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Since its formal inception in 1964–1965, Kohn-Sham density-functional theory (KS-DFT) has become the most popular electronic structure method in computational physics and chemistry. Its popularity stems from its beautifully simple conceptual framework and computational elegance. The rise of KS-DFT in chemical physics began in earnest in the mid 1980s, when crucial developments in its exchange-correlation term gave the theory predictive power competitive with well-developed wave-function methods. Today KS-DFT finds itself under increasing pressure to deliver higher and higher accuracy and to adapt to ever more challenging problems. If we are not mindful, however, these pressures may submerge the theory in the wave-function sea. KS-DFT might be lost. I am hopeful the Kohn-Sham philosophical, theoretical, and computational framework can be preserved. This Perspective outlines the history, basic concepts, and present status of KS-DFT in chemical physics, and offers suggestions for its future development. © *2014 AIP Publishing LLC*.
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I. INTRODUCTION

Density-functional theory (DFT) is a subtle, seductive, provocative business. Its basic premise, that all the intricate motions and pair correlations in a many-electron system are somehow contained in the *total electron density* alone, is so compelling it can drive one mad. I attended my first DFT conference in 1983, a two week NATO workshop in Alcabideche, Portugal.[1] The intensity of the debates and the level of scientific excitement at the meeting were impressive. I was hooked. It was about ten years before DFT made its big splash in computational chemistry. The field was new.[2] We were still finding our way.

The theoretical foundations had been laid by Hohenberg, Kohn, and Sham in 1964–1965[3,4] but the formative years were ~1980–2010. An analysis of Web of Science citation data undertaken at Tulane University reveals that DFT was the most active field in physics during this thirty-year period.[5] Of the top three most cited physicists,[6] the first (Perdew: 65 757 citations) and third (Becke: 62 581 citations) were density-functional theorists. The second was Richard Smalley (63 354). The top three most cited physics papers,[7] and eight of the top ten, were in the field of DFT. The Tulane analysis covers citations during, and to papers published within, the 1980–2010 window. The Hohenberg-Kohn-Sham (HKS) papers are therefore not included. Total citation counts for notable DFT papers, including the HKS papers, are shown in Table I, from Web of Science and Google Scholar as of January 1, 2014. The numbers speak for themselves. DFT is huge.

I will focus in this Perspective on the basic engine of Kohn-Sham DFT, the ground-state exchange-correlation functional, as it pertains to problems in chemical physics. I have been involved in its development since the "muffin-tin Xα" days of the late 1970s to the present and hopefully into the future. The narrative will have a historical and somewhat personal slant, but I intend for this article to be a teaching tool as well. Of course DFT is a much larger subject, and thankfully the recent Perspective of Burke[8] provides a broader overview. Also the Perspective of Klimes and Michaelides[9] on dispersion interactions in DFT is an excellent accompaniment.

The contributions to this special issue reflect the many colors of the modern DFT tapestry. It is all very good and increasingly powerful stuff. I wonder, however, if the heart and soul of Kohn-Sham DFT may be slipping from our grasp. Although it is not strictly so defined, I think KS-DFT is about *occupied orbitals only* (I hesitate to suggest the acronym "OOO"). Yet virtual orbitals are more and more being used: perturbation theory, random phase approximation, etc. My personal research philosophy has always been *occupied orbitals only*. It focuses the mind. It defines one's path. It is what gave KS-DFT its popularity and a share of the 1998 Chemistry Nobel prize to Walter Kohn. Let us not give up on the original spirit of Kohn-Sham DFT. Here is my take on the first fifty years. We use atomic units throughout, where $\hbar = m_e = e = 4\pi\varepsilon_0 = 1$.

II. IN THE BEGINNING

The intuitive origins of density-functional theory predate the seminal 1964–1965 Hohenberg-Kohn-Sham papers[3,4] by many decades. Thomas,[10] Fermi,[11] and Dirac[12] imagined that the kinetic and exchange energies of systems of many electrons could be *locally* modeled by their *uniform electron gas energy densities*. The result was an approximate theory of electronic structure ("TFD") depending only on the total electronic density $\rho(\boldsymbol{r})$. Though wonderfully simple, TFD fails qualitatively because it is unable to self-consistently reproduce atomic shell structure. Even with accurate input

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TABLE I. Total citations for notable DFT papers as of January 1, 2014. References are as follows: LYP,[67] B3PW91,[97] PBE,[59] B88,[63] KS,[4] HK.[3]

Paper	Web of Science	Google Scholar
LYP	43 123	49 703
B3PW91	42 642	52 028
PBE	30 575	37 771
B88	24 766	28 529
KS	21 670	31 251
HK	15 222	27 317

densities from other sources, TFD energies have errors of around 10%, too large for computational purposes. Furthermore, Teller deduced[13] that Thomas-Fermi theory cannot bind molecules. TFD is useful for rough estimates of atomic properties only.

Shell structure is a consequence of the Pauli exclusion principle and, as such, arises from electron pairs in orthonormal orbitals arranged in Slater determinants. Hartree-Fock (HF) theory is the simplest realization. Given the Hamiltonian operator, H, for N electrons in an external (nuclear) potential v_{ext}:

$$H = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v_{ext}(\boldsymbol{r}_i) + \frac{1}{2}\sum_{j\neq i}\sum_i \frac{1}{|\boldsymbol{r}_j - \boldsymbol{r}_i|},$$
(1)

we minimize the energy of a Slater determinant with respect to variations in the occupied spin orbitals $\psi_{i\sigma}$. The result is the famous HF orbital equation

$$-\frac{1}{2}\nabla^2\psi_{i\sigma}(1) + v_{ext}(1)\psi_{i\sigma}(1) + v_{el}(1)\psi_{i\sigma}(1)$$
$$-\sum_j \left[\int \frac{\psi_{j\sigma}^*(2)\psi_{i\sigma}(2)}{r_{12}}d2\right]\psi_{j\sigma}(1) = \varepsilon_{i\sigma}\psi_{i\sigma}(1),$$
(2)

$$v_{el}(1) = \int \frac{\rho(2)}{r_{12}}d2, \quad \rho = \sum_\sigma \rho_\sigma, \quad \rho_\sigma = \sum_i |\psi_{i\sigma}|^2,$$

with the summation over j in the exchange term over orbitals of parallel spin only. The total HF energy is given by

$$E_{HF} = -\frac{1}{2}\sum_\sigma\sum_i \int \psi_{i\sigma}^*\nabla^2\psi_{i\sigma} + \int v_{ext}\rho$$
$$+\frac{1}{2}\iint \frac{\rho(1)\rho(2)}{r_{12}}d1d2 + E_X,$$
(3)

$$E_X = -\frac{1}{2}\sum_\sigma \iint \frac{|\sum_i \psi_{i\sigma}^*(1)\psi_{i\sigma}(2)|^2}{r_{12}}d1d2,$$

where E_X is the Hartree-Fock *exchange* energy. The first three terms are the total kinetic energy, the interaction energy with the external potential, and the classical Coulomb self-interaction energy, respectively.

HF theory, while immensely more useful than TFD, is still not accurate enough for energy predictions in chemistry. Bond energies are significantly underestimated. Some molecules, F_2, for example, are not even bound at the Hartree-Fock level. Thus *post*-HF methods, adding to Hartree-Fock

numerous other determinants involving excited or "virtual" orbitals, are generally required for viable chemical computations. Post-HF technology is well developed (see, e.g., Refs. 14 and 15 for overviews) and capable of very high accuracy, but the development and computational costs are severe. Simply put, it is *complicated*, and the computer-time scaling with system size N is several orders larger than for Hartree-Fock depending on the method (i.e., the formal scaling[16] of HF is N^4, while post-HF methods scale like N^5 and higher as their sophistication increases). I will refer to HF and post-HF methods as *wave-function* methods, and the theory as *wave-function theory* (WFT). The more common terminology, *ab initio* theory, is regrettable as it denigrates density-functional theory. As we shall see in Secs. III and IV, DFT is as "*ab initio*" as WFT.

In the mid 1900s, computation of HF orbitals in condensed-matter systems was intractable. The problem is the orbital-dependent, nonlocal, exchange operator in Eq. (2). In 1951 Slater proposed a solution,[17] the Hartree-Fock-Slater (HFS) method, which in many respects is the ancestor of modern DFT. He replaced the HF exchange operator with an *orbital average*, deriving the following multiplicative exchange *potential*,

$$v_{X\sigma}^{Slater}(1) = -\frac{1}{\rho_\sigma(1)}\int \frac{|\sum_i \psi_{i\sigma}^*(1)\psi_{i\sigma}(2)|^2}{r_{12}}d2,$$
(4)

known as the Slater potential. We will see it again and again in this paper.

Slater observed that $v_{X\sigma}^{Slater}(1)$ is the Coulomb potential at $\boldsymbol{r}_1$ of an *exchange hole*:

$$h_{X\sigma}(1,2) = -\frac{|\sum_i \psi_{i\sigma}^*(1)\psi_{i\sigma}(2)|^2}{\rho_\sigma(1)},$$
(5)

whose depth at $\boldsymbol{r}_2 = \boldsymbol{r}_1$ is $-\rho_\sigma(1)$ and whose integrated charge is always -1:

$$\int h_{X\sigma}(1,2)d2 = -1.$$
(6)

This is easily proved using orthonormality of the orbitals. Then he modelled the spherical average of the hole, around $\boldsymbol{r}_1$, as follows:

$$h_{X\sigma}(1,r_{12}) = -\rho_\sigma(1)f(ar_{12}),$$
(7)

where $f(x)$ is some reasonable shape profile (square well, Gaussian, hyperbolic secant, etc.) with $f(0) = 1$ and "a" is determined by the hole normalization condition Eq. (6). An exchange potential of the form

$$v_{X\sigma}^{Slater} = -C_{X\sigma}\rho_\sigma^{1/3}$$
(8)

is obtained, where the constant $C_{X\sigma}$ depends on $f(x)$ but is rather insensitive to its shape. If we choose for $f(x)$ the exchange hole in the *uniform electron gas* (UEG), we obtain

$$v_{X\sigma}^{Slater} = -3\left(\frac{3}{4\pi}\right)^{1/3}\rho_\sigma^{1/3}.$$
(9)

In modern DFT parlance this is, except for a factor 2/3, the exchange-only "local (spin) density approximation" (LDA).

Slater anticipated much of what was later to transpire in Kohn-Sham DFT. His last book,[18] *The Self-Consistent Field for Molecules and Solids,* is an excellent DFT introduction, though restricted to exchange only. Slater's insights on the nature of the "hole," in compact and extended systems, inspired me and many others to enter DFT. Particularly fascinating was that HFS bond energies were superior to HF bond energies.[19] There was no clear underbinding or overbinding trend for HFS, and the errors were still unacceptably large, but this early victory over Hartree-Fock foreshadowed things to come.

