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Challenges for Density Functional Theory

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1. INTRODUCTION

Density functional theory (DFT) of electronic structure has made an unparalleled impact on the application of quantum mechanics to interesting and challenging problems in chemistry. As evidenced by some recent reviews,[1−11] the number of applications is growing rapidly by the year and some of the latest and most significant studies

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include the following: the understanding and design of catalytic processes in enzymes and zeolites, electron transport, solar energy harvesting and conversion, drug design in medicine, as well as many other problems in science and technology.

The story behind the success of DFT is the search for the exchange−correlation functional that uses the electron density to describe the intricate many-body effects within a single particle formalism. Despite the application and success of DFT in many branches of science and engineering, in this review we want to focus on understanding current and future challenges for DFT. If the exchange-correlation functional that is used was exact, then DFT would correctly describe the quantum nature of matter. Indeed, it is the approximate nature of the exchange−correlation functional that is the reason both for the success and the failure of DFT applications. Early developments of DFT focused on the most basic challenges in chemistry, in particular, the ability to have functionals that could give a reasonable description of both the geometries and dissociation energies of molecules. The next major challenge for DFT arose from the need to accurately predict reaction barrier heights in order to determine the kinetics of chemical reactions as well as to describe van der Waals interactions. Whether DFT can predict the small energy differences associated with van der Waals interactions or if additional corrections or nonlocal functionals of the density are needed has been the subject of much debate and current research. This interaction, although one of the weakest, is key to the accurate understanding of the biological processes involved in many drug−protein and protein−protein interactions.

All these challenges have been well-addressed by current developments, as described in the literature. However, it is our contention that there are even more significant challenges that DFT, and specifically the exchange−correlation functional, must overcome in order to fulfill its full promise. New and deeper theoretical insights are needed to aid the development of new functionals. These are essential for the future development of DFT. One way to facilitate this advance, as we will try to illustrate in this review, is to understand more deeply those situations where DFT exhibits important failures.

An intriguing aspect of DFT is that even the simplest systems can show intricacies and challenges reflecting those of much larger and complex systems. One example of this is the understanding encompassed in the widely used term, "strong correlation" found in the physics literature. Strong correlation is meant to refer to the breakdown of the single-particle picture, perhaps even of DFT itself, which is based on a determinant of single-particle Kohn−Sham orbitals. However, it is essential to see it only as a breakdown of the currently used density functional approximations. Strongly correlated systems offer significant new challenges for the functional. In this review we hope to demonstrate that the challenge of strong correlation for density functionals can be illustrated by the behavior of the energy of a single hydrogen atom. This understanding will help to realize the enormous potential of DFT.

The Schrödinger equation that describes the quantum nature of matter is

$$\hat{H}\Psi = E\Psi \tag{1}$$

where the Hamiltonian, $\hat{H}$, for a Coulombic system is given by

$$\hat{H} = -\sum_i \frac{1}{2}\nabla_i^2 - \sum_{iA} \frac{Z_A}{|\mathbf{r}_i - \mathbf{r}_A|} + \sum_{i>j} \frac{1}{r_{ij}} \tag{2}$$

with a specified set of nuclei with charges Z_A and positions $\mathbf{r}_A$ and number of electrons N. The task is to simply minimize the energy over all possible antisymmetric wave functions, $\Psi(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\ldots\mathbf{x}_N)$, where $\mathbf{x}_i$ contains the spatial coordinate $\mathbf{r}_i$ and spin coordinate σ_i. This enables us to find the minimizing Ψ and hence the ground state energy, E. However, technically, this is far from trivial, and has been summarized by Paul Dirac in the following quote:

> "The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved."

In DFT, the problem is reformulated in a philosophically and computationally different manner. The basic foundation of DFT is the Hohenberg−Kohn theorem,[12] which states that the external potential is a functional of the ground-state density. In other words, the density (an observable in 3D space) is used to describe the complicated physics behind the interactions between electrons and, therefore, determines everything about the system. As Kohn noted in his Nobel lecture, DFT "has been most useful for systems of very many electrons where wave function methods encounter and are stopped by the exponential wall".[13] In Kohn−Sham (KS) theory,[14] this is formulated as a simple expression for the ground state energy

$$E[\rho] = T_s[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \tag{3}$$

where the forms of some of the functionals are explicitly known. The kinetic energy for the KS noninteracting reference system is

$$T_s[\rho] = \sum_i \langle\phi_i| -\frac{1}{2}\nabla^2|\phi_i\rangle \tag{4}$$

in terms of $\{\phi_i\}$, the set of one electron KS orbitals. The electron density of the KS reference system is given by

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \tag{5}$$

The other two known energy components are the nucleus electron potential energy, expressed in terms of the external potential due to the nuclei, $v(\mathbf{r}) = -\Sigma_A(Z_A/|\mathbf{r} - \mathbf{R}_A|)$

$$V_{ne}[\rho] = \int \rho(\mathbf{r})\, v(\mathbf{r})\, d\mathbf{r}$$

and the classical electron−electron repulsion energy is

$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}'$$

Much is known about the key remaining term, the exchange−correlation functional, $E_{xc}[\rho]$, although no explicit form is available. It can be expressed in the constrained search formulation for density functionals[15]

$$\begin{aligned} E_{xc}[\rho] &= \min_{\Psi \to \rho} \langle\Psi|T + V_{ee}|\Psi\rangle - T_s[\rho] - J[\rho] \\ &= (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) \end{aligned}$$

It can also be expressed elegantly through the adiabatic connection[16,17]

$$E_{xc}[\rho] = \int_0^1 \langle\Psi_\lambda|V_{ee}|\Psi_\lambda\rangle\, d\lambda - J[\rho]$$

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Many density functional approximations (DFA) have been developed for practical applications. DFT applications have increased enormously in many areas of chemistry due to the excellent performance of these approximate functionals. However, it is important for DFT to fully connect to its roots as an exact theory rather than rest on its laurels as the "best semi-empirical" method, where the parameters are so successful because they are not system dependent. The approach is computationally very different from the direct solution of the Schrödinger equation, where the time is spent in a search over the whole of Hilbert space to find the wave function. In DFT, with a given form for E_{xc}, the search is only to find the three-dimensional density, which is a comparatively trivial problem.

In this review, we consider some of the challenges arising in the construction of approximations to the exact exchange−correlation functional. Despite the considerable success of currently used approximate functionals, there have also been a number of significant failures. We will focus on both of these aspects, but our primary emphasis will be on the failures. Before we begin the main body of the review, we also want to highlight some of the underlying themes that run throughout and also the important relationship between chemistry itself and DFT. To address the "challenges for DFT", one might expect us to list the chemically important molecules that DFT finds challenging. However, we do not do this; instead, we try to place DFT and more specifically the exchange−correlation functional, E_{xc}, at the forefront. It is in fact the challenges of the functional that we will attempt to understand. Despite the excellent progress to date in the field of chemistry, our knowledge of how to actually build a functional might still be quite limited. We know, in principle, we should be able to make a functional that works for the whole of chemistry, solid-state physics, and biology. But in practical applications, there are many failures. These are not breakdowns of the theory itself, but rather are only deficiencies of the currently used approximate exchange−correlation functionals. This can be most clearly seen in the two simplest molecules in the whole of the chemical universe, namely, stretched H_2^+ and stretched H_2. Even for these, all existing functionals fail. From this failure alone, it seems clear that more in-depth thinking, at quite a fundamental level, needs to be done on the nature of the functionals that we are trying to develop. It is here that chemistry can help us to understand the nature of the problem that we face. We attempt to use the challenges of simple molecules and simple questions about chemistry to probe the problems of the functional. Also, perhaps more importantly, any understanding gained will be useful in interpreting calculations and possible errors caused by the use of approximate functionals in cases of more complex chemistry. Understanding at the level of the functional is, of course, easier in principle than in practice. But this is the theme that we try to use throughout the review: a drive to simplify and to understand.

1.1. What Are the Challenges for Density Functional Theory?

In this section, we summarize some of the challenges that DFT faces. These range in nature from some that appear to have been already "solved", to others that are active current areas of research. In addition, there are even more that are less understood but are key to the continued development and the future use of DFT.

1.1.1. Challenge 1: To Develop a Functional That Performs Uniformly Better Than B3LYP. One of the main challenges for DFT is to keep as its cornerstone some element of simplicity. If DFT functionals become as complicated as full configuration interaction (FCI) then the theory begins to lose one of its main features, namely, its simplicity. This is especially true of its computational nature. However, this simplicity must not come at too great a cost, nor must it become an entirely empirical method either. The beauty and challenge of density functional theory as well as approximations to it, namely, DFA, is that they lie somewhere in between. To appreciate the current challenges for DFT, it is helpful to place them in an historical context. One of the first great challenges for DFT in chemistry was to provide an accurate description of geometries and binding energies of simple molecules. DFT was widely used in the solid-state physics community for many years before it was adopted by the computational chemistry community. This is largely due to the fact that the simplest functional, the local density approximation (LDA), did not perform well in many areas of chemistry. Although LDA gives good geometries, it massively overbinds molecules. The seminal work of Becke, Perdew, Langreth, and Parr in the 1980s, which introduced the first derivative of the density in the form of the generalized gradient approximation (GGA), was the first step enabling chemists to use DFT satisfactorily. The next major advance came with the inclusion of a fraction of Hartree−Fock exact exchange (HF) in the functional, as described by Becke in the early 1990s. This work lead to the development of B3LYP,[18,19] the most widely used of all the functionals. B3LYP has enjoyed a remarkable performance over a wide range of systems. Although new ideas have been introduced into more recent functionals of different complexity, B3LYP is still the most popular. Developing functionals that improve upon B3LYP will clearly provide a significant advance for DFT.

1.1.2. Challenge 2: The Need To Improve the Description of Reaction Barriers and Dispersion/van der Waals Interactions. However, in order to achieve a more complete description of chemistry, it is necessary to extend beyond a molecule at its equilibrium geometry and to also describe weakly interacting molecules as well as transition states in chemical reactions. The description of reaction barriers is problematic for LDA/GGA type functionals, because they systematically underestimate transition state barriers by several kilocalories/mole. This systematic error requires correction before the functionals can be used to describe potential energy surfaces. However, there are also some very important chemical processes that, although much smaller in the energetic scale, may be much more important for large systems. One of these is the weak but very important van der Waals force or London dispersion force, which has long been known to be a problem for approximate functionals. It is of key importance for the description of interactions between closed-shell species. The basic understanding of this problem can be seen from simple perturbation theory arguments dating back to London.[20] These stated that there should be an attractive part of the energy that asymptotically decays as $1/R^6$ when the distance between the interacting units increases ($R \rightarrow \infty$). Due to the local nature of the LDA or GGA functional form, it is not possible for these functionals to have this behavior. Nonlocal functionals involving Hartree−Fock are also completely wrong, since they all exhibit long-range repulsive behavior. The performance of most popular functionals on simple weakly bound dimers is extremely poor. The correct and efficient description of the van der Waals attraction, covalent bonding in chemistry and transition states all remain a challenge. This is especially true with the increasing application of DFT to areas of

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biological importance where all these interactions can occur simultaneously.

1.1.3. Challenge 3: To Understand the Significance of $E[\rho]$ vs $E[\{\phi_i,\epsilon_i\}]$, OEP, and Beyond. Both of the challenges described above are clearly to do with density functional approximations. This undoubtedly is the most important aspect of DFT and why it is such a widely used tool. However, in order to develop and understand new and better functionals, it is important not to forget the connection to the exact solution of the Schrödinger equation, namely, the exact exchange−correlation functional. Sometimes when attention is focused on a particular aspect of DFT, such as improved predictions of molecular energies, better properties of solid-state matter, or the fundamental aspects of the mathematical form of the exchange−correlation functional, this facet may easily stand out as the most important one while others are forgotten. However, DFT needs to be viewed in all possible ways. Currently, there are important challenges in understanding exactly how most widely used approximations fit in with some known properties of the exact functional. Some model systems, such as the uniform-electron gas or the slowly varying electron gas, the scaling relations, or systems with different electron−electron interactions, have all provided exact conditions, which have proved extremely useful in guiding the current development of functionals. At the very basis of the all the approximations used lies the important concept of noninteracting electrons, i.e., the reference system of Kohn and Sham as described by sets of orbitals $\{\phi_i\}$ and eigenvalues $\{\epsilon_i\}$. It is a basic challenge to understand the meaning, if any, of this reference system for chemistry. Alternatively, it may be considered merely as a pure mathematical construct to which one should not attach any other meaning than the density and its corresponding total energy. It is important to understand, after a DFT calculation is performed, if it is meaningful to look at anything else other than total energy, i.e., if the orbitals and eigenvalues have any further significance. It may be useful in this respect to invoke potential functional theory (PFT),[21] an alternative view of DFT that uses the potential, instead of the electron density, as the basic variable. The energy minimization can be carried out by minimizing the energy with respect to the potential. This provides the basis for the optimized effective potential method (OEP) and the understanding of orbital energies, which are functionals of the potential.

1.1.4. Challenge 4: Delocalization Error and Static Correlation Error. This brings us to another very interesting question raised by the performance of DFT, as highlighted by large errors for one-electron systems. Any system with a single electron is trivial and can be solved simply using the wave function. However, DFT does not treat individual electrons in the same way, but rather only considers their total density, ρ. So one-electron systems play no special role in DFT; in fact, a single electron can unphysically interact with itself, as has been known for a long time in terms of self-interaction error.[22] Of course the exact functional does not have any self-interaction; i.e., the exchange energy exactly cancels the Coulomb energy for one electron. This and similar errors are at the heart of many failures with the currently used approximations. We believe that for DFT to move forward into the future it is essential to see not just its good performances but also to seek out and understand its practical and theoretical inconsistencies. If we look back at some previous challenges, it is clear that significant effort has been made to improve performance on sets of many molecules as well as to understand and to implement the OEP equations. However, despite these efforts, most modern functionals can still have errors of 100 kcal/mol in extremely simple systems. These can be connected to systematic errors such as delocalization error and static correlation error in more complex systems. These simple systems must not be ignored, as they contain the key to a better understanding of the functional that will lead to improvements throughout chemistry.

1.1.5. Challenge 5: The Energy of Two Protons Separated by Infinity with One and Two Electrons: Strong Correlation. The challenge of strongly correlated systems is a very important frontier for DFT. To fully understand the importance of these systems, they must be looked at within the wider realm of electronic structure methods. Except for FCI and Valence Bond Theory,[23] most theories currently struggle to describe strongly correlated systems. This is evident from some very simple tests involving infinitely separated protons with varying numbers of electrons. Currently, all functionals fail even for the simplest of these, infinitely stretched H_2^+ and infinitely stretched H_2. Although these systems may seem trivial, they are, in our opinion, one of the great challenges for modern electronic structure theory. The integer nature of electrons is of great importance and it is key to understand this behavior for DFT. In order to satisfy exact fundamental conditions and not to suffer from systematic errors, the energy functionals must have the correct discontinuous behavior at integer numbers of electrons. This discontinuous behavior is key to give the energy gap and correctly describe strong correlation and, from our perspective, should never be ignored in the development of new theories.

2. THE ENTRANCE OF DFT INTO CHEMISTRY

From its earliest beginnings in the time of Thomas[24] and Fermi[25] to Slater,[26] the history of DFT has a checkered past. These were all based upon approximations and were not expected to give highly accurate results. However, this fundamentally changed upon the formulation of the Hohenberg−Kohn theorem, which showed that an exact quantum mechanical result could be obtained from a functional of the density. This was quickly followed by the Kohn−Sham (KS) equations, which offered a more constructive yet still exact formulation based on noninteracting electrons, thereby linking DFT to the familiar language and concepts of orbitals in chemistry. The Kohn−Sham paper clearly formulated the challenge being one requiring the construction of the exchange−correlation functional. Furthermore, the seminal paper suggested a simple path to begin tackling the problem, using the local density approximation. This idea quickly caught on as the basis of much of solid-state physics. It took time for the chemistry community to take notice, even though these ideas had been preceded in chemistry in the form of Slater's $X\alpha$ theory.

2.1. Exchange−Correlation Functionals

In this section, it is our aim is to provide a rough historical picture of the development of exchange−correlation functionals and their application in chemistry. We will therefore outline some of the key advances that have led to modern DFT in an attempt to formulate a framework, which can help us to gain insight into both the foundations and limitations of the theory.

2.1.1. LDA. Dating back to Dirac in 1930, the form of exchange for the uniform electron gas was known to be[27]

$$E_x^{\mathrm{LDA}}[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho^{4/3}\,\mathrm{d}\mathbf{r} \qquad (6)$$

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The functional for correlation was not derived from first principles, instead Monte Carlo simulations of the uniform gas[28] were used to parametrize interpolations between the known forms in the high- and low-density limits. There exist widely used LDA correlation functionals developed by Voskoet al.[29] and Perdew[30]

2.1.2. GGA. The uniform electron gas, although a beautiful model system that has played a key role in the development of functionals, has an incredibly different density to those found in atomic or molecular systems. It is interesting to note Bright-Wilson's "proof/conjecture"[31] proclaimed upon hearing the presentation of the Hohenberg−Kohn theorem, which can be summarized as: "I understand that the density tells you everything; the cusps of the density tell you where the nuclei are, the gradient of the density at the nucleus tells you what the nucleus is, and the integral of the density tells you how many electrons you have—therefore you have specified everything about your system and Hamiltonian and hence all is known." It should be noted that the Hohenberg−Kohn proof is more general, as it applies to any external potential not just the potential of nuclei (Coulombic systems). However, this offered an insight of great importance for chemistry: that knowledge of the gradient of the density, $\nabla\rho$, is needed at the most fundamental level. Nevertheless, there has been some confusion as to how to move on from the uniform electron gas, where analytic expansions[32] can give the exact coefficients that should apply to each term in a gradient expansion. The gradient expansion for the slowly varying uniform electron gas is carried out in terms of the dimensionless reduced gradient $x = |\nabla\rho|/\rho^{4/3}$ [or similarly $2(3\pi^2)^{1/3}s = x$] and has the form

$$E_x^{GEA} = -\int \rho^{4/3}\left[\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} + \frac{7}{432\pi(3\pi^2)^{1/3}}x^2 + \ldots\right] d\mathbf{r} \quad (7)$$

However, this idea gives rise to major problems when applied directly to atoms and molecules, because their densities are anything but slowly varying. This is not due to the nuclei, where x is well-defined, but rather to the atomic tails, as for any exponentially decaying density $x \rightarrow \infty$. Functionals that are useful for chemistry took a while to be developed, due in part to this problem. This is a useful illustration of one of the main challenges of this field, namely, the juxtaposition of three areas: mathematical derivation, challenges in chemistry (for this problem $x \rightarrow \infty$), and the different challenges in solid state physics, where x never diverges. Here the solution was the development of the generalized gradient approximation (GGA), which, for exchange, takes the simple form:

$$E_x^{GGA}[\rho, x] = \int \rho^{4/3}F(x)\, d\mathbf{r} \quad (8)$$

where $F(x)$ can be chosen to obey the gradient expansion (eq 7) in the low x limit. There are now many exchange functionals of the GGA type and the two most commonly used are B88[33]

$$E_x^{B88} = -\sum_{\sigma=\alpha,\beta}\int \rho_\sigma{}^{4/3}\left[\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3} + \frac{\beta x_\sigma{}^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma}\right] d\mathbf{r} \quad (9)$$

and PBE[34]

$$E_x^{PBE} = -\int \rho^{4/3}\left[\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} + \frac{\mu s^2}{1 + \mu s^2/\kappa}\right] d\mathbf{r} \quad (10)$$

As with LDA, the development of functionals for correlation has been more complex and taken longer to develop. Even the coordinate scaling relations for correlation[35,36] are much trickier and have not been widely used. Currently, there are two main functionals that are well-established, LYP[19] and PBE.[34] Many other GGA functionals have been developed and described in the literature.[19,33,34,37−51]

