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Book review

Parr, R. G., Yang, W.: Density-functional theory of atoms and molecules. Oxford University Press, New York Oxford Toronto 1989, 333 pp. (ISBN 0-19-504279-4) $55.00

This volume is no. 16 of *The International Series of Monographs on Chemistry*. The authors' goal of giving "a coherent account of the (density-functional) theory as it stands today" has been attained in this excellent book. The approach of Parr and Yang is to favor a precise description of the theory instead of showing many applications of it.

The first two chapters entitled "Elementary wave mechanics" and "Density matrices" along with appendices on functionals and second quantization set a firm ground for the remainder of the book. The Hohenberg–Kohn theorems are presented along the lines of the Levy constrained-search formulation in such a way that the generalization to finite temperature follows naturally. Chapters 4 and 5 deal with derivatives of the energy and of the density with respect to the number of electrons. This leads to the discussion of the related concepts of chemical potential, electronegativity, hardness, softness, the Fukui function and local softness and hardness, all of which have received major contributions from Parr, Yang and their coworkers. The Thomas–Fermi and related models that do not make use of orbitals are presented in chapter 6. The difficult problem of obtaining an accurate kinetic energy functional is appropriately emphasized. The next two chapters cover the Kohn–Sham method in which an accurate kinetic energy functional is obtained at the cost of introducing orbitals. A section on the integral formulation recently developed by Yang is included. The various approaches to an accurate exchange-correlation energy functional are especially well covered. Chapter 10 is more chemically oriented and consists largely of contributions from Parr and his coworkers to the understanding of chemical binding within DFT. It includes a definition of "atoms in molecules", a simple model on which is based a discussion of the rule "hard (soft) acids prefer hard (soft) bases" and a bond-charge model of the chemical bond. Various topics are treated in the remaining two chapters. Among others: excited states, time-dependent systems, density-matrix-functional theory, scaling relations and a maximum entropy approach to density-functional theory (DFT).

A commented bibliography of 22 main reviews and over 650 references complete the book.

The text presents the theory at an advanced level and brings the reader to the current state-of-the-art in DFT. A basic knowledge of quantum chemistry is necessary to its full appreciation. However, the very good introductory chapters and the appendices make this book reasonably self-contained and prior exposition to DFT is not necessary.

Parr and Yang's book should prove extremely valuable to researchers in the field of DFT for its unified presentation of the basic theory and many advanced topics and its extensive and up-to-date bibliography. In these respects it fills a gap in the literature of DFT. It could also form a good basis for a graduate level course but should be supplemented with additional readings and exercises.

We especially appreciated two qualities of this book. First the connection of DFT with the better known wavefunction approach to the quantum mechanics of many-body systems is stressed at the very beginning and emphasized throughout. The authors have been careful to state clearly the assumptions and approximations when they occur and to distinguish approximate from exact relations. This should prove particularly valuable for those who possess a background in quantum chemistry and want to learn DFT. Second, the authors stress the appealing and intuitive physical picture that comes with using the density instead of the wavefunction as the basic quantity. In particular, chapters 4, 5 and 10 support the authors' opinion expressed in their last sentence: "We expect the language of chemistry of the future to be replete with the idiom of density-functional theory."

Our only negative comment is that numerical results for molecules are too scarce. An additional chapter showing the most accurate results for a few well-chosen molecules (a tentative list could include: H_2, O_3, CH_2, Cr_2, a few representative "large" organic molecules, organo-metallic complexes and metal clusters) could illustrate the strong and weak points of DFT in its current state. Other interesting topics have received limited attention, as is unavoidable in a book of this size, but are appropriately mentioned at the end with key references.

Overall this is a very good book worth its price for anyone interested in density-functional theory.

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