Non-empirical hyper-generalized-gradient functionals constructed from the Lieb-Oxford bound

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A simple and completely general representation of the exact exchange-correlation functional of density-functional theory is derived from the universal Lieb-Oxford bound, which holds for any Coulomb-interacting system. This representation leads to an alternative point of view on popular hybrid functionals, providing a rationale for why they work and how they can be constructed. A similar representation of the exact correlation functional allows to construct fully non-empirical hyper-generalized-gradient approximations (HGGAs), radically departing from established paradigms of functional construction. Numerical tests of these HGGAs for atomic and molecular correlation energies and molecular atomization energies show that even simple HGGAs match or outperform state-of-the-art correlation functionals currently used in solid-state physics and quantum chemistry.

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I. INTRODUCTION

The modern understanding of materials is based on the detailed quantitative description of their electronic structure afforded by quantum-mechanics. Since electron-electron interactions play an essential role in shaping material properties, electronic structure must be dealt simultaneously with the many-body physics of interacting electrons. At the heart of this interface between many-body theory and electronic-structure theory is the exchange-correlation \( (xc) \) functional of density-functional theory (DFT) [1, 2, 3, 4].

This functional, \( E_{xc}[n] \), comprises the exchange energy \( E_x[n] \), which is known in terms of single-particle orbitals, and the correlation energy \( E_c[n] \), which is unknown, and must be approximated. An intense and multidisciplinary research effort is thus directed at developing ever better approximations for \( E_{xc}[n] \) or \( E_c[n] \). While the local-density approximation (LDA) [5] is still widely and successfully used for band-structure calculations, total-energy calculations require at least the accuracy afforded by generalized-gradient approximations (GGAs) [6, 7, 8]. Quantum-chemical applications of DFT to atoms and molecules make increasingly use of hybrid functionals [9, 10, 11] mixing a certain (often empirical) fraction of exact exchange with LDA or GGA.

To make progress beyond the GGA level, the concepts of meta-GGA (MGGAs) [12, 13] and hyper-GGA (HGGAs) [14, 15, 16] have been proposed for functionals employing the kinetic-energy density or the exchange-energy density, respectively, but few explicit examples of such functionals have been constructed. Established procedures of functional construction do not fully determine the form of GGAs, MGGAs and HGGAs, enhancing the need for introducing empirical parameters.

Here we propose a hitherto unexplored mode of functional construction, which provides additional insight into the structure of the exact \( xc \) functional and the nature of common approximations to it, and naturally gives rise to non-empirical hyper-GGA functionals.

In Sec. II we use the universal Lieb-Oxford (LO) bound [17] on the exchange-correlation energy of Coulomb-interacting systems to derive an exact representation of the universal exchange-correlation functional of DFT. As an immediate consequence, we also obtain an LO-based exact representation of the universal correlation-energy functional.

In Sec. III the LO-based representation of \( E_{xc}[n] \) is shown to lead naturally to a reconstruction of the generic global hybrid functional, providing additional insight into the meaning of the components of the hybrid. Local hybrids are shown to be describable in a similar way.

Section IV is devoted to using the LO-based representation of \( E_{xc}[n] \) to construct a family of orbital-dependent correlation functionals that in the Jacob’s ladder classification scheme [1] belong on the hyper-generalized-gradient approximation (HGGAs) rung. The resulting HGGA functional is of different form from other functionals on the same rung, and satisfies exact constraints such as scaling properties and recovery of the gradient expansion for weakly varying densities.

In Sec. VA we report numerical tests of the constructed HGGAs for atomic and molecular correlation energies and molecular atomization energies, and compare to common correlation functionals of the LDA, GGA and meta-GGA type. We also present, in Sec. VB two further LO-based HGGA correlation functionals, which perform better than that of the preceding section for specific properties. One of these employs an unusual multiplicative self-interaction correction, the other enhances the possibilities for error cancellation in combination with semilocal approximations for exchange.

Section VI contains our conclusions.
II. LIEB-OXFORD-BASED REPRESENTATIONS OF THE CORRELATION AND EXCHANGE-CORRELATION ENERGIES

The starting point of our analysis of $E_c$ is the Lieb-Oxford (LO) bound [17], according to which the exchange-correlation energy obeys

$$E_{xc}[n] \geq \lambda E_x^{LDA}[n], \quad (1)$$

where the Lieb-Oxford value for $\lambda$ is $\lambda_{LO} = 2.27$. Recent numerical evidence suggested that the LO bound can be further tightened [18, 19] and generalized to one and two-dimensional systems [20]. We therefore also report results obtained from the value $\lambda_{EL} = 1.9555 \approx 2.0$, which is the ratio of $E_{xc}$ to $E_x^{LDA}$ in the extreme low-density limit of the uniform electron liquid (EL), which was conjectured to provide the tightest universally applicable bound [19, 20].

