Chapter 3

Molecular symmetry and symmetry point group

Part B

(ref. *Chemical Application of Group Theory*, 3rd ed., F.A. Cotton, by John Wiley & Sons, 1990.)

§ 3.5 Group representation Theory and irreducible representation of point groups

3.5.1 Representations of a point group:

reducible vs. irreducible

For a point group,

- Each element is a unique symmetry operation (operator).
- Each operation can be represented by a square matrix.
- These *matrices* constitute a **matrix group**, i.e., a matrix representation of this **point group**.

Example: $C_i = \{E, i\}$ ~ a general point (x,y,z) in space.

$$\hat{i}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$

$$\left\{ \hat{i} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \hat{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\}$$

a matrix group

Example: C_i one unit vector ***x***

$$\hat{E}(x)=(1)(x)=(x) \quad \hat{i}(x)=(-1)(x)=(-x)$$

The corresponding matrix representation of C_i is $\{(1),(-1)\}$

Q1:How many representations can be found for a particular group?

A large number, limited on our ingenuity in devising ways to generate them.

Q2: If we were to assign three small unit vectors directed along the x, y and z axes to each of the atoms in H_2O and write down the matrices representing the changes and interchanges of these upon the operations, what would be obtained?

A matrix representation consisting of four 9x9 matrices would be obtained upon operating on a column matrix $(x_O, y_O, z_O, x_{H1}, y_{H1}, z_{H1}, x_{H2}, y_{H2}, z_{H2})$.

Example: C_{2v} three unit vectors (x,y,z) or a general point

$\{E, C_2, \sigma_{xz}, \sigma_{yz}\}$ Principal axis: z-axis.

$$\hat{E}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\hat{C}_2\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

$$\hat{\sigma}_{xz}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

$$\hat{\sigma}_{yz}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

⇨ a matrix representation of ***C_{2v}***

$$\left\{\begin{array}{cccc} \mathrm{E} & \mathrm{C}_2 & \sigma_{\mathrm{xz}} & \sigma_{\mathrm{yz}} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}\right\}$$

Bases, representations and their dimensions

- **Dimension of a representation = The order of matrices.**
- **Different basis → Different representation.**

Example: $\boldsymbol{C_{2v}}$ Basis ~ a general point or three unit vectors.

$$\begin{array}{cccc} E & C_2 & \sigma_{xz} & \sigma_{yz} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{array}$$

A 3-D rep.

Simple basis: a translational vector as **x**, **y**, or **z**, or a rotor ***R**z*

	Reduced to 1D matrices		irreducible representation			
x	[1] [-1] [1] [-1]	***1-D Reps.***	Γ_x = 1	-1	1	-1
y	[1] [-1] [-1] [1]	→	Γ_y = 1	-1	-1	1
z	[1] [1] [1] [1]		Γ_z = 1	1	1	1
			Γ_{Rz} = 1	1	-1	-1

Reducing of representations

- Suppose that we have a set of ***n***-dimensional matrices, ***A, B, C, …*** , which form a representation of a group. These ***n***-D matrices themselves constitute a matrix group Γ **= {*A*， *B*,…}.**

- If we make the same ***similarity transformation*** on each matrix, we obtain a new set of matrices，namely,

$$A' = X^{-1}AX,\ B' = X^{-1}BX,$$
$$C' = X^{-1}CX,\ \ ...$$

that forms a new matrix group: $\Gamma' = \left\{A',\ B', C', ...\right\}$

- Γ' is also a representation of the group!

- It is provable that if any of the matrix (e.g., ***A′***) in Γ' is a *block-factored* matrix, then all other matrices (e.g., ***B′,C′,…***) in Γ' are also blocked-factored.

$$A'=\begin{bmatrix}[A_1] & 0 & 0 & 0\\ 0 & [A_2] & 0 & 0\\ 0 & 0 & [A_3] & 0\\ 0 & 0 & 0 & [A_4]\end{bmatrix}, B'=\begin{bmatrix}[B_1] & 0 & 0 & 0\\ 0 & [B_2] & 0 & 0\\ 0 & 0 & [B_3] & 0\\ 0 & 0 & 0 & [B_4]\end{bmatrix}, C'=\begin{bmatrix}[C_1] & 0 & 0 & 0\\ 0 & [C_2] & 0 & 0\\ 0 & 0 & [C_3] & 0\\ 0 & 0 & 0 & [C_4]\end{bmatrix},\ldots\ldots$$

in which $A_1,A_2,A_3\ldots$ are $n_1,n_2,n_3\ldots$-order submatrices with $n = n_1 + n_2 + n_3 + \ldots.$

- These ***n***-order matrices can be simply expressed as

$A' = A_1 \oplus A_2 \oplus A_3 \oplus \ldots$, $\quad B' = B_1 \oplus B_2 \oplus B_3 \oplus \ldots$,

$C' = C_1 \oplus C_2 \oplus C_3 \oplus \ldots$, ……

(Direct sum of submatrices！)

- It is also provable that the various sets of submatrices, $\boldsymbol{T_1}=\{A_1,B_1,C_1\dots\}$, $\boldsymbol{T_2}=\{A_2,B_2,C_2\dots\}$, $\boldsymbol{T_3}=\{A_3,B_3,C_3\dots\}$, …,

  are in themselves representations of the group.

- We then call the set of matrices $\Gamma=\{A,B,C,\dots\}$ a reducible representation of the group, which breaks up into a direct sum of the representations, i.e., $\Gamma = \boldsymbol{T_1} \oplus \boldsymbol{T_2} \oplus \boldsymbol{T_3} \oplus \dots$

- If it is not possible to find a similarity transformation to reduce a representation in the above manner, the representation is said to be ***irreducible***.

- The irreducible representations of a point group are mostly countable and of fundamental importance!

Example: C_{2v} Is this 3-D Rep. reducible?

Yes. These matrices are block-factored!

$$\begin{array}{cccc} E & C_2 & \sigma_{xz} & \sigma_{yz} \\ \begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix} & \begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix} & \begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix} & \begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix} \end{array} \qquad \Gamma_{xyz}$$

Reduced to 1D matrices

x	[1] [-1] [1] [-1]
y	[1] [-1] [-1] [1]
z	[1] [1] [1] [1]

irreducible representation

Γ_x = 1 -1 1 -1

Γ_y = 1 -1 -1 1

Γ_z = 1 1 1 1

$$\Gamma_{xyz} = \Gamma_x \oplus \Gamma_y \oplus \Gamma_z$$

The 3-D rep. is reduced to 3 1-D rep.

Point group ***R*** **R={R$_A$, R$_B$, R$_C$, …}** (symm. ops.)

↓ Exerted on any set of bases

(e.g., AO′s, MO′s, vectors, rotations etc.)

A matrix group, $\Gamma = \{A, B, C, \ldots\}$

(a matrix rep. of group ***R***, dimension = order of the matrix)

↓ Similarity transformations (reducing of a representation!)

A block-factored matrix group, $\Gamma' = \{A', B', C', \ldots\}$

$(A' = A_1 \oplus A_2 \oplus \ldots,\ B' = B_1 \oplus B_2 \oplus \ldots,\ C' = C_1 \oplus C_2 \oplus \ldots, \ldots)$ and $\Gamma_1 = \{A_1, B_1, C_1, \ldots\}$, $\Gamma_2 = \{A_2, B_2, C_2, \ldots\}$ …

& $\Gamma' = \Gamma_1 \oplus \Gamma_2 \oplus \ldots$

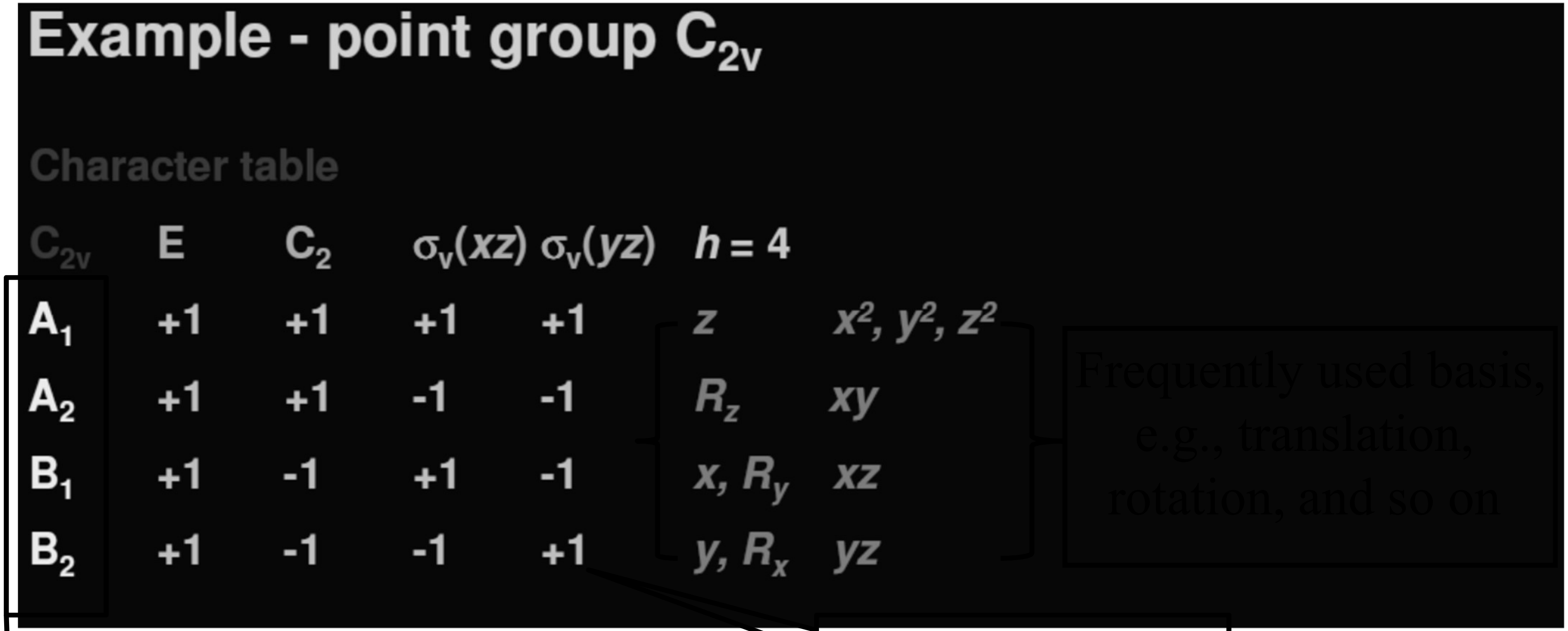
↓

Direct sum of irreducible representations!

The irreducible representations of a point group are mostly countable and of fundamental importance!!!

The character table of a point group lists up all essential information of its irreducible representations.

3.5.2. Character Tables of Point Groups



Example - point group C_{2v}

Character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$	
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

Frequently used basis, e.g., translation, rotation, and so on

Characters

Top line: point group
symmetry operations
order of group, ***h*** = number of symmetry operations

Symmetry species of irreducible representations.

Characters & reducing representation!

- **Character of a matrix *A*:** **(sum of its diagonal elements!)**

$$\chi(A)=\sum_i a_{ii}(A)$$

$$C_{2v}\qquad \overset{E}{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}}\quad \overset{C_2}{\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix}}\quad \overset{\sigma_{xz}}{\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}}\quad \overset{\sigma_{yz}}{\begin{bmatrix}-1&0&0\\0&1&0\\0&0&1\end{bmatrix}}$$

Γ_{xyz}

3-D Rep.

$\chi(E)=3$ $\quad\chi(C_2)=-1$ $\quad\chi(\sigma_{xz})=1$ $\quad\chi(\sigma_{yz})=1$

Reduced to 1D matrices

x [1] [-1] [1] [-1]

y [1] [-1] [-1] [1]

z [1] [1] [1] [1]

	E	C_2	σ_{xz}	σ_{yz}
B_1	1	-1	1	-1
B_2	1	-1	-1	1
A_1	1	1	1	1
Γ_{xyz}	*3*	*-1*	*1*	*1*

$$\Gamma_{xyz}=A_1\oplus B_1\oplus B_2$$

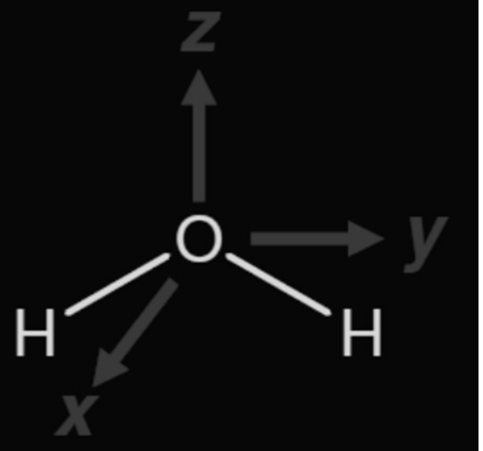
$$\text{If}\ \Gamma=\Gamma_1\oplus\Gamma_2\oplus\Gamma_3\oplus\ldots,\ \chi_{\Gamma}(R)=\sum_i\chi_{\Gamma_i}(R)$$

Γ_i---I.R.s

Translations

Movements of whole molecule – represent by vectors

e.g. y vector	E operation	y' (after operation) $= y$
	C_2	$y' = -y$ (i.e. $y' = -1 \times y$)
	$\sigma_v(xz)$	$y' = -y$
	$\sigma_v(yz)$	$y' = y$
z vector	all operations	$z' = z$
x vector	E operation	$x' = x$
	C_2	$x' = -x$
	$\sigma_v(xz)$	$x' = x$
	$\sigma_v(yz)$	$x' = -x$



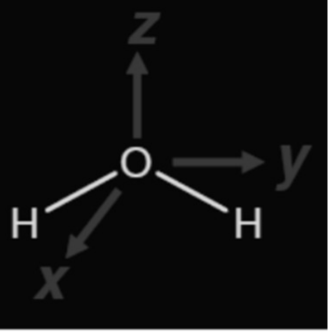
Translations

Consider effect of symmetry operation on the vector
Write +1 for no change, -1 for reversal

	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
z vector	+1	+1	+1	+1	A_1
y	+1	-1	-1	+1	B_2
x	+1	-1	+1	-1	B_1

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

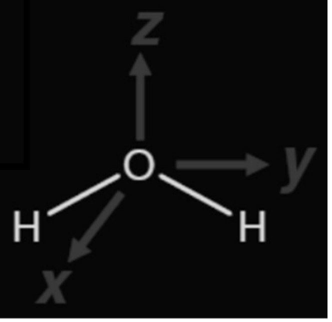
Labels A_1 etc. are *symmetry species*; they summarise the effects of symmetry operations on the vectors.



Rotations

Similarly for rotations of the molecules

	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
z vector	+1	+1	+1	+1	A_1
y	+1	-1	-1	+1	B_2
x	+1	-1	+1	-1	B_1
R_z	+1	+1	-1	-1	A_2
R_y	+1	-1	+1	-1	B_1
R_x	+1	-1	-1	+1	B_2



Characters

The numbers +1 and -1 are called *characters*.

The *character table* has all possible symmetry species for the *point group*. It is the same for all molecules belonging to the point group – e.g. C_{2v} for H_2O, SiH_2Cl_2, $Fe(CO)_4Cl_2$, etc.

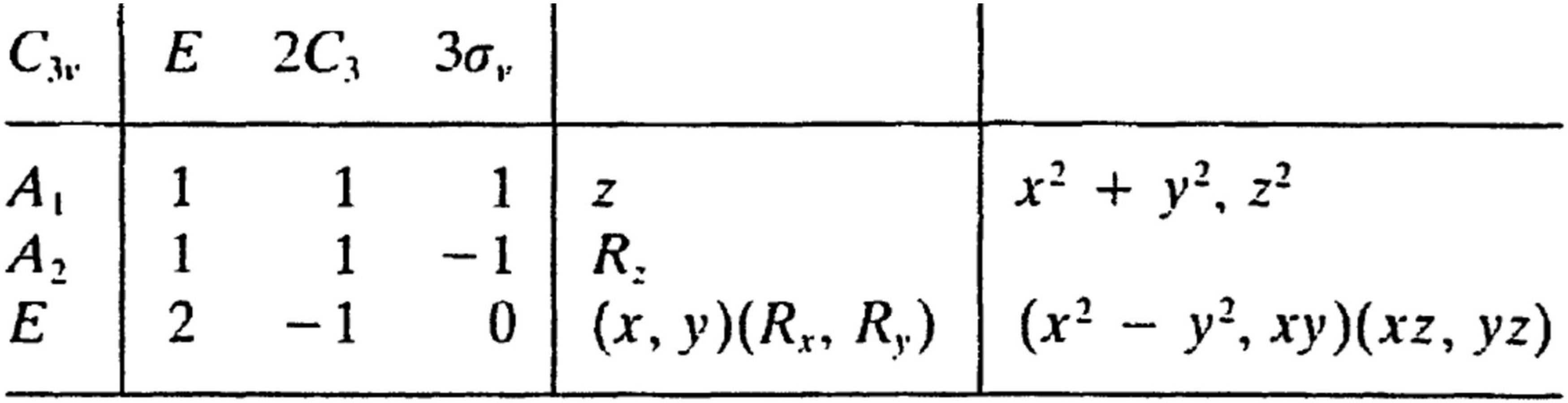
Note: the character table lists the symmetry species for translations and rotations.

