Orbital-free kinetic-energy functionals for the nearly free electron gas

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(Received 15 June 1998)

We present an improvement over the Wang-Teter, Perrot, and Smargiassi-Madden kinetic-energy functionals without going beyond linear-response theory and without introducing a density-dependent kernel. The improved functionals were tested on bulk aluminum, and excellent results were obtained. Accurate density-functional calculations using the new functionals on systems larger than one can study by traditional Kohn-Sham methods are demonstrated.

I. INTRODUCTION

The attractive feature of orbital-free (OF) density-functional schemes based on the original Hohenberg-Kohn (HK) theorem is that the computational effort essentially scales linearly \([O(N)]\) with system size. These \([O(N)]\) methods comprise a different group from the orbital-based \([O(N)]\) methods constructed on the traditional Kohn-Sham (KS) scheme. They also offer some benefits over these traditional KS methods. Being purely density based, no orbital localization, no orthonormalization and no Brillouin-zone sampling are required, and hence calculations can be done inexpensively.

However, practical realization of the HK theory requires a full knowledge of all the terms in the total-energy functional. In practice, this has not been possible except for a few model systems (e.g., one-electron systems), and suitable approximations have to be made. Over the years, a number of high-quality exchange-correlation functionals have been developed for all kinds of systems. By comparison, much less has been achieved for the kinetic-energy density functional (KEDF). Although many KEDF’s are available, they lack transferability and cannot be applied with the same merits in different scenarios. For example, the Thomas-Fermi (TF) functional, on the one hand, is only exact at the free-electron gas limit, and produces no binding for any system. The von Weizsäcker (vW) functional, on the other hand, is only exact for one- and two-electron ground-state systems, but fails for any many-electron environment. The conventional gradient expansion (CGE) (Ref. 14) about the uniform gas limit does improve the TF functional, but diverges after the fourth-order for exponentially decaying densities, and produces algebraically decaying densities and no shell structure for atoms. Moreover, these models do not have the correct linear-response (LR) behavior, and hence do not give rise to Friedel oscillations.

There are several KEDF’s (Refs. 1–6) with the correct LR built in. The KEDF’s due to Wang and Teter (WT), Perrot, and Smargiassi and Madden (SM) (Ref. 3) are very accurate for nearly-free-electron-gas-like systems (e.g., simple bulk metals), while more sophisticated ones by Chacón and co-workers and Carter and co-workers are nearly universal. KEDF’s based on higher-order response theories are also available. The only drawback with the universal KEDF’s (Refs. 5 and 6) is that they are computationally expensive, scaling quadratically with grid size. In this sense, the WT, Perrot, and SM KEDF’s are the optimal choices for simple bulk metals. In this paper, we propose a simple improvement over the WT, Perrot, and SM KEDF’s in terms of accuracy, while maintaining their practical efficiency.

II. BACKGROUND

The WT, Perrot, and SM KEDF’s can be conveniently written as

\[
T'_{\alpha}(\rho) = T^\omega_{TF}(\rho) + T_{vW}(\rho) + T^\alpha_{\chi}(\rho),
\]

\[
T^\omega_{TF}(\rho) = (T^w_{TF}(\rho) = \frac{\pi}{3}(3\pi^2)^2/5\langle\rho(\mathbf{r})^{5/3}\rangle),
\]

\[
T_{vW}(\rho) = \langle t_{vW}(\mathbf{r}) \rangle = 1/8\left(\frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})}\right),
\]

\[
T^\alpha_{\chi}(\rho) = \langle \Delta \rho(\mathbf{r})^\alpha \rangle K_a(\mathbf{r} - \mathbf{r}' - \mathbf{r})\Delta \rho(\mathbf{r})^\alpha
\]

