The University *of* Western Ontario
Department of Chemistry

CHEM 4474B: Advanced Quantum Chemistry and Spectroscopy
CHEM 9648B: Computational Quantum Chemistry

Winter 2023

Course Information

Instructor: Viktor N. Staroverov
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Office hours: by appointment (administrative matters)

Lectures: Monday, Wednesday, Friday, 12:30 pm–1:30 pm, ChB 9
Course web site: `http://owl.uwo.ca`
Prerequisite: CHEM 3374A (applies to undergraduate students)

Description: The course provides a systematic exposition of key concepts and computational methods of electronic structure theory: molecular orbitals, basis sets, many-electron wavefunctions, symmetry labels, *ab initio* methods, density-functional theory, atomic charges, and spin states.

Objectives and Outcomes: The course is designed for all students who intend to apply computational chemistry tools in their research and wish to:

(a) understand the capabilities and limitations of computational quantum chemistry;
(b) learn how to calculate molecular properties and study chemical reactions using quantum-chemistry software packages such as *Gaussian*;
(c) know how to choose an appropriate methodology and present calculations in a research paper;
(d) appreciate the role played by electronic structure theory in all branches of chemistry.

Course topics

1. *Introduction.* Basic principles of quantum mechanics. One-electron Schrödinger equation and methods for finding its exact and approximate solutions. Introduction to *Maple*.
2. *Symmetry in quantum chemistry*. Symmetry of molecules, orbitals, and electronic wave functions. Irreducible representations. Character tables. Symmetry labels. Molecular term symbols.
3. *Quantitative molecular orbital theory*. Many-electron Schrödinger equation. Slater determinants, Hartree–Fock self-consistent field method. Calculation of molecular orbital diagrams. Semiempirical methods and the Hückel approximation.
4. *Basis sets.* Slater-type and Gaussian-type orbitals, plane waves. Gaussian basis set nomenclature (STO-3G, 6-31G*, cc-pVQZ, etc.) Polarization and diffuse functions. How to choose a basis set.
5. *Spin in quantum chemistry.* Spin, spin operators, and spin states (singlets, doublets, triplets, etc.)
6. *Post-Hartree–Fock methods.* Correlation energy. Configuration interaction, perturbation theory, coupled-cluster theory, and other systematic techniques. Model chemistries.
7. *Density-functional methods*. Hohenberg–Kohn theorems and the Kohn–Sham scheme. Exchange and correlation functionals. Empirical and nonempirical density-functional approximations. Popular density functionals (B3LYP, PBE, etc.), their origin and scope of applicability.

8. *Standards for reporting quantum-chemical calculations*. Good practices for ensuring reproducibility. Numerical accuracy considerations. Computational chemistry databases.
9. *Potential energy surfaces*. Molecular geometry optimization. Stationary points: intermediates and transition states. The symmetry-breaking dilemma.
10. *Computational thermochemistry*. Prediction of atomization energies, standard enthalpies of formation, standard free energies, oxidation and reduction potentials, equilibrium and dissociation constants.
11. *Computational spectroscopy*. Simulation of electronic, vibrational and electronic spectra (absorption and emission). Time-dependent density-functional theory. Treatment of solvation effects.
12. *Analysis of electron distributions in molecules*. Calculation of atomic charges and bond orders. Atoms in molecules.

Course materials: All course materials including detailed lecture notes will be distributed through OWL.

Recommended literature

1. J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 3rd ed., Gaussian, Inc., Wallingford, CT, 2015.
2. I. N. Levine, *Quantum Chemistry*, 7th ed., Pearson–Prentice Hall, 2013.
3. D. A. McQuarrie, *Quantum Chemistry*, 2nd ed., University Science Books, Sausalito, CA, 2008

Method of evaluation

Assignments (6 in total)	30%	See the schedule below
Midterm Test 1 (in class, open book)	10%	Wednesday, February 15, in class
Midterm Test 2 (in class, open book)	10%	Monday, March 20, in class
Mini-project in computational chemistry	10%	See the schedule below
Final Exam (open book)	40%	To be scheduled by the Registrar (3 hours)

