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BOOK REVIEWS

Parallel Computing in Quantum Chemistry. By Curtis L. Janssen and Ida M. B. Nielsen (Sandia National Laboratories, Livermore, CA). CRC Press/Taylor & Francis Group: Boca Raton, FL. 2008. xx + 210 pp. $89.95. ISBN 978-1-4200-5164-3.

Computational chemistry has become a powerful tool for theorists and experimentalists alike for a number of reasons. Development of accurate *ab initio* and density functional techniques, coupled with advances in computer hardware and software, has made predictions of molecular structure and energetics feasible for a wide range of molecules. This book focuses on one aspect of these advances, parallel computing.

Its first part focuses on issues in computer science related to parallel computing. This includes a detailed description of different network architectures and message-passing schemes. Descriptions of computer architectures are not as detailed, but detailed enough to understand issues related to performance of parallel algorithms. This part ends with two informative chapters on evaluating parallel performance and parallel program design. In particular, the chapter on parallel program design does an excellent job of outlining the three primary issues with parallel computing: distribution of work, distribution of data, and communication.

The second part of this book focuses on parallel implementations of specific *ab initio* techniques. Strategies for evaluation of electron repulsion integrals (ERIs) and construction of Fock matrices are presented. The book also details approaches for transforming atomic orbital ERIs into the molecular orbital basis and their subsequent use in second-order Møller−Plesset perturbation theory. Methods involving multiple configurations, such as configuration interaction, are not discussed, although a discussion of such methods would have been useful since they present significantly different challenges compared to Hartree−Fock-based methods.

Besides being an excellent resource for those who are new to parallel computing, this book would be valuable for those who are new to writing any type of electronic structure code. The authors do an excellent job of describing the outlines of various basic electronic structure programs and discussing different strategies for their parallel implementation. Their use of diagrams and flow charts makes the book very accessible to those who have limited knowledge of computer science. This book would be an excellent first-read for those who intend to write electronic structure programs.

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JA809443M

10.1021/ja809443m

Ferrocenes: Ligands, Materials and Biomolecules. Edited by Petr Štěpnička (Charles University, Prague). John Wiley & Sons, Ltd.: Chichester. 2008. xii + 656 pp. $240. ISBN 978-0-470-03585-6.

This well-written and attractively produced book is billed as a sequel to, and update of, an earlier "Ferrocenes": a 1995 collection of review articles edited by Togni and Hayashi (reviewed in *J. Am. Chem. Soc.* **1996**, *118*, 6333−6334). Although the organization is similar to that of the previous volume, most of the contributors are new, providing a fresh viewpoint for much of the material covered. Also, the large majority of references cited were published after the earlier one was completed, with coverage running through 2006.

Part I (a little less than half the total) is devoted to ferrocene-based ligands with a strong emphasis on their role in catalytic applications, including asymmetric catalysis, which was treated extensively in the earlier monograph. The wide range of nickel- and palladium-catalyzed C−C and C−X coupling reactions are given particular focus—nearly all of the major advances in synthetic methodology that make use of this important subfield postdate the earlier book. Since ferrocene derivatives, especially 1,1′-bis(diphenylphosphino)ferrocene (dppf) and its analogues, have been found to be the ligands of choice in many cases, this part of the book would potentially be of considerable interest to researchers involved in organic synthesis and homogeneous catalysis.

Unfortunately, the presentation is not really very user-friendly. The material is organized according to the structural type of the ligand, e.g., monodentate ligands, dppf, dppf analogues, other bidentate ligands, etc., presumably to make life easier for the individual authors; however, readers looking for information on a particular reaction type will find the relevant examples scattered throughout the various chapters as a result. Organization based on reaction type would have been much more useful. The one adopted here makes it very difficult to discern patterns that might help one choose the best class of ligands to try out on a new reaction. It is even harder to see just what distinguishes species such as dppf from nonferrocene-based ligands. Many of the contributors do try to address this point—the "unique" conformational flexibility resulting from rotation of Cp rings about the metal-ring axis is most commonly mentioned—but none has been very successful in reaching any useful generalizations.

