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**Comment on “Single-point kinetic energy density functionals:  
a pointwise kinetic energy density analysis and numerical convergence investigation”  
Phys. Rev. B 91, 045124 (2015)**

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We suggest a more nuanced view of the merit and utility of generalized gradient approximations (GGAs) for the non-interacting kinetic energy than the critique of Xia and Carter (X-C). Specifically, the multiple-valuedness of the Pauli term enhancement factor (denoted  $G[n]$  by X-C), 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 pseudo-densities. The VT84F GGA, constructed with these constraints, does not have the numerical instability in our older PBE2 functional analyzed by X-C.

Part of Xia and Carter’s<sup>1</sup> (X-C 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

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

with  $\tau_{vW} = |\nabla n|^2/8n$  and  $\tau_{TF} = c_{TF}n^{5/3}$ , the canonical von Weizsäcker<sup>2</sup> and Thomas-Fermi<sup>3,4</sup> KE densities respectively and  $n(\mathbf{r})$  the electron number density. This is the Pauli term decomposition; see Ref. 5 and references therein. X-C’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  $s_{X-C} = |\nabla n|/n^{4/3}$ . See X-C’s Fig. 6 and associated discussion. (The subscript “X-C” distinguishes their gradient variable from the more common  $s$  variable used in our papers,  $s = \kappa s_{X-C}$ , with  $\kappa = 1/[2(3\pi^2)^{1/3}] = 0.16162$ . Behavior found at large  $s_{X-C}$  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 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<sup>6</sup>.

We believe that X-C’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 X-C found for PBE2 is eliminated in a fully constraint-based GGA, namely VT84F<sup>7</sup>.

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<sup>8</sup>. 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 X-C’s definition of  $\tau_s$ , X-C Eq. (11). Begin at  $s = 0$  and consider first only the lower branch of  $G([n]; \mathbf{r})$  as shown in X-C Fig. 6. There exists a global bound on the KS KE, conjectured by Lieb<sup>9</sup> and proved, at least to the rigor typical in physics, by the infinite particle limit of the inequality due to Gázquez and Robles<sup>10</sup>, namely

$$T_s \leq T_{vW} + T_{TF}. \quad (2)$$

To compel an approximate functional to be *universal*, that is to obey this bound for *all* possible densities, necessitates imposition of the constraint locally,  $\tau_s \leq \tau_{vW} + \tau_{TF}$ . This imposition corresponds to common usage of the Lieb-Oxford bound in GGA exchange functionals<sup>11,12</sup>. Though evidently not a necessary condition, this point-wise constraint yields a non-empirical 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  $F_\theta \leq 1$  because of the constraint.

In the case of xc GGAs, multivaluedness has been known for some time<sup>12,13</sup>, 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  $F_\theta \leq 1$ . First, the region of the lower branch in which X-C found  $G([n]; \mathbf{r})$  substantially in excess of unity is roughly  $s_{X-C} > 6 \rightarrow 10$  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  $0.26 \leq s \leq 1.30$ <sup>17</sup>. Where there are non-zero 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 use a smaller value<sup>7</sup>.) 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  $\lim_{s \rightarrow \infty} \tau^{GGA}(s) = \tau_{vW}$ . Physically this is because arbitrarily large  $s$  corresponds to density tail regions. Those are 1-electron densities, hence 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 pseudo-density properties that are qualitatively different from physical densities. X-C Fig. 6(b) shows that  $G$  for fcc Al is largest (roughly 14) for very small  $s$ , and X-C Figs. 2 and 3 confirm that this is true for small  $d = n_{pseudo}/n_0$ . X-C Fig. 8 shows that small  $n_{pseudo}$  occurs at the nuclear sites. Since for pseudo-densities  $\tau_{KS} \neq \tau_{vW}$  at those sites, but  $\tau_{TF}$  evaluated with that small pseudo-density is small,  $G$  from the pseudo-densities 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  $\tau_{vW}$  dominates in the near-nucleus region<sup>14</sup> and the corresponding  $G$  is much smaller than the  $G$  forced by the pseudo-density in that region. We note that VT84F<sup>7</sup> was parameterized in part against the Kato condition. (As an aside, we suspect that the pseudo-density also may be problematic for GGAs as well as functionals with higher-derivative dependence because of unphysical zeros of the pseudo-density gradient along bonds. This may be a real problem for the OFDFT agenda, since local pseudo-potentials 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 non-empirical 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, while 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. PBE2 has been supplanted by our VT84F, a non-empirical OFKE GGA functional which obeys all of the foregoing bounding and asymptotic properties<sup>7</sup>. X-C did not test it. We have. Fig. 1 shows that VT84F is fully stable against plane-wave cut-off. Note that this is precisely the same test as X-C did for PBE2, including use of their prescription for the local pseudopotential. (For reference, the calculated equi-

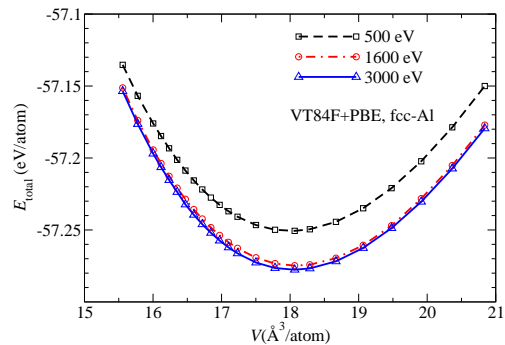


FIG. 1: Energy vs. unit-cell volume for fcc Al computed at three plane-wave cut-off energies using the VT84F OFKE functional and PBE exchange-correlation functional.

librium lattice constants in increasing order of the three cutoffs are 4.157 Å, 4.166 Å, 4.164 Å.) We had noted the stability distinction of VT84F versus PBE2 in Ref. 15. 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, Stott, and von Barth<sup>16</sup> had found such GGA OFKE instabilities earlier.

X-C also note that the near-nucleus density from PBE2 is peculiar. This is almost inevitable with any properly positive-definite GGA<sup>17</sup>. 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 pseudo-density is completely flat at nuclear sites, equivalent to  $s = 0$  there<sup>19</sup>. One example of removing the singularity is the GGA Pauli potential for the model pseudo-density in Ref. 16 with a particular parameter choice.

An essential difference between standard GGA KE functionals (e.g. P92<sup>20</sup> and E00<sup>21</sup> tested by X-C) and our GGAs (VT84F, PBE2) is that the former do not predict binding in small molecules at all, while the latter do predict semi-quantitatively correct binding in those molecules and simple solids<sup>6,17,18</sup>. This categorical distinction and the broad utility of these GGAs is suggestive of having achieved a universal functional (though certainly not a proof). X-C had a different goal, namely functionals which represent well the behavior of a class of periodically bounded materials. In fact, their fitted vWTF1 functional obeys the global Lieb-Gázquez-Robles bound<sup>22</sup> for such materials, but not for free molecules with a fixed parameter ( $\rho_0 = \rho_{max}$  in X-C notation). This non-universality can be viewed as a consequence of the different emphasis of their work and ours.

While 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, non-empirical GGA. The current situation is substantially better than the limitations of the mildly empirical PBE2 functional (which is almost 10 years old) analyzed by X-C. In particular, both the empirical parameterization and the numerical convergence limitations of PBE2 have

been eliminated in the entirely constraint-based VT84F functional<sup>7</sup>.

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