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

### Plan for Lecture 8:

**Examples of point groups and their characters – more details**

**Reading: Chapter 4 & 8 in DDJ**

1. **More details on basis functions**
2. **More details on symmetries of molecular vibrations**

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 | Chap. 4 & 8 | Symmetry of vibrational modes | #6 | 02/01/2017 |
| 9 | Wed: 02/01/2017 | | | | |



Point symmetry groups in physics

Notion of symmetry related basis functions*

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

*(Using notation in DDJ textbook)

Examples of basis functions based on Cartesian coordinates for the example of the triangular group: $P(3)=D_3$

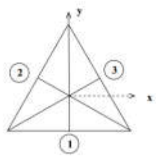



Figure 4.1: Symmetry operations of an equilateral triangle. The notation of this diagram defines the symmetry operations in Table 4.1.

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 $D_3$

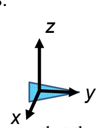
| $D_3(32)$ | | | $E$ | $2C_3$ | $3C_2'$ |
|---|---|---|---|---|---|
| $x^2+y^2, z^2$ | | $A_1$ | 1 | 1 | 1 |
| | $R_z, z$ | $A_2$ | 1 | 1 | $-1$ |
| $\left.\begin{matrix}(xz, yz)\\(x^2-y^2, xy)\end{matrix}\right\}$ | $\left.\begin{matrix}(x, y)\\(R_x, R_y)\end{matrix}\right\}$ | $E$ | 2 | $-1$ | 0 |

"Standard" notation for representations of $D_3$



Example basis functions:

$$|\Gamma_n j\rangle = x$$
$$|\Gamma_n j\rangle = y$$
$$|\Gamma_n j\rangle = z$$



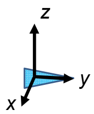

At the moment, we do not know that these basis functions belong to the same or different representations $\Gamma_n$

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

Assume integral implied by braket takes place over unit sphere and appropriate normalization constants will be applied.

For example:

$$\langle x | y \rangle = \int_{-1}^{1} d\cos\theta \int_{0}^{2\pi} d\phi \sin\theta \cos\phi \; \sin\theta \; \sin\phi = 0$$




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

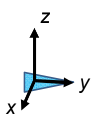
Example matrix elements:

$$\langle z|C_3|z\rangle = 1 \qquad \langle z|C_2|z\rangle = -1$$

$$\langle x|C_3|x\rangle = -\tfrac{1}{2} \qquad \langle y|C_3|x\rangle = \tfrac{\sqrt{3}}{2}$$

Note that basis functions related to irreducible representations follow: $D^{(\Gamma_n)}(R)_{j\alpha} = \langle \Gamma_n j|\hat{P}_R|\Gamma_n \alpha\rangle.$






The basis function $z$ can be used to generate the representation $\Gamma_{1'}$ (previously called $\Gamma^2$)

| | $E$ | $A$ | $B$ | $C$ | $D$ | $F$ |
|---|---|---|---|---|---|---|
| | | $C_{2(1)}$ | $C_{2(2)}$ | $C_{2(3)}$ | $C_3$ | $C_3^{-1}$ |
| $\Gamma_{1'}$ | 1 | $-1$ | $-1$ | $-1$ | 1 | 1 |

The basis function pair $(x,y)$ can be used to generate the representation $\Gamma_2$ (previously called $\Gamma^3$)

$$\Gamma_2(E)=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \quad \Gamma_2(A)=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \quad \Gamma_2(B)=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix}$$

$$\Gamma_2(C)=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix} \quad \Gamma_2(D)=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix} \quad \Gamma_2(F)=\begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}$$



$$\Gamma_2(B)=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix}$$

$$\langle x|B=C_{2(2)}|x\rangle = -\tfrac{1}{2}$$

$$\langle y|B=C_{2(2)}|x\rangle = \tfrac{\sqrt{3}}{2}$$

$$\Gamma_2(D)=\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}$$

$$\langle x|D=C_3^{-1}|x\rangle = -\tfrac{1}{2}$$

$$\langle y|D=C_3^{-1}|x\rangle = -\tfrac{\sqrt{3}}{2}$$

Extension to quadratic basis functions

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

Together with the cross functions $xy$, $xz$, $yz$, can show that the basis pairs $(xz, yz)$ or $((x^2-y^2), xy)$ generate the irreducible representation $\Gamma_2$.



