

国外化学经典教材系列（影印版）

3

计算化学

——分子和量子力学理论及应用导论

Computational Chemistry

Introduction to the Theory and Applications of
Molecular and Quantum Mechanics

(2nd Edition)

Errol G. Lewars

原著第2版



科学出版社

国外化学经典教材系列(影印版) 3

Computational Chemistry

Introduction to the Theory and Applications
of Molecular and Quantum Mechanics

(2nd Edition)

计算化学

——分子和量子力学理论及应用导论

(原著第2版)

Errol G. Lewars

常州大学图书馆
藏书章

科学出版社

北 京

图字: 01-2012-0174

Reprint from English language edition:

*Computational Chemistry: Introduction to the Theory and Applications of
Molecular and Quantum Mechanics*

by Errol G. Lewars

Copyright © 2011, Springer Netherlands

Springer Netherlands is a part of Springer Science+Business Media

All Rights Reserved

**This reprint has been authorized by Springer Science & Business Media for
distribution in China Mainland only and not for export therefrom.**

本影印版由施普林格科学商业媒体授权仅在中国大陆境内发行,不得出口。

图书在版编目(CIP)数据

计算化学:分子和量子力学理论及应用导论=Computational Chemistry:
Introduction to the Theory and Applications of Molecular and Quantum Me-
chanics:第2版:英文/(加)里沃斯(Lewars, E. G.)编著. —影印本. —北京:
科学出版社, 2012

国外化学经典教材系列 3

ISBN 978-7-03-033299-8

I. ①计… II. ①里… III. ①化学-计算机应用-高等学校-教材-英文
IV. ①O6-04

中国版本图书馆 CIP 数据核字 (2012) 第 001021 号

责任编辑:周强 / 责任印制:钱玉芬 / 封面设计:耕者设计室

科学出版社出版

北京东黄城根北街 16 号

邮政编码: 100717

<http://www.sciencep.com>

陈海印刷有限责任公司印刷

科学出版社发行 各地新华书店经销

*

2012 年 1 月第 一 版 开本: B5 (720×1000)

2012 年 1 月第一次印刷 印张: 42 1/2

字数: 854 000

定价: 150.00 元

(如有印装质量问题,我社负责调换)

*To Anne and John,
who know what their contributions were*

Preface

Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry – an aberration which is happily almost impossible – it would occasion a rapid and widespread degeneration of that science.

Augustus Comte, French philosopher, 1798–1857; in *Philosophie Positive*, 1830.

A dissenting view:

The more progress the physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of center to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility to which it may be submitted to calculation.

Adolphe Quetelet, French astronomer, mathematician, statistician, and sociologist, 1796–1874, writing in 1828.

This second edition differs from the first in these ways:

1. The typographical errors that were found in the first edition have been (I hope) corrected.
2. Those equations that should be memorized are marked by an asterisk, for example *(2.1).
3. Sentences and paragraphs have frequently been altered to clarify an explanation.
4. The biographical footnotes have been updated as necessary.
5. Significant developments since 2003, up to near mid-2010, have been added and referenced in the relevant places.
6. Some topics not in first edition, solvation effects, how to do CASSCF calculations, and transition elements, have been added.

As might be inferred from the word *Introduction*, the purpose of this book is to teach the basics of the core concepts and methods of computational chemistry. This is a textbook, and no attempt has been made to please every reviewer by dealing with esoteric “advanced” topics. Some fundamental concepts are the idea of a

potential energy surface, the mechanical picture of a molecule as used in molecular mechanics, and the Schrödinger equation and its elegant taming with matrix methods to give energy levels and molecular orbitals. All the needed matrix algebra is explained before it is used. The fundamental methods of computational chemistry are molecular mechanics, *ab initio*, semiempirical, and density functional methods. Molecular dynamics and Monte Carlo methods are only mentioned; while these are important, they utilize fundamental concepts and methods treated here. I wrote the book because there seemed to be no text quite right for an introductory course in computational chemistry suitable for a fairly general chemical audience; I hope it will be useful to anyone who wants to learn enough about the subject to start reading the literature and to start doing computational chemistry. There are excellent books on the field, but evidently none that seeks to familiarize the general student of chemistry with computational chemistry in the same sense that standard textbooks of those subjects make organic or physical chemistry accessible. To that end the mathematics has been held on a leash; no attempt is made to prove that molecular orbitals are vectors in Hilbert space, or that a finite-dimensional inner-product space must have an orthonormal basis, and the only sections that the nonspecialist may justifiably view with some trepidation are the (outlined) derivation of the Hartree–Fock and Kohn–Sham equations. These sections should be read, if only to get the flavor of the procedures, but should not stop anyone from getting on with the rest of the book.

