

CHEM 3070

Course Topics and Learning Objectives

Part 1: Introduction to Computational and Quantum Chemistry

Levine: I.N. Levine, *Quantum Chemistry*, 6th Edition, Prentice Hall, 2009.

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

Foresman: J.B. Foresman, Æ. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd Edition, Gaussian, Inc., 1996.

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

Section 1. Introduction to Computational Chemistry (9 fifty-minute lectures)

1.1. What is computational chemistry?

(Levine, section 1.1; pp. 1-2)

(Engel, section: 26.1; pp. 631-632)

Areas of application

Examples of combining experimental and computational work

Computational quantities: structure and chemical properties (“single molecule” properties, thermodynamic quantities and non-observables)

Three main problems for newcomers to computational chemistry

Questions you should be able to answer:

- What is computational chemistry?
- Explain some of the advantages of studying chemistry from a theoretical point of view.
- Mention different molecule-related quantities that can be computationally determined.
- Explain what are the three main problems for newcomers to computational chemistry.

1.2. What are calculations doing?

(Foresman, pp. 39-41; Engel, section: 26.2; pp. 632-636)

Potential energy surfaces (PES)

Questions you should be able to answer:

- Explain what a PES is.
- Explain what calculations do.

1.3. Chemically interesting stationary points on a PES

(Foresman, pp. 39-41)

Local and global minima

Local and global maxima

Saddle points

Important stationary points along the PES of a chemical system and a chemical reaction.

Questions you should be able to answer:

- Explain what are the stationary points of a function of several variables from a mathematical point of view and what do these points represent.
- How can minima (local and global), maxima (local and global), and saddle points be recognized when looking at a multi-dimensional PES.
- Indicate what do local and global minima, and first-order saddle points on a PES represent for a molecule and a chemical reaction.
- Identify the stationary points that can be calculated as an outcome of a geometry optimization.
- Identify the stationary points that are of chemical interest.

1.4. Types of calculations to characterize the PES

(Levine, section: 7.10; pp. 200-203)

Geometry optimizations: The energy gradient

Frequency calculations

The Hessian of the energy: Matrices and some basic properties

Mathematical definition and characterization of stationary points

Complex numbers and functions

Single-point energy calculations

Important data to be obtained from the different types of calculations

Questions you should be able to answer:

- Explain the different types of calculations that can be performed and the main results obtained in each case.
- Explain what happens during a geometry optimization and what is its main outcome.
- Explain what happens during a frequency calculation and what are the main properties calculated.
- Explain what happens during a single-point energy calculation.
- Given a molecular system, explain what the gradient of the energy in words and mathematically.
- How could you differentiate computationally between possible stationary points (minimum energy structures and saddle points) along a PES?
- What is the Hessian of the energy and why it needs to be calculated?
- Given a molecular system, obtain its Hessian matrix of the energy with respect to internal coordinates or Cartesian coordinates.

1.5. Minimum input for calculations

(Foresman, Appendix B, pp. 285-296)

(Young, sections: 8.1-8.2, Chapter 9; pp. 67-68, 73-76)

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

Questions you should be able to answer:

- Obtain the Z-matrix of any chemical system (taking symmetry into account) and *vice versa*.
Use dummy atoms when building the Z-matrix of certain systems (highly symmetric cyclic structures and linear configurations of more than three atoms).
- Explain what dummy atoms are and when they need to be used.
- Know some of the software used for preparing input files and visualizing output files.
- Given a chemical system, be able to determine its total number of electrons and its multiplicity.
- Explain what is the minimum amount of information that needs to be specified to run calculations in computational chemistry.

Section 2. The Postulates of Quantum Mechanics (11 fifty-minute lectures)

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

(Levine, sections: 1.2-1.3; pp. 2-8)

(Engel, sections: 12.1-12.7, 13.1, 17.2-17.4; pp. 293-311, 385-394)

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

Questions you should be able to answer:

- Explain fundamental differences between classical and quantum mechanics.
- Explain the uncertainty principle.
- What are some of the main discoveries that lead to the development of QM?
- Mention some of the scientists that contributed to the development of quantum mechanics and briefly explain some of their main accomplishments and their significance.

1.7. The wavefunction

(Levine, sections: 1.4-1.7, 3.8; pp. 8-19, 59-60)

(Engel, sections: 13.2, 13.3, 14.1; pp. 313-318, 332-333)

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

Questions you should be able to answer:

- Explain what a wf is and the essence of this postulate
- What are the mathematical requirements for an acceptable wf in QM? What are the reasons behind each of them?
- Explain what a normalized function is (normalization condition)
- Calculate complex conjugates of complex functions, Ψ^*
- Normalize a simple function.

1.8. Operators in quantum mechanics

(Levine, sections: 3.1, 3.3, 3.9; pp. 37-40, 42-47, 60-61)

(Engel, sections: 14.2, 17.1; pp. 333-334, 383-385)

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.

