Which functional should I choose?

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Abstract

Density functional methods have a long tradition in inorganic and bioinorganic chemistry. We introduce the density functional machinery and give an overview of most popular approximate exchange-correlation functionals. We present comparisons of density functionals for energies, structures, and reaction barriers of inorganic and bioinorganic systems, giving guidance on the title question. New development directions and current trends in density functional theory are reviewed.

1 Introduction

A central goal of modern electronic structure calculations is to find the ground-state energy of electrons in molecules. If we can do this accurately for any configuration of the nuclei, many basic properties of the molecule can be found, from bond lengths and angles to bond dissociation energies and transition state barriers.

From simple models and understanding of electronic behavior, one can construct usefully accurate empirical models for various properties, in which the parameters are taken from one experiment and used to predict others. But these days, systems of interest are large and complex, limiting the value of such models (too many parameters, or too little freedom). Thus there is increasing interest in *first principles* calculations, in which the only information taken from experiment is the nuclei and number of electrons, and the electronic structure is solved *ab initio*.

Direct solution of the Schrödinger equation for the electrons in a molecule is demanding because of the Coulomb repulsion between them. In Kohn-Sham (KS) density functional theory

(DFT),[1] we avoid this by solving a system of non-interacting electrons, but defined to have the same one-electron density as the true system. In this way, the calculation time is much shorter than that of a traditional direct approach, and so much larger systems (several hundred atoms) can be routinely handled.

In principle, this approach is exact,[2] and produces the exact ground-state energy and density, but in practice, one must approximate a small (but vital) contribution, called the exchange-correlation (XC) energy. The quality of the results depends on the quality of this approximation. Much of modern DFT research is devoted to developing such approximations, usually termed XC functionals. Unfortunately, there is presently no systematic approach, and so hundreds of different functionals have been proposed, leaving the bemused user to ask the title question.

In any practical case, the choice of functional strongly depends on the chemical system at hand. Due to the diversity of bonding situations in inorganic chemistry, ranging from covalently bonded isolated molecules to ionic crystals and metal clusters, a uniformly and usefully accurate approximate DFT description for all these systems is not yet available. For example, the strongly delocalized distribution of electron density in a chunk of tin oxide is very different from the localized bonding pattern of tris(2,2-bipyridyl)ruthenium. As a consequence, the features and formal properties of the XC functional that are important for extended solids are different from those relevant to small molecules with localized bonds. But since chemistry does not stop at the dividing lines of a formal classification, and both tin oxide and tris(2,2-bipyridyl)ruthenium must be included in a description of dye-sensitized solar cells, an accurate and universal description of all systems is the ultimate goal of DFT research. This universal description should be attainable at a higher level of approximation within the DFT framework. As of now, we choose a practical approach and consider different classes of inorganic and bioinorganic compounds separately.

The purpose of this chapter is to offer modern, up-to-date guidance on how to approach the title question, in the context of inorganic and bioinorganic systems. Like supplicants of the oracle at Delphi,[3] we are given no one simple answer: Each user must find his or her own way. A number of excellent reviews on applications of density functional methods in inorganic chemistry have appeared recently which illustrate some of the concepts outlined here.[4–11] Many additional applications are found in parts II and III of this book.

2 Functional Taxonomy

In this section, we mention several key points that help with choosing a functional. Throughout, we imagine we have enough computational power to be converged with respect to basis set, and ignore complications due to e.g., solvents or relativistic effects. (Such questions are addressed in more detail in the next section and in ia610 and ia613 of this book, respectively.)

2.1 Basics

(a) *All functionals used in practice are approximations.*

The value of DFT is in making the calculation much quicker than a direct solution. Evaluation of the exact functional would be as costly as direct solution, so we always use approximations in practice. Note this also means that reports of "failures of DFT" are in fact failures of approximations, not the theory.

(b) *No presently existing functional is highly accurate for all properties of interest.*

Because users apply existing technology to problems of immediate interest, functional development is always "behind the curve", i. e., there are always interesting new problems for which existing functionals fail.

(c) *Any functional can be applied to any electronic structure problem, without other input.*

This is the sense in which DFT is "*ab initio*". Of course, first it must be written down and coded. Thus we build up intuition and experience about when a given functional is expected to work and to fail.

2.2 Jacob's ladder

Functionals vary from very simple to very complex. On Jacob's ladder of approximations,[12,13] each rung represents a different level of approximation that should recover the results of lower rungs in the appropriate limits, but add more capabilities.

(a) The lowest rung is the local density approximation (*LDA*), in which the XC energy density depends only on the density at a point and is that of the uniform electron gas of that density. This is the simplest density functional,[1] and was used for a generation in materials science, but is insufficiently accurate for most chemical purposes. LDA typically overbinds molecules by about 30 kcal/mol, an unacceptable error for chemical applications.

(b) On the next rung are generalized gradient approximations (*GGAs*), which are formulas that use both the density and its gradient at each point. With this added information (and the cost of computing it), these are typically more accurate than LDA. Most importantly, they greatly reduce the bond dissociation energy error, and generally improve transition-state barriers. But, unlike LDA, there is no single universal form. Popular GGAs include PBE[14] and BLYP.[15,16]

(c) Next come *meta-GGAs*, which additionally depend on the Kohn-Sham kinetic energy density. Examples include TPSS.[17]

(d) We next encounter *hybrid* functionals, which mix some exact exchange with a GGA. The most popular functional in use today, B3LYP, is of this type. By mixing in only a fraction of exact exchange (about 20%), one can mimic effects of static correlation, and produce a highly accurate functional. This is more costly to compute because exact exchange is non-local, depending not only on the electron density but also on the density matrix, so additional approximations such as RI-J (see section 3) cannot be exploited as efficiently. The goal of meta-GGAs is to perform almost as well as hybrids, without this cost.

