Hartree potential dependent exchange functional

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We introduce a novel non-local ingredient for the construction of exchange density functionals: the reduced Hartree parameter, which is invariant under the uniform scaling of the density and represents the exact exchange enhancement factor for one- and two-electron systems. The reduced Hartree parameter is used together with the conventional meta-generalized gradient approximation (meta-GGA) semilocal ingredients (i.e. the electron density, its gradient and the kinetic energy density) to construct a new generation exchange functional, termed u-meta-GGA. This u-meta-GGA functional is exact for the exchange of any one- and two-electron systems, is size-consistent and non-empirical, satisfies the uniform density scaling relation, and recovers the modified gradient expansion derived from the semiclassical atom theory. For atoms, ions, jellium spheres, and molecules, it shows a good accuracy, being often better than meta-GGA exchange functionals. Our construction validates the use of the reduced Hartree ingredient in exchange-correlation functional development, opening the way to an additional rung in the Jacob’s ladder classification of non-empirical density functionals.

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I. INTRODUCTION

Kohn-Sham (KS) ground-state density functional theory (DFT)1–2 is one the most used methods in electronic calculations of quantum chemistry and condensed-matter physics. Its practical implementation is based on approximations of the exchange-correlation (XC) energy \( E_{xc} \), which is a subject of intense research3–5.

The simplest functionals, beyond the local density approximation (LDA), are those based on the generalized gradient approximation (GGA), which are constructed using the electron density \( n \) and its reduced gradients (e.g. \( s \) in Eq. (9)). These functionals can achieve reasonable accuracy for various energetical and/or structural properties of molecules and/or solids, at a moderate computational cost9–10. However, because of their simplicity, GGA functionals also show several important limitations, especially in terms of broad applicability. Moreover, they are based on a heavy error cancellation between exchange and correlation parts31.

To improve over GGAs, meta-generalized-gradient approximations (meta-GGAs) can be considered32–34. These are the most sophisticated semilocal functionals and use, as additional ingredient with respect to the GGA ones, the positive-defined kinetic energy density \( \tau = (1/2) \sum_{i=1}^N |\nabla \phi_i|^2 \) (with \( \phi_i \) being the KS orbitals and \( N \) the number of occupied KS orbitals). This quantity enters in the expansion of the angle-averaged exact exchange hole35, being thus a natural and important tool in the construction of XC approximations. Meta-GGA functionals incorporate important exact conditions and have an improved overall accuracy with respect to the GGA functionals. Moreover, because the kinetic energy density can be easily computed at any step of the KS self-consistent scheme, the meta-GGA functionals have almost the same attractive computational cost as any GGA.

Further improvements, beyond the meta-GGA level of theory, are usually realized abandoning the semilocal framework. Here we mention the so-called 3.5 Rung functionals36–59, that incorporate a linear dependence on the nonlocal one-particle density matrix, and non-local functionals based on the properties and modelling of the exchange-correlation hole60–65. Moreover, popular tools in computational chemistry are the hybrid functionals66–74, which mix a fraction of nonlocal Hartree-Fock exchange with a semilocal XC functional. Alternatively, even more complex possibilities can be considered, such as hyper-GGA functionals76–78 or orbital-dependent functionals79–82. In this way, a significant increase of the accuracy can be achieved. Nevertheless, because of the need to compute non-local contributions (e.g. the Hartree-Fock exchange), the computational cost of such methods is considerably larger than the one of semilocal functionals.

In this paper, we consider an alternative strategy to introduce non-local effects into a density functional, without affecting too much the final computational cost. The idea is to consider, as additional ingredient beyond the conventional meta-GGA level of theory, the Hartree potential

\[
u(r) = \int dr' \frac{n(r')}{|r - r'|}. \tag{1}
\]

The Hartree potential appears to be a natural input ingredient in the construction of exchange functionals for several reasons:

• For one- and two-electron systems, the exact ex-
change energy is\footnote{\textsuperscript{34}}
\begin{equation}
E_x[n] = -\frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) u(\mathbf{r}), \quad \text{for } N = 1 ,
\end{equation}
\begin{equation}
E_x[n] = -\frac{1}{4} \int d\mathbf{r} n(\mathbf{r}) u(\mathbf{r}), \quad \text{for } N = 2 ,
\end{equation}
where \( N \) is the number of electrons. Note that Eq. \( \text{(2)} \) is the basis of the self-interaction correction approach of Perdew and Zunger\footnote{\textsuperscript{35}}.

- The asymptotic decay of the Hartree potential
\begin{equation}
\lim_{r \to \infty} u(\mathbf{r}) = \frac{N}{r}
\end{equation}
is proportional to that of the exact exchange per particle and potential\footnote{\textsuperscript{36}},
\begin{equation}
\lim_{r \to \infty} \epsilon_{x}(\mathbf{r}) = -1/(2r)
\end{equation}
\begin{equation}
\lim_{r \to \infty} v_{x}(\mathbf{r}) = -1/r.
\end{equation}
In fact the Fermi-Amaldi potential\footnote{\textsuperscript{37,86}} which equals \( u(\mathbf{r})/N \), has been largely used to construct exchange and exchange-correlation functionals, see e.g. Refs. \textsuperscript{37,94}. However, the Fermi-Amaldi potential depends on \( N \), thus it is not size-consistent\footnote{\textsuperscript{38}}.

In this work we consider the construction of an exchange functional of the general form
\begin{equation}
E_x^{u-MGGA}[n] = \int n \epsilon_{x}^{u-MGGA}(n, \nabla n, \tau, u) d\mathbf{r} = (7)
\end{equation}
\begin{equation}
= \int n \epsilon_{x}^{LDA}(n) F_{x}(n, \nabla n, \tau, u) d\mathbf{r},
\end{equation}
where \( \epsilon_{x}^{LDA} = -(3/4\pi)(3\pi^2)^{1/3}n^{1/3} \) is the local density approximation for exchange and \( F_{x} \) is the exchange enhancement factor. The functional of Eq. \( \text{(7)} \) constitutes the prototype for a new class of functionals, that we name \textit{u-meta-GGA} (u-MGGA in short). The construction of a correlation \textit{u-meta-GGA} functional is also conceivable but it is a more complex task and it is left for future work. The \textit{u-meta-GGA} exchange functional is expected to have higher accuracy than conventional meta-GGAs, thanks to the inclusion of non-local effects via the Hartree potential. At the same time, because the Hartree potential must be anyway computed at every step of any KS calculation (even at the LDA level), it bears no essential additional computational cost with respect to meta-GGAs.