Several of the ligand-oriented chapters also refer to a role for the electronic properties of the ferrocene moiety, specifically the possibility of redox activity, but there are few, if any, examples where that factor exerts a clear effect upon catalytic properties. On the other hand, it *is* central to most of the topics covered in Part II: ferrocene-based sensors, electro-optical materials, polymers and dendrimers, liquid crystals, crystal engineering, and bioorganometallic chemistry. The chapters in this section vary considerably in length, as well as in the level and comprehensiveness of coverage. Some, particularly those on electro-optical materials and thermotropic liquid crystals, will be of interest primarily to specialists in their respective fields. Others give more attention to providing the background needed to appeal to a wider general audience. The chapter on ferrocene-based sensors in particular does a nice job of explicating the basic principles involved.

The article on the bioorganometallic chemistry of ferrocene is the longest single chapter in the book, but also the one that has virtually no parallel in the earlier volume, although the

10.1021/ja809443m CCC: $40.75

authors note that it is substantially based on their 2004 article in *Chemical Reviews*. It provides an extensive treatment of methods for preparing conjugates of ferrocene with biorelevant molecules, such as peptides and proteins, nucleic acids, carbohydrates, hormones, etc., and their applications, mainly as spectroscopic and/or redox-active probes. A section on possible medicinal uses of ferrocene derivatives, many of which involve replacing phenyl by ferrocenyl in known compounds, reports mostly negative findings, although there are a couple of intriguing leads: ferrocene-containing analogues of tamoxifen and chloroquine show interesting activity for treatment of breast cancer and malaria, respectively. There is some indication that the redox behavior of the ferrocene moiety plays an important role, at least in the former.

Although I doubt whether readers outside the ferrocene chemistry community will want to acquire this book, especially considering its rather steep price, or read it in its entirety, many may well find it rewarding to sample a few chapters that are relevant to their main interests or just to get an idea of what can still be done with this "classic" organometallic molecule.

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JA809247B

10.1021/ja809247b

Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach. By Yoshikata Koga (The University of British Columbia, Vancouver). Elsevier: Amsterdam. 2007. xiv + 296 pp. $225. ISBN 978-0-444-53073-8.

New insights can come from new information, but they can also come from looking differently at existing information. In this book, Koga tries to do exactly that. The fundamentals of chemical thermodynamics have been around for over a century, and their application to aqueous solutions has been studied numerous times. Here Koga gives a new twist to solution thermodynamics based on two considerations. The first is his opinion that excess Gibbs free energy is a better way to quantify the state of a solute than its activity. In the author's words: "The usage of a_i seems to us to have some apologetic connotation; apologetic in the fact that the reality does not follow [ideal solution theory]". The second consideration is the fact that subtle trends in a function can be highlighted by taking the derivative. Hence, Koga explores all the possible first, second, and third derivatives of the excess Gibbs free energy of various aqueous solutions and tries to extract information on the structure of the solution from the data. In this context, enthalpy is a derived quantity of the Gibbs free energy and so are entropy, volume, and the partial molar properties. One further derivative of the latter with respect to composition leads to solute−solute interaction properties, which play a major role in this book. A particularly interesting application of these interaction properties is the study of hydration of solutes, conducted with competitive hydration experiments using a probe molecule like 1-propanol.

The book is a mixed success. The author has produced an impressive body of work during his career, and he draws mainly from that work for this book, with about a quarter of the reference list being to his own work. This is both a strength and a weakness. Needless to say, Koga is more qualified than anyone to write this book, but this is at the expense of scientific detachment from the work that is being described. It is fair to say that Koga and his co-workers have developed their own scientific field over the past decade or two, but the number of researchers independent of Koga's group that have joined the field is limited; as a consequence, both the field and this book have suffered from this void. Some of Koga's interpretations of thermodynamic data are idiosyncratic at best, and facts are not clearly distinguished from speculations. While reading the book, I often found myself trying to formulate alternative explanations when I found the author's analysis unsatisfactory. Nevertheless, some powerful tools are developed, and some of the insights, especially from Koga's 1-propanol probing technique, are refreshing. In some cases the higher derivatives really do reveal transitions in liquid structure that would be difficult or impossible to discern from traditional analysis of thermodynamic data.

