

Jellium-with-gap model applied to semilocal kinetic functionals

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We investigate a highly nonlocal generalization of the Lindhard function, given by the jellium-with-gap model. We find a band-gap-dependent gradient expansion of the kinetic energy, which performs noticeably well for large atoms. Using the static linear response theory and the simplest semilocal model for the local band gap, we derive a nonempirical generalized gradient approximation (GGA) of the kinetic energy. This GGA kinetic-energy functional is remarkably accurate for the description of weakly interacting molecular systems within the subsystem formulation of density functional theory.

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I. INTRODUCTION

Density functional theory (DFT) [1,2] is the most used computational method for electronic structure calculations of molecular and extended systems, providing the highest accuracy–computational-cost ratio. In the conventional DFT formalism, the Kohn-Sham (KS) scheme [3], the ground-state electronic density $n(\mathbf{r})$ is determined from a set of auxiliary KS orbitals $\{\phi_i(\mathbf{r})\}$: the KS-DFT method is exact but for the approximations of the exchange-correlation (XC) functional. However, for large scale calculations, the computational cost of KS-DFT becomes unaffordable, as one needs to compute all the occupied KS orbitals in order to construct the density as $n(\mathbf{r}) = \sum_i^{\text{occ.}} f_i |\phi_i(\mathbf{r})|^2$, where f_i is the occupation number (2, for closed-shell systems).

Among other linear scaling methods [4–7], two DFT methods are attracting strong interest: (i) in the orbital-free version of DFT [8–12], $n(\mathbf{r})$ can be computed directly via the Euler equation [1], without the need of KS orbitals; (ii) in the subsystem version of DFT (Sub-DFT) [13–16], also known as frozen-density embedding (FDE), $n(\mathbf{r})$ is computed as the sum of the electronic densities of several (smaller) subsystems in which the total system is partitioned, which can be computed simultaneously. Both approaches allow in principle calculations of large systems, but the final accuracy depends directly on the approximations of the noninteracting kinetic-energy (KE) functional T_s (which are definitely more important than the ones for the XC energy, that are also present in standard KS calculations). We recall that the exact KS KE is

$$T_s^{\text{exact}} = \frac{1}{2} \sum_i^{\text{occ.}} \int f_i |\nabla \phi_i(\mathbf{r})|^2 d^3\mathbf{r}. \quad (1)$$

Thus the KE is explicitly known only as a function of ϕ_i but not as a functional of n .

On the other hand, in Sub-DFT the interaction between the subsystems is taken into account via the so-called embedding potentials [14–16], which depends on the nonadditive KE: in the case of just two subsystems (A and B) it is $T_s^{\text{nadd}}[n_A; n_B] = T_s[n_A + n_B] - T_s[n_A] - T_s[n_B]$.

The development of an accurate approximation of $T_s[n]$ (and/or $T_s^{\text{nadd}}[n_A; n_B]$) is one of the biggest DFT challenges

[17–19]. Nowadays, the most sophisticated KE approximations have been constructed to be exact for the linear response of the jellium model, by incorporating the Lindhard function in their fully nonlocal expressions [9,20–24]. We recall that the Lindhard function [9,25]

$$F^{\text{Lind}} = \left(\frac{1}{2} + \frac{1 - \eta^2}{4\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \right)^{-1}, \quad (2)$$

where $\eta = k/(2k_F)$ is the dimensionless momentum [$k_F = (3\pi^2 n)^{1/3}$ being the Fermi wave vector of the jellium model with the constant density n], is related to the Jellium density response χ^{Jell} via [9]

$$-\frac{1}{\chi^{\text{Jell}}} = \frac{\pi^2}{k_F} F^{\text{Lind}}. \quad (3)$$

The nonlocal KE functionals based on the Lindhard function are accurate for simple metals where the nearly free electron gas is an excellent model but they cannot describe well semiconductors and insulators, where the density response function behaves as [26,27]

$$-\frac{1}{\chi^{\text{Semicond}}(k)} \xrightarrow{k \rightarrow 0} \frac{b}{k^2}, \quad (4)$$

with b being positive and material dependent. Several KE functionals have been constructed to improve the description of semiconductors [27,28], but Eq. (4) has not been explicitly used in their expressions due to the lack of a sophisticated analytical form that can recover both the Lindhard function and Eq. (4).

In this paper, we will investigate the generalization of the Lindhard function for the jellium-with-gap model which satisfies Eq. (4).

The jellium-with-gap model [29] was developed outside the KS framework, using perturbation theory to take into account the band-gap energy. This model was used to have qualitative and quantitative insight for semiconductors [30–34], to develop an XC kernel for the optical properties of materials [35], and to construct accurate correlation energy functionals for the ground-state DFT [29,36–40]. We will show that the Lindhard function for the jellium-with-gap model (F^{GAP}), previously introduced by Levine and Louie [33] in

a different context (dielectric constant and XC potential), may be seen as a sophisticated analytical form suitable for KE approximations.

The paper is organized as follows. In Sec. II we discuss the properties of F^{GAP} , we derive its (band-gap-dependent) KE gradient expansion, and we assess it for large atoms. By using a local gap model, we propose a simple KE gradient expansion that is very accurate for the semiclassical atom theory.

In Sec. III we discuss the implications of this result in DFT by constructing a simple KE functional at the generalized gradient approximation (GGA) level of theory based on the gradient expansion of the jellium-with-gap model. GGA KE functionals are computationally very efficient and play a key role for the simulation of large systems. We mention that the development of semilocal KE functionals is nowadays an active field [41–50].

Finally, in Sec. IV we summarize our results.

II. THEORY

A. Properties and gradient expansions for the jellium model

For the conventional infinite jellium model, the Lindhard function behaves as

$$F^{\text{Lind}} \rightarrow 1 + \frac{1}{3}\eta^2 + \frac{8}{45}\eta^4 + O(\eta^6), \quad \text{for } \eta \rightarrow 0, \quad (5)$$

$$F^{\text{Lind}} \rightarrow 3\eta^2 - \frac{3}{5} - \frac{24}{175}\frac{1}{\eta^2} + O(\eta^{-4}), \quad \text{for } \eta \rightarrow \infty. \quad (6)$$

