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Semilocal kinetic energy functionals with parameters from neutral atoms

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We present a generalized gradient approximation kinetic energy functional family with a simple rational form and nonempirical parameter derived from the semiclassical energy expansion of neutral atoms. The family unifies the Pauli-enhancement-factor-based semilocal noninteracting kinetic energy functionals (known as Pauli functionals) that achieve good, balanced accuracy with respect to metallic and semiconductor systems. We show that these functionals' performance can be understood in terms of the small- s expansion, where s is the reduced density gradient. We derive Pauli functional parameters from the large- Z kinetic energy limits of neutral atoms, which prevents overfitting to bulk systems. These results spotlight the current state of the art for semilocal kinetic energy functionals. For the next generation of functionals, including more constraints and variables, these results would allow to fix second-order coefficients nonempirically and concentrate on exploring next-order terms in the small- s expansion.

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I. INTRODUCTION

Orbital-free density functional theory (OFDFT) is a density functional theory [1] that treats total energy as an explicit functional of density. This is in contrast to the Kohn-Sham (KS) scheme [2], which requires a noninteracting orbital ansatz. OFDFT only requires solving one pseudo-orbital (density's square root [3]), while KS orbitals require solving the entire eigensystem, which scales cubically in the number of electrons, N_e^3 . OFDFT enables much larger and faster *ab initio* molecular dynamics (AIMD) calculations [4] which can be used to simulate liquid metals and warm dense-matter systems when coupled with appropriate high-temperature corrections.

OFDFT's applicability is restricted by the kinetic energy functionals' accuracy that replaces the orbital-based KS kinetic energy expression. Current research proposes two types of kinetic energy functionals: Semilocal one-point functionals and two-point functionals. The energy density τ of semilocal functionals depends only on the density and its derivatives at one spatial point. In two-point functionals, though, the energy density τ depends explicitly on density at two spatially separated points.

Semilocal functionals are faster and, so far, attain broader applicability than two-point functionals although two-point functionals do have better performance within some categories like simple metals. Two recent semilocal Pauli functionals [5,6], for example, attained a low average mean

absolute relative error (MARE) on metals' and semiconductors' general properties.

Because we know the behavior of the exact kinetic energy density functional $T_s[n]$ in certain limits, we approach the problem with constraint-based development. On a generalized gradient approximation (GGA) level, similar to GGA exchange-correlation functionals, some exact constraints are hard to fulfill simultaneously. When constraints conflict with each other it is necessary to choose or modify them. Here we investigate kinetic energies of neutral atoms in a large- Z limit which is a constraint on any universal kinetic functional related to "charge-neutral" scaling [7]. Fulfilling this condition is a hard requirement on a GGA level functional and thus we relax the constraint as detailed in Sec. III.

The large- Z kinetic energy considerations for kinetic energy functionals were first introduced by Lee *et al.* [8]. Two main difficulties appeared. First, simple, one-parameter kinetic functionals were not able to reproduce the large- Z limit of kinetic energies completely. Second, the partial reproduction of the large- Z limit conflicts with second-order gradient expansion of kinetic energy functionals (GE2). Further analysis of such conflict revealed that kinetic functionals that recover the first two terms of the kinetic expansion are more accurate than those that recover GE2 [9] in frozen density embedding calculations. Here we consider the large- Z kinetic energy limit of neutral atoms as a desirable alternative constraint to the second-order gradient expansion constraint for OFDFT kinetic energy functionals. We apply functional parameters resulting from the large- Z limit to bulk systems with pseudopotentials.

We introduce a new functional family RATIONAL^{*p*} that unifies previously obtained results for these simple yet

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powerful semilocal Pauli functionals. We then obtain a relatively low average MARE on bulk properties for state-of-the-art semilocal functionals by finding the functional parameters with large- Z atomic constraints.

II. PAULI FUNCTIONALS

The Pauli term decomposition [10] for kinetic energy is $T_s = T_{vW} + T_\theta$, where T_{vW} is the von Weizsäcker term and T_θ is the Pauli energy. The von Weizsäcker term is $T_{vW} = \int d\mathbf{r} \tau_{TF} \frac{5}{3} s^2$ in terms of the reduced gradient $s = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$ and Thomas-Fermi kinetic energy density $\tau_{TF} = \frac{3}{10} (3\pi^2)^{2/3} n^{5/3}$. For semilocal GGA, the Pauli energy term is written with the help of the Thomas-Fermi kinetic energy density

$$T_\theta = \int d\mathbf{r} \tau_{TF}(\mathbf{r}) F_\theta(s(\mathbf{r})), \quad (1)$$

where $F_\theta(s)$ is the dimensionless Pauli enhancement factor. The enhancement factor ensures that the kinetic energy functional's uniform scaling rules are satisfied automatically [11]. In this paper, we call functionals constructed via this Pauli decomposition *Pauli functionals*.

Our proposed functional (along with two other functionals studied here) are all GGA Pauli functionals that satisfy these exact constraints:

(i) Positivity of the Pauli term $T_\theta \geq 0$ [10]. We impose this by using the more constraining simplification $F_\theta(s) \geq 0$.