Here, \(T^\omega_{TF}(\rho)\) is the TF functional, \(T_{vW}(\rho)\) is the vW functional, \(\Delta \rho(\mathbf{r})^\alpha = \rho(\mathbf{r})^\alpha - \rho_0^\alpha\), \(\rho_0\) is the average electron density, \(\alpha\) is a positive parameter that defines \(X = \text{Wang-Teter-Perrot}\) for \(\alpha = 2\), \(X^2 = \text{Perrot}\) for \(\alpha = 1\), and \(X = \text{SM}\) for \(\alpha = \frac{2}{3}\). The kernel \(K_a(\mathbf{r} - \mathbf{r}')\) is chosen such that \(T^\alpha_{\chi}\) satisfies the exact LR for a noninteracting electron gas without exchange.
and consequently,
\[ T^\alpha_s[\rho] = \langle \rho(r)^\alpha | K_s(r-r') | \rho(r')^\alpha \rangle, \]
which is in the form of the WT KEDF (Ref. 1) when \( \alpha = \frac{5}{6} \).

It has been shown that\(^3\) for a uniform system, \( T^\alpha_s \) reduces to \( T_{TF} \); for slowly varying densities, \( T^2_s \) yields the CGE up to second order (\( T_{TF} + \frac{1}{2} T_{vW} \)); and for rapidly varying densities, \( T_{vW} \) in \( T^\alpha_s \) will dominate. Since all the important limits can be reproduced using this family of KEDF’s, it is not surprising that they perform so well.\(^3\) However, a closer inspection shows that for bulk aluminum, \( T^\alpha_s \) performs better than \( T^{1/2}_s \) for most structures,\(^3\) even with the inclusion of quadratic response.\(^4\) At first glance, this seems illogical since \( T^{1/2}_s \) exactly reduces to the CGE for slowly varying densities while \( T^{5/6}_s \) does not,\(^3,4\) but the numerical evidence proves the opposite. Based on these results, one might easily conclude that there must be a defect in \( T^{1/2}_s \), and only use \( T^{5/6}_s \) in practical calculations. In the following, we will argue that both \( T^{5/6}_s \) and \( T^{1/2}_s \) are partially correct as well as incorrect, and a suitable combination of the two indeed yields excellent results. Furthermore, one can even generate an entire family of new functionals in the same spirit.

III. ANALYSIS AND DISCUSSION

To understand both the success and failure of the WT, Perrot, and SM KEDF’s,\(^1\)\(^-\)\(^4\) we reexpress the general \( T^\alpha_s \) in Eq. (1) in reciprocal space\(^4\) using Eqs. (2)–(8),

\[ T^\alpha_s[\rho] = \Omega \sum_\mathbf{q} \tilde{T}^\alpha_s(\mathbf{q}) = \Omega \sum_\mathbf{q} \{ \tilde{I}_{TF}(\mathbf{q}) + \tilde{I}_{vW}(\mathbf{q}) + \tilde{I}^\alpha_s(\mathbf{q}) \}, \]

where, in general, \( \tilde{T}(\mathbf{q}) \) and \( \rho^\alpha(\mathbf{q}) \) are the Fourier transforms of \( t(r) \) and \( \rho^\alpha(r) \), respectively. It can be readily shown\(^16\) that

\[ \lim_{q \to 0} \frac{1}{q^6} \int_{Lind} \rho^\alpha \left( \frac{k_F^2}{2\alpha^2} + \frac{q^2}{4} \right) = \frac{1}{3 \rho_0} \left( \frac{k_F^2}{y^2} + \frac{q^2}{12} \right), \]

\[ \lim_{q \to \infty} \frac{1}{q^6} \int_{Lind} \rho^\alpha \left( \frac{k_F^2}{3\alpha^2} - \frac{q^2}{4} \right) = \frac{1}{5 \rho_0} \left( \frac{k_F^2}{5} - \frac{q^2}{4} \right), \]

and hence for any \( \alpha \) value, there exists

\[ \lim_{q \to 0} \tilde{T}_s^\alpha(\mathbf{q}) = -\tilde{T}_{TF}(\mathbf{q}) - \frac{1}{2} \tilde{T}_{II}(\mathbf{q}), \]

\[ \lim_{q \to \infty} \tilde{T}_s^\alpha(\mathbf{q}) = \frac{1}{3} \tilde{T}_{II}(\mathbf{q}) - \tilde{T}_{III}(\mathbf{q}), \]