Equation (5) contains important physics that has been used in the construction of semilocal KE density functionals [9]. Thus, the KE gradient expansion which recovers the first three terms in the right-hand side of Eq. (5) can be easily derived [9] [see also Eqs. (15) and (16) in Sec. II C and the corresponding discussion]. It is

$$T_s^{\text{Lind}4}[n] = \int d\mathbf{r} \tau^{\text{TF}} \left(1 + \frac{5}{27}s^2 + \frac{8}{81}q^2 \right), \quad (7)$$

where $\tau^{\text{TF}} = \frac{3}{10}(3\pi^2)^{2/3}n^{5/3}$ is the Thomas-Fermi KE density [51,52], which is exact for the jellium model, and $s = |\nabla n|/[2k_F n]$ and $q = \nabla n^2/[4(3\pi^2)^{2/3}n^{5/3}]$ are the reduced gradient and Laplacian, respectively. Equation (7) resembles the second-order gradient expansion [53] (GE2)

$$T_s^{\text{GE2}}[n] = \int d\mathbf{r} \tau^{\text{TF}} \left(1 + \frac{5}{27}s^2 \right)$$

(derived also within the linear response of the jellium model), as well as the fourth-order gradient expansion [44,54,55] of the KE

$$T_s^{\text{GE4}}[n] = \int d\mathbf{r} \tau^{\text{TF}} \left(1 + \frac{5}{27}s^2 + \frac{8}{81}q^2 - \frac{1}{9}s^2q + \frac{8}{243}s^4 \right),$$

with the exception of the terms $\propto s^2q$, $\propto s^4$, which are beyond the linear response.

Note that $F^{\text{Lind}}(\eta = 0) = 1$ is the leading term in the expansion of Eq. (5) and it corresponds to the Thomas-Fermi local-density approximation, the linear response in the wave-vector space of which is just the Fourier transform of the second-functional derivative, i.e., $\delta^2 T_s^{\text{TF}}/\delta n(\mathbf{r})\delta n(\mathbf{r}') \sim k_F^{-1}\delta(\mathbf{r} - \mathbf{r}')$. We recall that the limit $\eta = 0$ is very powerful,

being also used in the construction of the adiabatic local-density approximation XC kernel of the linear response time-dependent DFT [56,57].

B. Properties of the Lindhard function for the jellium-with-gap model

Levine and Louie [33] proposed the density-response function $\chi^{\text{GAP}}(k, \omega)$ of the jellium-with-gap model, and the corresponding [i.e., from Eq. (3)] Lindhard function for the jellium-with-gap model is

$$\begin{aligned} 1/F^{\text{GAP}} = & \frac{1}{2} - \frac{\Delta [\arctan(\frac{4\eta+4\eta^2}{\Delta}) + \arctan(\frac{4\eta-4\eta^2}{\Delta})]}{8\eta} + \\ & + \left(\frac{\Delta^2}{128\eta^3} + \frac{1}{8\eta} - \frac{\eta}{8} \right) \ln \left(\frac{\Delta^2 + (4\eta + 4\eta^2)^2}{\Delta^2 + (4\eta - 4\eta^2)^2} \right), \end{aligned} \quad (8)$$

where $\Delta = 2E_g/k_F^2$ and E_g is the gap.

For a given Δ , a series expansion of F^{GAP} for $\eta \rightarrow 0$ gives

$$\begin{aligned} F^{\text{GAP}} \rightarrow & \frac{3\Delta^2}{16\eta^2} + \frac{9}{5} + \frac{3}{175} \frac{175\Delta^2 - 192}{\Delta^2} \eta^2 \\ & - \frac{64}{875} \frac{525\Delta^2 - 368}{\Delta^4} \eta^4 + O(\eta^6) \quad \text{when } \eta \rightarrow 0. \end{aligned} \quad (9)$$

Thus, for any system with $\Delta > 0$ we have that $F^{\text{GAP}} \propto \Delta^2 \eta^{-2}$. This term is correct [see Eq. (4)] and it has been also used in the jellium-with-gap XC kernel [35], which gives accurate optical absorption spectra of semiconductors and insulators. On the other hand, if we first perform a series expansion for $\Delta \rightarrow 0$, and then a series expansion for $\eta \rightarrow 0$ we obtain

$$\begin{aligned} F^{\text{GAP}} \rightarrow & \left[1 + \frac{1}{3}\eta^2 + \frac{8}{45}\eta^4 + \dots \right] \\ & + \Delta \left[\frac{\pi}{8}\frac{1}{\eta} + \frac{\pi}{12}\eta + \frac{7\pi}{120}\eta^3 + \dots \right] \\ & + \Delta^2 \left[\frac{\pi^2 - 4}{64}\frac{1}{\eta^2} + \frac{3\pi^2 - 16}{192} + \left(\frac{-17}{180} + \frac{13\pi^2}{960} \right) \eta^2 \right. \\ & \left. + \left(\frac{-383}{3780} + \frac{683\pi^2}{60480} \right) \eta^4 + \dots \right] + \dots \end{aligned} \quad (10)$$

Equation (10) confirms that, by construction, we have

$$F^{\text{GAP}} = F^{\text{Lind}}, \quad \text{when } \Delta = 0. \quad (11)$$

Inspection of Eqs. (9) and (10) clearly shows that

$$\lim_{\Delta \rightarrow 0} \lim_{\eta \rightarrow 0} F^{\text{GAP}} = \infty, \quad (12)$$

$$\lim_{\eta \rightarrow 0} \lim_{\Delta \rightarrow 0} F^{\text{GAP}} = 1, \quad (13)$$

meaning that F^{GAP} has an ‘‘order of limits problem.’’ Such a situation is common in DFT. For example, we recall that several meta-GGA XC functionals (e.g., TPSS [58], revTPSS [59,60], BLOC [61,62], SA-TPSS [63], VT{8,4} [64]) suffer from such an order of limits problem. Nonetheless, they are accurate for many systems and properties, showing realistic system-averaged XC hole models [62].

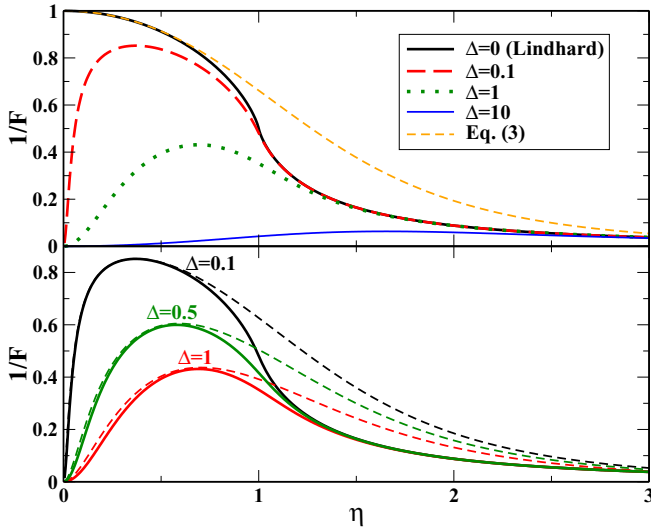


FIG. 1. Upper panel: $1/F^{\text{GAP}}$ vs η for various values of Δ . Also shown is the small- η expansion of Eq. (5). Lower panel: Comparison between F^{GAP} (solid lines) and the expansion (dashed lines) of Eq. (10), for $\Delta = 0.1, 0.5$, and 1 , respectively.

