Perspective on density functional theory

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Department of Chemistry, 1102 Natural Sciences 2, University of California, Irvine, California 92697, USA

Density functional theory (DFT) is an incredible success story. The low computational cost, combined with useful (but not yet chemical) accuracy, has made DFT a standard technique in most branches of chemistry and materials science. Electronic structure problems in a dazzling variety of fields are currently being tackled. However, DFT has many limitations in its present form: too many approximations, failures for strongly correlated systems, too slow for liquids, etc. This perspective reviews some recent progress and ongoing challenges. © *2012 American Institute of Physics.*
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I. INTRODUCTION

Over the past 20 years, density functional theory (DFT) has become a much used tool in most branches of chemistry.[1] Many experimental investigations in organic and inorganic chemistry routinely include such calculations, using a popular code, a standard basis, and a standard functional approximation.[2] A similar transformation is now underway in materials science where, in the past decade, improvements in both hardware and codes have made it possible to perform systematic comparisons with experiment across large ranges of materials, learning which approximations work and why, and allowing for true first-principles predictions of properties. Among notable recent successes are the prediction of new catalysts,[3] new Li battery materials[4] in the Materials Genome Project. A complementary aspect of this story is shown in Fig. 1, which shows the number of papers given by Web of Knowledge when DFT is searched as a topic (grey bars). This will soon reach 10 000 per year, vindicating the 1998 Nobel prize in chemistry, which was shared by Kohn[5] for inventing the theory and by Pople[6] for developing computational methods in quantum chemistry. The figure also marks the fraction of papers citing B3LYP,[7,8] currently the most popular approximation in chemistry, and PBE,[9] the most popular approximation in materials. Clearly, applications to materials will soon outstrip those in chemistry.

This perspective is for a general audience, and focuses on fundamental general aspects of DFT, rather than detailed computational procedures and results for specific systems. Because DFT is now applied so broadly, no such article can hope to be comprehensive. The topics covered here are designed to give a flavor of how the field works, and are mostly those I have personally worked in. Great longer reviews exist: for experts,[10–12] for users,[13] and for neophytes.[14,15] I work always within the Born-Oppenheimer approximation and the non-relativistic limit. I will not discuss convergence of basis sets, but blithely assume all calculations are converged. I use atomic units (lengths in bohr, energies in hartree) except where otherwise specified. For simplicity, I refer always to density functionals, but modern calculations and theory are always within spin-density functional theory, a generalization.[16]

II. A BRIEF HISTORY

Our story begins in 1926 with the creation of Thomas-Fermi theory,[17,18] an approximate method for finding the electronic structure of atoms using just the one-electron ground-state density, $\rho(\mathbf{r})$, but too crude to bind molecules.[19] In the 1950s, Slater[20] intuitively combined this idea with Hartree's orbital method[21] in the Xα scheme. Later, the Hohenberg-Kohn (HK) theorem[22] proved that an exact method based on $\rho(\mathbf{r})$ exists in principle. The modern version in use today is Kohn-Sham (KS) DFT, which defines self-consistent equations that must be solved for a set of orbitals whose density, $\rho(\mathbf{r})$ is defined to be exactly that of the real system.[23] In these equations, a small but vital contribution to the energy, the exchange-correlation (XC) energy, must be given in terms of $\rho(\mathbf{r})$. In principle, and for small systems, this functional can be found exactly, but turns out to be more expensive than direct solution of the Schrödinger equation.[24] In practical calculations, the XC contribution is approximated, and the results are only as good as the approximation used.

The simplest XC approximation is the local density approximation (LDA) (Ref. 23) which became the popular standard in calculations on solids in the 1970s and 1980s. But molecules in LDA are typically overbound by about 1 eV/bond, and in the late 1980s generalized gradient approximations (GGAs) (Ref. 25) produced an accuracy that was useful in chemical calculations. In the early 1990s, hybrids were introduced by Becke,[7] replacing a fraction of GGA exchange[26] with Hartree-Fock (HF) exchange, leading to the ubiquitous B3LYP,[8] the most popular approximation in use in chemistry today. On the other hand, the PBE GGA (Ref. 9) has come to dominate applications to extended systems (materials). We denote these three (LDA, PBE, and B3LYP) as the *standard* approximations, meaning that they are the most popular examples of each type of approximation, and dominate the user market, as shown by Fig. 1.

