Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

Spring Semester 2019
MWF 3:00 - 3:55 pm, 1045 McPherson Lab

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Course desription:
This course covers topics that describe advanced applications of quantum mechanics in chemistry and spectroscopy. Special emphasis will be placed on reviewing approximate methods for solving the nuclear and electronic time-independent Schrödinger equation and their application in spectroscopy of atoms and molecules. In addition to learning the course material, students are expected to learn how to write programs using Python and how to perform ab initio computations of molecules to solve problems in quantum chemistry and spectroscopy.

Suggested textbooks:
1. "Modern Quantum Chemistry", A. Szabo and N. S. Ostlund.
2. "Molecular Spectroscopy", I. N. Levine.
3. "Molecular Spectroscopy", J. L. McHale.
These books are available in the OSU library (in print and/or eBook formats) and in the bookstore, but you are not required to purchase them.

Grading scheme:
Quizzes: 5%;
Homework: 30%;
Programming projects: 15%;
Midterm: 20%;
Final Exam: 30%.

Quizzes:
There will be 4-5 quizzes given in class. The dates of the quizzes will be an-

nounced several days in advance. The quiz material is not intended to be challenging, but rather only to see if the students are familiar with the lecture material.

Homework:
There will be a total of 10 problem sets assigned on an approximately weekly basis. The due dates will be stated on each homework assignment. **Homework assignments will be demanding**, you should not wait until the last minute to complete them. Some of the problem sets will use various computational tools, please make sure that these tools are available during the first week of the course.

You are encouraged to work together on solving homework problems, but you must write their solutions separately. *Solutions that appear to be copied from another student will be considered as cheating, and may be subject to penalties under OSU's guidelines on academic misconduct.* **If a homework assignment is turned in late, 20 points will be deducted from its grade for every day it has been delayed**.

Programming projects:
In addition to homework assignments, you will be required to complete three programming projects:

1) Molecular geometry analysis program
2) Harmonic vibrational analysis program
3) Restricted Hartree-Fock theory program

Information about the programming projects and their due dates will be provided in class. Group work on completing these projects is encouraged, but the programs that appear to be copied from someone else will be considered as cheating. The programming assignments will be distributed approximately 3-4 weeks before they are due, **do not wait until the last day to complete them. If a programming project is turned in after the due date, 10 points will be deducted from the project's final grade for every day it has been delayed.** The programming assignments involve multiple steps and must be completed using Python.

Exams:
There will be one midterm exam and a final exam. Exams will be closed book. Both exams will take place outside of the regularly scheduled class time in a location to be determined. Tentative dates:

Midterm: February 25 - March 1,

Final exam: April 24 - 30.

Please plan your schedule accordingly. There will be no make-up exams, except due to extreme circumstances, which will be handled individually. If you are unable to attend, please notify Dr. Sokolov immediately.

Computer resources:
Q-Chem and ORCA will be used for some of the homework assignments. You will be provided with access to both programs. Python will be used for programming projects. To facilitate learning Python, you are strongly encouraged to complete one of the online tutorials listed below:

1) Python Codecademy – https://www.codecademy.com/learn/learn-python
2) Google's Python class – https://developers.google.com/edu/python

Carmen:
The course materials (syllabus, homework assignments, programming projects, etc.) will be uploaded on Carmen (carmen.osu.edu). To access Carmen, log in with your OSU username (last name.#) and password.

Attendance:
Attendance to every lecture is strongly encouraged. Some of the lecture material will not be in the textbooks or Carmen, but you are responsible for knowing all of it.

Disability services:
If you anticipate or experience academic barriers based on your disability (including mental health, chronic or temporary medical conditions), please let me know immediately so that we can privately discuss options. To establish reasonable accommodations, I may request that you register with Student Life Disability Services. After registration, make arrangements with me as soon as possible to discuss your accommodations so that they may be implemented in a timely fashion. SLDS contact information: slds.osu.edu; 614-292-3307; slds.osu.edu; 098 Baker Hall, 113 W. 12th Avenue.

Academic integrity:
It is the responsibility of the Committee on Academic Misconduct to investigate or establish procedures for the investigation of all reported cases of student academic misconduct. The term "academic misconduct" includes all forms of student

academic misconduct wherever committed; illustrated by, but not limited to, cases of plagiarism and dishonest practices in connection with examinations. Instructors shall report all instances of alleged academic misconduct to the committee (Faculty Rule 3335-5-487). For additional information, see the Code of Student Conduct http://studentlife.osu.edu/csc/.