(ii) Conjectured Lieb constraint $T_s \leq T_{vW} + T_{TF}$ [12]. For universality, we convert this to the form $F_\theta(s) \leq 1$.

(iii) Decay of the Pauli energy density $\lim_{s \rightarrow \infty} t_\theta = 0$. This is a constraint from many electron atoms, where at the density tail only one orbital dominates and the von Weizsäcker functional is the exact functional [3,13].

(iv) Small- s expansion of F_θ should be of the form $1 - C_2 s^2 + O(s^4)$. This ensures compatibility with the kinetic energy's GE2 [14]. We note that $F_\theta^{\text{GE2}} = 1 - \frac{8}{9} \frac{5}{3} s^2 \sim 1 - 1.48 s^2$.

We note that the constraints are valid for the positive-definitive definition of the Kohn-Sham kinetic energy density $\tau_s^{\text{KS}} = \frac{1}{2} \sum_{i=0}^{N_e} |\nabla \phi_i|^2$, where unit occupancy of each orbital is assumed.

Table I lists the investigated functionals, showing that they are identical to the second order and differing at the fourth order s^4 and beyond in the small- s expansion. The Luo-Karasiev-Trickey (LKT) functional by Luo *et al.* [6] has a parameter that corresponds to the value $C_2 = 0.845$ in the original work, where the main consideration is a balance

TABLE I. Pauli-type GGA functionals, where the functional has been expanded to a fourth order in the third column, small- s expansion.

Name	$F_\theta(s)$	Small- s expansion
LKT	$\cosh^{-1}(\sqrt{2C_2}s)$	$1 - C_2 s^2 + \frac{5}{6} C_2^2 s^4 + O(s^6)$
GAUSS	$\exp(-C_2 s^2)$	$1 - C_2 s^2 + \frac{1}{2} C_2^2 s^4 + O(s^6)$
RATIONAL ^{p}	$(1 + \frac{C_2}{p} s^2)^{-p}$	$1 - C_2 s^2 + (1 + \frac{1}{p}) \frac{1}{2} C_2^2 s^4 + O(s^6)$

between the positive Pauli potential and bulk performance. The GAUSS functional was previously introduced by Constantin *et al.* [5] with the name Pauli-Gaussian (PG). In their work, they performed a parameter scan on the PG with the most important parameters being $C_2 = 1$, a global optimum for bulk systems, and $C_2 = 1.48$, which is compatible with GE2. The functional RATIONAL ^{p} is a new functional in the context of Pauli-type functionals.

As reported in Refs. [5,6], these simple Pauli functionals perform quite well against two-point functionals, and the average MARE over metals and semiconductors is consistently better. Thus, here we focus on deriving parameters for the functionals from exact constraints and understanding the functionals' performance.

We use the RATIONAL ^{p} functional to emulate LKT and GAUSS functionals to the fourth order s^4 in the small- s expansion:

$$\text{RATIONAL}^{p=\frac{3}{2}} = \text{LKT} + O(s^6), \quad (2)$$

$$\lim_{p \rightarrow \infty} \text{RATIONAL}^p = \text{GAUSS} + O(s^6), \quad (3)$$

which are investigated to unify previous results and understand the small- s expansion's behavior at the fourth order. To emulate GAUSS we must choose finite p , and here we choose $p = 16$. Fourth-order s^4 behavior is not known *a priori* in GGA functionals, because the only clues of fourth-order behavior are from fourth-order gradient expansion (GE4) [15], which requires an additional variable (the reduced Laplacian of density q). We emphasize that in the following for each functional family LKT, GAUSS, RATIONAL ^{$p=\frac{3}{2}$} , and RATIONAL ^{$p=16$} we vary only the C_2 coefficient while the functional form stays fixed.

We also refer to the simplest GGA model: The Thomas-Fermi-von Weizsäcker (TF-vW) model:

$$F_\theta^{\text{TF-vW}}(C_2) = 1 - C_2 s^2. \quad (4)$$

The TF-vW functional is a lower-performant functional and does not satisfy constraints (i) and (iii), contrary to the functionals in Table I.

III. FUNCTIONAL PARAMETERS FROM SEMICLASSICAL AVERAGES

A. Introduction

In this section we detail a method to find functional parameters from a semiclassical consideration of model systems. The central concept is the *semiclassical average* which we define to be the smooth part of a quantity as a function of particle number N or atomic number Z . Formally this reads as

$$E(N) = \tilde{E}(N) + \delta E(N), \quad (5)$$

where \tilde{E} is the smooth part and δE is the oscillating part. In general, the smooth part gives the trend of the quantity and is a relatively simple function. The oscillating term depends on the exact quantum effects. For some quantities it is possible to extract the smooth part \tilde{E} completely by semiclassical methods and in some cases it can be extracted from oscillating data. A good example is the total energy of atoms as a function

of atomic number Z ,

$$\tilde{E}^{\text{atomic}}(Z) = -0.7687745Z^{7/3} + 0.5Z^2 - 0.2699Z^{5/3}, \quad (6)$$

which was derived by Schwinger via semiclassical methods [16,17] and later refined by Schwinger and Englert [18–20]. The second example is the ionization potential of atoms [21,22], which was extracted from Hartree-Fock atoms.