To give an idea of how much (or how little) progress is made in DFT development, we go back to the year of the Nobel prize, 1998. Some of the most prominent practical difficulties from back then include (i) fundamental gaps of bulk solids are underestimated, (ii) van der Waals interactions missing from popular functionals, (iii) strongly
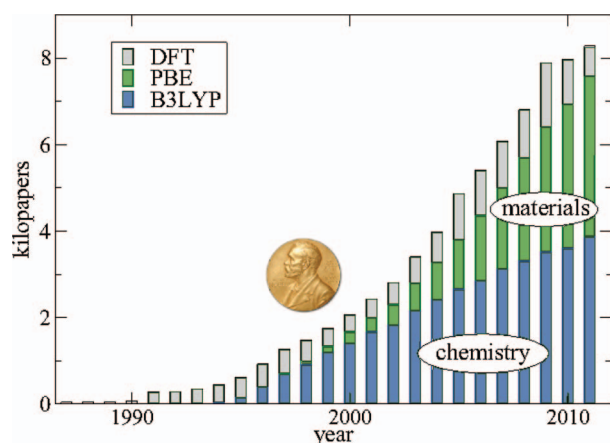
FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).

correlated systems poorly treated, and (iv) no good scheme for excitations. Of course, there are many others, but this sample will give us some idea of how things work. The rest of this article interweaves sections labeled *progress*, indicating areas where substantial progress has been made since that time, with *general background*, explaining relevant concepts, and *challenges*, areas that need improvement and where we can hope for progress in the next decade.

III. PROGRESS: MATERIALS AND NANOSCIENCE

As shown in Fig. 1, materials applications now share the limelight with chemistry. Nanoscience completely interweaves these two, such as when a molecule is adsorbed on a surface. Many areas of materials research, especially those related to energy, desperately need input from electronic structure methods. Most calculations of materials use codes that differ from traditional quantum chemistry codes, because they employ plane waves that satisfy periodic boundary conditions.[27] Such calculations converge much faster to the bulk limit than by taking ever larger finite clusters of the material. In fact, almost all popular codes are designed either for finite molecular systems[28] or for extended bulk systems,[29] although codes that treat both are beginning to appear.[30, 31]

In solid-state physics, DFT has always been more popular than traditional approaches to the Schrödinger equation, because the Hartree-Fock approximation has unpleasant singularities for zero-gap materials, i.e., metals. The next logical step[32] beyond the standard approximations are meta-GGAs, which include the kinetic energy density as an input, and can yield accurate ground-state energies simultaneously for molecules, solids, and surfaces.[33] But an outstanding failure has been DFT's inability to provide good estimates of the fundamental gaps of semiconductors and insulators, a crucial quantity for much materials research, such as impurity levels in doped semiconductors.[34]

The fundamental (or transport) gap is $I - A$, where I is the ionization potential and A is the electron affinity. It is well established that the KS gap, i.e., the difference between the KS HOMO and LUMO energies, does *not* equal this value, even with the exact XC functional.[35, 36] Calculations suggest

that the KS gap is typically substantially smaller (by about 50%) than the fundamental gap for semiconducting solids.[37] The LDA and GGA approximations yield accurate KS gaps, but it is the fundamental gap that is of real interest. In principle, $I - A$ can be found by adding and subtracting electrons from a large cluster of the material. Unfortunately, in LDA or GGA, this gap, found by total energy differences, incorrectly collapses to the KS gap, because these approximations wrongly allow electrons to completely delocalize over insulating solids. Such approximations lack a derivative discontinuity that prevents this over delocalization.[36]

A practical way around this problem is to use a hybrid, but treating the exchange term as orbital dependent, via generalized KS theory.[38] With mixing parameters of about 20%, this typically yields much better gaps for semiconductor materials. A recent functional, called HSE,[39, 40] not only mixes in some HF, but also performs a range-separation. Based on exact theorems of Savin,[41] the short-range part of the HF is treated exactly, while the long-range contribution is treated by approximate DFT. The resulting functional, used to calculate gaps in the generalized scheme, appears to work accurately for a large variety of moderate-gap semiconductors,[40] overcoming the problems of LDA and GGA. It yields accurate fundamental gaps when excitonic effects are negligible, and is closer to optical gaps when they are not.[42, 43]