2.1.3. Meta-GGA. In chemistry, the move from LDA to GGA brought about a massive improvement in functionals, of roughly an order of magnitude in binding energies. The next obvious step was to include higher-order derivatives of the density. This, however, did not provide the expected major advances in functional development. The term meta-GGA was coined by Perdew and Schmidt, when they proposed the famous Jacob's ladder of approximations[52] to the exact exchange−correlation functional. This is a ladder of functionals that progresses from the Hartree world, with no exchange−correlation, toward the "heaven" of chemical accuracy (within 1 kcal/mol for energetics). The ladder starts with the first rung as the LDA, the next rung GGA, and the third rung meta-GGA, which incorporates other local ingredients of the form $E_{xc}^{MGGA} = \int \rho^{4/3}F(\rho(\mathbf{r}),\nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}),\tau(\mathbf{r})\ldots)\, d\mathbf{r}$, including the kinetic energy density, $\tau = (1/2)\Sigma_i|\nabla\phi_i|^2$. This is followed by the fourth rung with nonlocal functionals of the occupied orbitals such as functionals that contain some Hartree−Fock exchange type terms (hyper-GGA) and the fifth rung that uses all the orbitals (both occupied and virtual) and their corresponding eigenvalues such as RPA (random phase approximation) and MP2 (second order many-body perturbation theory). The original proposition of a ladder is that each rung satisfies certain exact constraints and when a form for a certain rung on the ladder is given, the step up to the next rung should have functionals based on the previous rungs (to ensure satisfaction of the constraints). It is also hoped that each step up the ladder (maybe because it satisfies more exact constraints) should improve the performance and each level gets closer to the heaven of chemical accuracy. This concept in functional development has stimulated and inspired many ideas, even if they do not exactly stick to the full philosophy of the rungs as originally proposed. After that historical digression, we now return to the meta-GGA. At this level, we have functionals including the kinetic energy density, τ (sometimes defined without the factor of 1/2). There have been several functionals using τ, especially correlation functionals that use the fact that for one-orbital systems $\tau_\sigma = (\nabla\rho_\sigma)^2/8\rho_\sigma$ to eliminate $\sigma-\sigma$ correlation in one-orbital systems or regions. Functionals at this level originated with ideas from Becke such as B88C[53] or B95[54] or Becke−Roussel.[55] More recently, functionals have been derived by Perdew and coauthors,[56−59] including TPSS.[60] Several other meta-GGA functionals with somewhat different ideas have also been developed.[61−66]

2.1.4. Hybrid Functionals. Probably the last clear advance in the development of exchange−correlation funtionals came in 1993, with the inclusion of some Hartree−Fock exchange (HF) into the functional.

$$E_x^{HF} = -\frac{1}{2}\sum_{ij\sigma}\int\int \frac{\phi^*_{i\sigma}(\mathbf{r})\,\phi_{j\sigma}(\mathbf{r})\,\phi^*_{j\sigma}(\mathbf{r}')\,\phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}' \quad (11)$$

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The original idea came from Axel Becke, who used the adiabatic connection to argue that the functional should contain some E_x^{HF} and proposed a linear model that mixes it with some local DFA exchange and correlation type functionals.

$$E_{xc}^{BHH} = \frac{1}{2}E_x^{HF} + \frac{1}{2}W_1^{LDA} \tag{12}$$

This gave rise to functionals, such as BHLYP,[67] which did not perform uniformly better than GGA functionals. However, the next step that quickly followed was to introduce a little bit of experimental data to refine the idea,[18] giving rise to

$$E_{xc}^{B3} = aE_x^{HF} + (1-a)E_x^{LDA} + b\Delta E_x^{B88} + cE_c^{GGA} + (1-c)E_c^{LDA} \tag{13}$$

where the parameters a, b, and c were fitted to a set of experimental data, the G1 data set of Pople and co-workers. This was implemented into the Gaussian package[68] by

$$E_{xc}^{B3LYP} = 0.2E_x^{HF} + 0.8E_x^{LDA} + 0.72\Delta E_x^{B88} + 0.81E_c^{LYP} + 0.19E_c^{VWN} \tag{14}$$

using the LYP functional and also VWN [with some confusion over which parametrization (III or V) to use]. This functional has been incredibly successful and extremely widely used, to the extent that in many circles the term DFT is almost synonymous with running a B3LYP calculation. B3LYP has possibly outperformed all expectations, which is excellent for the field of chemistry as it has enabled numerous supporting and illuminating calculations to be carried out. However, B3LYP is successful as a result of some cancellation of errors, which creates a tremendous challenge for the development of new and better exchange−correlation functionals. There are also a large variety of other hybrid functionals found in the literature:[60,63,66,69−80]

2.1.5. Recent Developments in Functionals. We shall now elaborate some of the recent developments in functionals that have begun to make a significant impact in the field:

- Range separation: One idea, originally from the groups of Savin[81−83] and Gill,[84,85] has been to separate the electron−electron interaction into two parts, one long-range and the other short-range. A range separation based on the error function is most commonly used because of the simplicity in calculating the integrals in a Gaussian basis set

$$\frac{1}{r_{ij}} \equiv \underbrace{\frac{\mathrm{erf}(\mu r_{ij})}{r_{ij}}}_{\text{long range}} + \underbrace{\frac{\mathrm{erfc}(\mu r_{ij})}{r_{ij}}}_{\text{short range}}$$

and long-range Hartree−Fock is given by

$$E_x^{lr-HF} = -\frac{1}{2}\sum_{ij\sigma}\iint \frac{\phi^*_{i\sigma}(\mathbf{r}_1)\,\phi_{j\sigma}(\mathbf{r}_1)\,\mathrm{erf}(\mu r_{12})\,\phi^*_{j\sigma}(\mathbf{r}_2)\,\phi_{i\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\,d\mathbf{r}_1\,d\mathbf{r}_2 \tag{15}$$

The corresponding form of the long-range LDA exchange energy can be calculated from the explicit form of the LDA exchange-hole, to give[86]

$$E_x^{lr-LDA} = \frac{1}{2}\sum_\sigma \int \rho_\sigma^{4/3} K_\sigma^{LDA}\left(\frac{8}{3}a_\sigma\left[\sqrt{\pi}\,\mathrm{erf}\left(\frac{1}{2a_\sigma}\right) + 2a_\sigma(b_\sigma - c_\sigma)\right]\right)d\mathbf{r} \tag{16}$$

The key is then to treat the long-range part and the short-range part with different functionals. In atomic and molecular systems, the Hartree−Fock potential is correct in the asymptotic limit.[87] So one can mix long-range Hartree−Fock with short-range DFA to give a simple long-range corrected functional of the form

$$E_{xc}^{LC-DFA} = E_x^{DFA} + (E_x^{lr-HF} - E_x^{lr-DFA}) + E_c^{DFA} \tag{17}$$

In a similar but opposite manner, screened functionals utilize short-range HF and long-range DFA and are more widely used in solid-state calculations.[88−91] There are many range separated functionals in the literature,[83,86,89,92−98] and the area continues to gain many followers. Although these functionals may not improve the thermochemistry, they can give interesting improvements for other properties such as excitation energies.[99]

- Fitting: The challenges presented to the exchange−correlation functional by atomic and molecular systems remain largely unknown in their depth and complexity. It is very difficult to determine an accurate form of the exchange−correlation from first principles. A more practical approach is to take available experimental information to help determine and test the functional forms. The easiest way to do this is to apply some form of parametrization of the functional form to chosen sets of experimental data. This has proved very successful in the earliest development of functionals, with the three parameters in B3LYP fitted to the G1 set of experimental data. Becke later extended the idea to 10 parameters in his B97 functional.[69,100] However, for the problem of exchange−correlation, it is not obvious how many parameters are needed.[101] Will many thousands of parameters be required to describe correlation or perhaps none? Currently, the answer to this puzzling question is unknown. Some of the most successful functionals use a high level of parametrization, but this does not always have a good theoretical basis. However, this has led to the development of many interesting functionals, such as B98,[63] VS98,[64] and τ-HCTH.[65] Truhlar's group have combined and extended these ideas with parametrization to a large number of chemically important species to yield some useful functionals. Their performance with respect to many areas of chemistry is a significant improvement over the standard B3LYP functional. The efforts can be best seen in the M06 family of functionals: M06-L, M06, M06-2X, and M06-HF.[66,78,80,102]
- Adiabatic connection functionals: The last major advance in functional development came from the inclusion of a fraction of Hartree−Fock in the hybrid functional form. The argument for this arose from the adiabatic connection.[103] This may be a good indication that a deeper understanding and usage of the adiabatic connection may in fact help to guide other fruitful ideas in functional construction.

$$E_{xc} = \int_0^1 W_\lambda\,d\lambda \tag{18}$$

where $W_\lambda = \langle\Psi_\lambda|V_{ee}|\Psi_\lambda\rangle - J[\rho]$. Functionals can be built using models for the adiabatic connection integrand; the simplest idea coming from Becke[67] was to use a linear model

$$W_\lambda = a + b\lambda \tag{19}$$

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based on the knowledge of the exact W_0 and W_1^{LDA}. There are other ideas that could be used, such as building models using W_0, W_0', W_∞, and W_∞', as carried out by Perdew and co-workers.[104−106] We ourselves have also developed functionals[107] using a form

$$W_\lambda = a + \frac{b\lambda}{(1 + c\lambda)}$$

functionals W_0, W_0', and a chosen point W_{λ_p} from an approximate DFA, to give a highly nonlinear form:

$$E_{\mathrm{xc}}^{\mathrm{MCY}} = W_0 + \frac{W_0'}{\left(\frac{W_{\lambda_p} - \lambda_p W_0' - W_0}{\lambda_p(W_0 - W_{\lambda_p})}\right)} \times \left(1 - \frac{\ln\left(1 + \left(\frac{W_{\lambda_p} - \lambda_p W_0' - W_0}{\lambda_p(W_0 - W_{\lambda_p})}\right)\right)}{\left(\frac{W_{\lambda_p} - \lambda_p W_0' - W_0}{\lambda_p(W_0 - W_{\lambda_p})}\right)}\right) \tag{20}$$

Some interesting investigations of the exact adiabatic connection[108,109] have recently been carried out by Teale et al.[110,111] based on the theoretical formulation of Wu and Yang.[112] There is now renewed interest in the use of the strongly interacting limit, $\lambda \rightarrow \infty$, which can offer a new view on the exchange−correlation problem that may help to give more insight on strongly correlated problems.[113−115]

- Local hybrids: In general, hybrid functionals have been found to be a significant improvement over semilocal GGA type functionals. However, there are some systems where the fraction of Hartree−Fock exchange needs to be quite different. Another way of varying the amount of exact exchange is to use a variable amount at each point in space by defining a local variant of exact exchange (eq 11)

$$e_{\mathrm{x}}^{\sigma,\mathrm{HF}}(\mathbf{r}) = -\frac{1}{2}\sum_{ij}\int \frac{\phi_{i\sigma}^*(\mathbf{r})\,\phi_{j\sigma}(\mathbf{r})\,\phi_{j\sigma}^*(\mathbf{r}')\,\phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{r}' \tag{21}$$

with a local mixing function $a_\sigma(\mathbf{r})$, such that a local functional could be defined akin to B3LYP

$$E_{\mathrm{xc}}^{\mathrm{lH}} = \sum_\sigma \int (a_\sigma(\mathbf{r})\, e_{\mathrm{x}}^{\sigma,\mathrm{HF}}(\mathbf{r}) + (1 - a_\sigma(\mathbf{r}))e_{\mathrm{x}}^{\sigma,\mathrm{LDA}}(\mathbf{r}))\,\mathrm{d}\mathbf{r} + b\Delta E_{\mathrm{x}}^{\mathrm{GGA}} + E_{\mathrm{c}}^{\mathrm{GGA}}$$

This now places the challenge on the mixing function $a(\mathbf{r})$, and obviously if one chooses a constant, then normal hybrid functionals are recovered. Many interesting functionals and ideas have been developed using these ideas.[116−123] It is also possible, however, that there are some problems that still need to be fully overcome relating to a choice of gauge in the development of local hybrid functionals.[124]

- Functionals involving unoccupied orbitals and eigenvalues:[125−128] The fifth rung of Jacob's ladder utilizes the unoccupied orbitals and eigenvalues. The simplest functional of this form is the MP2 functional

$$E_{\mathrm{c}}^{\mathrm{MP2}} = \frac{1}{4}\sum_{ij}^{\mathrm{occ}}\sum_{ab}^{\mathrm{virt}} \frac{\langle ij||ab\rangle^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{22}$$

It should be pointed out that the eigenvalues used play a key role. If the eigenvalues on the bottom are from Hartree−Fock, then this is the MP2 energy expression. However, if the eigenvalues came from the a local potential, then this would be akin to the GL2 second-order correlation energy.[129] These two terms are really very different from each other (sometimes by hundreds of kilocalories/mole in a simple atomization energy). Unlike MP perturbation theory, GL perturbation theory can contain a contribution from single excitations; albeit a relatively minor effect. It has been shown to introduce improvements in some cases.[130] But, for example, in the breakdown of the GL2 for simple systems,[131] it only makes matters worse. There have been some quite successful fitted functionals that mix in a MP2/GL2 like correlation term represented by[126]

$$E_{\mathrm{xc}}^{\mathrm{B2PLYP}} = aE_{\mathrm{x}}^{\mathrm{HF}} + (1 - a)E_{\mathrm{x}}^{\mathrm{GGA}} + bE_{\mathrm{c}}^{\mathrm{GGA}} + (1 - b)E_{\mathrm{c}}^{\mathrm{PT2}}$$

The PT2 term is the MP2 expression, but the eigenvalues on the bottom of eq 22 come from a hybrid functional. Several newly developed functionals of the unoccupied orbitals (from old ideas[38,103,132−134]) use the idea of the fluctuation dissipation theorem[135−141]

$$E_{\mathrm{xc}}^{\mathrm{RPA}} = -\frac{1}{2\pi}\int_0^1\int_0^\infty\int\int \frac{1}{r_{12}}\chi_{\mathrm{xc}}^\lambda(\mathbf{r}_1,\mathbf{r}_2,i\omega)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\omega\,\mathrm{d}\lambda \tag{23}$$

which expresses the ground state correlation energy as an integral over frequency in an excitation energy type manner and leads to the random phase approximation (RPA)

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \tag{24}$$

where $A_{ia,bj} = (\epsilon_i - \epsilon_a)\delta_{ia,bj} + (ia|bj)$ and $B_{ia,jb} = (ia|jb)$. The RPA correlation energy is given by the difference between the many body and single particle excitations

$$E_{\mathrm{c}}^{\mathrm{RPA}} = \sum_{ia}\omega_{ia} - A_{ia,ia}$$

This method is often called direct RPA and there are other similar methods that differ in their choice of orbitals and eigenvalues such as full RPA (or RPAX or RPAE). There are also ideas connecting RPA to coupled cluster formulation, which can aid in understanding some of the successes and deficiencies of the method.[142] Other developments combine RPA with range-separation[143,144] or extended formalisms, such as second-order screened exchange, SOSEX.[141,145]

We have hopefully given the reader an overview of some of the major advances in functional development over the past few years. At the moment, it is not fully clear to us where exactly the future directions of functionals will be focused: Will it be along

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the directions outlined by the past development of functionals? Will they include range-separation or screening or fluctuation−dissipation arguments or hybrid functionals global or local? Will exact constraints or fitting be the path to future developments? Of course, the most likely answer is that a knowledge of all of these possible directions is important to help decide the best path forward, and clearly, it is important that no pathway is left unexplored in the quest for improved functionals. This is often done on philosophical grounds either with fitting parameters or introduction of exact exchange or, more recently, involving functionals of the unoccupied orbitals. For example, the introduction of unoccupied orbitals is often felt to lie outside of DFT. This is especially true in terms of practical calculations, where it reintroduces the basis set problem of quantum chemistry. For example, for the He atom, a HF or a normal DFT calculation with GGA or hybrid functional needs only *s* basis functions, whereas the complete description of the wave function needs all the higher angular momentum functions *p*, *d*, *f*, *g*, *h*, *i*.... However, there has been much recent progress in F12 methods that possibly means there are paths that simplify this problem both computationally and conceptually.

2.2. Performance with Respect to Chemistry

It is the major, all encompassing, challenge of DFT to construct a functional, $E_{xc}[\rho]$, that works for all densities ρ. In order to investigate this, a wide range of chemical systems are used to see how the approximate functional performs. For example, if we consider the atomization energy of water, the performance comes down to the subtle energy differences that are contained in $E_{xc}[\rho_{H_2O}]$ compared with $2E_{xc}[\rho_H]$ and $E_{xc}[\rho_O]$. In this review, we comment on some of the many published works that have tested functionals and use several well-known chemical data sets to illustrate the performances of many different functionals. To accomplish this, we evaluated all functionals using the same geometries and basis sets but also the same densities, ρ_{B3LYP}. Unless otherwise stated, we have performed B3LYP calculations with a large basis set (def2-qzvpp[146]). The energy differences are not computed from self-consistent densities. The key point is that this effect is really quite minor and much less than the errors between functionals. It should also be noted that the differences between $T_s[\{\phi_i^{B3LYP}\}]$ and the Kohn−Sham $T_s[\rho_{B3LYP}]$ are very small and the B3LYP orbitals are used to evaluate T_s. However, we wish to reemphasize the overriding main challenge for DFT always lies in E_{xc} rather than the secondary effects, which are seen in the relatively simple search for ρ. In this context, the assumption is that ρ_{B3LYP} is a good density and then the challenge is evaluating the functional for it. The currently used approximations define a small part of functional space that is easy to investigate with a fixed density. To exemplify this, consider a self-consistent B3LYP calculation for a particular molecule. The converged B3LYP energy is calculated from the sum of T_s, J, V_{ne}, V_{nn}, $0.2E_x^{HF}$, $0.8E_x^{LDA}$, $0.72\Delta E_x^{B88}$, $0.81E_c^{LYP}$ and $0.19E_c^{VWN}$. From these components, we can also construct the total energy from many other functionals, such as LDA, BVWN, BLYP, HFLYP, and BHLYP. If we also calculate other information such as $E_x^{PBE}[\rho_{B3LYP}]$ and $E_c^{PBE}[\rho_{B3LYP}]$, we can then evaluate even more functionals, such as PBE, PBE0, and BPBE. The calculation of a few more integrals with the B3LYP density matrix (including range-separated HF for several different range parameters, μ) allows the investigation of a large number of the functionals that are currently used in the literature. This is done without the intensive computation that is required in running self-consistent calculations for each functional, but more importantly, it helps to isolate the challenge of the energy of the exchange−correlation functional itself. The span of functionals that we calculate is somewhat representative of currently used functionals, but unfortunately is only a minuscule fraction of the full $\mathscr{R}^{\mathscr{R}^3}$ size of functional space.

2.2.1. Thermochemical Data Sets. In recent years, the development of functionals in chemistry has taken a useful and pragmatic approach. Approximate functionals have been tested over a wide variety of systems to indicate whether or not the functional will work well for the given type of problem. One of the initial challenges is to find high-quality experimental data with which to compare theoretical results. This approach was first used by Pople and collaborators, who developed the G*n* (n = 1, 2, 3...) wave function-based methods.[147,148] To aid the development of these model chemistries, they used sets of high-quality experimental data where the heats of formation were known to values better than 1 kcal/mol. This work started in the 1990s with the G1 and G2 sets[149] of mainly small molecules and has subsequently been extended to include larger molecules (generally organic). In the G3/99 set,[150] there are 222 heats of formation, 88 ionization energies, 58 electron affinities, and eight proton affinities. This set has played an important role in the early examination of functionals, both to fit the parameters of the functional and also to test the functionals. Other authors have also made extended databases of experimental data from Boese and Handy[46,47] and Truhlar's group.[66,151−155] Zhao and Truhlar also made smaller subsets that have representative errors of a much larger set (e.g., AE6 and BH6). Grimme also looked at making sets beyond those of normal chemistry, including arbitrarily generated molecules, where high-level quantum chemistry should work well enough to benchmark the performance of DFT functionals.[156,157]

2.2.2. Geometries. The prediction of geometries in DFT has been one of its great successes. This started out with LDA, which although it does not have a good energetic performance, it does give a very reasonable performance for geometries. In fact, in many cases the geometry with LDA is better than with GGA functionals, even though GGA functionals can give roughly an order of magnitude improvement in heats of formation. Hybrid functionals also have a very good performance for many geometric quantities, such that some high level quantum mechanical model methods (e.g., Gaussian-4 theory[158]) choose to use optimized geometries from DFT. There are several sets of accurately known geometries. In this work, we consider the T-96 set of Scuseria and co-workers,[159] which is of covalently bonded diatomic molecules and also some simple polyatomic molecules that due to symmetry have only one degree of freedom (e.g., CO_2, BCl_3, SF_6). Usually, in order to optimize the geometry one would carry out self-consistent calculations and evaluate the force using derivative theory.[160] However, we want to illustrate again that the challenge is not in the self-consistency or even the derivatives of the functional, but is encapsulated in the energy functional itself. Therefore, for all these molecules we use a def2-qzvpp basis set and calculate B3LYP densities for several geometries along the 1-D coordinate around the experimental geometry. For each of these densities, we then evaluate the energy of all the different functionals. The minimum energy geometry is determined for each energy functional. We are not suggesting that this is a general procedure. But in these cases, it worked extremely well in order to reproduce the fully self-consistent optimized geometries for each functional. This is hopefully a useful illustration of where the challenges for the functional lie, the main challenge being the energy functional form itself.

