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

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# Reply to 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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**Abstract**

We find that the multi-valued character of the $G$ factor as a function of the reduced gradient ($s$) still exists after accounting for pseudopotential artifacts and the kinetic energy global upper bound. We also find that the VT84F functional indeed exhibits stable convergence and more reasonable results for self-consistent bulk properties compared to other generalized gradient approximation (GGA) kinetic energy density functionals (KEDFs) that we tested earlier. However, VT84F generally yields overestimated equilibrium volumes, which may result from its inability (as with all GGAs) to reproduce the $G$-$s$ multi-valued character. The analogous failure to predict the multi-valued character of $G$ as a function of the reduced density ($d$) is also likely to be responsible for the inaccuracy of our vWGTF functionals reported earlier. Our multi-valuedness analysis therefore does not impugn any particular GGA KEDF. Instead, it merely confirms the importance of pointwise analysis for improving KEDFs, by emphasizing the need to resolve the multi-valuedness of $G$ with respect to various density variables.

In S. B. Trickey, V. V. Karasiev, and D. Chakraborty's interesting comment[1] on our previous paper,[2] two major issues are discussed: the multi-valuedness of the $G$ factor versus the reduced gradient $(s)^2$ and the numerical stability of the VT84F[3] kinetic energy density functional (KEDF). On one hand, we still believe in the existence and significance of $G$-$s$ multi-valuedness, despite possible pseudopotential artifacts and the global kinetic energy upper bound.[1] On the other hand, we are pleased to see the improved convergence of the VT84F KEDF and further perform a series of tests on it, as presented below.

First, we agree that using pseudopotentials may introduce artifacts in the $G$ distribution, especially around nuclei. The electron pseudodensities are generally very small around nuclei, which then lead to large $G$ values (see Fig. 2 in Ref. 2). However, even after removing the outer branch in $G$ versus $s$, the multi-valuedness still exists (e.g., see Figure 1, which is based on the data points in grey ($x$=0) in Fig. 6 in Ref. 2). It will be interesting to do a similar analysis in all-electron Kohn-Sham (KS) density functional theory (DFT), where we suspect the multi-valuedness also exists because any artifacts due to pseudopotentials will be confined to near-nucleus regions. It is possible that in all-electron cases, the multi-valuedness of $G$ versus $s$ will be lessened but it awaits more studies and data to confirm.

Second, we agree it is important to consider exact requirements when constructing KEDFs. However, we disagree that the data points with $G$>1 can be cut out or ignored due to the kinetic energy upper bound[4,5] of the Thomas-Fermi[6-8] plus von Weizsäcker KEDF.[9] As also mentioned in Ref. 1, the upper bound only applies to the total kinetic energy, while the corresponding pointwise upper bound for local kinetic energy density is only sufficient but

not necessary. In the Appendix, we provide a proof for the vWGTF1 KEDF proposed in our original paper,[2] which always satisfies the global upper bound but not the pointwise one, for any periodic or finite-volume system. The proof does not hold for isolated systems with infinite volumes where the average density is ill-defined. However, the vWGTF1 KEDF (simply using $\rho_0$ rather than $\rho_{max}$ in the scale function) still can be used for such systems in any practical calculations in which periodic or finite-volume unit cells are used as an approximation. The KEDF would be by no means accurate or physical in these calculations, but it still possesses the properties described above according to the proof. There are very possibly other KEDFs that can meet this criterion more rigorously for all systems. The exact KEDF (in KSDFT) should be one of them, at least in pseudopotential calculations as shown in Ref. 2. Furthermore, we pointed out in Ref. 2 that $G$ versus $d$ (the reduced electron density) has one desirable feature in our analysis: $G(d=1)=1$ in the materials we studied. For many regions where the densities are smaller than the average density, the $G$ value from KSDFT is larger than 1. Assuming the pseudopotentials only introduce differences near nuclei, it is therefore very possible that such $G$ values will also be present in all-electron cases.

