Coordination Chemistry Reviews 253 (2009) 523–525

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Preface

Theory and computing in contemporary coordination chemistry

1. DFT – the theory that changed chemistry

A volume like this one would have been unthinkable a mere 15–20 years ago. *Ab initio* wavefunction theory (WFT) reigned supreme during the 1980s and even around 1990, while density functional theory (DFT), often disdained as a semiempirical approach by *ab initio* quantum chemists, skulked in the background. Yet in another 5–7 years, DFT had taken chemistry by storm. Even such complicated systems as iron–sulfur clusters and single-molecule magnets could be efficiently and reasonably accurately modeled, thanks to broken-symmetry DFT methods. The operational simplicity of DFT meant that good-quality electronic-structure calculations on many transition metal systems, traditionally the realm of multiconfigurational *ab initio* theorists, could now be carried out by the average, computer-literate inorganic chemist. Indeed, by the end of the 1990s, DFT calculations had thoroughly permeated many areas of chemistry, including inorganic chemistry, while conventional WFT studies all but vanished from mainstream chemical journals. The late 1990s thus saw a remarkable turning of quantum chemical tables, with DFT, the underdog, clearly emerging on top. This state of affairs has continued into this decade and is fully reflected in the present volume. In other words, this special issue is unabashedly a celebration of DFT, applied to transition metal systems.[1]

2. An overview of this special issue

If I have sung DFT's praises a bit too loudly, let me take a step back: current DFT methods are far from perfect. For anyone involved with DFT calculations on open-shell transition metal systems, it is worth a reasonable amount of effort to get a basic idea of the fundamental theory as well as a sense of the performance of DFT vis-à-vis different molecular properties. The opening contribution by Neese provides just such an overview, aimed at an inorganic/bioinorganic audience. The next review, by Comba and Kerscher, provides additional examples of the performance of DFT. The next contribution, by Bendix and co-workers, provides an account of modern DFT-based ligand-field theory (LFT), which derives otherwise inaccessible ligand-field parameters from DFT, while emphasizing the simple physical insights afforded by LFT. Filatov's contribution is more specialized, focusing on first-principles calculations of Mössbauer isomer shifts, a most valuable exercise for a variety of iron-containing bioinorganic intermediates.

Next follow a series of reviews on some major topics in contemporary coordination chemistry and organometallic chemistry. Reidel and Kaupp discuss high-oxidation state transition metal complexes, while Sola and Matito discuss topological aspects of metal–ligand bonding. Of particular interest are cases where multiple reviews cover a given field, resulting in a wonderfully multifaceted picture. Thus, two reviews – by Lein and by Maseras and co-workers – present complementary perspectives of agostic interactions. Similarly, Bickelhaupt and Cavallo, along with their co-workers, present two different perspectives of N-heterocyclic carbene complexes. A valuable discussion of phosphine ligands and of the metal–phosphine bond has been presented by Harvey and coworkers, while Roithova and Schröder emphasize theory-experiment synergy vis-à-vis the gas phase chemistry of the coinage metals.

Four reviews cover important bioinorganic topics. Gherman and Cramer present a much-needed, comprehensive review of theoretical studies on $[Cu_2(\mu\text{-}O)_2]^{2+}$ intermediates. De Visser provides an account of iron-oxo intermediates of nonheme iron enzymes, a major mechanistic-bioinorganic observation of this decade. Interest in B_{12} chemistry continues unabated and theoretical studies continue to revolve around explaining the unexpectedly facile Co–C bond cleavage which is a key step in the catalytic cycles of many B_{12}-containing enzymes. Two reviews – by Jensen and Ryde and by Brunold and co-workers – provide complementary perspectives of this fascinating topic.

Finally, two reviews, by Deeth and co-workers and by Zimmer, address the issue of whether classical molecular modeling has a useful role to play in the DFT era. Perhaps surprisingly to some, the answer appears to be yes, if only because of the sheer speed of such calculations. Once force fields for transition metals (in their multitude of coordination geometries and spin states) are in place, classical molecular modeling of metalloproteins is clearly going to be far more efficient than any quantum approach (such as QM/MM and QM/MD), at least for the foreseeable future.

3. What remains to be done?

In case some contributors have taken DFT a bit too much for granted in this special issue, let me mention some of the main limitations of current DFT methods. DFT is normally viewed as excellent for ground-state structures and vibrational frequencies. On the other hand, the issue of spin-state energetics of open-shell transition metal complexes is a much more vexing issue. No known

[1] For a set of reviews on "Just how good is DFT?" aimed at a bioinorganic audience, see: A. Ghosh, J. Biol. Inorg. Chem. 11 (2006) 671–673.

