Preface to the Second Edition

The first edition of this book was written in the early 1980s. At that time molecular calculations were pretty much in the province of professional quantum chemists. An enormous change has occurred since that time. The explosive growth and availability of computer power has placed in the hands of undergraduate students the ability to carry out molecular calculations routinely that were unimaginable twenty years ago. This new edition incorporates this ability by discussing and encouraging the use of quantum chemistry programs such as Gaussian and WebMO, which most chemistry departments have access to. Not only can undergraduates do quantum chemical calculations nowadays, there is even a program in North Carolina, North Carolina High School Computational Chemistry Server (*http://chemistry.ncssm.edu*), that encourages high school students to do so.

In addition to these quantum chemistry programs, there are a number of general mathematical programs such as *MathCad* or *Mathematica* that make it easy to do calculations routinely that were formerly a drudgery. These programs not only perform numerical calculations, but they can also perform algebraic manipulations as well. They are relatively easy to learn and use and every serious scientific student should know how to use one of them. They allow you to focus on the underlying physical ideas and free you from getting bogged down in algebra. They also allow you to explore the properties of equations by varying parameters and plotting the results. There are a number of problems in this edition that require the use one of these programs.

Another product of the computer revolution is the availability of so much material on-line. We refer to a number of websites throughout the chapters, but one that is particularly useful is the Computational Chemistry Comparison and Benchmark Data Base (*http://srdata.nist.gov/cccbdb*) maintained by the National Institute of Science and Technology (NIST). This website lists numerical results of quantum chemical calculations for hundreds of molecules using a great variety of computational methods. It also has an excellent tutorial that discusses a number of topics that are not treated in this book. I have utilized this website a great deal in Chapter 12 , which treats ab initio molecular orbital theory. If a student can navigate around this website and understand, or at least appreciate, most of the material presented in it, then I will consider this book to have been successful. Websites have the distressing property of disappearing, and so I have usually included only websites that are government sponsored, but even these websites change their addresses every so often. I checked every website that I refer to just before the book went to press, but if you have difficulty finding one of them, putting the address into Google seems to work.

The early chapters of this revision do not differ significantly from the first edition. They have been well received and constitute a rather timeless introduction to basic quantum mechanics. One small addition, however, is the introduction of the Dirac bracket notation for state functions and integrals, which is used freely throughout the remainder of the book. Rather than devote a single chapter to molecular spectroscopy, I have included it in Chapter 5 (The Harmonic Oscillator and Vibrational Spectroscopy) and Chapter 6 (The Rigid Rotator and Rotational Spectroscopy). Chapter 7 (The Hydrogen Atom) discusses the hydrogen atomic orbitals as the solutions to the Schrödinger equation for this system , and also

uses the results of the Stern–Gerlach experiment and the fine structure of the spectrum of atomic hydrogen to motivate the introduction of electron spin. Chapters 8 and 9 (Approximation Methods and Many-Electron Atoms, respectively) are not too different from the earlier edition, except that a little more emphasis is placed on the Hartree–Fock method. Chapter 9 has an appendix that actually carries out a Hartree–Fock calculation for a helium atom step by step. Chapter 10 (The Chemical Bond: One- and Two-Electron Molecules) is a fairly detailed discussion of the bonding in H_2^+ and H_2, and we utilize these simple systems to introduce many of the techniques that are used in modern molecular calculations. The last section of the chapter carries out a minimal basis set Hartree–Fock–Roothaan calculation for H_2 step by step. Once a student carries through such a calculation for a two-electron system, calculations on larger molecules should pose no conceptual difficulties. Chapter 11 is a standard discussion of qualitative molecular orbital theory, molecular term symbols, and π-electron molecular orbital theory. The final chapter (The Hartree–Fock–Roothaan Method) introduces the use of basis sets consisting of Gaussian functions in modern molecular calculations and the use of computational chemistry programs such as Gaussian and WebMO. One goal of the chapter, and the book itself for that matter, is for a student to be comfortable in carrying out a Hartree–Fock calculation for a given basis set. Much of Chapter 12 is built around the NIST Computational Chemistry Comparison and Benchmark Data Base website that I mentioned previously.

As with the first edition, the mathematical background required of the students is one year of calculus, with no knowledge of differential equations. All the necessary mathematical techniques are developed in the text through a number of short units called MathChapters. These units are self-contained and present just enough material to give a student the ability and the confidence to use the techniques in subsequent chapters. The point of these units is to present the mathematics before it is required so that a student can focus more on the physical principles involved rather than on the mathematics. There are MathChapters on complex numbers, probability and statistics, vectors, series and limits, spherical coordinates, determinants, and matrices. Most of current computational chemistry is formulated in terms of matrices, and I have used matrix notation in a number of places, particularly toward the end of the book.

No one can learn this material (nor any thing else in the physical sciences for that matter) without doing lots of problems. For this reason, I have provided about 50 problems at the end of each chapter. These problems range from filling in gaps to extending the material presented in the chapter, but most illustrate applications of the material. All tolled, there are over 600 problems in the book. I have provided answers to many of them at the back of the book. In addition, Helen Leung and Mark Marshall of Amherst College have written a Solution Manual in which the complete solution to every problem is give.

A singular feature of the book is the inclusion of biographies at the beginning of each chapter. I wish to thank my publisher for encouraging me to include them and my wife, Carole, for researching the material for them and writing every one of them. Each one could easily have been several pages long and it was difficult to cut them down to one page.

You read in many prefaces that "this book could not have been written and produced without the help of many people" , and it is definitely true. I am particularly

grateful to my reviewers, Bill Fink of UC Davis, Scott Feller of Wabash College, Atilla Szabo of NIH, Will Polik of Hope College, Helen Leung and Mark Marshall of Amherst College, and Mervin Hansen of Humboldt State University, who slogged through numerous drafts of chapters and who made many great suggestions. I also wish to give special thanks to Gaussian, Inc., who gave me a copy of Gaussian 03 to use in the preparation of the manuscript and to Will Polik, who set me up to use WebMO. I also wish to thank Christine Taylor and her crew at Wilsted & Taylor Publishing Services and particularly Jennifer Uhlich for transforming a pile of manuscript pages into a beautiful-looking and inviting book without a hitch, Jane Ellis for dealing with many of the production details and procuring all the photographs for the biographies, Mervin Hansen for rendering hundreds of figures in *Mathematica* and keeping them all straight in spite of countless alterations, John Murdzek for a very helpful copyediting, Paul Anagnostopoulos for composing the entire book, and my publisher Bruce Armbruster and his wife and associate Kathy for being the best publishers around and good friends in addition. Finally, I wish to thank my wife, Carole, for preparing the manuscript in LaTex, for reading the entire manuscript, and for being my best critic in general (in all things).

There are bound to be both typographical and conceptual errors in the book and I would appreciate your letting me know about them so that they can be corrected in subsequent printings. I also would welcome general comments, questions, and suggestions at *mquarrie@mcn.org*, or through the University Science Books website *www.uscibooks.com*, where any ancillary material or notices will be posted.