Finally, we are glad to learn that the VT84F functional can exhibit better numerical convergence. It is unfortunate that the VT84F KEDF was not among the many tested in our original paper,[2] simply because there are too many KEDFs in the literature for all to be tested. After communication with S. B. Trickey, we implemented the VT84F KEDF in PROFESS[10] and confirmed its convergence. We then performed tests similar to those in Ref. 2 for VT84F (see Tables I-IV). Encouragingly, the non-self-consistent errors are significantly smaller than other generalized gradient approximation (GGA) KEDFs,[2] especially for Li phases. However,

the errors for the alloy and vacancy structures are slightly larger. In self-consistent calculations, the VT84F KEDF also provides reasonable results for bulk moduli and phase ordering energies, while the equilibrium volumes are overestimated, especially for Al, Mg, and their alloys, with errors around 10%. Overall, this GGA KEDF not only provides stable convergence but also offers much improved bulk properties compared to other GGA KEDFs. Although the results are not as good as the vWGTF and Wang-Govind-Carter (WGC) KEDFs,[2] the accuracy is rather impressive considering that it was not specifically designed for the systems tested.

To conclude, we show that the $G$ versus $s$ multi-valuedness still exists after considering pseudopotential artifacts and the kinetic energy upper bound. All-electron calculations may possibly share this multi-valuedness feature, which awaits future research to confirm. Such multi-valuedness was discussed previously in GGA exchange-correlation (XC) functional studies.[11-12] However, the accuracy requirement of XC functionals is much lower since the XC energy is smaller than the kinetic energy by orders of magnitude. For example, the local density approximation XC functionals work surprisingly well for many systems, while the counterpart in KEDFs (namely Thomas-Fermi) is of little practical use. Thus, the multi-valued character of $G$ is likely to be more important in KEDF development.

The multi-valuedness analysis does not aim to undervalue or discourage GGA KEDF development. More GGA KEDFs are being developed with improved stability and accuracy, such as the VT84F KEDF. Nevertheless, the VT84F KEDF still features considerable defects (overestimated equilibrium volumes) when describing bulk metals, which might be due to its failure to capture the multi-valuedness. Similarly, our vWGTF models[2] also fail to reproduce

the *G* versus *d* (the reduced density $\rho/\rho_0$) branching structure in alloys and defective structures. They thus yield unsatisfying results for such systems. By contrast, the WGC KEDF generally gives accurate results for pointwise *G* distributions, including remarkably the multivaluedness, which may be the underlying reason for its outstanding accuracy for main group metals. As a result, we, in our original paper,[2] did not intend to undervalue existing or future GGA KEDFs. Instead, we merely aim to emphasize the significance of analyzing pointwise distributions, including *G*, *s* as well as other density variables like *d* and the Laplacian of the density. Employing more density variables other than *s* may help to resolve the multi-valuedness problem and improve the accuracy of KEDFs.

## Acknowledgment

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Table I. The VT84F KEDF non-self-consistent total kinetic energy errors and mean absolute errors (MAEs) (in %) with respect to KSDFT benchmarks for bulk Al, Mg, and Li in the fcc, bcc, hcp, and sc structures at KSDFT equilibrium volumes. See numerical details in Ref. 2.

| KEDF | fcc Al | hcp Al | bcc Al | sc Al | hcp Mg | fcc Mg | bcc Mg | sc Mg | bcc Li | fcc Li | hcp Li | sc Li | MAE |
|------|--------|--------|--------|-------|--------|--------|--------|-------|--------|--------|--------|-------|-----|
| VT84F | 0.51 | 0.25 | -0.09 | 2.05 | 1.70 | 1.37 | 1.49 | -0.19 | -0.10 | -0.11 | -0.12 | -0.08 | 0.56 |

Table II. The VT84F KEDF non-self-consistent total kinetic energy errors and MAEs (in %) with respect to KSDFT benchmarks for fcc Al, hcp Mg, and bcc Li vacancy structures, as well as $Al_3Mg$, at KSDFT geometries.

| KEDF | $Al_3Mg$ | Al Vac | Mg Vac | Li Vac | MAE |
|------|---------|--------|--------|--------|-----|
| VT84F | 1.20 | 1.05 | 2.07 | -0.01 | 1.08 |

Table III. Equilibrium volumes ($V_0$), bulk moduli ($B$), and equilibrium total energies ($E_{min}$) for various Al, Mg, and Li phases calculated by self-consistent KSDFT and OFDFT-VT84F. See numerical details in Ref. 2.