(e) *Fully nonlocal functionals*: The previous rung requires input of the occupied KS orbitals, but fifth-rung functionals include unoccupied orbitals too. They are generally very expensive, but recent progress has been made (see section 5).

2.3 Functional flavors

Functionals come in different flavors: Non-empirical, a little empirical, and over-empirical. At each rung on the ladder, each of these types have been developed, leading to different functionals being favored by different communities.

(a) *Non-empirical functionals*: These include LDA, PBE, TPSS, and TPSSh, use only general rules of quantum mechanics and special limiting conditions to determine the parameters in a general form. These are not fit to any molecular properties. Such approximate functionals satisfy as many exact conditions as possible, including some well outside the region thought to be important for chemistry. All parameters are chosen based on inferences from other theoretical methods, or to maintain a simple shape for easier adaption to numerical methods. An invisible bias toward empirical data still exists, as any derived functionals that are inaccurate will be ignored. Successful functionals usually have errors that are quite systematic, e.g., LDA always overbinds. They can be considered controlled extrapolations away from known systems, and so their reliability for new systems and properties can often be predicted, or at least understood.

(b) *A few empirical parameters*: The second, including B88,[15] LYP,[16] and B3LYP,[18,19] use a few empirical parameters which have been fit by experts. This empiricism is totally different from that of semi-empirical methods as, once the functional is written down, it is universally applicable to all systems, i. e., there are no parameters fit to properties of the system being calculated. This can often speed up functional construction, and will reduce errors on systems similar to those which were used in the fitting. These errors, while smaller in magnitude, will typically be unsystematic. Such functionals represent an interpolation among known data points, and so can be less reliable when applied under new conditions.

(c) *Overfit functionals*: The third is where too many parameters are fit, and these are to be avoided always. Of course, we ignore the question, "How many is too many?".

There are two general implications about these flavors:

(a) *Good non-empirical functionals are widely applicable.*

At any given level (or rung), the approximation should be designed to be as general as possible. LDA has been shown to be a universal limit of *all* systems, including atoms and molecules.[20] The most universal GGA is PBE,[14] and is applied to both molecules and solids, including metals. It is neither the most accurate GGA for small organic molecules[21] nor the best for lattice parameters of bulk solids.[22] But the importance of being universal is that, once a functional works for a given property/system, it is inevitably then applied more generally. For example, organic reactions on metal surfaces are widely studied, and PBE (or some variant) is then needed to treat the bulk metal correctly.

(b) *Good empirical functionals are often more accurate*, at least for properties and systems that they've been designed for. Thus BLYP has smaller errors for main-group organic molecule energetics than PBE, and B3LYP has smaller errors still. But LYP does badly for the correlation energy of metals, and this failure is inherited by B3LYP.

3 Hard realities of computation

3.1 More approximations

In any practical DFT calculation, the XC functional is only one of several approximations used to model the system at hand. Most DFT calculations are performed with finite basis sets and discrete integration grids for numerical evaluation of XC contributions. For bulk solids, almost all calculations use plane waves for the basis. Moreover, additional approximations are often employed to reduce the computational cost of DFT calculations. We mention in particular the resolution-of-the-identity approximation for the Coulomb part (RI-J), also called the density-fitting approximation, which amounts to an expansion of the electron density into an auxiliary basis set. All these additional approximations affect the accuracy of the theoretical predictions and their respective uncertainties should be taken into account when interpreting the computational results. A reliable DFT calculation should be characterized by the following relation:

Error (functional) > Error (basis set) > Error (RI-J), Error(grid).

Two further common approximations must be mentioned. Most DFT studies are performed on condensed-phase systems making inclusion of solvation or environment effects particularly important, as these strongly influence structures and energetics of chemical systems. Powerful strategies to include solvation or environment effects in DFT calculations are quantum mechan-

Table 1: Overview of selected popular XC functionals. X is the exchange functional, C the correlation functional.

Functional	Authors	Ref.
Local Density Approximation (LDA) (I)		
SVWN[1]	X: Slater	[23]
	C: Vosko, Wilk, Nusair	[24]
PW[1]	Perdew, Wang	[25]
Generalized Gradient Approximation (GGA) (II)		
BP86	X: Becke	[15]
	C: Perdew	[26]
BLYP	X: Becke	[15]
	C: Lee, Yang, Parr	[16]
PW91	Perdew, Wang	[27,28]
PBE	Perdew, Burke, Ernzerhof	[14]
PBEsol	Perdew, Ruzsinszky *et al.*	[22]
RPBE	Hammer, Hansen, Nørskov	[29]
SOGGA	Zhao, Truhlar	[30]
Meta-Generalized Gradient Approximation (meta-GGA) (III)		
TPSS	Tao, Perdew, Staroverov, Scuseria	[17]
Hybrid Functionals (IV)		
B3LYP	Becke	[18,19]
PBE0	Perdew, Ernzerhof, Burke	[31]
HSE	Heyd, Scuseria, Ernzerhof	[32]
B97	Becke	[33]
TPSSh	Staroverov, Scuseria, Tao, Perdew	[34,35]
Fully nonlocal functionals (V)		
RPA	Bohm, Pines	[36]
B2PLYP	Grimme	[37]

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[a] Both SVWN and PW are different parameterizations for the exchange-correlation energy of uniform electron gas and give almost identical results.

ics/molecular mechanics (QM/MM) coupling schemes, which are subject of ia606, and continuum solvation models which are reviewed in ia613.

Finally, relativistic corrections are significant for systems with heavy elements, and approaches to include relativistic effects in quantum chemical calculations are described in ia610.

