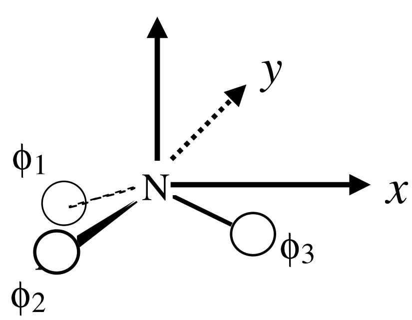
Transformation Matrices; Geometric and Otherwise

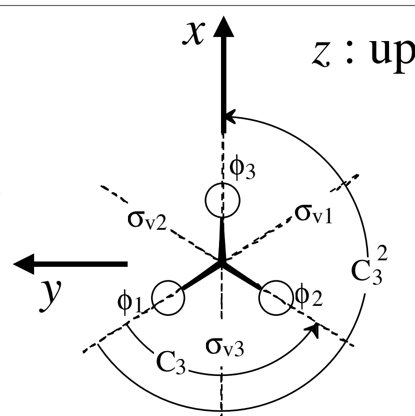
- As examples, consider the transformation matrices of the C_{3v} group. The form of these matrices depends on the *basis* we choose. Examples:
  - Cartesian vectors: $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$

$$\hat{\mathbf{x}} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \hat{\mathbf{y}} = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \quad \hat{\mathbf{z}} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

  - *p* orbitals on the N atom of NH_3
  - the three 1s orbitals on the hydrogen atoms of NH_3

$$\hat{\mathbf{x}} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \hat{\mathbf{y}} = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \quad \hat{\mathbf{z}} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$



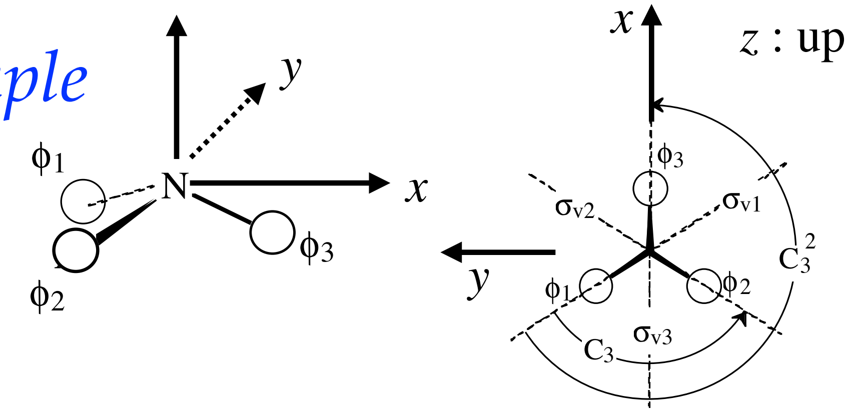


Cartesian basis:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

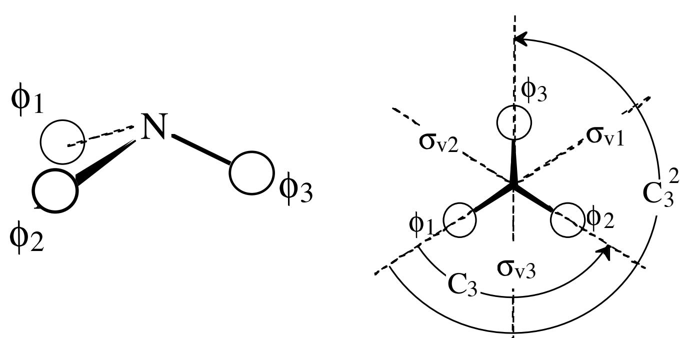
$$\sigma_{v1} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{v2} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{v3} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Example



