I. INSTRUCTOR

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II. COURSE TIMES

The class meets in Baker 219 on

Tuesday — 11:40 AM to 12:55 PM

Thursday — 11:40 AM to 12:55 PM

Office hours meet in 150 Baker. I will hold one or more office hour per week. I am happy to adjust office hours to accommodate your schedule. Let me propose:

Thursday — 6:00 PM to 7:30 PM

III. COURSE WEBPAGE

I will post course-related material to my public research notebook at

http://marohn-public.site44.com

Go to *Tags* and scroll down to *Chem 7940*. A link to the required and recommended texts can be found at

http://tinyurl.com/ms5fnkl

IV. OVERVIEW AND PHILOSOPHY

Chemistry 7940 is a course in time-dependent quantum mechanics, the interaction of molecules with radiation, and the interaction of molecules with other molecules. We will apply these ideas to understand time-domain spectroscopy (radiofrequency, infrared, and optical) and electron transfer.

Chemistry 7930 (or an equivalent first-semester graduate quantum mechanics course) is a prerequisite for this course.

In constructing the syllabus I have had to make some difficult choices. I have chosen to omit discussing the calculation of the electronic structure of molecules in any detail — not because it is not important (it is crucially important to chemists and is a topic of intense research), but because the topic is comparatively self-contained and excellent textbook treatments exist to get you started. Fortunately, a number of surprising optical spectroscopy experiments can be described without having to have full knowledge of the molecular wavefunction; a few matrix elements suffice to capture the essential phenomena. I have also chosen to omit group theory. Like electronic spectroscopy, the topic is self-contained with many excellent textbooks available.

In this course, we do not have time to treat systematically the fascinating and subtle rotational-vibrational-electronic spectra of diatomic and polyatomic molecules. Fortunately, Chemistry 7910, as taught every few years by Prof. Ezra, provides an in-depth treatment of the fundamentals of rotational-vibrational-electronic spectroscopy. Prof. Ezra's Chem 7910 also offers an introduction to scattering theory.

My goal with this course is to introduce you to new ideas (coherent multiple-pulse excitation, two dimensional spectroscopy) and phenomena (spin-lattice relaxation, spontaneous emission, electron transfer, energy transfer) as soon as possible using simple model systems. These ideas and phenomena have in common an underlying connection to time-dependent quantum mechanics.

V. PROBLEM SETS, LAB, AND GRADING

There will be weekly problem sets. These will make heavy use of Mathematica.

In addition, there will be a *lab*: you will carry out experiments on the Chemistry Department's nuclear magnetic resonance spectrometers that will illustrate many of the key ideas of time-domain quantum mechanics.

The course grade will be computed from your scores on

- homework
- lab
- preliminary and final exam
- final project

VI. COURSE OUTLINE

A. The Density Matrix

You are used to thinking of a quantum mechanical system in terms of its wavefunction. The problem with this approach is that the wavefunction for $\sim 10^{23}$ molecules in a test tube is just too large a mathematical object to deal with.

The density matrix gives you a way to capture the essential quantum mechanics of such a large ensemble of molecules in a much more compact and tractable way.

- From wavefunction to density matrix
- Calculating expectation values
- Pure states
- The random-phase approximation and mixed states
- Thermal equilibrium density operator

B. Unitary Time Evolution and the Two-level System

We are now ready to consider time evolution of a physical property. We will consider two example systems: 1) the electric dipole moment of a molecule, where we approximate the molecule as having only two electronic states, and 2) the magnetic moment of a proton. For properties to evolve in time, we need to excite the system into a superposition state. The superposition can be achieved in a number of ways by using an electromagnetic field, which we will treat classically.

- Lioville-von-Neumann equation of motion
- Semiclassical model for the interaction of a molecule with an electromagnetic field
- Oscillating magnetic and electric fields
- Application: Evolution of the molecular electric dipole moment
- Application: Evolution of proton magnetization in an NMR experiment
- Feynman-Vernon-Hellwarth theorem
- Interaction representation
- Rotating wave approximation
- Rabi frequency; pulsed excitation
- Effective field; adiabatic rapid passage
- Extension to multi-level systems: pseudo-two-level operators

C. Non-Unitary Evolution: Relaxation Processes and the Two-Level System

New phenomena appear when a quantum system is allowed to interact with its surroundings. For example, the electronic states of a molecule are perturbed by the electric dipole moments of solvent molecules undergoing translational and orientational diffusion nearby. Likewise, the magnetic moment of the proton is affected by paramagnetic ions moving by in solution which create local random magnetic fields. We will see that such perturbations lead to dephasing of the system's energy levels and to a decay of the excited states to equilibrium.

