

Challenges and Advances in Computational Chemistry and Physics

Volume 29

Series editor

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Transition Metals in Coordination Environments

Computational Chemistry and Catalysis
Viewpoints

 Springer

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Preface

From its very foundation, quantum chemistry has been closely accompanying experiment in search of properties of a coordinate bond and structures of coordination compounds. The impact of the molecular orbital concept exerted on the model crystal field theory converted it to the ligand field theory which paved the way to investigate transition metal (TM) systems from first principles. Already early and of necessity simplified wave function methods were applied to study structures and other properties of transition metal complexes, but only after the advent of robust density functional-based methods, the number of quantitative applications dramatically increased. The number of theoretical works devoted to transition metal coordination compounds, dealing with their intricate electronic structures, spectral and magnetic properties, and related catalytic activity has already exceeded ten thousand, with recent contributions reaching over 500 papers each year. This is an obvious direction since the electronic properties of coordinated transition metals are largely responsible for unique activity of TM sites in materials and bio- or inorganic catalysis, and fine control of an intricate TM chemistry is vital for the progress of society and environmental safety.

Wide demand for theory-based practical guidelines for designing modern materials in the fields of medicine, electronics, and sustainable technology compelled the studies on transition metal compounds to verge upon the limits. However, it was soon recognized that the exact description of advanced electronic and magnetic properties of TM sites in materials required involvement of high-level theoretical approaches, more demanding than standard density functional theory (DFT). This prompted us to design this book as a collection of chapters, dealing with both the advancements in correlated wave function theory, making it still more accurate but less costly, and summarizing the attempts to upgrade DFT methods to make them sufficiently accurate to become robust and reliable tools for quantitative predictions. On the other hand, the quest for exact description of electron density-based properties of coordinated transition metals is challenging to both theory and experiment; thus, the interplay between these two areas remains in the focus of consecutive chapters devoted to selected subfields, here spin-related phenomena, spectroscopic, electrochemical, and catalytic properties of TM in

various coordination environments. In this spirit, the following chapters are not strictly ordered either according to the level of theory or along formal distinction with respect to the branch of chemistry or physics, but cover rather related fields, combining various levels of theory and experiment.

The initial batch of five chapters deals with magnetic interactions, untypical systems, and related dedicated theoretical approaches. Chapter “[The Electronic Determinants of Spin Crossover Described by Density Functional Theory](#)” by Kasper P. Kepp deals with spin crossover (SCO) phenomenon which plays a vital role in living systems and in many emerging technologies. In line with the introductory paragraphs, the accurate prediction and design of SCO systems are of high current priority, while SCO tendency is extremely sensitive not only to the level of theory but also to its ability to cover such physical effects as dispersion, relativistic effects, and vibrational entropy for large molecular systems. It is shown that the density functional theory (DFT) is the tool of choice that can be predictive for this purpose only if the study is carried out scrupulously. A similar approach is taken in Chapter “[Anisotropic Magnetic Spin Interactions of Transition Metal Complexes and Metalloenzymes from Spectroscopy and Quantum Chemistry](#)” where Matthias Stein on example of transition metal-containing model complexes and metalloenzymes discusses the advancement of DFT computational approaches to calculate the parameters of the effective Spin Hamiltonian such as the electronic g - and hyperfine tensors in order to support the analysis and interpretation of complex magnetic resonance spectra. Chapter “[Non-covalent Interactions in Selected Transition Metal Complexes](#)” by Filip Sagan and Mariusz P. Mitoraj discusses how DFT is able to describe non-covalent chemical interactions in transition metal complexes where routine DFT methods have been known to occasionally fail. The authors illustrate on several examples of nonstandard bonds that good separation of donation (ligand to metal) and back-donation (metal to ligand) charge transfer processes, which govern this type of bonding, may be done by proper analysis of the deformation density.

