PHY 745 Group Theory
11-11:50 AM MWF Olin 102

Plan for Lecture 7:

Examples of point groups and their characters

Reading: Chapter 4 & 8 in DDJ

1. **Symmetry basis functions**
2. **Examples of point groups – molecules and their vibrational modes**

Note: In this lecture, some materials are taken from an electronic version of the Dresselhaus, Dresselhaus, Jorio text

PHY 745 Group Theory

MWF 11-11:50 AM | OPL 102 | http://www.wfu.edu/~natalie/s17phy745/

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Course schedule for Spring 2017

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	DDJ Reading	Topic	HW	Due date
1	Wed: 01/11/2017	Chap. 1	Definition and properties of groups	#1	01/20/2017
2	Fri: 01/13/2017	Chap. 1	Theory of representations		
	Mon: 01/16/2017		*MLK Holiday - no class*		
3	Wed: 01/18/2017	Chap. 2	Theory of representations		
4	Fri: 01/20/2017	Chap. 2	Proof of the Great Orthonality Theorem	#2	01/23/2017
5	Mon: 01/23/2017	Chap. 3	Notion of character of a representation	#3	01/25/2017
6	Wed: 01/25/2017	Chap. 3	Examples of point groups	#4	01/27/2017
7	Fri: 01/27/2017	Chap. 4 & 8	Symmetry of vibrational modes	#5	01/30/2017
8	Mon: 01/30/2017				

Point symmetry groups in physics

Notion of symmetry related basis functions

Previous notation | Dresselhaus notation

$\Gamma^i(R)_{\alpha\beta}$ $\quad$ $D^{(\Gamma_n)}(R)_{j\alpha}$ $\quad$ representation

Basis function for this representation and for group element R: $|\Gamma_n j\rangle$

Operator for group element R acting on basis function: $\hat{P}_R$

Properties:
$$\hat{P}_R|\Gamma_n\alpha\rangle = \sum_j D^{\Gamma_n}(R)_{j\alpha}|\Gamma_n j\rangle.$$

$$D^{(\Gamma_n)}(R)_{j\alpha} = \langle\Gamma_n j|\hat{P}_R|\Gamma_n\alpha\rangle.$$

Orthogonality:
$$\langle\Gamma_n j|\Gamma_{n'} j'\rangle = \delta_{n,n'}\delta_{j,j'},$$

Examples of basis functions based on Cartesian coordinates for the example of the triangular group:

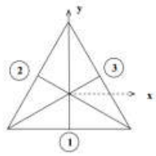


Figure 4.1: Symmetry operations of an equilateral triangle. The notation of this diagram defines the symmetry operations in Table 4.1.

Table 4.1: Symmetry operations of the group of the equilateral triangle on basis functions.

$\hat{P}_R/f(x,y,z)$	x	y	z	x^2	y^2	z^2
$E = E$	x	y	z	x^2	y^2	z^2
$C_3 = F$	$\frac{1}{2}(-x+\sqrt{3}y)$	$\frac{1}{2}(-y-\sqrt{3}x)$	z	$\frac{1}{4}(x^2+3y^2-2\sqrt{3}xy)$	$\frac{1}{4}(y^2+3x^2+2\sqrt{3}xy)$	z^2
$C_3^{-1} = D$	$\frac{1}{2}(-x-\sqrt{3}y)$	$\frac{1}{2}(-y+\sqrt{3}x)$	z	$\frac{1}{4}(x^2+3y^2+2\sqrt{3}xy)$	$\frac{1}{4}(y^2+3x^2-2\sqrt{3}xy)$	z^2
$C_{2(1)} = A$	$-x$	y	$-z$	x^2	y^2	z^2
$C_{2(2)} = B$	$\frac{1}{2}(x-\sqrt{3}y)$	$\frac{1}{2}(-y-\sqrt{3}x)$	$-z$	$\frac{1}{4}(x^2+3y^2-2\sqrt{3}xy)$	$\frac{1}{4}(y^2+3x^2+2\sqrt{3}xy)$	z^2
$C_{2(3)} = C$	$\frac{1}{2}(x+\sqrt{3}y)$	$\frac{1}{2}(-y+\sqrt{3}x)$	$-z$	$\frac{1}{4}(x^2+3y^2+2\sqrt{3}xy)$	$\frac{1}{4}(y^2+3x^2-2\sqrt{3}xy)$	z^2