In the form (11), the LO bound plays a key role in the development of some GGAs [1, 21, 22] and meta-GGAs [12, 13]. The form of these functionals is dictated by other considerations, but typically the value of an otherwise undetermined parameter in them is chosen such that the bound is obeyed for all possible densities. Here we make rather different use of the LO bound: instead of using it to fix the value of a parameter in a functional whose form is obtained in other ways, we use it to determine the form of the functional itself.

By combining the variational principle with the LO bound in its form (11), we find immediately

$$0 \geq E_x[n] \geq E_{xc}[n] \geq \lambda E_x^{LDA}[n]. \quad (2)$$

$E_{xc}$ is thus bounded from above and below, which allows us to cast it as

$$E_{xc}[n] = (1 - \beta[n])E_x[n] + \beta[n]\lambda E_x^{LDA}[n], \quad (3)$$

where $\beta[n]$ is a density functional taking values in the interval $[0, 1]$. By subtracting $E_x[n]$ we find for the correlation functional the exact representation

$$E_c[n] = \beta[n]\left(\lambda E_x^{LDA}[n] - E_x[n]\right), \quad (4)$$

Since these representations of $E_{xc}$ and $E_c$ are completely general, all exact constraints on these functionals become constraints on $\beta[n]$, with the difference that while $E_{xc}[n]$ and $E_c[n]$ have values ranging, in principle, from zero to $\infty$, $\beta[n]$ ranges from zero to one.

Although in principle $\beta[n]$ is as complex as $E_{xc}[n]$, we note that the maximum absolute error one can make in approximating a quantity varying from 0 to $\infty$ is $\infty$, while for a quantity varying from 0 to 1 is $1/2$. This observation suggests that it may be useful to develop simple models for $\beta[n]$, designed to recover as many exact properties as possible, in order to develop new approximations for $E_{xc}[n]$.

III. CONNECTION TO GLOBAL AND LOCAL HYBRIDS

Representations (3) and (4) have many interesting properties, of which we now explore a few. As a first application, we compare Eq. (3) with hybrid functionals, of which a typical single-parameter example can be written as [23, 24, 25]

$$E^{hyb}_{xc}[n] = (1 - a)E_x[n] + aE_x^{LDA}[n] + E_c^{approx}[n]. \quad (5)$$

Here $a$ is a (normally empirical) constant determining how much LDA exchange is mixed into exact exchange.

Expression (5) can be considered an approximation to the exact representation (3), consisting of three steps: (i) Replace the functional $\beta[n] \in [0, 1]$ by a parameter $a \in [0, 1]$. (ii) Replace the LO parameter $\lambda$ by unity, in the second term. According to the general LO bound, this means that the correlation energy is underestimated, i.e., the resulting energy is not low enough. (iii) This underestimate is compensated by adding an explicit correlation functional $E_c^{approx} \leq 0$.

This re-construction of the generic hybrid (5) starting from the exact representation (3) suggests an alternative interpretation of the individual contributions to the hybrid functional: $E_c^{approx}$ is not an approximation to the full correlation energy, but only to the part missed by replacing $\lambda = 2.27$ by 1. We stress that this is merely a change in perspective, as the final form is exactly the same. However, such a change may be useful in selecting correlation functionals to be used in conjunction with exchange hybrids, and in the construction of novel hybrids.

A related class of functionals, so-called local hybrids, are of the generic form [23]

$$E^{hyb}_{xc}[n] = \int d\mathbf{r}(1 - a(\mathbf{r}))e_x[n](\mathbf{r}) + a(\mathbf{r})e_x^{LDA}[n](\mathbf{r}) + E_c^{approx}[n](\mathbf{r}), \quad (6)$$

where lower-case letters indicate energy densities. These functionals, too, can be interpreted as particular approximations to the general LO-based representations, by starting from the local LO bound, $e_x[n](\mathbf{r}) \geq \lambda e_x^{LDA}[n](\mathbf{r})$. This local form of the bound (satisfaction of which guarantees satisfaction of the global one) is that also used in constructing PBE-GGA and TPSS meta-GGA. In terms of this bound, the different components of the local hybrid can be interpreted in the same way as for the global hybrid. However, we note that unlike the global LO bound, the local one is not a rigorous property of quantum mechanics, but may be violated. Thus, in this sense, local hybrids are less tightly connected to universal bounds than global hybrids.

