Book Reviews [*]

A Chemist's Guide to Density Functional Theory. By Wolfram Koch (German Chemical Society, Frankfurt am Main) and Max C. Holthausen (Humbolt University Berlin). Wiley-VCH: Weinheim. 2000. xiv + 294 pp. $79.95. ISBN 3-527-29918-1

More than a century ago, the great American physicist J. Willard Gibbs derived the phase rule, a central tenet of chemical thermodynamics. The phase rule proves that there *must be an equation* that relates the density of any pure substance to the pressure and temperature. Unfortunately, the phase rule does not tell us what this "equation of state" is, only that it must exist. Although the exact equation of state is still unknown for all substances, useful approximations have been derived empirically for many important materials by fitting mathematical functions to experimental data. Little or no theoretical justification exists for the specific form of these equations, which are generated with the simple objective of fitting experimental data better or in different ranges than presumably inferior approximations. This process ultimately leads to equations that have a good deal of predictive power and are useful in many branches of science and engineering.

A rather similar situation exists in modern density functional theory (DFT), which is the subject of this nice book by Koch and Holthausen. The Hohenberg−Kohn theorem was formulated about 40 years ago and shows that the total electronic energy of an atom or molecule is a function of the electron density. That is, there *must be an equation* that gives the energy in terms of the density, the latter being a quantity that depends only on the three spatial coordinates of the system in question. Since traditional methods for obtaining highly accurate solutions to the Schrödinger equation involve solving equations of considerably higher dimensionality, the search for the exact "exchange-correlation functional" (analogous to the equation of state) is an enticing goal. Although it is not yet known and may never be known, many useful approximations have been worked out by largely empirical means, and the generation of approximate exchange-correlation functionals is currently a cottage industry within the field of quantum chemistry. The accuracy of these equations has reached a point where DFT is usually more reliable than traditional Hartree−Fock (molecular orbital) calculations and comparable to that obtained when modest corrections have been added to Hartree−Fock results. It may safely be said that DFT is the best "semiempirical" approach yet developed for chemical applications, and the time for an overview of the theory and range of applicability of these methods has come.

A conspicuous hole in the computational chemist's library is nicely filled by this book, which provides a wide-ranging and pragmatic view of the subject. The book is broken into two parts. The first (Part A) deals with the Hohenberg−Kohn and Kohn−Sham theorems (the latter having significant computational importance), the treatment of spin in DFT approaches, a survey of most of the empirical exchange-correlation functionals in use today, and a very nice chapter (Chapter 7) that outlines exactly how most DFT calculations are carried out. Apart from the treatment of excited states, which I found to be a little bit behind the times, all of the most important subjects of DFT are covered competently and in an up-to-date fashion. The level of rigor found in this book is far below that in the classic treatment of Parr and Yang (*Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989), and this book is probably not the best choice for theoreticians who are trying to understand the intricacies of DFT. However, the book is really intended for practicing computational chemists, which nowadays includes many people with little or no formal theoretical training, and I believe that this community will be served well. A basic training in quantum mechanics equivalent to a typical first-semester graduate course provides all the background needed to read Part A and gain a basic understanding of modern DFT.

Part B provides a survey of the accuracy that can be achieved in DFT calculations, focusing first on the sort of examples usually used for benchmarking high-level calculations—structures, harmonic frequencies, thermochemistry, electrical and magnetic properties—and then dealing with some more involved areas of application, such as hydrogen bonding and relatively complicated organic reaction mechanisms. My only complaint about Part B is that most of the comparisons are made strictly among various combinations of exchange-correlation functionals and basis sets; much less effort is devoted to calibrating the accuracy of DFT against standard ab initio approaches. For example, I would have liked to have seen comparisons of DFT together with Hartree−Fock, second-order perturbation theory (MP2), and advanced coupled-cluster approaches such as CCSD(T), such as that found for NMR shifts of the pathological ozone molecule in Chapter 11 and the potential energy surface of malonaldehyde in Chapter 13.

In the field of traditional ab initio quantum chemistry—what DFT aficionados now call "wavefunction methods"—the standard books are *Modern Quantum Chemistry* by Szabo and Ostlund and two entitled *Quantum Chemistry* (one by Levine and the other by McQuarrie). The former is for the experts and goes into great detail about methodology, while the latter pair are written from a more practical perspective and are useful even to the nonspecialist. Now the field of density functional theory—the *haute couture* of quantum chemistry—has two such books. The comprehensive book by Parr and Yang that covers the subject in great detail is now complemented by this new book by Koch and Holthausen, which should justifiably become the favorite text on the subject for practitioners who aim to use DFT to solve chemical problems.