Basis-set requirements of density functional methods have been extensively investigated (see ia611), mostly for GGA and hybrid functionals. The sensitivity of DFT results to the size of the basis set is rather moderate. Atomic-centered basis sets comprising three basis functions per occupied atomic orbital (triple-zeta) and corresponding polarization functions provide structure parameters and reaction energies that are essentially converged with respect to the basis-set size; additional increase of basis sets usually does not lead to systematic improvement. This behavior was observed for Gaussian-type orbitals (GTO) of correlation-consistent hierarchy,[38,39] for segmented GTO basis sets,[40] for polarization-consistent GTO basis sets[41] as well as for Slater-type orbital (STO) basis sets.[42] The smaller double-zeta basis sets, having just two basis functions per occupied atomic orbital, are usually accurate to 1-2 pm in bond lengths and a few degrees in bond angles. Notable exceptions are van der Waals clusters and hydrogen-bonded systems, for which substantial basis-set superposition errors (BSSE) are observed with smaller basis sets.[43–46] BSSE lead in general to substantial overbinding and too-short bond distances in weakly bound systems, masking some deficiencies of present XC functionals in the description of weak interactions.[47] Reaction energies computed with triple zeta basis sets are typically within several kcal/mol from the basis set limit;[48,49] for very accurate calculations, the larger quadruple zeta basis sets may be employed.[39–42] The influence of numerical integration grids on the energies and structure is usually moderate beyond some minimum grid size, see section 7.4 of reference 50 and references therein.

Efficient approximate schemes for the Coulomb contribution to the Kohn–Sham equations are applicable if the XC functional has no orbital-dependent terms (first three rungs, section 2). They take advantage of the fact that the Coulomb term is equivalent to the classical electrostatic interaction of the electron density with itself. The common idea of all these schemes is to expand the electron density into an auxiliary basis while they vary how the expansion coefficients are determined. The earlier density-fitting scheme[51] used the overlap metric to fix the expansion coefficients. The resolution-of-the identity (RI-J) approximation[52,53] employs the Coulomb metric which ensures that the approximate Coulomb energy monotonically converges towards the exact result with increasing auxiliary basis-set size. Optimized auxiliary basis sets are available,[53,54] yielding errors of the RI-J approximation about one order of magnitude smaller than the corresponding basis-set errors.[54]

The accuracy of periodic DFT calculations using plane-wave basis sets[55–57] is controlled by the cut-off value in reciprocal space. An accurate description of the space regions near the nuclei requires rather high cut-off values which significantly increases the computational cost of such all-electron calculations. Replacing the core electrons by appropriately chosen pseudopotentials allows reduction of cut-off values quite significantly without affecting structures and energies.[55,58–60] A reliable periodic DFT calculation should consequently have

Error (functional) > Error (pseudopotential), Error (cut-off).

3.2 Refining expectations

Unlike good experimental data, theoretical results do not come with associated error bars. Assessing the methodical error inherent in approximate DFT is usually done *a posteriori* by comparison with accurate experimental values or high-level theoretical results. In this section we summarize DFT benchmark studies on solids, transition metal complexes and organometallics, metal clusters, and inorganic main group compounds. Most of them include statistical evaluations over a range of relatively small systems and reflect the overall performance on the given test set. An overview of some benchmark data for transition metals is given in table 4.1. In addition, it is highly advisable to perform benchmark calculations before tackling the target system. Comparisons to existing experimental or accurate theoretical data help to estimate methodical errors of approximate XC functionals and to determine basis set or ECP requirements, etc. While important for every computational study, calibration is vital for new compounds or unusual bonding types. Comparisons to similar chemical compounds are useful to develop experience on performance of DFT methods and quality of their results. A wealth of case studies may be found in parts II and III of this book.

The present enormous popularity enjoyed by density functional methods is due to a combination of useful accuracy with an enormous applicability range. However, average errors of present-day XC functionals exceed the gold standard of "chemical accuracy" (1 kcal/mol for large molecular thermochemistry test sets such as G3/99[21]) by a factor of 3–7.[34] Errors in reaction energies computed with DFT are typically in the range of 3–5 kcal/mol, which may serve as an estimate for the error bars of modern DFT calculations. Other conservative error estimates are 1 pm for covalent bonding distances and 50–100 cm^{-1} for vibrational frequencies (without scaling). Hence, it is important to define the expectations of a DFT calculation accordingly. The best average accuracy achievable with a given rung of Jacob's ladder is limited by the flexibility of the corresponding functional form. Seeking to obtain accuracy beyond this limit is like trying to wrap a smooth steel sheet around a delicate sculpture – it cannot possibly fit everywhere. Reducing methodical errors for a specific kind of chemical system and properties can lead to larger deviations in other cases. Many empirically fit functionals suffer from this shortcoming, since they are developed to minimize errors on a given training set of molecules and/or solids. For systems and properties outside the training set, errors may be considerable and careful validation of the methodology is indispensable. As a rule, interpolations between similar systems are usually smooth but extrapolations are prone to large and unpredictable deviations.

In contrast, errors of nonempirical functionals usually have a systematic tendency, e. g., bonding distances are usually overestimated and vibrational frequencies are mostly underestimated by PBE. This behavior makes it easier to estimate the target property. Moreover, relative quantities such as energy differences, bond length changes, or frequency shifts can be much more accurate with these functionals. Some semiempirical functionals also have this property, most notably B3LYP, due to extensive error cancellation. The good performance of B3LYP, especially for organic molecules, has been demonstrated in a large number of studies and made it the most-used XC functional of the past decade.[61] However, B3LYP shows larger and

less systematic errors for transition metal compounds, and its accuracy decreases for larger molecules.[62,63]

3.3 Test sets

The reliability of calculated properties clearly depends on how closely the method can match its physical model. Not so obvious is how closely that physical model resembles the experiment, and how large a difference between the two can be tolerated while still giving valuable results. To isolate the merits of one functional over another, test systems need to minimize complications (e.g. solvent, anharmonicity, thermal, and relativistic effects) that are generally handled with additional levels of modeling. For this reason, test calculations for molecules are generally gas phase, at 0 K, and with an appropriately large basis set. Corresponding experimental datasets should then also be from the gas phase, but adjusted (if possible) to represent 0 K, ground-state values. For (periodic) solids, the condensed phase is inherent to the model, but both thermal expansion and lattice defects must be addressed.

