Chemical Applications of Group Theory

Some Readings

Chemical Application of Group Theory

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Symmetry through the Eyes of a Chemist

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The Most Beautiful Molecule - an Adventure in Chemistry

H. Aldersey-Williams

Perfect Symmetry

J. Baggott

- The symmetry of molecules and solids is a very powerful tool for developing an understanding of bonding and physical properties
  - Used to predict the nature of molecular orbitals
  - Used to predict if electronic and vibration spectroscopic transitions can be observed
- We will cover the following material:
  - Identification/classification of symmetry elements and symmetry operations
  - Assignment of point groups
    - » The point group of a molecule uniquely and fully describes the molecules symmetry
  - Identifying polarity and chirality using point groups
  - Introduction to what a "Character Table" is
  - Assigning symmetry labels to "Symmetry adapted linear combination or orbitals"
  - Assigning symmetry labels to of vibration modes
  - Determining the IR and Raman activity of vibrational modes

- We have learnt the point group theory of molecular symmetry. We shall learn how to use this theory in our chemical research.

1. Representation of groups

1.1 Matrix representation and reducible representation

Total Representation for C_{2v}

Individually block diagonalized matrices

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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

Γ_{Rz} = 1 1 -1 -1

1.2 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.
- If we make the same similarity transformation on each matrix, we obtain a new set of matrices,

$$A' = \Gamma A \Gamma^{-1};\ B' = \Gamma B \Gamma^{-1}; C' = \Gamma C \Gamma^{-1} \quad \ldots$$

- This new set of matrices is also a representation of the group.
- If A' is a blocked-factored matrix, then it is easy to prove that B',C'… also are blocked-factored matrices.

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

$A_1, A_2, A_3 \ldots$ are $n_1, n_2, n_3 \ldots$-D submatrices with $n = n_1 + n_2 + n_3 + \ldots$

- Furthermore, it is also provable that the various sets of submatrices

  $\{A_1,B_1,C_1\ldots\}$, $\{A_2,B_2,C_2\ldots\}$, $\{A_3,B_3,C_3\ldots\}$, $\{A_4,B_4,C_4\ldots\}$,

  are in themselves representations of the group.
- We then call the set of matrices A,B,C, … a reducible representation of the group.
- 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 group is of fundamental importance.

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

Bases

Top line: point group

symmetry operations

order of group, h, = number of symmetry operations

2.1 Construction of Character Table

Total Representation for C_{2v}

Individually block diagonalized matrices

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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

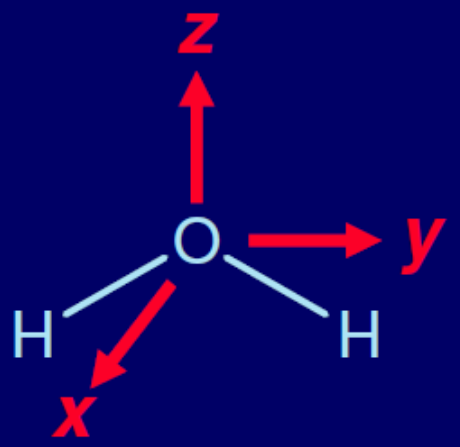
Γ_z = 1 1 1 1

Γ_{Rz} = 1 1 -1 -1

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 x 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



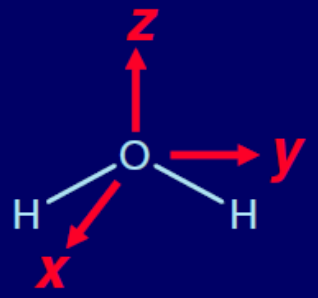
Translations

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.

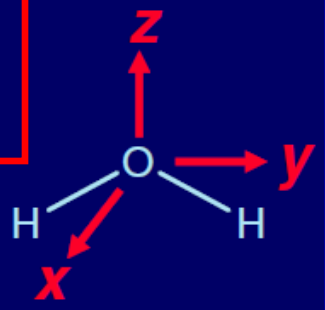


These translation vectors constitute a set of bases of C_{2v} group

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

2.2 symmetry species: Mulliken symbols

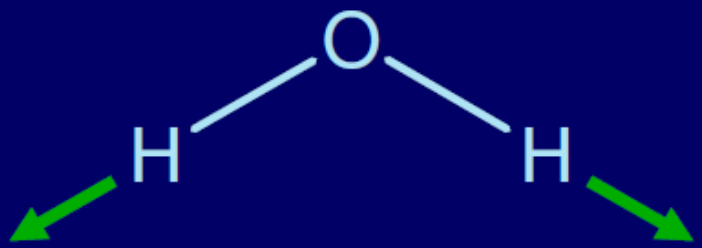
C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$
II		I		III	IV

- 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 σ_h

2.3 Symmetry of molecular properties

Translations and rotations can be assigned to symmetry species – and so can other molecular properties

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
symmetric stretch of O-H bonds	+1	-1	-1	+1	B_2

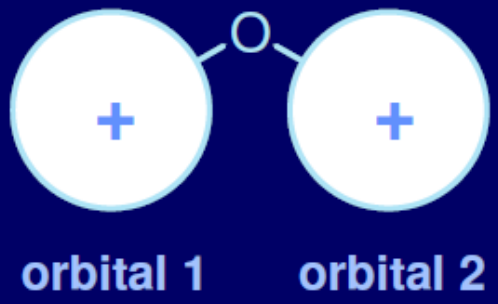


This set of characters is the *representation* of the symmetric stretch

Characters for more than one object or action

We can make representations of several things

e.g. H 1s orbitals in H_2O



E operation orbital 1' = orbital 1

orbital 2' = orbital 2

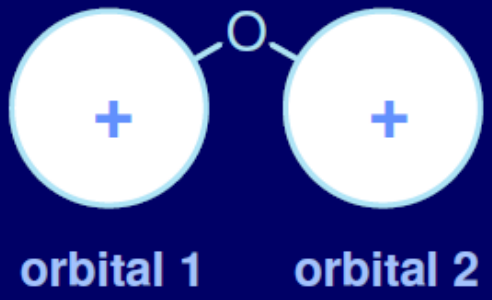
Each is unchanged (= 1 x itself), so the character is 2

[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 operation

orbital 1' = orbital 2

orbital 2' = orbital 1

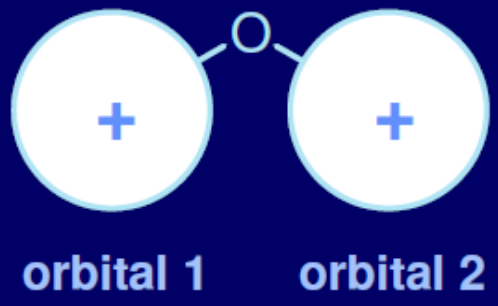
There is no contribution from the old orbital 1 to the new one (= 0 x itself), so the character is 0

[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



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

so overall:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
	+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

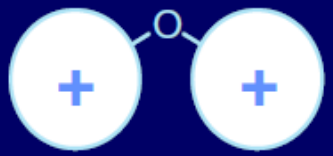
- but it can always be expressed as a sum of lines

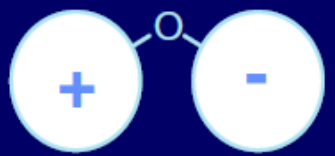
Character table

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

Reducing representations

The hard way – solve a set of simultaneous equations

The easy way – use the formula provided

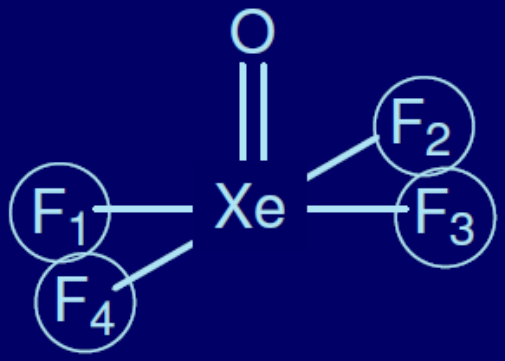
Formula is $$a_i = \frac{1}{h} \sum_R g_R \cdot \chi(R) \cdot \chi_i(R)$$

- a_i is the number of 'things' (orbitals etc.) of symmetry species I
- h is the order of the group
- g_R is the order of class *R* (the number of operations of that type)
- $\chi(R)$ is the character for operation *R* in the reducible representation
- $\chi_i(R)$ is the character for operation *R* in the character table for symmetry species *i*

- This formula was derived from the "Great orthorgonality theorem".

Reducing representations

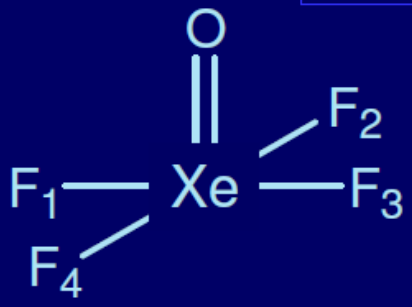
e.g. s orbitals on F atoms of $XeOF_4$



Point group ?

Point group algorithm – $XeOF_4$

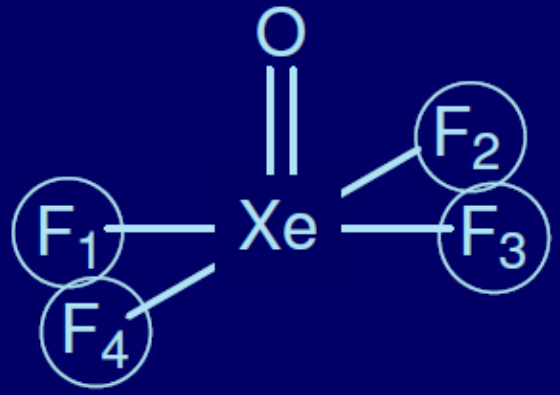
Start here



- linear ? — yes → infinite groups → i ? — yes → $D_{\infty h}$; no → $C_{\infty v}$
- no → 6 C_5 axes ? — yes → icosahedral groups → i ? — yes → I_h; no → I
- no → 3 C_4 axes ? — yes → octahedral groups → i ? — yes → O_h; no → O
- no → 4 C_3 axes ? — yes → tetrahedral groups → i ? — yes → T_h; no → $3S_4$? — yes → T_d; no → T
- no → rotation axis order, *n*, ≥2 ? — no → low-symmetry groups → σ ? — yes → C_s; no → i ? — yes → C_i; no → C_1
- yes → *n* C_2 axes ⊥ to the C_n axis ? — yes → D groups → σ_h ? — yes → D_{nh}; no → σ_h ? — yes → D_{nd}; no → D_n
- no → C and S groups → σ_h ? — yes → C_{nh}; no → $n\sigma_v$? — yes → C_{nv}; no → S_{2n} ? — yes → S_{2n}; no → C_n

Reducing representations

e.g. s orbitals on F atoms of $XeOF_4$



Point group C_{4v}

Symmetry operations		E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_{v'}$
E	all unchanged	character is +4 (+1 for each orbital)				
C_4	all move	character is 0				
C_2	all move	0				
$2\sigma_v$	2 move, 2 unchanged	2				
$2\sigma_{v'}$	all move	0				
Reducible representation is		4	0	0	2	0

- now reduce it!