A,B show symmetry with respect to rotation.
1,2 distinguish symmetry with respect to reflections

Character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$
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

Symmetry species: Mulliken symbols



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	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

- All ***1-D*** irreducible reps. are labeled by either ***A*** or ***B***, ***2-D*** irreducible rep. by ***E***, ***3-D*** irreducible rep. by ***T*** and so on.
- ***A***: symmetric with respect to C_n rotation, i.e., $\chi(C_n)=1$.
- ***B***: asymmetric with respect to C_n rotation, i.e., $\chi(C_n)=-1$.
- Subscriptions ***1*** or ***2*** designates those symmetric or asymmetric with respect to a $C_2\perp$ or a σ_v .
- Subscripts ***g*** or ***u*** for universal parity or disparity.
- Superscripts $'$ or $''$ designates those symmetric or asymmetric with respect to $\sigma_\mathbf{h}$

3.5.3 The “Great Orthogonality Theorem” and Its Consequences

广义正交定理

Some notations:

h – the order of a group; ***R*** – operations (elements) of a point group.

l_i – the dimension of ***i***th representation (i.e., the order of its matrices)

$\Gamma_i(R)_{mn}$ – the element in the ***m***th row and *n*th column of the matrix corresponding to the operation ***R*** in the ***i***th representation.

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}}\delta_{ij}\delta_{mm'}\delta_{nn'}$$

It means that in the set of matrices constituting any one irreducible representation, any set of corresponding matrix elements, one from each matrix, behaves as the components of a vector in a ***h***-dimensional space such that all these vectors are mutually orthogonal and each is normalized so that the square of its length is h/l_i.

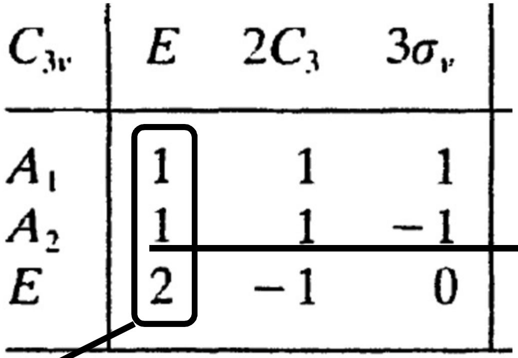
Five important rules

regarding irreducible representations and their characters:

Rule 1 – the sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of a group.

$$\sum_i l_i^2 = h$$

e.g., for C_{3v},



C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

$$\sum_i l_i^2 = 1^2 + 1^2 + 2^2 = 6 = h$$

$$\because \chi_i(E) = l_i \quad \Rightarrow \sum_i [\chi_i(E)]^2 = h$$

Rule 2 – the sum of the square of the characters in any irreducible representation of a group equals ***h***,

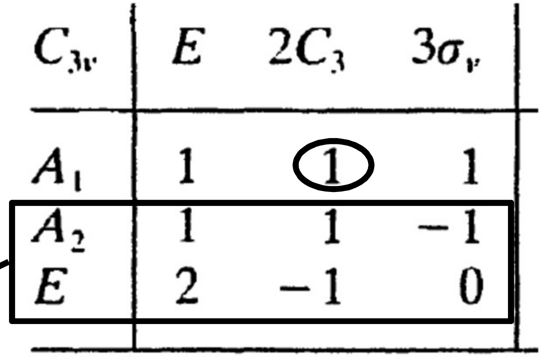
$$\sum_R [\chi_i(R)]^2 = h$$

$$e.g., A_2 \ for \ C_{3v}, 1^2 + 2\cdot 1^2 + 3\cdot(-1)^2 = 6$$

Five important rules

Rule 3 – the vectors whose components are the characters of two irreducible representations are orthogonal,

$$\sum_R [\chi_i(R)][\chi_j(R)] = 0$$



C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

e.g., The ***A*$_2$** and ***E*** I.R. of C_{3v} are orthogonal.

$$1(1\cdot 2) + 2(1\cdot(-1)) + 3((-1)\cdot 0) = 0$$

Rule 4 – In a given representation, the characters of all matrices belonging to operations in the same class are identical.

Rule 5 – the number of irreducible representations of a group is equal to the number of classes (of operations) in the group.

Illustration of the Five important rules

Example – Direct construction of the character table of C_{2v}

- ***Four*** classes of elements/operations: $\{E, C_2, \sigma', \sigma''\}$ & $h = 4$
- ***Rule 5*** → Four I.R.
- ***Rule 1*** → $\Sigma l_i^2 = h = 4$ → $l_{1\text{-}4} = 1$ → **4 1-D I.R.**
- ***There is always an all-symmetric representation,***

$$\Gamma_1 \quad \sum_R [\chi_1(R)]^2 = h = 4 \;\&\; \chi_1(R) = 1$$

C_{2v}	E	C_2	σ'	σ''
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

- ***Other 1-D I.R., $\chi_i(E) = 1$***

$$\because \sum_R [\chi_i(R)]^2 = h \Rightarrow \chi_i(R) = \pm 1$$

- ***Each of them is orthogonal to Γ_1 (rule3)***

$$\Rightarrow \sum_R \chi_i(R)\chi_1(R) = 0$$

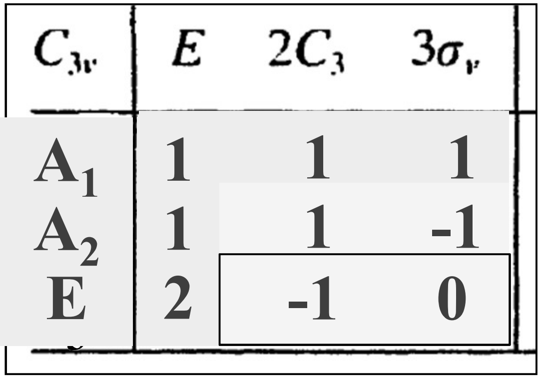
⇨ Two $\chi_i(R) = 1$, two $\chi_i(R) = -1$!

- ***If necessary, define the symmetry species (Mulliken symbols).***

Illustration of the Five important rules

Example – Direct construction of the character table of C_{3v}

- ***Three*** classes of elements/operations: $\{E, 2C_3, 3\sigma_v\}$ & $h=6$
- ***Rule 5*** → ***Three*** **I.R.**s
- ***Rule 1*** → $l_1^2 + l_2^2 + l_3^2 = 6$ → $l_1 = l_2 = 1$, $l_3 = 2$
- & $\chi_1(E)=\chi_2(E)=1$, $\chi_3(E)=2$
- ***There is always an all-symmetric 1-D I.R.***



C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$$\chi_1(E) = \chi_1(C_3) = \chi_1(\sigma_v) = 1 \quad (\Gamma_1 = \mathrm{A}_1)$$

- ***Another 1-D I.R. Γ_2 should follow rules 2 &3.***

$$\sum_R [\chi_2(R)]^2 = h \qquad \sum_R \chi_2(R)\chi_1(R) = 0$$

→ $\chi_2(C_3)=1$, $\chi_2(\sigma_v)=-1$

- ***Similarly for the 2-D I.R. Γ_3 ,*** → $\chi_3(C_3)=-1$, $\chi_3(\sigma_v)=0$
- ***If necessary, define the symmetry species (Mulliken symbols).***

An important practical relationship

Between any reducible representation and the I.R.s,

$$\chi(R)=\sum_j a_j\chi_j(R)$$

The number of times that the ***j***th I.R. occurs in a red. REP.

Character of a matrix corresponding to operation *R* in a red. REP.

Character of a matrix corresponding to operation ***R*** in the *j*th I.R..

$$\Rightarrow \sum_R \chi_i(R)\chi(R)=\sum_R \chi_i(R)\sum_j a_j\chi_j(R)=\sum_R a_i[\chi_i(R)]^2=ha_i$$

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

Rule 3

Rule 1

This relationship thus provides an easy way for reducing a representation of a group.

3.5.3 Symmetry of molecular properties & Application of the representation theory of group

- Translations and rotations can be assigned to symmetry species (of irreducible representations).

- So can other molecular properties, including molecular vibrations, hybrid orbitals, molecular orbitals and so on.

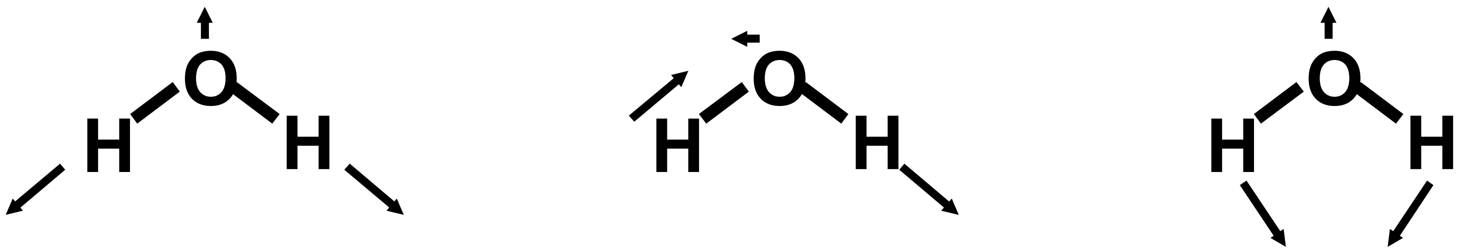
- The theory of molecular symmetry & point group facilitates the construction of hybrid orbitals, symmetry adapted MO’s, and analyses of molecular vibrations etc.

1. Vibrational spectroscopy

正则振动

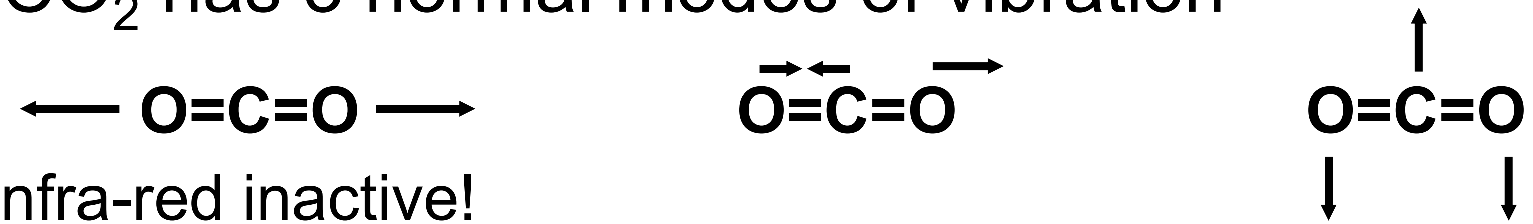
The normal vibrations (or normal modes of vibrations) of a molecule are the bases of I.R.s of the point group it belongs to.

* H_2O has (3N-6)=3 normal modes of vibration!



A_1 IR active **B_1** IR active **A_1** IR active

* CO_2 has 3 normal modes of vibration



Infra-red inactive!
no dipole change！

IR active

IR active

The Number **of active modes tells us about symmetry!**

IR – active:

The vibrations that induce a change in dipole moment.

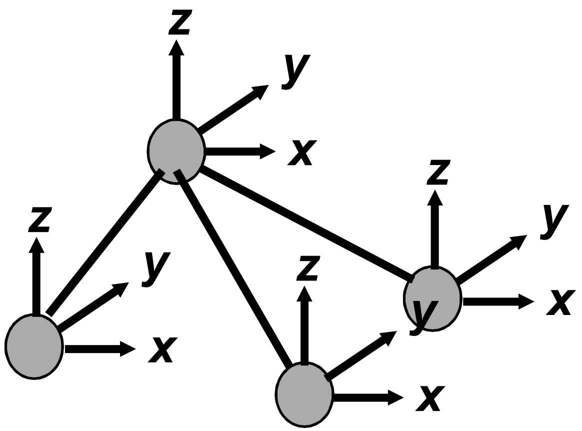
- A *IR-active* vibration and a component of *molecular dipole moment* (i.e., vectors x, y, z） belong to the same symmetry species.

Raman – active:

The vibrations that induce a change in polarizability.

- A *Raman-active* vibration and a component of *molecular polarizability* (i.e., x^2, y^2, z^2, xy, yz, xz and x^2-y^2 etc.） belong to the same symmetry species.

Molecular vibrations - number of modes



Each atom can move independently in *x, y,* z directions.

3N degrees of freedom for a N-atom molecule.

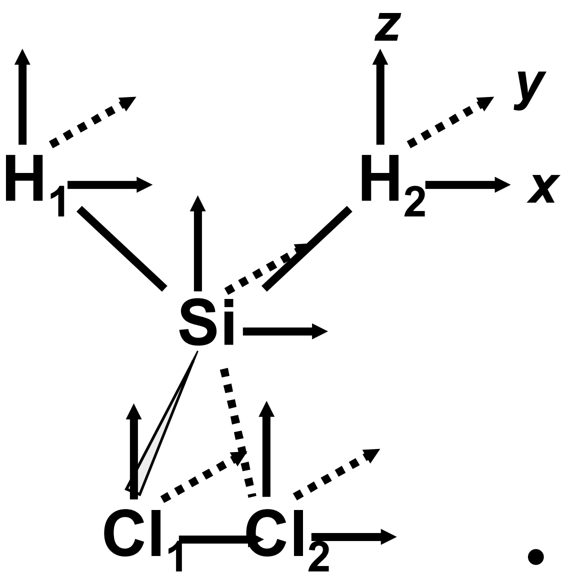
If atoms fixed, there are: 3 translational degrees

3 rotational degrees

and the rest (3N-6) are vibrational modes

No. of modes of each symmetry species

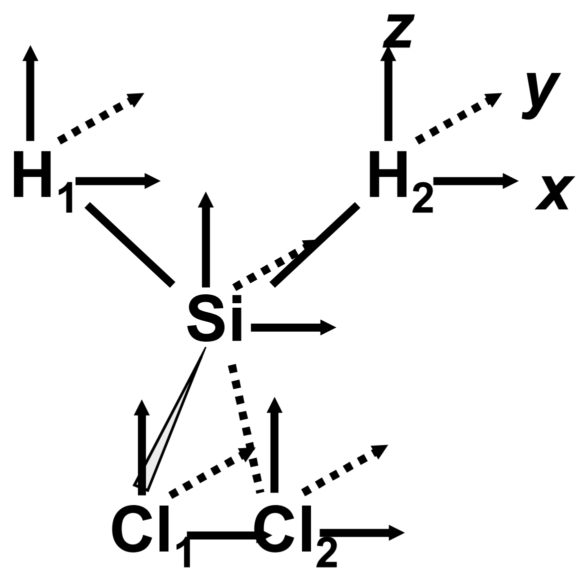
Example - SiH_2Cl_2 Point group C_{2v}



Character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$	
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

- Draw *x, y* and *z* vectors on all atoms.
- Perform symmetry operations.
- Count +1, -1, 0 if vector transforms to itself, minus itself, or moves.



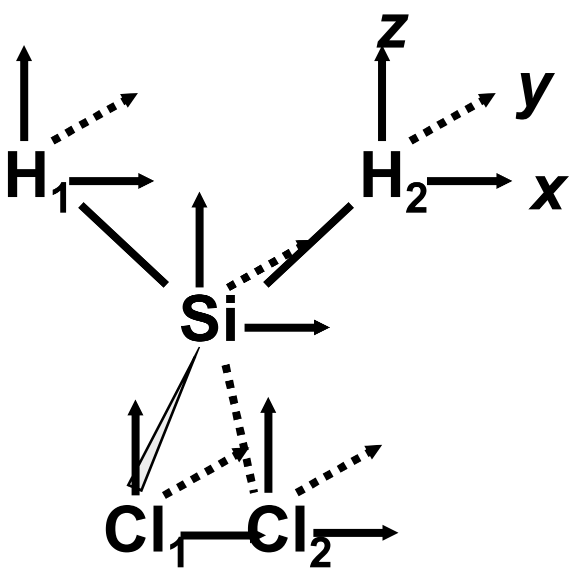
Character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$	
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

Operation E

Si atom	*x* transforms into Si *x*	count +1
	y transforms into Si *y*	count +1
	z transforms into Si *z*	count +1
		total +3

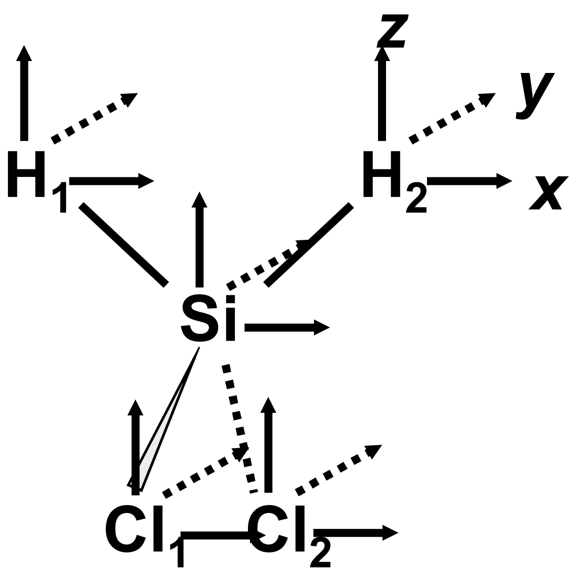
Same for other 4 atoms grand total +15



Character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$	
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

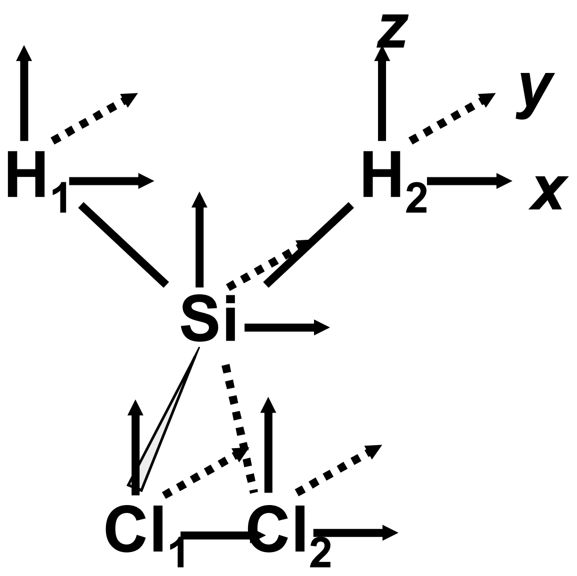
Operation C_2	**Si atom**	***x* transforms into Si -*x***	**count -1**
		y* transforms into Si -*y	**count -1**
		z* transforms into Si *z	**count +1**
			total -1
H_1 and H_2 move - swap places			**count 0**
Cl_1 and Cl_2 swap places			**count 0**
			grand total -1



Character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$	
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

Operation $\sigma_v(xz)$ Si atom	**x transforms into Si x**	**count +1**
	y transforms into Si $-y$	**count -1**
	z transforms into Si z	**count +1**
		total +1
H_1 and H_2 also lie in xz plane, and behave as Si		**count +1 each**
Cl_1 and Cl_2 swap places		**count 0**
		grand total +3



Character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$	
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

Operation $\sigma_v(yz)$ Si atom **x transforms into Si $-x$** **count -1**

y transforms into Si y **count +1**

z transforms into Si z **count +1**

total +1

H_1 and H_2 swap places **count 0**

Cl_1 and Cl_2 also lie in yz plane, and behave as Si **count +1 each**

grand total +3

No. of modes of each symmetry species

Example - SiH_2Cl_2 **Point group C_{2v}**

Overall we have:

E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
+15	-1	+3	+3

This is the *reducible representation* of the point group on the basis of the set of 3N (=15) atomic displacement vectors.

