Group theory 101

Suggested reading:

Landau & Lifshits, *Quantum Mechanics*, Ch. 12

Tinkham, *Group Theory and Quantum Mechanics*

Dresselhaus, Dresselhaus, Jorio, *Group Theory: Applications to the Physics of Condensed Matter*

Ramond, *Group Theory: a Physicist's Survey*

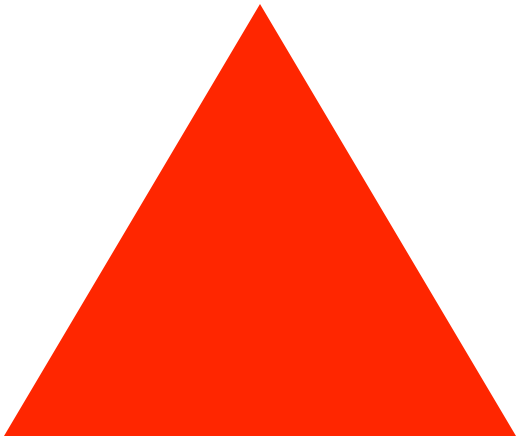
Definition

A (finite or infinite) sequence of elements *A,B,C…*form a group, if the following four conditions are satisfied

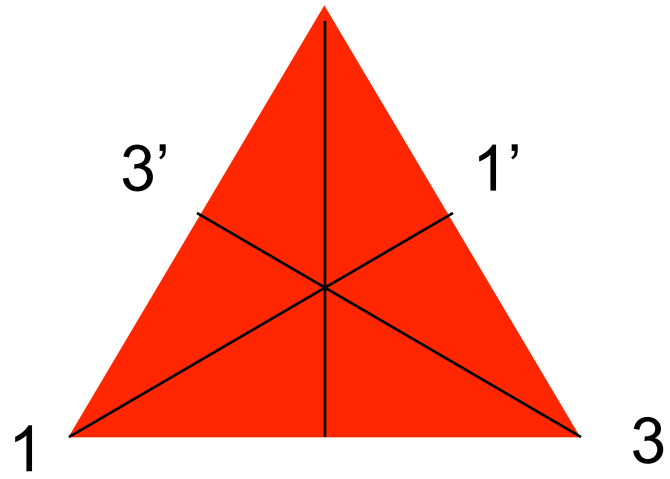
1. CLOSURE: If A and B are belong to the group, then $A \bullet B$ also belongs to the group.
2. ASSOCIATIVITY: If A, B and C belong to the group, then $(A \bullet B) \bullet C = A \bullet (B \bullet C)$.
3. IDENTITY: There is an element e of the group such that for any element a of the group
   $A \bullet I = E \bullet I = I$.
4. INVERSE: For any element A of the group there is an element A such that
   $A \bullet A^{-1} = A^{-1} \bullet \mathrm{A} = I$

Group of rotations of an equilateral triangle

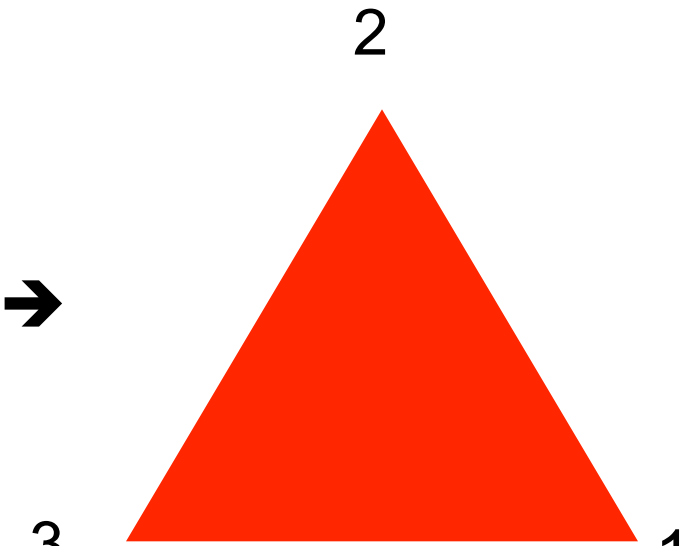
D_3



180 rotations2(flips)

