APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 717
Published online in Wiley InterScience
(www.interscience.wiley.com)

Book Review

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Computational chemistry of solid-state materials: a guide for materials scientists, chemists, physicists and others

Wiley-VCH, 2005,
294 pp; price £70.00/€105.00
ISBN 3-978-3-527-31410-2 (hardcover)

Computers are getting ever faster and ever cheaper, which means that most researchers now have access to the computer power required to apply quantum chemistry to molecular and solid-state problems. Software companies are keen to capitalize on this trend and provide packages that can use impressive graphical tools to display the results of the number crunching. However, assessing the reliability of the underlying methodology and interpreting the results in a chemically meaningful way remains a challenge. Several books are now available related to molecular calculations, not least Cramer's introductory text in the same series as the current title. There are fewer sources, however, for the materials chemist interested in the solid state. Dronskowski attempts to fill this gap with a book devoted largely to periodic electronic structure techniques.

Having tried to understand the results of periodic density functional theory calculations in terms of chemical bonding, I have always been grateful for the small monograph by Roald Hoffmann, who writes the introductory remarks for the current volume. Hoffmann took an almost cartoon-like approach to extending molecular orbital theory into the infinitely periodic solid state and allowed his readers to visualize the origin of band theory. This contrasts with the usual exposition of band theory based on the physics of the 'nearly free electron' derived for the treatment of simple metals. It is easy for such approaches to lose the reader from a chemistry background in the dark corners of reciprocal space before they have made the link to the more comfortable concepts of bonds and anti-bonds. In his preface Dronskowski pitches the new volume at the laboratory worker who is an experimentalist with an interest in computational approaches. There is certainly a growing number of people who fall into this category and this book sets off with a review of empirical models that will be familiar to them. He also extends the approach of Hoffmann by supplementing the orbital diagrams with more detailed mathematics and includes concepts such as exchange and correlation in a more rigorous, yet readable, manner.

In Chapter 1 basic ideas, such as the use of ionic radii and the radius ratio rule for predicting the structure types of ionic materials, are reviewed. This section is accompanied by handy tabulations of Shannon's ionic radii and bond-valence parameters. The introduction is quite gentle but is used to set the scene by discussing structures in terms of lattice energies and their decomposition into the classical contributions. The text moves in a quite standard way from strongly ionic (NaCl etc.) to systems in which covalent interactions are dominant (SiO_2 etc.). Here, cases in which covalency is prevalent are treated using Pauling's rules to explain why silica structures form predominantly corner-sharing tetrahedra, for example. Chapter 2 moves on to a discussion of quantum chemical approaches applied to the solid state. The approach is to move from Hückel theory of molecular systems to the tight binding approach in the solid state. The discussion introduces terms from computational chemistry, such as the widely used basis sets formed of Gaussian-type orbitals to describe molecular orbitals in a straightforward manner. The solid state arrives with Bloch's theorem to take the reader from the isolated molecule to the infinite periodic lattice. Band structures are considered with a few good pictorial descriptions reminiscent of Hoffmann's book. As pointed out earlier, this is a natural way for the chemist to approach band theory and the presentation here is logical and well written. The discussion requires the introduction of reciprocal space for which analogies from X-ray crystallography are drawn. Some concepts from practical computational chemistry, such as the use of *k*-point sampling, are slipped in here, but in general the practicalities of running programs are avoided. At the end of this chapter the author gives a more in-depth, mathematical, description of the material, and energy partitioning schemes are introduced using the density matrix approach. The concept of exchange and correlation energy is then used to lead into a comparison of Hartree Fock and density functional methods. Chapter 3 provides a series of examples largely drawn from the author's own work. Each section begins with a paragraph on the technological importance of the system being discussed, which defines the physical characteristics that the calculations aim to rationalize or predict. The first of these is a simple comparison of DFT calculation results on the structure of CaO to show that both back-of-the-envelope empirical methods (such as the radius ratio rule) and the sophisticated DFT computations correctly predict [NaCl] the preferred structure. The more complex examples concentrate on the magnetic properties of materials which are a particular interest of the author. Calculations allow comparisons that are impossible experimentally, and this is drawn out in a comparison of non-magnetic α-Fe and the true ferromagnetic system. This nicely illustrates how the exchange interaction leads to an imbalance in spin state populations through a comparison of density of states plots for the real and fictitious metals. Other examples cover metal–metal bonding in transition metal nitrides, alloys and nanocomposites. Each example gives clear explanations of the interpretation of the theoretical results using the band structure, density of states and COHP plots.

The text is written in a modern, almost flippant, style which keeps the reader's attention through the more conceptually difficult parts of the text. There are also useful tabulations of basic data such as the parameters required by extended Hückel theory for almost all of the periodic table. Its strength lies in linking basic chemical concepts to the band structure and density of states plots produced by density functional theory calculations. However it is not a manual on best practice, for example the assessment of the convergence of calculations with respect to basis set size and *k*-point sampling is absent. I did enjoy reading it myself and would recommend it as background material for new Ph.D. students whose research will involve applying quantum chemistry to solid-state problems.

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DOI:10.1002/aoc.1257