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On the Accuracy of Density Functional Theory in Transition Metal Chemistry

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Abstract. Density Functional Theory has become very widely used to study the electronic structure and related properties of transition metal complexes. Despite the many successes obtained using modern functionals, care is still needed as quite large errors can occur. These can be best understood by taking into consideration how density functional theory works, and how well it performs for the simpler case of main-group compounds. This serves to highlight the critical role of the exchange functional, which describes such varied effects as electron self-interaction, static (or non-dynamic) correlation, and dynamic correlation. A poor balance between these effects can lead to significant errors even for main-group compounds. This is even truer for transition metal compounds. Benchmark data published in the last year suggests that all existing functionals can lead to severe errors for some transition metal compounds. There is a slight trend for systems involving more static correlation to be treated better using second- or third-generation gradient-corrected or kinetic energy density functionals, rather than hybrid functionals. This trend is however quite variable from one type of compound to another. Computed spin-state splittings are highly variable from one functional to another, and this is also diagnostic of differences in the extent of static correlation. The increasing awareness of transition metal compounds by the developers of new exchange-correlation functionals should lead in the medium term to more accurate and hence (even) more useful functionals.

1. Introduction

The development of density functional theory (DFT) has led to a huge change in the field of theoretical transition metal chemistry. The development in the late 1980s and early 1990s of new, more accurate functionals and of efficient, user-friendly computer codes led to an explosion in the number and the breadth of applications. For example, a literature search reveals 356 papers published in 2005 in either Dalton Transactions, Inorganic Chemistry, or Organometallics, with the words 'density functional', 'DFT', or 'B3LYP' (perhaps the most popular density functional) in the title or abstract. Corresponding searches for 2000 and 1995 yield 170 and 29 papers, respectively, with none in 1990 or 1985.[1] DFT computations have become an accepted tool for analyzing structure, bonding, reactivity and properties, and are used both by specialized computational groups, and by mainly experimental groups. The reason for this remarkable development is that DFT is both relatively cheap and relatively accurate. This means that useful results can be obtained in a routine way for realistic models of the target molecule, or indeed for the latter.

Nevertheless, DFT is not an exact theory, and computations using the method are still often frustratingly inaccurate. The purpose of the present report is to summarize much of the present state of knowledge concerning the accuracy of DFT in the field of transition metal chemistry. A brief introduction to the formalism of DFT will be followed by a description of existing types of functional. The main part of the text will then focus on evaluating the accuracy of DFT in transition metal chemistry. Where required, insight will also be taken from broader discussions of accuracy

and DFT. A number of previous reviews address the topic of accuracy in DFT calculations on transition metal compounds.[2,3,4]

2. The formalism of DFT

Density functional theory is described in detail in many books and reviews[5] so this introduction will be very brief. The basic idea of DFT is that the energy of a system composed of fixed nuclei and mobile electrons can be expressed as a functional $E[\rho]$ of the electron density function. This represents a considerable simplification over traditional electronic structure theory, in which the central construct is the electronic wavefunction Ψ, which depends simultaneously on the coordinates of all the electrons (3N variables). The electronic density function ρ only depends on three variables.

The foundations of DFT are the two Hohenberg-Kohn theorems,[6] which show that the ground state density uniquely defines the system, and that the density can be derived from a variational procedure. However, the form of the exact functional is not clearly defined. In practice, the energy is usually written (eq. 1) as a sum of three well-defined terms and one smaller, less well understood term, the exchange-correlation energy, in which the uncertainties concerning the form of the functional are collected:

$$E[\rho] = \int v(r)\rho(r)dr + J(\rho) + T_S(\rho) + E_{XC}(\rho) \tag{1}$$

The first term on the right-hand side of eq. (1) represents the electromagnetic interaction of the electron density with the 'external potential' – in most cases, this simply corresponds to the Coulombic interactions between electrons and nuclei. The second term is the Coulomb energy, and represents the repulsion between the electron density and itself. This term is non-zero even for one-electron systems because it includes electron self-interaction. The next term is an approximation to the electronic kinetic energy. Early attempts to describe the latter directly as a functional of the density (e.g. Thomas-Fermi theory) were not very successful. Instead, the density is expanded in a set of orbitals, and the kinetic energy for this hypothetical system (in which the kinetic energy of the electrons is not affected by their interactions) is computed using the same expression as in traditional wavefunction methods. The final term, the exchange-correlation functional, corrects the first three terms. First, it contains a term for electronic exchange to reflect the fermionic nature of the electrons. This term also serves to correct for the spurious self-interaction introduced by the Coulomb energy. Next, it accounts for electron correlation. Finally, it could in principle correct for the approximate nature of the kinetic energy term, although common functionals do not usually contain a term explicitly aimed at correcting for this effect.

The energy expression given in equation (1) leads to a set of equations defining the shape of the orbitals that are used to expand the density. These are the Kohn-Sham equations[7] that are the foundation of all modern DFT applications discussed in the present work. Solving these equations leads in principle to the exact energy and density of the target system. The degree of accuracy obtained depends on the form given to the exchange-correlation functional.

3. Exchange-Correlation Functionals

3.1. *The Local Density Approximation*

In the first generation of exchange-correlation functionals, the energy is obtained from a purely *local* integral over the density, as shown in equation (2). In this equation, we introduce separate local exchange and correlation terms $\varepsilon_X\{\rho\}$ and $\varepsilon_C\{\rho\}$.

$$E_{XC}[\rho] = \int [\varepsilon_X\{\rho(r)\} + \varepsilon_C\{\rho(r)\}]\rho(r)dr \tag{2}$$

In local exchange-correlation functionals, ε_X and ε_C are functions which depend only on the scalar value of the electron density at a given point in space. Where open-shell systems are involved, separate expressions may be used for the exchange and correlation of the spin-up and spin-down electron density. A simple exchange functional is that due to Slater:[8]

$$\varepsilon_X\{\rho(r)\} = -\frac{3}{2}\left(\frac{3}{\pi}\rho(r)\right)^{\frac{1}{3}} \tag{3}$$

This expression can easily be understood in qualitative terms: overall, the exchange energy depends on the local density to the power 4/3, and is negative i.e. stabilizing: in regions of high electronic density, the Coulomb energy will overestimate the electron-electron repulsion energy, and this term corrects for that overestimation. The error arises because the Coulomb energy includes electron self-interaction, and because it neglects the effect whereby the probability of finding an electron of a given spin at a given place is highly dependent on the presence of other electrons of same spin in the vicinity. This effect is due to the Pauli principle, and gives rise to the so-called exchange hole, whereby the density of electrons of given spin in the vicinity of an electron of that spin is lower than in the surrounding space. The exact form of the functional was proposed based on general theoretical grounds.

The expressions used for local correlation functionals are more complicated and so will not be reproduced here. One of the most common of these functionals[9] has been parameterized to reproduce the highly accurate Monte Carlo results obtained for the homogeneous electron gas, so for this system with constant density, this functional is exact. The combination of the Slater local exchange functional[8] and the Vosko, Wilk and Nusair local correlation functional[9] is often referred to as the SVWN or LDA (local density approximation) functional.

The local density approximation and related functionals such as Xα are remarkably accurate methods given the relative simplicity of the energy functional. They lead to very good predicted molecular geometries, and to a reasonable description of molecular electronic structure and thermochemistry. However, bond energies (and atomization energies) are almost always overestimated compared to experiment, with a quite large deviation. Over the extended G3/99 set of 223 atomization energies, the SVWN functional yields a mean absolute deviation of as much as 121.85 kcal/mol.[10] At first sight, this is a very poor level of agreement with experiment. However, it should be realized that in many computational studies, the relative energies of interest are not atomization energies, which involve breaking many chemical bonds, but activation energies or reaction energies, in which only a few bonds are broken. The atomization energies for the G3/99 set are large because some of the molecules are quite large, and the SVWN error is cumulative over all the bond energies. The smaller G2/97 subset of 148 atomization energies of mostly smaller molecules yields a much lower mean absolute error of 83.71 kcal/mol.

