Chemistry 673
Symmetry and Group Theory in Chemistry

Instructor: Dr. Timothy Hughbanks
Time: TTh 12:45 - 2:00 PM; Room 2121
Office Hours: Tuesday 2:00 - 4:00. Other times are OK too, if I have time!

Texts: (1) F. A. Cotton, "Chemical Applications of Group Theory", 3rd Ed., Wiley: New York, 1990. (2) D. C. Harris and M. D. Bertolucci, "Symmetry and Spectroscopy; An Introduction to Vibrational and Electronic Spectroscopy", Dover: New York, 1989.

The course will provide an introduction to the fundamentals and applications of the theory of group representations in chemistry. After a brief introduction to the abstract theory of groups is given, applications of symmetry groups will constitute the major emphasis of the course. The student will be encouraged to develop both the formal skills of using group theory to "grind out answers" *and* to acquire some intuitive and pictorial sense of "what it all means". The text is well written and suitable for a course at this level, but students sometimes find phrases like "it is obvious that . . ." and "it is easily seen that . . ." to be frustrating. I would be pleased to spend time in my office explaining things that are not as "obvious" or "easily seen" as claimed. For the more mathematical (formal) first half of the course, the lectures will probably more closely follow the text than is often the case in graduate courses. For many topics, particularly with aspects of quantum mechanics and those dealing with solids, additional handouts and reference materials will be necessary.

Grades will be based on the homework (≈ 50%), midterm and final exams. The anticipated point breakdown should go as follows: 5 problem sets (60 pts each), one midterm exam (100 pts), and a final exam (200 pts). You are expected to make a serious attempt at every assigned homework problem before consulting with your peers, otherwise collaboration is permitted as long as significant contributions are made by all collaborators. *Do not expect to be able to do all problems in a problem set in a single sitting*.

Chemistry 673
Course Outline (including readings from Cotton's text)
(Tentative — the section on crystals will be covered if time permits)

<u>I. Basic Properties of Groups and Symmetry Groups</u> (Chapters 2 & 3) *~ 2 weeks*

A. Multiplication of elements
   closure, existence of an identity element and reciprocals, associative law
   noncommutation of operations
   multiplication tables
   subgroups and supergroups

B. Symmetry groups
   symmetry elements and operations
   assigning point groups (flow chart)
   examples of subgroups
   abelian groups, cyclic groups
   translation groups and crystals — introduction to k-space

C. Similarity transformations and classes
   similarity transformations
   geometrical significance of classes of symmetry operators

<u>II. Group Representations and Physical Implications</u> (Chapters 4, 5, & 6) *~ 3-4 weeks*

A. Matrices as representations for symmetry operations
   review of vector and matrix properties; matrix operations
   some special properties of matrices
   character (trace) of a matrix
   orthogonal matrices, matrices as geometric transformation operators
   inverses

B. Group representations
   reducible and irreducible representations
   the "Great Orthogonality Theorem" and its consequences
   character tables
   cyclic groups
   translation groups (just special cyclic groups)

C. Group theory as a tool in quantum mechanics
   operators in quantum mechanics
   the importance of operators that commute with the Hamiltonian
   symmetry operators as special cases of commuting operators
   the direct product and its uses
   bases for group representations and nonzero matrix elements
   transition probabilities - symmetry aspects

D. Symmetry-Adapted Linear Combinations (SALCs) and Bases for Irreducible Representations.
   projection operators - "complete" and "incomplete"

projection operators in the construction of SALCs
symmetry patterns, SALCs, and the intuitive nature of bases for irreducible representations - a pictorial survey

III. Selected Applications Group Theory: MO Theory, Band Theory, Vibrational Spectra

~ 6-7 weeks

A. Molecular Orbitals in Organic Molecules (Hückel Theory and Modest Extensions)
the LCAO method - secular determinants and the Hückel approximation
MO diagrams
using group theory to "block factor" secular determinants
carbocyclic molecules and other examples of π bonding
π carbon-based chains and layers (eg., polyacetylene and graphite)
more examples (e.g., heteroatoms, pericyclic reactions, etc.)

B. Molecular Orbitals in Inorganic Molecules and Solids (No spin worries)
MOs for octahedral and tetrahedral molecules
other molecular shapes (trigonal prisms, low coordination numbers)
π bonding ligands
clusters and cages
some basic organometallics
band structures for some basic inorganic solids

C. Ligand Field Theory (Some spin worries)
atomic states
connecting atomic states and molecular states
Slater determinants as bases for reducible and irreducible representations
high-spin and low-spin molecules
Jahn-Teller effects - applications of subgroups
selection rules for electronic transitions in molecules
selection rules for electronic transitions in solids
vibronic coupling and the solid state analog, electron-phonon coupling

D. Molecular Vibrations
normal modes
symmetries of normal modes
mixing of internal coordinates in normal modes
selection rules for vibrational spectra (IR and Raman)
mixing of internal coordinates in normal modes

IV. Crystals (time permitting) *~ 2 weeks*

A. Lattices and Reciprocal Lattices
2-D lattices and their reciprocals (translation groups in 2-D)
crystal symmetry classes
Grafting point groups on to lattices groups: symmorphic space groups
nonsymmorphic space groups (basic idea)

Chemistry 673 - Other Suggested Books (more advanced texts in italics)

Author(s)	**Title**
Ballhausen	Introduction to Ligand Field Theory
Ballhausen	Q. M. and Chemical Bonding in Inorganic Complexes
Bishop	Group Theory and Chemistry
Burdett	Molecular Shapes
Burns & Glazer	Space Groups for Solid State Scientists
Butler	Point Group Symmetry Applications
Carter	Molecular Symmetry and Group Theory
Figgis	Introduction to Ligand Fields
Flurry	Symmetry Groups
Franzen	Physical Chemistry of Solids, Basic Principles …
Hanna	Quantum Mechanics in Chemistry
Hoffmann	Solids and Surfaces, A Chemist's View…
Heine	*Group Theory in Quantum Mechanics (Dover)*
Kettle	Symmetry and Structure
Lax	*Symmetry Principles in Solid State and Molecular Physics*
McQuarrie & Simon	Physical Chemistry
Molloy	Group Theory for Chemists
Murrell, Kettle & Tedder	The Chemical Bond
Molloy	Group Theory for Chemists
Pearson	Symmetry Rules for Chemical Reactions
Tinkham	*Group Theory and Quantum Mechanics (Dover)*
Walton	Beginning Group Theory for Chemistry

See also:

• Herzfeld, C.M.; Meijer, P.H.E. "Group Theory and Crystal Field Theory." *Solid State Physics* **1961**, *12*, 1-89.