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Dendrimers II. Architecture, Nanostructure and Supramolecular Chemistry. Topics in Current Chemistry. Volume 210. By Fritz Vögtle (University of Bonn). Springer: Berlin, Heidelberg, and New York. 2000. x + 312 pp. $199.00. ISBN 3-540-67097-1

This book is the sequel to the first volume, entitled *Dendrimers*. In contrast to the earlier volume, which encompassed several topics unique to dendrimer chemistry, this volume reviews recent research in the dendrimer field and also covers several topical subfields for which dendrimer research makes a special contribution. Materials based on silicon, polyester, and organometallic dendrimers are highlighted with respect to their synthesis, reactivity, and physical properties. These materials are compared with other macromolecular systems, such as hyperbranched and linear polymers, to place the discussion in the broader context of macromolecular chemistry. Additionally, several exciting new applications of dendrimer scaffolds to problems in molecular recognition, supramolecular self-organization, catalysis, materials development, and diagnostics are discussed. Every chapter is extensively referenced and up-to-date and should fascinate chemists engaged in dendrimer or polymer research; however, nonspecialists interested in developing dendrimers for a specific application will find this resource particularly invaluable.

The first chapter, "Polyester and Ester Functionalized Dendrimers", introduces dendrimer research with a concise overview of synthetic strategies directed toward several early dendritic systems. The ready availability of ester-based dendrimeric materials makes these materials particularly attractive for a variety of bulk applications. With this in mind, the focus of this chapter emphasizes the synthesis and properties of dendrimers constructed with ester functionality at various locations throughout their structure. The development of these materials as unimolecular micelles, redox-active materials, radiation-curable resins, and liquid crystals is thoroughly reviewed. Furthermore, the application of ester-based dendritic cyclophanes and crowns to problems in molecular recognition is highlighted. Finally, the synthesis, classification, and chiroptical properties of chiral versions of these dendrimers are summarized. This chapter provides a comprehensive account of the current state of development of ester-based dendrimeric materials.

The second chapter, entitled "Silicon-Based Dendrimers", is similar in organization and content to the first chapter but emphasizes dendrimers containing silicon branch points. Synthetic strategies are outlined for all of the known classes of silicon-based dendrimers, including carbosilane, silane, silazane, and silatrane dendrimers. The review describes how the unique structure, connectivity, and flexibility of these novel materials create new opportunities for the development

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[*] Unsigned book reviews are by the Book Review Editor.

of modified materials, liquid crystals, and catalysts. In addition, contributions of these dendrimers to research in molecular recognition are included. Finally, the synthesis and properties of the structurally well-defined dendrimers are compared with their imperfect hyperbranched counterparts. This chapter thoroughly collates the vast literature associated with this class of dendrimers and would be an excellent resource for a nonspecialist seeking to become familiar with them.

In contrast to the first two chapters, Chapter 3, entitled "Host−Guest Chemistry of Dendritic Molecules", concentrates on how these novel structures contribute to studies in host−guest chemistry rather than discussing one particular structural motif. The discussion stresses how the internal void regions present in some dendrimers can be exploited in host−guest interactions and begins with a concise summary of the design of non-dendritic hosts that bind guest molecules through various noncovalent interactions, such as electrostatic, hydrophobic, and hydrogen-bonding interactions. Several controversial issues related to dendrimer conformation, such as whether dendrimers contain internal cavities, are addressed in the context of theoretical and experimental studies related to the conformational equilibria of dendrimers. The discussion also concentrates on the entrapment of molecules in dendrimers through both physical encapsulation as in "Meijer's dendritic box" and via hydrophobic interactions in unimolecular dendrimeric micelles. This review is not comprehensive but instead aims to present a critical discussion of how the conformational equilibria of dendrimer structures impact on host−guest interactions. An understanding of conformational equilibria of dendrimeric molecules will be crucial for most applications envisaged for these molecules, and this review does a good job of providing an excellent overview of the current state of knowledge in this area.

