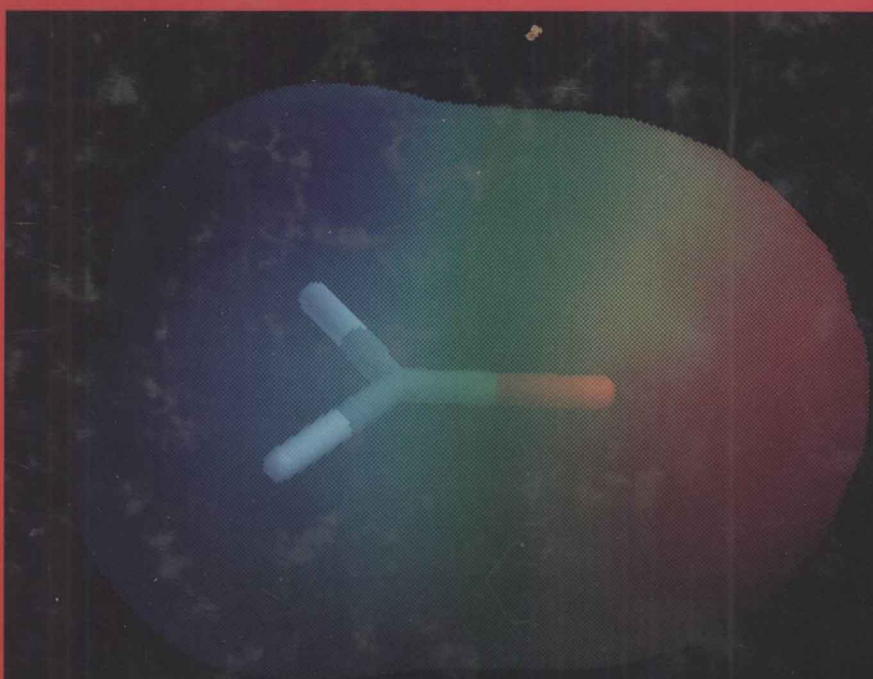
ELECTRONIC STRUCTURE MODELING

Connections Between Theory and Software



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Preface

Each of the authors has studied and taught the craft of electronic structure modeling for almost four decades. Becoming conscious of this deep subject in the 1960s, we have been witness to remarkable advances in quantum chemistry. One great change is that increasingly powerful electronic structure codes are now commodities, and machines to execute the code are widely available—potentially, to every reader, on his desktop or in her carryall.

This book is a response to the growing need for those pursuing experimental investigations to add to their methods and instruments the power of electronic structure modeling. We want to ensure that those who seek it can use this power for (their own) good. This may best be accomplished by a course of study that begins with a reminder of the foundations of the field and provides a leisurely look into the operation and structure of the most common electronic structure calculations. As aids to this exercise, we include two small-scale electronic structure programs. SCF1s is very tiny, but not quite a toy—it does real SCF calculations with a real basis set. It is just powerful enough to make some important features of SCF calculations intelligible. PCLOBE includes more sophisticated methods and can be (and has been) a medium for research-level modeling. Both grew out of the pioneering work of Lee Allen and his students at Princeton.

The first half of this book rests on the capabilities of these programs, and is a stepping stone to the insightful use of powerful modern codes, many of which are proof against tinkering—a consequence of the commercial importance and wide impact of electronic structure modeling.

We were given wise (if familiar) counsel by an architect of this field, H.F. Schaefer III. "Write what you know," he said. That would have made a shorter book. The second half of our work is mainly our effort to write what we learned. We know more now of density functional theory, coupled cluster methods, and modern means of calculation of properties such as NMR shielding and coupling, and electronic excitations by response theory. Finally, our discussion turns to a subject that has proved fascinating to one of us from the beginning and to the other in its resurgence just within the past few years. Circular dichroism, optical rotatory dispersion, and magnetic circular dichroism embrace a huge range of physical chemistry. The phenomena have attracted the attention of the best theoretical and experimental chemists for over almost 80 years, and were intriguing to Goethe, Pasteur, and Faraday. PCLOBE and the most modern codes grapple with these deep subtleties of light and matter. We hope that this survey of the workings of programs and their modern use will send the reader onto

independent study in electronic structure modeling, confident that powerful codes can be used in ways that are appropriate and meaningful.

