The University *of* Western Ontario
Department of Chemistry

CHEM 4474B: Advanced Quantum Chemistry and Spectroscopy

cross-listed as **CHEM 9648: Computational Quantum Chemistry**

Winter 2021

Course Information

(Tentative; statements of policies will appear in the final official version)

Instructor: Viktor N. Staroverov
Office: ChB 063
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Office hours: by appointment

Lectures: Monday, Wednesday, Friday, 11:30 am – 12:30 pm, ChB 9
Web site: `http://owl.uwo.ca`

Description: The course offers a practical exposition of electronic structure theory methods that are widely used as aids in chemical synthesis, characterization, and materials research. The lectures are designed to provide an accessible yet non-superficial understanding of molecular orbitals, basis sets, density-functional methods, computational thermochemistry and molecular spectroscopy, and applications of symmetry. The practical component consists of written and computer assignments that illustrate the concepts taught in class. **Prerequisite:** CHEM 3374A (applies to undergraduate students only).

Objectives: The course is intended for chemistry and science students who intend to apply computational chemistry tools in their research and wish to:

(a) understand the capabilities and limitations of modern quantum chemistry;
(b) learn how to calculate molecular properties and study chemical processes using *Gaussian 09*;
(c) have a good idea of how principal quantum-chemistry methods work;
(d) know how to choose an appropriate methodology and present your findings in a research paper;
(e) appreciate the role played by electronic structure theory in many branches of science

Method of evaluation:

Assignments (6 in total)	30%
Midterm test 1 (in class, open book)	10%
Midterm test 2 (in class, open book)	10%
Take-home mini-project in computational chemistry	10%
Final exam (open book)	40%

Course materials: All course materials will be distributed or provided as links to online resources.

Recommended texts:

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.

Course topics

1. *Introduction.* Basic principles of quantum mechanics. One-electron Schrödinger equation and methods for finding its exact and approximate solutions.
2. *Symmetry in quantum chemistry*. Symmetry of molecules, orbitals, and electronic wave functions. Irreducible representations. Character tables. Symmetry labels.
3. *Quantitative molecular orbital theory*. Many-electron Schrödinger equation. Slater determinants, Hartree–Fock self-consistent field method. Calculation of molecular orbital diagrams. Localized and delocalized molecular orbitals. Semiempirical methods. 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 eigenfunctions (singlets, doublets, triplets, etc.) Atomic and molecular term symbols.
6. *Post-Hartree–Fock methods.* Correlation energy. Configuration interaction, perturbation theory, coupled-cluster theory, and other techniques. Model chemistries.
7. *Density-functional methods*. Hohenberg–Kohn theorems. Kohn–Sham scheme. Exchange and correlation functionals. Empirical and nonempirical density-functional approximations: the local density approximation, generalized- and meta-generalized gradient approximations, hybrid functionals, range-separated hybrids. Popular density-functional approximations (B3LYP, PBE, etc.), their origin and scope of applicability. Choosing the density-functional approximation.
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.

Tentative schedule of assignments and exams

Assignments due:	January 25, February 1, February 8, March 15, March 22, March 29
Midterm test 1:	Wednesday, February 10, 11:30 am (in class)
Midterm test 2:	Wednesday, March 10, 11:30 am (in class)
Project presentations:	Friday, April 2 and Monday, April 5
Final exam:	3 hours, to be scheduled by the Registrar