Computational chemistry has become a tool used in much the same spirit as infrared or NMR spectroscopy, and to use it sensibly it is no more necessary to be able to write your own programs than the fruitful use of infrared or NMR spectroscopy requires you to be able to build your own spectrometer. I have tried to give enough theory to provide a reasonably good idea of how the programs work. In this regard, the concept of constructing and diagonalizing a Fock matrix is introduced early, and there is little talk of secular determinants (except for historical reasons in connection with the simple Hückel method). Many results of actual computations, most of them specifically for this book, are given. Almost all the assertions in these pages are accompanied by literature references, which should make the text useful to researchers who need to track down methods or results, and students (i.e. anyone who is still learning anything) who wish to delve deeper. The material should be suitable for senior undergraduates, graduate students, and novice researchers in computational chemistry. A knowledge of the shapes of molecules, covalent and ionic bonds, spectroscopy, and some familiarity with thermodynamics at about the level provided by second- or third-year undergraduate courses is assumed. Some readers may wish to review basic concepts from physical and organic chemistry.

The reader, then, should be able to acquire the basic theory and a fair idea of the kinds of results to be obtained from the common computational chemistry techniques. You will learn how one can calculate the geometry of a molecule, its IR and UV spectra and its thermodynamic and kinetic stability, and other information needed to make a plausible guess at its chemistry.

Computational chemistry is accessible. Hardware has become far cheaper than it was even a few years ago, and powerful programs previously available only for expensive workstations have been adapted to run on relatively inexpensive personal computers. The actual use of a program is best explained by its manuals and by books written for a specific program, and the actual *directions* for setting up the various computations are not given here. Information on various programs is provided in Chapter 9. Read the book, get some programs and go out and do computational chemistry.

You may make mistakes, but they are unlikely to put you in the same kind of danger that a mistake in a wet lab might.

It is a pleasure acknowledge the help of:

Professor Imre Csizmadia of the University of Toronto, who gave unstintingly of his time and experience,

The students in my computational and other courses,

The generous and knowledgeable people who subscribe to CCL, the computational chemistry list, an exceedingly helpful forum anyone seriously interested in the subject,

My editor for the first edition at Kluwer, Dr Emma Roberts, who was always most helpful and encouraging,

Professor Roald Hoffmann of Cornell University, for his insight and knowledge on sometimes arcane matters,

Professor Joel Liebman of the University of Maryland, Baltimore County for stimulating discussions,

Professor Matthew Thompson of Trent University, for stimulating discussions

The staff at Springer for the second edition: Dr Sonia Ojo who helped me to initiate the project, and Mrs Claudia Culierat who assumed the task of continuing to assist me in this venture and was always extremely helpful.

No doubt some names have been, unjustly, inadvertently omitted, for which I tender my apologies.

Ontario, Canada
April 2010

E. Lewars

Contents

1	An Outline of What Computational Chemistry Is All About	1
1.1	What You Can Do with Computational Chemistry	1
1.2	The Tools of Computational Chemistry	2
1.3	Putting It All Together	3
1.4	The Philosophy of Computational Chemistry	4
1.5	Summary	5
	References	5
	Easier Questions	6
	Harder Questions	7
2	The Concept of the Potential Energy Surface	9
2.1	Perspective	9
2.2	Stationary Points	13
2.3	The Born–Oppenheimer Approximation	21
2.4	Geometry Optimization	23
2.5	Stationary Points and Normal-Mode Vibrations – Zero Point Energy	30
2.6	Symmetry	36
2.7	Summary	39
	References	40
	Easier Questions	42
	Harder Questions	42
3	Molecular Mechanics	45
3.1	Perspective	45
3.2	The Basic Principles of Molecular Mechanics	48
3.2.1	Developing a Forcefield	48
3.2.2	Parameterizing a Forcefield	53
3.2.3	A Calculation Using Our Forcefield	57