For small organic and main group molecules, several experimental datasets exist[21] that contain various gas phase heats of formation, bond energies, structures, and reaction barrier heights. larger molecules, and those containing transition metals, are severely underrepresented due to the difficulty of creating the vapor phase, and the extremely limited selection of analytical techniques (gas-phase electron diffraction, microwave, infrared, and photoelectron spectroscopy).

Table 2: Comparison of XC functionals for transition metal compounds. Dissociation energies from reference 64. Bond lengths from reference 65.

Method	AE, kcal/mol		Bond lengths, pm	
	ME	MAE	ME	MAE
LDA	29.4	29.4	-2.63	2.96
BLYP			3.11	3.44
BP86	8.9	10.3	0.98	2.11
PBE	10.3	10.8	0.73	2.00
B3LYP	-6.6	12.0	1.17	2.15
PBE0			-1.05	1.81
TPSS	7.8	10.2	0.77	1.91
TPSSh	1.3	9.7	0.04	1.69

4 Which system do I have?

As explained above, many functionals have been fit for specific systems, or kinds of systems, so it is important to know which features are relevant to the system one is treating.

4.1 Transition Metal Complexes and Organometallics

Applications of density functional methods to transition metal complexes and organometallic compounds have been growing over the last two decades. A number of review articles have appeared on the topic.[4,5,7,9,11,50,69–72] In this section we focus on recent benchmark studies comparing the accuracy of different XC functionals for thermochemistry, molecular structures, and reaction barriers. Systematic studies are performed on relatively small isolated molecules and ions for which accurate gas phase

Table 3: Bond dissociation energies in kcal/mol of metal carbonyls $M(CO)_6$, M = Cr, Mo, W.[66] TZVPP basis sets[40] were used along with Stuttgart-Cologne effective core potentials[67] for Mo and W. Zero-point energy corrections were computed with PBE0 functional and TZVPP basis sets. Experimental dissociation energies from reference 68.

Method	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$
LDA	57.1	51.6	56.2
BLYP	34.4	33.8	38.2
BP86	40.6	38.5	43.1
PBE	42.6	39.9	44.6
B3LYP	34.1	34.3	39.1
PBE0	40.7	39.1	44.2
TPSS	41.3	39.9	44.8
TPSSh	40.5	39.5	44.5
Exp.	36.8±2	40.5±2	46.0±2

data exist. Even though most inorganic compounds of actual interest are larger and more complex than the test set examples, they represent many important bonding situations and provide guidance for real-world applications.

Most thermochemical comparisons include atomization energies and bond dissociation energies; results of a recent study including 18 dissociation energies of 3d transition metal compounds are shown in table 4.1.[64] Other studies[73,74] reached similar conclusions. LDA was shown to be least accurate, showing the typical overbinding tendency. GGAs correctly lower the dissociation energies and reduce the overbinding errors to 5–10 kcal/mol. Within the second rung, the performance of BP86 and PBE functionals is very similar, while BLYP typically yields lower dissociation energies.[73] The meta-GGA functional TPSS improves slightly upon GGA functionals, further reducing the overbinding tendency whereas the spread of the errors is essentially unchanged. Inclusion of exact exchange in hybrid functionals has the effect of weakening the bonds and usually improves agreement with experiment. Dissociation energies of small molecules are typically accurate to 3–5 kcal/mol with hybrid functionals. The TPPSh functional is closest to experiment in this study.

It should be noted, however, that atomization energies are rarely used as such in DFT applications. More relevant for chemistry are reaction energies and relative stabilities, which are more accurate due to error cancellation. The largest errors of semilocal functionals are typically in atoms, and atomization energies fully include these errors while reaction energies and energy differences are affected much less. If only the dissociation energies of table 4.1 that involve no free atoms are considered,

mean absolute errors of GGA and meta-GGA functionals are reduced to typically 3–5 kcal/mol.[64] Errors of hybrid functionals are somewhat larger for this test set, but are usually also in the range of 3–5 kcal/mol.[5,71]

A large amount of thermochemical data has been compiled for ligand dissociation reactions. We cite studies on carbonyl complexes,[68,75] substituted carbonyl complexes,[6,76,77] polynuclear clusters,[78] metal hydrides and small organometallic compounds.[5,79,80] As an example we consider the first ligand dissociation energies of homologous metal hexacarbonyls $M(CO)_6$, M = Cr, Mo, W, which are well characterized experimentally in the gas phase.[68] The first ligand dissociation energies describe the reaction $M(CO)_6 \rightarrow M(CO)_5 + CO$ and are shown in table 4.1. LDA again strongly overestimates the bond energies. The results of GGA, meta-GGA, and hybrid functionals agree to within 2 kcal/mol among each other; deviations from experiment are less than 4 kcal/mol for $Cr(CO)_6$ and less than 2 kcal/mol for $M(CO)_6$, M = Mo, W. A striking exception is the BLYP functional which underestimates the binding energy by 2–5 kcal/mol and passes on the underbinding to B3LYP.