Questions you should be able to answer:

- Explain postulate 2.
- What is an observable?
- What is an operator?
- What does it mean when we say that two operators commute?
- What is the relationship between observables and operators in QM?
- Determine if a pair of operators commute (evaluate their commutator), *i.e.*, determine if two physical quantities (represented by two operators) can be known exactly and simultaneously (section 1.9).
- Given the expression of a QM operator, derive another one related to it (the classical expressions of both properties would be provided, as well as the general expression for the components of the linear momentum operator).

1.9. Eigenvalues and eigenvectors

(Levine, sections: 3.2, 3.3, 3.7, 5.1-5.3, 7.2, 7.4, 7.9, 7.11; pp. 41-47, 56-59, 97-117, 167-173, 178-181, 196-200, 203-204)

(Engel, sections: 13.5-13.7, 14.2-14.4; pp. 320-326, 333-337)

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

Questions you should be able to answer:

- Explain postulates 3 and 4.
- What is an eigenvalue equation?
- Determine if a function is an eigenfunction (or eigenvector) of a given operator.
If so, determine its eigenvalue.
- What is a Hermitian operator?
- What is the expectation value of an observable and how can it be calculated.
- Express mathematically the notation: $\langle \Psi | A | \Psi \rangle$ and $\langle \Psi | \Psi \rangle$

1.10. The Schrödinger equation and the Hamiltonian of a molecule

(Levine, sections: 1.4, 1.5, 3.3, 3.4, 7.8, 13.1; pp. 8-15, 42-51, 192-196, 369-373)

(Engel, sections: 13.4, 13.5, 14.5, 26.3; pp. 318-321, 338, 636-638)

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

Questions you should be able to answer:

- Given the classical and QM expression of the linear momentum along x, y and z, determine the expression of the Hamiltonian for a particle moving in one and three dimensions, for N particles moving in 3 dimensions and for a given molecular system.
- What is the Hamiltonian of a molecule?
- What are the terms that normally appear in the Hamiltonian of a molecule?
- What is the Born-Oppenheimer approximation?
How is this approximation justified?
How does it simplify the molecular Hamiltonian and the solution to the time-independent SE?
- What is the approximation that allows the simplification of the Hamiltonian of a molecular system?
What does it state?
- Explain the different postulates of QM. (Levine, 7.8; Engel, Chapter 14)

1.11. The multielectronic wavefunction and the Slater determinant

(Levine, sections: 8.3, 8.4, 8.6, 8.7, 10.1-10.3, 10.5, 10.6; pp. 216-223, 230-238, 283-289, 292-297)
(Engel, sections: 21.1-21.3; pp. 483-489)

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

Questions you should be able to answer:

- What does it mean when we say that a multielectronic wf is antisymmetric with respect to the interchange of any two electrons?
- Explain what spin orbitals, molecular orbitals, and spin functions are.
- What is the Hartree product? Use a particular chemical system as an example.
- Explain why it is not correct to express a multielectronic wf as a Hartree product of spin orbitals.
- Solve determinants of order two and three.
- What is the simplest way to properly represent a multielectronic wf?
- Obtain the Slater determinant for a system of a given number of electrons.
- Explain the properties of the multielectronic wf that are satisfied in its Slater determinant representation.

- Given the ground electronic configuration of a system (with respect to occupied and virtual MOs), be able to obtain electronically excited configurations and obtain their Slater determinant representation.
- Explain the concepts: basis set in a vector space, complete basis set in QM.
- Express MOs as a linear combination of basis functions.
- Indicate the types of basis functions frequently used in QM.
- Explain the pros and cons of increasing the size of a basis set.
- Determine the number of basis functions, and the number of occupied and virtual MOs obtained as a result of performing a calculation on a molecular system using a minimal basis set.
- Provide examples (and provide details) of molecular properties can be calculated using MO energies.

Section 3. The Hartree-Fock Theory (2 fifty-minute lectures)

1.12. The Hartree-Fock (HF) theory

(Levine, sections: 11.1, 11.3; pp. 309-316, 319-322)

(Engel, sections: 21.5, 21.6, 26.3-26.5; pp. 491-501, 636-644)

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 (for self-study and Quiz)

Main sources of error for calculations

A frequently used notation

Be able to:

- Explain the main characteristics of the HF approximation.
- Explain how the multielectronic HF wavefunction is represented.
- Explain what the HF limit is.
- Explain the meaning of the main terms that appear in the HF equation (Fock operator, one-electron Hamiltonian, Coulomb operator, Exchange operator).
- Explain what the SCF method is and why it needs to be applied.
- Explain what the correlation energy is and how it is defined
- Explain the two main sources of error in QM calculations
- Explain the notation: Method 2/Basis Set 2 // Method 1/Basis Set 1 using a concrete example
- What does it mean when it is said that the HF method is variational?
- Explain some of the failures and successes when applying the HF approximation (homolytic bond dissociation energies, bond distances, frequencies, dipole moments).

