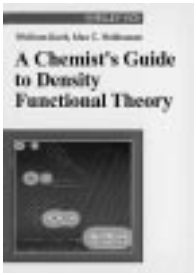
Chemical Solutions

A Chemist's Guide to Density Functional Theory. By *Wolfram Koch* and *Max C. Holthausen.* WILEY-VCH, Weinheim 2000. xiv+294 pp., hardcover DM 198.00.—ISBN 5-527-29918-1

During the past 15 years quantum chemistry has been transformed from a field for a relatively small number of specialists to an essential part of large sections of chemical research. Among other factors, developments in the methodology of approximate density functional theory (DFT) have played the most prominent role in this dramatic change. Almost as a natural consequence, the 1998 Nobel Prize for Chemistry was awarded jointly to John A. Pople, a pioneer of the more traditional ab initio quantum chemical methodology, and to Walter Kohn, the father of the conceptual basis of modern DFT.



Due to the remarkable success story of DFT in chemistry since the mid-eighties, DFT methods are now available in most of the generally accessible quantum chemistry programs. Therefore, more and more chemical researchers come into contact with DFT. They may not be quantum chemistry experts in terms of their prior education, but they are attracted by the enormous potential DFT holds for solving chemical problems.

This section contains book reviews and a list of new books received by the editor. Book reviews are written by invitation from the editor. Suggestions for books to be reviewed and for book reviewers are welcome. Publishers should send brochures or (better) books to the Redaktion Angewandte Chemie, Postfach 101161, 69451 Weinheim, Germany. The editor reserves the right of selecting which books will be reviewed. Uninvited books not chosen for reviews will not be returned.

While there exist a number of excellent textbooks on DFT,[1] these have traditionally been directed more towards physicists or specialists in quantum chemistry. A gap has existed in the textbook literature insofar as there have been no publications to guide chemists interested in the application of DFT to chemical problems. The present book by Koch and Holthausen attempts to bridge this gap. To anticipate the conclusion of this review, the authors have done an excellent service to the chemical community.

The book is divided into two major parts: Part A, "The Definition of the Model" and Part B, "The Performance of the Model". It is the well-balanced combination of these two parts that will make the book so valuable for chemists. In Part A the theoretical background of modern DFT is covered in a very logical way. After a very brief recapitulation of some elementary quantum chemistry in Section 1, the important concepts of the electron density, the pair density, and the Fermi and Coulomb holes are introduced in Section 2. The latter form the basis for a very pictorial approach to understanding electron correlation and exchange throughout the first part of the book. After a brief Section 3 covering early attempts at DFT, such as the Thomas–Fermi model and Slater's method, the Hohenberg–Kohn theorems are introduced in Section 4. The Kohn–Sham approach, which is the basis of all modern DFT methods, is described in detail in Section 5, followed in Section 6 by a thorough exposé on the search for approximations to the elusive exchange correlation functional of Kohn–Sham DFT. Section 7 concludes Part A with some important aspects of the technology involved in state-of-the-art implementations of DFT in quantum chemistry computer programs. Due to its pictorial style and the restriction to the essential points, Part A will be a very useful introduction to the concepts of DFT for many nonspecialists. This part benefits from the incorporation of some of the clearest recent treatments of DFT in the quantum chemistry literature by E. J. Baerends, A. D. Becke and others. A question of particular relevance to chemists, that of whether the Kohn–Sham orbitals provide a basis for chemical interpretations of electronic structure, is also discussed convincingly (Section 5.3.3).

Part B, equally as important for the target readership as Part A, deals with the accuracy that can currently be achieved or expected in DFT calculations. In particular, the performance of the available approximate exchange correlation functionals for computations of many different quantities of interest to chemists is analyzed in detail. This is done by bringing together the results of a vast number of systematic validation studies carried out during the past few years. Section 8 starts with molecular structures and vibrational frequencies. This is followed by relative energies and thermochemistry (Section 9, which includes not only quantities like atomization energies and bond strengths, but also ionization energies, electron affinities, and electronic excitation energies), electrical properties (Section 10), and magnetic properties (Section 11, covering NMR chemical shifts, nuclear spin–spin coupling constants, EPR *g*-tensors, and hyperfine coupling constants). Section 12 deals with hydrogen bonds and weakly bound systems, and Section 13 concludes the book by asking how DFT performs for questions of chemical reactivity, in particular for activation barriers (examples are taken mainly from organic chemistry, but H_2 activation by FeO^+ is also dealt with). Throughout these sections, the scope and limitations of current DFT approaches are treated in an honest and thorough way. Part B might seem frightening at first glance, due to the massive number of statistical comparisons of numerical data obtained