We reduce it to the *irreducible representations*, using a formula

Reduce the reducible representation

Formula is

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

Character table

C_{2v}	1E	$1C_2$	$1\sigma_v(xz)$	$1\sigma_v(yz)$		$h = 4$
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
Red. Rep. Γ	15	-1	3	3		

No. of A_1 motions = 1/4 [1.15.1 + 1.(-1).1 + 1.3.1 + 1.3.1] = 5

$$a_i = \frac{1}{h}\sum_c g_c \cdot \chi(c) \cdot \chi_i(c)$$

Character table

C_{2v}	1E	$1C_2$	$1\sigma_v(xz)$	$1\sigma_v(yz)$		*h* = 4
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
Red. Rep. Γ	15	-1	3	3		

No. of A_1 motions = 1/4 [1.15.1 + 1.(-1).1 + 1.3.1 + 1.3.1] = 5

No. of A_2 motions = 1/4 [1.15.1 + 1.(-1).1 + 1.3.(-1) + 1.3.(-1)] = 2

$$a_i = \frac{1}{h}\sum_{c} g_c \cdot \chi(c) \cdot \chi_i(c)$$

Character table

C_{2v}	1E	$1C_2$	$1\sigma_v(xz)$	$1\sigma_v(yz)$		$h = 4$
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
Red. Rep. Γ	15	-1	3	3		

No. of A_1 motions = 1/4 [1.15.1 + 1.(-1).1 + 1.3.1 + 1.3.1] = 5

No. of A_2 motions = 1/4 [1.15.1 + 1.(-1).1 + 1.3.(-1) + 1.3.(-1)] = 2

No. of B_1 motions = 1/4 [1.15.1 + 1.(-1).(-1) + 1.3.1 + 1.3.(-1)] = 4

No. of B_2 motions = 1/4 [1.15.1 + 1.(-1).(-1) + 1.3.(-1) + 1.3.1] = 4

Translations, rotations, vibrations

Symmetry species of all motions are:-

$5A_1 \oplus 2A_2 \oplus 4B_1 \oplus 4B_2$ - the *irreducible representation*

- 3 of these are *translations* of the whole molecule
- 3 are *rotations*
- Symmetry species of translations are given by vectors (*x, y, z*) in the character table.
- Symmetry species of rotations are given by R_x, R_y and R_z in the character table.

Translations, rotations, vibrations

Symmetry species **of all motions are:-**

$5A_1 + 2A_2 + 4B_1 + 4B_2$

Translations **are:-** $A_1 + B_1 + B_2$

Rotations **are:-** $A_2 + B_1 + B_2$

- so *vibrations* are:- $4A_1 + A_2 + 2B_1 + 2B_2$

Character table

C_{2v}	1E	$1C_2$	$1\sigma_v(xz)$	$1\sigma_v(yz)$		$h = 4$
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

Vibrational modes of SiH_2Cl_2

Symmetry species of vibrations
are:- $4A_1 + A_2 + 2B_1 + 2B_2$

What does each of these modes look like?

Two rules

(i) there is 1 stretching vibration per bond

(ii) must treat symmetry-related atoms together

Vibrational modes of SiH_2Cl_2

Two rules

(i) there is 1 stretching vibration per bond

(ii) we must treat symmetry-related atoms together

We therefore have:-

two stretching modes of the $SiCl_2$ group

two of the SiH_2 group

The remaining five modes must be deformations (angle bending vibrations)

Vibrational modes of SiH_2Cl_2

We therefore have:-

two stretching modes of the $SiCl_2$ group

We can stretch the two Si-Cl bonds

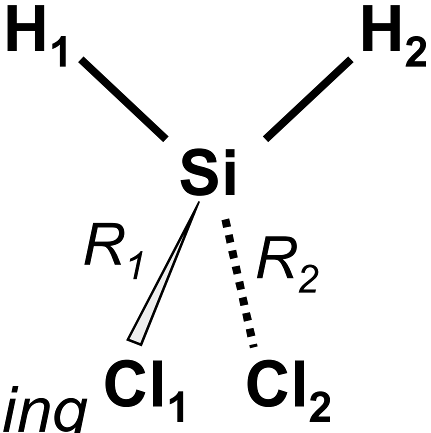
together *in phase*

or together *out of phase*

Why?

hint: 1) use the two Si-Cl bond stretching as basis set:

	E	**C_2**	**σ_{xz}**	**σ_{yz}**	
Γ_{2SiH}	**2**	**0**	**0**	**2**	→ $\Gamma_{2SiH} = A_1 + B_2$



2) Use the projection operator to work on R_1:

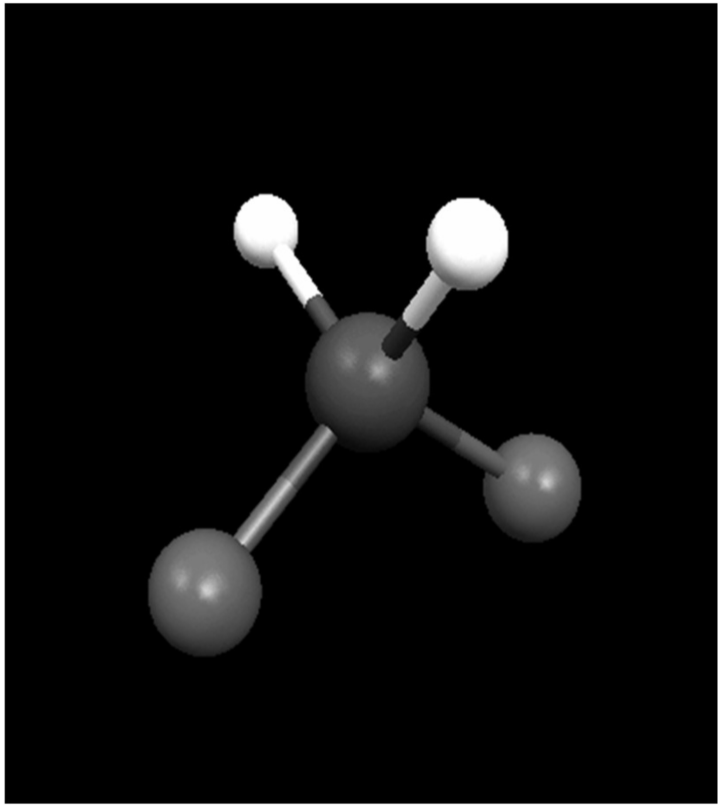
A_1 stretching = $(R_1 + R_2)/2$ *symmetric stretching*

B_2 stretching = $(R_1 - R_2)/2$ *anti-symmetric stretching*

Is vibration symmetrical with respect to each symmetry operation?

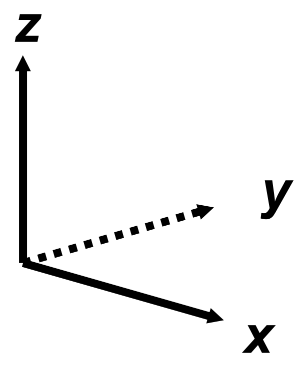
- if yes +1, if no -1

E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1



From the character table, this belongs to the symmetry species A_1

We call the mode of vibration ν_{sym} $SiCl_2$



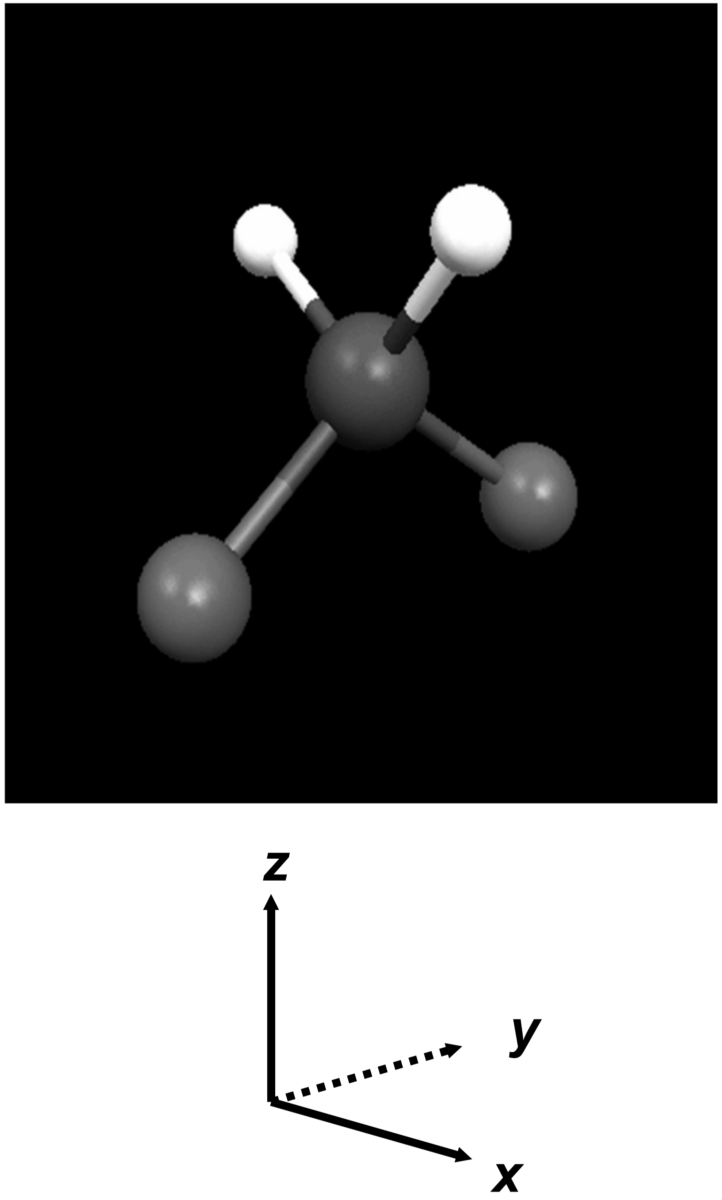
Is vibration symmetrical with respect to each symmetry operation?

- if yes +1, if no -1

E	C_2	σ_{xz}	σ_{yz}
+1	-1	-1	+1

From the character table, this belongs to the symmetry species B_2

We call the mode of vibration ν_{asym} $SiCl_2$



Vibrational modes of SiH_2Cl_2

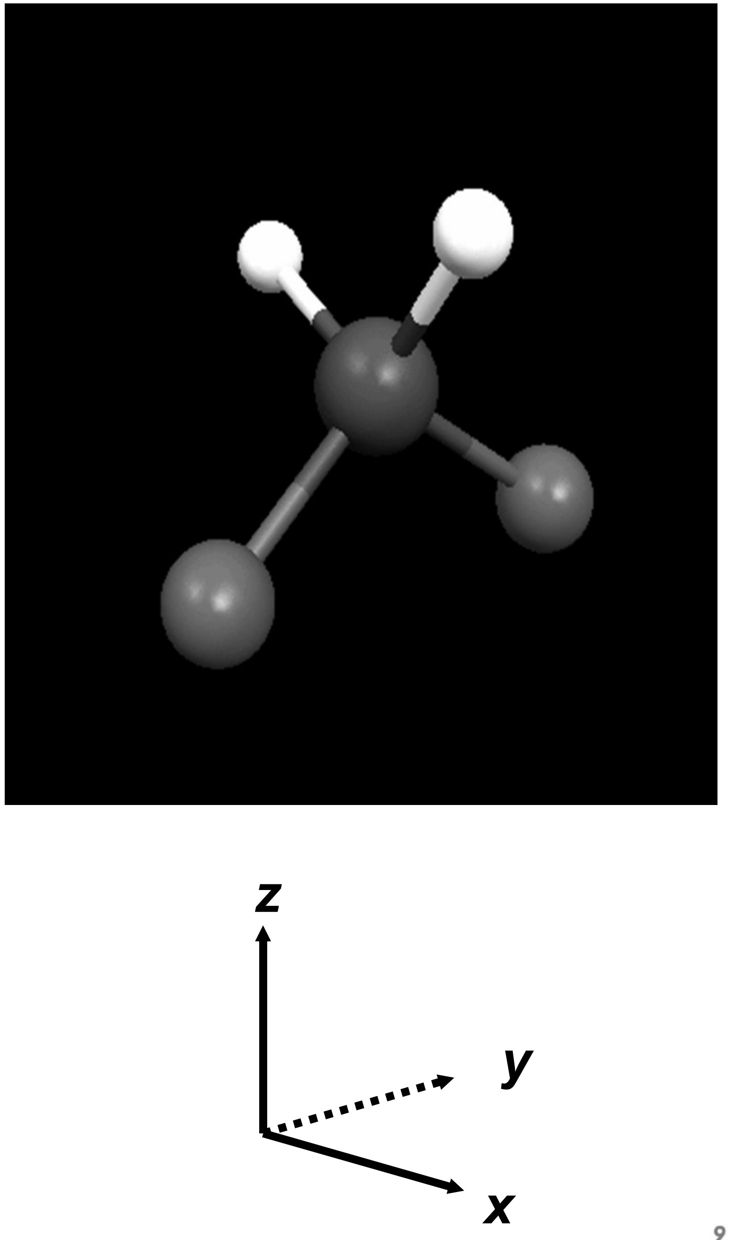
We therefore have:-

- **two stretching modes of the $SiCl_2$ group**
- **and two stretching modes of the SiH_2 group**

We can stretch the two Si-H bonds

- **together *in phase***
- **or together *out of phase***

E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1



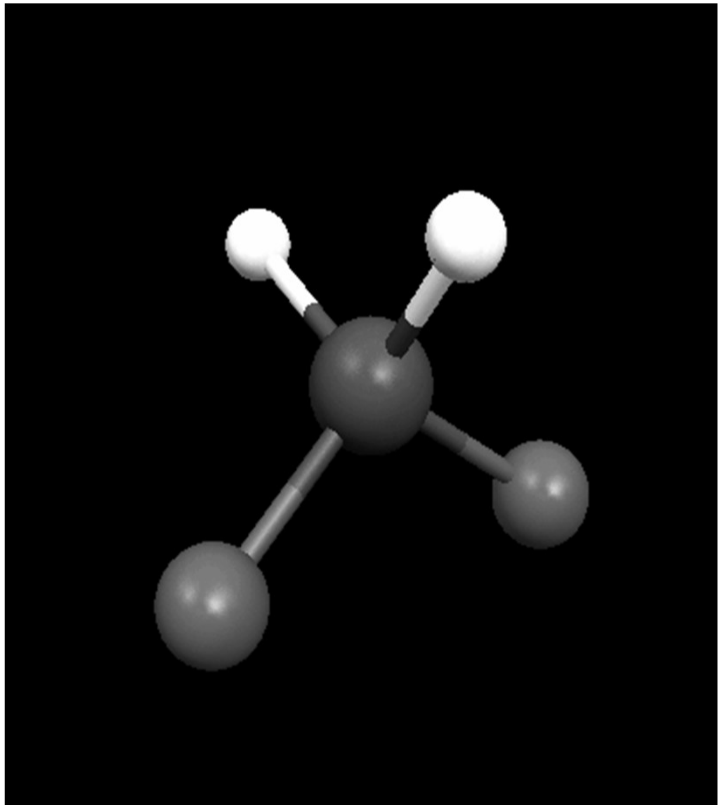
From the character table, this belongs to the symmetry species A_1

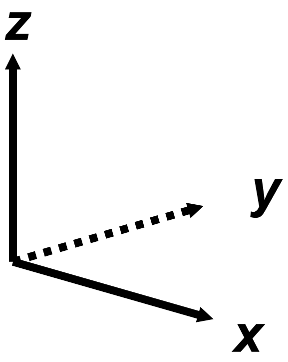
We call the mode of vibration ν_{sym} SiH_2