Readers may not agree with all the practices, interpretations, and conclusions put forward in the book. For instance, Koga takes the "coarse grain" concept from statistical thermodynamics and considers its size as if it is an actual material property instead of a theoretical concept. In the same vein, properties like $\langle(\Delta V)^2\rangle/k\langle V\rangle$ (the volume fluctuation, a microscopic interpretation of $T\kappa_T$, with κ_T as the isothermal compressibility) and $\langle(\Delta S)^2\rangle/k\langle V\rangle$ ($= C_{p,\mathrm{m}}/V_{\mathrm{m}}$), which are already normalized for volume, are divided once more by the molar volume to obtain a measure of what the author calls the "wavelength" of the fluctuation properties. No reasonable justification for this approach is given, and a check of the referenced papers reveals that Koga incorrectly assumes that ΔS (instead of $\langle(\Delta S)^2\rangle$) is the extensive property. Hence, I doubt that the concept of wavelength has any meaning at all in this context. Elsewhere in the book, Koga discusses "clusters" of solute molecules when the solute concentration is too high for clusters to be separated from each other. In several instances, he claims that Henry's law does not really exist. Upon careful examination of the evidence referenced in the book, this turns out to be a nonissue. Throughout the book, the math used in the data analysis is poor to nonexistent, and many of the fits of lines to data in the figures appear completely arbitrary, as if to confirm a preconceived idea rather than to test it. These quirks do not improve the palatability of the book, which could have used a critical peer review from a practitioner in the field not linked to Koga's group. Ironically, that weakness may turn out to be where the main value of the book lies. Now that the field of differential analysis of solution thermodynamics has been conveniently summarized, other researchers may be encouraged to contribute to the field and critically reappraise the insights developed to date. Suitable techniques of data analysis may improve the estimation of derived quantities from primary data, and the more speculative interpretations may be weeded out and replaced by more palatable ones. This may turn a somewhat quirky research program into a mature field of research.

I would not recommend this book to readers unless they have a solid background in chemical thermodynamics. The introductory chapter on the basics of thermodynamics is not the most insightful I have ever read and gives me the impression that, after years of applying unconventional thermodynamics, Koga's grasp of conventional thermodynamics is somewhat rusty. The differential approach that is the main subject of the book is not an easy one, and the reader must be prepared to make substantial

efforts to fully understand the book. The reward is a highly original, if somewhat speculative picture of aqueous solutions.

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JA809695U

10.1021/ja809695u

Molecular Recognition and Polymers: Control of Polymer Structure and Self-Assembly. Edited by Vincent Rotello and Sankaran Thayumanavan(University of Massachusetts, Amherst). John Wiley & Sons, Inc.: Hoboken, NJ. 2008. xlx + 436 pp. $125. ISBN 978-0-470-27738-6.

This book covers the recent developments of supramolecular polymers, their preparation, and functionality in a fascinating way. Although the book consists of contributions from 15 different principal authors, most of it reads like a monograph. The authors were carefully chosen to avoid thematic overlap. The selected topics are compiled into three parts, and the citations are thorough and cover the literature up to 2007 in several chapters. In one chapter, references to the primary literature of 2008 are also included.

The first part, Chapters 1−3, covers the basics of supramolecular chemistry related to material science, has many illustrations, and provides an early glimpse of the potential of the field using selected examples. The chapters are cross-linked to each other. In Chapters 4−11, the second part, formation of polymers and their self-assembly are discussed, and excellent reviews of functionalized block copolymers with hydrogen-bonding ability, self-assembled polymer-particle nanocomposites, metallosupramolecular polymers, polymeric capsules, and amphiphilic dendrimers are included.

The final part, Chapters 12−15, provides reviews of molecular recognition of biomolecules with polymers and comprises thorough overviews of colorimetric sensing and biosensing. The topics covered include the emerging field of pattern sensing, the current research efforts to modulate cellular recognition processes using multivalent displays of multiple carbohydrates for the creation of synthetic glycosystems, the dramatically expanded ability to design nanofibrous material from peptide derivatives, and recent achievements with molecularly imprinted polymers for sensing applications.