Part 2: Introductory Statistical Thermodynamics (7 fifty-minute lectures)

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

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

(LM&S, section: 15.1; pp. 784-785)

Translational energy

Rotational energy: principal axes and principal moments of inertia

Vibrational energy

Molecular degrees of freedom

Questions you should be able to answer:

- Given a molecule be able to determine the total number of degrees of freedom and their distribution among the different forms of molecular degrees of freedom (translations, rotations, vibrations).
- Know what the principal axes and principal moments of inertia of a molecule are.
- Calculate the principal moments of inertia of a molecule from its internal (bond distance, bond angles and dihedral angles) and Cartesian coordinates.
- Classify a molecule as a rotor according to the values of its principal moments of inertia (linear, spherical, asymmetric and symmetric rotors).

2.2. Introduction to statistical mechanics

Questions you should be able to answer:

- Understand the basic ideas, objectives and mode of action of statistical mechanics.

2.3. Classical thermodynamics and statistical thermodynamics:

The Boltzmann's equation

(LM&S, pp. 788, 828)

Questions you should be able to answer:

- Understand the main differences between classical and statistical thermodynamics and the equation that establishes the link between these two disciplines.
- Know what the Boltzmann equation is, identify the terms it relates and be able to explain its significance.

2.4. The Maxwell-Boltzmann distribution law

(LM&S, section: 15.2; pp. 789-795)

(Atkins, sections: 15.1, 15.5; pp. 564-568, 579-581)

Populations, configurations and weights. Dominant configuration

The Maxwell-Boltzmann (MB) distribution law

Questions you should be able to answer:

- Explain the concepts: populations, configurations, weights and dominant configuration.
- Understand the meaning of the MB distribution law, and in general terms, know how it is obtained.

- Be able to use the MB distribution to calculate (a) the fraction of particles on a given energy level and (b) differences and relative populations between energy levels.
- Know how to apply Stirling's approximation (formula provided).

LM&S: Prob. 15.20

2.5. The partition function

(LM&S, section: 15.3; pp. 795-798)

(Atkins, section: 15.2; pp. 568-574)

Definition, meaning, interpretation, temperature dependence

Questions you should be able to answer:

- Calculate the partition function (q) of simple systems at a given temperature.
- Explain how q changes as temperature increases and know what its value is at 0 K.
- Explain the meaning of the numerical value of q .

2.6. The molecular partition function

(LM&S, section: 15.5; pp. 802-810, 580)

(Atkins, section: 16.2; pp. 594-601)

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

Questions you should be able to answer:

- Derive the expression to calculate the molecular partition function from its different contributions.
- Describe the procedure followed in the derivation of the equations to calculate the different contributions to the molecular partition function: translational, rotational, and vibrational.
- Explain the meaning of each of these values and how they change with temperature.
- Explain the approximations made in the derivation of the equation for the molecular partition function and its contributions (model used, implications, mathematical approximations, etc).
- For each contribution (translational, rotational, vibrational) to the molecular partition function, explain the model adopted and discuss where the expression for the energy levels of these models come from. Comment on the degeneracies (if any) and the spacing between neighboring energy levels of the different types as per the models adopted.
- Explain why a given contribution is very large while others are small.
- Identify these equations and use them in calculations.
- Know how to work with the units of the different magnitudes involved.
- Given the Cartesian coordinates of a molecule and its harmonic frequencies, calculate its partition function.

- Explain the two adiabatic approximations studied: the Born-Oppenheimer approximation and the rigid rotor model.
- Explain the main differences between the harmonic and the anharmonic oscillator models.
- Why the harmonic oscillator model fails to properly describe molecular vibrations?
- What are the consequences of treating molecular vibrations as harmonic?
- Under which conditions it is okay to treat molecular vibrations as harmonic?

LM&S: Prob. 15.10 (1st part), 15.11, 15.12, 15.16, 15.19, *15.26

2.7. Ensembles and the canonical partition function (Q)

(LM&S, sections: 15.3, 15.10; pp. 797-798, 828-829)

(Atkins, section: 15.7; pp. 582-583)

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

Questions you should be able to answer:

- Given the value of the molecular partition function (q), calculate Q for the two systems studied.
- Obtain the expression of Q for a system of independent and distinguishable particles.

2.8. Calculation of thermodynamic quantities from canonical partition functions

(LM&S, sections: 15.4, 15.6-15.8; pp. 798-801, 811-826)

(Atkins, sections: 15.6, 16.1, 16.8; pp. 581-582, 592-594, 610-616)

Linking Q to the calculation of various thermodynamic quantities ($U-U_0$, $H-U_0$, $G-U_0$, S , p)

Partition functions and equilibrium constants (informative)

The statistical thermodynamic formulation of TST (informative)

Questions you should be able to answer:

- Given the expression for $\ln Q$ with respect to temperature or volume, calculate thermodynamic quantities ($U-U_0$, $H-U_0$, $G-U_0$, S , p) of a system of N independent and indistinguishable particles.
- Be able to verify some of these calculations using literature values or an alternative procedure (*e.g.*, $pV=nRT$).

LM&S: Prob. 15.27, 15.28, *15.29