III. THE BIRTH OF DENSITY-FUNCTIONAL THEORY

While intriguing in its simplicity and early successes, the Hartree-Fock-Slater method is a *model*, not a *theory*, of electronic structure. Where is dynamical correlation? Where is the correlation contribution to *kinetic* energy? HFS offers no answers to these questions. In their seminal 1964–1965 papers,[3,4] Hohenberg, Kohn, and Sham founded the rigorous theory that finally legitimized the intuitive leaps of Thomas, Fermi, Dirac, and Slater. Thus, 1964 is widely accepted as the birth year of modern DFT.

It was established in the 1964 paper of Hohenberg and Kohn[3] that the total electron density ρ completely and exactly determines all the (ground-state) properties of an N-electron system. Thus, ρ can be used as the fundamental "variable" in electronic structure theory. The much more complicated N-electron wave function is, in principle, superfluous. The logic is subtle. It goes something like this:

$$v_{ext} \rightarrow \Psi_0 \rightarrow \rho \quad \text{or} \quad v_{ext} \rightarrow \rho. \qquad (10)$$

For a system of N interacting electrons in an external potential, v_{ext}, and hence governed by the Hamiltonian of Eq. (1), there is a unique ground-state wave function Ψ_0 and associated density ρ. If the mapping from v_{ext} to ρ is "one-to-one" or reversible (see Ref. 3 for the proof), then

$$\rho \rightarrow v_{ext} \rightarrow \Psi_0 \rightarrow everything! \qquad (11)$$

i.e., ρ uniquely determines v_{ext}, which has a unique Ψ_0, and thus *in principle* we know everything.

The above is not enough however. For the theory to be self-contained, we need a variational principle. Corresponding to the first and last terms in the Hamiltonian, Eq. (1), the terms that do *not* involve the external potential, there exists a density functional for the total kinetic + total Coulomb interaction energy:

$$F(\rho) = T(\rho) + V_{ee}(\rho). \qquad (12)$$

From the WFT variational principle, it can be proved (see Ref. 3) that

$$F(\rho') + \int v_{ext}\rho' \geq F(\rho) + \int v_{ext}\rho = E_0, \qquad (13)$$

where ρ' is *not* the ρ corresponding to v_{ext}, but to some *other* external potential, and E_0 is the exact ground-state energy. This is the Hohenberg-Kohn density variational principle. Note that the Hohenberg-Kohn proofs were restricted to nondegenerate ground states, and that the mapping of Eq. (11)

inherently assumes "v-representable" densities, a subset of all conceivable Fermion densities. The later "constrained search" approach of Levy[20] relaxes this requirement.

That the functionals $T(\rho)$ and $V_{ee}(\rho)$ are known to exist *does not imply that we can write them down*! The requirement of v-representability (or the looser Fermion representability in the approach of Levy) on the densities is an additional difficulty. Nonrepresentable variational densities will collapse to the same shell-structureless densities obtained in Thomas-Fermi-Dirac theory. A year later, Kohn and Sham addressed both of these problems.[4]

Consider a single Slater determinant of orthonormal orbitals ψ_i with total density

$$\rho = 2 \sum_i |\psi_i|^2 \qquad (14)$$

and total kinetic energy

$$T_0 = -\frac{1}{2} \sum_i 2 \int \psi_i^* \nabla^2 \psi_i, \qquad (15)$$

where, for simplicity in this section and Sec. IV, we assume spin-neutral systems. A single Slater determinant connotes independent, noninteracting electrons. Nevertheless we presume that the density *expression* of Eq. (14) spans all possible N-electron densities, interacting or not. It is reasonable to assume that T_0 is a rather good approximation to $T(\rho)$ in the Hohenberg-Kohn energy functional $F(\rho)$. It is reasonable, also, to approximate $V_{ee}(\rho)$ by the classical Coulomb self energy

$$J(\rho) = \frac{1}{2} \iint \frac{\rho(1)\rho(2)}{r_{12}} d1 d2. \qquad (16)$$

Kohn and Sham called the error made by these approximations the *exchange-correlation* energy E_{XC}:

$$F(\rho) = T_0(\rho) + J(\rho) + E_{XC}(\rho),$$
$$\text{or} \quad E_{XC}(\rho) = T(\rho) + V_{ee}(\rho) - T_0(\rho) - J(\rho), \qquad (17)$$

where T_0, by extension of the Hohenberg-Kohn analysis to noninteracting systems, is a density functional also, and therefore so is E_{XC}. Note that E_{XC} is composed of both *kinetic* and potential energies.

Collecting all the above, the Kohn-Sham total energy functional is

$$E(\rho) = T_0(\rho) + \int v_{ext}\rho + J(\rho) + E_{XC}(\rho). \qquad (18)$$

The brilliance of this decomposition is that T_0 and J are given by exact expressions, Eqs. (15) and (16), and that the "unknown" functional, E_{XC}, is a relatively small part of the total. Variational minimization of Eq. (18) with respect to the orbitals ψ_i yields the Kohn-Sham (KS) orbital equation

$$-\frac{1}{2}\nabla^2 \psi_i + v_{KS}\psi_i = \varepsilon_i \psi_i, \qquad (19)$$

where v_{KS} is given by

$$v_{KS} = v_{ext} + v_{el} + \frac{\delta E_{XC}}{\delta \rho}, \qquad (20)$$

TABLE II. Atomic exchange energies, in a.u. (computed using LDA orbitals). Exact, Eq. (3). LDA, Eq. (38). B86,[56] Eq. (41). B86b,[60] Eq. (42). B88,[63] Eq. (47). PW86,[61] Eq. (43). revPW86.[62] PBE,[59] Eq. (49). BR.[81]

	Exact	LDA	B86	B86b	B88	PW86	revPW86	PBE	BR
He	-0.998	-0.862	-1.003	-0.999	-1.001	-1.009	-1.022	-0.990	-1.015
Ne	-12.01	-10.97	-12.09	-12.08	-12.06	-12.15	-12.29	-11.99	-12.12
Ar	-30.09	-27.81	-30.12	-30.12	-30.09	-30.23	-30.54	-29.93	-30.03
Kr	-93.68	-88.54	-93.71	-93.76	-93.77	-93.73	-94.57	-93.32	-92.77
Xe	-178.9	-170.5	-178.8	-178.9	-179.0	-178.5	-179.9	-178.2	-176.3

and $\frac{\delta E_{XC}}{\delta \rho}$ is the *functional derivative*[2] of E_{XC} with respect to ρ. The theory is now complete. Electrons in atoms, molecules, and solids can be viewed as *independent* particles, moving in the *effective* potential v_{KS}.

Kohn-Sham DFT is astounding in its simplicity. It is operationally an independent-particle theory, simpler even than Hartree-Fock. Yet it delivers, in principle, the exact density [through Eq. (14)] and exact total energy [through Eq. (18)] of any *interacting, correlated* electronic system. Everything hinges on the functional $E_{XC}(\rho)$ and its functional derivative. We are assured of its existence, but no explicit expression is known. In 1965, the quest for the holy grail of electronic structure theory began.

Kohn and Sham proposed a simple model for E_{XC}, the so-called "local density approximation" (LDA):

$$E_{XC}^{LDA} = \int e_{XC}^{UEG}(\rho), \qquad (21)$$

where $e_{XC}^{UEG}(\rho)$ is the exchange-correlation energy, per unit volume, of a uniform electron gas[21–23] having the local value $\rho(\mathbf{r})$ of the density. It is a reasonable first approximation, in the same vein as Thomas-Fermi-Dirac theory, certainly good for a very slowly varying $\rho(\mathbf{r})$. It is surprisingly good for atoms and molecules too, for reasons discussed in Sec. IV. In Tables II and III we compare local (spin) density exchange and correlation energies, respectively, of noble-gas atoms with exact values. The LDA is seen to be a reasonable start.

IV. THE EXCHANGE-CORRELATION HOLE

For two decades after its birth, KS-DFT was relatively unknown in quantum chemistry. Slater's HFS work[24] predated the Hohenberg-Kohn-Sham papers, and, in combination with the "muffin tin" (or "scattered wave") numerical implementation of Johnson,[25] had acquired some momentum. HFS implementations using standard atom-centered basis sets,[26,27] numerical atom-centered basis sets,[28] and high-precision numerical grids[19] were also under development. By the early 1980s, several reliable molecular HFS computer codes were up and running, but all this was largely ignored by the greater quantum chemistry community. The accuracy of the HFS model was no match for their well-established wave-function methods.

Solid-state physicists, on the other hand, made key advances in KS-DFT in its early decades. Reference 2 surveys the progress and literature of the period. Most importantly, a rigorous formula for the exchange-correlation energy E_{XC} in terms of quantum-mechanical pair density and an exchange-correlation "hole" was established in Refs. 29–33 (see also Refs. 34 and 35 for simpler derivations). It is called the "adiabatic connection" formula and its central role in KS-DFT cannot be overstated. Hohenberg, Kohn, and Sham proved the existence of E_{XC} but gave no prescription for finding it. The adiabatic connection provides the prescription. We outline the derivation in the paragraphs below.

Everything in Sec. III is formally rigorous. Yet there is an apparent "disconnect" between the interacting system with kinetic energy T and Coulomb interaction energy V_{ee}, and the *non*interacting KS reference system, Eq. (19), with kinetic energy T_0 and *no* Coulomb interaction. The connection is that they have the *same density*. The disconnect is that they have different Hamiltonians. The Hamiltonian of the interacting system is given by Eq. (1). The Hamiltonian of the noninteracting system is given by

$$H_0 = \sum_i \left(-\frac{1}{2}\nabla^2 + v_0 \right)_i, \qquad (22)$$

where, for reasons we will see momentarily, v_{KS} is denoted instead by v_0. Now imagine a manifold of *partially* interacting systems, all having the *same density*, but with a Coulomb interaction of partial strength λ:

$$H_\lambda = \sum_i \left(-\frac{1}{2}\nabla^2 + v_\lambda \right)_i + \lambda G, \quad G = \frac{1}{2}\sum_{j\neq i}\sum_i \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|}. \qquad (23)$$

Here, v_λ is the external potential that delivers the density ρ in the system of interaction strength λ. The Hamiltonians of the noninteracting KS reference system and the correlated "real" system are H_0 and H_1, respectively, with $v_0 = v_{KS}$ and $v_1 = v_{ext}$. At any given λ, the system has an N-electron wave function Ψ_λ and a pair density $P_2^\lambda(1, 2)$. It can be shown[34,35] that

$$E_{XC} = \frac{1}{2}\iint \frac{1}{r_{12}}\left[P_2^{avg}(1,2) - \rho(1)\rho(2) \right] d1\, d2, \qquad (24)$$

TABLE III. Atomic correlation energies, in a.u. (computed using LDA orbitals). Exact.[77] LDA.[23] Stoll.[57,58] PBE.[59] B88c(BR).[34,85]

	Exact	LDA	Stoll	PBE	B88c(BR)
H	0	-0.022	0	-0.006	0
He	-0.042	-0.111	-0.057	-0.041	-0.041
Ne	-0.391	-0.740	-0.380	-0.346	-0.362
Ar	-0.726	-1.423	-0.730	-0.703	-0.728

where $P_2^{avg}(1, 2)$ is the *coupling-strength averaged* pair density:

$$P_2^{avg}(1, 2) = \int_0^1 P_2^\lambda(1, 2)d\lambda. \qquad (25)$$

This is the "adiabatic (constant density) connection." Equation (25) literally "connects" the KS independent-particle reference state with the fully interacting correlated state through a coupling-strength integration.

