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Density functional theory
A powerful tool for theoretical studies in coordination chemistry

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Abstract

The development of molecular orbitals (MO) techniques and their applications to structural and reactivity problems in coordination chemistry has been greatly enhanced by the availability of density functional theory (DFT) methods. Whereas semi-empirical MO methods were used to provide symmetry based arguments in structural chemistry and reactivity, DFT has enabled theoretical chemistry to accurately predict the structures of clusters, organometallics and coordination compounds. This review summarizes the main features of DFT, giving a brief background to selected calculations illustrating some topical examples.

Keywords: Coordination chemistry; Density functional theory (DFT); Theoretical chemistry

1. Introduction

The first link of theoretical chemistry with coordination chemistry traces to the first development of crystal field theory [1] in the early 1950s. This has been a wonderful tool to give some insight into transition metal compound properties, provided the symmetry around the transition metal (TM) is sufficiently high. In particular, optical properties related to electronic properties like UV–visible spectroscopy have greatly benefit from such a simple model. The splitting of *d* orbitals in highly symmetric environments (and to a lesser extent of *f* orbitals) has been rationalized and crystal field theory has become a popular aid for the solid spectroscopists community. Nevertheless, the model becomes less and less accurate as the crystal compound is less ionic, and its variant, the ligand field model [2], has overtaken the crystal field in such a way that ligand field calculations are often called crystal field calculations instead. Models like Griffith's [3] and Tanabe and Sugano's [4,5] are the "musts" of such approaches, which make calls to fits of parameters to describe experimental spectra. According to the simplicity of the model, namely the three Racah parameters, this model has great power in rationalizing spectra, even though this power decreases with any descent in symmetry, which requires more parameters to be fitted. However, this model lacks accuracy when one is tempted to use it to predict spectra of new compounds or new impurities in a crystalline host. Nevertheless, this model is widely used, because more recent methods like semi-empirical extended Hückel theory (EHT) or ab initio Hartree–Fock (HF) are not able, although through a much larger computational effort, to provide significantly better results, if any: EHT needs a difficult choice of parameters, and generally HF fails in the description of optical spectra of TM complexes, because of the strong importance of electron correlation for *d* electrons, which is not taken into account. DFT methods, as we will see later, may provide sufficiently accurate results for a reasonable computational cost, provided the symmetry is not too low, and this has been shown indeed with the ancestors of the DFT methods, the so-called Xα methods (MSXα [6,7], DVXα [8] and their variants) in the 1980s.

The starting point of the application of theoretical chemistry methods to organometallic and coordination compounds (oriented towards the reactivity and stability of structures) may be traced to the well-known extended Hückel methodology in the 1970s. Whereas other semi-empirical methods were found adequate for rationalizing organic chemistry, the importance of the transition metals in coordination compounds has made the EHT method the most popular for the principal reason that most, if not all, the other semi-empirical methods (all the NDDO family, maybe ZINDO excepted [9]) are unable to describe the *d* and *f* orbitals correctly, whereas HF fails dramatically if no very expensive configuration interaction (CI) is performed in order to take into account some correlation. Therefore, the EHT model, popularized by Hoffmann and coworkers [10–14], has made an extensive use of symmetry properties of orbitals, and perturbation theory ideas. One should emphasize that such a model usually fails to accurately describe some crystal field splitting energies, as well as charges on atoms. Moreover, in the case of bimetallic compounds, it becomes very difficult to define the metal parameters properly, ...even if one does know the answer. However, the method provides a powerful tool to rationalize the bonding capabilities of ligands and metal fragments according to their symmetry in the coordination compound. In the mean time, it is also a powerful tool to understand the effects of any symmetry descent, which allows orbital mixing, and the effect of angular distortion in a molecule or a fragment, indicating the possibility of orbital interactions susceptible to control the chemical reactivity. These are the building blocks of the frontier theory introduced by Fukui [15,16] and the isolobal analogy suggested by Hoffmann [17]. These semi-empirical models have, however, strong limitations, such as the inadequacy to determine the most stable geometry structure of a complex, and, more generally, the bond lengths in molecules. Modified EHT methods have been proposed to cure these drawbacks, but the improvements are far from being universal [18–20].

The development of DFT methods bringing "chemical accuracy" at the beginning of the 1990s [21,22], and connected with the unbroken progress in computer technology, has made these methods the most powerful tools of the end of this century, and probably the beginning of the next decade, for the study of coordination compounds. The purpose of this paper is not to give an exhaustive review of the basic concepts of the DFT, which have been described extensively elsewhere, but to provide some hints as to the properties of coordination compounds which can be tackled by DFT methods, and to tentatively comment on why DFT is more successful than other conventional ab initio methods for this class of compounds. Finally, some limitations in the present state-of-the-art of the DFT, and the directions into which progress can be expected, are given.

2. Basis of the DFT

2.1. Basis of DFT

The basis of the DFT has been explored in many articles and books [23–36]. Accordingly, we will write as few equations as possible in this review. Let us just

summarize that the Hohenberg and Kohn theorem [37] establishes that the ground state of an (electronic) system is just a functional of the (electronic) density so that, in principle, one only needs a knowledge of the density to calculate all the properties of these systems. Splitting the energy functional into kinetic energy, potential energy (i.e. energy from nuclei–electron interaction and energy coming from external fields), classical Coulomb electrostatic repulsion energy and exchange-correlation energy (everything else) E_{xc} is the first step of the description of the electronic system.