This kind of progress is very welcome in an era in which we must accurately tackle moderately correlated systems. Transition metal oxides play vital roles in many energy-related problems, such as creation of efficient photovoltaics.[44] The standard approximations over-delocalize the *d*-electrons, leading to highly incorrect descriptions. Many practical schemes (HSE,[39] GGA + U,[45, 46] and dynamical mean-field theory (Ref. 47)) can correct these difficulties, but none has yet become a universal tool of known performance for such systems. Very recently, a promising non-empirical scheme has been suggested for extracting gaps using *any* approximate functional.[48]

An alternative approach to directly tackling such problems is to study them in simpler situations, and test suggested remedies on cases where exact, unambiguous answers can be easily obtained. Recently, an extremely powerful technique for direct solution of many-body problems, called density matrix renormalization group (DMRG), has been adapted to tackle a one-dimensional (1D) analog of the real world.[49] DMRG is powerful enough to calculate the exact XC functional on systems of 100 atoms or more.[24] We will see how the exact functional deals with strongly correlated insulators and which new approximations are working for the right reasons.

For more than a decade, researchers have been performing DFT calculations of molecular conductance, calculating the current in response to a bias applied to a molecule caught between two metal leads.[50] This problem is prototypically difficult for present electronic structure methods.[51] This is a steady state situation, not a ground-state one. Model Hamiltonians typically used to study this kind of physics are insufficiently accurate, as several hundred atoms must be treated to achieve chemical realism.[52] A standard approach, combining the Landauer formula[53] with ground-state DFT and often called non-equilibrium Green's functions (NEGF),[54] is

typically used, and avoids adjustable parameters. But especially in the case of organic molecules, there is every reason to believe that, for the reasons given above about bulk gaps, our standard approximations are simply wildly inaccurate for this problem. Recent calculations[55,56] including corrections based on non-DFT many-body theory[57] and simple exact results for simple models[58] are strong evidence that, at least for weak bias, the standard approach should yield accurate currents, once better DFT approximations are used.[59]

IV. BACKGROUND: EXACT THEORY

A KS calculation appears very similar to a Hartree-Fock calculation, but there is a crucial difference. The effective potential is *defined* to be one which makes the one-particle density $\rho(\mathbf{r})$ be the *exact* density of the system. By virtue of the HK theorem,[22] one can write the ground-state energy as

$$E = T_s + U + V_{nuc} + E_{xc}[\rho], \tag{1}$$

where T_s is the energy of the KS orbitals, U is the Hartree (a.k.a. Coulomb) energy, V_{nuc} is the attraction to the nuclei, and $E_{xc}[\rho]$ is everything else, defined to make the above exact. Then one finds the energy-minimizing orbitals are given by the celebrated KS equations:[23]

$$\left(-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right)\phi_j(\mathbf{r}) = \epsilon_j\phi_j(\mathbf{r}) \tag{2}$$

and

$$v_s(\mathbf{r}) = v_{nuc}(\mathbf{r}) + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[\rho](\mathbf{r}) \tag{3}$$

with $v_{xc}(\mathbf{r}) = \delta E_{xc}/\delta\rho(\mathbf{r})$. Thus, if the XC energy is known as a functional of the density, these form a closed set of self-consistent equations yielding the exact answer to the electronic structure problem, without ever calculating the electron-electron repulsion directly!

In Fig. 2, I show the *exact* KS potential for a He atom. The blue line in the bottom half is $v_{nuc}(r) = -2/r$ in atomic units, the attraction of the electrons to the nucleus. In the

top half, the red line indicates the exact radial density of the He atom, found by using sophisticated wavefunction techniques to directly solve the Schrödinger equation.[61] But the pink dashed line in the bottom is then the unique potential experienced by two fictitious *non-interacting* electrons that makes them have the exact ground-state density, i.e., $\phi_{1s}(\mathbf{r}) = \sqrt{\rho(\mathbf{r})/2}$. Every practical KS DFT calculation approximates $v_s(\mathbf{r})$, and *never* calculates the true many-electron wavefunction. (If you wish to annoy and confuse a traditional quantum chemist, ask "How much correlation is there in the KS wavefunction?")