$P_2^{avg}(1, 2) - \rho(1)\rho(2)$ is the difference between the correlated pair density (λ-averaged) and the *un*correlated pair density. The difference in the associated *conditional* pair densities, obtained by dividing through by $\rho(1)$, is

$$h_{XC}(1, 2) = \frac{P_2^{avg}(1, 2)}{\rho(1)} - \rho(2), \qquad (26)$$

and is called the exchange-correlation "hole." For an electron at r_1, $h_{XC}(1, 2)$ measures the effects of exchange and correlation on the probability of finding *another* electron at r_2 with respect to the classical probability $\rho(2)$. In terms of the hole:

$$E_{XC} = \frac{1}{2} \iint \frac{\rho(1)}{r_{12}} h_{XC}(1, 2)d1d2. \qquad (27)$$

Since ρ is independent of λ, the hole too may be expressed as a coupling-strength average as follows:

$$h_{XC}(1, 2) = \int_0^1 h_{XC}^\lambda(1, 2)d\lambda,$$

$$h_{XC}^\lambda(1, 2) = \frac{P_2^\lambda(1, 2)}{\rho(1)} - \rho(2). \qquad (28)$$

At all coupling strengths the hole is normalized, at all points r_1, to -1 electron:

$$\int h_{XC}^\lambda(1, 2)d2 = -1, \quad \int h_{XC}(1, 2)d2 = -1. \qquad (29)$$

This is a generalization of Slater's exchange-hole normalization of Eq. (6).

These concepts are tremendously important. They will inform the development of exchange-correlation functionals throughout Secs. V–X. An immediate benefit is an understanding of how the local density approximation, Eq. (21), works as well as it does in atoms and molecules. Atoms and molecules, especially of small nuclear charge, do not resemble uniform electron gases even locally. However, the normalization condition, Eq. (29), on the exchange-correlation hole is universal. The same constraint applies to the exact hole, at any r_1 in an atom or molecule, as applies to the UEG model hole that replaces it in the LDA. The success of the LDA is therefore no surprise at all.

The hole at the noninteracting $\lambda = 0$ limit is of special interest. This is called the Kohn-Sham "exchange only" or "pure exchange" (or just "exchange") limit since a noninteracting system has no correlation. The wave function of the noninteracting electrons is a Slater determinant, whose hole

is given by the following exact formula:

$$h_X(1, 2) = -2 \frac{\left| \sum_i \psi_i^*(1)\psi_i(2) \right|^2}{\rho(1)}, \qquad (30)$$

and has the same normalization as in Eq. (29):

$$\int h_X(1, 2)d2 = -1. \qquad (31)$$

This is the same exchange hole, Eq. (5), derived by Slater in 1951[17] by different means and for a different purpose [note, when comparing Eqs. (5) and (30), that in spin-neutral systems, as assumed in this section, $\rho = 2\rho_\sigma$].

The Kohn-Sham *correlation* hole is defined as the difference between the exchange-correlation hole and the exchange hole:

$$h_C(1, 2) = h_{XC}(1, 2) - h_X(1, 2). \qquad (32)$$

Since both holes on the right contain -1 electron, the correlation hole has *zero* normalization:

$$\int h_C(1, 2)d2 = 0. \qquad (33)$$

Partitioning of the exchange-correlation hole into exchange and correlation parts translates to the energy as well. We have

$$E_{XC} = E_X + E_C, \qquad (34)$$

where E_X and E_C are related to their respective holes by [see Eq. (27)]

$$E_{X/C} = \frac{1}{2} \iint \frac{\rho(1)}{r_{12}} h_{X/C}(1, 2)d1d2. \qquad (35)$$

E_X is the *exchange energy of the Slater determinant of the Kohn-Sham orbitals*, and E_C is everything else. Because the correlation hole integrates to zero and the exchange hole integrates to -1, $|E_C|$ is significantly smaller than $|E_X|$. We have therefore swept the remaining and unknown *correlation* effects into an even smaller part of the Kohn-Sham total energy.

The above has been restricted, for simplicity, to spin-neutral systems. Pair densities, holes, E_X, and E_C may be separated into parallel-spin and opposite-spin components for more detailed analysis and for treatment of spin-polarized systems. See Refs. 34 and 35 for a full discussion. Explicit spin dependence is convenient in the chemical literature (though not so much in the physics literature), as the building blocks of chemistry are *spin-polarized* atoms. We will therefore reinstate spin dependence in the rest of this article. In a spin-polarized system the exchange-correlation energy is a functional of both spin densities, i.e., $E_{XC}(\rho_\alpha, \rho_\beta)$, and the Kohn-Sham orbital equation, Eq. (19), becomes a pair of equations

$$-\frac{1}{2}\nabla^2\psi_{i\sigma} + v_{KS}^\sigma \psi_{i\sigma} = \varepsilon_{i\sigma}\psi_{i\sigma}, \qquad (36)$$

one for each spin, with the Kohn-Sham spin potential given by

$$v_{KS}^\sigma = v_{ext} + v_{el} + \frac{\delta E_{XC}}{\delta\rho_\sigma}. \qquad (37)$$

The total energy formula is the same as Eqs. (3) and (18), except that E_X in Eq. (3) and $E_{XC}(\rho)$ in Eq. (18) are replaced by $E_{XC}(\rho_\alpha, \rho_\beta)$.

V. GRADIENT APPROXIMATIONS: THE ASCENDENCY OF DFT

Let us introduce the acronym DFA at this point for "density-functional *approximation*." If you attend DFT meetings, you will know that Mel Levy often needs to remind us that DFT is *exact*. The failures we report at meetings and in papers are not failures of DFT, but failures of DFAs.

The most fundamental process in chemistry is the making and breaking of bonds. Computation of bond energies is therefore one of the greatest concerns of quantum chemists. It was not until the 1980s that software implementations of HFS (and hence KS-DFT) were up to the task of computing accurate molecular energies,[26–28] but by the end of the decade robust programs were in place[36–39] and dissociation energies were under test. The energy required to dissociate a molecule entirely to free atoms, i.e., break all its bonds, is called "atomization" energy. The accurate benchmarking of DFAs on atomization energies has been the driving force of DFA development for the past thirty years.

For consistency in our DFA assessments, we will use the G2/97 atomization-energy test set of Pople and co-workers[40] throughout this article. G2/97 is a compilation of 148 atomization energies of common organic and inorganic molecules, and radicals, from diatomics to molecules of about a dozen atoms. The source is experimental data with better than 1 kcal/mol precision. One kcal/mol (4.2 kJ/mol or 0.043 eV) is often referred to as "chemical accuracy" and is the target accuracy of quantum chemical methods. Our G2/97 assessments will be tabulated in Table IV, with the mean error (ME) and mean absolute error (MAE) listed for each method. All computations are performed with our grid-based NUMOL code[41–44] and are "post-LDA" [all energies computed using orbitals from the local (spin) density approximation, with the spin-dependent UEG exchange-correlation

TABLE IV. Mean error (ME) and mean absolute error (MAE), in kcal/mol, for 148 atomization energies of the G2/97 test set[40] and 41 hydrogen-atom-transfer (HAT) reaction barriers of Lynch and Truhlar[111] (computed using LDA orbitals). See text for explanation of the acronyms.

	G2/97(ME)	G2/97(MAE)	HAT(ME)	HAT(MAE)
HF	−158.9	158.9	22.4	22.4
HFS	−23.6	35.0	−12.8	13.0
LDA	82.9	82.9	−17.8	17.8
B86+PBE	5.4	8.0	−7.9	7.9
B86b+PBE	11.5	12.6	−8.7	8.7
B88+PBE	5.5	8.1	−7.6	7.6
PW86+PBE	5.7	8.7	−7.9	7.9
revPW86+PBE	3.1	7.7	−7.6	7.6
PBE+PBE	16.3	16.9	−9.5	9.5
BR+B88c(BR)	−5.9	9.0	−5.6	5.7
B3PBE	1.1	3.2	−3.7	3.8
PBE0	1.9	4.4	−3.6	3.6
B05	0.9	2.6	0.2	1.2
B13	0.8	3.8	0.9	1.8

energy parametrization of Perdew and Wang[23]]. All entries in Table II through Table IV have been specifically (re)computed for this Perspective.

Hartree-Fock theory is assessed first. We see, as expected, massive underbinding statistics, with ME = −158.9 and MAE = 158.9 kcal/mol. Hartree-Fock-Slater, essentially the exchange-only LDA [see Eq. (38) below] is a huge improvement, with ME = −23.6 and MAE = 35.0 kcal/mol. But there is no clear underbinding or overbinding trend. The LDA for exchange-correlation has a massive *over*binding trend, as observed, e.g., for diatomic molecules by Becke[45] in the mid 1980s. The G2/97 errors are ME = 82.9 and MAE = 82.9 kcal/mol. This large overbinding tendency is actually good news. It means something profound is awaiting discovery.

Since E_X dominates E_{XC}, and since it is given by the exact expressions of Eqs. (30) and (35), it is the natural first consideration for improvement. The LDA for pure exchange is

$$E_X^{LDA} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3} \int \left(\rho_\alpha^{4/3} + \rho_\beta^{4/3}\right). \qquad (38)$$

In free atoms E_X^{LDA} falls short of the exact E_X by typically 5%–10% (Table II). Might the local density *gradient* provide useful additional information? Dimensional analysis fixes the form of the lowest-order gradient correction (LGC) to the LDA as follows:

$$E_X^{LGC} = E_X^{LDA} - \beta \sum_\sigma \int \frac{(\nabla\rho_\sigma)^2}{\rho_\sigma^{4/3}} \qquad (39)$$

with a coefficient β one might hope to calculate from the theory of the slowly varying electron gas. In the 1970s and 80s, at least three different theoretical values[46–49] were published. Earlier, in 1969, the pragmatic approach of fitting β to *atomic* exchange energies had been taken by Herman *et al.*[50,51] The Herman value,

$$\beta = 0.003 \text{ to } 0.004, \qquad (40)$$

is at least twice as large as the later "theoretical" values, a conundrum that persists to this day.[52] There is no doubt, however, that the "theoretical" β is of little relevance in chemistry. Becke[53] has published a simple exchange hole model giving roughly the Herman value. See also Langreth and Mehl[54] and Hu and Langreth[55] for additional insights.