2.2.3. Kinetics and Reaction Barriers. Approximate functionals generally perform relatively well for atomization energies

Table 1. Performance, in Terms of Mean Absolute Errors (MAE) of a Wide Range of Functionals on Thermochemistry (G3 set[150]), Barriers (HTBH42[161] and NHTB38[151]), Geometries (T96[159]), Hydrogen Bonding[152] and Polarizabilities[178] all Evaluated Post-B3LYP and Post-PBE (see the text)

	post-B3LYP					post-PBE				
functional	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)	G3 (kcal/mol)	barriers- (kcal/mol)	T96 (a_0)	H bond- (kcal/mol)	α_{iso} (au)
LDA	72.24	14.36	0.0107	3.02	0.78	73.08	14.95	0.0114	3.19	0.83
GGA and Meta-GGA Functionals										
BLYP	6.64	7.37	0.0205	1.46	0.79	6.77	7.58	0.0216	1.49	0.83
HCTH	5.59	4.15	0.0119	2.22	0.48	5.51	4.31	0.0126	2.25	0.44
HCTH407	5.72	4.69	0.0107	1.05	0.50	6.20	4.84	0.0115	1.10	0.48
PBE	15.99	8.29	0.0148	1.24	0.63	16.22	8.58	0.0157	1.32	0.66
BP86	15.71	8.49	0.0158	1.39	0.66	16.11	8.76	0.0169	1.43	0.67
BPBE	7.55	6.81	0.0155	1.67	0.53	7.81	7.08	0.0167	1.71	0.51
OLYP	5.22	5.36	0.0142	2.21	0.53	5.39	5.51	0.0152	2.24	0.53
OPBE	8.86	5.21	0.0121	2.55	0.31	9.48	5.38	0.0132	2.59	0.30
TPSS	7.85	8.03	0.0123	1.16	0.44	8.04	8.01	0.0131	1.20	0.43
M06-L	5.87	3.82	0.0056	0.58	0.40	7.67	3.72	0.0060	0.60	0.33
Hybrid Functionals										
TPSSh	6.03	6.45	0.0082	0.98	0.30	6.05	6.19	0.0090	0.97	0.27
B3LYP	4.28	4.50	0.0097	1.01	0.37	4.38	4.22	0.0106	0.98	0.36
PBE0	6.37	4.11	0.0089	0.76	0.21	6.23	3.76	0.0096	0.71	0.19
B97−1	3.90	3.88	0.0093	0.75	0.28	3.85	3.61	0.0100	0.67	0.26
B97−2	4.31	2.79	0.0087	0.97	0.19	4.49	2.58	0.0093	1.07	0.19
B97−3	3.70	2.22	0.0087	0.92	0.26	3.96	2.00	0.0095	1.07	0.24
M06	4.78	2.03	0.0088	0.47	0.39	5.48	1.79	0.0093	0.48	0.33
M06-2X	3.34	1.37	0.0110	0.34	0.35	3.67	1.59	0.0123	0.60	0.34
M06-HF	6.26	3.14	0.0167	0.88	0.73	8.13	4.23	0.0185	1.57	0.74
HF	132.38	15.12	0.0277	3.15	1.01	134.36	17.78	0.0307	4.11	1.03
HFLYP	35.39	9.18	0.0423	1.13	1.36	37.38	11.52	0.0444	1.87	1.55
Range-Separated Functionals										
CAMB3LYP	4.04	2.51	0.0119	0.69	0.23	4.22	2.40	0.0132	0.88	0.22
LCBLYP	16.91	3.73	0.0169	0.90	0.31	16.40	3.44	0.0182	0.90	0.31
rCAMB3LYP	5.50	2.76	0.0225	0.78	0.37	6.04	3.57	0.0240	1.20	0.42
LC-PBE	16.69	3.07	0.0245	0.75	0.53	16.34	3.50	0.0271	1.16	0.62
HSE	4.37	3.43	0.0082	0.77	0.21	4.50	3.09	0.0093	0.77	0.19

but poorly for reaction barrier heights. This is true even for the simplest chemical reaction H + H_2 → H_2 + H, for which both experimental data and high-level calculations give a barrier of about 9.6 kcal/mol. However, functionals such as LDA and GGA can underestimate this barrier by 4−8 kcal/mol, a large systematic error. Hartree−Fock, on the other hand, overestimates the reaction barrier by around 10 kcal/mol. This illustrates a potential advantage of hybrid functionals, which mix together parts (and also errors) from GGA with HF and give improved results. However, despite this initial promise, hybrid functionals still underestimate the H + H_2 reaction barrier by around 3 kcal/mol. In terms of reaction rates, these functionals are all disastrous. Excellent work from Truhlar's group has investigated and addressed the problem of reaction barriers with some earlier functionals such as MPW1K (where the K stands for kinetics).[71] These tend to have a larger percent of exact exchange (around 50%). More recent work reported some important sets of hydrogen transfer barrier heights, HTBH42,[161] and non-hydrogen transfer barrier heights, NHTB38.[151] Truhlar also presented some functionals with an all around good performance, where the forms were optimized to give both thermochemistry and kinetics.[162]

2.2.4. Hydrogen Bonding. Hydrogen bonds are of the order 1−10 kcal/mol. They are much weaker than normal covalent and ionic bonds yet are still much stronger that the weak dispersion and van der Waals interactions found between nonpolar closed shell fragments (discussed later). The case of hydrogen bonds, where there is reasonable overlap of electron density as well as some electrostatic interactions between the fragments, has been a difficult challenge for functionals.[152] A wide difference between functionals that perform similarly on thermochemistry and geometries exists.

2.2.5. Other Sets. There are many other sets in the literature that offer a different challenge to functionals such as those for inorganic chemistry and transition metals. For the main periodic group and organic chemistry, there seems to be an improvement in going from semilocal functionals GGA to meta-GGA to hybrid functionals. With the inclusion of barriers, there is a definite push to increase the amount of Hartree−Fock exchange. For large parts of inorganic chemistry and some of the energy differences

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in transition-metal chemistry, it seems that the trend is reversed and functionals with smaller amounts of exchange perform better.[155,163−165]

2.2.6. Response Properties. The calculation of how a small perturbation can affect the ground-state energy allows one to calculate many very important properties with the use of linear response theory. For example, the dipole polarizability is given by the second derivative of the energy with respect to an electric field F_x, $\alpha_{xx} = \partial^2 E/\partial F_x^2$. Again, the performance of DFT has been evaluated for several standard sets related to response properties. The polarizability illustrates one of the basic problems of functionals: GGAs tend to overestimate the polarizability of standard small molecules, and this is improved by hybrid functionals, where generally a good performance is achieved. The overestimation observed with small molecules can be emphasized by examining the performance for chains or polymers of increasing length. This has been seen in one of the simplest possible chains $(H_2)_n$,[166−169] where the longitudinal polarizability becomes increasingly overestimated with LDA/GGA functionals and is largely corrected by HF and some hybrid functionals. Similar effects are also seen in long-distance charge-transfer excitations,[170−172] where the long-range error of LDA/GGA is seen with an incorrect missing $1/R$ behavior of the excitation energy. In all cases, LDA/GGA perform the worst, whereas hybrids, especially the newer range-separated hybrids, perform much better. There are other response properties where the opposite trend is seen. For example, in magnetic properties, such as NMR shielding constants,[173−177] the inclusion of exchange in hybrid functionals makes the performance worse. The exact nature of this reason is encapsulated in the type of response these energy expressions have to a magnetic field, where the Hartree−Fock expression has possibly a much too exaggerated response.

As an illustration of some of these properties, we have included the performance of functionals for the dipole polarizability calculated by finite difference using the B3LYP density (Table 1). Even in this derivative property, the density and self-consistency are very minor issues compared to the mathematical form of the energy functional.

2.2.7. Performance of Density Functional Approximations. The results in Table 1 demonstrate the performance for a wide range of properties of several illustrative functionals. LDA does not perform very well for many of the energetic differences that are important in chemistry, though it does surprisingly well for the geometries. At the GGA/meta-GGA level there is a marked improvement over LDA in terms of energetics, showing the importance of gradient corrections for many chemistry applications. Similarly to LDA, GGA/meta-GGA functionals tend to underestimate reaction barriers and overestimate polarizabilities. For most of the GGA/meta-GGA functionals, the geometries are actually worse than LDA with one notable exception to this being the M06-L functional. For the smaller energy differences seen in the hydrogen bonding and weak interaction set, there is quite a wide variance among the different GGAs and meta-GGAs. The inclusion of Hartree−Fock exchange in hybrid and range-separated functionals allows a much better description of a large part of the chemistry encapsulated in these assessments. This is particularly evident for the more recent functionals, such as M06-2X, which exhibit an excellent all around performance. Inclusion of some physically and theoretically motivated corrections in functionals, such as rCAMB3LYP and LC-BLYP, seems to come at the cost of a slightly worse description of chemistry in these testing sets, even though they may be important for chemical ideas outside of these. Also in Table 1 we show the performance not just post-B3LYP but also post-PBE ($E^{\mathrm{DFA}}[\rho_{\mathrm{B3LYP}}]$ and $E^{\mathrm{DFA}}[\rho_{\mathrm{PBE}}]$). The similarity between the two is quite striking and helps us to understand the true challenge of building a functional. The key is the energy expression. Other considerations, such as which density is used, are definitely secondary considerations.

2.3. Dispersion and van der Waals Forces

Is DFT capable of giving dispersion forces? The answer from one point of view is, of course, yes. The Hohenberg−Kohn theorems tells us that if we know the correct functional and minimize it we would then obtain the exact ground state energy and density of these systems. So it is not a problem for the exact theory, although it still remains a large challenge for approximate functionals. This is clear, as local and semilocal functionals cannot hope to capture the asymptotic $1/R^6$ behavior[179,180] (one can clearly see that for frozen monomer densities a GGA functional will incorrectly have no dependence on the intermonomer distance, leaving the interaction solely to the Coulomb terms. This does not capture the $1/R^6$ behavior). How this affects molecules where there is substantial overlap of the density is unknown but it is most definitely not a clear point from which to start. There is a clear correlation of the inability to describe van der Waals with the behavior of a GGA exchange functional in the region of small density and large reduced density gradient, x.[181] Possibly the understanding of dispersion needs to be traced to some more basic (or mathematical) flaw of the functional. However, the failure of LDA and GGA to give the correct energy for two fixed densities at long distance has led to some simple corrections.

Before discussing the popular approaches to tackling van der Waals interactions, it is pertinent to illustrate a point that is commonly known but perhaps slightly misinterpreted. On the basis of the Hellmann−Feynman theorem, the origin of the van der Waals long-range attraction can be clearly attributed to the accumulation of electron density between the two closed-shell systems.[180] This then seems to state that the challenge is in the description of the density. However, the challenge for approximate functionals can actually be quite different from that, as illustrated in Figure 1. Here, for Ar_2 around the equilibrium bond distance, we have two approximate functionals with completely different behaviors; PBE massively overbinds and BLYP is purely repulsive. Surely it is to be expected that they should have very different densities if van der Waals is related to the density. What we can see from a deeper consideration of Figure 1 is that this is not due to any difference in the density and is solely a property of the energy functionals themselves.

2.3.1. C_6/R^6 Corrections and Other Simple Corrections. It has been long noted that local density functionals (e.g., LDA or GGA) cannot describe the long-range behavior of the van der Waals interaction and will therefore miss the correct attractive $1/R^6$ behavior. This observation stimulated ideas to add on empirical pairwise corrections,[182−186] with the form

$$E_{\mathrm{xc}}^{\mathrm{disp}}(\mathrm{R}) = \sum_{ij} \left[\frac{C_6^{ij}}{R_{ij}^6}\right] f^{\mathrm{damp}}(R_{ij}) \tag{25}$$

which are functionals of the nuclear geometry and not purely of the density. This was also extended to include higher-order corrections

$$E_{\mathrm{xc}}^{\mathrm{disp}}(R) = \sum_{ij} \left[\frac{C_6^{ij}}{R_{ij}^6} + \frac{C_8^{ij}}{R_{ij}^8} + \frac{C_{10}^{ij}}{R_{ij}^{10}}\right] f^{\mathrm{damp}}(R_{ij}) \tag{26}$$

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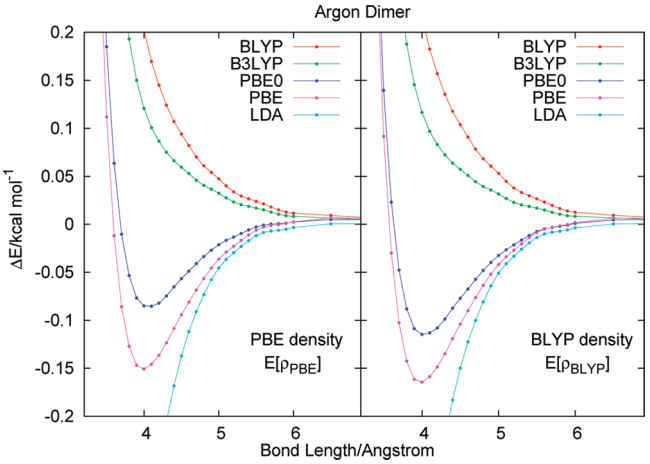

Figure 1. The role of the density in van der Waals forces: Binding curves of Ar_2 with several different energy functionals evaluated using two different densities, on the left the PBE density and on the right the BLYP density. There is very little observable difference; thus, the differing behavior of the functionals, in this region of the binding curve, is not attributable to their different densities but only the energies that they give.

One of the major questions in the application of these methods is the origin of the C_6 coefficients. They may be derived either from experimental information or calculated using ab initio methods.

There are many tabulated C_6 coefficients that together with an appropriate damping function allow the application of the above equations to a large range of interesting chemistry applications. However, C_6 coefficients can vary considerably depending on the chemical environment (for example sp^2 versus sp^3 bonded). It is unclear how one has to assign the bonding environment to apply the correct C_6 coefficient. Grimme has now extended this idea to cover the whole periodic table and to cover different bonding situations.[185] These functionals are often denoted by the name DFT-D.

Becke and Johnson[187−192] have developed nonempirical functionals for the dispersion coefficients based on the dipole moment of the exact exchange hole. For example

$$C_6^{ij} = \frac{\alpha_i \alpha_j \langle M^2 \rangle_i \langle M^2 \rangle_j}{\alpha_i \langle M^2 \rangle_j + \alpha_j \langle M^2 \rangle_i}$$

where the atomic expectation values of the multipole operators are given in terms of a functional of the density and orbitals

$$\langle M^2 \rangle_i = \sum_\sigma \int w_i(\mathbf{r})\, \rho_\sigma(\mathbf{r}) \times \left(\frac{1}{\rho_\sigma(\mathbf{r})} \sum_{kl} \phi_k(\mathbf{r})\, \phi_l(\mathbf{r}) \int \mathbf{r}' \phi_k(\mathbf{r}')\, \phi_l(\mathbf{r}')\, d\mathbf{r}' - \mathbf{r} \right)^2 d\mathbf{r}$$

Another practical idea is to capture the dispersion interaction by the addition of a suitably determined pseudopotential.[193,194] These are atom-centered potentials (developed for a few atom types) which combine a long-range weakly attractive potential with a shorter range weakly repulsive potential.

2.3.2. Explicit van der Waals Functionals. One of the first ideas in the development of explicit functionals came from explicitly considering the density of two separate fragments that are weakly interacting[195]

$$E_{xc}^{ALL} = \frac{6}{4(4\pi)^{3/2}} \int_{V_1} \int_{V_2} \frac{\sqrt{\rho_1(\mathbf{r}_1)\, \rho_2(\mathbf{r}_2)}}{\sqrt{\rho_1(\mathbf{r}_1)} + \sqrt{\rho_2(\mathbf{r}_2)}} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|^6} d\mathbf{r}_1\, d\mathbf{r}_2$$

However, this has the unattractive feature that we have to explicitly divide space into two species, which a priori are known to be weakly interacting. For example, what would one do if intramolecular van der Waals interactions are of interest, where space is not readily divided along the lines of the above equation? More recent ideas by Dion et al.[196] have reignited interest in this area with functionals that are exciting and promising. They devised a nonlocal van der Waals correlation functional

$$E_c^{nl} = \frac{1}{2} \int \int \rho(\mathbf{r})\, \phi(\mathbf{r}, \mathbf{r}')\, \rho(\mathbf{r})\, d\mathbf{r}\, d\mathbf{r}' \quad (27)$$

$$\phi(\mathbf{r}, \mathbf{r}') = \frac{2}{\pi^2} \int_0^\infty \int_0^\infty a^2 b^2 W(a,b)\, T(\nu(a), \nu(b), \nu'(a), \nu'(b))\, da\, db$$

where

$$\phi(\mathbf{r}, \mathbf{r}') = \phi(q(\mathbf{r}, \mathbf{r}')), \quad q(\mathbf{r}) = q(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))$$

but it can be expressed in a more compact manner using

$$E_{xc}^{nl} = \frac{1}{4\pi} \int_0^\infty \sum_{q,q'} [1 - (\hat{q}\cdot\hat{q}')^2] S_{q,q'}(iu)\, S_{q',q}(iu)\, du$$

There has been some very efficient implementation of these functionals by Soler and co-workers.[197]

Other ideas along these lines have led to similar functionals, which are being further developed to make them simpler and better[198−200]

$$E_c^{nl-VV} = \frac{3}{64\pi^2} \iint \frac{\omega_p^2(\mathbf{r})\, \omega_p^2(\mathbf{r}') D\left(\frac{|\mathbf{r} - \mathbf{r}'|}{2} \sqrt{\frac{\kappa(\mathbf{r})\, \kappa(\mathbf{r}')}{\kappa(\mathbf{r}) + \kappa(\mathbf{r}')}} \right)}{\omega_0(\mathbf{r})\, \omega_0(\mathbf{r}') [\omega_0(\mathbf{r}) + \omega_0(\mathbf{r}')] |\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}'$$

It is also a difficult task to find the best exchange and correlation functionals to go with the nonlocal piece that can describe the normal thermochemistry and geometries, as well as the weakly interacting systems.

Overall, there has been much success using some relatively new methods for treating dispersion interactions. For some of the prototypical examples, the prediction of binding in van der Waals complexes and biologically important complexes[201] is no longer outside the realm of DFT-based calculations. The refinement and a deeper understanding of these ideas will lead to developments and greater success in an increasing number of applications in important noncovalent interactions in both chemistry and biology.

3. CONSTRUCTING APPROXIMATE FUNCTIONALS AND MINIMIZING THE TOTAL ENERGY

In this section, we will explore further ways to progress the development of functionals. We have seen the advances that can be made in chemistry by considering the performance over greater numbers of chemical systems, including the addition of van der Waals. However, it is important to address the particularly challenging problem of exchange−correlation from other angles as well. To begin, let us consider some of the mathematical formulations that have underlined the exchange−correlation functional, starting from the simplest Kohn−Sham definition in terms of kinetic and electron−electron repulsion contributions

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) \quad (28)$$

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Here $T_s[\rho]$ denotes the kinetic energy of noninteracting electrons that have the same density as that of the physical system. It includes all the many-body contributions to both the kinetic energy and the electron−electron interaction terms. Probably the more important of the two is the electron−electron interaction term $V_{ee} = \Sigma_{i>j}(1/r_{ij})$. This led to the development of the adiabatic connection.