II. CONSTRUCTION OF THE U-META-GGA EXCHANGE FUNCTIONAL

A. The reduced Hartree ingredient

To start our work, we consider the construction of a proper reduced ingredient that depends on the Hartree potential and has the correct features to be usefully employed in the construction of density functionals. This is the \textit{Hartree reduced parameter}
\begin{equation}
\eta^u = \frac{u}{3\pi(3\pi^2)^{1/3}n^{1/3}}.
\end{equation}
This ingredient is invariant under the uniform scaling of the density \( n_{\gamma}(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r}) \), with \( \gamma > 0 \), i.e. it behaves as \( \eta^u(\gamma \mathbf{r}) = \eta^u(\mathbf{r}) \). This invariance is a key property for any input ingredient to be used in the development of semilocal DFT functionals. In fact, it is satisfied by all the semilocal ingredients:
\begin{equation}
s = \frac{|\nabla n|}{2 k_F n}, \quad z = \frac{\tau^W}{\tau}, \quad \alpha = \frac{\tau - \tau^W}{\tau^\text{unif}}, \quad \eta^u = \frac{u}{3\pi(3\pi^2)^{1/3}n^{1/3}}.
\end{equation}
where \( k_F = (3\pi^2 n)^{1/3} \) is the Fermi wavevector, \( \tau^\text{unif} = (3\pi^2)^{2/3} n^{5/3} \) is the Thomas-Fermi kinetic energy density, and \( \tau^W = \tau^\text{unif} 5^{2/3} / 3 \) is the von Weizsäcker kinetic energy density, width, and flow, respectively.

Additional important formal properties of \( \eta^u \) can be obtained considering its behavior under the coordinate and particle-number density scaling\footnote{\textsuperscript{95,96}} \( n_{\gamma}^{(\beta)}(\mathbf{r}) = \gamma^{3\beta + 1} n(\gamma^\beta \mathbf{r}) \), with \( \gamma > 0 \) and \( \beta \) being a parameter), which defines a whole family of scaling relations. Under this scaling, we have \( \eta^u \to \gamma^{2/3} \eta^u \), i.e. the Hartree reduced ingredient scales as \( N^{2/3} \), with \( N \) being the number of electrons. This result indicates that, unlike the semilocal parameters, \( \eta^u \) is a size-extensive quantity, increasing with the number of electrons. We note that, in spite of this feature, the reduced Hartree parameter is anyway behaving in a proper size-consistent way as shown in Appendix A.

Moreover, we can note that the scaling properties of \( \eta^u \) do not depend on the value of the parameter \( \beta \). Thus, for the uniform-electron-gas and the Thomas-Fermi scalings\footnote{\textsuperscript{95,96}}, where the \( \gamma \to \infty \) limit is important, large values of \( \eta^u \) are relevant; on the opposite, for the homogeneous and fractional-particle scalings\footnote{\textsuperscript{95,97}}, where \( \gamma \to 0 \), small values of \( \eta^u \) are important. These considerations will be significant to analyze the behavior of an \( \eta^u \)-dependent enhancement factor in different conditions.

In Fig. 1 we compare the behavior of \( \eta^u \) with that of the other semilocal ingredients for some atoms and dimers. It can be seen that \( \eta^u \) behaves rather different than the other conventional semilocal reduced parameters \( s, z, \) and \( \alpha \), being in general more shallowed and averaged: \( \eta^u \) is in fact a non-local ingredient and thus it contains, at every point of space, information on the whole system. Moreover, it is larger than zero at any point in space (unlike \( s \), for example): in the density tail asymptotic region we always have
\begin{equation}
\eta^u \to +\infty,
\end{equation}
like \( s \) but in contrast to \( \alpha \) which vanishes for iso-orbital density tails (e.g. for Be).

Thus, \( \eta^u \) appears to be an interesting tool for the construction of advanced functionals both to complement the
information available from standard semilocal reduced ingredient and to add information on the shape of the exchange enhancement factor.

The most important feature of $\eta^u$ is that the simple exchange enhancement factor

$$F_x = \eta^u$$

yields immediately Eqs. (2) and (3) [for the former, note that the exchange energy satisfies the spin-scaling relation~\cite{99} $E_x[n_\uparrow, n_\downarrow] = (E_x[2n_\uparrow] + E_x[2n_\downarrow])/2$. Hence, $\eta^u$ represents the exact exchange enhancement factor for any one- and two-electron system.

Finally, it is also useful to define the bounded ingredient

$$\upsilon_u = \frac{1}{1 + \eta^u},$$

that is small everywhere for large systems, but also in the tail of the density (where $\eta^u \to \infty$). In Fig. 2 we show $\upsilon_u$ for the noble atoms of the periodic table. One can see that in most of the space the curves are not intersecting, such that $\upsilon_u$ can be considered a good atomic indicator, being of interest for functional development.

B. The u-meta-GGA exchange functional

In the previous subsection we introduced the Hartree reduced parameter and we showed that it posses interesting properties that suggest its utility as input quantity in the construction of advanced density functionals. On the other hand, we have observed that in general $\eta^u$ is always large in magnitude. Thus, the proper use of this quantity in functional development is not trivial and the construction of a good u-meta-GGA functional represents instead a challenge.