We next discuss several relevant points about these equations:

- *Failures* of DFT are due to failures of approximations. The *exact* $E_{xc}[\rho]$ yields E and $\rho(\mathbf{r})$ exactly.
- Ground-state DFT calculations, even with the exact XC, yield *only* E and $\rho(\mathbf{r})$ and any property that can be extracted from them (such as the ionization potential).
- The KS *energies and orbitals* replace those of HF for understanding chemical reactivity,[62] even though they appear as mere constructs for $\rho(\mathbf{r})$. We also now know that orbital energy differences approximate *optical* transitions, via time-dependent DFT (TDDFT, Sec. VII).
- For most applications, one cares only about E as a function of the nuclear coordinates. This determines bond lengths, angles, vibrational frequencies, all reaction energies, transition-state barriers, etc., i.e., most of the properties of interest about a molecule or a material.

V. CHALLENGE: LARGER SYSTEMS

Although KS-DFT is just about the quickest way to get useful quantum calculations of electronic structure, its still too slow for a crucial application: molecular dynamics (MD) simulations of liquids. There is tremendous interest in performing calculations that mix KS-DFT with other methods. For example, molecular mechanics with classical force fields can routinely handle millions of atoms, but making and breaking bonds are usually unreliable. On the other hand, the field of *ab initio* molecular dynamics (AIMD), using the Car-Parrinello method[63] of combining DFT with MD, is thriving, but limited to a few hundred atoms per simulation. Thus, there is tremendous desire to perform mixed QM/MM simulations, in which the chemically active part of a larger system is treated in DFT. Many methods have been proposed, but many questions remain, especially when the interface between the classical and DFT regions involve covalent bonds. This very active area of research is reviewed in Ref. 64.

A related theme is that of *orbital-free DFT*, which looks backward to the original form of a pure DFT, as approximated by TF theory, and shown to be formally exact by the HK theorem. In a modern context, this means producing a sufficiently accurate approximation (much more accurate than TF theory) for the KS kinetic energy (T_s in the language of Sec. IV), thereby avoiding the need to solve the KS equations. If this could be done, then all DFT calculations would
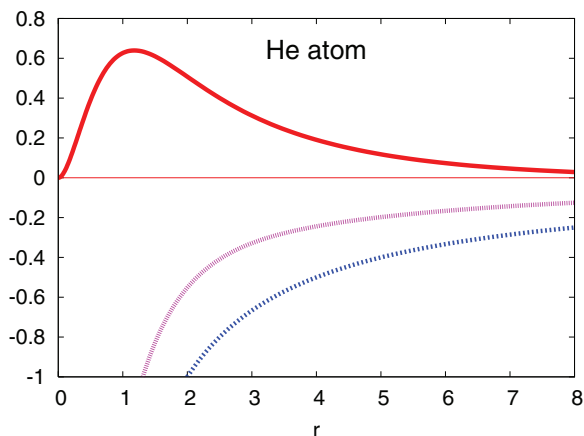
FIG. 2. Exact radial density, $4\pi r^2\rho(r)$, (red) and potentials (nuclear attraction, $v_{nuc}(r)$, is blue, while KS, $v_s(r)$, is pink) for the He atom in atomic units (bohr radii, 0.529Å). Two non-interacting fake electrons, doubly occupying the 1s orbital of $v_s(r)$, produce the *exact* ground-state density shown above.[60]

run much more quickly, and AIMD could be performed on much larger systems. This has been an active area of research for many decades,[11] with various empirical approaches being tried for such approximations. Most (if not all) attempts use reasoning similar to that used successfully to approximate XC contributions, but there is nothing to suggest (and much evidence to the contrary) that such methods can produce a general-purpose approximation sufficiently accurate for this purpose. Possibly a lower degree of accuracy could be acceptable for the larger system, and then a traditional KS treatment applied to the chemically active region. This *embedding* idea has been tried, especially when the system is weakly bonded to the environment.[65,66] An alternative is to switch the basic variable to the potential instead of the density,[67] so that semi-classical approximations (Sec. IX) can be directly applied to the atoms of interest.