Also, when comparing SVWN against the most simple wavefunction-based ab initio method (Hartree-Fock theory), it can be seen that it is actually of a quite good accuracy: the HF mean

absolute error on the G3/99 dataset is even larger, at 211.54 kcal/mol! This means that the simple LDA model of density functional theory, which is exact only for systems in which the electron density is constant throughout space, is nevertheless a more accurate theory of molecular structure than Hartree-Fock theory. LDA approaches have been used in a wide variety of applications for calculations on molecules and solids.

3.2. Gradient-corrected Functionals

A second generation of exchange correlation functionals include not only functions of the scalar density in the integrand of equation (2), but also functions of the gradient of the density. Whilst more fundamental theoretical reasons can be given for including the gradient terms, they can be justified in hand-waving terms based on the fact that the energy functional is expected to be different in regions such as those surrounding the nuclei (where the density varies rapidly) and those far from the nuclei (where it varies only slowly). Functionals including a gradient term are sometimes referred to as non-local as the gradient introduces a degree of non-locality into the energy expression. This is however somewhat misleading as the exchange-correlation term is still constructed as an integral (eq. (2)) that associates a defined energy contribution to the density residing in each infinitesimal volume within the molecular system. More generally, such functionals are referred to as gradient-corrected, and DFT methods using such functionals are said to use a Generalised Gradient Approximation or GGA.

Many different GGA exchange and correlation functionals exist. Some are defined as corrections to the local exchange and correlation functionals mentioned above, whereas some include both local and non-local effects. For example, one of the most popular exchange functionals, proposed in 1988 by Becke,[11] is written (eq. 4) in the following way as a sum of the local exchange of eq. (3) and a correction term that depends on the gradient of the density:

$$\varepsilon_X\{\rho\} = -\sum_\sigma \rho_\sigma^{\frac{1}{3}} \left(\frac{3}{2}\left(\frac{3}{4\pi}\right)^{\frac{1}{3}} + \frac{\beta x_\sigma^2}{\left(1 + 6\beta x_\sigma \sinh^{-1} x_\sigma\right)} \right) \tag{4}$$

In this equation, the index 'σ' refers to up- and down-spin, which are considered separately. The value x_σ is given by $\left|\nabla\rho_\sigma\right|/\rho_\sigma^{4/3}$. This functional was developed so as to reproduce the correct long-range behaviour of the Coulomb potential. As noted in the previous section, DFT functionals use a classical treatment of electron-electron interactions that effectively includes repulsion between an electron and itself. This self-interaction is partly, but not exactly, corrected by the exchange part of the functional. For example, for a hydrogen atom treated using the SVWN functional, the (non-physical!) Coulomb energy for this one-electron system is 0.298 atomic units. The Slater exchange term is –0.278 au and thereby nearly cancels out the self-interaction. It is difficult to devise exchange functionals that *exactly* remove the self-interaction, but the Becke functional of eq. (4) does lead to exact cancellation in the asymptotic region far from the nuclei. In fact, it also gives better agreement overall, with the parameter β chosen as 0.0042 so as to reproduce as exactly as possible the exchange energy for the rare gas atoms. For the H atom, a calculation using only the Becke (or 'B') exchange functional (no local or non-local correlation) gives a Coulomb energy of 0.307 au (the expression for this energy is of course the same as in the SVWN calculation, but the shape of the 1s orbital emerging from the self-consistent procedure is slightly different), and an exchange energy of –0.306 au, which thereby nearly cancel.

Many other gradient-corrected exchange functionals have been proposed. These differ from that of eq. (4) based on the number of parameters, the physical properties to which the parameters have been adjusted, the physical constraints that have been applied to the nature of the solutions (e.g. the long-range cancellation of self-interaction), and other design considerations.

Many non-local correlation functionals have also been proposed, including terms depending on the gradient of the density. As for the local correlation functionals, the form is more complex than for the corresponding exchange functionals, so will not be given here. Different design principles have been used to develop such functionals, including fitting to experimental data sets, and attempting to reproduce well-known physical principles. For example, the very commonly used functional of Lee, Yang and Parr[12] is based on ideas from conventional electronic structure theory relating to electron correlation in terms of the two-electron density matrix. This functional correctly predicts a correlation energy of zero for 1-electron systems. Thus the BLYP combination using the Becke exchange functional gives a quite accurate energy for the H atom, of –0.498 au.

When one takes into account that different overall density functionals are obtained by combining a given non-local (or local) exchange functional with a given correlation functional, it is already clear that the GGA approach encompasses a large number of different DFT methods. These differ somewhat in their performance, reflecting in part the fact that some of them have been developed with different target systems in mind. However, one remarkable feature of all these functionals (or at least the commonly used variants) is that they are much more accurate than the LDA, and indeed usually yield a very useful level of accuracy. To take an example, the mean absolute deviation from experiment for the 223 energy quantities in the G3/99 test set is of only 9.49 kcal/mol with the BLYP functional,[10] as compared to 121.85 with SVWN. The PW91 functional of Perdew et al.[13] (which includes exchange and correlation parts) gives a slightly less good mean deviation of 23.59 kcal/mol. Nevertheless, GGA functionals quite generally give a spectacular increase in accuracy compared to the LDA, and this means that DFT methods can be used with semi-quantitative accuracy for a wide range of problems in chemistry and materials science.

3.3. *Kinetic Energy Density Functionals*

We follow here an order of presentation of exchange-correlation functionals that can be referred to[14] as a "Jacob's Ladder" of increasing accuracy, leading from the first rung (the LDA) up to the hypothetical heaven of the exact functional. The second rung is constituted by the GGAs discussed above. The functionals corresponding to the third rung include two further functions of the density at each point in space, namely the Laplacian of the total density (or of the densities of spin-up and –down electrons) and the sum of the kinetic energy densities of the Kohn-Sham orbitals ψ_i. The first of these terms is intuitively expected given that it corresponds to the next term in the Taylor expansion of the density around a given point (eq. 5).

$$\varepsilon\{\rho\} = \varepsilon\left\{\rho_\sigma, \nabla\rho_\sigma, \nabla^2\rho_\sigma, \sum_i^{occ}|\nabla\psi_{i\sigma}|^2\right\} \tag{5}$$

The theoretical justification for the use of the second term is that it allows several theoretical constraints to be placed on the functional more easily.[14] In fact, the kinetic energy density is the only one of these terms to be used in one of the most frequently used of the so-called meta-GGA functionals, that suggested by Tao, Perdew, Staroverov and Scuseria (and hence called TPSS).[15]

Perhaps surprisingly given the extra complexity of these functionals, they do not yield a very large improvement in accuracy over GGA functionals, with a mean absolute deviation on the G3/99 atomization energies of 5.81 kcal/mol for the TPSS functional, as compared to e.g. 9.49 for BLYP.[14] Indeed, on the G2 subset of smaller compounds, where cumulative error is less of an issue, the difference is even smaller, with average errors of 7.27 and 5.98 for BLYP and TPSS.[14] However, the TPSS functional is not fitted to experimental data (it is referred to as a 'nonempirical' functional) and is thereby perhaps better compared to nonempirical GGA functionals such as PW91 or PBE, which give average errors of 23.59 and 22.22 on the G3/99 set.[14]

3.4. Hybrid Density Functionals

As discussed above, the use of local exchange and correlation functionals leads to significant overestimates of atomisation energies. Many GGAs also lead to the same type of overbinding, if to a lesser extent. At the same time, the Hartree-Fock method substantially underestimates these energies. This suggests that some combined treatment might yield improved thermochemical results, and this is indeed the case. It is also possible to put forward sophisticated theoretical arguments based on the adiabatic connection formula[16] in favour of using the resulting functionals, which are referred to as 'hybrid'. In the first application of such a method, the exchange-correlation energy was calculated using one half of the Hartree-Fock type exchange energy of the Slater Determinant formed from the Kohn-Sham orbitals, and one-half of the LDA exchange energy of the corresponding density, and this led to accurate results for a number of test cases. More sophisticated hybrid functionals were then developed, including the very popular B3LYP functional. This was based on an earlier three-parameter functional[17] in which the exchange-correlation energy was expressed as a combination of the local exchange-correlation energy, the HF exchange energy, and the gradient corrections to the exchange and correlation energies as shown in eq. (6):

$$E_{XC} = E_{XC}^{LSDA} + a_0\left(E_X^{HF} - E_X^{LSDA}\right) + a_X \Delta E_X^{B88} + a_C \Delta E_C^{PW} \qquad (6)$$

In the original form of this functional,[17] the non-local exchange and correlation terms were taken from the GGA exchange and correlation functionals of Becke[11] and of Perdew et al.,[13] respectively. The semi-empirical coefficients a_0, a_X and a_C were fit to reproduce as well as possible a set of ca. 100 atomization energies, ionization energies, proton affinities and atomic energies, yielding values of 0.20, 0.72 and 0.80 respectively. Other authors then used these same parameters and the same expression from eq. (6), but using the LYP correlation functional[12] instead of that of Perdew et al.,[13] to yield the well known B3LYP functional. This yields a quite low mean average deviation from experiment for the G3/99 set of atomization energies and other thermochemical properties of 4.93 kcal/mol.[10] This compares favourably to the 5.81 kcal/mol of the TPSS functional,[10] and was even more impressive at the time when it was first developed, by comparison to other functionals available at the time.

