Comment on "Single-point kinetic energy density functionals: A pointwise kinetic energy density analysis and numerical convergence investigation"

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We suggest a more nuanced view of the merit and utility of generalized gradient approximations (GGAs) for the noninteracting kinetic energy (KE) than the critique of Xia and Carter (XC) [Phys. Rev. B **91**, 045124 (2015)]. Specifically, the multiple valuedness of the Pauli term enhancement factor (denoted $G[n]$ by XC) with respect to the inhomogeneity variable s can be excluded by enforcement of a bound on the Kohn-Sham KE to achieve universality of the functional along with enforcement of proper large-s behavior. This is physically sensible in that the excluded G values occur for s values that correspond to low densities. The behavior is exacerbated by peculiarities of pseudodensities. The VT84F KE GGA, constructed with these constraints, does not have the numerical instability in our older PBE2 functional analyzed by XC.

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Part of Xia and Carter's [1] [(XC) hereafter] interesting recent investigation of single-point orbital-free kinetic energy (OFKE) density functionals involved writing the standard Kohn-Sham (KS) KE energy density as

$$\tau_s([n];\mathbf{r}) = \tau_{\mathrm{vW}}([n];\mathbf{r}) + G([n];\mathbf{r})\tau_{\mathrm{TF}}([n];\mathbf{r}), \qquad (1)$$

with $\tau_{\mathrm{vW}} = |\nabla n|^2/8n$ and $\tau_{\mathrm{TF}} = c_{\mathrm{TF}}n^{5/3}$ as the canonical von Weizsäcker [2] and Thomas-Fermi [3,4] KE densities, respectively, and $n(\mathbf{r})$ as the electron number density. This is the Pauli term decomposition; see Ref. [5] and references therein. XC's numerical exploration of $G([n];\mathbf{r})$ showed, in the example of fcc Al, that G is not a single-valued function of the reduced density gradient $s_{\mathrm{XC}} = |\nabla n|/n^{4/3}$. See XC's Fig. 6 and associated discussion. (The subscript XC distinguishes their gradient variable from the more common s variable used in our papers $s = \kappa s_{\mathrm{XC}}$ with $\kappa = 1/[2(3\pi^2)^{1/3}] = 0.161\,62$. Behavior found at large s_{XC} corresponds to intermediate s behavior. This becomes important below.) On this basis they concluded that "... it is not sensible to predict G using only s" and further that "... this multivalued character calls into question the validity of the GGA's $F(s)$." GGA is the generalized gradient approximation in which $G([n];\mathbf{r}) \approx F_\theta(s)$. Then, among various informative tests, they explored the convergence behavior (with respect to plane-wave cutoff) of the mildly empirical GGA OFKE functional PBE2 which came from our group several years ago [6].

We believe that XC's stance regarding GGAs is too harsh and that a more nuanced perspective is useful. In support of that view, we summarize here why it is both feasible and useful to deal with the double valuedness by application of physically relevant constraints to construct a GGA. In relation to that, we show that the lack of convergence with respect to plane-wave cutoff which XC found for the PBE2 is eliminated in a fully constraint-based GGA, namely, the VT84F [7].

At the outset we stipulate that no OFKE GGA can meet all the requirements derivable for the exact $G[n]$ any more

than an exchange-correlation (xc) GGA can meet all the exact requirements on it [8]. The issue is whether a useful GGA can be developed by judicious determination and use of the physically most important constraints. In that context, for simplicity of comparison with prior work, consider the behavior of G for which $x = 0$, x being the coefficient of $\nabla^2 n$ in XC's definition of τ_s, XC's Eq. (11). Begin at $s = 0$ and consider first only the lower branch of $G([n];\mathbf{r})$ as shown in XC's Fig. 6. There exists a global bound on the KS KE, conjectured by Lieb [9] and proved, at least to the rigor typical in physics, by the infinite particle limit of the inequality due to Gázquez and Robles [10], namely,