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

Reducible representation	4	0	0	2	0	
Character table C_{4v}	**1E**	**$2C_4$**	**$1C_2$**	**$2\sigma_v$**	**$2\sigma_v'$**	***h* = 8**
A_1	+1	+1	+1	+1	+1	*z*
A_2	+1	+1	+1	-1	-1	R_z
B_1	+1	-1	+1	+1	-1	
B_2	+1	-1	+1	-1	+1	
E	+2	0	-2	0	0	*(x, y) (R_x, R_y)*

No. of A_1 motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.1 + 2.0.1] = 1

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

Reducible representation	4	0	0	2	0	
Character table C_{4v}	**1E**	**$2C_4$**	**$1C_2$**	**$2\sigma_v$**	**$2\sigma_{v'}$**	***h* = 8**
A_1	+1	+1	+1	+1	+1	*z*
A_2	+1	+1	+1	-1	-1	R_z
B_1	+1	-1	+1	+1	-1	
B_2	+1	-1	+1	-1	+1	
E	+2	0	-2	0	0	*(x, y) (R_x, R_y)*

No. of A_1 motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.1 + 2.0.1] = 1

No. of A_2 motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.(-1) + 2.0.(-1)] = 0

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

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

No. of A_1 motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.1 + 2.0.1] = 1

No. of A_2 motions = 1/8 [1.4.1 + 2.0.1 + 1.0.1 + 2.2.(-1) + 2.0.(-1)] = 0

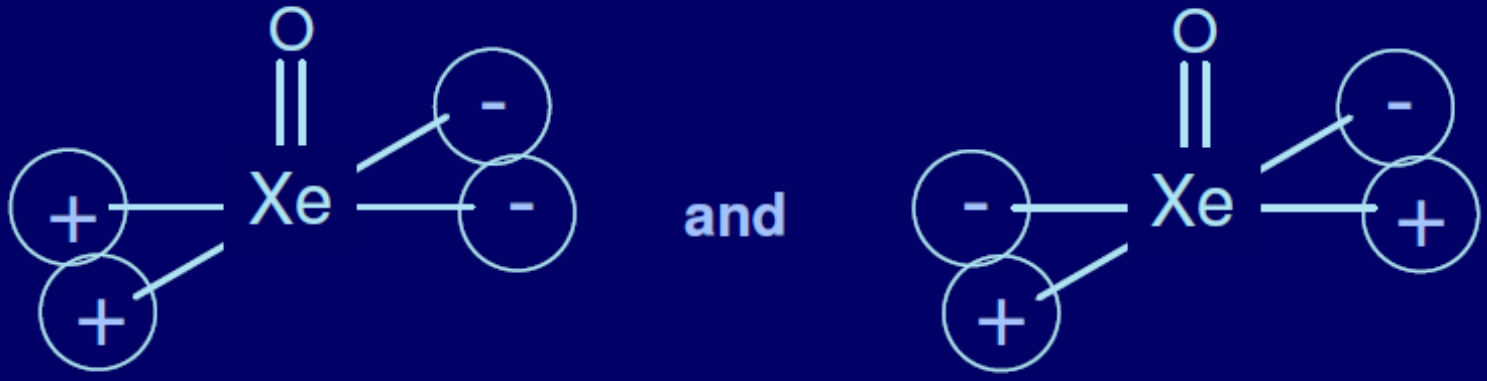
No. of B_1 motions = 1/8 [1.4.1 + 2.0.(-1) + 1.0.1 + 2.2.1 + 2.0.(-1)] = 1

No. of B_2 motions = 1/8 [1.4.1 + 2.0.(-1) + 1.0.1 + 2.2.(-1) + 2.0.1] = 0

No. of E motions = 1/8 [1.4.2 + 2.0.0 + 1.0.(-2) + 2.2.0 + 2.0.0] = 1

Character table C_{4v}	1E	$2C_4$	$1C_2$	$2\sigma_v$	$2\sigma_{v'}$
Reducible representation	4	0	0	2	0
Irreducible representation	$A_1 + B_1 + E$				

Note: E is *doubly degenerate* – accounts for two equivalent combinations of orbitals



3. Symmetry adapted Linear Combinations of AOs– A convenient way to construct MOs

Symmetry of wavefunctions of a molecule

Symmetry Operation on Schrödinger Eq.

$$\hat{H}\psi = E\psi \xrightarrow{R} R\hat{H}\psi = RE\psi$$

$$\downarrow$$

$$R\hat{H}R^{-1}R\psi = ER\psi$$

$$\downarrow$$

$$\hat{H}R\psi = ER\psi$$

$R\psi$ *is also an eigenvector of* $\hat{H}$*, with the same eigenvalue* E *as* ψ *corresponds to.*

Symmetry of wavefunctions

If eigenvalue E is not degenerate, then

$$R\psi = c\psi$$

Which means ψ is a basis for some 1-D I.R..

Symmetry of wavefunctions

If eigenstate E is l-fold degenerate, then

E $\Longleftrightarrow$ $\{\psi_1, \psi_2, \ldots, \psi_l\}$

$$R\psi_i = \sum_{j=1}^{l} r_{ij}\psi_j = \begin{bmatrix} r_{11} & r_{12} & \cdots & r_{1l} \\ r_{21} & r_{22} & \cdots & r_{2l} \\ \vdots & \vdots & \ddots & \vdots \\ r_{l1} & r_{l2} & \cdots & r_{ll} \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_l \end{bmatrix}$$

Which means set $\{\psi_1, \psi_2, \ldots, \psi_l\}$ is a basis for this l-D I.R.

Symmetry of wavefunctions

In LCAO approach of MO theory, we have

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

So we need to solve the secular equation

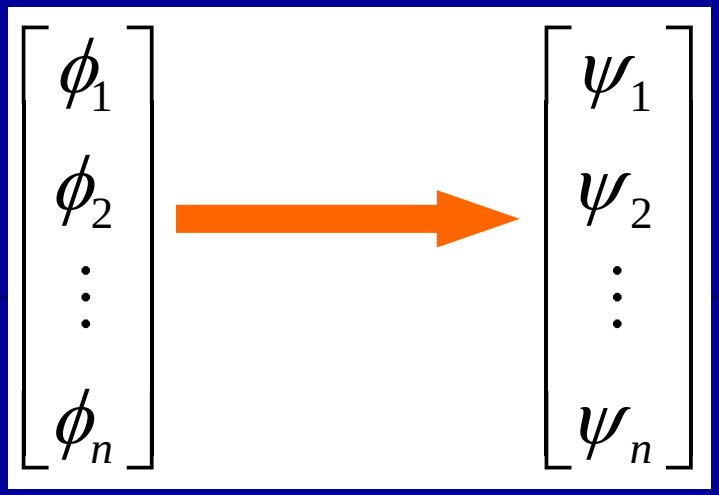
$$\sum_{i=1}^{n} c_i \left(H_{ir} - ES_{ir} \right) = 0, \qquad (r = 1, 2, \cdots, n)$$

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

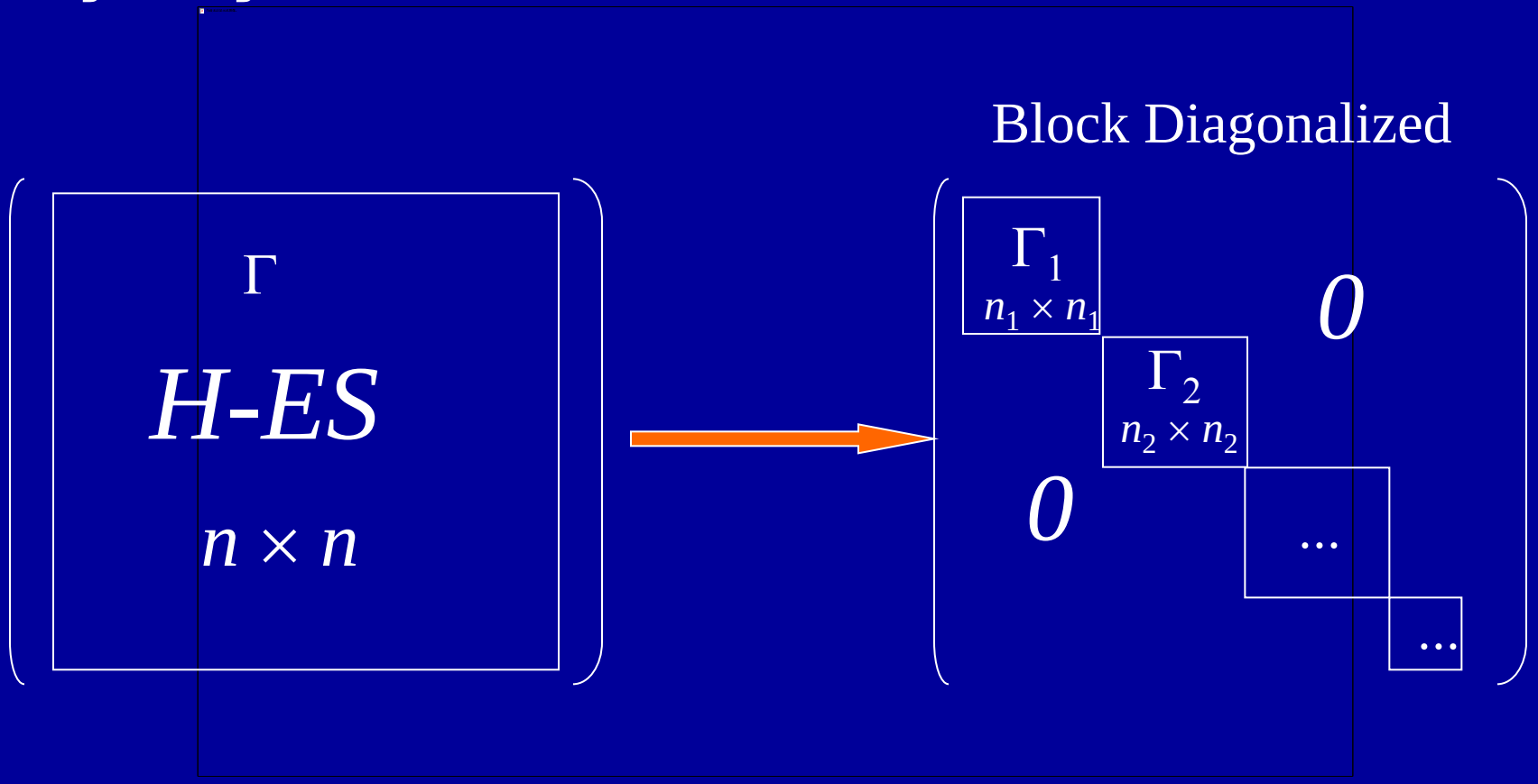
Symmetry of wavefunctions

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.