In this section we consider semiclassical averages of kinetic energy and use it to find parameters for kinetic functionals. Similar studies have been done in the past. First is Lee *et al.* [8], who investigated Kohn-Sham atoms and gradient expansions of kinetic energy. Later the method was applied to kinetic functionals in the context of frozen embedded density functional theory (DFT) [9].

Semiclassical averages are reproduced by the exact kinetic energy functional; thus they are a constraint on the kinetic energy functional. Then it is desirable to have functionals which do satisfy as many as possible of the constraints on relevant systems.

The section is structured as follows: We first detail how we determine semiclassical averages of the noninteracting isotropic harmonic oscillator as an illustrating example. Then we show how to find parameters by constraining the functionals to reproduce semiclassical averages of a harmonic oscillator. The method is adopted and extended from the original method by Lee *et al.* [8]. Finally we apply the method to obtain parameters for kinetic functionals from Kohn-Sham atoms which do include additional considerations. More details on the method are included in the Supplemental Material [23].

B. Semiclassical averages of a harmonic oscillator

We consider kinetic energies T although the method could apply to any quantity which contains a smooth part. Consider a noninteracting isotropic harmonic oscillator in three dimensions, $V_{\text{ext}} = \frac{1}{2}\omega^2 \mathbf{r}^2$. The smooth part of the total energy is given by

$$\tilde{E}^{\text{harmonic}}(N) = \frac{1}{4}\omega(3N)^{4/3} + \frac{1}{8}\omega(3N)^{2/3}, \quad (7)$$

where N is the particle number. The result can be obtained in multiple ways [24] but a straightforward way is to apply Thomas-Fermi theory to get the first term and apply quantum correction to the Thomas-Fermi result to obtain the second term.

The kinetic energy T^{harmonic} is obtained by applying the virial theorem $T = \frac{1}{2}E$. The analytically known kinetic energies are plotted in Fig. 1, where the smooth part and the oscillations are visible. Expression (7) is a semiclassical average and the smooth part is actually an *envelope* of valid values when we consider finite N .

Expression (7) is therefore not the only possible semiclassical average but there exist multiple equally valid semiclassical averages associated with different subsets of harmonic oscillators. We can study the possible semiclassical averages by extracting the limits: The upper and lower limits from $E(N)$. More quantitatively we can check how much their coefficient values can deviate from those given in (7).

To determine the upper and lower limits we choose harmonic oscillators from the upper and lower bounds of the

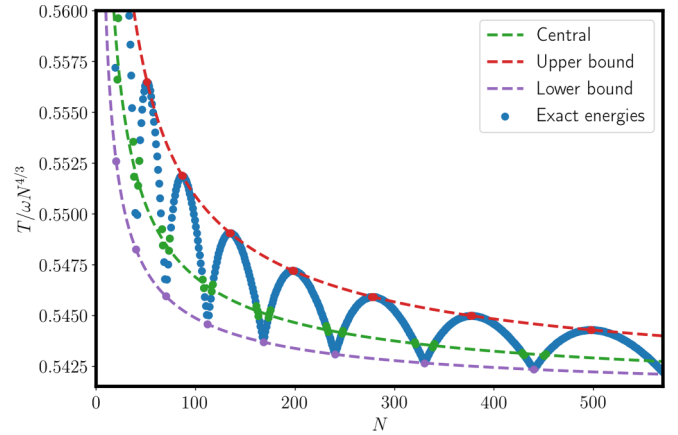


FIG. 1. Kinetic energies of a noninteracting isotropic harmonic oscillator in three dimensions. The central semiclassical average is shown in green and the upper and lower bounds are shown in red and violet. The central semiclassical average corresponds to the kinetic energy series T^{harmonic} (7). The harmonic oscillators chosen for each fit are shown with respective colors.

energy oscillations. We also choose harmonic oscillators where the T^{harmonic} crosses exact results in order to find how faithfully a fit to a finite amount of harmonic oscillators reproduces the semiclassical result. We then do a parabolic least-squares fit to $\frac{T}{N^{4/3}}$ in $N^{-1/3}$ to obtain the coefficients in

$$T_{\text{fit}}^{\text{harmonic}} = a_0 N^{4/3} + a_1 N + a_2 N^{2/3}.$$

The fits obtained from upper and lower limits are appropriately named upper and lower and we refer to the fit obtained from systems near semiclassical series, here T^{harmonic} , as “central.”

The results are shown in Table II. All three fits reproduce the Thomas-Fermi value $a_0 \sim 0.541$ correctly. The central fit reproduces a_2 of T^{harmonic} quite well which is not surprising considering how we chose the systems for the fit. The upper and lower limits show a difference in the a_2 coefficient. Reassuringly all the fits produce nearly zero a_1 value.