$$T_s \leqslant T_{\mathrm{vW}} + T_{\mathrm{TF}}. \qquad (2)$$

To compel an approximate functional to be *universal*, that is to obey this bound for *all* possible densities, necessitates imposition of the constraint locally $\tau_s \leqslant \tau_{\mathrm{vW}} + \tau_{\mathrm{TF}}$. This imposition corresponds to common usage of the Lieb-Oxford bound in GGA exchange functionals [11,12]. Although evidently not a necessary condition, this pointwise constraint yields a nonempirical GGA [for which $G([n];\mathbf{r}) \approx F_\theta(s)$] that automatically cuts out all of the values above unity on the lower branch of G since $F_\theta \leqslant 1$ because of the constraint.

In the case of xc GGAs, multivaluedness has been known for some time [12,13], yet there are highly successful xc GGAs. The corresponding issue for an OFKE GGA is whether anything useful is left after removing $G > 1$ by requiring $F_\theta \leqslant 1$. First, the region of the lower branch in which XC found $G([n];\mathbf{r})$ substantially in excess of unity is roughly $s_{\mathrm{XC}} > 6 \to 10$ or $s > 1$ to 1.6. But it is well documented that even many isolated systems, which have very diffuse density tails (hence, large s), have essentially zero density beyond roughly $s > 4$ and very little density for $s > 2.5$. See Fig. 6 in Ref. [12] as well as earlier work in Ref. [13]. Often the KS KE is nearly totally determined by the behavior of G over a smaller range of s. In the SiO molecule, for example, the KS KE is dominated by contributions from $0.26 \leqslant s \leqslant 1.30$ [14]. Where there are nonzero contributions to the KE density for larger values of s, what the cutoff in a proper GGA does is to approximate the lower branch of G in that region by unity, at most. (To meet other constraints, our actual GGAs

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use a smaller value [7].) The physical justification is that such contributions are comparatively small even though the lower branch of G substantially exceeds unity because n is small (hence one expects $n^{5/3}$ to be smaller yet), so a GGA underestimate of G in that region should be a satisfactory approximation. Note also that it is an exact requirement for any OFKE GGA that $\lim_{s\to\infty} \tau^{\mathrm{GGA}}(s) = \tau_{\mathrm{vW}}$. Physically this is because arbitrarily large s corresponds to density tail regions. Those are one-electron densities, hence they correspond to the von Weizsäcker KE density. Cutting off is eminently sensible therefore on grounds of both constraints.

What about the other branch of G? For small values of s on that branch, it appears that $G([n];\mathbf{r})$ is particularly large because of pseudodensity properties that are qualitatively different from physical densities. XC's Fig. 6(b) shows that G for fcc Al is largest (roughly 14) for very small s, and XC's Figs. 2 and 3 confirm that this is true for small $d = n_{\mathrm{pseudo}}/n_0$. ($n_0$ is the average density.) XC's Fig. 8 shows that small n_{pseudo} occurs at the nuclear sites. Since for pseudodensities $\tau_{\mathrm{KS}} \neq \tau_{\mathrm{vW}}$ at those sites, but τ_{TF} evaluated with that small pseudodensity is small, G from the pseudodensities is forced to be large. Such exaggerated behavior would not occur with the true all-electron density, which obeys the Kato cusp condition and has local maxima at the nuclear sites. Consequently τ_{vW} dominates in the near-nucleus region [15], and the corresponding G is much smaller than the G forced by the pseudodensity in that region. We note that the VT84F [7] was parametrized in part against the Kato condition. (As an aside, we suspect that the pseudodensity also may be problematic for GGAs as well as functionals with higher-derivative dependence because of unphysical zeros of the pseudodensity gradient along bonds. This may be a real problem for the OF density functional theory agenda since local pseudopotentials are technically very useful.)

