DFT: A Theory Full of Holes?

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Annu. Rev. Phys. Chem. 2015. 66:283–304

The *Annual Review of Physical Chemistry* is online at physchem.annualreviews.org

This article's doi: 10.1146/annurev-physchem-040214-121420

Keywords

electronic structure, approximations, nonempiricism, semiclassics, warm dense matter, density functional theory

Abstract

This article is a rough, quirky overview of both the history and present state of the art of density functional theory. The field is so huge that no attempt to be comprehensive is made. We focus on the underlying exact theory, the origin of approximations, and the tension between empirical and nonempirical approaches. Many ideas are illustrated on the exchange energy and hole. Features unique to this article include how approximations can be systematically derived in a nonempirical fashion and a survey of warm dense matter.

1. WHAT IS THIS ARTICLE ABOUT?

The popularity of density functional theory (DFT) as an electronic structure method is unparalleled, with applications that stretch from biology (1) to exoplanets (2). However, its quirks of logic and diverse modes of practical application have led to disagreements on many fronts and from many parties. Developers of DFT are guided by many different principles, while applied practitioners (i.e., users) are suspicious of DFT for reasons both practical [how can I pick a functional with so many choices? (3)] and cultural (with so many choices, why would I call this first principles?).

A modern DFT calculation (4) begins with the purchase of a computer, which might be as small as a laptop, and a quantum chemical code. Next, a basis set is chosen, which assigns predetermined functions to describe the electrons on each atom of the molecule being studied. Finally, a DFT approximation to something called the exchange-correlation (XC) energy is chosen, and the code starts running. For each guess of the nuclear positions, the code calculates an approximate energy (4). A geometry optimization should find the minimum energy configuration. With variations on this theme (5, 6), one can read out all molecular geometries, dissociation energies, reaction barriers, vibrational frequencies, etc. A modern desktop computer may do a calculation for a 100-atom system within a day. A careful user will repeat the most important parts of the calculation with bigger basis sets to check that answers do not change significantly.

2. WHERE DOES DENSITY FUNCTIONAL THEORY COME FROM?

Although DFT's popularity has skyrocketed since applications to chemistry became useful and routine, its roots stretch back much further (7–9).

2.1. Ye Olde Density Functional Theory

Developed without reference to the Schrödinger equation (10), Thomas-Fermi (TF) theory (11–13) was the first DFT. It is pure DFT, relying only on the electronic density, $\rho(\mathbf{r})$, as input. The kinetic energy was approximated as that of a uniform electron gas, while the repulsion of the electrons was modeled with the classical electrostatic Coulomb repulsion, again depending only on the electronic density as an input.

2.2. Mixing in Orbitals

Slater was a master of electronic structure, and his work foreshadowed the development of DFT. In particular, his X_α method (14) approximates the interactions of electrons in ground-state systems and improved upon the Hartree-Fock (HF) method (15, 16), one of the simplest ways to capture the Pauli exclusion principle. One of Slater's great insights was the importance of holes, a way of describing the depressed probability of finding electrons close to one another. Ahead of his time, Slater's X_α included a focus on the hole, satisfied exact conditions such as sum rules, and considered the degree of localization present in the system of interest.

2.3. A Great Logical Leap

Although Slater's methods provided an improvement upon the HF method, it was not until 1964 that Hohenberg & Kohn (17) formulated their famous theorems, which now serve as the foundation of DFT:

1. The ground-state properties of an electronic system are completely determined by $\rho(\mathbf{r})$.
2. There is a one-to-one correspondence between the external potential and the density.

We write this by splitting the energy into two pieces:

$$E_{\text{elec}}[\text{density}] = F[\text{density}] + \text{NucAtt}, \tag{1}$$

where E_{elec} is the total energy of the electrons, F is the sum of their exact quantum kinetic and electron-electron repulsion energies, and NucAtt is their attraction to the nuclei in the molecule being calculated. Square brackets denote some (very complex) dependence on the one-electron density, $\rho(\mathbf{r})$, which gives the relative probability of finding an electron in a small chunk of space around the point $\mathbf{r}$. F is the same for all electronic systems and thus is called universal. For any given molecule, a computer simply finds $\rho(\mathbf{r})$ that minimizes E_{elec} above. We can compare this to the variational principle in regular quantum mechanics. Instead of spending forever searching lots of wave functions that depend on all $3N$ electronic coordinates, one just searches over one-electron densities, which have only three coordinates (and spin).

The pesky thing about the Hohenberg-Kohn theorems, however, is that they tell us that such things exist without telling us how to find them. This means that to actually use DFT, we must approximate F[density]. We recognize that the old TF theory did precisely this, with very crude approximations for the two main contributions to F:

$$F[\text{density}] \sim \int d^3r\ \rho^{5/3}(\mathbf{r}) + \text{CoulRep} \quad \text{(TF)}, \tag{2}$$

where we do not bother with constants, etc. The first term is an approximation to the kinetic energy as a simple integral over the density. It is a local approximation, as the contribution at any point comes only from the density at that point. The other piece is the self-repulsion among electrons, which is simply modeled as the classical electrostatic repulsion, often called their Hartree energy or the direct Coulomb energy. Such simple approximations are typically good to within approximately 10% of the electronic energy, but bonds are a tiny fraction of this and so are not accurate in such a crude theory (18).

2.4. A Great Calculational Leap

Kohn and Sham proposed rewriting the universal functional to approximate only a small piece of the energy. They mapped the interacting electronic system to a fake noninteracting system with the same $\rho(\mathbf{r})$. This requires changing the external potential, so these aloof, noninteracting electrons produce the same density as their interacting cousins. The universal functional can now be broken into new pieces. Where, in the interacting system, we had kinetic energy and electron-electron interaction terms, in the Kohn-Sham (KS) system, we write the functional

$$F = \text{OrbKE} + \text{CoulRep} + XC, \tag{3}$$

where OrbKE is the kinetic energy of the fake KS electrons. XC contains all the rest, which includes both kinetic and potential pieces. Although it is small compared to the total, nature's glue (19) is critical to getting chemistry and physics right. The X part is (essentially) the Fock exchange from an HF calculation, and C is the correlation energy (i.e., that part that traditional methods such as coupled cluster usually obtain very accurately) (20).

