Book Reviews *

Computational Biochemistry and Biophysics. Edited by Oren M. Becker (Tel Aviv University), Alexander D. MacKerell, Jr. (University of Maryland), Benoît Roux (Cornell University), and Masakatsu Watanabe (Wavefunction, Inc.). Marcel Dekker: New York and Basel. 2001. xii + 512 pp. $195.00. ISBN: 0-8247-0455-X.

The first molecular dynamics simulation of a protein was published by McCammon, Gelin, and Karplus in 1977. This event followed by just 13 years the publication by Rahman of the first molecular dynamics simulation of a liquid. The ability to do molecular simulations at this level of detail on liquids was instrumental in creating a true physics of the liquid state. In biomolecules, the situation has been more complicated. The additional complexity has arisen from the wide range of time scales that are important in biomolecular function, combined with the number of different degrees of freedom for the internal motions of biomolecules. The application of standard statistical mechanical analysis to molecular dynamics simulations of proteins, although useful and important, provides insights into only a severely limited range of protein phenomena.

In the last couple of decades, the domain of applicability of computational studies of biomolecules has been extended by a community of workers who have essentially created a new field that might be called computational physical biochemistry. The foundations of this field reside in computer science (numerical analysis), statistical mechanics, and physical chemistry. Important developments, in addition to molecular dynamics, include Brownian dynamics, smart Monte Carlo, precise electrostatics calculations, improved atomic force fields, implicit solvent models for biomolecules, new tools for analyzing experimental data, automated molecular modeling software, and extension of these techniques from proteins and nucleic acids in solvated environments to the domain of membranes. All of these developments, applied in complementary fashion, will provide the basis for future advances in computational physical biochemistry.

The aim of *Computational Biochemistry and Biophysics* is to provide an authoritative presentation of these theories and computational techniques. Each chapter is provided by an author who has been a major contributor to an important component technique or body of theory in computational physical biochemistry. It is clear that each contributor was asked to provide a thorough and balanced background and not to unduly reflect on his or her own contribution. The result is a remarkable book. For a multiauthored book, the style is remarkably consistent. For a book by authors who are competitive people, the book is remarkably, if not completely, balanced. In any case, any emphasis there is on an author's own work is not so extreme that it pre-empts a careful reader's ability to achieve a balanced view.

It is clear that this book is designed to be useful for years to come, despite the rapid progress in its subject. Its longevity is enhanced by a choice of topics that are truly fundamental to the field and by grounding each topic in the relevant statistical mechanics, which can grow in application domain but cannot fundamentally change. In my judgment, this goal will be achieved. I certainly expect it to be a useful reference on my desk for years to come. Indeed, I will not lend my copy of the book to people in my lab, but will instead purchase a second copy for the lab commons area for reference by others.

The literature references are up-to-date to 1999, as a rule. Naturally, they will become significantly less up-to-date in a few years. Fortunately, there are now good tools on the Internet to keep topical bibliographies up-to-date if one has a reasonably recent starting point, and this book provides that.

As a reference work for workers in computational physical biochemistry at all levels of experience, from beginners to seniors, I give this book a thumbs up. As an introduction to computational physical biochemistry for an outsider who is not actually going to enter the field, however, this book is probably too detailed for most. As a textbook for a course in computational physical biochemistry, the topic coverage is about right, but the book is too expensive and too theoretical, and it does not have a sufficiently explicit presentation of how everything fits together. As a resource for students who want to dig deeper into particular aspects of the subject, however, this book will be good.

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Computational Chemistry: Reviews of Current Trends. Volume 5. Edited by Jerzy Leszczynski (Jackson State University). World Scientific: Singapore, New Jersey, London, Hong Kong. 2000. x + 326 pp. $68.00. 981-02-4371-5.

This is the fifth in a series of volumes that are peripherally associated with a very well-organized and excellent conference series having the same title, which is held annually in Vicksburg, Mississippi. The editor of the series of reviews also serves as the organizer of the conference, and there is understandably some overlap between past conference participants and contributors. In general, this platform gives people in computational chemistry the luxury of providing detailed descriptions of their research that go far beyond what would be published in a traditional peer-reviewed journal.