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**FIG. 1:** Plot of the reduced gradient ($s$), the $\alpha$ meta-GGA ingredient, and the Hartree reduced parameter $\eta^u$, for some atoms (top) and dimers (bottom), as functions of the position. The green cross in the bottom part of each dimer plot denotes the position of the atom (note that only half of the dimer is plotted).
The u-meta-GGA exchange functional has been costrued satisfying the following properties:

- For one and two electron systems \( z = 1 \), so that \( b = \beta = 0 \), yielding \( A = \eta^u \) and \( F_x^u = 1 \), therefore \( F_x^{u-MGGA} = \eta^u \) is exact (see Eq. (11));

- Under the uniform density scaling \( n_z(r) = \gamma^3 n(\gamma r) \), with \( \gamma > 0 \), it behaves correctly as \( E_x^{u-MGGA} = \gamma F_x^{u-MGGA} \);  

- It is size-consistent (see Appendix A);

- For many-electron systems, we can distinguish different regions:

  - In the slowly-varying density limit \((s \rightarrow 0 \), \( z \rightarrow 3s^2/4 + O(\n) \)), \( \alpha \rightarrow 1 + O(\n_4^2) \) we have \( b \rightarrow 1 \) and \( \beta \rightarrow 1 \), thus \( A \rightarrow 1 \) and

    \[
    F_x^{u-MGGA} \rightarrow F_x^1 \rightarrow 1 + \mu n^2 . \tag{19}
    \]

    Note that in the limit of large atoms \( \mu \rightarrow \mu^{MGE2} \), such that the semilocal atom theory is correctly recovered.

  - In the density tail asymptotic region with valence orbitals having a non-zero angular momentum quantum number \((s \rightarrow \infty, z < 1)\) so that \( \beta \rightarrow 0 \). We have also that \( \eta^u \rightarrow \infty \) and \( A \rightarrow 1 \) (as \( \beta^{(1/\eta^u)} \rightarrow 1 \)), thus

    \[
    F_x^{u-MGGA} \rightarrow F_x^1 \rightarrow \frac{2\pi \sqrt{\alpha}}{3 \sqrt{5} \sqrt{\ln(1+\alpha)}} . \tag{20}
    \]

Equation (20) is an exact meta-GGA constraint for metallic surfaces, making asymptotically exact both the exchange energy per particle and the potential, while for finite systems we found (see Appendix B) that the exchange energy per particle decays as \( e_x \rightarrow -C/p^{3/2} \), and the exchange potential decays as \( v_x \rightarrow -C/(2p^{3/2}) \), with \( C \) being a constant dependent on the angular momentum quantum number of the outer shell, if \( \alpha \rightarrow \infty \). Thus, for finite systems Eq. (20) is not an exact constraint. Nevertheless, this behavior is definitely more realistic than the usual exponential decay behavior of most semilocal functionals. In any case, we underline that the Hartree potential is not used to describe the asymptotic region, in contrast to functionals based on the Fermi-Amaldi potential: instead, the meta-GGA expression in Eq. (20) is used. Moreover, in this work we are only considering non self-consistent results, which are thus quite unaffected by the choice of the functional in the asymptotic region.
We note that the u-meta-GGA enhancement factor diverges for \( \eta^u \to +\infty \) and/or \( s \to +\infty \) (i.e. in the tail of the density). Therefore, unlike other functionals, it does not respect the local form of the Lieb-Oxford bound\(^{104-108}\). We note that this feature is anyway not an exact constraint and it is indeed also strongly violated by the conventional exact exchange energy density\(^{107}\). However, we recall that the global Lieb-Oxford bound, which is the true exact condition, is not tight, being usually fulfilled for all known physical systems, by most of the functionals\(^{108}\). As shown in the next section, the u-meta-GGA functional is accurate for atoms and molecules. Thus, it implicitly satisfies the Lieb-Oxford bound for these systems.

### C. Parametrization of the functional

Because the u-meta-GGA is exact for any one- and two-electron systems, we require it to be as accurate as possible also for four-electron systems. To this purpose, we consider the four-electron hydrogenic-orbital model (1s\(^2\)2s\(^3\)), with the following one-electron wavefunctions (\( \psi_{nlm} \) with \( n, l, \) and \( m \) being the principal, the angular, and the azimuthal quantum numbers respectively)

\[
\psi_{100}(r) = \sqrt{\frac{\pi}{2}} Z_1^{3/2} e^{-Z_1 r},
\]

\[
\psi_{200}(r) = \frac{1}{\pi} \sqrt{\frac{Z_2^{3/2}}{2}} e^{-Z_2 r/2}(2 - Z_2 r),
\]

with \( Z_1 \) and \( Z_2 \) being the nuclear charges seen by the 1s and 2s orbitals, respectively. Note that for the real beryllium atom, \( Z_1 \approx 4 \), and \( Z_2 \approx 2 \). This model system is analytical and simple, and can cover important physics by varying \( Z_1 \) and \( Z_2 \). In Appendix C we show in detail the case \( Z_1 = Z_2 = Z \). We also recall that the hydrogenic orbitals are important model systems in DFT, having been used to find various exact conditions\(^{102,103,109}\) and to explain density behaviors\(^{42,109}\).

The parameters \( a_1, a_2 \) and \( a_3 \) have been fitted by fixing \( Z_1 = 4 \) (as in the beryllium case) and varying \( Z_2 \) between 1 and 4. In Fig. 3 we show the resulting percent error (i.e. \( 100 \times (E_x\text{exact} - E_x\text{approx})/E_x\text{exact} \)) as a function of \( Z_2 \) and we compare the u-meta-GGA results with those of other popular functionals. All the considered meta-GGA exchange functionals (TPSS\(^{35}\), revTPSS\(^{36}\), BLOC\(^{28}\), MGGA\(_{MS}^{10,41}\), MVS\(^{42}\), and SCAN\(^{44}\)) perform similarly, while u-meta-GGA improves considerably, showing errors below 1.5 %.