When minimizing this new expression for the energy, one finds a set of orbital equations, the celebrated KS equations. They are almost identical to the HF equations, demonstrating that Slater's idea could be made exact (if the exact functional were known). The genius of the KS scheme is that, because it calculates orbitals and gives their kinetic energy, only XC, a small fraction of the total energy, needs to be approximated as a density functional. The KS scheme usually produces excellent self-consistent densities, even with simple approximations such as local

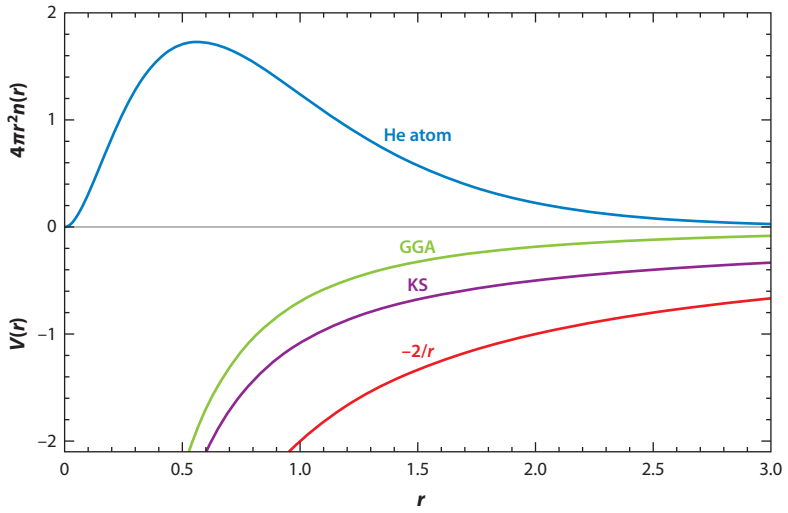

Figure 1

Radial densities and potentials for the helium atom (energies in Hartree, distances in Bohr). The red line is $-2/r$, the attraction of real electrons to the nucleus. The purple line is the exact Kohn-Sham (KS) potential. Two fake electrons in the 1*s* orbital of this potential have the same ground-state density as real helium. The green line is the potential of a typical approximation [generalized gradient approximation (GGA)], which, although inaccurate, yields a highly accurate density.

density approximation (LDA), but approximate potentials for this noninteracting KS system are typically very different from the exact KS potential (**Figure 1**).

2.5. Popular Approximations for Exchange Correlation

Despite the overwhelming number of approximations available in the average DFT code, most calculations rely on a few of the most popular approximations. The sequence of these approximations is

$$\begin{aligned} XC &\sim XC^{\text{unif}}(\rho) \quad \text{(LDA)}, \\ &\sim XC^{\text{GGA}}(\rho, |\nabla\rho|) \quad \text{(GGA)}, \\ &\sim a(X - X^{\text{GGA}}) + XC^{\text{GGA}} \quad \text{(hybrid)}. \end{aligned} \tag{4}$$

The first approximation was the third major step in the foundation of DFT in the mid-1960s and was invented by Kohn & Sham (21). It was the mainstay of solid-state calculations for a generation and remains popular for some specific applications even today. It is (almost) never used in quantum chemistry, as it typically overbinds by approximately 1 eV per bond. The LDA (21) assumes that the XC energy depends on the density at each position only, and that dependence is the same as in a uniform electron gas.

Adding another level of complexity leads to the more accurate generalized gradient approximations (GGAs) (22, 23), which use information about both the density and its gradient at each point. Hybrid approximations mix a fraction (*a*) of exact exchange with a GGA (24). These maneuvers beyond the GGA usually increase the accuracy of certain properties with an affordable increase in computational cost (25). [Meta-GGAs try to use a dependence on the KS kinetic energy density to avoid calculating the Fock exchange of hybrids (26, 27), which can be very expensive for solids.]

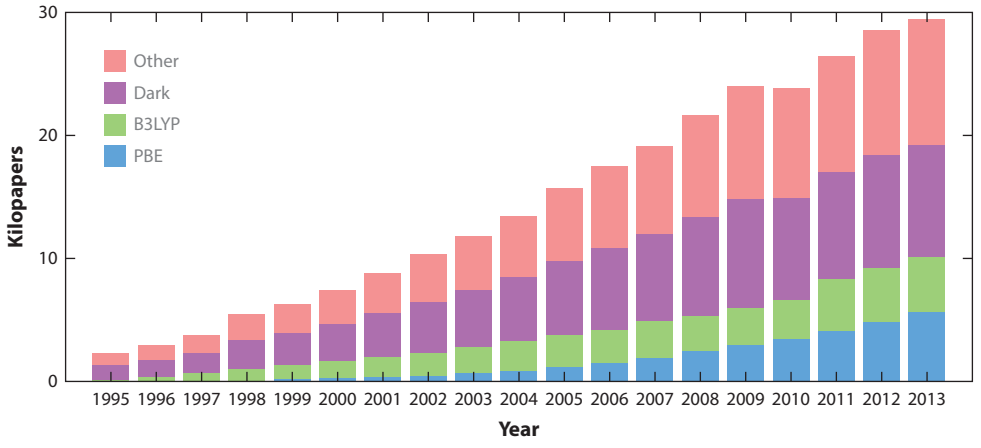

Figure 2

The number of density functional theory (DFT) citations has exploded (as have ab initio methods). PBE represents the number of citations of Reference 28, and B3LYP represents the number of citations of Reference 24. Dark indicates papers using either of these approximations without citing the original papers, and Other represents citations to all other DFT papers. All numbers are estimates. We note the contrast with figure 1 of Reference 7, which missed almost two-thirds of these citations.

Figure 2 shows that the two most popular functionals, PBE (28, 29) and B3LYP (24, 30), comprise a large fraction of DFT citations each year (about two-thirds), even though they are now cited only about half the time they are used. PBE is a GGA, whereas B3LYP is a hybrid (24). As a method tied to HF, quantum chemists' old stomping grounds, and one with typically higher accuracy than PBE, B3LYP is more often a chemist's choice. PBE's more systematic errors, mathematical rationale, and lack of costly exact exchange have made it most popular in solid-state physics and materials science. In reality, both are used in both fields and many others as well.

