Semilocal Pauli-Gaussian Kinetic Functionals for Orbital-Free Density Functional Theory Calculations of Solids

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Abstract

Kinetic energy (KE) approximations are key elements in orbital-free density functional theory. To date, the use of non-local functionals, possibly employing system dependent parameters, has been considered mandatory in order to obtain satisfactory accuracy for different solid-state systems, whereas semilocal approximations are generally regarded as unfit to this aim. Here, we show that instead properly constructed semilocal approximations, the Pauli-Gaussian (PG) KE functionals, especially at the Laplacian-level of theory, can indeed achieve similar accuracy as non-local functionals and can be accurate for both metals and semiconductors, without the need of system-dependent parameters.

Graphical TOC Entry
The kinetic energy (KE) functional is a fundamental quantity in electronic structure theory. It plays a prominent role in subsystem and embedding theories, hydrodynamic models, information theory, machine learning techniques for Fermionic systems, potential functional theory, various extensions of the Thomas-Fermi (TF) theory, and especially orbital-free density functional theory (OF-DFT). The applicability of these methods is strongly limited by the lack of accurate and simple KE approximations.

The OF-DFT allows an efficient description of the ground state of any electronic system via the solution of the Euler equation:

\[
\frac{\delta T_s[n]}{\delta n} + v_{\text{ext}}(r) + \int \frac{n(r')}{|r - r'|} d^3r' + \frac{\delta E_{\text{xc}}[n]}{\delta n} = \mu ,
\]

where \(n\) is the ground-state electron density, \(T_s\) is the non-interacting KE functional, \(v_{\text{ext}}\) is the external (e.g. nuclear) potential, \(E_{\text{xc}}\) is the exchange-correlation functional, and \(\mu\) is the chemical potential.

The vast majority of the OF-DFT calculations employ non-local (or two-point) KE functionals, that are rather accurate and display a logarithmic \(O(N \ln(N))\) scaling behavior with system size \(N\). However, these functionals are based on the Lindhard response function of the non-interacting homogeneous electron gas (HEG). Thus, most of them depend on the average density in the unit cell \(n_0\) and therefore they are not adequate for finite systems or even for anisotropic solid-state systems such as interfaces, surfaces or layered materials, where \(n_0\) may be not well defined or may be not representative for the system. Moreover, very accurate results are often obtained only using system-dependent parameters.

On the other hand, unlike for the exchange-correlation energy case where semilocal approximations have experienced a huge success in the context of Kohn-Sham (KS) DFT, semilocal KE approximations, which scale linearly with system size, and can be easily implemented in both real-space and wave-vector formalisms, are barely used in OF-DFT calculations. This traces back to the fact that the actual state-of-the-art semilocal function-
als (e.g. VT84f,\textsuperscript{40} vWGTF1/vWGTF2\textsuperscript{41}) may encounter severe failures for various systems (e.g. semiconductors) and properties (e.g. bulk modulus, vacancy energy\textsuperscript{41}).

In this Letter, we show that this limitation is not a fundamental feature of the semilocal functionals but it is just related to the approximations employed so far. Indeed, we show that even a simple combination of the local Thomas-Fermi (TF)\textsuperscript{42,43} and gradient-dependent von Weizsäcker (W)\textsuperscript{44} functionals can outperform the actual state-of-the-art semilocal functionals in solid-state calculations. Moreover, we show that a simple non-empirical Laplacian-level semilocal KE functional can easily approach the accuracy of non-local KE approximations, achieving a broad accuracy and applicability. These results shed a completely new light on the topic of KE functionals, showing that with a careful development semilocal KE functionals can be applied with good accuracy in large-scale OF-DFT applications.