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with different DFT approaches. However, it is clear that a judicious use of DFT presently has to rely heavily on such comparisons. As there is no systematic way of approaching the elusive exact exchange correlation potential of Kohn–Sham theory, present-day DFT has a degree of semi-empirical character. On the other hand, it may well be argued that it is also by far the most successful "semi-empirical" quantum chemical theory. Therefore it is mandatory for the chemist using DFT methods to acquire some background knowledge on the merits and shortcomings of the various functionals in use. The extensive data compilations in Part B should help the nonexpert to choose the best methodology to answer a given chemical question.

What is missing from the book? There are certainly some intricate features of the theory which have not been treated. For example, two aspects that are not covered adequately are: a) the DFT-based derivation of qualitative chemical concepts such as electronegativity or hardness by Parr and his school, and b) the topological analysis of the electron density and of quantities derived from it. And, as the authors state in their foreword, the growing field of plane-wave approaches and of DFT-based ab initio molecular dynamics simulations (Car–Parrinello and related methods) is outside the scope of the book. These omissions appear unavoidable, given the relatively modest size of the book (294 pp.). Some of these points have already been addressed in detail in other books.[1,2] Others should find their entry into future editions. Future updates will undoubtedly be required to keep up with the remarkable pace of development in the field.

Overall, *A Chemist's Guide to Density Functional Theory* is exactly what the title suggests. It should be an invaluable source of insight and knowledge for many chemists using DFT approaches to solve chemical problems. In view of the growing importance of DFT in many areas of chemistry, it can be warmly recommended as a textbook for parts of courses on computational chemistry. In this context, its price will not make the book very attractive to students. A more affordable paperback student edition would therefore be highly desirable.

[1] R. M. Dreizler, E. K. U., *Gross Density Functional Theory*, Springer, Heidelberg **1995**; R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York **1989**; E. S. Kryachko, E. V. Ludena, *Energy Density Functional Theory of Many-Electron Systems*, Kluwer Academic Press, Dordrecht **1990**.

[2] R. W. F. Bader, *Atoms in Molecules, A Quantum Theory*, Clarendon Press, Oxford **1994**.

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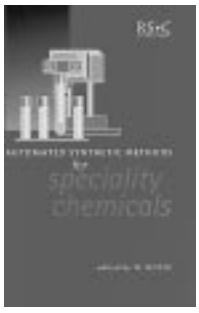
Automated Synthetic Methods for Speciality Chemicals. Edited by *William Hoyle*. Royal Society of Chemistry, Cambridge 2000. viii+114 pp., hardcover £ 49.50.—ISBN 0-85404-825-1

This small and relatively low-priced book describes the application of high-throughput experimentation for research and development in the specialty chemicals industry and by one catalyst producer. In the first part, short and useful definitions of terms used in this book and the literature are given. In the following chapters, which are based on a two-day symposium, several quite diverse articles about microreactors for the gas and liquid phase, as well as solution-phase robots, are presented. Then, a number of case studies describing the testing of heterogeneous catalysts, developments in the synthesis of dyes, as well as applications to various reactions in process development, are described.



The description of the robots and the various uses is easy to read, and gives a helpful overview of the possibilities of automated methods, even though the connection to specialty chemicals is not always obvious. What is somewhat missing in this book is a critical assessment of the various approaches, indicating which applications might be useful and where one should rather not try. Furthermore, it would be important for the reader to know the different systems presently on the market, what they cost, and how they compare (usually there is only one specific brand described in each article). The most serious drawback of the book is that there is only very little discussion about the problems associated with the acquisition, processing, and storage of the enormous amounts of data generated by such robots. This is certainly an aspect of automated methods and high-throughput testing which needs much consideration.

The book contains a useful index, giving easy access to the corresponding chapters. Unfortunately, the quality of some of the (in principle useful) illustrations is unbelievably low . It certainly does not meet today's standard, especially not for a book about high-tech applications.

In conclusion, this small book is very easy to read and brings the reader up to date about many practical aspects of automated synthetic methods and a number of specific microreactors and robotic systems. The chapters on the applications of these machines in the various areas of chemistry are especially useful for R & D managers who have to decide whether to invest in this technology or not (yet). It is clear, however, that with the current speed of innovation in this area the book will not remain up-to-date for very long.

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