2.6. Cultural Wars

The LDA was defined by Kohn and Sham in 1965; there is no controversy about how it was designed. However, adding complexity to functional approximations demands choices about how to take the next step. Empirical functional developers fit their approximations to sets of highly accurate reference data on atoms and molecules. Nonempirical developers use exact mathematical conditions on the functional and rely on reference systems, such as the uniform and slowly varying electron gases. The PBE GGA is the most popular nonempirical approximation, whereas the most popular empirical functional approximation is the B3LYP hybrid. Modern DFT conferences usually include debates about the morality of this kind of empiricism.

Both philosophies have been incredibly successful, as shown by their large followings among developers and users, but each success is accompanied by failures. No single approximation works well enough for every property of every material of interest. Many users sit squarely and pragmatically in the middle of the two factions, taking what is best from both of their accomplishments and insights. Often, empiricists and nonempiricists find themselves with similar end products, a good clue that something valuable has been created with the strengths of both.

To illustrate this idea, we give a brief allegory from an alternative universe. Since at least the 1960s, accurate HF energies of atoms have been available owing to the efforts of Froese Fischer

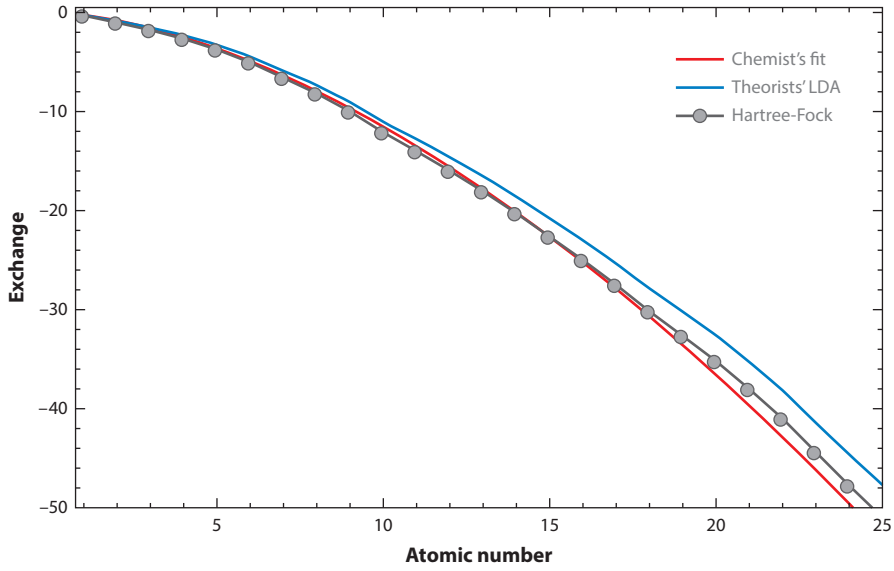

Figure 3

Exchange energy (in Hartrees) of atoms from a Hartree-Fock calculation as a function of Z, the atomic number, and two local density approximation (LDA) X calculations: one with the theoretical asymptote and the other fitted by the chemist in our story.

(31, 32) and others. A bright young chemistry student plots these X energies as a function of Z, the atomic number, and notices they behave roughly as $Z^{5/3}$, as in **Figure 3**. She is an organic chemistry student, and mostly cares only about main-group elements, so she fits the curve by choosing a constant to minimize the error on the first 18 elements, finding $E_X = -0.25Z^{5/3}$. Much later, she hears about KS DFT and the need to approximate the XC energy. A little experimentation shows that if

$$X^{\text{opt}} = C_0 \int d^3r\ \rho^{4/3}(\mathbf{r}), \tag{5}$$

this goes as $Z^{5/3}$ when Z is large, and choosing $C_0 = -0.80$ makes it agree with her fit.

In our alternate timeline, a decade later, Dirac (33), a very famous physicist, proves that for a uniform gas, $C_0 = A_X = -(3/4)(3/\pi)^{1/3} = -0.738$. Worse still, Schwinger (34) proves that inserting the TF density into Dirac's expression becomes exact as $Z \to \infty$, so that $E_X \to -0.2208Z^{5/3}$. Thus, theirs is the official LDA for X, and our brave young student should bow her head in shame.

Or should she? If we evaluate the mean absolute errors in exchange for the first 20 atoms, her functional is significantly better than the official one (35). If lives depend on the accuracy for those 20 atoms, which would you choose?[1]

[1] In fact, sadly, the young chemist is unable to find a permanent position, and she ends up selling parameterized functionals for food on the streets. Conversely, the physicists all celebrate their triumph over empiricism with a voyage on a brand new ship, which has been designed with materials whose properties have been calculated using DFT. Because the local approximation, as given above, underestimates the magnitude of the exchange energy, the brittle transition temperature is overestimated. When the new ship sails through icy waters, its hull is weakened and damaged by an iceberg, so all of them drown. (The interested reader may find more information on the ductile-to-brittle transition in Reference 135 and other works by Kaxiras and colleagues).

This simple fable contains the seeds of our actual cultural wars in DFT derivations:

1. An intuitive, inspired functional need not wait for an official derivation. One parameter might be extracted by fitting, and later derived.
2. A fitted functional will usually be more accurate than the derived version for the cases where it was fitted. The magnitude of the errors will be smaller, but less systematic.
3. The fitted functional will miss universal properties of a derived functional. We see in Section 6 that the correct LDA for exchange is a universal limit of all systems, not just atoms.
4. If one wants to add the next correction to LDA, starting with the wrong constant will make life very difficult (see Section 6).

3. WHAT IS AT THE FOREFRONT?

3.1. Accurate Gaps

Accurate energy gap calculations and self-interaction errors are notorious difficulties within DFT (36). Self-interaction error stems from the spurious interaction of an electron with itself in the Coulomb repulsion term. Orbital-dependent methods often cure most of this problem, but they can be expensive to run. The so-called gap problem in DFT often stems from treating the KS gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as the fundamental gap, but the difference in the HOMO and LUMO of the KS system is not the same as the difference between the ionization potential and the electron affinity (36). Ad hoc methods are often used to correct DFT gaps, but these methods require expensive additional calculations, empirical knowledge of one's system, or empirical tuning. However, it has recently been shown that some classes of self-interaction error are really just errors due to poor potentials leading to poorer densities (37, 38). Such errors are removed by using more accurate densities (**Figure 4**).