The chapters in this volume lack a common theme and range from an extremely detailed analysis of coupled cluster methods to (necessarily) relatively low-level calculations of weak interactions between nucleic acids. The former subject is covered in the first chapter by Piecuch and Kawolski. In this work, the authors discuss a problem of some practical and considerable mathematical interest: the existence of multiple solutions to the coupled-cluster equations. Although some computational chemists may think that there is just *the* coupled-cluster wave function, the equations defining the method are nonlinear, and other solutions may well exist. What these are and, perhaps more importantly, what they mean are the subjects of this paper. The authors present a highly mathematical and detailed investigation of these issues. Although their work may be readable only by aficionados of many-body theory with additional training in the mathematics of nonlinear equations, it answers many questions about these extra solutions.

The second chapter of the monograph, which also touches on fundamental aspects of quantum chemical theory, is written by Weatherford and Ritchie. They explore the use of time-dependent methods to obtain solutions to the two-particle Schroedinger equation. Although methods of this sort—propagator theory—have a long history in quantum chemistry, several new and interesting ideas are presented, and hopefully, numerical results will soon become available that shed light on the practicality of these novel approaches.

The third chapter is written by Gianinetti, Vandoni, Femulari, and Raimondi and presents an interesting approach to calculations on weakly bonded systems. This has long been a problem because of what the quantum chemists refer to as the basis set superposition error (BSSE). Whether to include this effect and how to do it are subjects that inspire considerable debate among some theoreticians, who often defend their ideas with nearly religious fervor. Gianinetti, et al., totally circumvent the problem here using a new—and, I think, promising—treatment.

The remainder of the volume deals more with application-related issues and contains two chapters authored by the editor and his collaborators. The first covers the stacking and hydrogen-bonding preferences of nucleic acids and investigates the pros and cons of various computational approaches for studying this set of problems. The conclusion arising from this work that the stacking of bases is probably treated quite adequately by the standard modeling programs in use today should be of interest to people in biochemical modeling. In the second chapter by Leszczynski and collaborators, they deal with the nonbiological problem of the molecular structure and vibrational spectra of halomethanes, halosilanes, and halogermanes. Again, an impressive arsenal of methods is applied to the problems, and some general trends emerge that can be used to guide the choice of methods in studying compounds of this sort.

Sandwiched between the two chapters by the editor's group is a discussion of how to model biochemical dynamics using the idea of

*Unsigned book reviews are by the Book Review Editor.

"direct ab initio dynamics". This is the name given to a class of methods in which potential energy surfaces, which govern the forces that ultimately guide the nuclear motion that we call "chemistry", are calculated as the dynamics proceed. This is to be contrasted with other types of simulations, in which the potential is modeled by some analytic function that greatly speeds up the simulation at the cost of reduced accuracy. In this chapter, Truong and Maity outline their procedure, which is based on the QM/MM (quantum mechanics/molecular mechanics) ideas that have taken hold in computational chemistry and the variational transition state approach developed by Truhlar.

The breadth of subjects in this volume is such that almost everyone in the field of computational chemistry will find something of interest here, but I suspect that few people will pore through all of the chapters in great detail. Nevertheless, the reviews and articles that are included are all well-written and cover their subjects expertly and in great depth.

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Transition Metal and Rare Earth Compounds: Excited States, Transitions, Interactions I and II. Topics in Current Chemistry. Volumes 213 and 214. Edited by Harmut Yersin (University of Regensburg). Springer-Verlag: Berlin. 2001. Information for Volume 213: x +186 pp. $109.00. ISBN: 3-540-67986-3. Information for Volume 214: x + 190 pp. $109.00. ISBN: 3-540-67976-6.