Having been made swiftly available to the community in several popular computational chemistry packages, the B3LYP functional was rapidly taken up and widely used – the original paper by Becke, ref. 17, has been cited more than fifteen thousand times at the time when this review was written! This is partly due to its overall good accuracy for a wide range of problems, and its status as a kind of 'gold standard' within modern computational chemistry, which is recognized and trusted by many experts as well as by experimental scientists. Many other hybrid functionals have been developed and some of them have also been widely used. As well as hybrid functionals based on GGA and local exchange-correlation functionals, others have been developed based on the kinetic energy density functionals, with e.g. a hybrid based on the TPSS functional, TPSSh,[10] giving a still lower average error of 3.90 kcal/mol. It should also be noted that promising methods have been developed in which more complicated (spatially resolved) mixing of Hartree-Fock and GGA exchange is used.[18,19]

Finally, we should note that various methods have been developed which go beyond the Kohn-Sham framework by also including excited Slater determinants within a DFT framework.[20]

3.5. Inaccuracies in DFT

The description above of the four types of functional suggests that there has been constant development of more and more accurate functionals, with the latest developments leading to methods that can be used as 'black-box' tools yielding very high accuracy for all sorts of problems.

This is in part true: computational electronic structure methods can be and are now used in a straightforward and relatively inexpensive way to learn more about the chemistry of almost any system. However, some problems remain that affect the accuracy of DFT. These problems have been widely discussed in many places so our presentation will be brief. For convenience, the errors are presented as being due to three separate shortcomings, although in reality these aspects are linked as they are all due to deficiencies in the treatment of exchange-correlation. The implications of these problems for computational transition metal chemistry will be discussed in the following section.

The first problem is that pure dispersion interactions between unbound chemical species are not well reproduced by common functionals. There has been considerable discussion as to whether such forces *can* be reproduced correctly as a matter of principle when using standard Kohn-Sham DFT. Also, extensive work has been put into developing functionals or methods to describe dispersion in a Kohn-Sham framework.[21] A pragmatic way of dealing with the problem is to use a normal functional, which does not describe dispersion, but to include additional molecular mechanics terms to treat this effect.[22] This leads to a hybrid DFT-empirical approach similar in some respects to QM/MM methods.

The second problem relates to the poor cancellation between the electron self-interaction present in the Coulomb term of eq. (1) and the exchange energy. In wavefunction-based methods such as Hartree-Fock theory, this interaction cancels exactly. In DFT, it does not, and there remains a residual self-interaction term that leads to sometimes significant errors. One of the most common manifestations of this error is an effect whereby electronic configurations with one or more localized unpaired electrons are incorrectly destabilized compared to situations in which these electrons are delocalized or paired up. A number of known pathological results associated with this effect concern the potential energy surface of systems in which an electron is localized in some configurations and delocalized in others. A simple example is the H_2^+ one-electron system.[23] The potential energy curve of this ion, which is treated exactly using Hartree-Fock theory, has a non-physical maximum at intermediate range with many DFT functionals, and the asymptote is artificially low, by ca. 55 kcal/mol, compared to the molecular cation or to the fragments, $H^+ + H$. This is because the Kohn-Sham equations lead to a solution in which the one electron is delocalized over both centres.

A related situation arises for a number of radical abstraction reactions $X^\bullet + Y–Z \rightarrow X–Y + Z^\bullet$, in which the TS has a delocalized electronic structure that is thereby artificially lowered in energy using DFT methods. The prototypical example is the $H + H_2$ reaction, for which some density functionals find the H—H—H TS to be a stable minimum, while almost all calculate its relative energy to be far too low.[24] Many other reactions of this type display abnormally low barriers, as do some reactions of closed-shell species, such as the S_N2 substitution reaction $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$.[25] It should however be noted that contrary to what is often stated, this problem does *not* occur for *all* transition states (or perhaps not even for most of them).

The self-interaction problem can be corrected, leading to so-called self-interaction corrected DFT methods. These greatly improve the barrier heights for the problematic reactions.[24,25] However, such methods are also much less accurate on the G2 and G3 benchmark tests for atomization energies[26] and ionization potentials.[27] For example, the mean absolute deviation from experiment for B3LYP and self-interaction corrected B3LYP for the G2 enthalpies of formation are respectively 2.2 and 18.7 kcal/mol! This indicates that introducing self-interaction free DFT methods, and thereby avoiding the difficulties that this unphysical effect undoubtedly creates, is not straightforward.

The third problem is that even the best current exchange-correlation functionals still lead to unacceptably large energy errors for a significant number of 'outlier' species, even when dispersion and self-interaction do not appear to be involved. For example, the maximum deviations from experiment for the heats of formation in the G3/99 benchmark set are as large as 41.0, 81.1, 20.8, 22.9 and 22.0 kcal/mol, respectively, for the BLYP, PW91, B3LYP, TPSS and TPSSh functionals,[10] respectively. These deviations appear for species, namely octane, azulene, sulphur hexafluoride, chlorine trifluoride, and tetrafluorosilane, in which fairly 'normal' bonding would be expected. There is considerable anecdotal evidence that such outliers crop up relatively often when using density functional theory. To take one example from our own research, we have found[28] that the dimerisation energy of diaminocarbenes to give tetraminoethylenes is underestimated by ca. 15 kcal/mol. Many other examples could be mentioned from the work of other groups.

To understand why such large errors occur occasionally even for quite accurate functionals, it is necessary to understand a bit better why methods such as BLYP and B3LYP give such good results in general, despite their simplicity as compared to correlated wavefunction methods. This has been explored in some detail by Kraka and Cremer in a series of papers.[29] Only the main results of their analysis can be given here, but they are of great importance for understanding the general topic of accuracy in DFT. The description given above of Kohn-Sham theory suggests that the exchange part of a functional covers (en gros) the self-interaction energy erroneously introduced through the Coulomb energy, as well as the exchange energy, while the correlation part covers all correlation effects, both dynamic (short range instantaneous effects) and static or non-dynamic (longer range 'left-right' correlation, as e.g. in the H_2 molecule at extended internuclear distance). Detailed analysis of electron densities as well as the exchange hole shows that this picture is incorrect.[29] In fact, as well as covering the self-interaction and exchange effects, local and GGA exchange functionals also account for a large part of non-dynamic correlation, and even for some dynamic correlation.

In fact, the self-interaction 'error' discussed above is also shown to be critical to the accuracy of common functionals, as removing it tends to remove the treatment of non-dynamic correlation. This may explain the poor accuracy mentioned above for completely self-interaction free functionals.[26,27] It is also shown that including Hartree-Fock exchange, as is the case in hybrid functionals, tends to mimic the effect of introducing a partial self-interaction correction.[29] This explains why hybrid functionals seem to give better results than 'pure' GGAs in many cases, as some correction for self-interaction seems to improve accuracy. Indeed, in cases such as those mentioned above where self-interaction leads to pathological results, e.g. in the radical abstraction reactions, hybrid functionals with a very large (ca. 50%) amount of exact exchange give much improved barrier heights.[30]

In this context, the overall good accuracy of common functionals such as BLYP and B3LYP can be seen as resulting from the fact that the mix of static and dynamic correlation in the electronic structure of the molecules contained in benchmark tests sets and indeed in many other species is fairly constant. Also important is that the residual self-interaction error is usually fairly constant, so that it cancels out. The systems for which large errors occur can therefore be seen as resulting either from large changes in the self-interaction error or from a different balance of static and dynamic correlation. In this picture, it is difficult to distinguish between errors due to self-interaction and those due to shortcomings in the treatment of exchange and correlation, and we will therefore discuss these two types of error together.

