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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

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by Errol G. Lewars
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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 Compte, 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

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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 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,
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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

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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.

E.G. Lewars, *Computational Chemistry*,
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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

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