CHAPTER NINE

Frank Discussion of the Status of Ground-State Orbital-Free DFT

Valentin V. Karasiev*, **Samuel B. Trickey***,[1]
*Quantum Theory Project, Departments of Physics and of Chemistry, University of Florida,
Gainesville, Florida, USA
[1]Corresponding author: e-mail address: trickey@qtp.ufl.edu

Contents

Abstract

F.E. Harris has been a significant partner in our work on orbital-free density functional approximations for use in *ab initio* molecular dynamics. Here we mention briefly the essential progress in single-point functionals since our original paper (2006). Then we focus on the advantages and limitations of generalized gradient approximation (GGA) noninteracting kinetic energy (KE) functionals. We reconsider the constraints provided by near-origin conditions in atomic-like systems and their relationship to regularized versus physical external potentials. Then we seek the best empirical GGA for the noninteracting KE for a modest-sized set of molecules with well-defined near-origin behavior of their densities. The search is motivated by a desire for insight into GGA limitations and for a target for constraint-based development.

Advances in Quantum Chemistry, Volume 71
ISSN 0065-3276
http://dx.doi.org/10.1016/bs.aiq.2015.02.004

1. INTRODUCTION

1.1 Background

At the Harris Workshop (10–12 December 2014), the second author spoke about recent progress by the University of Florida orbital-free density functional theory (OFDFT) group of which Frank Harris is a member. Substantially all that work is reported in Refs. 1–3 and references therein. Earlier work and voluminous references for context are in two review articles from our group.[4,5]

Rather than recapitulate the talk and publications, here we provide a particular perspective on what has been learnt. The phrase "near origin" rather than "cusp condition" is a clue to the role the external potential plays in enforcing behavior upon generalized gradient approximations (GGAs) for the noninteracting kinetic energy (KE). We present some new results on near-origin conditions applied to GGAs. These extend work we did with Frank Harris.[6–8] Then we explore implications of a generic regularization of the usual external potential (from a nuclear array) by empirical determination of the most nearly optimal GGA for a set of molecular data. That continues the study of binding in simple molecules by non-self-consistent OFDFT with key ingredients of the methodology introduced in our previous publications.[6–8] Those ingredients, besides the near-origin analysis of the Pauli potential, include (i) the use of a set of nuclear spatial configurations for the same molecule; (ii) the use of Gaussian Kohn–Sham (KS) molecular densities as input; (iii) so-called ΔE criterion which enforces binding; and (iv) the E criterion which enforces correct absolute energies. See also the recent work of Borgoo et al.[9] in which the relationship between binding and the effective homogeneity of approximate noninteracting KE functional is considered.

Though our research agenda emphasizes functionals for free energy DFT[10] primarily for use in the warm dense matter regime, here we restrict attention to ground-state OFDFT. There are three reasons. First, ground-state OFDFT is a hard challenge (as history going all the way back to Thomas[11] and Fermi[12] demonstrates). That challenge is worsened by going to finite-T (one must devise an entropy functional and incorporate the intrinsic T-dependence of other functionals). Third, the ground-state approximations must be reliable and well-founded if there is to be a sensible $T = 0$ K limit for approximate free energy functionals.

1.2 Basics and Notation

For context and to set notation, the Levy–Lieb version of the Hohenberg–Kohn universal functional[13–15] is

$$\mathcal{E}[n] = T[n] + U_{\mathrm{ee}}[n] \tag{1}$$

with $T[n]$, $U_{\mathrm{ee}}[n]$, and $n(\mathbf{r})$ the total KE, total Coulomb energy (Hartree, exchange, and correlation), and the electron density at point $\mathbf{r}$, respectively ($\int d\mathbf{r} n(\mathbf{r}) = N_{\mathrm{e}}$, with N_{e} the number of electrons). Assuming that the sum is bounded below, addition of an external potential energy $E_{\mathrm{ext}}[n]$ gives the usual DFT variational principle,

$$\min_n \{\mathcal{E}[n] + E_{\mathrm{ext}}[n]\} = E_0[n_0]. \tag{2}$$

Zero subscripts indicate ground-state values.

The KS[16] rearrangement of $\mathcal{E}$ invokes an auxiliary noninteracting Fermion system with the same density as the physical system. This raises so-called v-representability requirements which we assume to be satisfied. The KS system has KE and exchange (X) energies T_{s}, E_{x}, which enable the regrouping of (1) into

$$\mathcal{E}[n] = T_{\mathrm{s}}[n] + E_{\mathrm{H}}[n] + E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n] \tag{3}$$

$$E_{\mathrm{c}}[n] := U_{\mathrm{ee}}[n] - E_{\mathrm{H}}[n] - E_{\mathrm{x}}[n] + T[n] - T_{\mathrm{s}}[n] \tag{4}$$

$$E_{\mathrm{H}}[n] := \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{5}$$

$$E_{\mathrm{x}}[n] := \langle \boldsymbol{\Phi}_{\mathrm{s}}[n] | \hat{V}_{\mathrm{ee}} | \boldsymbol{\Phi}_{\mathrm{s}}[n] \rangle - E_{\mathrm{H}}[n]. \tag{6}$$

E_{c} is the DFT correlation energy. It often is useful to write $E_{\mathrm{xc}} = E_{\mathrm{x}} + E_{\mathrm{c}}$. $\hat{V}_{\mathrm{ee}}$ is the electron–electron Coulomb interaction. The KS Slater determinant $\boldsymbol{\Phi}_{\mathrm{s}}[n]$ is comprised of orbitals from the KS system Euler equations,

$$h_{\mathrm{KS}}[n]\varphi_i = \varepsilon_i \varphi_i, \quad n(\mathbf{r}) = \sum_i f_i |\varphi_i(\mathbf{r})|^2. \tag{7}$$

Here the $f_i = 0,1,2$ are occupation numbers in the non-spin-polarized case.[17,18] The KS potential is

$$\begin{aligned} v_{\mathrm{KS}} &= v_{\mathrm{H}} + v_{\mathrm{xc}} + v_{\mathrm{ext}} \\ v_{\mathrm{H}} &= \int d\mathbf{r}_2 \frac{n(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|}, \quad v_{\mathrm{xc}} = \frac{\delta E_{\mathrm{xc}}}{\delta n}, \end{aligned} \tag{8}$$

For now, we leave v_{ext} unspecified. Finally, the KS KE is

$$T_{\mathrm{s}}[\{\varphi_i\}] = \frac{1}{2}\sum f_i \int \mathrm{d}\mathbf{r} |\nabla\phi_i(\mathbf{r})|^2 := \int \mathrm{d}\mathbf{r} t_{\mathrm{orb}}[n(\mathbf{r})] \tag{9}$$

in Hartree atomic units. This positive-definite integrand form of T_{s} is preferable for OFDFT because the integrand of the ordinary Laplacian form of T_{s} can have both signs. The two forms differ by a surface integral which is zero for physically significant systems.

1.3 Essential Challenge of OFDFT

Posed succinctly, the OFDFT opportunity is that the computational costs of direct minimization of Eq. (3) scale with system size. In contrast, solution of the KS equations, (7), has computational cost scaling as N_{e}^3 or worse.