- Spin-lattice relaxation (T_1) versus dephasing (T_2)
- Stochastic Hamiltonians and the molecule-bath coupling
- Fluctuations and correlation functions
- Bloembergen-Purcell-Pound theory of relaxation
- Application: relaxation of proton magnetization by, for example, transition metal ions
- Application: dephasing of a molecular vibration by stochastic electric fields and field gradients
- Temperature-dependent relaxation: the surprising T_1 minimum
- Bloch equations (both optical and magnetic)
- Low-power irradiation – heterodyne detection and continuous-wave absorbtion
- High-power irradiation – saturation and hole-burning
- Hahn spin echoes and stimulated echoes

D. Time-Dependent Perturbation Theory I: Average Hamiltonian Theory

- Coupled linear equations with time-dependent coefficients
- The Magnus expansion
- Application: The Bloch-Siegert shift — beyond the rotating wave approximation
- Application: The Waugh-Huber-Haeberlen experiment — selective averaging of internal Hamiltonian with multiple-pulse irradiation
- The toggling-frame interaction representation
- Feynman diagrams

E. Multi-Dimensional Time-Domain Spectroscopy

Multiple-pulse irradiation schemes can be used to dissect the congested spectra of multi-level quantum systems; two-dimensional spectroscopy is another powerful tool. We can use these spectroscopic tools to study coupled spins (with the goal of determining the full three dimensional structure of complicated organic molecules) and coupled molecular vibrations (which has the same goal, but has only recently become possible with the advent of pulsed infrared lasers).

1. *Theory of Two-Dimensional Spectroscopy*

- Magnetic resonance imaging
- Coupled-spin Hamiltonian
- Löwdin projection-operator theorem and the 1D spectrum of two coupled spins
- The three pulse heteronuclear correlation experiment and the 2D spectrum of two coupled spins
- Possible extensions: polarization transfer; multidimensional vibrational spectroscopy

2. *Liquid-state 1D and 2D NMR experiments*

- Faraday-Law detector
- Probe
- Receiver: mixers; phase-sensitive detection
- Transmitter: quadrature pulses
- Spectrometer demonstration: quadrature detection and echoes
- Lab: free induction decay and COSY experiments

F. Time-Dependent Perturbation Theory II: Fermi's Golden Rule

Another type of time-dependent perturbation theory that we will derive from first principles.

- Step-function perturbation
- Harmonic perturbation
- Application: Stimulated absorbtion and emission

G. Marcus-Jortner Theory of Electron Transfer

Time-dependent quantum mechanics underlies not just modern spectroscopy, but a wide range of physical/chemical phenomena: electron transfer, energy transfer, transition-state theory, intermolecular forces, and scattering (a powerful tool for understanding intermolecular potentials and dissecting chemical reactions in quantum detail). Here we will focus on using time-dependent quantum mechanics to derive, from first principles, an expression for the rate of electron transfer between two molecules.

- Electron-vibration coupling model
- The sudden approximation
- A transformation to decouple electronic and vibrational Hamiltonians
- Implimenting Fermi's Golden Rule to get a reaction rate
- Low-temperature limit: tunneling
- High-temperature limit: activated rates
- The Marcus reorganization energy idea
- Solvent effects on electron transfer

H. Electromagnetic Radiation Interacting with Matter I – Classical Field

We continue by taking another look at the interaction of electronic states with the electromagnetic field. Einstein developed a simple ad-hoc argument that predicts the phenomena of stimulated emission and spontaneous emission.

- Einstein A and B coefficients
- Spontaneous emission and stimulated emission
- Oscillator strength

I. Electromagnetic Radiation Interacting with Matter II – Quantizing the Field

So far we have treated the matter-molecule interaction semiclassically: the molecule has been modeled quantum mechanically but the radiation has been modeled classically. Important new phenomena such as stimulated emission appear naturally when the radiation is modeled quantum mechanically. Here we pass from treating the radiation classically to treating it quantum mechanically.

1. *Classical Electromagnetic Field*

- Vector fields; divergence, and curl
- Helmholtz theorem; vector potential and scalar potential
- Maxwell's equations; output, inputs, and constants
- Gauge transformations; Lorentz gauge and Coulomb gauge
- Solving Maxwell's equations
- A charged particle in a field
  - Force
  - Lagrangian
  - Hamiltonian
- Semiclassical matrix elements
  - Electric dipole transitions
  - Magnetic dipole transitions
  - Electric quadrupole transitions
- From classical to quantum-mechanical particle-in-a-field Hamiltonian

2. *Quantized Electromagnetic Field*

- Plane waves in a box; polarization
- Fields as a superposition of modes
- Energy of the field confined to a box
- Quantized-field raising and lowering operators
- Fock states
- Vector potential in terms of raising and lowering operators
- Coherent states of the quantized electromagnetic field

J. Electromagnetic Radiation Interacting with Matter III – Quantum Optics

The phenomena of spontaneous emission and stimulated emission now follow naturally from first principles if we couple a molecule to a quantized electromagnetic field. Fascinating nonlinear phenomena such as superradiance, Raman scattering, and even van der Waals forces can be derived straightforwardly using quantum optics.