Many of these ideas are unified in a new approach to the issue of subsystems within electronic structure, called partition DFT (PDFT). Originally developed by Cohen and Wasserman to resolve difficult issues in chemical reactivity theory,[68] this formalism unifies several distinct concepts in chemistry, including atoms in molecules, effective charges, chemical identity, localization of bonds, etc. To date, only calculations on model systems[69] and diatomic molecules[70] have appeared, but interest is growing rapidly.[71] An interesting challenge is to adapt PDFT to include external electric fields, as it seems ideally suited to the molecular electronics problems of Sec. III.

VI. BACKGROUND: THE USERS' LAMENT

But the popular success of DFT has bred its own set of problems. As codes become faster and easier to use, DFT is applied to a huge number of situations. Figure 1 includes applications to protein folding,[72] astrophysics,[73] dyes,[74] and dirt,[75] to name just a few. As experience builds with each given functional, the accuracy and reliability come to be known, as well as the qualitative failures. For example, it was very early recognized that standard approximations do not yield long-range dispersion.[76] The local nature of the standard approximations implies an exponential decay of the interaction. Progress in this area only came recently, and is described in Sec. X. Another example is that of anions, which are technically unbound with standard approximations,[77] and yet for which accurate results can still be obtained.[78] Only recently has this puzzle been addressed and a solution proposed.[79]

Naturally, users would like an all-purpose tool that provides answers of a prescribed quality in all situations. Present DFT calculations are a far cry from this. Table I shows a list of features that most users will unfortunately recognize. Throughout its history, DFT has provided approximations that work for some problems and fail for others, in largely mysterious ways. At any given moment, the most popular approximations fail for the most interesting systems, such as the moderately correlated oxides mentioned in Sec. III.

VII. PROGRESS: EXCITATIONS

Because an excited-state density does not uniquely determine the potential,[80] there is no general analog of HK for ex-

TABLE I. List of things users despise about DFT calculations. Please rank in order of induced frustration. The extreme left column indicates the users' response to these "features," the right denotes that of developers.

:(	No simple rule for reliability	♡
:(	No systematic route to improvement	♡
:(	Decades between each generation	♡
:(	Full of arcane insider jargon	♡
:(	Too many approximations to choose from	♡
:(	Can only be learned from a DFT guru	♡

cited states. Many different ways to approach the calculation of excited states in DFT have been developed over the years, including ensembles[81,82] ΔSCF,[83] and min-max principles[84] and others. However, since the mid-1990s, TDDFT has become extremely popular.[85] Because the methodology is technically very similar to that of time-dependent HF, TDDFT was very rapidly implemented in quantum chemical codes such as Turbomole,[86] and is now a standard part of any code. A useful reference and pedagogical tool is Ref. 87, while a popular review is Ref. 85.

TDDFT is based on a similar (but distinct) theorem to HK, the Runge-Gross theorem,[88] which establishes that, in a time-dependent quantum problem, all observables are functionals of the time-dependent density (under certain conditions). Then, considering the linear-response of a molecule to a time-dependent electric field, one finds simple formulas that correct the KS eigenvalue differences into the (in principle, exact) optical excitations of the system,[89] but requiring (of course) another unknown functional, called the XC kernel.[90] All practical calculations employ the adiabatic approximation, and almost all use the same approximation for both the ground-state and the TD part of a DFT calculation.[91]

Practical TDDFT often produces good excitation spectra. Typical errors in individual energies are higher than for the ground-state (0.3 eV),[92] but properties are excellent (bond lengths, dipole moments, etc.), and even roughly accurate spectra can be sufficient to identify the dominant excitations in the optical spectra of large molecules.[91] About 10% of all DFT calculations now include TDDFT as well, as its computational cost is not many times more than a single calculation of a ground-state energy. The procedure can even be extended to continuum states[93] to accurately predict electron-atom elastic scattering.

