Testing the kinetic energy functional: Kinetic energy density as a density functional

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A new method for defining an energy density for the noninteracting kinetic energy of density functional theory is given. The resulting energy density is a density functional determined completely by the kinetic energy functional itself. Although this method is not constructive, it allows for a direct comparison between exact and approximate functionals pointwise in space. For simple systems, the new energy density is calculated exactly, and compared with traditional choices, on both formal and physical grounds. Finally, the energy densities of both the gradient expansion and the von Weizsäcker approximation are calculated, and compared with the exact quantity. The errors in the von Weizsäcker approximation are identified. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Density functional theory is a very popular method for finding the ground-state of electronic systems.[1] In most modern density functional calculations, the Kohn–Sham equations[2] are solved for a set of orbitals, the sum of whose densities equals (in principle) the exact ground-state density $n(\mathbf{r})$, and from which the ground-state energy can be extracted. The only approximation in this scheme is to the exchange-correlation energy as a functional of the density. A large part of the total energy, the kinetic energy of the Kohn–Sham orbitals, T_s, is treated exactly, but at the computational cost of needing to solve the Kohn–Sham equations for N orbitals, where N is the number of electrons. However, if a sufficiently accurate approximation to T_s as a functional of the density were known, then one would only need to solve a single integrodifferential equation directly for the density, without recourse to constructing the orbitals. Such a method would be, by design, an order N method, meaning that the computational cost would scale with the number of electrons in the system, and be far faster than present Kohn–Sham calculations for large systems. The search for accurate approximations to $T_s[n]$ has a long history,[3,4] and remains an active area of research.[5–13]

A useful tool in this search for an accurate approximation to T_s is the kinetic energy density. By a kinetic energy density, we mean any function over real space that integrates to T_s:

$$T_s = \int d^3r \, t_s(\mathbf{r}). \tag{1}$$

Such a definition does not determine $t_s(\mathbf{r})$ uniquely. Addition of any function whose integral vanishes, e.g., $\nabla^2 n(\mathbf{r})$, to a valid $t_s(\mathbf{r})$ produces another valid kinetic energy density. Two popular choices are

$$t_s^{\text{WFI}}(\mathbf{r}) = -\tfrac{1}{2} \sum_{i=1}^{N} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) \tag{2}$$

and

$$t_s^{\text{WFII}}(\mathbf{r}) = \tfrac{1}{2} \sum_{i=1}^{N} |\nabla \phi_i(\mathbf{r})|^2, \tag{3}$$

where $\phi_i(\mathbf{r})$ is the ith Kohn–Sham orbital in an N-electron system. The label WF refers to wave function, because these definitions explicitly employ the KS orbitals. Both these definitions are valid and are useful in different contexts. For finite systems these forms integrate to the same global kinetic energy, but they differ locally and are related to each other via[3]

$$t_s^{\text{WFI}}(\mathbf{r}) = t_s^{\text{WFII}}(\mathbf{r}) - \tfrac{1}{4} \nabla^2 n(\mathbf{r}). \tag{4}$$

The kinetic energy densities based on these choices are plotted in Fig. 1 for a single particle in a finite rectangular potential well. The first choice has the advantage of being the form of the kinetic energy that appears explicitly in the Schrödinger equation, while the latter enjoys the benefit of being positive everywhere. Plots of such densities often provide insight into solutions of the Kohn–Sham equations and the mechanisms by which chemical reactions proceed.[16,17] The nonuniqueness of the kinetic energy density has been studied extensively in the literature. For example, Yang *et al.*[18] thoroughly examined wave-function-based definitions, showing that pointwise energy conservation and a specific asymptotic behavior uniquely constrain the choice of wave-function-based kinetic energy density.

However, the present paper tackles an entirely different question: How does one define the kinetic energy density as a *density* functional? The traditional wave function choices of Eqs. (2) and (3) are *not* explicit density functionals. (They are orbital functionals, and so only implicit density functionals.[20]) A fundamental difficulty in discussing ap-
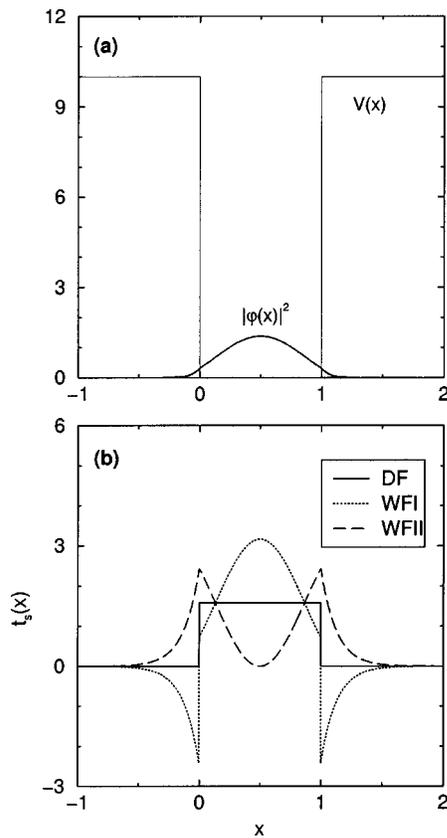
FIG. 1. Comparison of different choices of kinetic energy density for single particle in a one-dimensional finite box potential well: (a) Rectangular potential well (thin line) and the ground state density (thick line) and (b) kinetic energy densities (atomic units).