3.2. Range-Separated Hybrids

Range-separated hybrids (40) improve fundamental gaps calculated via the DFT HOMO-LUMO gap (41). Screened range-separated hybrids can even achieve gap renormalization when moving between gas-phase molecules and molecular crystals (42). The basic range-separated hybrid scheme divides the troublesome Coulomb interaction into long-range and short-range pieces. The screened version enforces exact conditions to determine where this separation occurs and incorporates the dielectric constant as an adaptive parameter. This technique takes into account increased screening as molecules form solids, resulting in reduced gaps critical for calculations geared toward applications in molecular electronics.

3.3. Weak Interactions

Another classic failing of DFT is its poor treatment of weak interactions (43, 44). Induced dipoles and the resulting dispersion interactions are not captured by the most popular approximations of Equation 4. This prevents accurate modeling of the vast majority of biological systems, as well as a wide range of other phenomena, such as surface adsorption and molecular crystal packing. GGAs and hybrids are unable to model the long-range correlations occurring between fluctuations induced in the density. The nonempirical approach based on the work of Langreth, Lundqvist, and colleagues (45–48) and the empirical DFT-D of Grimme (49, 50) have dominated the advances in this area, along with the more recent, less empirical approach of Tkatchenko & Scheffler (51, 52).

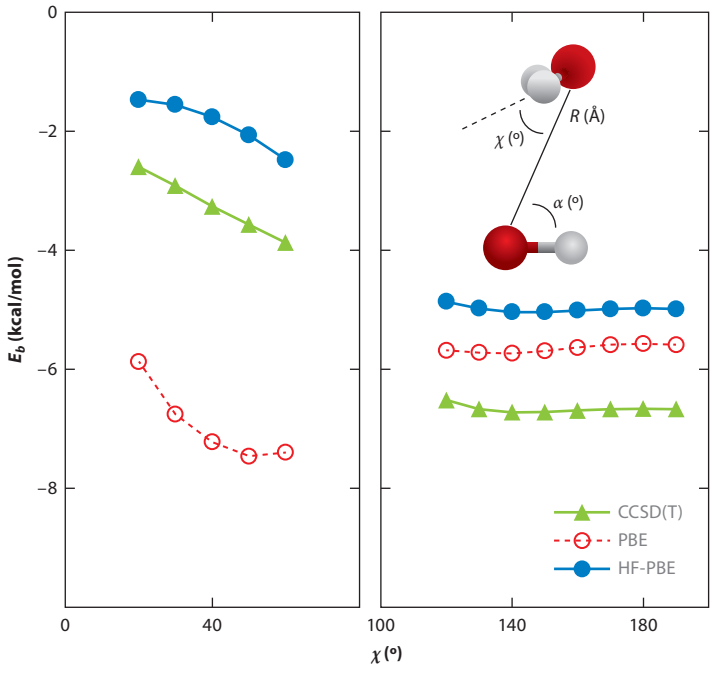

Figure 4

When a density functional theory (DFT) calculation is abnormally sensitive to the potential, the density can go bad. Usually, DFT approximate densities are better than Hartree-Fock (HF) (39), as in Figure 1. Here, self-consistent PBE results for OH-H_2O interactions yield the wrong geometry, but PBE on HF densities fixes this (38).

4. REDUCING COST: IS LESS MORE?

No matter how much progress is made in improving algorithms to reduce the computational cost of DFT calculations, there will always be larger systems of interest, and even the fastest calculations become prohibitively expensive. The most glaring example is molecular dynamics (MD) simulation in biochemistry. With classical force fields, these can be run for nano- to milliseconds, with a million atoms, with relative ease. But when bonds break, a quantum treatment is needed, and the first versions of these were recognized in the 2013 Nobel Prize in Chemistry (53–55). These days, many people run Car-Parrinello MD simulations (56, 57), with DFT calculations inside their MD simulations. Although new algorithms and architectures are being leveraged to greatly speed up ab initio MD, even on desktop computers (58), including these DFT calculations often reduces tractable system sizes to a few hundred atoms.

Thus, there remains a great deal of interest in finding clever ways to keep as much accuracy as needed while simplifying computational steps. One method for doing so involves circumventing the orbital-dependent KS step of traditional DFT calculations. Alternatively, one can save time by only doing those costly steps (or even more expensive procedures) on a system's most important pieces, while leaving the rest to be calculated using a less intensive method. The key to both approaches is to achieve efficiency without sacrificing precious accuracy.

4.1. Removing the Orbitals

Orbital-free methods (6, 59–63) such as TF reduce computational costs but are often not accurate enough to compete with KS DFT calculations. Current methods search for a similar solution,

by working on noninteracting kinetic energy functionals that allow continued use of existing XC functionals (64). [An intriguing alternative is to use the potential as the basic variable (65, 66) (see Sections 6 and 7).]

4.2. Embedding

Partitioning and embedding are similar procedures, in which calculations on isolated pieces of a molecule are used to gain understanding of the molecule as a whole (67). One might want to separate out molecular regions to look more closely at pieces of high interest or to find a better way to approximate the overall energy with density functionals. Parsing a molecule into chunks can also allow for entirely new computational approaches not possible when dealing with the molecule as a whole.

Partition DFT (68) is an exact embedding method based on density partitioning (69, 70). Because it uses ensemble density functionals (71, 72), it can handle noninteger electron numbers and spins (73, 74). The energy of the fragments is minimized by using effective potentials consisting of a fragment's potential and a global partition potential that maintains the correct total density. This breakdown into fragment and partition energies allows approximations that are good for localized systems to be used alongside those that are better for the extended effects associated with the partition potential.

Whereas partition DFT uses DFT methods to break up the system, projector-based wave-function-theory-in-DFT embedding techniques combine wave-function and DFT methods (75, 76). This multiscale approach leverages the increased accuracy of some wave-function methods for some bonds, for which high accuracy is vital, without extending this computational cost to the entire system. Current progress in this field has been toward the reduction of the errors introduced by the mismatch of methods between subsystems. This type of embedding has been recently applied to heterolytic bond cleavage and conjugated systems (77). Density matrix embedding theory on lattices (78) and its extension to full quantum mechanical chemical systems (79) use ideas from the density matrix renormalization group (80, 81), a blazingly fast way to exactly solve low-dimensional quantum mechanics problems. This shifts the interactions between fragments to a quantum bath instead of dealing with them through a partition potential.