3.3 Examples of the Use of Molecular Mechanics	60
3.3.1 To Obtain Reasonable Input Geometries for Lengthier (Ab Initio, Semiempirical or Density Functional) Kinds of Calculations	61
3.3.2 To Obtain Good Geometries (and Perhaps Energies) for Small- to Medium-Sized Molecules	64
3.3.3 To Calculate the Geometries and Energies of Very Large Molecules, Usually Polymeric Biomolecules (Proteins and Nucleic Acids).....	65
3.3.4 To Generate the Potential Energy Function Under Which Molecules Move, for Molecular Dynamics or Monte Carlo Calculations	65
3.3.5 As a (Usually Quick) Guide to the Feasibility of, or Likely Outcome of, Reactions in Organic Synthesis.....	66
3.4 Geometries Calculated by MM	67
3.5 Frequencies and Vibrational Spectra Calculated by MM	72
3.6 Strengths and Weaknesses of Molecular Mechanics	73
3.6.1 Strengths.....	73
3.6.2 Weaknesses.....	74
3.7 Summary	78
References.....	79
Easier Questions	82
Harder Questions.....	82
 4 Introduction to Quantum Mechanics in Computational Chemistry	85
4.1 Perspective	85
4.2 The Development of Quantum Mechanics. The Schrödinger Equation	87
4.2.1 The Origins of Quantum Theory: Blackbody Radiation and the Photoelectric Effect.....	87
4.2.2 Radioactivity	91
4.2.3 Relativity	91
4.2.4 The Nuclear Atom.....	92
4.2.5 The Bohr Atom.....	94
4.2.6 The Wave Mechanical Atom and the Schrödinger Equation.....	96
4.3 The Application of the Schrödinger Equation to Chemistry by Hückel.....	102
4.3.1 Introduction.....	102
4.3.2 Hybridization	103
4.3.3 Matrices and Determinants.....	108
4.3.4 The Simple Hückel Method – Theory	118
4.3.5 The Simple Hückel Method – Applications	133
4.3.6 Strengths and Weaknesses of the Simple Hückel Method.....	144

4.3.7 The Determinant Method of Calculating the Hückel c's and Energy Levels.....	146
4.4 The Extended Hückel Method	152
4.4.1 Theory	152
4.4.2 An Illustration of the EHM: the Protonated Helium Molecule..	160
4.4.3 The Extended Hückel Method – Applications.....	163
4.4.4 Strengths and Weaknesses of the Extended Hückel Method	164
4.5 Summary	165
References.....	168
Easier Questions	172
Harder Questions.....	172
5 Ab initio Calculations	175
5.1 Perspective	175
5.2 The Basic Principles of the Ab initio Method	176
5.2.1 Preliminaries.....	176
5.2.2 The Hartree SCF Method	177
5.2.3 The Hartree–Fock Equations.....	181
5.3 Basis Sets.....	232
5.3.1 Introduction.....	232
5.3.2 Gaussian Functions; Basis Set Preliminaries; Direct SCF.....	233
5.3.3 Types of Basis Sets and Their Uses.....	238
5.4 Post-Hartree–Fock Calculations: Electron Correlation	255
5.4.1 Electron Correlation.....	255
5.4.2 The Møller–Plesset Approach to Electron Correlation	261
5.4.3 The Configuration Interaction Approach To Electron Correlation – The Coupled Cluster Method	269
5.5 Applications of the Ab initio Method.....	281
5.5.1 Geometries	281
5.5.2 Energies	291
5.5.3 Frequencies and Vibrational Spectra.....	332
5.5.4 Properties Arising from Electron Distribution: Dipole Moments, Charges, Bond Orders, Electrostatic Potentials, Atoms-in-Molecules (AIM)	337
5.5.5 Miscellaneous Properties – UV and NMR Spectra, Ionization Energies, and Electron Affinities.....	359
5.5.6 Visualization.....	364
5.6 Strengths and Weaknesses of Ab initio Calculations.....	372
5.6.1 Strengths.....	372
5.6.2 Weaknesses.....	372
5.7 Summary	373
References.....	373
Easier Questions	388
Harder Questions.....	389