In the opposite limit, i.e., for $\eta \rightarrow \infty$, we have

$$F^{\text{GAP}} \rightarrow 3\eta^2 - \frac{3}{5} + \left(-\frac{24}{175} + \frac{3}{16}\Delta^2\right)\frac{1}{\eta^2} + O\left(\frac{1}{\eta^4}\right). \quad (14)$$

Therefore, in this limit, F^{GAP} always behaves as F^{Lind} for $\Delta = 0$.

In the upper panel of Fig. 1, we show $1/F^{\text{GAP}}$ for several values of Δ . The plots are all smooth. At large η , F^{GAP} recovers the Lindhard function [see Eq. (14)], while at small η it is driven by the term $\propto \eta^{-2}$. The plot of the linear response of $T_s^{\text{Lind}4}[n]$ [Eq. (5)] is also given for comparison. In the lower panel of Fig. 1 we report the accuracy of Eq. (10), considering only the terms explicitly indicated in the equation, for $\Delta = 0.1, 0.5$, and 1 . Even for the case $\Delta = 1$, this expansion is still very accurate for $\eta \leq 1$.

C. Kinetic-energy gradient expansions from the linear response of the jellium-with-gap model

Next we proceed to build the linear response jellium-with-gap KE gradient expansion, that should recover Eq. (7) when $\Delta = 0$. To this purpose, we consider the GAP4 expansion, with the general form of the KE fourth-order gradient expansion:

$$T_s^{\text{GAP4}}[n] = \int d\mathbf{r} \tau^{\text{TF}} \left(\frac{a_1}{s^2} + \frac{a_2}{s} + a_3 + a_4 s + a_5 q + a_6 s^2 + a_7 s q + a_8 s^3 + a_9 s^4 + a_{10} q^2 + a_{11} s^2 q \right). \quad (15)$$

Performing the linear response of such a functional

$$F(\eta) = \frac{k_F}{\pi^2} \mathcal{F} \left(\left. \frac{\delta^2 T_s[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \right|_{n_0} \right), \quad (16)$$

where \mathcal{F} represents the Fourier transform, we can find the coefficients a_i , by comparing term by term with Eq. (10). Nevertheless, the straightforward calculation of Eq. (15) requires a tedious and long algebra [65,66]. Instead, a more elegant and simpler way to obtain the linear response of a given semilocal functional has been proposed in Ref. [67]: consider a small perturbation in density at $\mathbf{r} = \mathbf{0}$, of the form $n = n_0 + n_k e^{i\mathbf{k}\mathbf{r}}$, such that $\nabla n = n_k i\mathbf{k} e^{i\mathbf{k}\mathbf{r}}$, and $\nabla^2 n = -n_k k^2 e^{i\mathbf{k}\mathbf{r}}$, with $n_k \ll n_0$. Thus, at $\mathbf{r} = \mathbf{0}$, these expressions are simply $n = n_0 + n_k$, $\nabla n = n_k i\mathbf{k}$, and $\nabla^2 n = -n_k k^2$. Inserting them in the functional expression, the linear response is obtained as twice the second-order coefficient of the series expansion with respect to n_k/n_0 . After some algebra, the KE gradient expansion which gives the linear response of Eq. (10) is found to be

$$\begin{aligned} T_s^{\text{GAP4}}[n] &= \int d\mathbf{r} \tau^{\text{TF}} \left\{ \Delta^2 \frac{27}{91} \frac{\pi^2}{64} \frac{1}{s^2} + \Delta \frac{5\pi}{72} \frac{1}{s} + 1 \right. \\ &+ \Delta^2 \left(\frac{\pi^2}{64} - \frac{1}{12} \right) + \Delta \frac{5\pi}{36} s \\ &+ \left[\frac{5}{27} + \Delta^2 \left(\frac{-17}{324} + \frac{13\pi^2}{1728} \right) \right] s^2 \\ &\left. + \Delta \frac{-7\pi}{216} s q + \left[\frac{8}{81} + \Delta^2 \left(\frac{-383}{6804} + \frac{683\pi^2}{108864} \right) \right] q^2 \right\}. \quad (17) \end{aligned}$$

The terms $\propto s^{-2}$ and $\propto s^{-1}$ account for the terms $\propto \eta^{-2}$ and $\propto \eta^{-1}$ of Eq. (10). These terms contribute only for a nonzero gap, i.e., in semiconductors and insulators, but not in metals. At $\Delta = 0$, $T_s^{\text{GAP4}}[n]$ correctly recovers $T_s^{\text{Lind}4}[n]$.

To test $T_s^{\text{GAP4}}[n]$, we perform calculations for noble atoms, up to $Z = 290$ electrons, using LDA orbitals and densities, in the Engel code [68,69]. We consider $\Delta = 2E_g/k_F^2(\mathbf{r})$ with E_g being the KS band gap of the atoms. Because the gradient expansion is well defined only at small gradients and small Δ , we perform all the integrations over the volume V defined by the conditions $-1 \leq q \leq 1$ and $\Delta \leq 1$, in a similar manner as in Ref. [70]. The results are reported in Table I. For small atoms (Ne and Ar), the GE2 is more accurate than $T_s^{\text{Lind}4}[n]$ and $T_s^{\text{GAP4}}[n]$. However, we recall that in the case of a small number of electrons, the semiclassical and statistical concepts beyond the gradient expansions do not hold. In fact, for larger atoms (Kr to the noble atom with 290 electrons), both T_s^{GAP4} and $T_s^{\text{Lind}4}$ outperform GE2. In particular, T_s^{GAP4} shows the best performance, improving over $T_s^{\text{Lind}4}[n]$ and proving that, due to the inclusion of the gap, F^{GAP4} contains important physics beyond $F^{\text{Lind}4}$.