E	C_2	σ_{xz}	σ_{yz}
+1	-1	+1	-1

From the character table, this belongs to the symmetry species B_1

We call the mode of vibration ν_{asym} SiH_2





Vibrational modes of SiH_2Cl_2

We now have:-

two stretching modes of the $SiCl_2$ group

two of the SiH_2 group

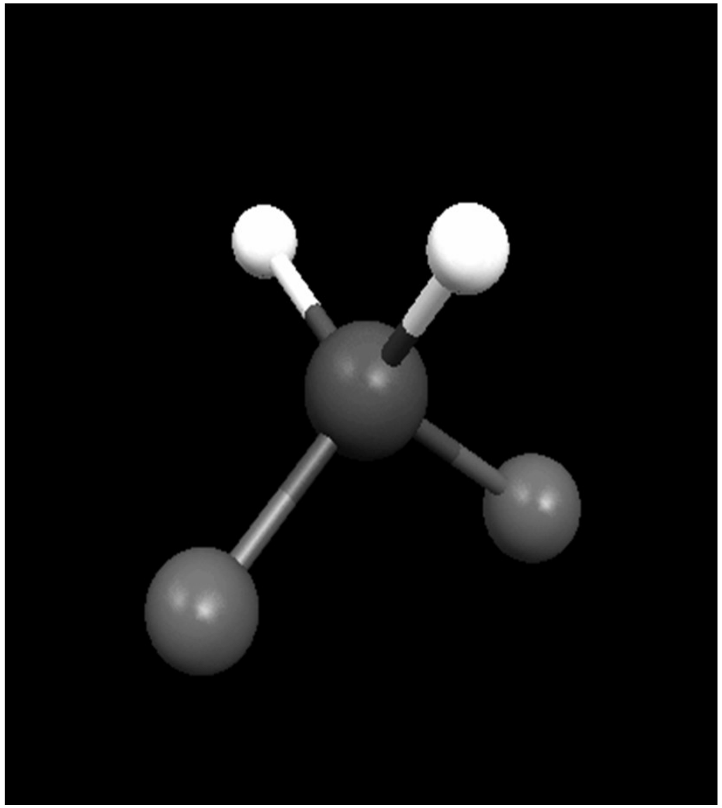
The remaining five modes must be deformations (angle bending vibrations)

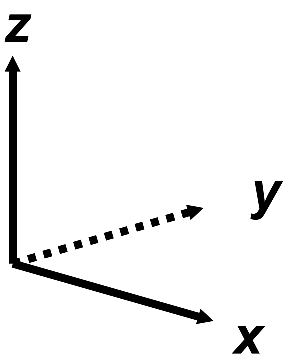
As with stretches, we must treat symmetry-related atoms together

E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1

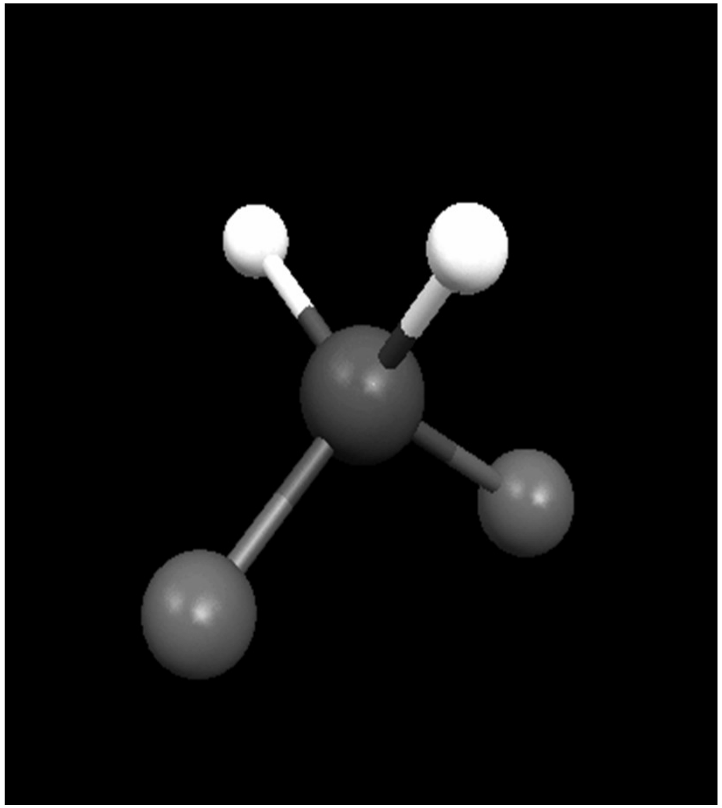
From the character table, this belongs to the symmetry species A_1

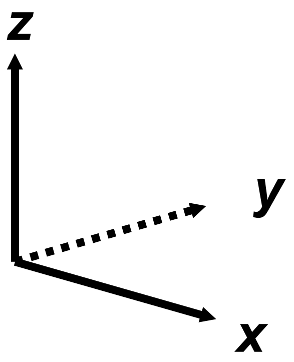
We call the mode of vibration δ_{sym} $SiCl_2$ (or $SiCl_2$ scissors)





E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1

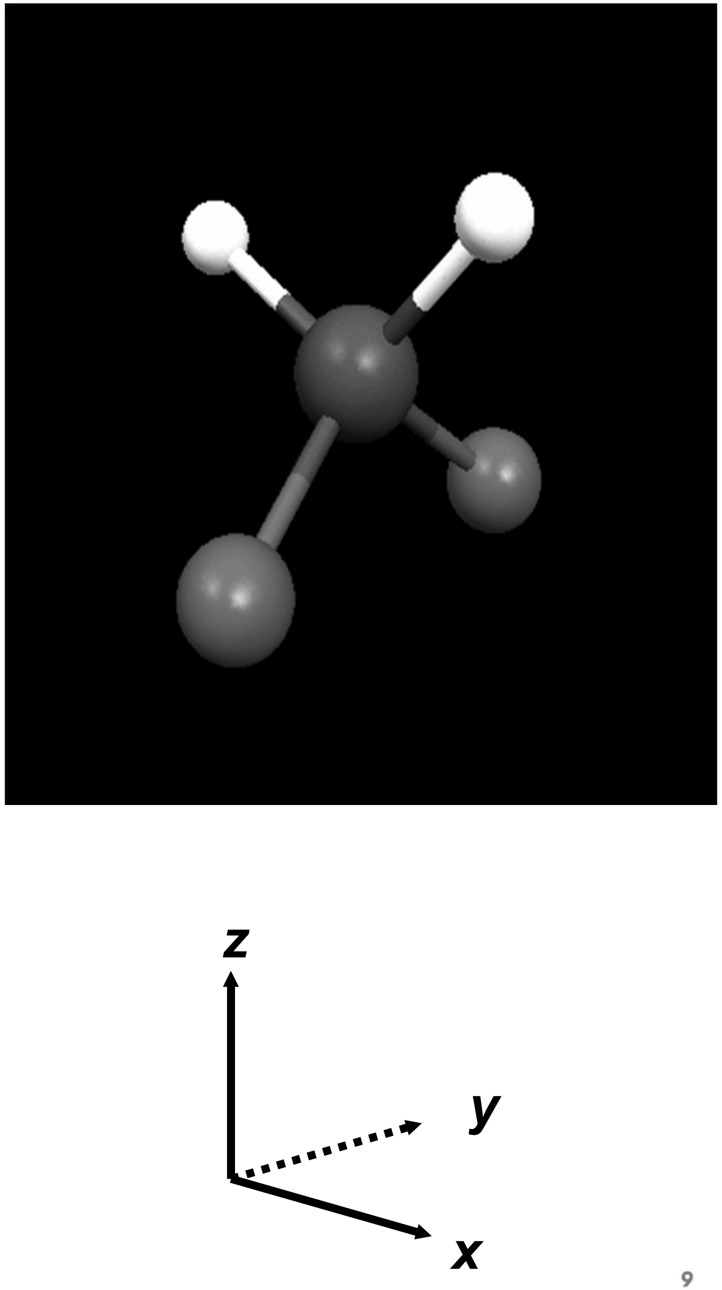




From the character table, this belongs to the symmetry species A_1

We call the mode of vibration δ_{sym} SiH_2 (or SiH_2 scissors)

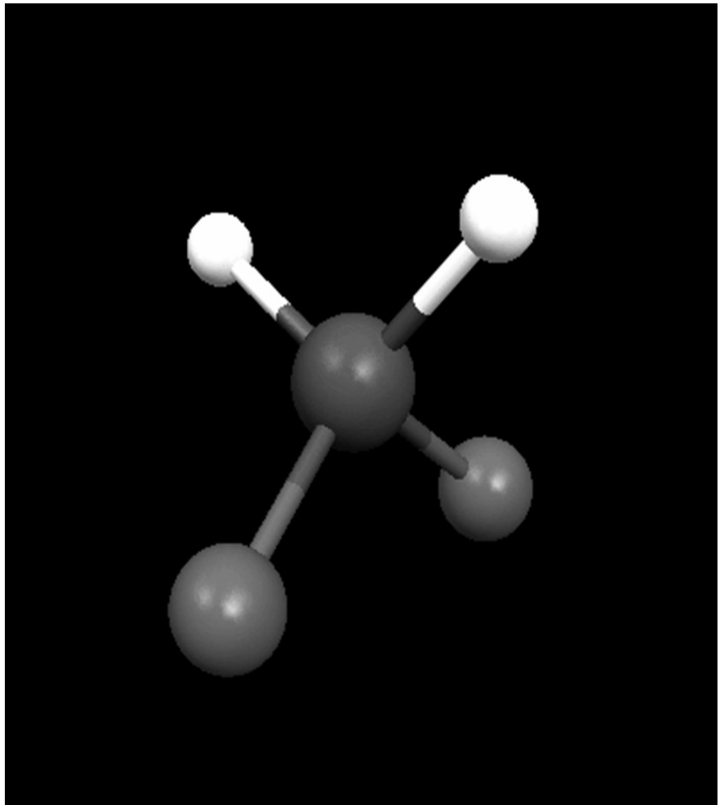
E	C_2	σ_{xz}	σ_{yz}
+1	-1	+1	-1



From the character table, this belongs to the symmetry species B_1

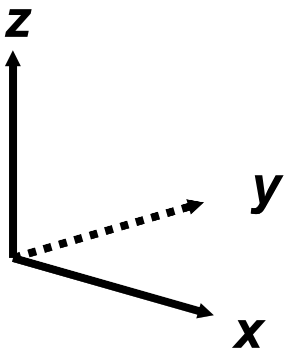
We call the mode of vibration ω SiH_2 (or SiH_2 wag)

E	C_2	σ_{xz}	σ_{yz}
+1	-1	-1	+1

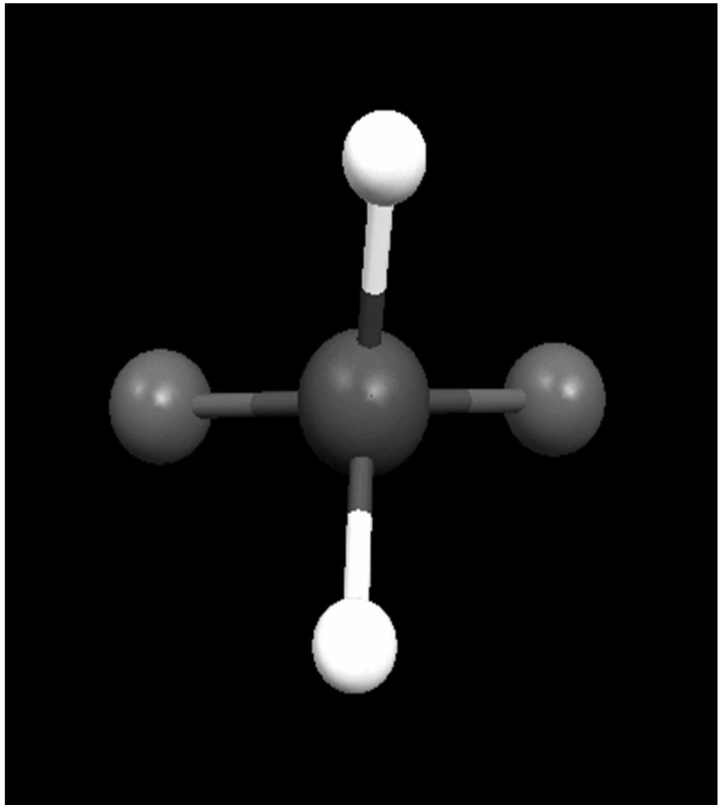


From the character table, this belongs to the symmetry species B_2

We call the mode of vibration ρ SiH_2 (or SiH_2 rock)

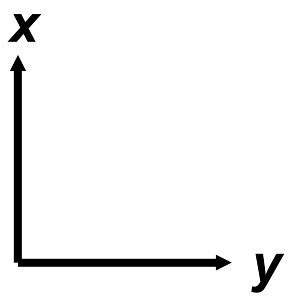


E	C_2	σ_{xz}	σ_{yz}
+1	+1	-1	-1



From the character table, this belongs to the symmetry species A_2

We call the mode of vibration τ SiH_2 (or SiH_2 twist)



Vibrational modes of SiH_2Cl_2

Overall, we now have:-

two stretching modes of the $SiCl_2$ group

$A_1 + B_2$

two of the SiH_2 group

$A_1 + B_1$

five deformation modes

$2A_1 + A_2 + B_1 + B_2$

Together, these account for all the modes we expect:

$$4A_1 + A_2 + 2B_1 + 2B_2$$

Observing vibrations

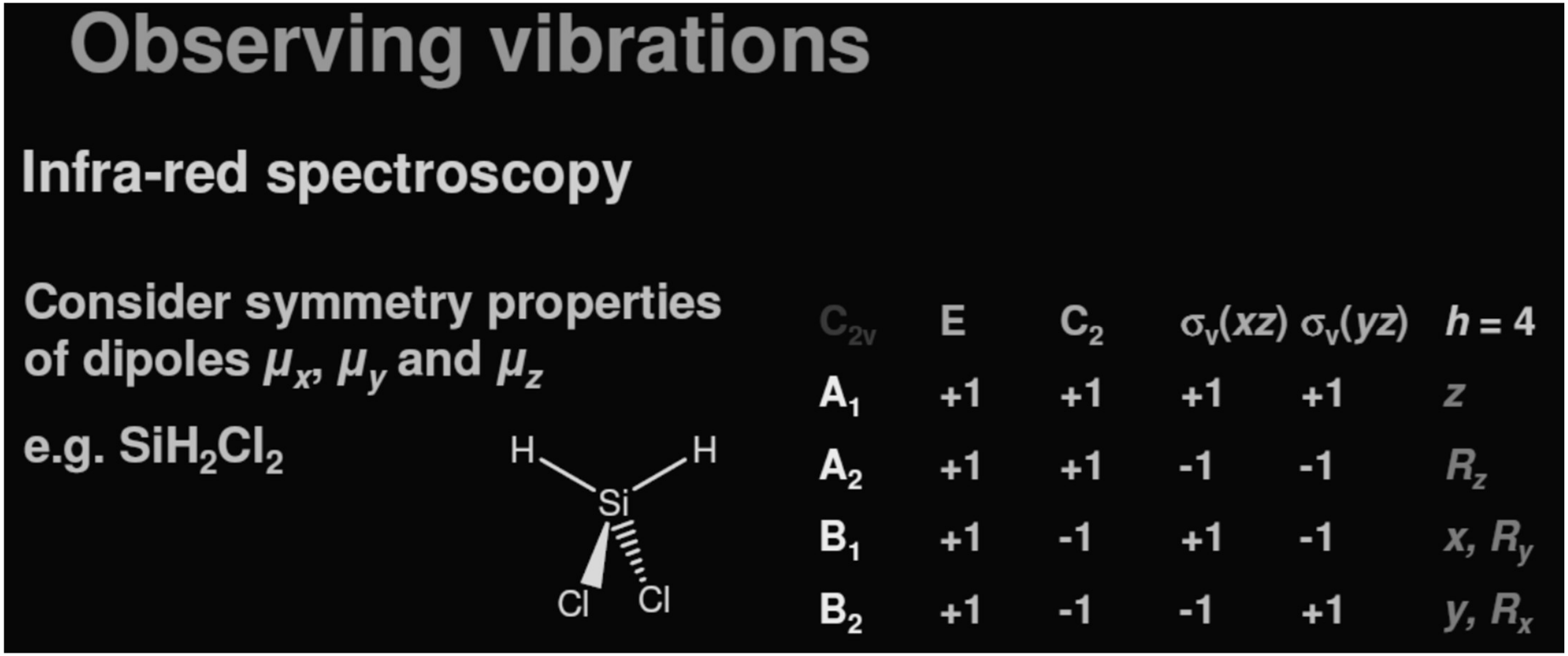
Infra-red spectroscopy

Process – quantum of energy is absorbed by exciting a vibration

– may also increase or decrease rotational energy

IR radiation → sample → $h\nu$ absorbed

Activity – absorption possible if and only if the vibration involves a dipole change