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 |
| $(xz, yz)$, $(x^2-y^2, xy)$ | $(x,y)$, $(R_x, R_y)$ | $E$ | 2 | −1 | 0 |

"Standard" notation for representations of $D_3$

In this case, $R_x$, $R_y$, $R_z$ behave as axial vectors along *x, y, z.*



Example of $H_2O$

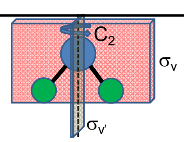
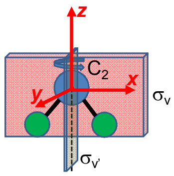



Table 3.14: Character Table for Group $C_{2v}$

| $C_{2v}$ (2mm) | | | $E$ | $C_2$ | $\sigma_v$ | $\sigma_v'$ |
|---|---|---|---|---|---|---|
| $x^2, y^2, z^2$ | $z$ | $A_1$ | 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 $C_{2v}$

Basis functions for this case --




$$P_{C_2}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-x\\-y\\z\end{pmatrix}$$

$$P_{\sigma_v}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}x\\-y\\z\end{pmatrix}$$

$$P_{\sigma_{v'}}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-x\\y\\z\end{pmatrix}$$



Basis functions for $C_{2v}$ – *continued* --

$$\langle x|P_E|x\rangle=1\quad \langle x|P_{C_2}|x\rangle=-1\quad \langle x|P_{\sigma_v}|x\rangle=1\quad \langle x|P_{\sigma_{v'}}|x\rangle=-1$$

$$\langle y|P_E|y\rangle=1\quad \langle y|P_{C_2}|y\rangle=-1\quad \langle y|P_{\sigma_v}|y\rangle=-1\quad \langle y|P_{\sigma_{v'}}|y\rangle=1$$

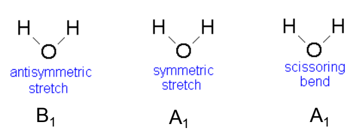
$$\langle z|P_E|z\rangle=1\quad \langle z|P_{C_2}|z\rangle=1\quad \langle z|P_{\sigma_v}|z\rangle=1\quad \langle z|P_{\sigma_{v'}}|z\rangle=1$$

| $C_{2v}$ (2mm) | | | $E$ | $C_2$ | $\sigma_v$ | $\sigma'_v$ |
|---|---|---|---|---|---|---|
| $x^2, y^2, z^2$ | $z$ | $A_1$ | 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 |



Vibrational modes

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



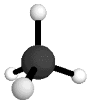

Normal modes in terms of generalized coordinates $q_i$

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

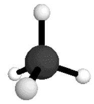
## Another example – $CH_4$ (tetrahedral symmetry)

http://www2.ess.ucla.edu/~schauble/MoleculeHTML/CH4_html/CH4_page.html

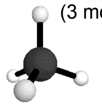
**$o_1$ = 3025.5 cm$^{-1}$**
***$A_1$* Symmetry**



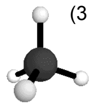
**$o_2$ = 1582.7 cm$^{-1}$**
***E* Symmetry** (2 modes)



**$o_3$ = 3156.8 cm$^{-1}$**
***$T_2$* Symmetry** (3 modes)



**$o_4$ = 1367.4 cm$^{-1}$**
***$T_2$* Symmetry** (3 modes)





## Symmetry analysis of vibrations of $CH_4$

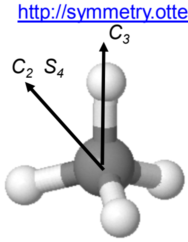
Table 3.34: Character Table for Group $T_d$