The OFDFT challenge can be stated succinctly too. $E_{\mathrm{x}}[n]$ is *defined* in terms of the KS orbitals and hence is known exactly only as an implicit functional of n. $T_{\mathrm{s}}[n]$ is an implicit functional as well. $E_{\mathrm{c}}[n]$ is *defined* in terms of those two. One might try reversion to $\mathcal{E}[n]$ for construction of approximations, but most rigorous knowledge about $\mathcal{E}$ (scaling, bounds, limits, etc.) is in terms of the KS rearrangement. Roughly a half century of effort has been devoted to finding good approximations to E_{x} and E_{xc}. Abandoning the KS decomposition would discard that resource and, worse, disconnect the result from a huge literature of calculations with such functionals. And T_{s} has several rigorously demonstrable properties which serve as stringent constraints on approximations.[4,6–8]

In short, retention and use of the KS decomposition is practically inescapable. OFDFT thus aims at reliable approximations for KS DFT quantities without explicit dependence on the KS orbitals. The allowed variables therefore are n and its spatial derivatives. For E_{xc}, the consequence is a restriction to the meta-generalized-gradient approximation (mGGA) rung of the widely quoted Perdew–Schmidt Jacobs' ladder of complexity.[19] mGGAs depend upon n, $|\nabla n|$, $\nabla^2 n$, and the KS KE density t_{orb}. Immediately, the OFDFT challenge is in play: an explicit functional for t_{orb} is required.

In practice, the highest spatial derivative dependence that so far has been useful for t_{orb} is a GGA, to wit

$$\begin{aligned} T_{\mathrm{s}}^{\mathrm{GGA}}[n] &= c_{\mathrm{TF}} \int \mathrm{d}\mathbf{r}\, n^{5/3}(\mathbf{r}) F_{\mathrm{t}}(s(\mathbf{r})) \\ c_{\mathrm{TF}} &= \frac{3}{10}(3\pi)^{2/3}. \end{aligned} \tag{10}$$

F_t is called the enhancement factor. For $F_t = 1$, $T_s^{GGA} = T_{TF}$, the Thomas–Fermi functional. The dimensionless reduced density gradient is

$$s := \frac{1}{2(3\pi^2)^{1/3}}\frac{|\nabla n|}{n^{4/3}} \equiv \kappa\frac{|\nabla n|}{n^{4/3}}. \tag{11}$$

Remark: The s variable occurs in GGA X functionals also. They have the same form as Eq. (10) but with $n^{4/3}$ rather than $n^{5/3}$, F_x rather than F_t, and a different prefactor, $c_x = -(3/4)(3/\pi)^{1/3}$.

Equation (10) is a one-point GGA functional. In the OFKE literature, there is extensive work on two-point functionals, generically $\int d\mathbf{r}d\mathbf{r}' n^{\alpha}(\mathbf{r})K(\mathbf{r},\mathbf{r}')n^{\beta}(\mathbf{r}')$. See Section 2.3 of Ref. 4 for brief discussion and references. One readily can imagine constructing a GGA for two-point functionals, but we are unaware of effort along that line. Instead, the emphasis has been on constructing $K(\mathbf{r},\mathbf{r}')$ via constraints, mostly to match response properties of the weakly perturbed homogeneous electron gas.

Motivated to optimize computational performance, our group has focused on finding and exhausting the limits of single-point GGAs for T_s. The remaining discussion assesses what we have found, with a focus on the surprising nonuniversality of approximate OFKE functionals, implications for their common use with external potentials of regularized Coulomb form, and an empirical attempt to ascertain the limits of GGA performance for a particular kind of regularized potential.

2. QUALITATIVE DISTINCTIONS AMONG GGAs FOR t_{orb}

Our work began[6] by testing multiple published T_s^{GGA} functionals. A rough classification introduced then was standard GGA and modified-conjoint GGA (mcGGA). The latter term stems from conjoint functionals,[20] i.e., those for which $F_t \propto F_x$. Standard GGAs include the second-order gradient approximation (SGA)

$$T^{SGA} = T_{TF} + \frac{1}{9}T_W \tag{12}$$

$$T_W[n] := \frac{1}{8}\int d\mathbf{r}\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} \tag{13}$$

and the von Weizsäcker KE T_W itself, along with most of the GGAs of the modern era, e.g., that by Perdew,[21] the PW91 KE functional based on the Perdew–Wang X functional,[22] and those from DePristo and Kress,[23] Thakkar,[24] and Tran and Wesolowski,[25] and the APBEK functional based on the PBE X functional.[26] Modified conjoint GGAs arise from altering or refining the conjointness conjecture (which is not strictly correct; see Ref. 8). These include $T_{\mathrm{TF}} + T_{\mathrm{W}}$ and our PBE2, KST2,[6,8] and VT84F[3] functionals.

The two functional types have qualitatively different performance. Ordinary GGAs predict the KE order of magnitude correctly but fail to give binding for simple molecules and solids. There are some exceptions for solids in which a pseudo-density is used. mcGGAs do bind simple molecules as well as many solids at least semi-quantitatively, but they overestimate the KE strongly. As a consequence, the total energy also is strongly overestimated (too high). We also have found that these functionals exhibit peculiar sensitivity to the type of pseudo-potential used, behavior found by others as well.[27]

The main difference between ordinary GGAs and the mcGGAs is the enforcement of positivity constraints on the mcGGAs. Enforcement is via imposition of requirements upon the density in the case that the external potential is Coulombic,

$$v_{\mathrm{ext}}(\mathbf{r}) = -\sum_{\alpha} \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} \tag{14}$$

with Z_α the atomic number of the nucleus at site $\mathbf{R}_\alpha$. Such approximate $T_{\mathrm{s}}^{\mathrm{GGA}}$ functionals therefore are not guaranteed to be universal, even though T_{s} is. Two questions then arise. Are both the overly large KE and sensitivity to pseudo-potentials of mcGGAs connected with this nonuniversality? Is there an example of a $T_{\mathrm{s}}^{\mathrm{GGA}}$ that has both the good KE magnitudes of an ordinary GGA and the good binding properties of an mcGGA? We address these two issues in the remainder of this chapter.

3. POSITIVITY AND NEAR-ORIGIN CONDITIONS

The Pauli term decomposition

$$T_{\mathrm{s}}[n] = T_{\mathrm{W}}[n] + T_\theta[n], \tag{15}$$

provides a rigorous bound,[28–32]

$$T_\theta[n] \geq 0, \tag{16}$$

because T_{W} is a lower bound to the KS KE.[33–36] T_{W} also is the exact T_{s} for one electron, a fact that will become useful shortly. (It also is exact for a two-electron singlet.) The Pauli term potential also is rigorously non-negative:

$$v_\theta(\mathbf{r}) := \frac{\delta T_\theta[n]}{\delta n(\mathbf{r})} \geq 0, \quad \forall \mathbf{r}. \tag{17}$$

These are universal properties of T_s. For a GGA, the Pauli term separation corresponds to a T_θ^{GGA} with energy density t_θ and enhancement factor

$$F_\theta(s) = F_{\mathrm{t}}(s) - \frac{5}{3}s^2. \tag{18}$$

Though $T_\theta \geq 0$, it is not necessarily the case that the associated Pauli term energy density t_θ obeys the same positivity $t_\theta \geq 0$ because energy densities are defined only up to additive functions which integrate to zero. Refs. 31,36,37 chose the canonical form for t_θ (i.e., that which comes from the KS equation), which is positive semi-definite. We adopted that argument in Ref. 38. The consequence, to which we return in Section 4, is

$$F_\theta(s(\mathbf{r})) \geq 0, \quad \forall \mathbf{r}. \tag{19}$$

To have enough additional constraints to determine a useful approximate F_θ, we used[3,6,8,38] requisites of physical many-electron systems, i.e., those with an external potential given by Eq. (14). Nonuniversality enters.

The nuclear-cusp condition[39] density

$$n(r) \sim \mathrm{e}^{-2Zr} = (1 - 2Zr) + O(r^2). \tag{20}$$

gives $v_\theta^{\mathrm{GGA}}(r) \sim a/r$, where a is a constant which depends on the specific enhancement factor.[8] So far as we know, the first mention of this consequence was by Levy and Ou-Yang (see the latter part of Section III of Ref. 31).

