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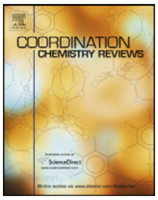

Review

Consistent descriptions of metal–ligand bonds and spin-crossover in inorganic chemistry

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Contents

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ABSTRACT

Density functional theory (DFT) is today the unchallenged tool for routinely obtaining molecular information on chemical stability, reactivity, and electronic structure across the Periodic Table. The chemical bond is the fundamental unit of molecular structure and reactivity, and thus, large-scale DFT studies of inorganic systems in catalysis and bioinorganic chemistry rely directly on the ability to balance correlation effects in the involved bonds across the s-, p-, and d-blocks. This review concerns recent efforts to describe such bonds accurately and consistently across the s-, p-, and d-blocks. Physical effects and ingredients in functionals, their systematic errors, and approaches to deal with them are discussed, in order to identify broadly applicable methods for inorganic chemistry.

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1. Introduction

The last two decades have been characterized by the massive diffusion of density functional theory (DFT) [1–3] into all fields of chemistry, a development that already in 1998 led to Walter Kohn sharing the Nobel Prize in chemistry with John Pople for their pioneering efforts in DFT and general quantum chemistry, respectively [4].

The current status 14 years later is that DFT is the unchallenged method for describing electronic structure in medium- and large-size molecular systems [5,6]. Its unique combination of computational speed and accuracy affects most areas of molecular science from molecular physics and chemistry to biochemistry, nanochemistry, and materials science. As an illustration, state-of-the-art DFT is an invaluable complementary and supporting tool for spectroscopic methods that have greatly contributed to shaping the field of bioinorganic chemistry [7,8].

DFT can describe molecular systems with an accuracy that often competes with experimental data, e.g. for local geometries of metal centers in proteins [9,10]. However, due to the formulation of DFT, there is no rigorous hierarchy of accuracy of functionals corresponding to the many-electron space of configuration state functions in wave function theory (WFT), although DFT is variational for each functional separately. Thus, no universal functional is available in algorithm to accurately describe any given electron density [1,3]. Scientists today rely on a relatively large arsenal of functionals with various strengths and weaknesses, depending on molecular systems and electronic properties studied, as reviewed before [6,11–23].

Functionals can be categorized according to their design and mathematical complexity [14]. In terms of complexity, one can distinguish (i) local uniform functionals (local spin density approximations [24]) with the energy being a functional of the electron density [25–27]; (ii) functionals that depend also on the gradient of the density (generalized gradient approximation, GGA) [28–30]; (iii) functionals that also depend on more or higher derivatives, e.g. the Laplacian of the density [31] or the kinetic energy density (meta functionals) [32]; (iv) functionals that substitute part of the exchange functional with non-local exchange from a determinant, typically from a Hartree–Fock (HF) procedure (hybrid functionals) [33]; and (v) functionals that substitute also part of the correlation energy for WFT correlation, e.g. from MP2 (double hybrids) [34]. Further levels of complexity also occur, e.g. range-corrected hybrids [35,36].

One can also distinguish a priori and a posteriori functionals: the a priori functionals fulfill physical bounds on the energy and density or its derivatives without violating fundamental laws [37–39], risking poor accuracy for specific, perhaps important classes of systems in exchange for a sound platform for further improvement. Representative functionals include PBE [40], TPSS [41], and to some extent their hybrid counterparts, PBE0 [42] and TPSSh (containing only one parameter, the amount of HF exchange) [43]. The a posteriori functionals use several (>1) fitted parameters and pragmatically and efficiently reproduce vital observables, guaranteeing good accuracy for systems and properties within the data sets used for developing the functionals, but possibly restricted from expanding this accuracy beyond their parameterization range [44]. Some representative functionals are B3LYP [33,45–47] of the hybrid type and M06 [48], a meta hybrid.