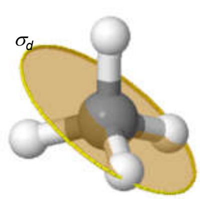
| $T_d$ ($\bar{4}3m$) | | $E$ | $8C_3$ | $3C_2$ | $6\sigma_d$ | $6S_4$ |
|---|---|---|---|---|---|---|
| | $A_1$ | 1 | 1 | 1 | 1 | 1 |
| | $A_2$ | 1 | 1 | 1 | −1 | −1 |
| | $E$ | 2 | −1 | 2 | 0 | 0 |
| $(R_x, R_y, R_z)$ | $T_1$ | 3 | 0 | −1 | −1 | 1 |
| $(x, y, z)$ | $T_2$ | 3 | 0 | −1 | 1 | −1 |

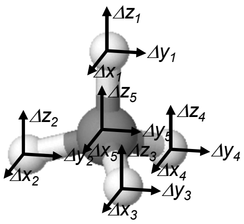


## Visualization of symmetry elements

http://symmetry.otterbein.edu/tutorial/methane.html



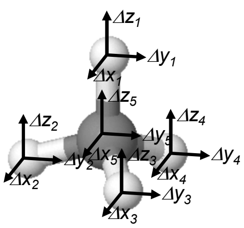





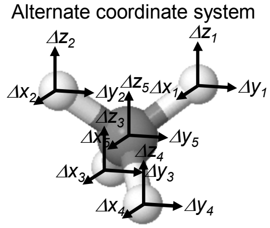

Construct 15-component vector V describing the 3-dimensional motion of the 5 atoms in $CH_4$

$$V = \begin{pmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \Delta z_2 \\ \Delta x_3 \\ \vdots \\ \Delta z_5 \end{pmatrix}$$






Alternate coordinate system




Compute characters of transformations:

$\chi(E)=15 \quad \chi(C_3)=0 \quad \chi(C_2)=-1 \quad \chi(\sigma_d)=3 \quad \chi(S_4)=-1$



| $T_d$ ($\bar{4}3m$) | | $E$ | $8C_3$ | $3C_2$ | $6\sigma_d$ | $6S_4$ |
|---|---|---|---|---|---|---|
| | $A_1$ | 1 | 1 | 1 | 1 | 1 |
| | $A_2$ | 1 | 1 | 1 | −1 | −1 |
| | $E$ | 2 | −1 | 2 | 0 | 0 |
| $(R_x, R_y, R_z)$ | $T_1$ | 3 | 0 | −1 | −1 | 1 |
| $(x, y, z)$ | $T_2$ | 3 | 0 | −1 | 1 | −1 |
| $\chi$ | | 15 | 0 | −1 | 3 | −1 |

Decomposition of the displacement representation into irreducible representations

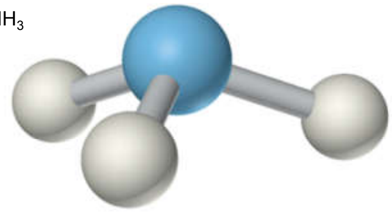
$$\chi(R) = \sum_i a_i \chi^i(R)$$

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

All motions: ➔ $A_1+E+T_1+3T_2$
Translations: $T_2$
Rotations: $T_1$
Vibrations: $A_1+E+2T_2$

Symmetry of $NH_3$

$C_{3v}$



Ammonia

http://wps.prenhall.com/wps/media/objects/602/616516/Media_Assets/Chapter19/Text_Images/FG19_07-12UN.JPG



Table 3.15: Character Table for Group $C_{3v}$

| $C_{3v}$ $(3m)$ | | | $E$ | $2C_3$ | $3\sigma_v$ |
|---|---|---|---|---|---|
| $x^2+y^2, z^2$ | $z$ | $A_1$ | 1 | 1 | 1 |
| | $R_z$ | $A_2$ | 1 | 1 | −1 |
| $(x^2-y^2, xy)$ $(xz, yz)$ | $(x, y)$ $(R_x, R_y)$ | $E$ | 2 | −1 | 0 |
| | | $\chi$ | 12 | 0 | 2 |