Three 1s orbitals on the hydrogen atoms of NH_3

Example, Answers



$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3 = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \quad C_3^2 = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}$$

$$\sigma_{v1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \quad \sigma_{v2} = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \quad \sigma_{v3} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Transformation of d orbitals

$$d_0\ (l=2, m_l=0) \propto \tfrac{1}{4}\sqrt{\tfrac{5}{\pi}}(3\cos^2\theta-1)$$

$$d_{\pm1}\ (l=2, m_l=\pm1) \propto (\mp)\tfrac{1}{2}\sqrt{\tfrac{15}{2\pi}}\sin\theta\cos\theta e^{\pm i\varphi}$$

$$d_{\pm2}\ (l=2, m=\pm2) \propto \tfrac{1}{4}\sqrt{\tfrac{15}{2\pi}}\sin^2\theta\ e^{\pm2i\varphi}$$

see, e.g., Atkins & de Paula, *Physical Chemistry*

$$d_{xz} = \tfrac{1}{\sqrt{2}}[-d_1+d_{-1}] \propto \tfrac{1}{2}\sqrt{\tfrac{15}{\pi}}\sin\theta\cos\theta\tfrac{1}{2}[e^{i\varphi}+e^{-i\varphi}] = \tfrac{1}{2}\sqrt{\tfrac{15}{\pi}}\sin\theta\cos\theta\cos\varphi \propto \tfrac{1}{4}\sqrt{\tfrac{15}{\pi}}\times 2xz$$

$$d_{yz} = \tfrac{-1}{i\sqrt{2}}[d_1+d_{-1}] \propto \tfrac{1}{2}\sqrt{\tfrac{15}{\pi}}\sin\theta\cos\theta\tfrac{1}{2i}[e^{i\varphi}-e^{-i\varphi}] = \tfrac{1}{2}\sqrt{\tfrac{15}{\pi}}\sin\theta\cos\theta\sin\varphi \propto \tfrac{1}{4}\sqrt{\tfrac{15}{\pi}}\times 2yz$$

$$d_{x^2-y^2} = \tfrac{1}{\sqrt{2}}[d_2+d_{-2}] \propto \tfrac{1}{4}\sqrt{\tfrac{15}{\pi}}\sin^2\theta\tfrac{1}{2}[e^{2i\varphi}+e^{-2i\varphi}] = \tfrac{1}{4}\sqrt{\tfrac{15}{\pi}}\sin^2\theta\cos2\varphi \propto \tfrac{1}{4}\sqrt{\tfrac{15}{\pi}}\times(x^2-y^2)$$

$$d_{xy} = \tfrac{1}{i\sqrt{2}}[d_2-d_{-2}] \propto \tfrac{1}{4}\sqrt{\tfrac{15}{\pi}}\sin^2\theta\tfrac{1}{2i}[e^{2i\varphi}-e^{-2i\varphi}] = \tfrac{1}{2}\sqrt{\tfrac{15}{\pi}}\sin^2\theta\sin2\varphi \propto \tfrac{1}{4}\sqrt{\tfrac{15}{\pi}}\times 2xy$$

$$d_{z^2} = d_0 \propto Y_{20} \propto \tfrac{1}{4}\sqrt{\tfrac{5}{\pi}}\left(3\cos^2\theta-1\right) \propto \tfrac{1}{4}\sqrt{\tfrac{15}{\pi}}\times\tfrac{1}{\sqrt{3}}\left(3z^2-r^2\right)$$

$$d_1 = -\tfrac{1}{\sqrt{2}}[d_{xz}+id_{yz}] \quad ; \quad d_{-1} = \tfrac{1}{\sqrt{2}}[d_{xz}-id_{yz}]$$

$$d_2 = \tfrac{1}{\sqrt{2}}[d_{x^2-y^2}+id_{xy}] \quad ; \quad d_{-2} = \tfrac{1}{\sqrt{2}}[d_{x^2-y^2}-id_{xy}]$$

Group Representations

- Representation: A set of matrices that “represent” the group. That is, they behave in the same way as group elements when products are taken.
- A representation is in correspondence with the group multiplication table.
- Many representations are in general possible.
- The order (rank) of the matrices of a representation can vary.

