Meta-Local Density Functionals: A New Rung on Jacob’s Ladder

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ABSTRACT: The homogeneous electron gas (HEG) is a key ingredient in the construction of most exchange-correlation functionals of density-functional theory. Often, the energy of the HEG is parameterized as a function of its spin density \( n_\sigma \) leading to the local density approximation (LDA) for inhomogeneous systems. However, the connection between the electron density and kinetic energy density of the HEG can be used to develop the LDA by evaluating it on a geometric average of the HEG and which form a new rung of functionals [AIP Conf. Proc. 2001, 577, 1]. The first functional of this ladder, the local \( \tau \) approximation (LTA) of Ernzerhof and Scuseria [J. Chem. Phys. 1999, 111, 911] that corresponds to \( \tau = 1 \) is unfortunately not stable enough to be used in self-consistent field calculations because it leads to divergent potentials, as we show in this work. However, a geometric averaging of the LDA and LTA densities with smaller values of \( \tau \) not only leads to numerical stability of the resulting functional but also yields more accurate exchange energies in atomic calculations than the LDA, the LTA, or the tLDA functional (\( \tau = 1/4 \)) of Eich and Hellgren [J. Chem. Phys. 2014, 141, 224107]. We choose \( \tau = 0.50 \) as it gives the best total energy in self-consistent exchange-only calculations for the argon atom. Atomization energy benchmarks confirm that the choice \( \tau = 0.50 \) also yields improved energetics in combination with correlation functionals in molecules, almost eliminating the well-known overbinding of the LDA and reducing its error by two thirds.

1. INTRODUCTION

The homogeneous electron gas (HEG) has a special place in the history of the study of many-electron systems in general, and density-functional theory in particular. In fact, the development of accurate exchange-correlation functionals typically begins with the local (spin) density approximation (LDA), whose construction is based on the exchange-correlation energy of the HEG. This is then modified by an enhancement factor that depends on the gradient of the density in the generalized gradient approximation (GGA); the mega-GGA approximation adds further dependence on the local kinetic energy density and/or the Laplacian of the electron density.3–5

LDAs, GGAs, and meta-GGAs form the first three rungs of the so-called Jacob’s ladder of the density-functional theory,6 each rung generally leading to approximations with better accuracy. Although GGAs and meta-GGAs add more physical information into the density-functional approximation (DFA), they are typically constructed to maintain the exactness for the exchange-correlation energy of the HEG. In fact, it can be even argued that this is one of the most important exact conditions that a functional should fulfill.

In this work, we investigate the accuracy of an ansatz, which, like the LDA, is derived from considerations of the HEG only, but which adds a further dependence on the local kinetic energy density as in meta-GGAs. These functionals, which we term meta-LDA functionals, thus constitute a new rung on Jacob’s ladder of density functionals.7,8

The work is organized as follows. We will describe the theory behind the meta-LDA approach in Section 2. The implementation of the meta-LDA functionals and the details of our computations are described in Section 3. The accuracy of the novel functionals is then assessed by benchmarking the exchange energies of atoms and atomization energies of molecules in Section 4. A brief summary and conclusions are presented in Section 5. Atomic units are used throughout the manuscript, unless specified otherwise.

2. THEORY

The LDA for the exchange energy is derived for the HEG as7,8...
The kinetic energy density of the gas is also known

\[ C_{\text{HEG}} \frac{5}{3} \tau \]

where

\[ C_{\text{HEG}} = \frac{3}{10} \left( 3\pi^2 \right)^{2/3} \]

Since eq 3 establishes a link between the kinetic energy density and the electron density, Ernzerhof and Scuseria\(^9\) proposed an exchange functional similar to eq 1, where eq 3 is used to replace the local density dependence by

\[ \tilde{n}(r) = \left[ \frac{\tau(r)}{C_F} \right]^{3/5} \]

yielding the local r approximation (LTA) exchange functional

\[ E_x^{\text{LTA}}[\tau] = -C_x \int \left[ \frac{\tau(r)}{C_F} \right]^{4/5} d^3r \]