Course content:
The schedule below lists topics that we will attempt to cover each week, but depending on the pace of coverage it can change. *You are strongly encouraged to refresh group theory, as well as linear algebra, operators, and eigenfunctions*. **We will not be covering these topics in class.** Please read Szabo & Ostlund Ch. 1 and week 1 handouts before or during the first week of class.

Week 1: Review of foundations
Reading: Szabo Ch. 1, Levine Chs. 1.1-1.3, 2, handouts
Materials:

- Topics covered in handouts, but not in class:
  - Linear vector algebra, complex vector spaces, Dirac notation
  - Change of basis, eigenvalue problem
  - Orthogonal functions, eigenfunctions, and operators
  - Time-dependent and time-independent Schrödinger equation
  - Measurements, observables
  - Atomic units
- Mathematics of the Born-Oppenheimer approximation

Week 2-3: Rotations of polyatomic molecules
Reading: Levine Ch. 5, McHale Ch. 8, handouts
Materials:

- Applications in microwave spectroscopy
- Classical mechanics of rigid rotations: moments of inertia, types of rigid rotors
- Quantum mechanics of rigid rotations: angular momentum operators, commutation relations, Euler angles
- Solutions of the rotational Schrödinger equation for different types of rotors
- Selection rules in rotational spectroscopy
- Vibration-rotation interaction

Week 4-6: Vibrations of polyatomic molecules
Reading: Levine Ch. 6, McHale Chs. 9 and 10, handouts
Materials:

- Applications in infrared spectroscopy
- Classical treatment of molecular vibrations: normal coordinates and normal modes
- Quantum mechanical treatment of molecular vibrations: multidimensional harmonic approximation
- Vibrational wavefunctions for polyatomic molecules: symmetry and normal vibrations
- Selection rules and band shapes for infrared spectra of polyatomic molecules
- Anharmonicity of molecular vibrations: overtone, combination bands, vibration-rotation coupling, Fermi resonance, inversion doubling

Week 7-8: Advanced electronic structure theory
Reading: Szabo 2.1 - 2.3, 3.1 - 3.4, handouts
Materials:

- Brief recapitulation of the Hartree-Fock theory
  - The electronic Schrödinger equation, the variation method
  - The Hartree approximation, spin-orbitals and spatial orbitals
  - Antisymmetry, Pauli exclusion principle, Slater determinant
  - The Hartree-Fock approximation, energy expression, one- and two-electron integrals
  - The Hartree-Fock equations
  - Atom-centered basis sets, gaussian-type orbitals
  - Closed-shell (restricted) Hartree-Fock (RHF)
  - The self-consistent field algorithm (SCF)
- Form of the exact wavefunction: full configuration interaction (FCI)
- Electron correlation, Slater-Condon rules, Brillouin's Theorem

Week 9-11: Electronic spectroscopy of atoms and molecules
Reading: Levine Ch. 7, McHale Chs. 7, 11, handouts
Materials:

- Review of spin and orbital angular momentum theory:
  - One-electron and many-electron operators

  - Raising and lowering operators
  - Commutation relations and eigenfunctions
- Atomic term symbols for various electronic configurations
- Hund's rule, particle-hole symmetry
- Diatomic term symbols
- Polyatomic term symbols: abelian and non-abelian point groups
- Spin-orbit coupling, effect of external fields
- Selection rules for electronic transitions
- Vibrational structure in electronic spectra

Week 12-14: Beyond the Hartree-Fock approximation
Reading: Szabo Chs. 4, 6.1 - 6.5, coupled cluster review by Crawford, handouts
Materials:

- Approximate configuration interaction (CI)
- Size-consistency and size-extensivity
- Rayleigh-Schrödinger perturbation theory, second-order Møller-Plesset perturbation theory (MP2)
- Second quantization, normal ordering, Wick's theorem
- Coupled cluster theory (CC): foundations and hierarchy of approximations
- Breakdown of the Hartree-Fock approximation: static electron correlation
- Multi-reference methods: multi-configurational self-consistent field methods (MCSCF), multi-reference perturbation theory