IV. CONSTRUCTION OF A HYPER GGA

As a second application, we use representation (4) to construct a class of non-empirical hyper-GGAs by enforcing constraints on $\beta[n]$. Occasionally, the expression
hyper-GGA is meant to refer to any functional employing exact exchange. In this sense, the global and local hybrids just discussed are already hyper-GGAs. However, we here adopt a more restrictive definition, in which hyper-GGA refers specifically to correlation functionals that use the exchange-energy density as an ingredient.

A first approximation to the functional \( \beta[n] \) is obtained by requiring that the resulting \( E_x[n] \) has the correct uniform density limit. On uniform densities \( \tilde{n} \) the exact and general representation \([1]\) becomes

\[
E_x[\tilde{n}] = \beta[\tilde{n}] \left( \lambda E^{LDA}_x[\tilde{n}] - E_x[\tilde{n}] \right),
\]

and since by definition \( E_c[\tilde{n}] = E^{LDA}_c[\tilde{n}] \) and \( E_x[\tilde{n}] = E^{LDA}_x[\tilde{n}] \), we find

\[
\beta[\tilde{n}] = \frac{E^{LDA}_c[\tilde{n}]}{(\lambda - 1) E^{LDA}_x[\tilde{n}]}.
\]

The use of this \( \beta \) in Eq. (1) also for nonuniform densities leads to a LO-based functional that correctly recovers the uniform gas limit.

In the same way, we can build in the gradient expansion for weakly nonuniform densities \( \tilde{n}(r) \), where the tilde means that the density is such that the low-order gradient-expansion approximation (GEA) is adequate. On such densities representation (4) becomes

\[
E_x[\tilde{n}] = \beta[\tilde{n}] \left( \lambda E^{LDA}_x[\tilde{n}] - E_x[\tilde{n}] \right),
\]

and since by definition \( E_c[\tilde{n}] = E^{GGA}_c[\tilde{n}] \) and \( E_x[\tilde{n}] = E^{GGA}_x[\tilde{n}] \), we can construct an approximation to \( \beta[n] \) from any functional that on weakly varying densities correctly reduces to the gradient expansion. The simplest choice would be the gradient expansion itself, leading to

\[
\beta[\tilde{n}] = \frac{E^{GGA}_c[\tilde{n}]}{\lambda E^{LDA}_x[\tilde{n}] - E^{GGA}_x[\tilde{n}]}. \tag{10}
\]

The use of this \( \beta \) in Eq. (4) also for strongly nonuniform densities leads to an explicit functional correlation functional recovering the uniform and the weakly nonuniform limits, in addition to the LO bound.

However, the denominator of this prefactor can have zeros at some values of the reduced gradient \( s \). The prefactor \( \beta[n] \) diverges at such densities, in contradiction to the Lieb-Oxford bound. Thus, this bound requires to construct \( \beta \) from a functional that has the correct gradient expansion at small gradients, and does not produce divergences at large ones. This problem is solved by using GGA instead of GEA, i.e.,

\[
\beta[\tilde{n}] = \frac{E^{GGA}_c[\tilde{n}]}{\lambda E^{LDA}_x[\tilde{n}] - E^{GGA}_x[\tilde{n}]}, \tag{11}
\]

which is also exact for weakly varying densities. The use of this \( \beta \) in Eq. (4) for arbitrary densities leads to the approximate functional

\[
E^{HGGA1}_c[n] = \frac{E^{GGA}_c[n]}{\lambda E^{LDA}_x[n] - E^{GGA}_x[n]} \left( \lambda E^{LDA}_x[n] - E_x[n] \right). \tag{12}
\]

By construction, this functional recovers the uniform limit and the gradient expansion to the order built into GGA. This is an important caveat, since actually very few GGAs recover the GEA both for exchange and correlation. In fact, the requirement that both the exchange and correlation functional used in constructing \( \beta[n] \) reproduce the low-order gradient expansion excludes popular GGAs such as PBE, PBEsol and BLYP, and almost uniquely singles out PW91 as the only widely used GGA suitable for the construction [24].

Numerically, we have explored many other variations, employing different choices of ingredient functionals of \( \beta[n] \) that do not fully recover the gradient expansion, such as PBE. This empirical analysis confirms that the choice of PW91 in \( \beta[n] \) is near-optimal (and certainly better than PBE) independently of, but in agreement with, the above construction based on recovering exact constraints.

With this choice, Eq. (12) has become an explicit correlation functional expressed in terms of other known density functionals, in particular the exact exchange functional \( E_x \). For this reason, it belongs into the class of hyper-GGAs. Interestingly, while representations [3] and [4] thus rather naturally lead to a connection with hybrids and to hyper-GGA type functionals, they do not involve any explicit use of kinetic energy densities, i.e., the present functionals belong to the fourth rung of Jacob’s ladder [4, 14, 29] without having passed through the third (meta-GGA) rung.

