5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #29: A Sprint Through Group Theory

Bernath 2.3-4, 3.3-8, 4.3-6. I'll touch on highlights

Symmetry

odd vs. even integrands $\rightarrow$ 0 integrals

selection rules for matrix representation of any operator

* transition moment
* $\hat{\mathbf{H}} \leftarrow$ block diagonalization

generation of symmetry coordinates

how to deal with totality of

- exact $[\hat{O}, \hat{\mathbf{H}}] = 0$
- approx. $[\hat{O}, \hat{\mathbf{H}}^\circ] = 0$
- convenient $[C_2^{a,b,c}, \hat{\mathbf{H}}^{ROT}] = 0$ symmetries

Chapter 2: Molecular Symmetry

rotation $\hat{C}_n$ (axis) rotation by $\frac{2\pi}{n}$ radians about (specified) axis ($\hat{C}_n \hat{C}_n = \hat{C}_n^2$ etc.)

reflection $\hat{\sigma}$ (plane) reflect thru plane

- σ_v vertical (includes highest order C_n axis)
- σ_h horizontal ($\perp$ to highest order C_n axis)
- σ_d dihedral (also vertical, bisects angle between 2 C_2 axes $\perp$ to C_n)

contrast to **I** - inversion in lab (parity)

inversion in body $\hat{i} = \hat{C}_2 \hat{\sigma}_h$ inversion (C_2 axis $\perp$ to plane of $\hat{\sigma}_h$)

improper rotation $\hat{S}_n = \hat{\sigma}_h \hat{C}_n = \hat{C}_n \hat{\sigma}_h$ (C_n axis $\perp$ to plane of $\hat{\sigma}_h$) [$i = S_2$]

identity $\hat{E}$ do nothing

Groups: Closure

Associative Multiplication

Identity Element

Inverse of every element R.

Rigid isolated molecules — **point** groups — all symmetry elements intersect at one **point**

[distinct from translational symmetries — periodic lattices

CNPI - nonrigid molecules (Complete Nuclear Permutation-Inversion)

MS - (Molecular Symmetry Group) subgroup of CNPI, isomorphic with point group, but more insightful (especially when dealing with transitions between different point-group structures)]

Point Group notation

C_s,	C_i,	C_n,	D_n,	C_{nv},	C_{nh},	D_{nh},	D_{nd}
$\downarrow$	$\downarrow$		$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$	$\downarrow$
1 plane	inversion		$nC_2 \perp C_n$	$n\sigma_v$	$C_n + \sigma_h$	$C_n + nC_2\perp + \sigma_h$	$C_n + nC_2\perp + \sigma_d$

S_n	T_d	O_h	I_h	K_h
	tetrahedral	octahedral	icosohedral	spherical

[Flow Chart: Figure 2.11, page 52 of Bernath]

Bernath Chapter 3. Matrix Representations

$$\mathbf{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \text{ which means } \mathbf{r} = \underset{x_1}{x}\,\underset{\hat{e}_1}{\hat{i}} + \underset{x_2}{y}\,\underset{\hat{e}_2}{\hat{j}} + \underset{x_3}{z}\,\underset{\hat{e}_3}{\hat{k}} = \underset{\substack{i \\ \text{convenient} \\ \text{notation}}}{\sum} x_i \hat{e}_i$$

Apply symmetry operator, $\hat{R}$, to coordinates of an atom ("Active")

$$\hat{R}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} x_1' \\ x_2' \\ x_3' \end{pmatrix} = D(\hat{R})\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$$

$D(\hat{R})$ is a 3×3 matrix representation of the $\hat{R}$ symmetry operator.

$$D(\hat{\sigma}(12)) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$D(\hat{C}_\theta(\underset{\substack{\uparrow \\ \boxed{\text{3 axis}}}}{3})) = \begin{pmatrix} c\theta & s\theta & 0 \\ -s\theta & c\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$D(\hat{C}_\theta(3)^{-1}) = \begin{pmatrix} ? \end{pmatrix}$$

$$\boxed{\begin{array}{l} \theta \to -\theta \\ U^{-1} = U^\dagger \end{array}}$$

What is the inverse of $D(\hat{C}(3))$?
What are the characteristics of a unitary transformation?
* normalized rows and columns
* rows (and columns) are orthogonal

$$D(\hat{i}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$D(\hat{S}_\theta(3)) = \begin{pmatrix} c\theta & s\theta & 0 \\ -s\theta & c\theta & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{difference between } \hat{S}_\theta \text{ and } \hat{C}_\theta$$

$$D(\hat{E}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

We have been considering the effect of symmetry operations on coordinates of a point. We generated matrices which represent the symmetry operations by producing the intended effect on coordinates. These matrices have the same multiplication table as the symmetry operations themselves. The matrices form a representation of the group that includes these symmetry operations .