AO SALC



Symmetry of wavefunctions



$$\Gamma = n_1\Gamma_1 + n_2\Gamma_2 + \cdots$$

Symmetry of wavefunctions

Step 1 Reduce the REP spanned by the AO basis.

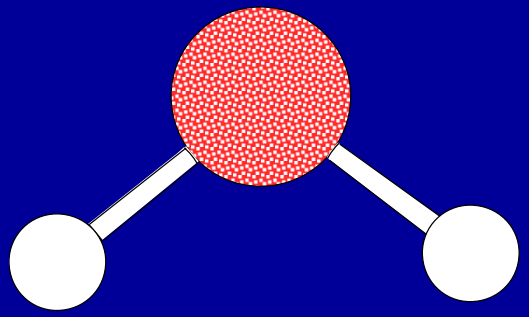
Obtain the n_i's for each I.R.

Step 2 Construct n_i SALCs for each I.R..

Step 3 Transform the hamiltonian matrix into block diagonalized form, and solve it.

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}

- Neglecting the O 1s orbital/electrons.

H_2O

e.g. p_z orbital on O atom of H_2O

Unchanged by all operations

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
	+1	+1	+1	+1	A_1

p_y orbital

	+1	-1	-1	+1	B_2

Character Table

C_{2v}	I	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 : $2p_y$

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

C_{2v}	I	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
χ(R)	2	0	0	2	

$$n_{A_1} = \frac{1}{4}(1\times 2 + 1\times 0 + 1\times 0 + 1\times 2) = 1 \qquad n_{A_2} = \frac{1}{4}(1\times 2 + 1\times 0 - 1\times 0 - 1\times 2) = 0$$

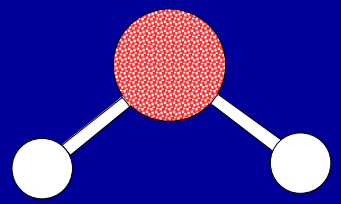
$$n_{B_1} = \frac{1}{4}(1\times 2 - 1\times 0 + 1\times 0 - 1\times 2) = 0 \qquad n_{B_2} = \frac{1}{4}(1\times 2 - 1\times 0 - 1\times 0 + 1\times 2) = 0$$

$$\Gamma = A_1 + B_2 \longrightarrow \text{Two 1-D REPs}$$

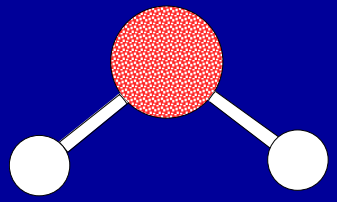
SALC - *Symmetry Adapted Linear Combination of AOs*

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

A_1: $\frac{1}{\sqrt{2}}\left(1s_A + 1s_B\right)$



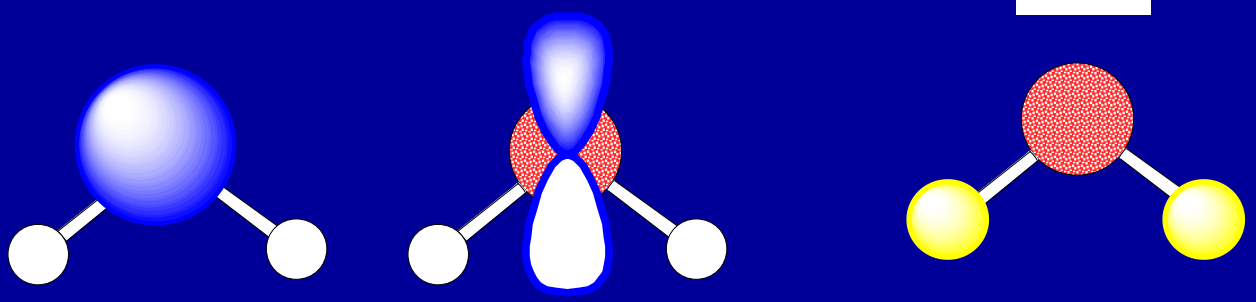
B_2: $\frac{1}{\sqrt{2}}\left(1s_A - 1s_B\right)$



H2O

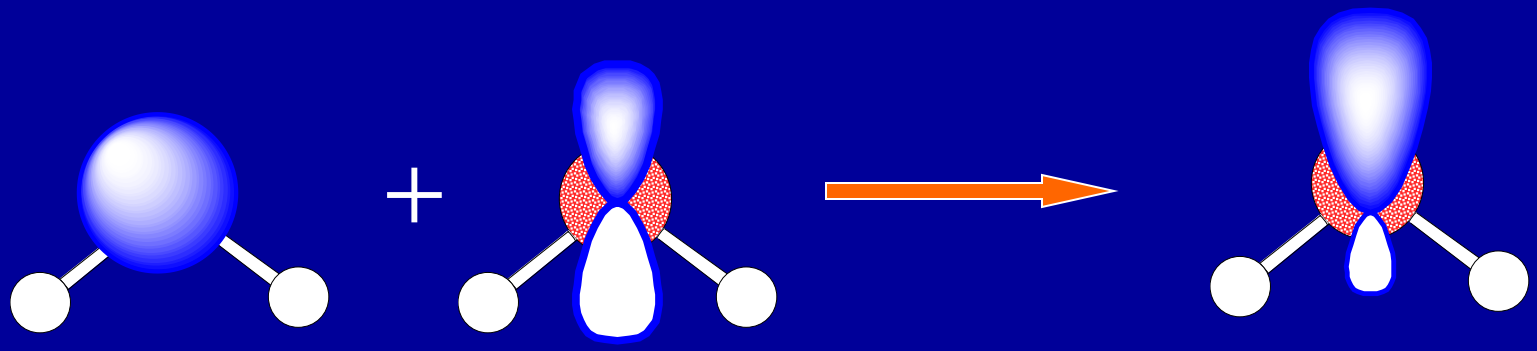
A_1 symmetry AOs or SALCs for LCAO

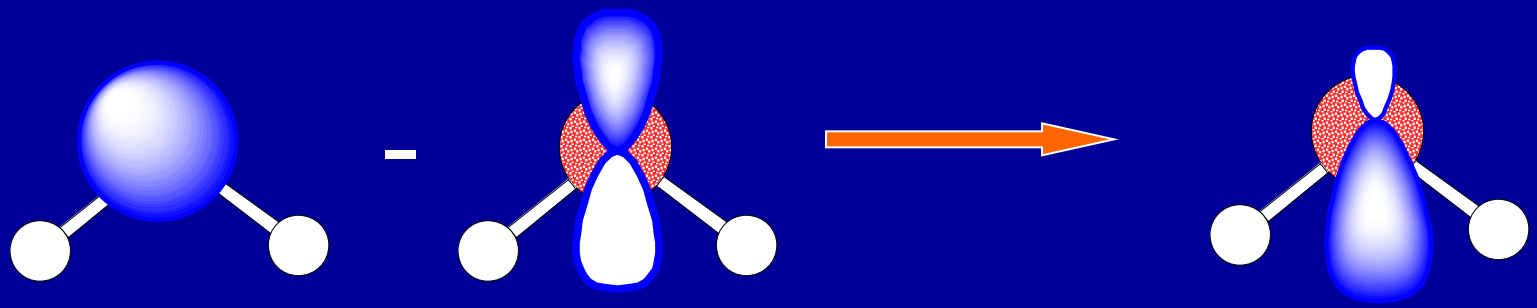
A_1 : O2s, O2p_z ϕ_{A_1}



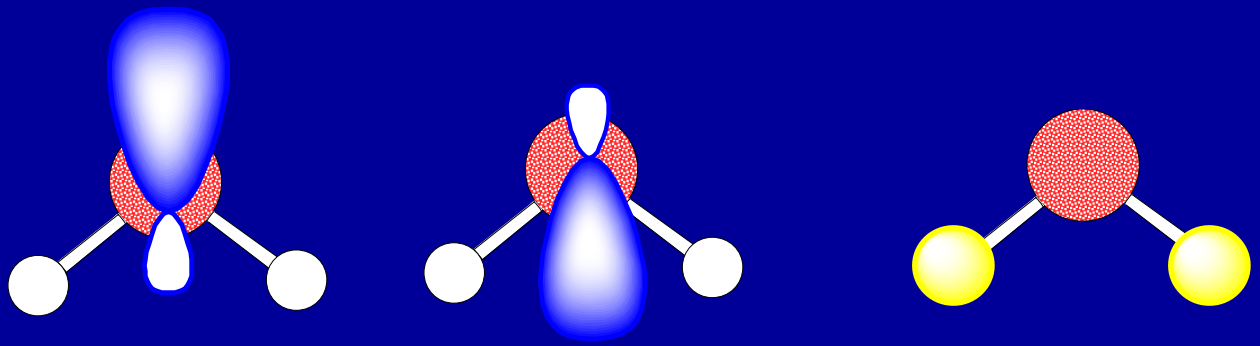
Too complicated for analysis!