We note that the LO bound is incorporated in the correlation functional (12) through its structure, not by choice of a parameter, as in common GGAs and MGGA. It also makes use of the bound for correlation, unlike PW91 GGA, PBE GGA and TPSS meta-GGA, which use it for exchange. Moreover, Eq. (12) employs only the global LO bound, which has been rigorously proven for all possible densities [17], and does not make use of the local LO bound.

We also observe that under Levy coordinate scaling \([27]\) \( n(r) \rightarrow n_\gamma(r) = \gamma^3 n(\gamma r) \), both \( E^{LDA}_x \) and \( E^{PW91}_x \) correctly scale as \( E_x[n_\gamma] = \gamma^3 E_x[n] \). Thus, on scaling the present \( E^{HGGA1}_c[n] \) the exchange scaling factors cancel, and \( E^{HGGA1}_c[n] \) appropriately inherits all scaling properties of the correlation functional used in \( \beta \).

Overall, Eq. (12) is a nonempirical (in the sense of not containing any fitted parameters) correlation functional that recovers the uniform and the weakly nonuniform limits by construction, correctly scales as a correlation functional, and obeys the LO bound for structural reasons.

On the down side, in its present form the functional is not size consistent. However, we note that size-consistent versions of all our functionals can be constructed by replacing the component energy functionals by their respective energy densities, and integrating over the result, very similar to the step leading from a global hybrid to a local hybrid. In the specific case of HGGA1, this leads
TABLE I: Comparison of our HGGA1 functional with standard LDA, GGA and MGGA correlation functionals. First row: negative correlation energy of the H atom, in milliHartree. Second row: mean absolute relative error (mare) of the correlation energy of 17 atoms, from He \((Z=2)\) to Ar \((Z=18)\). Third row: mare of the correlation energy of 35 molecules for which highly precise correlation energies are available \([32]\). Fourth row: correct for the electron liquid \((y/n)\).

|            | LDA | PW91 | PBE | LYP | TPSS | HGGA1\((\lambda_{LO})\) | HGGA1\((\lambda_{LO})\) | HGGA1\((\lambda_{EL})\) | HGGA1\((\lambda_{EL})\) |
|------------|-----|------|-----|-----|------|--------------------------|--------------------------|--------------------------|--------------------------|
| H atom \((\text{mH})\) | 21.66 | 6.33 | 5.71 | [0] | [0] | 6.24 | 0 | 6.20 | 0 |
| atoms \((\text{mare }\%)\) | 119.7 | 4.9 | 6.8 | 3.9 | 5.4 | 4.75 | 4.38 | 4.70 | 4.37 |
| molecules \((\text{mare }\%)\) | 102.5 | 7.4 | 9.7 | 6.7 | 9.0 | 7.0 | 6.6 | 6.8 | 6.5 |
| electron liquid | Y | Y | Y | N | Y | Y | Y | Y | Y |

The second row reports mean absolute relative errors (mare) for atoms He to Ar. As benchmark data we used the standard set of CI atomic correlation energies of Ref. \([31]\). HGGA1 performs better than LDA, PW91, PBE and even TPSS MGGA, but loses to LYP. LYP, unlike all the other functionals tested here, contains empirical parameters fitted to the He atom, which explains its superior performance when applied to isolated atoms.

The third row reports molecular correlation energies for a set of 35 molecules for which highly precise correlation energies are available \([32]\). Encouragingly, we find that on this set HGGA1 achieves a lower error than all tested nonempirical functionals, including the highly sophisticated TPSS MGGA. The fourth row reports whether the tested functional is correct for the uniform electron liquid. All correlation functionals except for LYP (which was not designed to be correct in this limit) pass this test. Finally, we note that the performance of HGGA1 is systematically improved by lowering the value of \(\lambda\). This improvement is particularly encouraging, as a constraint-based functional should indeed deliver better results when the constraint it is based on is sharpened.

