THOMPSON RIVERS UNIVERSITY

Department of Physical Sciences (Chemistry)

CHEM 3070 – 3 Credits
Physical Chemistry 2 (3,0,0)
Winter 2024

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Office Hours:	Tue, Fri (2:15 - 2:45 PM)
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	(in S-254 or via Zoom)

Description

Chemistry is the science dealing with the transformation and properties of molecules. Theoretical chemistry is the subfield where mathematical methods are combined with fundamental laws of physics to study processes of chemical relevance. Computational chemistry is the application of any computational method (algorithm implemented on a computer) in chemistry. So far in your studies, you have been exposed to various experimental approaches for learning about chemical systems. The first part of this course will introduce you to the theoretical side of studying chemistry, covering basic aspects of computational and quantum chemistry.

Statistical thermodynamics is a branch of physical chemistry that applies probability theory to the study of the thermodynamic behavior of systems composed of a large number of particles. It provides a molecular-level interpretation of macroscopic thermodynamic quantities such as work, heat, free energy, and entropy. This ability to make macroscopic predictions based on microscopic properties is the main advantage of statistical thermodynamics over classical thermodynamics. The second part of this course will be an introduction to statistical thermodynamics.

Prerequisites

CHEM 2160 (C- minimum) and CHEM 3060 (C- minimum)
MATH 2120 (Linear Algebra) is highly recommended.

The practical component of this course is acquired in CHEM 3080. Therefore, it is strongly recommended that students take this course together with CHEM 3080.

<u>**Lectures**</u> (3 hours/week)

The official scheduled time for this class is:

Tuesday	1:00 – 2:15 PM	S-278
Friday	1:00 – 2:15 PM	S-278

This course might have blended components, in which recorded lectures will be made available for some sections before class discussions.

<u>**Assessment**</u>

Grades will be assigned on the following basis:

Moodle Quizzes	15%	(one attempt allowed before the due date)
Test 1	25%	(Tue, Feb 13; Part 1: Section 1)
Take-home exam 1	5%	(tentative due date: Tue, Feb 27)
Take-home exam 2	5%	(tentative due date: Tue, Mar 12)
Test 2	30%	(Tue, Mar 19; Part 1: Sections 2, 3)
Take-home exam 3	5%	(tentative due date: Tue, Mar 26)
Test 3	15%	(Fri, Apr 5; Part 2)

*An aggregate total of at least **50%** (35/70) must be achieved on the <u>**sum**</u> of Tests 1 to 3 to receive a passing grade.

A letter grade will be awarded using the TRU Grading System (Policy ED-3-5) on p. 24 of the TRU Calendar. This one-semester course is worth 3 credits.

<u>**Moodle**</u>

Any electronic course-related materials will be available through Moodle.
Moodle course: CHEM 3070 - Physical Chemistry 2
To access Moodle on the Internet, use the Moodle quick link from the TRU homepage (www.tru.ca).

<u>**Reference Texts**</u>

Particularly useful references, listed below, can be found in the library.

Part 1: Introduction to Quantum and Computational Chemistry

I.N. Levine, *Quantum Chemistry*, 6th Edition, Prentice Hall, 2009.
T. Engel and P. Reid, *Physical Chemistry*, 3th Edition, Pearson, 2013.

Part 2: Introductory Statistical Thermodynamics

K.J. Laidler, J.H. Meiser and B.C. Sanctuary, *Physical Chemistry*, 4th Edition, Houghton Mifflin, 2003.
P.W. Atkins and J. de Paula, *Physical Chemistry*, 9th Edition, W.H. Freeman, 2010.

<u>**Course Topics**</u>

(This outline is provisional and may change as the course progresses)

Part 1: Introduction to Computational and Quantum Chemistry

Section 1. Introduction to Computational Chemistry

1.1.   Introduction

Theoretical and computational chemistry
Areas of application of computational chemistry
Examples of combining experimental and computational work
Computational quantities: structure and chemical properties ("single molecule" properties, thermodynamic quantities and non-observables)

1.2.   What are calculations doing?

Potential energy surfaces (PES)

1.3.   Chemically interesting stationary points on a PES

Local and global minima
Local and global maxima
Nth-order saddle points
Important stationary points along the PES of a chemical system and a chemical reaction.
Geometry optimizations: The energy gradient