Unfortunately, the exchange-correlation energy functional, which should be universal, is not known and practical (and approximate) solutions are obtained by the use of the so-called Kohn–Sham (KS) orbitals, which differ from other kinds of orbitals mostly by the fact that the sum of the squares of the occupied KS orbitals is the true density of the system, an assumption which is only approximated in other quantum chemical methods such as Hartree–Fock. The Kohn–Sham method was introduced in 1965 [38], and lets us solve the problem through a Schrödinger equation which differs from the well-known Hartree–Fock equations by replacement of the exchange potential term by a more general exchange-correlation potential term which is, in principle, simpler because it is only a function of the density. The spin orbitals, $\psi_{i\sigma}(\boldsymbol{r})$, are solutions of KS equations:

$$[-\tfrac{1}{2}\nabla^2 + V_{\text{eff}}(\boldsymbol{r})]\psi_{i\sigma}^{\text{ks}} = \epsilon_{i\sigma}^{\text{ks}}\psi_{i\sigma}^{\text{ks}} \tag{1}$$

where the effective potential, V_{eff}, is the sum of the external potential $v(\boldsymbol{r})$, the Hartree potential for electrons $V_{\text{H}}(\boldsymbol{r})$ and the exchange-correlation potential $V_{\text{xc}\sigma}(\boldsymbol{r}) = \{\delta E_{\text{xc}}[\rho_\sigma(\boldsymbol{r})]/\delta\rho_\sigma(\boldsymbol{r})\}$ (with $\rho_\sigma = \Sigma_{i\sigma}\,|\psi_\sigma|^2$, σ being the spin index). The power of this approach lies in the fact that this latter potential includes not only the exchange in the Hartree–Fock sense, but also the correlation (which is referred to all that is missed by the Hartree–Fock approach), and also the difference between the exact kinetic energy of the system and the one calculated from the KS orbitals.

Let us recall that the exchange-correlation potential is the way to describe the fact that every electron tries to both maximize the attraction from the nuclei, and minimize the repulsion from the other electrons, during its movement within a molecule. More precisely, the exchange-correlation potential describes the exchange-correlation hole which is the zone around each electron into which no other electron is allowed. Indeed, a careful examination of the concepts introduced lets us observe that the KS exchange differs slightly from the HF exchange, because the first is only a functional of the exact density whereas the second is a functional of the orbitals, and also because the KS and HF orbitals which are the required intermediates of the calculations are not totally identical. The same can be said for the KS correlation which, according to the definitions, should be larger (more negative) than the HF-defined correlation. For an enlightening discussion of these subtleties, see Baerends and coworkers [39,40].

The important point is that, in any case, the differences between these KS orbitals and the others are small, so that *all the concepts which have been elaborated through more approximate (semi-empirical) methods can be used*. We will later highlight this point. To illustrate this, one can cite Cinal who showed that atomic KS and HF

orbitals cannot be differentiated on a graph [41]; see also Zhao and Parr [42,43]. Similarly, a long time ago, Salahub and coworkers [44] showed that the KS energies of both KS and HF orbitals of ozone were very similar, as well as the HF energies of both KS and HF orbitals of ozone, although the HF energies were significantly different from the KS energies. Use of a less simple exchange-correlation potential than the Xα used at that time would not change this feature. Indeed, one should remember that Slater introduced his Xα theory [45] in 1951, before the DFT was established [46].

Finally, relativistic corrections can be introduced into the DFT equations through various approximations according to the accuracy requested and the cost accepted for the calculation [47–52].

2.2. Functionals

Since the exchange-correlation energy functional is not known, one has to use as accurate approximations as possible, and the elaboration of new functionals is still an area of intense active work. The exchange-correlation energy functionals have been classified by Ziegler [53] into three generations.

- The first generation of functionals is the local density approximation (LDA). This approximation involves the Dirac functional for exchange, which is nothing else than the functional proposed by Dirac [54] in 1927 for the so-called Thomas–Fermi–Dirac model of the atoms. For the correlation energy, some parametrizations have been proposed, starting in the earlier 1970s, and the formula proposed by Vosko et al. [55], Perdew and Zunger [56] or Perdew and Wang [57] in the beginning of the 1980s can be considered as the limit of what can be obtained at this level of approximation (i.e. a functional of only the third power of the density). The Xα approximation, already cited, falls into this category, since the correlation is approximated by a given percentage of the exchange energy.
- The second generation of functionals makes use of both the density and its gradients. However, a simple gradient expansion, already tested in the beginning of the 1970s by Sham [58] or Herman et al. [59], was not successful, and much effort has been spent trying to elucidate this issue. Levy, Perdew and others have shown that various relations, which can be divided into sum rules, scaling properties and asymptotic properties, are satisfied by the LDA, but not by a simple gradient expansion, so that it is necessary to parametrize the gradient expansion in order to satisfy most of these relations [60,61]. The first gradient-corrected energy functionals were proposed in 1986 by Becke [62] and Perdew and Wang [63] for exchange and Perdew [64] for correlation. The most popular functionals at the present time are those of Becke for exchange [65], Perdew for correlation [64], Lee et al. [66] for correlation, as well as Perdew and Wang for exchange and correlation [67,68]. Following Perdew, they are all often called generalized gradient approximations (GGAs).
- The third generation of exchange-correlation energy functionals is the generation of functionals "beyond the GGA". It comprises various options, some giving rise to more accuracy through sophistication and computational cost. The most

important ones are the hybrid functionals, which we will describe in the following section, and the functionals which are dependent on the density, its gradients and its laplacians [69]. Hybrid functionals are energy functionals which contain both a DFT exchange (i.e. an LDA part and a GGA part) and a Hartree–Fock type exchange calculated from the orbitals. The justification of this approach lies in the so-called adiabatic connection scheme first defined by Langreth and Perdew [70] in 1977, but practically introduced by Becke [71] in 1993, and generalized within hybrid functionals in which the weight of the various contributions to the total exchange-correlation energy is obtained by a fit of energies of a reference data set. In 1998, the most popular hybrid functional is definitely the so-called B3LYP functional, available for the first time in the Gaussian package in 1994 [72] which introduces this family of acronyms. It writes:

