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BOOK REVIEWS

Scanning Tunneling Microscopy in Surface Science, Nanoscience and Catalysis. Edited by Michael Bowker and Philip R. Davies (both at Cardiff University, United Kingdom). WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim. 2010. xiv + 244 pp. $195.00. ISBN 978-3527-31982-4.

As we approach the 30-year mark since scanning tunneling microscopy (STM) was invented in 1981, many books can be found throughout the literature detailing the basic principles of STM and describing how the technique has been pivotal in the birth of the field of nanoscience. With the ability to both image and manipulate single atoms and molecules, STM has proven time and time again to be an invaluable asset in many fields across the broad disciplines of physics and chemistry.

This book, as the title suggests, can be considered a state-of-the-art overview of STM-related advances in surface science, nanoscience, and catalysis. Although this review will not necessarily teach the reader how to use STM by belaboring the basics, it covers in detail the advances in many areas in which STM has been established as an important experimental method. Each chapter is a survey of the current literature in a variety of fields, from chiral surfaces to catalysis and the challenges of using STM to study oxides. The authors, which include Baddeley and Richardson, Becker and Wandelt, Yang and Goodman, Teobaldi, Lin and Hofer, Kolb and Simeone, Netzer and Sumev, Somorjai, Tao and Butcher, and Pang and Thornton, have been carefully chosen as leaders in their respective fields. Eight 30−50-page chapters provide fairly comprehensive, up-to-date reviews and extensive references for each topic.

The first chapter on chiral surface chemistry is an excellent summary of this relatively small but rapidly advancing field. The Somorjai chapter provides ample details on the construction of a unique high-pressure STM used to interrogate surface reconstructions and reactions at catalytically relevant pressures. Also of special interest to any experimentalist who uses STM is a chapter on the theory surrounding simulating STM images. The authors of this chapter detail the capabilities and complications of using computational methods to imitate the biased interaction of a scanning probe tip and a conducting surface. This is a must-read for those who have never personally attempted to simulate an STM image.

In summary, this book is a very useful addition to your bookshelf if you or your collaborators use or even refer to scanning tunneling microscopy data in research and publications. Whether you read only the one chapter related to your area or the entire book to gain an appreciation of the vast utility of STM, you are bound to learn something new about this unique instrument and its continued impact on nearly every aspect of surface science and nanoscience as well as its ever-increasing contributions toward understanding catalysis.

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JA106375E

10.1021/ja106375e

Quantal Density Functional Theory II. Approximation Methods and Applications. By Viraht Sahni (City University of New York, Brooklyn). Springer-Verlag: Berlin, Heidelberg, New York. 2009. xviii + 426 pp. $159.00. ISBN 978-3-540-92228-5.

In Volume I of *Quantal Density Functional Theory* (QDFT), we are presented with a unique view on the nature of density functional theory (DFT). In Volume II, we find the inner workings of that theory. With this volume, the reader continues to benefit from the same great clarity of thought and consistency of ideas that characterize the first volume. To its credit, *QDFT II* possesses an even greater expansiveness and richness of explanation that many readers will find very agreeable.

Such scope begins immediately with the Introduction, where we find a detailed roadmap of the basic ideas behind QDFT. Not only does the map point the reader forward to the material in *QDFT II*, it also provides valuable references to *QDFT I*. This chapter is insightful, as well as concise. I cannot recommend strongly enough starting here so that readers will be at liberty to peruse the volume at their discretion.

Sahni also provides a number of diagrams, both depicting QDFT and relating it to traditional views of the foundations of DFT. Figures 1.1 and 1.2 clarify the generality of QDFT, which comes from the virial-theorem foundations of QDFT, the origins of novelty in Sahni's point of view. Another figure (4.3) depicts the generalization of the fundamental theorems of Hohenberg and Kohn. These generalizations come from gauge transformation arguments and do not appear in *QDFT I*.

There are a great many other useful figures, which I do not have the space to describe here. That said, there is little doubt that Figure 6.1 is the most crucial and the most telling. It is a "wiring diagram" of the complete inner workings of QDFT that shows both its strengths and its present limitations. The foundations of QDFT are illustrated in the top of the diagram as a set of model wave functions with undetermined parameters and referred to as wave function functionals. These functionals are constrained to yield one or more average properties, such as normalization to the number of electrons, the Coulomb sum rule, etc. The process of constraining is a difficult one that the community as a whole is working to advance. Given a reduction process to generate the electron density and associated quantal sources and fields, one constructs the companion noninteracting system that is analogous to the Kohn−Sham (KS) equations. In spite of the formal similarities, the foundations are very different, as is stressed many times, with the KS equations grounded in the variational arguments of the Hohenberg−Kohn theorem and QDFT grounded in the differential virial theorem.

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The route backward to the wave function functionals from fields, sources, and densities closes the loop in the iterative process between these states and the effective potentials of the noninteracting system. This part of the route is even less well-known than the reduction process from wave functions to sources and electron density. To be slightly more complete in notation, the χ parameters in the wave function functionals should be carried into the orbitals describing the noninteracting system via the effective potential $v_{\mathrm{ee}}(\mathbf{r})$.

In spite of these difficulties, Sahni and co-workers have managed to produce a large set of examples that have been worked out in great detail and are wonderfully illustrated. Among the most interesting to me are the hydrogen molecule and the metal−vacuum interface systems. In the example of the hydrogen molecule, the ground-state wave function at the equilibrium bond length of the molecule is reduced to generate the required QDFT quantities. The accuracy of the reduction process is remarkable, as is the structure of the various distribution functions for this highly inhomogeneous system. In the metal−vacuum interface system, one is faced with an extended system. In the system treated at the level of the jellium model, one finds unexpected, counterintuitive properties for the delocalization of electron holes near the interface. Such a result has been very difficult to achieve by other approaches. There are many other such examples presented in this book.

When one has a unique point of view such as that with QDFT, the opportunities for lines of research are virtually limitless. Sahni hints at some of these opportunities in the Epilogue, and a few others come to my mind. For instance, one might wonder about the relationship of the QDFT point of view to contracted Schrödinger equations. The importance of the electron−nuclear cusp condition is demonstrated very convincingly in this book. It seems that the electron−electron coalescence cusps might play a pivotal role as well. Also it seems possible that a constraint, such as diamagnetic susceptibility, might limit which excited states are accessible. Finally, studies of electron gases and the hydrogen molecule from the QDFT point of view that undergo the complete cycle as illustrated in Figure 6.1 and an investigation of excited states would be most interesting. These are daunting tasks to be sure, but the results would be hugely insightful, if they can be achieved. Regardless of the specific paths pursued, more fascinating developments from QDFT will undoubtedly be following.

This book could serve two readerships. One would clearly be serious students and practitioners of density functional theories because *QDFT II* is replete with fresh ideas and insights, regardless of whether one subscribes to the QDFT view. The other type of readership could very well be beginning students of the subject. The basic concept of QDFT rests on a concept in quantum mechanics that is commonly covered in introductory courses. In *QDFT II*, the examples serve to illustrate the many components of the general theory and may serve as the route to understanding the formal theory of QDFT. They are also self-contained, permitting the reader to select topics as desired and according to interests. I recommend this volume to anyone with interests in or curiosities about density functional theories.

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JA105861Z

10.1021/ja105861z