There is a problem with Eq. (39) that renders it unacceptable in any case. The functional derivative (i.e., the KS potential) of the gradient term diverges in the exponential tails of finite systems.[50] This is not just a computational nuisance. It reflects a fundamental failure of the LGC functional form. Becke[56] suggested a simple modification in 1986 that fixes the problem:

$$E_X^{B86} = E_X^{LDA} - 0.0036 \sum_\sigma \int \rho_\sigma^{4/3} \frac{\chi_\sigma^2}{\left(1 + 0.004\chi_\sigma^2\right)},$$
$$\chi_\sigma = \frac{|\nabla\rho_\sigma|}{\rho_\sigma^{4/3}}, \qquad (41)$$

known as "B86," with parameters fit to atomic data (Table II). The B86 "β" (0.0036) is in good agreement with the Herman value, Eq. (40). Particularly exciting, however,

was that B86, in combination with an opposite-spins-only LDA correlation functional,[57,58] gave excellent bond energies in diatomic molecules.[56] In Table IV we present G2/97 statistics for B86 in combination with the more recent "PBE" correlation functional[59] to be discussed later. The MAE of "B86+PBE" is 8.0 kcal/mol, an *order of magnitude better* than for the exchange-correlation LDA. Reference 56 was the first indication, since its birth more than twenty years earlier, that DFT might be a useful tool in computational chemistry.

Becke published a second gradient-corrected E_X the same year[60] ("B86b"):

$$E_X^{B86b} = E_X^{LDA} - 0.00375 \sum_\sigma \int \rho_\sigma^{4/3} \frac{\chi_\sigma^2}{\left(1 + 0.007\chi_\sigma^2\right)^{4/5}}. \tag{42}$$

The G2/97 performance of B86b+PBE is similar to that of B86+PBE (Table IV). That different gradient-corrected E_X functionals perform similarly in molecular systems will be an important thread in our G2/97 tests.

At the same time, Perdew and Wang[61] took another approach. The exchange hole always has negative value, Eq. (30), and is always normalized to −1 electron, Eq. (31). Upon deriving an expression for the exchange hole in an electron gas with a small density gradient, they found that this lowest-order (in the density gradient) hole was *not* negative definite and did *not* satisfy the normalization condition. They zeroed the positive regions, restored proper normalization by truncating the rest, and numerically integrated the truncated hole to obtain an E_X approximation. Then the numerical results were fit with the following functional form:

$$E_X^{PW86}(\rho) = \int e_X^{LDA}(1 + 1.296s^2 + 14s^4 + 0.2s^6)^{1/15}, \tag{43}$$

$$e_X^{LDA} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3}, \quad s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}},$$

known as "PW86." Perdew and co-workers, as is the convention of physicists, write their exchange functionals as spin-neutral total-density functionals. In spin-polarized systems, one uses

$$E_X(\rho_\alpha, \rho_\beta) = \frac{1}{2}[E_X(2\rho_\alpha) + E_X(2\rho_\beta)]. \tag{44}$$

Without any parameters fit to atomic data, PW86 atomic exchange energies compare well to those of B86 and B86b (Table II). In Table IV, we see that the G2/97 statistics for PW86+PBE are also in line with the other gradient approximations. The model underpinning PW86 has been revisited by Murray, Lee, and Langreth[62] and the parameters in Eq. (43) slightly adjusted. We refer to the adjusted functional as "revPW86" in Tables II and IV.

Exchange functionals of density and density gradient have the general form, in Perdew's notation,

$$E_X(\rho) = \int e_X^{LDA}(\rho)f_X(s), \tag{45}$$

where "s" [see Eq. (43)] is a *dimensionless* or "reduced" density gradient, and $f_X(s)$ is called the "exchange enhancement factor." This form is stipulated by dimensional analysis. The UEG limit requires that $f_X(0) = 1$, and analyticity requires that

$f_X(s)$ is an *even* function, expandable in powers of s^2. PW86 is explicitly written in this form. B86 and B86b can be cast in this form as well. In a finite system such as an atom or molecule, s behaves in a manner contrary to the gradient itself. Near nuclei, where $\nabla\rho$ is largest, s is relatively small. Far from nuclei, where $\nabla\rho$ approaches zero, s diverges to infinity. In other words, electron densities are most "homogeneous" near atomic nuclei, and most "*in*homogeneous" in exponential tails. The functional form of Eq. (45) is known as the "generalized gradient approximation" (GGA), because it goes beyond the lowest-order gradient correction, Eq. (39). GGAs can be viewed as resummations of presumed infinite-order gradient expansions in s^2.

The exchange enhancement factor interpolates between $s = 0$, the UEG limit, and the asymptotic $s = \infty$ limit in the exponential tails of finite systems. The physics in the asymptotic limit is interesting. When an electron is far from a finite system ($r \to \infty$) the exchange hole remains pinned to the system and the electron sees an asymptotic Coulomb potential $-1/r$. Thus the exchange energy density goes to [see Eq. (35)]

$$e_X \approx -\frac{1}{2}\frac{\rho}{r}. \tag{46}$$

Remarkably, this behavior can be captured by a density-gradient correction.[63] Given that the asymptotic density is exponential, $\rho_\sigma \to Ae^{-ar}$, it can be shown that the following exchange functional,

$$E_X^{B88} = E_X^{LDA} - \beta \sum_\sigma \int \rho_\sigma^{4/3} \frac{\chi_\sigma^2}{(1 + 6\beta\chi_\sigma \sinh^{-1}\chi_\sigma)}, \tag{47}$$

has the correct $r \to \infty$ limit, Eq. (46), regardless of the exponential decay constants. If the single parameter β is fit to exact atomic exchange energies,[63] $\beta = 0.0042$ is obtained, in good agreement with the Herman value, Eq. (40), and with B86 and B86b. This exchange functional is known as "B88." Like all proper gradient-corrected exchange functionals, it can be written in the GGA form, Eq. (45). The G2/97 statistics for B88+PBE in Table IV are similar to the previous GGAs in the table.

Does B88 capture, in addition, the exact $-1/r$ asymptotic *functional derivative*? Engel *et al.*[64] have shown that, unfortunately, no GGA can give the exact asymptotic exchange energy density *and* the exact functional derivative. The functional derivative of B88 falls off like $-1/r^2$.

Despite the dramatic rise of exchange GGAs through the 1980s, quantum chemists, and physicists, were reluctant to adopt them. Ziegler[65] was their sole advocate during this time, applying GGAs to challenging problems in inorganic and organometallic chemistry. But everything was about to change. At the International Congress of Quantum Chemistry in Menton, France, 1991, I reported GGA atomization-energy benchmarks on Pople's older "G1" test set. Pople was present, and we had a memorable conversation that week, the first of what would be many. It was the boost that DFT needed.

Within a year, Pople and co-workers[66] combined B88 exchange with the "LYP" correlation functional of Lee, Yang, and Parr[67] (based on earlier work of Colle and Salvetti[68]), as modified by Miehlich *et al.*[69] to create "BLYP." This

was quickly followed[70] by tests of a larger variety of functionals using the modest but efficacious 6-31G* basis set. Their software platform was the ubiquitous GAUSSIAN program, requiring only minor modifications of its Hartree-Fock technology[71] and the implementation of numerical integration grids[41] to incorporate DFAs. With the consequent release of GAUSSIAN 92/DFT, density-functional theory was widely launched into the chemistry community. This was a turning point. Virtually any chemist in the world could now do DFT computations.

In 1996, Perdew, Burke, and Ernzerhof[59] (PBE) obtained an exchange GGA and a correlation GGA (the latter is the "PBE" correlation functional in Table IV) by enforcing selected theoretical constraints. Among them is the Lieb-Oxford (LO) bound[72,73] on total exchange-correlation energies:

$$|E_{XC}| \leq 2.28|E_X^{LDA}|. \tag{48}$$

The functional form of B86, Eq. (41), is convenient (but not necessary!) for enforcing this bound and PBE used it for their exchange functional:

$$f_X^{PBE}(s) = 1 + 0.804 - \frac{0.804}{1 + 0.21951s^2/0.804}. \tag{49}$$

Whereas the parameters in B86 were fit to atomic data, PBE was fit to UEG linear response and the Lieb-Oxford bound. The PBE+PBE G2/97 statistics in Table IV are noteworthy. The PBE exchange GGA gives atomization-energy errors twice as large as the other GGAs in the table.

The LO bound is a divisive issue in DFT. Atomic and molecular exchange energies are well within this bound[74] by about a factor of two. Any reasonable exchange functional will satisfy Eq. (48) for any real chemical or physical density. Just examine the data in Table II. Proponents of the LO bound therefore apply it locally, even though the energies in Eq. (48) are total energies. This is okay, if you understand that the *local* LO bound is a *manufactured* bound; a sufficient but *not necessary* constraint in functional design. Unfortunately not everyone does. The DFT literature is permeated by absurd statements that, e.g., PW86, B86b, B88, etc. "violate" the (local) LO bound. Those who make these statements ignore the inconvenient fact that the *exact* exchange energy density also "violates" the (local) LO bound, in the tail of any finite system [see Eq. (46)]. It is the local Lieb-Oxford bound that "violates" exact exchange!

All matter in our terrestrial world is composed of atoms, few in number and well defined. Atomic exchange energies are computable with arbitrarily high precision. Atomic correlation energies are accurately known up to Ar[75-77] and are known with reasonable accuracy beyond.[78] My philosophy of DFA design, and that of many others, is that *atoms* are the logical calibration targets. This philosophy is often labeled "empirical." Yet atoms are no less sacred than uniform or nearly uniform electron gases, or the sufficient-but-not-necessary local Lieb-Oxford bound. The "nonempiricists" work with selected theoretical/mathematical constraints and, in the end, assess their functionals on the *same data* as the "empiricists." Both groups are really doing the same thing, except that the nonempiricists need more iterations to get there.

There is considerable literature on gradient-corrected *correlation* DFAs as well. This is a much more difficult problem than the exchange problem. Correlation functionals do not have the simple dimensionality of exchange functionals because, unlike exchange, correlation involves the interelectronic coupling strength to all orders. Even the uniform electron gas is a challenge, with quantum Monte Carlo simulations the only systematic route to the "right" answer. UEG parametrizations are available,[21-23] as are correlation GGAs,[54,55,59,79,80] predominantly from the Perdew group. The 1996 PBE correlation GGA[59] is our current favourite. "PW91"[80] was our pre-1996 favourite. Fortunately E_C is of much less importance than E_X, so minimal discussion of E_C will be offered here. The next two paragraphs will suffice.

In low-Z atoms the correlation LDA makes a huge relative error, a factor of roughly two (too large), compared to the $\sim$10% error of the exchange LDA. Stoll *et al.*[57,58] offered an enlightening explanation. About half the UEG correlation energy is between *parallel-spin* electrons, essentially smoothing out long-range oscillations in the UEG *exchange* hole. In finite systems, especially low-Z atoms, this parallel-spin UEG effect is inoperative. Stoll *et al.*[57,58] suggested that the correlation LDA for *opposite spins only* be used in chemical applications. Thus, DFAs for E_C must attenuate the full correlation LDA by about a half, or more, in light atoms. Indeed, the correlation energy of a hydrogen atom is zero.