Summary of basis functions associated with character table for D_3

$D_3(32)$			E	$2C_3$	$3C_2'$
x^2+y^2, z^2		A_1	1	1	1
	R_z, z	A_2	1	1	-1
$\left.\begin{matrix}(xz, yz)\\(x^2-y^2, xy)\end{matrix}\right\}$	$\left.\begin{matrix}(x, y)\\(R_x, R_y)\end{matrix}\right\}$	E	2	-1	0

"Standard" notation for representations of D_3

Example of H_2O

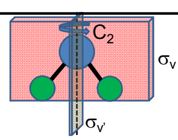


Table 3.14: Character Table for Group C_{2v}

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

"Standard" notation for representations of C_{2v}

Lattice vibrations of H_2O:

3 modes:
- 3x3 degrees of freedom
  - 3 translations
  - 3 rotations

Symmetric stretch: ν=3685 cm^{-1}

Sissors bend: ν=1885 cm^{-1}

Asymmetric stretch: ν=3506 cm^{-1}

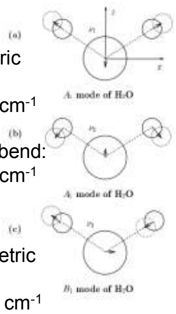
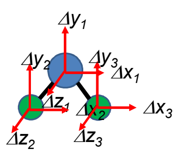
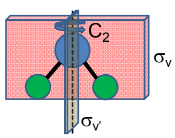


Figure 9.1: Normal modes for the H_2O molecule with 3 vibrational degrees of freedom. (a) The breathing mode with symmetry A_1, which changes only bond lengths. (b) The symmetric stretch mode of H_2O with A_1 symmetry, which changes bond angles. (c) The anti-symmetric stretch mode with B_1 symmetry.

Symmetry analysis





$$R \begin{bmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \Delta z_2 \\ \Delta x_3 \\ \Delta y_3 \\ \Delta z_3 \end{bmatrix}$$

$$E \begin{bmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \Delta z_2 \\ \Delta x_3 \\ \Delta y_3 \\ \Delta z_3 \end{bmatrix} = \begin{bmatrix} 1&0&0&0&0&0&0&0&0 \\ 0&1&0&0&0&0&0&0&0 \\ 0&0&1&0&0&0&0&0&0 \\ 0&0&0&1&0&0&0&0&0 \\ 0&0&0&0&1&0&0&0&0 \\ 0&0&0&0&0&1&0&0&0 \\ 0&0&0&0&0&0&1&0&0 \\ 0&0&0&0&0&0&0&1&0 \\ 0&0&0&0&0&0&0&0&1 \end{bmatrix} \begin{bmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \Delta z_2 \\ \Delta x_3 \\ \Delta y_3 \\ \Delta z_3 \end{bmatrix}$$

$\chi(E)=9$

$$C_2 \begin{bmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \Delta z_2 \\ \Delta x_3 \\ \Delta y_3 \\ \Delta z_3 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \Delta z_2 \\ \Delta x_3 \\ \Delta y_3 \\ \Delta z_3 \end{bmatrix}$$

$\chi(C_2)=-1$

Similarly: $\chi(\sigma_v)=3$
$\chi(\sigma_{v'})=1$

Decomposition of the displacement representation into irreducible representations

$$\chi(R) = \sum_i a_i \chi^i(R)$$

$$a_i = \frac{1}{h}\sum_R \left(\chi^i(R)\right)^* \chi(R)$$

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xz	R_y, x	B_1	1	−1	1	−1
yz	R_x, y	B_2	1	−1	−1	1
$\chi(R)$			9	−1	3	1

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$\chi(R)$			9	−1	3	1

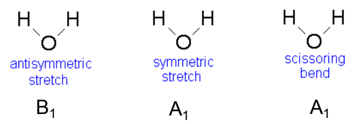
$\Rightarrow$ Coordinate representation$=3A_1 + A_2 + 3B_1 + 2B_2$

translations $=A_1 + B_1 + B_2$

rotations $=A_2 + B_1 + B_2$

vibrations $=2A_1 + B_1$

From:
http://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Spectroscopy/Vibrational_Spectroscopy/Vibrational_Modes



Normal modes in terms of generalized coordinates q_i

$$\sum_j \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial q_i \partial q_j} q_j = \omega^2 q_i$$