Computational Inorganic and Bioinorganic Chemistry

This volume of the encyclopedia of computational quantum chemistry in bioinorganic and inorganic chemistry is a work of wide scope comprising 614 pages in short chapters on a variety of computational aspects in this burgeoning scientific field. The volume constitutes a valiant effort to present a snapshot of a field that is extremely rich, dynamic, and rapidly developing. It is divided pedagogically into three parts: Part 1—Methods, Part 2—Bioinorganic Case Studies, and Part 3—Inorganic Chemistry Case Studies. In all there are 40 chapters written by experts on many areas of bioinorganic chemistry and inorganic chemistry. Most chapters make reference to others, so that in the end there is a sense of a unified work. Even though the chapters are short, they generally have a good list of references so that the reader can consult the original literature. The chapters have a uniform structure, and they generally possess a list of suggested reading and a glossary of terms. The index at the end of the encyclopedia is good, and the index of abbreviations and acronyms is helpful (although there is some lack of consistency).

Part 1 consists of 14 chapters on methods. There are three chapters dealing with QM/MM, three on DFT methodology, four on wave function theoretical methods such as ab initio and semiempirical methods, three chapters on applications of theory to NMR, IR, pK_a, and redox potentials, one chapter on energy decomposition analysis, and one on a potential new MM method for inorganic/bioinorganic complexes.

The chapter by Ryde on QM/MM is very didactic. It describes the ways of handling the QM–MM junction and the corrective treatments of the electrostatics around the junction. It discusses the errors in X-ray structure determination that are useful as inputs for QM/MM, and suggests a method of refining these structures. The chapter also includes a discussion of the pitfalls of QM/MM, for example in a case where a distant water molecule suddenly gains a new hydrogen bond, and gives a set of practical instructions on how to run QM/MM calculations.

The chapters by Morokuma and Lundberg and by Neese et al. include more applications; the first one emphasizes the method ONIOM, while the second also includes a short discussion of the important application of QM/MM in spectroscopy. The chapter by Neese et al. points out an important pitfall of QM/MM calculations, namely that since the parameters are not published it is not easy to reproduce results of other groups. In fact, since the supporting information of a QM/MM paper does not include the coordinates of the MM part, it is impossible to repeat an existing QM/MM result. In my opinion, even though the three chapters emphasize somewhat different aspects of QM/MM, there is still a good degree of overlap between the chapters. That is certainly unavoidable, but perhaps in the next edition one should consider providing a single comprehensive review.

The DFT-related chapters deal with the arsenal of DFT functionals (Rappoport et al.), with TDDFT (Autschbach), and with applications to NMR spectroscopy (Kaupp and Bühl). Some of the material is too technical for the general reader from the bioinorganic/inorganic community. The chapter on TDDFT gives a good account of the pros and cons of DFT compared with wave function theory (WFT). For example, in DFT the Jacob's Ladder is not a systematic one, while in WFT one soon hits the "scaling wall". The rest of the chapter is devoted to TDDFT and to its main problem in charge-transfer transitions. A few useful take-home lessons are mentioned at the end.

The chapter by Rappoport et al. is entitled "Which Functional do I Use?", and is written with humor as it tries to guide the "bemused user" who has to choose one from the "hundreds of different functionals that have been proposed". The authors' functional taxonomy is explained in terms of the Jacob's Ladder, but the categories are also characterized as "non-empirical", "a little empirical", and "over-empirical", and they give examples of the different classes, with tables of average deviations that rank selected functionals. Here my feeling is that they failed to emphasize that B3LYP does extremely well in heme enzymes and synthetic systems (on a par with highly correlated WFT methods), is not bad for non-heme systems, and is still the most widely preferred functional in bioinorganic chemistry, as the applications chapters show. The review on NMR spectroscopy shows how computations can be a real partner of experiment in structural assignment of complex molecules and enzymatic species. With the exception of the NMR chapter, my feeling is that there is a significant degree of overlap between the two DFT chapters, and a single comprehensive review on the methodology aspects might have been more effective.

