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Review

Covalency and chemical bonding in transition metal complexes: An ab initio based ligand field perspective

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N-electron valence perturbation theory to second order (NEVPT2)

ABSTRACT

In this work, a general, user-friendly method – ab initio ligand field theory (AILFT), is described and illustrated. AILFT allows one to unambiguously extract all ligand field parameters (the ligand field one-electron matrix $\boldsymbol{V}_{LFT}$, the Racah parameters B and C, and the spin-orbit coupling parameter ζ) from relatively straightforward multi-reference ab initio calculations. The method applies to mononuclear complexes in d^n or f^n configurations. The method is illustrated using complete active space self-consistent field (CASSCF) and N-electron valence perturbation theory (NEVPT2) calculations on a series of well documented octahedral complexes of Cr^{III} with simple ligands such as F^-, Cl^-, Br^-, I^-, NH_3 and CN^-. It is shown that all well-known trends for the value of $10Dq$ (the spectrochemical series) are faithfully reproduced by AILFT. By comparison of B and ζ for Cr^{III} in these complexes with the parameters calculated for the free ion Cr^{3+}, the covalency of the Cr-ligand bond can be assessed quantitatively (the non-relativistic and relativistic nephelauxetic effects). The variation of ligand field parameters for complexes of 3d, 4d and 5d elements is studied using MCl_6^{3-} ($M = Cr^{III}, Mo^{III}, W^{III}$) as model examples. As reflected in variations of $10Dq$, B and ζ across this series, metal-ligand covalency increases from $CrCl_6^{3-}$ to $MoCl_6^{3-}$ to WCl_6^{3-}. Using the angular overlap model, the one-electron parameters of the ligand field matrix are decomposed into increments for σ- and π- metal-ligand interactions. This allows for the quantification of variations in σ- and π-ligand donor properties of these ligands. Using these results, the well documented two-dimensional spectroscopic series for complexes of Cr^{III} is quantitatively reproduced. Comparison of the results obtained using CASSCF and NEVPT2 reveals the importance of dynamic electron correlation. Finally, the limitations of the AILFT method for complexes with increasing metal-ligand covalency are analyzed and discussed.

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1. Introduction

Ligand field theory [1–8] is a model designed for an entire *class* of compounds – namely coordination complexes of d-block transition metals (TM) in oxidation states that are not too high or too low, typically II and III. The electronic structure of the free ions with charges +2 and +3 has been studied in great detail by atomic spectroscopy, more specifically by discharge spectra, which display sharp d-d transitions [9–11]. For example, for the Cr(III) ion, which we will focus on in the present review, all S = 3/2 (^4F and ^4P) and S = 1/2 states (except of b^2D) could be identified in the spectra, including their splitting into spin-orbit coupled multiplets. Such spectroscopic studies served as a basis for the development of the quantum theory of atomic structure [12].

The electronic structures of the free ions change in a characteristic way upon embedding in a coordination complex with neutral or anionic ligands. Such complexes often display geometries of high symmetry – octahedral (O_h) or tetrahedral (T_d). This enables the use group theory for the classification of localized ground- and excited electronic levels, commonly referred to as terms or multiplets [13]. For predominantly ionic (Werner type) complexes, the nd^q ($\underline{n}$ = 3, 4, 5, q = 1–9) electronic configurations were shown by spectroscopy to be well defined [14]. The d^n configurations then give rise to a multitude of electronic states and to electronic transitions in the visible or near infra-red (IR) spectral region referred to as d-d or ligand field transitions [15]. Such transitions are manifested in absorption bands which gives rise to the beautiful and rich colors that are characteristic of coordination complexes with open d-shells. As they are partly filled, the nd^q configuration also leads to ground and excited electronic states with both spin and only partially quenched orbital angular momenta, and therefore exhibit a magnetic response to an applied external magnetic field [16,17]. Numerous experimental techniques such as near IR, visible, UV (UV–VIS) absorption and emission spectroscopies, magnetic circular dichroism (MCD) [18], and electron paramagnetic resonance (EPR) [19,20] have been employed widely to probe the electronic structures of transition metal complexes.

The early view of theory designed to interpret and classify the spectroscopic and magnetic properties of transition metal complexes considered “d-electrons” as completely localized on the metal [13]. As such, they were deemed to be solely affected by electrostatic interactions with surrounding ligands, where the latter have been modeled by point charges or point dipoles. In addition to parameters accounting for the Coulomb repulsion between the d-electrons, the potential due to ligand charges and dipoles has been used to explicitly calculate the splitting of the nd orbitals in the complex [21–23]. This led to a static picture of the d-electronic states in complexes where overlap between wave functions located at transition metal and the ligands is ignored, also known as crystal field theory [24,25].

It was soon realized that such a localized description leads to energy effects (e.g. term energy splitting in crystals) that are too small compared to those seen experimentally [26]. Electron paramagnetic resonance spectroscopy, which probes transitions between spin-levels in a homogeneous magnetic field, is another method that proved unambiguously that metal-ligand covalency does exist [19,27]. Metal-ligand hyperfine interactions manifested in the EPR spectra of Cu^{2+}(d^9) and Ir^{4+}(low-spin d^5) complexes with ^{19}F and $^{35,37}Cl$ (both possessing nuclear spins, I = 1/2 and 3/2, respectively) provided information about the delocalized spin-density, and correspondingly on the transferred hyperfine field that a ligand nuclei experiences from the spin of the transition metal bound to it [19]. This was the first *direct* manifestation of metal-ligand covalency. Note, that if the mechanism of spin-transfer to the ligand would be spin-polarization, one would expect negative spin density at the position of the ligands (as, for example, in the methyl radical, where the hydrogen atoms reside in a node of the singly occupied molecular orbital). However, positive spin-density at the directly coordinating ligand atoms must come from symmetry-allowed covalent delocalization. In order to account for such effects, molecular orbital theory was developed to include these effects in a straightforward and transparent manner. When applied to transition metal complexes, the resulting treatment was referred to as “ligand field theory” [1,3,25].

Ligand field spectra and ligand field parameters extracted from a best fit of these parameters to experimental energies of electronic transitions provided the first indirect information about metal-ligand bond at a time where neither density functional theory (DFT) nor ab initio methods were broadly in use [14,15]. Ligand field parameters consist of 10*Dq* (parametrizing the splitting of the 3d-orbitals in octahedral and tetrahedral ligand fields) and the Racah parameters *B* and *C*, which quantify interelectronic repulsion. Systematic studies of these parameters allowed the classification and ordering of TM complexes into series of increasing 10*Dq* and B/B_o (B_o the free ion value)–the spectrochemical [14,15] and nephelauxetic [28], series.

The reduction of the parameter *B* with respect to free ion values, $1 - B/B_o$ of the same element, otherwise known as the nephelauxetic effect, lead to the concept of ‘cloud expansion’ for the d-electrons, which provided a first attempt at determining metal-ligand covalency on a rigorous experimental basis [14,15]. Yet, the information content of the ligand field parameters deduced