On the basis of the work of Ernzerhof and Scuseria, Eich and Hellgren\(^10\) suggested another exchange functional, where only the energy per unit particle is written as a function of the fictitious density of eq 5, yielding the tLDA exchange functional

\[ E_x^{\text{tLDA}}[n, \tau] = -C_x \int n(r) \tilde{n}^{1/3}(r) d^3r \]

In this work, we show the power of this idea by generalizing the approach of Ernzerhof, Scuseria, Eich, and Hellgren. We thus replace the electron density by an effective density \( n^{\text{eff}}(r) \) formed as a weighted combination of the electron density \( n(r) \) and the fictitious density computed from \( \tau(r) \) as

\[ n(r) \rightarrow n^{\text{eff}}(r) = \tilde{n}(r)n^{1-x}(r) \]

This form interpolates between the LDA (\( x = 0 \)), tLDA (\( x = 1/4 \)), and LTA (\( x = 1 \)) in the case of the exchange functional. Furthermore, it can also be employed within any LDA correlation functional, allowing us to generate a complete exchange-correlation ansatz.

We note here that the family of functionals generated by eq 8 is actually a member of a general family of functionals that have the form of an LDA, but which are based on a transformed density variable

\[ f_{\text{mLDA}}(C_F) = 1 \]

Because this procedure generates a meta-GGA-type functional without gradient dependence from a LDA, we will term these functionals as meta-LDAs.

3. COMPUTATIONAL DETAILS

The effective density of eq 8 can be rewritten in the form of eq 9 as

\[ f(t) = \left( \frac{t}{C_F} \right)^{3x/5} \]

The resulting meta-LDA version of the local exchange functional can be easily rewritten in terms of an enhancement function.

Figure 1. Errors in the self-consistent total (blue solid line) and exchange (red solid line) energies of Ne, Ar, and Kr, as well as in the perturbative exchange energy calculated on top of the HF density (dashed red line). The vertical dashed blue line shows the critical value \( x = 0.625 \), see the main text. The location of the smallest error for the self-consistent total and exchange energies are shown as blue and red squares, respectively, and that for the perturbative exchange energy as red diamonds; however, since the optimal value is close to \( x = 1/2 \) for all cases, the markers are on top of each other.
\[ F(t; x) = \left[ \frac{t}{C_F} \right]^{3e/5} = \left( \frac{t}{C_F} \right)^{4s/5} \] (13)

The generalization of the Perdew‒Wang 1992 correlation functional\(^{11}\) is equally trivial; the density used to evaluate the energy density is merely re-expressed using eq 8. These new functionals have been implemented in version 5.1.0 of the LI\(\text{BX}\) library of exchange-correlation functionals.\(^{12}\) In LI\(\text{BX}\), the derivatives of the functional are evaluated analytically using the MAPLE symbolic algebra program, as is the case for all other functionals in LI\(\text{BX}\) as well. Combined with a basis set, these derivatives can be used to minimize the total energy variationally with respect to the orbital coefficients within a self-consistent field approach; we refer to ref 13 for discussion.

Fully numerical,\(^{13}\) fully variational calculations on closed and partially closed shell atoms from H to Sr were performed with the finite-element method as implemented in the HELFEM program,\(^{15}\) which allows for an efficient approach to the complete basis set limit.\(^{16,17}\) The atomic calculations employed five radial elements, yielding 69 numerical radial basis functions, which suffice to converge the energy to better than \(\mu\)E\(\text{h}\) precision for these systems.