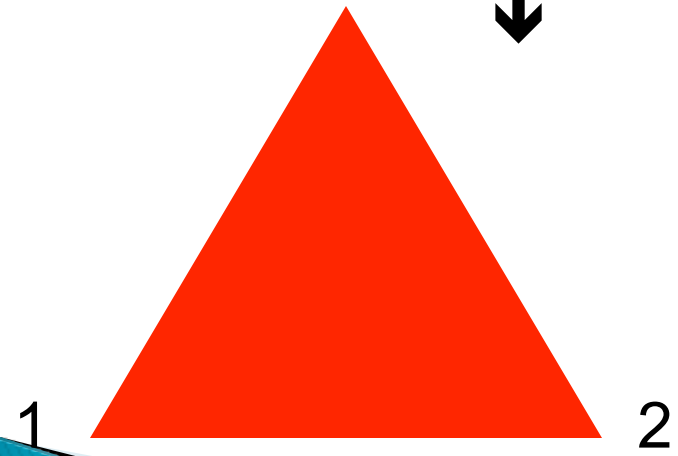


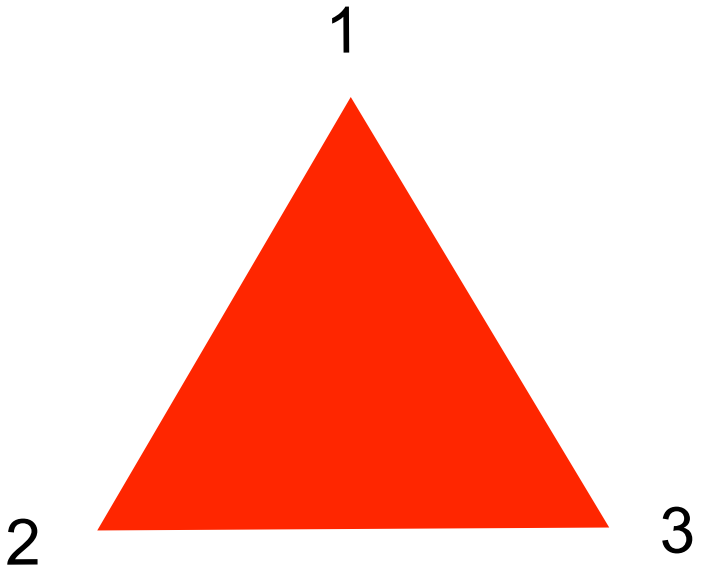
→A→

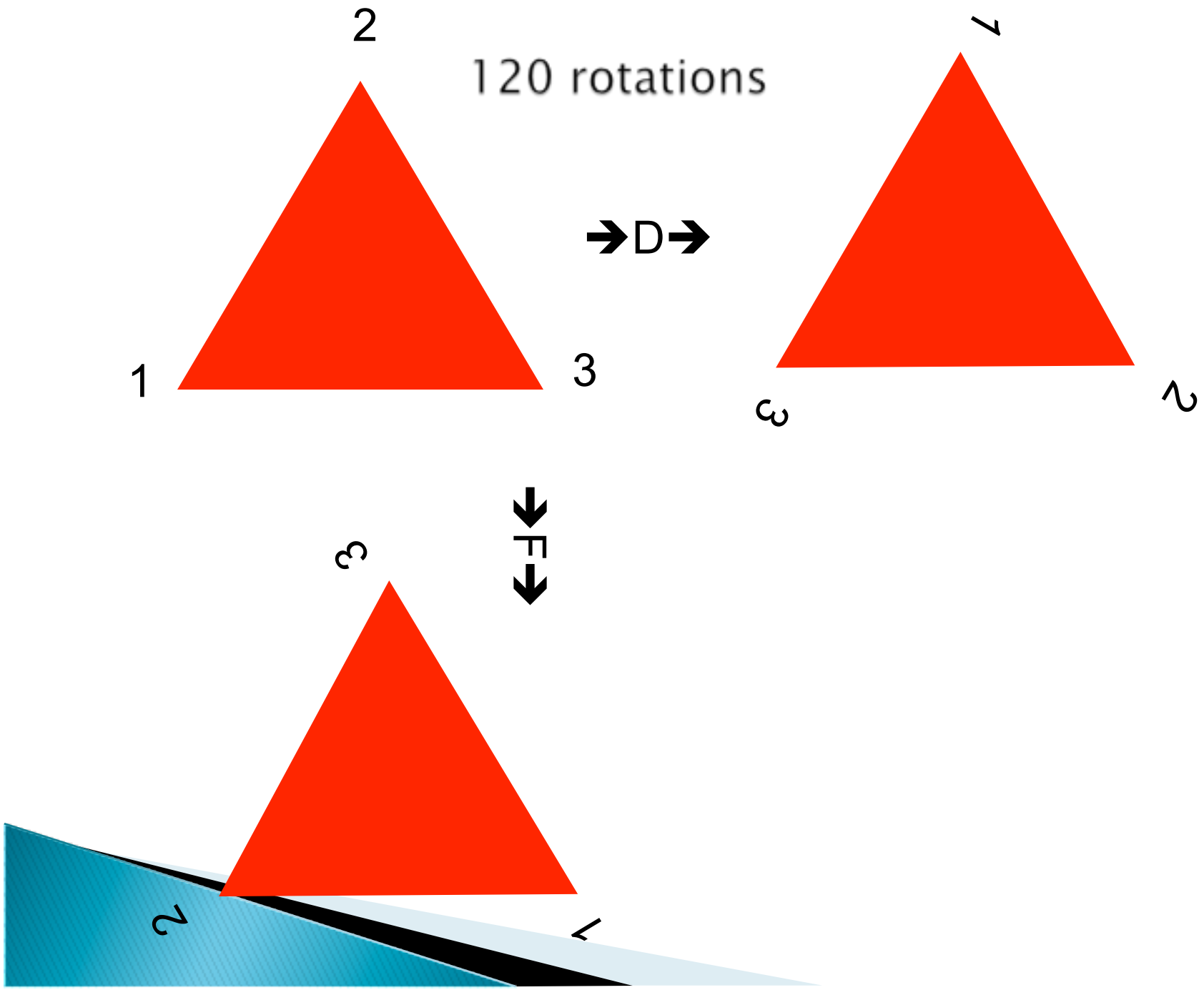


C

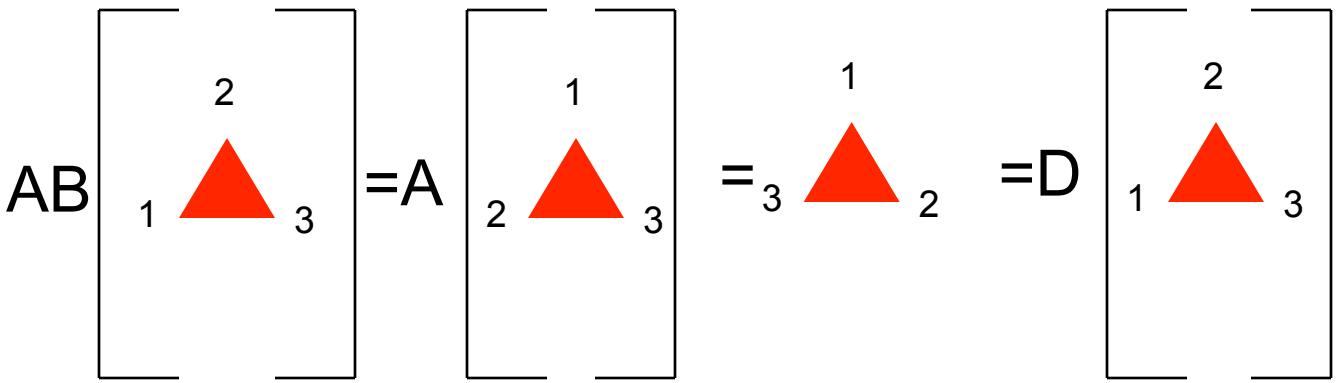
→B→






2
120 rotations
1
3
→D→
1
3
2
F
3
2
1

Closure property



Six elements: identity, three filps, two rotations
Group of order 6

Cayley (multiplication) table

classes

I $3C_2$ $2C_3$

Left

Right

	I	A	B	C	D	F
I	I	A	B	C	D	F
A	A	I	D	F	B	C
B	B	F	I	D	C	A
C	C	D	F	I	A	B
D	D	C	A	B	F	I
F	F	B	C	A	I	D

Three classes: 1) identity (E), 2) three 180 rotations (A,B,C), 3) 120 rotation (D) and 240 rotation (F)

Isomorphic groups

Two groups *G* and *G'* are called isomorphic, if there is one-to-one correspondence between their elements

$$G = \{A, B, C \ldots P \ldots\}$$
$$G' = \{A', B', C' \ldots P' \ldots\}$$
$$A \Leftrightarrow A'$$
$$B \Leftrightarrow B'$$
$$\ldots.$$
$$AB = P$$
$$A'B' = P'$$

Example: D_3 is isomorphic to C_{3v} (rotations by 120° + reflections in three vertical planes)

Basis

Let $\psi_1(\mathbf{x})$ is an arbitrary (single-valued) function of $\mathbf{x}$.

Take an element R of group G (order g)

Apply the operator $P(R)$ to $\psi_1(\mathbf{x})$ defined as

$$P(R)\psi_1(\mathbf{x}) \equiv \psi_1\left(R^{-1}\mathbf{x}\right) \equiv \Phi_R(\mathbf{x})$$

Operators $P(R)$ form a group which is isomorphic to G: $P(S)P(R) = P(SR)$

Proof:

$$P(S)P(R)\psi_1(\mathbf{x}) = P(S)\Phi_R(\mathbf{x}) = \Phi_R\left(S^{-1}\mathbf{x}\right) = \psi_1\left(R^{-1}S^{-1}\mathbf{x}\right) = \psi_1\left((SR)^{-1}\mathbf{x}\right) = P(SR)\psi_1(\mathbf{x})$$

Applying all symmetry operations to ψ_1, we get a set of r linearly indepedent functions

$$\underbrace{\{\psi_1 \ldots \psi_r\}}_{\text{BASIS}}$$

In general, $r \le g$.

NB : choice of ψ_1 is arbitrary.

Representation of a group

Applying a symmetry operation to the basis function, we get a linear superposition of basis functions

$$P(S)\psi_i = \sum_{k=1}^{r} G_{ki}(S)\psi_k$$

Matrices $G(S)$ form a representation of the group.

Representation of a group is as arbitrary as the choice of the basis function.

If a matrix of particular representation cannot be reduced to a block-diagonal form by any similarity transformations, such a representaton is called *irreducible.*

Irreducible represenations of D_3

1) consider a function which does not change either upon rotations or flips

$$f(x,y,z) = 1, x^2 + y^2, z^2, \ldots$$

This function generates a trivial 1D representation

$$G(I) = G(A) = G(B) = G(C) = G(D) = G(F) = 1$$

2) consider a function which is invariant with respect to 120 rotations but changes its sign upon flips

$$f(x,y,z) = z$$

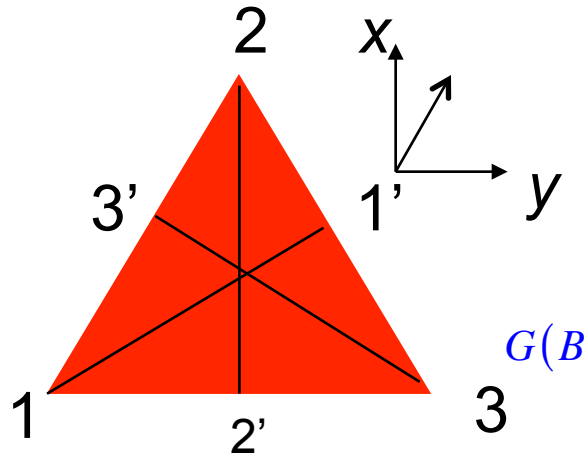
This function generates another 1D representation

$$G(I) = G(D) = G(F) = 1$$

$$G(A) = G(B) = G(C) = -1$$

Irreducible representations of D_3 ,continued…

3) 2D representations are formed by two basis functions which transform as elements of a vector *(x,y)*



$$G(I)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix};\ \mathrm{Tr}=2$$

identity

$$G(A)=\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix};\ \mathrm{Tr}=0$$

22' flip: x→-x,y→y

$$G(B)=\begin{pmatrix}1/2 & -\sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \mathrm{Tr}=0$$

33' flip

$$G(C)=\begin{pmatrix}1/2 & \sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \mathrm{Tr}=0$$

11' flip

$$G(D)=\begin{pmatrix}-1/2 & \sqrt{3}/2\\ -\sqrt{3}/2 & -1/2\end{pmatrix};\ \mathrm{Tr}=-1$$

120 rotation

$$G(F)=\begin{pmatrix}-1/2 & -\sqrt{3}/2\\ \sqrt{3}/2 & -1/2\end{pmatrix};\ \mathrm{Tr}=-1$$

240 rotation

Characters

Character=trace of an irreducible representation matrix

Traces are invariant➔characters do not depend on the choice of basis functions

Reading character tables

A,B: 1D representations (*A* is even upon rotation, *B* is odd)
E: 2D representation (not to be confused with identity!)
F: 3D representation…

Group

Class

D_3		I	$2C_3$	$3C_2$
1	A_1	1	1	1
z	A_2	1	1	-1
(x,y)	E	2	-1	0

Basis function

irrep

Trace of irrep

Orthogonality of characters

Take trace^2, multiply by the number of the elements in the class, and sum over classes

D_3		I	$2C_3$	$3C_2$
1	A_1	1	1	1
z	A_2	1	1	−1
(x,y)	E	2	−1	0

same irrep

$$1\times 1^2 + 2\times 1^2 + 3\times 1^2 = 6 = g$$

$$1\times 1^2 + 2\times 1^2 + 3\times (-1)^2 = 6 = g$$

$$1\times 2^2 + 2\times (-1)^2 + 3\times 0^2 = 6 = g$$

$$\sum_C \underbrace{N_C}_{\text{number of elements in } C} |\chi^\alpha(\underbrace{C}_{\text{class}})|^2 = g$$

different irreps

$$A_1 \text{ and } A_2:\ 1\times(1\times 1)+2\times(1\times 1)+3\times(1\times(-1))=0$$

$$A_1 \text{ and } E:\ 1\times(1\times 2)+2\times(1\times(-1))+3\times(1\times 0)=0$$

$$\sum_C \underbrace{N_C}_{\text{number of elements in } C} [\chi^\beta(C)]^* \chi^\alpha(\underbrace{C}_{\text{class}}) = g\delta_{\alpha\beta}$$

Also,

$$1^2 + 1^2 + 2^2 = 6 = g$$

$$\sum_{\alpha:\text{ over irreps}} \underbrace{f_\alpha^2}_{\text{dim of irrep}} = g$$

Van Vleck orthogonality theorem for irreps

$$\sum_{R\text{: symmetry elelements}} \left[G_{ik}^{\alpha}(R)\right]^{*} G_{lm}^{\beta}(R) = \frac{g}{f_{\alpha}} \delta_{\alpha\beta}\delta_{il}\delta_{km}$$

Set $i = k, l = m$ and take a trace $\Rightarrow$

$$\sum_{R\text{: symmetry elelements}} \left[\chi^{\alpha}(R)\right]^{*} \chi^{\beta}(R) = g\delta_{\alpha\beta}$$

All elements of the same class (C) have the same characters $\Rightarrow$

$$\sum_{C\text{: classes}} N_C \left[\chi^{\alpha}(C)\right]^{*} \chi^{\beta}(C) = g\delta_{\alpha\beta}$$

Decomposition theorem

Let $\bar{G}$ be a reducible representation of dim f with character χ_R .

A reducible representation can be expanded over irreps

$$\bar{G} = \sum_\alpha a_\alpha G_\alpha$$

or, since dims of G may be different,

$$\bar{G} = a_1 G_1 \oplus a_2 G_2 \oplus \ldots \qquad \oplus \equiv \text{direct sum}$$

$$A \oplus B = \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix}$$

Applying trace,

$$\chi_R = \sum_\alpha a_\alpha \chi^\alpha$$

How many times an irrep G^α is contained in $\bar{G}$? Using orthogonality of characters,

$$a_\alpha = \frac{1}{g} \sum_{C:\text{all classes of } G^\alpha} N_C \chi_R \left[\chi^\alpha(C)\right]^*$$

Applications in Quantum Mechanics

$$\hat{H}\psi = E\psi$$

Wavefunctions must obey all symmetry properties of the Hamiltonian.

A proper description of a degenerate state is a linear superposition of wavefunctions.