Schedule of assignments and presentations

Assignments due:	January 30, February 6, February 13, March 6, March 13, March 27 (in class, as paper copies)
Project presentations:	3 final classes (April 3, April 5, April 10)

Conditions required to pass the course

The assignments, projects, and exams are essential components of this course. You must submit at least 4 of the 6 assignments, write at least 1 of the 2 midterm tests, present the research project, and write the Final Exam. Students who fail to meet any of these requirements without a proper excuse for the missed work will receive a course grade of not greater than 40%, even if the calculated grade is higher. A student who is unable to submit the required minimum number of assignments, tests, and projects for medical or compassionate reasons, and who wishes to complete the missed work, will need to apply for Incomplete Standing (a grade of INC) by submitting a written request to the Dean of the Faculty of Registration. If Incomplete Standing is granted, the student will be able to complete the missed items the next time the course is offered. A student who is unable to write the Final Exam must apply for permission to write a Special Final Examination (SPC Exam).

Policies

Student absences and missed work. Students who are unable to meet their academic responsibilities due to medical or compassionate reasons may submit a request for academic consideration. For each missed piece of work **worth 10% or more** of the total course grade, you must apply for such consideration by providing valid medical or supporting documentation to the Academic Counselling Office of your Faculty of Registration. For each missed piece of work **worth less than 10%** of the course grade (i.e., an assignment), you do not need to provide any medical documentation or contact the Academic Counselling Office, but you must send a written explanation of your absence to the instructor within 48 hours of the due date to be excused. Note that *all* accommodations for absence, regardless of who grants them, are subject to the *Conditions required to pass the course* detailed above.

Accommodation for students with disabilities. Students with disabilities are encouraged to contact Accessible Education, which provides recommendations for accommodation based on medical documentation or psychological and cognitive testing. In cases where a student misses a piece of work for reasons related to the disability on file with Accessible Education, the student should request accommodation by contacting Accessible Education instead of the Academic Counselling Office.

Missed assignments. There are no make-up assignments. If you miss an assignment and are granted academic accommodation, the weight of the missed assignment will be transferred to the Final Exam.

Missed midterm test. If you miss a midterm test and are granted academic accommodation, the weight of the missed test will be transferred to the Final Exam. A cumulative 50-min make-up midterm test will be offered to those students who miss each of the two scheduled midterms and receive accommodation for both. For the purpose of evaluation, this make-up test will be weighted as one regular midterm.

Missed final exam: If you miss the Final Exam, contact the Academic Counselling office of your Faculty of Registration as soon as possible. They will assess your eligibility to write the Special Examination. You may also be eligible to write the Special Exam if you are in a "Multiple Exam Situation" (e.g., more than 2 exams in 23-hour period, more than 3 exams in a 47-hour period).

Late assignments. Late submissions will be accepted within 24 hours after the due date without penalty, but will be rejected afterwards. Students with applicable accommodations recommended by Accessible Education can request a longer one-time deadline extension. This extension cannot exceed 7 days after the regular due date because graded assignments will normally be returned by that time. Students with disability accommodations who ask for a longer extension will be excused instead, subject to the *Conditions required to pass the course*.

Use of electronic devices. Only basic scientific calculators are permitted on all tests and exams. All other electronic devices (cell phones, laptops, tablets, cameras, etc.) are prohibited.

Scholastic offences. The University will take all appropriate measures to promote academic integrity and deal appropriately with scholastic offences. For definitions of what constitutes a scholastic offence, see *http://www.uwo.ca/univsec/pdf/academic_policies/appeals/scholastic_discipline_undergrad.pdf*

Support services. Detailed information on academic considerations for absences, religious accommodation, exam conflicts, appeals, and other academic matters may be found on the Science & Basic Medical Sciences Academic Counselling webpage: *https://www.uwo.ca/sci/counselling*. Students who are in emotional/mental distress should refer to Mental Health@Western (*https://uwo.ca/health*) for help.