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BOOK REVIEWS

Chemical Reactivity Theory: A Density Functional View. Edited by Pratim Kumar Chattaraj (Indian Institute of Technology, Kharagpur). CRC Press (an imprint of Taylor & Francis Group): Boca Raton, FL. 2009. xviii + 576 pp. $161.96. ISBN 978-1-4200-6543-5.

The popularity enjoyed by density functional theory (DFT) today probably could not have been foreseen 30 years ago when it was met with skepticism by the quantum chemistry community. Today, the alphabet soup of modern density functionals has become the workhorse for the accurate theoretical study of a myriad of chemical systems extending from materials to biomolecules. As a contribution to this field, *Chemical Reactivity Theory: A Density Functional View* was not meant to serve as a guide for the novice on how to perform successful density functional theory calculations, but rather as an exposition on conceptual density functional theory or how chemical reactivity concepts can be derived from the electron density.

The first chapter of the book, written by Parr, one of the pioneers in the field, provides an interesting historical account of the birth of conceptual DFT. The remainder of the text is devoted to theoretical developments of the properties of electron density and chemical reactivity indices with examples of their application. Chapters 2−7 provide a satisfying primer to concepts related to DFT and the exchange-correlation potential, a review of bonding and quantum chemistry, and an introduction to time-dependent DFT (TDDFT) for molecules. Chapter 6 is a short review of the basic formalisms of TDDFT of many-electron systems for time-dependent scalar potentials as well as electric and magnetic fields. However, it is deficient in its description of the linear response theory that is currently enjoying overwhelming popularity for the prediction of excitation energies and oscillator strengths. Moreover, recent advances in the theory for calculation of excited state properties from TDDFT are omitted (Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117*, 7433). These omissions exclude a rapidly expanding area of the field. Chapter 8 is a description of the interesting connection between TDDFT and Bohmian mechanics and provides several timely references on the subject.

Chapters 11−20 present a well-organized compendia of chemical reactivity descriptors including chemical hardness (Chapter 11), Fukui functions and local softness (Chapter 12), electrophilicity (Chapter 13), population analyses (Chapter 15), molecular quantum similarity (Chapter 16), molecular electrostatic potential (Chapter 17), and the following functions: Fukui (Chapter 18), shape (Chapter 19), and electron localization (Chapter 20). A chapter on the structure, bonding, and reaction mechanisms of the bent metallocenes is embedded among these. It provides an interesting account of the authors' accomplishments in the area; however, it seems oddly placed because the chemical descriptors described elsewhere in this section are not invoked in these studies. Thus, it contributes little to the conceptual theme of the volume.

Discussion of the individual chemical reactivity descriptors is followed, in my view, by a group of very exciting chapters on electric field (Chapter 25) and solvent (Chapter 26) effects on chemical reactivity. In Chapter 27, Geerlings provides a well-written, concise summary of relevant applications of conceptual DFT to understand hydrogen bonding, $\pi-\pi$ stacking, and dispersion interactions. These principles undoubtedly form the basis for the application of conceptual DFT to study intermolecular interactions and biochemical phenomena. Moreover, Geerlings recently contributed to a review summarizing the application of these chemical descriptors to understanding enzyme mechanisms and discussed their complementarity to methods such as hybrid quantum mechanics/molecular mechanics (see Roos, G.; Geerlings, P.; Messens, J. *J. Phys. Chem. B* **2009**, *113*, 13465). Although relatively simple examples of biological relevance are illustrated, e.g., $\pi-\pi$ stacking of the benzene−cytosine dimer, examples like those given in this review would have been of value to experimentalists.

The remaining chapters provide a broader interpretation of chemical reactivity descriptors, including discussions on aromaticity and quantitative structure−activity relationships. Chapter 28 is a concise survey of aromaticity in organic molecules and provides useful discussion of currently tested descriptors. These include simple chemical models, e.g., Clar's π-sextet rule, to more sophisticated examples based on calculations of electronic structure. Furthermore, remaining controversies surrounding aromaticity in metallabenzenes and all-metal clusters are discussed. Complementary to this discussion is an interesting case study of aromaticity in boron clusters and application of an adaptive natural density partition method that is described in Chapter 29.

Despite some overlap of the material covered in many of the chapters, *Chemical Reactivity Theory: A Density Functional View* is a contemporary treatise on the rapidly emerging field of conceptual DFT. The book is moderately well organized with an encyclopedic flavor in some sections. I would not recommend its use as the primary text in an advanced undergraduate or early postgraduate course. However, it will be a useful addition to the libraries of both experimental and theoretical practitioners of DFT methods.

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