

Department of Physical Sciences (Chemistry)

CHEM 3070 – 3 Credits
Physical Chemistry 2 (3,0,0)
Winter 2019

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Office Hours: Mon, Wed, Fri 2:30 – 3:30 pm
Additional office hours are available by appointment.

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 3060 (C- minimum), MATH 2120 (Linear Algebra) is highly recommended. See the TRU Calendar for details.

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.

Lectures

3 hours/week Tue, Fri 11:30 – 12:45 pm OM 1792

Assessment

Grades will be assigned on the following basis:

Quizzes	10%
Assignments	15%
Test 1	30% (Fri, Mar 1)
Test 2	30% (Fri, Apr 5)
Test 3	15% (Fri, Apr 12)

*An aggregate total of at least **50%** (42.5/85) must be achieved on the **sum** of the quizzes and the tests in order to receive a passing grade.

Test 2 will evaluate all the topics covered from the start of the course, with emphasis on materials not yet examined.

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.

Reference Texts

Particularly useful references, listed below, can be found in the library with the materials on reserve.

Part 1: Introduction to Quantum and Computational Chemistry

I.N. Levine, *Quantum Chemistry*, 6th Edition, Prentice Hall, 2009. [QD 462 .L48 2009]

T. Engel and P. Reid, *Physical Chemistry*, 3th Edition, Pearson, 2013.

Additional reference texts:

J.B. Foresman, Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd Edition, Gaussian, Inc., 1996. [QD 462.6 .D38 F67 1996]

D.C. Young, *Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems*, John Wiley & Sons, 2001. [QD 39.3 .M3 Y68 2001]

Part 2: Introductory Statistical Thermodynamics

K.J. Laidler, J.H. Meiser and B.C. Sanctuary, *Physical Chemistry*, 4th Edition, Houghton Mifflin, 2003. [QD 453.2 .L338 2003] (Chapter 15)

P.W. Atkins and J. de Paula, *Physical Chemistry*, 9th Edition, W.H. Freeman, 2010. (Chapters 15 and 16)

Moodle

Any electronic course-related materials will be available through Moodle. You have to enroll in the Moodle course “CHEM 3070 - Physical Chemistry 2” by using the enrolment key: 2019-CHEM3070. To access Moodle on the Internet, use the Moodle quick link from the TRU homepage (www.tru.ca).

Course Topics

(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. What is computational chemistry?

Areas of application

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. Types of calculations to characterize the PES

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

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

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

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

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