3.1. Adiabatic Connection

In the adiabatic connection[17,202] of Langreth and Perdew,[103] the key idea is that the interaction between electrons is allowed to vary

$$V_{ee}^{\lambda} = \sum_{i>j} \frac{\lambda}{r_{ij}} \tag{29}$$

with a family of Hamiltonians defined by

$$H_\lambda = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v_\lambda(\mathbf{r}_i) + \sum_{i>j}\frac{\lambda}{r_{ij}} \tag{30}$$

$$H_\lambda \Psi_\lambda = E_\lambda \Psi_\lambda \tag{31}$$

and minimizing wave function Ψ_λ such that $\rho_\lambda(\mathbf{r}) = \rho(\mathbf{r})$ for all λ. It is then easy to show that the exchange−correlation energy can be expressed as an integral over the coupling constant, λ, going from the noninteracting Kohn−Sham system at $\lambda = 0$ to the real physical system at $\lambda = 1$.

$$E_{xc}[\rho] = \int_0^1 W_\lambda \, d\lambda \tag{32}$$

where $J[\rho] + W_\lambda = \langle\Psi_\lambda|(\partial V_{ee}^{\lambda}/\partial\lambda)|\Psi_\lambda\rangle = \langle\Psi_\lambda|V_{ee}|\Psi_\lambda\rangle$. There are some important properties of W_λ that are known:[35,129,203,204]

$$W_0[\rho] = E_x[\Psi_0]$$

$$W_0'[\rho] = 2E_c^{GL2}[\Psi_0] = \frac{1}{2}\sum_{ij}^{occ}\sum_{ab}^{virt}\frac{\langle ij||ab\rangle^2}{\epsilon_i^{KS} + \epsilon_j^{KS} - \epsilon_a^{KS} - \epsilon_b^{KS}}$$

$$W_\lambda[\rho] = \frac{\partial}{\partial\lambda}\{\lambda^2 E_{xc}[\rho_{1/\lambda}]\}$$

where the scaled density is defined as $\rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r})$. The adiabatic connection is also often written at the level of the exchange−correlation hole

$$E_{xc} = \int_0^1 d\lambda \int\int \frac{\rho(\mathbf{r})\,\rho_{xc}^{\lambda}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$$

Modeling W_λ or $\rho_{xc}^{\lambda}(\mathbf{r},\mathbf{r}')$ gives rise to different functional approximations. It is also possible to use other connections beyond the simple linear form of eq 29, such as in the generalized adiabatic connection,[205] which also offers a direct link to the use of range-separated interactions in functional construction.[94,97]

3.2. Methods for Minimizing Energy Functionals

In the ground-state energy functional, eq 3, the Kohn−Sham kinetic energy is expressed as an explicit functional of the one-electron orbitals of the noninteracting reference system. The noninteracting Kohn−Sham first-order reduced density matrix of the reference system is given by

$$\rho_s(\mathbf{r}',\mathbf{r}) = \sum_{i\sigma} n_{i\sigma}\phi_{i\sigma}(\mathbf{r}')\,\phi_{i\sigma}^*(\mathbf{r}) \tag{33}$$

and the physical density $\rho(\mathbf{r})$ is equal to the Kohn−Sham density $\rho_s(\mathbf{r})$, which is the diagonal element of $\rho_s(\mathbf{r}',\mathbf{r})$

$$\rho(\mathbf{r}) = \rho_s(\mathbf{r}) = \rho_s(\mathbf{r},\mathbf{r}) = \sum_{i\sigma} n_{i\sigma}\phi_{i\sigma}(\mathbf{r})\,\phi_{i\sigma}^*(\mathbf{r}) \tag{34}$$

Since T_s is an implicit functional of electron density, it is impractical to just use the electron density as the basic computational variable. The practical approach for obtaining the minimum was originally developed by Kohn and Sham,[14] where the orbitals $\{|\phi_{i\sigma}\rangle\}$ are the eigenstates of one-electron local potentials $v_s^{\sigma}(\mathbf{r})$

$$\left(-\frac{1}{2}\nabla^2 + v_s^{\sigma}(\mathbf{r})\right)|\phi_{i\sigma}\rangle = \epsilon_{i\sigma}|\phi_{i\sigma}\rangle \tag{35}$$

The KS potential $v_s^{\sigma}(\mathbf{r})$ is related to the exchange−correlation potential $v_{xc}^{\sigma}(\mathbf{r})$

$$v_s^{\sigma}(\mathbf{r}) = v_{xc}^{\sigma}(\mathbf{r}) + v_J(\mathbf{r}) + v(\mathbf{r}) \tag{36}$$

where

$$v_{xc}^{\sigma}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho_\sigma(\mathbf{r})} \tag{37}$$

For E_{xc} that is an explicit functional of the electron density, either a local functional such as LDA, a semilocal functional such as GGA, or a nonlocal functional, $\delta E_{xc}[\rho]/\delta\rho_\sigma(\mathbf{r})$ can be directly evaluated and the energy minimization can thus be achieved by the self-consistent solution of the KS equations, eqs 35 and 36.

Going beyond the limitations of current local or semilocal approximations, a promising approach for the systematic development of exchange−correlation functionals is based on implicit density functionals. Here the energy functional has an explicit dependence on the reference single-electron orbitals and orbital energies $E_{xc}[\{\phi_j,\epsilon_j\}]$, as in $T_s[\{\phi_j\}]$. The prototypical example of an implicit density functional is that of exact exchange, EXX, which takes the form of the Hartree−Fock energy expression but is evaluated using KS orbitals. While EXX itself is a rather poor approximation of E_{xc}, compatible correlation functionals of orbitals such as those derived from many-body perturbation theory[206,131,207] or random phase approximation[136] or constructed using exchange holes[119] or from the adiabatic construction[107] clearly demonstrate the promise of this approach. More complicated functional forms also offer new challenges for minimizing the energy.

One way to carry out energy minimization with orbital functionals is the optimized effective potential (OEP) method.[208,209] This follows the original KS equations for the orbitals as eigenstates of a local potential $v_s(\mathbf{r})$. Now $v_{xc}(\mathbf{r})$ can be formally expressed through the following chain rule

$$v_{xc}^{\sigma}(\mathbf{r}) = \sum_i^N \int\int \frac{\delta E_{xc}[\phi_j]}{\delta\phi_{i\sigma}(\mathbf{r}')}\frac{\delta\phi_{i\sigma}(\mathbf{r}')}{\delta v_s^{\sigma}(\mathbf{r}'')}\frac{\delta v_s^{\sigma}(\mathbf{r}'')}{\delta\rho_\sigma(\mathbf{r})}\,d\mathbf{r}'\,d\mathbf{r}'' \tag{38}$$

which can be simplified to obtain the OEP integral equation[208]

$$\sum_i^N \int \phi_{i\sigma}^*(\mathbf{r}')\left[v_{xc}^{\sigma}(\mathbf{r}') - \frac{1}{\phi_{i\sigma}^*(\mathbf{r}')}\frac{\delta E_{xc}[\phi_{j\sigma}]}{\delta\phi_{i\sigma}(\mathbf{r}')}\right]G_{KS}^{i\sigma}(\mathbf{r}',\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}) = 0 \tag{39}$$

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where the Kohn−Sham Green's function is given by

$$G_{\mathrm{KS}}^{i\sigma}(\mathbf{r}',\mathbf{r}) = \sum_{j\neq i}^{\infty} \frac{\phi_{j\sigma}^{*}(\mathbf{r})\,\phi_{j\sigma}(\mathbf{r}')}{\epsilon_{i\sigma}-\epsilon_{j\sigma}}$$

The basis set expansion for the exchange−correlation potential $v_{\mathrm{xc}}^{\sigma}(\mathbf{r})$ was first used in conjunction with eq 39 in successful implementations of finite-basis set OEP calculations for molecules.[210,211] An alternative view of OEP is to take the variable of the optimization as the local potential $v_{\mathrm{s}}^{\sigma}(r)$, since both the orbitals and orbital energies $\{\phi_{j\sigma},\epsilon_{j\sigma}\}$ are functional of $v_{\mathrm{s}}^{\sigma}(\mathbf{r})$. The ground-state energy is just given by the following minimum

$$E_{\mathrm{gs}} = \min_{v_{\mathrm{s}}^{\sigma}(\mathbf{r})} E[\{\phi_{j\sigma}\}]$$

The theoretical foundation for the potential-centric view of the DFT has been rigorously established as the potential functional theory (PFT).[21] Here two versions of the PFT using the external potential and the one-electron potential were shown to parallel the results of Hohenberg−Kohn and Kohn−Sham. Calculation of OEP by minimization of an object functional was done by Colle and Nesbet;[212] their object functional was not the total energy but was constructed as a quadratic functional consistent with the linearized OEP equations eq 39 and an additional constraint of the HOMO eigenvalue. The direct minimization of the energy over all possible potentials can be carried out effectively by the direct optimization of the coefficients $\{b_t\}$ in the basis set expansion[213]

$$v_{\mathrm{s}}^{\sigma}(\mathbf{r}) = v(\mathbf{r}) + v_{0}^{\sigma}(\mathbf{r}) + \sum_{t} b_{t}^{\sigma} g_{t}(\mathbf{r}) \qquad (40)$$

where $v(\mathbf{r})$ is the external potential due to the nuclei and $v_{0}^{\sigma}(\mathbf{r})$ is a fixed reference potential that can be used to describe the correct long-range behavior. The exact analytic derivatives $\partial E/\partial b_t^{\sigma}$ and approximate second derivatives have been derived to allow efficient optimization.[213,214] The conditions of the vanishing first-order energy gradients also lead to the natural algebraic equations for finite basis set formulation of the OEP,[214] which is different from the direct projection of the OEP equations, eq 39, with a finite basis set expansion of the exchange−correlation potential[210,211] and other methods.[215,216] However, with the introduction of finite basis sets for orbitals, the ill-posed inverse nature of the OEP manifests itself with the generation of nonphysical energies and potentials.[217,218] A successful determination of OEPs relies on a choice of balanced orbital and potential basis sets.[219,220] In addition, there exists an efficient method for determining physically meaningful OEPs for arbitrary orbital and potential basis sets with a regularization approach.[221,220]

Instead of determining the local OEP, one can perform the following optimization for the ground-state energy using the orbitals as the optimization variables,

$$E_{\mathrm{gs}}^{\mathrm{GKS}} = \min_{\{\phi_{j\sigma}\}} E[\{\phi_{j\sigma}\}]$$

For functionals of $\rho_{\mathrm{s}}(\mathbf{r}',\mathbf{r})$, such as EXX, one obtains the Generalized Kohn−Sham (GKS) equations,[222] which are also called Hartree−Fock−Kohn−Sham equations,[223] with a nonlocal potential $v_{\mathrm{s}}^{\sigma,\mathrm{NL}}(\mathbf{r},\mathbf{r}') = v_{\mathrm{xc}}^{\sigma}(\mathbf{r},\mathbf{r}') + v_J(\mathbf{r}) + v(\mathbf{r})$ for the orbitals:

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}^{\sigma,\mathrm{NL}}(\mathbf{r},\mathbf{r}')\right)|\phi_{i\sigma}\rangle = \epsilon_{i\sigma}^{\mathrm{GKS}}|\phi_{i\sigma}\rangle \qquad (41)$$

For example, for the most cited functional in the literature, B3LYP, when the calculation is carried out to minimize the energy as is routinely done, it will not fall within the regime of Kohn−Sham theory, as the potential in the minimizing equation is nonlocal. It has been carried out within the GKS framework.

There is one scenario where the KS-OEP approach appears to be the only computational approach for minimization of the energy. This is when the energy functional is $E[\{\phi_{j\sigma},\epsilon_{j\sigma}\}]$, also dependent on the eigenvalues of the one-electron orbitals, such as in the RPA and MP2 correlation functionals. Since $\{\phi_{j\sigma},\epsilon_{j\sigma}\}$ are functional of $v_{\mathrm{s}}^{\sigma}(\mathbf{r})$, the OEP approach is well-defined.[131,206,207]

We feel it is important to point out that for a functional such as B3LYP, in terms of the total energy,[224] there is very little to choose between GKS and OEP, even in the case of a well-regularized (or balanced basis set description) potential. The two methods are not identical but they are very similar!

All calculations in Table 2 [atomic energies H−Ne, 93 set of energies, BH42 set of barriers, geometries of small molecules.[225] and a small set of isotropic dipole polarizabilities calculated by finite difference (ΔF = 0.001 au)] are carried out using a modified version of the NWChem package[226] with a pVTZ basis set for both the orbital and potential basis sets . We can see from the results that the OEP and GKS calculations are not identical (as would happen with a much larger potential basis set in an unregularized calculation), but they are very similar. The OEP total energy must be higher, as it has an extra constraint on top of the GKS calculation, that is, that the potential in the KS equation, $v_{\mathrm{s}}^{\sigma}(\mathbf{r})$, is local. However, this has a minor effect on total energies and energy differences. The effects on the molecules and the properties shown here are much smaller than the effects of a change in a functional. Although it is appealing to run an OEP(B3LYP) calculation to place the most famous functional more firmly in the theoretical setting of Kohn−Sham theory, there do not appear to be any practical advantages. The extra computational effort to run the OEP calculation means that we cannot see much reason at all for running OEP calculations. There was one property where the use of OEP seemed to offer some practical advantages, namely, in the calculation of magnetic properties.[227−231] This no doubt comes down to the uncoupled manner in which the calculation is carried out and to the use of the OEP rather than GKS eigenvalues.

Table 2. OEP versus GKS: Mean Absolute Error for Several Molecular Sets Is Shown for the OEP and GKS Minimizations of Three Different Approximate Functionals, B3LYP, MCY2, and HF[a]

	B3LYP		MCY2		HF	
property	GKS	OEP	GKS	OEP	GKS	OEP
atom E/kcal mol^{-1}	2.63	2.63	3.48	3.47	101.00	101.19
93 set/kcal mol^{-1}	3.30	3.21	2.26	2.16	74.00	75.15
barrier/kcal mol^{-1}	4.65	4.58	1.93	1.86	12.91	14.14
R_{e}/au	0.0042	0.0041	0.0049	0.0050	0.0165	0.0172
α/au	0.2967	0.2953	0.2053	0.2020	0.9107	0.9979

[a] Differences in minimizing an energy expression using either OEP or GKS are clearly minor compared with changing functional.

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3.3. Kohn−Sham and Generalized Kohn−Sham Eigenvalues

Eigenvalues play an important role in density functional theory without completely fulfilling their full potential. This is in part due to the inconsistencies of approximate functionals currently used in the literature. However, there is some access to the exact Kohn−Sham orbitals and eigenvalues also from a potential-driven calculation. From high-level quantum chemical methods (or even from experiments), we can obtain accurate densities, and in the true spirit of Kohn−Sham, we can find the $v_s(\mathbf{r})$ that gives it back by minimizing the noninteracting kinetic energy, as was first done in a practical scheme by Zhao et al.[232] as well as similar schemes.[224,233−235] In the work by Wu and Yang,[112] this is done by maximizing the functional

$$W = \langle \Psi_s | \hat{T} | \Psi_s \rangle + \sum_\sigma \int v_s^\sigma(\mathbf{r})(\rho_{s,\sigma}(\mathbf{r}) - \rho_\sigma^{\text{in}}(\mathbf{r}))\, d\mathbf{r} \tag{42}$$

with respect to the Kohn−Sham potential v_s^σ. Here v_s^σ plays the role of a Lagrange multiplier to satisfy the constraint that the Kohn−Sham density is the same as the highly accurate input density, $\rho_\sigma^{\text{in}}(\mathbf{r})$. This density usually comes from a high-quality ab initio calculation, such as MP2 or CCSD, or it could even be a density as measured by experiment. Once $v_s^\sigma(\mathbf{r})$ is determined from this density, we can get the exact Kohn−Sham potential and also the exact Kohn−Sham orbitals and the exact Kohn−Sham eigenvalues.

We can also obtain approximate eigenvalues from calculations with approximate functionals, for example, from LDA or GGA functionals

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_J(\mathbf{r}) + \frac{\delta E_{\text{xc}}^{\text{GGA}}[\rho]}{\delta \rho_\sigma(\mathbf{r})} \right) \phi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}\phi_{i\sigma}(\mathbf{r}) \tag{43}$$

This raises the question how similar are these eigenvalues to the exact ones? Note that Kohn−Sham eigenvalues must have come from a potential, $v_s^\sigma(\mathbf{r})$, that is multiplicative. This is the case for LDA and GGA, where the exchange−correlation is a functional of the density. However, for orbital functionals, the direct minimization carried out in a standard Hartree−Fock calculation (or a B3LYP calculation)

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_J(\mathbf{r}) + \frac{\delta E_{\text{xc}}^{\text{B3LYP}}[\phi_i]}{\delta \rho_\sigma(\mathbf{r},\mathbf{r}')} \right) \phi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}^{\text{GKS}}\phi_{i\sigma}(\mathbf{r}) \tag{44}$$

has a potential $v_s(\mathbf{r},\mathbf{r}')$ that is nonmultiplicative and is not of the Kohn−Sham type but rather of a generalized Kohn−Sham (GKS) nature. The ϵ^{GKS} are generally very different from the Kohn−Sham ϵ. A rather straightforward rearrangement of the above equation gives

$$\epsilon_{i\sigma}^{\text{GKS}} = \langle \phi_{i\sigma} | -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_J(\mathbf{r}) + \frac{\delta E_{\text{xc}}^{\text{B3LYP}}[\phi_{i\sigma}]}{\delta \rho_\sigma(\mathbf{r},\mathbf{r}')} | \phi_{i\sigma} \rangle$$

or more generally

$$\epsilon_{i\sigma}^{\text{GKS}} = \langle \phi_{i\sigma} | H_{\text{eff}}^\sigma | \phi_{i\sigma} \rangle \tag{45}$$

and also for Kohn−Sham eigenvalues

$$\epsilon_{i\sigma} = \langle \phi_{i\sigma} | H_s^\sigma | \phi_{i\sigma} \rangle \tag{46}$$

Table 3. Orbitals and Eigenvalues Originating from Different Methods: Eigenvalues (in eV) for the Fluorine Atom Calculated Using $\langle \phi_f | H_{\text{eff}} | \phi_f \rangle$ with Different Combinations of H_{eff} and $\{\phi_{j\sigma}\}$[a]

	$\epsilon_{\text{HOMO}} = \langle \phi_{\text{HOMO}} \vert H_{\text{eff}} \vert \phi_{\text{HOMO}} \rangle$			$\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}$		
H_{eff}	ϕ_{BLYP}	ϕ_{B3LYP}	$\phi_{\text{LC-BLYP}}$	ϕ_{BLYP}	ϕ_{B3LYP}	$\phi_{\text{LC-BLYP}}$
LDA	−10.01	−9.86	−10.19	−0.06	−0.10	−0.09
BLYP	**−10.13**	−9.97	−10.30	**−0.84**	−0.87	−0.85
PBE	−10.11	−9.96	−10.28	−0.90	−0.94	−0.93
B3LYP	−12.19	**−12.04**	−12.35	−4.71	**−4.69**	−4.69
CAM-B3LYP	−14.20	−14.06	−14.37	−8.56	−8.51	−8.52
LC-BLYP	−14.56	−14.41	**−14.74**	−9.45	−9.44	**−9.44**
rCAM-B3LYP	−16.28	−16.14	−16.45	−12.75	−12.68	−12.70
HF	−18.81	−18.70	−18.95	−20.85	−20.56	−20.64

[a] The numbers corresponding to true eigenvalues (when ϕ and H_{eff} come from the same method) are bold. The different methods give vastly different eigenvalues; however, the orbitals themselves can be quite similar and the only factor of importance is the nature of H_{eff}.

Here we express the eigenvalues in terms of expectation values of the one-electron operators. An illustration of the importance of this understanding is given in Table 3.

3.3.1. Janak's Theorem. If fractional occupations are included in a KS or a GKS scheme such that the density is given by

$$\rho(\mathbf{r}) = \sum_{i\sigma} n_{i\sigma} |\phi_{i\sigma}(\mathbf{r})|^2$$

where the n_i can be fractional, then we can evaluate the modified Kohn−Sham energy by minimizing

$$E_{\text{Janak}} = \sum_{i\sigma} n_{i\sigma} \langle \phi_{i\sigma} | \hat{T} | \phi_{i\sigma} \rangle + \int v_{\text{ext}}(\mathbf{r})\, \rho(\mathbf{r})\, d\mathbf{r} + J[\rho] + E_{\text{xc}}[\rho] \tag{47}$$

and we can take derivatives of the above from the usual Kohn−Sham starting point $\{n_{i\sigma}\} = 1,0$ to simply find that[236]

$$\frac{\partial E[\rho]}{\partial n_{i\sigma}} = \epsilon_{i\sigma} \tag{48}$$

This constitutes the Janak theorem. It is also easy to extend Janak's result to orbital functionals and similarly find[237]

$$\frac{\partial E[\{\phi_{j\sigma}\}]}{\partial n_{i\sigma}} = \epsilon_{i\sigma}^{\text{GKS}} \tag{49}$$

Before we consider how the eigenvalues agree with electron removal and addition, let us consider a few implications. First, are they something that only comes from a full self-consistent calculation, or can we view them in a different manner? In Table 3 we want to highlight the implication of eqs 45 and 46, which is that "eigenvalues" can often be calculated in a much simpler manner. As we have seen previously, it is not actually a challenge for the density (or the orbitals) but again more a challenge for the energy expression (in this case the derivative $H_{\text{eff}}[\phi_{i\sigma}]$). The HOMO−LUMO gap here is insensitive to the type of orbitals; it only depends on the H_{eff}. The physical meaning of KS and GKS eigenvalues and their relation to experimental observables will be further discussed in (Section 4.1.4).