D. Local band gap

In order to use Eq. (17) in semilocal DFT, we need to replace the true band gap E_g , with a density dependent local band gap. There are several models for the local band gap [36,40], constructed from the exponentially decaying density behavior [36] or from conditions of the correlation energy [40]. In the slowly varying density limit, they behave

TABLE I. Comparison of several linear-response KE gradient expansions. All integrations are performed over the volume V , defined by $-1 \leq q \leq 1$ and $\Delta \leq 1$. We show the exact KE (T_s^{exact}) and the errors $E_s^{\text{approx}} = T_s^{\text{approx}} - T_s^{\text{exact}}$ (in hartree). The GAP4 and LGAP functionals are defined in Eqs. (17) and (20), respectively. The best result of each line is shown in bold style. We use LDA orbitals and densities.

Atom	T_s^{exact}	E_s^{GE2}	E_s^{Lind4}	E_s^{GAP4}	$E_s^{\text{LGAP-GE}}$
Ne	125.8	-0.2	1.2	4.0	1.9
Ar	512.2	4.3	8.1	12.0	11.4
Kr	2742.3	-21.1	-6.7	1.0	10.3
Xe	7214.4	-50.7	-19.6	-8.9	23.2
Rn	21829.6	-146.5	-72.4	-56.8	48.9
Uuo	46259.6	-298.4	-162.3	-139.6	81.1
168 e^-	106907.1	-636.4	-369.8	-336.9	158.9
218 e^-	198077.5	-1065.9	-622.5	-579.7	318.9
290 e^-	389072.0	-1888.9	-1114.7	-1056.4	630.1

as $E_g \sim |\nabla n|^m$, with $m \geq 2$. However, none of them can be considered accurate in this density regime.

On the other hand, under a uniform density scaling $n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda\mathbf{r})$, the local band gap should behave as $E_g \sim \lambda^2$. This condition is fulfilled by the general formula

$$E_g(\mathbf{r}) = a|\nabla n(\mathbf{r})|^m / n(\mathbf{r})^{2(2m-1)/3}, \quad m \geq 0, \quad a \geq 0. \quad (18)$$

Because other exact conditions of the local gap in the slowly varying density limit are not known, we use Eq. (18) in the expression of T_s^{GAP4} , considering the case with $m = 2$. We fix the parameter a requiring that the gradient expansion should recover the first two terms of the kinetic-energy asymptotic expansion for the large, neutral atom [51,52,71–78]:

$$T_s = c_0 Z^{7/3} + c_1 Z^2 + c_2 Z^{5/3} + \dots, \quad (19)$$

where Z is the number of electrons. The first term in Eq. (19) is the Thomas-Fermi one [51,52], the second is the Scott correction due to the atomic inner core [71], and the last term accounts for quantum oscillations [72–75]. The exact coefficients are shown in the first line of Table II. As in Ref. [77], we assume that any gradient expansion that is exact for the uniform electron gas should have the exact c_0 coefficient. The calculation of c_1 and c_2 has been done using the method proposed in Ref. [77]. We recall that the semiclassical atom theory has been often used in the development of exchange functionals [41,70,79–82] and occasionally also for kinetic-energy functionals [42]. Finally, we mention that these gradient expansions are models for the total KE, and not for the KE density, where the use of the reduced Laplacian q

TABLE II. The coefficients c_0 , c_1 , and c_2 of the large- Z expansion of the kinetic energy [see Eq. (19)].

	c_0	c_1	c_2
Exact	0.768745	-0.500	0.270
GE2	0.768745	-0.536	0.336
LGAP-GE	0.768745	-0.500	0.283

(which is not present in linear response of the jellium model) is essential [47,49,83,84].

Using the procedure described above, we find $a = 0.0075$, and we obtain the following gradient expansion (denoted as LGAP-GE):

$$\begin{aligned} T_s^{\text{LGAP-GE}} &= \int d\mathbf{r} \tau^{\text{TF}} \left[1 + a \frac{5\pi}{72} s + \left(\frac{5}{27} + a^2 \frac{27}{91} \frac{\pi^2 - 4}{64} \right) s^2 \right. \\ &\quad \left. + a \frac{5\pi}{36} s^3 + O(|\nabla n|^4) \right] \\ &= \int d\mathbf{r} \tau^{\text{TF}} [1 + 0.0131s + 0.18528s^2 + 0.0262s^3]. \end{aligned} \quad (20)$$

Note that in Eq. (20) only terms up to s^3 are considered [terms in Eq. (17) proportional to q or q^2 are neglected, as these terms will correspond to s^4].

As shown in Table II, LGAP-GE gives a very accurate large- Z expansion, having the c_2 coefficient close to exact. The results for noble atoms are reported in Table I. LGAP-GE is reasonably accurate for all atoms and, as expected due to the inclusion of the semiclassical atom theory, the accuracy increases with the number of electrons.

One additional observation is that LGAP-GE contains odd powers of the reduced gradient, in contrast with F^{Lind4} . Nevertheless, Ou-Yang and Levy have already shown that, using nonuniform coordinates scaling requirements [85], the GE4 terms in the KE gradient expansion can be replaced by an s -only dependent term [86], the coefficient of which must be positive (and was fitted to the Xe atom). The resulting simple KE functional, that behaves better than GE4 for the nonuniform density scaling, has the following enhancement factor ($F_s = \tau^{\text{approx}} / \tau^{\text{TF}}$):

$$F_s^{\text{OL1}} = 1 + \frac{5}{27} s^2 + cs, \quad (21)$$

with $c = 0.01459$ being slightly bigger than its LGAP-GE counterpart. Anyway, we need to acknowledge that, since the kinetic potential of a GGA functional (with the enhancement factor F_s) has the general form

$$\frac{\delta T_s}{\delta n} = \frac{\partial \tau^{\text{TF}}}{\partial n} F_s(s) + \tau^{\text{TF}} \frac{\partial F_s}{\partial s} \frac{\partial s}{\partial n} - \nabla \cdot \left[\frac{1}{s} \frac{\partial F_s}{\partial s} \cdot \frac{\nabla n}{n^{8/3}} \right], \quad (22)$$

a necessary condition for it to be well defined is $|\frac{1}{s} \frac{\partial F_s}{\partial s}| < \infty$. This is not satisfied by the LGAP-GE (and OL1). Thus, the term $\propto s$ gives a diverging kinetic potential ($\delta T_s / \delta n \rightarrow \infty$) at $s = 0$. This is due to the high nonlocality of Eq. (17), which was not fully suppressed by the local gap model of Eq. (18) with $m = 2$. Note that this divergence is a direct consequence of the jellium-with-gap theory. Nevertheless, for molecular systems $s = 0$ only at the middle of bonds, and it has been found that this divergence is not important in real calculations of weakly bounded molecular systems [87]. In fact, the same problem is shared by other well-known KE functionals [45,86,88].

