Rapid Communications

A simple generalized gradient approximation for the noninteracting kinetic energy density functional

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A simple, unconventional, nonempirical, constraint-based orbital-free generalized gradient approximation (GGA) noninteracting kinetic energy density functional is presented along with illustrative applications. The innovation is adaptation of constraint-based construction to the essential properties of pseudodensities from the pseudopotentials that are essential in plane-wave-basis *ab initio* molecular dynamics. This contrasts with constraining to the qualitatively different Kato-cusp-condition densities. The single parameter in the proposed functional is calibrated by satisfying Pauli potential positivity constraints for pseudoatom densities. In static lattice tests on simple metals and semiconductors, the LKT (for the authors' initials) functional outperforms the previous best constraint-based GGA functional, VT84F [Phys. Rev. B **88**, 161108(R) (2013)], is generally superior to a recently proposed meta-GGA, is reasonably competitive with parametrized two-point functionals, and is substantially faster.

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Introduction. Hohenberg-Kohn density functional theory (DFT) [1,2] has come into prominence mainly in Kohn-Sham (KS) orbital form [3]. However, driving *ab initio* molecular dynamics (AIMD) [4–7] with KS DFT exposes a computational cost-scaling burden. The KS computational cost scales no better than N_e^3 with N_e the number of electrons or number of thermally occupied bands. Additionally there is reciprocal space sampling cost or equivalent costs from large real-space unit cells used with Γ-point sampling. In contrast, orbital-free DFT (OF-DFT) offers linear scaling with system size [8,9] for use of AIMD on arbitrarily large systems.

The long-standing barrier to widespread use of OF-DFT has been the lack of reliable nonempirical approximate kinetic energy density functionals (KEDFs). In terms of the KS orbitals φ_j, the reference, positive-definite KS kinetic energy (KE) density is

$$t_s[n] = t_s^{\text{orb}} \equiv \frac{1}{2}\sum_{j=1}^{N_e} |\nabla\varphi_j|^2, \quad (1)$$

in Hartree atomic units with $n(\mathbf{r})$ the electron number density (and unit occupation for simplicity). Two types of approximate KEDFs have been explored; semilocal (one point)

$$T_s[n] = \int d\mathbf{r}\, t_s[n(\mathbf{r}), \nabla n(\mathbf{r}), \ldots] \quad (2)$$

and two point with a nonlocal term

$$T_{NL}[n] = c_{TF}\iint d\mathbf{r}\, d\mathbf{r}' n^{\alpha}(\mathbf{r}) K[n(\mathbf{r}), n(\mathbf{r}'), \mathbf{r}, \mathbf{r}'] n^{\beta}(\mathbf{r}') \quad (3)$$

with $c_{TF} = \frac{3}{10}(3\pi^2)^{2/3}$. For a dimensionless K, $\alpha + \beta = 8/3$. Most approximate Ks are parametrized (see Refs. [9–16] for details as well as brief discussion below). In this Rapid Communication, we propose an unconventional nonempirical one-point KEDF and show that it is competitive with current two-point KEDFs, generally better than other one-point functionals, more transferable, and notably faster.

Generalized gradient approximations. The simplest one-point functionals are Thomas-Fermi [17–19]

$$T_{TF}[n] := \int d\mathbf{r}\, t_{TF}(\mathbf{r}), \quad t_{TF}(\mathbf{r}) := c_{TF} n^{5/3}(\mathbf{r}), \quad (4)$$

and von Weizsäcker [20]

$$T_W[n] := \frac{1}{8}\int d\mathbf{r}\, \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} \equiv \int d\mathbf{r}\, t_W(\mathbf{r}). \quad (5)$$

Neither is satisfactory as a general KEDF. As with approximate exchange-correlation (XC) functionals [21], the gradient expansion of the weakly inhomogeneous electron gas KE leads to consideration of generalized gradient approximations (GGAs) for T_s,

$$T_s^{\text{GGA}}[n] = \int d\mathbf{r}\, t_{TF}(\mathbf{r}) F_t[s(\mathbf{r})]. \quad (6)$$

Here $F_t(s)$ is the GGA KE enhancement factor, a function of the dimensionless reduced density gradient $s := \frac{|\nabla n|}{2nk_f} \equiv \frac{1}{2(3\pi^2)^{1/3}}\frac{|\nabla n|}{n^{4/3}}$ familiar from GGA X functionals. GGA KEDFs so constructed automatically satisfy T_s uniform scaling requirements [22]. In GGA form the von Weizsäcker KE becomes $F_W(s) = \frac{5}{3}s^2$.