Gorelsky, Schlegel et al., Peterson, and Roos contributed the WFT chapters. The chapter by Gorelsky discusses three ab initio methods, from HF all the way to CASPT2 and RASSCF in three pages, and then to semiempirical methods in five pages. The chapter by Roos focuses on CASSCF/CASPT2 for molecules containing heavy elements. The chapter by Peterson discusses Gaussian basis sets, while Schlegel discusses spin contamination, its meaning, and its extent in WFT compared with DFT. Again, I could not avoid the feeling that there

Computational Inorganic and Bioinorganic Chemistry Edited by Edward I. Solomon, Robert A. Scott and R. Bruce King. John Wiley & Sons, Hoboken 2009. 614 pp., hardcover € 155.00.—ISBN 978-0470699973

is significant overlap between the individual chapters.

Finally, there are single chapters on various topics, by Frenking et al., Lehnert, and Deeth. Frenking's chapter discusses applications of energy decomposition analysis to bonding, whereas the discussion of the method itself is less emphasized. Perhaps this didactic chapter would have fitted better in the inorganic applications part (Part 3) rather than in the methods part. Lehnert's chapter deals with the implementation of centered normal coordinate analysis for vibrational spectroscopy, while Deeth describes his recent development of the ligand-field molecular mechanics method, which will certainly be a welcome addition in the future.

Part 2 consists of 13 chapters on applications to bioinorganic chemistry, which is probably the fastest developing field in chemistry. A great variety of enzymes are covered. The first chapter by Friesner describes the QM(DFT)/MM methodology and its principles, difficulties, and limitations, and then gives short applications to P450 and MMO. In this sense, the chapter would have fitted equally in Part 1, along with the other chapters on QM/MM, to provide a cluster of papers on QM/MM technology. The chapter by Noodleman and Case discusses the broken symmetry (BS) approach to create spin ladders in multispin systems, as well as methods for determining redox potentials and pK_a values, and continues with applications to [*n*Fe,*m*S] redox clusters. Again, perhaps the more fitting place for this chapter is in Part 1, back-to-back with the Schlegel chapter on spin contamination. Also, I would have reminded readers that the construction of a state from BS wave functions is a valence-bond idea.

The chapter by Siegbahn on the oxygen evolution center is a detective story, which shows how the interplay between computations, structural chemistry, and mechanistic information can lead to a reasonable resolution of a key problem in nature. Solomon and co-authors describe the use of L-edge X-ray absorption spectroscopy (XAS) to determine the degree of covalency of M–L bonds, and they apply this method to the iron(III)–catecholate bonds in a few enzymes and to their reactivity patterns. The chapter by Brunhold describes the utilization of DFT and QM/MM to probe the mechanisms of the AdoCbl and MeCbl cofactors, and the origins of the highly efficient catalysis of the former. Kirk et al. describe reactivity studies on molybdenum enzymes, sulfite oxidase, and xanthine oxidase. This is followed by a chapter by Tuczek on electronic structure and mechanisms of nitrogenases, a chapter by Bruschi et al. on hydrogenases, one by Mantri and Baik on cisplatin, and a didactically written chapter by Mujika et al. on modeling of zinc-containing enzymes. There are two chapters on modeling proton and Ca^{2+} pumping, by using different approaches. Quennville and co-authors use a QM(DFT)/MM-related theory to tackle the proton-pumping issues in cytochrome C oxidase (CcO), showing that the dependence of the pK_a value of the His ligand (of Cu) on the redox state of Cu, along with the repulsion between the "chemical" proton (which converts the HO ligand into H_2O) and the one on His creates a free-energy change that overcomes the differences in electrochemical potential across the membrane and allows the proton pumping to occur. The second chapter, by Bu and Cukier, tackles similar problems by using a QM/MD method wherein, for example, the protons are described by a "proton wave function", whereas all the heavy atoms are described by MM. Part 2 ends with a very interesting chapter by Jensen on chemical evolution of metal sites, wherein the author tries to show that using computations of very simple descriptors such as BDE, IP, reorganization energies, spin-state gaps, etc., as "chemistry first principles" enables one to outline an overview of how the various enzymes evolved and how ligand and metal co-evolved.