In recent work, Friesner has analyzed the B3LYP errors with respect to experiment for the compounds in the G2 benchmark and found that they can be understood in terms of the expected amount of static correlation.[31] Hand-waving arguments as well as analysis of the bonding in terms

of localised orbitals can be used to predict how much non-dynamic correlation should be present, and this can then be correlated with systematic errors on a bond-per-bond basis with a small number of empirical parameters. Where a large amount of correlation can be expected, e.g. in polar covalent bonds with a large bond length, B3LYP tends to underestimate the stability of the bond. For example, static correlation is quite important in the C–C single bond, and this explains the quite large discrepancies with respect to experiment for the heats of formation of larger alkanes.[32] Conversely, for short bonds, there is a tendency to overestimate the stability. In some cases, delocalization of bonding pairs into the anti-bonding orbitals of adjacent bonds is also expected to be important (e.g. in poly-halo alkanes such as CCl_4), and here too, B3LYP underestimates the stability due to the extensive non-dynamical correlation associated with this effect.

To summarize, modern DFT functionals provide unexpected accuracy for a low computational cost, but do still lead to significant errors. Much progress is being achieved in terms of understanding how these errors arise, and it can be hoped that future developments will build on this insight to produce even more accurate functionals. We now consider the situation concerning the accuracy of DFT methods for transition metal compounds.

4. DFT for Transition Metal Compounds

As mentioned in the introduction, many applications of DFT to problems in molecular transition metal chemistry have been published since the pioneering period in the 1980s. The fact that so many papers have been published is in itself a testament to the fact that DFT has in some sense been judged by the authors to be sufficiently accurate for the purposes of their studies. Most computational papers attempt to reproduce some or other known experimental observation, and to then make novel predictions based on the same or further computations. Most serious work of this type will involve some attempt to gauge how well the chosen method agrees with experiment. It will also try to examine whether agreement with experiment is due to mere accidental cancellation of error, or whether the chosen method is quite generally accurate for the type of target systems and observables being calculated. Although this type of calibration is usually informal and may sometimes incorrectly lead to the conclusion that the method is accurate 'enough', hence leading to incorrect predictions, it does provide at least some support for the fact that DFT gives reasonable accuracy for many problems in the field.

For example, some years ago we studied[33] the question of the relative stability of isomeric alkyl-metal complexes R–[M] (see Scheme 1), in an attempt to understand whether the generally observed preference for primary 'linear' isomers vs. secondary 'branched' isomers was due to a steric or electronic effect. To do so, it was essential to be able to reproduce fairly precisely the relative stability of such isomers for some cases where the equilibrium constant was known from experiment. We did indeed find that relatively simple calculations gave good results, with an accuracy approaching 1 kcal/mol based on agreement with experiment! We compared gas-phase energy computations using the B3LYP functional with condensed-phase free energies, so it is of course possible that agreement was fortuitous, with e.g. solvent effects cancelling an incorrect DFT description of the relative energy. It is also obvious that this is a very favourable case as the electronic structure of the isomeric metal complexes is likely to be very similar and most sources of error are expected to cancel. Nevertheless, the success of this project serves to demonstrate, if only in a very loose way, that the B3LYP functional provides a reasonably accurate description of the target systems. This is just one of many examples showing that DFT can be successfully used as a tool to understand organometallic chemistry in a qualitative and even nearly quantitative way.
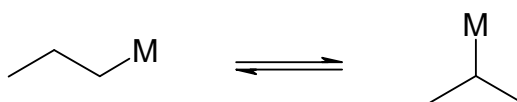
Scheme 1.

It should also be noted in this context that many studies of transition metal chemistry involve processes in which extensive changes in bonding occur in the ligand sphere as well as between the ligands and the metal. The description of the former changes is of course expected to be most accurate using the same functionals as yield good results for main-group compounds. Hence in many cases, using a well-validated functional such as B3LYP may be the best choice even though, as we shall see below, this functional is not always the most accurate in describing the metal itself and its bonding to ligands. In the future, it can be hoped that such choices and compromises will become unnecessary, because functionals will become available which provide adequate accuracy for both the metal centre and the ligands.

4.1.   Difficulties in Benchmark Studies of TM Compounds

Compared to the broad range of applications and *ad hoc* testing just mentioned, rather little *systematic* testing of DFT has been made in transition metal chemistry. By systematic, we mean that computations have been made on a large dataset of well-validated experimental systems involving a range of transition metal elements and a range of bonding types, using large basis sets and if possible comparing several different functionals. The borderline between such studies and smaller-scale tests is difficult to define, and we should point out that we are aware of many papers[34] and reviews[2,3] addressing the topic of DFT accuracy in transition metal chemistry, which are however not discussed here in detail.

There are several reasons for the lack of broad-ranging benchmark studies of the type mentioned. First of all, even simple transition metal compounds tend to be larger than is strictly desirable in a benchmark set from the point of view of computational expense. Their electronic structure is also more complicated than that of most main-group compounds and convergence of the Kohn-Sham equations can be hard to achieve. Also, scalar and spin-orbit relativistic effects can be substantial and are not always readily computed. Hence carrying out the large number of DFT computations needed for benchmarking many functionals is challenging. This was perhaps true to a greater extent some years ago, when DFT applications were in their infancy. Modern codes and powerful computers mean that DFT calculations on medium sized (less than 20-50 atoms) molecular systems are essentially trivial nowadays. Nevertheless, the early benchmark sets of compounds did not include transition metal compounds, and the understandable conservatism in this respect has led to little change in the composition of typical test sets.

One aspect involved in performing 'benchmark' quality DFT calculations that is not always sufficiently taken into account is the need to use saturated basis sets. For wavefunctions methods, the basis set needs to be able to describe the interelectronic cusp, and this requires a large number of functions including very high angular momentum basis functions. The situation for DFT is different, in that all that is needed is sufficient flexibility to describe the one-particle Kohn-Sham orbitals. This limit is in principle fairly easy to reach; indeed, in some cases rather small basis sets of e.g. double-zeta polarized quality will appear to represent the basis set limit for a given property. However, such favourable convergence is not always achieved and in some other cases, experience suggests that basis set saturation will be achieved only with quadruple zeta sets including two sets of polarization functions (*f* and *g* functions for transition metals) as well as diffuse primitives to eliminate basis set superposition errors. As geometries are less sensitive to basis set quality, tests

can be carried out as single-points at geometries derived at a lower level. Some tests of DFT accuracy unfortunately use smaller basis sets and may be unreliable for this reason.

Another difficulty is that high-quality gas-phase geometries and thermochemical data for transition metal compounds is somewhat lacking. One of the most striking aspects of one of the more comprehensive reviews on transition metal thermochemistry[35] is the low amount and often poor quality of data compared to that available for simpler main-group compounds, due to the difficulty of carrying out experiments in this field. In some cases, experimental observations do not relate to the electronic ground state of the considered molecule or fragment, and solvent or other medium effects can be large.

A final factor is that it is far more difficult to carry out benchmark accuracy *ab initio* studies of transition metal compounds than it is for small main-group species. Even for main group compounds, the successful description of bonding to within chemical accuracy requires the use of very large basis sets and very high levels of correlation.[36] For transition metal compounds, this requirement is if anything more severe (e.g. the basis set should be at the very least of triple zeta size, and include *f* and *g* functions, and much larger basis sets may be needed). Also, in many cases a more complicated multi-reference treatment of correlation is required. Taken together, this means that obtaining well converged wavefunction-based results is too difficult for this approach to provide a straightforward and abundant source of high accuracy data with which to test DFT.