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4. INSIGHT INTO LARGE SYSTEMATIC ERRORS OF FUNCTIONALS

In section 2 we have seen that DFT has enjoyed much success using approximate functionals. One path to progress is to refine the performance of DFT in areas where it is already quite successful (e.g., improving G3 MAE from 4 kcal/mol toward a chemical accuracy of 1 kcal/mol). Although the field of DFT is now reaching maturity due to such success, it is critical and perhaps even more important to understand the errors. This realization can help to establish a philosophically different approach to functional construction. By definition, the errors in DFT all arise from the approximate nature of the functionals that are used in the calculations. Understanding the true nature and root cause of these errors in the functional approximation can offer insight to help improve the physics and chemistry contained in newer functionals. We now discuss the principal large systematic errors of functionals beyond the average errors seen in the near-equilibrium geometries of the G3 set and the slightly larger errors found in reaction barriers due to molecules in their transitions states. We believe that understanding and eradicating the basic errors of currently used approximations is key for the advancement of DFT.

4.1. Stretched H_2^+ and Delocalization Error

What better place to start than the simplest molecule in chemistry: H_2^+. This molecule with one electron, that should be trivial to solve, is in fact one of those problems whose failure could well indicate that something is fundamentally flawed with currently used functionals (Figure 2). The size of the failure is also worrying. In the quest for average errors of 1 kcal/mol, large errors of 50−60 kcal/mol are found for the dissociation of H_2^+ with all GGA type functionals. This is not solely a problem restricted to just the prototypical one electron system H_2^+, but can also be clearly seen in many other systems. Even in other stretched odd electron systems such as He_2^+ and $(H_2O)_2^+$,[238] they all show massive errors on stretching. Rather than using the fact that the chemistry in the G3 set is hopefully different in nature to the stretching of molecules, let us instead consider it in more detail in an attempt to shed some light on the problem. Hence, we will now focus on the *functional* rather than the chemistry.

4.1.1. Self-Interaction. The classic way of viewing the problem of H_2^+ is to consider it a one-electron system. Any error made is because the electron interacts with itself in an unphysical manner, a problem well-known in the literature as the self-interaction error (SIE).[239−242] One way to correct it would be to include the full amount of exact Hartree−Fock exchange, since this would exactly cancel the Coulomb term in any one electron system. Perdew and Zunger[22] suggested a correction term that removes all the one-electron self-interaction terms present in any approximate functional

$$E_{xc}^{PZ}[\rho] = E_{xc}[\rho] - \left(\sum_{i\sigma} J[\rho_{i\sigma}, 0] + E_x[\rho_{i\sigma}, 0] \right) \quad (50)$$

This would have no effect on the exact functional. It has been applied to LDA and GGA functionals and the results give some interesting properties. First, the correction unfortunately means that the functional is no longer of a Kohn−Sham nature, as the potential is now orbital-dependent. However, the energy can be directly minimized allowing for rotations of the occupied orbitals.[243−245] Second, the self-interaction corrected functionals often perform worse than the parent functionals for the standard tests, such as thermochemistry and geometries. This situation has stimulated further work along these lines with attempts to scale down the correction.[246,247]

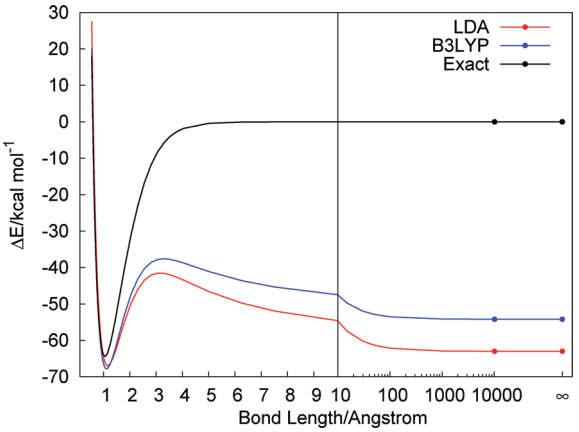

Figure 2. Binding energy curves of stretched H_2^+, calculated with LDA, B3LYP, and exact (HF). After 10 Å the x axis changes to a logarithmic scale and the final point at infinity is from an explicitly fractional charge calculation ($2 \times H[^1/_2\alpha,0]$).

The essence of self-interaction can also be understood from the behavior of the energy of one electron. In this case the exact exchange−correlation functional is known, for $0 < N < 1$, $E_{xc}[\rho] = -J[\rho]$. However, the behavior of the energy for one-electron systems can be more clearly seen if we consider the homogeneity scaling[248] of functionals between 0 and 1 electrons, $\rho_q = q\rho$, $0 < q < 1$.[242] With a knowledge of the explicit forms of the T_s, V_{ne}, and J functionals and also the exact behavior of the total energy, a scaling relation for the exact exchange−correlation functional can be easily found,

$$E_{xc}[\rho_q] = qE_{xc}[\rho] + q(1-q)J[\rho] \quad (51)$$

This equation reveals that there are two parts to the correction of $E_{xc}[\rho]$: a linear correction and a quadratic correction to counteract the behavior of the Coulomb term. In this case, the Coulomb term for one electron is not removed, rather, it is corrected to become a linear interpolation between the integers as well as the exchange, and of course, in up to one-electron systems the exchange and Coulomb cancel exactly. There is much to be understood even from systems with only one electron. In density functional theory, which is based on the average of all electrons, one-electron densities are not very different from other densities. They offer some illuminating challenges which, as always, translate into a challenge for the exchange−correlation functional.

4.1.2. Many-Electron Self-Interaction Error. The concept of self-interaction is simplest and clearest in the one-electron case. However, the effects can also be seen in many-electron systems. In such cases, are there, in fact, effects present other than those arising just from each electron interacting with itself? An answer to this question can be obtained by looking in functional space. There are approximate functionals upon which the Perdew−Zunger correction eq 50 has no effect. These functionals are correct for one-electron systems. Some examples are the adiabatic connection functional MCY2[107] or the position-dependent exact-exchange functional B05.[119] The key point is that these functionals are a long way from being correct for the self-interaction problems of systems with more than one electron,

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and in such cases, the Perdew−Zunger correction cannot possibly help. This observation helped lead to the concept of "many-electron self-interaction error".[107,247,249−251] The idea that all the error is due to electrons interacting with themselves is very hard to formalize mathematically for many electrons and is a difficult way to view the problem. We believe that a better understanding comes from the term "delocalization error", because it better captures the physical bias of the functionals commonly used in the literature.[252] We will discuss the concept of delocalization error in (section 4.1.6), after introducing fractional charges and associated exact conditions.

4.1.3. Fractional Charges. Having identified some chemical systems where functionals exhibit a poor performance, it is important to attempt to move from what we term chemical space (the molecules) to functional space. In other words, we need to identify the real underlying cause of the failure in terms of the mathematical nature of the functional. Although it is useful to identify a system or set of systems where the functional exhibits errors, it is more beneficial to have a deeper understanding of the underlying cause of those errors. Otherwise, we remain at the level of only seeing an error in H_2^+ and then a similar error in $(C_{60})_2^+$ and again a similar error in the band gap of solid diamond, but without a true understanding of the connection between them. However, it should be acknowledged that recognition of the error helps and is the first step to understanding the problem inherent to the functional that gives rise to that error.

The question now arises, what further can we learn from infinitely stretched H_2^+, other than it is a system where LDA/GGAs fail? One main advantage of DFT is that unlike ab initio quantum chemistry, which is based on the wave function in the many-dimensional Hilbert space, we can look in real space at orbitals and densities and therefore at the functional that acts upon these real space objects. Although the complexity of the functional is unknown, some understanding can be gained from looking at the real space picture of what is happening in a particular molecular system. For example, at the infinite limit of stretched H_2^+, the electron density is spread out over both centers, and there is half an electron on each proton.[242] In this infinite limit, we really have two fractional systems, two $H^{1/2+}$ atoms, and it is evident that DFT struggles to give the correct energy for this fractional system.

On the basis of the seminal work of Perdew et al. in 1982,[253] the exact energy for a system with a fractional number of electrons has been known for many years. This work shows that for a fractional number of electrons $N + \delta$, $0 \le \delta \le 1$

$$E(N + \delta) = (1 - \delta)E(N) + \delta E(N + 1) \tag{52}$$

This means the total energy is a linear interpolation in between integer points. The elegant and informative proof uses the grand-canonical ensemble with a bath of electrons to allow electron numbers to fluctuate. This directly utilizes the underlying Schrödinger equation to help understand subsidiary considerations about the energy expression within DFT.[254] A pure-state proof using size-consistency was also given by Perdew.[255] Later work from Yang et al.[256] using size-extensivity proved the same final result but from a pure state perspective, namely, that of infinitely stretched degenerate systems with varying numbers of electrons. As for H_2^+, an additional requirement (which is physically correct) is that of size-extensivity. Although this proof only covers the rational numbers, an alternative proof that covers the irrational fractions has been provided by Ayers.[257] To summarize these proofs, we can consider Figure 3, which illustrates some elements of the different views of the problem.

It should be noted, for the more mathematically inclined, that all the proofs also rely on the convexity of E vs N at the integers, which is thought to be generally true for electronic systems. Currently, there are no known counterexamples in nature, although this is yet to be proven. This proof is difficult, although there are no known counterexamples for the Schrödinger Hamiltonian (with electron−electron interaction $\Sigma_{i>j}(1/r_{ij})$. There are known counterexamples for other types of electron−electron interaction.[258] Therefore, if convexity is true for all systems, it is not a general property of all Hamiltonians but relies upon the Coulomb nature of the electron−electron repulsion.

To some degree, the extension of DFT to fractional charges looks like a foray into a world outside of physical systems. A chemical system that has a fractional number of electrons does not in fact exist. So how can this help us? What is the essence behind the perspective of fractional charges? Although these are complex questions, it is important to understand that this foray into fractional charges is an attempt to look at the properties of the *functional* rather than at the *chemistry*. In this case, the pure state proof of Yang et al. is valuable, as it highlights a clear connection to a real molecule. In fact $H^{1/2+}$, which is a fractional system, is directly connected to a real system, namely, infinitely stretched H_2^+. It may also (via the functional) be connected to other real systems without such a clear link (for example, the delocalized density in part of an aromatic organic molecule). This highlights the fact that a consideration of fractional charges in DFT is key to understand some properties and failures of the functional. It is evident that if we can construct an LDA or GGA functional that works for $H^{1/2+}$, then it will also work for a real integer system H_2^+ (this clearly follows as all the pieces are size consistent). Furthermore, if it gives too low an energy for $H^{1/2+}$, then it will fail for H_2^+ dissociation. This direct connection is important as it enables us to trace the error from functional space into chemical space: from a fictional fractional system to a real chemical system.

Band Gap in Terms of Chemical Potential. It is also important to realize that the fundamental band gap (or chemical hardness) can be understood clearly from the behavior of E vs N,[259] as in Figure 3. The fundamental gap is given by the difference between the ionization energy and electron affinity

$$\begin{aligned} E_{\text{gap}}^{\text{integer}} &= I - A \\ &= [E(N-1) - E(N)] - [E(N) - E(N+1)] \end{aligned}$$

which can be compared with the derivatives at N, taking the difference between the derivative to the left and the right

$$E_{\text{gap}}^{\text{deriv}} = \left.\frac{\partial E}{\partial N}\right|_{N+\delta} - \left.\frac{\partial E}{\partial N}\right|_{N-\delta} \tag{53}$$

For the exact functional, $E_{\text{gap}}^{\text{integer}} = E_{\text{gap}}^{\text{deriv}}$ due to the straight line nature of the exact energy. This is a key result that may help us understand some of the failings of approximate functionals. This is especially true for describing the band gap of solids.

KS-DFT for Fractional Charges. The initial and simplest way used to calculate fractional charges with approximate functionals was to perform a calculation on molecules with odd numbers of electrons and stretch them to infinity.[250] This approach has absolutely no problems with size-consistency, as the form of all the approximate functionals used is rigorously size-consistent, so

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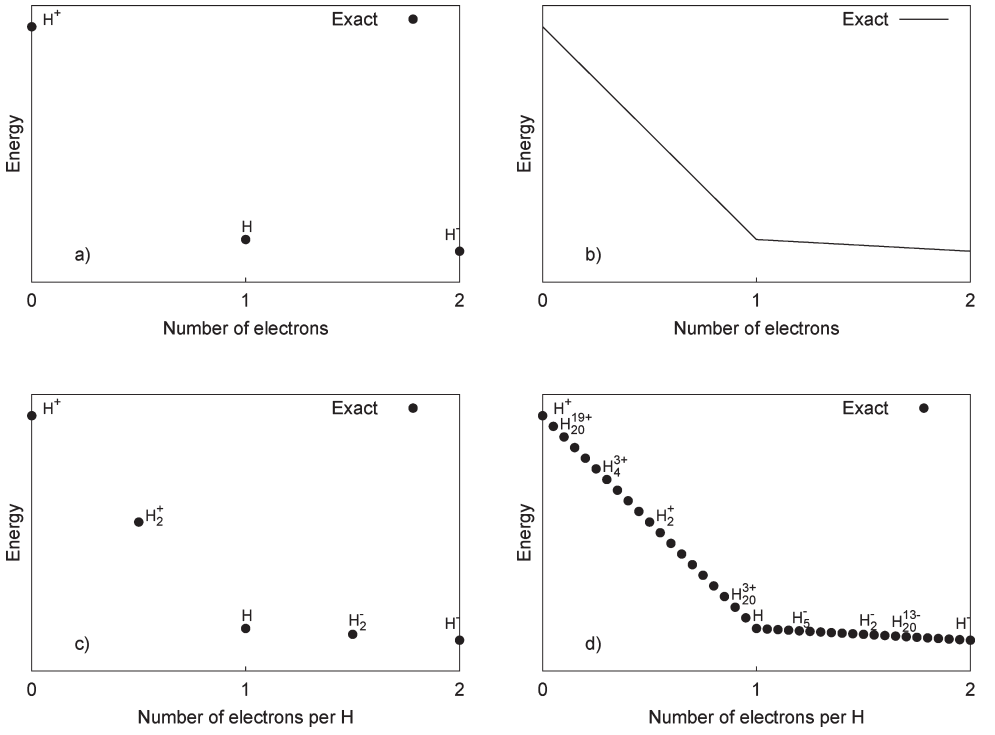

Figure 3. Energy vs number of electrons (E vs N) curve for (a) solution of the Schrödinger equation for integer species, (b) DFT for fractional species from eq 52, (c) including stretched molecules H_2^+ and H_2^-, and (d) the Yang, Zhang and Ayers[256] extension showing many stretched molecules.

the only issue is whether the calculation can in fact be carried out. These calculations can be performed without any changes to the code and with the usual integer idempotent density matrices that are widely used in DFT and HF calculations. However, the stretching to infinity often causes minor technical challenges; with some determination these can be overcome. On the other hand, a simpler and more direct route to carry out such calculations involves a minor modification of any DFT code to explicitly use fractional occupations.[251] In some way, the Kohn−Sham scheme must be extended to account for fractional occupations, since the original stipulation is that the occupation numbers of the orbitals should either be 1 or 0. A generalization to fractional numbers of electrons is easily achieved using fractional occupation of the frontier orbital (the highest occupied/lowest unoccupied orbital)[236]

$$n_i = \begin{cases} 1 & \text{for} \quad \epsilon_i < \epsilon_F \\ \delta & \text{for} \quad \epsilon_i = \epsilon_F \\ 0 & \text{for} \quad \epsilon_i > \epsilon_F \end{cases} \tag{54}$$

Since the occupation numbers in eq 54 are between 0 and 1, the extension is explicitly for the regime of *spin DFT*. Here and in the rest of this section, we have suppressed the spin index σ to simplify the notation. Thus, the spin index is implicit in the orbital index i and the calculations are spin-polarized calculations. With these occupation numbers for the density, $\rho = \sum_i n_i \phi_i^2$, we can minimize the modified Janak-type Kohn−Sham energy

$$E = \sum_i n_i \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle + \int v_{ext}(\mathbf{r})\, \rho(\mathbf{r})\, d\mathbf{r} + J[\rho] + E_{xc}[\rho] \tag{55}$$

with Kohn−Sham equations for fractional charges

$$\left(-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + v_J(\mathbf{r}) + v_{xc}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \tag{56}$$

The only difference from the normal Kohn−Sham equations is due to the dependence of v_J and v_{xc} on the density, which in this case is fractional. For example,

$$v_J(\mathbf{r}) = \int \frac{\sum_i n_i \phi_i^2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{57}$$

The execution of some DFT calculations for fractional charges is quite revealing in the performance of many different functionals. Figure 4 shows the behavior of the energy of the carbon atom with between five and seven electrons ($3\alpha 2\beta \rightarrow 4\alpha 2\beta \rightarrow 5\alpha 2\beta$). In this case, the gap is given by the gap in the α spin spectrum. However, it should be noted that the gap is not always given by either of the gaps in the spin spectrum. For example, for the nitrogen atom ($4\alpha 2\beta \rightarrow 5\alpha 2\beta \rightarrow 5\alpha 3\beta$) it would be given by a mixed gap $E_{gap} = \partial E/\partial N|_{N_\beta+\delta} - \partial E/\partial N|_{N_\alpha-\delta}$.

The behavior of the curves with approximate functionals is far from correct as the initial slopes do not correctly point to the integer values. This has two effects, first the eigenvalues will not correspond to the correct values. Second, and more importantly, the error for fractional charges highlights a real energetic error in a larger system: for example, infinitely stretched C_2^+ or infinitely stretched C_{100}^-. The fact that the initial slopes are incorrect leads to an energetic error in a real stretched molecule.

4.1.4. Chemical Potential and Physical Meaning of the Frontier KS and GKS Eigenvalues. Electron removal and addition are two fundamental electronic processes in chemistry

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and material science. For solids, the difference between the ionization potential and the electron affinity is the fundamental band gap. On the other hand for molecules, it is the chemical hardness identified by Parr and Pearson,[260] a factor of one-half is neglected. The band gap plays a critical role in determining the properties of electron transport, structure and energetics of defects and interfaces, and many electromagnetic responses.[261] Hardness, chemical potential,[262] and Fukui functions[263] are the key quantities of the chemical reactivity theory.[223,264,265]

The chemical potential is the derivative of the total energy with respect to particle number when the external potential is fixed

$$\mu = \left(\frac{\partial E_v(N)}{\partial N}\right)_v \tag{58}$$

As a consequence of the linearity condition (eq 52), μ is a constant between the integers and has a derivative discontinuity at the integers

$$\mu(N) = \begin{cases} -I(N_0) = E(N_0) - E(N_0 - 1), & \text{if} \quad N_0 - 1 < N < N_0 \\ -A(N_0) = E(N_0 + 1) - E(N_0), & \text{if} \quad N_0 < N < N_0 + 1 \end{cases} \tag{59}$$

where $I(N_0)$ is the ionization potential of the N_0-electron system and $A(N_0)$ is its electron affinity.

For the Kohn−Sham reference system with a local potential $v_s(\mathbf{r})$, here we use the potential functional formulation.[21] The electron density $\rho_s(\mathbf{r})$ can be represented as the set of orbitals and occupation numbers $\{\phi_i,n_i\}$ or, equivalently, by the local potential and total particle number $\{v_s(\mathbf{r}),N\}$. Thus the total energy functional, formally in terms of the density as $E_v[\rho_s(\mathbf{r})]$, can be equivalently expressed as $E_v[v_s(\mathbf{r}),N]$. The ground state energy is the minimum of the KS energy functional, expressed (explicitly or implicitly) in terms of the local potential $v_s(\mathbf{r})$:

$$E_v(N) = \min_{v_s} E_v[v_s,N] = E_v[v_s^{gs},N] \tag{60}$$

where the minimizer v_s^{gs} is the optimized effective potential (OEP), as established.[21] The variational nature of v_s^{gs} means that $(\delta E_v[v_s,N])/(\delta v_s(r))|_{v_s{}^{gs}} = 0$, simplifying the calculation of the derivative:[237]

$$\left(\frac{\partial E_v}{\partial N}\right)_v = \int \left.\frac{\delta E_v[v_s,N]}{\delta v_s(\mathbf{r})}\right|_{v_s^{gs}} \frac{\partial v_s^{gs}(\mathbf{r})}{\partial N}\,\mathrm{d}\mathbf{r} + \left(\frac{\partial E_v[v_s^{gs},N]}{\partial N}\right)_{v_s^{gs}} = \left(\frac{\partial E_v[v_s^{gs},N]}{\partial N}\right)_{v_s^{gs}} \tag{61}$$

We will drop the superscript gs for the ground state quantities in cases where there is no confusion.