The one-electron character of the tail region of a many-electron atom[37] forces the approximate functional to go over to T_{W} in that region.[18] For a GGA therefore we may require,

$$\lim_{s \to \infty} F_\theta(s) = 0. \tag{21}$$

Kato cusp behavior Eq. (20) is not exhibited by any density that results from a regularized potential, e.g., a pseudo-potential. See, for example, Eq. (6) in Ref. 40 and associated discussion. Removing that cusp to allow use of compact basis sets (especially a plane-wave basis) is the motive for pseudo-potentials. Densities from expansion in a finite Gaussian-type basis set, even in all-electron calculations that use Eq. (14), also do not have Kato cusp behavior. Similarly, the proper tail behavior, also exponential, is not found in any finite Gaussian expansion density. Here we focus on the former issue, the near-origin behavior of atomic-like systems.

Consider one-center N_e electron densities of the flexible form

$$n_f(\mathbf{r}) := A_f \exp(-\lambda r^\gamma), \quad 1 \leq \gamma \leq 2 \tag{22}$$

$$A_f = \frac{N_e \gamma \lambda^{3/\gamma}}{4\pi\Gamma(3/\gamma)}, \tag{23}$$

The norm follows from Ref. 41, with the usual Γ function. With $\gamma = 1$, $\lambda = 2N_e$, $N_e = 1$, this is the H atom density in the central field approximation. For $\gamma = 2$, it is pure Gaussian. For use in what follows, the von Weizsäcker potential for densities of this form is

$$v_W = \frac{\delta T_W}{\delta n} = \frac{\lambda\gamma}{8} r^{\gamma-2}[2(\gamma+1) - \lambda\gamma r^\gamma] \, . \tag{24}$$

With densities of the form (22), we can explore two simple but illuminating issues. The first is to determine the external potential that corresponds to the given density for the case $N_e = 1$. Recall the bijectivity of the external potential and the density guaranteed by the first Hohenberg–Kohn theorem.[13] The central-field hydrogenic case is obvious but it is instructive to do it in the context of OFKE functionals. The Euler equation is

$$\frac{\delta(\mathcal{E} + E_{\text{ext}})}{\delta n} = v_W + v_\theta + v_H + v_{xc} + v_{\text{ext}} = \mu, \tag{25}$$

with μ the Lagrangian multiplier for charge normalization. T_W is exact for the one-electron case, so $v_\theta = 0$. Exact exchange cancels the Hartree self-interaction, so $v_H = -v_x$, and there is no correlation, $v_c = 0$. The von Weizsäcker potential (24) for the hydrogenic densities ($\gamma = 1$, $\lambda = 2N_e$) is

$$v_W = \frac{N_e}{r} - \frac{N_e^2}{2}. \tag{26}$$

For H, $\mu = -\frac{1}{2}$, $N_e = 1$, (25) gives the expected result:

$$0 = \frac{1}{r} - \frac{1}{2} + v_{\text{ext}}(r) - (-\frac{1}{2}) \Rightarrow v_{\text{ext}}(r) = -\frac{1}{r}. \tag{27}$$

Redoing the argument with $\gamma = 2$, $N_e = 1$ gives

$$v_W = \frac{\lambda}{2}(3 - \lambda r^2) \Rightarrow v_{\text{ext}} = \frac{1}{2}\lambda^2 r^2 + (\mu - \frac{3\lambda}{2}), \tag{28}$$

the expected quadratic dependence for v_{ext}.

This elementary exercise illustrates a significant point for approximate functionals. Repeat the argument for $\gamma = 2$ but now with the physically important external Coulomb potential imposed and with an approximate T_θ functional (not necessarily a GGA; for the moment, the discussion is general). Then the Euler equation becomes

$$\mu = -\frac{1}{r} - \frac{1}{2}\lambda^2 r^2 + \frac{3\lambda}{2} + v_\theta^{\mathrm{approx}}(r). \tag{29}$$

The only way this can be satisfied is for there to be an *incorrect*, i.e., nonzero, $v_\theta^{\mathrm{approx}}$ for the one-electron case.

In the case of pseudo-potentials, the argument runs in reverse. Suppose a pseudo-potential prescription to be used at the so-called one-electron level, i.e., one electron outside the core, and suppose it to deliver the form (28). Assume that one can contrive a satisfying approximate functional with the property that for $N_e = 1$, the approximate functional respects rigorous constraints for the corresponding pseudo-density. Now shift to an all-electron pseudo-potential and shrink the core toward the bare Coulomb potential. In an arbitrarily small region around the origin, the pseudo-density will remain harmonic but the pseudo-potential in almost all space will be essentially Coulombic, leading to the kind of mismatch given in Eq. (29). Even at this level (two pseudo-potentials with the same regularization procedure but significantly different core radii and populations), there is a lack of universality for the approximate T_θ.

For arbitrary γ dependence, $1 \le \gamma \le 2$, the imputed external potential is

$$v_{\mathrm{ext}} = \mu - v_{\mathrm{W}} = \mu + \frac{\lambda\gamma}{8} r^{\gamma-2}[\lambda\gamma r^\gamma - 2(\gamma+1)], \tag{30}$$

(with suitably adjusted μ of course). Similar mismatch difficulties will occur for all intermediate γ values, as will the singularities for $\gamma \neq 2$.

Now consider GGA functionals with arbitrary N_e. The GGA Pauli potential is[8]

$$v_\theta^{\mathrm{GGA}}(s^2) = c_0 n^{2/3}\left\{\frac{5}{3}F_\theta(s^2) - \left(\frac{2}{3}s^2 + 2p\right)\frac{\partial F_\theta}{\partial(s^2)} + 4\left(\frac{4}{3}s^4 - q\right)\frac{\partial^2 F_\theta}{\partial(s^2)^2}\right\}, \tag{31}$$

with higher-order reduced density derivatives

$$p := \kappa^2 \frac{\nabla^2 n}{n^{5/3}}, \quad q := \kappa^4 \frac{\nabla n \cdot (\nabla\nabla n) \cdot \nabla n}{n^{13/3}}. \tag{32}$$

Evaluation with the flexible density (22) yields

$$s^2(r) = \kappa^2 \lambda^2 \gamma^2 r^{2(\gamma-1)} n_{\mathrm{f}}^{-2/3}(r), \tag{33}$$

$$p(r) = \kappa^2 \lambda \gamma r^{\gamma-2} [\lambda \gamma r^\gamma - (\gamma+1)] n_{\mathrm{f}}^{-2/3}(r), \tag{34}$$

and

$$q(r) = \kappa^4 \lambda^3 \gamma^3 r^{3\gamma-4} [\lambda \gamma r^\gamma - (\gamma-1)] n_{\mathrm{f}}^{-4/3}(r). \tag{35}$$

Except for a negative sign, the coefficient of $\partial F_\theta / \partial s^2$ in Eq. (31) is

$$\frac{2}{3} s^2 + 2p = 2\kappa^2 \lambda \gamma r^{\gamma-2} \left[\frac{4}{3} \lambda \gamma r^\gamma - (\gamma+1) \right] n_{\mathrm{f}}^{-2/3}(r). \tag{36}$$

Notice the singularity at the origin for $\gamma < 2$. Up to a factor of 4, the coefficient of $\partial^2 F_\theta / \partial (s^2)^2$ in Eq. (31) is

$$\left[\frac{4}{3} s^4 - q \right] = \kappa^4 \lambda^3 \gamma^3 r^{3\gamma-4} \left[\frac{\lambda\gamma}{3} r^\gamma + (\gamma-1) \right] n_{\mathrm{f}}^{-4/3}. \tag{37}$$

This is nonsingular only for $\gamma \geq 4/3$.