Basis functions of a given irrep are transformed into each other under group operations➔

Degenerate states form a basis of a given irrep➔

Dimensionality of a given irrep gives us immediately degeneracy of the corresponding energy level

A,B: 1D representations ➔ non-degenerate levels

E: 2D representation ➔ two-fold degeneracy

F: 3D representation ➔ three-fold degeneracy

Lifting of degeneracy by perturbation

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

Symmetry of $\hat{H}'$ < Symmetry of $\hat{H}_0 \Rightarrow$

Representations of $\hat{H}'$ are contained in $\hat{H}$

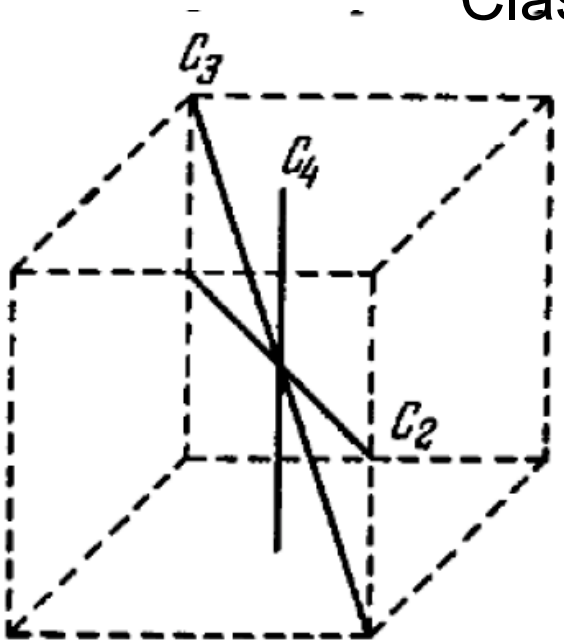
In general, a representation of $\hat{H}'$ is a reducible representation of $\hat{H}_0$

Decomposing representations of $\hat{H}'$ into irreps of $\hat{H}_0$,

we find which degeneracies are lifted.

Example: lifting of cubic degeneracy

$\hat{H}_0(O)$: Rotational group of a cube (without inversion and reflection symmetries)



Classes:

$$4\ C_3\ \text{axes} \Rightarrow 8C_3\ (4\underbrace{C_3}_{120} + 4\underbrace{C_3^2}_{240})$$

$$6\ C_2\ \text{axes} \Rightarrow 6C_2$$

$$3\ C_4\ \text{axes} \Rightarrow 6C_4\ (3C_4 + 3C_4^3)$$

$$\Rightarrow 3C_2\ (=3C_4^2)$$

O	I	$8C_3$	$3C_2$	$6C_2$	$6C_4$	
$A_1(\Gamma_1)$	1	1	1	1	1	} non-degen.
$A_2(\Gamma_2)$	1	1	1	−1	−1	
$E(\Gamma_{12})$	2	−1	2	0	0	} 2-fold
$F_1(\Gamma_{15})$	3	0	−1	−1	1	} 3-fold
$F_2(\Gamma_{25})$	3	0	−1	1	1	

$\hat{H}'(D_3)$: A strain is applied along the main diagonal

How does the strain split the degenerate levels?

Lifting of 3-fold degeneracy

Group O contans all the elements of D_3 $[E, 2C_3, 3C_2]$

For example, irrep F_2 of O is a reducible representation of D_3

O	I	$8C_3$	$3C_2(=3C_4^2)$	$6C_2$	$6C_4$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
E	2	−1	2	0	0
F_1	3	0	−1	−1	1
F_2	3	0	−1	1	−1

D_3	I	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

Decomposition formula: $a^\alpha = \frac{1}{g} \sum_{C:\text{all classes of } G^\alpha} N_C \chi_R(\bar{C}) \left[\chi^\alpha(C)\right]^*$

$$a(A_1) = \frac{1}{6}\left[\overbrace{\underbrace{1}_{N_C} \times \underbrace{3}_{\chi(I)} \times \underbrace{1}_{\chi^{A_1}(I)}}^{I} + \overbrace{\underbrace{2}_{N_C} \times \underbrace{0}_{\chi(8C_3)} \times \underbrace{1}_{\chi^{A_1}(2C_3)}}^{2C_3} + \overbrace{\underbrace{3}_{N_C} \times \underbrace{1}_{\chi(6C_2)} \times \underbrace{1}_{\chi^{A_1}(3C_2)}}^{3C_2}\right] = 1$$

$$a(A_2) = \frac{1}{6}\left[3\times 1 + 2\times 0\times 1 + 3\times 1\times(-1)\right] = 0$$

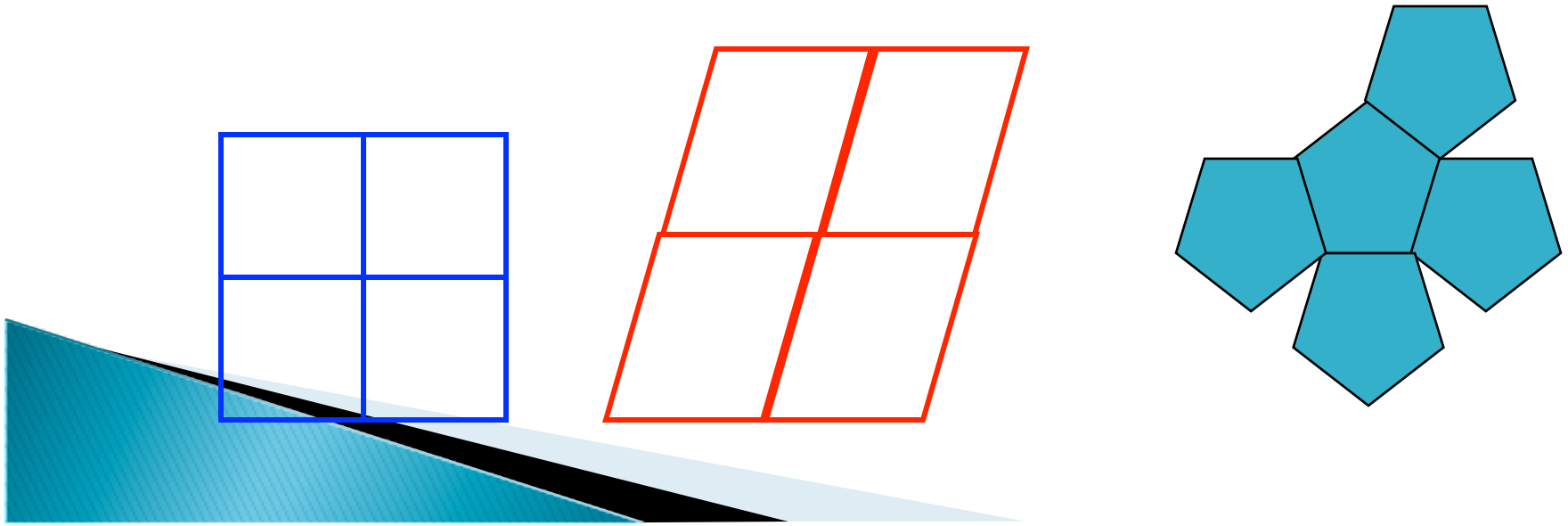
$$a(E) = \frac{1}{6}\left[3\times 2 + 2\times 0\times(-1) + 3\times 1\times 0\right] = 1$$

$F_2(\times 3) \longrightarrow A_1(\times 1) + E(\times 2)$

Lattice symmetries

Rotational symmetries of building blocks (polygons) must be consistent with translational symmetry

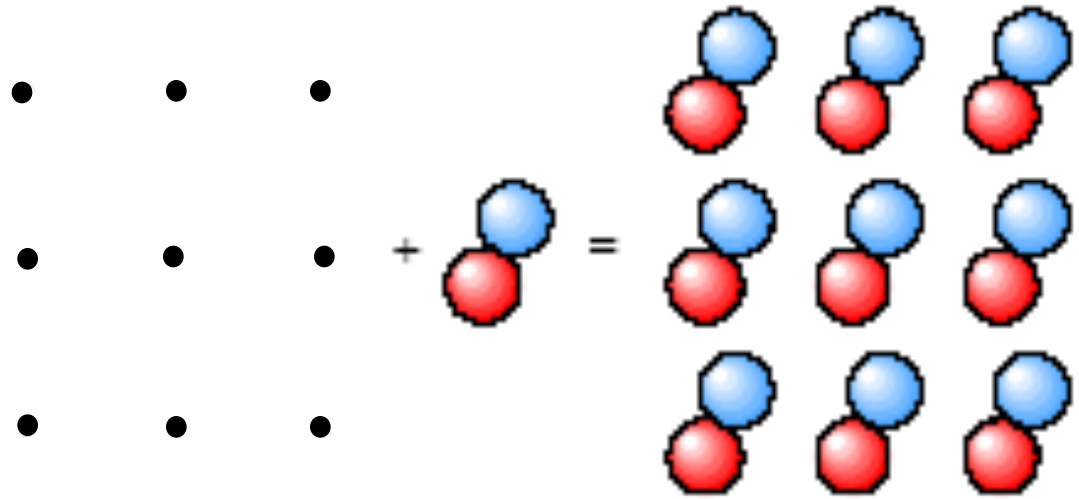
crystallographic restriction theorem: lattice can have only 2, 3, 4, and 6-fold rotational symmetries



Crystal Structure

Crystal structure can be obtained by attaching atoms or groups of atoms --basis-- to lattice sites.

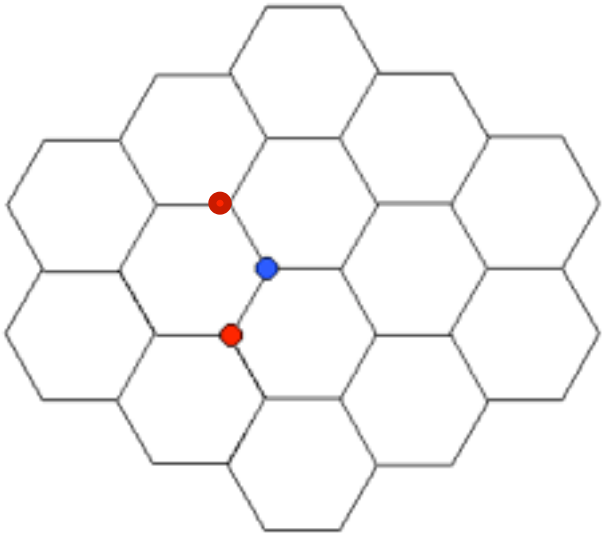
Crystal Structure = Crystal Lattice • + Basis