For our more advanced examples we have used GAUSSIAN and ADF software, with which we have longstanding familiarity. We are grateful to those who produced results specifically for our use with GAMESS, ACES II, PSI3, and deMON. Many other powerful software suites are available, including the commercial products SCHRÖEDINGER, Q-CHEM, HYPERCHEM, and JAGUAR. Many active research groups maintain and share their own software: these include CADPAC, COLUMBUS, DALTON, MOLCAS, MOLPRO, NWCHEM, and TURBOMOL. Links to sources may be found at http://ws1.kist.re.kr among many other sites. We have found that SPARTAN software provides a particularly gentle way to gain experience with electronic structure modeling. Its excellent graphics and powerful molecule builder add to its appeal; the electrostatic potential mapped on a charge density isosurface appearing on the cover of this book is a small example.

Like everyone who writes, we are not free from debt to those who have led the way and helped us along. The study and practice of electronic structure modeling have brought us into the presence of great teachers and scientists. Some of them made a deeply personal impact, and others inspired us by example through their published work. The first group must include our mentors and colleagues. Donald Shillady thanks Walter Kauzmann, his ideal of the gentleman scientist, and John Bloor for proving that an organic chemist only needs a diagonalization routine to become a quantum chemist. Fred Richardson inspired his interest in trying to solve all the problems proposed in Kauzmann's 1940 review of optical activity, and his longtime mentor and chairman Larry Winters maintained his interest in problems of physical organic chemistry while continuing the Drexel link to Virginia Commonwealth University. The impact of Jerry Whitten's work with lobe basis sets and his encouragement of this work are also gratefully acknowledged.

The second group must include those authors of books that we have come back to again and again. Carl Trindle salutes Linus Pauling and E. Bright Wilson Jr. for a first notion of the power of quantum chemistry, Charles Coulson for a sense of adventure in applying such power, Wilson again with Decius and Cross for opening his eyes to the power of symmetry, and Frank Pilar for his example of clarity of exposition. He also thanks Abramowitz and Stegun for compiling a work of everlasting value.

We acknowledge with appreciation our colleagues who were so patient with our naïve questions, and so generous with their help. Their names appear in the chapters most relevant to their contributions. Personal thanks for making this work possible go first to Lance Wobus of Taylor & Francis, unfailing in encouragement. Barbara Body went as far as saying that writing this book could be valuable, and not only to the authors. She made time for Carl to write during vacations and weekends, lent a sympathetic ear, and supplied affectionate dogs to help console him. Nancy Shillady supported

Don throughout the work and helped in a thousand practical ways, especially in the clerical work of securing permissions. Don's son, Doug Shillady, constructed the Visual Basic® interface for PCLOBE, essential to its user's welcome. His former student Sherry Baldwin was the best possible reader. Professor Zikri Altun and the physicists at the University of Marmara heard and improved a version of this work presented in Istanbul in 2005. Not least, Toshiba made machines that survived the ordeal.

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Authors

Carl Trindle studied at Grinnell College, Tufts University, Yale University, and Argonne National Laboratory. Professor K.H. Illinger of Tufts guided his dissertation on the theory of line broadening in microwave spectra. The University of Virginia has been his professional home; he is currently professor of chemistry and principal of Brown College there. He has taught the range of physical chemistry, especially applications of quantum mechanics, in the chemistry department and an assortment of seminars on scientific ethics, the history of nuclear weaponry, and more general subjects for the residential college.