For small s, one usually enforces gradient expansion behavior on F_θ,

$$F_\theta = 1 + as^2 \tag{38}$$

and only the first derivative term in v_θ, Eq. (31), is at issue. After a bit of manipulation,

$$p(r) = s^2 \left[1 - \frac{\gamma+1}{\lambda\gamma r^\gamma} \right] \Rightarrow \frac{2}{3} s^2 + 2p = 2s^2 \left[\frac{4}{3} - \frac{\gamma+1}{\lambda\gamma r^\gamma} \right]. \tag{39}$$

The singularity structure in v_θ then is evident. The general result is

$$v_\theta^{\mathrm{GGA}}[n_{\mathrm{f}}] = c_0 n_{\mathrm{f}}^{2/3} \left\{ \frac{5}{3} + a\kappa^2 \gamma^2 \lambda^2 r^{2(\gamma-1)} n_{\mathrm{f}}^{-2/3} \left[\frac{2(\gamma+1)}{\lambda\gamma r^\gamma} - 1 \right] \right\}. \tag{40}$$

For convenience, the two limiting cases are

$$v_\theta^{\mathrm{GGA}}[n_{\mathrm{f}}, \gamma = 1] = c_0 n_{\mathrm{f}}^{2/3} \left\{ \frac{5}{3} + a\kappa^2 \lambda^2 n_{\mathrm{f}}^{-2/3} \left[\frac{4}{\lambda r} - 1 \right] \right\} \tag{41}$$

and

$$v_\theta^{\mathrm{GGA}}[n_{\mathrm{f}},\gamma=2]=c_0 n_{\mathrm{f}}^{2/3}\left\{\frac{5}{3}+4a\kappa^2\lambda n_{\mathrm{f}}^{-2/3}\left[3-\lambda r^2\right]\right\}. \tag{42}$$

The takeaway point is that if one sets out to build an approximation constrained to behave properly for $\gamma = 1$ (the physical case), the singularity is inevitable and the near-origin positivity is determined by the sign of the gradient expansion coefficient a. Our mcGGAs are built to have $a > 0$. However, if the actual density is regularized and has Gaussian form near the origin, then if that density is "cuspy" enough, i.e., has large λ, even with $a > 0$ and positivity constraints enforced on building the approximation, there still can be small-r regions for which $v_\theta^{\mathrm{approx}} < 0$.

4. EMPIRICAL EXPLORATION OF THE LIMITS OF GGA KE

4.1 Methodology

Our approach to the development of GGA OFKE functionals has been to adopt some suitable analytical form for the KE enhancement factor F_{t} with a few parameters determined from imposing constraints (e.g., correct scaling if applicable, correct small-s and large-s behavior) and, if unavoidable, fitting to a small set of training data. Interpolation between small- and large-s is defined by the chosen analytical form for F_{t}. The analytical forms usually are relatively simple with deliberately limited flexibility to avoid introduction of nonphysical kinks or other artifacts in that interpolation. In this sense, the properties are analogous to those of standard finite basis sets (see, for example, Refs. 3,6,7,21,23–25).

The unwelcome effects of limited flexibility can be avoided, at least in principle, by use of a numerical enhancement factor given on a mesh $s_0 = 0, s_1, \ldots, s_n = s_{\max}$. There is a practical barrier however. To determine such a numerical F_{t} requires numerical integration in real space of the complicated $(n, |\nabla n|)$ dependence of the KE functional integrand t_{orb}, Eq. (9), evaluated on a numerical s-mesh. Experience demonstrates that the result is unphysical, noisy, numerically unstable. One can see the difficulty simply by considering the numerical integration of an s "density of states" on a mesh of points s_i:

$$\mathcal{D}(s_i) := \int d\mathbf{r}\,\delta(s_i - s(\mathbf{r})) \approx \sum_j w_j \delta_{s_i, s(\mathbf{r}_j)}, \tag{43}$$

with w_j the quadrature weights. Numerical experiment shows that a modest change in even a very fine **r** or s mesh (or both) leads to distinctly different results.

An effective alternative is Padé approximants[42] of high orders such as were used recently for analytical representation of common Fermi–Dirac integral combinations.[43] They provide the simultaneous flexibility and smoothness required by the numerical integration in **r**. Numerical exploration led to the Padé approximant

$$F_t(s) = \frac{1 + \sum_{i=1}^{k} a_i s^i}{1 + \sum_{i=1}^{l} b_i s^i}, \tag{44}$$

of order [9,10] in the variable s ($k = 9$, $l = 10$) as a workable compromise between flexibility and number of free parameters.

Only a few parameters in the approximant can be determined from imposition of constraints. The remainder must be obtained by fitting. For this study, the *only* constraint imposed on Eq. (44) is recovery of the correct second-order gradient expansion at small s,

$$F_t(s) \approx 1 + \frac{5}{27} s^2, \quad s << 1. \tag{45}$$

This is accomplished by setting $a_1 = b_1$, $a_2 = (5/27) + b_2$. To allow maximal freedom for the fitted F_t, we have not imposed the large-s von Weizsäcker limit given in Eq. (21). Studies of X GGA functionals[44] show that the distribution of s, Eq. (43), is negligible above about $s = 3$ for most systems of interest, thus suggesting that such large-s behavior constraints are not critically important, at least for fitting. Also note well that in what follows, we have *not* imposed *any* of the positivity constraints, Eqs. (16), (17), and (19). The motivation is to make the empirical fitting as unconstrained as possible.

The absolute KE versus binding energy dilemma posed at the end of Section 2 has implications for the fitting criteria to be used. The usual *KE* fitting criterion is equivalent to the *total energy* or *E* criterion,[6] namely to minimize the squared energy difference between nonself-consistent OFDFT and reference KS energies at system equilibrium geometries (from standard KS calculations). The procedure is nonself-consistent for the OFDFT calculations because KS densities are used as input. The obvious flaw in the *E* criterion (which was investigated in Ref. 8) is that it forces OFDFT total energies at KS equilibrium configurations to be as nearly correct as possible but ignores the shape of the KS binding energy curve near equilibrium.

In Refs. 6–8, Frank Harris and two of us introduced what was called the ΔE criterion. In it, the objective function to be optimized is formed from energy differences between a point away from equilibrium and the equilibrium point as predicted by the reference conventional KS calculation. The objective function has two of those energy differences, one from OFDFT and the other from the KS calculations. Obviously, the ΔE criterion enforces binding upon the OFDFT approximation while leaving the total energy uncontrolled. The result can be an excessively high total energy.

In this work, we address these two limitations by making a convex sum of average versions of the two criteria. The averages are calculated over all atoms and molecules (and their geometries) in a training set. To put the two criteria on the same scale, we use the mean absolute relative error (MARE) of energy differences rather than average absolute energy differences,

$$\omega_{\Delta E} = \frac{1}{N}\sum_{M,i\neq e}\frac{\left|\Delta E^{\mathrm{KS}}_{M,i} - \Delta E^{\mathrm{OF-DFT}}_{M,i}\right|}{\left|\Delta E^{\mathrm{KS}}_{M,i}\right|}. \tag{46}$$

Here, for the nuclear spatial configuration i of molecule M, $\Delta E_{M,i} = E_{M,i} - E_{M,e}$, with $E_{M,e}$ the energy associated with the equilibrium nuclear configuration as predicted from conventional KS computations, and N the total number of terms in the sum (Eq. 46). Similarly, the mean absolute relative error of the total energy is

$$\omega_{E} = \frac{1}{N}\sum_{M,i}\frac{\left|E^{\mathrm{KS}}_{M,i} - E^{\mathrm{OF-DFT}}_{M,i}\right|}{\left|E^{\mathrm{KS}}_{M,i}\right|}. \tag{47}$$

The objective function is a convex combination of both

$$\omega(\alpha) = \alpha\omega_E + (1-\alpha)\omega_{\Delta E}, \tag{48}$$

with $\alpha \in [0,1]$. Minimization of $\omega(0)$ is essentially the ΔE criterion and conversely for $\omega(1)$. One expects, or at least hopes, that some intermediate α will provide a KE functional with both reasonable binding and reasonable absolute energy errors.