proximate *density* functional kinetic energy densities is to know which of the infinitely many choices allowed by Eq. (1) that a given approximate kinetic energy density is trying to approximate.[19] This is particularly important if one is developing density functional approximations for $T_s[n]$ that are not based on approximations to a specific wave function choice of energy density. A desirable feature of any density-functional choice of kinetic energy density is a degree of near-sightedness.[14,15] A choice that changes drastically as a result of a perturbation far away is unlikely to provide useful physical insight. This paper demonstrates how one goes about constructing kinetic energy densities that are explicit *density* functionals, $t_s^{DF}[n](\mathbf{r})$, determined by the kinetic energy functional itself. For example, in one-dimension for noninteracting v-representable densities, $t_s^{DF}[n](x)$ can be chosen to satisfy the relationship,

$$\frac{dt_s^{DF}[n](x)}{dx} = -\frac{n(x)}{2}\frac{dv_s[n](x)}{dx}, \tag{5}$$

where $v_s(x)$ is the Kohn–Sham potential. Since $v_s(x) = -\delta T_s/\delta n(x)$ modulo a constant μ, the chemical potential, this is an explicit density functional determined by $T_s[n]$. Later, we will prove that $T_s[n] = \int dx\, t_s^{DF}[n](x)$. Such a choice is not only an explicit density functional, but also has some useful features for physical interpretation. In Fig. 1, it can be seen that our choice is extremely near-sighted,[15] almost as near-sighted as the potential itself. For particles in an

infinite well, using Eq. (5) yields a constant kinetic energy density for any number of electrons, whereas either of the wave function choices become uniform only in the interior when there are a large number of particles in the box. While $t_s^{DF}[n](x)$, defined by Eq. (5), is not constructive (because we do not know the exact v_s as a functional of density) it is useful for being both extremely near-sighted and allowing a pointwise comparison for different approximations to $T_s[n]$, independent of their various origins and any assumptions made in their construction.

The paper is divided as follows: In Sec. II, we describe how kinetic energy densities that are density functionals can be designed with specific properties. In Sec. III we illustrate several simple one-dimensional examples as well as the three-dimensional hydrogen atom. Section IV discusses exact conditions and the Thomas–Fermi kinetic energy density which is exact for a uniform electron gas. In Sec. V the details of our calculations are explained and in Sec. VI we discuss convergence of the semiclassical gradient expansion for the kinetic energy density of the hydrogen atom. In Sec. VII the von Weizsäcker approximation is thoroughly examined and its correction terms are derived. Finally, summary and outlook appear in Sec. VIII. We use atomic units throughout this paper ($e^2 = m_e = \hbar = 1$).

II. CONSTRUCTION

The Euler equation for noninteracting electrons is[21]

$$\frac{\delta T_s}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) = \mu, \tag{6}$$

where μ is the chemical potential. Therefore the functional derivative of the kinetic energy is just the negative of the Kohn–Sham potential, up to a constant. As we restrict ourselves here to density changes that leave the total number of electrons N fixed, this constant is irrelevant.

Performing an integration by parts on the defining relation for an energy density, Eq. (1), leads to

$$T_s = \int d^3r\, t_s(\mathbf{r}) = -\int d^3r\, \mathbf{r}\cdot\nabla t_s(\mathbf{r})/D, \tag{7}$$

where D is the dimensionality of the space. To satisfy the scaling relation $T_s[n_\gamma](\mathbf{r}) = \gamma^2 T_s[n](\mathbf{r})$ where $n_\gamma = n(\gamma\mathbf{r})$, the virial theorem for noninteracting electrons with v-representable densities is usually written as[21]

$$2T_s = \int d^3r\, n(\mathbf{r})\mathbf{r}\cdot\nabla v_s(\mathbf{r}). \tag{8}$$

The integrand of Eq. (8) can be determined from the density and one may attempt to use it as a definition for $t_s^{DF}(\mathbf{r})$. However, this integrand is origin-dependent and this is problematic for systems with more than one nucleus. On the other hand, since $n(\mathbf{r})\nabla v_s(\mathbf{r})$ is a well-defined vector field throughout space, vanishing outside finite systems, it can be written as the gradient of a scalar plus the curl of a vector,[22]

$$-\frac{D}{2}n(\mathbf{r})\nabla v_s(\mathbf{r}) \equiv \nabla t_s^{DF}(\mathbf{r}) + \nabla\times\mathbf{a}_s(\mathbf{r}) \tag{9}$$

with the auxiliary condition that $t_s(\mathbf{r})\to 0$ as $r\to\infty$. Inserting Eq. (9) into Eq. (8) and comparing with Eq. (7), we see that Eq. (9) does indeed define a kinetic energy density. The curl term in Eq. (9) plays no role in the energy density. An easy way to see this is to take the divergence of both sides of Eq. (9), yielding

$$\nabla^2 t_s^{\text{DF}}(\mathbf{r}) = -\frac{D}{2}\nabla\{n(\mathbf{r})\nabla v_s(\mathbf{r})\},\tag{10}$$

i.e., $t_s^{\text{DF}}(\mathbf{r})$ satisfies a Poisson equation whose source is the gradient of the KS force density. This methodology was originally devised to produce an exchange-correlation energy density from the corresponding potential.[23] It is important to note that the choice of $t_s^{\text{DF}}(\mathbf{r})$ in Eq. (9) is not unique, e.g., one may add $\nabla^2 n$ to $t_s^{\text{DF}}(\mathbf{r})$ and still have a density-functional kinetic energy density. This is always true because the gradient of the density is always zero where $r\to\infty$ and the integral of the Laplacian is equivalent to the surface integral of the gradient,

$$\int d^3 r \nabla^2 n(\mathbf{r}) = \int d\mathbf{S}\cdot\nabla n(\mathbf{r}).\tag{11}$$