We can form a matrix representation of any group by selecting any set of:

BASIS VECTORS;
coordinates of each atom in molecule;
each equivalent bond;
each equivalent angle;
anything convenient. (over-complete is OK)

Before generating lots of matrix representations, we must consider ACTIVE vs. PASSIVE coordinate transformations.

ACTIVE: move the object ($r \to r'$). Change the coordinates of the object.

PASSIVE: move the axis system. ($\hat{\mathbf{e}} \to \hat{\mathbf{e}}'$)

Equivalence of the two kinds of transformation: the coordinates of the untransformed object in the new axis system are identical to the coordinates of the transformed object in the old coordinate system.

$$\underline{r} = \sum \hat{e}_i x_i \Rightarrow \underline{r} = \underline{e}^t \underline{x} \qquad \text{in matrix notation}$$

$$\underline{r}' = \hat{R}\underline{r} = \underline{e}^t\left[\underline{D}(\hat{R})\underline{x}\right] = \underline{e}^t\underline{x}' \qquad \text{active (transformation applied to the object)}$$

$$= \left[\underline{e}^t\underline{D}(\hat{R})\right]\underline{x} \qquad \text{passive (transformation applied to the coordinate system)}$$

$$= \underline{e}'^t\underline{x}$$

$$\underline{e}'^{t} \equiv \underline{e}^{t}\,\underline{D}\left(\hat{R}\right)$$

take transpose

$$\underline{e}' = \left[\underline{e}^{t}\,\underline{D}(R)\right]^{t} = \underline{D}^{t}(R)\,\underline{e} = \underline{D}\left(R^{-1}\right)\underline{e} \quad !$$

same as inverse for *unitary* matrix

$\hat{R}$ acts on the coordinate system in the <u>inverse sense</u> to the way it acts on the object.

We are now ready to construct $3N \times 3N$ dimension matrix representations of effects of symmetry operations on an N-atom molecule.

We are going to simplify things soon to the traces or characters of these matrices, $\chi(\hat{R})$:

$$\chi\left(\hat{R}\right) \equiv \sum_{i=1}^{3N} \underline{D}\left(\hat{R}\right)_{ii}$$

Keep this in mind when we focus on only what appears along the diagonal of $\underline{D}\left(\hat{R}\right)$!

If a symmetry operation causes 2 atoms α, β to be permuted, all information about this is in the α, β <u>off-diagonal</u> 3×3 block.

$$\begin{pmatrix} \boxed{\alpha} & & \boxed{\alpha,\beta} & \\ & \ddots & & \\ \boxed{} & & \boxed{\beta} & \\ & & & \ddots \end{pmatrix}$$

no contribution to character, χ

NON-LECTURE

What about the effect of a symmetry operation on a function?

f(x) = a number

active: move the function f(x′) = a different #

passive: move the coordinate system, which changes the function so that f′(x) ≠ f(x) [but it must be true that f′(x) = f(x′)]

We want to find out what f′(x) is in terms of a complete orthogonal set of basis functions. How do we do this?

We require that f(x) = f′(x′). The new function operating in the new coordinate system gives the same number as the old function operating in the old coordinate system.

See pages 75-76 in Chapter 3 of Bernath for how to derive the new functions in terms of old coordinates

f(x,y,z) = xyz for example

$$\hat{O}_{C_3(z)} f(x,y,z) = f'(x,y,z) = \left(-\left(3^{1/2}/2\right)x_1^2 + \left(3^{1/2}/2\right)x_2^2 + x_1 x_2\right)x_3/2$$

So we know how to derive a matrix representation of any symmetry operation.

NOT unique, but it doesn't matter because regardless of what set of orthogonal basis vectors we use to generate our matrices, the matrices

* have the same trace (sum of eigenvalues)
* have the same eigenvalues (and determinant which is product of eigenvalues)
* differ from each other by at most a similarity transformation

$$D' = T^{-1}DT \qquad \underbrace{T^{-1} = T^{\dagger} \text{ (unitary)}}_{\text{a special case.}}$$

Suppose we have generated a set of 3N × 3N matrix representations of all symmetry operations, $\hat{R}$.

Perhaps there is a special unitary transformation **T** that causes all matrices to take the same block diagonal form. Reduced dimension representations.

Group Theory helps us to find these simplest possible "irreducible representations."