Nevertheless, some authors do try to use accurate wavefunction computations to test the accuracy of DFT. In many cases discrepancies with DFT are found and it is often concluded that the DFT methods are wrong. In many cases, an equally plausible interpretation is that the wavefunction computation is deficient, either due to the use of small basis sets or to an inadequate description of correlation.[37] This problem can be illustrated by an example. A number of enzymes involve binding of dioxygen to a dinuclear copper (I) centre to give an adduct that can exist in two forms, as shown in Figure 1. Experiment suggests that the more stable form has a bridging doubly negative peroxide ligand with an oxygen-oxygen bond. The bis-oxo form, in which this bond in broken and the copper ions are formally in the +3 oxidation state, is a possible intermediate in various oxidation reactions.
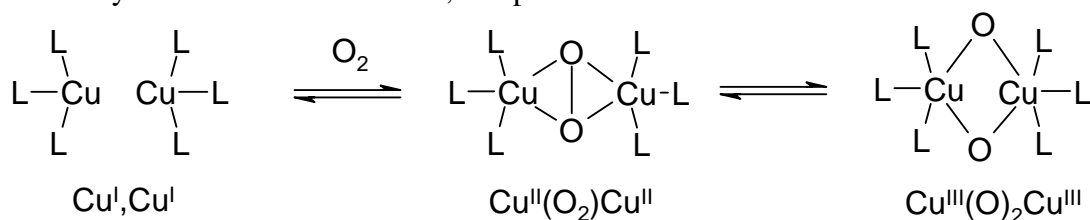

Figure 1. Peroxide and bis-μ-oxo forms of dicopper oxygen adducts. The ancillary ligands L are protein sidechains such as histidine-derived imidazole.

Density functional calculations on these dicopper complexes identify two minima corresponding to the different isomers. Using the B3LYP functional, the peroxide form is significantly more stable than the dioxo form, by 18.7 kcal/mol, when L = ammonia.[38] The same authors found the dioxo form to be favoured by as much as 12.7 kcal/mol using the CASPT2 multireference wavefunction method. This suggests that B3LYP is in error by more than 30 kcal/mol. This system has however been reinvestigated using a more accurate multi-reference configuration interaction method using large basis sets, and the peroxide structure has then been found to be more stable, by an amount similar to that found using B3LYP.[39] The authors suggest that with the necessarily rather limited active space used in the earlier study, the correlation treatment of the two isomers is unbalanced. In general, the well-known difficulties of treating transition metal compounds with traditional wavefunction correlated methods means that great caution is needed before such a calculation is used to decide that a particular DFT method has 'failed' (or that it is highly accurate!).

4.2. Accuracy of Computed Molecular Geometries

The accuracy of DFT methods can obviously be assessed separately for many different molecular properties: geometry, bonding energy, spectroscopic properties, etc. The bulk of this review focuses on energetics, as this is perhaps the most challenging property to calculate accurately. In consequence, there is much less discussion of the other aspects, despite their importance. By and large, the experience with transition metal compounds is that most common DFT functionals yield rather good geometries for most traditional coordination and organometallic compounds.[2,3] Of course, there are some cases where the potential energy surface is rather flat along a given coordinate, and in this case, a very small error concerning the relative energy of two points along this coordinate can lead to quite large discrepancies between the calculated optimum geometry and the correct value. Indeed, in such cases, the error can also be due to experimental effects such as solvation or crystal packing.

4.3. Dispersion Interactions and DFT

In the section on Inaccuracies in DFT, three main shortcomings of contemporary DFT functionals were mentioned. The second and third of these, the treatment of electron self-interaction and the inaccuracy of the exchange-correlation functional, were recognized to be linked. These aspects are probably the most problematic and their impact will be discussed at length below. The other problem, whereby most common functionals do not account for dispersion interactions, is also important in many contexts but we will not discuss it in detail here. For small molecules, this problem is mainly important when studying molecular clusters and intermolecular interactions. As such effects are not usually covered by benchmark datasets, this problem is not mentioned at length in most studies of DFT accuracy (including the present one!).

However, for larger molecules, such as many organometallic complexes, dispersion forces are certainly present between different parts of the molecule, e.g. between two bulky ligands on a single metal site, as shown in Scheme 2. Standard DFT calculations on such complexes will perhaps not reproduce the correct interaction between the two ligands, and this may alter the geometry at the active site. In such cases, the calculated energetics for dissociation of the bulky ligand may be incorrect, and indeed energetics for other reactions may be perturbed also.
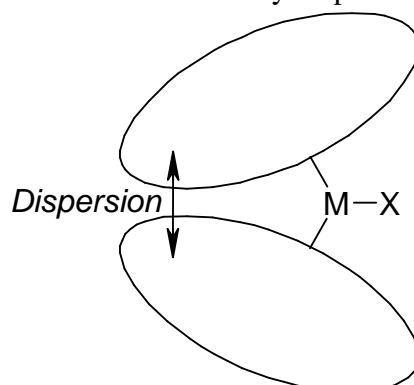
Scheme 2.

In our study[40] of tricyclohexyl phosphine dissociation from the Grubbs metathesis catalysts $(Cy_3P)_2Ru(Cl)_2(CHPh)$ and $(Cy_3P)(IMes)Ru(Cl)_2(CHPh)$, we found evidence that such effects are indeed important. These catalyst systems are very large molecules in which the ligands CHPh, Cy_3P and IMes are in van der Waals contact. Our all-QM DFT computations of the M–P bond energies yield values of 17.3 and 15.9 kcal/mol, respectively. Using a hybrid QM/MM method in which the bulky side-chains are treated using a molecular mechanics forcefield and only the core atoms are treated with DFT, the respective bond energies are 30.7 and 28.5 kcal/mol. In the QM/MM

calculations, the van der Waals interactions between the side-chains are treated using the forcefield, including non-bonded Lennard-Jones dispersion terms, and inspection of the geometries shows that this leads to a more favourable interaction between these ligands. The computed energies and geometries are also in better agreement with experiment. Clearly, the absence of dispersion in the all-DFT computations accounts for the large change in bond energy.

Anecdotal evidence suggests that similar effects occur more broadly when studying large transition metal complexes, and that this is in fact a reason why QM/MM treatments are to be preferred over all-DFT studies.[41] However, detailed studies, including comparison between DFT, QM/MM and correlated wavefunction methods for a broad range of cases are not yet available.

4.4. Exchange-Correlation Functionals and Binding in Transition Metal Compounds

At the end of the section concerning inaccuracies of DFT functionals, we mentioned that the cause of many poor results from DFT computations was that the system under consideration was in some sense abnormal in terms either of the degree of electron self-interaction, or of the balance between dynamic and non-dynamic (static) correlation. The LDA as well as GGA methods involve a substantial self-interaction error, and also account quite well for static correlation effects.[29] In fact, in some cases, such functionals appear to exaggerate the magnitude of static correlation effects and thereby can lead to overbinding. Introduction of a correction for self-interaction does not improve agreement with experiment[26,27] as it removes much of the treatment of static correlation. Introduction of Hartree-Fock exchange, as in hybrid functionals, mimics the effects of a partial removal of self-interaction,[29] and, for main-group compounds, an optimum at values of the exact exchange of ca. 20% leads to improved agreement with experiment as compared to GGAs. However, this optimum only applies to situations where the balance of genuine exchange effects, self-interaction and static and dynamic correlation is roughly constant. In cases where static correlation is more important, significant errors can occur even for accurate functionals such as B3LYP.