Errors of approximate functionals may be offset by neglect of relativistic effects which are particularly significant in heavy elements. Relativistic corrections increase bond strengths by about 10 kcal/mol in 5d transition metal compounds, while the stabilization is only about 1 kcal/mol in 4d transition metals and almost negligible for 3d transition metals.[9] Neglect of relativistic effects in 5d compounds artificially weakens the bonds and partially cancels the overestimation typical to LDA and to a smaller amount to GGA functionals. Indeed, a non-relativistic calculation predicts $W(CO)_6$ to be more weakly bound than

$Cr(CO)_6$.[75] A significant part of relativistic stabilization is due to scalar relativistic effects, which can be captured by using relativistic effective core potentials (ECPs) at little additional computational cost.[6] An extensive discussion of relativistic effects may be found in ia610.

Critical tests for DFT methods are energy differences between states of different spin. Ground state configurations of transition metal atoms,[64,81] spin-state splittings in mononuclear transition metal complexes,[82,83] and exchange couplings in binuclear complexes[84,85] are very sensitive to the choice of the XC functional. Functionals that do not include exact exchange significantly stabilize low-spin states, while the Hartree–Fock (HF) method and hybrid functionals favor high-spin states. Moreover, it has been shown that the energy difference between the high-spin state and the low-spin state increases linearly with the amount of exact exchange in many mononuclear[82,86] and binuclear[84] transition metal complexes. The optimal range of mixing coefficients was determined as 10–15 % exact exchange.[86]

A series of recent studies provides an extensive assessment of molecular structures of 3d, 4d, and 5d transition metal complexes.[65,87,88] LDA underestimates bond lengths by as much as 3 pm. The GGA functionals BP86 and PBE give very similar results, which are within 1 pm of experimental data, while BLYP predicts bonds to be significantly too long and offers no improvement over LDA. For coordinatively bound ligands such as NH_3 or halides, larger deviations up to 3–5 pm have been found with GGA functionals.[11] The meta-GGA functional TPSS performs quite similarly to PBE. Hybrid functionals predict bonds to be slightly too long, but are generally in very good agreement with experiment. The choice between GGA/meta-GGA functionals and hybrid functionals depends on the row of the transition metal. Complexes of 3d elements are better described by GGA/meta-GGA functionals[87] while hybrid functionals yielded somewhat smaller deviations from the experiment for 4d and 5d element compounds.[65,88] Particular care must be taken if the computed bond lengths are compared to experimental x-ray data. The deviations between the gas-phase structures and crystal structures are usually moderate for neutral molecules and singly-charged ions. In contrast, for multiply charged ions, the presence of counterions and crystal packing effects shrink the bond lengths by as much as 2–10 pm and should be taken into account by including the counterions or by using continuum solvation models.

The accuracy of DFT predictions of reaction energy barriers[69,70,89] has been assessed in a number of benchmark studies, mostly using organic reactions as test examples.[90–94] The general observation is that LDA systematically underestimates activation energies of bimolecular reactions by as much as 10–20 kcal/mol. In contrast, barrier heights of unimolecular processes such as conformational changes or electrocyclic reactions are much better reproduced by LDA. The underestimation of activation energies by LDA may be understood in terms of differential XC effects which favor the delocalized transition state structures relative to the more compact electron density distributions of the reactants. This effect is large for associative bimolecular reactions or bond dissociations but plays a minor role for torsional barriers.[95] In most applications, however, LDA is deemed not accurate enough for activation energies. GGA and meta-GGA functionals improve upon LDA for reaction barriers, reducing the absolute errors to 5–10 kcal/mol.

While they still systematically underestimate activation energies, GGA and meta-GGA functionals usually yield transition-state structures in good agreement with accurate post-HF correlation methods.[91,93]

The preference of LDA for higher-coordinated, more delocalized transition state structures (which is inherited by GGA and meta-GGA functionals) is attributed to spurious self-interaction. This explanation is corroborated by the much improved accuracy of self-interaction corrected (SIC) XC functionals.[96] Inclusion of exact exchange in the hybrid functionals partially ameliorates the self-interaction problem and leads to useful estimates of activation energies, which are accurate to ca. 5 kcal/mol. It was argued in several studies, that increasing the amount of the exact exchange to 40–50 % significantly improves the agreement with experimental activation barriers. Besides the BHLYP functional of Becke[97] a series of "special purpose" functionals was developed for chemical kinetics calculations.[98,99] We note, however, that these functionals, while in general increasing and thus improving reaction barrier heights[98–101] perform rather poorly for minimum structures and energetics.[37,101] Exchange-correlation functionals with a high percentage of exact exchange are particularly problematic for transition metal compounds[87,102] and yield unreliable spin state splittings.[82]

4.2 Metal and Semiconductor Clusters

Inorganic clusters vary in their metallic content, from molecules with a noticeable abundance of metal atoms, to small chunks of an extended solid, perhaps with an organic ligand coating. No well-defined test sets exist, and what data are available tends to be strongly affected by real experimental conditions. One

would expect that the recommendations for molecular coordination and organometallic compounds of the previous section should be an excellent starting point for clusters. A major caveat is that cluster cores tend to behave like the solids from which they are derived (often the whole point of synthesizing the cluster), and so, if metallic, functionals that are incorrect for the uniform gas will fail badly here (see next section).

DFT calculations on large clusters are still highly demanding, and it is not unexpected that systematic comparisons of the application of various functionals are rare. One such study[103] invokes very high symmetry to enable efficient computation of phosphorus and arsenic allotropes based on $(X_2X_8)_n$ and $(X_2X_{10})_n$ polymeric structure types. As there was no reliable experimental data for these clusters, spin-component-scaled MP2 (SCS-MP2)[104] energies at B3LYP geometries were chosen as a reference. It was found that standard MP2 overestimated the stability of P_{120} by 16.5 kJ/mol per P_4 equivalent (495 kJ/mol total error), and As_{120} by 18.8 kJ/mol per As_4. B3LYP, on the other hand underestimates their stabilities by 32.2 kJ/mol (per P_4) and 45.7 kJ/mol (per As_4). BP86 does surprisingly well with underestimations of 16.0 kJ/mol (P_4) and 33.7 kJ/mol (As_4). These errors are attributed to an overcorrection (MP2) or neglect (B3LYP, BP86) of dispersion. B3LYP-D (empirical dispersion terms added to B3LYP) has roughly the same error magnitude as B3LYP, but on the other side of SCS-MP2.