The fundamental properties of transition metal and rare earth complexes have long drawn the interest of photophysical scientists, not only for the intellectual challenges they inspire but also for the childlike delight in seeing the emission of light. Luminescent materials also have important roles in practical applications, such as display screens, and show promise for future technology, such as optical computing. In this context, Volumes 213 and 214 are the third and fourth in the series on the chemistry and spectroscopy of transition metal and rare earth excited states edited by Professor Hartmut Yersin, the earlier ones being volumes 171 (1994) and 191 (1997).

Volume 213 consists of three reviews. The first is from K. L. Bray on applications of high-pressure probes of transition metal and lanthanide electronic structure and luminescence properties. The focus is on the effect of very high pressures (up to ~300 kbar) on solid luminescent materials using diamond anvil cells. This valuable review begins with a discussion of the methodology and principles of the high-pressure experiments and illustrates these with examples involving spectra and lifetimes of d → d, d → f, and f → f electronic transitions. The second review is by M. Glasbeek on optically detected magnetic resonance (ODMR) techniques applied to the excited-state spectroscopy and exited-state dynamics of Rh(III) and Pd(II) chelates. The author begins with an interesting discussion of methods and theory and then focuses on specific applications of this high-resolution technique for probing the radiative character of triplet-state sublevels. The third review by A. Vogler and H. Kunkely is an insightful survey of different electronic configurations and excited states from which luminescence is seen for transition metal complexes. Although more qualitative than the previous two articles, it will remind the specialist of the remarkable diversity of luminescent systems and serve as a short primer for a newcomer to the solid-state or solution photophysics of transition metal systems.

Volume 214 consists of three review articles. The first is an article from D. R. Gamelin and H. U. Güdel on upconversion processes in transition and rare earth metal-doped halide lattices. Upconversion, that is, the generation of short-wavelength light from longer wavelengths by sequential absorptions or energy transfers involving metastable excited states, has considerable interest in materials applications. This review is both a nice introduction for the uninitiated as well as a timely update by a leader in the field (Güdel). The second article is a short review from M. J. Riley on different spectroscopic studies of Jahn−Teller distorted six-coordinate copper(II) complexes, and the third is a discussion by H. Yersin and D. Donges of the low-lying excited states of the homologous complexes $Pd(2\text{-thpy})_2$ and $Pt(2\text{-thpy})_2$ ($2\text{-thpy}^- =$ 2-(2-thienyl)-pyridinate) as studied by tour de force high-resolution electronic/vibronic spectroscopy, ODMR, and other high-resolution techniques. The two case studies, presented with an appropriate background introduction, represent a remarkable level of effort using a variety of techniques and very nicely demonstrate the details of electronic excited-state character, structure, and dynamics that one may thus obtain.

The articles are, with one exception, quantitatively photophysical, reflecting the editor's bent in this direction. These volumes are valuable contributions to the literature of transition metal and rare earth excited states and would be very worthwhile additions to the science library of any major research institution.

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Localized to Itinerant Electronic Transition in Perovskite Oxides. Structure and Bonding, Volume 98. Edited by J. B. Goodenough (University of Texas at Austin). Springer-Verlag: Heidelberg, New York. 2001. xii + 240 pp. $149.00. ISBN 3-540-67522-1.

The topic of this monograph has been a favorite of the volume editor, who has not only made outstanding original contributions to this area, but who also wrote some seminal articles on the subject several years ago. The localized-to-itinerant transition is based on the fact that ligand field theory and band theory represent two limiting behaviors of electrons in solids; clearly, there is a continuum between the two extremes. The book features a long article on transport properties by Goodenough and Zhou, which is well-written, but I have a feeling that some literature references to some contributors to the area are missing or minimal. I would like to have seen a detailed discussion of phase segregation and charge-ordering in the manganates because these phenomena are important and fascinating. In particular, phase segregation poses interesting questions regarding the causes and effects. In the following two chapters, the role of local structure in determining properties such as CMR is discussed by Egami, and Cooper provides a valuable review on optical spectroscopy of metal−insulator transition. Although the last two articles are useful, a comprehensive discussion of the electronic structures of manganates, cuprates, and related systems, including the results from photoelectron spectroscopy and related techniques, would have been valuable.