- Coupling of matter to a quantized electromagnetic field
- The Jaynes-Cummings Hamiltonian (lab and rotating frame)
- Evolution of the matter-radiation density operator
- Bloch-like equations
- Single-atom spontaneous emission
- Possible extensions: dressed states, multiple-atom spontaneous emission and Dicke superradiance, raman scattering

VII. TEXTS

A. Required

[Weissbluth]
Photon-Atom Interactions
Mitchel Weissbluth
Academic Press, Inc. (1989)
IBSN 0-12-743660-X
[link to the publisher]
[link to Amazon]
Seminal treatment of second quantization and dephasing.

B. Recommended

[Schatz & Ratner]
Quantum Mechanics in Chemistry
George C. Schatz and Mark A. Ratner
Dover Publications, Inc. (1993; 2002)
IBSN 0-486-42003-5 (pbk.)
[link to the publisher]
[link to Amazon] ($17 paperback)
Excellent treatment of spins, reaction rates, and electron transfer.

C. References

These texts will be placed, as needed, on reserve in the Physical Sciences Library in Clark Hall.

[Allen and Eberly]
Optical Resonance and Two-Level Atoms
L. Allen and J. H. Eberly
Dover Publications, Inc. (1975; 1987)
IBSN 0-486-65533-4 (pbk.)

Only $15 [link to Amazon]
A wonderful book: short, readable, great pictures.

[Atkins and Fridman]
Molecular Quantum Mechanics (4th Edition)
Peter Atkins and Ronald Friedman
Oxford University Press (2005)
IBSN 10: 0-19-927498-3
Molecular structure, electronic structure calculations, magnetic and optical properties of molecules.

[Craig and T···]
Molecular Quantum Electrodynamics: An Introduction to Radiation-Molecule Interactions
D. P. Craig and T. Thirunamachandran
Dover Publications, Inc. (1984; 1998)
IBSN 0-486-40214 (pbk.)
Interactions between molecules and optical activity.

[Goldman]
Quantum Description of High-Resolution NMR in Liquids
Maurice Goldman
Oxford University Press (1988)
IBSN 0-19-855652-7 (Pbk)
Concise treatment of 2D correlation spectroscopy.

[Mukamel]
Principles of Nonlinear Optical Spectroscopy
Shaul Mukamel
Oxford University Press, Inc. (1995)
IBSN 0-19-513291-2 (pb)
Absolutely definitive (impenetrable).

[Slichter]
Principles of Magnetic Resonance (3rd Edition)
C. P. Slichter
Springer-Verlag (1978; 1990)
IBSN 0-387-50157-6
Relaxation theory and pulse sequences.

[Steinfeld]
Molecules and Radiation: An Introduction to Modern Molecular Spectroscopy
Jeffrey I. Steinfeld
Dover Publications, Inc. (1974; 1985)
IBSN 0-486-44152-0 (pbk.)
Nice chapters on the optical Bloch equations and optical echoes.

[Tannor]
Introduction to Quantum Mechanics: A Time Dependent Perspective
David J. Tannor
University Science Books (2007)
IBSN 10: 1-891389-23-8
$76.05 hardcover [link to publisher] [link to author] [link to Amazon]
Long-awaited book; an intuitive and mathematical of modern electronic and vibrational spectroscopy.

D. Books You Should Know About

Standard texts that you should know about.

[Bishop]
Group Theory and Chemistry
David M. Bishop
Dover Publications, Inc. (1973; 1993)
IBSN 0-486-67355-3

[Bohm]
Quantum Theory
David Bohm
Dover Publications, Inc. (1951; 1979)
IBSN 0-486-65969-0

[CTDL]
Quantum Mechanics, Volumes I and II
Claude Cohen-Tannououdji, Bernard Diu, and Franck Laloë
John Wiley and Sons, Inc. (1977)
IBSN 2-7056-5833-5
Volume 1 [Cornell eBook]
Volume 2 [Cornell eBook]

[Harris & Bertolucci]
Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy
Daniel Harris and Michael D. Bertolucci
Dover Publications, Inc. (1978; 1989)
IBSN 0-486-66144-X

[Zare]
Angular Momentum: Understanding the Spatial Aspects in Chemistry and Physics
Richard N. Zare
John Wiley and Sons, Inc. (1988)
IBSN 0-471-85892-7

VIII. ABOUT THE INSTRUCTOR

Professor Marohn earned a

- B.S. in Chemistry from the University of Rochester
- B.A. in Physics from the University of Rochester
- Ph.D. in Chemistry at Caltech.

He did postdoctoral work at the U.S. Army Research Laboratory and joined the Cornell faculty in 1999.

His research interests include charge generation, transport, injection, and trapping in semiconductors; fuel cell membranes and catalysts; dielectric fluctuations and nanoscale friction; and nanoscale magnetic resonance imaging. He is a huge fan of multidimensional time-domain spectroscopy.

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