III. KINETIC-ENERGY FUNCTIONAL CONSTRUCTED FROM THE LGAP GRADIENT EXPANSION

A. The LGAP GGA

To show the importance of the LGAP-GE, we construct a simple GGA functional (named LGAP-GGA or simply LGAP) that recovers the LGAP-GE in the slowly varying density regime. We consider the RPBE exchange enhancement factor form [89], $F_x^{\text{RPBE}} = 1 + \kappa(1 - e^{-\mu_s^2/\kappa})$, and we fix $\kappa = 0.8$ from the Lieb-Oxford bound [90], using the approximate link between the kinetic and exchange energies (i.e., the *conjointness conjecture* [41,91,92]). Note that, to our knowledge, the RPBE functional form has not been yet used in the development of kinetic functionals. The LGAP kinetic enhancement factor is therefore defined as

$$F_s^{\text{LGAP}} = 1 + \kappa(1 - e^{-\mu_1 s - \mu_2 s^2 - \mu_3 s^3}), \quad (23)$$

where $\mu_1 = b_1/\kappa$, $\mu_2 = b_2/\kappa + \mu_1^2/2$, and $\mu_3 = b_3/\kappa + \mu_1\mu_2 - \mu_1^3/6$, such that it recovers the LGAP-GE in the slowly varying density limit. Here $b_1 = 0.0131$, $b_2 = 0.18528$, and $b_3 = 0.0262$ [see Eq. (20)].

B. The kinetic-energy benchmark

In order to assess the LGAP KE functional, we consider several known tests.

For total KE, we have the following.

(1) The benchmark set of atoms and ions [42,44,93]. All calculations employed analytic Hartree-Fock orbitals and densities [94].

(2) The Na jellium clusters ($r_s = 3.93$) set with magic electron numbers 2, 8, 18, 20, 34, 40, 58, 92, and 106, used in Refs. [42,44,93]. We use exact exchange orbitals and densities.

(3) The set of two interacting jellium slabs at different distances [44]. Each jellium slab has $r_s = 3$ and a thickness of $2\lambda_F$. Here $\lambda_F = 2\pi/k_F$ is the Fermi wavelength. The calculations were performed using the orbitals and densities resulting from numerical Kohn-Sham calculations within the local-density approximation [3] for the XC functional.

(4) The set of molecules (H_2 , HF, H_2O , CH_4 , NH_3 , CO, F_2 , HCN, N_2 , CN, NO, and O_2) used in Refs. [44,93,95]. The noninteracting kinetic energies of test molecules were calculated using the PROAIMV code [96]. The required Kohn-Sham orbitals were obtained by Kohn-Sham calculations performed with the uncontracted 6-311 + $G(3df,2p)$ basis set, the Becke 1988 exchange functional [81], and the Perdew-Wang correlation functional [97].

For KE differences, we have (1) the disintegration kinetic energy (DKE) of a jellium cluster [44,98]; (2) the jellium surfaces test with bulk parameter $r_s = 2, 4$, and 6 into the liquid drop model (LDM), as in Refs. [42,44,93]; (3) the dissociation KE (dKE) of a jellium slab into two pieces (as in Ref. [44]); and (4) the atomization KE (AKE) of molecules [44,93,95].

For nonadditive KE, we employ the LGAP functional in subsystem DFT calculations, using the TURBOMOLE [99] program, together with FDE script [100]. The FDE calculations have been performed with a supermolecular def2-TZVPPD [101,102] basis set and the Perdew-Burke-

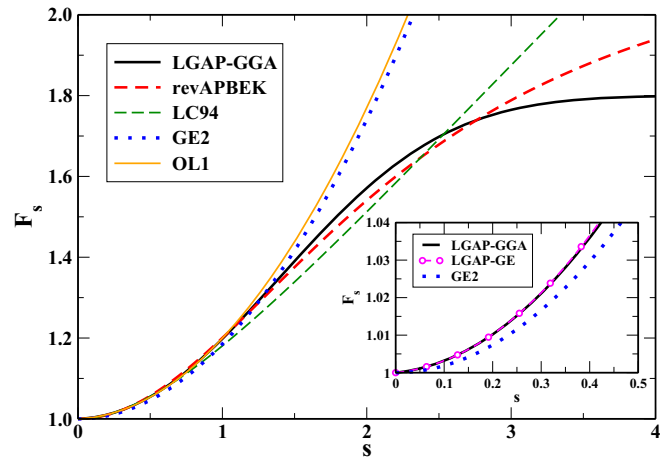


FIG. 2. Comparison of kinetic enhancement factors.

Ernzerhof [103] XC functional. Five weakly interacting groups of molecular complexes are considered as a benchmark [42,44,84,104–107]: WI, weak interaction [He-Ne , He-Ar , Ne_2 , Ne-Ar , $\text{CH}_4\text{-Ne}$, $\text{C}_6\text{H}_6\text{-Ne}$, $(\text{CH}_4)_2$]; DI, dipole-dipole interaction [$(\text{H}_2\text{S})_2$, $(\text{HCl})_2$, $\text{H}_2\text{S-HCl}$, $\text{CH}_3\text{Cl-HCl}$, $\text{CH}_3\text{SH-HCN}$, $\text{CH}_3\text{SH-HCl}$]; HB, hydrogen bond [$(\text{NH}_3)_2$, $(\text{HF})_2$, $(\text{H}_2\text{O})_2$, HF-HCN , $(\text{HCONH}_2)_2$, $(\text{HCOOH})_2$]; DHB, double hydrogen bond (AlH-HCl , AlH-HF , LiH-HCl , LiH-HF , $\text{MgH}_2\text{-HCl}$, $\text{MgH}_2\text{-HF}$, $\text{BeH}_2\text{-HCl}$, $\text{BeH}_2\text{-HF}$); CT, charge transfer ($\text{NF}_3\text{-HCN}$, $\text{C}_2\text{H}_4\text{-F}_2$, $\text{NF}_3\text{-HCN}$, $\text{C}_2\text{H}_4\text{-Cl}_2$, $\text{NH}_3\text{-F}_2$, $\text{NH}_3\text{-ClF}$, $\text{NF}_3\text{-HF}$, $\text{C}_2\text{H}_2\text{-ClF}$, HCN-ClF , $\text{NH}_3\text{-Cl}_2$, $\text{H}_2\text{O-ClF}$, $\text{NH}_3\text{-ClF}$).