But, just as with ground-state DFT, along with success comes challenges. Important ones are that the standard functionals are inaccurate for charge transfer excitations, leaving them so low so that they contaminate other parts of the spectrum. Double excitations are also excluded by the adiabatic approximation. Calculations of the optical response of solids using standard approximations produce results similar to those found using the random phase approximation (see Sec. XI), in which XC effects are set to zero, and which fails to describe excitonic effects in solids. For applications beyond linear response (strong fields), the standard approximations cannot be used because of their poor quality potentials. Furthermore, sometimes the quantity of interest is not a simple functional of the time-dependent one-electron density, such as the double ionization probability.[94]

But all these are open areas of research and progress is being made continuously. Many papers have been published on the charge transfer issue, and several range-separated schemes seem to handle these excitations well.[95] The basic form of the kernel needed to handle double excitations was deduced years ago,[96] and has been generalized and systematized successfully.[97] With much effort, the nature of the error for solids was deduced,[98] and a new approximation to the kernel (the nanoquanta kernel) can be found from many-body perturbation theory.[99] In a very recent development, a bootstrap approximation for the kernel in terms of the dielectric function appears to produce accurate excitons in all but the largest gap insulators.[100]

VIII. BACKGROUND: FIRST PRINCIPLES OR UNPRINCIPLED?

Over the decades since the introduction of the Schrödinger equation, many excellent methods have been developed for directly solving the electronic structure problem, including configuration interaction, Møller-Plesset perturbation theory, the coupled-cluster expansion, and quantum Monte Carlo.[101] Such methods rarely suffer from any of the difficulties listed in Table I. But because of the coupling between coordinates in the many-electron Schrödinger equation, the computational cost of such methods is usually significantly more than that of DFT. Loosely, the more accurate the method is, the more rapidly the cost rises with number of atoms. Thus, without some algorithmic breakthrough, DFT will always allow more atoms (often by a factor of 10) to be treated, no matter how fast our processors get, or how many we have.

This does not make direct solutions obsolete. They provide crucial benchmarks for testing approximate functionals for smaller systems, and give crucial insight into the nature of errors, both quantitative and qualitative. In chemistry, it is traditional to refer to standard approaches as *ab inito*, while DFT is regarded as empirical. Because solid-state calculations are more demanding, for many decades DFT was the only possible approach. Thus, DFT calculations are referred to as *ab initio* in solid-state physics and materials science. This explains how there is a solid-state code ABINIT (Ref. 102) which performs *only* DFT calculations. (When teaching chemistry students, I explain that DFT is some algorithm meaning unreliable, while *ab initio* is Latin for *too expensive*.)

A sore point is whether or not approximate DFT should be called *empirical*. Even if an approximate functional includes parameters that have been fit to some data set, once the final form has been written down, that approximation can be applied to every possible electronic structure problem, without adjusting parameters for each specific calculation. Thus DFT, with a fixed approximate functional, is still first principles, in the sense that the user only chooses the atoms, and the computer predicts all properties of the molecule or solid.

As mentioned above, the first approximation was LDA,[23] and the formula for this is determined by properties of the uniform electron gas. No one disputes that DFT with LDA is non-empirical.[103,104] But even just the next step up Jacob's ladder[32] of functional sophistication, the GGA has no unique form. There are two major schools of thought here. Purists like to use exact conditions of quantum mechanics to derive the parameters in their approximate functionals, and so claim to be non-empirical. This school has been championed by John Perdew, with a lifetime of very successful approximations.[9,104,105] On the other hand, pragmatists such as Axel Becke and Bob Parr have allowed one or two parameters to be fit to specific systems, such as in B88 for exchange[26] and LYP for correlation.[8] Such approximations have been based on sound physical reasoning *underlying* the structure of the approximation. I have even had the pleasure of *deriving* some of these parameters much later.[106,107] By fitting, one usually finds higher accuracy for systems similar to those fitted (often by a factor of 2), but greater inaccuracies far away. For example, LYP correlation[8] works very well as part of B3LYP in chemistry, but fails badly for bulk metals. The PBE approximation[9] works passably well for many materials purposes, but can be a factor of 2 or more worse than BLYP for dissociation energies.