In Eq. (9) $t_s^{\text{DF}}(\mathbf{r})$ is determined from the density and the Kohn–Sham potential, which allows one to compare different functional approximations on the same ground and to explain how functionals with poor potentials can still obtain good energies. It is also devised in such a way that in the limit of a uniform gas, the exact Thomas–Fermi (TF) kinetic energy density is recovered.

The above derivation applies to the density functional for the kinetic energy. Spin-density results are easily extracted from the exact spin-scaling relation,[21]

$$T_s[n_\uparrow,n_\downarrow] = \tfrac{1}{2}(T_s[2n_\uparrow] + T_s[2n_\downarrow]),\tag{12}$$

where the right-hand terms are density functionals with $n_\uparrow(n_\downarrow)$ being spin-up (spin-down) density. Since the virial theorem applies to each density functional on the right-hand-side separately, the spin-density functional for the kinetic energy density is

$$t_s^{\text{DF}}[n_\uparrow,n_\downarrow](\mathbf{r}) = \tfrac{1}{2}(t_s^{\text{DF}}[2n_\uparrow](\mathbf{r}) + t_s^{\text{DF}}[2n_\downarrow](\mathbf{r})).\tag{13}$$

In particular, for a fully polarized system,

$$t_s^{\text{DF,pol}}[n,0](\mathbf{r}) = \tfrac{1}{2}t_s^{\text{DF}}[2n](\mathbf{r}).\tag{14}$$

We conclude this section by relating the formalism to other work. Our DF construction is closely related to analysis of the microscopic stress tensor.[24,25] The ambiguity in the energy density mirrors the more general ambiguity in the stress tensor at a point. To see the relationship, note that a microscopic stress tensor must satisfy

$$\mathbf{f}(\mathbf{r}) = -\nabla\cdot\vec{\vec{\sigma}}(\mathbf{r}),\tag{15}$$

where $\mathbf{f}(\mathbf{r})$ is the force density, $-n(\mathbf{r})\nabla v(\mathbf{r})$, and $\vec{\vec{\sigma}}$ is the symmetric stress tensor. Clearly one can add any symmetric tensor with vanishing divergence to the right of Eq. (15) and find a new stress tensor. The formal link to the specific case here can be seen by considering the KS stress tensor on the right, whose divergence is the KS force density. Compared to Eq. (9) and taking divergence of both sides, we find
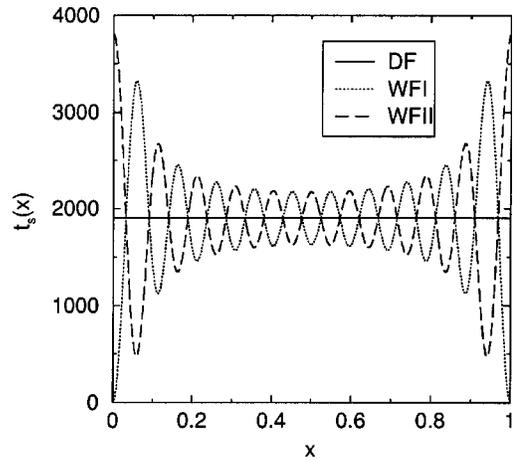
FIG. 2. Same as Fig. 1(b), but for ten spinless fermions in an infinite potential well.

$$t_s^{\text{DF}}(\mathbf{r}) = \frac{2}{D}\int d^3 r' \frac{\partial_i\partial_j\sigma_{ij}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}.\tag{16}$$

The source of this ambiguity has been nicely identified by Rogers and Rappe.[26] Only if one allows unphysical distortions of space (leading to nonflat metrices) can one unambiguously determine a stress tensor. But physical systems *do* have flat metrices, and the remaining formal ambiguity has been identified.[26] On the other hand, one may resort to physical arguments to choose a certain energy per particle extracted from the wave function, and discuss the remaining ambiguity.[27] All these efforts[26,27] consider the energy density as a functional of the wave function, rather than as a *density* functional.

III. ILLUSTRATIONS

To better understand the behavior of the exact $t_s^{\text{DF}}(\mathbf{r})$, we consider several simple examples. The two traditional wave function definitions of $t_s^{\text{WF}}(x)$ are compared with $t_s^{\text{DF}}(x)$. In one dimension, Eq. (9) reduces to Eq. (5). Note that $t_s^{\text{DF}}(x)$ is constant whenever $v_s(x)$ is constant which is not the case for the traditional kinetic energy densities. In Fig. 1, kinetic energy densities of a single particle in a finite potential well illustrate this behavior due to the constant potential within the box. Note that our kinetic energy density is finite only inside the box, making it more near-sighted (in this example) than the other two densities.