6	Semiempirical Calculations	391
6.1	Perspective	391
6.2	The Basic Principles of SCF Semiempirical Methods	393
6.2.1	Preliminaries	393
6.2.2	The Pariser-Parr-Pople (PPP) Method	396
6.2.3	The Complete Neglect of Differential Overlap (CNDO) Method	398
6.2.4	The Intermediate Neglect of Differential Overlap (INDO) Method	399
6.2.5	The Neglect of Diatomic Differential Overlap (NDDO) Methods	400
6.3	Applications of Semiempirical Methods	412
6.3.1	Geometries	412
6.3.2	Energies	419
6.3.3	Frequencies and Vibrational Spectra	423
6.3.4	Properties Arising from Electron Distribution: Dipole Moments, Charges, Bond Orders	426
6.3.5	Miscellaneous Properties – UV Spectra, Ionization Energies, and Electron Affinities	431
6.3.6	Visualization	434
6.3.7	Some General Remarks	435
6.4	Strengths and Weaknesses of Semiempirical Methods	436
6.4.1	Strengths	436
6.4.2	Weaknesses	436
6.5	Summary	437
	References	438
	Easier Questions	443
	Harder Questions	443
7	Density Functional Calculations	445
7.1	Perspective	445
7.2	The Basic Principles of Density Functional Theory	447
7.2.1	Preliminaries	447
7.2.2	Forerunners to Current DFT Methods	448
7.2.3	Current DFT Methods: The Kohn–Sham Approach	449
7.3	Applications of Density Functional Theory	467
7.3.1	Geometries	468
7.3.2	Energies	477
7.3.3	Frequencies and Vibrational Spectra	484
7.3.4	Properties Arising from Electron Distribution – Dipole Moments, Charges, Bond Orders, Atoms-in-Molecules	487
7.3.5	Miscellaneous Properties – UV and NMR Spectra, Ionization Energies and Electron Affinities, Electronegativity, Hardness, Softness and the Fukui Function	491
7.3.6	Visualization	509

7.4 Strengths and Weaknesses of DFT.....	509
7.4.1 Strengths.....	509
7.4.2 Weaknesses.....	510
7.5 Summary.....	510
References.....	512
Easier Questions.....	518
Harder Questions.....	518
8 Some “Special” Topics: Solvation, Singlet Diradicals, A Note on Heavy Atoms and Transition Metals	521
8.1 Solvation.....	521
8.1.1 Perspective.....	522
8.1.2 Ways of Treating Solvation.....	522
8.2 Singlet Diradicals.....	535
8.2.1 Perspective.....	535
8.2.2 Problems with Singlet Diradicals and Model Chemistries	535
8.2.3 (1) Singlet Diradicals: Beyond Model Chemistries. (2) Complete Active Space Calculations (CAS).....	537
8.3 A Note on Heavy Atoms and Transition Metals.....	547
8.3.1 Perspective.....	547
8.3.2 Heavy Atoms and Relativistic Corrections	548
8.3.3 Some Heavy Atom Calculations	549
8.3.4 Transition Metals.....	550
8.4 Summary.....	552
References.....	553
Solvation	558
Easier Questions	558
Harder Questions	558
Singlet Diradicals	558
Easier Questions	558
Harder Questions	559
Heavy Atoms and Transition Metals	559
Easier Questions	559
Harder Questions	560
9 Selected Literature Highlights, Books, Websites, Software and Hardware	561
9.1 From the Literature.....	561
9.1.1 Molecules.....	561
9.1.2 Mechanisms	566
9.1.3 Concepts.....	568
9.2 To the Literature.....	572
9.2.1 Books.....	572
9.2.2 Websites for Computational Chemistry in General.....	576

9.3 Software and Hardware	577
9.3.1 Software	577
9.3.2 Hardware	581
9.3.3 Postscript	582
References.....	582
Answers	585
Index	655

Chapter 1

An Outline of What Computational Chemistry Is All About

Knowledge is experiment's daughter
Leonardo da Vinci, in *Pensieri*, ca. 1492
Nevertheless:

Abstract You can calculate molecular geometries, rates and equilibria, spectra, and other physical properties. The tools of computational chemistry are molecular mechanics, *ab initio*, semiempirical and density functional methods, and molecular dynamics. Computational chemistry is widely used in the pharmaceutical industry to explore the interactions of potential drugs with biomolecules, for example by docking a candidate drug into the active site of an enzyme. It is also used to investigate the properties of solids (e.g. plastics) in materials science. It does not replace experiment, which remains the final arbiter of truth about Nature.

