Simple meta-generalization of local density functionals

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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 density, 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 generalize the LDA by including a fraction $x$ of the kinetic energy density. This leads to a new family of functionals that we term meta-local density approximations (meta-LDAs), which are still exact for the HEG. The first functional of this kind, the local $\tau$ approximation (LTA) of Ernzerhof and Scuseria [J. Chem. Phys. 111, 911 (1999)] is unfortunately not stable enough to be used in self-consistent field calculations. However, we show in this work that geometric averaging of the LDA and LTA densities with $x = 1/2$ 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 $\tau$-LDA ($x = 1/4$) of Eich and Hellgren [J. Chem. Phys. 141, 224107 (2014)]. Furthermore, atomization energy benchmarks confirm that the choice $x = 1/2$ 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. Our functional form can also be used as a starting point to construct new meta-generalized gradient functionals by including further dependence on the gradient of the density.

I. INTRODUCTION

The homogeneous electron gas (HEG) has a special place in the history of the study of many-electron systems in general, and of density-functional theory in particular.\textsuperscript{1,2} 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 electron density Laplacian.\textsuperscript{3–5} Nevertheless, these most sophisticated functionals are often constructed to maintain 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.

The LDA for the exchange energy is derived for the HEG with Hartree–Fock (HF) theory as\textsuperscript{6,7}

$$E_x^{\text{LDA}}[n] = -C_x \int n^{4/3}(r) \, d^3r$$

(1)

where

$$C_x = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3}.$$  

(2)

The kinetic energy density of the gas is also known,

$$\tau^{\text{HEG}} = C_F n^{5/3}$$

(3)

where

$$C_F = \frac{3}{10} \left( \frac{3\pi^2}{2} \right)^{2/3}.$$  

(4)

Since equation (3) establishes a link between the kinetic energy density and the electron density, Ernzerhof and Scuseria\textsuperscript{8} proposed an exchange functional similar to equation (1) where equation (3) is used to replace the local density dependence by

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

(5)

yielding the local $\tau$ approximation (LTA) exchange functional

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

(6)

Based on the work of Ernzerhof and Scuseria, Eich and Hellgren\textsuperscript{9} suggested another exchange functional where only the energy per unit particle is written as a function of the fictitious density of equation (5), yielding the tLDA exchange functional

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

(7)

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 a weighted combination of the electron density $n(r)$ and the fictitious density from $\tau(r)$ as

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

(8)
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 equation \((\text{8})\) 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

\[ n(r) \rightarrow n(r) f^{\text{mLDA}}(t(r)), \quad (9) \]

where \(t(r)\) is the (dimensionless) reduced kinetic energy density

\[ t(r) = \frac{\tau(r)}{n^{3/5}(r)}. \quad (10) \]

It is easily seen that LDA functionals operating on a density transformed according to equation \((\text{8})\) are exact for the HEG if the function \(f^{\text{mLDA}}\) reduces to one for the HEG, i.e.

\[ f^{\text{mLDA}}(C_F) = 1. \quad (11) \]

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

The remainder of this work is organized as follows. We describe the implementation of the functionals arising from equation \((\text{8})\) and the details of our computations in section \((\text{II})\). The accuracy of the novel functionals is then assessed by benchmarking exchange energies of atoms and atomization energies of molecules in section \((\text{III})\). A brief summary and conclusions are presented in section \((\text{IV})\). Atomic units are used throughout the manuscript, unless specified otherwise.

\section{Computational Details}

The effective density of equation \((\text{8})\) can be rewritten in the form of equation \((\text{10})\) as

\[ f(t) = \left( \frac{t}{C_F} \right)^{3x/5}. \quad (12) \]

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

\[ F(t; x) = \left[ \left( \frac{t}{C_F} \right)^{3x/5} \right]^{4/3} = \left( \frac{t}{C_F} \right)^{4x/5}. \quad (13) \]

The generalization of the Perdew–Wang 1992 correlation functional\(^{10} \) is equally trivial. These new functionals were implemented in the development version of the Libxc library of exchange-correlation functionals\(^{11} \) and will be included in the next release of the library. In Libxc, functional derivatives are evaluated using computer algebra\(^{11} \), which ensures the correctness of the implementation.

Fully numerical\(^{12} \) 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\(^{13} \) which allows for an efficient approach to the complete basis set limit\(^{14,15} \). The atomic calculations employed five radial elements, yielding 139 numerical radial basis functions which suffice to converge the energy to better than \(\mu E_h\) precision for these systems.

Molecular calculations on the 183 non-multireference molecules in the W4-17 dataset\(^{16} \) were performed with the Psi4 program\(^{17} \). The Psi4 calculations employed the quadruple-\(\zeta\) aug-pcseg-3 basis set\(^{18,20} \) and a \((100,590)\) quadrature grid. Density fitting\(^{21} \) was used to accelerate the Psi4 calculations; a universal auxiliary basis set was used for this purpose\(^{22} \).

\section{Results}

\subsection{Atomic Calculations}

The errors of exchange-only density functional calculations compared to unrestricted 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.\(^15 \). Due to the similarity of the results, data is shown here only for the noble gases Ne, Ar, and Kr in figure\((\text{I})\), the rest of the data can be found in the Supplementary Material. In addition to the self-consistent data, figure\((\text{I})\) also shows the perturbative evaluation of the exchange energy computed on top of the HF density. Although the self-consistent calculations diverge for large fractions \(x\) of the LTA density, it is noteworthy that in addition to being quasi-optimal for all systems, \(x = 1/2\) is still numerically stable for all the studied atoms. This choice 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.