The critical notion here is the fact that the coefficient a_2 can actually have a value within the range (0.22, 0.08) and all these coefficient values for a_2 produce a reasonable *semiclassical average*. We apply the semiclassical averages

TABLE II. Semiclassical averages for harmonic oscillator and Kohn-Sham atoms. For more details see text.

	a_0	a_1	a_2
<i>Harmonic oscillator</i>			
T^{harmonic}	0.5408	0.0000	0.1300
Upper	0.5409	−0.0001	0.2157
Central	0.5407	0.0008	0.1327
Lower	0.5408	0.0000	0.0866
<i>Kohn-Sham atom</i>			
T^{atomic}	0.7688	−0.5000	0.2699
Upper		−0.5002	0.2586
Central		−0.5000	0.2699
Lower		−0.5015	0.2799

TABLE III. Thomas-Fermi–von Weizsäcker model coefficients and fits for the three different semiclassical averages.

	TF-vW			
	C_2	a_0	a_1	a_2
Upper	1.149	0.5404	0.0182	0.2157
Central	1.032	0.5381	0.0477	0.2600
Lower	1.489	0.5405	0.0068	0.0866

as a constraint on kinetic energy functionals to find values for free parameters.

C. Constraining kinetic functionals to reproduce semiclassical average of harmonic oscillator

Ideally the kinetic energy functional would satisfy fully the constraint imposed by semiclassical averages by reproducing the correct oscillations. We use a more relaxed condition: The kinetic energy functional should reproduce a semiclassical average, not necessarily all of them.

We now detail the method of fitting functional parameters to a semiclassical average, which is a variant of the method presented by Lee *et al.* [8]:

(1) Find a semiclassical average: Choose a set of systems $\{N_i\}$ and find the semiclassical average of the kinetic energies $T_{\text{fit}}(\{N_i\})$.

(2) Use the densities of those same systems to evaluate the kinetic energy functional $T_s^\alpha[n]$ non-self-consistently (perturbatively), where α is the functional parameter to be adjusted. Then adjust parameter α until $T_{\text{fit}}^\alpha(\{N_i\})$ and $T_{\text{fit}}(\{N_i\})$ agree to the desired accuracy.

We can apply the above procedure to all semiclassical averages we can find. Naturally the central case and the limiting values hold the most interest. By fitting parameters to multiple semiclassical averages we address two issues: (i) from the semiclassical point of view multiple parameter values are valid and (ii) the densities contain shell oscillations which might affect the results from the kinetic energy functional. The second point is sensitivity analysis: How sensitive the functional parameter is to the choice of systems $\{N_i\}$. By using multiple semiclassical averages the method estimates how large of variations the shell effects can induce in the functional parameters.

We return to the harmonic oscillator example. We apply the method to the three semiclassical averages upper, central, and/lower in Table II to find the range of functional parameters. Results for the procedure with the TF-vW kinetic energy functional are shown in Table III. The Thomas-Fermi coefficient a_0 is reproduced within reasonable accuracy. The variation in the C_2 parameter is quite large, ~ 0.5 . There is discrepancy between the analytical derivation and the parameters found from fitting. Analytically the TF-vW functional with $C_2 \sim 1.481$ (GE2) produces (7) [24] but the central semiclassical average produces $C_2 = 1.032$.

As we discussed earlier, for simple functionals, with only one parameter, we have to choose among multiple constraints. In the case of the harmonic oscillator the numerical results for a lower semiclassical average agree with the analytical

considerations so we consider the lower semiclassical average to be the preferred choice as a constraint.

Studied Pauli functionals are unable to reproduce the a_2 coefficients, which shows that some universality is already lost with the functional form which is not surprising due to constraint (iii). We can still check how precisely the Thomas-Fermi coefficient a_0 is reproduced. Remember that constraint (iv) should impose the correct Thomas-Fermi limit. We find that all the Pauli functionals reproduce $a_0 \sim 0.541$ with varying C_2 values. Thus constraint (iv) does agree reasonably well with the semiclassical Thomas-Fermi limit given by T^{harmonic} .

D. Kinetic functional parameters from semiclassical average of Kohn-Sham atoms

We now apply the method to obtain the kinetic functional's parameters from constraining the functionals to reproduce the semiclassical average of Kohn-Sham atoms. Noninteracting atoms are not an option because the quantum correction term of size $Z^{5/3}$ vanishes [22]. We calculate neutral Kohn-Sham atoms with Dirac exchange up to atomic number $Z = 181$ [25]. Following [8] we apply the virial theorem to (6) to obtain

$$T_s^{\text{atomic}} = 0.7687745Z^{7/3} - 0.5Z^2 + 0.2699Z^{5/3} + O(Z^{4/3}) \quad (8)$$

for the Kohn-Sham kinetic energy T_s . We want to use the atomic kinetic energy T_s^{atomic} and the related semiclassical averages as a constraint to find the functional parameters. However, we do not require full reproduction of the semiclassical average but only the coefficient of the last term $Z^{5/3}$. We assume that the first term coefficient is fixed to 0.7687745 due to the limited amount of calculated atoms and we are not interested in the value of the second term for orbital-free kinetic energy functionals because of more fundamental reasons. We discuss both aspects in the following. Instead of the fit introduced in the case of the harmonic oscillator we do a parabolic least squares fit to $\frac{T_s}{Z^{7/3}}$ in $Z^{-1/3}$ to find coefficients of the expression $a_0Z^{7/3} + a_1Z^2 + a_2Z^{5/3}$.