5. WHAT IS THE UNDERLYING THEORY BEHIND DENSITY FUNCTIONAL THEORY APPROXIMATIONS?

Given the Pandora's box of approximate functionals, many found by fitting energies of systems, most users imagine DFT as an empirical hodgepodge. Ultimately, if we end up with a different functional for every system, we will have entirely defeated the idea of first-principles calculations. However, prior to the mid-1990s, many decades of theory were developed to better understand the local approximation and how to improve on it (43). Here we summarize the most relevant points.

The joint probability of finding one electron in a little chunk of space around point A and another in some other chunk of space around point B is called the pair probability density. The exact quantum repulsion among electrons is then

$$\text{ElecRep} = \frac{1}{2}\int dA \int dB \frac{P(A,B)}{|\mathbf{r}_A - \mathbf{r}_B|}. \tag{6}$$

But we can also write

$$P(A,B) = \rho(A)\,\rho_{\text{cond}}(A,B), \tag{7}$$

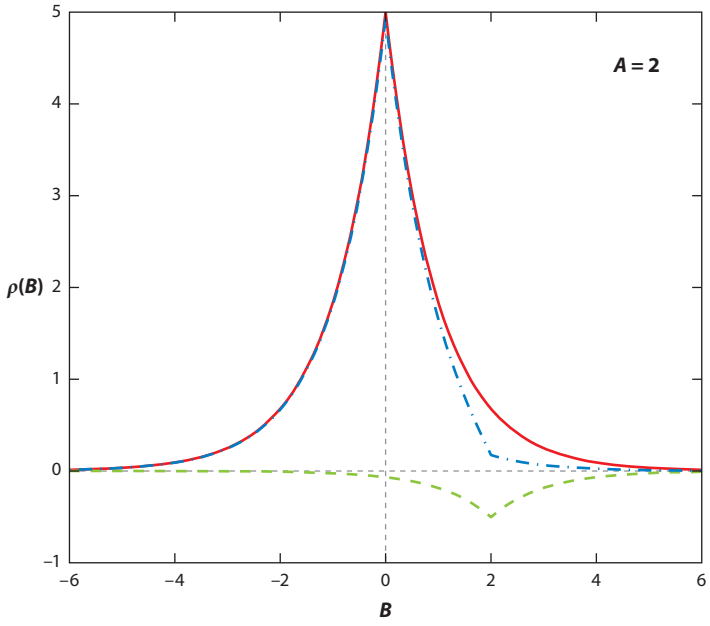

Figure 5

Illustration of a one-dimensional 10-electron density (*solid red line*), the conditional density (*dot-dashed blue line*) given an electron at $A = 2$, and its hole density (*dashed green line*).

where $\rho(A)$ is the density at $\mathbf{r}_A$ and $\rho_{cond}(A, B)$ is the probability of finding the second electron at B, given that there is one at A. [If you ignore the electron at A, this is just $\rho(B)$, and Equation 6 gives the Coulomb repulsion in Equations 2 and 3.] We write this conditional probability as

$$\rho_{cond}(A, B) = \rho(B) + \rho_{XC}(A, B), \tag{8}$$

where $\rho_{XC}(A, B)$ is called the hole around A. It is mostly negative and represents a missing electron (it integrates to -1), as the conditional probability integrates to $N - 1$. With a little math trick, called the adiabatic connection (82, 83), we can fold the kinetic correlation into the hole so that

$$XC = \frac{1}{2}\int dA \int dB \frac{\rho(A)\rho_{XC}(A, B)}{|\mathbf{r}_A - \mathbf{r}_B|}. \tag{9}$$

Because the XC hole tends to follow an electron around (i.e., be centered on A as in **Figure 5**), its shape is roughly a simple function of $\rho(A)$. If one approximates the hole by that of a uniform gas of density $\rho(A)$, Equation 9 above yields the LDA for the XC energy. So the LDA approximation for XC can be thought of as approximating the hole by that of a uniform gas (43, 84).

Although the XC is roughly approximated by LDA, the energy density at each point in a system is not, especially in systems of low symmetry. However, from Equation 9, the energy depends only on the average of the XC hole over the system, and **Figure 6** shows such a system-averaged hole for the helium atom (integrate over A and the angular parts of B in Equation 9). The LDA hole is not deep enough, and neither is the LDA energy. This is the effect that leads to LDA overbinding of molecules.

5.1. Generalized Gradient Approximation Made Briefer

The underlying idea behind the Perdew series of GGAs was to improve on the LDA hole (86). Adding gradient corrections to the hole violates certain sum rules (the negativity of the exchange

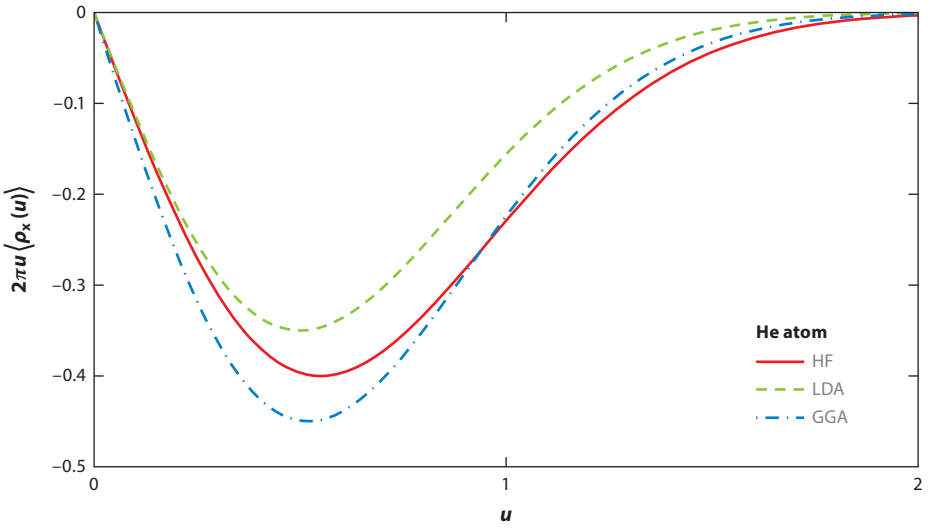

Figure 6

Illustration of system-averaged radial exchange holes for the helium atom (85), weighted by the Coulomb repulsion, so that the area equals the exchange (X) energy. Compared to accurate Hartree-Fock (HF) (*solid red line*), the local density approximation (LDA) hole (*dashed green line*) is not deep enough, reflecting that the LDA underestimates the magnitude of the X energy. The generalized gradient approximation (GGA) hole (*dotted-dashed blue line*) is substantially better, but a little too deep.