1.1 What You Can Do with Computational Chemistry

Computational chemistry (also called molecular modelling; the two terms mean about the same thing) is a set of techniques for investigating chemical problems on a computer. Questions commonly investigated computationally are:

Molecular geometry: the shapes of molecules – bond lengths, angles and dihedrals.

Energies of molecules and transition states: this tells us which isomer is favored at equilibrium, and (from transition state and reactant energies) how fast a reaction should go.

Chemical reactivity: for example, knowing where the electrons are concentrated (nucleophilic sites) and where they want to go (electrophilic sites) enables us to predict where various kinds of reagents will attack a molecule.

IR, UV and NMR spectra: these can be calculated, and if the molecule is unknown, someone trying to make it knows what to look for.

The interaction of a substrate with an enzyme: seeing how a molecule fits into the active site of an enzyme is one approach to designing better drugs.

The physical properties of substances: these depend on the properties of individual molecules and on how the molecules interact in the bulk material. For example, the strength and melting point of a polymer (e.g. a plastic) depend on how well the molecules fit together and on how strong the forces between them are. People who investigate things like this work in the field of materials science.

1.2 The Tools of Computational Chemistry

In studying these questions computational chemists have a selection of methods at their disposal. The main tools available belong to five broad classes:

Molecular mechanics is based on a model of a molecule as a collection of balls (atoms) held together by springs (bonds). If we know the normal spring lengths and the angles between them, and how much energy it takes to stretch and bend the springs, we can calculate the energy of a given collection of balls and springs, i.e. of a given molecule; changing the geometry until the lowest energy is found enables us to do a geometry optimization, i.e. to calculate a geometry for the molecule. Molecular mechanics is fast: a fairly large molecule like a steroid (e.g. cholesterol, $C_{27}H_{46}O$) can be optimized in seconds on a good personal computer.

Ab Initio calculations (ab initio, Latin: "from the start", i.e. from first principles") are based on the Schrödinger equation. This is one of the fundamental equations of modern physics and describes, among other things, how the electrons in a molecule behave. The ab initio method solves the Schrödinger equation for a molecule and gives us an energy and *wavefunction*. The wavefunction is a mathematical function that can be used to calculate the electron distribution (and, in theory at least, anything else about the molecule). From the electron distribution we can tell things like how polar the molecule is, and which parts of it are likely to be attacked by nucleophiles or by electrophiles.

The Schrödinger equation cannot be solved exactly for any molecule with more than one (!) electron. Thus approximations are used; the less serious these are, the "higher" the level of the ab initio calculation is said to be. Regardless of its level, an ab initio calculation is based only on basic physical theory (quantum mechanics) and is in this sense "from first principles".

Ab initio calculations are relatively slow: the geometry and IR spectra (= the vibrational frequencies) of propane can be calculated at a reasonably high level in minutes on a personal computer, but a fairly large molecule, like a steroid, could take perhaps days. The latest personal computers, with 2 or more GB of RAM and a thousand or more gigabytes of disk space, are serious computational tools and now compete with UNIX workstations even for the demanding tasks associated with high-level ab initio calculations. Indeed, one now hears little talk of "workstations", machines costing ca. \$15,000 or more [1].

Semiempirical calculations are, like *ab initio*, based on the Schrödinger equation. However, more approximations are made in solving it, and the very complicated integrals that must be calculated in the *ab initio* method are not actually evaluated in semiempirical calculations: instead, the program draws on a kind of library of integrals that was compiled by finding the best fit of some *calculated* entity like geometry or energy (heat of formation) to the *experimental* values. This plugging of experimental values into a mathematical procedure to get the best calculated values is called *parameterization* (or *parametrization*). It is the mixing of theory and experiment that makes the method “semiempirical”: it is based on the Schrödinger equation, but parameterized with experimental values (*empirical* means experimental). Of course one hopes that semiempirical calculations will give good answers for molecules for which the program has *not* been parameterized.