A simple example of a first principles approach is given by the B3LYP approximation (and its materials counterpart, PBE0 (Ref. 108)). The crucial part of a hybrid, which mixes HF exchange with a GGA, is the fraction of exact exchange, a, which is about 20%. This was fixed once and for all in the definition of the functional, and all the thousands of papers using B3LYP in Fig. 1 are gathering information on the same functional. The amount of mixing can be rationally related to other aspects of atomization energies.[109] If authors *adjust* the amount of mixing to improve their results for some system or property, this is *not* first principles.

Many of these tensions have been highlighted in recent years by the Minnesota functionals developed by Truhlar and coworkers, reviewed in Ref. 110. These use the same basic ingredients as the standard approximations, but optimize performance on a training set of energies by fitting up to several dozen parameters. These often produce more accurate results on systems close to those trained on and beyond, by employing functional forms that are more complex than those of the standard functionals, and challenge orthodoxy concerning the limitations of given levels of approximation.[110] I consider these first principles, because the functionals contain no parameters adjusted to the system being calculated. (Interestingly, I have recently co-authored an approximation with about 10^5 "empirical" parameters.[111] Don Truhlar, eat your heart out!)

Figure 3 shows just a random selection of some of the hundreds of XC approximations that have been suggested over the years. Many of these are in popular codes, some of which even allow you to *design* your own functional. Clearly, when calculating a property to compare with experiment, one could keep trying functionals until agreement with the measured value is reached. Not only is this contrary to the entire spirit of DFT, it is certainly not first principles, and is the worst form of empiricism. The literature today is (mildly) infected with such calculations, and the existence of so many approximations, with so little guidance, makes it ever more difficult for non-specialists to separate the silver from the dross. Users should stick to the standard functionals (as most do, according to Fig. 1), or explain very carefully why not.

FIG. 3. The alphabet soup of approximate functionals available in a code near you. Figure used with permission from Peter Elliott.

IX. CHALLENGE: DIGGING DEEPER

As we have seen, the practice of modern DFT suffers a lack of detailed understanding of how to approximate functionals. We begin from local approximations, and then create more accurate, sophisticated versions. Based on insight and intuition, combining either exact conditions from quantum mechanics, or fitting specific systems, we make progress, but only very slowly, and rarely without ambiguity. A formally exact theory exists (Sec. IV), but provides only limited guidance about approximations.

I believe that a fundamental principle underlies the success of DFT, which is that local approximations are a peculiar type of *semiclassical* approximation to the many-electron problem. For the last 6 years, with both my group and many collaborators, I have been trying to uncover this connection, and make use of it. The underlying math is very challenging, and some must be invented.

Basic quantum textbooks have separate chapters on perturbation theory and semiclassical approximations, but never relate the two.[112] All modern many-body methods have their roots in treating the interaction as a perturbation, since we find solving non-interacting problems relatively easy. But such treatments ignore the fact, proven by Lieb more than a quarter of a century ago,[113] that TF theory (see Sec. II) becomes relatively exact for neutral atoms as $Z \to \infty$. As detailed by Schwinger,[114] this *is* the semiclassical limit[115] mentioned above. Dramatic confirmation of this fact is that TF also appears to yield the exact ionization potential of atoms (averaged across a row) in this limit, and that LDA-X recovers the HF result, including the oscillations across a row.[116] Most of our results so far have been confined to 1D systems,[117] but this insight lead to the restoration of the gradient expansion in PBEsol, which cures many of the PBE problems with lattice parameters,[118] and a derivation of the parameter in the B88 functional.[107]

X. PROGRESS: WEAK INTERACTIONS

The ability to treat van der Waals interactions is a recent (and ongoing) success story for DFT. In the 1990s, it was well-known that the standard functionals could not yield correct long-range dispersion forces,[76] i.e., their binding energy curves decay exponentially (with density overlap) instead of $-C_6/R^6$, where R is the separation and C_6 is the van der Waals coefficient, determined from the frequency-dependent polarizabilities of the fragments.[119] Because this excluded such a huge number of important systems and properties (such as DNA, physisorption on surfaces, most biochemistry, etc.), there were always *ad hoc* methods for adding back in dispersion, simply using pair potentials between atoms.[120]

