# Supplemental Materials
# Towards accurate orbital-free simulations: a generalized gradient approximation for the noninteracting free energy density functional

Kai Luo,[1,*] Valentin V. Karasiev,[2] and S.B. Trickey[3]
[1] *Geophysical Laboratory, Carnegie Institution, 5251 Broad Branch Road NW, Washington D.C. 20015*
[2] *Laboratory for Laser Energetics, University of Rochester, Rochester, NY 14623*
[3] *Quantum Theory Project, Department of Physics and Department of Chemistry, University of Florida, Gainesville, FL 32611*
(Dated: December 4, 2019)

## I. NUMBER OF BANDS IN THE SIMULATIONS

In the static lattice calculations, the number of bands used for *fcc* Al and *cd* Si at each temperature is shown in Table I. Table II shows the corresponding values used in the deuterium (D) AIMD simulations at two densities. The result is that the smallest occupation number used always was less than $10^{-6}$.

TABLE I. The number of bands used for *fcc* Al at $\rho = 2.3$ g/cm$^3$ and *cd* Si at $\rho = 2.0$ g/cm$^3$. For higher densities, the same were used.

| T (eV) | *fcc* Al | *cd* Si |
|---|---|---|
| 01 | 20 | 60 |
| 02 | 50 | 120 |
| 03 | 90 | 160 |
| 04 | 100 | 240 |
| 05 | 150 | 320 |
| 06 | 180 | 400 |
| 07 | 200 | 440 |
| 08 | 220 | 500 |
| 09 | 240 | 540 |
| 10 | 260 | 650 |

TABLE II. The number of bands used for deuterium (D) at various conditions. The simulation cell contains 128 D atoms.

| T (kK) | $r_s = 1.1$ bohr | $r_s = 1.4$ bohr |
|---|---|---|
| 5 | 90 | 110 |
| 10 | 90 | 110 |
| 15.625 | 100 | 130 |
| 31.25 | 160 | 210 |
| 62.5 | 200 | 480 |
| 95.25 | 340 | 600 |
| 125 | 470 | |

## II. VIOLATIONS OF THERMODYNAMIC RELATIONS

Because the construction of the non-interacting free energy starts with the ground-state non-interacting kinetic energy (KE) functional, once the kinetic free energy generalization is done, there is a route to the non-interacting entropic contribution. It starts with enforcement of the Maxwell relation

$$\mathcal{S}_{\mathrm{s}}^{\mathrm{GGA}} = -\frac{\partial \mathcal{F}_{\mathrm{s}}^{\mathrm{GGA}}}{\partial \mathrm{T}}\Big|_V = -\frac{\partial \mathcal{T}_{\mathrm{s}}^{\mathrm{GGA}}}{\partial \mathrm{T}}\Big|_V + \frac{\partial (\mathrm{T}\mathcal{S}_{\mathrm{s}}^{\mathrm{GGA}})}{\partial \mathrm{T}}\Big|_V . \qquad (1)$$

That gives

$$\frac{\partial \mathcal{T}_{\mathrm{s}}^{\mathrm{GGA}}}{\partial \mathrm{T}}\Big|_V = \mathrm{T}\frac{\partial \mathcal{S}_{\mathrm{s}}^{\mathrm{GGA}}}{\partial \mathrm{T}}\Big|_V . \qquad (2)$$

and thus to a required relationship between the enhancement factors $F_\tau$ and $F_\sigma$ such that the two are proper kinetic and entropic contributions respectively, namely

$$\begin{aligned} &\xi'(t)F_\tau(s_\tau) + \xi(t)F'_\tau(s_\tau)\,\tfrac{\partial s_\tau}{\partial t} \\ &\quad = -\tfrac{1}{t}\zeta(t)F_\sigma(s_\sigma) + \zeta'(t)F_\sigma(s_\sigma) + \zeta(t)F'_\sigma(s_\sigma)\,\tfrac{\partial s_\sigma}{\partial t} , \end{aligned} \qquad (3)$$

This last relationship is Eq. (35) of Ref. [1]. Even if satisfied by a particular approximation, that clarity of identification does not provide any guarantee on the accuracy or inaccuracy of the non-interacting free energy provided by the two approximations combined.

The LKTF functional developed in this work does not satisfy Eq. (3) exactly. The same is true with the earlier VT84F[2] and KST2[1] functionals. All three used the approximation

$$F_\sigma(s_\sigma) = 2 - F_\tau(s_\sigma) \qquad (4)$$

Two questions then arise. To what extent does use of this approximation result in loss of identification of the $F_\tau$ and $F_\sigma$ terms as kinetic and entropic and does such loss matter for the overall accuracy of the approximation?

For insight at least as to the first question, we compare the left- and right-hand sides of Eq. (3) to see the difference. Fig. 1 shows the results for KST2. This is a reproduction and extension of Fig. 3 in Ref.[1]]. (We note that the analytical representations of the functions $\xi(t)$ and $\zeta(t)$ used here are from Ref. [3], not the older fits given by Perrot and Dharma-wardana[4] and extended.) For small $s$ (weak spatial density variation) and low $t$. Eq. (3) is violated only mildly. As $s$ increases, the largest deviation happens around $t = 0.4$ for $s = 1.0$. Similarly, Fig. 2 shows that LKTF exhibits vanishing left-hand versus right-hand side differences, for $s = 0.5$. For $s = 2.0$, the difference reaches its maximum magnitude around $t = 0.4$.