The training set we used includes nine molecules comprised of first- and second-row atoms and of diverse bonding types along with three closed shell atoms, $M = \{$LiH, CO, N_2, LiF, BF, NaF, SiO, H_4SiO, H_4SiO$_4$, Be, Ne, Ar$\}$. A set of six bond lengths was used for each molecule. Molecular geometries were changed by varying the single bond length in the diatomics, the central bond length R(Si–O) in H_4SiO, and by varying R(Si–O_i) in H_4SiO_4 deformed in the T_d mode. This set is small by comparison with the training sets used in the Minnesota series of XC functionals[45] because our purpose is different. We do not seek a broadly useful empirical functional. The issue here is narrower, namely whether there exists an OFDFT GGA functional which does well both on absolute energies and binding even on a small sample of systems.

One other technical point is that the enhancement factor F_t which results from fitting is checked for poles on the interval $s \in [0,1000]$. If the denominator of Eq. (44) has a root on that interval, the corresponding set of parameters is rejected.

All reference KS calculations were done in the local density approximation (LDA) for XC (see Refs. 16,46–52) using a triple-zeta Gaussian-type basis with polarization functions (TZVP).[53–55] Orbital-free KE integrals were calculated by numerical quadrature, as in our previous work.[6] Weight functions, $w_I(\mathbf{r})$, localized near each center with the properties that $w_I(\mathbf{r}) \geq 0$ and $\sum_I w_I(\mathbf{r}) = 1$ are used to represent the multicenter integrals exactly as a sum of atom-centered contributions[56]

$$T_s^{GGA}[n] = \sum_{I=1}^{N_{atoms}} c_{TF} \int d\mathbf{r} w_I(\mathbf{r}) n^{5/3}(\mathbf{r}) F_t(s(\mathbf{r})). \tag{49}$$

Radial integration of the resulting single-center forms was via a Gauss–Legendre procedure, while integration over the angular variables used high-order quadrature formulae.[57] A dense mesh consisting of 150 radial and 434 angular grid points was used to calculate atom-centered integrals. These computations used routines developed by Salvador and Mayer[58] and included in their code Fuzzy.

Before proceeding to results, one should note the implications of these numerical procedures. The finite Gaussian-type basis inexorably yields Gaussian near-origin behavior of the density. Yet the calculations are all-electron in the bare Coulomb external potential (14). This is precisely the inconsistency between external potential and near-origin density behavior discussed in Section 3.

4.2 Results

There are 17 independent parameters left in Eq. (44) after constraining to the second-order gradient expansion. Those were optimized to minimize the objective function $\omega(\alpha)$. Figure 1 shows the ω_E and $\omega_{\Delta E}$ MAREs,

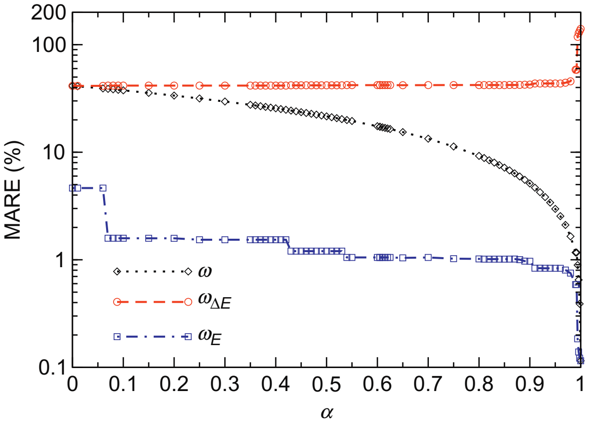

Figure 1 Minimum $\omega(\alpha)$ and corresponding $\omega_{\Delta E}$ and ω_E values as functions of α.

Eqs. (47) and (46), respectively, as functions of α. The minimum $\omega(\alpha)$ value also is shown. It decreases monotonically from 41% to 0.12%. Up to about $\alpha = 0.97$, ω_E decreases slowly with a few jumps (from about 5% to 0.8%), while $\omega_{\Delta E}$ is almost flat (from 41% to 44%). Unsurprisingly, they diverge as $\alpha \to 1$ ($\omega_{\Delta E} = 140\%$, $\omega = 0.12\%$), an illustration of the absolute energy versus binding energy dilemma.

Figure 2 shows the fitted F_t and F_θ for selected α values. Notice the violation of $F_\theta \geq 0$, a consequence of the unconstrained fitting. Notice also the structure in F_t for $\alpha < 1.0$.

Figure 2A clearly shows the separation of enhancement factors into two groups corresponding to $\alpha \leq 0.99$ and $\alpha = 1.0$. The $\alpha = 1.0$ curve is almost a line (F_θ is shown as a function of s^2) and is practically indistinguishable from the SGA curve (shown for comparison) for $s < 1.5$. F_θ (and F_t) has some structure (oscillations around the SGA curve) for $s \leq 1.5$ and $\alpha \leq 0.99$, though that may change upon changing the training set and/or the analytical form for the enhancement factor. Also, during the optimization process we noted the existence of many significantly different enhancement factors which cannot be discriminated clearly by the objective function $\omega(\alpha)$.

Any choice of $0.1 \leq \alpha \leq 0.98$ corresponds to the required KE functional, namely one which provides semi-quantitative binding, $\omega_{\Delta E} \approx 44\%$, and reasonable absolute energy error ($\omega_E \approx 1\%$). Table 1 lists the ω_E and $\omega_{\Delta E}$ values for the systems from the training set corresponding to the optimized $\omega(\alpha = 0.95)$. The highest $\omega_{\Delta E} = 85\%$ corresponds to LiH. Values for the optimized $\omega(\alpha = 1.0)$ are also shown for comparison. All $\omega_{\Delta E}$ values for $\alpha = 1.0$

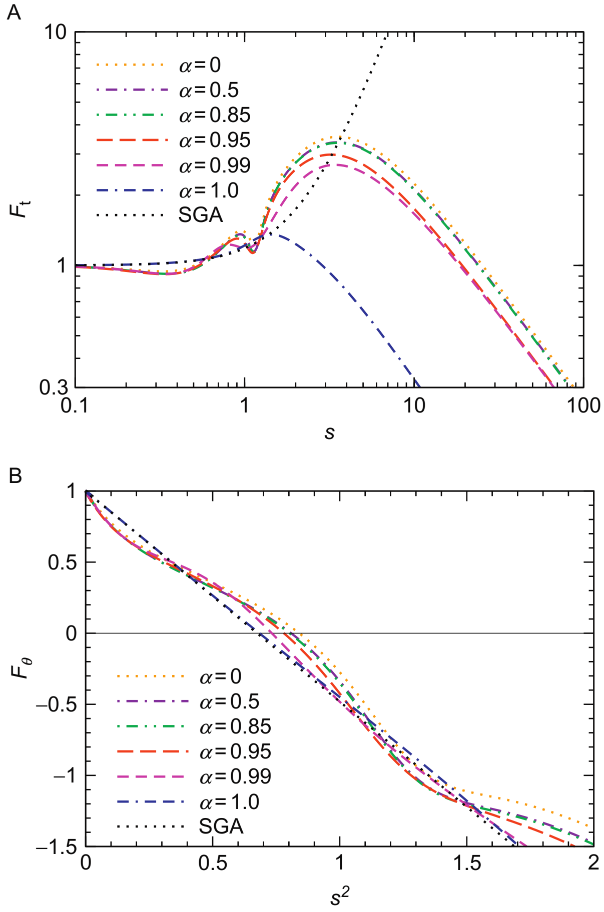

Figure 2 Noninteracting kinetic energy (A) and Pauli term (B) enhancement factors, F_t and F_θ, as functions of s and s^2, respectively.

(except the LiH molecule) are between 110% and 200%, signifying no binding.