Each of the contributions is authoritative and will be of value to specialists in the area. The contributions assume a certain knowledge of solid state science on the part of the reader. The monograph, however, could have been made more useful and appealing to a general audience of chemists, physicists, and materials scientists because of the wide significance of this important subject. This would require not only a more detailed introduction, but a presentation that would gradually bring in various concepts and experimental results, ultimately ending by showing what we understand and what we do not. I realize, however, that in a multi-authored contribution it is difficult to develop the material in the manner one prefers. I have made these comments mainly because it is unlikely that there will be another monograph of this title edited by someone more knowledgeable. I have no doubt, however, that the monograph will be valuable to the solid state and materials chemistry community.

Unfortunately, the very high price of this volume precludes its purchase by many individuals, and I wish that publishers would find ways of reducing costs in order to remove this barrier.

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Near-Infrared Applications in Biotechnology. Edited by R. Raghavachari (Corning Microarray Technology, Corning, NY). Marcel Dekker: New York and Basel. 2001. xviii + 382 pp. $165.00. ISBN 0-8247-0009-0.

For many years, near-infrared spectroscopy was the Rodney Dangerfield of analytical chemistry, that is, it "got no respect". This lack of respect stemmed from the poor quality of the chemical information

available from this spectral range, particularly in comparison to the bordering visible and mid-infrared regions of the electromagnetic spectrum. Recent advances in both technology and chemistry have enabled high-quality optical measurements within the near-infrared spectrum, thereby rendering this spectral region attractive for a multitude of analytical problems. This monograph describes these advances and details their impact on analytical chemistry.

The 13 chapters in this book can be divided into two categories. The first includes chapters associated with the development of molecular probes that have strong absorption or fluorescence characteristics in the near-infrared spectrum. The second group deals with extracting analytical information from near-infrared absorbance spectra collected from samples of complex chemical matrixes. These two classes of measurements differ greatly in terms of their instrumentation, data analysis, and applications. There has been virtually no effort to coordinate the underlying principles of these two types of measurements, which is understandable, because the former is based on low-energy electronic transitions (of both intra- and intermolecular origin), whereas the latter is based on overtones and combinations of vibronic transitions. The majority of the text (nine chapters) is devoted to the development and utility of near-infrared molecular probes. Although a couple of 1999 citations are provided, most of the citations are dated 1998 and before.

After a brief introductory chapter, the second chapter provides a nice description of fluorescence. Issues discussed include energy levels, the impact of molecular aggregation, fluorescence resonance energy transfer, steady-state measurements, lifetime measurements (both phase-resolved and time-resolved), and the impact of restricted molecular rotation. This treatment of fluorescence is general in nature and offers no specific information about near-infrared measurements. Chapter 3, on the other hand, is devoted to a discussion of the chemistry of dyes that fluoresce in the near-infrared region of the spectrum. A wealth of information is provided for several major classes of compounds. Particular attention is given to polymethine dyes. In addition to documenting the structure, basic spectroscopic properties, and general synthetic pathways for these dyes, the author provides a synopsis of the chemical factors that contribute to their fluorescence properties.

Chapters 4 through 10 cover the major applications of near-infrared sensitive dyes. The principal driving force behind the development of these dyes, which is expressed repeatedly in these various chapters, is 2-fold. First, the development of inexpensive and durable solid-state lasers provides a convenient and high-powered monochromatic source to measure these dyes via their fluorescence. Second, natural samples exhibit virtually no background fluorescence when exposed to light at near-infrared wavelengths. Taken together, these factors provide an effective means for measuring these molecules with high sensitivity and low limits of detection. Some of the applications covered include using these dyes as labels for immunoassays (Chapter 4) and DNA sequencing (Chapter 5), as reagents for photodynamic therapy and flow cytometry (Chapter 6), and for detecting single molecules (Chapter 7). Chapter 6 also discusses imaging with near-infrared light via photon migration and Raman spectroscopy. Chapter 8 focuses on lifetime measures of fluorescent dyes in general and briefly discusses lifetime measurements of near-infrared dyes to probe chemical environments. Materials generated by embedding near-infrared dyes within polymeric matrixes are described in Chapters 9 and 10. Chapter 9 mainly covers the potential of polymer-bound near-infrared dyes as lasing materials, whereas Chapter 10 surveys the many current and potential applications of these dyes, such as optical recording (both write-once and erasable recording strategies), color-copy systems, leuco dyes for thermal printing and bar-coding, heat absorption, plasma display panels, and photovoltaic cells.