| Al | | fcc | hcp | bcc | sc |
|----|----|-----|-----|-----|-----|
| $V_0$ (Å$^3$) | KSDFT | 16.575 | 16.733 | 17.025 | 19.937 |
| | VT84F | 18.101 | 18.116 | 18.163 | 19.638 |
| $B$ (GPa) | KSDFT | 77 | 75 | 70 | 57 |
| | VT84F | 90 | 90 | 90 | 81 |
| $E_{min}$ (eV/atom) | KSDFT | -57.202 | 0.024 | 0.081 | 0.334 |
| | VT84F | -57.273 | -0.001 | 0.022 | 0.574 |
| Mg | | fcc | hcp | bcc | sc |
| $V_0$ (Å$^3$) | KSDFT | 22.899 | 23.073 | 22.839 | 27.107 |
| | VT84F | 25.425 | 25.385 | 25.300 | 27.432 |
| $B$ (GPa) | KSDFT | 38 | 38 | 38 | 24 |
| | VT84F | 33 | 34 | 33 | 28 |
| $E_{min}$ (eV/atom) | KSDFT | -24.246 | 0.013 | 0.029 | 0.408 |
| | VT84F | -24.204 | -0.001 | 0.009 | 0.332 |
| Li | | fcc | hcp | bcc | sc |
| $V_0$ (Å$^3$) | KSDFT | 19.397 | 19.308 | 19.324 | 19.932 |
| | VT84F | 19.417 | 19.304 | 19.331 | 20.229 |
| $B$ (GPa) | KSDFT | 16 | 17 | 17 | 17 |
| | VT84F | 16 | 16 | 16 | 16 |
| $E_{min}$ (eV/atom) | KSDFT | -7.550 | -0.001 | 0.000 | 0.136 |
| | VT84F | -7.553 | -0.002 | -0.001 | 0.129 |

Table IV. Equilibrium volume ($V_0$), bulk modulus ($B$), and alloy formation energy ($E_{\text{fm}}$) for Al$_3$Mg calculated by

self-consistent KSDFT and OFDFT-VT84F.

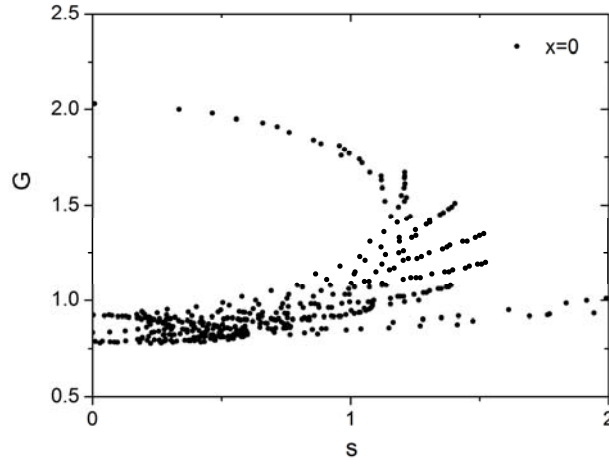|  | $B$ (GPa) | $V_0$ (Å$^3$) | $E_{\text{fm}}$ (eV/atom) |
|---|---|---|---|
| KSDFT | 63 | 71.828 | -0.019 |
| OFDFT-VT84F | 78 | 77.073 | 0.083 |



Figure 1. KSDFT $G$ versus $s$ with $x$=0 for fcc Al (zoomed in for Fig. 6 in Ref. 2).

Appendix

*Proposition*: Consider the vWGTF1 KEDF[2]

$$T_{\text{vWGTF1}} = T_{\text{vW}} + \int G \cdot \tau_{\text{TF}} d\mathbf{r} = T_{\text{vW}} + C_{\text{TF}} \int a\left(\frac{\rho}{\rho_0}\right)^b \cdot \rho^{5/3} d\mathbf{r}, (1)$$

where $a = 0.9892$ and $b = -1.2994$. Although the local pointwise $G$ factor can be any positive value (including those greater than 1), the total kinetic energy always satisfies the TFvW upper bound, namely

$$T_{\text{vWGTF1}}[\rho] \leq T_{\text{vW}}[\rho] + T_{\text{TF}}[\rho] \text{ for } \forall \rho , (2)$$

for all periodic or finite-volume systems.