The quality of energy curves for the CO and H_4SiO molecules corresponding to the $\alpha = 0.95$ functional is shown in Fig. 3. The $\alpha = 1$ curves (functional parameters fitted to optimize $\omega(\alpha = 1)$, i.e., pure E criterion) are shown for comparison. They have no minima. For the CO molecule, the minimum in the $\alpha = 0.95$ curve is too shallow compared to the reference KS result. In contrast, for H_4SiO the agreement between the $\alpha = 0.95$ optimized functional and KS results is excellent. Figure 4 shows a similar comparison for two molecules not in the training set. For the simplest, H_2, both

Table 1 MARE Values ω_E and $\omega_{\Delta E}$ (in %) Calculated Individually for Each System, with Parameters from Minimization of $\omega(\alpha = 0.95)$ and $\omega(\alpha = 1.0)$

	$\alpha = 0.95$		$\alpha = 1.0$	
System	ω_E	$\omega_{\Delta E}$	ω_E	$\omega_{\Delta E}$
LiH	4.2	85	0.2	85
CO	0.2	28	0.3	150
N_2	0.2	35	0.3	150
LiF	0.1	80	0.1	200
BF	0.1	15	0.1	160
NaF	0.1	25	0.03	180
SiO	0.02	32	0.04	120
H_4SiO_4	0.3	41	0.04	120
H_4SiO	0.02	50	0.6	110
Be	4.0	–	0.2	–
Ne	0.1	–	0.02	–
Ar	0.7	–	0.1	–
Average	0.83	44	0.12	140

functionals ($\alpha = 0.95$ and $\alpha = 1.0$) provide qualitatively correct binding, but the minimum is too shallow and there are large discrepancies at the dissociation limit relative to the KS result. Single-bond stretching in H_2O is described qualitatively roughly correctly only by the $\alpha = 0.95$ functional. As expected, the $\alpha = 1.0$ functional fails to give binding.

Table 2 lists the set of coefficients in the KE enhancement factor (Eq. 44) for the optimized $\omega(\alpha = 0.95)$.

5. SUMMARY DISCUSSION

A GGA OFKE form is the simplest one-point functional which explicitly includes effects of electron density inhomogeneity. The GGA form, with parameters determined by constraints, has been very successful for approximate XC functionals, to the point that such functionals dominate in practical calculations. A crucial distinction with respect to OFKE is the order of magnitude of the XC energy, about 10% of the total energy.

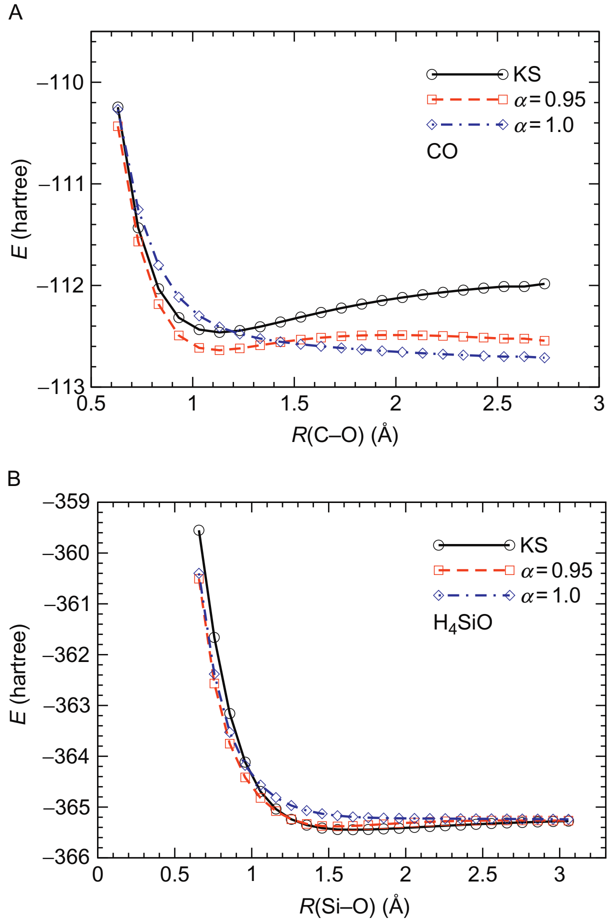

Figure 3 Total energy as a function of bond distance for the CO (A) and H_4SiO_4 (B) molecules from the training set obtained from a KS LDA calculation and from the post-KS orbital-free calculation with approximate GGA functionals.

The ground-state KE, however, has the same order of magnitude as the total energy and the KS KE is a large fraction of the total KE. Hence, a relative error of even a few percent in an approximate OFKE functional will have much bigger impact on calculated properties than would the same relative error in an approximate XC functional.

This distinction has significant implications for the constraint-based development of GGA OFKE functionals. There is a related, but perhaps less-obvious distinction. Because exchange in physical systems is purely Coulombic and correlation (as defined in DFT; recall Eq. 4) is mostly

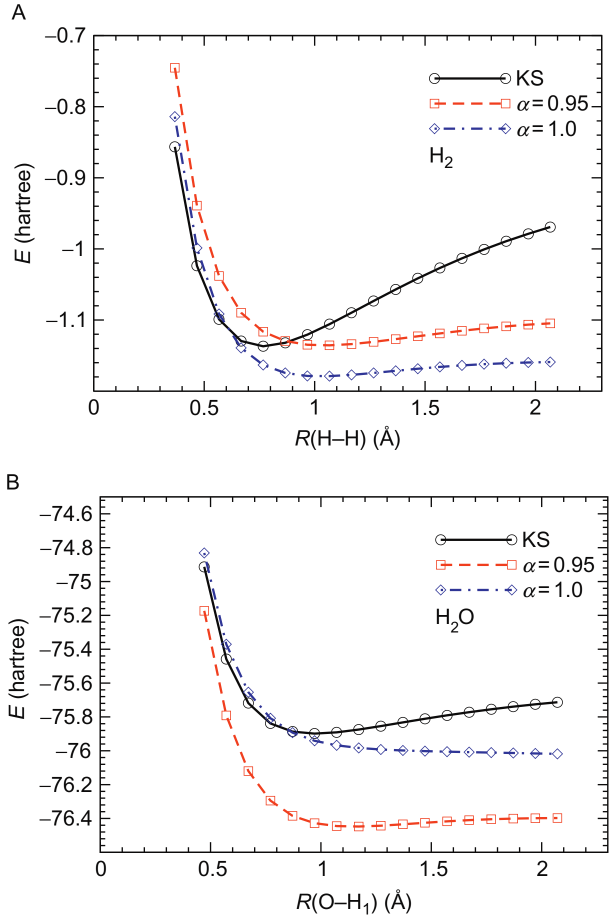

Figure 4 Total energy as a function of bond distance for the H_2 (A) and H_2O (B) molecules (neither in training set) obtained from a KS LDA calculation and from the post-KS orbital-free calculation with approximate GGA functionals.

Coulombic (the KE contribution is small), it is eminently sensible to impose Coulombic constraints on an approximate E_{xc}. The resulting functional should be applicable to a broad range of v_{ext}, if not truly universal. Experience shows that to be the case. Good GGA E_{xc} functionals deliver variations in MARE over classes of properties and types of bonding but they are broadly applicable.

