Introduction

CHEM 325 Physical Chemistry 2

Preliminaries

- Housekeeping
  - Syllabus
  - Course calendar
- Keys to Success
  - Read the book
  - Do the problems in the book
  - Ask questions
  - Don't panic
  - Don't be afraid of the math
  - Remember the system

> "I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of Science, whatever the matter may be."
>
> Sir William Thomson
> Lord Kelvin

What is Physical Chemistry?

- Description of the Chemical World
  - Interaction of energy with matter
  - How chemical/physical change occurs
  - Change over time
- Accurate, Precise Measurements of Physical Phenomena
- Mathematical Models
  - State functions and state variables (p, V, n, T)
  - Ideal case to non-ideal cases

Divisions of Physical Chemistry

- Classical Physical Chemistry
  - Developed before 1900
  - Thermodynamics, kinetics, equilibrium
  - Focused on macroscopic observables
- Modern Physical Chemistry
  - Mainly developed after 1900
  - Also called chemical physics
  - Derived from spectroscopy
  - Includes quantum mechanics, bonding, spectroscopy and statistical mechanics

- For those who are not shocked when they first come across quantum theory cannot possibly have understood it.

  -Niels Bohr

- Not only is the universe stranger than we imagine, it is stranger than we can imagine.

  -Sir Arthur Eddington

Mathematics of Quantum Mechanics

- New this Semester
  - – Complex numbers and functions
  - – Vectors
  - – Matrix algebra
  - – Group theory
  - – Combinatorial functions
- Don’t forget first Semester Calculus Topics
  - – See Appendix 2 in Atkins for review

Linear Algebra

- Mathematics of Matrices
  - – Important for quantum mechanics
- Definition of a Matrix
  - – Array of numbers of *n* rows by *m* columns
- Examples of special *n* x *m* Matrices
  - – 1 x 1 = Scalar
  - – 3 x 1 = Vector (also 4 x 1)
  - – *n* x *n* = Tensor

Linear Algebra

- Matrix Addition
  - – Undefined if matrices aren’t same size
- Scalar Multiplication

$$x\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} xa \\ xb \end{bmatrix}$$

- Matrix Multiplication
  - – Undefined when *n* of first matrix ≠ *m* of second
  - – Commutative law does not necessarily hold

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}\begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} = \begin{bmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \end{bmatrix}$$

Square Matrices

- Matrices where $n = m$
  - Most useful for quantum mechanics
- Identity Matrix: $I = [\delta_{ij}]$
  - Kronecker delta: δ_{ij}
- Inverse of a Matrix, A^{-1}
  - Definition: $A \cdot A^{-1} = A^{-1} \cdot A = I$
  - Not all matrices are invertible
- Diagonal Matrix
  - Matrix $[a_{ij}]$ where if $i = j$ $a_{ij} \neq 0$, but if $i \neq j$ $a_{ij} = 0$

Square Matrices

- Transpose of a Matrix, A^T
  - Definition: $A^T = [b_{ij}]$, where $b_{ij} = a_{ji}$
  - Flip rows and columns
- Adjoint of a Matrix, A^*
  - Definition: $A^* = [b_{ij}]$ with $b_{ij} = \bar{a}_{ji}$
  - Take transpose and flip sign i, too
  - For a real matrix $A^* = A^T$
- Symmetric Matrix: $A = A^T$
- Hermitian Matrix: $A = A^*$ (self-adjoint)

Determinants

- Scalar Derived from a Matrix

$$\det A = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}$$

- For Larger Matrices break into 2 x 2 Matrices as follows
  - Note on row/column choice

$$\det A = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

Vector Spaces

- Set of Objects (Vectors) with two Operations defined: Scalar Multiplication and Vector Addition
- Basis Set
  - Subset of the vector space whose members are *linearly independent* (*orthogonal*) and which *span the set*
  - Can write all other members of the vector space as linear combinations of this subset

Linear Transformations

- Function (Matrix) that converts one Vector Space to another Vector Space
  - Function called an *operator*
  - Transformation is called an *operation*
  - Linear transformation = matrix multiplication
- Properties of Linear Transformations
  - Associative and distributive laws hold
  - Commutative law not necessarily true
  - Zero and identity transformations