Observing vibrations

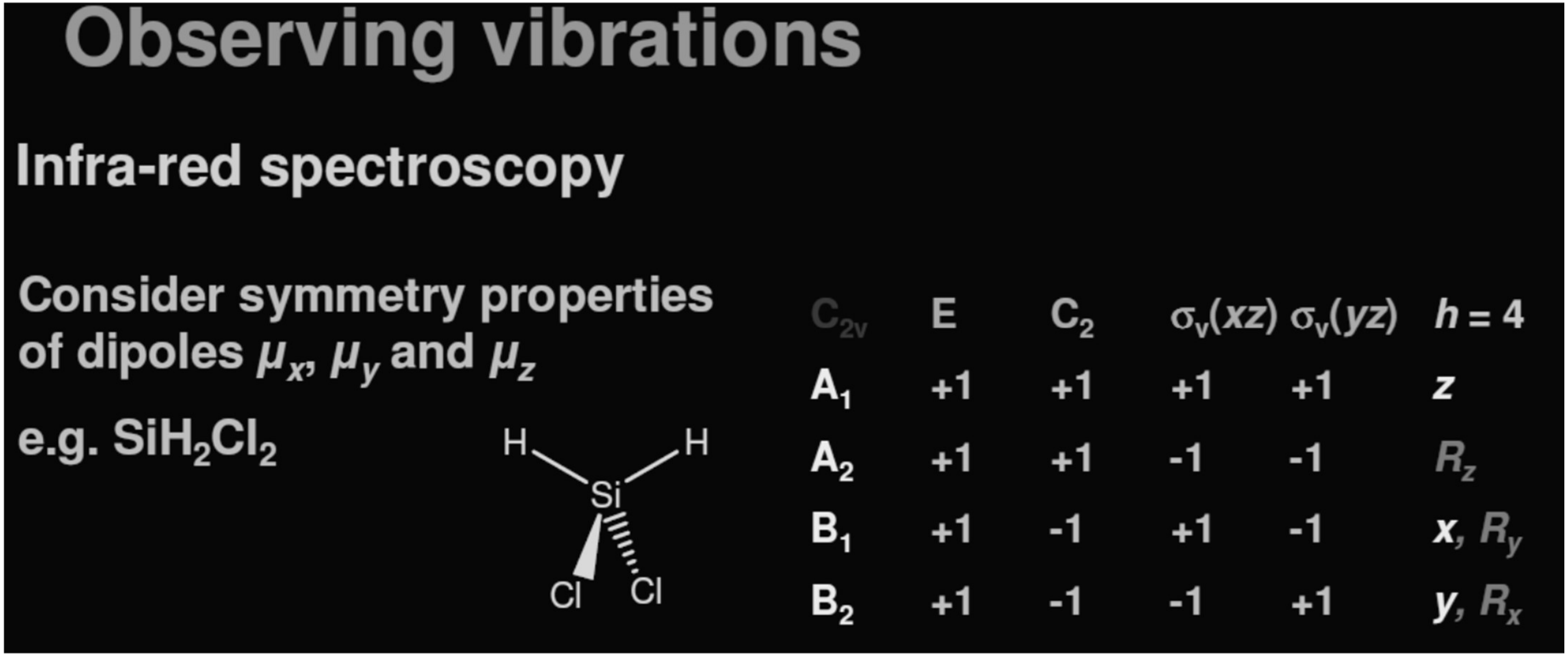
Infra-red spectroscopy

Consider symmetry properties of dipoles μ_x, μ_y and μ_z

e.g. SiH_2Cl_2

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$
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

- Dipoles are vectors, with same symmetry properties as x, y, and z. In this case, μ_z has A_1 symmetry.
- Those A_1 vibrations involve dipole changes along the z axis and so all A_1 modes must be ***infra-red active***.



Observing vibrations

Infra-red spectroscopy

Consider symmetry properties of dipoles μ_x, μ_y and μ_z

e.g. SiH_2Cl_2

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$
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

- Similarly B_1 and B_2 modes involve dipole changeds along x and y axes, and so must be ***infra-red active***.
- $\boldsymbol{A_2}$ modes cannot involve dipole changes, and are *infra-red inactive.*
- For any point group, no more than ***3*** IR-active symmetry species.

Observing vibrations

Infra-red spectroscopy

Example 1: SiH_2Cl_2

$$\Gamma_{vib} = 4A_1 + A_2 + 2B_1 + 2B_2$$

4 + 2 + 2 active modes

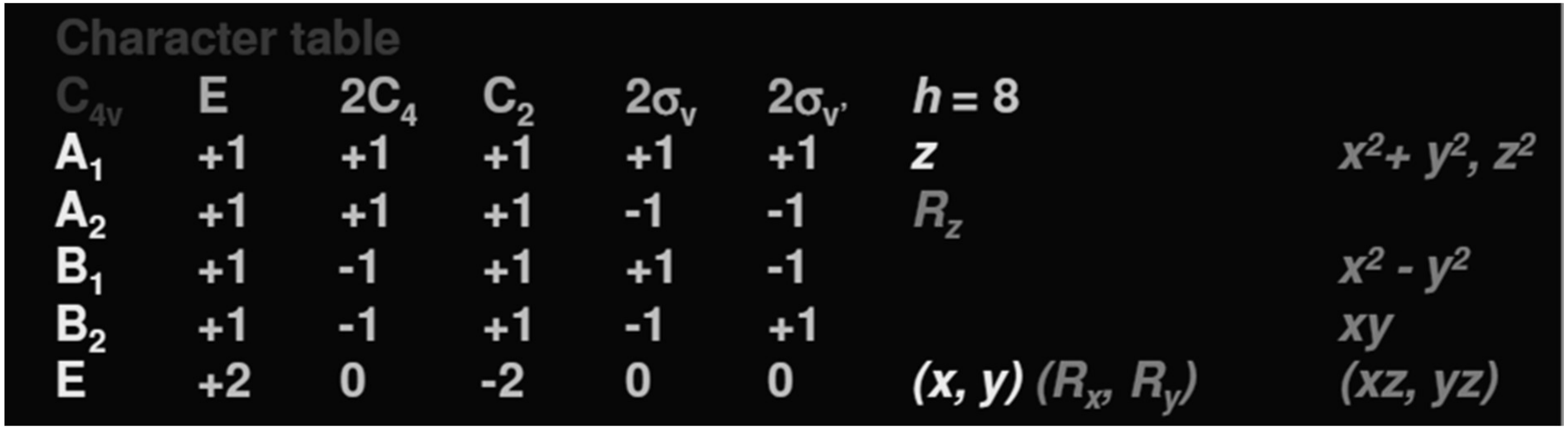
8 absorption bands in IR spectrum

Example 2: $XeOF_4$

$$\Gamma_{vib} = 3A_1 + 2B_1 + B_2 + 3E$$

3 + 3 active modes

6 absorption bands in IR spectrum



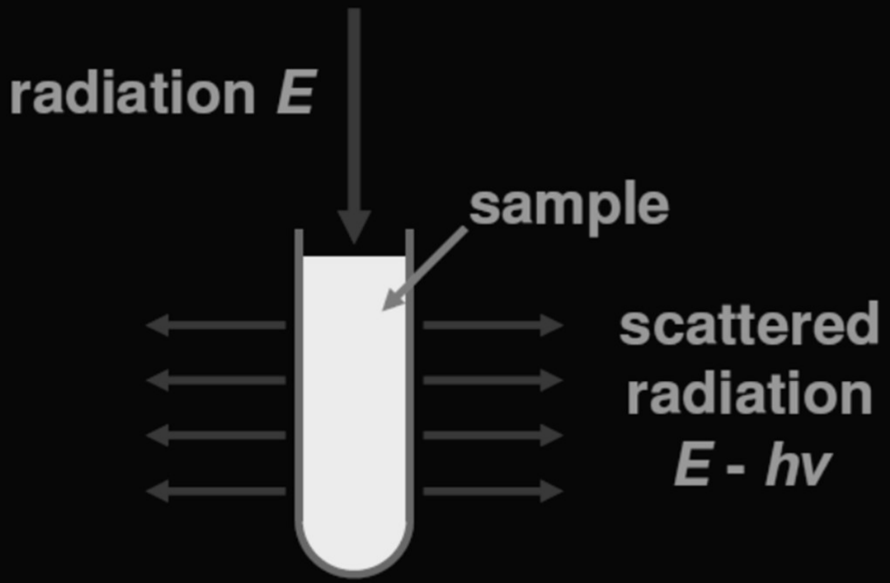
Character table

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_{v'}$	$h = 8$	
A_1	+1	+1	+1	+1	+1	z	$x^2 + y^2, z^2$
A_2	+1	+1	+1	-1	-1	R_z	
B_1	+1	-1	+1	+1	-1		$x^2 - y^2$
B_2	+1	-1	+1	-1	+1		xy
E	+2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)

Observing vibrations

Raman spectroscopy

Process – large quantum of energy E is scattered with energy E - *hv*



radiation *E*

sample

scattered radiation *E - hv*

Sample usually liquid, occasionally solid or gas

Activity – vibrational mode active if and only if it involves a polarisability change

Observing vibrations

Raman spectroscopy

Dipoles are vectors - μ_x etc. – symmetry properties as x, y, z

Polarisabilities are tensors – α_{xx}, α_{xy} etc. – properties as xx, xy

- listed in final column of character table

SiH_2Cl_2 $\Gamma_{vib} = 4A_1 + A_2 + 2B_1 + 2B_2$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$	
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

2. Molecular orbitals (wavefunctions) as the bases of irreducible representations of molecular point group.

Symmetry of wavefunctions of a molecule

Symmetry Operation ***R*** on Schrödinger ***Eq.***

$$\begin{tikzcd}
\hat{H}\psi_i = E_i\psi_i \arrow[r, "\boldsymbol{R}"] & \boldsymbol{R}\hat{H}\psi_i = \boldsymbol{R}E_i\psi_i \arrow[d] \\
\hat{H}\boldsymbol{R}\psi_i = E_i\boldsymbol{R}\psi_i \arrow[d] & \boldsymbol{R}\hat{H}\boldsymbol{R}^{-1}\boldsymbol{R}\psi_i = E_i\boldsymbol{R}\psi_i \arrow[l] \\
{} &
\end{tikzcd}$$

$\boldsymbol{R}\psi_i$ *is also an eigenfunction of* $\boldsymbol{\hat{H}}$, *with the same eigenvalue* $\boldsymbol{E}_i$ *as* ψ_i *corresponds to.*

Symmetry of wavefunctions

- If eigenvalue E_i is not degenerate, as ψ_i is normalized, it requires

$$\boxed{R\psi_i = c\psi_i = \pm 1\,\psi_i}$$

in order that $R\psi_i$ is also normalized.

- Hence, by applying each of the operations of the group to an eigenfunction ψ_i with a nongenerate eigenvalue, we generate a 1-D representation of the group with each matrix, $\Gamma_i(R)$, equal to +/-1.
- That is, each of the nondegenerate eigenfunctions is a basis of a 1-D I.R. of the very group!

Symmetry of wavefunctions

If the eigenvalue $\boldsymbol{E_i}$ is $\boldsymbol{k}$-fold degenerate with the eigenfunctions $\{\psi_{i1}, \psi_{i2}, \ldots, \psi_{ik}\}$,

$$\hat{H}\psi_{im} = E_i\psi_{im} \xrightarrow{R} \hat{H}R\psi_{im} = E_iR\psi_{im}$$

where $\boldsymbol{R}\psi_{im}$ may be a linear combination of ψ_{ij} $(j=1,2,\ldots,k)$.

$$\boxed{R\psi_{im} = \sum_{j=1}^{k} r_{jm}\psi_{ij}} \Longrightarrow \boxed{R\begin{bmatrix} \psi_{i1} \\ \psi_{i2} \\ \cdots \\ \psi_{ik} \end{bmatrix} = \begin{bmatrix} r_{11} & r_{12} & \cdots & r_{1k} \\ r_{21} & r_{22} & \cdots & r_{2k} \\ \cdot & \cdot & \cdots & \cdot \\ r_{k1} & r_{k2} & \cdots & r_{kk} \end{bmatrix}\begin{bmatrix} \psi_{i1} \\ \psi_{i2} \\ \cdots \\ \psi_{ik} \end{bmatrix}}$$

That is, the set of eigenfunctions $\{\psi_{i1}, \psi_{i2}, \ldots, \psi_{ik}\}$ is a basis for this $\boldsymbol{k}$-dimensional irreducible representation!

Symmetry of wavefunctions

In LCAO approach of MO theory, each of the MOs can be express as

$$\psi = \sum_{i=1}^{n} c_i \phi_i \quad (\text{AOs}: \phi_1, \phi_2, \dots, \phi_n)$$

So we need to solve the secular equation

$$\sum_{i=1}^{n} c_i \left(H_{ri} - E S_{ri} \right) = 0 \quad (r = 1, 2, \cdots, n)$$

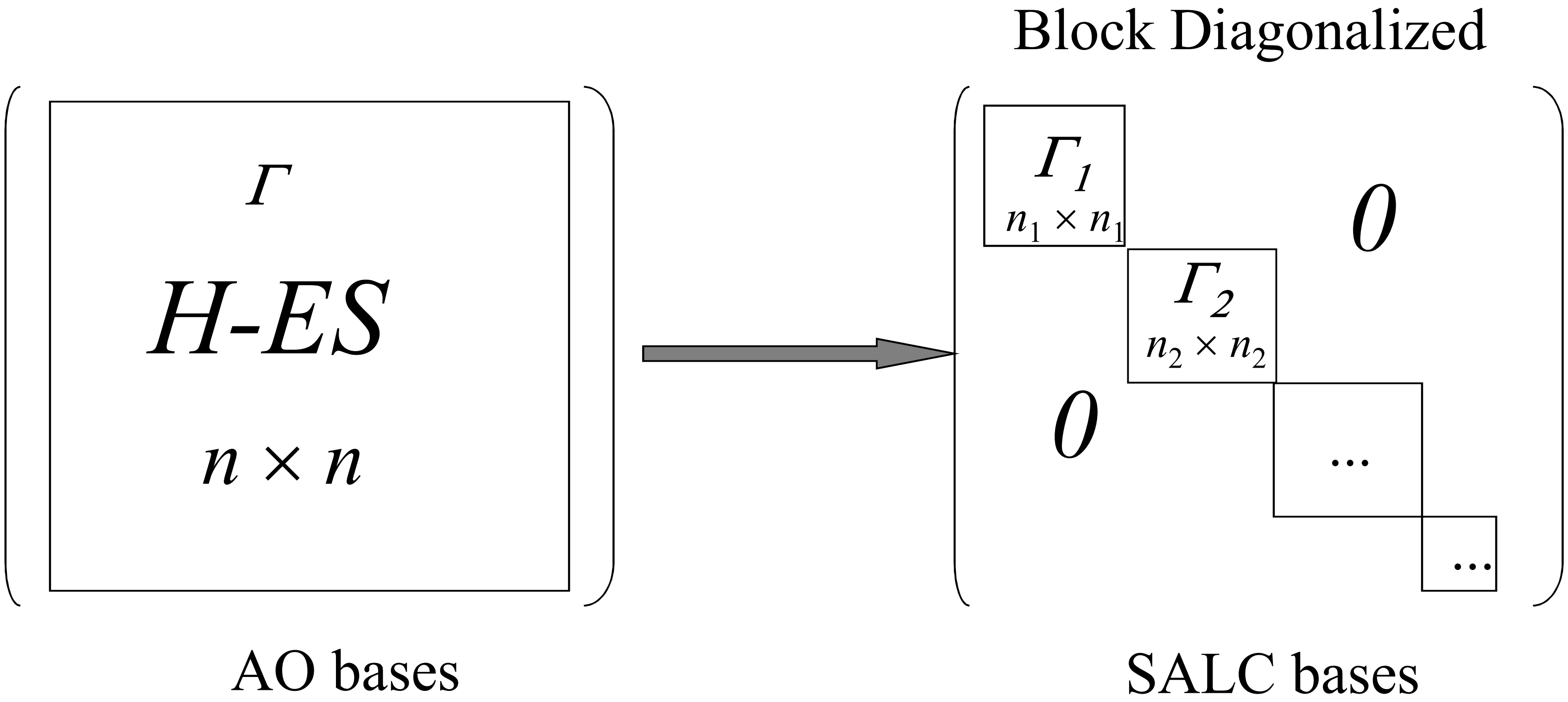
$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \cdots & H_{nn} - ES_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = 0$$

Symmetry of wavefunctions

We can transform the original bases of AO's into Linear Combinations of AO's which have the same properties of some I.R.s (Symmetry Adapted Linear Combination), therefore the Secular Equation is block-diagonalized.

$$\begin{array}{ccc} \text{AO} & & \text{SALC(MO)} \\ \begin{bmatrix}\phi_1\\ \phi_2\\ \vdots\\ \phi_n\end{bmatrix} & \xrightarrow{\quad ? \quad} & \begin{bmatrix}\psi_1\\ \psi_2\\ \vdots\\ \psi_n\end{bmatrix} \end{array}$$

Symmetry of wavefunctions



Block Diagonalized

Γ

$H-ES$

$n \times n$

Γ_1

$n_1 \times n_1$

0

Γ_2

$n_2 \times n_2$

0

...

...

AO bases

SALC bases

$$\Gamma = n_1\Gamma_1 \oplus n_2\Gamma_2 \oplus \ldots\ldots$$

Symmetry of wavefunctions

Step 1 Obtain the REP spanned by a set of AO basis (normally called basis set!)

Step 2 Reduce the REP spanned by the AO basis.

Obtain the n_i's for each **I.R.**

Step 3 Construct n_i SALCs for each **I.R.**.

Step 4 Transform the hamiltonian matrix into block diagonalized form, and solve it.

Symmetry greatly facilitates the computations!