Generating useful constraints on a GGA OFKE functional that preserve universality has not been as straightforward so far as for the XC functionals. One way to see the underlying difficulty is that T_s is a noninteracting system

Table 2 Coefficients in Eq. (44) from Optimizing $\omega(\alpha = 0.95)$

Coefficient	**Value**
$a_1 = b_1$	12.100994770272
$a_2 = 5/27 + b_2$	10.829496969896
a_3	− 27.327919841144
a_4	73.841590552393
a_5	25.096089580269
a_6	− 45.306369888376
a_7	− 77.901835391837
a_8	− 20.862438996553
a_9	67.083330246208
b_1	12.100994770272
b_2	10.644311784711
b_3	14.896876304511
b_4	5.5830951758904
b_5	− 24.558524755221
b_6	− 31.914940553009
b_7	4.3293607988211
b_8	17.169012815532
b_9	2.4210601059537
b_{10}	3.2527234245842

quantity, whereas E_{xc} is, as just remarked, predominantly a Coulombic quantity. This means a lack of specificity for T_s compared to E_{xc}. Surmounting that lack is what we have done by abandoning universality and imposing conditions that follow from Coulombic v_{ext}. Precisely because they are nonuniversal conditions, use of pseudo-potentials or Gaussian-type basis sets immediately introduces inconsistencies. In Section 3, we have shown how the consequences can be delineated clearly with simple one-center densities.

Section 4 then considered whether any GGA can have acceptable errors in both total energies and binding energies. The result is not as encouraging as we would like. For a small training set, the best empirical OFKE GGA we have been able to develop so far provides a relatively small MARE for the total energy ($\omega_E \approx 0.8\%$) but only semi-quantitative binding ($\omega_{\Delta E} \approx 44\%$). The use of mixed $E - \Delta E$ criteria is essential to get both correct total energies and roughly reasonable binding simultaneously.

The correct second-order gradient expansion was the only constraint imposed on the KE enhancement factor. The result is violation of a constraint, $F_\theta \geq 0$, (Eq. 19) which depends on a particular choice of t_θ. We have not checked whether $v_\theta \geq 0$ is violated for the empirical GGA, but are certain that it will be violated because of the negative slope of $F_\theta^{\text{empirical}}$ for $s^2 \leq 1$. One might hope that incorporation of more constraints should make the functional better or, at least, more nearly universal in the limited sense of improving its transferability to different systems and/or conditions. The counterargument is that, except for the high-order Padé form itself, the empirical functional was not restricted in any other way, a fact which should facilitate optimization (even at the cost of realism or transferability).

A weak caveat is that we have not yet tested the empirical functionals in SCF calculations. This may be important because the large-s behavior of the empirical functionals for Padé approximants of different orders might be very different, while the ω_E and $\omega_{\Delta E}$ errors are very similar. That difference in large-s behavior might be important for SCF calculations, but not for post-KS calculations. However, the somewhat disappointing performance on post-KS binding energy curves makes this, in our judgment, a somewhat problematic conjecture.

During minimization of $\omega(\alpha)$ with respect to the independent parameters of the Padé enhancement factor (at fixed α of course), we encountered three main difficulties. First is the precision of numerical integration required (very dense radial and angular meshes) to handle roughness in the KE enhancement factor. Second is that, for any given α, the optimization process very frequently sticks in local minima. Optimizations therefore were run for multiple values of α. Those results were analyzed to find one or a few superior parameter sets (based on values of ω_E and $\omega_{\Delta E}$). Then those parameter sets were used as initial ones to start a repeat optimization for all α. Eventually, this "by hand" procedure yielded optimal sets of parameters for every α. Third, the existence of multiple enhancement factors which deliver very similar values of the objective function $\omega(\alpha)$ despite being very different functions of s makes the final functional for each α sensitive to the choice of the training set. Increasing the size of the training set might help to overcome that difficulty. But we note again that our purpose here is not to attempt a general, widely applicable empirical GGA for OFKE but simply to find the best for a modest selection of molecules. Even with that narrow goal, the outcome seems to be that there are significant limits on what can be expected of a GGA OFKE functional.

ACKNOWLEDGMENTS

We thank the University of Florida High-Performance Computing Center for computational resources and technical support. We thank Keith Runge for help with the title. This work was supported by U.S. Department of Energy grant DE-SC0002139.

REFERENCES

1. Karasiev, V. V.; Sjostrom, T.; Dufty, J.; Trickey, S. B. Accurate Homogeneous Electron Gas Exchange-Correlation Free Energy for Local Spin-Density Calculations. *Phys. Rev. Lett.* **2014**, *112,* 076403(1–5).
2. Karasiev, V. V.; Sjostrom, T.; Trickey, S. Finite-Temperature Orbital-Free DFT Molecular Dynamics: Coupling PROFESS and Quantum Espresso. *Comput. Phys. Commun.* **2014**, *185*, 3240–3249.
3. Karasiev, V. V.; Chakraborty, D.; Shukruto, O. A.; Trickey, S. B. Nonempirical Generalized Gradient Approximation Free-Energy Functional for Orbital-Free Simulations. *Phys. Rev. B* **2013**, *88*, 161108(R)(1–5).
4. Karasiev, V. V.; Chakraborty, D.; Trickey, S. B. Progress on New Approaches to Old Ideas: Orbital-Free Density Functionals. In: Delle Site, L.; Bach, V. Eds.; *Many-Electron Approaches in Physics, Chemistry, and Mathematics: A Multidisciplinary View*; Springer: Heidelberg, 2014; pp 113–134.
5. Karasiev, V. V.; Chakraborty, D.; Dufty, J. W.; Harris, F. E.; Runge, K.; Trickey, S. B. Innovations in Finite-Temperature Density Functionals. In: Graziani, F. et al., Eds.; *Frontiers and Challenges in Warm Dense Matter*; Springer Verlag: Heidelberg, 2014; pp 61–85.
6. Karasiev, V. V.; Trickey, S. B.; Harris, F. E. Born-Oppenheimer Interatomic Forces from Simple, Local Kinetic Energy Density Functionals. *J. Comput. Aided Mater. Des.* **2006**, *13*, 111–129.
7. Karasiev, V.; Jones, R. S.; Trickey, S. B.; Harris, F. E. Recent Advances in Developing Orbital-Free Kinetic Energy Functionals. In: Paz, J. L.; Hernández, A. J. Eds.; *New Developments in Quantum Chemistry*; Transworld Research Network: Kerala, India, 2009; pp 25–54.
8. Karasiev, V. V.; Jones, R. S.; Trickey, S. B.; Harris, F. E. Properties of Constraint-Based Single-Point Approximate Kinetic Energy Functionals. *Phys. Rev. B* **2009**, *80,* 245120 (1–17); Erratum *ibid.* **2013**, *87*, 239902.
9. Borgoo, A.; Green, J. A.; Tozer, D. J. Molecular Binding in Post-Kohn-Sham Orbital-Free DFT. *J. Chem. Theory Comput.* **2014**, *10*, 5338–5345.
10. Mermin, N. D. Thermal Properties of Inhomogeneous Electron Gas. *Phys. Rev.* **1965**, *137*, A1441–A1443.
11. Thomas, L. The Calculation of Atomic Fields. *Proc. Camb. Philos. Soc.* **1927**, *23*, 542–548.
12. Fermi, E. Un metodo statistico per la determinazione di alcune proprietá dell'atomo. *Atti Accad. Nazl. Lincei* **1927**, *6*, 602–607.
13. Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871.