The first correlation DFA giving zero correlation energy for the H atom, or any one-electron system, is from Becke[34] ("B88c"). Previous DFAs giving zero H-atom correlation energy, e.g., LYP[67] and Stoll *et al.*,[57,58] ignored parallel spins altogether. B88c is also the first DFA explicitly based on the adiabatic connection, through λ-dependent cusp conditions. "Self-correlation error" can only be expunged properly if *kinetic* energy density,

$$\tau_\sigma = \sum_i |\nabla \psi_{i\sigma}|^2, \tag{50}$$

is included in E_C along with ρ and $\nabla \rho$, as demonstrated in the B88c paper[34] [note that we do *not* include a 1/2 factor in Eq. (50), nor in our other papers]. Functionals that do not incorporate τ, namely, the correlation LDA and all correlation GGAs, give a spurious nonzero H-atom E_C (Table III). Functionals incorporating τ are known as "meta"-GGAs. B88c is not modeled on the uniform electron gas and is therefore not, strictly speaking, a meta-GGA. This leads naturally to Sec. VI.

VI. OTHER STROKES

All GGA and meta-GGA functionals, by definition, are corrections to the LDA. They all revert to the uniform electron gas at zero density gradient. Might other contexts be better, or at least equally well, suited to chemistry? In 1989, Becke and Roussel[81] introduced an exchange hole model *exact for any hydrogenic atom*, but not exact for the UEG. It misses the UEG exchange energy by 2%–3%.[82]

The Becke-Roussel ("BR") model is completely nonempirical. Picture an exponential function, $-Ae^{-ar}$, centered at a distance b from some reference point $\mathbf{r}_1$. The spherical

average, around r_1, is easily obtained and Taylor expanded. The Taylor expansion, to second order, of the *exact* spherically averaged exchange hole around r_1 is given by[53]

$$h_{X\sigma}(1, r_{12}) = -\rho_\sigma - Q_\sigma r_{12}^2 + ...$$

$$Q_\sigma = \frac{1}{6}\left[\nabla^2\rho_\sigma - 2\tau_\sigma + \frac{1}{2}\frac{(\nabla\rho_\sigma)^2}{\rho_\sigma}\right], \quad (51)$$

with τ_σ as defined in Eq. (50). If the second-order Taylor expansions of the model hole and the exact hole are equated, and if normalization to -1 is enforced, then parameters A, a, and b are uniquely defined. This is the BR exchange hole model.

At first glance, the BR model might seem concocted and unnecessarily complicated. It depends on all of ρ, $\nabla\rho$, $\nabla^2\rho$, and τ. Notice, however, that a normalized off-center exponential is precisely the exchange hole in a hydrogenic atom. Thus the BR hole is exact in two respects. It replicates the second-order Taylor expansion in r_{12} of the exact exchange hole in general, and it fully replicates the exact exchange hole in any hydrogenic atom. Formulas for A, a, b, and E_X^{BR} may be found in Ref. 81, but are not expressible in closed analytical form. Imposition of the BR constraints yields a 1D nonlinear equation that must be solved by, e.g., the Newton-Raphson method. This is easily done. Becke-Roussel atomic exchange energies are about an order of magnitude better than the exchange LDA, but not as accurate as B88 (Table II).

To discard the uniform electron gas as a reference system, or not, is a personal choice. After a conference talk some years ago on the functionals OPTX[83] and OLYP[84] that do not respect the UEG limit, Nicholas Handy verbalized his own choice as follows: "I don't know about you chaps in America, but at Cambridge we have never been able to synthesize jellium!" It should be added, though, that the performance of OPTX/OLYP deteriorates for heavy atoms because the LDA *does* become exact, in a relative-error sense, in the infinite Z limit. It was the view of the Handy group that this deterioration resides in the cores and is of little chemical importance. The same would apply to the BR functional.

BR has been successful in myriad subsequent applications. It has been spliced into[85] the correlation functional B88c[34] [called B88c(BR) in Tables III and IV]. It has been generalized, in a logical and nonempirical manner, to include paramagnetic current density[86] ("BRj"). It was shown by Becke[87] and by Johnson, Dickson, and Becke[88] that BRj solves a long-standing fundamental problem with the LDA and GGAs in open-shell atomic states. The LDA and GGAs give large energy discrepancies between atomic open-shell Slater determinants that should be degenerate! BRj fixes this. In the "reverse" direction, BR has become the foundation of our latest work on exchange-correlation DFAs based on *exact* exchange (see Sec. VIII). Last, but not least, BR has been used to "density functionalize" the dispersion model of Becke and Johnson (see Sec. IX).

Meanwhile the group of Perdew, after honing the GGA functional class to its PBE form,[59] worked on meta-GGAs. Employing their favored strategy, satisfaction of UEG and other theoretical constraints, they obtained the "TPSS" functional[89–91] and the "revTPSS" functional,[92] among others. Both these functionals give the correct exchange energy

of the hydrogen atom in addition to the UEG, and their MAEs on the G2/97 atomization energies are $\sim$5 kcal/mol, slightly better than typical GGAs.

The functional derivative of τ-dependent DFAs is problematic, because the functional $\tau(\rho)$ is not known. It was the BR functional that prompted Neumann, Nobes, and Handy[93] to circumvent the problem through differentiation with respect to orbital expansion coefficients instead of functional differentiation with respect to the density. This is the trick that made Hartree-Fock theory practical long ago. Formally it is not Kohn-Sham theory, but in practice should be very close. The same strategy was employed by Adamo, Ernzerhof, and Scuseria[94] to implement meta-GGAs in the GAUSSIAN program. Alternatively, Arbuznikov and Kaupp[95] have implemented an "optimized effective potential" (OEP) for meta-GGAs that is equivalent to the Kohn-Sham potential. Total DFT energies are rather insensitive to the orbitals, self-consistent, non-self-consistent, or OEP, but properties such as nuclear shielding constants are much less so.[95] In a recent paper on a meta-GGA relativistic kinetic-energy approximation, Becke[96] has derived a variational orbital equation applicable to meta-GGAs which, again, is not the Kohn-Sham equation but should generate orbitals that are very close.

VII. HYBRID FUNCTIONALS

In 1993, Becke[97] observed that GGAs, while dramatically reducing the massive overbinding tendency of the LDA, show a small overbinding tendency still. This can be understood from the adiabatic connection formulas, Eqs. (27) and (28). E_{XC} depends on the *coupling-strength averaged* exchange-correlation hole. The $\lambda = 0$ exact exchange hole is relatively *delocalized* ("nonlocal") in multicenter systems. In H_2, for example, $h_X(1, 2)$ is spread equally over both centers regardless of the electron's position r_1 [see Eq. (30)]. Electron correlation then localizes the hole as it evolves from $\lambda = 0$ to $\lambda = 1$. GGA holes, however, are *inherently localized at all* λ, including $\lambda = 0$, and are therefore too compact. This explains why exchange-correlation GGAs, despite their sophistication, are slightly overbinding. The delocalized character of the exchange-correlation hole at $\lambda = 0$ can only be captured by replacing a small amount of DFA exchange by *exact* exchange!

In 1993 we proposed[97] the following replacement:

$$E_{XC}^{B3PW91} = E_{XC}^{LDA} + a\left(E_X^{exact} - E_X^{LDA}\right) + b\Delta E_X^{B88}$$

$$+ c\Delta E_C^{PW91},$$

$$a = 0.20, \quad b = 0.72, \quad c = 0.81. \quad (52)$$

This preserves the UEG limit, but reduces the amount of the B88 gradient *correction* ΔE_X^{B88} and the PW91 gradient *correction* ΔE_C^{PW91} because substitution of exact exchange reduces their importance. The three parameters a, b, and c were fit to atomization-energy data. This functional is known as "B3PW91" in deference to its three fitted parameters. In Table IV we report performance statistics for "B3PBE," a variant of B3PW91 that replaces PW91 correlation with the more recent PBE correlation.[59] B3PBE significantly reduces

the G2/97 errors to ME = 1.1 and MAE = 3.2 kcal/mol, about three times better than for the pure GGAs.

Frisch and co-workers[98] reworked B3PW91 using the LYP[67] correlation DFA instead of PW91. The reworked functional employs the same three parameters as in Eq. (52) and is known as "B3LYP." For the past two decades, B3LYP has been the most popular exchange-correlation DFA in computational chemistry.[8]

Perdew, Ernzerhof, and Burke[99] argued that 25% exact exchange was preferable to the 20% in B3PW91. Combined with the PBE exchange-correlation GGA,[59] and fixing $b = 0.75$ and $c = 1$, the corresponding functional is called "PBE0."[100] The slightly higher exact-exchange fraction, $a = 0.25$, in PBE0 compensates for the distinctive overbinding tendency (Table IV) of the pure PBE+PBE GGA.

These functionals are called "hybrid" functionals for obvious reasons. They mix GGA exchange with explicitly nonlocal exact exchange. Also, their implementation in the GAUSSIAN program, and in other programs, was a hybrid of technologies. The exact exchange part was implemented with well-developed Hartree-Fock techniques (differentiation with respect to orbital expansion coefficients) and the rest was KS-DFT.[71] As such the E_X^{exact} part is *not Kohn-Sham* exact exchange.[101] The orbitals are nevertheless close to true Kohn-Sham orbitals. Mixing of BR-type functionals[85] and meta-GGAs with exact exchange has also been widely tested. An excellent review of GGA and meta-GGA hybrids can be found in Ref. 102. It appears that meta-GGAs need less exact exchange than GGAs. The kinetic energy density in meta-GGAs can crudely sense exact exchange nonlocality, as Van Voorhis and Scuseria[103] and Becke[104] have pointed out.

The parameter fitting in B3PW91 crosses a philosophical line. All the functionals in Tables II and III were determined by whatever means (fitting to atoms or fitting to theoretical constraints) once and for all time. They were *not* fit to *molecular* data. With B3PW91, fitting to molecular data was initiated. Many wish this door had never been opened. Unlike the comfortably small number of noble-gas atoms employed in the fitting of B86, B86b, or B88, there are uncountably many molecules! But there was little choice. The exact-exchange mixing fraction cannot be determined from atomic data. A few years later Becke went further,[105,106] introducing a flexible form for GGA-hybrid functionals ("B97") and for second-order GGA-hybrids ("B98") that allowed systematic fitting of even more parameters. He stopped at ten, beyond which symptoms of overfitting set in. Some have gone further.[103,107] Some have, arguably, gone too far[108] ("20, 30, or even 50" parameters[108]).

In an essay entitled "*Obituary: Density Functional Theory (1927-1993)*" in 2001,[109] Gill pronounced that hybrid functionals marked the death of DFT. It is a purist view that has some merit. However, the heart of Kohn-Sham DFT is not necessarily that E_{XC} is explicitly density dependent, but that *only the occupied orbitals* are used, and that E_{XC} is *invariant with respect to unitary orbital transformations*. Hybrid functionals, meta-GGA and BR-type functionals, and the much more complicated nonlocal functionals in Secs. VIII–X, preserve these. It will take several more years,

until Sec. IX of this article, before Kohn-Sham DFT finds itself in peril.