$$E_{xc} = a_0 E_{HF} + a_1 E_{X(LSD)} + a_2 E_{X(GGA)} + a_3 E_C \quad (2)$$

remembering that the exchange-correlation energy is everything other than the potential energy, kinetic energy and Coulomb electrostatic energy in the total energy, and where: (i) $E_{X(HF)}$ stands for the pure exchange energy, i.e. Hartree–Fock like, calculated with the KS orbitals; (ii) $E_{X(LSD)}$ stands for the local exchange energy, taken as Dirac exchange [54]; (iii) $E_{X(GGA)}$ stands for gradient corrections to the exchange energy, namely the Be88 [65] form; (iv) E_C stands for the gradient corrected correlation, namely the Lee–Yang–Parr (LYP) functional [66]. Eq. (2), with $a_1 = 1.0 - a_0$ relationship, is the classic form adopted by most practitioners of hybrid functionals, in order to keep the Dirac exchange [54] of the electron gas part complementary to pure exchange. Therefore, the number of fitted parameters adds up to three, as indicated in the acronym. Whereas $a_1 = 0.20$ is widely used, the 0.25 value may be supported by a stronger theoretical basis [73–75]. B3LYP was proven to lead to quite reasonable results for coordination compounds, although the "pure DFT" functionals, i.e. not containing pure exchange (e.g. second generation GGAs), which are less accurate for organic thermochemistry, are of comparable efficiency for most organometallic compounds.

2.3. Dynamical density functional methods

As we will recall later, DFT is a powerful tool to optimize (static) geometrical structures and compute stationary points and relative energies along a reaction path. It is also a powerful tool through ab initio molecular dynamics (MD) calculations, as Car and Parrinello (CP) first described the methodology in 1985 [76]. Whereas standard molecular dynamics describe trajectories of atoms as hard objects within a classical interaction potential (i.e. with the help of a precalculated and fitted potential), CP calculations are molecular dynamics which involve the movements of both nuclei and electrons. For the latter, the DFT model is used, usually, but not necessarily, at the LDA level of approximation, and the control of the kinetic energy of both electrons and nuclei is controlled in an identical way, through the use of fictitious masses, in order to save computational time, i.e. to span large portions of

configuration space within a minimum of time. Although more demanding in computational effort, ab initio molecular dynamics calculations are a very powerful tool for the localization of reaction pathways. For numerical efficiency, plane waves are usually used for the description of the valence orbitals, whereas frozen cores [77] or pseudo-potential approximations [78] are used for taking into account the core electrons. CP dynamics allow efficient reaction path scans, free energy calculations and simulations covering subpicosecond fluxionality.

A combined Car–Parrinello quantum mechanics/molecular mechanics (QM/MM) implementation for ab initio molecular dynamics (MD) simulation of extended systems has been successfully applied to transition metal catalysis by Ziegler and coworkers [79]. In this last approach, the core of the molecular system is treated at the DFT level while the (usually large) substituted chains or rings are treated with a molecular mechanics force field. QM/MM is an efficient way to take bulky ligands into account for both "static" calculations and "dynamic" simulations. It is an active area of methodological development, in particular when the QM/MM boundary crosses bonds [80–83]. The combination of CP and QM/MM models is certainly one of the most promising theoretical tools available for theoretical coordination chemistry.

3. Applications to coordination compounds

3.1. Bond energies

Bond dissociation energies are the key properties which have recently made DFT the most widespread approximate theoretical tool for theoretical thermochemistry. The important point is that accuracy, which could easily be tested on small organic molecules, was definitely insufficient at the LDA level of approximation. Consequently, the DFT methods were not routinely used until gradient corrected functionals were introduced, then allowing DFT to provide the so-called "chemical accuracy". It is important to underline that the efficiency of DFT with modern functionals applies to chemicals involving the whole Mendeleev periodic table, whereas traditional ab initio methods, i.e. Hartree–Fock and post-Hartree–Fock (MP2, etc), which are quite accurate for (small) organic molecules, fail to give, at least at reasonable computing cost, satisfactory energies for transition metal compounds, these last being the building blocks of coordination chemistry.

Concerning calculations of bond energies, the general trend is that, on the one hand, Hartree–Fock bond energies are underestimated, especially for multiple bonded molecules, as shown by Buijse and Baerends [84], and on the other hand, LDA bond energies are overestimated, roughly speaking, by nearly 100%. It is worth noticing that most hybrid functionals were designed mainly to reproduce bond energies, and they contain at least one (free) parameter which was fitted on thermochemical data, as is the wide spread B3xxx type functional [71]. One may also underline that most of the improvement comes from the exchange functional, which controls an energy almost 10 times larger than the correlation energy, and that this

improvement is more important for the constituting atoms than for the molecules themselves [85]. In an impressive comparison of calculations restricted to 105 first-row and second-row molecules, heats of reactions of more than 300 systems were calculated with some of the most popular DFT functionals. The authors [86] showed that energies of reaction could be calculated within an accuracy better than 20 kJ mol^{-1} with a hybrid functional and a large basis set. No comparison has been made for a similarly large set of coordination compounds. However, for this category of molecules, most calculations with hybrid functionals were successfully performed [87], an unexpected result since Becke's parametrization of B3xxx functionals was obtained for only a panel of molecules which did not contain transition metal atoms. In order to be considered, new functionals belonging to the so-called third generation of functionals have to produce accuracy in bond energies at least as good as 20 kJ mol^{-1}.

As an illustration, Table 1 shows some bond energies for a typical organometallic, namely ferrocene, as recently calculated [88] by DFT methods, in comparison to highly sophisticated post-Hartree–Fock calculations, which at the price of a huge computational effort and the required use of a rather medium quality basis set [89] cannot provide more accurate values.

