PC$_3$ Introductory Modules Outline

Department of Chemistry

COURSE CODE: COURSE NAME

Fall 2025 (Sept - Dec 2025)

Instructors:

The local instructor at UNIVERSITY NAME is Dr. INSTRUCTOR NAME (EMAIL).

Content will be presented by several external instructors:

Instructors: Dr. Richard Bowles (Part I, richard.bowles@usask.ca), Dr. Joshua Hollett (Part II, j.hollett@uwinnipeg.ca), and Dr. Robert Szilagyi (Part III, robert.szilagyi@ubc.ca)

Lectures:

Synchronous lectures will be held on Mondays and Thursdays from 10:30 AM to 12:00 PM (Pacific Time) over Zoom. Class starts on September 4 and ends on December 4. There will be no class on October 2, October 13 (Thanksgiving Day), and November 6. Links will be provided to the class by email. Students are expected to have a working microphone and webcam for discussion. **Instructors may require that students keep their cameras on during lectures.**

Module length: full semester

Prerequisite Knowledge: Students entering the PC$_3$ program should have an undergraduate-level understanding of:

- Linear Algebra, Calculus of multiple variables, Basic quantum chemistry
- Intro level quantum chemistry, electronic structure and bonding theories (some level of physical organic or inorganic chemistry)

Pre-work: This section outlines work students should do prior to joining the course. This is self-directed learning that prepares them for the course and may constitute readings and exercises to be completed to support their learning.

For Part III, select a molecule or interacting molecules of interest via weak interactions to be evaluated at various functionals and approximate DFT potentials.

Topics:

Part I: Dr. Richard Bowles

This part of the course focuses on molecular mechanics, including potential energy functions and geometry optimization. It also introduces statistical mechanics with applications to calculations of the molecular partition function, thermodynamics, as well as molecular dynamic and Monte Carlo simulation methods.

Introduction

- Schrodinger equation (brief introduction to motivate molecular mechanics)
- Potential Energy Surfaces

Molecular Mechanics potential Energy Function

Different components of MM:

- Bonded interactions
  Bond stretching
  Angle bending
  Torsional terms
  Cross Terms
- Intermolecular potential energies
  Van der Waals interactions
  Buckingham potential
  Lennard Jones potential
  XDX and D3 Models
- Electrostatic interactions
  Ewald sum methods
  Other methods (reaction field, Lekner, Wolf)
- Empirical Force Fields
  Parameterization strategies
  Common Force Fields (MM2, AMBER, OPLS, CHARMM)
  Machine Learning Force Fields
- Geometry Optimization
  Optimization methods
  Transition states
  Conformational Search

Review of Statistical Mechanics

- From microscopic to macroscopic
- Micro-states and phase space
- Postulates of statistical mechanics
- Ensembles
- Canonical partition function
- Boltzmann distribution
- Averages

Molecular Partition function

- Zero Point energy
- Non-interacting systems
  Molecular electronic partition function
  Molecular Translational partition function
  Molecular Rotational partition function/Hindered rotation.
  Molecular Vibrational partition function

Thermodynamics

Energy
Entropy
Free energies

Including Temperature

Molecular Dynamics
- Basic integration schemes
- Tricks of the trade
- Dynamic quantities

Monte Carlo
- Basics of MC integration
- Metropolis Sampling

Part II: Dr. Joshua Hollett

This part of the module is dedicated to the introduction of wavefunction based methods, and practical aspects such as basis sets. A focus will be placed on which methods are applicable in various scenarios (e.g. size, accuracy, desired property) and why they may not be suitable. Emphasis will also be placed on the computational cost/scaling of each method.

Born-Oppenheimer Approximation

- Potential Energy Surface
- Total molecular Schrodinger Equation

Electronic Schrodinger Equation

Variation Theorem

Hartree-Fock Approximation

- Indistinguishability, antisymmetry and electron spin
- Slater determinants
- HF energy expression and one- and two-electron integrals
- HF equations
- SCF
- RHF, ROHF, UHF
- limitations of HF

Basis functions

- Atom-centred vs. plane wave basis functions
- GTO vs. STO
- Basis sets: Pople, Dunning, Ahlrichs, etc. (polarization, diffuse, core)
- Pseudopotentials (ECPs etc.)
- Completeness and extrapolation to the CBS limit
- BSSE

Post-HF

- electron correlation
- Configuration Interaction
    - electron configurations (occupied and virtuals orbitals, active and frozen)
    - full and truncated CI
    - selected CI
    - size consistency and extensivity
- Coupled-Cluster
- Moller-Plesset Perturbation
- Multireference methods
    - CASSCF, RASSCF, MRCI and MRPT
    - DMRG

1) Exercise (using ORCA) exploring cost of HF calculations (timing)
    - compare timings of SCF for HF/cc-pVnZ calculations (n=2 to 5)
    - compare energies (or other properties) and extrapolate (exponential ansatz)
2) Exercise exploring effect of BSSE
    - determine effect of BSSE for small molecule complex (basis set extrap, CP and CHA corrections)
3) Exercise exploring single and multireference post-HF

  - calculation of energy barrier for single ref system (not sure yet) using CC, MPn (frozen and active core)
  - calculation of energy barrier for multi ref system (not sure yet) using CC, MPn, MRSCF and MRPT2

Part III: Dr. Robert Szilagyi

This section will focus on electron density-based description of energy, geometry, and properties. Both the density functional tight binding and "ab initio" density functional methods will be introduced. Firstly, the performance of various repulsive potentials will be compared and contrasted using examples selected by the students (if parameters are available). Secondly, the density functionals will be discussed using Perdew's Jacob's ladder concept and contrasted with the conceptually converging series of Pople's model chemistry.