Although all contributions are exclusively from authors in the United States, research accomplishments from noncontributing experts in the field in the US, Europe, and other parts of the world are also incorporated into the text through both illustrations and references. Most chapters start with eye-catching cartoons that are supported by accompanying structures to explain concepts and terminology. Nonexperts in the field and students will therefore easily understand the interdisciplinary material that ranges from material science to organic chemistry and biochemistry. References to background literature are frequently provided; however, the text can be easily understood without consulting these.

Overall, this book is an excellent up-to-date source for scientists in the field, as well as for teachers and graduate students of advanced organic chemistry or material science. Industrial researchers might also find the thorough reviews of emerging fields stimulating. The mix of reviews and their graphics are very appealing. It would have been beneficial, however, if more illustrations had been in color and if the index had included more cross-references. Nevertheless, the contents meet the objectives of the editors, and thus, the book should serve as a very valuable source and reference in any institutional or personal library.

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JA809837B

10.1021/ja809837b

Primary Processes of Photosynthesis: Principles and Apparatus, Parts 1−2. Edited by Gernot Renger (Technische Universität Berlin). From the Comprehensive Series in Photochemistry and Photobiology, Volumes 8−9. Edited by Donat P. Häder and Giulio Jori. Royal Society of Chemistry: Cambridge. 2008. xxii + 474 (Part 1) and xxii + 570 pp (Part 2). $649. ISBN 978-0-85404-364-4 (set).

In his Introduction, Gernot Renger calls this offering "an ambitious attempt to provide a synoptic state-of-the-art picture of the primary processes of photosynthesis", and these volumes certainly go a long way toward fulfilling that goal. Renger has assembled a stellar team of authors, who have put together 22 chapters covering the light-driven processes that precede metabolism, with topics from the photophysical to evolution of the apparatus. I benefited from all the chapters and learned a great deal about the new science in diverse areas, especially those in which my own expertise is limited, but I especially enjoyed the accounts of research in areas in which I have been involved.

Volume 1 covers light harvesting, from photophysical aspects to antenna structure and function. Gernot Renger provides an informative and useful introduction, and Thomas Renger provides a succinct account of physical principles of excitation energy and electron transfer, with a nice introduction to the "hard" bits, although even the more physicochemically adept biologists will find this "simplified" description challenging. Nevertheless, it was useful to get a feel for the approximations that underlie the treatments that are practical, and the aficionados will find the chapter useful. In the next chapter, Scheer discusses the chemistry, spectra, energy levels, synthetic pathways, etc. of chlorophylls and relates this usefully to the functional context. Koyama et al. then provide a more detailed discussion of how some very sophisticated spectroscopies of carotenoids — and the information derived from these approaches — can provide insights into both excitation transfer and protective functions at the molecular level.

The chapters on structural aspects of light harvesting (LH) complexes put the pigments into their structural and functional contexts. There have been exciting developments in these areas in both bacteria and plants. Law and Cogdell have a nice account of bacterial systems, although the chapter seems to have been completed before some of the more recent AFM studies of LH and reaction center complexes *in situ* became available. Mimura et al. extend the picture to the cyanobacteria and the phycobilisome apparatus, Morosinotto and Bassi to the photosystem I antenna, and van Amerongen and Croce to photosystem II LH proteins. All of these contributions are nicely done. The volume is completed by chapters on the role of light harvesting complexes in photo protection by Gilmore and Li and by Vass and Aro.

Volume 2 covers the electron transfer component of the "light reactions", including the photochemical reactions, intermediates involved in electron transfer, and ATP synthesis. The main