H2O- Hybridization of Oxygen's $2s$ and $2p_z$





H2O- Hybridization of Oxygen's $2s$ and $2p_z$



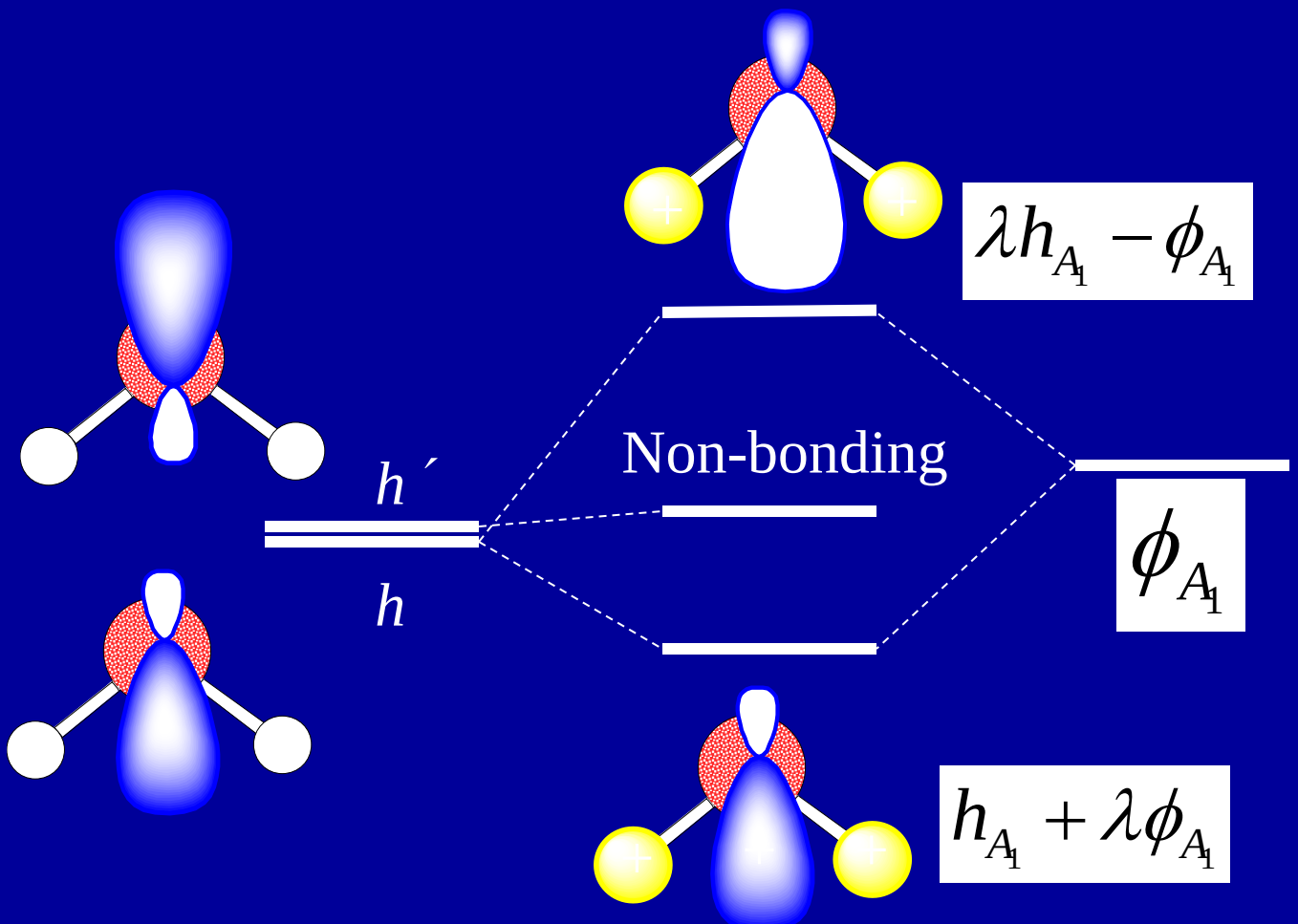
h' h ϕ_{A_1}

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

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

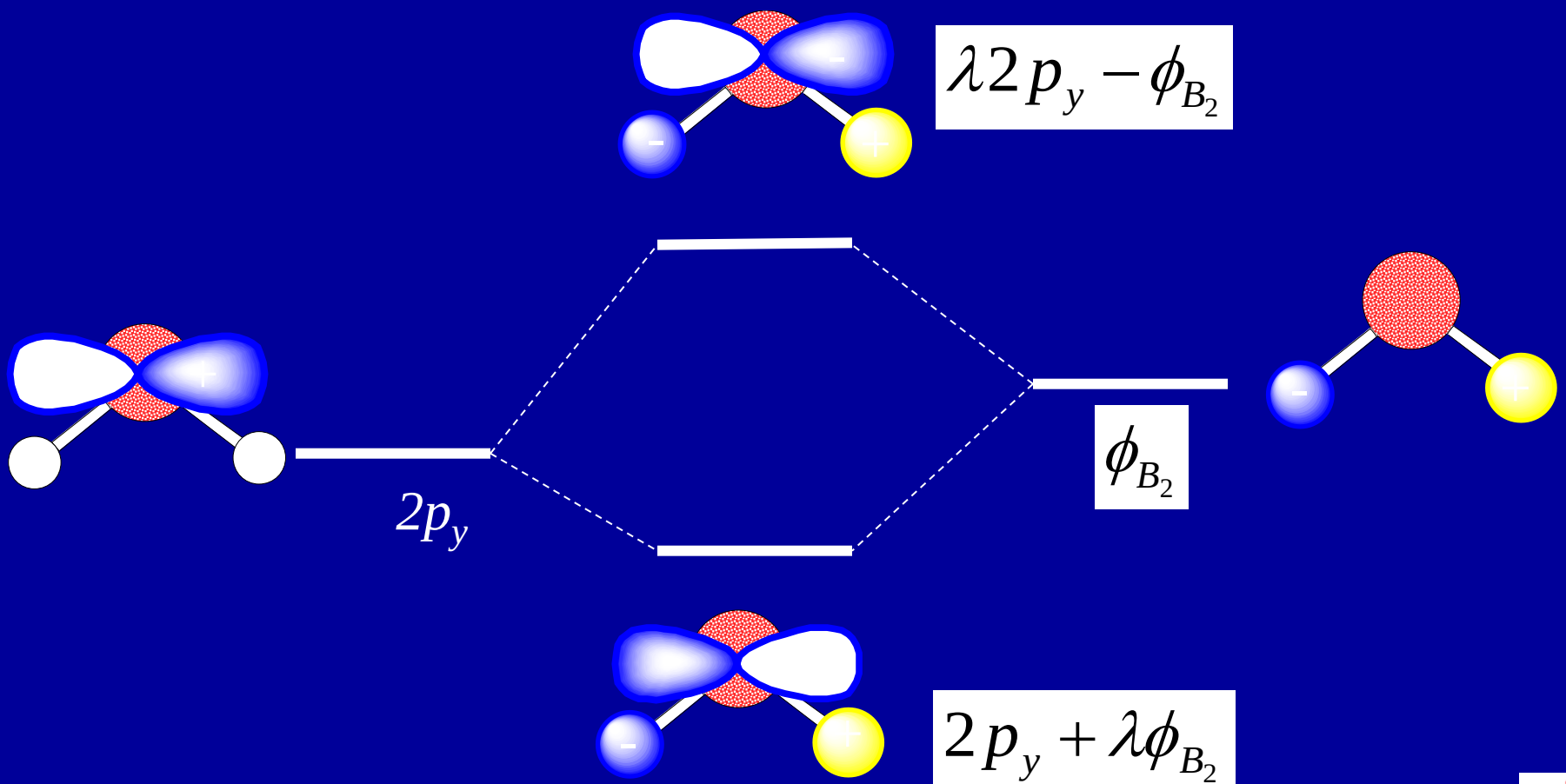
H2O- Chemical Bonding in A_1 REP

$$0 \leq \lambda \leq 1$$

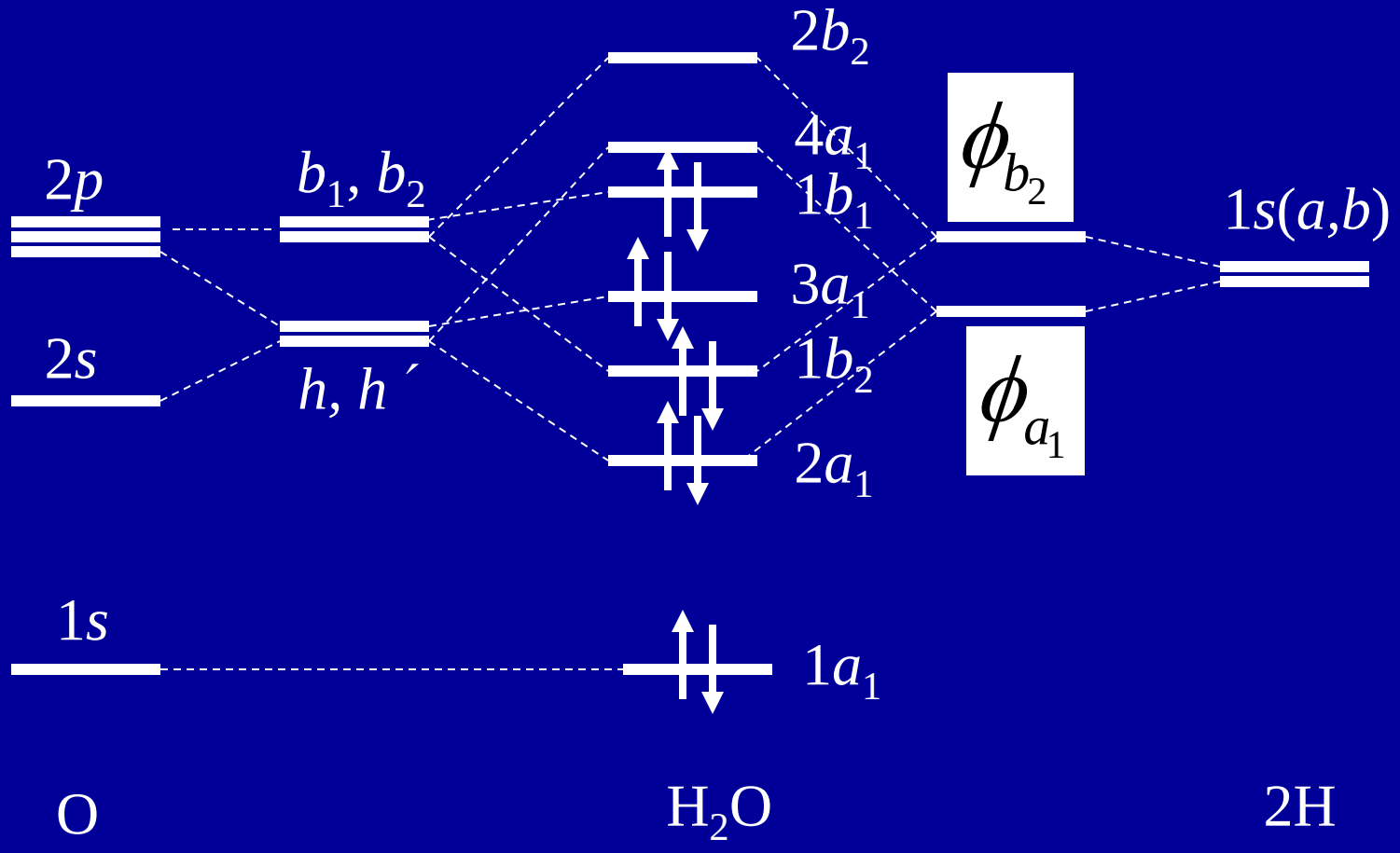


H2O- Chemical Bonding in B_2 REP

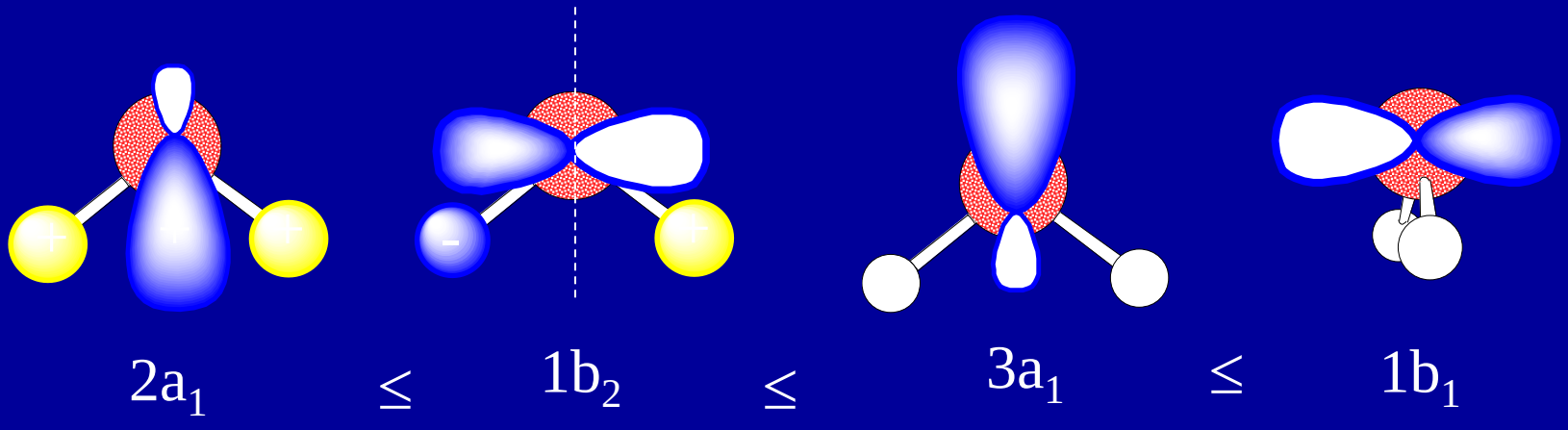
$$0 \leq \lambda \leq 1$$

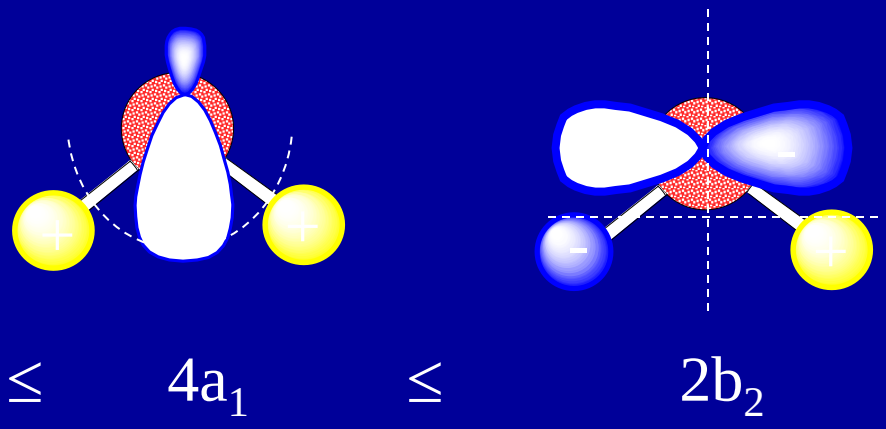


H2O- Summary on Chemical Bonding



H2O- Summary on Molecular Energy Level Sequences





Use Projection operator to construct SALCs

- Definition:

$$\hat{P}^j = \frac{l_j}{h} \sum_R \chi(R)^j \hat{R}$$

for j-th ir. rep. of the point group. This equation was derived from the "great orthogonality theorem".

- A non-normalized SALC can be constructed from bases set by the formula:

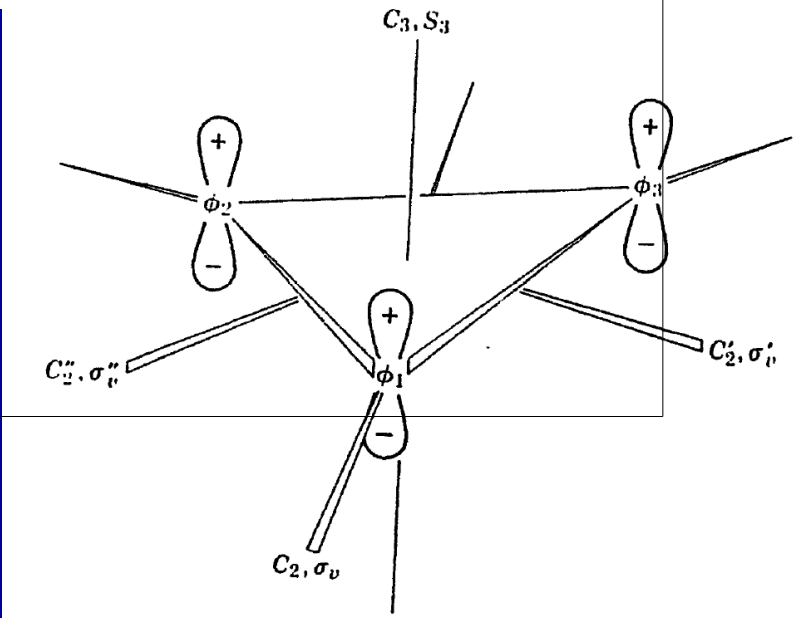
$$\Psi_{SALC}^{j} = \hat{P}^j \phi_i = \frac{l_j}{h} \sum_R \chi(R)^j \hat{R} \phi_i$$

Example: π-MOs of C_3H_3 (D_{3h})

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1		
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)
Γ	3	0	−1	−3	0	1		

- $\Gamma = A_2'' + E''$
- However, it is more convenient to reduce its symmetry to D_3. Then we have

$$\Gamma = A_2 + E$$



D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	−1	z, R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$
Γ_π	3	0	-1		$\Gamma_\pi = A_2 + E$

$$\hat{P}^{A_2}\phi_1 = \frac{1}{6}\sum_R \chi(\hat{R})^{A_2}\hat{R}\phi_1$$

$$= \frac{1}{6}(E\phi_1 + C_3^1\phi_1 + C_3^2\phi_1 - C_2\phi_1 - C_2^{'}\phi_1 - C_2^{''}\phi_1)$$

$$= \frac{1}{6}(\phi_1+\phi_2+\phi_3+\phi_1+\phi_2+\phi_3) = \frac{1}{3}(\phi_1+\phi_2+\phi_3)$$

$$\Psi^{A_2} = A\bullet\hat{P}^{A_2}\phi_1$$

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

$$\hat{P}^{E}\phi_1 = \frac{1}{6}\sum_R \chi(\hat{R})^{E}\hat{R}\phi_1$$

$$= \frac{2}{6}(2E\phi_1 - C_3^1\phi_1 - C_3^2\phi_1) = \frac{1}{3}(2\phi_1-\phi_2-\phi_3)$$

$$\Psi_1^E = A\bullet\hat{P}^{E}\phi_1$$

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

Using orthogonality and normalization, we have

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

Another way to derive the third MO:

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

$$C_3^1\Psi_1^E = \frac{1}{\sqrt{6}}(2\phi_2 - \phi_3 - \phi_1)$$

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

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

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

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

A general simplification

- Reducing the symmetry to C_3 subgroup.

C_3	E	C_3	C_3^2		$\varepsilon = \exp(2\pi i/3)$
A	1	1	1	z, R_z	$x^2 + y^2, z^2$