In Fig. 4 we report the u-meta-GGA exchange enhancement factor for the Be atom, comparing it to the exact one (obtained as the ratio of the conventional exact exchange and the LDA exchange energy densities) and the popular TPSS meta-GGA. This is a difficult and important example for the u-meta-GGA, because in the atomic core the density varies rapidly, the 1s and 2s orbitals overlap strongly, showing a significant amount of non-locality. Thus, \( s \) and \( \alpha \) are large (\( s \approx 2 \) at \( r = 0.8 \), and \( \alpha \approx 7 \) and \( r = 1 \)), while \( z \) is relatively small (\( z \approx 0.34 \) at \( r = 1 \)). See also Fig. 4 \( F_x^{u-MGGA} \) is smooth and more realistic than the TPSS one, at every point in space. Remarkably, the u-meta-GGA can also describe well the atomic core. Using the PBE\(^{10}\) orbitals and densities, the total exchange energies for Be atom are: \( E_x^{\text{exact}} = -2.659 \) Ha, \( E_x^{TPSS} = -2.673 \) Ha, and \( E_x^{u-MGGA} = -2.655 \) Ha.

## III. COMPUTATIONAL DETAILS

All calculations for spherical systems (atoms, ions, and jellium clusters) have been performed with the numerical Engel code\(^{110,111}\), using PBE orbitals and densities.

All calculations for molecules have been performed with the TURBOMOLE program package\(^{112,113}\) using
TABLE I: Relative errors \(10^3 \times \left(\frac{E_{x}^{\text{approx}} - E_{x}^{\text{exact}}}{E_{x}^{\text{exact}}}\right)\) for the exchange energy of the H, G, and C one-electron densities.

| Functional   | H    | G    | C    |
|--------------|------|------|------|
| u-meta-GGA   | 0.0  | 0.0  | 0.0  |
| TPSS         | 0.0  | 0.3  | -3.6 |
| revTPSS      | 0.0  | 1.5  | -3.3 |
| MS2          | 0.0  | -9.4 | -7.0 |
| MVS          | 0.0  | -5.9 | -5.5 |
| SCAN         | 0.0  | -3.5 | -4.8 |

PBE\(^{10}\) orbitals and densities and a def2-TZVPP basis set\(^{114,115}\). Similar results (not reported) have been found using LDA and Hartree-Fock orbitals and densities.

Following a common procedure in DFT calculations, we have set a minimum threshold (\(10^{-20}\)) for the electron density in order to avoid divide-by-zero overflow errors in tail regions and one-electron systems. All results are completely insensitive to the value of the threshold.

IV. RESULTS

A. One- and two-electron systems

For one- and two-electron systems, the u-meta-GGA functional satisfies the exact condition in Eq. (11). This is a very powerful exact constraint, that cannot be achieved at the GGA and meta-GGA levels of theory. In fact, even if some meta-GGAs have been fitted to the exchange energies of the hydrogen atom (e.g. TPSS\(^{35}\), revTPSS\(^{36}\), BLOC\(^{38,54}\), and Meta-VT\(^{8,4}\)\(^{34}\)), they are not exact for many other interesting one- and two-electron densities. On the contrary, the u-meta-GGA functional is exact, not only for total exchange energies, but also for exchange energy densities and potentials, by construction, in all cases.

To make this point more clear, we consider briefly some relevant examples of one- and two-electron densities. The first case concerns the hydrogen (H), Gaussian (G), and cuspless hydrogen (C) one-electron densities, that are defined as

\[
n_H(r) = \frac{e^{-2r}}{\pi}, \quad n_G(r) = \frac{e^{-r^2}}{\pi^{3/2}}, \quad n_C(r) = \frac{(1+r)e^{-r}}{32\pi}.
\]  

These densities are models for atomic, bonding, and solid-state systems\(^{23,28,35}\). They have analytical exchange energies \(E_H = -5/16\), \(E_G = -1/\sqrt{2\pi}\), and \(E_C = -63/512\). Thus, we have used them to test the performance of several functionals (see Table I). Inspection of the table immediately shows that only the u-meta-GGA is exact in all cases, whereas the other functionals can at most perform exactly in a single case, by virtue of a targeted parametrization. Note that any meta-GGA cannot give the exact exchange potential of any one- or two-electron densities.

Another example is shown in Fig. 5, where we plot the dissociation curve of the \(H_2^+\) molecule, which is the simplest possible molecule. This is a notoriously difficult problem for semilocal functionals\(^{116}\), being related to the delocalization error. Nevertheless, because the u-meta-GGA is exact for any one-electron density, it yields the exact description for this difficult case.

Finally, we report in Fig. 6 the exchange energy computed for the non-uniformly scaled hydrogen atom versus the scaling parameter \(\lambda\)\(^{117}\). This is a model for quasi-two-dimensional systems and to study the three-dimensional to two-dimensional crossover\(^{29}\). All functionals, including meta-GGAs, are very accurate at \(\lambda = 1\) (i.e. the conventional three-dimensional hydrogen atom). However, for larger values of the confining parameter only u-meta-GGA is exact (by construction). The meta-GGA functionals instead fail badly even for mild and moderately large values of \(\lambda\).
FIG. 7: Upper panel: Percent exchange energy error \((100(E_x^{\text{exact}} - E_x^{\text{approx}})/E_x^{\text{LDA}})\) versus \(Z^{-1/3}\) for all periodic table atoms \((2 \leq Z \leq 118)\). Lower panel: Percent exchange energy error \((100(E_x^{\text{exact}} - E_x^{\text{approx}})/E_x^{\text{LDA}})\) versus \(Z^{-1/3}\), for noble atoms \((2 \leq Z \leq 290)\).

Other examples of two-electron densities of interest in DFT are the Hooke’s atom, the Loos-Gill model, and the strictly-correlated two-electrons model. In all these cases, the u-meta-GGA functional yields, by construction, an exact description of exchange.