Table 1
Energetics and structural features of eclipsed (D_{5h}) and staggered (D_{5d}) $FeCp_2$ calculated at two levels of theory: LDA and B88-PW91. The differences between calculated and experimental values are given in parentheses

		Eclipsed (D_{5h})			Staggered (D_{5d})		
	Exp.	LDA [88]	B88-PW91 [88]	CCSD [89]	Exp.	LDA [88]	B88-PW91 [88]
Energy[a]							
a.u.		−5.30097	−4.86692			−5.29880	−4.86532
kJ mol^{-1}		−13904	−12766			−13899	−12762
Dissociation enthalpy	3065	2770	2655				
[b]	[92]	(+15.4%)	(+4.4%)				
d (pm)	[90]				[91]		
Fe–X[c]	166.0	160.6	166.1	166.0		161.2	166.6
		(−5.4)	(+0.1)			(−4.8)	(+0.6)
Fe–C	206.4	201.2	206.1			201.6	206.5
		(−5.2)	(−0.3)			(−4.8)	(+0.1)
C–C	144.0	142.5	143.5	144.8		142.4	143.4
		(−1.5)	(−0.5)			(−1.6)	(−0.6)
C–H	110.4	109.1	108.6			109.1	108.6
		(−1.3)	(−1.8)			(−1.3)	(−1.8)

[a] Bonding energy relative to the spherically averaged ground state atoms.
[b] Heterolytic dissociation enthalpy: binding energy relative to an Fe^{2+} fragment in its closed shell D_{5h} like electronic configuration and two Cp^- fragments at their geometry in $FeCp_2$ (kJ mol^{-1}).
[c] X is a dummy atom located in the center of the Cp ring.
Data from ref. [88].

3.2. Molecular structures

Determination of molecular structure is a major issue for theoretical chemistry codes, and is now available thanks to automatic procedures based on energy gradient calculations. Indeed, the implementation of analytical gradients and analytical second derivatives enables us to accurately optimize the geometry of complex molecules. This was possible in ab initio Hartree–Fock codes much earlier than in DFT ones. However, whereas Hartree–Fock calculations lead to satisfactory bond lengths for organic molecules (as accurate as 2 pm), this is far from true for organometallics, as already noticed in Ziegler's review [21].

The general trend is that LDA calculations perform well for bond distances which do not involve hydrogen atoms, leading generally to slightly too short bonds, which are usually lengthened when gradient-corrected functionals are used. However, one can notice that this lengthening is generally small, and that although it generally improves the bond lengths, it worsens them if the initial LDA lengths are too long. This trend is somewhat enlarged for Werner type transition metal complexes, relative to organometallic species [92]. Conversely, the LDA approximation leads to too long bond lengths connecting hydrogen atoms, and these lengths remain more or less unchanged when gradient-corrected functionals are used [86]. Since Hartree–Fock calculations lead to overestimated bond lengths, one is not surprised to see that hybrid functionals, which contain 20% or more of Hartree–Fock type exchange, could be claimed to be the best choice for bond distances [86]; however, one should underline that hybrid functionals are more sensitive to the quality of the basis set than are pure DFT functionals (i.e. LDA or GGAs), and such dependence is strongly related to the amount of pure (i.e. Hartree–Fock like) exchange retained in the calculations. It is known that Hartree–Fock calculations are sensitive to the quality of the basis set, and post-Hartree–Fock significantly more so, whereas pure DFT calculations are much less sensitive to the basis set. Bond lengths rely strongly upon the quality of the calculated density, and consequently the quality of the KS orbitals. These orbitals are mainly controlled by the exchange-correlation potential (indeed by the exchange part of the exchange-correlation potential) in the Kohn–Sham equations, and this potential is the functional derivative of the exchange-correlation energy. However, in some DFT codes, and for some functionals, because of computing time efficiency (or other reasons), the XC potential is restricted to an LDA quality, so that the bond lengths do not differ significantly from the LDA ones.

While such "static" structure determinations are more and more widely and successfully used, a rather good initial guess for the structure is required then to be refined by the calculation. A second technique to determine structures is the use of quantum dynamic calculations with a Car–Parrinello type method. Whereas these methods can be used to actually simulate a dynamic for a few femtoseconds (for example the movements of the cyclopentadienyl rings of berylocene [93–95]), they are often used to locate energy minima structures. This procedure, which is certainly more computer time consuming, is generally used only at the LDA level, but unlike static optimization, it enables the systems to cross energy barriers, and then to find

energy minima belonging to structures which can significantly differ from input structure neighbors [96].

Thanks to the increased computer power, DFT calculations can now be used to examine the nature of bonds in rather big complexes {e.g. $Au_5(C_5H_5)_5$ [97] or $Ti_8C_{12}(C_6H_6)_8$ [98]} and to indicate whether polymetallic molecular clusters may involve metal–metal interactions besides metal–ligand bonds [97,99]. As an illustration, Table 1 displays some bond lengths for ferrocene.

3.3. Potential energy surfaces and reaction profiles

In coordination chemistry, the use of DFT electronic structure calculations at least qualitatively to evaluate catalytic mechanisms (such as the most favorable mode of nucleophilic or electrophilic attack) was pioneered by Trogler through Xα calculations in the 1980s [100,101]. With more elaborate functionals, many calculations lead to a better understanding of elimination, exchange or insertion of small ligands such as H_2 [102] or CO [103,104], but bigger ligands have also been successfully tackled [105], some including taking into account solvation [106]. The characterization of a chemical reaction should require the determination of the potential energy surface (PES) for the system made of the reactants and the products, as a function of the nuclear coordinates. Indeed, one generally determines the PES around the reactants, the product(s) and the transition state (TS) which is a saddle point in the PES. In some cases, an intermediate structure which corresponds to a minimum in the PES may also be found, and it is connected by two transition states to both the reactants and the products. The lowest energy pathway connecting the transition state(s) to the energy minima is then determined. Such a determination is now routinely performed in molecular codes, provided good guesses for TS structures are given. One should point out that semi-empirical methods are not suited for such determinations, because their parametrization is designed to mimic stable structures (energy minima) of organic chemical species. Similarly, the ab initio Hartree–Fock method is generally inadequate for reactivity studies of organometallic compounds, because of the poor accuracy of geometries and bond energies which are obtained.

Therefore, DFT methods turn out to be the most suitable for such studies: indeed, this is only partly true for TS structure determination, which is generally rather satisfying, although experimental ones are not extensively known, but the energy barriers are generally significantly underestimated. In the worst cases, LDA barriers may be found negative (i.e. the TS is found as an energy minimum) and, in general, most GGA barriers are still too small. As far as hybrid functionals are concerned, this could be traced back to the nature of the data set used for parametrization of the functional. For example, for the widely used B3xxx functional, the parametrization bore only on bond energies [71]. A new functional designed by Becke, which contains 10 parameters, uses a data set which includes at least one energy barrier [107]. One can predict that new functionals under development will certainly more efficiently take care of energy barriers, and consequently will improve the description of energy profiles of chemical reactions.