Now we would like to express the result of eq 61 in terms of $\{\phi_i,n_i\}$. Consider a change in the total number of electrons $N = N_0 + \delta$. At the fixed v_s^{gs}, all the orbitals $\{\phi_i^{gs}\}$ as its eigenstates are fixed. Since $\rho_s(\mathbf{r})$ is the ground-state density of the reference potential v_s^{gs}, only the frontier level occupation n_f is allowed to change $\delta = \delta n_f$, thus

$$\mu = \left(\frac{\partial E_v}{\partial N}\right)_v = \left(\frac{\partial E_v[\{\phi_i^{gs},n_i\}]}{\partial n_f}\right)_{\{\phi_i^{gs}\}} \tag{62}$$

where the frontier orbital is either the lowest unoccupied molecular orbital (LUMO) or the highest occupied molecular orbital (HOMO):

$$n_f = \begin{cases} n_{LUMO} & \text{if} \quad \delta > 0 \\ n_{HOMO} & \text{if} \quad \delta < 0 \end{cases} \tag{63}$$

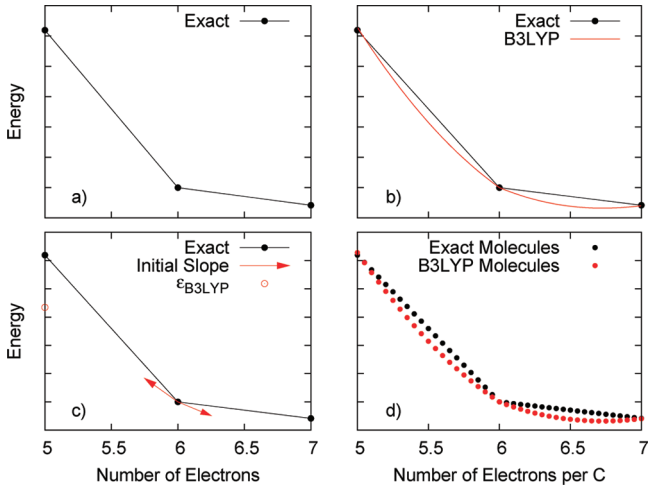

Figure 4. Failures of an approximate functional, B3LYP, for fractional charges. (a) The exact fractional charge behavior for the carbon atom. (b) B3LYP predicts accurate energies at the integers but fails for the energy of fractional charges. (c) The initial slope of the B3LYP curve at $N = 6$ does not give an eigenvalue that agrees with the ionization energy. (d) B3LYP gives too low energies for real stretched molecules.

Equation 62, obtained by Cohen et al.,[237] is a key result linking the chemical potential to quantities in the KS or GKS reference systems. Applying eq 62 to the total energy expression and using the results of the Janak theorem for KS (eq 48) and its extension to GKS (eq 49) result in an important conclusion regarding the physical meaning of the frontier KS or GKS eigenvalues. Namely, that they are the corresponding chemical potentials:[237] when E_{xc} is an explicit functional of the electron density, $\rho(\mathbf{r})$, either local or nonlocal

$$\mu = \epsilon_f \tag{64}$$

and when E_{xc} is an explicit and differentiable functional of the noninteracting density matrix $\rho_s(\mathbf{r},\mathbf{r}')$ (or orbital functionals)

$$\mu = \epsilon_f^{GKS} \tag{65}$$

These two scenarios cover all commonly used functionals, but further extension is necessary for functionals that are not differentiable and are needed for describing strong correlation; see section 5. Note that for differentiable functionals of the orbitals or density matrix, it is possible to carry out KS calculations via OEP, but the resulting frontier OEP eigenvalues are not equal to the chemical potentials; a correction is needed.[237]

Expanding these relations and *assuming* that the functionals under discussion satisfy the exact linearity condition (eq 52) and are simply differentiable, for functionals depending explicitly on the electron density $\rho(\mathbf{r})$ we now have

$$\epsilon_{HOMO} = -I \tag{66}$$

$$\epsilon_{LUMO} = -A \tag{67}$$

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and for functionals depending explicitly on the electron density matrix $\rho_s(\mathbf{r}',\mathbf{r})$

$$\epsilon_{\mathrm{HOMO}}^{\mathrm{GKS}} = -I \tag{68}$$

$$\epsilon_{\mathrm{LUMO}}^{\mathrm{GKS}} = -A \tag{69}$$

While the connection of the KS HOMO eigenvalue to $-I$ has been well established,[253,223] the physical meaning of the KS LUMO eigenvalue and both frontier GKS eigenvalues have only been developed recently.[237] How well these frontier KS and GKS eigenvalues approximate the experimental values of $-I$ and $-A$ is a different question. The answer depends on how well the functional satisfies the linearity condition.

We have seen in Figure 4 that commonly used functionals, for a system such as the carbon atom, do not obey the assumption in eqs 66−69, because they do not have the correct linear behavior in between the integers. For small systems, the eigenvalues from a GGA functional will typically underestimate I by about 100 kcal/mol and overestimate A by a similar amount. However, several functionals have now been developed that have improved straight line behavior. For molecules, these have tended to include some amount of long-range Hartree−Fock exchange, e.g., rCAM-B3LYP or BNL.[94,266] These functionals give a good prediction of frontier eigenvalues.[94,237,267] Other approaches use similar ideas.[268−270] A fixed amount of range separation does not always result in consistently good results, and this has led to the possibility of tuning the range separation for the systems of interest.[271,272] This understanding and approach for molecules is very enlightening and useful, although, it must be acknowledged that there is some way to go before it fully helps to correct the band gap across the whole range of systems including those in the solid state. These often present a slightly different challenge. Continuing along this direction of thought, a nonempirical scaling correction method, inspired by eq 51, has been developed to restore the straight-line behavior of the total energy. It is applicable to a variety of mainstream density functional approximations.[273] A scaled version of a modified LDA predicts band gaps with a an accuracy consistent for systems of all sizes, ranging from atoms and molecules to solids. The scaled modified LDA thus provides a promising tool to quantitatively characterize the size-dependent effect on the energy gaps of nanostructures.

4.1.5. Fractional Occupations vs Ensemble. The question now arises, which one is correct, the fractional or the ensemble view of DFT? This a key question and really at the heart of understanding some of the key issues. It is important to appreciate that although the energy of an isolated fractional system is of key importance, the real interest lies in understanding the results of calculations on real integer systems that, from the point of view of the density (or the density matrix Γ_1), appear to have separated into fractional pieces. If we pose the question "what do functionals predict for hydrogen with half an electron?", the ensemble approach would require us to calculate a system with no electrons (which as far as we know no functional gets incorrect!) and then the hydrogen atom with one α electron for which all functionals (e.g., PBE, B3LYP, etc.) do a very reasonable job. The linear combination of these would give an excellent prediction for the energy of $H^{1/2+}$. However, the very same functionals applied to stretched H_2^+ would give qualitative failure, as seen in Figure 2. This alone seems to us to highlight the relevance of understanding the importance of functionals for calculations with fractional *but* only because of their appearance in real integer calculations. This idea is simply encapsulated by

$$\Gamma_1^N(\mathrm{A}\cdots\mathrm{B}) = \Gamma_1^{J+\delta}(\mathrm{A}) + \Gamma_1^{K+(1-\delta)}(\mathrm{B})$$

As all the usual functional forms such as E_x^{HF} satisfy size consistency if A and B are well separated

$$E_x^{\mathrm{HF}}[\Gamma_1^N(\mathrm{A}\cdots\mathrm{B})] = E_x^{\mathrm{HF}}[\Gamma_1^{J+\delta}(\mathrm{A})] + E_x^{\mathrm{HF}}[\Gamma_1^{K+(1-\delta)}(\mathrm{B})]$$

$$E_x^{\mathrm{LDA}}[\Gamma_1^N(\mathrm{A}\cdots\mathrm{B})] = E_x^{\mathrm{LDA}}[\Gamma_1^{J+\delta}(\mathrm{A})] + E_x^{\mathrm{LDA}}[\Gamma_1^{K+(1-\delta)}(\mathrm{B})]$$

and the resultant total energies in an integer system suffer from the fractional errors of the functionals. However, at infinite separation these errors are just an illustration of a deeper error that can be seen at all distances such as at very finite distances (even at 3 Å the functionals are already in large error by 20 kcal/mol).

Hartree−Fock for Fractional Charges and Ensembles. One question that often arises is how it is possible for a wave function based method, such as Hartree−Fock, to be carried out for fractional numbers? By its very nature the wave function is only definable for an integer number of electrons. This is analogous to the situation that arises in Kohn−Sham DFT, where if we restrict ourselves to integer occupation of Kohn−Sham orbitals, fractional calculations are not possible. When we get to the level of the Hartree−Fock equations and energy expression, which come from a wave function, they can in fact be written exactly in terms of the one-particle density matrix and easily extended to fractional occupations.

Consider the exchange part of the Hartree−Fock energy, which can be written as below in terms of the one-particle density matrix, $\rho_s(\mathbf{r},\mathbf{r}') = \Sigma_i \phi_i(\mathbf{r})\,\phi_i(\mathbf{r}')$

$$E_x^{\mathrm{HF}}[\rho_s] = -\frac{1}{2}\int\int \frac{\rho_s(\mathbf{r},\mathbf{r}')^2}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$$

For two possible integer number of electrons N and $N+1$ with two wave functions $\Psi^N \rightarrow \rho_s^N$ and $\Psi^{N+1} \rightarrow \rho_s^{N+1}$, we can consider a fractional system in terms of

$$\begin{aligned} E_x^{\mathrm{frac}}[\rho_s^{N+\delta}] &= -\int\int \rho_s^{N+\delta}\rho_s^{N+\delta}/2r_{12}\,d\mathbf{r}_1\,d\mathbf{r}_2 \\ &= -\int\int [(1-\delta)\rho_s^N + \delta\rho_s^{N+1}] \\ &\quad \times[(1-\delta)\rho_s^N + \delta\rho_s^{N+1}]/2r_{12}\,d\mathbf{r}_1\,d\mathbf{r}_2 \\ &= -\int\int [(1-\delta)^2\rho_s^N\rho_s^N + 2\delta(1-\delta)\rho_s^N\rho_s^{N+1} \\ &\quad + \delta^2\rho_s^{N+1}\rho_s^{N+1}]/2r_{12}\,d\mathbf{r}_1\,d\mathbf{r}_2 \end{aligned}$$

However, the ensemble energy is given by

$$\begin{aligned} E_x^{\mathrm{ensemble}}[\rho_s^{N+\delta}] &= (1-\delta)E_x[\rho_s^N] + \delta E_x[\rho_s^{N+1}] \\ &= -\int\int [(1-\delta)\rho_s^N\rho_s^N + \delta\rho_s^{N+1}\rho_s^{N+1}]/2r_{12}\,d\mathbf{r}_1\,d\mathbf{r}_2 \end{aligned}$$

The first case corresponds to the fractional perspective, whereas the second one refers to the ensemble mixture. They give different results for approximate functionals. The key result is the understanding that, for a system that separates into fractional pieces, such as stretched H_2^+, an approximate functional that is not linear in its basic variable (the Coulomb is quadratic in ρ, Hartree−Fock is quadratic in ρ_s, all DFT pieces

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are nonlinear in ρ) *will* have a difference between the ensemble and fractional energies.

This important understanding also has implications for various other methods, for example, many-body theories such as RPA, where the basic variable in this case is the single particle Green's function G_0 for the noninteracting reference system. For these methods, the valid and undoubtedly most important way to understand the fractional pieces found in H_2^+ is again to take the ensemble at the level of the basic variable and evaluate the energy of the ensemble Green's function. $G_0^{N+\delta} = (1 - \delta)G_0^N + \delta G_0^{N+1}$, $E^{\text{frac}}[G_0^{N+\delta}]$.[274] Again, for approximate methods this fractional result may well be different from the ensemble at the level of the energy, as has been seen for RPA in stretched H_2^+.[275]

4.1.6. Delocalization Error. Commonly used approximate functionals deviate from the exact linearity condition for fractional charges with a convex behavior.[251,252] This convex behavior means approximate functionals will give too low energies for a delocalized charge distribution, and/or tend to favor fractional charges or delocalized charge distributions over the integer or localized ones. This results in the definition of the delocalization error, as related to the negative deviation of the $E(N)$ curve from the exact linearity condition for fractional charges. Conversely, for functionals with concave behavior for fractional charges, such as HF, delocalization of the charge will raise the energy. Such functionals tend to predict too localized charge distributions and hence give rise to *localization error*.[252]

An understanding of this deviation from linearity can be viewed as a problem of fractional charges. It may well be key for the future development of functionals. However, one usually does not carry out a calculation on an explicitly fractional system, and furthermore, for normal calculations of real molecules we cannot explicitly see such separation in these fractional pieces. For example, in H_2^+ we can only make the division into two fractionally charged atoms as the internuclear separation approaches ∞. However, there are errors throughout the binding curve. For example, at 2 Å, LDA/GGA already have an error of 20 kcal/mol. Another useful way of understanding the problem is from a perspective of the electron delocalizing. Consider a typical GGA calculation on a single proton and a single electron (a Hydrogen atom), a case that exhibits no important error. However, if we add a second proton infinitely far away, which should of course have no effect on the energy, it gives the electron the possibility to delocalize. The GGA functional takes this possibility into consideration and puts half an electron on each proton. Very importantly, this electron delocalization is coupled with a massive drop in energy. If another proton is added, the electron will delocalize further with a third of an electron on each proton and an even lower energy with the GGA functional. All of these cases should be energetically the same, but the GGA functional gives an incorrect lowering of the energy the more the electron delocalizes.

Another prototypical example where the systematic error can be seen clearly is the ionization of clusters of He atoms at finite distances, as seen in the case of Figure 5 for an 8 × 8 square of He atoms separated by 2 Å . The density difference illustrates nicely the error of a GGA functional, such as PBE, which will spread out the electron density. However, the error in the density is actually secondary, since it is driven by the energy. This can be seen from the ionization energy from the different methods: from CCSD it is 500 kcal/mol and for PBE (which is very similar to other GGA functionals) it is 340 kcal/mol, and this only changes by around 10 kcal/mol if the HF density is used. The density (although visually illustrative) is only a secondary factor, because the overriding problem is the energy given by the functional.

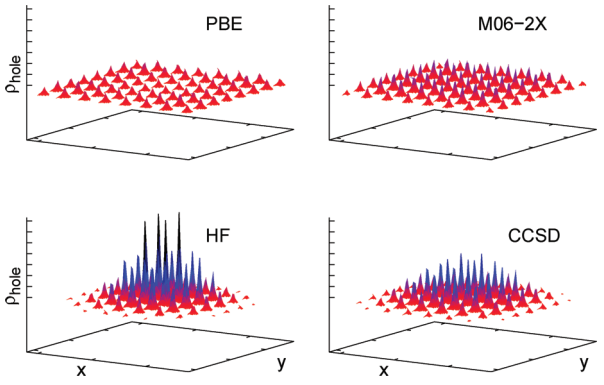

Figure 5. Visualization of the delocalization error: The density difference or hole, $\rho_{\text{hole}} = \rho_N - \rho_{N-1}$, for the ionization process $He_{64} \rightarrow He_{64}^+$ is shown for four different methods. CCSD gives a good description of ρ_{hole} in this system. In comparison a GGA functional, such as PBE, overdelocalizes ρ_{hole}, whereas Hartree−Fock overlocalizes ρ_{hole}. A hybrid functional, such as M06-2X, which has quite a large amount of exchange (58%), still does not adequately describe ρ_{hole}.

The delocalization error is not just intrinsic to stretched systems or odd electron systems. It is clearly seen in these cases, but these are just examples of delocalized densities. Any system with a delocalized density may be affected by similar errors, perhaps even metallic solids. However, it is possible to see some trends in much smaller systems, for example, in closed-shell organic molecules, which are often thought to be relatively simple in terms of their electronic structure. Despite this there have been several problems identified in the literature.[276,277] One such problem for DFT is the case of the isomers of [10]-annulene.[278,279] For example, let us consider the twist and heart conformations; one has a density that is localized and the other delocalized. The results with many approximate functionals relative to CCSD(T) calculations are given in Table 4. CCSD(T) gives the twist isomer a lower value than the heart conformation by about 6 kcal/mol, whereas GGA functionals predict the opposite by around 8 kcal/mol, an error of around 14 kcal/mol. This reflects the tendency of GGA functionals to give too low an energy for delocalized charge distributions. This is a quite large and systematic error. Furthermore, from the results presented in Table 3 the performance of functionals can be seen to be highly related to the error on a fractionally charged system (in this case the ionization of methane, $CH_4^+ \rightarrow CH_4$). This is the key understanding of the delocalization error that relates these two problems and highlights the fundamental issue that a mathematical error of the functional for fictitious systems relates in fact to problems in chemistry, not just the hypothetical chemistry of infinitely stretched molecules but, in this case, an important isomerization energy of a real organic molecule. Overall, the delocalization error of approximate functionals is very important and has clear physical consequences. It is also important to realize that the distribution of the electron density can actually be dictated by errors of the functional rather than the underlying physics of the problem.

4.2. Stretched H_2 and Static Correlation Error

Many of the problems regarding DFT applications reported in the literature can be explained from the perspective of delocalization error or similar issues. However, there are many other

Table 4. Seeing the Delocalization Error in Organic Chemistry: Errors of Many Functionals for the Twist to Heart Isomerization Energy of [10]-Annulene, $C_{10}H_{10}$[a]

functional	annulene	error[CH_4^{frac}]
LDA	−14.27	−15.97
GGA and Meta-GGA Functionals		
BLYP	−13.95	−15.62
HCTH	−14.37	−15.54
HCTH407	−14.47	−15.42
PBE	−14.08	−15.54
BP86	−14.12	−15.44
BPBE	−14.05	−15.48
OLYP	−14.93	−15.59
OPBE	−15.04	−15.45
TPSS	−14.47	−14.97
M06-L	−11.44	−14.61
Hybrid Functionals		
TPSSh	−12.75	−13.08
B3LYP	−10.60	−11.76
PBE0	−9.91	−10.66
B97−1	−10.34	−11.74
B97−2	−10.60	−11.70
B97−3	−9.35	−10.69
M06	−6.86	−10.92
M06−2X	−2.74	−6.23
M06-HF	2.66	1.19
HF	3.90	4.38
HFLYP	2.70	3.83
Range-Separated Functionals		
CAMB3LYP	−3.23	−5.19
LCBLYP	2.33	−0.99
rCAMB3LYP	4.66	1.89
LCPBE	3.83	0.60
HSE	−10.33	−11.93

[a] The third column gives the error of many different functionals for fractional CH_4, error[CH_4^{frac}] = $\sum_{i=0}^{i=10} E[CH_4^{(i/10)+}] - \{(1-0.1i)E[CH_4] + 0.1iE[CH_4^+]\}$. There is a strong indication in the errors that the error of delocalization in the aromatic vs nonaromatic isomerization is related to the delocalization error of fractional charges.

molecules where this does not apply, especially in terms of the performance of functionals. Probably the simplest illustration of this is provided by the closed-shell stretching of H_2 (Figure 6).[116,137,280−282]

Most approximate functionals fail to properly stretch H_2. Of course there is the possibility of breaking the spin symmetry, which may be allowable at infinite separation, but this solution does not give the correct ground state for any other distance. Both from experiment and also accurate wave function calculations, the ground state of H_2 should be closed-shell with zero spin density everywhere $[\rho_\alpha(\mathbf{r}) - \rho_\beta(\mathbf{r}) = 0, \forall\, \mathbf{r}]$. If we look again at infinity, it becomes clear that the true problem is that many states that should be degenerate are not; they are given different energies by approximate functionals.

4.2.1. Static Correlation and Degeneracies. The usual understanding of stretching H_2 and related problems is that of static correlation. From a quantum chemistry perspective, it corresponds to a situation that is inherently multideterminental, and single determinant approaches will fail. For example, for infinitely stretched H_2, HF has an error of around 190 kcal/mol. Perturbation theory built from this erroneous starting point breaks down, and in fact, the MP2 energy goes to $-\infty$ because of the degeneracy of the orbitals.[283] The quantum chemical methods used to treat these difficult cases are generally built upon a multiconfigurational starting point such as CASSCF. This gives rise to methods such as CASPT2, MRCI, or MRCCSD. There have also been some success in combining these wave function ideas with DFT to give methods such as CASDFT.[284−286] However, in these cases, it is a deeper understanding of Kohn−Sham DFT that is required. It has even been questioned if Kohn−Sham DFT applies in these difficult situations involving degeneracies and near-degeneracies. We believe this is merely a challenge for the exchange−correlation functional, which is formalized in the next section in terms of fractional spins fully within Kohn−Sham DFT.