Different approach is taken by Vera Krewald and Dimitrios A. Pantazis (Chapter “[Applications of the Density Matrix Renormalization Group to Exchange-Coupled Transition Metal Systems](#)”). This chapter deals with inherently multireference problem, like oligonuclear transition metal complexes containing magnetically coupled open-shell ions, not always tractable by broken-symmetry DFT. In such cases, the use of multireference methods remains the deal to treat the exchange coupling. However, the applicability of these methods has been severely restricted due to their computational cost, and only in recent years, the introduction of the density matrix renormalization group (DMRG) to quantum chemistry has enabled the multireference treatment of exchange-coupled transition metal systems. The first detailed applications of DMRG-based methods to exchange-coupled systems are reviewed, and the lessons learned so far regarding the applicability, apparent limitations, and future promise of this approach are discussed. In the same spirit, Chapter “[New Strategies in Modeling Electronic Structures and Properties with Applications to Actinides](#)” is written by Aleksandra Leszczyk, Paweł Tecmer, and Katharina Boguslawski. After a short overview of relativistic Hamiltonians,

frequently applied to account for relativistic effects, the authors review conventional and unconventional single- and multireference approaches, developed to model the multireference nature of actinide compounds and their ground- and excited-state electronic structures, finishing with geminal-based approaches. In addition, concepts of quantum information theory are introduced, providing a qualitative understanding of complex electronic structures of actinide compounds using the picture of interacting orbitals.

The set of next four chapters is generally devoted to spectroscopic issues where the interplay between experiment and theory is frequently indispensable for the interpretation of the spectra and translates the gained information into chemical insights. In Chapter “[Computational Versus Experimental Spectroscopy for Transition Metals](#)” Maja Gruden, Wesley R. Browne, Marcel Swart, and Carole Duboc discuss a variety of examples where different spectroscopy techniques aided by computations allow to determine intricate and elusive properties, like the oxidation state, spin state, or coordination environment around redox-active metal ions such as iron, manganese, or nickel.

Marcus Lundberg and Mickaël G. Delcey show in Chapter “[Multiconfigurational Approach to X-ray Spectroscopy of Transition Metal Complexes](#)” how close correlation between theoretical modeling and X-ray experiment allows for the identification of the electronic and geometric structure of transition metal system through their spectral fingerprint from the core excitation energies. Compared to ground state calculations, modeling of X-ray spectra is complicated by the presence of the core hole, which typically leads to multiple open shells and large effects of spin-orbit coupling. Thus, reliable fingerprinting requires a theoretical model that is accurate enough, and the authors show that multiconfigurational wave function approaches, recently extended to model a number of X-ray processes of transition metal complexes, are suitable for that purpose. Chapter “[Assessing Electronically Excited States of Cobalamins via Absorption Spectroscopy and Time-Dependent Density Functional Theory](#)” by Megan J. Toda, Pawel M. Kozłowski, and Tadeusz Andruniów is specifically devoted to one type of systems, B12 chemistry. Due to the complexity and the size of the cobalamins, the computational analysis is almost exclusively represented by DFT and time-dependent DFT (TD-DFT) methods; thus, the proper choice of exchange-correlation functional discussed by authors is of paramount importance in predicting electronic transitions and simulating the full spectrum reliably. Chapter “[Photodeactivation Channels of Transition Metal Complexes: A Computational Chemistry Perspective](#)” by Daniel Escudero which concludes this section deals with the fate of the excited states in a transition metal compound, deactivating via a plethora of interconnected relaxation processes, competing with each other and controlled by the subtle interplay of electronic and geometrical rearrangements. The author provides critical overview of the state-of-the-art quantum chemical and reaction dynamic methods to study the photodeactivation dynamics in transition metal compounds and illustrates the progress and challenges in this field with recent examples on a variety of excited states in photoactive iridium and ruthenium complexes.

Finally, the third section of the book is devoted to computational approaches to catalysis by transition metal compounds, with enzymatic and biomimetic systems allocated as the last, separate part. The section opens with Chapter “[Mechanism and Kinetics in Homogeneous Catalysis: A Computational Viewpoint](#)” where Jeremy N. Harvey critically reviews the use of computational methods based on electronic structure theory and statistical mechanics to study reaction mechanisms and kinetics in homogeneous catalysis, especially organometallic catalysis and organocatalysis. The chapter is based on suitably selected examples from the authors’ own group, which are discussed in the perspective of progress and still open challenges for computational chemistry to model actual chemistry. A careful reading of this chapter may be especially recommended as a warning to researchers pursuing this domain of computational modeling because it draws their attention to still existing (and occasionally even growing) number of doubts and pitfalls awaiting inexperienced users of “user-friendly” computational, half-automated tools. The main line set in the introductory chapter for this part is actually followed in consecutive three chapters which are devoted to complicated reaction patterns found in catalytic systems and summarize attempts to allow various extended environments into the modeling.