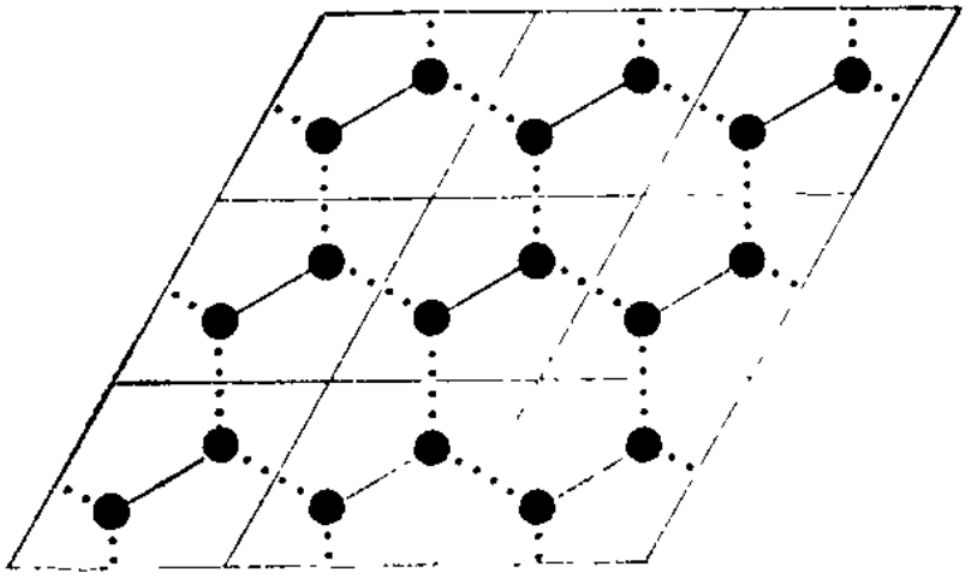


Partially from Prof. C. W. Myles (T... Tech) course presentation

Bravais lattices: monoatomic basis

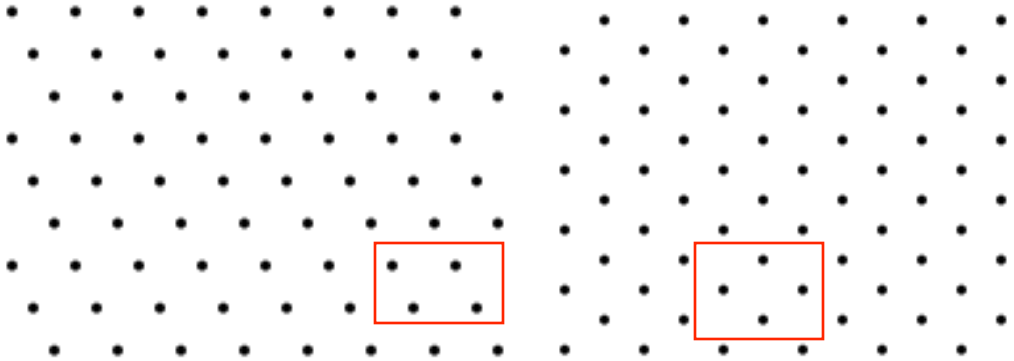
Non-Bravais lattices: polyatomic basis





Graphene: Honeycomb

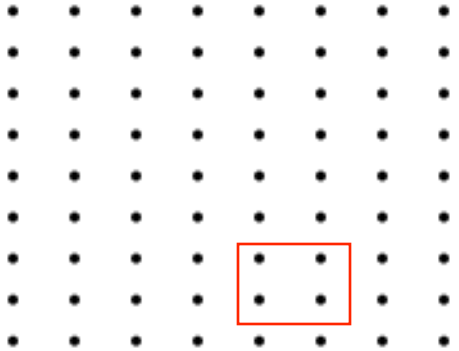
Five 2D Bravais lattices



Oblique

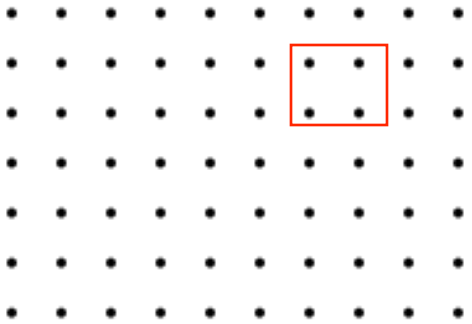
$180^\circ = \frac{2\pi}{2}\ 180^\circ = \frac{2\pi}{2} \Rightarrow 2-\text{fold axis}$

Rhombohedral



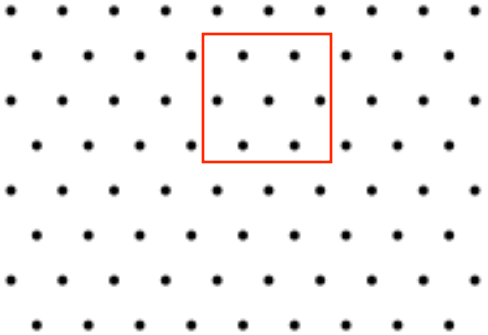
Orthorhombic (Rectangular)

$180^\circ = \frac{2\pi}{2}$



Tetragonal (Square)

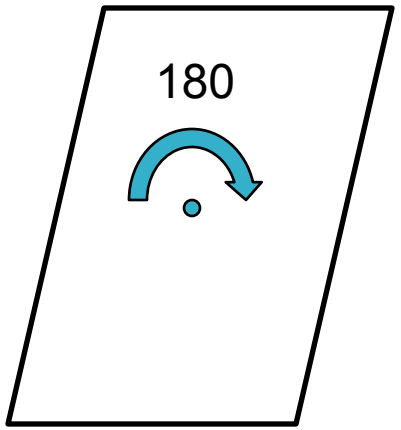
$90^\circ = \frac{2\pi}{4} \Rightarrow 4\text{-fold axis}$



Hexagonal (Triangular)

$60^\circ = \frac{2\pi}{6} \Rightarrow 6\text{-fold axis}$

Oblique



Elements of symmetry: C_2 rotations

Group: C_2

Ohm's law on a lattice:

$$j_i = \sigma_{ij} E_j$$

Conductivity tensor

$$\hat{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \tag{1}$$

How many independent components does an oblique lattice have?

The only symmetry operation is the 180 rotation about z.

Matrix of rotation about z by θ:

$$U_\theta = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \Rightarrow \tag{2}$$

$$U_{180} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} = -1 \times \mathbb{1} \tag{3}$$

Transformation of the Ohm's law under rotation

$$\hat{U}\vec{j} = \hat{U}\hat{\sigma}\hat{U}^{-1}\hat{U}\vec{E} \Rightarrow \hat{\sigma} \rightarrow \hat{U}\hat{\sigma}\hat{U}^{-1} \tag{4}$$

For rotations, $\hat{U} \hat{=} U^{-1} \Rightarrow$

$$\hat{\sigma} = \hat{U}\hat{\sigma}\hat{U} \tag{5}$$

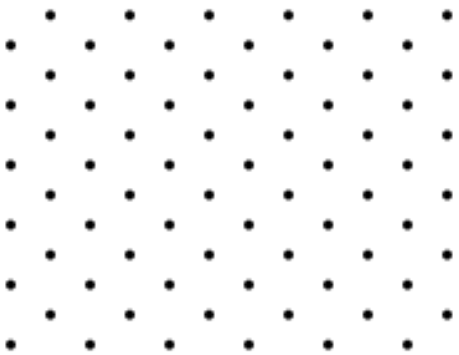
$$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} = \hat{U}_{180}\hat{\sigma}\hat{U}_{180} = (-1)\begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix}(-1)$$
$$= \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \quad (6)$$

$\Rightarrow$ lattice symmetry imposes no constrains on $\hat{\sigma}$.

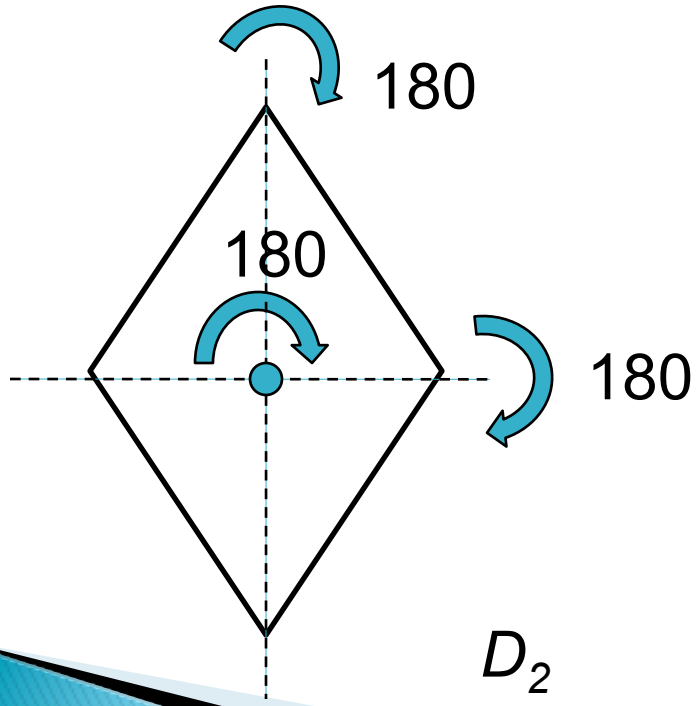
Time-reversal symmetry
(symmetry of Onsager kinetic coefficients):

$$\sigma_{ij} = \sigma_{ji} \Rightarrow \quad (7)$$

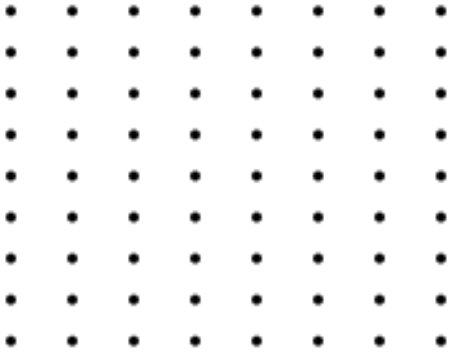
$$\hat{\sigma}_{\text{oblique}} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{xy} & \sigma_{yy} \end{pmatrix} \quad (8)$$



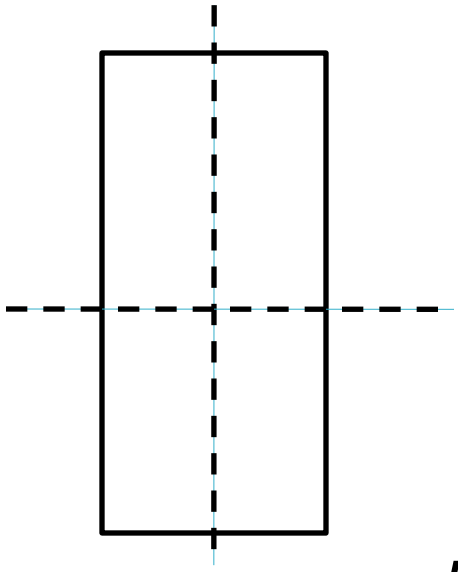
Rhombohedral



D_2

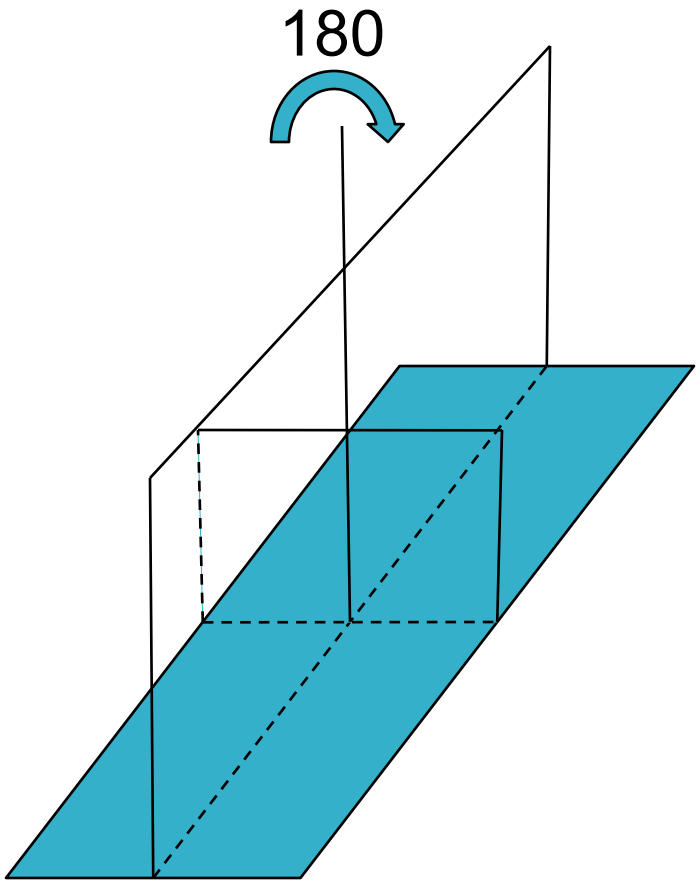


Orthorhombic (Rectangular)