4.2.2. Fractional Spins. Another key way to view the problem of static correlation is by considering the division of infinitely stretched H_2 into two closed-shell hydrogen atoms. Each of these subsystems is a hydrogen atom with one electron, but with $^1/_2$ spin up and $^1/_2$ spin down ($H[^1/_2\alpha, ^1/_2\beta]$). It is obvious that the closed-shell hydrogen atom could be calculated using a restricted calculation but with an odd number of electrons. However, we can extend the fractional occupation formalism to have more than one orbital fractionally occupied. The general principle is that for a degenerate orbital one can have fractional occupation of more than one frontier orbital. In the case of a g-fold degeneracy.

$$n_i = \begin{cases} 1 & \text{for} \quad \epsilon_i < \epsilon_F \\ \delta_i & \text{for} \quad \epsilon_i = \epsilon_F \\ 0 & \text{for} \quad \epsilon_i > \epsilon_F \end{cases} \qquad \sum_i^g \delta_i = 1 \tag{70}$$

The formal occupation numbers apply only in the case of an exact degeneracy. However, we can also extend the idea to a case of near degeneracy or maybe in approximate DFT calculations when orbitals that should be degenerate are not exactly so. For example, consider the case of a fractional spin hydrogen atom, $H[0.6\alpha,0.4\beta]$, which, from Figure 7, would come from the degenerate wave function $\Psi = [(0.6)^{1/2}\Psi_1 + (0.4)^{1/2}\Psi_2]$. From the same arguments as above for stretched H_2, it of course must be degenerate in energy with a normal hydrogen atom. This gives rise to an exact condition that should be satisfied by exchange−correlation functionals; the constancy condition for fractional spins[282]

$$E\left[\sum_{i=1}^{g} c_i\rho_i\right] = E[\rho_j] = E^0(N), \quad j = 1, \ldots, g \tag{71}$$

In the case of the energy of the H atom, $E[n_\alpha n_\beta]$, it can be expressed as

$$E[1,0] = E[0,1] = E\left[\frac{1}{2},\frac{1}{2}\right] = E[\gamma,(1-\gamma)] \tag{72}$$

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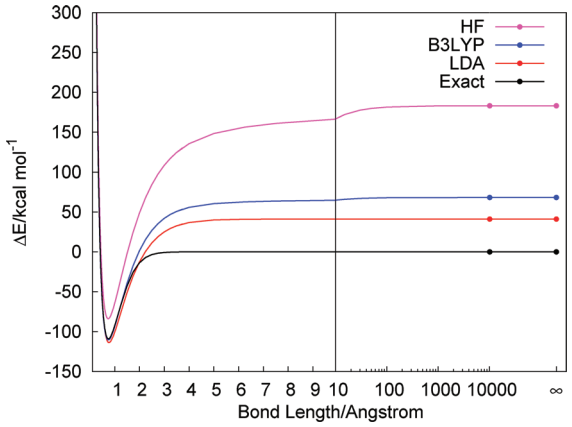

Figure 6. Binding energy curves of closed-shell stretched H_2, calculated using LDA, B3LYP, and EXX (all from B3LYP density and orbitals), to be compared with an exact curve (FCI in a cc-pVQZ basis set). After 10 Å the x axis changes to a logarithmic scale and the final point at infinity is from an explicitly fractional spin calculations ($2 \times H[^1/_2\alpha, ^1/_2\beta]$).

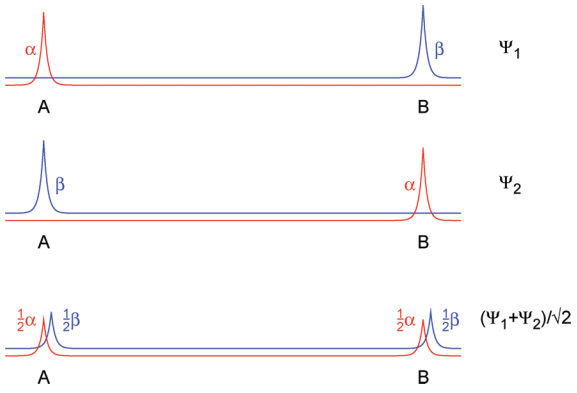

Figure 7. Fractional spins in stretched H_2. Ψ_1 and Ψ_2 are two degenerate and orthogonal wave functions. Any combination of these two wave functions is degenerate in energy. One example given is $(\Psi_1 + \Psi_2)/2^{1/2}$, which yields a very different looking density. The degeneracy is obvious from the wave function (in Hilbert space) but is a real challenge for the energy functional (in 3D space).

where $0 \leq \gamma \leq 1$. It can clearly be seen that the error of stretched H_2 is nothing more than a failure to satisfy the exact fractional spin constancy condition.

It is also possible to have fractional-spin states arising from an ensemble of states that are degenerate because of other symmetries, such as spatial degeneracies. This can be understood by considering an isolated open-shell atom, such as the boron atom,[282] which has a 3-fold spatial degeneracy between the p_x, p_y, and p_z. DFAs gives rise to lower energy nonspherical solutions such as $p_x^1 p_y^0 p_z^0$ that should be degenerate with many other states such as the spherical one, $p_x^{1/3} p_y^{1/3} p_z^{1/3}$ that has a fractional occupation of each p orbital. However, violation of the constancy condition, eq 71, by DFAs means they give an incorrectly higher energy to all fractionally occupied states, including the spherical one. The fractional spin error is a basic error and, like the fractional charge error, can produce qualitatively wrong density distributions.

Fractional spins have been used to describe the spin state splitting in open-shell singlet molecules successfully with normal DFA, thus preventing spin contamination associated with normal broken symmetry calculations of the same functional.[287]

4.3. Coming in from Infinity

The fractional understanding clearly relates to molecules at the infinite distance limit, but it is also evident that there are clear related deficiencies as one comes in from infinity toward finite distances. Again, let us consider stretched H_2^+. Here the failure of local functionals is not just the value of the energy at infinity but also the asymptotic behavior as one approaches infinity. In fact, for LDA and GGA functionals, we can restate the problem that they have an incorrect asymptotic R^{-1} behavior[288] (which is of course coupled with the incorrect $R = \infty$ behavior). This is because they fail to correct for the asymptotic behavior of the Coulomb term. The challenge of the asymptotic behavior of the functional can be seen in the contrasting behavior of functionals in stretched H_2. In this case, LDA and GGA functionals have the correct asymptotic behaviors (just the wrong $R = \infty$ behavior). It is Hartree−Fock this time that has the incorrect R^{-1} behavior, as now the Coulomb interactions between electrons and nuclei are correct at the level of the Coulomb term and an additional R^{-1} from the Hartree−Fock term is incorrect. To reiterate, the long-range interaction contained in the Hartree−Fock exchange energy gives the *correct* behavior for stretched H_2^+, but the *incorrect* behavior for stretched H_2.

In this simple case of two protons with one and two electrons, this long-range asymptotic behavior for DFA illustrates a difficult challenge in functional construction. This raises the question of whether to use long-range Hartree−Fock exchange or not. Solid-state systems have a very different external potential and there is no doubt that the screening of long-range electron−electron interactions[289,88,290] plays an important role and must also be understood from this perspective.

5. STRONG CORRELATION

We have just illustrated some massive failures of DFT functionals for two of the simplest systems in chemistry, which can be understood from the perspectives of fractional charges and fractional spins. Simultaneous understanding of both of these concepts is of key importance and is perhaps the simplest manifestation of a term coming from the physics community: "strong correlation". A strongly correlated system conjures up an image of a system in which electron interactions are particularly difficult to describe. However, in DFT, the nature of the problem changes, and it can be viewed from the perspective of the *functional*. The challenge of strong-correlation in DFT is actually to find *one* functional that works for all systems. The simplest test of this concept is to ask if a single functional can simultaneously work for two systems, infinitely stretched H_2 and H_2^+ or, equivalently, a hydrogen atom simultaneously with fractional charge and fractional spin. More broadly, we would like to see functionals with significant simultaneous reduction of the delocalization and the static correlation error for all systems.

The understanding of correlation arising from a quantum chemistry perspective divides the correlation energy into dynamic correlation and nondynamic correlation (also called left−right or static correlation). In quantum chemistry, the correlation energy, E_c, is defined by

$$E_c = E_{\text{exact}} - E^{\text{HF}} \tag{73}$$

However, the division into dynamic and static correlation is not defined rigorously. In terms of "hand-waving" arguments,

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dynamic correlation is roughly associated to "simple" correlations, describable by atomic-like correlation (due to Coulomb repulsion). On a DFT level, it is describable by correlation functionals such as $E_c^{LYP}[\rho]$ or $E_c^{PBE}[\rho]$, not unlike the correlations that would be seen in the uniform electron gas. Static correlation appears in situations where multiple determinants associated with degeneracy or near degeneracy are needed.[291] The classic extreme example is that of dissociating H_2. First at equilibrium distance, HF is improved by MP2 to give a very good description and also happens to be reasonably corrected by HF + $E_c^{LYP}[\rho]$. However, as H_2 is stretched, the basic Hartree−Fock description gets even worse, HF + MP2 breaks down, and HF + LYP is basically just as wrong as HF. This is often described as pure nondynamical correlation or left−right correlation.[48] This gives rise to some important questions. What does a DFT view have to add to this understanding? Can we shed any light on the connection or difference between static correlation of quantum chemistry and strongly correlated physics? Are they the same or different?

While the general and precise definition of static correlation energy is difficult, a clear and rigorous definition of *static correlation error* of density functionals has been given: it is the deviation from the constancy condition for fractional spins.[282] It is peculiar that we cannot define static correlation energy itself clearly, but we can detect if a DFA correctly or incorrectly describes it.

5.1. Errors for H_2^+ and H_2 at the Same Time

The errors seen in the previous section for H_2^+ (delocalization error) and H_2 (static correlation error) are extremely important. However, it is our contention that a much deeper understanding comes from a consideration of both at the same time. In chemistry, the simplest atom has one proton and the simplest molecule has two protons with one or two electrons. The simplest distance mathematically is either 0 or ∞; 0 represents another atom. Therefore, our simplest molecule has two protons separated by ∞ with one or two electrons. So infinitely stretched H_2^+ and infinitely stretched H_2 are the two simplest possible molecules in the chemical universe. The trivial exact solutions to the Schrödinger equations give the energies of these systems, $-0.5E_h$ and $-1E_h$, respectively, as well as exact densities that are known in closed form. It is surprising that these two simple and trivial molecules are still an incredible challenge for DFT. To consider more clearly these two molecules as one conceptual challenge, we will group them together as the hydrogen test set (HTS). To test an approximate functional for this set, one can carry out molecular calculations for the molecules at a very large bond length, making sure to impose symmetry. Alternatively, one can carry out explicit fractional charge and spin calculations for the atom, which is often much easier.

Strong correlation has been phrased in many different ways.[292−294] However, the simultaneous consideration of the energies of the two simplest molecules in the chemical universe, H_2^+ and H_2, poses the question of strong correlation in an extremely useful manner. Table 5 and Figure 8 show the performance of different approximate functionals for the HTS. Currently, there is no functional that is even remotely capable of describing these two systems. The performances on the standard thermochemistry and kinetics can give errors as small as 3 kcal/mol. However, for these two simple and trivial molecules, the average error is around 60 kcal/mol. This average error is virtually constant, irrespective of the individual performance on either system or the particular form of the functional, whether it be GGA or hybrid or range-separated and whether it be semiempirical or parameter-free. The error analyzed here is not dependent on these aspects of the functional, although, of course, we have seen that there is much of chemistry that is, for example, improvement on the sets in section 2. Furthermore, this particular view of the error has not been used in the construction of functionals. We have also included some performance of functionals of the unoccupied orbitals and eigenvalues, mainly to illustrate that despite their increased complexity they do not satisfy this issue either. This is also true for other methods beyond DFT, such as functionals of the first-order density (1RDMFT). Here, the simplest such approximation, known as the Müller functional, corrects H_2 but only at the cost of a massive error

Table 5. All Functionals Fail for the Simplest Molecules: Individual Errors (in kcal/mol) for Infinitely Stretched H_2^+ and H_2 as Well as the Mean Absolute Error of Both, the Hydrogen Test Set (HTS)[a]

functional	H_2^+	H_2	HTS
LDA	−62.96	40.91	51.93
GGA and Meta-GGA Functionals			
BLYP	−68.86	44.52	56.69
HCTH	−69.80	46.15	57.97
HCTH407	−69.25	48.32	58.79
PBE	−66.70	51.69	59.20
BP86	−66.64	43.99	55.32
BPBE	−67.68	51.05	59.36
OLYP	−69.82	43.19	56.50
OPBE	−68.64	49.72	59.18
TPSS	−63.87	52.50	58.19
M06-L	−62.61	63.17	62.89
Hybrid Functionals			
TPSSh	−57.31	63.64	60.48
B3LYP	−54.17	67.93	61.05
PBE0	−49.29	81.88	65.59
B97-1	−53.90	77.50	65.70
B97-2	−55.14	76.72	65.93
B97-3	−49.92	81.45	65.68
M06	−53.16	77.01	65.08
M06-2X	−36.65	103.45	70.05
M06-HF	−15.83	140.80	78.31
HF	1.77	182.58	92.17
HFLYP	1.77	165.90	83.83
Range-Separated Functionals			
CAMB3LYP	−30.40	110.39	70.40
LCBLYP	−14.76	139.77	77.26
rCAMB3LYP	−5.21	157.03	81.12
LCPBE	1.96	169.49	85.72
HSE	−56.08	70.19	63.13
Functionals of the Unoccupied Orbitals			
RPA	−108.0	0.0	54.0
RPAE	0.0	120.0	60.0
MP2	0.0	−∞	∞

[a] $\text{error}_{HTS}(H_2^+) = (E_{H_2^+}^{DFA} - E_H^{DFA})$ and $\text{error}_{HTS}(H_2) = (E_{H_2}^{DFA} - 2E_H^{DFA})$. Although the individual errors for each molecule depend on the particular functionals, the mean absolute error for both, the HTS column, is very similar and disastrous for all functionals.

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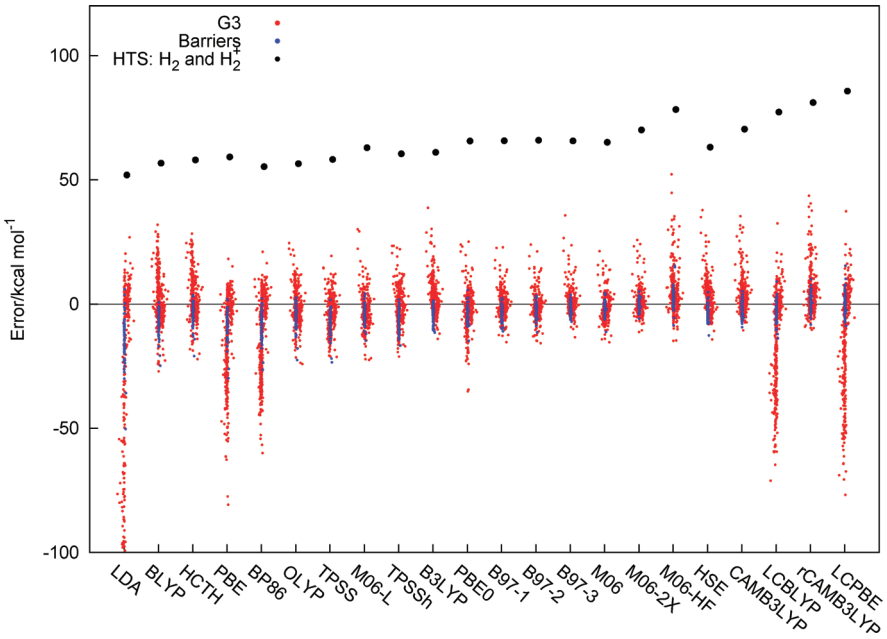

Figure 8. Errors of approximate functionals. All the individual errors of the G3 set and set of barriers are shown along with the MAE for the two molecules of the HTS. Despite the improvement on the G3/barriers, all functionals fail for the two simplest molecules in the whole of chemistry.

for H_2^+. Similar results are found for functionals of the second-order density matrix (2-RDM) with approximate N-representability conditions. Without additional corrections,[295] they are only able to tackle problems of static correlation[296] at the cost of failure, with too low energies, for stretching of systems that can dissociate to give fractional charges.[297,298] This is an incredible challenge!

Of course, this challenge presented by two protons with one and two electrons captures some of the most difficult physics required for functionals to reproduce. It even poses the fundamental question, is it possible to do it fully within the realm of KS DFT? Of course, the Hohenberg−Kohn theorem and the other foundational theorems of DFT provide us with the knowledge and determination that at least it is not an impossible problem. However, the performance of the common list of functionals provides us with what is truly a great challenge. Indeed, it is evident that we need a different perspective and new ideas in functionals. For example, we cannot just refit the parameters in functionals and hope that they can successfully give both H_2 and H_2^+. In this regard, we feel it is extremely important to see the connection between H_2 and H_2^+ that arises naturally in DFT by the use of the same exchange−correlation functional. We do this in the following section by considering more general fractional occupation of orbitals, incorporating both fractional charges and fractional spins simultaneously. This allows us to consider a single hydrogen atom with fractional occupations, exactly what is found at the stretched limit of both H_2 and H_2^+, which clearly shows the strong connection between the two systems.

5.2. Fractional Charges and Fractional Spins

The previous behavior for fractional charges[253] and fractional spins[282] has been combined in to one unified condition, which is called the flat-plane condition[299]

$$E\left[\frac{1}{q}\sum_{i=1}^{g_N} c_i\rho_{N,i} + \frac{1}{q}\sum_{j}^{g_{N+1}} d_j\rho_{N+1,j}\right] = \frac{q-p}{q}E(N) + \frac{p}{q}E(N+1) \tag{74}$$

Here, p, q, c_i, and d_i are all positive real numbers, $\sum_j^{g_{N+1}} d_j = p$, and $\sum_{i=1}^{g_N} c_i = q - p$. The degeneracy is g_N for the N electron system and is g_{N+1} for the $N+1$ electron system. The degeneracies in the flat-plane condition go beyond the spin symmetry and include all other degeneracies, either symmetry-related or not. This is an exact condition for the energy from any method, which is most readily understood for the hydrogen atom. The energy of the H atom where the number of electrons is between 0 and 1 or 1 and 2 can be represented by the following two equations respectively,

$$E[\delta(\gamma\rho^{\mathrm{H}}_{\alpha,0} + (1-\gamma)\rho^{\mathrm{H}}_{0,\beta})] = \delta E[\mathrm{H}] \tag{75}$$

$$E[(1-\delta)(\gamma\rho^{\mathrm{H}}_{\alpha,0} + (1-\gamma)\rho^{\mathrm{H}}_{0,\beta}) + \delta\rho^{\mathrm{H}^-}_{\alpha,\beta}] = (1-\delta)E[\mathrm{H}] + \delta E[\mathrm{H}^-] \tag{76}$$

Here, $0 \le \gamma \le 1$, $0 \le \delta \le 1$, and $\rho^{\mathrm{H}}_{\alpha,\beta}$ is the density of hydrogen atom with occupation α/β for spin up and spin down orbital. These equations are easiest to understand when represented pictorially, such as in Figure 9, where the behavior of the energy of the hydrogen atom is shown as a function of fractional occupation numbers.

Previously, we noted an alternative view (Figure 3d) of fractional systems, which directly connects to the energy of integer systems. The same argument holds here. In Figure 10 we consider stretched molecules in symmetric arrangements. One such example is infinitely stretched $H_{20}{}^{8+}[7\alpha,5\beta]$ in which all the electrons are symmetrically distributed. This corresponds to 20 identical fractional systems H[0.35,0.25] and a total energy of $-6E_h$ or $-0.3E_h$ per H atom. In practice, we could attempt to carry out DFT calculations on the $^3H_{20}{}^{8+}$ at infinite separation. But, as previously illustrated for H_2^+, it is simpler to utilize explicit fractional occupations.

We now need to emphasize the significance of Figures 9 and 10, which illustrate some of the most important concepts in DFT. In these figures, a discontinuous derivative of the functional is transformed into energetic performances for real molecules.

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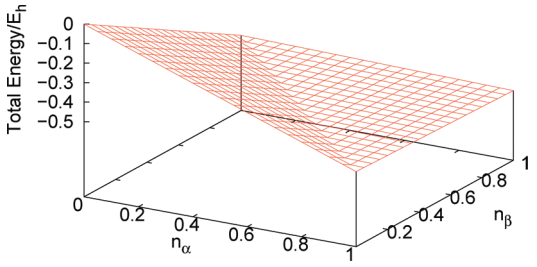

Figure 9. The flat-plane condition. The exact energy of the hydrogen atom with between zero and two electrons.

Thus, the dots in Figure 10 represent energies of numerous stretched molecules, whose correct solution is a pivotal challenge for the exchange−correlation functional. The errors for H_2^+ and H_2 in Table 5 are a particular subset of the flat plane (Figure 10) and perhaps represent the most challenging molecules for approximate functionals. Although we previously realized the importance of the solution of these two molecules (ref 300), we did not quite fully appreciate the challenge of having a single functional capable of simultaneously solving both H_2^+ and H_2. This is due to the connection between the exchange−correlation functional of these two systems. This is clearly illustrated in Figure 9.