The origin of different terms in (6) is well known: The first is the Thomas-Fermi term $a_0 = 0.7687745$; the second term, $a_1 = 0.5$, the Scott term, is coming from the atomic inner core; and the last term, $a_2 = 0.2699$, is due to the first semiclassical correction to the Thomas-Fermi and Dirac exchange. The first and last terms are similar to the harmonic oscillator case (Thomas-Fermi term and its correction) but there is no equivalent of the Scott term in the harmonic oscillator.

We have only a limited amount of Kohn-Sham atoms available and obtaining the limiting Thomas-Fermi coefficient a_0 is difficult so we follow Lee *et al.* [8,9] and fix $a_0 = 0.7687745$ for all fits. For Kohn-Sham kinetic energies this is not problematic. For kinetic energy functionals we confirmed with harmonic oscillators that constraint (iv) coincides with producing the correct Thomas-Fermi coefficient a_0 in the semiclassical average.

The kinetic energies of Kohn-Sham atoms are shown in Fig. 2. We use similar naming as in the case of the harmonic oscillator: Central refers to the semiclassical average related to T_s^{atomic} (8) and lower and upper refer to the limiting

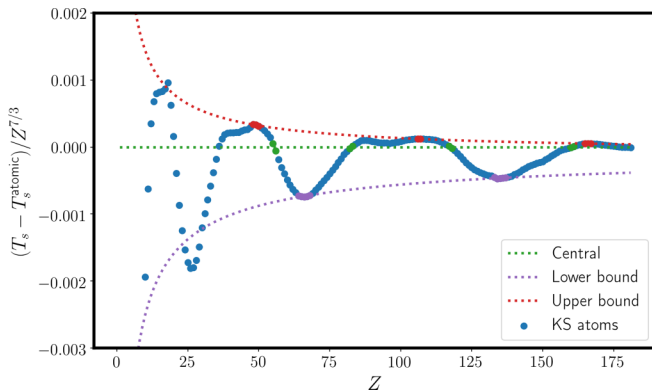


FIG. 2. Kinetic energies of Kohn-Sham atoms with semiclassical averages. The central semiclassical average is shown in green and the lower and upper bounds in violet and red. The central semiclassical average corresponds to the kinetic energy series T^{harmonic} (8). The Kohn-Sham atoms chosen for each fit are shown with respective colors.

semiclassical averages. The resulting semiclassical averages are in Table II. It is reassuring that the a_1 is consistently correct. The variation of a_2 is within the range (0.2586, 0.2799) which is a smaller range than in the harmonic oscillator case. We did not use low- Z atoms ($Z < 40$) to find the semiclassical averages as small- Z oscillations are quite prominent and as a result the lower bound crosses the oscillations at $Z \sim 30$. The discrepancy with the harmonic oscillator case can be attributed to the different treatment of electronic interaction.

We now discuss the Scott term in depth and its implications for our procedure.

1. Atomic inner core

The atomic inner core is the region of the atom where the effective potential is $V \sim \frac{Z}{r}$. The electrons which are mostly in the inner core are called strongly bound electrons (SBEs) [22]. It was shown by Schwinger that this region is unambiguously responsible for the Scott term in the total energy (6).

We also assume that the corresponding Scott term of size Z^2 in the kinetic energy expression (8) is mostly because of strongly bound electrons. This is hard to show directly but there is some supporting evidence.

We apply GGA kinetic functionals to Thomas-Fermi densities, which do not contain SBEs, to obtain a fit where $a_1 \sim 0$. This is a direct consequence of charge-neutral scaling [7]. On the other hand, Thomas-Fermi densities are not usable for detailed GGA analysis due to well-known unphysical behavior near the atomic nucleus. Thus if no SBEs are present in the density then the coefficient a_1 is zero. When applying kinetic energy functionals to realistic atom densities the coefficient a_1 is nonzero.

The typical example of SBEs involves the electrons of the first hydrogenic shell with the density $n_0 = \frac{Z^3}{\pi} e^{-2Zr}$. By applying typical functionals T^{TF} and T^{vW} to n_0 we see that they produce nonzero a_1 : $T^{\text{TF}}[n_0] = \frac{81}{1250}(3\pi)^{2/3}Z^2$ and $T^{\text{vW}}[n_0] = \frac{1}{2}Z^2$. It is in general difficult to point out which orbitals have strongly bound electrons and which do not as the

TABLE IV. Parameter C_2 values for kinetic energy functionals by using semiclassical averages.