\[ \lim_{q \to 0} \tilde{T}_s^\alpha(\mathbf{q}) = \tilde{T}_{TF}(\mathbf{q}) + \tilde{T}_{vW}(\mathbf{q}) - \frac{8}{5} \tilde{T}_{III}(\mathbf{q}), \]

\[ \lim_{q \to \infty} \tilde{T}_s^\alpha(\mathbf{q}) = \tilde{T}_{TF}(\mathbf{q}) + \tilde{T}_{vW}(\mathbf{q}) - \frac{8}{5} \tilde{T}_{II}(\mathbf{q}). \]

It can be further shown that

\[ T_{III} = \frac{5}{9 \alpha^2} \tilde{T}_{TF}(\mathbf{q}) + \frac{5}{9 \alpha^2} \tilde{T}_{vW}(\mathbf{q}) + \frac{5}{9 \alpha^2} \tilde{T}_{II}(\mathbf{q}) + \frac{5}{9 \alpha^2} \tilde{T}_{III}(\mathbf{q}), \]

\[ T_{II} = \frac{5}{9 \alpha^2} \tilde{T}_{TF}(\mathbf{q}) + \frac{5}{9 \alpha^2} \tilde{T}_{vW}(\mathbf{q}) + \frac{5}{9 \alpha^2} \tilde{T}_{II}(\mathbf{q}) + \frac{5}{9 \alpha^2} \tilde{T}_{III}(\mathbf{q}), \]

where \( \sigma(r) = \rho(r)/\rho_0 \), and \( \delta \sigma = \sigma(r) - 1 \). For the nearly free electron gas, \( |\delta \sigma| \) will be normally much less than 1, and both Eqs. (22) and (23) will be quite accurate up to third order with a moderate \( \alpha \) value (\( \alpha \sim 1 \)). Therefore, for the \( q \to 0 \) region,

\[ T^0_s \rightarrow T_{TF} + \frac{1}{2} T_{vW} - \frac{16}{9 \alpha^2} (\alpha - \frac{1}{2}) \langle \delta \sigma | t_{vW} \rangle \]

\[ - \frac{16}{9 \alpha^2} (\alpha - \frac{1}{2}) \langle \delta \sigma^2 | t_{vW} \rangle + O(\delta \sigma^3), \]

and for the \( q \to \infty \) region,

\[ T^\alpha_s \rightarrow T_{TF} + \frac{1}{2} T_{vW} - \frac{16}{9 \alpha^2} (\alpha - \frac{1}{2}) \langle \delta \sigma | t_{vW} \rangle \]

\[ - \frac{16}{9 \alpha^2} (\alpha - \frac{1}{2}) \langle \delta \sigma^2 | t_{vW} \rangle + O(\delta \sigma^3), \]

A few conclusions can be drawn from the above derivations. First, Eqs. (22) and (24) show that for any \( \alpha \) value, \( T^\alpha_s \)
always reduces to the CGE up to second order. However, this reduction is exact only when \( \alpha = \frac{1}{2} \), implying that there are no higher-order spurious terms involving \( \delta \sigma \). Specifically, Eq. (22) with \( \alpha = \frac{5}{7} \) has been recognized before, but it was not emphasized enough in later studies. Second, though the choice of \( \alpha = \frac{5}{6} \) removes all the spurious \( \delta \sigma \) terms in Eqs. (23) and (25), \( T_{5/6}^{5/6} \) does not yield the correct large-\( q \) limit (CLQL). \( T_{vW}^{1/2} \) corresponds to the second-order CGE at the \( q \to 0 \) limit, while others correspond at the \( q \to \infty \) limit.

There is a subtle point that needs further explanation. Though Eq. (5) shows that \( T_{5/6}^{5/6} \) always satisfies the exact LR (\( \chi_{Lind} \)) for any \( \alpha \) value, its limiting forms, however, do not necessarily have the same property, as clearly demonstrated by Eq. (25) and Fig. 1. Similar behavior has also been observed before for the functional derivatives of the Becke exchange functional and the DePristo-Kress KEDF. In this sense, these functionals are not designed self-consistently at all limits. In the following, we will present a solution for this problem by explicitly enforcing this self-consistency.

