

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,

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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.

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