C. Results

We compare our results with revAPBEk [41] and LC94 [108] GGAs, which are considered state-of-the-art KE functionals for FDE [42], as well as with GE2 [53,55] and OL1 [86]. The KE enhancement factors of the considered functionals are reported in Fig. 2. In the inset of Fig. 2, we show that LGAP and LGAP-GE are identical (by construction) at relatively small values of the reduced gradient ($0 \leq s \leq 0.5$), both differing significantly from the GE2 behavior. Consequently, LGAP shows a bigger enhancement factor than both LC94 and revAPBEk (i.e., $F_s^{\text{LGAP}} \gg F_s^{\text{revAPBEk}} \gg F_s^{\text{LC94}}$) when $s \leq 2.5$. Such a feature has been proved to be essential for jellium surfaces [109]. On the other hand, the LGAP enhancement factor recovers its maximum value $F_s \rightarrow 1 + \kappa$ at $s \approx 3$, faster than revAPBEk.

In Table III we report the numerical results of all the tests. For total KE tests, LGAP gives the best overall performance, among the considered functionals, being the best for jellium clusters, jellium slabs, and molecules. For KE differences LGAP is the most accurate for jellium surfaces and dissociation KE of jellium slabs. We also mention that LGAP performs reasonably well for all the other tests, being in line with revAPBEk.

Finally, LGAP outperforms the other functionals for the FDE theory, being especially accurate for dipole-dipole, dihydrogen bond, and charge-transfer interactions. These latter results show that, in agreement with the finding of Ref. [87],

TABLE III. Mean absolute relative errors (MARE) of the non-self-consistent benchmark tests, and mean absolute errors (MAE in millihartree) of FDE self-consistent tests, given by several KE functionals. The best result of each group is highlighted in bold style.

	GE2	revAPBek	OL1	LC94	LGAP
Total KE (non-self-consistent calculations)					
Atoms and ions	1.1	1.2	1.1	0.8	1.1
Jellium clusters	1.0	0.8	1.0	0.9	0.8
Jellium slabs	0.6	0.5	0.5	0.5	0.4
Molecules	0.9	0.4	0.7	0.5	0.2
KE differences (non-self-consistent calculations)					
Jellium cluster DKE	27.2	23.1	28.9	21.3	22.6
Jellium surfaces	3.3	3.6	3.4	3.8	3.1
Jellium slabs dKE	5.0	3.5	4.7	4.1	3.4
Molecules AKE	184	155	185	154	159
FDE results for molecular systems ^a (self-consistent calculations)					
Weak interactions (WI)	2.46	0.13	2.49	0.36	0.21
Dipole interactions (DI)	6.48	0.48	6.59	0.67	0.45
Hydrogen bonds (HB)	10.68	1.27	10.90	1.34	1.69
Dihydrogen bonds (DHB)	4.39	3.08	4.50	2.92	2.58
Charge transfer (CT)	5.05	2.61	6.94	2.79	1.95
MAE FDE	5.66	1.72	6.31	1.82	1.50

^aEmbedding energy errors $\Delta E = E^{\text{FDE}} - E^{\text{KS}}$ (in millihartree) for different KE functionals and complexes. In the last line, the mean absolute error (MAE) is reported.

the divergence at $s = 0$ of the LGAP kinetic potential is not important for calculations of weakly bounded molecular systems. Moreover, results indicate that the LGAP-GE gradient expansion can be successfully used in the kinetic-energy functional construction, which performs relatively well in FDE theory.

IV. CONCLUSIONS

In conclusion, we have investigated the linear response of the jellium-with-gap model, in the context of semilocal kinetic functionals. We have shown that the Levine and Louie [33] analytical generalization of the Lindhard function (F^{GAP}) contains important physics beyond the jellium model, and in particular we mention the following properties:

(i) F^{GAP} recovers the Lindhard function when the band gap is zero (i.e., $E_g = 0$).

(ii) F^{GAP} has the correct behavior [see Eq. (4)] at small wave vectors, expressing the material-dependent constant b in terms of the band gap.

(iii) In the regime of small band-gap energy (i.e., $E_g \leq E_F$, with E_F being the Fermi energy), F^{GAP} gives the GAP4 gradient expansion of the kinetic energy [see Eq. (17)], which is band-gap dependent, and performs remarkably well in the atomic regions where the density varies slowly, improving over T_s^{Lind4} of Eq. (7) (see Table I).

These features show that F^{GAP} should be further investigated and exploited in the field of nonlocal kinetic functionals [9,20–24,27,28,110–116], and we would like to address this important issue in further work.

Finally, by considering a local band-gap model, and a simple enhancement factor form, we have constructed the nonempirical LGAP GGA kinetic-energy functional, derived from the linear response of the jellium-with-gap model (i.e., the GAP4 gradient expansion). This functional showed the best performance in the context of FDE theory. Thus, it can be further used in real applications.