Of course, these two diagnoses (on the lower and upper branches) of the sources of large G and how to control them do not entirely eliminate the challenge of the multivaluedness of the exact KS G. The diagnoses do help understand how a meaningful nonempirical GGA is feasible. The detail lost by exclusion is offset, at least in part, by the addition of guaranteed physical behavior via the constraints. Thus, although a GGA cannot reproduce all the exact KS OFKE functional behaviors, it can represent the most important part of G on the most important range of densities and gradients.

We turn to instability of our PBE2 GGA with respect to plane-wave cutoff. The PBE2 has been supplanted by our VT84F, a nonempirical OFKE GGA functional which obeys all of the foregoing bounding and asymptotic properties [7]. XC did not test it. We have. Figure 1 shows that the VT84F is fully stable against plane-wave cutoff. Note that this is precisely the same test as XC performed for the PBE2, including use of their prescription for the local pseudopotential. (For reference, the calculated equilibrium lattice constants in increasing order of the three cutoffs are 4.157, 4.166, and 4.164 Å.) We had noted the stability distinction of the VT84F vs the PBE2 in Ref. [16]. There the passage just below Fig. 3 reads "Our . . . PBE2 . . . [has] worse numerical convergence than VT84F because of the same wrong large-s limit." Wang *et al.* [17] had found such GGA OFKE instabilities earlier.
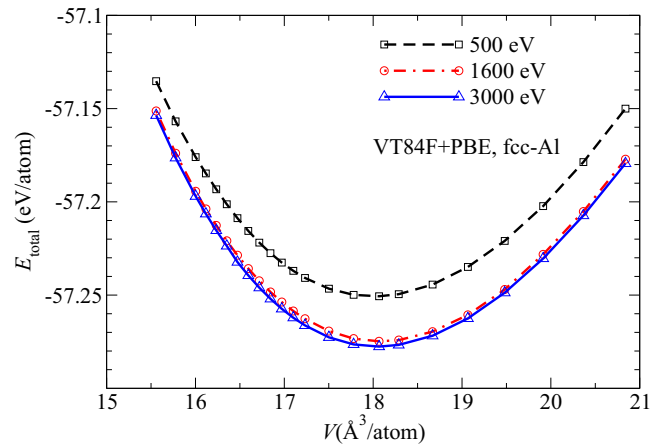

FIG. 1. (Color online) Energy vs unit-cell volume for fcc Al computed at three plane-wave cutoff energies using the VT84F OFKE functional and the PBE exchange-correlation functional.

XC also note that the near-nucleus density from the PBE2 is peculiar. This is almost inevitable with any properly positive-definite GGA [14]. A singularity at the origin in the Pauli potential causes the artifact. It is on a very small scale. Only a specially selected pseudopotential construction can remove it. It is removed if the pseudodensity is completely flat at nuclear sites, equivalent to $s = 0$ there [18]. One example of removing the singularity is the GGA Pauli potential for the model pseudodensity in Ref. [17] with a particular parameter choice.

An essential difference between standard GGA KE functionals (e.g., P92 [19] and E00 [20] tested by XC) and our GGAs (VT84F and PBE2) is that the former do not predict binding in small molecules at all, whereas the latter do predict semiquantitatively correct binding in those molecules and simple solids [6,14,21]. This categorical distinction and the broad utility of these GGAs are suggestive of having achieved a universal functional (although certainly not a proof). XC had a different goal, namely, functionals which represent well the behavior of a class of periodically bounded materials. In fact, their fitted vWGTF1 functional obeys the global Lieb-Gázquez-Robles bound [22] for such materials but not for free molecules with a fixed parameter ($\rho_0 = \rho_{\mathrm{max}}$ in XC's notation). This nonuniversality can be viewed as a consequence of the different emphasis of their work and ours.

Although there are distinct limitations on what can be expected of a GGA OFKE functional, the multivaluedness of G is not a prohibitive barrier to a useful nonempirical GGA. The current situation is substantially better than the limitations of the mildly empirical PBE2 functional (which is almost 10 years old) analyzed by XC. In particular, both the empirical parametrization and the numerical convergence limitations of the PBE2 have been eliminated in the entirely constraint-based VT84F functional [7].

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