Use Projection operator to construct SALCs

- Projection operator:

$$\hat{P}^{j} = \frac{l_j}{h}\sum_{R}\chi_j(R)\hat{R}$$

j-th I.R. of the group

derived from the "*great orthogonality theorem*".

- A non-normalized ***SALC*** can be constructed from AO-basis set by using the formula:

$$\Psi^{j}_{SALC} = \hat{P}^{j}\phi_i = \frac{l_j}{h}\sum_{R}\chi_j(R)\hat{R}\phi_i$$

An AO from the set of AO bases.

Example 1: H_2O

LCAO with the following atomic orbitals

O: $2s$; $2p_x$, $2p_y$, $2p_z$

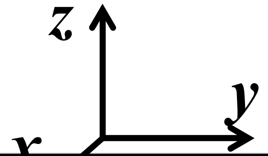
2H: $1s_a$, $1s_b$

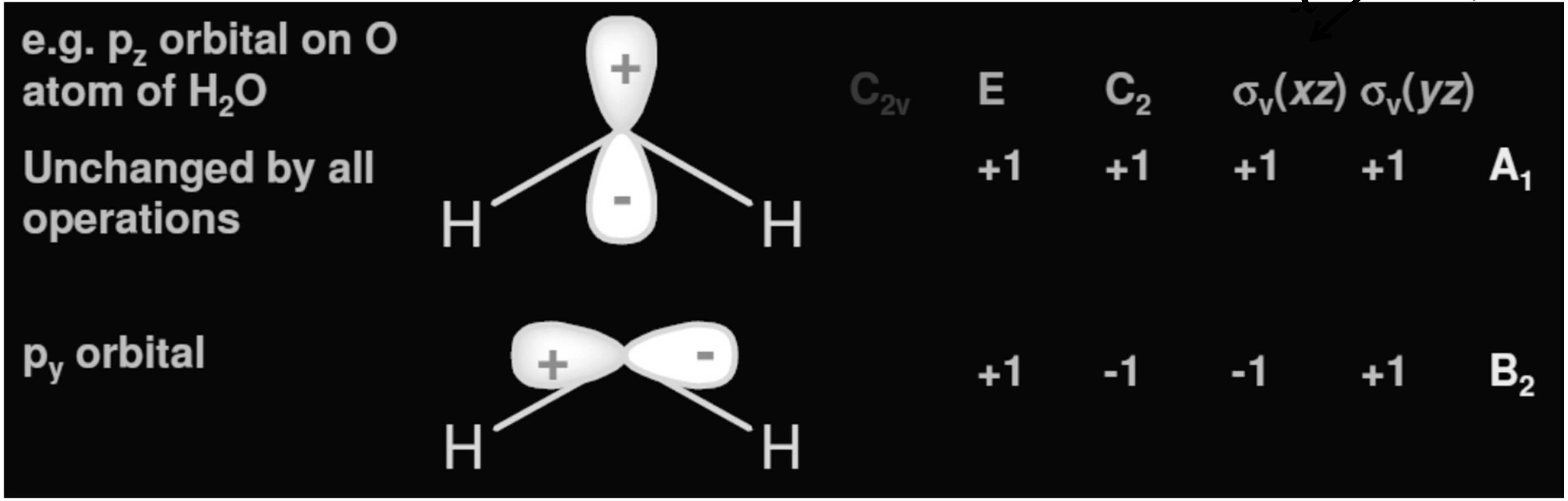
Symmetry: C_{2v}

First classify these AOs according to symmetry!

- Neglecting the O 1s orbital/electrons.

H_2O





	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
e.g. p_z orbital on O atom of H_2O Unchanged by all operations		+1	+1	+1	+1	A_1
p_y orbital		+1	-1	-1	+1	B_2

Character Table

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

Symmetry of AOs from Oxygen

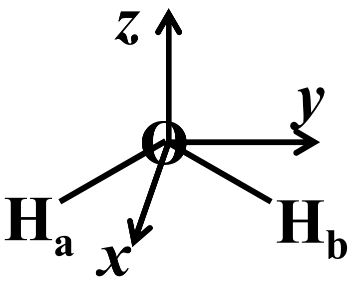
A_1 : $2s,\ 2p_z$

B_1 : $2p_x$

B_2 : $2p_y$

2H: $1s_a$, $1s_b$

Symmetry Reduction of 2-D Basis Set $\{1s_a, 1s_b\}$



C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz
Γ	**2**	**0**	**0**	**2**	

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

$$n_{A_1} = (1\times2+1\times0+1\times0+1\times2)/4 = 1$$

$$n_{B_1} = 0 \,\&\, n_{A_2} = 0$$

$$n_{B_2} = (1\times2-1\times0-1\times0+1\times2)/4 = 1$$

$$\boxed{\therefore \Gamma = A_1 \oplus B_2}$$

→ Two 1-D I.R.s

SALC - *Symmetry Adapted Linear Combination of AOs*

For this trivial problem, it is very simple. We intuitively determined the new basis as

***A*₁**: $\boxed{\frac{1}{\sqrt{2}}\left(1s_A + 1s_B\right)}$ + +

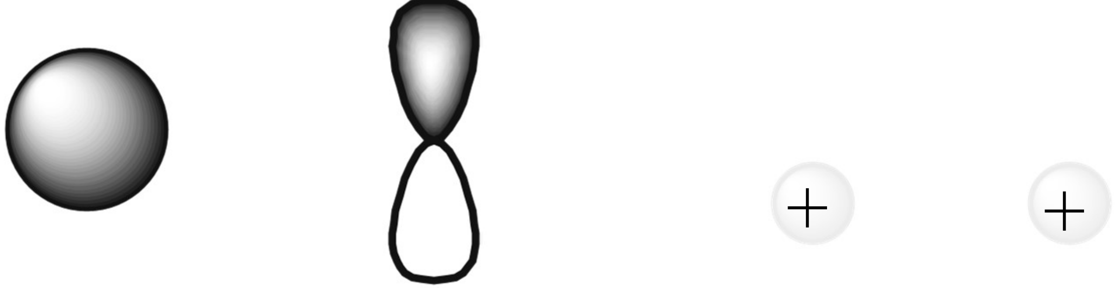
***B*₂**: $\boxed{\frac{1}{\sqrt{2}}\left(1s_A - 1s_B\right)}$ - +

For more complicated problem, the projection operator can be used to construct SALC of AOs. Plz confirm the above two SALCs by using the projection operator.

H_2O

A_1 symmetry AOs or SALCs for LCAO

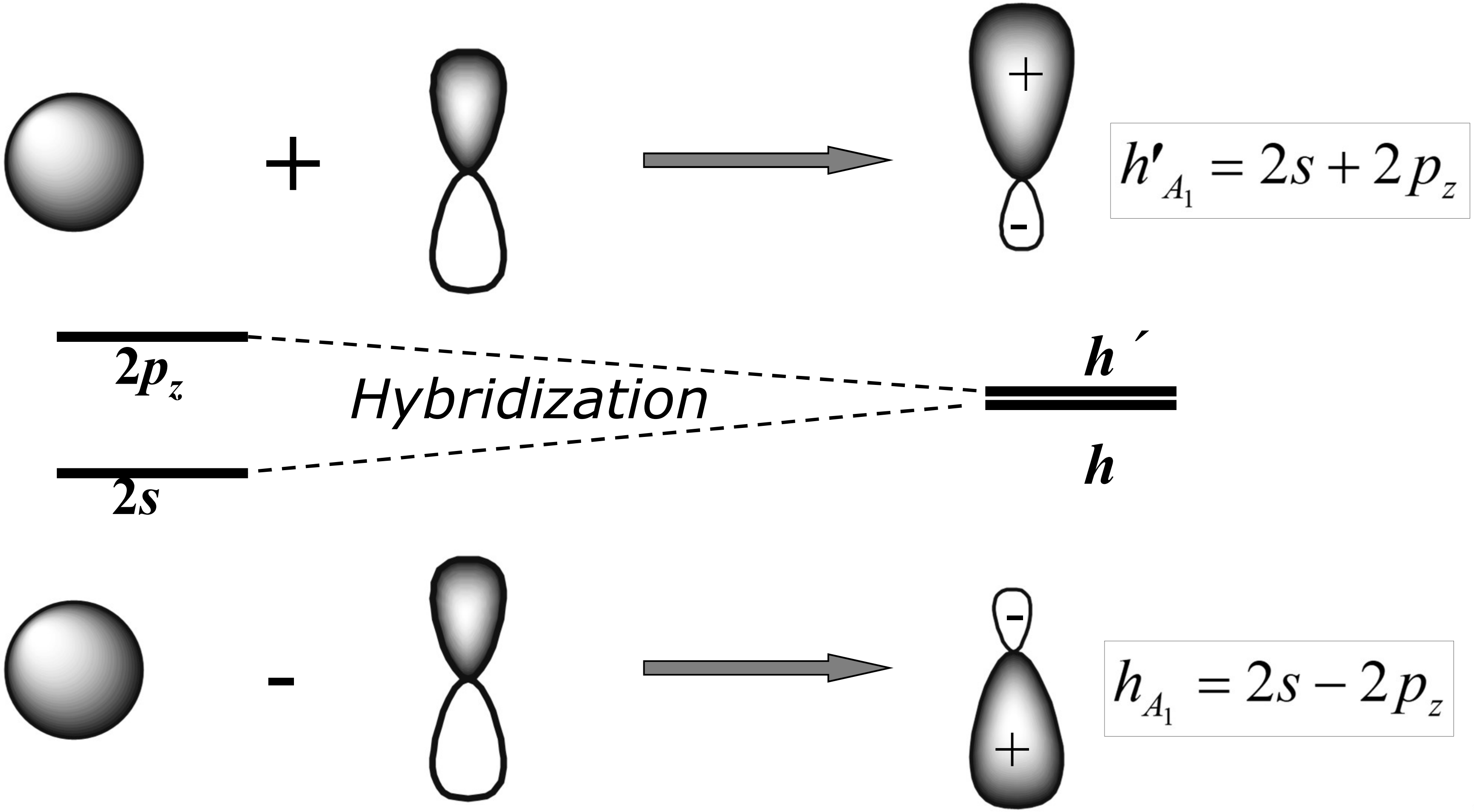
A_1 : **O2*s*,** **O2p_z** $\boxed{\phi_{A_1}}$



- Both AOs of the O atom can interact with the SALC of H 1s AOs.

- Hybridization of the two AOs of O atom is needed!

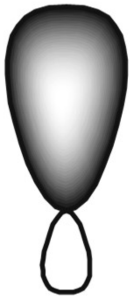
H_2O- Hybridization of Oxygen’s 2*s* and 2p_z



$$h'_{A_1} = 2s + 2p_z$$

$$h_{A_1} = 2s - 2p_z$$

H_2O- Hybridization of Oxygen’s 2*s* and $2p_z$



h´

h

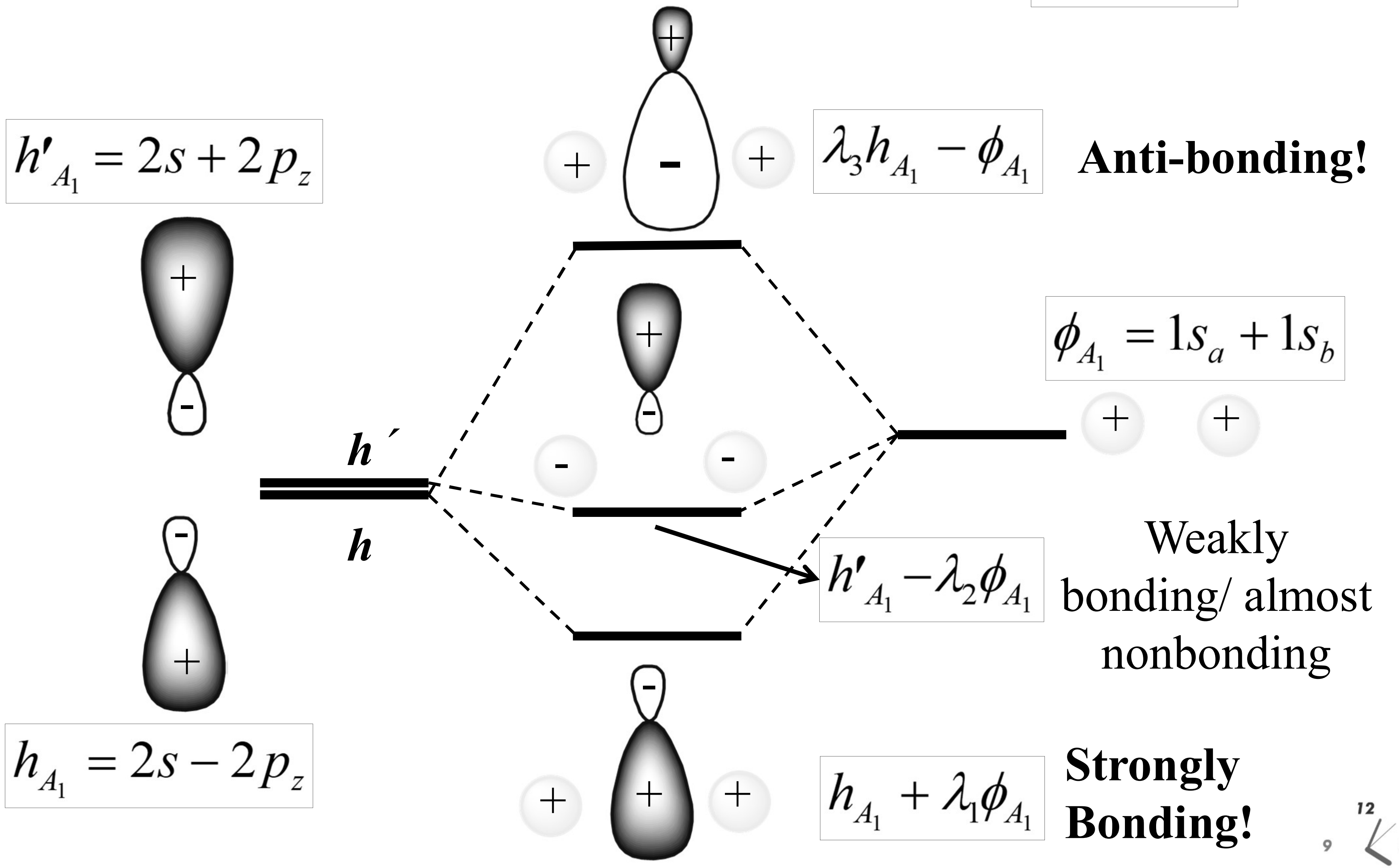
ϕ_{A_1}

$\int h'^{*} \phi_{A_1} d\tau$ ***Small***, not effective bonding

$\int h^{*} \phi_{A_1} d\tau$ ***Large***, effective bonding

H_2O- Chemical Bonding in A_1 REP

$0 < \lambda_i < 1$



$h'_{A_1} = 2s + 2p_z$

$h_{A_1} = 2s - 2p_z$

$\lambda_3 h_{A_1} - \phi_{A_1}$ **Anti-bonding!**

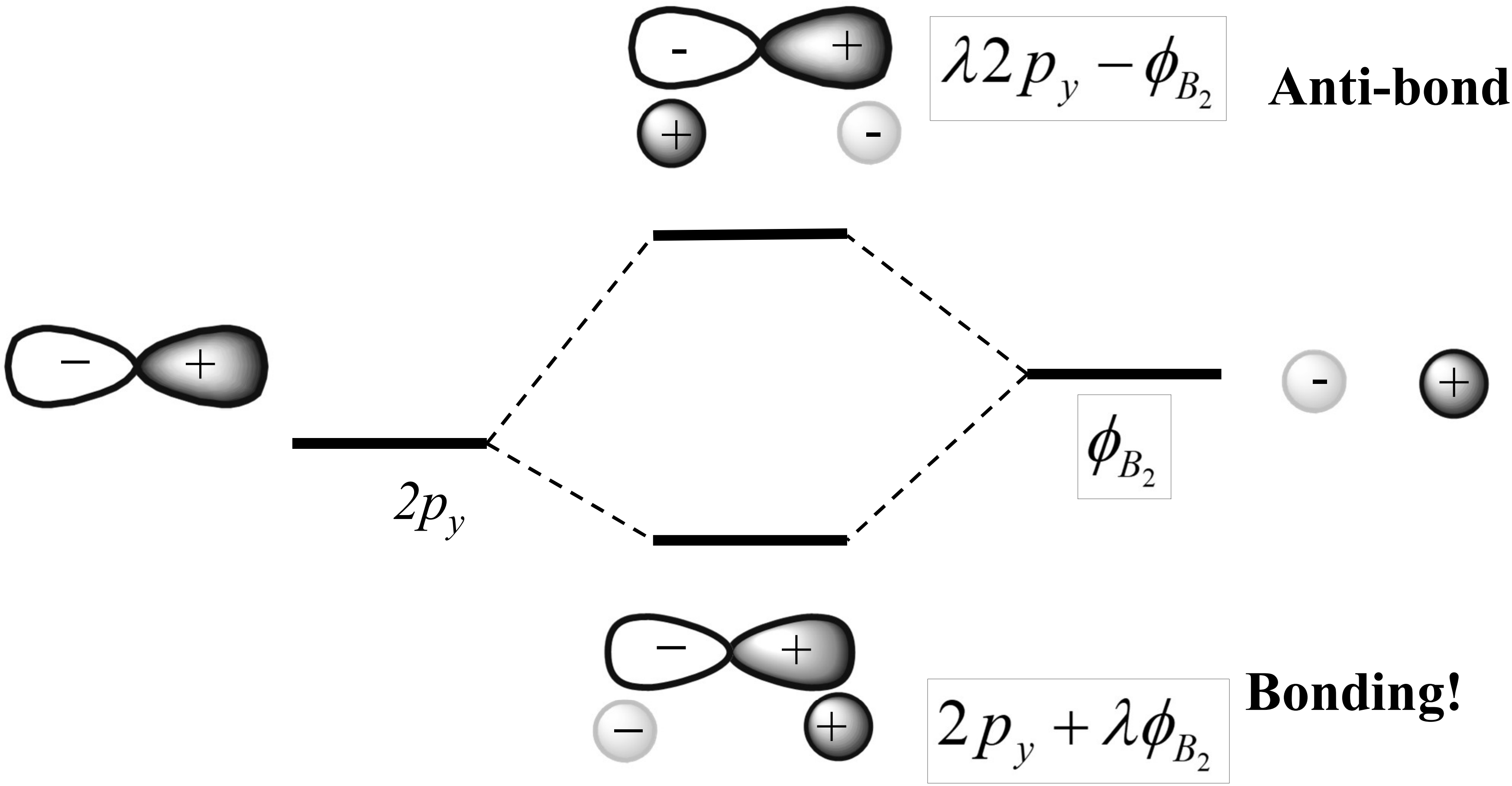
$\phi_{A_1} = 1s_a + 1s_b$

$h'_{A_1} - \lambda_2 \phi_{A_1}$ Weakly bonding/ almost nonbonding

$h_{A_1} + \lambda_1 \phi_{A_1}$ **Strongly Bonding!**

H_2O- Chemical Bonding in B_2 REP

$0 \le \lambda \le 1$



$\lambda 2p_y - \phi_{B_2}$

Anti-bonding!