The fundamental principles of near-infrared spectroscopy are presented in Chapter 11. This succinct presentation covers all the major issues, including the molecular origin of overtone and combination absorption bands, the instrumentation for acquiring these spectra, and the multivariate calibration methods and procedures used to extract the desired analytical information. The author does a nice job of explaining all the major issues, except in his discussion of chemometrics, which is rather weak and superficial; the interested reader will need to supplement this material. Unfortunately, no references are provided to aid the reader in this regard. Chapters 12 and 13 present a variety of applications of near-infrared absorption spectroscopy for analytical measurements in the biomedical sciences (Chapter 12) and in the pharmaceutical industry (Chapter 13), which include (1) measuring glucose in blood, (2) measuring oxygen in blood and tissues, (3) characterizing the chemical state of various tissues and organs, (4) in situ measurements within bioreactor systems, (5) verifying the homogeneity of pharmaceutical blends, (6) characterization of molecular polymorphism in pharmaceutical preparations, (7) particle size analysis, and (8) dosage forms in intact tablets and capsules.

Overall, the chapters in this book are targeted to those interested in either near-infrared dyes or near-infrared spectral analysis. As with many multi-authored monographs, the quality of these chapters varies considerably. For the most part, however, this text provides very good tutorials on the major topics at hand.

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Chemiluminescence in Analytical Chemistry. Edited by Ana M. Garcia-Campana (University of Granada) and Willy R. G. Baeyens (Ghent University). Marcel Dekker: New York and Basel. 2001. xiv + 621 pp. $225.00. ISBN 0-8247-0464-9.

According to the editors, this book aims to provide a wide overview of light-producing chemical reactions, with emphasis on their analytical uses and recent applications, and to appeal to a wide variety of readers, ranging from undergraduate and graduate students to researchers.

The 20 chapters in this book, each with extensive references, make it a comprehensive source on the topic. The chapter on bioluminescence (BL) stands out in particular, with over 270 references, almost all in the 1990s. Analytical methods illustrated with instrument diagrams are emphasized throughout the book; however, figures of organic structures showing their chemical reactions are prominent. Major subject areas that are covered include (1) fundamentals of chemiluminescent analysis, including a historical account; (2) standard chemical systems, such as peroxyoxalate, electrogenerated, BL, and gas-phase; (3) chemiluminescence (CL) enhancement involving photosensitizers and organized media; and(4) instrumental approaches, such as kinetics, flow injection, liquid chromatography, capillary electrophoresis, and sensors.

The chapter on CL in organic analysis is too short (14 pages of text) and does not cover important aspects of this topic, such as luminol CL, in enough detail. Fortunately, some of the other chapters make up for this shortcoming. Only one chapter, on the applications of novel acridan esters as CL reagents for immunoassay, covers a field that is too specialized. For an edited book, there is some probably unavoidable repetition of reaction diagrams but remarkably little overlap of analytical material. For example, the specific assays and diagrams in the flow injection and liquid chromatography chapters are different from those in the peroxyoxalate and electrogenerated CL chapters. Particularly recent CL topics featured in this book include the use of CCD cameras and their hardware specifications; CL detection for capillary electrophoresis, with a brief mention of micromachining; CL and BL for imaging and detecting hybridized DNA; and gas, as well as liquid-based, CL sensors.