hole and integration to −1, and integration to zero for the correlation hole), so the real-space cutoff procedure was designed to restore these conditions. This is an effective resummation of the gradient expansion, producing the numerical GGA. The popular functional PBE was derived from imposing exact conditions on a simple form (28, 29) but should be believed because it mimics the numerical GGA. **Figure 6** shows how the GGA hole roughly improves on LDA, reducing typical energy errors by a factor of three.

GGAs not only show how important good hole models can be, they also demonstrate that good approximations can satisfy different exact conditions, so picking which to satisfy is nontrivial. For instance, B88 (23), PW91 (87, 88), and PBE (28, 29) give similar values for exchange energy when densities do not get too small or vary too quickly. However, once they do, each behaves very differently. Each approximation was sculpted to satisfy different exact conditions in this limit. Becke decided a good energy density for exponential electronic densities was important. Perdew and coworkers first thought that a particular scaling behavior was important (89) and then thought that satisfying a certain bound was better (28). Without a systematic way to improve our approximations, these difficult choices guide our progress. But starting from a model for the XC hole is an excellent idea, as such a model can be checked against the exact XC hole (90).

5.2. Exchange-Hole Dipole Moment Method

A recent, parameter-free approach to capturing dispersion is the exchange-hole dipole moment method (91–94), in which perturbation theory yields a multipole-multipole interaction, and quantum effects are included through the dipole moment of the electron with its exchange hole. Using these in concert with atomic polarizabilities and dipole moments generates atomic pair dispersion coefficients that are within 4% of reference C_6 values (95). Such a model has an

advantage over the more popular methods mentioned in Section 3 because its assertions about the hole can be checked.

5.3. Random Phase Approximation and Other Methods

Originally put forth in the 1950s as a method for the uniform electron gas, random phase approximation (RPA) can be viewed as a simplified wave function method or a nonlocal density functional approach that uses both occupied and unoccupied KS states to approximate the correlation energy. RPA correlation performs extremely well for noncovalent, weak interactions between molecules and yields the correct dissociation limit of H_2 (96), two of the major failures of traditional DFT approximations (97).

Although computational expense once hindered the wide use of RPA, resolution-of-identity implementations (98, 99) have improved its efficiency, making it accessible to researchers interested in large molecular systems. RPA gives good dissociation energy for catalysts involving the breaking of transition-metal-ligand and carbon-carbon bonds in a system of over 100 atoms (100). Although RPA handles medium- and long-range interactions very well, its trouble with short-range correlations invites the development of methods that go beyond RPA. RPA used in quantum chemistry usually describes only the particle-hole channel of the correlation, but another recent approach to RPA is particle-particle RPA (101). This approach is missing some correlation, which causes errors in the total energies of atoms and small molecules. This nearly cancels out in reaction energy calculations and yields fairly accurate binding energies (102).

RPA and its variations will likely lead to methods that work for both molecules and solids, and their computational costs will be driven down by algorithmic development. However, RPA is likely to remain substantially more expensive than a GGA calculation for the indefinite future. Although RPA methods may rise to fill an important niche in quantum chemistry, producing comparably accurate energetics to modern functionals without any empiricism, such methods will not replace DFT as the first run for many calculations. Moreover, as with almost all methods that are "better" than DFT, there appears to be no way to build in the good performance of older DFT approximations.

6. IS THERE A SYSTEMATIC APPROACH TO FUNCTIONAL APPROXIMATION?

A huge intellectual gap in DFT development has been in the theory behind the approximations. This, as detailed above, has allowed the rise of empirical energy fitting. Even the most appealing nonempirical development seems to rely on picking and choosing which exact conditions the approximation should satisfy. Lately, even Perdew and colleagues (103, 104) have resorted to one or two parameters in the style of Becke to construct a meta-GGA. Furthermore, up until the mid-1990s, many good approximations were developed as approximations to the XC hole, which could then be tested and checked for simple systems.

However, in fact, there is a rigorous way to develop density functional approximations. Its mathematical foundations were laid down 40 years ago by Lieb & Simon (105–107). They showed that the fractional error in the energy in any TF calculation vanishes as $Z \to \infty$, keeping $N = Z$. Their original proof is for atoms but applies to any molecule or solid, once the nuclear positions are also scaled by $Z^{1/3}$. Their innocuous statement is in fact quite profound. This very complicated many-body quantum problem, in the limit of large numbers of electrons, has an almost trivial (approximate) solution. And although the world finds TF theory too inaccurate to be useful, and performs KS calculations instead, the equivalent statement (not proven with rigor) is that the fractional error in the LDA for XC vanishes as $Z \to \infty$. XC, like politics, is entirely local in this limit.

These statements explain many of the phenomena seen in modern DFT:

1. LDA is not just an approximation that applies for uniform or slowly varying systems but is instead a universal limit of all electronic systems.
2. LDA is the leading term in an asymptotic expansion in powers of $\hbar$ (i.e., semiclassical). Such expansions are notoriously difficult to deal with mathematically.
3. The way in which LDA yields an ever smaller error as Z grows is very subtle. The leading corrections are of several origins. Often the dominant error is a lack of spatial quantum oscillations in the XC hole. However, as Z grows, these oscillations get faster, so their net effect on the XC energy becomes smaller. Thus, even as Z grows, LDA should not yield accurate energy densities everywhere in a system (and its potential is even worse, as in **Figure 1**), but the integrated XC energy will become ever more accurate.
4. The basic idea of the GGA as the leading correction to LDA makes sense. The leading corrections to the LDA hole should exist as very sophisticated functionals of the potential, but whose energetic effects can be captured by simple approximations using the density gradient. This yields improved net energetics, but energy densities might look even worse, especially in regions of high gradients, such as atomic cores.