$T_s[n]$	Upper	Central	Lower
TF-vW	1.2681	1.2854	1.3364
GAUSS	0.8350	0.8403	0.8852
RATIONAL ^{$p=16$}	0.8261	0.8311	0.8758
LKT	0.7630	0.7659	0.8089
RATIONAL ^{$p=\frac{3}{2}$}	0.7658	0.7687	0.8118

definition of strongly bound electrons is based on the potential and not on the orbitals [22].

The strongly bound electrons are not relevant for pseudopotential applications due to the simple fact that pseudodensities do not contain such electrons. In general it is much easier to use kinetic energy functionals to describe kinetic energies and potentials of densities that vary slowly on the scale of the Fermi wavelength [7], while strongly bound electrons are highly localized near the atomic nucleus. Thus we are not interested in fixing the value of coefficient a_1 when searching for functional parameters. The underlying assumption is that most of the effects coming from strongly bound electrons are contained in the a_1 coefficient.

2. Parameters for Pauli functionals

We apply the fitting procedure to semiclassical averages of atoms in Table II. The results for different functionals are shown in Table IV. There is much smaller variation in the TF-vW functional than in the harmonic oscillator case. Again there is the discrepancy between the analytical derivation $C_2 \sim 1.481$ of (6) and the fitted values $C_2 = 1.2681 \sim 1.3364$. One possible explanation is that including the electronic interaction self-consistently modifies the densities to this degree but such exploration is beyond the scope of this paper.

For Pauli functionals the variation of C_2 values is smooth: $C_2(\text{lower}) > C_2(\text{central}) > C_2(\text{upper})$. The upper and central values are quite close to each other. The similarity in functional forms is seen here: GAUSS results are close to RATIONAL ^{$p=16$} results and similarly LKT and RATIONAL ^{$p=\frac{3}{2}$} results are almost identical.

In the next section we study the bulk performance and we consider only C_2 values from central and lower sets as the central and upper values are practically identical.

IV. PAULI POTENTIAL

Another important, exact constraint on the kinetic energy functional $T_s[n]$ is the Pauli potential's positivity:

$$V_\theta(\mathbf{r}) = \frac{\delta T_\theta[n(\mathbf{r})]}{\delta n(\mathbf{r})} \geq 0. \quad (9)$$

Although it is not included in our initial list of constraints, we are interested in assessing how the functional's quality depends on its satisfaction.

The Pauli potential is an important quantity for self-consistent OFDFT calculations, especially numerically. Violating the exact constraint $v_\theta \geq 0$ can cause convergence

TABLE V. Parameter values for which there is a transition in the Pauli potential of a lithium pseudoatom. Smaller values (than the ones given here) of coefficient C_2 yield a completely positive Pauli potential. The GAUSS is a special case, because it has a small negative region near the nucleus, which we do not take into account in this analysis.

Name	Coefficient C_2
LKT	0.66
GAUSS*	0.66
RATIONAL $^{p=\frac{3}{2}}$	0.66
RATIONAL $^{p=16}$	0.66

problems [26]. Thus, creating a functional with a positive Pauli potential is important for the functional's physicality and convergence. Here, we look only at self-consistent Pauli potentials.

We look at the lithium pseudoatom, which is the most demanding test for a self-consistent Pauli potential out of the elements that have bulk-derived local pseudopotentials (BLPSs) (Li, Mg, Al, In, P, Ga, and As). In our experience, if the Pauli potential's positivity is fulfilled self-consistently for a lithium pseudoatom, then it is fulfilled self-consistently for all pseudoatoms. The exact Pauli potential is zero for a lithium pseudoatom, because it only contains one electron in the valence. All of the chosen functionals have a positive Pauli potential for lithium if the C_2 parameter is chosen below a maximum value shown in Table V.

Figure 3 shows the Pauli potential for an LKT and RATIONAL $^{p=\frac{3}{2}}$ functional with parameter $C_2 = 0.93$. The Pauli potential has a negative feature at $r \sim 1.8$ bohr where the reduced gradient s goes to zero (shown in Fig. 4).

It is comforting that we can tune each of these functional parameters to have a positive Pauli potential. More impor-

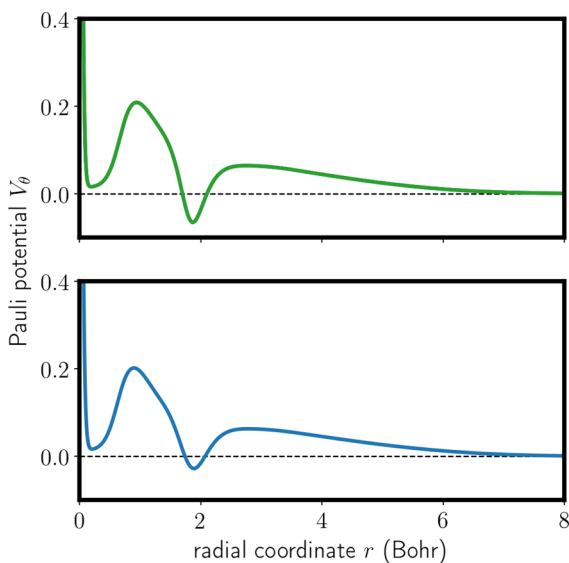


FIG. 3. Top: Self-consistent Pauli potential for a RATIONAL $^{p=\frac{3}{2}}$ functional with $C_2 = 0.93$. Bottom: Self-consistent Pauli potential for an LKT functional with $C_2 = 0.93$. All the functionals in Table V have quite similar Pauli potentials.