From the Pauli term decomposition [8,23,24],

$$T_s[n] = T_W[n] + T_\theta[n], \quad (7)$$

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three constraints follow [25]:

$$T_\theta[n] \geqslant 0, \tag{8}$$

$$v_\theta(\mathbf{r}) \geqslant 0 \quad \forall\, \mathbf{r}, \tag{9}$$

$$v_\theta(\mathbf{r}) \geqslant \frac{t_\theta(\mathbf{r})}{n(\mathbf{r})} \quad \forall\, \mathbf{r}, \quad t_\theta := t_s^{\rm orb} - t_W, \tag{10}$$

with the Pauli potential defined as $v_\theta(\mathbf{r}) := \delta T_\theta[n]/\delta n(\mathbf{r})$ and the Pauli enhancement factor is $F_\theta(s) = F_t(s) - F_W(s)$.

To date, perhaps the best constraint-based GGA KEDF is VT84F (evaluated at $T = 0$ K, of course) [26]. It is successful in finite-T AIMD simulations [27] and is the only nonempirical GGA KEDF that yields reasonable binding in simple solids. It was constrained to satisfy Eqs. (8) and (9) for physical atom densities, i.e., those that obey the Kato cusp condition [28]. VT84F also was constrained to respect $\lim_{s\to\infty} F_\theta(s)/F_W(s) = 0$. This comes from the one-electron tail region of a many-electron atom [29] where t_θ/t_W must vanish, hence $t_s \to t_W$ [30].

In terms of the universal Hohenberg-Kohn-Levy density functional, such a physically motivated constraint is nonuniversal: the Kato cusp condition is specific to an external Coulomb potential. Such nonuniversality is rational for material and molecular property calculations. But the ubiquitous use of pseudopotential plane-wave-basis methods in AIMD simulations means that it is not the optimal nonuniversality for them. OF-DFT calculations in fact require a local pseudopotential (LPP). The OF-DFT Euler equation then implies that v_θ is closely related to the LPP $v_{\rm ext}^{\rm pseudo}$ and that v_θ is evaluated with the corresponding pseudodensity. Thus any constraint based on density characteristics should be specific to a particular type or class of pseudopotential.

Reference [31] explored some elementary consequences for constraint satisfaction (or violation) with non-Kato densities. Difficulties with simpler one-point KEDFs (linear combinations of T_{TF} and T_W) used with orbital-free projector augmented-wave pseudodensities also have been reported [32]. So far as we know, no approximate KEDF has been constructed by explicit satisfaction of the foregoing constraints, Eqs. (8) and (9), for a specified type of pseudodensities. Nor has Eq. (10) been used.

New GGA KEDF. We resolve this pseudopotential AIMD deficiency by devising a GGA KEDF constrained to satisfy Eqs. (8) and (9) for pseudodensities of a particular kind and show that in most spatial regions its v_θ satisfies Eq. (10) as well. The proposed GGA KEDF enhancement factor is

$$F_t^{\rm LKT}(s) = \frac{1}{\cosh(a\,s)} + \frac{5}{3}s^2 \tag{11}$$

with parameter $a > 0$. Figure 1 compares $F_\theta^{\rm LKT}$ with the VT84F and APBEK [33] enhancement factors. It satisfies the obvious homogeneous electron gas constraint $\lim_{s\to 0} F_{t/\theta}(s) = 1$ and obeys $0 \leqslant F_\theta^{\rm LKT} \leqslant 1$ so as to satisfy the bound conjectured by Lieb [34,35]:

$$T_s \leqslant T_{TF} + T_W. \tag{12}$$

$F_t^{\rm LKT}$ also satisfies [25,29,36] $t_\theta([n];\mathbf{r}) \geqslant 0\ \forall\, \mathbf{r}$, thus $T_\theta^{\rm LKT} \geqslant 0$.