Chapter “[Computational Modelling of Structure and Catalytic Properties of Silica-Supported Group VI Transition Metal Oxide Species](#)” by Jarosław Handzlik deals with chromium, molybdenum, and tungsten oxides supported on amorphous silica, the catalysts for many reactions, including large-scale industrial processes. Although these systems have been extensively studied for many years, there are still unresolved issues, concerning mainly the nature of the active sites and mechanisms of their formation. Computational studies, using carefully selected cluster or periodic models to represent the catalyst surface, are helpful in interpretation of spectroscopic data and can provide complementary information about the catalytic process and lead to complex structure–activity relationships. Nevertheless, even if a great progress has been achieved in modeling of these systems, theoretical determining of complex reaction mechanisms using surface models with representative distribution of metal sites is still a challenge for computational catalysis. Chapter “[Catalytic Properties of Selected Transition Metal Oxides—Computational Studies](#)” by Witold Piskorz and Filip Zasada constitutes the review of computational methods applied specifically to transition metal oxides (most abundant in heterogeneous catalysis, used as bulk or supported oxides) and is focused on the influence of the environment on the transition metal cation properties. The shortcomings of the DFT level of theory, most commonly used for modeling, are discussed, and its extensions toward more realistic environment are presented. The modern reactive force field methods are also mentioned, and the embedding schemes most commonly found in the quantum chemical or classical description of the heterogeneous processes are discussed. It is shown that in all discussed systems, the appropriately applied Hubbard DFT GGA+U methods are successful provided that the Hubbard correction is carefully tuned for modeling of particular properties. In turn, Chapter “[Molecular Electrochemistry of Coordination Compounds—A Correlation Between Quantum Chemical Calculations and Experiment](#)” by

Piotr P. Romańczyk and Stefan S. Kurek describes the progress in efficient solvation models that helped to develop effective computational protocols allowing for accurate reproduction of experimental redox potentials of mono- and dinuclear complexes, including electrocatalytically relevant systems and mixed-valence compounds. Examples of such computational protocols that use DFT combined with continuum solvent models, as well as a mixed, discrete-continuum approach, are shown in this contribution. The ferrocenium/ferrocene system, widely used as an internal standard, is discussed, followed by the presentation of intriguing properties of mono- and bimetallic Mo/W scorpionates, in particular electrochemical communication between metal centers and a baffling dehalogenation, the mechanism of which was elucidated only owing to the application of DFT-D3 calculations.

The end section of the book entails four chapters and discusses enzymatic and biomimetic systems. The topic is singled out even if problems intrinsic to very large systems incorporating transition metals are generally common; nevertheless, transition metals in bio- or bioinorganic complexes share several specific properties and specific techniques common among them but distinctive from inorganic transition metal complexes. This part opens with Chapter [“The Quest for Accurate Theoretical Models of Metalloenzymes: An Aid to Experiment”](#) by Matthew G. Quesne and Sam P. de Visser. The chapter reviews two key computational approaches to metalloenzymes, namely quantum mechanics/molecular mechanics (QM/MM) on complete enzyme structures and QM cluster models on active site structures only. The former take the structure of the full enzyme with a solvent layer into consideration, whereas the latter only include key features of the first and second coordination sphere. The examples are discussed where the QM cluster approach worked well; however, for systems where substrate binding is tight and or a network of hydrogen-bonding interactions exists, a complete QM/MM approach may be more appropriate. The following Chapter [“Applications of Computational Chemistry to Selected Problems of Transition-Metal Catalysis in Biological and Nonbiological Systems”](#) by Hajime Hirao describes as well recent attempts to study the structure and catalytic properties of transition metal-containing systems of different sizes, including metalloenzymes but also metal–organic frameworks (MOFs). Similar techniques (DFT and hybrid techniques for embedding) are used, but examples are selected specifically and substantially broaden the spectrum of applications, increasing the pool for critical analyses and benchmarking. The same concerns Chapter [“How Metal Coordination in the Ca-, Ce-, and Eu-Containing Methanol Dehydrogenase Enzymes can Influence the Catalysis: A Theoretical Point of View”](#) written by Tiziana Marino, Mario Prejanò, and Nino Russo, where the pool of examples is farther enriched with studies on lanthanide-containing enzymes where relativistic effects played a significant role.