Eigenvalue Problems

- Certain Linear Transformations obey the Relationship $\hat{\mathbf{L}}\mathbf{x} = \lambda\mathbf{x}$
  - Matrix **x** is called an *eigenvector*
  - Scalar λ is called an *eigenvalue*
  - Eigenvectors form *eigenspace* (subset of the original vector space of which **x** is a member)
- Procedure for solving Eigenvalue Problem
  - Use determinant to find eigenvalues (*diagonalize the matrix*)
  - Substitute eigenvalues in to find eigenvectors

Group Theory

- What is it?
  - Mathematics of symmetry
- How does it apply to Chemistry?
  - Wavefunctions have shapes
  - Molecules also have shapes
- Two Fundamental Terms
  - Symmetry element
  - Symmetry operation

Symmetry

- Identity
  - Element = E
  - Operation = Ê

$$(x,y,z)\xrightarrow{\hat{E}}(x,y,z)$$

- Inversion (Point)
  - Element = i
  - Operation = î

$$(x,y,z)\xrightarrow{\hat{i}}(-x,-y,-z)$$

Symmetry

- Rotation (Line)
  - Element = C_n (n fold rotation)
  - Operation = $\hat{C}_n$ (clockwise rotation by $2\pi/n$)
  - Highest order axis

$$(x,y,z)\xrightarrow{\hat{C}_4(z)}(-y,x,z)$$

  - C_n generates more than one operation corresponding to number of times rotation performed or direction of rotation

$$\hat{C}_4^1, \hat{C}_4^2\left(=\hat{C}_2\right), \hat{C}_4^3, \hat{C}_4^4\left(=\hat{E}\right)$$

Symmetry

- Reflection (Plane)
  - Element = σ
  - Operation = $\hat{\sigma}$
  - Planes || to highest order axis ≡ σ_v
  - Planes ⊥ to highest order axis ≡ σ_h

$$(x,y,z) \xrightarrow{\hat{\sigma}(xy)} (x,y,-z)$$

$$\hat{\sigma}^2 = \hat{E}$$

Symmetry

- Improper Rotation (Line and Plane)
  - Element = S_n
  - Operation = $\hat{S}_n$ $2\pi/n$ rotation followed by reflection in plane ⊥ to rotation axis
  - Equivalent to $\hat{\sigma}_h\hat{C}_n$ (when operations performed in order from right to left)

$$\begin{tikzcd}(x,y,z) \arrow[r, "\hat{C}_2(z)"] \arrow[rr, bend right, "\hat{S}_2 = \hat{i}"'] & (-x,-y,z) \arrow[r, "\hat{\sigma}_h"] & (-x,-y,-z)\end{tikzcd}$$

Symmetry Group

- Complete Set of Symmetry Operations needed to describe an Object
- Vector Space with the Properties
  - All binary products (defined right to left) of group members are also in the group
  - Contains the identity ($\hat{E}$)
  - Associative law of multiplication holds
  - Every member has an inverse ($A^{-1}A=AA^{-1}=E$)
  - Commutative law (Abelian)

Symmetry Groups

- Additional Definitions
  - Order of group, *h*
  - Dihedral mirror plane (σ_d)

$$\begin{tikzcd}(x,y,z) \arrow[r, "\hat{C}_4(z)"] \arrow[rr, bend right, "\hat{\sigma}_d"'] & (-y,x,z) \arrow[r, "\hat{\sigma}_v(yz)"] & (y,x,z)\end{tikzcd}$$

- Schoenflies Notation
  - Special symbols for high-symmetry groups
  - D vs. C designation for groups
- Hermann-Mauguin Notation

Symmetry Groups

- Related Groups
  - Nonaxial groups: C_1, C_s, C_i
  - Cubic groups: T_h, T, T_d, O, O_h
  - “Linear” groups: $C_{\infty v}$, $D_{\infty h}$
  - Icosahedral groups: I_h, I
  - Pure rotation groups: I, T, O, C_n, D_n
- Useful to Divide a Group into Classes
  - Class: a subset of group all members of which are conjugates related by similarity transform

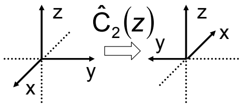
$$\hat{P}^{-1}\hat{A}\hat{P} = \hat{B}$$