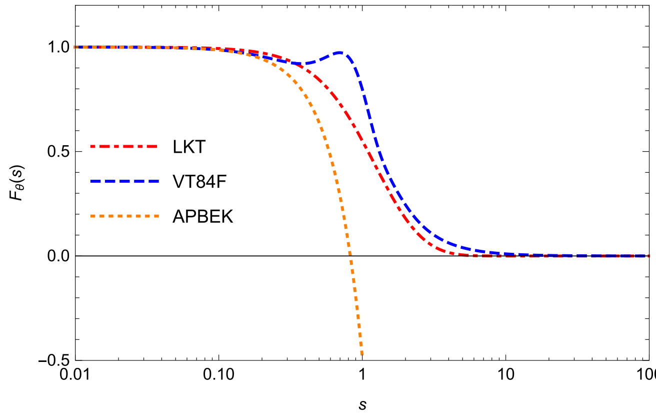

FIG. 1. Pauli enhancement factors for LKT ($a = 1.3$; red dot-dashed), VT84F (blue dashed), and APBEK (orange dotted).

The sole parameter $a = 1.3$ (which was used throughout all the subsequent calculations) was determined as follows. A set of pseudodensities was generated for the atoms H through Ne with a typical Hamann norm-conserving nonlocal pseudopotential scheme [37] using default radii in the APE code [38] and the Perdew-Zunger (PZ) XC local density approximation (LDA) [39]. Then a was found such that all the post–self-consistent-field (post-scf) Pauli potentials from those pseudodensities satisfied $v_\theta \geqslant 0\ \forall\, r$. Importantly, as long as an a value gave $v_\theta \geqslant 0$ for the H atom, positivity also was met for all the heavier atoms. For Li $a < 1.4$ is required, while for H, $a \leqslant 1.3$ is needed to get a post-scf $v_\theta \geqslant 0$. For He, the a value does not seem to matter within the range tested. While the a value is nonuniversal, we expect reasonable transferability to those other pseudopotential types for which the pseudodensities are similar, specifically those with nearly flat pseudodensities near the nucleus. The expectation is confirmed by post-scf and scf calculations for atoms.

Although the reference atom set, H-Ne, encompasses 1–8 pseudoelectrons, equally good performance for other elements is not assured. Post-scf determination of a also is distinct from self-consistent calculation, which might vitiate the supposedly constrained behavior. Atomic tests are the first line of investigating these issues. For a given pseudopotential and XC approximation, self-consistent solution of the KS equation provides the reference KS t_θ and the ingredients to construct the reference KS Pauli v_θ [see Eq. (35) in Ref. [23]. Those are the standards against which to judge t_θ and v_θ from an approximate KEDF. In anticipation of the OF-DFT calculations on periodically bounded systems reported below, we focused upon the bulk-derived LPP (BLPS) [40,41] for two atoms, Al and Li. Here we discuss Al because it was not in the a calibration. Li discussion is in the Supplemental Material [42]. [The Li pseudoatom is challenging because it is a one-orbital system ($2s^1$) for which T_θ should vanish.] Again the XC functional is PZ.

Figure 2 displays the reference t_θ/n and v_θ for the BLPS Al pseudoatom in the $3s^2\,3p^1$ configuration and the post-scf results with that pseudodensity for both VT84F and LKT. Note several features. Although VT84F was constructed to satisfy $v_\theta^{VT84F} \geqslant 0$ near a nucleus for Kato-cusped densities, it also satisfies that constraint arbitrarily close to the nucleus

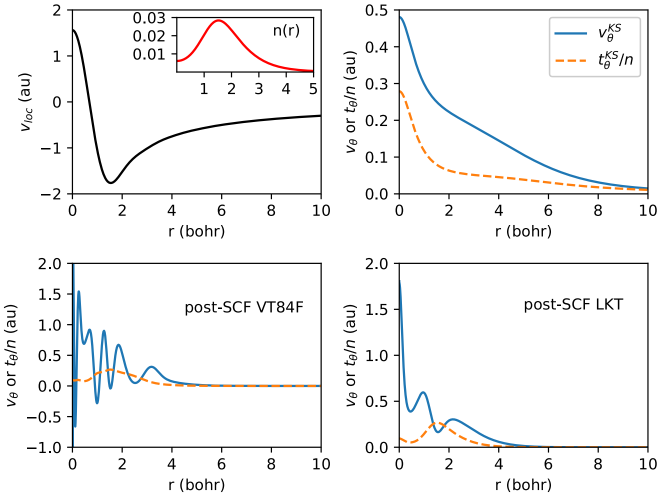

FIG. 2. Upper left: Al BLPS as a function of radial position (inset: KS pseudodensity). Upper right: reference KS v_θ and t_θ/n. Lower left: post-scf v_θ (solid) and t_θ/n for VT84F (dashed). Lower right: same for LKT.