Semiempirical calculations are slower than molecular mechanics but much faster than *ab initio* calculations. Semiempirical calculations take roughly 100 times as long as molecular mechanics calculations, and *ab initio* calculations take roughly 100–1,000 times as long as semiempirical. A semiempirical geometry optimization on a steroid might take seconds on a PC.

Density functional calculations (DFT calculations, density functional theory) are, like *ab initio* and semiempirical calculations, based on the Schrödinger equation. However, unlike the other two methods, DFT does not calculate a conventional wavefunction, but rather derives the electron distribution (electron *density* function) directly. A *functional* is a mathematical entity related to a function.

Density functional calculations are usually faster than *ab initio*, but slower than semiempirical. DFT is relatively new (serious DFT computational chemistry goes back to the 1980s, while computational chemistry with the *ab initio* and semiempirical approaches was being done in the 1960s).

Molecular dynamics calculations apply the laws of motion to molecules. Thus one can simulate the motion of an enzyme as it changes shape on binding to a substrate, or the motion of a swarm of water molecules around a molecule of solute; quantum mechanical molecular dynamics also allows actual chemical reactions to be simulated.

1.3 Putting It All Together

Very large biological molecules are studied mainly with molecular mechanics, because other methods (*quantum mechanical* methods, based on the Schrödinger equation: semiempirical, *ab initio* and DFT) would take too long. Novel molecules, with unusual structures, are best investigated with *ab initio* or possibly DFT calculations, since the parameterization inherent in MM or semiempirical methods makes them unreliable for molecules that are very different from those used in the parameterization. DFT is relatively new and its limitations are still unclear.

Calculations on the structure of large molecules like proteins or DNA are done with molecular mechanics. The motions of these large biomolecules can be studied with

molecular dynamics. Key *portions* of a large molecule, like the active site of an enzyme, can be studied with semiempirical or even *ab initio* methods. Moderately large molecules like steroids can be studied with semiempirical calculations, or if one is willing to invest the time, with *ab initio* calculations. Of course molecular mechanics can be used with these too, but note that this technique does not give information on electron distribution, so chemical questions connected with nucleophilic or electrophilic behaviour, say, cannot be addressed by molecular mechanics alone.

The energies of molecules can be calculated by MM, SE, *ab initio* or DFT. The method chosen depends very much on the particular problem. Reactivity, which depends largely on electron distribution, must usually be studied with a quantum-mechanical method (SE, *ab initio* or DFT). Spectra are most reliably calculated by *ab initio* or DFT methods, but useful results can be obtained with SE methods, and some MM programs will calculate fairly good IR spectra (balls attached to springs vibrate!).

Docking a molecule into the active site of an enzyme to see how it fits is an extremely important application of computational chemistry. One could manipulate the substrate with a mouse or a kind of joystick and try to fit it (dock it) into the active site, with a feedback device enabling you to feel the forces acting on the molecule being docked, but automated docking is now standard. This work is usually done with MM, because of the large molecules involved, although selected portions of the biomolecules can be studied by one of the quantum mechanical methods. The results of such docking experiments serve as a guide to designing better drugs, molecules that will interact better with the desired enzymes but be ignored by other enzymes.

Computational chemistry is valuable in studying the properties of materials, i.e. in materials science. Semiconductors, superconductors, plastics, ceramics – all these have been investigated with the aid of computational chemistry. Such studies tend to involve a knowledge of solid-state physics and to be somewhat specialized.

Computational chemistry is fairly cheap, it is fast compared to experiment, and it is environmentally safe (although the profusion of computers in the last decade has raised concern about the consumption of energy [2] and the disposal of obsolescent machines [3]). It does not replace experiment, which remains the final arbiter of truth about Nature. Furthermore, to *make* something – new drugs, new materials – one has to go into the lab. However, computation has become so reliable in some respects that, more and more, scientists in general are employing it before embarking on an experimental project, and the day may come when to obtain a grant for some kinds of experimental work you will have to show to what extent you have computationally explored the feasibility of the proposal.

1.4 The Philosophy of Computational Chemistry

Computational chemistry is the culmination (to date) of the view that chemistry is best understood as the manifestation of the behavior of atoms and molecules, and that these are real entities rather than merely convenient intellectual models [4]. It is