VIII. NONLOCALITY

After the heady decades of the 1980s and 1990s, it was easy to be complacent about the "standard" DFT approximations. As DFT applications multiplied, however, the list of failures of the standard GGA and hybrid functionals grew: overstabilization of molecular radicals, poor treatment of charge transfer processes, and, most troubling of all, the inability to account for dispersion interactions (to be discussed separately in Sec. IX). All of these are truly *nonlocal* effects, extending beyond *intra*atomic to *inter*atomic distances. They cannot be treated by local functionals depending on ρ, or even by functionals depending additionally on $\nabla \rho$, $\nabla^2 \rho$, and/or τ. All such functionals are "local" as they use information only *at* each integration point $\boldsymbol{r}_1$. Truly nonlocal effects must be sensed by explicitly sampling, at each integration point, all other points $\boldsymbol{r}_2 \neq \boldsymbol{r}_1$.

It has been known for some time[110] that local DFAs give a much too low barrier for the simplest hydrogen-atom-transfer (HAT) reaction in chemistry, $H_2 + H \rightarrow H + H_2$. The transition state is a linear H_3 arrangement with an unpaired electron in an orbital concentrated on the end hydrogens. Because the electron is unpaired, electron correlation cannot localize this highly delocalized hole. It is *delocalized for all* λ. Therefore local DFAs, with their inherently localized exchange-correlation holes, seriously overstabilize the transition state. A valuable benchmark set of HAT reaction barriers, compiled by Lynch and Truhlar,[111] underscores these problems. Table IV lists MEs and MAEs of HAT barriers in addition to G2/97 statistics. All the local DFAs, and also the hybrids derived from them, significantly underestimate the HAT barriers.

What about locality/nonlocality of the orbitals? Local DFAs prefer delocalized self-consistent orbitals relative to exact exchange. Exact exchange must *localize the orbitals* in order to *localize the hole* and hence lower the energy. The localized holes underlying local DFAs, on the other hand, obviate the need to localize the orbitals. In homonuclear dissociations of closed-shell molecules, this is a good thing. The Coulson-Fischer point in diatomic molecules (the internuclear separation at which spin-restricted orbitals break symmetry in order to lower energy) for local DFAs is much further out than for Hartree-Fock. In *hetero*nuclear dissociations, however, local DFA orbitals are *too* delocalized. In charge-transfer complexes, for example, too much delocalization leads to too much transferred charge and too much stabilization. An early computational study of charge-transfer complexes by Ruiz *et al.*[112] foretold this. A much more recent study[113] of charge transfer in the TTF/TCNQ complex, as a function of exact-exchange mixing fraction, nicely illustrates (see Fig. 5 in Ref. 113) that local DFAs transfer too much charge.

By far the most embarrassing failure of local DFAs is the energy curve of the simplest bond in chemistry, H_2^+, plotted in Figure 1. Near the equilibrium internuclear separation, standard DFAs perform well, giving a good bond energy. As
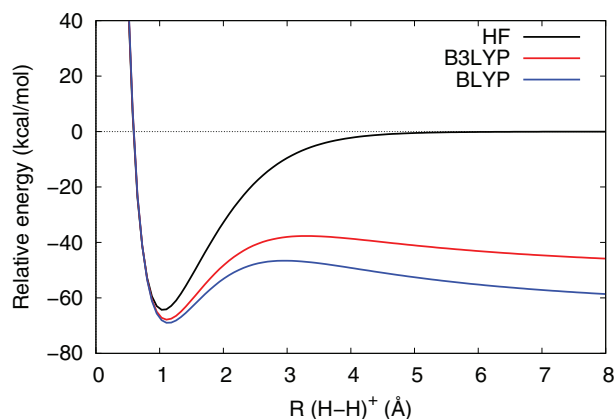
FIG. 1. Dissociation curve of H_2^+.

H_2^+ is stretched, however, a typical local-DFA energy curve (e.g., BLYP in Fig. 1) falls increasingly below the exact curve, displays an artifactual maximum, and dives to an erroneous asymptote almost as deep as the bond minimum itself! This is the worst possible case of a highly delocalized hole whose extent cannot be sensed by local DFAs. Local DFA holes, in this worst case, are far too compact and local DFAs overstabilize stretched H_2^+ horribly.

Hybrid DFAs are a slight improvement, but not nearly enough. See the B3LYP curve in Figure 1. "Long range corrected" (LRC) methods have been proposed[114–122] that divide the interelectronic interaction $1/r_{12}$ into a short-range part and a long-range part:

$$\frac{1}{r_{12}} = \frac{1 - erf(\omega r_{12})}{r_{12}} + \frac{erf(\omega r_{12})}{r_{12}}. \qquad (53)$$

Modified density-functional approximations are used at short range. Long range is handled exactly. LRC methods have attracted much attention, but are not the final answer. Just as the exact-exchange mixing fraction in GGA-hybrids is really not a molecule-independent constant, the range parameter ω in LRC functionals is not a constant either. Its optimum value in different systems may be difficult to discern, especially given that ω is a nonlinear parameter.

All the failures of local DFAs reside in the *exchange* part. Also, most of the parameters in DFAs, whether "empirical" or "nonempirical," are related to the exchange part. An overwhelming proliferation of DFAs has diluted the DFT literature in recent years. The flexibility of meta-GGAs, in particular, invites endless reworking and endless refitting. The "Minnesota" functionals are fit to almost a thousand data points, in over fifty different sets, by dozens of parameters.[108] The Perdew group has also published a bewildering number of meta-GGAs. Broad applicability to solid-state and surface physics[123] and to metallic and non-covalent in addition to covalent bonds[124] is their objective. Good intentions notwithstanding, things are spinning out of control. How, and when, will it stop?

If "100%" *exact* exchange were used in DFAs instead of GGA, meta-GGA, LRC, or other exchange approximations, nonlocality errors would be eliminated. Contentious parameter fitting would, for the most part, be eliminated as

well. Furthermore, exact exchange is the *only* way to ensure that *any one-electron* system is properly treated. However, exact exchange must be coupled with entirely new kinds of correlation functionals. Local electron-gas-like functionals describe short-range *dynamical* correlations only, and will not suffice. To be partnered with exact exchange, correlation functionals must be as *nonlocal* as exact exchange itself, in order to describe multicenter *non*dynamical (or "static") correlation effects.

With two publications in 2003 and 2005,[125] we developed a 100% exact-exchange-based correlation model that performs admirably on the G2/97 tests ("B05" in Table IV). At every point in a molecule, B05 applies a "reverse" BR procedure to the exact exchange-hole potential, namely, the Slater potential $v_{X\sigma}^{Slater}$ of Eq. (4), to extract an effective local exchange-hole normalization $N_{X\sigma}^{eff}$. This is a measure of exchange-hole localization or *de*localization. If $N_{X\sigma}^{eff}$ is close to 1, the exchange hole is localized and there is no nondynamical correlation. If $N_{X\sigma}^{eff}$ is smaller than 1, the exchange hole is *de*localized to other centers and nondynamical correlation kicks in. The details are unimportant here, but B05 has the following form:

$$E_{XC}^{B05} = E_X^{exact} + a_{NDC}^{opp} U_{NDC}^{opp} + a_{NDC}^{par} U_{NDC}^{par} + a_{DC}^{opp} E_{DC}^{opp}$$
$$+ a_{DC}^{par} E_{DC}^{par}. \qquad (54)$$

Each of the four correlation terms represents an explicit correlation hole model for opposite-spins and parallel-spins, nondynamical and dynamical correlations, respectively. The nondynamical terms (NDC) are *nonempirical*. The dynamical terms (DC) are B88c(BR),[34,85] with one parameter in each adjusted to the correlation energies of the He, Ne, and Ar atoms.

To add flexibility, linear prefactors were inserted in Eq. (54) and fit to the G2/97 data. The best-fit values are fascinating:[125]

$$a_{NDC}^{opp} = 0.514, \quad a_{NDC}^{par} = 0.651,$$
$$a_{DC}^{opp} = 1.075, \quad a_{DC}^{par} = 1.113. \qquad (55)$$

It transpires that a_{DC}^{opp} and a_{DC}^{par} are very near 1, indicating that the dynamical correlation models are obviously sound. The best-fit a_{NDC}^{opp} and a_{NDC}^{par} are very near 1/2, in agreement with the *virial* theorem if the nondynamical terms are interpreted as pure *potential* energies of correlation (hence the designation U instead of E for the NDC terms). These results are gratifying. B05 is essentially nonempirical. "Fine tuning" is a more appropriate terminology than "fitting" for the calibration of B05 on the G2/97 data. The B05 MAEs for both the G2/97 atomization energies and the HAT barriers are the best in Table IV.

However, B05 is a very complicated functional. It depends on ρ, $\nabla\rho$, $\nabla^2\rho$, τ, and the Slater potential, Eq. (4). It is $v_{X\sigma}^{Slater}$ that communicates the nonlocality of the exchange hole to the B05 nondynamical correlation model, allowing the coupling of E_C^{B05} with E_X^{exact}. Is the effort of evaluating this complicated functional worth it? With no reparametrization whatsoever, B05 gives the best HAT reaction barriers[126] in Table IV by far. B05 appears to treat delocalized radical systems very well, as was the hope for this new class of

functionals. Also, B05 is exact for any one-electron system. The highly embarrassing H_2^+ problem is no problem for B05. It is noteworthy too that, beginning with B05, absolutely nothing from the uniform electron gas is used in our functionals. Becke-Roussel and B88c ideas are used throughout.

Exact-exchange-based functionals have also been studied by Mori-Sanchez, Cohen, and Yang[127, 128] (MCY2). MCY2 is based on modeling of the adiabatic connection and contains three empirical parameters. It has the advantage over B05 that the Slater potential is not required. Therefore, MCY2 is similar in cost to standard hybrid functionals.

Perdew and co-workers have pursued the construction of exact-exchange-based functionals as well. The first of these is from Perdew *et al.*[129, 130] (PSTS) and contains five empirical parameters. Like B05, PSTS requires the Slater potential. More recent work by Odashima, Capelle, and others[131, 132] is "nonempirical." Their results are exploratory so far, with G2/97 MAEs exceeding 10 kcal/mol. Perdew has called this class of functionals "hyper GGAs," an unsuitable name because they do not resemble GGAs at all. Rather, exact exchange replaces GGA exchange altogether, and the full nonlocality of the exact exchange energy density is input to the correlation part. "Exact-exchange-based" (EXX-based), "true correlation," or "pure correlation" are better names.

B05, MCY2, and PSTS have been assessed by Liu *et al.*,[133] using an efficient RI (resolution of the identity) implementation of Proynov *et al.*[134–136] for *self-consistent* computations. They find that B05, MCY2, and PSTS do not perform quite as well as heavily parametrized meta-GGAs or LRC GGAs on standard thermochemical tests. The EXX-based functionals are significantly better, however, in dissociation curves, including H_2^+ and the equally problematic He_2^+. Also, B05 and MCY2 give the correct singlet ground state for the NO dimer, a well-known stringent test of nondynamical correlation, and a reasonable binding energy. PSTS gives the singlet ground state but too much binding. All the meta-GGAs and LRC GGAs qualitatively fail the NO-dimer test.[133]

With these explicitly nonlocal, exact-exchange-based functionals looking promising, it is tempting to proclaim that "universal" DFAs are in sight. But there is one more nonlocality to consider.