**B. Atoms**

Computing the absolute energies of atoms can be expected to be quite a hard task for the u-meta-GGA functional. In fact, the functional is exact for one- and two-electron system (i.e. H and He atoms) but for increasingly large atoms the Hartree reduced parameter becomes soon very large (see Fig. 7). Therefore, a particular care is required to balance the contribution of this ingredient in different cases.

To check this issue, we have calculated the exchange energy of all periodic table atoms \((2 \leq Z \leq 118)\) and we have compared the u-meta-GGA results to those of some meta-GGA functionals. The results are reported in the upper panel of Fig. 7 and in Table II.

The u-meta-GGA performs remarkably well for all the periodic table atoms, being one of the most accurate functionals, with a mean absolute error (MAE) of 7.6 mHa/electron, slightly worse than MVS and SCAN meta-GGAs (with MAE=2.8 mHa/electron and MAE=4.8 mHa/electron, respectively). Moreover, in Fig. 7, we show the exchange energy error \((100(E_x^{\text{exact}} - E_x^{\text{approx}})/E_x^{\text{LDA}})\) for noble atoms with \(2 \leq Z \leq 290\). This plot shows that, in case of large atoms \((118 \leq Z \leq 290)\), the u-meta-GGA becomes the most accurate functional, due to the semiclassical atom theory which it incorporates.

**C. Isoelectronic series and Jellium clusters**

We consider the first 17 ions of the isoelectronic series of Beryllium \((4 \leq Z \leq 20)\), Nitrogen \((7 \leq Z \leq 23)\), Neon \((10 \leq Z \leq 26)\), and Copper \((29 \leq Z \leq 45)\). The results for all systems are reported in Fig. 8 while the MAEs are shown in Table II. The u-meta-GGA is very accurate in all cases, outperforming most of the other semilocal functionals for Be and Ne. For N (Cu) the best functional is SCAN (MVS) and u-meta-GGA is the second best one. Note that the case of Cu is the most difficult one, because u-meta-GGA performs modestly for the Cu atom (see Fig. 7). Nevertheless, for increasing \(Z\) values it soon becomes very accurate.

We also tested the u-meta-GGA for magic jellium clusters with 2, 8, 18, 20, 34, 40, 58, and 92 electrons for bulk parameters \(r_s = 1\) and \(r_s = 4\). The error statistics are reported in Table II. In both cases u-meta-GGA is accurate, being in line with the best semilocal functionals.

**D. Molecules**

In Table III we report the exchange atomization energies of the systems constituting the AE6 test set, as computed with several methods. One can see that the u-meta-GGA functional performs quite well in this case, being often superior to meta-GGA functionals and yielding overall the best MAE. This result shows that the u-meta-GGA functional provides a well balanced description of atoms and molecules, at the exchange level. We note that this success goes beyond the exactness of this functional for one- and two-electron systems, since in the present case this feature concerns only the computation of the H atom energy, which is exact also for all the other tested meta-GGAs.

As additional test, we consider in Table IV the exchange-only barrier heights and reaction energies of the systems defining the K9 test set. This is a harder test than the previous one, since transition-state structures display rather distorted geometries and are therefore characterized by a different density regime than ordinary molecules. Inspection of the table shows that the errors on reaction energies display a similar trend as for the atomization energies, even though the differences between the functionals are smaller because of the smaller magnitude of the computed energies. Instead, for barrier heights no clear trend can be extracted. Nevertheless, the u-meta-GGA functional shows a reasonable performance being similar to meta-GGAs. This finding supports the robustness of the construction presented in Section II B.
TABLE II: Mean absolute errors (mHa) for various systems and properties.

| System                       | Property | TPSS  | revTPSS | BLOC  | MS2   | MVS   | SCAN  | u-MGGA |
|------------------------------|----------|-------|---------|-------|-------|-------|-------|--------|
| Atoms ($2 \leq Z \leq 118$)  | $E_x/Z$  | 12.4  | 27.3    | 23.4  | 18.9  | 2.8   | 4.8   | 7.6    |
| Noble atoms ($2 \leq Z \leq 290$) | $E_x/Z$  | 21.5  | 34.2    | 31.6  | 27.2  | 5.5   | 8.8   | 5.1    |
| $4e^-$-ions ($4 \leq Z \leq 20$) | $E_x$    | 50.5  | 29.8    | 56.8  | 51.1  | 65.1  | 37.6  | 2.5    |
| $7e^-$-ions ($7 \leq Z \leq 23$) | $E_x$    | 23.3  | 64.9    | 25.0  | 13.7  | 68.8  | 4.3   | 8.6    |
| $10e^-$-ions ($10 \leq Z \leq 26$) | $E_x$    | 30.6  | 156.0   | 35.4  | 39.7  | 59.3  | 76.9  | 12.2   |
| $29e^-$-ions ($29 \leq Z \leq 45$) | $E_x$    | 203.8 | 754.0   | 483.5 | 448.2 | 63.4  | 225.8 | 191.1  |
| Jellium clusters $r_s = 4$ ($2 \leq Z \leq 92$) | $E_x/Z$  | 1.1   | 1.3     | 1.1   | 0.9   | 2.0   | 1.3   | 1.0    |
| Jellium clusters $r_s = 1$ ($2 \leq Z \leq 92$) | $E_x/Z$  | 2.7   | 4.7     | 3.4   | 3.8   | 2.7   | 1.7   | 2.1    |

FIG. 8: Exchange errors ($E_{exact}^x - E_{approx}^x$) versus nuclear charge $Z$, for Beryllium (top-left panel), Nitrogen (top-right panel), Neon (bottom-left panel), and Copper (bottom-right panel) isoelectronic series.

V. COMPATIBILITY OF THE U-META-GGA WITH SEMILOCAL CORRELATION FUNCTIONALS

In this section we investigate the possibility to combine the u-meta-GGA exchange with an existing semilocal correlation functional. Thus, we consider the performance of different combinations of the u-meta-GGA exchange with an existing semilocal correlation functional, for the description of molecular properties, namely the AE6\cite{123,125} and K9\cite{124,125} test sets. In more detail, we consider the following correlation functionals: PBE\cite{10}, PBElo\cite{31}, GAPlo\cite{27}, TCA\cite{16}, vPBE\cite{41} (the semilocal correlation of the MGGA-MS functional), PBEso\cite{11}, LYP\cite{19} [GGA functionals], TPSS\cite{35}, revTPSS\cite{36,37}, BLOC\cite{38}, MS\cite{39,42} [meta-GGA functionals].