First principle MD is also a powerful tool for the determination of potential energy surfaces and the identification of TS and intermediate states. It has been used by Campana et al. [108] to study the effect of the presence of various monovalent cations inside a zeolite offretite framework. These authors could show that the relative stability of the cation binding sites depends on the nature of the counterion as well as the Al/Si ratio of the zeolite. Margl et al. [109] showed recently in a study bearing on metallocene dihydrogen complexes that CP calculations could allow us to discover (unexpected) novel reaction pathways. With the combined CP QM/MM approach, Ziegler and coworkers [79] could determine the free energy barrier of the chain termination process in a nickel diimine based ethylene polymerization catalyst.

3.4. Vibration frequencies

Calculations of vibration frequencies in the harmonic approximation are now available in most molecular DFT codes, following the experience gained from ab initio codes in the 1980s. Let us recall that Hartree–Fock frequencies have to be scaled by a factor of 0.88 in order to be compared with experiment. This is sometimes referred to anharmonicity corrections, but is mainly related to the deeper curvature of the PES at the Hartree–Fock level of approximation. Moreover, when inorganic elements are involved, the estimated frequencies are rather poor. On the contrary, such an adjustment is not needed for LDA frequencies, and good agreement is usually reached with experiment. These frequencies are generally not significantly modified when GGA functionals are used, although, in some cases, especially for transition metal compounds, more accurate theoretical frequencies are obtained with GGA functionals. In that case, this comes mostly from the improved geometry [110] and for a small part from the contribution of the gradient corrections to the energy Hessian. Nevertheless, when hybrid functionals such as B3xxx (which introduces an amount of Hartree–Fock like exchange) are used, frequencies have to be scaled by a factor amounting to 0.96 to best compare with experiment. As a matter of fact, the scaling factor should be even smaller if the amount of pure exchange in the hybrid functional is larger than the usual 0.20 coefficient [111]. Wong [112] has given optimal scaling factors for various exchange-correlation functionals, based on analysis of 1000 frequencies of 100 molecules (mostly organic). Bérces and Ziegler [110] have achieved a whole force field calculation for complexes like ferrocene or benzene–chromium–tricarbonyl.

Vibrational spectra can also be extracted from MD simulations by Fourier transform of the atomic velocity autocorrelation function [113–115]. An illustration may be found in the work cited previously relating cations in zeolite framework [108].

3.5. UV–visible spectroscopy

The optical spectra of transition metal complexes have long been interpreted by means of DFT calculations; indeed, Xα methods, also called "Hartree–Fock–Slater" methods when used in an LCAO formalism, have been most suitable for the calculation of excitation energies of complexes (with reasonable success), whereas traditional

ab initio methods fail. The MnO_4^- anion has been a crucial test case, being first successfully interpreted by Johnson and Smith in 1970 [116] with the MSXα method, whereas, as just said, Hartree–Fock and post-Hartree–Fock methods have failed so far to estimate the excitation energies with satisfactory accuracy. Buijse and Baerends [84] in 1990 gave an analysis of the errors inherent to Hartree–Fock calculations. Calculations of optical spectra of heavy metal complexes were feasible in the early 1980s, since relativistic corrections were introduced in some Xα codes at that time [117–119], allowing a rather quantitative description of spectra which was not available through other ab initio methods.

There are, however, strong limitations to DFT approaches since Kohn–Sham orbitals are calculated in order to describe the ground state within a single determinental wave function. The evaluation of space and spin multiplets is then difficult to perform in an unambiguous way. Moreover, strictly speaking, the DFT has been established only for the ground state, and the lowest states within a symmetry class [120,121]. Therefore one approach, first proposed by Ziegler et al. [122], is to use the relation between the exchange energies of multiplets and the exchange energies of the determinants (i.e. configurations) for the exchange-correlation energies. More precisely, one may write:

$$E_X^{LDA}(D_i) = \sum_j C_{ij} E_X^{LDA}(M_i) \tag{3}$$

where $E_X^{LDA}(D_i)$ and $E_X^{LDA}(M_i)$ are the energies of the determinants and the corresponding multiplets, respectively. The C_{ij} coefficients are given by Slater's rules and group theory. Inverting Eq. (3) leads to the multiplet energies. Table 2 shows a typical successful assignment of the $IrCl_6^{2-}$ spectrum obtained in 1984 [123]. Such a procedure has now been generalized by Daul [124] and automated within DFT codes like ADF. This approach has been successfully used for many purposes [125], such as the photochemistry of organometallic compounds, allowing a full assignment (ligand–field vs. charge transfer) of the spectra {e.g. $Cr(CO)_6$ [126]}, or the spectroscopy of n*d* impurities in crystalline matrices [127]. However, the success of the method relies on the presence of a point symmetry in the metal ion environment. When the description of the electronic system requires more than one determinant, for instance the magnetic coupling of weakly interacting metal centers, similar concepts can also be used: Noodleman and Norman [128] developed in 1979 a broken symmetry method based on spin-projection techniques which has been successfully applied to polymetal complexes such as ferrodoxin [129,130].

A totally different approach to determine electronic spectra is the use of the linear response theory. This has been the subject of recent theoretical developments [131], and the first results look promising. Casida and coworkers, who obtained quite convincing results for N_2 [132], wrote an exhaustive review on the subject [133].

