Chemistry 634
Physical Methods in Inorganic Chemistry

Instructor: Dr. Timothy Hughbanks
Time: TTh 11:10 - 12:25 PM; Room 2122
Office Hours: Tuesday 2:00 - 4:00. Other times are OK too, as available

Texts (loosely followed):
J. Iggo, “NMR Spectroscopy in Inorganic Chemistry”;
A. F. Orchard, “Magnetochemistry”;
Harris & Bertolucci, “Symmetry and Spectroscopy, An Introduction to Vibrational and Electronic Spectroscopy”.
Other resources: Numerous handouts, book chapters – detailed in lecture notes posted online.

The course will provide an introduction to methods of determining of molecular and crystal structures and physical properties of inorganic compounds. Because this is a survey course, a single textbook that adequately discusses all topics covered is difficult to identify. Students are especially encouraged to read from the broader readings in the attached reading list and to identify other sources for themselves.

The grades will be based on the homework (~25%), term paper (~15%) midterm and final exams (~60%). The anticipated point breakdown should go as follows: ~4-5 problem sets (~125 pts total), term paper (~75 pts), a one-hour midterm exam (100 pts), and a final exam (160 pts). [Note: the term paper is still tentative, subject to possible cancellation.] 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. The homework will be a mix of straightforward exercises combined with a couple of more challenging problems in each set; for the latter, you should budget time to do them in more than a single sitting.
Chemistry 634
Course Outline

I. X-ray Diffraction and Space Groups ~ 4-5 weeks

A. Lattices and Space Groups
   Bravais lattices
   Plane Groups
   Space Groups – “simple” symmorphic cases w/examples
   Structures vs lattices
   Glide Planes and screw axes w/examples
   Survey of examples of space groups applied to structures

B. Reciprocal lattices and Diffraction
   Mathematical definition of reciprocal lattices
   and geometric relationships to direct (Bravais) lattices
   Role of reciprocal lattice in diffraction
      – the condition for constructive interference
   Fraunhofer diffraction vs. Bragg/Laue diffraction – an optical analogy
   Structure factors
   Systematic Absences and symmetry

C. A Conceptual walk through ‘typical’ crystal structure determinations
   Data collection
   Unit cell and symmetry
   Intensities
   Data Reduction
   Structure Solution
   Finishing Touches

II. Electronic Structure and Spectroscopy of TM Complexes ~ 2-3 weeks

A. MO Theory
   Ligand Field Theory
   Valence Bond Theory (deficiencies of elementary approach)

B. Ligand Effects; Metal Effects
   σ-donors
   π-donors
   π-acceptors
   Metal-dependent trends

C. Electronic States of TM complexes
   d-d transitions; connecting atomic states and molecular states
   High-spin and low-spin molecules
   Jahn-Teller effects - applications of subgroups
   Selection rules for electronic transitions in molecules
   LMCT and MLCT transitions
   Aspects of solid-state spectroscopy
III. EPR Spectroscopy ~ 2-3 weeks

A. Background
   What is EPR?
   Electronic Structure of Atoms and open-shell ions
   Spin-Orbit Coupling
   $g$-values in atoms
   Zeeman interaction

B. Hyperfine coupling
   Connection to wavefunctions
   Simple radicals
   Hyperfine anisotropy – dipolar contributions
   Complex cases

C. The $g$-tensor
   Phenomenological meaning of $g$-values
   Why are $g$-values anisotropic in molecules?
   Relationship between $g$-tensor, “fictitious” spin, and “true” spin
   Spin-orbit coupling, electronic structure, and $g$-value anisotropy
   Examples

IV. Magnetism ~ 2 weeks

A. Phenomenological survey
   Ideal paramagnets (Curie Law) and weakly interacting paramagnets (Curie-Weiss)
   Ferromagnets, antiferromagnets, and ferrimagnets
   Basics of magnetic measurements

B. Mechanisms of magnetic coupling
   Coupling in dimers
   Magnetostructural correlations – whether by design or by discovery

V. Nuclear Magnetic Resonance Spectroscopy ~ 2 weeks

A. Fundamentals
   Energy levels, transitions, sensitivity issues, timescales
   Chemical shielding and shifts, basics and a few advanced ideas
   Spin-spin coupling and decoupling
   Basics of relaxation and the vector model

B. Structure Determination
   Trends in chemical shifts
   Factors influencing coupling constants
   Chemical and magnetic equivalence
   First- and second-order spectra
   Relaxation and structure

C. Other topics
   Dynamic processes
   NMR of paramagnetic compounds
### Chemistry 634 - Other Suggested Books

<table>
<thead>
<tr>
<th>Author(s), Editors</th>
<th>Title</th>
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<tbody>
<tr>
<td>Abragam &amp; Bleaney</td>
<td>Electron Paramagnetic Resonance of Transition Ions</td>
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<td>Brisdon</td>
<td>Inorganic Spectroscopic Methods</td>
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<td>Canet</td>
<td>Nuclear Magnetic Resonance Concepts and Methods</td>
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<tr>
<td>Carrington &amp; McLachlan</td>
<td>Introduction to Magnetic Resonance</td>
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<td>Cheetham &amp; Day</td>
<td>Solid-State Chemistry Techniques</td>
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<tr>
<td>Clegg</td>
<td>Crystal Structure Determination</td>
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<tr>
<td>Cotton</td>
<td>Chemical Applications of Group Theory, 3rd Edition</td>
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<tr>
<td>Drago</td>
<td>Physical Methods for Chemists, 2nd Edition</td>
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<tr>
<td>Ebsworth, Rankin &amp; Cradock</td>
<td>Structural Methods in Inorganic Chemistry, 2nd Ed.</td>
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<tr>
<td>Friebolin</td>
<td>Basic One-and Two-Dimensional NMR Spectroscopy, 5th Ed.</td>
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<tr>
<td>Keeler</td>
<td>Understanding NMR Spectroscopy, 2nd Ed.</td>
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<tr>
<td>Housecroft &amp; Sharpe</td>
<td>Inorganic Chemistry, 4th Ed.</td>
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<tr>
<td>Orton</td>
<td>Electron Paramagnetic Resonance</td>
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<td>Giacovazzo, Monaco, Viterbo, Scordari, Gilli, Zanotti, Catti</td>
<td>Fundamentals of Crystallography</td>
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<td>Solomon &amp; Lever, eds.</td>
<td>Inorganic Electronic Structure and Spectroscopy, Volumes I &amp; II</td>
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<tr>
<td>Stout &amp; Jensen</td>
<td>X-Ray Structure Determination-A Practical Guide</td>
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<tr>
<td>Wertz &amp; Bolton</td>
<td>Electron Spin Resonance</td>
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<td>Weltner</td>
<td>Magnetic Atoms and Molecules</td>
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