14. Levy, M. Universal Variational Functionals of Electron Densities, First-Order Density Matrices, and Natural Spin-Orbitals, and Solution to the v-Representability Problem. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6062–6065.
15. Lieb, E. H. Density Functionals for Coulomb Systems. *Int. J. Quantum Chem.* **1983**, *24*, 243–277.
16. Kohn, W.; Sham, L. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.
17. Parr, R.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford: New York, 1989.
18. Dreizler, R.; Gross, E. *Density Functional Theory*; Springer-Verlag: Berlin, 1990.
19. Perdew, J. P.; Schmidt, K. Jacob's Ladder of Density Functional Approximations for the Exchange-Correlation Energy. *A.I.P. Conf. Proc.* **2001**, *577*, 1–20.
20. Lee, H.; Lee, C.; Parr, R. G. Conjoint Gradient Correction to the Hartree-Fock Kinetic- and Exchange-Energy Density Functionals. *Phys. Rev. A* **1991**, *44*, 768–771.
21. Perdew, J. P. Generalized Gradient Approximation for the Fermion Kinetic Energy as a Functional of the Density. *Phys. Lett. A* **1992**, *165*, 79–82.
22. Lacks, D. J.; Gordon, R. G. Tests of Nonlocal Kinetic Energy Functionals. *J. Chem. Phys.* **1994**, *100*, 4446–4452.
23. DePristo, A. E.; Kress, J. D. Kinetic-Energy Functionals via Padé Approximations. *Phys. Rev. A* **1987**, *35*, 438–441.
24. Thakkar, A. J. Comparison of Kinetic-Energy Density Functionals. *Phys. Rev. A* **1992**, *46*, 6920–6924.
25. Tran, F.; Wesolowski, T. A. Link Between the Kinetic- and Exchange-Energy Functionals in the Generalized Gradient Approximation. *Int. J. Quantum Chem.* **2002**, *89*, 441–446.
26. Constantin, L.; Fabiano, E.; Laricchia, S.; Sala, F. D. Semiclassical Neutral Atom as a Reference System in Density Functional Theory. *Phys. Rev. Lett.* **2011**, *106,* 186406 (1–4).
27. Lehtomäki, J.; Makkonen, I.; Caro, M. A.; Lopez-Acevedo, O. Orbital-Free Density Functional Theory Implementation with the Projector Augmented-Wave Method. *J. Chem. Phys.* **2014**, *141,* 234102(1–7).
28. Tal, Y.; Bader, R. F. W. Studies of the Energy Density Functional Approach. I. Kinetic Energy. *Int. J. Quantum Chem.* **1978**, *S12*, 153–168.
29. Bartolotti, L.; Acharya, P. K. On the Functional Derivative of the Kinetic Energy Density Functional. *J. Chem. Phys.* **1982**, *77*, 4576–4585.
30. Harriman, J. The Interface Between Reduced Density Matrices and Density Functional Theory. In: Erdahl, R.; Smith, J. V. Eds.; *Density Matrices and Density Functionals*; D. Reidel: Dordrecht, 1987; pp 359–373.
31. Levy, M.; Ou-Yang, H. Exact Properties of the Pauli Potential for the Square Root of the Electron Density and the Kinetic Energy Functional. *Phys. Rev. A* **1988**, *38*, 625–629.
32. Baltin, R. The 3-Dimensional Kinetic-Energy Density Functional Compatible with the Exact Differential-Equation for Its Associated Tensor. *J. Chem. Phys.* **1987**, *86*, 947–952.
33. Hoffmann-Ostenhof, M.; Hoffmann-Ostenhof, T. Schrödinger Inequalities" and Asymptotic Behavior of the Electron Density of Atoms and Molecules. *Phys. Rev. A* **1977**, *16*, 1782–1785, see Eq. (2.20). See also; Romera, E.; Dehesa, J. S. Weizsacker Energy of Many-Electron Systems. *Phys. Rev. A* **1994**, *50*, 256–266.
34. Sears, S. B.; Parr, R. G.; Dinur, U. On the Quantum-Mechanical Kinetic Energy as a Measure of the Information in a Distribution. *Isr. J. Chem.* **1980**, *19*, 165–173.
35. Harriman, J. E. A Kinetic Energy Density Functional. *J. Chem. Phys.* **1985**, *83*, 6283–6287.

36. Herring, C. Explicit Estimation of Ground-State Kinetic Energies from Electron Densities. *Phys. Rev. A* **1986**, *34*, 2614–2631.
37. Levy, M.; Perdew, J. P.; Sahni, V. Exact Differential Equation for the Density and Ionization Energy of a Many-Particle System. *Phys. Rev. A* **1984**, *30*, 2745–2748.
38. Trickey, S. B.; Karasiev, V. V.; Jones, R. S. Conditions on the Kohn-Sham Kinetic Energy and Associated Density. *Int. J. Quantum Chem.* **2009**, *109*, 2943–2952.
39. Kato, T. On the Eigenfunctions of Many-Particle Systems in Quantum Mechanics. *Commun. Pure Appl. Math.* **1957**, *10*, 151–177.
40. Lambert, F.; Clérouin, J.; Zérah, G. Very-High-Temperature Molecular Dynamics. *Phys. Rev. E* **2006**, *73,* 016403(1–5).
41. Gradshteyn, I.; Ryzik, I. *Table of Integrals, Series, and Products*. Academic Press: New York, 1980, Corrected and enlarged edition by A. Jeffrey (entry 3.478).
42. Baker, G., Jr.; Gammel, J. L. *The Padé Approximant in Theoretical Physics*; Academic Press: New York, 1970.
43. Karasiev, V. V.; Chakraborty, D.; Trickey, S. B. Improved Analytical Representation of Combinations of Fermi-Dirac Integrals for Finite-Temperature Density Functional Calculations. *Comput. Phys. Commun.* **2015**, *192*, 114–123. URL: http://dx.doi.org/10.1016/j.cpc.2015.03.002.
44. Gázquez, J.; del Campo, J.; Trickey, S.; Alvarez-Mendez, R.; Vela, A. Analysis of the Generalized Gradient Approximation for the Exchange Energy. In: Ghosh, S. K.; Chattaraj, P. K. Eds.; *Concepts and Methods in Modern Theoretical Chemistry*; 1, CRC Press: Boca Raton, FL, 2013; pp 295–311(In honor of Prof. B. M. Deb).
45. Peverati, R.; Truhlar, D. G. Quest for a Universal Density Functional the Accuracy of Density Functionals Across a Broad Spectrum of Databases in Chemistry and Physics. Philos. Trans. R. Soc. A, 372(20120476).
46. Slater, J. C. A Simplification of the Hartree-Fock Method. *Phys. Rev.* **1951**, *81*, 385–390.
47. Slater, J. C. Magnetic Effects and the Hartree-Fock Equation. *Phys. Rev.* **1951**, *82*, 538–541.
48. Slater, J. C. Suggestions from Solid-State Theory Regarding Molecular Calculations. *J. Chem. Phys.* **1965**, *43*, S228.
49. Gáspár, R. Über eine approximation des Hartree-Fockschen potentials durch eine universelle potentialfunktion (On an Approximation of Hartree-Fock Potentials Through a Universal Potential Function). *Acta Phys. Hung.* **1954**, *3*, 263–286.
50. Tong, B.; Sham, L. Application of a Self-Consistent Scheme Including Exchange and Correlation Effects to Atoms. *Phys. Rev.* **1966**, *144*, 1–4.
51. Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.
52. Ceperley, D. M.; Alder, B. J. Ground State of the Electron Gas by Stochastic Method. *Phys. Rev. Lett.* **1980**, *45*, 566–569.
53. Schäfer, A.; Horn, H.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets for Atoms Li to Kr. *J. Chem. Phys.* **1992**, *97*, 2571–2577.
54. Schäfer, A.; Huber, C.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets of Triple Zeta Valence Quality for Atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829–5835.
55. Taken from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, funded by the U.S. Department of Energy (contract DE-AC06-76RLO). See URL: http://www.emsl.pnl.gov/forms/basisform.html.

56. Becke, A. D. A Multicenter Numerical Integration Scheme for Polyatomic Molecules. *J. Chem. Phys.* **1988**, *88*, 2547–2553.
57. Lebedev, V. I.; Laikov, D. N. Quadrature Formula for the Sphere of 131st Algebraic Order of Accuracy. *Dokl. Akad. Nauk* **1999**, *366*, 741–745.
58. Salvador, P.; Mayer, I. Energy Partitioning for "Fuzzy" Atoms. *J. Chem. Phys.* **2004**, *120*, 5046–5052.