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| <p>[1] R. G. Parr and W. Yang, <i>Density-Functional Theory of Atoms and Molecules</i> (Oxford University Press, Oxford, 1989).</p> <p>[2] R. M. Dreizler and E. K. U. Gross, <i>Density Functional Theory</i> (Springer, New York, 1990).</p> <p>[3] W. Kohn and L. J. Sham, <i>Phys. Rev.</i> 140, A1133 (1965).</p> <p>[4] W. Yang, <i>Phys. Rev. Lett.</i> 66, 1438 (1991).</p> <p>[5] S. Goedecker, <i>Rev. Mod. Phys.</i> 71, 1085 (1999).</p> <p>[6] D. R. Bowler, T. Miyazaki, and M. J. Gillan, <i>J. Phys.: Condens. Matter</i> 14, 2781 (2002).</p> <p>[7] J. Kussmann, M. Beer, and C. Ochsenfeld, <i>Wiley Interdiscip. Rev.: Computat. Mol. Sci.</i> 3, 614 (2013).</p> <p>[8] E. Smargiassi and P. A. Madden, <i>Phys. Rev. B</i> 49, 5220 (1994).</p> <p>[9] Y. A. Wang and E. A. Carter, in <i>Theoretical Methods in Condensed Phase Chemistry</i> (Springer, New York, 2002), pp. 117–184.</p> <p>[10] V. Gavini, K. Bhattacharya, and M. Ortiz, <i>J. Mech. Phys. Sol.</i> 55, 697 (2007).</p> <p>[11] T. A. Wesolowski and Y. A. Wang, <i>Recent Progress in Orbital-Free Density Functional Theory</i> (World Scientific, Singapore, 2013).</p> | <p>[12] M. Chen, X.-W. Jiang, H. Zhuang, L.-W. Wang, and E. A. Carter, <i>J. Chem. Theor. Comput.</i> 12, 2950 (2016).</p> <p>[13] P. Cortona, <i>Phys. Rev. B</i> 44, 8454 (1991).</p> <p>[14] T. A. Wesolowski, in <i>Chemistry: Reviews of Current Trends</i>, edited by J. Leszczynski (World Scientific, Singapore, 2006), Vol. 10, pp. 1–82.</p> <p>[15] A. Krishtal, D. Sinha, A. Genova, and M. Pavanello, <i>J. Phys.: Condens. Matter</i> 27, 183202 (2015).</p> <p>[16] T. A. Wesolowski, S. Shedge, and X. Zhou, <i>Chem. Rev.</i> 115, 5891 (2015).</p> <p>[17] V. Karasiev and S. Trickey, <i>Comput. Phys. Commun.</i> 183, 2519 (2012).</p> <p>[18] J. Xia, C. Huang, I. Shin, and E. A. Carter, <i>J. Chem. Phys.</i> 136, 084102 (2012).</p> <p>[19] J. M. G. Lastra, J. W. Kaminski, and T. A. Wesolowski, <i>J. Chem. Phys.</i> 129, 074107 (2008).</p> <p>[20] Y. A. Wang, N. Govind, and E. A. Carter, <i>Phys. Rev. B</i> 58, 13465 (1998).</p> <p>[21] G. S. Ho, V. L. Lignères, and E. A. Carter, <i>Phys. Rev. B</i> 78, 045105 (2008).</p> |
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- [22] P. García-González, J. E. Alvarellos, and E. Chacón, *Phys. Rev. B* **53**, 9509 (1996).
- [23] P. García-González, J. E. Alvarellos, and E. Chacón, *Phys. Rev. B* **57**, 4857 (1998).
- [24] D. Garcia-Aldea and J. E. Alvarellos, *Phys. Rev. A* **77**, 022502 (2008).
- [25] J. Lindhard, Kgl. Danske Videnskab. Selskab Mat.-Fys. Medd. **28**, 8 (1954).
- [26] R. M. Pick, M. H. Cohen, and R. M. Martin, *Phys. Rev. B* **1**, 910 (1970).
- [27] C. Huang and E. A. Carter, *Phys. Rev. B* **81**, 045206 (2010).
- [28] I. Shin and E. A. Carter, *J. Chem. Phys.* **140**, 18A531 (2014).
- [29] J. Rey and A. Savin, *Int. J. Quantum Chem.* **69**, 581 (1998).
- [30] J. Callaway, *Phys. Rev.* **116**, 1368 (1959).
- [31] D. R. Penn, *Phys. Rev.* **128**, 2093 (1962).
- [32] G. Srinivasan, *Phys. Rev.* **178**, 1244 (1969).
- [33] Z. H. Levine and S. G. Louie, *Phys. Rev. B* **25**, 6310 (1982).
- [34] A. Tsolakidis, E. L. Shirley, and R. M. Martin, *Phys. Rev. B* **69**, 035104 (2004).
- [35] P. E. Trevisanutto, A. Terentjevs, L. A. Constantin, V. Olevano, and F. Della Sala, *Phys. Rev. B* **87**, 205143 (2013).
- [36] J. B. Krieger, J. Chen, G. J. Iafrate, and A. Savin, in *Electron Correlations and Materials Properties* (Springer, New York, 1999), pp. 463–477.
- [37] J. B. Krieger, J. Chen, and S. Kurth, *AIP Conf. Proc.* **577**, 48 (2001).
- [38] J. Toulouse, A. Savin, and C. Adamo, *J. Chem. Phys.* **117**, 10465 (2002).
- [39] J. Toulouse and C. Adamo, *Chem. Phys. Lett.* **362**, 72 (2002).
- [40] E. Fabiano, P. E. Trevisanutto, A. Terentjevs, and L. A. Constantin, *J. Chem. Theor. Comput.* **10**, 2016 (2014).
- [41] L. A. Constantin, E. Fabiano, S. Laricchia, and F. Della Sala, *Phys. Rev. Lett.* **106**, 186406 (2011).
- [42] S. Laricchia, E. Fabiano, L. Constantin, and F. Della Sala, *J. Chem. Theor. Comput.* **7**, 2439 (2011).
- [43] V. V. Karasiev, D. Chakraborty, O. A. Shukruto, and S. B. Trickey, *Phys. Rev. B* **88**, 161108 (2013).
- [44] S. Laricchia, L. A. Constantin, E. Fabiano, and F. Della Sala, *J. Chem. Theor. Comput.* **10**, 164 (2013).
- [45] A. Borgoo and D. J. Tozer, *J. Chem. Theor. Comput.* **9**, 2250 (2013).
- [46] A. Borgoo, J. A. Green, and D. J. Tozer, *J. Chem. Theor. Comput.* **10**, 5338 (2014).
- [47] A. Lindmaa, A. E. Mattsson, and R. Armiento, *Phys. Rev. B* **90**, 075139 (2014).
- [48] F. Della Sala, E. Fabiano, and L. A. Constantin, *Phys. Rev. B* **91**, 035126 (2015).
- [49] A. C. Cancio, D. Stewart, and A. Kuna, *J. Chem. Phys.* **144**, 084107 (2016).
- [50] S. Śmiga, E. Fabiano, L. A. Constantin, and F. Della Sala, *J. Chem. Phys.* **146**, 064105 (2017).
- [51] L. H. Thomas, in *Mathematical Proceedings of the Cambridge Philosophical Society* (Cambridge University Press, Cambridge, 1927), Vol. 23, pp. 542–548.
- [52] E. Fermi, *Rend. Accad. Naz. Lincei* **6**, 32 (1927).
- [53] D. Kirzhnits, *Sov. Phys. JETP* **5**, 64 (1957).
- [54] C. Hodges, *Can. J. Phys.* **51**, 1428 (1973).
- [55] M. Brack, B. Jennings, and Y. Chu, *Phys. Lett. B* **65**, 1 (1976).
- [56] K. Burke, J. Werschnik, and E. Gross, *J. Chem. Phys.* **123**, 062206 (2005).
- [57] L. A. Constantin and J. M. Pitarke, *Phys. Rev. B* **75**, 245127 (2007).
- [58] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).
- [59] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, L. A. Constantin, and J. Sun, *Phys. Rev. Lett.* **103**, 026403 (2009).
- [60] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, L. A. Constantin, and J. Sun, *Phys. Rev. Lett.* **106**, 179902(E) (2011).
- [61] L. A. Constantin, E. Fabiano, and F. Della Sala, *J. Chem. Theor. Comput.* **9**, 2256 (2013).
- [62] L. A. Constantin, E. Fabiano, and F. Della Sala, *Phys. Rev. B* **88**, 125112 (2013).
- [63] L. A. Constantin, E. Fabiano, J. M. Pitarke, and F. Della Sala, *Phys. Rev. B* **93**, 115127 (2016).
- [64] J. M. del Campo, J. L. Gázquez, S. Trickey, and A. Vela, *Chem. Phys. Lett.* **543**, 179 (2012).
- [65] V. U. Nazarov and G. Vignale, *Phys. Rev. Lett.* **107**, 216402 (2011).
- [66] S. Karimi and C. A. Ullrich, *Phys. Rev. B* **90**, 245304 (2014).
- [67] J. Tao, J. P. Perdew, L. M. Almeida, C. Fiolhais, and S. Kümmel, *Phys. Rev. B* **77**, 245107 (2008).
- [68] E. Engel and S. H. Vosko, *Phys. Rev. A* **47**, 2800 (1993).
- [69] E. Engel, in *A Primer in Density Functional Theory* (Springer, New York, 2003), pp. 56–122.
- [70] L. A. Constantin, A. Terentjevs, F. Della Sala, P. Cortona, and E. Fabiano, *Phys. Rev. B* **93**, 045126 (2016).
- [71] J. M. C. Scott, *Philos. Mag. J. Sci.* **43**, 859 (1952).
- [72] J. Schwinger, *Phys. Rev. A* **22**, 1827 (1980).
- [73] J. Schwinger, *Phys. Rev. A* **24**, 2353 (1981).
- [74] B.-G. Englert and J. Schwinger, *Phys. Rev. A* **29**, 2339 (1984).
- [75] B.-G. Englert and J. Schwinger, *Phys. Rev. A* **32**, 26 (1985).
- [76] P. Elliott, D. Lee, A. Cangi, and K. Burke, *Phys. Rev. Lett.* **100**, 256406 (2008).
- [77] D. Lee, L. A. Constantin, J. P. Perdew, and K. Burke, *J. Chem. Phys.* **130**, 034107 (2009).
- [78] E. Fabiano and L. A. Constantin, *Phys. Rev. A* **87**, 012511 (2013).
- [79] J. Sun, A. Ruzsinszky, and J. P. Perdew, *Phys. Rev. Lett.* **115**, 036402 (2015).
- [80] J. Sun, J. P. Perdew, and A. Ruzsinszky, *Proc. Natl. Acad. Sci. USA* **112**, 685 (2015).
- [81] A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- [82] A. C. Cancio, C. E. Wagner, and S. A. Wood, *Int. J. Quantum Chem.* **112**, 3796 (2012).
- [83] A. C. Cancio and J. J. Redd, *arXiv:1605.07751* (2016).
- [84] S. Śmiga, E. Fabiano, S. Laricchia, L. A. Constantin, and F. Della Sala, *J. Chem. Phys.* **142**, 154121 (2015).
- [85] HuiOu-Yang and M. Levy, *Phys. Rev. A* **42**, 155 (1990).
- [86] H. Ou-Yang and M. Levy, *Int. J. Quantum Chem.* **40**, 379 (1991).
- [87] A. W. Gotz, S. M. Beyhan, and L. Visscher, *J. Chem. Theor. Comput.* **5**, 3161 (2009).
- [88] A. J. Thakkar, *Phys. Rev. A* **46**, 6920 (1992).
- [89] B. Hammer, L. B. Hansen, and J. K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999).
- [90] E. H. Lieb and S. Oxford, *Int. J. Quantum Chem.* **19**, 427 (1981).
- [91] H. Lee, C. Lee, and R. G. Parr, *Phys. Rev. A* **44**, 768 (1991).