Example - show that the matrices found earlier are a representation

$$\text{eg.,}\quad C_3C_3^2 = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = E$$

$$(\sigma_{v1})^{-1}C_3\sigma_{v1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} = C_3^2$$

Reducible and Irreducible Reps.

- If we have a set of matrices, {**A**, **B**, **C**, ...}, that form a representation of a group and we can find a transformation matrix, say **Q**, that serves to “block factor” <u>all</u> the matrices of this representation <u>in the same block form</u> by similarity transformations, then {**A**, **B**, **C**, ...} is a <u>reducible</u> representation. If no such similarity transformation is possible then {**A**, **B**, **C**, ...} is an <u>irreducible</u> representation.

Similarity Transformation maintains a Representation

Suppose the group multiplication rules are such that **AB = D**, **BC = F** , etc ...

- Now perform similarity transforms using the transformation matrix **Q**:

  $\mathbf{A}' = \mathbf{Q}^{-1}\mathbf{A}\mathbf{Q}$, $\mathbf{B}' = \mathbf{Q}^{-1}\mathbf{B}\mathbf{Q}$, $\mathbf{C}' = \mathbf{Q}^{-1}\mathbf{C}\mathbf{Q}$, etc.

- Multiplication rules preserved:

  $\mathbf{A}'\mathbf{B}' = (\mathbf{Q}^{-1}\mathbf{A}\mathbf{Q})(\mathbf{Q}^{-1}\mathbf{B}\mathbf{Q}) = (\mathbf{Q}^{-1}\mathbf{D}\mathbf{Q}) = \mathbf{D}'$

  $\mathbf{B}'\mathbf{C}' = (\mathbf{Q}^{-1}\mathbf{B}\mathbf{Q})(\mathbf{Q}^{-1}\mathbf{C}\mathbf{Q}) = (\mathbf{Q}^{-1}\mathbf{F}\mathbf{Q}) = \mathbf{F}'$, etc.

Reducing a Representation by Similarity Transformations

$$\mathbf{Q}^{-1}\mathbf{A}\mathbf{Q} = \left[\begin{array}{c|c|c} \mathbf{A}_1 & & \\ \hline & \mathbf{A}_2 & \\ \hline & & \mathbf{A}_3 \end{array}\right]$$

$$\mathbf{Q}^{-1}\mathbf{C}\mathbf{Q} = \left[\begin{array}{c|c|c} \mathbf{C}_1 & & \\ \hline & \mathbf{C}_2 & \\ \hline & & \mathbf{C}_3 \end{array}\right]$$

$$\mathbf{Q}^{-1}\mathbf{B}\mathbf{Q} = \left[\begin{array}{c|c|c} \mathbf{B}_1 & & \\ \hline & \mathbf{B}_2 & \\ \hline & & \mathbf{B}_3 \end{array}\right]$$

"Blocks" of a Reduced Rep. are also Representations

This must be true because any group multiplication property is obeyed by the subblocks. If, for example, $\mathbf{AB} = \mathbf{C}$, then $\mathbf{A}_1\mathbf{B}_1 = \mathbf{C}_1$, $\mathbf{A}_2\mathbf{B}_2 = \mathbf{C}_2$ and $\mathbf{A}_3\mathbf{B}_3 = \mathbf{C}_3$.