interest in the past few years has been in the additional information about these functions that comes from new structural data, with structures for the green plant — or cyanobacterial — reaction centers and the Cytochrome b_6f complexes providing the primary focus. The recent higher resolution structures from the bc_1 complex from *Rhodobacter* were unfortunately too recent to be included. The interpretation of the structures of green plant reaction centers and their function still depend heavily on prior work on bacterial reaction centers, and this aspect is covered in a nice review of the earlier work and recent advances by Lancaster. I particularly enjoyed the discussion of the Q_B-site. Parson follows this with a succinct and lucid summary of functional aspects. The structure and function of photosystem I are nicely covered by Fromme and colleagues and by Sétif and Leibl, respectively. Gernot Renger has a nice account of photosystem II function, and in another chapter with Messinger, they provide a beautiful review of recent progress in the mechanism of O_2 evolution. Recent structures of photosystem II are covered by Zouni, who also includes some recent information suggesting that radiative reduction has changed the state of the Mn-cluster, which is also covered by Messinger and G. Renger. The remainder of the volume is devoted to chapters on intermediate electron transfer systems and phosphorylation, with bacterial systems covered nicely by Verméglio and cyanobacteria by Peschek. There are also stellar contributions by Cramer et al. on the b_6f complex and by Junge on the ATP-synthase.

I can certainly recommend the set to colleagues and would think it a "must" for any library serving a scientific community with serious interests in this area. My only quibble is that some of the chapters were clearly submitted earlier than others and are a bit dated, likely because those who met a target deadline suffered at the expense of the tardier. References in most chapters finish in 2004, but a few include work up to 2007.

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JA809545U

10.1021/ja809545u

Nanostructured Design: Methods and Protocols. Methods in Molecular Biology, 474. Edited by Ehud Gazit and Ruth Nussinov (Tel Aviv University, Israel). Humana Press (a part of Springer + Business Media, LLC): New York. 2008. xiv + 268 pp. $79.95. ISBN 978-1-934115-35-0.

Nanostructured Design: Methods and Protocols represents a new volume in the well-established *Methods in Molecular Biology* series. The principal stated goal of this book is to bring together in a single reference the major experimental, theoretical, and computational techniques for the design, characterization, and technological development of well-defined nanosized materials based on biological motifs. This approach to nanoscale design is maturing into an established field; therefore such an undertaking at this time is warranted.

The volume is divided into two major sections: "Experimental approach" (Chapters 1−6) and "Computational approach" (Chapters 7−12). The first three chapters deal with the preparation of protein/peptide fibers, Chapter 4 covers the preparation of nanoparticle−bimolecular conjugates, and Chapter 6 reviews the preparation of gold nanoparticle−DNA scaffolds. Although the subject of Chapter 5 formally concerns the synthesis of self-assembled peptide-based hydrogels, the authors mostly explore general aspects of automated solid-phase peptide synthesis and purification. The protocols in these chapters should be easily followed by those with experience in general biochemical procedures, peptide synthesis, and purification. However, I would suspect that those not familiar with these techniques may have difficulty in successfully performing the protocols, and more discussion may have been warranted.

The remaining chapters concern theoretical aspects of biomolecular nanostructured design. Many of these chapters concern the use of theory to direct experimental investigations. Chapter 7 is an insightful and useful tutorial on constructing RNA-based structures, whereas Chapter 8 explores protocols for fusing homo-oligomers to construct three-dimensional structures. Chapter 11 is a broad overview of computer modeling in biotechnology and nanoengineering, which, although lacking in protocols, is probably the most engaging chapter in the text. The final chapter concerns the investigation of β-rich structures for the design of interfaces. The other two chapters in this section (9 and 10) are concerned with computational methods to probe amyloid formation and properties. Although there is a substantial amount of theory in this section, the chapters are relatively easily understood by the nontheoretician. It should be noted that, as with the experimental protocols, nonexperts in the field may have difficulty in actually *performing* the computational protocols outlined.

The text is well referenced and up-to-date, with many of the references dating from 2004 on. As with other compilations containing chapters written by different authors, there is a dramatic difference in writing style from chapter to chapter. Although effort was taken to ensure a consistent format, the actual content of the chapters range wildly from short recipe-like protocols to full-on review articles.

There are two major weaknesses of the monograph. One is the fact that several key aspects of bioinspired nanostructure design are absent. For example, there is no mention of the use of virus particles for the production of semiconductors and other constructs or of biomineralization. Another weakness is that the text is divided into two major sections: experimental and computational approaches. Although this field requires both experimental and theoretical insights for fully exploiting the power of using biological constructs in nanostructured design, the two sections are largely orthogonal to their respective target audiences. Both of these failings could have been circumvented if the present work had been expanded or if two different volumes—a theoretical and experimental volume, for example—had been compiled.