An important feature of these energy densities is their behavior as the number of particles grows. In particular, if one wishes to treat both solids, including metals, and molecules, they should behave well in the thermodynamic limit of systems with delocalized orbitals. Figure 2 shows the two WF and our DF kinetic energy densities for ten spinless fermions in an infinite well. All three definitions give the same constant density in the thermodynamic limit ($N\to\infty,N/L\to n$), but the DF choice is uniform for *all* finite N, whereas the WF definitions exhibit strong oscillations.

To demonstrate the effect of nonconstant potentials, in Fig. 3 we present the results from one particle in a harmonic potential well. While the ground state density and $t_s^{\text{DF}}(x)$
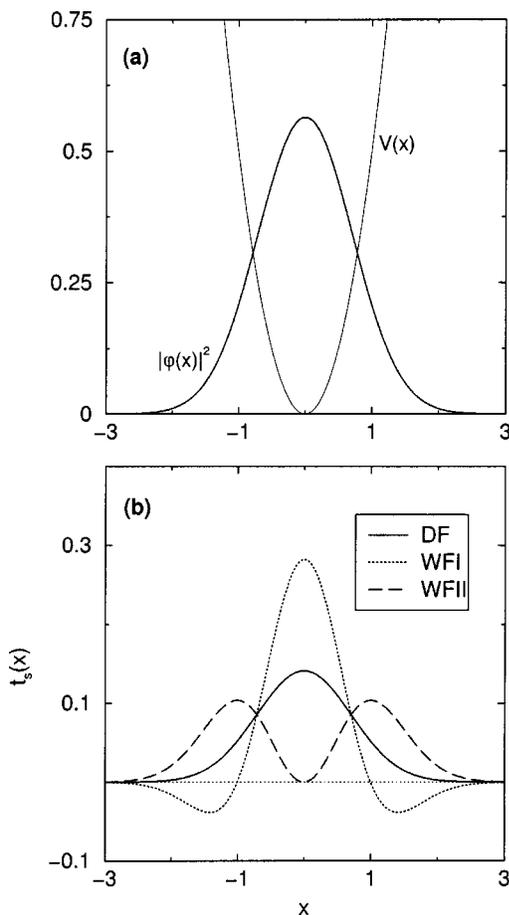
FIG. 3. Same as Fig. 1, but for a single particle in harmonic oscillator potential well of $k = 1$.

have Gaussian shapes, wave function definitions give negative values or zero at the potential minimum where the density has the maximum value. The DF curve is nicely peaked where the maximum of the density is peaked, but does not vanish anywhere. In one-dimension, for any number of electrons we find (see Appendix) that $t_s^{DF}(x)$ is the average of the two wave function kinetic energy densities,

$$t_s^{DF}(x) = \tfrac{1}{2}[t_s^{WFI}(x) + t_s^{WFII}(x)]. \tag{17}$$

In the Appendix it is shown that this result is valid for a particle in a one-dimensional potential well and, furthermore, that $t_s^{DF}(x)$ can be expressed as

$$t_s^{DF}(x) = \frac{1}{16 n(x)}\left(\frac{dn(x)}{dx}\right)^2 + \frac{1}{2}[E - v(x)]n(x), \tag{18}$$

which clearly shows that $t_s^{DF}(x)$ is positive in the classical region.

Although for some three-dimensional systems, e.g., a particle in a harmonic oscillator potential well, $t_s^{DF}(\mathbf{r})$ is also the average of $t_s^{WFI}(\mathbf{r})$ and $t_s^{WFII}(\mathbf{r})$, this is not always the case. But for any spherical system, the equation for our kinetic energy density is very simple,

$$\frac{dt_s^{DF}}{dr}(r) = -\frac{3}{2}n(r)\frac{dv_s(r)}{dr} \tag{19}$$

yielding

$$t_s^{DF}(r) = -\frac{3}{2}\int_r^{\infty} dr'\, n(r')\frac{dv_s(r')}{dr'}. \tag{20}$$

As our final illustration in this section, we consider the simplest one-electron system in three dimensions: the hydrogen atom. The exact results can be found analytically with the ground state density,

$$n(r) = \frac{1}{\pi}e^{-2r}, \tag{21}$$

from which the wave function kinetic energy densities are obtained

$$t_s^{WFII}(r) = \frac{1}{2\pi}e^{-2r} \tag{22}$$

and

$$t_s^{WFI}(r) = \left(\frac{2}{r} - 1\right)t_s^{WFII}(r). \tag{23}$$

As the hydrogen atom has only one electron, the Kohn–Sham potential is $-1/r$, therefore, one can easily calculate the density-functional kinetic energy density,

$$t_s^{DF}(r) = \frac{3}{2\pi r}e^{-2r} - \frac{3}{\pi}\mathrm{Ei}(2r), \tag{24}$$

where the exponential integral is defined as

$$\mathrm{Ei}(x) = \int_x^{\infty} dx'\frac{e^{-x'}}{x'}. \tag{25}$$

In the Appendix we also show that in general for a particle in a three-dimensional spherically symmetric potential well,

$$t_s^{DF}(r) = \frac{3}{2}[t_s^{WFI}(r) + t_s^{WFII}(r)] - 3\int_r^{\infty} dr'\frac{1}{r'}\left(\frac{d\phi}{dr'}\right)^2. \tag{26}$$

In Fig. 4(a) we plotted the $-1/r$ potential and the ground state density of the hydrogen atom, while in Fig. 4(b) compared the three definitions of radial kinetic energy density. Once again we find the DF choice combines the virtues of the other two: it is peaked where the density is, yet never goes negative.