E	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{matrix} \varepsilon \\ \varepsilon^* \end{matrix}$	$\begin{matrix} \varepsilon^* \\ \varepsilon \end{matrix}$	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(yz, xz)$

Γ_π 3 0 0 $\qquad\qquad$ $\Gamma_\pi = A + E$

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

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

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

$$\Psi_1^A = A\hat{P}^A\phi_1$$

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

$$\Psi_1^E = A(\hat{P}^{E(1)}\phi_1 + \hat{P}^{E(2)}\phi_1)$$

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

$$\Psi_2^E = A(\hat{P}^{E(1)}\phi_1 - \hat{P}^{E(2)}\phi_1)$$

$$= Ai(2\sin(\frac{2\pi}{3})\phi_2 - 2\sin(\frac{2\pi}{3})\phi_3) = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

Example 2: 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) (R_x, R_y)	(xz, yz)
	1	ε^*	$-\varepsilon$	−1	$-\varepsilon^*$	ε		
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 $\Gamma_\pi = A + B + E_1 + E_2$

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

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

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

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

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) (R_x, R_y)	(xz, yz)
	1	ε^*	$-\varepsilon$	−1	$-\varepsilon^*$	ε		
E_2	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		(x^2-y^2, xy)
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		

Γ	6	0	0	0	0	0

$\Gamma = A + B + E_1 + E_2$

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

$$= \phi_1 + \varepsilon\phi_2 - \varepsilon^*\phi_3 - \phi_4 - \varepsilon\phi_5 + \varepsilon^*\phi_6$$

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

$$= \phi_1 + \varepsilon^*\phi_2 - \varepsilon\phi_3 - \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6$$

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

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

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

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

Similarly, we have

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

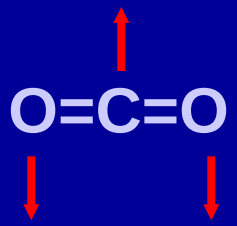
$$\Psi^{E_2}(2) = A(\phi_5 - \phi_6)/i = \frac{1}{2}(-\phi_2 + \phi_3 - \phi_5 + \phi_6)$$

Vibrational spectroscopy

CO_2 has 3 modes of vibration

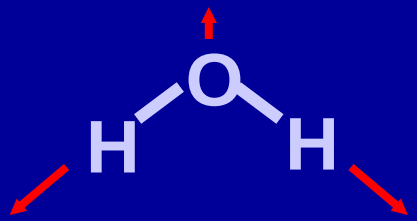
Infra-red inactive - no dipole change

IR active

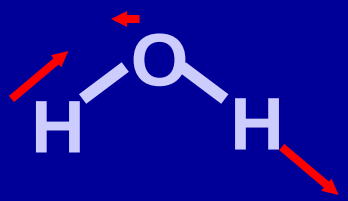


IR active

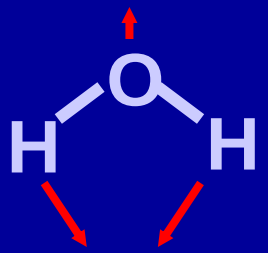
H_2O has 3 modes of vibration



IR active



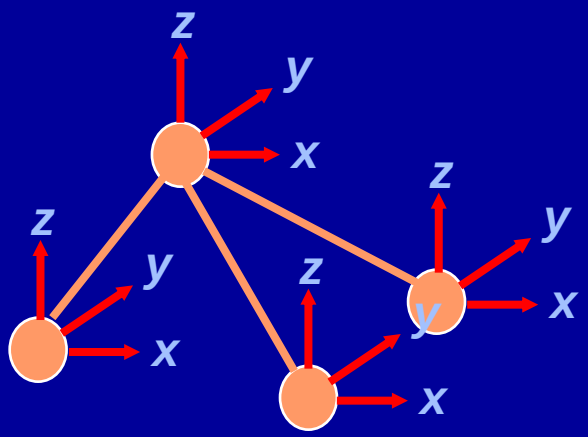
IR active



IR active

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

Molecular vibrations - number of modes



4 atoms - can move independently in *x*, *y*, z directions

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

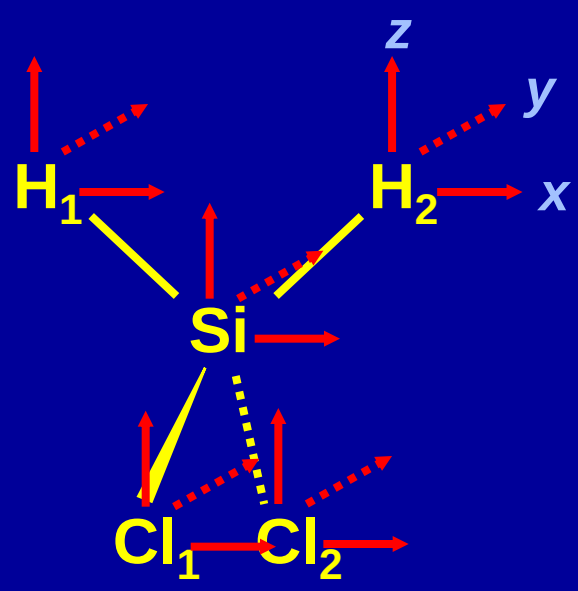
If atoms fixed, there are: 3 translational degrees