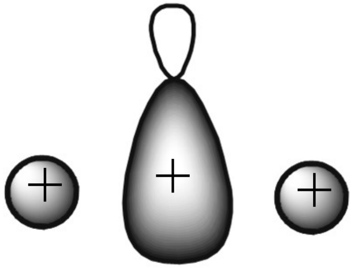
$2p_y$

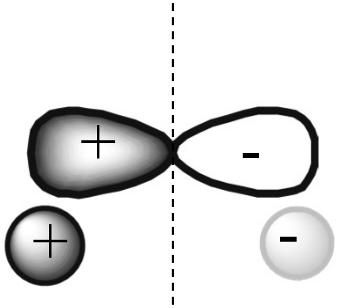
ϕ_{B_2}

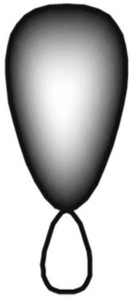
$2p_y + \lambda \phi_{B_2}$

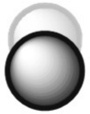
Bonding!

H_2O- Summary on Molecular Energy Level Sequences



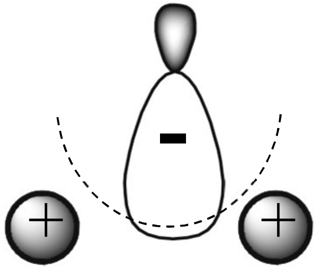


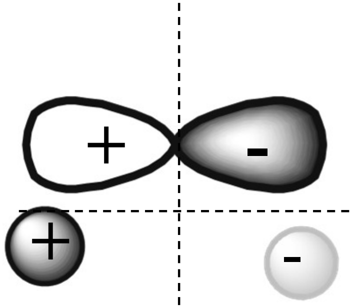




$2a_1$ $\leq$ **$1b_2$** $\leq$ **$3a_1$** $\leq$ **$1b_1$**

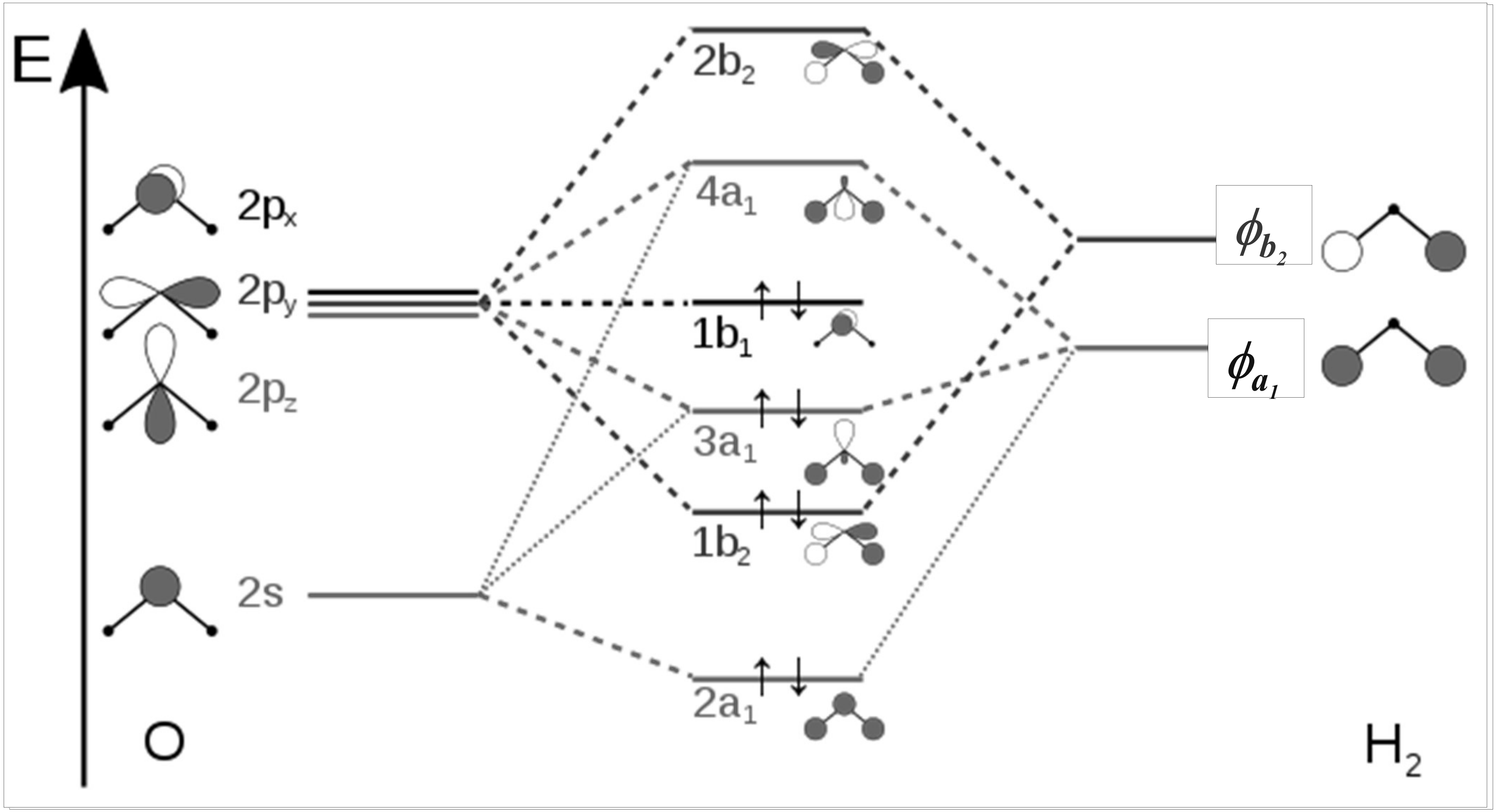
(O $2p_x$)





$\leq$ **$4a_1$** $\leq$ **$2b_2$**

H_2O- Summary on Chemical Bonding



The lowest energy transitions are broad at ***7.61*** and ***9.36 eV*** for the ***$4a_1 \leftarrow 1b_1$*** and ***$4a_1 \leftarrow 3a_1$*** transitions respectively for the gas phase and at **8.09** and ***9.74 eV*** in the liquid.

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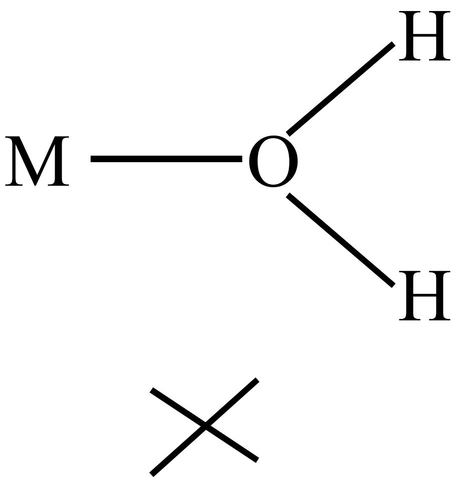
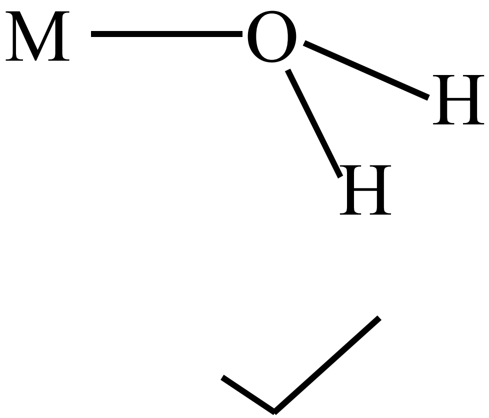
Questions

- For H_2O, which two MOs of its MO model can be regarded as equivalence of the two lone pairs of its VB model?
- H_2O can form hydrated cations with metal cations in aqueous solution. However, it is seldom to find the M-H_2O bonding in the coplanar manner. Why?

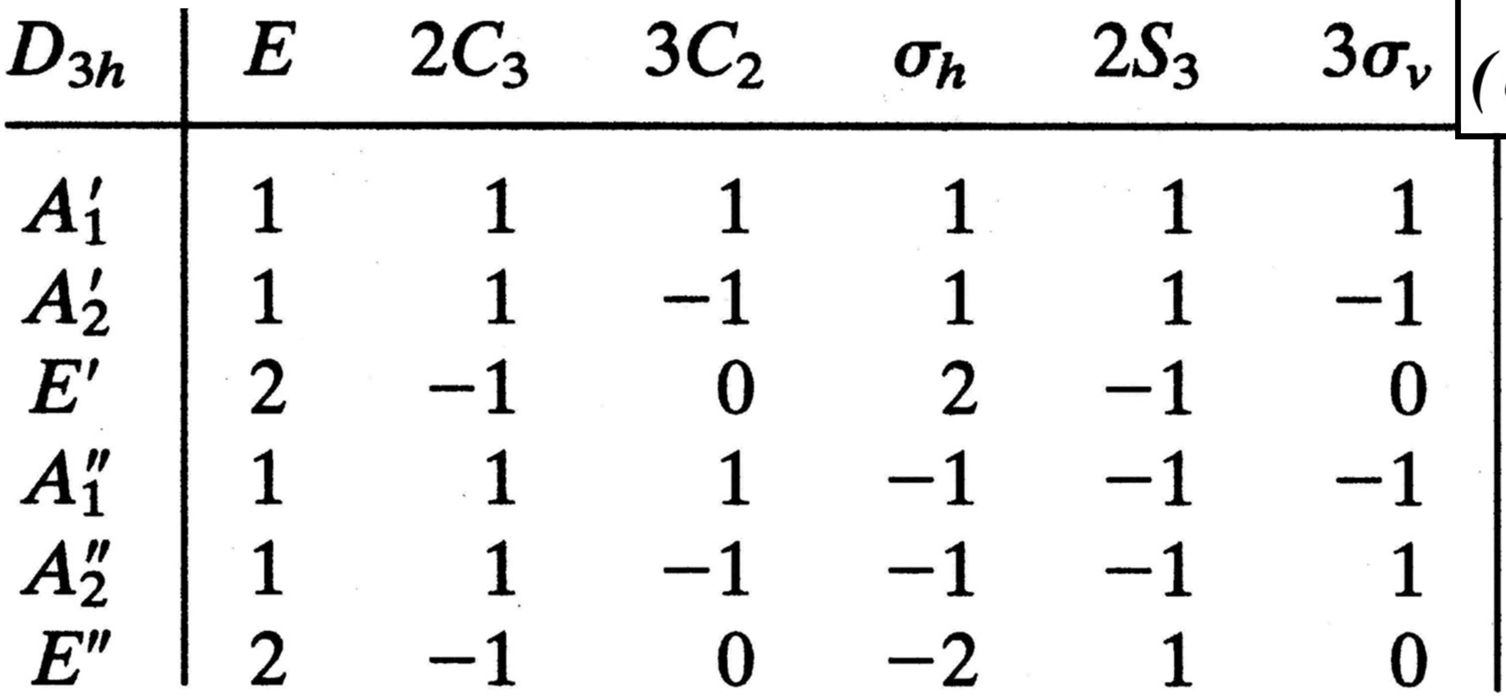




Example 2: π-MOs of C_3H_3 (D_{3h})

$$\Psi = \sum_i c_i\phi_i$$

$$(\phi = p_\pi = p_z)$$



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0
A_1''	1	1	1	−1	−1	−1
A_2''	1	1	−1	−1	−1	1
E''	2	−1	0	−2	1	0
Γ	**3**	**0**	**–1**	**–3**	**0**	**1**

Basis set

{ϕ_1, ϕ_2, ϕ_3}

Step 1: get the REP.

Reducible!

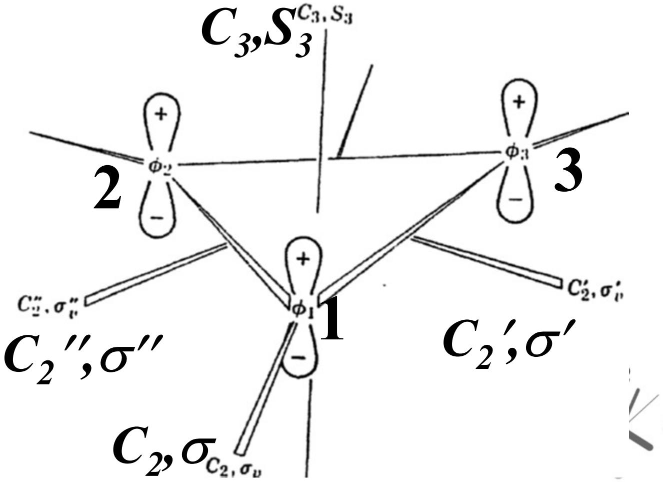
- *Step 2: By applying to **all** I.R.s, we have*

$$a_i = \frac{1}{h}\sum_c g_c \cdot \chi(c) \cdot \chi_i(c)$$

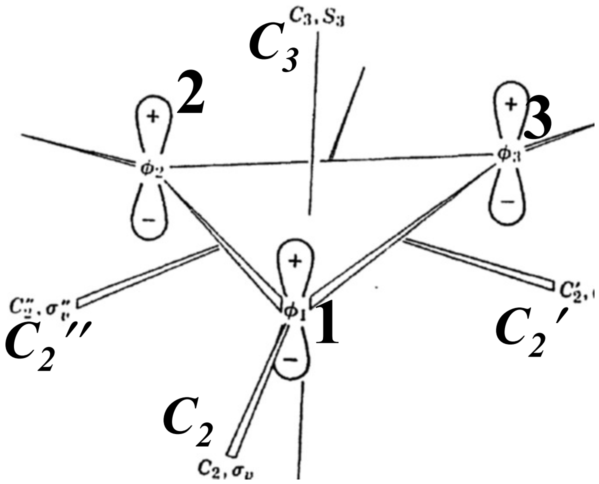
$$\Gamma = A_2'' \oplus E''$$

$$\hat{P}^{\Gamma_i}\phi_1 = \frac{l_i}{h}\sum_R \chi_i(\hat{R})\hat{R}\phi_1$$

- Step 3: use projection operator to obtain SALCs. (a bit tedious!)



To save time, use subgroup D_3



sym. op. → count ***1,-1,0*** if an AO transforms to itself, minus itself or moves.