Γ symbolizes a representation

$$\Gamma^{\text{red}} = \left\{\underline{D}\left(\hat{R}_1\right), \underline{D}\left(\hat{R}_2\right), \ldots\right\}$$ a set of same-dimensional matrices

$$\Gamma^{\text{red}} = \Gamma^{(1)} \oplus \Gamma^{(2)} \oplus \cdots \Gamma^{(n)}$$ blocks assembled along diagonal

$$= \sum_{\nu} a_{\nu}\Gamma^{(\nu)}$$ ⊕ means direct sum of representations

Great Orthogonality Theorem (**GOT**) ⇒ helps to find the irreducible representations and, most importantly, to reduce the reducible representations to a sum of irreducible representations.

specific irreducible representation

complex conjugate

order of group (# of symmetry operations)

$$\text{GOT}: \sum_{\hat{R}} D_{ik}^{\mu}\left(\hat{R}\right)\left[D_{jm}^{\nu}\left(\hat{R}\right)\right]^{*} = \frac{g}{n_{\mu}}\delta_{\mu\nu}\delta_{ij}\delta_{km}$$

g terms in sum

row and column of matrix

dimension of μ-th irreducible representation

$$\sum_{\nu} n_{\nu}^{2} = g$$ (sum of squares of dimensions of irreducible representations is order of group)

Simplify to characters (because characters are all we need for most applications).

$$\chi^{\mu}\left(\hat{R}\right) \equiv \sum_{i=1}^{n_{\mu}} D_{ii}^{\mu}\left(\hat{R}\right)$$

n_{μ} is the dimension of the μ-th irreducible representation

For characters, we have a simplified form of the GOT:

$$\text{GOT}: \sum_{\hat{R}} \chi^{\mu}\left(\hat{R}\right)\left[\chi^{\nu}\left(\hat{R}\right)\right]^{*} = g\delta_{\mu\nu}$$

$$\chi^{\text{red}}\left(\hat{R}\right) = \sum_{\nu} a_{\nu}\chi^{\nu}\left(\hat{R}\right)$$

sum over all irreducible representations

$$a_\mu = \frac{1}{g}\sum_{\hat{R}} \chi^{red}(\hat{R})\chi^{\mu}(\hat{R})^*$$

be careful about classes

# of times μ-th irreducible representation appears in initial reducible representation

Example:

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$
A_1	1	1	1
A_2	1	1	–1
E	2	–1	0

3 classes, 3 irreducible representations

Condensed according to "classes". To find the members of the class that contains $\hat{R}$, perform $\hat{R}'^{-1}\hat{R}\hat{R}'$ for all $\hat{R}'$

# of classes: k

members of each class: g_i

$$\sum_i g_i = g$$

# of irreducible representations: r

$r = k$ ($\therefore$ condensed character table is square!)

$\sum n_\mu^2 = g$

Mulliken Notation for irreducible representations.

1 dimensional: A or B

$\chi(\hat{C}_n) = +1$ (for A) -1 (for B) (n is highest order rotation)

2 dimensional: E

3 dimensional: T or F

if $\hat{i}$ is present $\chi(\hat{i}) = \underset{g}{+1}$ or $\underset{u}{-1}$ (e.g. A_g, A_u)

$\hat{\sigma}_h$ $\chi(\hat{\sigma}_h) = \underset{\prime}{+1}$ or $\underset{\prime\prime}{-1}$ (e.g. A′, A″)

$_1$ and $_2$ labels — no special rule except by convention for problematic point groups.

NH_3 [C_{3v}] 12×12 reducible Cartesian representation

	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$
χ^{red}	12	0 (from H's)	2–1 (for N)
		$1 + 2\cos\frac{2\pi}{3} = 0$ (from N)	2 – 1 (for one H)
	12	0	2

χ^{red} = [12, 0, 2]

Decompose χ^{red}

$$a_{A_1} = \frac{1}{g}\sum_{\hat{R}} \chi^{\text{red}}\left(\hat{R}\right)\chi^{A_1}\left(\hat{R}\right)^* \qquad g = 6 \text{ (one E, two } C_3\text{, three } \sigma_v\text{)}$$

$$= \frac{1}{6}[12\cdot 1 + \mathbf{2}\cdot 0\cdot 1 + \mathbf{3}\cdot 2\cdot 1] = \frac{1}{6}[12 + 6] = 3$$

$$a_{A_2} = \frac{1}{6}\left[12\cdot 1 + 2\cdot 0\cdot 1 + 3\cdot 2\cdot(-1)\right] = 1$$

$$a_E = \frac{1}{6}\left[12\cdot 2 + 2\cdot 0\cdot(-1) + 3\cdot 2\cdot 0\right] = 4$$

3 + 1 + 2(4) = 12

Next: remove rotations and translations.