IX. DISPERSION INTERACTIONS: THE FLOODGATES OPEN

The great promise of DFT is the simulation of complex systems of very large size: biological systems, materials, surfaces, and interfaces. In areas such as these, van der Waals (vdW) interactions play a crucial role. Standard DFAs treat hydrogen-bonding interactions fairly well,[137] as their origin is largely electrostatic. Dispersion interactions, on the other hand, are highly problematic for conventional functionals. I have heard it said that "chemistry of the 20th century was about *intra*molecular interactions; chemistry of the 21st century will be about *inter*molecular interactions" (Mark Ratner in a 2004 seminar). It is absolutely critical that DFAs be able to treat dispersion interactions.

Kristyan and Pulay published an early warning in 1994,[138] stating the more-or-less obvious fact (but it needed to

be said) that local DFAs cannot give an asymptotic dispersion interaction of London form, $-C_6/R^6$. The asymptotic interaction energy of local DFAs falls off exponentially instead. Undeterred, a few studies of conventional DFAs and noble-gas vdW curves appeared in the DFT literature.[139–142] Some functionals, including the LDA, bound noble-gas dimers. Some did not. Agreement with experimental data, when binding was observed, was haphazard at best. It was all very confusing.

A few papers were enlightening. Lacks and Gordon[143] suggested that *pure exchange* DFAs should be assessed on their ability to reproduce *exact*-exchange noble-gas curves, which are repulsive. Their best picks were PW86 and B86b, whose enhancement factors $f_X(s)$ both have the same asymptotic behavior, $s^{2/5}$. The important influence of asymptotic $f_X(s)$ behavior on noble-gas curves was highlighted by Zhang, Pan, and Yang[144] as well. But the fact remained that no known correlation functional could generate the London $-C_6/R^6$ dispersion energy.

In 2002, Wu and Yang[145] resorted to adding an empirical dispersion correction

$$E_{disp} = -\sum_{j>i} f_{damp}(R_{ij}) \frac{C_{6ij}}{R_{ij}^6} \tag{56}$$

to a number of conventional exchange-correlation DFAs. The interatomic C_{6ij} coefficients were obtained by fitting to accurate reference molecular C_6 coefficients. A damping function $f_{damp}(R_{ij})$ is also required in order to tame the R_{ij}^{-6} divergences at small internuclear separations. Grimme[146, 147] added a similar empirical dispersion correction to a variety of functionals, with a scaling parameter that absorbed differences in how each native functional handled vdW interactions. He obtained his best results with "B97-D," in which the native DFA is Becke's 1997 flexible 10-parameter GGA hybrid.[105]

Strategies to add dispersion in a less empirical way were also investigated. Moller-Plesset (MP2) perturbation theory and Goerling-Levy second-order Kohn-Sham perturbation theory[148] account for dispersion. Indeed MP2 tends to overestimate it. Several groups therefore introduced *double* hybrid functionals combining GGAs, exact exchange, and second-order perturbation theory.[149–151] Goerigk and Grimme have reviewed these methods in Ref. 152. Double hybrid DFAs are, in my opinion, undesirable. Their formal computer-time scaling is an order higher than Hartree-Fock or KS-DFT. They are philosophically undesirable as well, from the "occupied-orbitals-only" point of view.

Meanwhile an independent approach to dispersion interactions, known as "vdW-DF," originated in papers by Andersson, Langreth, and Lundqvist[153] and Dobson and Dinte.[154] Subsequent developments are numerous. See, for example, Refs. 155 and 156. The vdW-DF approach does not add an explicit London-type correction to standard exchange-correlation functionals. It computes the beyond-LDA contribution to the correlation energy, *dynamical plus dispersion*, by a double integration

$$E_{XC}^{vdWDF} = E_X^{GGA} + E_C^{LDA} + E_C^{nl},$$
$$E_C^{nl} = \int\int \rho(1) K_C^{nl}(1,2) \rho(2) d1d2, \tag{57}$$

with an explicitly nonlocal kernel $K_C^{nl}(1, 2)$ from electron gas theory. With no empirical parameters, the method generates good C_6 dispersion coefficients in a seamless manner. The "revPBE" exchange GGA[157] was used in vdW-DF initially. A recent variation called vdW-DF2[158] uses "revPW86."[62] Other studies of exchange GGAs in vdW-DF make other recommendations.[159,160] Steady advances, particularly the algorithmic improvements of Soler,[161] have produced a powerful plane-wave-based technology for investigations of complex systems. As the name implies, however, vdW-DF is specialized to vdW interactions. It cannot be used in ordinary chemical applications.

The group of Tsuneda and Hirao[162,163] have combined the Andersson-Langreth-Lundqvist[153] underpinnings of vdW-DF with the LRC functional of Ref. 117 to build a general Gaussian-type-orbitals methodology going beyond just vdW interactions. Also in the vdW-DF family and designed for general chemical applications, are the functionals of Vydrov and Van Voorhis.[164]

Outside the vdW-DF family, many researchers continued to work on corrections of the London, Eq. (56), form. A nonempirical way to obtain interatomic dispersion coefficients, employing only occupied Kohn-Sham orbitals, was needed. Becke and Johnson developed a nonempirical approach in a series of papers beginning in 2005.[165,166] The concept is simple. The exchange hole, $h_X(1, 2)$, of an electron at r_1 in a nonuniform system is generally *not* centered on the electron. Hence the electron plus its hole is a neutral entity with a nonzero r_1-dependent "exchange-hole dipole moment," $d_{XDM}(r_1)$, easily calculable from Eq. (30). This position-dependent XDM moment, if taken in each of two distinct atoms, generates a dipole-dipole interaction which, when inserted into second-order perturbation theory, generates a dispersion energy.[167]

That $h_X(1, 2)$ is not centered on r_1 is perfectly manifested by the Becke-Roussel exchange hole model of Sec. VI. Indeed the magnitude of $d_{XDM}(r_1)$ is, to a very good approximation, just b in the BR model, and its direction is towards the nucleus. Thus the XDM dispersion model is a *density-functional* model.[168] Moreover, it can be extended to higher order $-C_8/R^8$ and $-C_{10}/R^{10}$ terms,[167,169] and to atoms *in molecules*, thus reflecting their molecular environments.[169] The end result is the XDM dispersion correction

$$E_{disp}^{XDM} = -\sum_{j>i} \left(\frac{C_{6ij}}{R_{vdw,ij}^6 + R_{ij}^6} + \frac{C_{8ij}}{R_{vdw,ij}^8 + R_{ij}^8} + \frac{C_{10ij}}{R_{vdw,ij}^{10} + R_{ij}^{10}} \right) \tag{58}$$

in which all dispersion coefficients are computed nonempirically "on the fly" using the molecular ρ, $\nabla\rho$, $\nabla^2\rho$, and τ. The separations $R_{vdw,ij}$ controlling the damping of each term are related, ultimately, to only two universal constants.[169]

The initial XDM work of Johnson and Becke employed exact (HF) exchange, the B88c(BR) dynamical correlation DFA,[34,85] and the above dispersion correction. The subsequent goal of Kannemann and Becke[170–172] was to find an optimum exchange-correlation *GGA* with which to partner

XDM. There is enormous variability between exchange DFAs and their noble-gas interaction curves; everything from massive over-repulsion to massive artifactual binding. Kannemann and Becke concluded,[170] as did Lacks and Gordon,[143] that PW86 is the optimum exchange GGA for reproducing exact-exchange (Hartree-Fock) noble-gas curves. Murray *et al.*[62] concluded the same in consideration of intermolecular interaction curves. They therefore revisited Perdew's original model[61] and reparametrized it[62] in the light of more recent knowledge ("revPW86" in Tables II and IV), and inserted revPW86 into vdW-DF2.[158] The choice of GGA for dynamical correlation is not critical. Kannemann and Becke chose PBE.[59] The PW86+PBE+XDM combination was tested with Gaussian-type-orbitals in Ref. 172, and has been fully developed into an efficient and powerful general-purpose chemical tool in Ref. 173.

Following quickly after XDM, other nonempirical dispersion models appeared: Tkatchenko and Scheffler[174] ("TS"), Sato and Nakai[175] ("LRD"), and Grimme *et al.*[176,177] ["D3" and "D3(BJ)"], each based on a different underlying strategy. TS[174] employs a volume ratio trick [Eq. (7) in Ref. 174] to determine atom-in-molecule dispersion coefficients and vdW radii from *free*-atom values. This trick is from Becke and Johnson [Ref. 167 (1st paper) and Ref. 169]. The LRD (local response dispersion) method of Sato and Nakai[175] is related to the vdW-DF family but avoids the double integration in Eq. (57). The D3 model of Grimme *et al.*[176] uses precomputed reference data for dispersion coefficients, and the concept of "fractional coordination number" to mimic the environment of an atom in a molecule. D3(BJ)[177] is a refinement of D3 that incorporates the rational damping, Eq. (58), of Johnson and Becke.[169] Grimme's models are garnering popularity among chemists, as they are the simplest of the above to implement.

All of this was a dramatic reversal of fortune. Circa 2000, with nothing in sight but empirical dispersion corrections, the future of DFT was bleak. By 2010, everything had changed for the better.

Applications of DFT dispersion methods are rapidly growing[9] and theoretical progress continues unabated. The thermochemistry benchmark sets[40] that were indispensible for DFA development in the past have been joined by vdW benchmark sets. The S66 set of Rezac, Riley, and Hobza[178] for biochemical systems, the set of supramolecular complexes of Risthaus and Grimme,[179] and the molecular solids set of Otero-de-la-Roza and Johnson[180] are a few examples. *Three*-center dispersion interactions, in addition to two-center interactions, are being studied.[176,181–183] Screening effects are being studied as well.[184] I think the jury is still out on the importance of three-center interactions and screening. The balance between these latter effects, higher-order C_8 and C_{10} terms, damping functions, and the exchange-correlation DFAs themselves, is incredibly delicate.

The dispersion problem has also stimulated great interest in the "random phase approximation" (RPA) of the physicists[185] and its application to molecular systems.[186] RPA invokes the virtual orbitals and, like all WFT methods that use the virtuals, naturally incorporates dispersion. The RPA literature is complicated, confusing (at least to me!), and

growing fast. Early explorations of RPA in a DFT context were made by Langreth and Perdew.[30] Recent flavors of the subject may be found in Refs. [187–191]. The floodgates are open now. The virtual orbitals are pouring in. Double hybrids were just the first step. The ultimate conclusion of combining DFT and WFT is what Bartlett calls[192] "*ab initio* DFT," a mathematical and theoretical framework that exploits the best of both worlds and seeks a systematic route to improving both. Operationally though, it is not in the occupied-orbitals-only spirit of Kohn and Sham.

Gill's pronouncement[109] of the death of DFT was perhaps premature, but not unfounded. The dispersion problem has, in large part, plunged DFT into an identity crisis. Have we forgotten why Kohn-Sham theory is popular in the first place? If employment of the virtual orbitals increases, I am afraid the beauty and simplicity of the Kohn-Sham vision will be lost.