Part 3 contains 13 chapters devoted to inorganic chemistry, with some emphasis on main-group elements, and a few chapters on transition metals and their complexes. The chapter by Ghosh et al. deals with transition-metal nitrosyl complexes, the issue of oxidation-state formalism compared with the Enemark–Feltham notation, and structures and properties of heme and non-heme complexes. This chapter could also have fitted in Part 2. The second chapter, by Szilagyi, discusses the issue of non-innocent ligands, their experimental characterization by XAS, and calculations by DFT. This term refers to strong mixing of the d orbitals with ligand orbitals to such an extent that the bonding–antibonding ordering is reversed compared with the conventionally expected view (low-lying ligand orbitals with some contribution of the metal d orbitals to the bonding character). It discusses Fe,S clusters, and Ni and Cu pincer-type complexes. For some reason it leaves out the high-valent oxo–heme complexes where the porphyrin is non-innocent.

McGrady discusses multiple M–M bonding of transition metals and f-block metals, highlighting the new bond types (such as δ and ϕ), while Sliaghi-Dumitrescu discusses multiple bonding of main-group elements of Groups 13 and 14 and emphasizes the roles of donor–acceptor orbital interactions and fragment promotion energies. There are three chapters on metal and metalloid clusters, which are didactically written. Gutier and co-authors discuss transition-metal clusters, in terms of the polyhedral skeletal electron pair (PSEP) theory, which is based on electron-counting theoretical rules (Wade–Mingos rules, etc.) which were

developed to improve the understanding of cluster stability. Shameema and Jemmis discuss electron-counting rules, including the mno rules, Hoffmann's concept of preferred fragments for relative isomer stability, and Jemmis's concept of orbital (overlap) compatibility. A related chapter is that by Zubarov and Boldyrev, on the extension of the aromaticity/anti-aromaticity concept, etc., to metallic and metalloid elements, and on the analytical tool of adapting natural density partition as devised by the same authors to understand these molecular features. Another related chapter is the one on poloxometalate anions, written by Poblet and López, who contribute a lucid discussion of the electronic structure principles, isomerism, and reactivity of these very large clusters (the largest to date consists of more than 2300 atoms).

The chapter by Mariano et al. begins with a discussion of gas-phase reactivity patterns of bare and ligated metal ions, with some emphasis on the two-state reactivity issues. It continues with a discussion of modeling of enzymatic reactions of methionine diamino peptidase, and examines the reason why Zn^{2+} appears to be the best metal ion for this function. This chapter could have fitted well in Part 2. The chapter by Dolg and Cao is a nicely written work on calculations of atoms and molecules of lanthanides and actinides. Its major part is devoted to methodology aspects, and its appropriate place seems to be in Part 1, although it is somewhat connected to the following chapters by Kaltsoyanis, Chantal, and Dixon, which deal with advanced calculations including effects of correlation, relativistic terms, spin–orbital coupling, etc. on the properties of compounds of heavy elements.

In conclusion, this is a great work that will find its place in all libraries and laboratories. The reader will benefit from an enormous wealth of information on the application of theory to problems in bioinorganic and inorganic chemistry, and on the arsenal of methods that are now available to deal with these problems. In many chapters on applications there is too much emphasis on the technical details and less on insights and general principles. Consequently, many of the chapters are not easy to read, and may not be sufficiently accessible to the general readership. Furthermore, many of the chapters end up discussing similar technical features and pitfalls of DFT, which seems a bit repetitive when one attempts to seriously study significant parts of the volume. However, these features are perhaps necessary in an encyclopedia and for keeping the integrity of chapters independently of others. In any event, these features, as well as some possible reorganization of the chapters, may be reconsidered in future editions. Finally, adding short abstracts to the chapters should be helpful to readers and explorers of this encyclopedia. One major challenge will be the process of updating this project, especially in the sections on applications and DFT methodology, which are in a state of constant change.

Sason Shaik
Institute of Chemistry, Lise Meitner Minerva Center for Computational Quantum Chemistry
The Hebrew University, Jerusalem (Israel)

DOI: 10.1002/anie.201000436