**IV. NEW FUNCTIONALS**

We therefore propose the following general trial KEDF:

\[
T_s^{(\alpha)} = T_{TF} + T_{vW} + \sum \alpha T_N^\alpha.
\]

where \( \{ \alpha \} \) are parameters, and \( \{ \lambda, \alpha \} \) are the corresponding expansion weights. To keep the LR intact, the weights have to satisfy

\[
\sum \lambda_\alpha = 1.
\]

Additionally, to yield the CLQL and to minimize the effects of those spurious \( \delta \sigma \) terms in Eqs. (24) and (25), the weights further need to satisfy

\[
\sum \alpha \lambda_\alpha (\alpha - \frac{1}{2}) = \varepsilon_1,
\]

\[
\sum \alpha \lambda_\alpha (\alpha - \frac{1}{2}) (\alpha - 1) = \varepsilon_2,
\]

\[
\sum \alpha \lambda_\alpha \frac{\alpha - 5/6}{\alpha^2} = \varepsilon_3,
\]

\[
\sum \alpha \lambda_\alpha \frac{\alpha - 5/6}{\alpha^2} (\alpha - 4/3) = \varepsilon_4 = -\frac{3+26\varepsilon_3}{12}.
\]
where \( \{e_i\} \) are small numbers close to 0. Figure 1 shows that the CLQL approximates \( \chi_{\text{Ind}} \) quite well for most of \( \eta \) values larger than 1, while the second-order CGE is only good for a tiny area close to 0. Hence, setting \( e_3 = 0 \) is an appropriate and reasonable assumption, and consequently \( e_4 = -\frac{1}{2} \). In the following, we will solve Eqs. (27)–(29) and (31) for the two-parameter and three-parameter cases, and then judge the quality of the selections of \( \{\alpha\} \) and \( \{\lambda_{\alpha}\} \) based on the smallness of \( e_1 \) and \( e_2 \). Equation (30) is not explicitly solved because it is of second order.

If there are only two terms in the sum of Eq. (26), the solution of Eqs. (27)–(29) and (31) is

\[
\lambda_\alpha = \frac{\alpha^2}{\beta - \alpha} \left( \frac{2}{3} \beta - \epsilon_1 - \frac{1}{2} \right), \tag{33}
\]

\[
\lambda_\beta = \frac{\alpha^2}{\beta - \alpha} \left( \frac{2}{3} \alpha - \epsilon_1 - \frac{1}{2} \right), \tag{34}
\]

\[
\alpha = \frac{3}{2} - 2 \epsilon_1 + \sqrt{Q}, \tag{35}
\]

\[
\beta = \frac{3}{2} - 2 \epsilon_1 - \sqrt{Q}, \tag{36}
\]

\[
Q = \left( 2 \epsilon_1 + \frac{1}{3} \right)^2 - \frac{\pi}{2}, \tag{37}
\]

where \( \epsilon_1 \) is chosen to be within the two domains: \((-\infty, -[(\sqrt{5}+1)/12]]\) and \([(\sqrt{5}-1)/12, \infty)\), to ensure that \( Q > 0 \) and \( \alpha \neq \beta \). Figures 2 and 3 show \( \alpha, \beta, \lambda_\alpha, \lambda_\beta, \epsilon_2 \) [via Eq. (30)] as functions of \( \epsilon_1 \). Figures 2 and 3 show that in the positive domain, \( |\epsilon_1| \) has smaller values and \( |\epsilon_2| \) is uniformly close to zero. To keep the magnitudes of \( \lambda_\alpha \) and \( \lambda_\beta \) small and to ensure a reasonable separation between \( \alpha \) and \( \beta \), we choose \( \epsilon_1 = 0.105 \), which is just slightly larger than \((\sqrt{5}-1)/12\). The corresponding values for \( \alpha, \beta, \lambda_\alpha, \lambda_\beta, \epsilon_2 \) are listed in Table I. For the sake of comparison, we also include some one-parameter cases as well as a two-parameter case: \( \{\alpha, \beta\} = \{\frac{3}{2}, \frac{1}{2}\} \) whose weights are calculated via Eqs. (27) and (28),