The section is finalized by Tomasz Borowski and Maciej Szaleniec in Chapter [“Challenges in Modelling Metalloenzymes”](#) which gives a critical summary of the entire process of constructing a reliable computational model for metalloenzymes. This contribution, complementary to preceding chapters, nicely illustrates and validates the key decisions and steps one has to take in such projects: validating

X-ray structures, re-refining metal sites, determining residues protonation state, modeling missing loop regions or whole proteins by comparative modeling, performing MD simulations, choosing representative snapshots and constructing QM models. While this list is by no means exhaustive, the content of this chapter, combined with the material covered in other chapters of this book offers a more comprehensive view on modeling metalloenzymes and may supply additional suggestions for modeling other systems related to modern materials.

In the closing paragraph of this Preface, the reader deserves some remarks justifying the need for publishing (and reading!) still new book on modeling transition metals in various coordination environments despite that many works on the topic have already appeared. We hope we succeed in constructing the book as a collection of chapters well obeying the balance between methodological and practical information. The first nine chapters deal with advancements in correlated wave function and DFT methods making them applicable to nonstandard problems, whereas the next eight contributions bring as well instructive examples of their applications as practical guidance (and warnings!) to prospective users of modeling protocols in related disciplines.

We are very grateful to all authors for their contributions shaping this book and for their patience.

Kraków, Poland

Ewa Broclawik
Tomasz Borowski
Mariusz Radoń

Contents

| | |
|--|-----|
| The Electronic Determinants of Spin Crossover Described by Density Functional Theory | 1 |
| Kasper Planeta Kepp | |
| Anisotropic Magnetic Spin Interactions of Transition Metal Complexes and Metalloenzymes from Spectroscopy and Quantum Chemistry | 35 |
| Matthias Stein | |
| Non-covalent Interactions in Selected Transition Metal Complexes | 65 |
| Filip Sagan and Mariusz P. Mitoraj | |
| Applications of the Density Matrix Renormalization Group to Exchange-Coupled Transition Metal Systems | 91 |
| Vera Krewald and Dimitrios A. Pantazis | |
| New Strategies in Modeling Electronic Structures and Properties with Applications to Actinides | 121 |
| Aleksandra Leszczyk, Paweł Tecmer and Katharina Boguslawski | |
| Computational Versus Experimental Spectroscopy for Transition Metals | 161 |
| Maja Gruden, Wesley R. Browne, Marcel Swart and Carole Duboc | |
| Multiconfigurational Approach to X-ray Spectroscopy of Transition Metal Complexes | 185 |
| Marcus Lundberg and Mickaël G. Delcey | |
| Assessing Electronically Excited States of Cobalamins via Absorption Spectroscopy and Time-Dependent Density Functional Theory | 219 |
| Megan J. Toda, Paweł M. Kozłowski and Tadeusz Andruniów | |

| | |
|--|-----|
| Photodeactivation Channels of Transition Metal Complexes: A Computational Chemistry Perspective | 259 |
| Daniel Escudero | |
| Mechanism and Kinetics in Homogeneous Catalysis: A Computational Viewpoint | 289 |
| Jeremy N. Harvey | |
| Computational Modelling of Structure and Catalytic Properties of Silica-Supported Group VI Transition Metal Oxide Species | 315 |
| Jarosław Handzlik | |
| Catalytic Properties of Selected Transition Metal Oxides—Computational Studies | 345 |
| Witold Piskorz and Filip Zasada | |
| Molecular Electrochemistry of Coordination Compounds—A Correlation Between Quantum Chemical Calculations and Experiment | 409 |
| Piotr P. Romańczyk and Stefan S. Kurek | |
| The Quest for Accurate Theoretical Models of Metalloenzymes: An Aid to Experiment | 439 |
| Matthew G. Quesne and Sam P. de Visser | |
| Applications of Computational Chemistry to Selected Problems of Transition-Metal Catalysis in Biological and Nonbiological Systems | 463 |
| Hajime Hirao | |
| How Metal Coordination in the Ca-, Ce-, and Eu-Containing Methanol Dehydrogenase Enzymes Can Influence the Catalysis: A Theoretical Point of View | 487 |
| Tiziana Marino, Mario Prejanò and Nino Russo | |
| Challenges in Modelling Metalloenzymes | 503 |
| Tomasz Borowski and Maciej Szaleniec | |
| Index | 527 |

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