To this purpose, we have performed OF-DFT calculations for simple metals\textsuperscript{41} (Li, Mg and Al, in simple-cubic (sc), face-centered-cubic (fcc), and body-centered-cubic (bcc) configurations) and III-V semiconductors\textsuperscript{36,37} (AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, and InSb with the cubic zincblende unit cell), comparing our results to KS-DFT values obtained using the same computational set up. These systems have been largely employed to assess the accuracy of non-local KE functionals\textsuperscript{32,35–37,41}. We considered four properties: cell volume ($V_0$), bulk modulus ($B$), total energy at equilibrium volume ($E_0$) and density error ($D_0$). The first three properties have been previously considered in the assessment of functionals.\textsuperscript{32,35–37,41} The last quantity is defined as

$$D_0 = \frac{1}{N_e} \int |n^{KS}(\mathbf{r}) - n^{OF-DFT}(\mathbf{r})|d^3\mathbf{r},$$

and it is computed at the KS lattice constant for both KS and OF-DFT. Here $N_e$ is the electron number in the unit cell. The density error is a very hard test for the quality of the KE functional, describing how well the OF-DFT calculations converge to the exact density. For each quantity $p \in \{V_0, B, E_0, D_0\}$, we considered the mean absolute relative
error (MARE$_p$) with respect to the reference KS values averaging over all systems (metals or semiconductors). Finally, in order to have a global indicator for all the properties, we considered a relative MARE (RMARE) obtained normalizing to the average values of the Smargiassi and Madden (SM)\textsuperscript{30} and the Huang and Carter (HC)\textsuperscript{37} functionals, i.e.

\[
RMARE = \sum_p \frac{MARE_p}{(1/2)(MARE_{pSM} + MARE_{pHC})}.
\]

(3)

The HC (with universal parameters $\lambda = 0.01177$ and $\beta = 0.7143$\textsuperscript{36}) and SM functionals have been chosen as references, since they bind both metals and semiconductors\textsuperscript{33} and do not employ system-dependent parameters (actually, HC does not even depend on the average density $n_0$). Thus, a functional with RMARE=1 shows a performance between HC and SM.

Figure\textsuperscript{[1]} reports the RMAREs for metals and semiconductors of different semilocal functionals commonly used in OF-DFT calculations, namely VT84f,\textsuperscript{40} TFW, TF(1/5)W (the latter being combinations of the TF functional with W and W/5, respectively), as well as for the non-local references HC and SM. Note that other functionals from literature, not only semilocal, but also WT,\textsuperscript{28} WGC,\textsuperscript{45} and vWGTF\textsuperscript{41} do not bind semiconductors,\textsuperscript{33,36} so they cannot be included in Fig.\textsuperscript{[1]} Clearly the non-local functionals give the lowest RMAREs, with SM being especially accurate for metals and HC for semiconductors. On contrast, the semilocal functionals (TF(1/5)W, TFW, VT84f) perform much worse (VT84f is quite accurate only for metals).

Next we consider more general semilocal functionals. Any Generalized Gradient Approximation (GGA) or Laplacian-level meta-GGA semilocal KE functional that behaves correctly under the uniform density scaling (i.e. $T_s[n_\gamma(r)] = \gamma^2 T_s[n(r)]$,\textsuperscript{46,47} where $n_\gamma(r) = \gamma^3 n(\gamma r)$, with $\gamma \geq 0$) can be written

\[
T_s[n] = T_s^W + \int \tau^{TF} F_s^p(s, q) d^3r,
\]

(4)

where $\tau^{TF} = (3/10)k_F^2 n$ is the TF KE density,\textsuperscript{42,43} with $k_F = (3\pi^2 n)^{1/3}$ being the Fermi
wave vector, \( s = |\nabla n|/(2k_F n) \) and \( q = \nabla^2 n/(4k_F^2 n) \) are the reduced gradient and Laplacian, \( T_s^W = \int \tau^F(5s^2/3)d^3r \) is the von Weizsäcker kinetic energy (which is exact for one and two electron systems, as well as for any bosonic system), and \( F_p \) is the Pauli KE enhancement factor.\(^{24} \) The exact condition \( T_s \geq T_s^W \) requires that \( F_p > 0 \). However, this constraint is satisfied only by few semilocal approximations,\(^{40,41,48} \) and it is even violated by some non-local KE functionals.\(^{49} \)