Carl Trindle was named an Alfred P. Sloan fellow and was a National Academy of Sciences exchange fellow at the Institute Rudjer Boškoviç in Zagreb. He has lectured in India under the sponsorship of the Fulbright Foundation, spent a semester at the Technion in Haifa, and a summer at King's College (London), and has maintained a long-standing collaboration with Turkish scientists. He has served as an American Chemical Society tour speaker and, like his coauthor, was recognized by the Virginia Section of the ACS with its Distinguished Service Award.

His research interests include the computational characterization of the structures of highly reactive systems including dianions and dications, bonding in triplet carbenes and diradicals, and electronic influences on regioselectivity. Most recently he has been studying UV absorption spectra and circular dichroism of high-symmetry chiral systems.

Donald D. Shillady is an emeritus professor of chemistry at Virginia Commonwealth University in Richmond, Virginia. He has been interested in optical activity and magnetically induced optical activity since his PhD thesis in 1969 but later expanded his interests to the larger field of quantum chemistry. He enjoys teaching physical chemistry and quantum chemistry. He has carried out a few experimental spectroscopic studies of magnetic circular dichroism but has mainly devoted his career to writing programs for computation of ORD, CD, MCD, CASCI, and MCSCF results. So far he has written 77 publications and has edited two books. His past interests include the biological effects of electromagnetic waves, determination of the absolute configuration of large organic molecules, integral transform wave functions, properties of metal atom clusters, and the relationship between valence bond and configuration interaction methods in chemistry. Although retired, he occasionally teaches a chemistry course and the preparation of this text has brought him up to date with active areas of research in quantum chemistry.

His computer program PCLOBE which accompanies this text includes many features of his research over the years. This program builds orbitals from Gaussian lobes, which eases exploration of new areas of electronic structure modeling. It is a connection between theory and software.

The CD and installation instructions are located on the back inside cover and facing page respectively.

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Chapter 4 Gaussian-Lobe Basis Sets

Chapter 5 A Very Simple MO Program

Chapter 6 Geometry Optimization and Vibrational Frequencies by SCF

1

One-Dimensional Quantum Mechanics: A Short Review

We want to provide a compact reminder of the framework of molecular electronic structure theory to those turning to computational chemistry. This chapter contains an account of the fundamental assumptions of quantum mechanics, including some of the rather few exact solutions to model problems, the algebra of operators, and an illustration of the uncertainty principle.

Quantum mechanics is well outside our human intuition, and we salute those adventurous scientists who were able to see so deeply into its strange world. The adventure begins with Planck's amazing account of the blackbody radiation spectrum based on the idea that energy is exchanged in parcels (1901) [1] and Einstein's adoption of that principle to explain the photoelectric effect in 1905 [2]. Bohr's daring model of the hydrogen spectrum, incorporating quantization of angular momentum (1913) [3], recaptured the numerical representation of H atom absorption and emission frequencies observed by Balmer (1885) [4]. All these advances made reference to the constant h that Planck had used to fit the blackbody radiation spectrum.

This constant played a role in resolving the curious duality of wave and particle at the very small scale. Prince Louis De Broglie [5] proposed that every object with momentum had also an associated wavelength.*

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

The De Broglie wavelength λ is immeasurably small for macroscopic objects such as baseballs, ball bearings, or rifle bullets, and classical mechanics is excellent for describing these macroscopic objects. However, for subatomic particles, and in particular the electron, the De Broglie wavelength is comparable in size to chemical bonds.

*De Broglie arrived at this relationship by consideration of an oddity in relativity theory. [http://www.davis-inc.com/physics/]. It of course seems magical. Consider that the circular Bohr orbit with circumference $2\pi r$ accommodates one wavelength. Then the momentum is $p = h/(2\pi r)$ and the kinetic energy T is $h^2/[2m(2\pi r)^2]$. The potential V is $-Z/r$. The minimum energy $T + V = -m(2\pi Z)^2/2h^2$ is in agreement with Bohr's fit. Hey presto!