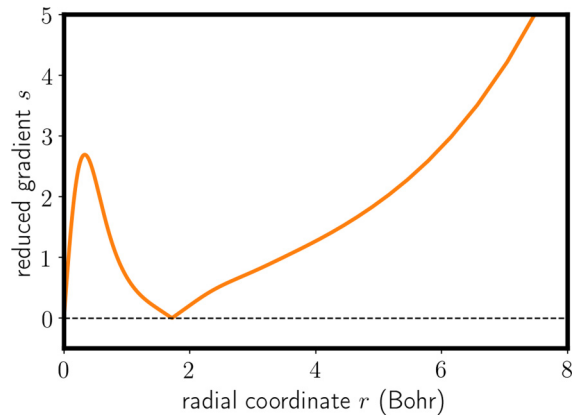


FIG. 4. Reduced gradient s for a lithium pseudoatom calculated with Kohn-Sham with a Perdew-Zunger local density approximation (LDA) and local pseudopotential. The reduced gradient is quite similar in self-consistent functionals.

tantly, even if we do not tune the parameters, the resulting Pauli potential is negative on a very small range of s according to our tests (see Fig. 3).

V. BULK RESULTS

We calculate bulk systems to evaluate the effect of parameter choice on different functionals. Specifically, we calculate the metallic systems Li, Mg, and Al in sc, fcc, bcc, and hcp phases and semiconductor systems GaAs, GaP, GaSb, InAs, InP, InSb, AlAs, AlP, and AlSb in the zincblende phase. We evaluate the equilibrium volume V_0 , energy E_0 , and bulk modulus B against the KS reference from [6,27]. The quantities are obtained by expanding the structures around equilibrium volume by $\pm 10\%$ with 15 points, which are then fitted to a Birch-Murnaghan equation of state. All the calculations use a Perdew-Zunger LDA exchange correlation. We chose two values of C_2 from references for comparison, where $C_2 = 0.85$ corresponds to the LKT parameter $a = 1.3$ in [6], and $C_2 = 1.00$ corresponds to $\mu = 1$ in [5].

We chose a few other C_2 values for comparison: GE2 coefficient $C_2 = 1.48$, C_2 coefficients from central and lower semiclassical averages in Table IV, and $C_2 = 0.66$, which guarantees the Pauli positivity for all pseudoatoms. For all C_2 coefficients, we use two decimals, which are enough to assess the performance. We perform all the calculations with a PROFESS calculator [28] and BLPS [29,30] with a plane-wave cutoff of 1600 eV. Table VI details the best mean average error (MAREs) for metals and semiconductors.

The presented functionals and parameters in Table VI have quite similar performance. It is clear from these results that the C_2 parameters from central and lower semiclassical averages produce competitive results in terms of average MARE for this selection of functionals and parameters. These results validate the relevance of the large- Z expansion (8) for pseudopotential kinetic energy functional development.

Table VI also evaluates the fourth-order coefficient's effect. The functional RATIONAL $^{p=\frac{3}{2}}$ has the same fourth-order coefficient as LKT, which we see in the results: They are practically identical. The functional RATIONAL $^{p=\frac{3}{2}}$ has

TABLE VI. Results for bulk systems for LKT and GAUSS functionals. The column containing C_2 type indicates where we obtained the value. The best mean average error (MARE) is in bold.

Functional	C_2		Metals MARE			Semiconductors MARE			Average (%)
	Type	Value	V0 (%)	E0 (%)	B0 (%)	V0 (%)	E0 (%)	B0 (%)	
LKT	GE2	1.48	7.45	1.16	8.89	1.78	0.95	5.07	4.22
	Reference	0.85	4.02	0.20	7.67	2.08	2.50	4.23	3.45
	Lower	0.81	4.05	0.17	8.08	2.10	2.59	4.44	3.57
	Central	0.77	4.09	0.14	8.58	2.13	2.69	4.70	3.72
	Pauli positivity	0.66	4.02	0.20	7.72	2.08	2.50	4.40	3.49
GAUSS	GE2	1.48	8.30	1.45	13.48	4.22	0.54	14.14	7.02
	Reference	1.00	4.30	0.40	6.19	2.65	2.08	6.73	3.73
	Lower	0.89	3.97	0.33	6.90	2.62	2.25	6.67	3.79
	Central	0.84	3.82	0.28	7.39	2.44	2.38	5.87	3.70
	Pauli positivity	0.66	4.02	0.11	9.60	2.22	2.88	4.85	3.95
RATIONAL ^{$p=16$}	GE2	1.48	7.46	1.15	9.24	1.74	0.96	4.01	4.09
	Reference	1.00	4.51	0.50	5.92	2.93	1.95	8.11	3.99
	Lower	0.88	3.96	0.31	7.02	2.48	2.29	6.02	3.68
	Central	0.83	3.80	0.26	7.52	2.31	2.42	5.19	3.58
	Pauli positivity	0.66	4.04	0.10	9.62	2.22	2.89	4.88	3.96
RATIONAL ^{$p=\frac{3}{2}$}	GE2	1.48	7.46	1.15	9.24	1.74	0.96	4.01	4.09
	Reference	0.85	4.04	0.20	7.67	2.08	2.50	4.25	3.46
	Lower	0.81	4.05	0.17	8.05	2.10	2.58	4.45	3.57
	Central	0.77	4.10	0.14	8.55	2.13	2.69	4.70	3.72
	Pauli Positivity	0.66	4.26	0.10	9.72	2.20	2.99	6.21	4.25