Next, we continue the allegory from Section 2.6. To do so, we subtract the LDA exchange energy from our accurate ones, so we can see the next correction, and plot this, per electron, in **Figure 7**. Now, a bright young chemist has heard about the GGA, cooks up an intuitive correction to LDA, and fits one parameter to the noble gas values. Later, some physicists derive a different GGA, which happens to also give the correct value. Later still, a derivation of the correction for large Z is given, which can be used to determine the parameter (and turns out to match the empirical value within 10%). The only difference from the original allegory is that this is all true.

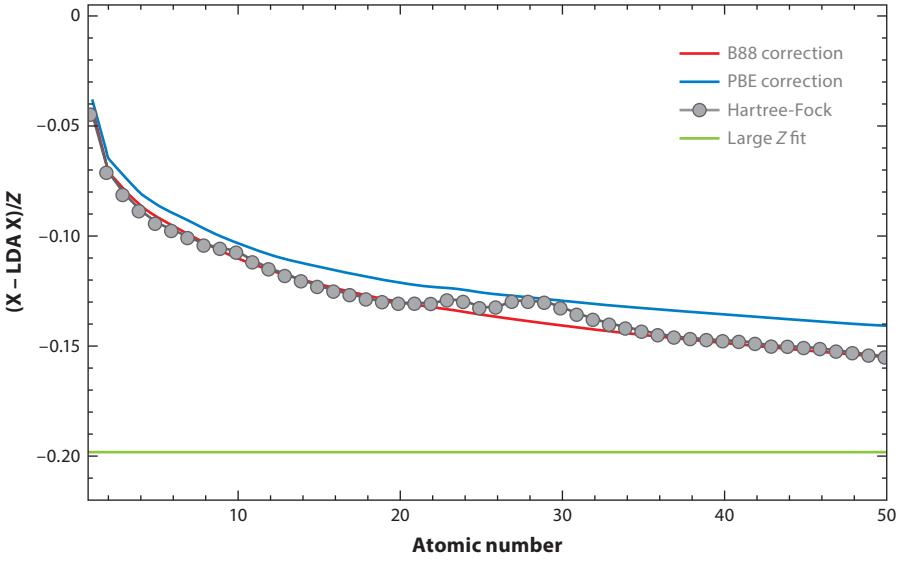

Figure 7

The nonlocal exchange energy, exchange minus local density approximation (LDA) X, per electron of atoms with atomic number Z (compare with **Figure 3**). The PBE functional tends to the theoretical limit ($Z \to \infty$) (*horizontal green line*), but B88 is more accurate for $Z < 50$ because of fitting (108).

The chemist was Becke; his fitted functional is B88 (23). The derived functional is PBE (28), and the derivation of the parameter in B88 is given in Reference 108.

This true story validates both Becke's original procedure and the semiclassical approach to density functional approximation. We note that even the correction is evaluated on the TF density to find the limiting behavior. The PBE exchange functional also yields the leading correction to the exchange energy of atoms. PBEsol was created by throwing this away and restoring the (different) gradient expansion for slowly varying gases (109).

6.1. Semiclassical Approximations

New approximations driven by semiclassical research can be divided into density approaches and potential approaches. In the density camp, we find innovations such as Armiento & Mattsson's (110–112) approximations, which incorporate surface conditions through their semiclassical approach. In the potential functional camp, we find highly accurate approximations to the density, which automatically generate approximations to noninteracting kinetic energies (65, 66, 113). Because these approaches use potential functionals, they are orbital-free and incredibly efficient but apply only in one dimension (see also Section 7). Current research is focused on extension to three dimensions and semiclassical approximations in the presence of classical turning points, as well as semiclassical approximations to exchange and correlation energies.

7. WARM DENSE MATTER: A HOT NEW AREA?

Although we do not live at icy absolute zero, most chemistry and physics happens at low-enough temperatures that electrons are effectively in their ground state. Most researchers pretend to be at zero temperature for their DFT work with impunity. But some people, either those working at high-enough temperatures and pressures or those interested in low-energy transitions, cannot ignore thermal effects. Those of us caught up in these warmer pursuits must tease out where temperature matters for our quantum mechanical work.

In 1965, Mermin (114) proved a finite-temperature version of the Hohenberg-Kohn theorem, and the finite-temperature LDA was shown in the original KS paper (21). However, many people continue to rely on the zero-temperature approximations, although they populate states at higher energy levels using finite-temperature weightings. **Figure 8** shows how these high-energy populations affect electronic densities as temperatures rise. Better understanding and modeling of the finite-temperature XC hole could lead to improvement in some of the finer details of these calculations, such as optical and electronic properties (115).

7.1. Warm Dense Matter and Molecular Dynamics

One area that has seen great recent progress with DFT is the study of warm dense matter (WDM) (116, 117). WDM is intermediate to solids and plasmas, inhabiting a world where both quantum and classical effects are important. It is found deep within planetary interiors, during shock physics experiments, and on the path to the ignition of inertial confinement fusion. Lately, the use of DFT MD has been a boon to researchers working to simulate these complicated materials (118–124). Most of these calculations are performed using KS orbitals with thermal occupations, ignoring any temperature dependence of XC, in hopes that the kinetic and Coulomb energies will capture most of the thermal effects. Agreement with experiment has been excellent, although there is great interest in seeing if temperature-dependent XC approximations affects these results.