D_2

Equivalently, one can do reflections in vertical planes



D_2=C_{2v} (=means “isomorphic”)

$D_2 = (C_{2v})$ **group**
(rhombohedral and orthorhombic lattices)

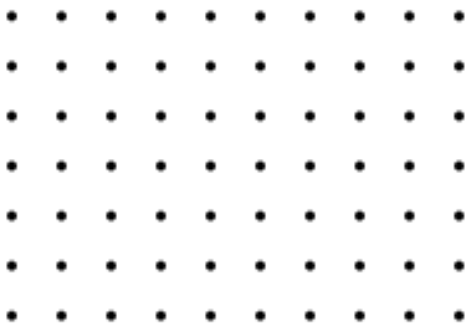
We already know that $\hat{U}_{180}$ about z axis imposes no constraints.

180 rotation about the x axis: $x \to x$, $y \to -y$

$$\hat{U}^x_{180} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{9}$$

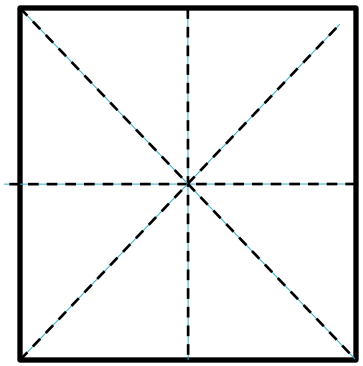
$$\begin{aligned} \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} = \hat{U}^x_{180}\hat{\sigma}\hat{U}^x_{180} &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \sigma_{xx} & -\sigma_{xy} \\ \sigma_{yx} & -\sigma_{yy} \end{pmatrix} \\ &= \begin{pmatrix} \sigma_{xx} & -\sigma_{xy} \\ -\sigma_{yx} & \sigma_{yy} \end{pmatrix} \Rightarrow \sigma_{xy} = 0, \quad \sigma_{yx} = 0 \end{aligned} \tag{10}$$

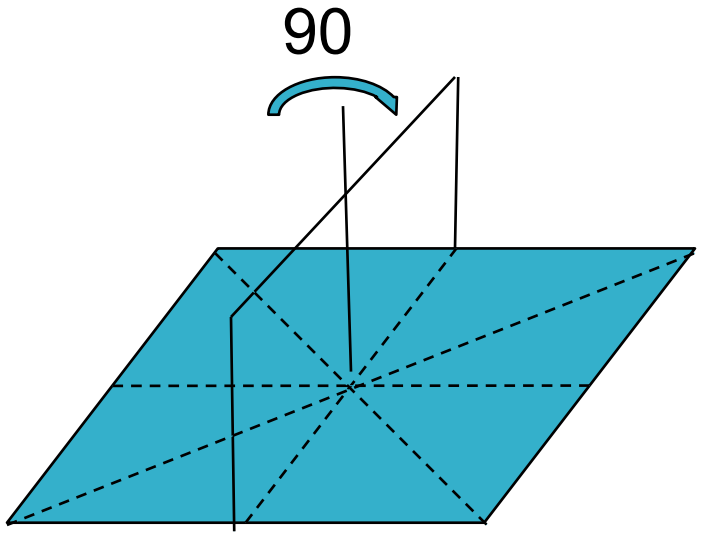
$$\hat{\sigma}_{\text{rhombo/ortho}} = \begin{pmatrix} \sigma_{xx} & 0 \\ 0 & \sigma_{yy} \end{pmatrix} \tag{11}$$



Tetragonal (Square)

Symmetry operations:
3×90 rotations
180 rotations about 4 horizontal axes
→D_4





Symmetry operations:
3×90 rotations
Reflections in 4 Vertical planes
→C_{4v}

D_4=C_{4v}

$$D_4 = C_{4v}$$

(tetragonal)

D_4 (C_{4v}) already contains all symmetries of D_2 (C_{2v}). $\Rightarrow$ At least, we must have

$$\hat{\sigma}_{\text{tetra}} = \begin{pmatrix} \sigma_{xx} & 0 \\ 0 & \sigma_{yy} \end{pmatrix} \tag{12}$$

However, we have additional symmetries: 180 rotations about diagonals (or reflections in the diagonal vertical planes).

Reflection in a diagonal vertical plane: $x \to y$, $y \to x$

$$\hat{R} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\hat{R} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} y \\ x \end{pmatrix} \tag{13}$$

$$\begin{pmatrix} \sigma_{xx} & 0 \\ 0 & \sigma_{yy} \end{pmatrix} = \hat{R}\hat{\sigma}\hat{R} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \sigma_{xx} & 0 \\ 0 & \sigma_{yy} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & \sigma_{xx} \\ \sigma_{yy} & 0 \end{pmatrix} = \begin{pmatrix} \sigma_{yy} & 0 \\ 0 & \sigma_{xx} \end{pmatrix}$$

$$\Rightarrow \sigma_{xx} = \sigma_{yy} \tag{14}$$

$$\hat{\sigma}_{\text{tetra}} = \begin{pmatrix} \sigma_{xx} & 0 \\ 0 & \sigma_{xx} \end{pmatrix} \tag{15}$$

Any tensor describing physical properties of the lattice

- dielectric permittivity $\hat{\varepsilon}$
- elastic moduli
- electron effective mass $\hat{m}$
- ...

have the same symmetries.

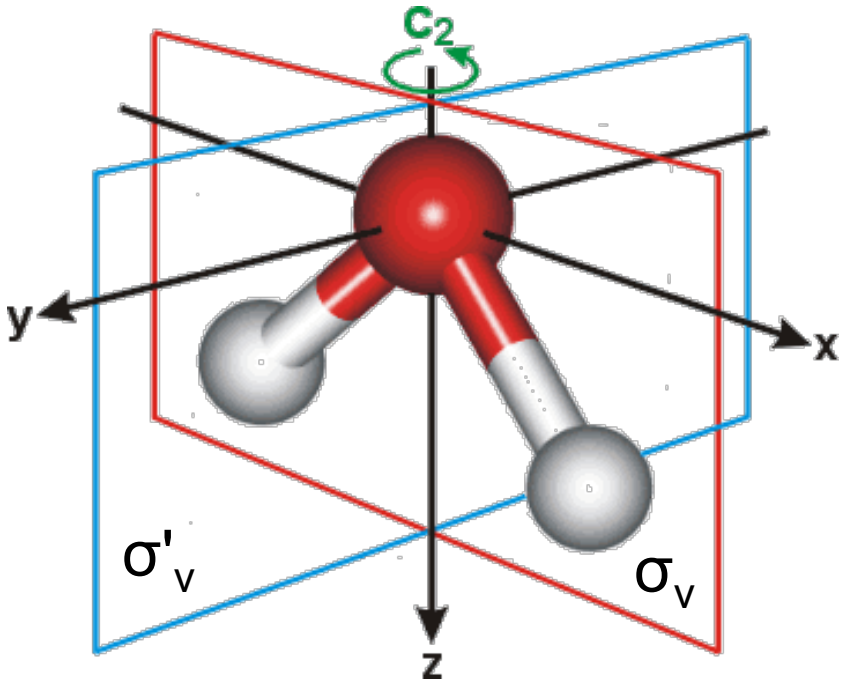
Exercise: work out symmetries of $\hat{\sigma}$ for the hexagonal lattice.

Vibrational modes of the H_2O molecule

System of *N* particles (not on the same line):
3N degrees of freedom
3 translational
3 *rotational*
# of vibrational modes: $N_v = 3N-3-3=3N-6$
For H_2O: $N=3 \rightarrow N_v=3$

What are those 3 modes?

H_2O



C_2 axis+2 vertical planes (σ_v and σ'_v)

→ C_{2v} group

Symmetry operations of C_{2v} group: I, C_2, σ_v, and σ_v'. $g = 4$.

Special property: C_{2v} is *cyclic* group.

Cyclic group:

Take one symmetry element, S.

All other elements are given by S^k, $k = 1, 2...$

Cyclic groups have only 1D irreps.

C_{2v} is particularly simple:

applying any element twice, we get I.

$$C_2^2 = I, \quad \sigma_v^2 = I, \quad (\sigma_v')^2 = I.$$

Let ψ be any basis function.

$$S(S\psi) = S^2\psi = \psi$$

Irreps are numbers such that $G^2 = 1 \Rightarrow G = \pm 1$.

$$\sum_{\text{irreps}} \dim^2(\text{irrep}) = g$$

$$\sum_{\text{irreps}} 1 = 4 \Rightarrow \#\text{ of irreps} = 4$$

How do the group elements act on coordinates?

$$C_2: \quad x \to -x,\ y \to -y$$
$$\sigma_v: \quad x \to x,\ y \to -y$$
$$\sigma_v': \quad x \to -x,\ y \to y$$

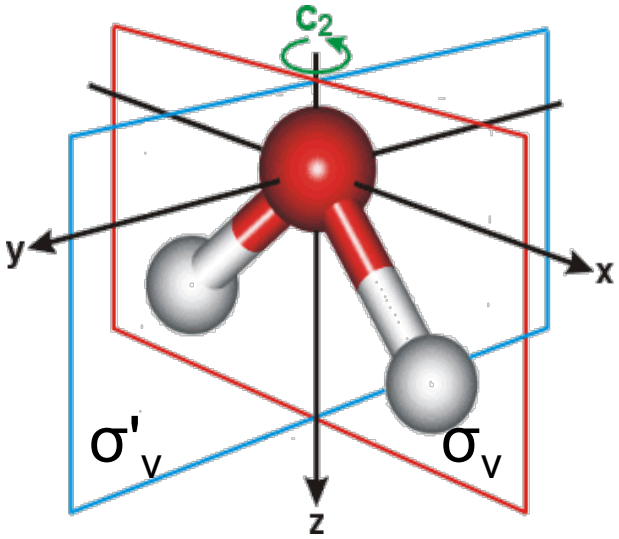
For all operations, $z \to z$.