These principles provide a useful heuristic principle for assessing the likely accuracy of DFT methods for transition metal compounds. The latter have a complicated electronic structure that furthermore is highly variable from one species to another. The relatively small size of the *d* orbitals, especially for the metals of the first transition series (Sc – Cu) and even more so for those on the right-hand side of the series (e.g. Cr to Cu) leads to relatively poor overlap and hence to near-degeneracy effects. In other words, bonding in transition metal compounds frequently involves substantial static correlation. This is well supported by *ab initio* wavefunction studies of their electronic structure.[42,43]

Non-dynamical correlation arises in several contexts in transition metal chemistry. First, metal-nonmetal multiple bonds (as e.g. in diatomic oxides[44]) involves significant mixing between configurations with $\ldots\pi^2\pi^{*0}$ and $\ldots\pi^0\pi^{*2}$ (or $\ldots\pi^2\pi^{*1}$ and $\ldots\pi^1\pi^{*2}$) occupations, due to left-right correlation within the π bond. This explains why single-reference treatments give such poor results for many of these compounds: the bond energy in VO_2^+ is calculated[45] to be -66 kcal/mol with Hartree-Fock, and 201 kcal/mol with MP2, against an experimental estimate of ca. 70-90 kcal/mol. Such effects are also very important in metal-metal bonding, as in the notorious case of the chromium dimer Cr_2, which has a $^1\Sigma_g^+$ ground state with a formal sextuple bond, with extreme left-right correlation between the formally 'bonding' and 'anti-bonding' $\pi - \pi^*$ and $\delta - \delta^*$ orbital pairs.[46]

A less obvious source of non-dynamic correlation is the so-called 'double-shell' effect.[43,47] Hartree-Fock calculations on systems containing doubly-occupied d orbitals tend to lead to an incorrect exaggerated size for these orbitals, due to the absence of correlation. Correlation treatment based on this inappropriate reference then leads to poor results. Better results are obtained using a multi-reference treatment in which the d electrons are also allowed to occupy a second shell of d orbitals in the reference wavefunction. This is in fact not really a case of static correlation, merely an extreme example of dynamic correlation.

As well as intervening in metal-element multiple bonding, static correlation also plays an important role in metal-ligand single bonds, whether dative or covalent.[43] Finally, it also affects metal to ligand back-bonding interactions.[43]

All of these types of static correlation involve somewhat different orbitals and atoms, and it can be expected that the description of the different types of correlation by a given functional may be of different quality. With this background, it might be expected that the description of bonding in transition metal compounds would require DFT functionals with a lesser amount of Hartree-Fock exchange than is typically needed for man-group compounds, due to the greater prevalence of non-dynamic correlation. Also, it may be expected that performance of a given functional may vary from one system to another even if the overall contribution from static correlation is similar, due to the fact that the pattern of correlation is different.

4.5. Benchmark studies of DFT for Transition Metal Compounds

We mentioned previously that most benchmark studies of DFT have not used datasets containing transition metal compounds. This has however changed in the last year, as several studies have appeared that are highly pertinent to the present topic. The first, by Cundari et al., involves a dataset of 26 heats of formation of small inorganic and organometallic molecules, such as TiF_4, $Cr(CO)_6$, ferrocene and $Pt(NH_3)_2Cl_2$.[48] This paper is designed as a test of the accuracy of two different families of effective core potentials and only uses a single functional (B3LYP). The basis sets used are too small to obtain quantitative results, so no conclusions about accuracy of the functional can be reached. However, the set of compounds chosen cover a broad range of bonding types and could usefully be integrated in a future benchmarking exercise.

Two papers by Schultz, Zhao and Truhlar address bonding in respectively eight transition metal dimers[49] and twenty-one small molecules containing metal-element bonds, such as CoO^+, $CrCH_3^+$ and $Ni(CO)_4$.[50] Furche and Perdew present a dataset with 18 reaction energies involving processes such as metal dimer, metal monohydride, mononitride and monoxide dissociation, and ligand dissociation.[51] Unlike the study mentioned above,[48] the latter two surveys, and especially that by Furche and Perdew,[51] use reasonably large basis sets which should be close to the basis set limit for DFT.

Whilst these databases are still somewhat too small to be able to assess DFT accuracy for the wide range of bonding environments encountered in transition metal compounds, they do yield valuable insight. First, all functionals in all studies are able to predict geometries with very good accuracy, if perhaps somewhat less so than would be the case for main-group compounds. This is in general agreement with many observations and we will not discuss this point further. Likewise, we will not discuss the data on vibrational frequencies or dipole moments that is available in some of the studies as accuracy for these properties tends to be reasonably well correlated with accuracy for energies. Instead, we will focus on the latter, for which the situation is as expected less good than it is for main group compounds.

For the combined set of 29 energies in the Schultz, Zhao and Truhlar datasets,[49,50] the mean absolute errors using a triple zeta basis set range from 5.3 kcal/mol for the best functional tested (the B97-2 hybrid functional[52]) to 32.2 kcal/mol for the LDA. The commonly used B3LYP functional has a medium level of accuracy (11.4 kcal/mol mean absolute error) and has a tendency to underbind, that is to predict too low bond energies (mean *signed* error −8.6 kcal/mol, that is, the calculated bond energies are on average too small by this amount). The authors suggest that GGA and meta-GGA functionals give better results than hybrid functionals. This conclusion is perhaps not clearly demonstrated, as some of the hybrid functionals (e.g. B97-2 and B3LYP) give results that are not significantly worse than those obtained with the GGA and meta-GGA functionals, especially when the relatively small size of the database (and hence poor statistical significance) is taken into account. However, what is clear is that unlike for main-group benchmarks such as the G3/99 set, hybrid functionals such as B3LYP are no better than commonly used GGA functionals such as BP86 (9.8 kcal/mol mean absolute error) or BLYP (6.9 kcal/mol). The mean signed errors for these pure functionals indicate a degree of *over*binding (+8.7 and +6.9 kcal/mol, respectively).

Although a larger dataset would clearly be preferable, it does appear that many hybrid functionals (although not all – the B97-2 functional gives good results) tend to predict too low bond energies. The authors suggest that this is due to the fact that introducing some Hartree-Fock exchange removes the non-dynamic correlation effects described by the GGA functionals. In fact, they also suggest that hybrid functionals give better results for systems demonstrating less static correlation, with GGA functionals outperforming them for cases with more near-degeneracy effects. To quantify the occurrence of such effects, they introduce a 'B_1' diagnostic, the difference per bond in calculated bond energy with the BLYP GGA and B1LYP hybrid functionals. This diagnostic is analogous to the well known T_1 diagnostic of coupled-cluster theory,[53] with larger values (larger differences between BLYP and B1LYP bond energies) corresponding to a larger degree of near-degeneracy effects. For at least some of the compounds (the metal dimers), there is a trend for better results with hybrid functionals where there is little static correlation, and less good results when there is more such correlation, but the statistics are poor and detailed analysis of such effects will need to wait for larger datasets.

The study by Furche and Perdew[51] covers fewer functionals but a broader range of bonding situations, and concentrates on the computationally more problematic first-row transition metals (Sc – Cu, with some additional K, Ca and Zn compounds). For metal dimers, as in the study by Schultz et al.,[49] B3LYP is found to underbind (by 11.6 kcal/mol on average!), whereas the GGAs and meta-GGAs overbind, with TPSS overall the most accurate but still having a mean absolute error of 9.0 kcal/mol. For metal monohydrides, all functionals overbind by ca. 10 kcal/mol on average. For diatomic nitrides and oxides, the trend towards larger bond energies for GGAs and smaller ones for B3LYP returns, but the pattern of agreement with experiment is different. For the four nitrides considered (ScN, TiN, VN and CrN), B3LYP gives too low bond energies by 15.8 kcal/mol, BP86 overbinds by 9.1 kcal/mol on average, and TPSS is quite accurate (3.0 kcal/mol average error, largest error 6.8 kcal/mol). For the ten oxides (CaO to CuO), however, B3LYP is very accurate (mean error 4.0 kcal/mol, maximum error 8.3 kcal/mol), whereas the GGAs and meta-GGAs all overbind, e.g. by 13.4 kcal/mol on average for TPSS. *A priori*, one might have predicted that the pattern of bonding in diatomic metal oxides and nitrides might be rather similar, so it is surprising that such a different level of performance between the functionals is obtained for these two groups of compounds.

The authors also consider some more complicated species, e.g. metal carbonyls where B3LYP tends to underbind, and GGAs and TPSS are quite accurate, and some π-bonded complexes such as dibenzene chromium and ferrocene where B3LYP again gives much too low bonding energies.