Another paper[105] critically evaluated the use of B3LYP for MnO clusters related to the oxygen-evolving complex in photosystem II (see ia192). They determined that the B3LYP optimized geometries of model compounds could faithfully reproduce the X-ray crystal structures of those same models. Calculations of simplified (ligand-truncated) structures deviated more significantly, but the Mn_xO_y cores were still within a few pm in bond distance and a few degrees in bond angles. More importantly, the high-spin low-spin splitting was completely incorrect. This particular hybrid functional severely overstabilizes the high-spin state.

4.3 Extended Solids

The natural choice of basis functions for (non-hybrid) DFT calculations on periodic systems are periodic plane waves. This basis can be systematically improved by adding functions with ever shorter wavelengths (thus higher energy), up to a cutoff energy. Compared to Gaussian- or Slater-type basis functions, integral evaluation is extremely quick. However, this is balanced by the relatively huge number of plane waves needed to reach the same level of energy accuracy. The large number of basis functions also makes the Hartree-Fock exact exchange calculations needed for hybrid functionals extremely costly. Switching to the standard AO-based basis sets normally used for molecules is possible, but they tend to have diffuse tails that are inappropriate for solids and must be truncated and re-optimized.

In a test of 8 simple, main-group solids,[30,106] LSDA overestimated cohesive energies by 0.7 eV/atom on average, PBE was almost exact (-0.04 eV/atom), while the solids-oriented PBEsol[22] and SOGGA[30] overestimated by 0.26 and 0.30 eV/atom, respectively. The TPSS meta-GGA brought the overestimation down to 0.17 eV/atom. The direct calculation of cohesive energies involves the energy difference between the energy of the solid and the energy of its free constituent atoms, two extremes of chemistry that limited functional forms simply cannot model well simultaneously. Far more important and useful are relative energies of solid phases, which are more closely related to lattice constants (see below), where functionals with diminished gradient dependence (PBEsol and SOGGA) should do much better.

Hybrid functionals including LYP correlation tend to perform worse than non-hybrid GGAs due to LYP's failure to handle the uniform electron gas limit, which is most relevant for metals and small-gap semiconductors. For main-group metals, hybrids tend to fail, and for transition metals, fail miserably. This is where recovering the uniform gas limit becomes important.

Most structural test sets used to compare functionals are heavily biased toward simple crystals with few structural parameters not fixed by space group, and most of those are cubic or tetragonal. Still, as many properties of the solid are sensitive to lattice constants (e.g. bulk moduli and magnetic coupling), getting them right is critical. A set of 18 such solids (4 main group metals, 4 transition metals, 5 semiconductors, and 5 ionic solids), with lattice constants from 3.451 to 5.646 Å, has been used to evaluate several non-empirical functionals.[22,30,106] LSDA consistently underestimates the lattice constant, on average by about 1%, while GGA PBE and meta-GGA TPSS overestimate by about the same amount. The reformulation of PBE for solids, PBEsol,[22] halves the error of TPSS and shifts the error distribution for metals close to 0 (as likely to underestimate as to overestimate), but still consistently overestimates the size of the unit cell for semiconductors and ionic solids. SOGGA, a more elaborate derivative of PBE containing bits of RPBE[29] and PBEsol that also is directed at solids, shifts the error distribution of all but transition metals (which it generally underestimates) close to zero, with a similar absolute error to PBEsol. Bulk moduli are about 15% too large for LSDA, half that (and too small) for anything else.

Lattice constants in the more extensive SC/40 test set for semiconductors are best matched with hybrid functionals. The LSDA, PBE, TPSS, and HSE average errors are (respectively) -4.6, 7.6, 6.3, and 3.5 pm. Although it was not tested with this particular set, PBEsol should reduce the overestimation of unit cell size of PBE, but will almost certainly have the same severe underestimation of the band gap.

Perhaps the most useful property of an insulating solid to predict is its fundamental gap. This is $I - A$, the difference between ionization energy and electron affinity for a macroscopic chunk of that solid. This gap would be given exactly by adding and removing an electron from such a chunk, if we had the *exact* XC functional. On the other hand, the Kohn–Sham band gap, defined as the HOMO–LUMO difference, is *not* equal to the fundamental band gap, even with the *exact* XC.[107] While the HOMO energy computed with the exact XC functional is equal to the negative ionization potential I, the LUMO energy is not equal to the electron affinity A, even when the exact functional is used. In general the Kohn–Sham band gap is smaller than the fundamental gap and, in an extreme case (Mott insulator), can vanish, while correlation effects still make the solid an insulator.

Semi-local functionals suffer from self-interaction, and over delocalize electrons. In these approximations, $I - A$ collapses to the KS band gap as the cluster size grows. The most notorious case is the indirect band gap of Si, which LDA underestimates by about 50%. Inclusion of some fraction of exact exchange would help localize the electrons in the cluster calculation, slightly improving $I - A$, but not by much.