I. Introduction to density functional theory
  - Philosophy, electron density vs. wave function, compare and contrast to HF theory and post-HF theory.
  - Early Approximations
  - Kohn-Sham self-consistent field methodology

II. Approximate DFT = DFTB
  - Tight binding theory, DFTB2 vs. DFTB3
  - Performance - best and worst case scenarios
  - Molecular dynamics using DFTB level of theory (connection to Richard's section)

III. "ab initio" DFT
  - exchange-correlation functionals
  - Jacob's ladder: LDA, GGA, metaGGA, hyperGGA, double hybrid, RPA
  - Excited state calculations: orbital energies, ΔSCF, TD-DFT
  - Performance - Ionic, covalent, magnetic bonding and interactions
  - Broken-symmetry DFT calculations for multi-spin paramagnetic system

3- DFTB: DFTB+ - https://dftbplus.org/about-dftb

Learning Outcomes: Upon completion of this module, student should be able to:

Part I:

- Describe the potential energy surface and its topology.
- Describe the bonded and non-bonded interactions used in MM
- Identify the best optimization methods for a given problem.
- Perform conformational search on a simple molecular system.
- Describe principles of statistical mechanics.
- Calculate probabilities, and thermodynamic properties of simple molecules using the molecular partition function.
- Describe the principle of molecular dynamics
- Describe the principles of Monte Carlo simulation

Part II:

- describe the origin of the potential energy surface and its role in computational chemistry.
- identify scenarios where the Born-Oppenheimer approximation breaks down.
- identify the components of the electronic Schrodinger Equation.
- describe the role of the variation theorem in computational chemistry.
- describe the approximation made in Hartree-Fock theory and its consequences.
- identify the most time-consuming part of a Hartree-Fock calculation.
- decide which form of HF is appropriate for a system, RHF ROHF or UHF.
- describe the advantages and disadvantages of using GTOs over STOs.
- determine the appropriate basis set for a particular calculation, considering accuracy and compute time.
- identify calculations in which BSSE is significant.
- apply basis set extrapolation to energies and other properties.
- describe the different forms of electron correlation and identify systems exhibiting each.
- describe how to determine a CI wave function and the pros and cons of such an approach.
- describe size consistency and extensivity, and identify calculations for which they are important.
- describe the form of the coupled-cluster wave function.
- identify systems for which a multireference wave function is required for accurate modelling.
- choose an appropriate active-space for a CAS, RAS or DMRG calculation.

Part III:

- Describe the key differences among MO and electron density based description of electronic structure
- Identify some of the earliest attempts to express electron-electron interactions using electron density
- Describe the first Hohenberg-Kohn Theorem as proof of existence for functional to describe all properties of a system
- Describe the second Hohenberg-Kohn Theorem as the variational principle
- Identify the essential elements of the Kohn-Sham approach
- Compare and contrast DFTB and DFTB approaches
- Select the appropriate DFTB repulsive potentials and calculate molecular properties, such as ground state structure, interpret the associated energy, atomic charges and spin densities
- Describe the concept of Jacob's ladder for exchange and correlation functionals
- Differentiate among local density, gradient-corrected, and hybrid density functionals; give examples for each
- Identify the conceptual sources of error in DFT (self-interaction, asymptotic behaviour, delocalization error)
- Demonstrate with calculations the functional dependence of ionic, covalent, magnetic bonding interactions
- Evaluate the performance of functionals in calculating spectroscopic (IR, UV-vis, core level excitations) features
- Perform broken-symmetry DFT calculations for open shell singlet systems with multiple unpaired electrons, project out to the pure spin state using the expectation value of the spin operator.

Software:

Part I:

GROMACS, VMD.

Part II:

ORCA, Avogadro.

Part III:

Gaussian-16, DFTB+, ORCA may also be used.

Assignments:

Part II:

Assignments based on the suggested exercises (described above), with follow-up questions

Part III:

Written reports (manuscript style: Introduction - why the chosen molecules; Methods - key highlights; Results and Analysis - DFTB vs. DFT and potential and functional dependence, respectively; Discussion - what is the level of theory choice for a given system and why, Conclusion/take home messages) and follow up presentation (conference/meeting presentation of the results) for selecting the most reasonable (as defined by experiment, high level MO theory) for the specific molecules students chose and calculated/predicted properties.

Assessment based on demonstrating understanding of concepts and proficiency of executing tasks as outlined by learning outcomes.