Table of characters

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

$A_{1,2}$ even under C_2, $B_{1,2}$ odd under C_2.

We know that $N_v = 3$ but we have 4 irreps.
Some of the irreps do not correspond to molecular vibrations!
Need to get rid of irreps that correspond to translations and rotations rather than to vibrations.



Equivalence ("atomic site") representation (G_{eq}) is formed by vibrational displacements of all atoms consistent with the symmetry operations of the group.

In general, G_{eq} is reducible. Expand G_{eq} over irreps.

$$C_{2v}: \quad G_{eq} = a_1 A_1 + a_2 A_2 + a_3 B_1 + a_4 B_2$$

Some of the coefficients should be zero.
Consider rotation by angle θ
about some symmetry axis of the molecule in 3D

$$U_\theta = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Its character:

$$\chi(U_\theta) = \mathrm{Tr} U_\theta = 1 + 2\cos\theta$$

If there are N_a atoms on the same axis,

$$\chi(U_\theta) = N_a(1 + 2\cos\theta)$$

Each of the N_a atoms was subjected not only to vibrations but also to translations and rotations $\Rightarrow$
$\chi(U_\theta)$ contains extra degrees of freedom.

Translation is a vector $\vec{u} = (u_x, u_y, u_z)$. U_θ transforms its as any other vector. The corresponding character is

$$1 + 2\cos\theta$$

Rotation by an infinitesimally small angle $\delta\phi$ is described by vector $\delta\vec{\phi}$ of magnitude $\delta\phi$ and along the axis of rotation. $\delta\vec{\phi}$ is a polar vector but, under rotations, it transforms as a polar vector. Its transformation adds another $1 + 2\cos\theta$ term to $\chi(U_\theta)$.

Subtracting $2(1 + 2\cos\phi)$ from $\chi(U_\theta)$, we obtain a character of *purely vibrational* degrees of freedom

$$\chi_v = N_a(1 + 2\cos\theta) - 2(1 + 2\cos\theta) = (N_a - 2)(1 + 2\cos\theta)$$

Equivalence representation of C_{2v}

$$\chi_v = (N_a - 2)(1 + 2\cos\theta)$$

Identity (I): $N_a = N$, $\theta = 0 \Rightarrow$

$$\chi_v(I) = 3$$

. C_2 contains 1 oxygen: $\Rightarrow N_a = 1,\ \theta = 180 \Rightarrow$

$$\chi_v(C_2) = -1(1 - 2) = 1$$

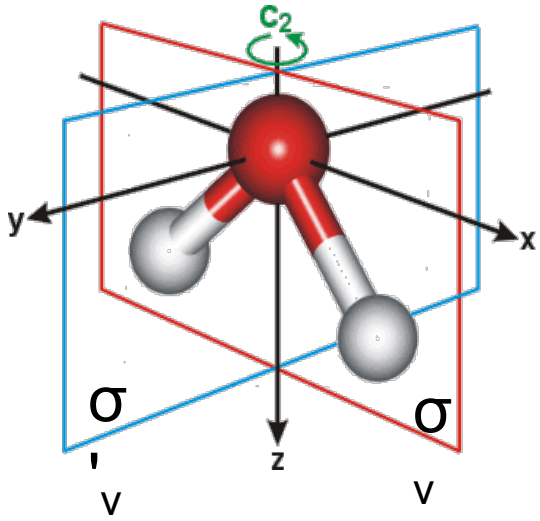
σ_v leaves all atoms intact$\Rightarrow$

$$\chi_v(\sigma_v) = \chi_v(I) = 3$$

σ'_v is equivalent to $C_2 \Rightarrow$

$$\chi_v(\sigma'_v) = \chi_v(C_2) = 1$$

C_{2v}	I	C_2	σ_v	σ'_v
G_{eq}	3	1	3	1



Last part: decompose G_{eq} into irreps of C_{2v}

C_{2v}	I	C_2	σ_v	σ'_v
z, A_1	1	1	1	1
xy, A_2	1	1	-1	-1
x, B_1	1	-1	1	-1
y, B_2	1	-1	-1	1

C_{2v}	I	C_2	σ_v	σ'_v
G_{eq}	3	1	3	1

$$G_{eq} = a_1 A_1 + a_2 A_2 + a_3 B_1 + a_4 B_2$$

Decomposition formula

$$a_\alpha = \frac{1}{g} \sum_C N_C \chi_v(C) \left[\chi_\alpha(C)\right]^*$$

$$g = 4,\ N_C = 1$$

$$a_1 = \frac{1}{4}(3 \times 1 + 1 \times 1 + 3 \times 1 + 1 \times 1) = 2$$

$$a_2 = \frac{1}{4}(3 \times 1 + 1 \times 1 - 3 \times 1 - 1 \times 1) = 0$$

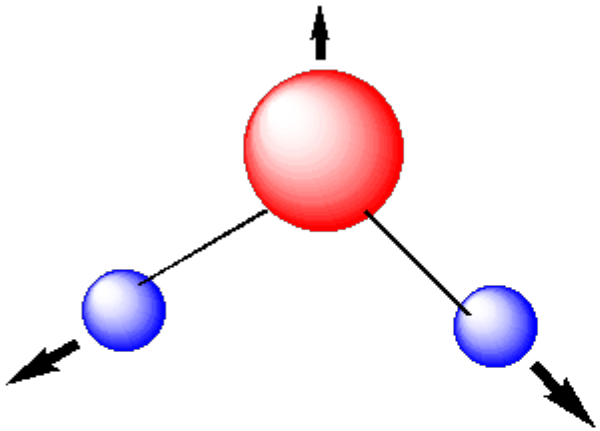
$$a_3 = \frac{1}{4}(3 \times 1 - 1 \times 1 + 3 \times 1 - 1 \times 1) = 1$$

$$a_4 = \frac{1}{4}(3 \times 1 - 1 \times 1 - 3 \times 1 + 1 \times 1) = 0$$

$$G_{eq} = 2A_1 + B_1 \Rightarrow$$

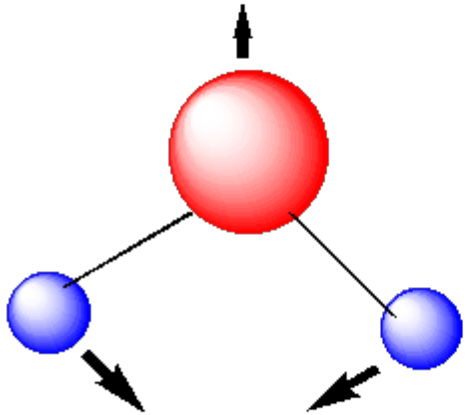
Two vibrational modes with symmetry A_1, one with symmetry B_1, none with A_2 and B_2.

A_1



Symmetric Stretch
3657 cm^{-1}

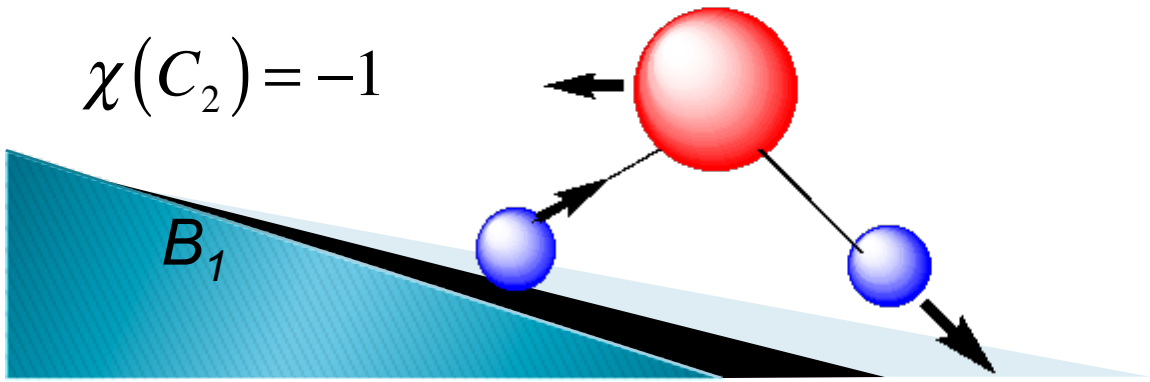
$\chi(C_2) = +1$



Bend 1595 cm^{-1}

A_1

$\chi(C_2) = -1$



Asymmetric Stretch
3756 cm^{-1}

Selection Rules

Consider a basis function ψ_i^α $(i = 1...f)$ of the an f dimensional representation ψ_i^α.

Theorem 1: The integral of ψ_i^α over an entire configurational space of the system

$$\int \psi_i^\alpha dq$$

is non-zero is non-zero if and only if Γ^α is the identical (or symmetric) representation, Γ_1.

Proof: Assume that $\Gamma^\alpha \neq \Gamma_1$. Since the integral must be the same in any coordinate system (it is over all space), we can say

$$\int \psi_i^\alpha dq = \int \hat{\Gamma}^\alpha \psi_i^\alpha dq = \int \sum_k \Gamma_{ki}^\alpha \psi_k^\alpha$$

where $\hat{\Gamma}$ transforms the function by acting as a matrix product. Now we sum the last equation over all symmetry elements of group G:

$$\sum_G \int \psi_i^\alpha dq = \sum_G \int \Gamma_{ki}^\alpha \psi_k^\alpha dq$$

On the LHS, we simply get the group order (g) times the original integral,

$$g \int \psi_i^\alpha dq = \int \sum_G \Gamma_{ki}^\alpha \psi_k^\alpha dq$$

Recall the orthogonality theorem

$$\sum_G \left(\Gamma^\beta_{ik}\right)^* \Gamma^\alpha_{jl} = \frac{g}{f_\beta} \delta_{\alpha\beta}\delta_{ij}\delta_{kl}$$

If $\Gamma^\beta = \Gamma_1$, then

$$\sum_G \Gamma^\alpha_{jl} = g\delta_{\alpha 1} = \begin{cases} g, & \alpha = 1 \\ 0, & \alpha \neq 1 \end{cases}$$

Because of this, it immediately follows that

$$\int \psi^\alpha_i dq = \frac{1}{g} \int \sum_G \Gamma^\alpha_{ki} \psi^\alpha_k dq = 0$$

if $\Gamma^\alpha \neq \Gamma_1$. Hence, $\Gamma^\alpha = \Gamma_1$.
Consider the Hamiltonian

$$H = H_o + H'$$

where H_o has group G and H' has some lower symmetry group. Define the matrix elements

$$M = \int \psi^\beta_k H' \psi^\alpha_i dq$$

The direct product (or tensor product or Kronecker product) of representations is denoted by

$$C = A \otimes B \quad , \quad C_{sr} = A_{ij} B_{kl}$$

for $1 \leq (i, j, k, l) \leq (m, n, p, q)$ and so

$1 \leq (s,r) \leq (mp, nq)$. For example,

$$A \otimes B = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \otimes \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} = \begin{pmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{pmatrix}$$

$$= \begin{pmatrix} a_{11} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} & a_{12} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} \\ \\ a_{21} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} & a_{22} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} \end{pmatrix} \tag{16}$$