The rehabilitation of semilocal KE functionals for OF-DFT. In a first attempt, we have considered the family of functionals \( TF\lambda W \) which are defined by

\[
F_{s,\lambda}^p = 1 + (\lambda - 1)\frac{5}{3} s^2 .
\]
This class of functionals has been investigated for atomic/molecular systems\textsuperscript{50,51} but not for bulk systems with pseudopotentials. The performance for various values of $\lambda$ is reported in Fig. 1. The first interesting result of this Letter, is that the RMAREs can be strongly reduced varying $\lambda$, reaching for $\lambda = 0.6$ a RMARE$\approx 1.2$, and 1.9 for metals and semiconductors, respectively. Thus a very simple functional, TF(0.6)W is already better than the current semilocal state-of-the-art (VT84f).

However, the Pauli enhancement factor of TF\textsubscript{W} becomes negative whenever $s^2 \geq 0.6/(1 - \lambda)$. The relevant values of $s^2$ for solids are comprised in the interval $[0:1]$, as shown in Fig. 2 by an $s$-decomposition of the TF KE energy $t[n](s)$, so that\textsuperscript{52}

$$T_s[n] = \int_{0}^{+\infty} ds \ t[n](s) \ F_s(s) . \quad (6)$$

Thus, as shown in Fig. 2 the Pauli enhancement factor for TF(0.6)W is always positive, which could explain its relative good performance. Nevertheless, the tendency of $F_{s,\lambda}^p$ to become rather small and with high slope at high $s$ may limit its performance in particular for semiconductors, that are characterized by larger values of $s$.

To overcome this problem, a new class of functionals (named Pauli-Gaussian, PG\textsubscript{$\mu$}) can be constructed considering the positive-defined Pauli enhancement factor

$$F_s^p(s) = e^{-\mu s^2} \geq 0 . \quad (7)$$

When $\mu \approx 1.96\lambda^2 - 5.33\lambda + 3.37$, then $F_{s,PG\mu}^p \approx F_{s,\lambda}^p$ for $0 \leq s \leq 1$. As expected, the PG\textsubscript{$\mu$} functionals are significantly better than TF\textsubscript{W} for semiconductors and have similar accuracy for simple metals, as shown in Fig. 1. The best global performance is obtained approximately with $\mu = 1$ (which defines the PG1 functional). However, this functional does not satisfy the second-order gradient expansion (GE2), which is instead an important exact property to be retained.\textsuperscript{53} On the other hand, the functional with $\mu = 40/27 \approx 1.48$ (named PGS, from Pauli-Gaussian Second order) satisfies the GE2 constraint, is very good
for semiconductors but quite bad for metals (see Fig. 1).

While we do not exclude that further optimizations of $F^p_s(s)$ could lead to improved results, here we follow a different path, and we move to the Laplacian-meta-GGA level of theory, considering the PGSL/$\beta$ (from Pauli-Gaussian Second order and Laplacian) class of functionals, defined by

$$ F^p_s(s, q) = e^{-40/27s^2} + F(q) \approx e^{-40/27s^2} + \beta q^2 + ... $$  \hspace{1cm} (8)
In Eq. (8), $F(q)$ represents a generic function of the reduced Laplacian, which can be expanded in Taylor series because $q$ is always small in solids. The linear term in $q$ does not contribute to the energy nor to the potential,\textsuperscript{27} thus the $q^2$ term considered here is just the lowest-order correction. Note that the $q^2$ term in Eq. (8) would cause a divergence near the cusp of an electronic density (i.e. at the nuclei). However, this shortcoming is not present using pseudopotentials. In the tail of an exponentially decaying density (e.g. far away from an atom or a surface) $q$ is diverging, but the full kinetic contribution $\tau^{TF}q^2$ is still exponentially decaying, being integrable.\textsuperscript{51,52} We also recall that the HEG fourth-order gradient expansion has been successfully applied to metallic clusters in the OF-DFT context.\textsuperscript{55}