for the cuspless pseudodensity. However, v_θ^{VT84F} with that pseudodensity becomes negative near $r = 0.1$ bohr, a clear example of the crucial nonuniversality. LKT does not have that problem. Second, v_θ^{LKT} is much smoother than v_θ^{VT84F}, although not as smooth as v_θ^{KS}. Third, except for a small region around $r = 1.8$ bohr, v_θ^{LKT} respects the Pauli potential inequality, Eq. (10), whereas v_θ^{VT84F} violates it in four regions that span much of the significant density magnitude.

Note also that, unlike some other GGA KEDFs, e.g., E00 [43], PBE2 [24], and APBEK, $v_\theta^{\text{LKT}}(r)$ decays correctly to zero asymptotically for an atom. This may be useful in the AIMD simulation of low-density regions of matter. Although v_θ^{VT84F} decays similarly, its rapid oscillations in the dominant density region might slow scf convergence rates as well as cause other difficulties.

Self-consistent OF calculations for the BLPS Al pseudoatom show that v_θ^{LKT} stays positive, although it exhibits oscillations quite similar to those seen in the post-scf case (see Fig. 3). The LKT Pauli energy per particle is far from the KS value. However, the inequality Eq. (10) is violated only around $r = 1.8$ bohr as in the post-scf case. We did not insist on strict imposition of this constraint because doing so would require $a \lessapprox 0.8$, a value that materially worsens results for solids.

Performance on solids. Validation of the LKT functional for AIMD requires accuracy tests on extended systems. We therefore did KS-DFT and OF-DFT calculations on simple metals and semiconductors. Conventional KS calculations were done with ABINIT [44] and the OF-DFT calculations used PROFESS [45] and/or PROFESS@QUANTUM-ESPRESSO [46]. Again the PZ LDA XC functional and BLPS were used. For comparison we included the Wang-Govind-Carter (WGC) [13], Huang-Carter (HC) [14], and Constantin *et al.* KGAP [16] two-point KEDFs and the one-point Constantin *et al.* SOF-CFD [47] meta-GGA (Laplacian-dependent) KEDF. Technical details and parameter values are in the Supplemental Material [42].

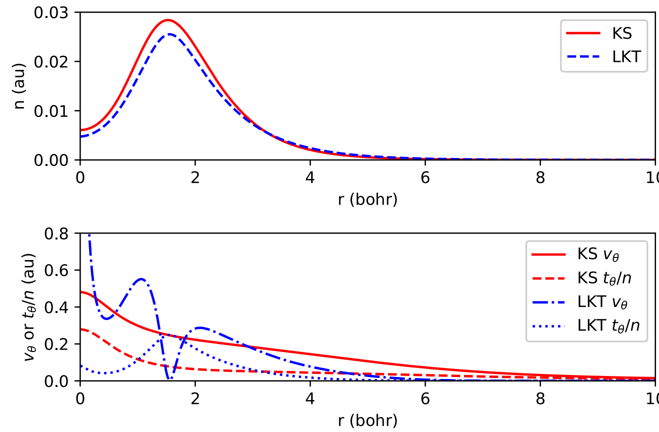

FIG. 3. Top: Al KS (solid, red) and LKT (dashed, blue) pseudodensities as a function of radial position. Bottom: KS vs LKT v_θ (solid red vs dash-dotted blue, upper pair) and similarly t_θ/n (dashed red vs dotted blue; lower pair).