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}**



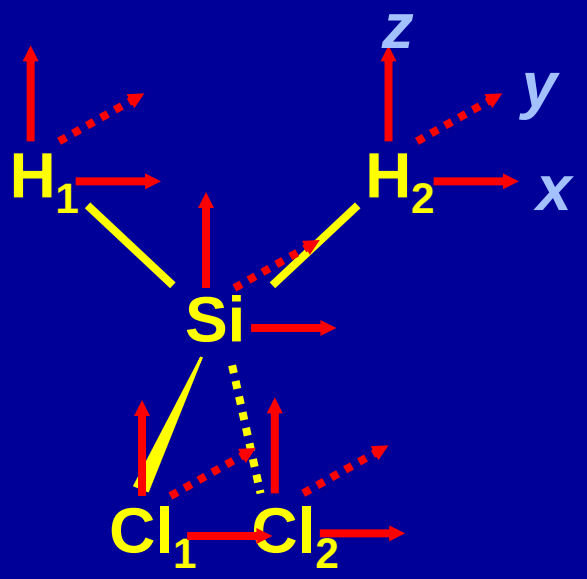
Character table

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

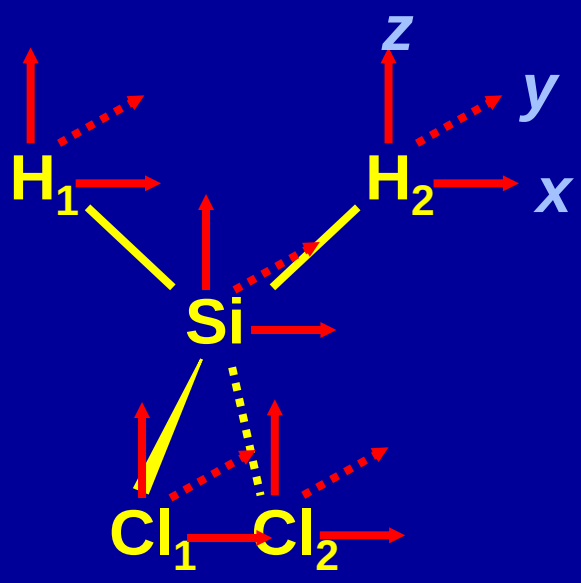
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	$h = 4$	
A_1	+1	+1	+1	+1	z	x^2, y^2, z^2
A_2	+1	+1	-1	-1	R_z	xy
B_1	+1	-1	+1	-1	x, R_y	xz
B_2	+1	-1	-1	+1	y, R_x	yz

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

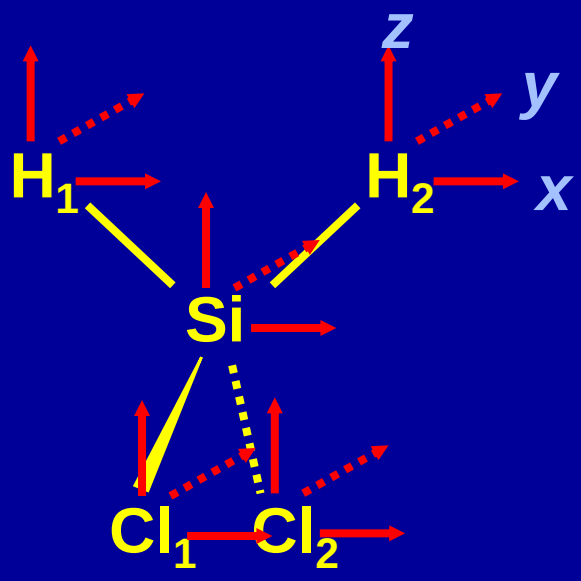


Character table

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

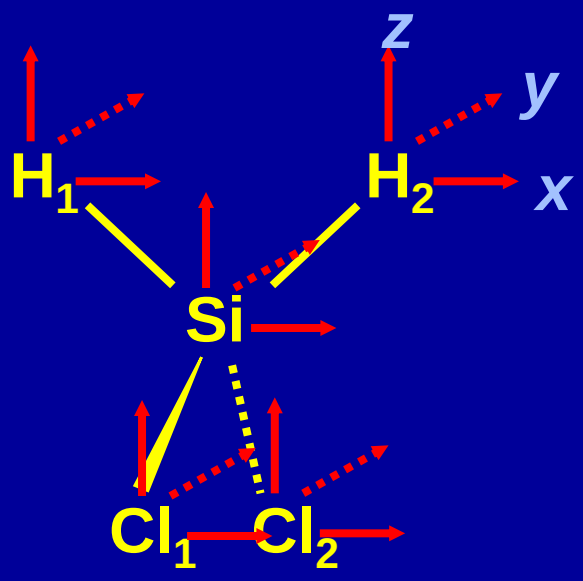
z transforms into Si z count +1

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 set of 3N (=15) atomic displacement vectors

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

Reduce the reducible representation

Formula is

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

Reducible representation 15 -1 3 3

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

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

Formula is

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

Reducible representation 15 -1 3 3

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

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

Formula is

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

Reducible representation 15 -1 3 3

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

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:-**

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

2 rules

(i) there is 1 stretching vibration per bond

(ii) must treat symmetry-related atoms together

Vibrational modes of SiH_2Cl_2

2 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*

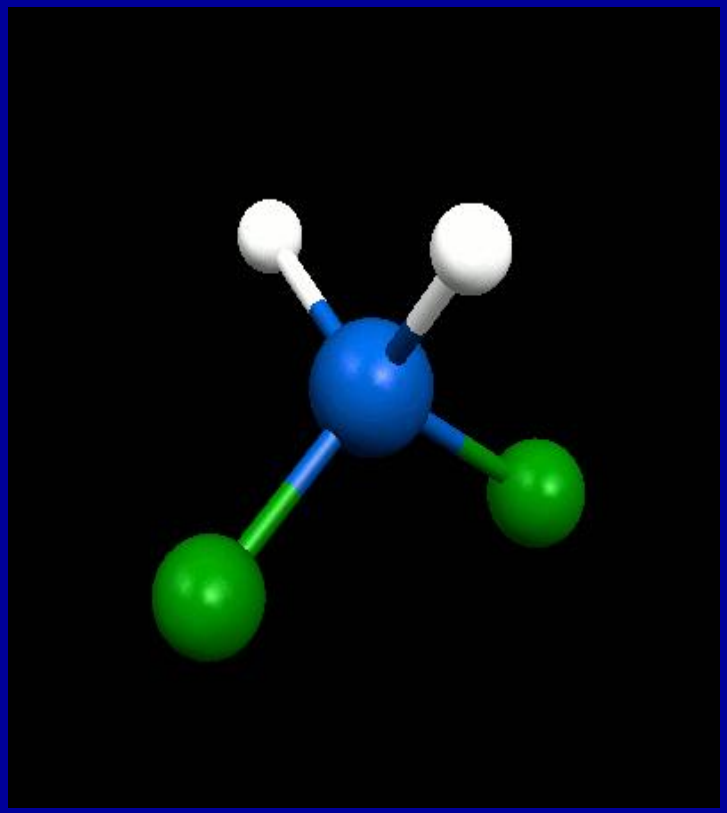
Is vibration symmetrical with respect to each symmetry operation?

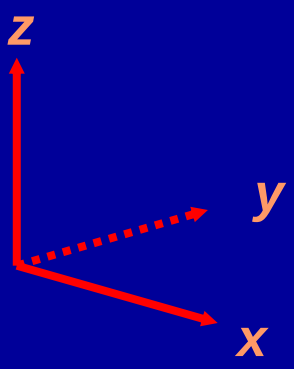
- if yes +1, if no -1

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} $SiCl_2$





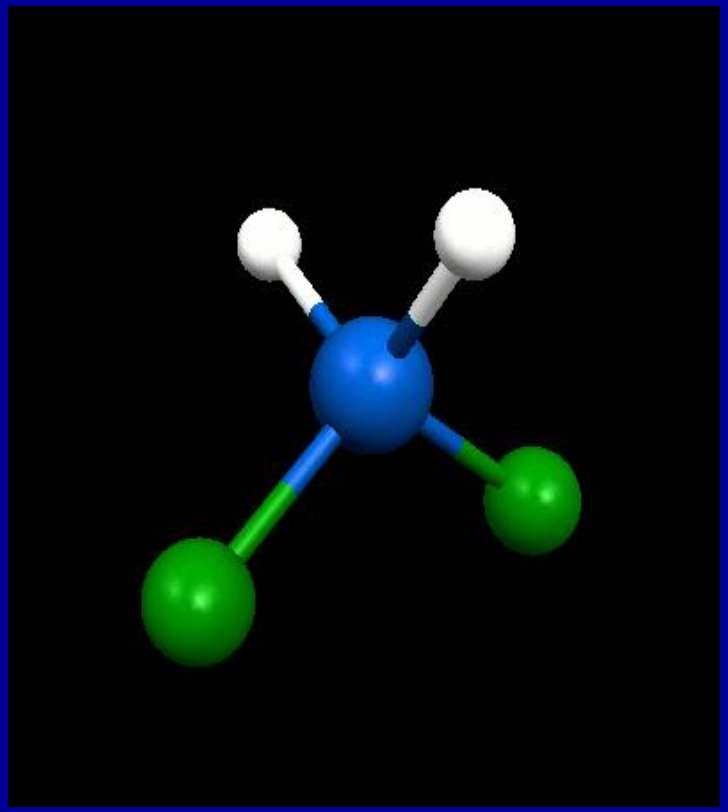
Is vibration symmetrical with respect to each symmetry operation?