IV. EXACT CONDITIONS

We may prove the analogous formulas for the behavior of Coulombic systems as are done in the traditional case. Far out in the tail of a neutral atom or molecule,

$$v_s(r) \rightarrow -1/r \tag{27}$$

and

$$n(r) \rightarrow |\phi^{HOMO}(r)|^2, \quad r \rightarrow \infty, \tag{28}$$

therefore,

$$t_s^{DF}(r) = \int_r^{\infty} dr'\frac{3|\phi^{HOMO}(r')|^2}{2r'^2}, \quad r \rightarrow \infty. \tag{29}$$
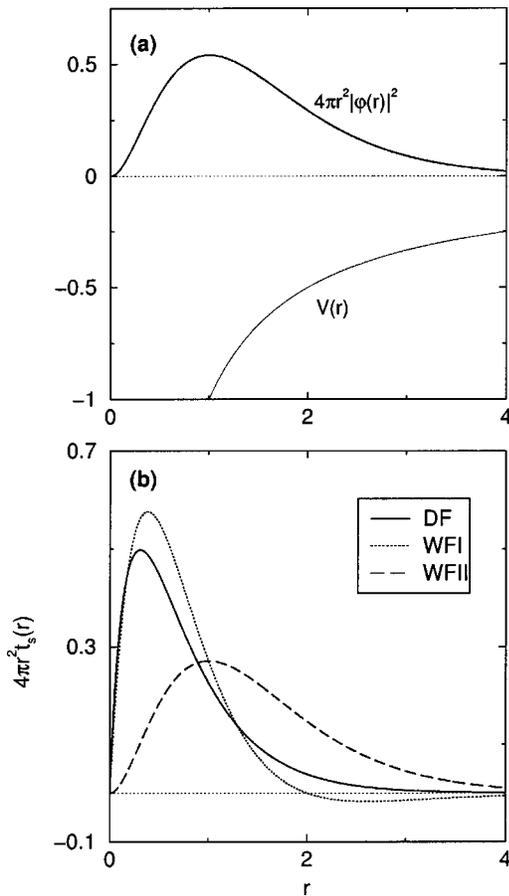
FIG. 4. Same as Fig. 1, but for the hydrogen atom.

For a neutral atom or molecule, $\phi^{\mathrm{HOMO}}(r) \approx A r^\beta e^{-\alpha r}$, $\alpha = \sqrt{2I}$, $\beta = 1/\alpha - 1$ with I being the ionization energy, yielding

$$t_s^{\mathrm{DF}}(r) = \frac{3}{2} A^2 \frac{e^{-2\alpha r}}{2\alpha} r^\gamma \left\{ 1 + \frac{\gamma}{2\alpha r} + \frac{\gamma(\gamma-1)}{(2\alpha r)^2} \right.$$
$$\left. + \frac{\gamma(\gamma-1)(\gamma-2)}{(2\alpha r)^3} + \cdots \right\}, \quad r \to \infty \text{ and } \beta \leq 1,$$
(30)

where $\gamma = 2(\beta - 1)$.

On the other hand, near a nucleus the KS potential is dominated by the external contribution, $-Z/r$, while the density becomes $n(r) = n(0)(1 - 2Zr + \cdots)$ via Kato's cusp condition.[28] This yields

$$t_s^{\mathrm{DF}}(r) = 3n(0)Z\left(\frac{1}{2r} + Z \log(r) + \cdots \right), \quad r \to 0. \quad (31)$$

The singularity at the origin is shared by WFI; in Fig. 4(b) this is damped by $4\pi r^2$.

At the other extreme is the uniform gas, the paradigm for solid state systems. Our specific choice of density-functional $t_s^{\mathrm{DF}}(\mathbf{r})$ was made to recover the usual formula for the uniform gas[29,30]

$$t_s^{\mathrm{DF}} = A_s n^{5/3}, \quad A_s = \frac{3}{10}(3\pi^2)^{2/3}. \quad (32)$$

This ensures the near-sightedness demonstrated in Fig. 2.

V. TESTING APPROXIMATIONS

So far, we have discussed only exact properties of our new DF definition for a kinetic energy density. For the rest of the paper, we use it to analyze the performance of several common approximations to the kinetic energy functional. To do this, we use the output of any standard Kohn–Sham calculation. For the particular cases studied here, namely atoms, we use the fully numerical OEP code of Engel[31] to solve the KS equations with exact exchange and no correlation, but we could be equally solving within the local (spin) density approximation. At the self-consistent solution, the KS potential is the exact KS potential for the self-consistent density (even though that is *not* the exact density for the original physical problem). Thus we can construct the exact $t_s^{\mathrm{DF}}(\mathbf{r})$ for that density via Eq. (4).

To construct an approximate $t_s^{\mathrm{DF}}(\mathbf{r})$, we begin by functionally differentiating the approximation for $T_s[n]$, to yield the corresponding approximate $v_s[n](\mathbf{r})$. We then evaluate this on the KS density mentioned above, and solve Eq. (9) for the corresponding $t_s^{\mathrm{DF}}[n](\mathbf{r})$. This typically leads to an energy density that differs from the traditional choice for the given approximation.