We now consider the performance of four approximate functionals for the flat-plane condition (Figure 11). These four approximate functionals completely fail to give the exact behavior for the flat plane. This is due to the fact that they miss the correct discontinuous behavior on going through one electron. All the other functionals tested (those in Table 5) also fail for the flat plane (data not shown), which is also to be expected as they fail for H_2^+ and H_2.

5.3. Derivative Discontinuity and Mott Insulators

We have seen in the previous sections 4.1.3 and 4.1.4 how the fractional charge perspective offers insight into the prediction of the band gap for which most density functional approximations fail. The main understanding of the gap is that there is a key change in the derivative when the orbital changes from the HOMO to the LUMO. For example, in the case of the He atom, where the HOMO is the 1s orbital and the LUMO is the 2s orbital, each term of the total energy contributes to the gap

$$\left.\frac{\partial T_s}{\partial N}\right|_{N+\delta} - \left.\frac{\partial T_s}{\partial N}\right|_{N-\delta} = \langle \phi^{1s}| -\frac{1}{2}\nabla^2|\phi^{1s}\rangle - \langle \phi^{2s}| -\frac{1}{2}\nabla^2|\phi^{2s}\rangle \tag{77}$$

$$\left.\frac{\partial V_{ne}}{\partial N}\right|_{N+\delta} - \left.\frac{\partial V_{ne}}{\partial N}\right|_{N-\delta} = \langle \phi^{1s}|v_{ext}|\phi^{1s}\rangle - \langle \phi^{2s}|v_{ext}|\phi^{2s}\rangle \tag{78}$$

$$\left.\frac{\partial J}{\partial N}\right|_{N+\delta} - \left.\frac{\partial J}{\partial N}\right|_{N-\delta} = \langle \phi^{1s}|v_J|\phi^{1s}\rangle - \langle \phi^{2s}|v_J|\phi^{2s}\rangle \tag{79}$$

$$\left.\frac{\partial E_x^{LDA}}{\partial N}\right|_{N+\delta} - \left.\frac{\partial E_x^{LDA}}{\partial N}\right|_{N-\delta} = \left\langle \phi^{1s}\left|\frac{4}{3}c_D\rho^{1/3}\right|\phi^{1s}\right\rangle - \left\langle \phi^{2s}\left|\frac{4}{3}c_D\rho^{1/3}\right|\phi^{2s}\right\rangle \tag{80}$$

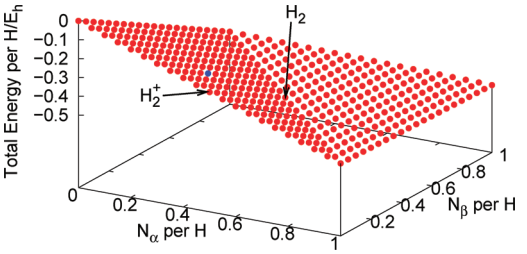

Figure 10. Flat-plane condition from the perspective of stretched molecules. All the dots correspond to an infinitely separated hydrogen clusters with up to two electrons per hydrogen. $^3H_{20}^{8+}$ as discussed in the text is represented by a blue dot.

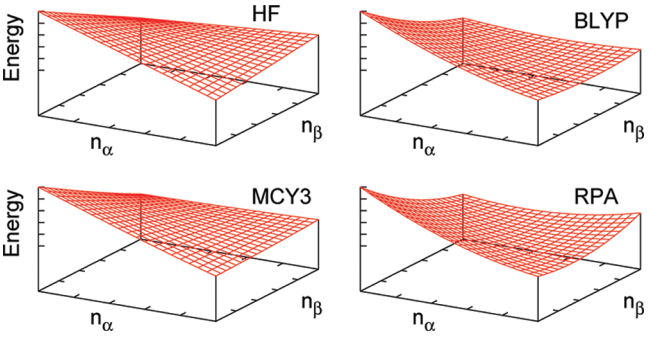

Figure 11. Performance of some representative approximate functionals for the flat plane condition All functionals are qualitatively wrong and are missing the correct discontinuous behavior. This means that no functional is capable of giving the energies of the stretched H_2^+ and H_2.

$$\left.\frac{\partial E_x^{HF}}{\partial N}\right|_{N+\delta} - \left.\frac{\partial E_x^{HF}}{\partial N}\right|_{N-\delta} = (\phi^{1s}\phi^{1s}|\phi^{1s}\phi^{1s}) - (\phi^{1s}\phi^{2s}|\phi^{1s}\phi^{2s}) \tag{81}$$

Each functional contributes to the gap because the HOMO is different from the LUMO, which is summarized by a discontinuity in the density matrix

$$\frac{\partial \rho_s(\mathbf{r},\mathbf{r}')}{\partial N} = \begin{cases} \phi_{1s}(\mathbf{r})\,\phi_{1s}(\mathbf{r}') & \text{if} \quad 1 < N < 2 \\ \phi_{2s}(\mathbf{r})\,\phi_{2s}(\mathbf{r}') & \text{if} \quad 2 < N < 3 \end{cases}$$

However, it is informative to consider a chemical species in which the HOMO and LUMO are degenerate, which is exactly the case for the closed shell H atom (or He^+ ion). There is no derivative discontinuity in the electron density and

$$\frac{\partial \rho_s(\mathbf{r},\mathbf{r}')}{\partial N} = \begin{cases} \phi_{1s}(\mathbf{r})\,\phi_{1s}(\mathbf{r}') & \text{if} \quad 0 < N < 1 \\ \phi_{1s}(\mathbf{r})\,\phi_{1s}(\mathbf{r}') & \text{if} \quad 1 < N < 2 \end{cases}$$

Consequently, the differences in all these terms are zero

$$\left.\frac{\partial T_s}{\partial N}\right|_{N+\delta} - \left.\frac{\partial T_s}{\partial N}\right|_{N-\delta} = 0 \tag{82}$$

$$\left.\frac{\partial V_{ne}}{\partial N}\right|_{N+\delta} - \left.\frac{\partial V_{ne}}{\partial N}\right|_{N-\delta} = 0 \tag{83}$$

$$\left.\frac{\partial J}{\partial N}\right|_{N+\delta} - \left.\frac{\partial J}{\partial N}\right|_{N-\delta} = 0 \tag{84}$$

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$$\left.\frac{\partial E_x^{LDA}}{\partial N}\right|_{N+\delta} - \left.\frac{\partial E_x^{LDA}}{\partial N}\right|_{N-\delta} = 0 \quad (85)$$

$$\left.\frac{\partial E_x^{HF}}{\partial N}\right|_{N+\delta} - \left.\frac{\partial E_x^{HF}}{\partial N}\right|_{N-\delta} = 0 \quad (86)$$

An equivalent system that is sometimes useful in clarifying this idea is closed-shell infinitely stretched H_2, where the HOMO orbital is $\phi_{HOMO} = \sigma_g = (1/\sqrt{2})(\eta_A + \eta_B)$ and the LUMO orbital is $\phi_{LUMO} = \sigma_u = (1/\sqrt{2})(\eta_A - \eta_B)$. This means that $\rho_{HOMO} = \rho_{LUMO}$ and also $\langle\phi_{HOMO}|-(1/2)\nabla^2|\phi_{HOMO}\rangle = \langle\phi_{LUMO}|-(1/2)\nabla^2|\phi_{LUMO}\rangle$. Therefore, in this system clearly there can be no gap due to the terms T_s, V_{ne}, and J or terms like E_x^{LDA} or E_x^{HF}. However, there must be a gap because the hydrogen atom (or two hydrogen atoms in the case of stretched H_2) has an ionization energy $I = 0.5E_h$ and an electron affinity $A = 0.028E_h$. Hence, it must have a large gap, $E_{gap} = 0.472E_h = 12.8$ eV = 296 kcal/mol. Where does this gap come from? Is it possible to obtain within DFT? Let us look at the KS type equations for the HOMO and LUMO orbitals, for example, with a hybrid functional mixing 80% LDA with 20% HF:

$$\left(-\frac{1}{2}\nabla^2 + v_{ext} + v_J + 0.8c\left(\frac{1}{2}\phi_\alpha{}^2\right)^{1/3} + 0.2\int \frac{\frac{1}{2}\phi_\alpha(\mathbf{r}')\,\phi_\alpha(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,P_{\mathbf{r},\mathbf{r}'}\right)\phi_{i\alpha} = \epsilon_{i\alpha}\phi_{i\alpha}$$

$$\left(-\frac{1}{2}\nabla^2 + v_{ext} + v_J + 0.8c\left(\frac{1}{2}\phi_\beta{}^2\right)^{1/3} + 0.2\int \frac{\frac{1}{2}\phi_\beta(\mathbf{r}')\,\phi_\beta(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,P_{\mathbf{r},\mathbf{r}'}\right)\phi_{i\beta} = \epsilon_{i\beta}\phi_{i\beta}$$

Clearly these equations show that the α Fock matrix and the β Fock matrix are equivalent through symmetry and hence so are all the orbitals and eigenvalues. Most importantly, so are the frontier eigenvalues $\epsilon_{1s\alpha} = \epsilon_{1s\beta}$. By analogy, due to spatial symmetry, this also applies to stretched H_2, whereby the frontier eigenvalues are equivalent $\epsilon_{\sigma_g} = \epsilon_{\sigma_u}$. In fact, for any odd-electron system, this will be the case. This encapsulates the problem of Mott insulators, where "band-theory" (i.e., the eigenvalue picture) breaks down.[259,299] If we return to the case of stretched H_2, we can clearly see that the $I - A = 296$ kcal/mol and $\epsilon_{HOMO} - \epsilon_{LUMO} = 0$ are not the same. That is

$$I - A \neq \epsilon_{HOMO} - \epsilon_{LUMO}$$

Using eq 53 for predicting the gap from the chemical potential discontinuity and the linearity condition for the exact functional eq 52, we arrive at

$$E_{gap} = I - A = \left(\frac{\partial E}{\partial N}\right)_v\Big|_+ - \left(\frac{\partial E}{\partial N}\right)_v\Big|_-$$

which is true for the exact functional. However, we note that $\epsilon_{HOMO}/\epsilon_{LUMO}$ or $\epsilon_{HOMO}^{GKS}/\epsilon_{LUMO}^{GKS}$ are the chemical potential only when the condition for eq 64 or 65 is satisfied. Therefore, we have to conclude that for Mott insulators, the condition for the validity of eq 64 or 65 cannot be satisfied. The exact functional *cannot* be an *explicit and differentiable functional* of the electron density $\rho(\mathbf{r})$, or the noninteracting density matrix $\rho_s(\mathbf{r},\mathbf{r}')$, for all physical densities or density matrices.[299]

The only place for functionals to be nondifferentiable is in the unknown E_{xc}. Thus, we can now write down the more general equations for the prediction of the gap,[299]

$$E_{gap} = I - A = \epsilon_{HOMO} - \epsilon_{LUMO} + \Delta_{xc} + \mathscr{D}_{xc}$$

for KS (or OEP) calculations and

$$E_{gap} = I - A = \epsilon_{HOMO}^{GKS} - \epsilon_{LUMO}^{GKS} + \mathscr{D}_{xc}$$

for GKS calculations. $\epsilon_{HOMO}^{GKS} - \epsilon_{LUMO}^{GKS}$ is the difference in the GKS frontier eigenvalues and incorporates all the discontinuity due to a change of orbitals, including the smooth part, Δ_{xc}, of an orbital dependent exchange−correlation term. Furthermore, $\mathscr{D}_{xc}$ represents only the explicit discontinuity of the exchange−correlation term and, hence, goes beyond previous work.[237,259] So for a pure Mott insulator, where the eigenvalue difference $\epsilon_{HOMO}^{GKS} - \epsilon_{LUMO}^{GKS}$ is zero,

$$I - A = \mathscr{D}_{xc}$$

It is only a change in the exchange−correlation functional that can possibly offer a gap. This implies that there is a change in the functional itself; not just a change in the density or orbitals that the functional acts on. This is a difficult concept still requiring clarification. For example, does this imply that we need a different functional for every N? Have we simply returned to performing a different FCI calculation for every different number of electrons? Or is this a different type of change in the functional? In fact, it is only that the functional has to change more than just changing the density or the density matrix put in to it.

The problem of the gap in Mott insulators is encapsulated in the energies of the flat plane. This is illustrated, in an intuitive manner, as shown in Figure 12 by a specific line of the flat planes. Namely, the closed shell line from 0 to 2, i.e. $H^+[0,0] \rightarrow H[^1/_2,^1/_2] \rightarrow H^-[1,1]$ with $n_\alpha = n_\beta = N/2$. The curves with approximate functionals in Figure 12 are, however, completely wrong. The error in the energy at one electron is exactly the static correlation error that one would see in infinitely stretched H_2 (note the RPA total energy for the spin unrestricted H atom is the same as the closed shell H atom $E_H^{RPA} = -0.52E_h$). However, the key deficiency of all the functionals is that they completely miss any discontinuous behavior as they pass through the integer $N = 1$, as can be seen in Figure 12. That is they give $\mathscr{D}_{xc} = 0$. The common error of these functionals is that the slope on either side of the integers is the same, i.e. $(\partial E/\partial N)|_{1+\delta} = (\partial E/\partial N)|_{1-\delta}$. Although discontinuous behavior is a key challenge for functionals, it is not an impossible one and we have previously presented a model illustrative functional for the H atom to correctly reproduce the flat plane behavior.[299] In another effort to satisfy the flat-plane condition, an interesting functional has also been developed recently.[301]

5.4. Integer Nature of Electrons and the Right Form for E_{xc}

The integer nature of electrons is of course present in an N-body wave function, but the transformation of this into functionals of the density is an incredible challenge. If we consider the first step along the path of approximate DFT, which is the Thomas−Fermi theory, we can see that without knowledge of

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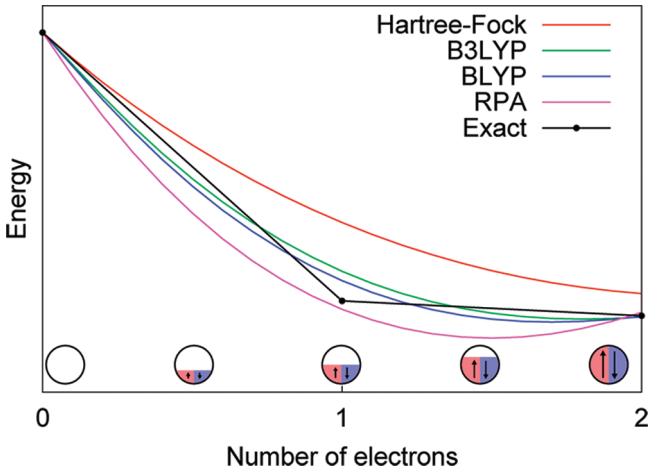

Figure 12. E vs N for the closed shell H atom, $H^+[0,0] \rightarrow H[^1/_2,^1/_2] \rightarrow H^-[1,1]$. The error seen in the value of the energy at 1 is exactly the static correlation error. However, the discontinuous behavior is missing from all the functionals and can be seen in derivatives to the left and the right at $N = 1$. The hallmark of the failures of density functional approximations for strong correlation.

the orbitals, the correction to the kinetic energy is massive and all the integer nature of electrons is missing. With the introduction of Kohn−Sham theory, even at the simplest level such as LDA, the concept of the orbital helps the kinetic energy massively and introduces some discontinuous behavior. In this case, the integer nature comes in at every two electrons. Spin DFT, the extension of LDA to LSDA, then makes this discontinuous at every single electron. However, the discontinuous behavior of LSDA, and analogously of most functionals in the literature, is not correct for all situations. We can see this above in the case of the fractional hydrogen atom (Figure 11), where the corners of the flat plane are correct but not the whole line at $N = 1$. What is needed is a new framework and better functionals that have discontinuities of the right nature at each electron number. Ultimately, this will allow the correct description of electron addition and removal and hence many other phenomena in chemistry.

5.5. Contrast between DFT and Ab Initio Quantum Chemistry

Before we conclude, we feel it is important to offer what we see as some of the differences between DFT and ab initio quantum chemistry. From one point of view, the two methods appear almost identical. In fact, the rapid rise of DFT is because of the computational similarity of solving the KS equations to the simplest possible ab initio method, HF. This similarity means that many DFT codes currently in use started out as HF and post-HF codes. However, despite this similarity, it is important to stress the philosophical difference that we see in their approaches to the electronic structure problem,

$$E_{xc}[\rho] \quad \text{versus} \quad \Psi$$

From the quantum chemistry point of view, the electronic structure challenge is clear: for a particular chemical system (specifying v and N in the Schrödinger equation), the main effort is to find the FCI wave function, Ψ. Great work has gone into this very clear challenge from both a practical and conceptual route.[302−305] This challenge for finding Ψ^{FCI} is greatest for systems that are strongly correlated.

Let us contrast this with the DFT perspective. Assuming we are given the exact $E_{xc}[\rho]$, then for each system there is a relatively trivial search to minimize the energy over density ρ. However, it is exactly the same functional that works for each and every system; therefore, it is the functional that is of the same complexity as doing FCI on all possible systems. What actually shows up is a very clear connectedness between systems. In DFT this link is through the functional E_{xc}. We can see now that the challenge is concentrated on the search and determination of the E_{xc}. Thus, the computational challenge of CI calculations for Ψ is turned into a theoretical challenge of constructing one universal $E_{xc}[\rho]$ that is exact for all densities.

For new functionals we feel it will be important to directly consider this connection between different systems as a central piece of their development, rather than hoping it somehow arises in a random consideration of molecules throughout chemistry. Of course, the functional has to work for all these individual molecules, but it is at the level of the functional that the connectedness needs to be understood and exploited. The extension to fractional charges and fractional spins is one such idea and probably there are even more connections that can play an illuminating role in functional development. Even we did not fully comprehend this connection in our earlier work.[300] Actually viewing the problems of H_2^+ and H_2 separately overlooks the true connection: the fact that it needs one functional to do both systems.

6. CONCLUSIONS

In this review, we have attempted to show some of the successes and challenges of DFT, both of which can be attributed to the exchange−correlation functional, E_{xc}. Currently, using DFT with approximate functionals means it performs well for a wide range of properties from energetics and geometries of molecules to reaction barriers and van der Waals interactions. However, we have emphasized some important problems, such as delocalization error and static correlation error, in which the currently used functionals fail.

The ability to describe the energies of stretched H_2^+ and H_2 has been shown to be a simple way of explaining the concept of strong correlation. Table 5 and Figure 8 recognize that currently no known functional is able to simultaneously describe these two systems. It is the key contribution of this review to demonstrate that the inability to correctly describe H_2^+ and H_2 has the same root in the functional as the failures of DFT in relation to strong correlation.

The basic errors highlighted in this review may not generally have a large effect at the equilibrium geometries of the most widely studied molecules. However, they will have a much greater impact as the range of molecules studied increases and the electronic structures becomes more complex, for example, in systems containing transition metals. To combat this problem, we need to develop better functionals. This, of course, requires a deeper understanding of why current functionals fail. It is this understanding that offers a path forward in functional development. For example, the formulating of relevant exact constraints, such as the flat-plane condition, and understanding what the relevant challenges of such conditions are to functionals. In this review, we have shown that the failure of all currently used functionals for the flat-plane condition highlights the need for a derivative discontinuity in the functional to give the energy of H_2^+ and H_2 and, more generally, accurately describe strong correlation. We believe innovative radically different functionals are necessary for the advancement of DFT.

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BIOGRAPHIES

Aron J. Cohen received his Bachelor's degree in Natural Sciences (Chemistry) from the University of Cambridge in the United Kingdom. He completed his Ph.D. with Prof. Nicholas C. Handy before going to Duke University to carry out 5 years of postdoctoral research with Prof. Weitao Yang. He has now returned to the University of Cambridge as a Royal Society University Research Fellow. His research focuses on the basic development of DFT and related electronic structure methods.

Paula Mori-Sánchez received her Bachelor's Degree in Chemistry from the Universidad de Oviedo in Spain, where she also did a Ph.D. on the nature of chemical bonding in molecules and crystals. She then went to Duke University in North Carolina for 7 years, working with Prof. Weitao Yang, first as a Fulbright Fellow and then as a postdoctoral researcher. She is now at the Universidad Autónoma de Madrid in Spain, where she is a Ramón y Cajal Research Fellow. She is interested in quantum electronic structure and density functional theory.

Weitao Yang is the Philip Handler Professor of Chemistry at Duke University. He held visiting professorships from many universities and has received numerous awards, including the 2010 International Solvay Chair in Chemistry and the 2012 ACS Award for Computers in Chemical and Pharmaceutical Research. He is an elected member of the International Academy of Quantum Molecular Science and an elected fellow of American Association for the Advancement of Science. Prof. Yang is recognized by ISI as a Highly Cited Researcher. His interests are in development of quantum theory and particularly density functional theory and applications to complex problems.

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