Though this clearly indicates a failure of the Eq. (4) approximation to be a solution of Eq. (3) when used to construct

LKTF from ground-state LKT, how to interpret that failure is not entirely clear. What the non-zero difference, LHS - RHS of Eq. (3), shows is only that the combination of a given pair $F_\tau$, $F_\sigma$ with the "2 - F" approximation of Eq. (4) violates the exact relationship. That violation does not provide a diagnostic as to whether it is the form of the pair of enhancement factors or the "2-F" approximation that is the cause. For example, if Eq. (3) were to be solved exactly but with a rather inaccurate $F_\tau$ to start, the result almost certainly would be inaccurate forces in AIMD simulations. This follows, in part, from the fact that Eq. (3) results from interchange of integration and differentiation.

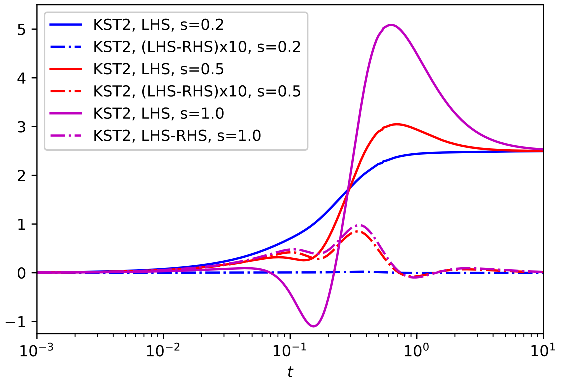

FIG. 1. Values of the left side of Eq. (3) and the difference between the left and right sides of that equation. Note that the differences for $s = 0.2$ and $s = 0.5$ are magnified by 10.

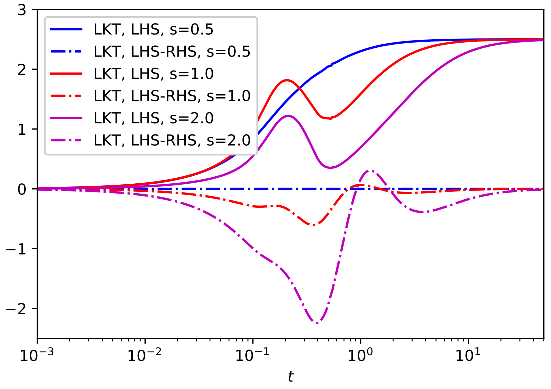

FIG. 2. As in Fig. (1) for LKTF but on a different range of $s$.

In turn that leads back to Eq. (45) of Ref. [1], namely the difference of entropic free energy between the thermodynamically correct entropic part from a given GGA and the contribution from the nominally entropic term:

$$\begin{aligned}\mathrm{T}\Delta\mathcal{S}_{\mathrm{s}} := \int \Big[ &-\xi'(t)F_\tau(s_\tau) - \xi(t)F'_\tau(s_\tau)\frac{\partial s_\tau}{\partial t} \\ &+\zeta'(t)F_\sigma(s_\sigma) + \zeta(t)F'_\sigma(s_\sigma)\frac{\partial s_\sigma}{\partial t} \\ &-\frac{1}{t}\zeta(t)F_\sigma(s_\sigma)\Big] t\tau_0^{\mathrm{TF}}(n)d\mathbf{r}^3 \,. \qquad (5)\end{aligned}$$

From Table III, the largest violation happens around T = 4eV for LKTF, and T = 5eV for VT84F. Comparing the absolute value, the violation for LKTF is certainly not worse than VT84F.

---

[*] kluo@carnegiescience.edu

[1] V. V. Karasiev, T. Sjostrom, and S. B. Trickey, Physical Review B **86**, 115101 (2012).
[2] V. V. Karasiev, D. Chakraborty, O. A. Shukruto, and S. B. Trickey, Physical Review B **88**, 161108 (2013).
[3] V. V. Karasiev and S. Trickey, Computer Physics Communications **183**, 2519 (2012).
[4] F. m. c. Perrot and M. W. C. Dharma-wardana, Phys. Rev. A **30**, 2619 (1984).

TABLE III. The deviation $T\Delta\mathcal{S}$ as computed in Ref. [1] for cd Si at $\rho = 2.0$ g/cm$^3$. LKTF and VT84F are included. For higher densities, similar trends were observed.

| T (eV) | T$\mathcal{S}^{LKTF}$ (eV) | T$\Delta\mathcal{S}^{LKTF}$ (eV) | T$\mathcal{S}^{VT84F}$ (eV) | T$\Delta\mathcal{S}^{VT84F}$ (eV) |
|---|---|---|---|---|
| 01 | 11.37 | 0.39 | 12.68 | 1.23 |
| 02 | 42.89 | 0.75 | 46.28 | 2.84 |
| 03 | 95.80 | 1.29 | 103.52 | 5.65 |
| 04 | 168.42 | 1.71 | 180.50 | 8.29 |
| 05 | 256.04 | 1.51 | 269.66 | 8.57 |
| 06 | 355.14 | 1.04 | 367.76 | 7.00 |
| 07 | 463.55 | 0.58 | 473.94 | 4.83 |
| 08 | 579.61 | 0.23 | 587.25 | 2.58 |
| 09 | 702.18 | 0.02 | 707.32 | 0.86 |
| 10 | 830.37 | -0.09 | 833.47 | -0.29 |