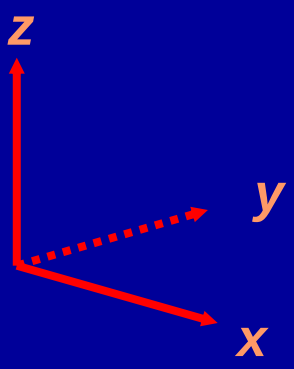
- if yes +1, if no -1

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

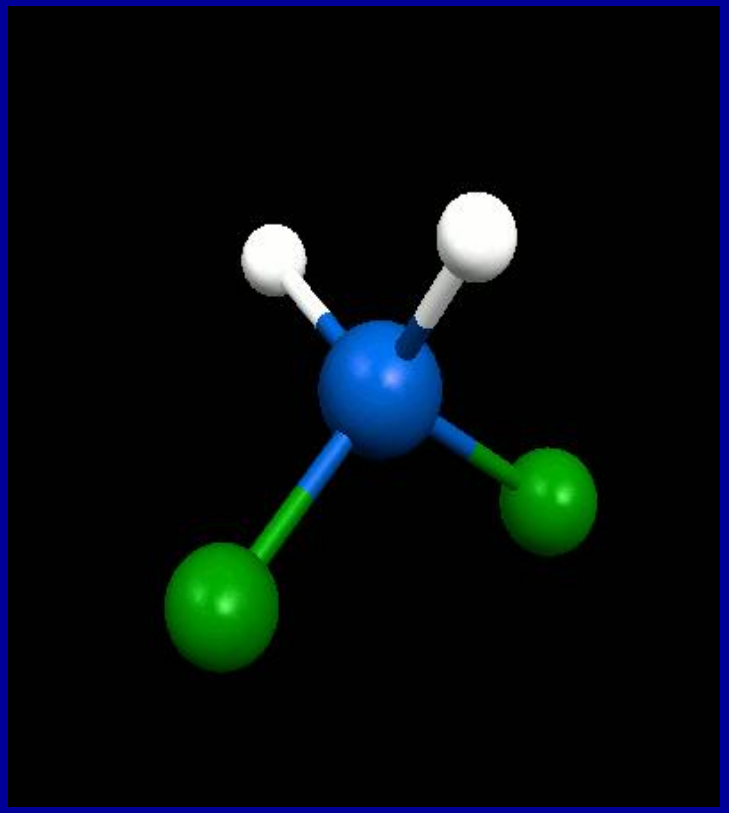
and two stretching modes of the SiH_2 group

We can stretch the two Si-H bonds

together *in phase*

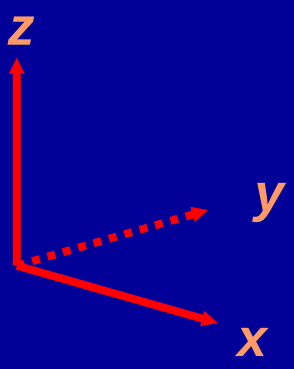
or together *out of phase*

E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1

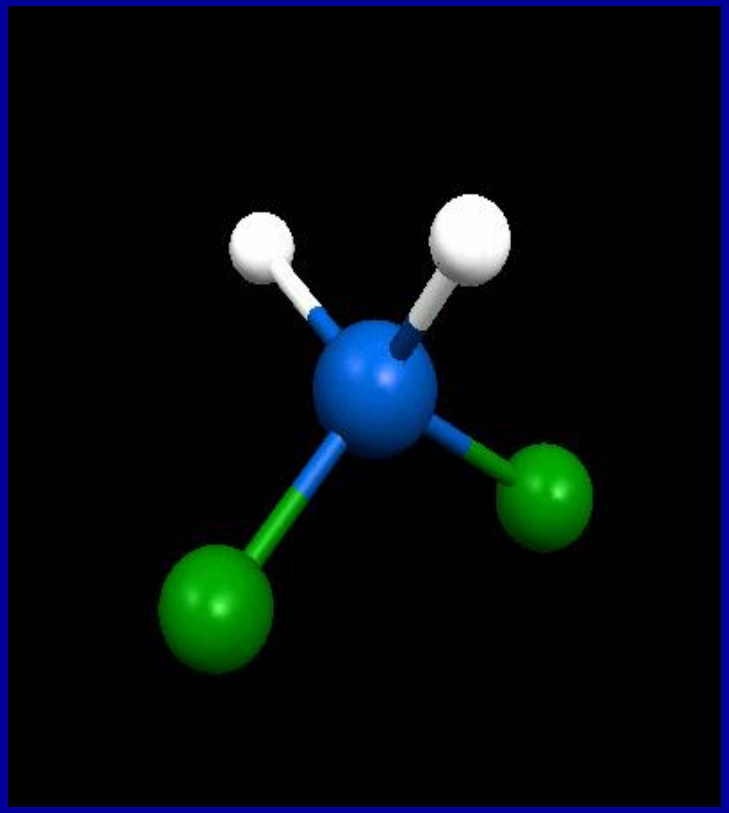


From the character table, this belongs to the symmetry species A_1

We call the mode of vibration ν_{sym} SiH_2

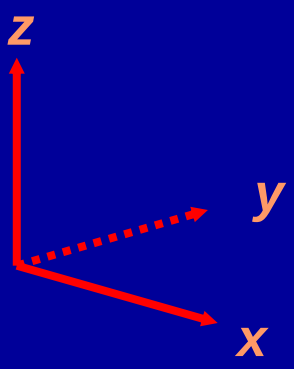


E	C_2	σ_{xz}	σ_{yz}
+1	-1	+1	-1



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

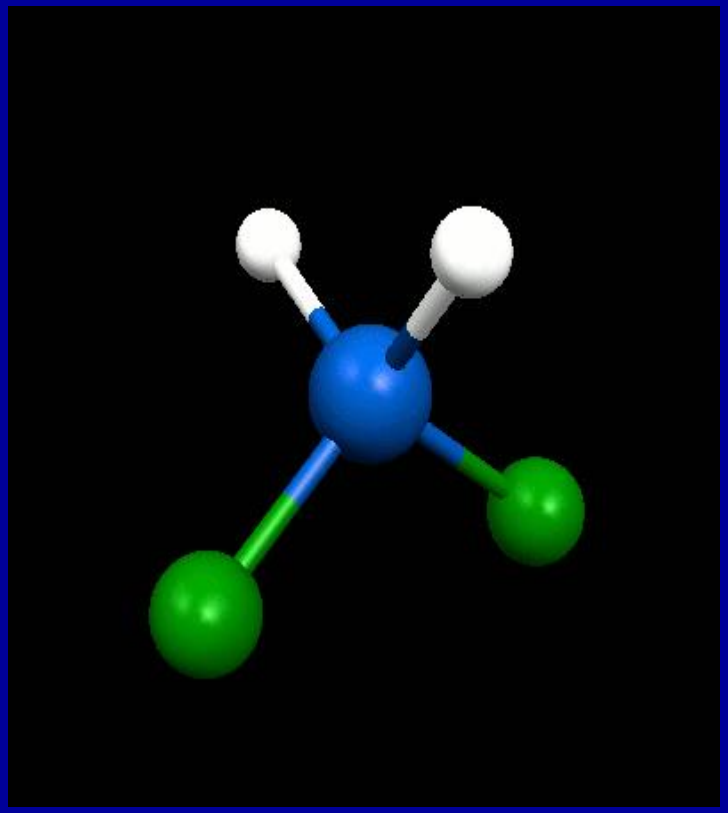
We now have:-

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

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

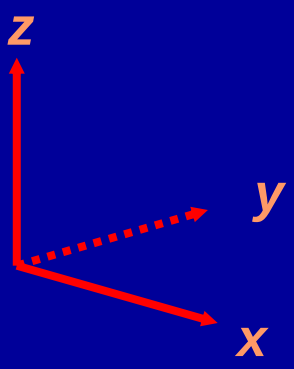
As with stretches, we must treat symmetry-related atoms together