a slightly lower average error for the same C_2 parameter. The corresponding functional for GAUSS, RATIONAL ^{$p=16$} , performs similarly (but not identically) to GAUSS, because $p \rightarrow \infty$ is only approximated. For the average MARE, which is dominated by the error on the bulk modulus, the values from references are slightly better than the semiclassical ones. This is no surprise as the C_2 values from references do include the bulk systems in their consideration for the best coefficient. In this light the semiclassical C_2 parameters do perform quite well. The functional RATIONAL ^{$p=16$} is an exception but the reference value is tuned for GAUSS and not for RATIONAL ^{$p=16$} .

We conclude that the RATIONAL ^{p} functional captures the LKT functionals' behavior. This underscores that most of the performance information on bulk systems already is contained in the fourth-order small- s expansion. GAUSS and RATIONAL ^{$p=16$} have a slightly lower performance on average for MARE, when compared to LKT and RATIONAL ^{$p=\frac{3}{2}$} , mostly because of the higher error on the semiconductors' bulk modulus. During the course of investigation, we studied other values of p , too, but for this test set it seems that $p = \frac{3}{2}$ (and consequently, LKT) are quite optimal.

What is clear from the set is that for Pauli functionals satisfying condition (iii) the coefficient of the fourth-order term in the small- s expansion is more relevant than how exactly $F_\theta(s)$ decays to zero in the limit $s \rightarrow \infty$.

We assess the performance in more detail for each quantity. For semiconductor volumes there is no obvious pattern over all results. For both metals and semiconductors only the GE2 gives differentiation results: Considerably higher error for metals and lower error for semiconductors. The bulk modulus is the most volatile for calculational details but it

is also the most interesting as it probes the flexibility of the functional beyond simple equilibrium volume and its error for metals has minima in the range $C_2 = 0.66$ – 1.48 . The semiconductor bulk modulus also has error minima in the range $C_2 = 0.66$ – 1.48 for LKT and RATIONAL ^{$p=\frac{3}{2}$} but for GAUSS and RATIONAL ^{$p=16$} the error minima seems to have shifted below $C_2 = 0.66$. For energy the pattern is clear: The KS values are reached below $C_2 = 0.66$ for metals and above $C_2 = 1.48$ for semiconductors.

VI. DISCUSSION AND CONCLUSION

Our new family of functionals, RATIONAL ^{p} , captures LKT and GAUSS functionals' behavior. The difference in performance on bulk systems for these functionals is mostly determined by the fourth-order term in the small- s expansion. For functional development, this implies that continued efforts in this direction will involve more variables to improve accuracy, such as a reduced Laplacian q .

Large- Z methodology has been applied in the literature multiple times before, but this is the first time it is applied by explicitly targeting kinetic energy functionals to use with pseudopotentials. We have clarified and extended the method proposed by Lee *et al.* [8]. The concept of the semiclassical average does provide an explanation from a semiclassical perspective of why there are multiple coefficient values for the TF-vW model in the literature [31], even for the same system.

We found the large- Z methodology easy to apply, making it a convenient check for future functionals. It provides another reference system in addition to the bulk system, albeit a non-self-consistent one. We expect that our investigations and

improvements upon the large- Z methodology are useful for future studies.

For future work, a few points do deserve deeper discussion. First, large- Z energies can be derived from GE2. From this viewpoint, the method's applicability as a guideline beyond order $O(s^2)$ in functional development is doubtful. As such, it does serve as a useful tool either to prevent overfitting to bulk systems or to find parameters for a functional. In the current approach, we only roughly account for errors but we do provide an estimate for the variation of C_2 .

The C_2 parameters found from the large- Z method perform quite well considering that they are applied to a bulk environment. While good parameters can be found with numerical minimization of target properties it is reassuring that similar parameters can be found from semiclassical considerations. There is also the subtle promise that parameters obtained via these methods perform well also on properties that are not explicitly targeted.

Overall, simple Pauli functionals do perform well, and, considering their simplicity, they perform excellently. This is especially true for RATIONAL^P, which does not require any special functions. Pauli functionals offer significant improvements, and they are the current state of the art of GGA functionals; here, with the help of Pauli functionals, we shed light on how to find coefficients without overly relying on bulk system performance.

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