Assigning Objects to a Point Group

- Flow Chart on Handout
- Keys
  - Recognize special cases (linear, O_h, T_d)
  - Look for C_n first, then for $C_2 \perp$ to C_n
  - Next look for mirror planes
  - But go with whatever you find first
  - Note: pure rotation groups are relatively rare
- Practice

Matrix Representations

- Symmetry Operations can be written as Matrix Multiplication
  - Example: $\hat{C}_2$ about z axis



$$(x,y,z) \xrightarrow{\hat{C}_2(z)} (-x,-y,z)$$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

Matrix Representations

- Replace Geometric Operations with Matrix Multiplication
  - Serial application of operations becomes serial matrix multiplication
- Irreducible Representations (IRs)
  - Basis set for vector space
- Reducible Representations
  - Linear combinations of IRs
  - Any function can be reduced to a smaller number of functions within the group

Matrix Representations

- Symmetry Group C_{2v}
  - Symmetry operations: $\hat{E}, \hat{C}_2(z), \hat{\sigma}_v(xz), \hat{\sigma}'_v(yz)$

$$\hat{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \hat{C}_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\hat{\sigma}_v(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \hat{\sigma}_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

No operation interchanges two directions $\therefore$diagonal.

Matrix Representations

- Matrices are always Block Diagonal
  - Identifies members of basis set
  - Shows which functions belong to which irreducible representation

$$\hat{E} = \begin{bmatrix} \boxed{1} & 0 & 0 \\ 0 & \boxed{1} & 0 \\ 0 & 0 & \boxed{1} \end{bmatrix}$$ x, y and z belong to different IRs

$$\hat{C}_4 = \left[\begin{array}{cc|c} 0 & -1 & 0 \\ 1 & 0 & 0 \\ \hline 0 & 0 & \boxed{1} \end{array}\right]$$ x and y belong to one IR, but z belongs to a different IR

Matrix Representations

- Need only Consider Trace (*Character*) of each <u>Submatrix</u>
  - Trace: sum of diagonal matrix elements

$$\chi = \sum_i A_{ii}$$

$$\hat{E} = \begin{bmatrix} \boxed{1} & 0 & 0 \\ 0 & \boxed{1} & 0 \\ 0 & 0 & \boxed{1} \end{bmatrix}$$ Trace of each submatrix = 1

$$\hat{C}_4 = \left[\begin{array}{cc|c} 0 & -1 & 0 \\ 1 & 0 & 0 \\ \hline 0 & 0 & \boxed{1} \end{array}\right]$$

Trace of xy submatrix = 0

Trace of z submatrix = 1

Character Tables

- Collection of IRs for a Symmetry Group and their Characters
  - Number of IRs in character table must equal order of group
- Derivation of C_{2v} Character Table

$$\hat{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \hat{C}_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\hat{\sigma}_v(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \hat{\sigma}_v(yz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Character Tables

- Irreducible Representations designated by Mulliken Symbols as follows

$\chi(\hat{E}) = 1$ A or B

$\chi(\hat{E}) = 2$ E

$\chi(\hat{E}) = 3$ T

For one-dimensional IRs

$\chi(\hat{C}_n^1) = +1$ A

$\chi(\hat{C}_n^1) = -1$ B

Character Tables

One dimensional IRs continued

$\chi(\perp\hat{C}_2, \text{if none } \hat{\sigma}_v) = +1$ subscript 1

$\chi(\perp\hat{C}_2, \text{if none } \hat{\sigma}_v) = -1$ subscript 2

$\chi(\hat{i}) = +1$ subscript g (*gerade* = symmetric)

$\chi(\hat{i}) = -1$ subscript u (*ungerade*)

If no inversion

$\chi(\hat{\sigma}_h) = +1$ superscript ′

$\chi(\hat{\sigma}_h) = -1$ superscript ″

Character Tables

- Special Notes for Linear Groups
  - 1 Dimensional: Σ
  - 2 Dimensional: Π
  - 3 Dimensional: Δ

$\chi(\hat{\sigma}_v) = +1$ superscript +

$\chi(\hat{\sigma}_v) = -1$ superscript -

For $D_{\infty h}$

$\chi(\hat{i}) > 0$ subscript g

$\chi(\hat{i}) < 0$ subscript u

Mulliken Symbols

- Contain all Information found in Character Table
- Example: A_2' in D_{3h}

A	$\chi(\hat{E}) = +1$	$\chi(\hat{C}_3^1) = +1$
Subscript 2	$\chi(3\hat{C}_2) = -1$	$\chi(3\hat{\sigma}_v) = -1$
Superscript ′	$\chi(2S_3) = +1$	$\chi(3\hat{\sigma}_h) = +1$