Molecular calculations on the 183 non-multireference molecules in the W4-17 data set\(^{18}\) were performed with the Ps\(\text{i}4\) program.\(^{19}\) The Ps\(\text{i}4\) calculations employed the quadruple-\(\zeta\) aug-pcseg-3 basis set\(^{20}–22\) and a (100, 590) quadrature grid. Density fitting\(^{23}\) was used to accelerate the Ps\(\text{i}4\) calculations; a universal auxiliary basis set was used for this purpose.\(^{24}\)

### 4. RESULTS

#### 4.1. Atomic Calculations

The errors of exchange-only density-functional calculations compared to the unrestricted Hartree–Fock (HF) total and exchange energies for atoms from H to Sr were studied with HELFEM; the reference unrestricted HF total energies have been recently reported in ref 17. Due to the similarity of the results, data is shown here only for the noble gases Ne, Ar, and Kr in Figure 1; the rest of the data can be found in the Supporting Information. In addition to the self-consistent data, Figure 1 also shows the perturbative evaluation of the exchange energy computed on top of the HF density.

Following Becke\(^{25}\) and Sun et al.\(^{26}\) among others, we fit the parameter \(x\) for our meta-LDAs by optimizing the total energy of the argon atom to the Hartree–Fock reference value, leading to the choice \(x = 0.50\). It is noteworthy that in addition to being quasi-optimal for all systems, \(x = 0.50\) is also numerically stable for all of the studied atoms. Finally, it also leads to uniformly smaller errors in the exchange energy than in the LDA and tLDA, which uniformly underestimate the energy, while LTA grossly overestimates the energy.

As already implied above, the self-consistent calculations diverge for large fractions \(x\) of the LTA density. We have analyzed the instability observed in the calculations; see the Appendix for a formal analysis. It turns out that the functional form is inherently unstable for \(x > 0.625\), since for such values of \(x\), the potentials corresponding to both \(n\) and \(r\) diverge asymptotically to \(-\infty\) for \(r \to \infty\). However, it is clear from the results that the optimal value of \(x\) for the exchange functional is found at \(x < 0.625\).

#### 4.2. Molecular Calculations

The application of the functional to atomization energies

\[ E_{\text{fit}} = \sum_{\text{atoms } A} E(A) - E(\text{molecule}) \] (14)

of the non-multireference part of W4-17 yields

\[ \Delta E_{\text{fit}} = E_{\text{fit}}(\text{DFT}) - E_{\text{fit}}(\text{W4-17}) \] (15)

shown in Table 1. Due to the higher cost of the molecular calculations compared to that of the atomic calculations, the table is divided into exchange-only calculations and exchange-correlation functionals.

| Functional | \(x\) | \(\Delta E_{\text{fit}}\) (kcal/mol) | \(\Delta E_{\text{fit}}\) (kcal/mol) |
|------------|------|----------------|----------------|
| LDA-PW92   | 28.966 | -12.015        |
| hlTA exchange\(^a\) | 71.235 | -67.512        |
| tLTA exchange\(^b\) | 47.504 | -35.863        |
| qLTA exchange\(^c\) | 42.181 | -26.070        |
| HF         | 144.848 | -144.848       |
| B88 exchange | 98.177 | -98.177        |
| PBE exchange | 87.958 | -87.958        |

\(^{a}\)The data for the exchange-only hLTA calculation excludes CH\(_2\)NH\(_2\) for which the SCF procedure did not converge. \(^{b}\)qLTA is the same as the tLDA of Eich and Hellgren. \(^{c}\)The data is divided into exchange-only calculations (A), and calculations including both exchange and correlation (B). See the main text for the legend of the functionals shown. To clarify the notation, the used values for \(x\) in the meta-LDA exchange and correlation functionals are also shown.
molecules due to the complete neglect of electronic correlation effects, while LDA overbinds them. Due to the overbinding, exchange-only LDA calculations are more accurate than those that explicitly include also correlation contributions, although the LDA exchange by itself is slightly underbinding. In contrast, while gradient-corrected exchange functionals yield bad results if used alone, when they are combined with a good gradient-corrected correlation functional, they achieve good accuracy. Jacob’s ladder\(^6\) is also visible in the results: more accurate atomization energies are obtained in the sequence LDA → PBE → TPSS.