E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1

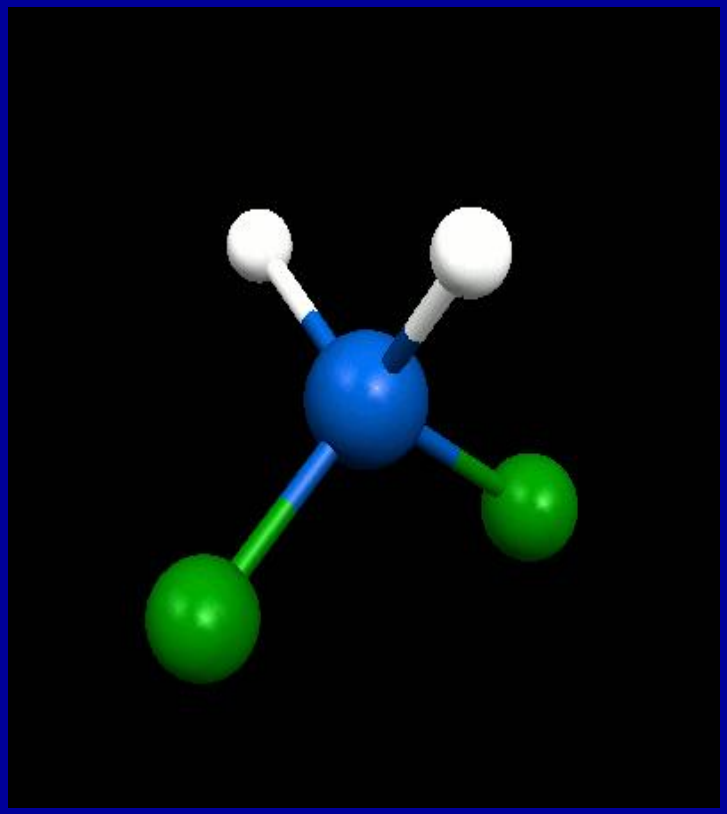


From the character table, this belongs to the symmetry species A_1

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

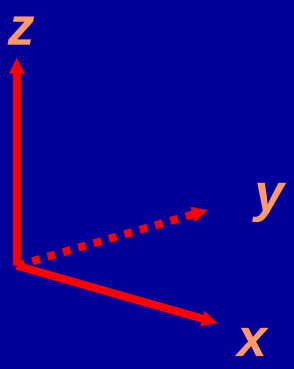


E	C_2	σ_{xz}	σ_{yz}
+1	+1	+1	+1

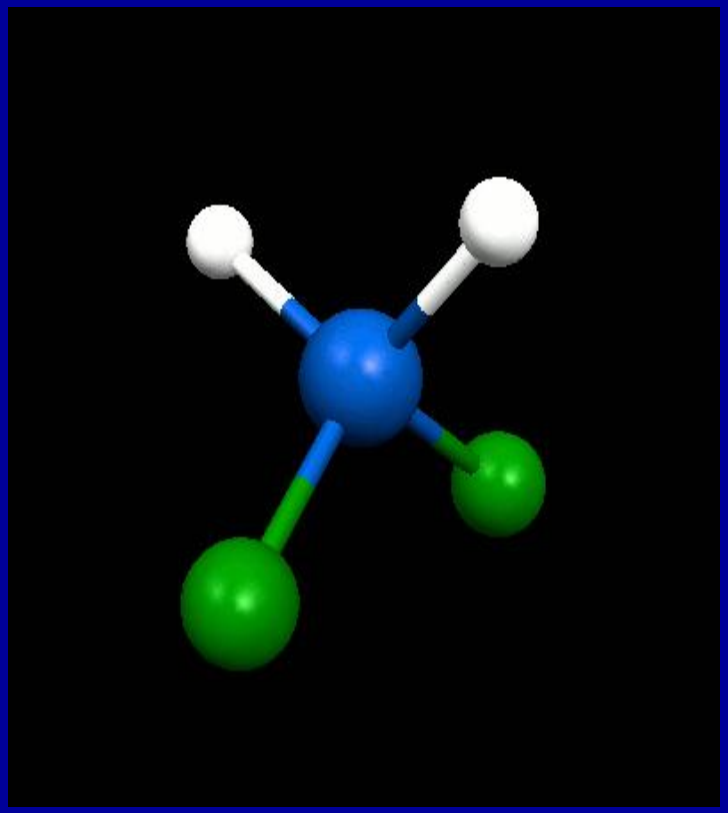


From the character table, this belongs to the symmetry species A_1

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

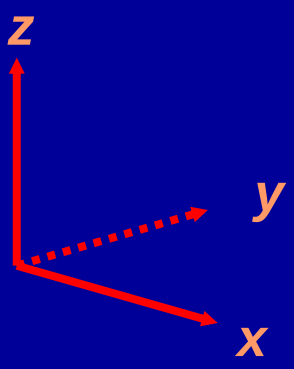


E	C_2	σ_{xz}	σ_{yz}
+1	-1	+1	-1

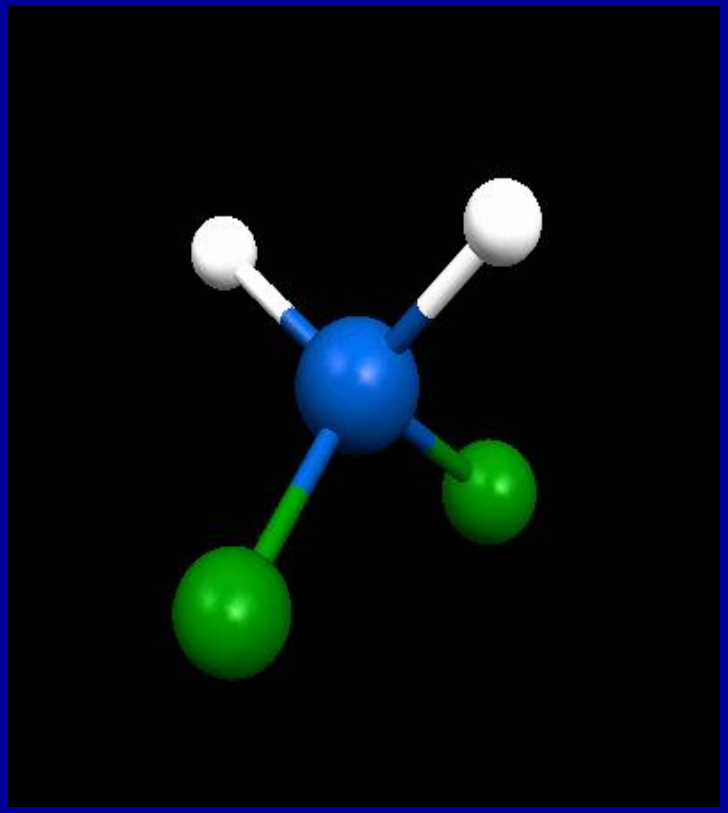


From the character table, this belongs to the symmetry species B_1

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

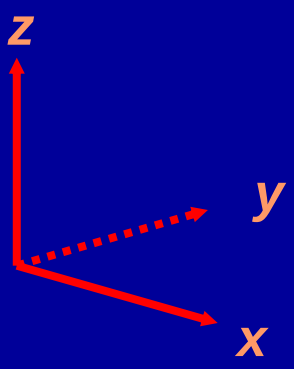


E	C_2	σ_{xz}	σ_{yz}
+1	-1	-1	+1

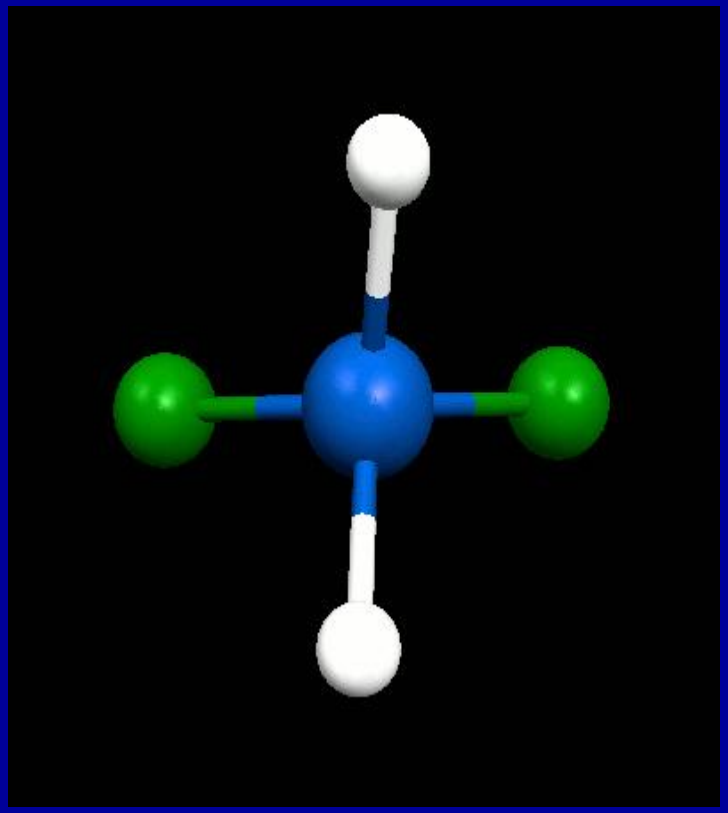


From the character table, this belongs to the symmetry species B_2

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

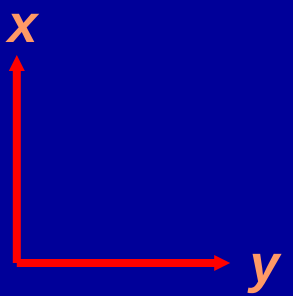


E	C_2	σ_{xz}	σ_{yz}
+1	+1	-1	-1



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:

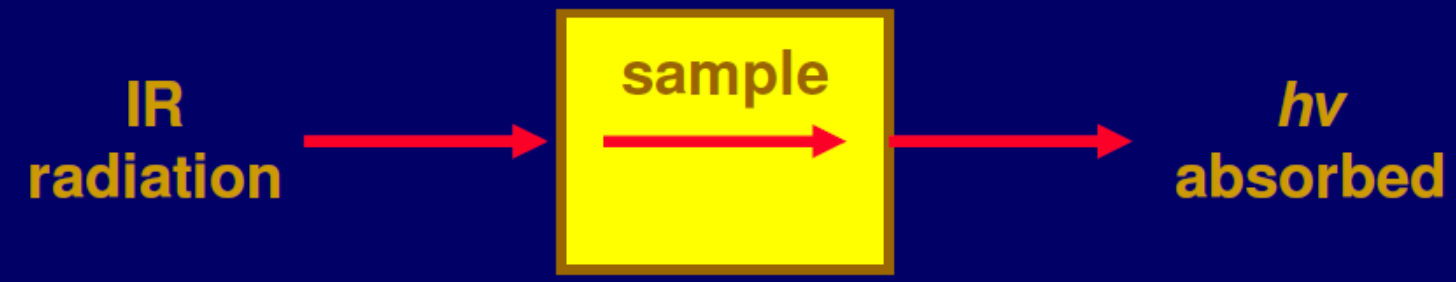
$4A_1 + A_2 + 2B_1 + 2B_2$

Observing vibrations

Infra-red spectroscopy

Process – quantum of energy is absorbed by exciting a vibration

– may also increase or decrease rotational energy



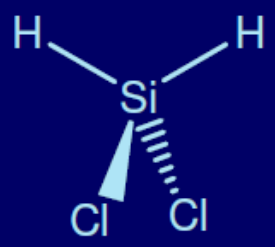
Activity – absorption possible if and only if the vibration involves a dipole change

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, z

In this case, μ_z has A_1 symmetry

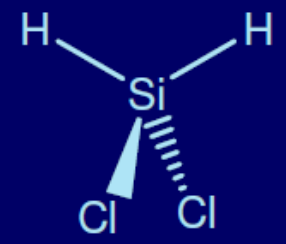
Therefore A_1 vibrations involve dipole changes along the z axis, and so all A_1 modes must be *infra-red active*.

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 changes along *x* and *y* axes, and so must be ***infra-red active***.

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

Our examples

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

4 + 2 + 2 active modes

8 absorption bands in IR spectrum

$XeOF_4$ $\Gamma_{vib} = 3A_1 + 2B_1 + B_2 + 3E$

3 + 3 active modes

6 absorption bands in IR spectrum

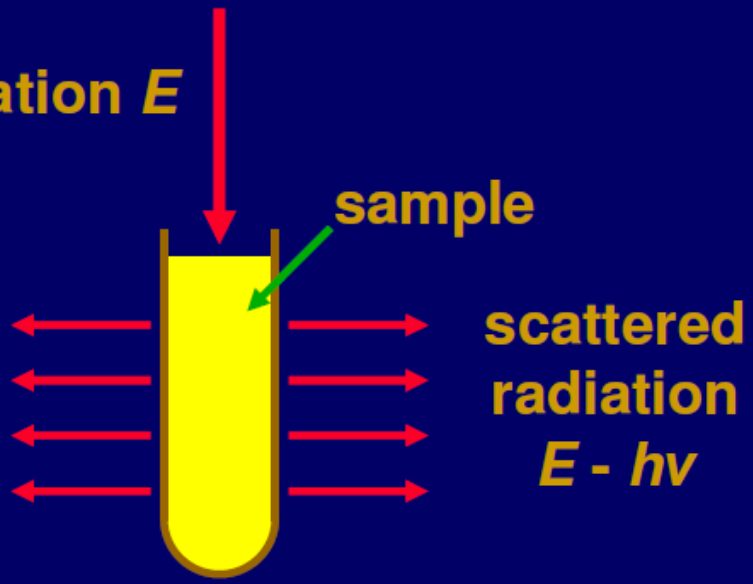
Character table

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*



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

all symmetry species are Raman-active

9 bands in Raman spectrum

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*

Good Luck In the Final Exam!

Final Exam

- Content: Chapters 5-9
- Time: June 13, 8:00-10:00
- Venue: 群贤二-102
- Tools: 科学计算器、笔等普通文具
- 考前答疑: June 10-12,
  嘉锡楼316(圆弧形办公室)