Note that WGC was parametrized for main-group metals and yields poor binding curves for semiconductors, while HC was parametrized for semiconductors. KGAP is parametrized to experimental direct band gaps. Results from the one-point functionals E00, APBEK, and PBE2 are omitted because of unrealistic binding curves for the former two and computational instability problems for the latter one. KGAP comparisons are from Tables I and II of Ref. [16]. SOF-CFD values are from Table I of Ref. [47]. Equilibrium volumes, energies, and bulk moduli for other functionals were generated by varying ±5% around the equilibrium volume to obtain 11 energy-volume points, which then were fitted to the Birch-Murnaghan equation of state [48].

The metals were Li, Mg, and Al in the simple cubic, body-centered cubic, face-centered cubic, and hexagonal close-packed structures. Nine III-V semiconductors in zinc-blende structures were treated: AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, and InSb.

With KS quantities as references, Table I shows the mean absolute relative error (MARE) percentages for equilibrium volume V_0, energy E_0 per atom (for metals) or per cell (for semiconductors), and bulk moduli B_0 from WGC, HC, KGAP, VT84F, SOF-CFD, and LKT. These are calculated as

TABLE I. KEDF performance on solid metals and semiconductors: MARE of equilibrium volumes V_0, energies E_0, and bulk moduli B_0, as percentages. See text for notation.

	Metals			Semiconductors		
KEDF	V_0	E_0	B_0	V_0	E_0	B_0
WGC	0.7	0.0	2.7			
HC	5.5	0.6	12.3	1.5	0.5	4.9
KGAP[a]	4.0		5.1	3.0		16.2
VT84F	6.0	0.1	11.6	10.5	3.6	56.4
SOF-CFD[a]	5.2	0.6	8.5	3.4	0.9	10.0
LKT	4.0	0.2	7.7	2.1	2.8	4.3

[a]Note: only metals with cubic symmetry were included and PBE XC was used.

$|(Q_{\mathrm{OF}} - Q_{\mathrm{KS}})/Q_{\mathrm{KS}}| \times 100/N_{\mathrm{systems}}$, where Q is V_0, E_0, or B_0. (More detailed tabulations are in the Supplemental Material [42].) For V_0 and B_0, LKT is a significant improvement over VT84F. The V_0 and B_0 MAREs are reduced by 33% in metals. The reduction is more dramatic in the semiconductors, a factor of 5 for V_0 and 13 for B_0. The semiconductor E_0 MARE is reduced by 22% but worsened slightly from 0.1% to 0.2% for the metals. Except for performance on semiconductor E_0, it also is clear that the LKT GGA is superior to the more-complicated nonempirical SOF-CFD meta-GGA KEDF. Despite noticeable discrepancies in absolute energies for semiconductors, it is important to note that LKT OF-DFT gives the same phase ordering as does conventional KS (see Table III in the Supplemental Material).

Regarding the two-point functionals, WGC outperforms all the other functionals on the metals but is inapplicable on semiconductors; recall above [13]. Conversely, HC with averaged parameters exhibits balanced error, with all three MAREs within 5% (except B_0 for metals). KGAP does well on volumes in both classes but not B_0. Remarkably, LKT exhibits performance competitive with both HC and KGAP in prediction of equilibrium volumes for both material classes. Moreover, LKT outperforms HC for B_0 and is much more balanced than KGAP for B_0. (Comparison with the recent MGP two-point functional is of no avail, since its parametrization is tuned to match KS results for each system [15].)

For the case of AlP, we found that LKT converges for relatively smaller energy cutoff than needed with VT84F and HC. Typically, LKT also requires fewer self-consistent iterations for solution to a given tolerance than are needed by either HC or VT84F and each LKT iteration is typically about one-fifth the time of an HC iteration. Thus the one-point LKT is more useful as a broadly applicable functional than the highly parametrized two-point HC KEDF or the experimentally parametrized two-point KGAP KEDF yet is simpler, faster, and mostly better than the SOF-CFD one-point KEDF. LKT seems therefore to be currently the most promising candidate for general AIMD OF-DFT use or with small-box algorithms [49]. Although it remains to be tested, we anticipate the finite-T generalization [50] of LKT will be of value for warm dense matter simulations.

As to limitations, LKT does not yield a good value of V_0 for bcc Li with a three-electron LPP. So far as we know, all GGA KEDFs developed so far share this limitation. The extent of transferability to another distinct class of pseudopotential, along with the post-scf determination of a, remains to be examined.

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