- [92] N. March and R. Santamaria, *Int. J. Quantum Chem.* **39**, 585 (1991).
- [93] J. P. Perdew and L. A. Constantin, *Phys. Rev. B* **75**, 155109 (2007).
- [94] E. Clementi and C. Roetti, *Atom. Data Nucl. Data Tables* **14**, 177 (1974).
- [95] S. S. Iyengar, M. Ernzerhof, S. N. Maximoff, and G. E. Scuseria, *Phys. Rev. A* **63**, 052508 (2001).
- [96] F. W. Biegler-König, R. F. W. Bader, and T.-H. Tang, *J. Comput. Chem.* **13**, 317 (1982).
- [97] J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- [98] L. A. Constantin and A. Ruzsinszky, *Phys. Rev. B* **79**, 115117 (2009).
- [99] TURBOMOLE ver. 6.2, 2009, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- [100] S. Laricchia, E. Fabiano, and F. Della Sala, *J. Chem. Phys.* **133**, 164111 (2010).
- [101] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- [102] D. Rappoport and F. Furche, *J. Chem. Phys.* **133**, 134105 (2010).
- [103] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [104] S. Laricchia, E. Fabiano, and F. Della Sala, *Chem. Phys. Lett.* **518**, 114 (2011).
- [105] S. Laricchia, E. Fabiano, and F. Della Sala, *J. Chem. Phys.* **137**, 014102 (2012).
- [106] S. Laricchia, E. Fabiano, and F. Della Sala, *J. Chem. Phys.* **138**, 124112 (2013).
- [107] E. Fabiano, L. A. Constantin, and F. Della Sala, *J. Chem. Theor. Comput.* **10**, 3151 (2014).
- [108] A. Lembarki and H. Chermette, *Phys. Rev. A* **50**, 5328 (1994).
- [109] L. Vitos, B. Johansson, J. Kollár, and H. L. Skriver, *Phys. Rev. A* **61**, 052511 (2000).
- [110] J. A. Alonso and L. A. Girifalco, *Phys. Rev. B* **17**, 3735 (1978).
- [111] E. Chacón, J. E. Alvarillos, and P. Tarazona, *Phys. Rev. B* **32**, 7868 (1985).
- [112] V. V. Karasiev, D. Chakraborty, and S. B. Trickey, in *Many-Electron Approaches in Physics, Chemistry and Mathematics* (Springer, New York, 2014), pp. 113–134.
- [113] V. V. Karasiev, T. Sjöström, and S. B. Trickey, *Comput. Phys. Commun.* **185**, 3240 (2014).
- [114] V. V. Karasiev and S. B. Trickey, *Adv. Quantum Chem.* **71**, 221 (2015).
- [115] A. Cangi, D. Lee, P. Elliott, and K. Burke, *Phys. Rev. B* **81**, 235128 (2010).
- [116] R. F. Ribeiro and K. Burke, *Phys. Rev. B* **95**, 115115 (2017).