Over about 20 years of research and many papers, the late David Langreth with Bengt Lundqvist[121] and many other collaborators, developed an approximate non-local ground-state density functional, call it LL, that has the right decay behavior and reasonably accurately captures these effects.[122] LL is entirely non-empirical, using results from the uniform gas and interactions between slabs of that gas to find such a form from first principles. While the initial implementation of this functional was computationally expensive, a recent algorithm of Soler *et al.*[123] made it much faster, so much so that its cost is negligible beyond about 100 atoms. This led to immediate implementation in many codes worldwide, and there is now a plethora of calculations with LL.[124]

Simultaneous with this development, in quantum chemistry, Grimme[125] developed his DFT-D methodology that provides an empirical correction to DFT results in a highly systematic and accurate fashion. The results for small molecules in the S22 data set[126] are extremely good. DFT-D is much more accurate for these systems than LL, but LL can be applied to all matter (except possibly metals), including situations where pair-potentials cannot work. A less empirical alternative to Grimme has been proposed by Tkatchenko and Scheffler,[127] which produces a scheme for calculating an additive correction for *any* functional and has only slight empiricism. This has recently been extended to include even metals.[128] Over the next five years, one (or possibly two) of these schemes is likely to become the standard method for including weak interactions in DFT calculations.

XI. CHALLENGE: TIME FOR A PARADIGM SHIFT?

The KS equations, combined with the local density approximation, were a reformulation of the electronic structure problem relative to TF theory. By producing a more demanding computational algorithm while lessening the fraction of the total energy that needs approximating, a great leap forward in accuracy and reliability was achieved. But that was back in 1965. Perhaps we are at the end of that road in terms of useful approximations, and what is needed now is a new paradigm which uses a different starting point from which approximations are to be found.

A. Optimized effective potential (OEP)

At some point, exact exchange (loosely, evaluating an orbital-dependent functional in the KS scheme) seemed like a strong candidate, because it allowed exchange to be evaluated exactly, instead of being approximated.[129, 130] This cures a multitude of problems with local and semilocal

approximations, such as better orbital energies, avoiding self-interaction error, and better approximations to the derivative discontinuity. However, the technology for solving the OEP equations efficiently has existed for at least a decade,[131–133] but no general-purpose correlation approximation has been found that works well with exact exchange in all situations. Even worse, there are questions about how well-defined the equations are in a basis.[134]

B. Random phase approximation (RPA)

A more recent development,[135] driven primarily by improvements in hardware and algorithms, is the ability to solve the RPA equations efficiently for systems up to about a hundred atoms. These can now be done *faster* than a conventional Hartree-Fock calculation. Moreover, bare RPA has many excellent features, including exact exchange and a van der Waals contribution, but also has problems with atomization energies. RPA is now implemented in both materials[136] and chemical codes.[28] RPA makes a promising candidate for a new baseline calculation, to which further inexpensive approximations can be added, because it incorporates more traditional theory (here, coupled cluster[137]) at low computational cost.

C. Density-matrix functional theory (DMFT)

A darling of the chemistry community, and of increasing interest in physics, is DMFT,[138] in which impressive results have been gotten over the years. The formalism is well-founded, using the same variational principles as DFT, due to Gilbert,[139] and a sequence of successive approximations and refinements have produced excellent results at equilibrium bond lengths and for total energies of closed-shell systems.[140] Even gaps of insulators seem to come out well.[141] But the methods are not yet developed for general purpose, as open shell systems and size-consistency remain issues. If this methodology ever does become popular, it would represent a true paradigm shift, as it does not even use KS equations. But, for this reason, it is difficult to see how many of the impressive results of DFT approximations could be retained.

XII. THE FUTURE

So, where does this leave us? It is clearly both the best and worst of times for DFT. More calculations, both good and bad, are being performed than ever. One of the most frequently asked questions of developers of traditional approaches to electronic structure is: "When will DFT go away?." Judging from Fig. 1, the answer is clearly no time soon. Although based on exact theorems, as shown in Fig. 2, these theorems give no simple prescription for constructing approximations. This leads to the many frustrations of the now manifold users listed in Table I. Without such guidance, the swarm of available approximations of Fig. 3 will continue to evolve and reproduce, perhaps ultimately undermining the entire field. But I expect that some of the many excellent ideas being developed by the DFT community will come to fruition, i.e., produce *new* and more general standard approximations, well before that happens.

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