Notice that

$$\mathrm{Tr}\{A \otimes B\} = \sum_i a_{ii} \sum_j b_{jj} = \mathrm{Tr}\{A\}\,\mathrm{Tr}\{B\}$$

Suppose we have two representations Γ^{α}_{ij} and Γ^{β}_{kl}. The direct product of two representations

$$\Gamma = \Gamma^{\alpha} \otimes \Gamma^{\beta}$$

is a matrix given by the direct product of matrices corresponding to Γ^{α} and Γ^{β}.
Going back to the matrix element,

$$M = \int \psi^{\beta}_{k} H' \psi^{\alpha}_{i} dq$$

we note that $M \neq 0$ if and only if the integrand transforms as Γ_1. Suppose that H' transforms as some representation

$\Gamma^{H'}$ which, in general, is a *reducible* representation of the Hamiltonian group G. The integrand transforms as a triple direct product

$$\Gamma^{\beta} \otimes \Gamma^{H'} \otimes \Gamma^{\alpha}$$

According to Theorem 1, the matrix element is non-zero if and only if this triple product contains an identical representation

$$\Gamma^{\beta} \otimes \Gamma^{H'} \otimes \Gamma^{\alpha} = \Gamma_1 \oplus \dots$$

Now we have practical way to find if the matrix element is non-zero: we must decompose the triple product into irreps of G, and see if Γ_1 occurs in the decomposition. If it does, then $M \neq 0$; if it does not, $M = 0$.
This procedure can be simplified further if we observe that the direct product of some representation Γ with itself, $\Gamma \otimes \Gamma$, must necessarily contain Γ_1. Indeed, let us decompose $\Gamma \otimes \Gamma$ into irreps

$$\Gamma \otimes \Gamma = a_1\Gamma_1 \oplus a_2\Gamma_2 \oplus \cdots$$

The weight of Γ_1 in this decomposition is found as

$$a_1 = \frac{1}{g} \sum_G \chi_{\Gamma\otimes\Gamma}(G)\chi^*_{\Gamma_1}(G)$$

For a direct product of two matrices, $\mathrm{Tr}\,(A \otimes B) = \mathrm{Tr}(A)\mathrm{Tr}(B)$. (To convince yourself in the validity of this identity have a look at the example of the direct product of 2×2 and 3×3 matrices.) Therefore,

$\chi_{\Gamma\otimes\Gamma} = \chi_\Gamma^2$ while, by definition, $\chi_{\Gamma_1} = 1$. By the orthogonality property of characters,

$$\frac{1}{g}\sum_G \chi^2_{\Gamma^\alpha} = 1.$$

Therefore,

$$a_1 = \frac{1}{g}\sum_G \chi_{\Gamma\otimes\Gamma} = \frac{1}{g}\sum_G \chi^2_\Gamma = \frac{1}{g}g = 1,$$

which means that Γ_1 contains in $\Gamma\otimes\Gamma$ once.
Thus the condition $\Gamma^\beta\Gamma^{H'}\Gamma^\alpha = \Gamma_1 \oplus \dots$ can be replaced by an equivalent one

$$\Gamma^{H'}\otimes\Gamma^\alpha = \Gamma^\beta \oplus \dots$$

Indeed, in this case, $\Gamma^\beta \otimes \left(\Gamma^{H'}\otimes\Gamma^a\right)$ must necessarily contain Γ_1.

A. Dipole selection rule

Consider am electron system subject to a weak electromagnetic field. In the transverse gauge, $\nabla\cdot\vec{A} = 0$,

$$H = \frac{1}{2m}\left(\vec{p} + \frac{e}{c}\vec{A}\right)^2 = \underbrace{\frac{p^2}{2m}}_{H_o} + \underbrace{\frac{e}{mc}\vec{A}\cdot\vec{p}}_{H'} + O(A^2)$$

The matrix element of the transition is

$$\langle\beta, j|H'|\alpha, i\rangle = \frac{e}{mc}\vec{A}\cdot\langle\beta, j|\vec{p}|\alpha, i\rangle$$

Vector $\vec{p}$ is a polar vector which transforms as the radial vector, $\vec{r} = (x, y, z)$. A representation of a polar vector is

denoted by Γ'. We need to decompose Γ' into irreps of H. Recall the character table of the C_{2v} group which described the H_2O molecule. The x, y, and z components of $\vec{r}$ transform as B_1, B_2, and A_1. Therefore,

$$\Gamma'(C_{2v}) = A_1 \oplus B_1 \oplus B_2$$

On the other hand, for the D_3 group

$$\Gamma'(D_3) = A_2 \oplus E$$

Suppose that the initial state of the H_2O molecule is A_1. Then we need to find

$$\Gamma' \otimes A_1 = (A_1 \oplus B_1 \oplus B_2) \otimes A_1$$

Here is one more useful property:

$$\Gamma_\alpha \otimes \Gamma_1 = \Gamma_\alpha, \ \forall \Gamma_\alpha$$

Proof: Decompose $\Gamma_\alpha \otimes \Gamma_1$ into irreps

$$\Gamma_a \otimes \Gamma_1 = \sum_\beta a_\beta \Gamma_\beta$$

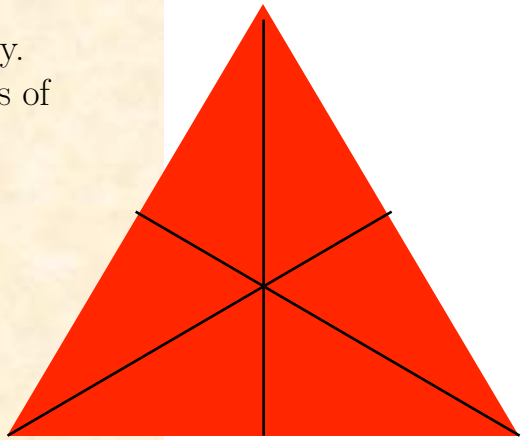
where

$$a_\beta = \frac{1}{g} \sum_G \chi_{\Gamma_\alpha \otimes \Gamma_1} (\chi_{\Gamma_\beta})^* = \frac{1}{g} \sum_G \chi_{\Gamma_\alpha} \underbrace{\chi_{\Gamma_1}}_{=1} (\chi_{\Gamma_\beta})^* = \delta_{\alpha\beta}$$

Then, $(A_1 \oplus B_1 \oplus B_2) \otimes A_1 = A_1 \oplus B_1 \oplus B_2$. Vibrational normal modes transform as A_1 and B_1. This means that the final state can be either A_1 or B_1: each of these modes has a non-zero overlap with $\Gamma' \otimes A_1$. In other words, all vibrational modes of H_2O are infrared-active.

I. EXAMPLE: DIPOLE TRANSITIONS IN A D_3 MOLECULE

Consider a (hypothetical) molecule with D_3 symmetry. Determine possible transitions between electronic states of this molecule.



D_3		I	$2C_3$	$3C_2$
1	A_1	1	1	1
z,	A_2	1	1	-1
(x, y),	E	2	-1	0

A polar vector transforms as

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

.

Suppose that the initial state is A_1.

$$\Gamma' \otimes A_1 = \Gamma' = A_2 \otimes E$$

Allowed transitions: $A_1 \to A_2$ and $A_1 \to E$.
Initial state: A_2.

$$\Gamma' \otimes A_2 = (A_2 \oplus E) \otimes A_2 = A_2 \otimes A_2 \oplus E \otimes A_2$$

$$\chi_{A_2 \otimes A_2} = \chi^2_{A_2} = 1$$

for all symmetry classes $\Rightarrow$

$$A_2 \otimes A_2 = A_1$$

D_3		I	$2C_3$	$3C_2$
1	A_1	1	1	1
z,	A_2	1	1	-1
(x, y),	E	2	-1	0
$E \otimes A_2$		2	-1	0

$$\Rightarrow E \otimes A_2 = E$$

$$\Gamma' \otimes A_2 = A_1 + E$$

Allowed transitions

$$A_2 \to A_1, \; A_2 \to E$$

Initial state: E

$$\Gamma' \otimes E = (A_2 \oplus E) \otimes E = \underbrace{A_2 \otimes E}_{=E} \oplus E \otimes E = E \oplus E \otimes E$$

Decomposing $E \otimes E$

D_3	I	$2C_3$	$3C_2$
$1 \quad A_1$	1	1	1
$z, \quad A_2$	1	1	-1
$(x,y), \quad E$	2	-1	0
$E \otimes E$	4	1	0

$$E \otimes E = \sum_\alpha a_\alpha G_\alpha$$

$$a_\alpha = \frac{1}{6} \sum_G \chi_{E\otimes E} \chi_{\Gamma_\alpha}$$

$$a_{A1} = \frac{1}{6} \left(\underbrace{4 \times 1}_{I} + \underbrace{2 \times 1 \times 1}_{2C_3} \right) = 1$$

$$a_{A_2} = \frac{1}{6} \left(\underbrace{4 \times 1}_{I} + \underbrace{2 \times 1 \times 1}_{2C_3} \right) = 1$$

$$a_E = \frac{1}{6} \left(\underbrace{4 \times 2}_{I} - \underbrace{2 \times 1 \times 1}_{2C_3} \right) = 1$$