Interestingly, also the meta-LDA functionals show monotonic behavior. Going from LDA to qLTA to tLTA and, finally, hLTA in exchange-only calculations leads to systematically increasing underbinding. The same effect holds also in the presence of correlation: while LDA-PW92 is greatly overbinding, as already established above, the overbinding decreases systematically in the sequence LDA-PW92 → qLTA-qPW92 → tLTA-tPW92 → hLTA-hPW92. Like in the case of the atomic exchange energies, the half-and-half ratio \(x = 1/2\) yields quasi-optimal results for both atoms and molecules, almost fully eliminating the overbinding of LDA and reducing the mean absolute error in the atomization energies to a third of the original.

Meta-LDAs could also be seen as a better starting point for the inclusion of an extra dependency in the gradient of the density (as in a standard GGA), and in the Laplacian of the density and the kinetic energy density (as in a standard meta-GGA). Due to the extra flexibility, we can expect that these perform better than the parent functionals. For example, the new degree of freedom introduced with the meta-LDAs could play an important role for, e.g., semi-empirical functionals fitted to the experimental data. In many of these cases (see for example in refs 34–36), the functionals do not reduce to the LDA for homogeneous densities, as this would compromise the accuracy of the functional for other systems. By replacing the standard LDA with a meta-LDA form in full or in part could, in principle, obey the exact condition without compromising the accuracy, and at the same time increase the transferability of the functionals to solids. Of course, the GGA or meta-GGA enhancement functionals have to be redesigned (or at least reoptimized) to take the new form into account. Work along these lines has already started.

5. SUMMARY AND CONCLUSIONS

We have proposed a new class of functionals as generalizations of the established class of local density approximations (LDAs) by including a fraction \(x\) of fictitious density computed from the local kinetic energy density via a relation derived for the homogeneous electron gas (HEG). The resulting so-called meta-LDA functionals maintain the exactness of LDA for the HEG, and are derived from HEG data only (with the exception of the one parameter \(x\) that is fitted to the total exchange-only energy of the argon atom) but afford much improved accuracy for inhomogeneous systems, thus forming a new rung on Jacob’s ladder of density functionals in between LDAs and GGA. Benchmarks on both perturbative and self-consistent atomic exchange energies and molecular atomization energies in the presence of a correlation functional showed that the half-and-half ratio \(x = 1/2\) yields quasi-optimal results for both atoms and molecules, almost fully eliminating the overbinding of LDA and reducing the mean absolute error in the atomization energies to a third of the original.

Meta-LDAs could also be seen as a better starting point for the inclusion of an extra dependency in the gradient of the density (as in a standard GGA), and in the Laplacian of the density and the kinetic energy density (as in a standard meta-GGA). Due to the extra flexibility, we can expect that these perform better than the parent functionals. For example, the new degree of freedom introduced with the meta-LDAs could play an important role for, e.g., semi-empirical functionals fitted to the experimental data. In many of these cases (see for example in refs 34–36), the functionals do not reduce to the LDA for homogeneous densities, as this would compromise the accuracy of the functional for other systems. By replacing the standard LDA with a meta-LDA form in full or in part could, in principle, obey the exact condition without compromising the accuracy, and at the same time increase the transferability of the functionals to solids. Of course, the GGA or meta-GGA enhancement functionals have to be redesigned (or at least reoptimized) to take the new form into account. Work along these lines has already started.

APPENDIX: INSTABILITY OF THE LOCAL \(\tau\) APPROXIMATION

The Kohn–Sham electron density is known to behave asymptotically as \(n(r) \propto e^{-2\sqrt{-2\epsilon_{\text{HOMO}}}}r\) due to the highest occupied molecular orbital (HOMO), which behaves as \(\psi_{\text{HOMO}} \propto e^{-\sqrt{-2\epsilon_{\text{HOMO}}}r}\).\(^37\) For simplicity, we will study hydrogenic orbitals of the form

\[
\psi_n(r) = \frac{2^{3/2}e^{-\zeta r}}{\sqrt{4\pi}}
\]

