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Review

Density functional theory applied to calculating optical and spectroscopic properties of metal complexes: NMR and optical activity☆

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Contents

Abstract

A short overview of the theoretical approach to calculate linear response properties (double perturbation properties) for molecules is given. The importance of response calculations to determine various spectroscopic parameters is outlined. The formalism covers static (time-independent) and dynamic (time-dependent) perturbations. Two areas of research where such theoretical methods are of practical importance are the computation of NMR parameters and computations of response functions that govern the optical activity of a molecule. An account of recent work by the author and collaborators based on density functional theory as applied to the computation of NMR chemical shifts and spin–spin coupling and to circular dichroism and optical rotation of metal complexes is presented. Among other topics, relativistic effects, solvent effects, and vibrational corrections are discussed.

Keywords: Transition metal complexes; Computational chemistry; NMR; Optical activity; Relativistic effects; Solvent effects; DFT computations

1. Introduction

The computation of properties of metal complexes by utilizing first-principles (ab initio) quantum theoretical methods has traditionally met with great challenges. Even as recent as 10–15 years ago, most first-principles computations on metal

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complexes have not been able to match the expectations of experimental chemists in their ability to reproduce experimental data, to predict yet unavailable measurements with confidence, or to support assignments of spectra and analyses of optical and spectroscopic properties with the help of theoretical results that agree well with experiment. Instead, semi-empirical methods were in widespread use. It is fair to state that the situation has changed tremendously in the meantime; few chemists today question the value of ab initio theoretical support in their research.

It is widely recognized that both the advances in affordable computer hardware and many break-through method developments in quantum chemistry have contributed to the success-story of ab initio computational coordination chemistry. This article will focus on applications of some of the quantum chemical methods developed during recent years. It is now possible not only to explore the chemistry of metal complexes computationally – a task defined in the context of this paper as the computation of the energy of a metal system as a function of geometry, i.e. isomers, conformers, reactants, products, transitions states, and so on – but also to a satisfactory degree their optical and spectroscopic properties. Such properties can be defined as derivatives of the energy (or a suitably defined time-dependent quasi-energy), for example with respect to the presence of electric and magnetic fields, or nuclear positions, to name a few of the most important examples.

High-level correlated wave-function based ab initio computational methods have occasionally been applied to calculate properties of metal complexes. However, because of the scaling behavior of most of these methods with system size it is clear that the main tool for most of present-day computational coordination chemistry is density functional theory (DFT), both in its static version as applied to the electronic ground state (structures, energies) and in its time-dependent version (TD-DFT) as applied to determine excitation energies and dynamic properties. Consequently, the present article will focus on applications of DFT and TDDFT in the coordination chemistry field.

Ab initio computational chemistry of coordination compounds is a research field that has diversified to a point where it would be difficult to review most of the pertinent literature in a single article. A selection of reviews on more specialized topics is the following: Rosa et al. have reviewed the computation of excitation spectra of metal complexes [1]; Autschbach [2,3], and Autschbach and Ziegler [4–6] have reviewed computations of energy and many energy-derivative properties (NMR, EPR, optical, chiral, and others); Bühl, Kaupp, et al. have reviewed the computation of NMR in metal systems [7,8]; the results of experimental and computational NMR studies performed by Bagno et al. on systems containing ^{99}Ru, ^{103}Rh, ^{181}Ta, ^{183}W, and ^{199}Hg and $^{203/205}$Tl, among others, have been summarized by Bagno and Saielli [9]; and a number of researchers have reviewed computational work on EPR parameters of open-shell molecules in Ref. [10]; see for instance Neese's chapter on applications in bioinorganic chemistry [11]. A selection of reviews on a variety of topics including general aspects of transition metal complex modelling can be found, for example, in the February 2000 thematic issue of *Chem. Rev.* entitled "Computational Transition Metal Chemistry" and in a "Theoretical and Computational Chemistry" special issue of *Coord. Chem. Rev.* (vols. 238/239, March 2003). The modelling of reaction inorganic mechanisms has been reviewed, e.g., by Ziegler in Ref. [12]. For the field of magnetic resonance (both NMR and EPR), a book edited by Kaupp, Bühl, and Malkin, Ref. [10], provides a convenient collection of reviews (including some of the articles cited above) which contain many references to work on metal complexes. The "Chemist's Guide to Density Functional Theory" by Koch and Holthausen [13] quotes numerous benchmark data for structure, energy, reactivity, and optical and spectroscopic data obtained with DFT for metal complexes. A two-volume special issue of *Structure and Bonding* on "Principles and Applications of Density Functional Theory in Inorganic Chemistry" contains many references to original research articles dealing with coordination chemistry (vols. 112/113, 2004). It has already been pointed out that DFT has become the major theoretical tool to study metal complexes which is clearly reflected in the available reviews.

The present article is mainly concerned with recent advances made by the author and his collaborators in the first-principles modelling of NMR parameters and of the optical activity of transition metal complexes. It provides an account of topics presented by the author in a keynote lecture at the 37th International Congress of Coordination Chemistry that took place in Cape Town, South Africa, in August 2006. Some related studies by other research groups will also be discussed. The two research areas that are the subject of this article may seem only loosely connected at first sight, but it will be shown in Section 2 that their theoretical treatment is closely related. Specific studies of metal complexes and their main results will be discussed in Sections 3 and 4. Some general concluding remarks can be found in Section 5. Section 2 is not essential for reading Sections 3 and 4 and may be skipped, although this section provides some useful theoretical background.

2. Computation of linear response properties: a quick overview

A detailed overview of the theoretical approach to calculating so-called second-order properties (also termed linear response properties or double perturbation properties) of general molecules, with a focus on metal complexes, has been given by Autschbach and Ziegler in this Journal [4]. We summarize some of the main steps here but also extend upon the discussion of theoretical methods presented in Ref. [4]. The reader is referred to Refs. [4,14] for further details. We will restrict the discussion to the Born–Oppenheimer approximation, i.e. the nuclei are considered to be fixed and only the electronic degrees of freedom are included in the quantum mechanical formalism. Electromagnetic fields are treated semi-classically. Dimensionless atomic units with the electronic charge $e = 1$, electronic mass $m_e = 1$, Planck's constant $h = 2\pi$, $4\pi\epsilon_0 = 1$ and the speed of light $c \approx 137.036$ will be used throughout the theoretical section. Consequently, factors of $e, m_e, \hbar = h/(2\pi) = 1$ and $4\pi\epsilon_0$ will often be omitted in the equations. In these atomic units the fine structure constant α equals $1/c$. Boldface notation is used for vectors.

Definitions of molecular properties are related to the energy and the wavefunction via the system's Hamiltonian and the