3.6. Dipole moments, UV–visible intensities, polarizabilities

Dipole moments are known to be sensitive to the quality of the method. Taking care to use a large enough basis set, i.e. sets containing diffuse and polarization

Table 2
Electronic spectrum of $IrCl_6^{2-}$: calculated ligand field excitation energies and LMCT electronic excitation energies calculated at the Xα level of approximation and experimental peaks (cm^{-1})

	Transitions[b]		Calc. values[a]		Exp. peak positions
$E''(^2T_{2g})$	$\rightarrow U'_g(^2T_{1g})$	FA	18500		17300
	$\rightarrow E'_g(^2T_{1g})$	FF	19200		
$E''(^2T_{2g})$	$\rightarrow U'_u(^2T_{1u})$	AA	21000		20400
	$\rightarrow E'_u(^2T_{1u})$	AF	22200		
$E''(^2T_{2g})$	$\rightarrow U''_u(^2T_{2u})$	AA	23400		23200
	$\rightarrow U'_u(^2T_{2u})$	AA	24000		23800
$E''(^2T_{2g})$	$\rightarrow U'_u(^2T_{1u})$	AA	30900		$\cong$32000
	$\rightarrow U'_u(^2T_{1u})$	AF	33900		
$E''(^2T_{2g})$	$\rightarrow[1t_{1g}^5 2t_{2g}^5 3e_g^1]$[c]	F	43000		
$E''(^2T_{2g})$	$\rightarrow[4t_{1u}^5 2t_{2g}^5 3e_g^1]$[c]	A	43900		$\cong$43100
$E''(^2T_{2g})$	$\rightarrow[3t_{1u}^5 2t_{2g}^5 3e_g^1]$[c]	A	46400		
Excited state	Calc. value[a]	Exp. peak positions	Excited state	Calc. value[a]	Exp. peak positions
$U'_g(^4T'_{1g})$	20030	20400[d]	$U'_g(^4T'_{1g})$	31600	
$U'_g(^4T'_{1g})$	22500		$E'_g(^2T_{1g})$	32100	
$U'_g(^4T'_{2g})$	24700	23500[d]	$U'_g(^2T''_{2g})$	32600	
$E'_g(^4T'_{1g})$	25000		$E''_g(^4T_{2g})$	33900	
$U'_g(^4T'_{1g})$	25800	24400[d]	$U'_g(^2T'_{1g})$	34300	
$E'_g(^4T_{2g})$	26500		$E'_g(^2A_{1g})$	34800	
$U'_g(^2T_{1g})$	26700	28000 sh	$E'_g(^2T_{2g})$	36100	
$E''_g(^4T_{1g})$	29100		$E'_g(^2T_{1g})$	37500	
$U'_g(^2E''_g)$	29100		$U'_g(^2E'_g)$	38900	41000[d]
$E''_g(^2A_{2g})$	30900	32000[d]	$E''_g(^2T_{2g})$	37500	

[a] Values from ref. [123].
[b] A = allowed; F = forbidden.
[c] Average energy over the LMCT states related to this configuration.
[d] Experimental wide band (also) assigned to LMCT transitions; sh = shoulder.

functions, dipole moments can be reproduced with good accuracy within DFT calculations. Gradient-corrected functionals lead in general to better dipole moments [134,135], but one has to remember that dipoles are probes of the density, which depend on the quality of the exchange-correlation potential in the KS equations. According to the status of the present XC functionals, whereas GGAs and hybrid energy functionals have already gained a respectable accuracy, perhaps due to cancellation of some errors, there is still room for improvement of the XC potential.

In the same vein, transition moments and UV–visible intensities are also sensitive to the quality of the calculation, but they rely on the hypothesis that the DFT excited states are well-defined, an assumption which is certainly approximately true, according to the huge amount of data accumulated, but which may not be rigorous, and has never been proved. Gardet et al. [136] have recently calculated theoretical intensities of some lithium clusters, using an approximation in the evaluation of the virtual orbital energies proposed by Fritsche [137]. Application to organometallic complexes is under progress. As noted above, another promising approach to repro-

duce optical spectra, including intensities, involves the linear response theory within DFT. Casida [133] indeed obtained a good description of optical spectra for small systems [132], and application to coordination compounds should be straightforward.

3.7. X-ray spectroscopy

Organometallic compounds and complexes exhibit X-ray absorption spectra and photoemission spectra which are fingerprints of their structure which depend on both the formal oxidation state of the metal(s) and the geometry itself (symmetry, bond lengths, bond angles). Determination of theoretical spectra, or at least interpretation of experimental spectra, requires all-electron type calculations, and this is a severe limitation on standard calculations which use either the frozen core approximation or pseudo-potentials for the description of the inner electronic shells. The multiple scattering approach, which severely approximates the potential through the "muffin-tin" approximation, leads to a description of the valence orbitals which has not the accuracy we are now used to. In particular, the choice of the sphere radii has a small taste of semi-empiricism and unfortunately is responsible for the non-variational evolution of the total energy with respect to the muffin-tin sphere size, precluding its use for geometry optimization. On the other hand, this method, which has been widely used with the Xα approximation, is very fast, and optimizes quite well core orbitals which are just constrained to vanish at the sphere radii. Therefore, this is still a good method for calculating XPS or X-ray absorption spectra. Besides, the multiple scattering formalism lets us analyze the role of the second or third shells of ligands in the shape of the spectra, pointing out the importance of constructive and destructive interferences between the scattered waves around the absorber. As an example of such an analysis, among others, the XANES of TiO_2 in its two crystalline structures, apatite and rutile, has recently been published [138]. Discussion of the importance of the bond lengths and the oxidation state of Fe in iron chlorides may be found in ref. [139]. Such calculations are also, however, now possible within a LCAO formalism, and some results bearing on chemisorbed molecules recently appeared [140].

3.8. Ionization potentials, electron affinities

This section is related to the previous one dealing with XPS, since photoelectron spectroscopy is a privileged tool to determine ionization potentials. Again, quite accurate ionization energies were obtained in the past through Xα methods, in particular in connection with Slater's transition state method [141] which, through a self-consistent calculation of a state in which half of an electron has been removed, exhibits directly the ionization energy as the HOMO eigenvalue. This technique effectively takes into account the electronic relaxation occurring through the ionization process, and removes the self-interaction energy [142] which is responsible for the excessively high energies of Kohn–Sham orbitals with respect to their "experimental" energies. This technique uses Janak's theorem [143] which generalizes the

transition state concept to any DFT calculation of ionization or excitation energies, and permits us to calculate these energies through orbital energy differences instead of total energy differences, necessarily less accurate. Indeed, Williams et al. [144] showed that with a transition state with a 2/3 fractional occupation of the occupied orbital (and 1/3 for the empty orbital towards which the transition occurs), one can even obtain a more accurate transition energy (equal to a linear combination of the eigenvalues). Following this procedure, Chong and Bureau recently calculated core electron binding energies of a series of carbonyl and nitrosyl complexes [145,146]. It appears that the calculation of ionization potentials is not very sensitive to the choice of the exchange-correlation functional (at least if it belongs to established functionals [147]).