(16)

to show that the exponentially decaying asymptotic region leads to problems for \(r \to \infty\) for the local \(\tau\) exchange
functional. The electron density of the wave function in eq 16 is
\[ n_0(\mathbf{r}) = \frac{\zeta^3 \exp(-2\zeta r)}{\pi} \]  
while the kinetic energy density is
\[ \tau_0(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \psi_i(\mathbf{r})|^2 = \frac{\zeta^3 \exp(-2\zeta r)}{2\pi} \]  
The self-consistent implementation of the meta-LDAs is based on the potentials \( v^e_\mu \) and \( v^c_\mu \), which are defined as the derivatives of the exchange energy density arising from the substitution of eq 8 into eq 1 with respect to \( n_0 \) and \( \tau_0 \) respectively. It is easy to show using, e.g., computer algebra (we used MAPLE 20 to obtain these results), that when evaluated on an electron density and kinetic energy density of the form of eqs 17 and 18, both of the potentials \( v^e_\mu \) and \( v^c_\mu \) contain a factor of the form \( \exp\left(16x - 10 rz/15\right) \), which diverges in the limit \( r \to \infty \) whenever \( x > x_{\text{cr}} \) with the critical value \( x_{\text{cr}} = 5/8 = 0.625 \).

Interestingly, also the choice of a HOMO with a Gaussian form \( \psi_\mu \propto \exp(-r^2) \) leads to divergent potentials, only now of a stronger kind \( \exp\left(16x - 10 rz^2/15\right) \), and yields the same critical value \( x_{\text{cr}} = 5/8 \). In fact, it can be shown that all asymptotic wave functions of the kind \( \psi_\mu \propto \exp(-\zeta_\mu r^p) \) with \( p > 0 \) lead to divergences of the kind \( \exp\left(16x - 10 rz^p/15\right) \) in \( v^e_\mu \) and \( v^c_\mu \). The total exchange energy, however, is finite in each case.

For \( x > x_{\text{cr}} \), one then has \( v^e_\mu \to -\infty \) and \( v^c_\mu \to -\infty \) for \( r \to \infty \) because the potentials are negative everywhere (as expected for an exchange functional). This divergence causes convergence problems. Assuming an orthonormal basis set \( \{\chi_\mu\} \), the potentials \( v^e_\mu \) and \( v^c_\mu \) contribute to the Kohn–Sham–Fock matrix as
\[ F^\mu_\nu \propto \left[ \int \psi^e_\mu(\mathbf{r}) \chi^*_\nu(\mathbf{r}) \chi_\nu(\mathbf{r}) + \frac{1}{2} \psi^c_\mu(\mathbf{r})[\nabla \chi^*_\nu(\mathbf{r}) \cdot \nabla \chi_\nu(\mathbf{r})] \right] d^3r \]  
The tentative physical interpretation of the divergent potentials is that displacing electron density toward \( r \to \infty \) would lead to a decrease in the energy. Now, if a Gaussian-type or Slater-type orbital basis set is employed, \( \chi_\mu \) and its gradient will decay asymptotically as \( \exp(-\alpha_\mu r) \) or \( \exp(-\zeta_\mu r) \), respectively, where \( \alpha_\mu \) and \( \zeta_\mu \) are the Gaussian- and Slater-type exponents, with analogous expressions for \( \nabla \chi_\mu \). Evaluating eq 19 then requires quadrature of an expression with an exponentially decaying part and an exponentially increasing part, which is numerically unstable, as the resulting value may be either small or large. The finite-element calculations with HELE.EM, in turn, feature localized basis functions also at large values of \( r \). This leads to exponentially increasing elements of the Kohn–Sham–Fock matrix, making the self-consistent field algorithm unstable.

In contrast, the potentials arising in the asymptotic region for \( x < 0.625 \) decay exponentially (like they do in the local density approximation), making self-consistent field calculations stable.

**ASSOCIATED CONTENT**

### Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.0c01147.

Further plots on the accuracy of the meta-LDA exchange functional with varying fractions \( x \) of LTA density for atoms from H to Sr, and the raw data for the atomization energies (PDF).

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**Notes**

The authors declare no competing financial interest.

The data that supports the findings of this study is available within the article and its supporting material.

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