Overall, the authors have computed average errors for a set of 18 reaction energies, and find that B3LYP underbinds by 6.6 kcal/mol on average, with a mean average error of 12.0 kcal/mol, and the other functionals tested tend to overbind and give roughly similar mean average errors. As discussed in the preceding text, though, these average results mask some quite diverse levels of performance for different classes of compounds and indeed individual species. Another aspect that needs to be considered is that the statistics are not as reliable as they would be if the dataset was much larger. Nevertheless, the same trend as in the previous study is quite apparent, namely that the B3LYP functional, which for main group compounds in the G3/99 (and especially G2) benchmark set is far more accurate than GGAs such as BP86, is here only of comparable accuracy to these functionals. Also, B3LYP has a clear tendency to predict too low bond energies, and this could conceivably be attributed to an underestimate of static correlation effects.

One quite limited study of binding energetics in transition metal compounds concerns a series of aquo and hydroxyl-manganese complexes, in which experimental data for O−H bond energies are available. These bond energies have been calculated by Lundberg and Siegbahn using a variety of functionals.[54] Agreement with experiment is good in all cases except one, where the experimental data is of dubious quality, for B3LYP, whereas GGA functionals *under*estimate the bond energy. This unusual sign for the discrepancy between GGAs and experiment is due to the fact that the metal-oxygen bond energy is not probed directly here. In fact, the GGAs presumably *over*estimate the Mn−O bond energy in the fragment (where there is a covalent metal-oxygen bond) compared to that in the molecule (in which there is merely a water of hydroxide ligand). B3LYP seems to provide a more balanced description.

In conclusion to this section, the first systematic surveys of DFT functionals for transition metal binding energetics and related properties have started to appear in the very recent past. Much more work of this type is needed but some clear trends already emerge. First, transition metal compounds are clearly very challenging for DFT, with large errors of 10-20 kcal/mol or more appearing for individual compounds even with the most sophisticated functionals. Next, performance varies considerably from one class of compounds to another, suggesting that the nature of correlation in a given species has a big effect on the accuracy of a given functional. Finally, static correlation is clearly more important than for main-group compounds, as shown by the reduced tendency of functionals such as BP86 to overbind, and the appearance of a clear trend for underbinding with hybrid functionals such as B3LYP. A similar conclusion is reached for a much smaller dataset as part of a wider study by Boese and Martin.[55]

4.6. *Relative Spin-State Energetics*

One very useful energetic property that is not included in the surveys discussed in the previous section, yet could be of great use in testing DFT functionals, is the relative energy of different spin states of a given metal complex. This energy is known very accurately for a number of species that display the property of spin equilibrium, that is, they exist as a mixture of spin states depending on the temperature. The multiplicity of the ground state of a number of other complexes is also known. The compounds involved are fairly 'normal' species with a full coordination sphere, unlike the gas-phase species mostly covered in the benchmark sets discussed above. This is useful given that the electronic structure of the latter species is possibly somewhat untypical. Finally, spin-state energetics are of interest because they are very highly variable from one functional to another, and they thereby represent a very challenging observable with which to test DFT accuracy.

This topic is of interest to us due to our work on understanding the kinetics of reactions involving changes in spin state.[56] Reactivity in such cases depend on the topology of the potential energy surfaces of the individual spin states involved, and especially on the relative energy of the

regions where these surfaces cross. In turn, this strongly depends on the spin-state splitting of the corresponding minima on the potential energy surfaces. As well as discussing the accuracy of DFT for predicting this key property in some of our papers concerning reactivity, we have reviewed this topic in some detail two years ago.[4] The present section covers the main points of our previous review, presents some new developments, and makes a link with the conclusions from the benchmark calculations in the previous section.

After having been informally noticed by a number of authors, it was first pointed out by Reiher, Salomon and Hess in 2001[57] that the calculated spin-state splitting for a given complex varies almost linearly with the proportion of exact (Hartree-Fock) exchange included in an otherwise constant functional. Increased exact exchange contributions lead to lower relative energies for higher-spin states (or higher energies for low-spin states). This is a large effect: for an octahedral iron (II) complex with two thiolate, two thioether, one carbonmonoxy and one amino ligand, the calculated[57] spin-state splitting between the low-spin singlet and high-spin quintet states varies from more than 25 kcal/mol in favour of the singlet with a modified B3LYP functional with 0% exact exchange to more than 10 kcal/mol in favour of the quintet with 25% exact exchange! This complex is known to have a low-spin ground state, which means that the correct result for this compound is obtained only when the proportion of exact exchange is lower than 17%. The authors carried out similar calculations for a number of related species and found that only functionals with ca. 15% exact exchange correctly predict the ground state for all of them. They consequently proposed that a modified B3LYP functional with 15% exact exchange, named B3LYP*, should be widely used.

In further work,[58] the same authors showed that this modified functional provides almost equally good results for the G2 test set as the original B3LYP, showing that main-group bonding is less sensitive than spin-state splittings to exact exchange admixture. The authors also computed spin-state splittings for several metallocenes $M(C_5H_5)_2$ and dibenzene-metal complexes $M(C_6H_6)_2$. Again, they found that a functional with a proportion of exact exchange of ca. 15% gives results consistent with experiment, and indeed argued that other values would lead to results inconsistent with experiment. We argued previously[4] that the latter conclusion is reliant on the data for manganocene, $Mn(C_5H_5)$, so may be partly misleading because although the calculations[58] consider an isolated species, the experimental data[59] is complex, with different ground states in the gas phase and under different conditions in the solid state.

Extensive literature was cited in our earlier review[4] supporting the observation that calculated spin-state splittings in transition metal compounds tend to depend very strongly on the proportion of exact exchange. Further examples of this have appeared in the intervening time.[60, 61] We note in particular the extensive work by the Reiher[62] and Casida[63] groups. In our own work, we have also found increased exact exchange admixture to lead to lower relative energies for high-spin states compared to low-spin states. We observed this effect for the 16-electron species $Fe(CO)_4$,[64] $CpCo(CO)$ and the isoelectronic $Tp'Co(CO)$,[65] for the myoglobin active site model iron porphine-imidazole adduct[66] and for organometallic species such as $CrCl_2(dmpe)_2$.[67] It should be noted that the dependence is strongest in the case of complexes of metals from the first transition series. For example, for the isoelectronic 16-electron species $M(CO)_4$ (M = Fe, Ru and Os), the change in spin-state splitting from functionals with no exact exchange to those with ca. 50% is of the order of 25 kcal/mol with the first-row iron compound, yet only 5 or 8 kcal/mol with the second- and third-row ruthenium and osmium derivatives.[4] This can be understood loosely because the pairing energy for the second- and third-row species is lower,[68] so that exchange effects are less important. The lower pairing energy also explains the lower prevalence of species with high-spin ground states in second- and third row compounds. Hence the cases where it is most often chemically important to identify

the ground state and compute the spin-state splitting are also those where the greatest variability in computed splittings is obtained.

Although spin-state splitting is clearly strongly dependent on exact exchange admixture, it is important to be cautious and aware that other factors may also be important. For example, we pointed out[4] that the trend is only expected to apply for cases where the two spin states involved correspond to different ligand-field pairing of the metal d orbitals. Where one or more unpaired electrons are on another atom, or the spin-states differ in the redox state of the metal, other effects may appear. Also, different GGA functionals can sometimes yield fairly different results, and meta-GGA functionals may also display different behaviour. Nevertheless, to a first approximation, the most important effect is that of exact exchange.

Is it possible to discern any trends concerning the most accurate functionals? Previously, we suggested[4] that the safest way to approach a problem requiring the identification of the (experimentally unknown) ground spin-state of a species was to calculate this property with more than one functional, preferably a GGA-type functional and a hybrid functional. In case of large differences between the two results, caution was required, and in the absence of other evidence, the most reliable way to make the prediction would be to use a functional such as B3LYP* with 15% exact exchange. This was based on the significant support for the accuracy of such functionals.[57,58]

This however assumes that there is a single value of the exact exchange admixture that is the optimum value for all complexes. Already, there is evidence that no such single value exists for providing an accurate description of all observables for all species. For example, very high exact exchange admixtures are required in order to reproduce barrier heights for some simple reactions.[30] A more detailed analysis of the extensive studies appearing in the literature seems to confirm that even for spin states of transition metal compounds, different amounts of exact exchange are optimal for different metals and ligand environments. Moreover, it is possible to rationalise the different amounts required for different species based on the type of bonding and the likely amount of non-dynamic correlation, based on the discussion in previous sections.