0010-8545/$ – see front matter
doi:10.1016/j.ccr.2009.01.006

Fig. 1. A cartoon view of functionals and their antics. The cartoon was drawn by Mr. Odd Klaudiussen, based on design directives from AG.

exchange-correlation functional provides a good description of the spin-state energetics of even a moderately wide range of transition metal complexes. Less well-known is the fact that even issues related to molecular structure may be occasionally troublesome. For example, in an ongoing study of spin-crossover $Fe^{II}(salen)(py)_2$ (where py is a substituted pyridine) complexes in our laboratory,[2] we found that whereas many pure functionals give reasonable geometries for the S = 0, 1 and 2 states, the energies are poor, inconsistent with the observed spin-crossover behavior of the complexes. In contrast, hybrid functionals gave poor geometries for some of the higher-spin states: the axial Fe–N_{py} bonds were so long that the pyridines almost appeared to have fallen off. The pragmatic but inelegant solution that we ended up with was to obtain structures with a pure functional and then to obtain single-point energies with a hybrid functional such as B3LYP or B3LYP*. I had a good banter about the problem with my friend and noted *ab initio* theorist Peter Taylor (University of Warwick) and Fig. 1 presents a cartoon view of the conversation. Despite his tongue-in-cheek comment (that he never invented a functional), many leading quantum chemistry groups are currently (and justifiably!) hard at work developing improved exchange-correlation functionals.

[2] B. Weber, F.A. Walker, Inorg. Chem. 46 (2007) 6794–6803.

Another well-known limitation of DFT is vis-à-vis van der Waals (or dispersion) interactions. A number of ingenious approaches have been devised to tackle this issue. *Ab initio*–DFT hybrid methods, currently under development in a number of groups, are one approach to the problem. Another empirical but very efficient and apparently quite accurate approach called DFT-D (D for dispersion) has been reported by Grimme, where interatomic potentials of the form C_6R^{-6} are used in conjunction with regular gradient-corrected density functionals to describe dispersion energies.[3]

Excited states and photochemistry are yet another frontier for quantum chemistry. Although DFT is essentially a ground-state theory, a variety of formalisms including time-dependent DFT (TDDFT) and DFT/MRCI have been developed, which allow calculations of excited states and electronic spectra. Very recently, even TDDFT gradients have been implemented in a number of DFT codes, although actual calculations of excited-state structures and potential energy surfaces remain fraught with a variety of problems. Not all of these methods have been implemented for open-shell systems, which limits their application significantly to coordination chemistry, but this should change with time.

There are many other areas of inorganic chemistry where methodological advances in quantum chemistry would be particularly useful. Surface chemistry and heavy element chemistry (especially actinides) are just two examples of such areas.

In concluding, let me return to the issue of WFT: is there a future for *ab initio* WFT (as far as mainstream inorganic chemists are concerned)? At present, high-level *ab initio* methods such as CASPT2 and CCSD(T) provide valuable calibration of DFT-derived spin-state energetics for transition metal systems. Even more important, multiconfigurational theory can clarify electronic structures where DFT results, even if they eventually turn out to be essentially correct, cannot be trusted. A good example is oxyheme, whose electronic structure has remained uncertain for decades. By comparing multiconfigurational *ab initio* and DFT results, Shaik and co-workers have brought much-needed clarity to this system; as it happens, both the *ab initio* and DFT natural orbitals are very similar, indicating that the DFT picture of the bonding is indeed quite good.[4] A similar example is provided by chloroiron corrole. On the basis of a detailed CASSCF/CASPT2 study, Roos, I and our collaborators have shown that this complex does not contain a high-valent Fe(IV) center (nor indeed does any of its low-lying excited states); instead, the complex is best described as spin-coupled Fe^{III}-corrole$^{\bullet 2-}$.[5] These examples illustrate that WFT, though reduced in importance, remains useful in certain niche applications. In a year or two, I hope to assemble another set of reviews offering a more in-depth look at the role of *ab initio* WFT calculations vis-à-vis transition metal systems – stay tuned!

Abhik Ghosh*
Department of Chemistry and the Center for Theoretical and Computational Chemistry, University of Tromsø, N-9037 Tromsø, Norway

* Tel.: +47 77644072; fax: +47 77644765.
E-mail address: abhik@chem.uit.no

2 January 2009
Available online 15 January 2009

[3] S. Grimme, J. Comp. Chem. 25 (2004) 1463–1473.

[4] H. Chen, M. Ikeda-Saito, S. Shaik, J. Am. Chem. Soc. 130 (2008) 14778–14790.

[5] B.O. Roos, V. Veryazov, J. Conradie, P.R. Taylor, A. Ghosh, J. Phys. Chem. B 112 (2008) 14099–14102.