\[
\lambda_\alpha = \frac{\alpha^2}{\beta - \alpha} \left( \frac{2}{3} \beta - \epsilon_1 - \frac{1}{2} \right), \tag{38}
\]

\[
\lambda_\beta = \frac{\alpha^2}{\beta - \alpha} \left( \frac{2}{3} \alpha - \epsilon_1 - \frac{1}{2} \right), \tag{39}
\]

\[
\alpha = \frac{3}{2} - 2 \epsilon_1 + \sqrt{Q}, \tag{35}
\]

\[
\beta = \frac{3}{2} - 2 \epsilon_1 - \sqrt{Q}, \tag{36}
\]

\[
Q = \left( 2 \epsilon_1 + \frac{1}{3} \right)^2 - \frac{\pi}{2}, \tag{37}
\]

where \( \epsilon_1 < \frac{3}{4} \) and \( \epsilon_1 \neq \frac{1}{2} \), to keep \( \gamma \) positive and different from the fixed values of \( \alpha \) and \( \beta \). Figure 4 plots \( \gamma, \lambda_\alpha, \lambda_\beta, \lambda_\gamma, \epsilon_2 \) as functions of \( \epsilon_1 \). Since \( \epsilon_1 \) cannot attain a null value, we choose two small numbers, \( \pm \frac{1}{15} \), for tests,

\[
\begin{array}{|c|c|c|c|c|}
\hline
\{\alpha, \beta, \gamma\} & \{\lambda_\alpha, \lambda_\beta, \lambda_\gamma\} & \epsilon_1 & \epsilon_2 & \epsilon_3 & \epsilon_4 \\
\hline
\{1\} & \{1\} & 0.500 & 0.000 & 0.167 & -0.056 \\
\{\frac{3}{2}\} & \{1\} & 0.333 & -0.056 & 0.000 & 0.000 \\
\{\frac{1}{2}\} & \{1\} & 0.000 & 0.000 & -1.333 & 1.111 \\
\{\sqrt{5}/3\} & \{1\} & 0.245 & -0.062 & -0.158 & 0.093 \\
\{\frac{3}{2}, \frac{1}{2}\} & \{\frac{5}{2}, \frac{9}{11}\} & 0.286 & -0.048 & -0.188 & 0.156 \\
\{0.511, 0.402\} & \{1.857, -0.857\} & 0.105 & -0.060 & 0.000 & -0.250 \\
\{\frac{3}{2}, \frac{1}{2}, \frac{1}{2}\} & \{\frac{11}{8}, -\frac{1}{2}, -3\} & -0.042 & -0.243 & 0.000 & -0.250 \\
\{\frac{3}{2}, \frac{1}{2}, \frac{1}{2}\} & \{-\frac{12}{11}, -\frac{9}{11}, -4\} & 0.042 & -0.118 & 0.000 & -0.250 \\
\hline
\end{array}
\]

FIG. 3. The negative domain for the two-parameter case.

However, if there are three terms in the sum of Eq. (26), there will be no definite solution for Eqs. (27)–(29) and (31) since the unknowns outnumber the equations. We can nonetheless fix \( \alpha = \frac{3}{2} \) and \( \beta = \frac{1}{2} \) based on the previous discussions [Eqs. (22)-(25)]. Then, the unique solution is

\[
\gamma = \frac{3}{2} - 4 \epsilon_1, \tag{40}
\]

\[
\lambda_\gamma = \frac{\gamma^2}{8 \epsilon_1(2 \gamma - 1)}, \tag{41}
\]

\[
\lambda_\beta = \frac{3}{8(1 - 2 \gamma)}, \tag{42}
\]

\[
\lambda_\alpha = 1 - \lambda_\beta - \lambda_\gamma, \tag{43}
\]

TABLE I. Parameters for the trial KEDF’s.
which correspond to \( g = \frac{7}{3} \) and 1, respectively. Other pertinent parameters are given in Table I.