\subsection{Molecular Calculations}

The application of the functional to atomization energies

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

of the non-multireference part of W4-17 yields the errors

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

shown in table\((\text{II})\). Due to the cost of the molecular calculations, the new family of meta-LDA functionals is
Figure 1: Errors in 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 location of the smallest error for the self-consistent total and exchange energies are shown as the blue and red squares, respectively, and the one 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.

| Functional       | MAE (kcal/mol) | ME (kcal/mol) |
|------------------|----------------|---------------|
| $h\text{LTA}$ exchange$^a$ | 71.235         | -67.512       |
| HF               | 144.848        | -144.848      |
| B88 exchange     | 98.177         | -98.177       |
| PBE exchange     | 87.958         | -87.958       |
| LDA-PW92         | 79.879         | 79.879        |
| qLTA-qPW92       | 61.089         | 60.897        |
| tLTA-tPW92       | 50.207         | 49.494        |
| qLTA exchange    | 42.181         | -26.070       |
| hLTA-PW92        | 31.388         | 23.913        |
| LDA exchange     | 28.966         | -12.015       |
| hLTA-hPW92       | 26.907         | 14.088        |
| B88-P86          | 19.173         | 18.899        |
| PBE-PBE          | 18.028         | 17.052        |
| TPSS-TPSS        | 12.427         | 11.180        |
| B88-LYP          | 8.176          | 1.714         |

Table I: Mean absolute error (MAE) and mean error (ME) in atomization energies of the non-multireference part of the W4-17 test set, computed in the aug-pcseg-3 basis with density fitting and a (100,590) grid. See the main text for the legend. $^a$The data for the exchange-only $h\text{LTA}$ calculation excludes CH$_2$NH$_2$ for which the SCF procedure did not converge.

only studied at select points, indicated by a prefix to the name of the exchange and correlation functionals. Data are presented for the LDA exchange functional as qLTA (same as Eich and Hellgren’s tLDA), tLTA, and hLTA for $x = 1/4$, $x = 1/3$, and $x = 1/2$, respectively, both for exchange-only calculations and when combined with the Perdew–Wang (PW92) correlation functional$^{20}$, which also admits meta-LDA generalizations to qPW92, tPW92 and hPW92 for $x = 1/4$, $x = 1/3$, and $x = 1/2$, respectively.

For comparison, data is also included on the Perdew–Burke–Ernzerhof exchange-correlation functional$^{23,24}$, combinations of the Becke’88 (B88) exchange functional$^{25}$ with the Perdew’86(P86) and Lee–Yang–Par (LYP) correlation functionals; as well as the Tao–Perdew–Staroverov–Scuseria (TPSS) exchange-correlation functional$^{29,30}$.

Starting out with the basics, the table demonstrates the well-known characteristics of HF and LDA: HF severely underbinds 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 LDA exchange by itself is slightly underbinding. In contrast, while the 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$^{31}$ is also visible in the results: more accurate atomization energies are obtained in the sequence LDA $\rightarrow$ PBE $\rightarrow$ TPSS.

Also the meta-LDA functionals interestingly 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 was already established above, the overbinding decreases systematically in the se-
quence LDA-PW92 → qLTA-qPW92 → tLTA-tPW92 → hLTA-hPW92. Like in the case of the atomic exchange energies, the half-and-half $x = 1/2$ mixture of the electron density with the $\tau$-based density as in the hLTA-hPW92 functional yields the best results with a mean absolute error almost three times smaller than in the original LDA-PW92 calculation. This finding is underlined by the error histograms shown in figure 2, while LDA-PW is consistently overbinding, the errors for hLTA-hPW are almost symmetric, even though the error scale is still large compared to established GGA functionals.

IV. 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, but afford much improved accuracy for inhomogeneous systems. Benchmarks on both perturbative and self-consistent atomic exchange energies, as well as molecular atomization energies in the presence of a correlation functional, show that a 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.

Even though the errors in the atomization energy in the meta-LDA functionals are larger than with established GGA functionals like B88-P86 (BP86) and B88-LYP (BLYP), gradient dependence can in principle be included on top of the meta-LDA form to form a meta-GGA functional with improved accuracy, which may be addressed in future work.

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SUPPLEMENTARY MATERIAL

The errors of exchange-only density functional calculations compared to unrestricted HF total and exchange energies for atoms from H to Sr are shown in figure 2 for closed-shell atoms (excluding Ne, Ar, and Kr that were presented in the main text), and figures 4 and 5 for the partially closed-shell atoms. In addition to the self-consistent data, figures 3 to 7 also show a perturbative evaluation of the exchange energy computed on top of the HF density.

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Figure 2: Error histograms for the atomization energies of the non-multireference part of W4-17 in the aug-pcseg-3 basis set.

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Figure 3: Errors in self-consistent total (blue solid line) and exchange (red solid line) energies of closed-shell atoms, as well as in the perturbative exchange energy calculated on top of the HF density (dashed red line). The location of the smallest error for the self-consistent total and exchange energies are shown as the blue and red squares, respectively, and the one for the perturbative exchange energy as red diamonds.
Figure 4: Errors in self-consistent total (blue solid line) and exchange (red solid line) energies of partially closed-shell atoms, as well as in the perturbative exchange energy calculated on top of the HF density (dashed red line). The location of the smallest error for the self-consistent total and exchange energies are shown as the blue and red squares, respectively, and the one for the perturbative exchange energy as red diamonds.
Figure 5: Errors in self-consistent total (blue solid line) and exchange (red solid line) energies of partially closed-shell atoms, as well as in the perturbative exchange energy calculated on top of the HF density (dashed red line). The location of the smallest error for the self-consistent total and exchange energies are shown as the blue and red squares, respectively, and the one for the perturbative exchange energy as red diamonds.