No g/u so no inversion

Character Table

Symmetry (point) group

Irreducible representations

C_{2v}	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v'(yz)$	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	xy, R_z
B_1	1	-1	1	-1	x, xz, R_y
B_2	1	-1	-1	1	y, yz, R_x

Character of IRs under each symmetry operation

Important functions (R_i = rotations)

Character Table Theorems

- Sum of the Squares of the Dimensions of IRs of Group Equals Order of Group

Dimension of i^{th} IR = $\chi_i(\hat{E})$

$$h = \sum_i [\chi_i(\hat{E})]^2$$

In C_{2v}: $h = (1)^2 + (1)^2 + (1)^2 + (1)^2 = 4$

- Sum of the Squares of Characters of any IR equals Order of Group

$$h = \sum_R [\chi_i(R)]^2$$

In C_{2v}: with B_2 $h = (1)^2 + (-1)^2 + (-1)^2 + (1)^2 = 4$

Character Table Theorems

- Vectors whose Components are Characters of two Different IRs are mutually Orthogonal

$$\sum_{R} \chi_i(R)\chi_j(R) = 0 \quad \text{for } i \neq j$$

In C_{2v}: $B_2 \times A_2 = (1)(1)+(-1)(1)+(-1)(-1)+(1)(-1)=0$

- For any Representation, Characters of all Matrices belonging to Same Class are Identical
- Number of IRs equals Number of Classes in Group

Binary Multiplication

- Multiplication of Matrices
  - Often only symmetry of result is needed
  - Know symmetry of functions in group can find symmetry of product by simple multiplication of characters
- To Determine Direct (Binary) Product multiply Character of each Operation for the two Functions

$$\chi_{DP}(\hat{R}) = \chi_1(\hat{R})\chi_2(\hat{R})$$

Binary Multiplication

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y) (R_x,R_y)	(x^2-y^2,xy) (xz,yz)

What is $A_1 \times A_2$ in C_{3v} symmetry?

	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$
A_1	1	1	1
A_2	1	1	-1
$A_1 \times A_2$	1	1	-1

In general: $A_{1(g)} \times \Gamma_i = \Gamma_i$

Binary Multiplication

What is E x E in C_{3v} symmetry?

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$
E	2	-1	0
E	2	-1	0
E x E	4	1	0

Not an irreducible representation!

This reducible representation must be a linear combination of irreducible representations. But which ones?

Reducing Reducible Represenations

- Great Orthogonality Theorem
  - a_i = number of times i^{th} IR appears in reducible representation
  - h = order of the group
  - n_i = number of operations in class
  - χ_{RED} and χ_i are characters of each operation

$$a_i = \frac{1}{h}\sum_{R} n_i \chi_{RED}(\hat{R})\chi_i(\hat{R})$$

Reducing Reducible Represenations

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y) (R_x,R_y)	(x^2-y^2,xy) (xz,yz)
E x E	4	1	0		

$$a_{A_1} = \frac{1}{6}\big((1)(4)(1)+(2)(1)(1)+(3)(1)(0)\big) = 1$$

$$a_{A_2} = \frac{1}{6}\big((1)(4)(1)+(2)(1)(1)+(3)(0)(-1)\big) = 1$$

Reducing Reducible Represenations

C_{3v}	$\hat{E}$	$2\hat{C}_3$	$3\hat{\sigma}_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y) (R_x,R_y)	(x^2-y^2,xy) (xz,yz)
E x E	4	1	0		

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

E x E = A_1 + A_2 + E

Group Multiplication Tables

- Work out all Possible Direct Products in a Group
  - Symmetric about diagonal
  - A_1 appear only on diagonal these are only direct products that contain A_1

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	A_1+A_2+E

Importance of Linear Algebra to Quantum Mechanics

- Solutions to the Schrödinger Equation form a Vector Space
- Linear Algebra/Group Theory can be used to simplify Problems
  - What transitions can be observed?
  - What orbitals can combine? (MO Theory)
  - Predicting optical activity and molecular polarity