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Book review

Christopher J. Cramer: Essentials of Computational Chemistry: Theories and Models

Wiley, New York, 2002. 562 pp (ISBN 0-471-48551-9) $110.00

David Chatfield

Chemistry Department, Florida International University, FL 33199, USA

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This is an excellent text for graduates or advanced undergraduates in any field of chemistry and for researchers desiring an introduction to computational chemistry. The author conveys the conceptual basis of force field and electronic structure calculations, with attention to issues of accuracy and performance, such that a student can approach practical research at the end of a course. Particular strengths are the author's ability to convey the principles of theory without heavy reliance on equations, close connection with chemical examples, useful performance data, and presentation of the state of the art (e.g., polarized molecular mechanics solvent models and recent self-consistent reaction field and quantum mechanical/molecular mechanics techniques). The topics are presented in the order force field methods, electronic structure methods, physical properties, solvation methods, and advanced topics. Nearly every chapter contains useful guides to the performance and limitations of the methods and concludes with a case study from the literature. Cramer's verbal prowess and dry wit make the book an amusing and insight-bringing read. Some may find the book too loosely discursive at times, but on the whole the conceptual presentation will immensely benefit noncomputational chemists. The author provides a URL where example problems can be found. The book is independent of a particular software package, as that choice depends on the instructor's experience.

The book attempts to bridge the gap between texts whose mathematics is overwhelming for the noncomputational chemist, and texts that are so purely conceptual that a user cannot learn to make informed judgments. When equations are presented, they are interpreted (the author makes a pledge in this regard). Experts may disagree about particular choices and even about the philosophy of such an approach, but Cramer is to be commended for taking a big step in the direction of making computational chemistry accessible to the nonexpert.

Force field methods are presented with a historical and physical motivation sometimes lacking in other books, and they serve as a springboard for discussing optimization, molecular dynamics, and Monte Carlo techniques. Discussion of electronic structure methods, the core of the text, begins with a brief review of basic molecular orbital theory, building on concepts from a first course in quantum mechanics and setting the framework for discussion of semiempirical methods.

Semiempirical methods are presented historically and thus in a natural conceptual sequence, and the section concludes with ongoing developments in theory. Useful comparison between the performance of various neglect of diatomic differential overlap models will allow students to make informed choices. Discussion of Hartree–Fock methods begins with the philosophy of basis-set building and competing nomenclatures. Practical issues such as self-consistent-field (SCF) convergence and uses of symmetry are discussed, and open-shell methods are presented.

Particularly for correlated methods (configuration interaction, multiconfigurational SCF, MPx, coupled cluster), the focus is on the principles and on issues of usage. (A more complete derivation is provided for MPx methods.) Multilevel methods (e.g., G2) are also discussed. The density functional theory (DFT) chapter is discursive but complete. The basic ideas are carefully developed, with attention to, for example, jellium and Xα methods, before modern functionals are considered. One example of the latter is given in order to show that at this level the mathematical expression is not enlightening. The local density approximation, generalized gradient approximation, and adiabatic connection methods are discussed. Very useful price/performance comparisons are presented and tabulated for all of these methods, including a selection of DFT methods.

Two chapters are devoted to properties: the first to charge distributions and spectroscopic properties (NMR, ESR, vibrational frequencies); the second to

Correspondence to: D. Chatfield
e-mail: chatfiel@fiu.edu

thermodynamic properties. Cramer devotes many pages to partial atomic charges, as he has done much fine work in this area. Given the importance of charge in rationalizing chemical mechanisms and the temptation for the uninformed to overinterpret Mulliken populations, this is a useful section. A very brief review of statistical mechanical expressions leads to a discussion of thermodynamic properties. Conventions for heats of formation and reaction, a potentially confusing issue, are given careful discussion. Practical matters such as isodesmic reactions and errors in low-frequency motions are treated. The accuracy of various methods for predicting properties is discussed at length, with a very helpful series of tables.

Two chapters are devoted to solvation. Implicit solvent models, an area to which Cramer has contributed substantially, are covered thoroughly (polarizable-continuum-model-type, generalized Born, SM*x* models). The principles are developed well, although the discussion would benefit from more focus. A range of explicit solvent models, classical and quantal, polarizable and nonpolarizable, are outlined. Free-energy perturbation, thermodynamic integration, and slow growth are treated. These are advanced techniques unlikely to be used except by experts, but it is perhaps useful for the novice to become acquainted with the principles.

The book concludes with three chapters on advanced topics. One is a thorough and easily understandable introduction to the menagerie of quantal/classical models. The others are on excited electronic states and adiabatic reaction dynamics. It is unlikely that a 1-semester course would cover all of these topics, but they provide a selection for an instructor's choice.

In summary, Cramer's *Essentials of computational chemistry* is just that: the essentials for performing meaningful computational experiments, with a sense for the state of the art. The text provides an excellent introduction to the field for students and researchers in any area of chemistry. The many tables comparing the performance of the methods are a big plus. This is a fine and practical book, and the reviewer intends to use it as a text in fall 2002.