$$E \otimes E = A_1 \oplus A_2 \oplus E$$

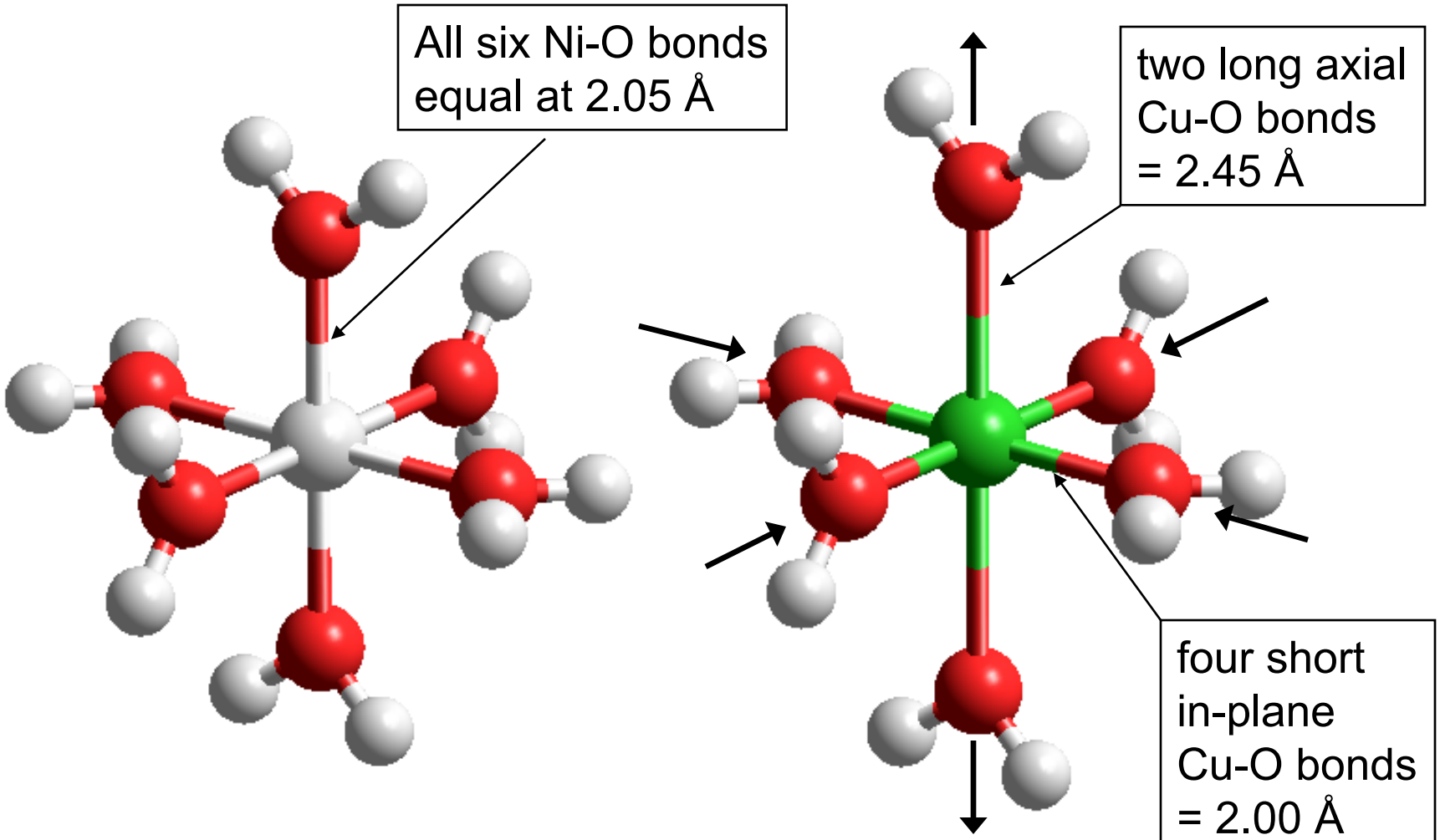
$$\Gamma' \otimes E = E \oplus A_1 \oplus A_2 \oplus E = A_1 \oplus A_2 \oplus 2E$$

Transitions

$$E \to A_1, E \to A_2, E \to E$$

Jahn-Teller Effect

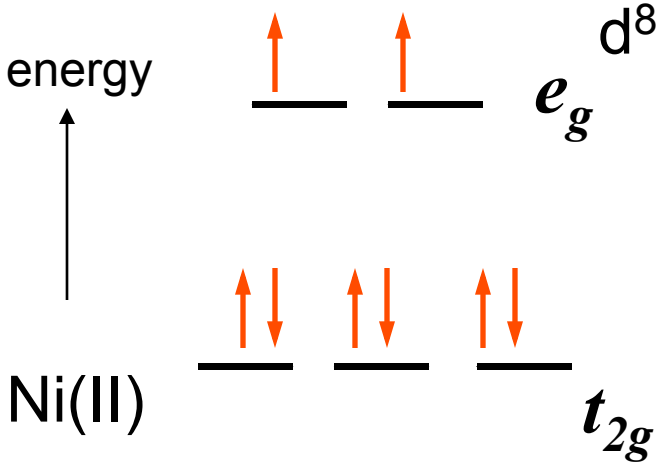
From Prof. Hancock
Chemistry, UNC-Wilmington



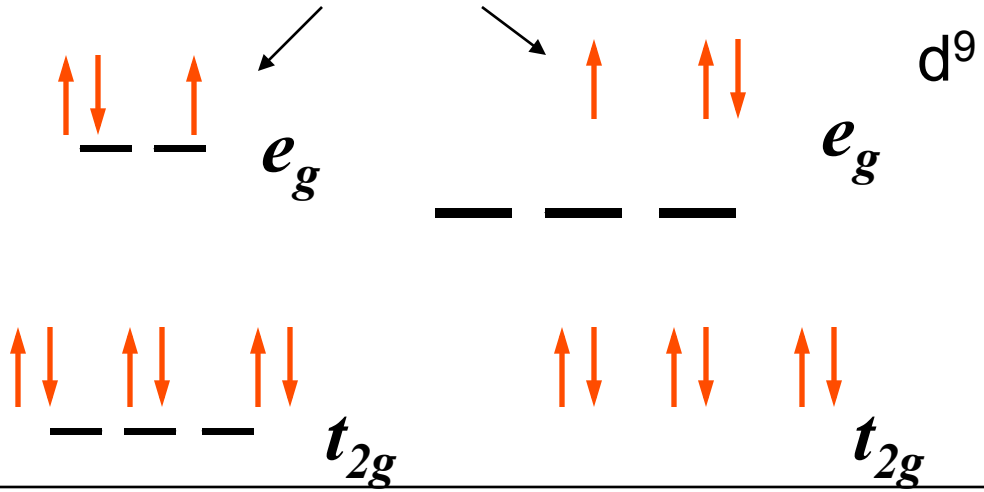
$[Ni(H_2O)_6]^{2+}$

$[Cu(H_2O)_6]^{2+}$

High-spin Ni(II) – only one way of filling the e_g level – not degenerate, no J-T distortion



Cu(II) – two ways of filling e_g level – it is degenerate, and has J-T distortion



Jahn-Teller Theorem (1937)

Symmetric configurations of molecules
with degenerate electron states are *unstable*

$\Rightarrow$The nuclei in the molecule will distort
to remove the degeneracy.

Let q_i^α be the normal modes of molecular vibrations ($i = x, yz$, α labels the irreducible representation) We are interested only in asymmetric positions of ions: Γ_1 is not considered

Electron Hamiltonian: H_0 Suppose that the electrons are in one the multidimensional representations

$$\Gamma_\beta,\ \dim(\Gamma_\beta) > 1$$

$$\Gamma_b = E, F, T, \ldots$$

Suppose that the molecule get distorted

$$H = H_0 \to H = H_0 + \sum_{\alpha,i} V_{\alpha i} q_{\alpha i} + \sum_{\alpha,\beta,i,j} W_{\alpha i,\beta j} q_{\alpha i} q_{\beta j} + \ldots$$

Is the matrix element of the linear in q term finite?
If it is, the energy will always be lowered (the sign of q can always be chosen negative) for small enough q.
(Higher-order terms–non-linear JT-effect)
Coefficients V_α transform as one of the equivalence representations of the symmetry group

$$V_\alpha \propto \Gamma_\alpha^{\text{eq}}$$

Reminder: an equivalence representation describes purely vibrational modes and exclude translations and vibrations

$\mathrm{H_2O}$ (C_{2v})

C_{2v}	I	C_2	σ_v	σ_v'
Γ^{eq}	3	1	3	1

$$\Gamma^{eq} = 2A_1 \oplus B_1$$

If the electron state is degenerate, the energy splitting due to a deformation is

$$\Delta E = \langle \beta, b | V_{\alpha,i} | \beta, a \rangle$$

where $|\beta, a\rangle$ $(a = 1...f_\beta)$ is the basis function

$$\Delta E \neq 0$$

if and only if

$$\Gamma_\beta \otimes \Gamma_\alpha^{eq} \otimes \Gamma_\beta \supset \Gamma_1$$

Equivalently,

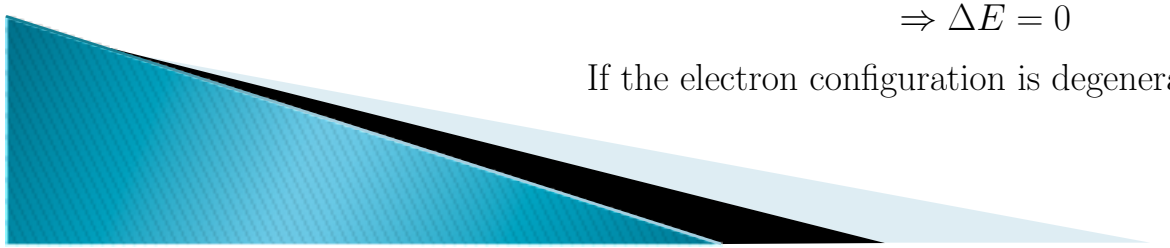
$$\Gamma_\beta \otimes \Gamma_\beta \supset \Gamma_\alpha^{eq}$$

Non-degenerate electron configuration $\Rightarrow$no JT distortion
JT distortion: an asymmetric configuration of nuclei $\Rightarrow$ $\Gamma_\alpha^{eq} \neq \Gamma_1$
If the electron configuration is non-degenerate, Γ_β is a 1D representation and

$$\Gamma_\beta \otimes \Gamma_\beta = \Gamma_1$$

$$\chi_{\Gamma_B}(G) = \pm 1 \Rightarrow \chi_{\Gamma_\beta \otimes \Gamma_\beta} = \chi^2_{\Gamma_\beta}(G) = 1 \Rightarrow \Gamma_\beta \otimes \Gamma_\beta = \Gamma_1$$
$$\Rightarrow \Delta E = 0$$

If the electron configuration is degenerate, $\Delta E \neq 0$



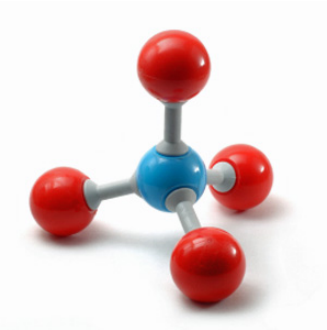


FIG. 1. Methane molecule

Example: CH_4 (methane)
Vibrational modes

$$\Gamma^{eq} = A_1 \oplus E \oplus 2T_2$$

Excluding the symmetric mode

$$\Gamma^{eq} = E \oplus 2T_2$$

Degenerate electron configurations: E,T

$$E \otimes E = A_1 \oplus E \supset E$$

$$T_1 \otimes T_1 = T_2 \otimes T_2 = A_1 \oplus E \oplus T_2 \supset T_2$$

$\Rightarrow$ symmetric molecule is unstable

Td symmetry

This document is provided by the **Chemical Portal** www.webqc.org

Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

You may print and redistribute verbatim copies of this document.