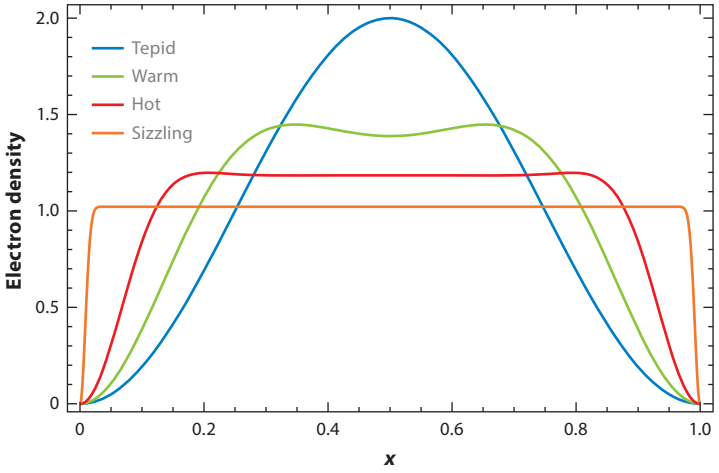

Figure 8

The density of a single electron in a flat box spreads toward the infinite walls as temperatures rise.

7.2. Exact Conditions

Exact conditions have been derived (115, 125–127) for finite-temperature systems that seem very similar to their ground-state counterparts. However, a major difference in thermal systems is that when one squeezes or compresses the length scale of the system, there is an accompanying scaling of the temperature. This is further reflected in the thermal adiabatic connection, which links the noninteracting KS system to the interacting system through scaling of the electron-electron interaction. At zero temperature, this allows us to write the XC energy in terms of the potential alone, as long as it is accompanied by appropriate squeezing or stretching of the system's length scale (see Section 5). With the temperature-coordinate scaling present in thermal ensembles, the thermal adiabatic connection requires not only length scaling, but also the correct temperature scaling.

7.3. Orbital-Free Methods

Orbital-free methods, discussed in Section 4, are of particular interest in the WDM community. Solving the KS equations with many thermally populated orbitals is repeated over and over in DFT MD, leading to prohibitive cost as temperatures rise. The focus on free energies for thermal ensembles has led to two different approaches to orbital-free approximations. One approach uses two separate forms for kinetic and entropic contributions (127). Following this path, one can make approximations either empirically (128) or nonempirically (129). Another approach enforces a particular type of response in the uniform gas limit (130). If one wishes to approximate the kentropy, the free energy consisting of kinetic energy and temperature-weighted entropy (115), as a whole, one can use temperature-dependent potential functional theory to generate highly accurate approximations from approximate densities generated semiclassically or stochastically (131, 132). **Figure 9** shows the accuracy of a semiclassical density approximation, which captures the quantum oscillations missed by TF theory and still present as temperatures rise.

8. WHAT CAN WE GUESS ABOUT THE FUTURE?

The future of DFT remains remarkably bright. As **Figure 2** shows, the number of applications continues to grow exponentially, with three times as much activity than previously realized (7,

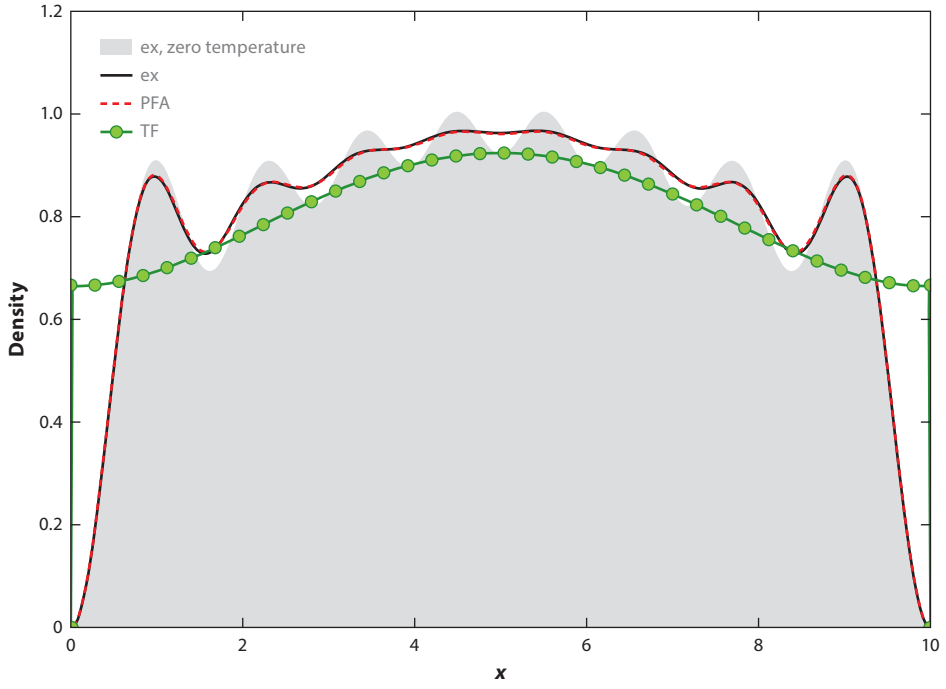

Figure 9

Eight electrons in the potential $-2\sin^2(\pi x/10)$ in a one-dimensional box. At zero temperature (*gray*), the density exhibits sharp quantum oscillations, which wash out as the temperature increases (*black line*). This effect is much weaker near the edges. Thomas-Fermi (TF) theory (*green line*) is used in many warm simulations but misses all oscillations, vital for accurate chemical effects. The orbital-free, finite-temperature potential functional approximation (PFA) (*red line*) of Reference 125 is almost exact here.

figure 1). Although empiricism has generated far too many possible alternatives, the standard well-derived approximations continue to dominate.

To avoid losing insight, we need to further develop the systematic path to approximations, which eschews all empiricism and expands the functional in powers of $\hbar$, Planck's constant. This will ultimately tell us what we can and cannot do with local-type approximations. There is huge room for development in this area, and any progress could impact all those applications.

Meanwhile, new areas have been developed (e.g., weak interactions) or are being developed (WDM). New methods, such as the use of Bayesian statistics for error analysis (133) or machine learning for finding functionals (63, 134), are coming online. Such methods will not suffer the limitations of local approximations and should be applicable to strongly correlated electronic systems, an arena where many of our present approximations fail. We have little doubt that DFT will continue to thrive for decades to come.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

A.P.-J. thanks the US Department of Energy (DE-FG02-97ER25308), and K.B. thanks the National Science Foundation (CHE-1112442). We are grateful to Cyrus Umrigar for data on the helium atom and to Min-Cheol Kim for **Figure 4** and Attila Cangi for **Figure 9**.

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Annual Review of
Physical Chemistry
Volume 66, 2015

Contents

Indexes

Errata

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