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JA809618Z

10.1021/ja809618z

Probes and Tags to Study Biomolecular Function for Proteins, RNA, and Membranes. Edited by Lawrence W. Miller (University of Illinois, Chicago). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xvi + 178 pp. $130. ISBN 978-3-527-31566-6.

Four types of biopolymers—proteins, nucleic acids, polysaccharides, and lipids—are pivotal to a cell's storing and processing of biological information at levels ranging from gene expression

to cell recognition. In order to understand how the biopolymers function inside cells, it is essential to know the rates of biopolymer production and degradation, their intracellular localization, as well as their partners in biomolecular interactions and the dynamics of such interactions. The major approach to comprehensive studies of biopolymers in living cells is fluorescent microscopy, in which only molecules of interest are visualized by attaching fluorophores to them. Attaching a fluorophore to a biopolymer with high selectivity may seem like a technical step; however, this step is often so challenging that it becomes the sole focus of many research groups in molecular and cell biology and organic chemistry. In general, this operation can be achieved in three ways: (i) covalent attachment of a fluorophore, (ii) noncovalent attachment of an affinity probe, covalently labeled with a fluorophore, and (iii) genetic fusion with a polypeptide tag that either is fluorescent, e.g., a fluorescent protein, or can be made fluorescent through covalent or affinity labeling. The area of fluorescent labeling of biopolymers is well established but continues to develop rapidly with novel interesting approaches emerging with surprising regularity. The body of literature describing different methods is large, but there is a continuous need for reviews and generalizations to keep up with new works.

This book is a valuable addition to the body of literature on fluorescent labeling of biopolymers. It focuses on a few selective new methods for fluorescent labeling of lipids, proteins, and mRNA. It should be noted that "a probe" is used in this book solely as a fluorescently labeled lipid that retains the function of an unlabeled lipid. This meaning is very narrow and different from that of an affinity probe, e.g., molecular probe, hybridization probe, antibody, aptamer, etc., mentioned above. The methods described in this book have been previously reviewed; however, this is the first collection of them in a single volume in which basic principles, state-of-the-art procedures, useful examples, and detailed protocols are described. The literature citations in the book are comprehensive and mostly limited to recent articles. I think the book will be useful to a wide readership including researchers currently practicing in the area, novices in the area interested in microscopy studies of fluorescently labeled biopolymers, and graduate students studying relevant subjects. I personally learned quite a bit from the book and recommended selective chapters to my graduate students for examples of how the knowledge of molecular biology and biochemistry can fuel the area of fluorescent labeling of biopolymers. In my view, the book is important and timely.

I have a few critical comments that I hope will help the reader to adjust expectations and experience more efficient reading. The title of the book is somewhat nondescriptive. First, it misses two words that are key to the subject: "living cell". Novel probes and tags for visualizing membrane components, proteins, and RNA in *living cells* are described here. In only a single instance, when describing protein modification with non-natural functionalities in a cell-free *in vitro* protein expression system, do the authors deviate from living cells. Also, although the title mentions "biomolecular function", some chapters do not refer to biomolecular function or at least do not refer to it explicitly. There is an imbalance among the three subjects—membranes, proteins, and RNA—as well: three chapters on membranes take up nearly half of the nine-chapter book, whereas the visualization of RNA is addressed in a single chapter and only a single method is described. I am guessing this imbalance reflects, to some extent, both the personal interests of the editor and the status of the area. The book reads more as a collection of independent works rather than as a set of logically linked chapters. For example, the introductions to the five protein chapters are very similar. The book would gain considerably from an editorial introduction to the three parts—lipids, protein, and RNA—of the book. The reader should also be prepared to find some nondefined abbreviations and sentences with missing words. The quality of the chapters is not even.

Despite the above criticism, the overall quality of the book is good and its importance to the chemical community is high. I congratulate the editor on his first book. I am sure I will return to this book many times in the future.

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JA809727X

10.1021/ja809727x