X. INTO THE FUTURE

With dispersion interactions in place, the future looks bright. But we cannot, quite yet, forget the basics. The focus of ground-state DFA developers has shifted to what I hope is the last frontier, "strong" correlation. Strong correlation refers to substantial mixing of configurations in systems with a small HOMO-LUMO gap. Chemical problems in which the gap approaches zero include dissociation of homonuclear bonds and "avoided-crossing" reactions. Systems with a large number of low-lying virtual states are especially troublesome. The chromium dimer, Cr_2, is a nightmare test of strong-correlation methods in quantum chemistry.[193,194] We will visit this nightmare below.

In the context of Kohn-Sham DFT, strong correlation can be defined in terms of the adiabatic connection. Consider Figure [2], which plots

$$W_C^\lambda = \frac{1}{2} \iint \frac{\rho(1)}{r_{12}} h_C^\lambda(1,2) d1 d2 \qquad (59)$$

as a monotonically decreasing function of the coupling strength. At zero coupling strength there is no correlation and $W_C^0 = 0$. At unit coupling strength, $W_C^1 = U_C$ is the *potential* energy of correlation in the "real" system. The total correlation energy E_C (kinetic + potential) is the area under the curve from $\lambda = 0$ to $\lambda = 1$. In atoms and molecules that are not strongly correlated, the curve is almost a straight line and $E_C \cong \frac{1}{2} U_C$. In *strongly* correlated systems, the curve drops
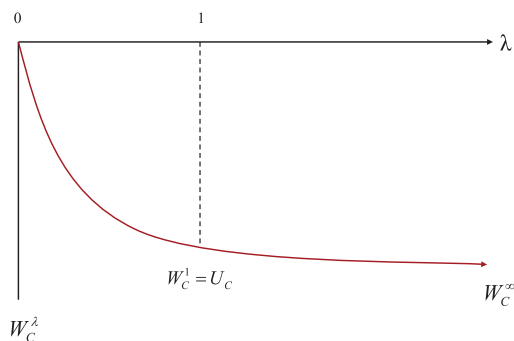

FIG. 2. Typical correlation-energy adiabatic connection curve.

quickly to U_C and $E_C \cong U_C$. In general,

$$U_C \le E_C \le \frac{1}{2} U_C. \qquad (60)$$

Models of the curve have been helpful in understanding hybrid functionals.[195,196] The slope at $\lambda = 0$ is particularly useful[195] but is given by second-order perturbation theory and calls for the virtual orbitals. Recently, the Helgaker group has extensively analyzed adiabatic connection curves in a variety of systems[197] and there are many fine plots in their paper. The coupling-strength region $\lambda > 1$ is not physically relevant. Nevertheless, an understanding of this unphysical region can inform the physical part of the curve and provide measures of strong correlation. The "strictly" correlated limit, $\lambda \to \infty$, has been studied[198,199] as a possibly useful source of information. Reference [200] is an up-to-date look.

Within the last year, we have proposed a simple local relationship between E_C and U_C, in accord with Eq. [(60)], that looks promising as a harbinger of strong correlation.[201] The "B13" functional resembles B05. It is based on exact exchange and has the following correlation part:

$$E_C^{B13} = a_{NDC}^{opp} U_{NDC}^{opp} + a_{NDC}^{par} U_{NDC}^{par} + a_{DC}^{opp} U_{DC}^{opp}$$
$$+ a_{DC}^{par} U_{DC}^{par} + \Delta E_C^{strong}, \qquad (61)$$

with a strong-correlation correction, ΔE_C^{strong}, that recognizes strongly correlated situations automatically. ΔE_C^{strong} is expandable in a polynomial series, but one or two terms appear to be sufficient (five or six linear parameters altogether). B13 has been fine tuned to G2/97 atomization energies and *spin-depolarized atoms*: i.e., the spin-restricted dissociation limits of molecular bonds.[201] Some G2/97 accuracy is sacrificed compared to B05 (see Table [IV]), but the potential universality of B13 is intriguing. A preliminary *spin-restricted* B13 binding-energy curve for Cr_2 has a minimum at 1.64 Å (experiment 1.68) and a bond energy of 54.9 kcal/mol (experiment 34.6). Considering that spin-restricted Hartree-Fock is unbound by over 400 kcal/mol, and that B05 is unbound by ~15 kcal/mol (unpublished calculations), the B13 result is very encouraging. The multireference WFT computations of Refs. [193] and [194] used, respectively, over 1×10^9 and almost 3×10^9 configurations!

Like B05, the five (or six) parameters in B13 are "fine tuning" linear prefactors with logical values rooted in the adiabatic connection. All of a_{NDC}^{opp}, a_{NDC}^{par}, a_{DC}^{opp}, and a_{DC}^{par} have value ~0.6, the prefactor in ΔE_C^{strong} has value ~0.4, and it is no accident that these add up to ~1. B13 is essentially nonempirical.

Systems at "avoided crossings" have a zero HOMO-LUMO gap and are challenging strong-correlation problems. An excellent discussion of the energy surface of the prototypical H_4 system, with an avoided-crossing transition state at the square geometry, can be found in Ref. [202]. *Fractional occupancies*[202,203] are implicated in this and other avoided-crossing problems.[204] It is not possible to represent the D_{4h} density of the open-shell square H_4 structure, or structures near it, without fractional occupancies.[202,204] The B13 barrier of 141.2 kcal/mol in this H_4 system (unpublished) is in fair agreement with the high-level WFT barrier[202] of

147.6 kcal/mol. A few other B13 avoided-crossing barriers can be found in the very recent Ref. 204.

Like B05, B13 is a functional of ρ, $\nabla\rho$, $\nabla^2\rho$, τ, and the Slater potential $v_{X\sigma}^{Slater}$, Eq. (4). Direct computation of the Slater potential on all grid points is costly, and differentiating B05 (or B13) with respect to orbital expansion coefficients for the purpose of self-consistent computations is daunting. Yet both of these tasks have been accomplished for B05[134–136, 205] and are therefore in hand for B13. Self-consistent B05/B13 computations are a few times lengthier than, e.g., B3LYP, but are not intractable thanks to RI (resolution of the identity) bases. If self-consistency is not desired, then post-LDA B05/B13 computations are a fast alternative.[133–136]

The distributed Slater potential may also be computed in an indirect manner by a literal implementation of Slater's original orbital-averaged HF-potential concept (Sec. II). A simple reorganization of the HF equations is all that is required.[206–208] Thus, *post-Hartree-Fock* implementations of EXX-based functionals like B05, B13, or PSTS are conceivable at essentially no cost beyond HF itself (plus, perhaps, an additional HFS computation to correct for basis-set artifacts[207, 208]). Post-Hartree-Fock DFT is not new. The 1992 implementation of BLYP by Gill *et al.*[66] was post-HF, followed by Oliphant and Bartlett[209] and others. Numerous DFT researchers had used HF orbitals long before then. Post-Hartree-Fock DFT has advantages over self-consistent DFT. As Verma, Perera, and Bartlett[210] have reminded us, HF requires no numerical integration grids and therefore has high speed and orbital precision (i.e., no grid noise). However if forces are required, perturbations of the HF orbitals need to be computed and some advantage is lost.[210] Overall, though, post-Hartree-Fock DFT chemistry and self-consistent DFT chemistry are of similar cost. Future prospects for nonlocal EXX-based DFAs employing the Slater potential, whether implemented post-HF, post-LDA, or self-consistently, are exciting.

Looking back thirty years to the genesis of DFA growth, I am amazed at where we have come. Our goal back then was to replace all things WFT, including Hartree-Fock, with simpler density-functional approximations. I did not imagine, until 2003, that I would ever espouse the use of exact exchange. Yet this is my position, today, on how to proceed into the future. We have come "full circle" back to exact exchange or, if you prefer, Hartree-Fock. Figure 3 plots the path. Post-Hartree-Fock *W*FT, circa 1980, involved (still does) configuration mixing. Post-Hartree-Fock *D*FT, circa 2010, is a very different thing. Pure, nonlocal correlation functionals are DFT at its best. Everything we have learned about GGAs, meta-GGAs, BR, etc., these past thirty years is *in* these functionals. To understand nonlocality, you have to understand locality first. Although we have come full circle ultimately, the thirty intervening years were well spent.

XI. SUMMARY

DFT detractors complain that the linchpin of KS-DFT, the exchange-correlation functional and its underlying hole, will never be expressible in closed analytical form and is not amenable to systematic improvement. DFA development *has*, in fact, been systematic, as the history in this Perspective has hopefully shown. We started with the LDA, which samples only the density at each grid (integration) point. GGAs sample density *gradient* information in addition to the density. Remarkably, the gradient helps us capture the physics of the exchange energy density *out to the asymptotes* of finite systems (B88). Next we included kinetic energy density, τ, to ensure zero correlation energy in one-electron systems and to exploit its crude knowledge of nonlocality. The BR functional includes $\nabla^2\rho$ as well, exactly sampling the exchange-hole Taylor expansion as far as second order in r_{12}. The *full* multicenter nonlocality of the exact exchange hole is partially incorporated into hybrid functionals. Recent "100%" EXX-based functionals, and functionals including dispersion and even virtual orbitals, are truly nonlocal. We have progressed from the LDA to full nonlocality in a rational and systematic manner, climbing the rungs of "Jacob's DFT ladder" (an image, popularized by Perdew,[211] recounting the above advances as successive rungs in Jacob's biblical ladder) as we reach for DFT heaven.

But DFT heaven is probably unattainable. DFAs, local or nonlocal, will never be exact. Users are willing to pay this price for simplicity, efficacy, and speed. As we strive to make DFAs more robust, will their accuracy and speed continue to satisfy users? Will Kohn-Sham DFT, in its pristine occupied-orbitals-only form, survive the pressure? Or will DFT and WFT transform each other and merge into a single entity. The next fifty years will be as interesting as the first.

ACKNOWLEDGMENTS

FIG. 3. Full circle, from Hartree-Fock back to Hartree-Fock.

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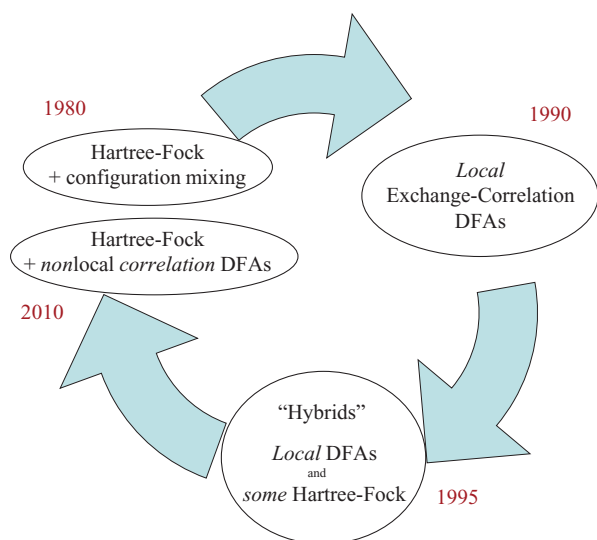²R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
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