The fourth chapter, entitled "Supramolecular Dendrimer Chemistry—A Journey Through the Branched Architecture", expands the discussion in Chapter 3 to the effect of the three topologically distinct regions of a dendrimer (e.g., periphery, internal branch segments, and central core) on molecular recognition events. The potential for cooperative enhancement in the strength of binding interactions at the periphery of a dendrimer is explored, followed by a discussion of the effect of the branch segments and the central core on recognition events that take place in these regions. The chapter concludes with a review of how noncovalent interactions can drive dendrimer self-assembly. The conceptual discussions presented in Chapters 3 and 4 provide an invaluable source of information for researchers interested in developing functional materials from dendrimeric molecules.

Chapter 5, entitled "The First Organometallic Dendrimers: Design and Redox Functions", focuses on the synthesis of metallodendrimers and metallostars for applications in redox and catalytic processes. The primary emphasis of the chapter is on work performed in the author's laboratory directed at incorporating cyclopentadienyl metal sites at the periphery of dendrimers and stars. Applications of these novel structures to molecular recognition and catalysis are also addressed.

The book concludes in Chapter 6, "Dendrimers in Diagnostics", by describing research on the application of dendrimers as contrast agents for magnetic resonance imaging, scintigraphy, and X-ray techniques. A critical analysis of the limitations of current low-molecular-weight contrast agents is presented with regard to the tremendous potential of larger dendrimeric agents to modify pharmacokinetic and distribution behaviors. The chapter provides a succinct description of the recent success in developing dendrimeric contrast agents for medical diagnostics and should appeal to a broad readership interested in medical applications of dendrimeric materials.

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Organosilicon Chemistry IV: From Molecules to Materials. Edited by Norbert Auner (Johann Wolfgang Goethe-Universität, Frankfurt) and Johann Weis (Wacker-Chemie GmbH, München). Wiley-VCH: Weinheim. 2000. xviii + 834 pp. $155.00. ISBN 3-527-29854-1

This volume is a compilation of the lectures and poster contributions presented at the IV. Münchner Silicontage in April 1998. The synthesis and reactivity of new organosilicon compounds and their chemical applications are covered, as are some of the latest trends in silicon chemistry, like silicon biotechnology. To make the material current with the publication date, the references have been updated to include papers published during the past two years.

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Capillary Electrophoresis for Food Analysis: Method Development. By Richard A. Frazier, Jennifer M. Ames, and Harry E. Nursten (The University of Reading). Royal Society of Chemistry: Cambridge, UK. 2000. xiv + 128 pp. $99.00. ISBN 0-85404-492-2

This handbook is designed to help food analysts use capillary electrophoresis (CE) to develop new separation methods and should be useful to both novices and current practitioners in the field. Accordingly, the book proceeds from introductory chapters that describe the theory and background of CE to more detailed ones that explain the process of developing new CE methods. Step-by-step examples of CE method development are provided in three appendices, and a troubleshooting guide is also included.

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Annual Review of Physical Chemistry. Volume 51, 2000. Edited by Herbert L. Strauss (University of California, Berkeley), Gerald T. Babcock (Michigan State University), and Stephen R. Leone (University of Colorado, Boulder). Annual Reviews: Palo Alto, CA. 2000. xiv + 868 pp. $64.00 Individual Price. $134.00 Institutional Price. ISBN 0-8243-1051-9

This latest volume of *Annual Reviews* opens with a reminiscence by Dudley Herschbach of his 50-year career in physical chemistry. As with previous volumes, the remaining 25 chapters cover a broad range of topics at the forefront of physical chemistry, from gas-phase kinetics to the chemistry and microphysics of polar stratospheric clouds and cirrus clouds. This publication will be a valuable addition to the collections of individual researchers and libraries alike.

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Asymmetric Fluoroorganic Chemistry. Synthesis, Applications, and Future Directions. Edited by P. V. Ramachandran (Purdue University). American Chemical Society: Washington, DC. 2000 (Distributed by Oxford University Press.) 2000. x + 310 pp. $125.00. ISBN 0-8412-3639-9

This book contains 20 chapters from leading experts in fluoroorganic chemistry who participated in the Asymmetric Synthesis of Fluoroorganic Compounds symposium held in August 1998. The topics explored include reagent- and substrate-controlled asymmetric synthesis, synthesis of fluoroorganic targets, bioorganic synthesis of asymmetric fluoroorganic compounds, and asymmetric fluoroorganic chemistry in materials chemistry, agrochemistry, and pharmacy.

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