However, many hybrid functionals give better estimates for $I - A$. This is because the Hartree–Fock (HF) gap is typically much *larger* than $I - A$. (The HF gap is *not* a KS gap). By mixing a small fraction of HF exchange with a semilocal approximation, one gets a hybrid gap that is about right. Unfortunately, it is not even remotely clear that there is an optimal fraction to add. It is tempting to adjust the hybrid fraction to get the right band gap, but this risks destroying the accurate description of the rest of the system. Until functionals with the ability to dynamically (and rationally!) adapt the fraction of HF to local conditions are available[108] it is better to use a non-hybrid functional with good solids performance (PBE → PBE0, TPSS → TPSSh), accepting that the gap is too low. Another alternative is to use a functional specifically designed to be computationally efficient with periodic systems, such as HSE,[32,109] a derivative of PBE with only short-range HF exchange.

In reference 110, an extensive selection of 40 main group semiconductors (SC/40) was evaluated with LSDA, PBE, TPSS, and HSE. As expected, the non-hybrids underestimated the band gap on average by 1.14, 1.13, and 0.98 eV respectively, whereas the hybrid HSE was too low by only 0.17 eV. The experimental gaps of InAs (0.41 eV) and InSb (0.23 eV) were very well reproduced by the hybrid (0.39 and 0.29 eV), but disappeared with the other functionals.

The general recommendations given above may work fine for high-symmetry crystals with one or two atoms per unit cell, but what about non-cubic systems with larger unit cells? One particularly difficult example is CeO_2 and Ce_2O_3.[111] The fluorite-structure CeO_2 is an insulator with a band gap measured at 6.0 eV. LSDA and PBE underestimate by around 0.4 eV, while

PBE0 and HSE overestimate this gap by a surprising amount (gaps of 7.93 eV and 6.96 eV respectively). For cell volume, the hybrids underestimate by only 1.1%, while LSDA is too small by 2.2% and PBE too large by 3.3%.

Ce_2O_3 is much more complex due to the additional electron per cerium atom placed in the 4f electron band in the middle of the 6 eV gap. In the real system, these electrons are anti-ferromagnetically coupled, and the band gap is 2.4 eV. The hybrids get the gap about right (PBE0: 3.5 eV; HSE: 2.5 eV) and correctly predict the anti-ferromagnetic coupling to be more stable (by 6 and 5 meV). LSDA and PBE incorrectly predict Ce_2O_3 to be a metal or semi-metal and stabilize ferromagnetic coupling by 60 and 110 meV respectively. Geometrically, the hybrids give a unit cell volume for this cerium oxide also 1% too small, but LSDA and PBE shrink significantly to 8.9% and 2.7% too small. The free parameters for Ce and O positions are also noticeably closer to experiment in the hybrids than PBE, and LSDA is significantly off. Thus, for Ce_2O_3, hybrid functionals correct qualitative errors of GGAs.

5 Various directions in DFT development

There are always many different and new ideas being proposed and tested in DFT development, and it is impossible to report them all. Here we provide a sampling of some of those relevant to inorganic and bioinorganic chemistry.

5.1 Semi-local functionals

Universal GGAs such as PBE work for a wide range of systems, but their accuracy is limited. There is a growing awareness

that this limitation may be caused by the restrictive functional form of GGAs.[112] One approach is to devise GGAs that are specialized for certain classes of compounds. The recently proposed PBEsol GGA[22] is an example of this strategy: PBEsol recovers the original gradient expansion for exchange, and its correlation piece is adjusted to reproduce jellium surface energies accurately.[113] Due to its diminished gradient dependence, PBEsol is biased towards solids and yields better lattice constants and other equilibrium properties of densely packed solids than PBE.[114] However, PBEsol is generally less accurate for molecular bond energies, although molecular bond distances are comparable to PBE.[30] The best of both worlds requires a more flexible functional form and can only be achieved at the meta-GGA level. For example, the TPSS meta-GGA combines accurate molecular properties and good surface energies.[106,115]

Certain chemical applications benefit from the diminished gradient dependence of PBEsol. For example, energy differences between sterically crowded and linear alkanes and other stereo-electronic effects are improved by PBEsol.[116] A striking example from inorganic chemistry is the 2D-3D transition in gold cluster anions Au_n^-.[117] This phase transition, which occurs at an unusually large number of $n = 12$ gold atoms, plays a crucial role for the catalytic activity of small gold clusters. PBEsol, TPSS, and, maybe surprisingly, LSDA correctly predict the transition to occur at $n = 12$, while most GGAs and hybrid functionals fail.[118] This suggests that a diminished gradient dependence and accurate jellium surface energies are important for dimensionality transitions in finite molecular clusters. However, all attempts to improve accuracy by applying different functionals to different situations[119] eventually fail, because such schemes cannot handle more general systems that include both situations (see section 4).

5.2 Self-interaction correction

It has long been known that spurious Coulomb interaction of an electron with its own charge distribution severely limits the accuracy of molecular properties computed using semi-local functionals.[120] While the notion of self-interaction depends on the basis of molecular orbitals used and is therefore not unique, necessary conditions for self-interaction freedom of XC functionals may be found. A simple condition is one-electron self-interaction freedom, which states that, for a one-electron system, exchange should completely cancel the Coulomb energy and correlation should vanish, because there is no electron interaction in this case.[13] Recently, "many-electron self-interaction freedom" has been associated with linearity of the ground-state energy as a function of the electron number N for non-integer N.[121] This condition is strongly violated by semi-local functionals, which is related to the well-known failure of these functionals to describe one- and three-electron bonds,[122] localization vs. delocalization,[64,123] e.g. in mixed-valence compounds, and charge transfer complexes. Yang et al. have proposed a functional that is more many-electron self-interaction free and improves upon most of these shortcomings, but is heavily parameterized.[124] The use of exact exchange is another way to remove most many-electron self-interaction error, but popular hybrids include only a fraction of exact exchange.