D_3	E	$2C_3$	$3C_2'$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
Γ_π	**3**	**0**	**−1**

Basis set $\{\phi_1, \phi_2, \phi_3\}$

Now reduce Γ_π by using the formula,

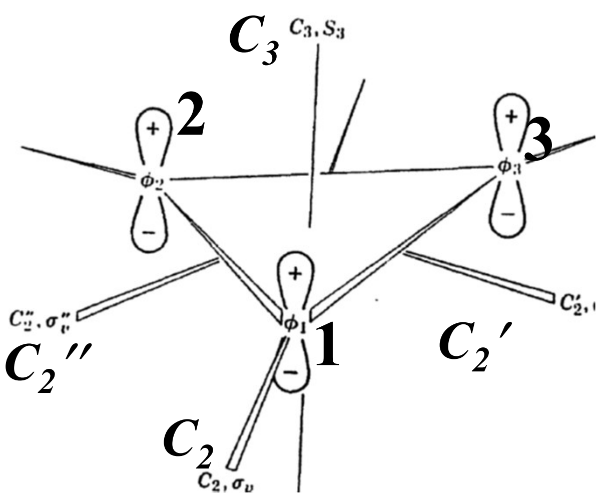
$$a_i = \frac{1}{h}\sum_c g_c \,.\, \chi(c) \,.\, \chi_i(c)$$

$$a_{A_1} = \frac{1}{6}\{3\cdot 1+2\cdot(0\cdot 1)+3\cdot(-1)\cdot 1\}=0$$

$$a_{A_2} = \frac{1}{6}\{3\cdot 1+2\cdot(0\cdot 1)+3\cdot(-1)(-1)\}=1$$

$$a_E = \frac{1}{6}\{3\cdot 2+2\cdot 0\cdot(-1)+3(-1)\cdot 0)\}=1$$

⇨ $\Gamma_\pi = A_2 \oplus E$



	E	$2C_3$	$3C_2'$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
Γ_π	**3**	**0**	**–1**

Basis set

$\{\phi_1, \phi_2, \phi_3\}$

$$a_i = \frac{1}{h}\sum_c g_c \cdot \chi(c) \cdot \chi_i(c)$$

$$\Gamma_\pi = A_2 \oplus E$$

- Now use the projection operator to derive the SALCs (MOs).

$$\hat{P}^{\Gamma_i}\phi_1 = \frac{l_i}{h}\sum_R \chi_i(\hat{R})\hat{R}\phi_1$$

$$\hat{P}^{A_2}\phi_1 = \frac{l_{A_2}}{h}\sum_R \chi_{A_2}(\hat{R})\hat{R}\phi_1 = \frac{1}{6}(E\phi_1 + C_3^1\phi_1 + C_3^2\phi_1 - C_2\phi_1 - C_2'\phi_1 - C_2''\phi_1)$$

$$= \frac{1}{6}(\phi_1 + \phi_2 + \phi_3 + \phi_1 + \phi_3 + \phi_2)$$

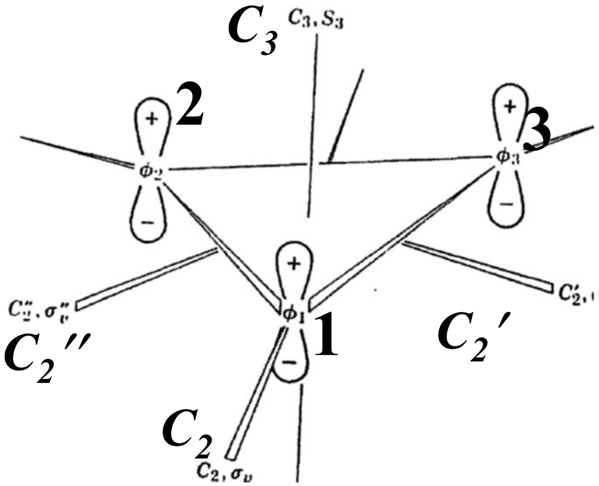
$$= \frac{1}{3}(\phi_1 + \phi_2 + \phi_3)$$

(not normalized yet!)

$$\text{suppose} \int \phi_i \phi_j d\tau \approx \delta_{ij}$$

$$\xrightarrow[\textit{Normalization}]{\textit{Hückel approx.}}$$

$$\boxed{\Psi^{A_2} = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)}$$



	E	$2C_3$	$3C_2'$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
Γ_π	**3**	**0**	**−1**

Basis set

$\{\phi_1, \phi_2, \phi_3\}$

$$a_i = \frac{1}{h}\sum_c g_c \cdot \chi(c) \cdot \chi_i(c)$$

$$\Gamma_\pi = A_2 \oplus E$$

$$\hat{P}^{\Gamma_i}\phi_1 = \frac{l_i}{h}\sum_R \chi_i(\hat{R})\hat{R}\phi_1$$

For one of the E-type MOs, we have

$$\hat{P}^E\phi_1 = \frac{l_E}{h}\sum_R \chi_E(\hat{R})\hat{R}\phi_1 = \frac{2}{6}(2E\phi_1 - C_3^1\phi_1 - C_3^2\phi_1)$$

$$= \frac{1}{3}(2\phi_1 - \phi_2 - \phi_3)$$

Normalization

$$\Psi_1^E = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$$

- Using orthogonality and normalization, we have

$$\Psi_2^E = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

Yet not simple!

Another way to derive the third MO:

Step 1. Find an operation to covert the second wavefunction into an nonequivalent one (not +/- of the original one). A C_3 operation works well. Then we have

$$C_3^1 \Psi_1^E = (2\phi_2 - \phi_3 - \phi_1)$$

Step 2. A linear combination of this new one and the original one gives rise to

$$C_3^1 \Psi_1^E + A \bullet \Psi_1^E = (2\phi_2 - \phi_3 - \phi_1) + (\frac{1}{2})(2\phi_1 - \phi_2 - \phi_3)$$

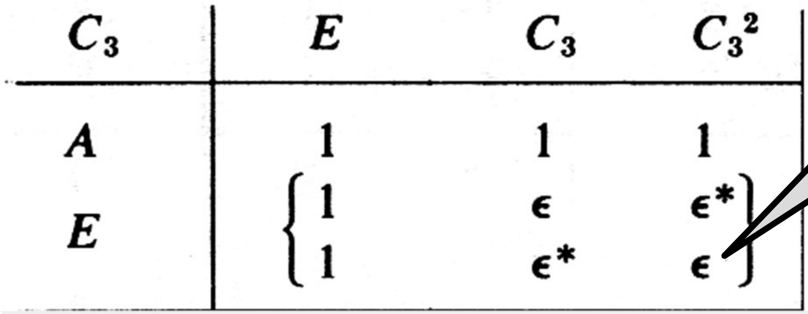
$$= \frac{3}{2}(\phi_2 - \phi_3) \xrightarrow[\text{normalization}]{} \Psi_2^E = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

For high-symmetry molecules that have degenerate MOs pertaining to 2- or 3-D I.R.s, it is more convenient to make use of cyclic group REP!

A general simplification

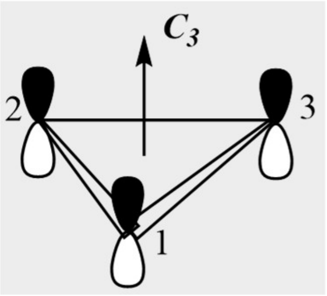
- Further reducing the symmetry to C_3 subgroup, a cyclic group.

(* I.R.s of a cyclic group can sometimes have complex characters.)



C_3	E	C_3	C_3^2
A	1	1	1
E	$\begin{cases}1 \\ 1\end{cases}$	$\begin{matrix}\epsilon \\ \epsilon^*\end{matrix}$	$\begin{rcases}\epsilon^* \\ \epsilon\end{rcases}$

$\varepsilon = e^{2\pi i/3}$



Γ_π 3 0 0

$\Gamma_\pi = A \oplus E$

$$\hat{P}^{\Gamma_i}\phi_1 = \frac{l_i}{h}\sum_R \chi_i(\hat{R})\hat{R}\phi_1$$

$$\hat{P}^{A}\phi_1 \approx \sum_R \chi(\hat{R})^{A}\hat{R}\phi_1 = E\phi_1 + C_3^1\phi_1 + C_3^2\phi_1 = \phi_1 + \phi_2 + \phi_3$$

$$\hat{P}^{E(1)}\phi_1 \approx \sum_R \chi(\hat{R})^{E(1)}\hat{R}\phi_1 = \phi_1 + \varepsilon C_3^1\phi_1 + \varepsilon^* C_3^2\phi_1 = \phi_1 + \varepsilon\phi_2 + \varepsilon^*\phi_3$$

$$\hat{P}^{E(2)}\phi_1 \approx \sum_R \chi(\hat{R})^{E(2)}\hat{R}\phi_1 = \phi_1 + \varepsilon^*\phi_2 + \varepsilon\phi_3$$

$$\Psi_1^A = A\hat{P}^A\phi_1$$
$$= A(\phi_1 + \phi_2 + \phi_3) = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$$

A for normalization!

(Note that the Hückel approximation is used in the normalization of these MOs!)

$$\text{define } \int \phi_i \phi_j d\tau \approx \delta_{ij}$$

$$\Psi_1^E = A(\hat{P}^{E(1)}\phi_1 + \hat{P}^{E(2)}\phi_1)$$
$$= A(2\phi_1 + 2\cos(\frac{2\pi}{3})\phi_2 + 2\cos(\frac{2\pi}{3})\phi_3) = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$$

$$\Psi_2^E = A(\hat{P}^{E(1)}\phi_1 - \hat{P}^{E(2)}\phi_1)$$
$$= Ai(2\sin(\frac{2\pi}{3})\phi_2 - 2\sin(\frac{2\pi}{3})\phi_3) = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

Now Let's return to the D_{3h} point group. we can prove that Ψ_1^A belongs to A_2'', and $\{\Psi_1^E, \Psi_2^E\}$ belongs to E''.

Example 2: C_6H_6 D_{6h} → C_6 Basis set $\{\phi_1, \phi_2, \ldots, \phi_6\}$

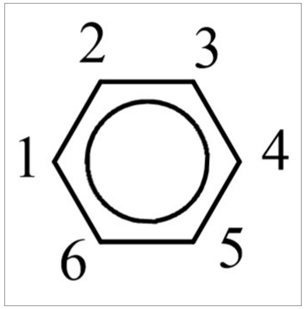
C_6	E	C_6	C_3	C_2	C_3^2	C_6^5		$\varepsilon = exp(2\pi i/6)$
A	1	1	1	1	1	1	z, R_z	x^2+y^2, z^2
B	1	-1	1	-1	1	-1		
E_1	1	ε	$-\varepsilon$	-1	$-\varepsilon$	ε^*	(x, y)	(xz,yz)
	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε	(R_x, R_y)	
E_2	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		(x^2-y^2, xy)
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		
Γ_π	6	0	0	0	0	0	$\Gamma_\pi = A \oplus B \oplus E_1 \oplus E_2$	

$$\hat{P}^A \phi_1 \approx \sum_R \chi(\hat{R})^A \hat{R}\phi_1 = E\phi_1 + C_6^1\phi_1 + C_6^2\phi_1 + C_6^3\phi_1 + C_6^4\phi_1 + C_6^5\phi_1$$

$$= \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 \Rightarrow \Psi^A = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\hat{P}^B \phi_1 \approx \sum_R \chi(\hat{R})^B \hat{R}\phi_1 = E\phi_1 - C_6^1\phi_1 + C_6^2\phi_1 - C_6^3\phi_1 + C_6^4\phi_1 - C_6^5\phi_1$$

$$= \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 \Rightarrow \Psi^B = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$



$$\phi_i = p_\pi$$

C_6H_6 D_{6h} → C_6

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5		$\varepsilon = exp(2\pi i/6)$
A	1	1	1	1	1	1	z, R_z	x^2+y^2, z^2
B	1	-1	1	-1	1	-1		
E_1	1	ε	$-\varepsilon$	-1	$-\varepsilon$	ε^*	(x, y)	(xz,yz)
	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε	(R_x, R_y)	
E_2	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		(x^2-y^2, xy)
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		
Γ_π	6	0	0	0	0	0	$\Gamma_\pi = A \oplus B \oplus E_1 \oplus E_2$	

$$\hat{P}^{E_1(1)}\phi_1 \approx \sum_R \chi(\hat{R})^{E_1(1)}\hat{R}\phi_1 = E\phi_1 + \varepsilon C_6^1\phi_1 - \varepsilon^* C_6^2\phi_1 - C_6^3\phi_1 - \varepsilon C_6^4\phi_1 + \varepsilon^* C_6^5\phi_1$$
$$= \phi_1 + \varepsilon\phi_2 - \varepsilon^*\phi_3 - \phi_4 - \varepsilon\phi_5 + \varepsilon^*\phi_6$$

$$\hat{P}^{E_1(2)}\phi_1 \approx \sum_R \chi(\hat{R})^{E_1(2)}\hat{R}\phi_1 = E\phi_1 + \varepsilon^* C_6^1\phi_1 - \varepsilon C_6^2\phi_1 - C_6^3\phi_1 - \varepsilon^* C_6^4\phi_1 + \varepsilon C_6^5\phi_1$$
$$= \phi_1 + \varepsilon^*\phi_2 - \varepsilon\phi_3 - \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6$$

$$\Psi^{E_1}(1) = A(\hat{P}^{E_1(1)}\phi_1 + \hat{P}^{E_1(2)}\phi_1) = 2A(\phi_1 + \cos(\frac{\pi}{3})\phi_2 - \cos(\frac{\pi}{3})\phi_3 - \phi_4 - \cos(\frac{\pi}{3})\phi_5 + \cos(\frac{\pi}{3})\phi_6)$$

$$= \frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)$$

$$\Psi^{E_1}(2) = A(\hat{P}^{E_1(1)}\phi_1 - \hat{P}^{E_1(2)}\phi_1) = 2Ai(-\sin(\frac{\pi}{3})\phi_2 - \sin(\frac{\pi}{3})\phi_3 + \sin(\frac{\pi}{3})\phi_5 + \sin(\frac{\pi}{3})\phi_6)$$

$$= \frac{1}{2}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

Similarly, we have

$$\Psi^{E_2}(1) = A(\phi_5 + \phi_6) = \frac{1}{\sqrt{12}}(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 + \phi_6)$$

$$\Psi^{E_2}(2) = A(\phi_5 - \phi_6)/i = \frac{1}{2}(-\phi_2 + \phi_3 - \phi_5 + \phi_6)$$

Assignments:

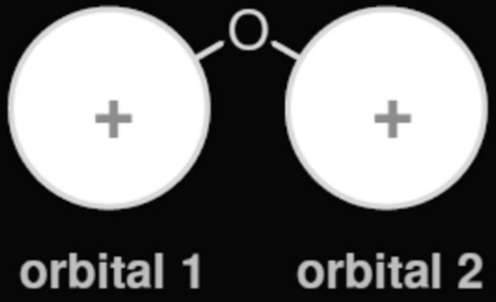
- Please figure out all the normal vibrations of NH_3 and discern whether they are IR- or Raman-active!
- Construct the π-MOs of Naphthalene with the p_π AOs of carbon atoms.

The End of Chapter 3!

Characters for more than one object or action

We can make representations of several things

e.g. H 1s orbitals in H_2O



$$E\begin{pmatrix} 1s_1 \\ 1s_2 \end{pmatrix} = \begin{pmatrix} 1s_1 \\ 1s_2 \end{pmatrix}$$

$$\Rightarrow E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

E operation orbital 1’ = orbital 1

orbital 2’ = orbital 2

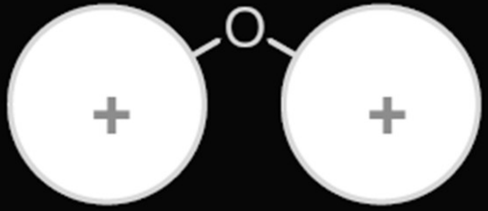
Each is unchanged (= 1 x itself), so the character is 2

[Strictly speaking the character is the *trace* (sum of diagonal terms) of the *transformation matrix*. $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$]

Characters for more than one object or action

Representations of several things

e.g. H 1s orbitals in H_2O



$$C_2 \begin{pmatrix} 1s_1 \\ 1s_2 \end{pmatrix} = \begin{pmatrix} 1s_2 \\ 1s_1 \end{pmatrix}$$

$$\Rightarrow C_2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

C_2 operation

orbital 1' = orbital 2

orbital 2' = orbital 1

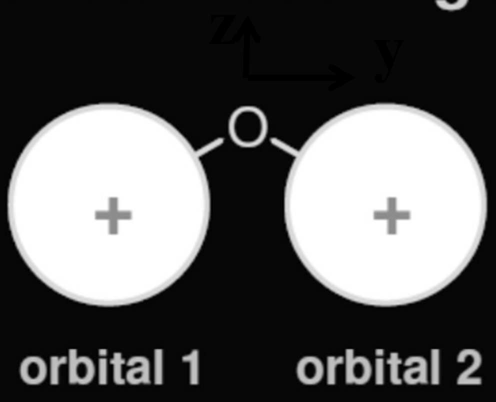
There is no contribution from the old orbital 1 to the new one (= 0 x itself), so the character is 0

[The trace of the transformation matrix is zero. $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$]

Characters for more than one object or action

Representations of several things

e.g. H 1s orbitals in H_2O



$$\sigma_{xz}\begin{pmatrix}1s_1\\1s_2\end{pmatrix}=\begin{pmatrix}1s_2\\1s_1\end{pmatrix}$$

$$\Rightarrow \sigma_{xz}=\begin{pmatrix}0&1\\1&0\end{pmatrix} \quad \chi(\sigma_{xz})=0$$

$$\sigma_{yz}\begin{pmatrix}1s_1\\1s_2\end{pmatrix}=\begin{pmatrix}1s_1\\1s_2\end{pmatrix}$$

$$\Rightarrow \sigma_{yz}=\begin{pmatrix}1&0\\0&1\end{pmatrix} \quad \chi(\sigma_{yz})=2$$

E operation	character is +2
C2	0
$\sigma_v(xz)$	0
$\sigma_v(yz)$	+2

	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
so overall:		+2	0	0	+2

This the *reducible representation* of the set of 2 orbitals.

Reducible representations

This set of characters does not appear in the character table

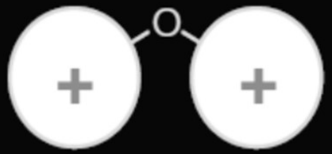
- but it can always be expressed as a sum of lines

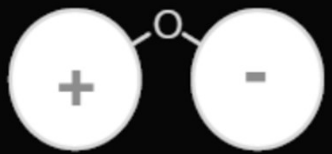
Character table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$
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

Must be an A and a B to make the second number = 0

Must then be $A_1 + B_2$ to make final number = 2





A_1 is the symmetric combination

B_2 is the asymmetric combination

$A_1 + B_2$ is the *irreducible representation* of the two orbitals