Example: Show that the matrix at left, $\mathbf{Q}$, can reduce the matrices we found for the representation given earlier.

$$\mathbf{Q} = \begin{bmatrix} 1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ -1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ 0 & 2/\sqrt{6} & 1/\sqrt{3} \end{bmatrix}$$

A Block Factoring Example

$$\mathbf{Q}^{-1}\mathbf{C}_3\mathbf{Q} = \begin{bmatrix} 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ -1/\sqrt{6} & -1/\sqrt{6} & 2/\sqrt{6} \\ 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ -1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ 0 & 2/\sqrt{6} & 1/\sqrt{3} \end{bmatrix}$$

$$\mathbf{Q}^{-1}\mathbf{C}_3\mathbf{Q} = \left[\begin{array}{cc|c} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ \hline 0 & 0 & 1 \end{array}\right] \qquad \mathbf{Q}^{-1}\sigma_{v1}\mathbf{Q} = \left[\begin{array}{cc|c} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ \hline 0 & 0 & 1 \end{array}\right]$$

Significance of Transformations

- Irreducible Representations are of pivotal importance
- Chosen properly, similarity transformations can reduce a reducible representation into its irreducible representations
- With the proper first choice of basis, the transformation would not be necessary
- Important Future goal: finding the basis functions for irreducible representations

Great Orthogonality Theorem

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

2 Proofs: Eyring, H.; Walter, J.; Kimball, G.E. *Quantum Chemistry*; Wiley, 1944.
http://www.cmth.ph.ic.ac.uk/people/d.vvedensky/groups/Chapter4.pdf

$\Gamma_i(R)$ — matrix that represents the operation R in the i^{th} representation. Its form can depend on the basis for the representation.

$[\Gamma_i(R)_{mn}]$ — matrix element in m^{th} row and n^{th} column of $\Gamma_i(R)$

l_i — the dimension of the i^{th} representation

h — the order of the group (the number of operations)

δ_{ij} = 1 if i=j, 0 otherwise

Great Orthogonality Theorem - again

- Vectors formed from matrix elements from the mth rows and nth columns of different irreducible representations are orthogonal:

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{mn}]^* = 0 \text{ if } i \neq j$$

- Such vectors formed from different row-column sets of the same irreducible representation are orthogonal and have magnitude h/l_i:

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

The First Sum Rule

The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group, that is,

$$\sum_i l_i^2 = l_1^2 + l_2^2 + l_3^2 + \cdots = h$$

this is equivalent to:

$$\sum_i \left[\chi_i(E)\right]^2 = h$$

Second Sum Rule

The sum of the squares of the characters in any irreducible representation equals h, the order of the group $\sum_R [\chi_i(R)]^2 = h$

"Proof" – From the GOT:

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

let $m=m'=n=n'$: $\sum_R [\Gamma_i(R)_{mm}][\Gamma_i(R)_{mm}]^* = (h/l_i)$

Characters of Different Irreducible Representations are Orthogonal

The vectors whose components are the characters of two different irreducible representations are orthogonal, that is,

$$\sum_R \chi_i(R)\chi_j(R) = 0 \text{ when } i \neq j$$

Proof

Setting $m = n$ in first GOT statement:

$$\sum_R \Gamma_i(R)_{mm}\Gamma_j(R)_{mm} = 0 \text{ if } i \neq j$$

compare this to the statement ($i \neq j$):

$$\sum_R \chi_i(R)\chi_j(R) = \sum_R \left\{ \left[\sum_m \Gamma_i(R)_{mm} \right] \left[\sum_m \Gamma_j(R)_{mm} \right] \right\}$$

$$= \sum_m \left[\sum_R \Gamma_i(R)_{mm}\Gamma_j(R)_{mm} \right] = 0$$

Matrices in the Same Class have Equal Characters

- This statement is true whether the representation is reducible or irreducible
- This follows from the fact that all elements in the same class are conjugate and conjugate matrices have equal characters.

of Classes = # of Irred. Reps.

The number of irreducible representations of a group is equal to the number of classes in the group.

$$\sum_R \chi_i(R)\chi_j(R) = h\delta_{ij}$$

if the number of elements in the m^{th} class is g_m and there are k classes,

$$\sum_{p=1}^{k} \chi_i(R_p)\chi_j(R_p)g_p = h\delta_{ij}$$