With respect to the readership, the book should be very understandable to graduate students and practicing analytical chemists, and the first three chapters give an overview of CL that is well-suited for undergraduate students. As an active researcher in CL, I found this book to be an excellent compilation of the well-established areas of CL and also an educational update of some CL chemistry and applications.

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Molecular Switches. Edited by Ben L. Feringa (University of Groningen). Wiley-VCH: Weinheim and New York. 2001. xxii + 454 pp. $187.95. ISBN 3-527-29965-3.

Current manufacturing methods will be reaching the physical limits of miniaturization for silicon-based microchips in a few years. Will we be forced to accept the eventual demise of Moore's law and abandon our expectations of increasingly cheaper computer memory and more powerful processors? Only time will tell. In the meantime, a growing number of chemists have been working to find molecular solutions to

the problem of miniaturization of circuit elements to sizes within a few nanometers. The Holy Grail of this field is to develop the molecular switch, a device whose operation relies on a single bistable molecule with two (or more) states, accessible through a reversible mechanism that can be controlled by external stimuli. The two states (on/off, 0/1) must exhibit properties sufficiently different to enable readout operations. As it turns out, there are a large number of bistable or switchable molecules that have already been reported in the literature, and this book provides an excellent compilation of recent work in this area.

The volume consists of 13 review chapters written by leading scientists in the field and complemented with recent and appropriate reference lists. Edited books usually suffer from variable writing quality and repetition of topics, concepts, or ideas. The editor has done a very good job here at minimizing these problems. In terms of content, the book is strongly oriented toward photochemically switchable molecules, which are discussed almost exclusively in 10 out of the 13 chapters. Bistable molecules relying on electrochemical, chemical, or other switching mechanisms are comparatively underrepresented. This book suggests that, if molecular switches become a practical reality, photonics will certainly replace electronics in the not-so-distant future. Throughout the book, the reader will find some discussion of the serious problems that remain to be solved in order to integrate switchable molecules into real circuits. Obviously, the development of a switchable molecule does not automatically translate into a working molecular switch because of the daunting problems associated with addressing (stimulating and reading) a single molecule, as well as issues related to chemical stability upon cycling and other practical difficulties. These problems do not constitute the main focus of this volume and, thus, are not treated in depth. In any instance, the book is a very comprehensive look at the state-of-the-art from the standpoint of organic chemistry and should be very useful to those involved or simply interested in this type of exciting research work.

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Handbook on Metalloproteins. Edited by Ivano Bertini (University of Florence), Astrid Sigel, and Helmut Sigel (University of Basel). Marcel Dekker: New York, Basel. 2001. xxx + 1182 pp (plus 16 color plates). $265.00. ISBN: 0-8247-0520-3.

This book, written by 43 experts in the field of metalloproteins, provides structural information on proteins and their metal coordination spheres and gives particular focus to their corresponding structure−function relationships. The authors of the Handbook concentrate on metals that are indispensable to life, although others used as substitution probes in studies of metal ion−protein interactions, such as Rb^+, are also considered. The beginning chapter, titled "Scope and Use of the Handbook", provides an introduction to the organization of the book as well as a list of useful Web sites for further information. The book ends with a chapter that explores developing themes and patterns in metalloprotein research. References are current through 2000, and an index is provided.

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Fluorine Chemistry at the Millennium. Fascinated by Fluorine. Edited by R. E. Banks (University of Manchester Institute of Science and Technology, U.K.). Elsevier: Amsterdam, New York. 2000. xvi + 644 pp. $259.00. ISBN: 0-08-043405-3.

In the words of the Editor, *"Fascinated by Fluorine* is a Festschrift in honour of all who have contributed directly to the massive developments in fluorine chemistry and technology witnessed by the past 50 years." This labor of love on the part of Professor Banks contains 32 chapters written by a variety of authors in a highly readable mixture of styles—biographical, autobiographical, historical, and scientific—describing important progress and events in fluorine chemistry since WWII.

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