Fig. 1 shows the occurrence of topical words in papers from Thomson's Web of Science 1990–2011 as a very rough estimate of the overall trends in use of various theoretical methods (the absolute numbers may be affected by search strategy). To the left, various general methods are compared: while semi-empirical methods such as PM3 [49,50] are in decline due to DFT outcompeting them for widely studied medium-size systems (~10–100 atoms), MP2, with its N^5 size-restriction, maintains a steady use of ~1000/year due to its accuracy and stringent interpretation. DFT passed MP2 in the nineties and has grown super-linearly since then to reach ~6000/year. Coupled-cluster methods ("CCSD" keyword) display modestly increasing use, but a declining market share due to the massive increase in the use of DFT the last ten years.

The center and right parts of Fig. 1 show trends of a few individual functionals (they were all searched as "method synonym" + "dft", reducing total hits against "dft" alone to eliminate bias from other acronym uses). B3LYP has for many years been almost synonymous with DFT and remains by far the most applied functional, although during the last 2–3 years, new functionals are quickly conquering market shares. PBE was a first contender, which now seems to be overrun by the Minnesota functionals (M0x series) [51], but the trends are not completely established yet.

The chemistry community currently faces a transition from an almost uniform standard during the "golden age" of B3LYP to a new, refreshingly vibrant, but highly fragmented and confused market place of density functionals with numerous persuasive vendors. No new golden standard will arise soon, as judging from Fig. 1, and this could damage the credibility of theoretical chemists to their experimental colleagues and may divert productivity away from

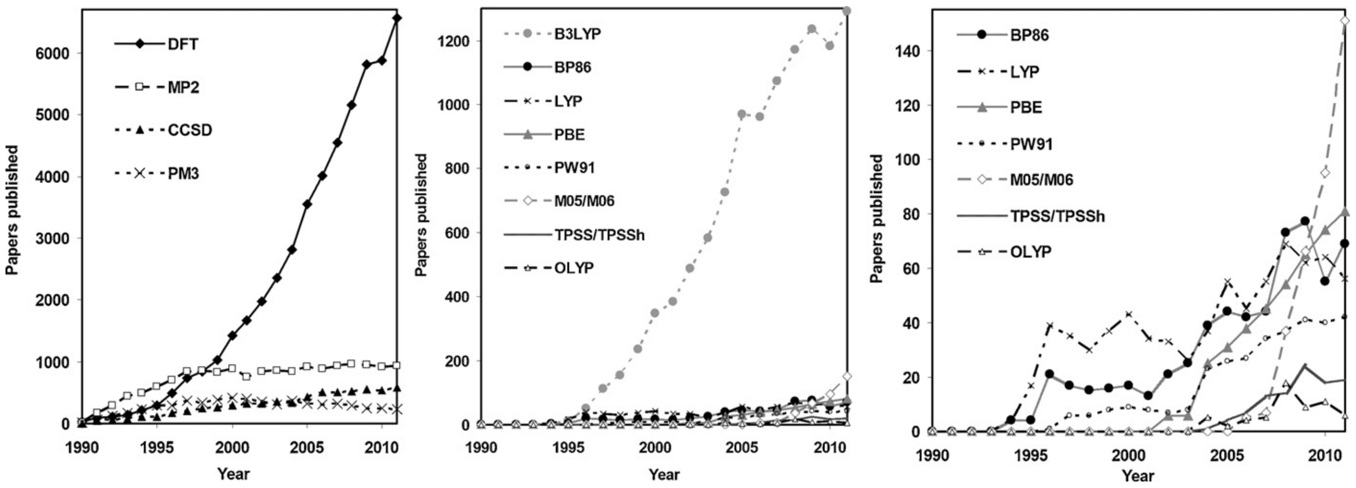

Fig. 1. Papers published 1990–2011 containing keywords corresponding to various electronic-structure methods; from Thomson Web of Science. Left: total counts of general methods: DFT, MP2, CCSD, and PM3. Center: DFT methods. Right: DFT methods without B3LYP.