To fix the $\beta$ coefficient in a non-empirical way we could note that setting $\beta = 8/81 \approx 0.1$ in Eq. (8), the corresponding functional recovers the fourth-order linear response of the non-interacting HEG, i.e. the Lind4 functional, see Ref.\textsuperscript{56}

As shown in Fig. 1, the Laplacian plays an important role. Varying $\beta$ from 0 to 0.25 we observe a large improvement of simple metal properties (the RMARE decreases from 3 to 1.2) and correspondingly a very small change in the accuracy of semiconductors (RMARE increases from 0.9 to 1.2). The functional PGSL0.25 ($\beta = 0.25$) is competitive with HC and SM, being only 20% worse than their average. This is the second main result of this work: a very simple Pauli KE functional (a sum of an exponential and a Laplacian-dependent quadratic term) is almost as accurate as complicated and sophisticated non-local expressions.

The good performance of the PGSL0.25 functional can be rationalized considering the exact density-density response function the HEG system which is $\chi(\eta) = (k_F/\pi^2)(1/F^{Lind}(\eta))$, with $\eta = k/2k_F$ and $F^{Lind}$ being the dimensionless wave vector and the Lindhard function,\textsuperscript{57} respectively. Figure 3 reports the behavior of the linear response function for different functionals. We see that TF(0.6)W and PG1 are good for $\eta > 1$, while PGS and VT84f are good for $\eta < 1$: thus none of the gradient-dependent functionals considered is able to reproduce the exact behavior for all $\eta$. On the other hand, a significant improvement is obtained by
moving to the Laplacian level of theory: the PGSL0.25 functional describes accurately both the low- and the high-\( \eta \) regions.

In more details, in Table 1 we report the accuracy of the various functionals for the all the considered properties, separately (results for all systems are reported in Supporting Information). For simple metals all the semilocal functionals introduced in this Letter give quite accurate results, being comparable to the non-local KE functionals. On the other hand, semiconductors are more difficult systems and all the MARE are larger (but the errors for \( V_0 \), which are comparable). Among the semilocal functionals considered, only PGSL0.25 gives always consistently accurate results. In particular, it performs better than 1/2(SM+HC) for both lattice constants and bulk moduli; for energies and densities (the hardest test), it
Table 1: Mean absolute relative errors (in %) for equilibrium volumes ($V_0$), bulk moduli ($B$), total energies ($E_0$) and density errors ($D_0$) of the simple metals and semiconductors test sets. The best results from semilocal functionals are shown in bold style, and a star indicates accuracy comparable or better than 1/2(HC+SM).

|            | Simple Metals |            | Semiconductors |
|------------|--------------|------------|----------------|
|            | $V_0$  | $B$  | $E_0$ | $D_0$ | $V_0$  | $B$  | $E_0$ | $D_0$ |
| TFW        | 4.8   | 20.3 | 0.91  | 4.4   | 5.7   | 30.8 | 5.35  | 23.4  |
| VT84f      | *4.4  | 15.8 | *0.14 | 3.9   | 10.5  | 63.5 | 3.56  | 22.1  |
| TF(0.6)W   | *2.6  | 12.1 | *0.35 | 3.1   | *2.9  | *9.2 | 2.99  | 16.1  |
| PG1        | *3.6  | *7.3 | 0.45  | 3.7   | *3.1  | *8.2 | 2.03  | 14.7  |
| PGSL0.25   | *4.4  | *7.4 | *0.35 | 2.8   | *2.5  | *5.7 | 1.62  | 13.3  |
| 1/2 (HC+SM)| 4.3   | 7.8  | 0.34  | 1.7   | 4.5   | 21.1 | 0.63  | 7.9   |
| SM         | 3.4   | *4.2 | 0.21  | *1.4  | 7.6   | 37.7 | 0.80  | *7.6  |
| HC         | 5.0   | 11.5 | 0.47  | 2.0   | *1.6  | *4.5 | *0.46 | 8.3   |

is twice worse than 1/2(HC+SM), but still much more accurate than any other semilocal functionals. (A comparison of GaAs densities is reported in the Supporting Information.)