In Fig. 9 we report the MAE on the AE6 test versus the MAE for the K9 test as obtained by the different
TABLE III: Errors (kcal/mol) and error statistics for the exchange atomization energies of the AE6 test. The best result of each line is highlighted in bold style.

| System   | TPSS | revTPSS | BLOC | MS2  | MVS  | SCAN | u-MGGA |
|----------|------|---------|------|------|------|------|--------|
| CH₄      | -3.1 | -1.9    | -2.8 | -3.0 | 3.8  | 5.6  | -15.6  |
| SiO      | 31.8 | 30.5    | 27.8 | 26.7 | 38.4 | 34.3 | 12.9   |
| S₂       | 17.4 | 18.2    | 15.1 | 14.4 | 25.1 | 14.3 | 3.6    |
| C₃H₄     | 20.2 | 15.2    | 16.0 | 25.4 | 42.1 | 45.5 | -1.3   |
| C₂H₂O₂   | 60.2 | 56.9    | 51.9 | 66.0 | 78.2 | 83.6 | 16.3   |
| C₄H₆     | -2.8 | -8.5    | -11.2| 21.3 | 34.2 | 48.4 | -47.6  |
| MAE      | 13.8 | 13.6    | 12.1 | 12.8 | 19.4 | 16.0 | 5.7    |

TABLE IV: Errors (kcal/mol) and error statistics of several exchange functionals for the K9 representative test. The best result of each line is highlighted in bold style.

| System               | TPSS | revTPSS | BLOC | MS2  | MVS  | SCAN | u-MGGA |
|----------------------|------|---------|------|------|------|------|--------|
| **Forward barriers** |      |         |      |      |      |      |        |
| OH⁺CH₄ → CH₃⁺H⁺O    | -12.5| -11.6   | -10.5| -10.2| -11.1| -12.1| -1.0   |
| H⁺OH → O⁺H₂         | -2.7 | -8.1    | -6.8 | **-2.2**| -5.5 | -3.0 | -8.4   |
| H⁺H₂S → H₂⁺HS       | **-1.0**| -3.6    | -4.1 | -3.4 | -4.5 | -5.0 | -3.1   |
| MAE                  | 8.0  | 7.8     | 7.1  | 5.3  | 7.0  | 6.7  | **4.2**|
| **Backward barriers**|      |         |      |      |      |      |        |
| OH⁺CH₄ ← CH₃⁺H⁺O    | -7.6 | -8.1    | -6.8 | -10.3| 2.1  | -5.5 | **3.6**|
| H⁺OH ← O⁺H₂         | -10.4| -9.9    | -12.2| -15.7| -13.6| -16.6| -16.9  |
| H⁺H₂S ← H₂⁺HS       | -2.2 | **6.3**| -1.6 | -8.2 | -2.9 | -7.0 | -3.7   |
| MAE                  | 7.3  | 6.3     | 6.9  | 8.9  | 8.7  | 9.7  | 8.1    |
| **Reaction energies**|      |         |      |      |      |      |        |
| Δ(OH⁺CH₄-CH₃⁺H⁺O)    | -4.9 | -3.5    | -3.7 | **0.1**| -13.2| -6.5 | -4.6   |
| Δ(H⁺OH-O⁺H₂)         | 7.7  | **1.8**| 5.3  | 11.4 | 10.2 | 13.6 | 8.5    |
| Δ(H⁺H₂S-H₂⁺HS)       | -2.0 | -2.7    | -2.5 | -0.5 | 3.7  | 2.1  | **0.6**|
| MAE                  | 3.9  | **2.7**| 3.8  | 4.0  | 9.0  | 7.4  | 4.6    |
| **Overall statistics**|      |         |      |      |      |      |        |
| MAE                  | 6.4  | **5.6**| 6.0  | 6.1  | 8.3  | 7.9  | **5.6**|

The best performance is found for PBEloc, GAPloc, and BLOC. These are indeed the only correlation functionals that allow to achieve for both tests results that are better than the simple PBE XC ones (13.4 kcal/mol for AE6 and 7.5 kcal/mol for K9), which we have used here as a reference. This result indicates that a more localized correlation energy density may favor the compatibility with the u-meta-GGA in finite systems. This conclusion can be traced back to the fact that the localization constraint in the PBEloc, GAPloc, and BLOC correlation functionals has been introduced to enhance the compatibility of the semilocal correlation with exact exchange, thus it also improves the compatibility with the u-meta-GGA exchange which is rather close to the exact one.

Nevertheless, we find that none of the semilocal correlation functionals can yield highly accurate results, when used with the u-meta-GGA exchange. This is not much surprising since the usual error cancellation that occurs at the semilocal level between exchange and correlation contributions cannot work properly in this case because the u-meta-GGA functional is exact for one- and two-electron systems. This suggests the need for the construction of a proper u-meta-GGA correlation functional being able to include the non-local effects on equal footing with the exchange part. Such a development is any-
VI. CONCLUSIONS

The success of semilocal DFT is mainly based on the correctness of the semiclassical physics that it incorporates (e.g. gradient expansions derived from small perturbations of the uniform electron gas), and on the satisfaction of several formal exact properties (e.g. density scaling relations). However, it also relies on a heavy error cancellation between the exchange and correlation parts. Thus, semilocal DFT can often achieve good accuracy for large systems, where the semiclassical physics is relevant, but not for small systems, that are usually treated with hybrid functionals.