First of all, it seems that for Werner-type coordination compounds, with ligands fairly low in the spectrochemical scale, such as halides, water, ammonia, or other nitrogen-based ligands, it appears that functionals with close to 20% exact exchange provide accurate results. For example, in our work on heme-imidazole complexes, we and others[61,66] find low-spin ground states when using GGA functionals, which is inconsistent with the experimental observation that pentacoordinate deoxyheme has a high-spin quintet ground state. QM/MM calculations show that the protein environment does not significantly affect the energetics.[69] Also, B3LYP QM/MM calculations for the heme−CO bond energy[69b] are in good agreement with experiment, providing further support that this hybrid functional describes the relative energy of the quintet fragments and singlet CO adduct accurately. Finally, large basis set CCSD(T) calculations on a small model of the iron-heme system are in good agreement with B3LYP calculations, whereas GGA functionals overestimate the stability of the low-spin singlet state.[66a]

Other examples concern the $Fe(OH_2)_6^{2+}$ iron hexaaquo ion. Accurate *ab initio* calculations using the CASPT2 and SORCI methods predict[63a] that this ion has a quintet ground state, with the singlet state lying ca. 12000 cm^{-1} (or 34 kcal/mol) higher. B3LYP calculations predict a splitting of ca. 11500 cm^{-1}, whereas GGAs such as BP86, BLYP or PW91 give values closer to 9000 cm^{-1}, that is, they overestimate the stability of the singlet. The same authors obtain similar results for the hexammine complex $Fe(NH_3)_6^{2+}$.[63b] Thiel et al. show that only hybrid functionals predict reasonable energetics for the active site of the cytochrome P450 enzymes.[60f,h]

This observation may also explain the generally good agreement with experiment obtained when using the B3LYP functional to study reactivity in bioinorganic systems, in which the metal ligands are generally low in the spectrochemical series (weak-field ligands).[70]

Coordination compounds such as these will of course display significant non-dynamic correlation effects, but these will occur mainly on the metal centre itself, and perhaps in the metal-ligand dative σ bond.

Turning to organometallic systems or other complexes with high-field ligands such as the carbonyl group, there is increasing evidence that better results are obtained for the spin-state splitting when using GGA functionals rather than hybrid ones. In our own work, large-basis CCSD(T) calculations on CpCo(CO) predict a triplet ground state with a singlet lying ca. 15 kcal/mol higher in energy.[65] CASPT2 and MCPF calculations predict a slightly larger splitting of 21 kcal/mol,[71] but the small basis set used in that work will favour the triplet ground state, so we feel our value of 15 kcal/mol should be close to the correct value. With B3LYP, we obtain a splitting of 25.7 kcal/mol, which is far too large, whereas BP86 and PW91 are in good agreement with the CCSD(T) value, at respectively 14.9 and 14.8 kcal/mol. For $Fe(CO)_4$, accurate *ab initio* results are difficult to obtain as it is hard to converge the results with respect to the size of the basis set. Using large-basis CCSD(T) values and also some indirect experimental data, we predict[64b] that the splitting between the ground triplet state of this unsaturated fragment and the excited singlet state should be of the order of 2 – 3 kcal/mol. This again is closer to the values obtained[64a] with GGA functionals (BP86: 0.92 kcal/mol; BLYP: 1.43 kcal/mol) than those derived from hybrid functionals (B3LYP: 9.78 kcal/mol).

Insufficient evidence is available to prove that this trend is true for all complexes of high-field ligands (see however ref. 60a), but this difference with respect to the less covalently bound Werner coordination compounds mentioned above is certainly plausible. Metal-carbonyl and indeed metal-phosphine binding involves back-bonding interactions between the metal's *d* electrons and vacant orbitals on the ligand, leading to delocalized electrons and additional non-dynamic correlation.[43] Also, it can be expected that more of this correlation will be present in the low-spin forms of the complexes. Given that including exact exchange tends to lead to a decreased treatment of this type of correlation, it is perhaps not surprising that hybrid functionals tend to underestimate the stability of the low-spin form.

5. Conclusions

The previous section covers some of what is known concerning the accuracy of DFT and different functionals for transition metal chemistry. Overall, the calculation of bond energies and heats of formation is considerably less accurate than for main-group compounds. Whereas bond energies for a single bond in a main-group compound are rarely in error by more than 10 kcal/mol with modern GGA, hybrid and meta-GGA functionals, such deviations are relatively common in transition metal chemistry.

A complementary discussion of the accuracy of DFT for describing spin-state splittings in transition metal complexes suggests that the main difficulty for DFT in this field is the diversity in the magnitude and the nature of static correlation effects. It can by and large be stated that for systems in which such correlation is stronger, GGA and meta-GGA functionals perform better, because the inclusion of Hartree-Fock exchange in hybrid functionals has the effect of decreasing the self-interaction error and thereby the description of static correlation. However, this trend is not

straightforward, as some systems involving extensive static correlation, e.g. metal oxides, are well described using hybrid functionals, whereas very similar cases, such as metal nitrides, are not.

It should of course be remembered that 'static correlation' is not a simple phenomenon. For pragmatic purposes, it can be defined in wavefunction theory as the occurrence of large weights of doubly excited determinants with respect to the Hartree-Fock reference. Such near-degeneracy effects can however cover a wide range of bonding situations, depending on the size, location and shape of the 'donor' orbital and the corresponding properties of the 'acceptor'. For metal-ligand bonding, the most notable types of static correlation involve[43] metal-element $\sigma-\sigma*$ and $\pi-\pi*$ interactions, metal-centered d orbital 'double-shell' correlation, and metal-ligand d – acceptor backbonding. All of these cases involve orbitals of very different shapes and energies, so it is perhaps not surprising that the degree of admixture of exact exchange – a single, rather crude, parameter to regulate static correlation in DFT treatments – cannot provide a high-quality description of all of these types of binding.

The development of many of the DFT functionals in common use nowadays has involved explicit parameterization to reproduce as well as possible experimental properties for a more or less large group of compounds mostly involving main-group elements. Other functionals are instead non-empirical in the sense that they have instead been developed to respect as many physical constraints as possible, and have only been tested with respect to experiment *post hoc*. Nevertheless, even for the latter type of functional, testing on benchmark sets of main-group compounds will have played a certain role in choosing the constraints and improving the functionals from one generation to another. It can be postulated that the benchmark compounds involve a fairly constant amount and type of static correlation. Indeed, where modern functionals such as B3LYP are less accurate, this can be traced back to small variations in the amount of this type of correlation.[31] It is not clear to what extent the currently used types of functional are able to accurately take into account the more extensive and more varied static correlation in transition metal compounds. However, it does seem likely that including such species in the sets of compounds used for parameterisation or testing should lead to improved results for transition metal compounds, but perhaps also for main-group species. A particularly useful quantity to include in parameterisation is spin-state splitting as extensive experimental data is available, this property is very sensitive to the type of functional used, and different complexes are at present described optimally by different functionals.

Overall, DFT is already a tremendously useful method for studying structure, properties, and reactivity in metallic compounds, in such diverse areas as inorganic, organometallic and bioinorganic chemistry. Even non-expert users can easily predict geometries, binding energies, mechanisms and activation energies to a useful level of accuracy. It should however be realised that all currently used functionals are still liable to yield very inaccurate results, especially for energetic quantities. This type of problem occurs more often for transition metal compounds than for other species. As a consequence, all computational projects should include at least some attempt to benchmark the chosen method by comparing to experimental data. Where this is not available or ambiguous, comparison between several different functionals is also useful. Unlike in main-group chemistry, where hybrid functionals give a somewhat better description of energetics, especially for transition states, there are clearly some cases in transition metal chemistry where GGA (or meta-GGA) functionals give better results so these should also be considered in some cases.

6. Acknowledgements

7. References

[1] This is partly a reflection of the search terms used, and does not mean that no DFT calculations were being reported at that time – for example, one of the foremost and earliest proponents of the application of DFT to organometallic chemistry published two papers on bonding in metal carbonyls and metal-phosphine complexes in these journals in 1985: T. Ziegler, *Organometallics,* 1985, **4**, 675-680; T. Ziegler, *Inorg. Chem.*, 1985, **24**, 1547-1552.

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