Finally, in order to verify the broader applicability of the PGSL0.25 functional, we considered additional systems and properties. In Table 2, we report the MARE for several silicon phases (sc, fcc, bcc and cd, for cubic diamond) and vacancy formation energies for fcc Al, hcp Mg, and bcc Li. Again, for all properties, PGSL0.25 is the best semilocal functional, being always competitive with the non-local HC and SM functionals. In particular, PGSL0.25 is performing well in case of the vacancy formation energies of metals, which is a severe test for most KE functionals (here HC has a MARE of 88% error and it also incorrectly predicts a negative Al-fcc vacancy formation energy; for all results see the Supporting Information).

In conclusion, we have shown that it is possible to achieve a realistic description of the KE of both metals and semiconductors at the Laplacian semilocal level of theory, without system-dependent parameters. This is an important result in view of future OF-DFT applications on large and complex systems (e.g. hybrid interfaces). Moreover, semilocal functionals of the type considered here can also easily be implemented in any real-space or plane-wave code. Finally, new developments can be considered starting from the present work. A first step concerns a further optimization of the $F(q)$ function in Eq. (8) and/or considering
Table 2: MARE for equilibrium volumes ($V_0$), bulk moduli ($B$), total energies ($E_0$) and density errors ($D$) for Si phases (sc, fcc, bcc, and cd). Last column report the MARE for vacancy formation energies for fcc Al, hcp Mg, and bcc Li. The best results from semilocal functionals are shown in bold style, and a star indicates the best functional.

|        | $V_0$ | $B$   | $E_0$ | $D$  | $E_{vac}$ |
|--------|-------|-------|-------|------|------------|
| TFW    | 9.48  | 103.24| 2.28  | 12.9 | 133.8      |
| VT84F  | 6.51  | 86.49 | 0.94  | 8.9  | 74.5       |
| PG1    | 2.56  | 36.0  | 0.69  | 6.1  | 52.2       |
| PGSL0.25 | 2.94 | **18.13** | **0.53** | **5.4** | **30.5** |
| HC     | 5.51  | *10.41*| 0.28  | 4.4  | 88.5       |
| SM     | 5.11  | 19.76 | *0.21*| *2.6*| *25.1*     |

more complicated functional products of both $s$ and $q$. To this end, systems with stronger inhomogeneity (i.e. larger $q$ values) will be needed. A natural next step is thus the extension of the proposed functional to interfaces or finite systems. Preliminary calculations carried out on molecular dimers have indeed shown that the PGSL0.25 functional can describe rather well the equilibrium bond length of dimers, with an accuracy similar to HC. Nevertheless, for further applications in this context, a more careful treatment of exponentially decaying density regions (where both $s$ and $q$ diverge) must be considered.

After this work has been completed, we have acknowledged the development of the LKT GGA functional. The LKT functional form is numerically close to PG0.75 one (for $s < 1$). An extensive assessment of various KE functionals will be presented in a forthcoming article.

**Computational Details.** All calculations have been performed using the PROFESS 3.0 code. For a better comparison with literature results, we have chosen the Perdew-Burke-Ernzerhof (PBE) XC functional for simple metals, and the Perdew and Zunger XC LDA parametrization for semiconductors. We use bulk-derived local pseudopotentials (BLPSs), as in Refs. and plane wave basis kinetic energy cutoffs of 1600 eV. Equilibrium volumes and bulk moduli have been calculated by expanding and compressing the optimized lattice parameters by up to about 30% to obtain twenty energy-volume points, fitted using a birch-Murnaghan’s equation of state expanded to 6th-order. The ref-
ference KS density have been computed using the Abinit program. In this case denser grids have been used (10 grid-points per angstrom).

Supporting Information

Full results for simple metals, semiconductors, Si phases, and vacancies; plot of the self-consistent electron densities of GaAs.

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