### V. APPLICATIONS

The trial KEDF’s shown in Table I were tested on the bulk phases of aluminum and compared with the KS results to find the best parameter set. The Goodwin-Needs-Heine local pseudopotential\(^{20}\) together with a plane-wave cutoff of 400 eV were used for both the OF-HK calculations and the KS calculations. The exchange-correlation effects were treated at the LDA level.\(^{21}\) Details of the implementation of the OF-HK scheme are given in Refs. 3 and 7. Five bulk phases of aluminum were studied, and the results are summarized in Tables II and III.

We specifically included the hcp structure in the comparison, since its energy is only slightly above the more stable fcc structure, making it an excellent test case for our trial KEDF’s. The experimentally well-characterized vacancy formation energy was also computed to further assess the quality of the trial KEDF’s. The \( \text{vf} \) energy was calculated using a 32-site cell \( (31 \text{ atoms} - 1 \text{ vacancy}) \) via the expression\(^{22}\)

\[
E_{\text{vf}} = E \left( N - 1, 1, \frac{n}{N} \right) - \frac{N - 1}{N} E(N, 0, \Omega),
\]

where \( E(N, n, \Omega) \) is the energy of the system of \( N \) atoms and \( n \) vacancies occupying \( (N + n) \) sites in a volume \( \Omega \). Since the change in the \( \text{vf} \) energy due to ionic relaxation is minimal,\(^{22}\) we kept the lattice fixed.

The calculated lattice constants are shown in Table II, and they all agree quite well with the KS results. Table III shows that \( T_s^{5/6} \) is marginally wrong in the ordering of the hcp and bcc structures, which clearly depicts its internal deficiency. Since the energy gaps for the five phases are not drastically different with respect to the different trial KEDF’s, the \( \text{vf} \) energy provides a unique way to differentiate them. Table III clearly shows that our optimally interpolated KEDF’s are all within 0.1 eV of the well-converged KS result\(^{22}\) and the

![FIG. 5. Contour plots of the KS (solid lines) and the OF-HK (broken lines) electron densities for fcc aluminum in the (100) plane. The trial KEDF is \( T_s^{5/6,1/2,2/3} \).](image)
showing the differences between the KS and the T\textsuperscript{58,12,2/3} energies, experimental value.\textsuperscript{23} Figures 5 and 6 are contour plots around the vacancy for a 256-site simulation cell are well converged. Figure 7 shows the OF-HK electron density around the vacancy for a 256-site simulation cell (255 atoms + 1 vacancy). A KS calculation on this cell would be fairly expensive indicating the utility of OF-HK calculations on large systems. In addition, we found that the calculated fcc bulk moduli are all within the envelope of 0.74±0.02 Mb, which is very close to the experimental value 0.725 Mb.\textsuperscript{16,24} Overall, in terms of lattice constants, bulk moduli and energies, T\textsuperscript{58,12,2/3} appears to be the best choice.

FIG. 6. Contour plots of the KS (solid lines) and the OF-HK (broken lines) electron densities around the vacancy in aluminum. The trial KEDF is T\textsuperscript{58,12,2/3}.

FIG. 7. Contour plot of the OF-HK electron density around the vacancy in aluminum for a 256-site cell (255 atoms + 1 vacancy). Dark areas represent low electron densities and light areas represent high electron densities.

VI. CONCLUSION

In conclusion, we have pointed out certain interesting features of the Wang-Teter, Perrot, and Smargiassi-Madden kinetic-energy functionals and a simple yet sound way of enhancing their performance without going beyond linear-response theory and without introducing a density-dependent kernel. The functionals will be useful for O(N) methods of first-principles molecular dynamics for the nearly free electron gas.

ACKNOWLEDGMENTS

We thank Dr. Asbjørn Christensen for some of the KS results. Financial support for this project was provided by the National Science Foundation, the Army Research Office, and the Air Force Office of Scientific Research.