Electron affinity is a property traditionally difficult to calculate accurately for molecular systems. This is related to the necessity of evaluating energies of both the neutral molecule and its corresponding anion, whose (relaxed) geometry must be optimized. The latter is more difficult to describe since standard basis sets, optimized for neutral systems, are not flexible enough, and more diffuse functions are required to correctly describe the more loosely bonded electrons of anions. According to theory, electron affinity should be equal to the energy of the empty orbital accepting the supplementary electrons. However, all the present exchange-correlation functionals are still unable to correctly remove the self-interaction energy, so that a positive eigenvalue of this orbital does not necessarily mean an instability of the negatively charged species. Electron affinity has to be calculated from energy differences between the anion and the neutral molecule, or, as with ionization energies, via a Slater's transition state calculation. Scheffer et al. recently showed the stability of anions within DFT calculations and the corresponding electron affinities were in good agreement with experimental data [148].

Electron affinity and ionization potentials are master pieces for the calculation of two global reactivity indexes which are deduced on the basis of DFT, electronegativity, and hardness. Let us recall that the first is simply approximated as $\xi=(I+A)/2$, I and A being the ionization potential and the electron affinity, respectively [23]. Hardness was defined by Parr and Pearson [149] from the difference $\xi=(I-A)$ (with the 1/2 factor now omitted in recent publications).

One may underline that spin polarization calculations need to be carried out, since either the molecule or its anion have an odd number of electrons, but spin-polarization calculations are the standard approach for the KS orbitals.

3.9. ESR, NMR

As shown by Vignale et al. [150], the inclusion of currents in DFT is required whenever a large magnetic field coexists with a strongly inhomogeneous electronic structure. However, the elaboration of a current density functional theory is not simple since one has to formulate a gauge invariant theory in terms of gauge invariant variables. To overcome this approach which, involving approximations for exchange-correlation functionals as functionals of both the density and current density, would be very time-consuming, some developments have recently been

suggested by Malkin et al. [151–153] and Schreckenbach et al. [154–156]. These works go beyond the uncoupled DFT [157] with the use of a model for the magnetic field linear response, e.g. through the so-called sum over the states density functional perturbation theory [151]. NMR shifts and ESR hyperfine tensors [158] are now available from DFT calculations and may be expected to be routinely calculated in the near future. A review of the inherent problems occurring in the calculation of NMR and ESR spectroscopy parameters within DFT, and how they can be solved, has recently been published [159].

3.10. Electrochemistry

This domain has not yet been widely investigated by theoretical calculations in the field of coordination chemistry, although, within DFT, electronegativity is rigorously equal to the chemical potential. In reality, one has seen that KS eigenvalues, and consequently electronegativity, are too high because the self-interaction energy introduced by the LDA is not completely canceled by gradient corrections (GGAs). Consequently, one cannot expect to get a kind of (electro)chemical accuracy with the functional presently used (LDA, GGAs, hybrid functionals, etc.), but trends should be correctly described. Bureau et al. recently showed that the acidic or basic behavior of some systems — at least metal surfaces — could in principle be driven by the electrode potential, this last being closely related to the chemical potential [160]. Ji et al. [161] recently presented a calculation of redox potentials and pK_a values of hydrated transition metal cations combining DFT and continuum dielectric models. The development of potential functionals with correct asymptotic behavior [162,163] should lead to better estimations of Kohn–Sham eigenvalues, and consequently to better chemical potentials [164]. Moreover, for molecular systems and insulators, the position of the chemical potential within the band gap is usually not clearly defined, if one excepts the newly proposed approach deriving it from a self-consistent procedure [165].

3.11. Other properties

There are many other one-electron properties which have been successfully calculated within DFT approaches. To cut a long story short, one can recall Xα calculations of electric field gradients [166,167], or Mössbauer spectra [168], two important properties for an unfortunately limited group of coordination compounds possessing the isotopes permitting the determination of molecular properties from nuclear spectroscopies. More accurate results have been obtained by more modern DFT calculations, belonging either to (physics' side) band structure [169] or to (chemists' side) molecular electronic structure [170] types of computation.

3.12. Reactivity indices

As we have seen, various reactivity indices can be unambiguously defined within DFT approaches. The most widely used are of course the orbital eigenvalues, which

are the building blocks of the frontier orbitals theory first introduced in the ab initio formalism [15,171]. Indeed, the KS orbitals, which are representative of a system of fictitious independent electrons, describe the electronic structure of molecules better than any other method involving independent electrons because the correlation, although approximate, is self-consistently included in the calculations. Although this is not yet admitted by all experts in DFT [172], the KS orbitals consequently give more chemical insight than any other type of orbital (in particular Hartree–Fock orbitals). Baerends and Gritsenko gave a very documented comparison of the properties of orbitals in the two models [39].

Let us recall that, in DFT, the orbital eigenvalues are the derivatives of the total energy of the molecular system with respect to their electron number, i.e. their occupation, and in particular the eigenvalue of an open shell HOMO (highest occupied molecular orbital) is equal to the chemical potential of the system. On the other hand, the derivative of the total energy with respect to the external potential is equal to the density (for a fixed number of electrons) [23,173].