VI. CONVERGENCE OF GRADIENT EXPANSION FOR ATOMS

In the extreme of a uniform or slowly-varying electron gas, the gradient expansion for the first-order density matrix has been calculated in a semiclassical expansion up to sixth-order.[3,19] The traditional energy density in terms of the first-order density matrix is given up to sixth-order. The lowest order is the Thomas–Fermi functional,[29,30] which becomes exact as the number of electrons $N \to \infty$ in any fixed potential. The next order yields $\frac{1}{9}$ of the von Weizsäcker correction; the fourth-order[32] and the sixth-order terms[33] have also been determined explicitly. Unfortunately for atoms and molecules, finding better accuracy for the kinetic energy functional through gradient corrections ends at the fourth-order because the sixth-order gradient correction for atoms is known to diverge.

Because our construction was designed to recover the usual energy density for a uniform gas, the density-functional kinetic energy density for the TF approximation is simply the conventional one, i.e., $A_s n^{5/3}(\mathbf{r})$ with no additional terms integrating to zero. However, this is not true for any higher-order terms. In Fig. 5, one can easily see the poor behavior of the gradient expansion as higher-order correction terms are included. The addition of the second-order correction generally improved the energy density. But the fourth-order correction does little, except to add an unphysical singularity near the nucleus and make the energy density diverge at large r.
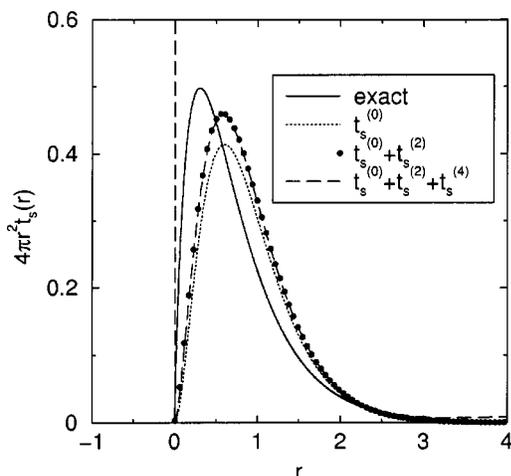
FIG. 5. Gradient expansion and exact density-functional kinetic energy densities (radial) for the hydrogen atom. The vertical line at the origin represents a δ-function contribution from the fourth-order correction term.

FIG. 6. Radial kinetic energy densities of the Be atom: solid line is the exact DF kinetic energy density, dashed line is the von Weizsäcker approximation to that energy density.

We conclude that our new methodology clearly demonstrates that, for real finite systems, the second-order gradient correction improves the energy density of the zeroth-order, but that even fourth-order terms worsen it.

VII. ANALYSIS OF THE VON WEIZSÄCKER APPROXIMATION

For two unpolarized electrons, there is only one relevant orbital, $\phi(\mathbf{r}) = \sqrt{n(\mathbf{r})/2}$, yielding in Eq. (3),

$$t_s^{\mathrm{VW}}(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})} \tag{33}$$

whose integral is the von Weizsäcker functional.[34] This functional is well-known to be exact in the tail of any Coulombic system, because the density matrix is dominated by the HOMO, whose decay is least rapid. In the traditional approach, the von Weizsäcker approximation also becomes exact as $r \rightarrow 0$, because by inserting the nuclear cusp condition $n(r \rightarrow 0) = n(0)(1 - 2Zr) + O(r^2)$ into the von Weizsäcker functional, it is readily verified that $t_s^{\mathrm{VW}}(\mathbf{r})$ satisfies the exact cusp condition,[3]

$$t_s(r \rightarrow 0) = \tfrac{1}{2}Z^2 n(0). \tag{34}$$

Applying our methodology, the DF energy density for T_s^{VW} is defined by

$$\nabla t_s^{\mathrm{VW,DF}}(\mathbf{r}) = -\frac{D}{16} n(\mathbf{r}) \nabla \left[\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^2} - \frac{2\nabla^2 n(\mathbf{r})}{n(\mathbf{r})} \right]. \tag{35}$$

Note how it depends on much higher gradients than the traditional choices. Equation (29) shows that $t_s^{\mathrm{VW,DF}}(\mathbf{r})$ is also exact in the von Weizsäcker approximation at large r. Since the derivation of Eq. (31) does not depend on the number of electrons, the von Weizsäcker approximation becomes exact near a nucleus as well. This behavior is clearly illustrated in Fig. 6 for the Be atom. As $r \rightarrow 0$ and as $r \rightarrow \infty$, $t_s^{\mathrm{VW,DF}}(\mathbf{r})/t_s^{\mathrm{DF}}(\mathbf{r}) \rightarrow 1$, with deviations only occurring in the intershell region near $r = 1$.