Proof: to show Equation (2) is true, we rewrite the Equation (1) as

$$T_{\text{vWGTF1}} = T_{\text{vW}} + T_{\text{TF}} + C_{\text{TF}} \int \left[ a\left(\frac{\rho}{\rho_0}\right)^b \cdot \rho^{5/3} - \rho^{5/3} \right] d\mathbf{r} . (3)$$

We only need to show

$$\int \left[ a\left(\frac{\rho}{\rho_0}\right)^b \cdot \rho^{5/3} - \rho^{5/3} \right] d\mathbf{r} \leq 0 \text{ for } \forall \rho , (4)$$

or equivalently

$$\int \rho^{5/3} d\mathbf{r} - \int a\rho_0^{-b} \rho^{5/3+b} d\mathbf{r} = \int \rho^{5/3} d\mathbf{r} - \int a\left(\frac{\int \rho d\mathbf{r}}{V}\right)^{-b} \rho^{5/3+b} d\mathbf{r} \geq 0 , (5)$$

where $V$ is the unit cell volume. Since $-b=1.2994>1$, the function $f(x)=x^{-b}$ is convex. We thus have

$$\left(\frac{\int \rho d\mathbf{r}}{V}\right)^{-b} \leq \frac{\int \rho^{-b} d\mathbf{r}}{V} . (6)$$

Along with the fact that $a<1$ and that all densities are always nonnegative, we have

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$$\int \rho^{5/3}d\mathbf{r} - \int a\left(\frac{\int \rho d\mathbf{r}}{V}\right)^{-b}\rho^{5/3+b}d\mathbf{r} \geq \int \rho^{5/3}d\mathbf{r} - \int a\frac{\int \rho^{-b}d\mathbf{r}}{V}\rho^{5/3+b}d\mathbf{r}$$

$$\geq \int \rho^{5/3}d\mathbf{r} - \frac{1}{V}\int \rho^{5/3+b}d\mathbf{r}\int \rho^{-b}d\mathbf{r} = \frac{1}{V}\int\int \rho(\mathbf{r})^{5/3}d\mathbf{r}d\mathbf{r'} - \frac{1}{V}\int\int \rho(\mathbf{r})^{-b}\rho(\mathbf{r'})^{5/3+b}d\mathbf{r}d\mathbf{r'} \qquad . (7)$$

$$= \frac{1}{2V}\left[\int\int \rho(\mathbf{r})^{5/3}d\mathbf{r}d\mathbf{r'} + \int\int \rho(\mathbf{r'})^{5/3}d\mathbf{r}d\mathbf{r'} - \int\int \rho(\mathbf{r})^{-b}\rho(\mathbf{r'})^{5/3+b}d\mathbf{r}d\mathbf{r'} - \int\int \rho(\mathbf{r'})^{-b}\rho(\mathbf{r})^{5/3+b}d\mathbf{r}d\mathbf{r'}\right]$$

$$= \frac{1}{2V}\int\int \left[\rho(\mathbf{r})^{5/3+b} - \rho(\mathbf{r'})^{5/3+b}\right]\left[\rho(\mathbf{r})^{-b} - \rho(\mathbf{r'})^{-b}\right]d\mathbf{r}d\mathbf{r'}$$

Since 5/3+b>0 and –b>0, $\left[\rho(\mathbf{r})^{5/3+b} - \rho(\mathbf{r'})^{5/3+b}\right]$ and $\left[\rho(\mathbf{r})^{-b} - \rho(\mathbf{r'})^{-b}\right]$ always have the same

sign, which gives

$$\int \rho^{5/3}d\mathbf{r} - \int a\left(\frac{\int \rho d\mathbf{r}}{V}\right)^{-b}\rho^{5/3+b}d\mathbf{r} \geq \frac{1}{2V}\int\int \left[\rho(\mathbf{r})^{5/3+b} - \rho(\mathbf{r'})^{5/3+b}\right]\left[\rho(\mathbf{r})^{-b} - \rho(\mathbf{r'})^{-b}\right]d\mathbf{r}d\mathbf{r'} \geq 0 \ \text{for} \ \forall \rho \ . (8)$$

Equation (5), (4), and (2) are thus true. QED