1.4.   Main types of calculations

Single-point energy calculations
Geometry optimizations
Frequency calculations
The Hessian of the energy: Matrices and some basic properties
Mathematical definition and characterization of stationary points
Complex numbers and functions
Important data to be obtained from the different types of calculations

1.5.   Minimum input for calculations

Minimum input for calculations: level of theory, charge, multiplicity, molecular geometry
Level of theory
Molecular geometry: Cartesian coordinates and Z-matrices
Internal coordinates
Graphic interfaces
Number of electrons: Charge and multiplicity of a chemical system
Constructing the Z-matrix of any system
Dummy atoms: Applications

Section 2. The Postulates of Quantum Mechanics

1.6.   Historic background of quantum mechanics (for self-study)

Differences between classical and quantum mechanics (QM)
Historic background of QM: Wave nature of light; Planck's theory of quantization; dual wave-particle behavior of microparticles (De Broglie's equation).
The Heisenberg uncertainty principle

1.7.   The wavefunction (for self-study)

Postulate 1: The wavefunction (wf) or state function, Ψ
Characteristics of a well-behaved wf
Physical significance of Ψ
Probability density: Complex conjugates
Normalization condition

1.8.   Operators in quantum mechanics (for self-study)

Postulate 2: Observables and QM operators
Operators and some properties (sum, product, commutation)
Evaluation of commutators
Operators in QM: linear momentum operators, the Hamiltonian operator.

1.9.   Eigenvalues and eigenvectors (for self-study)

Eigenvalue equations: Eigenvalues and eigenvectors.
Hermitian operators
Postulate 3: Measurement, observable, operator, eigenvalue
Consequence of operators that commute: Simultaneous specification of several exact properties
Postulate 4: Expectation (average) value

1.10.   The Schrödinger equation and the Hamiltonian of a molecule

Postulate 5: The Schrödinger equation (time-dependent and time-independent versions)
The Hamiltonian (total energy) operator: expression for several systems (for a particle moving in one and three dimensions, for N particles moving in 3 dimensions)
The Hamiltonian operator of a molecule
The Born-Oppenheimer approximation

1.11.   The multielectronic wavefunction and the Slater determinant

Postulate 6: The multielectronic wf is antisymmetric
Molecular orbital (MO) theory: Molecular orbitals, spin functions and spin orbitals
The Hartree product of spin orbitals
Determinants: Solving determinants of order two and three.
Properties of determinants
Slater determinants
Linear algebra concepts: basis sets
The LCAO (linear combination of atomic orbitals) approximation

MOs as a linear combination of basis functions
Molecular properties that can be calculated from MOs energies: ionization energy, electron affinity, electronegativity, hardness, softness
Basis functions frequently used in QM: STOs and GTOs
Examples of basis sets used
Effects of increasing the size of a basis set

Section 3. The Hartree-Fock Theory

1.12.   The Hartree-Fock (HF) theory

The HF approximation: Main features
The correlation energy
The HF equations: identification and understanding of every term
The self-consistent-field (SCF) method
The Roothaan-Hall Equations
Examples of limiting HF calculations
Main sources of error for calculations
A frequently used notation

Part 2: Introductory Statistical Thermodynamics

2.1.   Forms of molecular energy and degrees of freedom of a molecule

Translational energy
Rotational energy: principal axes and principal moments of inertia
Vibrational energy
Molecular degrees of freedom

2.2.   Introduction to statistical mechanics

2.3.   Classical thermodynamics and statistical thermodynamics: The Boltzmann's equation

2.4.   The Maxwell-Boltzmann distribution law

Populations, configurations and weights. Dominant configuration
The Maxwell-Boltzmann's distribution law

2.5.   The partition function

Definition, meaning, interpretation, temperature dependence

2.6.   The molecular partition function

Adiabatic approximations
The rigid rotor approximation
Factorization of the molecular partition function
Translational partition function
Rotational partition function
The harmonic and the anharmonic oscillators
Vibrational partition function
Electronic partition function

2.7.   Ensembles and the canonical partition function (Q)

Calculation of Q for some special cases: independent and distinguishable particles, independent and indistinguishable particles

2.8.   Calculation of thermodynamic quantities from canonical partition functions

2.9.   Statistical thermodynamic formulation of TST