We can go further and explore the differences between the exact and von Weizsäcker density-functional kinetic energy densities in terms of the orbitals. Consider the Schrödinger equation for the Bose orbital[35,36] $\varphi(\mathbf{r})$ of an N particle system by defining $\varphi(\mathbf{r}) = \sqrt{n(\mathbf{r})/N}$ such that $\int d^3 r |\varphi(\mathbf{r})|^2 = 1$,

$$\{-\tfrac{1}{2}\nabla^2 + v_{\mathrm{VW}}(\mathbf{r})\}\varphi(\mathbf{r}) = \epsilon_N \varphi(\mathbf{r}), \tag{36}$$

where $v_{\mathrm{VW}}(\mathbf{r})$ is the von Weizsäcker potential and ϵ_N is the eigenvalue of the HOMO. Rewrite the Kohn–Sham orbitals using the Bose orbital by introducing the orbital fractions $\eta_i(\mathbf{r})$,

$$\phi_i(\mathbf{r}) = \eta_i(\mathbf{r})\varphi(\mathbf{r}), \tag{37}$$

where the orbital fractions satisfy the sum rule $\Sigma_{i=1}^N |\eta_i(\mathbf{r})|^2 = N$ and $|\eta_i(\mathbf{r})|^2$ represents the fraction of density in the ith orbital. If $|\eta_i(\mathbf{r})|$ is close to unity for a single i, it is an isoorbital region. In Fig. 7 we show the Kohn–Sham orbitals and their corresponding orbital fractions for the Be atom. Only near $r = 1$ is there much change in any $\eta_i(\mathbf{r})$.

Substituting Eq. (37) into the Kohn–Sham orbital equation leads to

$$-\tfrac{1}{2}\{\eta_i \nabla^2 \varphi + 2\nabla \eta_i \nabla \varphi + \varphi \nabla^2 \eta_i\} + v_s(\mathbf{r})\eta_i \varphi = \epsilon_i \eta_i \varphi. \tag{38}$$

Applying $\Sigma_{i=1}^N \eta_i$ on both sides and using the sum rule, one can rewrite Eq. (38) as

$$-\frac{1}{2}\nabla^2 \varphi + \frac{1}{2N} \varphi \sum_{i=1}^N |\nabla \eta_i|^2 + v_s(\mathbf{r})\varphi = \frac{1}{N} \sum_{i=1}^N \epsilon_i |\eta_i|^2 \varphi. \tag{39}$$

Comparing Eq. (36) and Eq. (39) gives the difference between the exact and von Weizsäcker potential in terms of the orbital fractions and their gradients,

$$v_s(\mathbf{r}) = v_{\mathrm{VW}}(\mathbf{r}) + v_{\mathrm{GRAD}}(\mathbf{r}) + v_{\mathrm{EIGEN}}(\mathbf{r}), \tag{40}$$

where
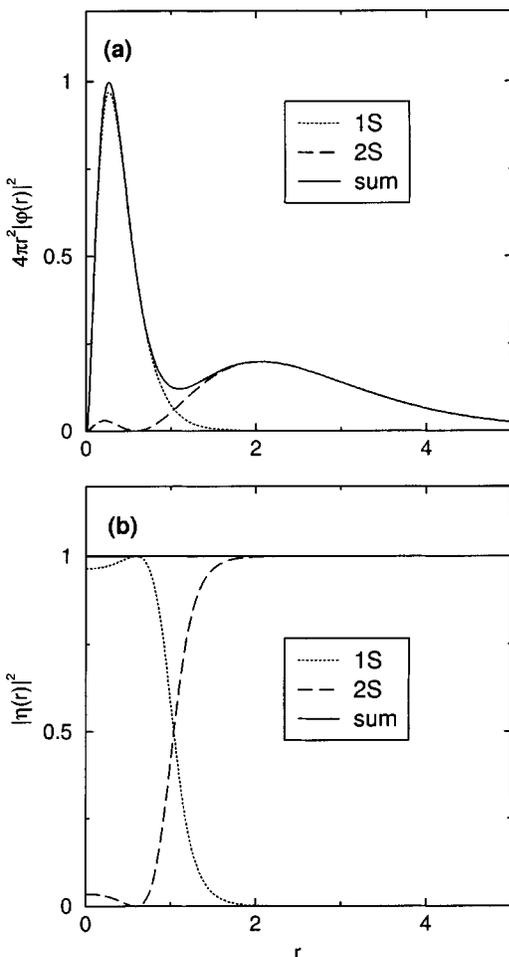
FIG. 7. Kohn–Sham orbitals of the Be atom and their corresponding orbital fractions [see Eq. (37)].

FIG. 8. (a) Kohn–Sham potential and (b) radial DF kinetic energy density contributions in the Be atom: solid line is the result of the exact Kohn–Sham calculation, dashed line is the von Weizsäcker approximation, dotted and dot–dashed lines corresponds to the gradient and eigencorrection terms, respectively, in Eq. (40).

$$v_{\mathrm{GRAD}}(\mathbf{r}) = -\frac{1}{2}\sum_{i=1}^{N} |\nabla \eta_i|^2 \qquad (41)$$

and

$$v_{\mathrm{EIGEN}}(\mathbf{r}) = -\frac{1}{N}\sum_{i=1}^{N-1} (\epsilon_N - \epsilon_i)| \eta_i|^2. \qquad (42)$$

The gradient correction term is due to the gradient of the orbital fractions. This term is small in iso-orbital regions, but produces a strong dip in intershell regions. The eigenvalue correction term is more steplike when moving from one orbital to the next. Both are always negative, so that $v_{\mathrm{VW}}(\mathbf{r}) > v_s(\mathbf{r})$,[36] but this is not true for the corresponding contribution to $t_s^{\mathrm{DF}}(\mathbf{r})$ which are found by inserting Eq. (40) into Eq. (9).