Further derivatives may be taken, leading also to useful chemical concepts. Senet [173] has gathered some of the relationships one may find between these further derivatives. In particular, the second derivative of the total energy with respect to the external potential is the linear response of the electron to a change of the external potential, whereas the second derivative of total energy with respect to the number of electrons is the hardness, as already mentioned. Finally, the mixed derivative, which is the derivative of the chemical potential with respect to the external potential, and also the derivative of the density with respect to the number of electrons, is the (linear) Fukui function:

$$f^{\alpha}(\boldsymbol{r}) = \left[\frac{\delta\mu}{\delta v(\boldsymbol{r})}\right]_N = \left[\frac{\partial\rho(\boldsymbol{r})}{\partial N}\right]_{v(\boldsymbol{r})} \tag{4}$$

Physically, it is a measure of the first order variation of the HOMO or LUMO energies (we would say the Fermi level in solid state physics) due to a change of the Kohn–Sham potential at constant number of electrons. At zeroth order, as suggested by Fukui [171], it is consequently equal to the KS frontier orbital densities $|\phi_{\mathrm{F}}^{\alpha}(\boldsymbol{r}, s)|^2$ (F = HOMO or LUMO, s = spin index), according to the sign α of the variation of the number of electrons [electrophile if $\Delta N > 0$ ($\alpha > 0$), and nucleophile for $\Delta N < 0$]. At first order, Fukui functions involve the derivatives of all the occupied KS orbitals:

$$f^{\alpha}(\boldsymbol{r}) = \sum_{s} |\phi_{\mathrm{F}}^{\alpha}(\boldsymbol{r}, s)|^2 + \sum_{i,s}^{\mathrm{occ}} \left[\frac{\partial|\phi_i(\boldsymbol{r}, s)|^2}{\partial N}\right]_{v_{\mathrm{ext}}}^{\alpha} \tag{5}$$

but other expressions can be found [173].

Alternatives to the Fukui functions are the condensed Fukui functions f_k^{α}, proposed by Yang and Mortier [174] and which reduce the information to numbers related to constituting atoms. They are based on an approximation of finite differences in Eq. (4) obtained through the Mulliken population analysis of the cation

and anion corresponding to the studied neutral species:

$$f_k^+ = q_k(N+1) - q_k(N)$$

$$\text{for } f^+(\boldsymbol{r}) = \left[\frac{\partial \rho(\boldsymbol{r})}{\partial N}\right]_v^+ \quad \text{(for a nucleophilic attack)}$$

$$f_k^- = q_k(N) - q_k(N-1)$$

$$\text{for } f^-(\boldsymbol{r}) = \left[\frac{\partial \rho(\boldsymbol{r})}{\partial N}\right]_v^- \quad \text{(for an electrophilic attack)}$$

and

$$f_k^0 = \frac{1}{2}\left[q_k(N+1) - q_k(N-1)\right]$$

$$\text{for } f^0(\boldsymbol{r}) = \left[\frac{\partial \rho(\boldsymbol{r})}{\partial N}\right]_v^0 \quad \text{(for a radical attack)}$$

$q_k(N)$ being the charge associated with atom k for the molecular system with N electrons.

In principle, though much easier to calculate than the true Fukui functions, the condensed Fukui functions suffer from some of the well-known difficulties associated with a Mulliken population analysis, in particular their basis set dependences. However, the use of numerical integration schemes seems to lead to condensed Fukui functions which do not suffer from these troubles [175]. Most of the capacity of the Fukui functions as a reactivity index is not lost upon integration, leading to the corresponding condensed functions [176]. Until now, these concepts, which are derived from DFT, have been used mostly with calculated data obtained from Hartree–Fock or semi-empirical methods.

The orbitally resolved hardness tensor is the second derivative of the electronic energy relative to the occupation number

$$\eta_{ij} = \frac{\partial^2 E}{\partial n_i n_j}$$

and is related to the global hardness η by [177]:

$$\eta = \sum_i \sum_j \left(\frac{\partial n_i}{\partial N}\right)_{v_{\text{ext}}} \left(\frac{\partial n_j}{\partial N}\right)_{v_{\text{ext}}} \eta_{ij} \tag{6}$$

or other relationships [173,178–181]. In order to calculate the hardness tensor, numerical techniques using the Janak theorem [182,165,183] and the so-called thermal density functional theory [165] have recently been developed. Following the internal orbitally resolved charge sensitivity analysis proposed by Nalewjaski et al. [179,184], Grigorov et al. showed [165] that four normal orbitals — which are obtained by a diagonalization of the hardness tensor — account for the reactivity

towards hard (respectively soft) electrophiles (respectively nucleophiles) and, taking ferrocene as an example, could successfully connect the reactivity properties of this coordination compound to these normal orbitals. These normal orbitals do not account for the electronic flows between the reactants, but are the channels of polarization of the electronic density at the very beginning of a chemical reaction [165].

4. Conclusions

The electronic structure of a coordination compound defines its static structure and most of its properties, such as spectroscopic properties including electronic spectra and vibrational spectra as well as more local properties such as NMR, ESR or MCD spectra. Moreover, since the pioneer work of Car and Parrinello, some dynamic properties can now be investigated, including the energetics of stationary states and transition states and some estimation of the energy barriers. Finally, an increasing knowledge of the chemical bond is now readily accessible through the extensive calculation of analytic properties such as Fukui functions or the hardness tensor. For this purpose, DFT (in its Kohn–Sham formulation) has become one of the most efficient tools for applied theoretical chemistry, since it includes some of the advantages of semi-empirical methods, namely the use of a monodeterminental wave function as well as the corresponding simplicity of interpretation of properties which are related to a simple basis set of (spin) orbitals. These advantages come along with a high reliability for the figures obtained from pure ab initio approaches, since no special use of system-dependent parameters is made (the parameters included in some functionals are, in principle, universal). Such reliability was only the privilege of the so-called post-Hartree–Fock methods, even though a huge computational cost is to be paid, especially when TM are involved, making these methods poorly adapted for standard theoretical coordination chemistry. DFT is now implemented in most program packages and, accordingly, is used by an increasing number of practitioners. However, much still remains to be done to study large systems, to develop new and more accurate functionals, e.g. for handling weak bonds like van der Waals systems (still poorly described), or to describe excited states, as well as transition states. Following the tremendous increase of theoretical efforts now devoted to DFT, one can be confident that DFT will become one of the most powerful tools available for studies in coordination chemistry.

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