While our functional is, by construction, a correlation functional, and thus should be, as a matter of principle, compared to other correlation functionals, in practice it is clearly important to also test its performance for molecular atomization energies. As a test set we employed the well established set of 20 molecules that was used in the original PBE work \([6]\). Atomization energies are calculated from total energies, which in turn require choosing an exchange functional in addition to a correlation functional. To compare like with like, we combine all correlation functionals included in Table I with the same exchange functional. Since the spirit of HGGA \([26]\) is to provide a correlation functional to be combined with exact (Fock) exchange, we first calculated all total and atomization energies combining \(E_{\text{approx}}\) with the exact \(E_{\text{EL}}\). Results are reported in the first line of Table I. HGGA1 performs better than LDA, PW91, PBE and BLYP, while HGGA1-MSIC also improves on TPSS. When combined with exact exchange, the present HGGA functionals thus provide, comparatively, the best atomization energies.

to

\[
\int d^3r \frac{E_{\text{HGGA1-SC}}[n]}{\lambda e_{\text{LDA}}[n](r) - e_{\text{LDA}}[n](r)} = E_{\text{HGGA1}}[\lambda_{LO}] - e_{\text{LDA}}[n](r), \tag{13}
\]

which is size consistent (but, as any other approximate density functional available, not guaranteed to be size extensive).

V. NUMERICAL TESTS

A. HGGA1 correlation functional

In this section we present numerical tests of our HGGA1 functional. Since this is a correlation functional, the most direct and stringent test is the calculation of atomic and molecular correlation energies, to which we turn first.

A selfconsistent implementation of orbital functionals such as Eq. \((12)\) is possible by means of the optimized effective potential method and its simplifications \([26]\), or by the scaled selfconsistency approach \([28]\). Alternatively, such functionals can be implemented post-selfconsistently on LDA or GGA densities. Below, we evaluate all component-functionals of our HGGA1 post-selfconsistently on PW91 densities and orbitals.

Table I compares our HGGA1 correlation functional to a set of widely used correlation functionals: LDA, PW91 GGA, PBE GGA, LYP GGA, and TPSS MGGA, for 18 atoms, 35 molecules and the electron liquid. All DFT calculations were performed with GAUSSIAN 03 \([24]\) using the aug-cc-pVQZ basis set (except for the molecules from Ref. \([30]\), which uses cc-pVTZ).

The first row of Table I reports correlation energies of the hydrogen atom, which we display separately from those of other atoms because they are exclusively due to self-interaction, and thus permit to assess the self-interaction error. We note that already HGGA1, without any self-interaction correction, has a lower self-correlation error than LDA and PW91 GGA. HGGA1-MSIC, which by construction has zero self-correlation error, is explained in Sec. V.B below.
B. Variants exploiting error cancellation and the one-electron limit

On the other hand, it is well known that error cancellation allows to obtain much better atomization energies from local and semi-local correlation functionals by combining them with approximate local or semi-local exchange functionals, instead of with exact exchange. Results obtained in this way are reported in the second line of Table I, where LDA, PW91, PBE and TPSS correlation were combined with the corresponding exchange functionals, LYP correlation was combined with B88 exchange, and all HGGA’s were combined with PW91 exchange.

Evidently, all semilocal functionals benefit hugely from this error cancellation. The same applies to HGGA1, but the degree of improvement is slightly smaller than for GGAs and MGGA. However, we note that our choice of LYP GGA, must be interpreted with caution, since LYP erroneously predicts zero correlation energy for any fully polarized system, while the local one-electron indicator used in TPSS MGGA recognizes only one-electron systems with real orbitals, but fails for complex (current-carrying) orbitals. Thus, the correct entry 0 for TPSS MGGA, and even more so that for LYP GGA, must be interpreted with caution, signaled in Table II by [0]. The global one-electron indicator $E_x[n^{(1)}] = -E_H[n^{(1)}]$, used in our MSIC, does not suffer from either problem.

The resulting HGGA1-MSIC functional is a product of three factors, one stemming directly from the LO bound, one ($\beta$) from the electron liquid, and one ($F$) from the one-electron limit. HGGA1-MSIC spoils the recovery of the gradient expansion achieved by HGGA1, but does correctly recover the one-electron limit. (HGGA functionals achieving both properties are currently under investigation in our group.) As Table II shows, HGGA1-MSIC combines better with exact exchange than any of the other functionals, which is the behaviour expected from a HGGA. However, when combined with semilocal exchange it is still inferior to functionals exploiting error cancellation.

VI. CONCLUSIONS

All of the above suggests that the present HGGA functionals (with or without the MSIC factor) deliver competitive correlation and atomization energies, matching or outperforming those from sophisticated state-of-the-art functionals. We stress, however, that in spite of this encouraging conclusion we consider the present HGGA functionals merely as illustrations of the use of our representations and in the construction and analysis of functionals, and not as the final word in this regard.

Future development of other functionals based on the same representations (including novel hybrids) seems...
promising. The way our HGGAs are constructed from the global Lieb-Oxford bound represents a radical departure from traditional modes of functional construction in quantum chemistry and solid-state physics which is only beginning to be explored.

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