In Fig. 8 the exact Kohn–Sham calculation and the von Weizsäcker approximation results are compared. It is interesting to see that in Fig. 8(a) the von Weizsäcker potential has more features than the Kohn–Sham potential. It is also noteworthy that, near the nucleus, there is a constant contribution from $v_{\mathrm{EIGEN}}(r)$ due to the $1s$ orbital, which decreases as the dominating orbital shifts from $1s$ to $2s$. Meanwhile, $v_{\mathrm{GRAD}}(\mathbf{r})$ has most of the contribution at the intershell region near $r=1$. Although the potential correction terms appear to

have simple valley- and steplike features, Fig. 8(b) shows that the corresponding corrections in $t_s^{\mathrm{DF}}(r)$ are not necessarily as predictable. For atoms with complicated shell structures, more than three or four orbital fractions may contribute to the corrections as shown in the Ar atom case in Fig. 9, which makes it difficult to estimate the shape of the correction terms.

VIII. SUMMARY AND OUTLOOK

In this paper, we have provided a novel route to defining the energy density of the noninteracting kinetic energy density functional. Our method is not directly constructive. We have not suggested in this work any new kinetic energy density functional, and our method does not provide a systematic route toward one. It simply provides a method for studying and understanding the success and limitations of suggested approximations for $T_s[n]$.

We have compared our method to the traditional approach, on both formal and physical grounds. Since our method produces a density functional determined completely by the kinetic energy functional itself, we have been able to assess the performance of the traditional approximations to the kinetic energy pointwise in real space. We directly see the failure of the gradient expansion to converge for finite
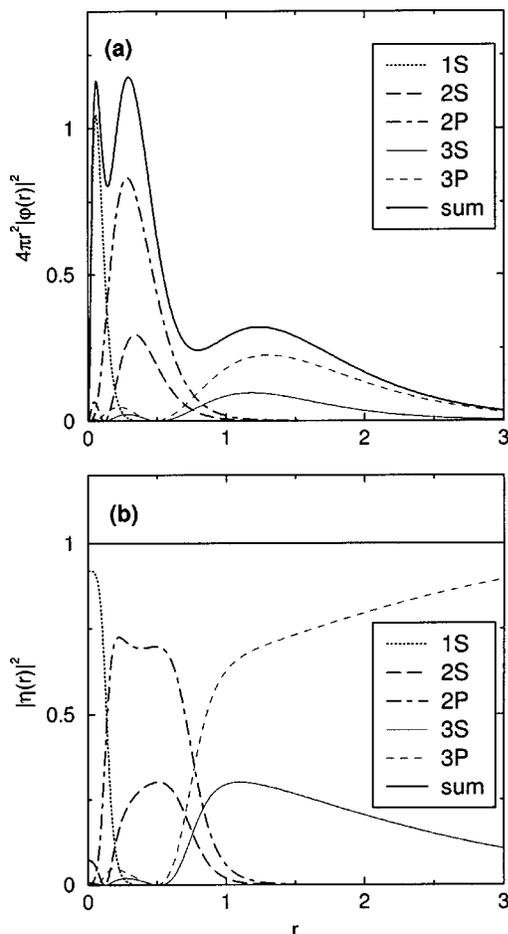
FIG. 9. Kohn–Sham orbitals of the Ar atom and their corresponding orbital fractions.

systems, and the breakdown of the von Weizsäcker approximation in regions dominated by more than one orbital. We recommend that the many recent suggestions in the literature be subjected to this test. For spherical systems, the only non-trivial requirement is calculation of the functional derivative, i.e., the Kohn–Sham potential.

We note also that one cannot simply suggest functional approximations for the density functional kinetic energy itself. One can only suggest approximations for the total kinetic energy, then functionally differentiate, and so construct the corresponding approximate $t_s^{DF}[n](\mathbf{r})$. This can look very different from the original energy density, and it is this that one is trying to make more accurate. A successful universal approximation to $T_s[n]$ will surely have an accurate $t_s^{DF}[n](\mathbf{r})$.

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APPENDIX: RELATIONSHIP BETWEEN DEFINITIONS OF KINETIC ENERGY DENSITY

In this Appendix, we construct an explicit relationship between the density functional and wave function definitions of kinetic energy. The density functional kinetic energy density $t_s^{DF}(x)$, for a particle in a one-dimensional potential well is defined by

$$\frac{dt_s^{DF}}{dx} = -\frac{1}{2} n(x) \frac{dv_s}{dx} = -\frac{1}{2} \phi^2 \frac{dv_s}{dx}. \qquad (A1)$$

The inverted Schrödinger equation is

$$v_s(x) = E + \frac{1}{2\phi} \frac{d^2 \phi}{dx^2}. \qquad (A2)$$

Differentiating and multiplying by $|\phi|^2$, yields Eq. (17) and also can be written as Eq. (18). More generally, for spherically symmetric systems, we find

$$t_s^{DF}(\mathbf{r}) = \frac{D}{2} [t_s^{WFI}(\mathbf{r}) + t_s^{WFII}(\mathbf{r})]$$

$$- \alpha \sum_{i=1}^{N} \int_r^\infty dr' \frac{1}{r'} \left(\frac{d\phi_i}{dr'} \right)^2, \qquad (A3)$$

where D is dimensionality and $\alpha = 0, 1, 3$ for the one-, two-, and three-dimensional cases.

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