Using the reduced Hartree parameter \( \eta_u(r) \) [Eq. \( \text{[20]} \)] as a new ingredient in the construction of DFT functionals, can guarantee the exactness of the exchange functional for any one- and two-electron systems. This is an important exact condition, also related to the homogeneity density scaling\(^{95,97,98} \), the delocalization and many-electron self-interaction errors\(^{116} \), and it can boost the accuracy of the functional.

Hence, we have constructed a prototype u-meta-GGA exchange functional, showing that it is possible and useful the use of the reduced Hartree parameter \( \eta_u(r) \). Note that even if \( \eta_u(r) \) is non-local, we have shown that it is compatible with the semilocal quantities. The u-meta-GGA has been tested for a broad range of finite systems (e.g. atoms, ions, jellium spheres, and molecules) being better than, or comparable with, the popular meta-GGA exchange functionals.

Nevertheless, we have showed that \( \eta_u(r) \) is a size-extensive quantity, increasing with the number of electrons. This fact represents a real challenge for functional development, limiting the applicability of the present formalism to periodic (infinite) systems. This limitation can be removed only by a large screening. Such a screening is given, in the present work, [Eqs. \( \text{[13]-[17]} \)] by the function \( \beta(s, z) \). An alternative way will be the use of the screened reduced Hartree potential \( x^u(r) \), defined by

\[
x^u(r) = \frac{1}{3(3a(r)/\pi)^{1/3}} \int dr' \frac{n(r')}{|r-r'|} e^{-a \alpha(r') k_F(r')^3 |r-r'|^\beta},
\]

where \( a, b, \) and \( \beta \) are other positive constants. Note that \( x^u(r) = \eta_u(r) \) for any one- and two-electron systems, and \( x^u(r) \) is realistic at the nuclear region\(^{103} \). However, such an approach, which is theoretically more powerful, is significantly more complex. In addition, it is also computationally more expensive since the bare Hartree potential is computed at every step of the Kohn-Sham self-consistent method, and thus its use does not affect the speed of the calculation, whereas the screened Hartree potential should be calculated separately for the only purpose of constructing the functional.

We also note that the bounded ingredient \( v^u \) of Eq. \( \text{[12]} \), can by itself be of interest for the development of exchange-correlation and even kinetic functionals, since it is a powerful atomic indicator. In this sense, a further investigation of this issue may be worth. Construction of the exchange enhancement factors of the form \( F_x(s, v^u) \) should be much simpler, because \( v^u \) is bounded, and should reveal the importance of the non-locality contained in this ingredient.

In any case, the u-meta-GGA exchange functional defined in Eqs. \( \text{[13]-[15]} \) is just a first attempt, and other simpler and/or better functional forms could possibly be developed. Thus, the class of u-meta-GGA functionals may represent a new semi-rung on the Jacob’s ladder: it is above the third one as it includes the Hartree potential to describe exactly the exchange for any one- and two-electron systems, but with a computational cost lower than functionals dependent on exact exchange. In this work, all calculations are non-self consistent. In a future work we will consider the functional derivative of the u-meta-GGA functionals.
Appendix A: Size consistency

Because the Hartree reduced parameter $\eta^u$ is a size extensive quantity, it is important to prove that the unmeta-GGA functional is properly size consistent. That is, given two systems, $A$ and $B$, separate by an infinite distance and whose densities are not overlapping, we have

$$E^{u-MGGA}_x[A + B] = E^{u-MGGA}_x[A] + E^{u-MGGA}_x[B],$$  \hspace{1cm} (A1)

where $E^{u-MGGA}_x = \int n^u_x L^{DA} F^{u-MGGA}_x \, dr$. To show this, we can use the fact that the integrand is finite everywhere ($n^u_x L^{DA}$ decays exponentially, while in the evanescent density regions $F^{u-MGGA}_x$ behaves according to Eq. (A2), to write

$$E^{u-MGGA}_x[A + B] = \int_{\Omega_A} n^u_x L^{DA} F^{u-MGGA}_x \, dr + \int_{\Omega_B} n^u_x L^{DA} F^{u-MGGA}_x \, dr,$$

where $\Omega_A$ and $\Omega_B$ are the space domains where $n_A$ and $n_B$, respectively, are not zero. Then, considering any $r \in \Omega_A$ (analogous considerations hold for $\Omega_B$), we have

$$\eta^{u}_{A+B}(r) = \frac{\int_{\Omega_A} n_A^{u}(r') \, dr'}{3(3/\pi)^{1/3} (n_A(r) + n_B(r))^{1/3}}$$

$$= \frac{\int_{\Omega_A} n_A^{u}(r') \, dr'}{3(3/\pi)^{1/3} (n_A(r) + n_B(r))^{1/3}}.$$  \hspace{1cm} (A3)

Now, because $r \in \Omega_A$, we have that $n_B(r) = 0$; moreover, because the two systems lay at infinite distance from each other, $|r - r'| = \infty$ for any $r' \in \Omega_B$. Hence,

$$\eta^{u}_{A+B}(r) = \frac{\int_{\Omega_A} n_A^{u}(r') \, dr'}{3(3/\pi)^{1/3} n_A(r)}.$$  \hspace{1cm} (A4)

In the same way, for $r \in \Omega_B$ we have $\eta^{u}_{A+B}(r) = \eta^{u}_{B}(r)$. At this point, since all the other input quantities are semilocal, Eq. (A2) immediately yields Eq. (A1).