Charge transfer is a fundamental process for the conversion of electrical, mechanical, or light energy into chemical energy and vice versa. Unfortunately, most conventional density functionals are troubled by self-interaction error when applied to these problems. Van Voorhis and co-workers have developed a simple and useful solution to this problem by constraining charges to certain parts of a molecule.[125–127] This constraint leads to an extra "constraint potential" which is added to the external potential of the nuclei and enforces the proper charge distribution. But at present it is unclear how to merge this method with standard DFT calculations in an ab initio fashion.

5.3 Hybrid Functionals

Recently, a number of range-separated hybrid functionals have been proposed. These functionals separate the electron Coulomb interaction into a short- and a long-range part by a switching function, usually an error function.[128,129] After that, different approximations are used for different interaction ranges. At short range, most functionals contain a high fraction of GGA exchange, while at long range, a high fraction of exact exchange is typical.[130–132] In contrast, the screened exchange HSE hybrid uses an inverse range separation.[32] Post-HF correlation methods such as configuration interaction (CI)[129,133] and coupled cluster (CC)[134,135] have also been proposed for the long-range part. The underlying hypothesis of range-separated hybrids is that semi-local functionals work best at short electron separations. Indeed, range-separated hybrids improve over global hybrids in certain properties, e.g. for long-range charge transfer excitation energies.[136,137] Fine-tuning is possible by multiple range separation.[138,139] However, the range separation procedure introduces at least one additional empirical parameter that may not be system-independent.

Another related class of functionals are local hybrids.[140–143]

These "hyper-GGAs" use a hybrid mixing coefficient that depends on local ingredients such as the density and its gradients and multiplies the exchange energy density. While this additional freedom seems appealing, the proper behavior of these functionals in various regions of space is difficult to control.[108,144] At the same time, local hybrids are computationally even more demanding than global hybrids because they require evaluation of the exact exchange energy density on the molecular grid.

A new global hybrid of the empirical kind is Grimme's Becke three-parameter hybrid with second order perturbation correction (B2PLYP).[37] This functional is a re-parameterized B3LYP hybrid mixed with MP2 correlation. B2PLYP seems to improve upon both B3LYP and MP2, especially for organic main-group chemistry,[145,146] and has successfully been applied to a number of molecular properties.[147,148] Unfortunately, B2PLYP is not the method of choice for small-gap problems such as many transition metal compounds, metal clusters, and radicals. The MP2 correlation part has a much steeper formal N^5 scaling of computational cost with the system size than GGA correlation functionals, although this is significantly alleviated by approximations such as RI-MP2.[149]

5.4 Dispersion Effects

Long-range dispersion effects are notoriously difficult to capture with semi-local functionals. Due to their dependence on the *local* density at a given point in space $\mathbf{r}$ and other local ingredients, these functionals cannot account for XC effects due to the presence of electrons in remote parts of a molecule. Ad hoc attempts have been made to correct this by adding a van der Waals attraction between the nuclei to the nuclear potential energy, in the spirit of classical force fields.[150–154] Just like force fields, these methods can give accurate results for a restricted class of compounds, but their successful use generally requires extensive calibration and expert knowledge.

Becke and Johnson recently presented a semi-classical argument to derive dispersion coefficients from the exchange-hole dipole moment.[46,155] They integrated their model into a new general purpose functional called DF07 that includes dynamical, non-dynamical, and dispersion interactions.[156] DF07 contains 100% of exact exchange and is remarkably accurate for a wide range of energetic and kinetic data of main-group compounds with relatively few empirical parameters.[157]

A fully non-local non-empirical dispersion correction to GGAs was proposed by Langreth, Lundqvist, and co-workers in 2004.[158,159] This functional explicitly depends on the densities and their gradients at all pairs of coordinates $(\mathbf{r}, \mathbf{r}')$ and exhibits qualitatively correct behavior for non-overlapping subsystems. Promising results for a number of van-der-Waals complexes have been reported.[160] Open questions include sensitivity of the results to the choice of short-range GGA, and ways to reduce the cost of the required six-dimensional numerical quadrature.[161]

5.5 Random-Phase Approximation (RPA)

A systematic way to go beyond semi-local approximations is to construct functionals that treat a part of the electron correlation exactly for all systems. The random-phase approximation (RPA)[36] arises as a natural starting point for this class of functionals.[162] It relies on the zero-temperature fluctuation-dissipation theorem and the KS version was first proposed by Langreth and Perdew in 1975.[163,164] Unlike perturbation theory, RPA works for small-gap systems including the uniform electron gas, and it is most accurate in the high-density or weak correlation limit, where most semi-local functionals exhibit large errors. RPA is compatible with exact exchange and thus does not require the error compensation between semilocal exchange and correlation that affects molecular properties in many GGA calculations. It includes dispersion interactions in a seamless fashion, i. e., there are no empirical damping or other parameters. While bare RPA yields little improvement over GGA bond energies, it is an excellent starting point for refined functionals that model beyond-RPA correlation, which is typically an order of magnitude smaller than the full correlation energy.[165] Perdew, Dobson and co-workers recently presented inhomogeneous Singwi-Tosi-Land-Sjölander (ISTLS) functionals representing a local-field correction to RPA.[166]

The relatively high computational cost of RPA was previously considered a central limitation for applications to chemistry.[167] However, very recently, new methods have become available that substantially reduce the computational complexity of RPA, making it comparable in cost to MP2.[168] Also, it has been recognized that RPA is equivalent to a simplified coupled cluster doubles method, making RPA calculations with coupled cluster codes straightforward.[169]

6 Concluding Remarks

DFT is certainly no mythical "black box" that can be mindlessly applied to current problems of interest in inorganic and bioinorganic chemistry, and practical considerations always limit choices. Clearly, there is no single answer to the title question.

At any given time, and for any given property and system, there is at most a "best" answer. Experience and benchmarking are always needed to find that best answer. We hope we have given the reader some help in answering the title question.

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