Appendix B: Asymptotic behavior

In case of spherical systems in a central potential (e.g. atoms, jellium spheres), the following equation holds

$$\tau - \tau^W = \frac{l(l+1)}{2} \frac{n}{r^2},$$  \hspace{1cm} (B1)

in the asymptotic region. Here $l$ is the angular momentum quantum number of the outer shell, and the density decays exponentially $n \sim e^{-br}$, when the radial distance is large ($r \to \infty$). Here $b = 2\sqrt{2\mu}$, with $\mu$ being the ionization potential. Then, for any $l \neq 0$, $\alpha$ diverges as

$$\alpha = \frac{l(l+1)}{2C_x n^{2/3} r^2},$$  \hspace{1cm} (B2)

where $C_x = \frac{3}{4} (3\pi^2)^{2/3}$. Considering the enhancement factor of Eq. (20), i.e. $F^{x-MGGA}_x(\alpha)$, the exchange energy per particle

$$\epsilon_x = -C_x n^{1/3} F^{x-MGGA}_x(\alpha) \quad \text{with} \quad C_x = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3},$$  \hspace{1cm} (B3)

decays as

$$\epsilon_x \to -\frac{\sqrt{2}}{4} \frac{\sqrt{l(l+1)}}{\sqrt{b}} \frac{1}{r^{3/2}} + O\left( \frac{1}{r^{5/2}} \right).$$  \hspace{1cm} (B4)

Concerning the exchange potential, we consider the generalized Kohn-Sham framework to write

$$v_x \phi_i = \frac{\partial(n\epsilon_x)}{\partial n} \phi_i - \nabla \cdot \left[ \frac{\partial(n\epsilon_x)}{\partial \nabla n} \phi_i + \frac{1}{2} \frac{\partial(n\epsilon_x)}{\partial \tau} \nabla \phi_i \right] + \left( \frac{\partial(n\epsilon_x)}{\partial \tau} \right) \nabla \phi_i.$$  \hspace{1cm} (B5)

Using the following equations

$$\frac{\partial(n\epsilon_x)}{\partial n} = -C_x \frac{4}{3} n^{1/3} F^{x-MGGA}_x(\alpha) - C_x n^{4/3} \frac{dF^{x-MGGA}_x(\alpha)}{d\alpha} \frac{\partial \alpha}{\partial n},$$

$$\frac{\partial(n\epsilon_x)}{\partial \tau} = -C_x n^{4/3} \frac{dF^{x-MGGA}_x(\alpha)}{d\alpha} \frac{\partial \alpha}{\partial \tau},$$

$$\frac{\partial \alpha}{\partial n} = \frac{\nabla n^2}{8n^2 \tau^\text{unif}},$$

$$\frac{\partial \alpha}{\partial \tau} = -\frac{\nabla n}{4n \tau^\text{unif}},$$

$$\tau^\text{unif} = C_x n^{5/3},$$

we obtain after some simple algebra

$$v_x \phi = -C_x n^{1/3} \frac{4}{3} F^{x-MGGA}_x - \frac{5}{3} \frac{dF^{x-MGGA}_x(\alpha)}{d\alpha} \phi - C_x n^{4/3} \frac{dF^{x-MGGA}_x(\alpha)}{d\alpha} \frac{\nabla n}{2n \tau^\text{unif}} \left[ \nabla \phi - \nabla \phi \right] - \nabla \cdot \left[ C_x n^{4/3} \frac{dF^{x-MGGA}_x(\alpha)}{d\alpha} \frac{1}{2n \tau^\text{unif}} \left( \nabla n \phi - \nabla \phi \right) \right],$$

where $\phi$ is the highest occupied orbital. Then, the asymptotic density is $n = f \phi^2$ (with $f$ being the occupation number) and

$$\nabla n \phi - \nabla \phi = 0.$$  \hspace{1cm} (B8)

The final formula for the exchange potential is

$$v_x = -C_x n^{1/3} \left( \frac{4}{3} F^{x-MGGA}_x - \frac{5}{3} \frac{dF^{x-MGGA}_x(\alpha)}{d\alpha} \right),$$  \hspace{1cm} (B9)

which is valid for any exchange enhancement factor that depends only on the $\alpha$ ingredient. Then, the exchange potential of $F^{x-MGGA}_x$ defined in Eq. (20) behaves at $r \to \infty$ as

$$v_x \to -\frac{\sqrt{2}}{8} \frac{\sqrt{l(l+1)}}{\sqrt{b}} \frac{1}{r^{3/2}} + O\left( \frac{1}{r^{5/2}} \right).$$  \hspace{1cm} (B10)
Appendix C: Hydrogenic orbitals

The system of Eq. (21), with \( Z_1 = Z_2 = Z \) has the following density

\[
n(r) = 2 \frac{Z^3 (e^{-rZ})^2}{\pi} + \frac{Z^3 (e^{-1/2rZ})^2 (2 - rZ)^2}{16\pi}, \quad (C1)
\]

kinetic energy density

\[
\tau(r) = \frac{Z^5 (e^{-rZ})^2}{\pi} + \frac{1}{128} \frac{Z^5 e^{-rZ} (-4 + rZ)^2}{\pi}, \quad (C2)
\]

Hartree potential

\[
u(r) = \frac{1}{4r} (16 - 6ve^{-v} - 8e^{-v} - 2v^2 e^{-v} - 8ve^{-2v} - 8e^{-2v} - v^3 e^{-v}), \quad (C3)
\]

and exchange energy density

\[
e_x(r) = n(r)\nu(r) = -\frac{Z^3}{6912\pi} \left\{ 864ve^{-v} - 864ve^{-v} + 6048e^{-2v} + 216v^2 e^{-v} + 216ve^{-2v} + 1024ve^{-3v} - 768v^3 e^{-3v} - 6912v^4 e^{-4v} + 1024ve^{-3v} + 216ve^{-2v} - 27v^3 e^{-2v} - 54v^3 e^{-2v} + 54v^4 e^{-2v} \right\}, \quad (C4)
\]

where \( v = Zr \). The Hartree, exact exchange and LDA exchange energies are

\[
U = \frac{49565}{20736}Z = 2.39029Z,
\]

\[
E_x = -\frac{305797}{373248}Z = -0.8192864Z,
\]

\[
E_x^{LDA} = -0.7183437428Z. \quad (C5)
\]

Note that all the exchange ingredients \( (s, z, \alpha, \eta^v) \) are only functions of \( v = Zr \), such that for any exchange enhancement factor \( F_x(s, \alpha, z, \eta^v) \), the total exchange energy will be \( E_x = -constant \ Z \).

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