I. INTRODUCTION

The exchange-correlation (XC) energy functional is the key quantity in Kohn-Sham density functional theory (DFT) and is subject to intense research. The simplest functionals of practical utility are those based on the generalized gradient approximation (GGA) which are constructed using the electron density and its gradient. At present, there exist GGA functionals that are rather accurate for molecules and solids, interfaces, and even low-dimensional systems. However, in general no GGA functional can be simultaneously accurate for many of these problems, due to the extreme simplicity of the GGA level. Meta-generalized-gradient-approximations (meta-GGAs) are the most sophisticated semilocal functionals, incorporating important exact conditions, and having an improved overall accuracy with respect to the GGA functionals, with almost the same attractive computational cost. These functionals use as an additional ingredient to the GGA ones, the kinetic energy density functional (named PBEloc), having the physically motivated correction parameter (atomic units are used throughout)

\[ \beta(r_s, t) = \beta_0 + a t^2 (1 - e^{-r_s^2}) \]  

with \( \beta_0 = 0.0375 \) obtained from the linear response of the local density approximation (LDA), \( a = 0.08 \) obtained by jellium surface analysis (so that PBEloc/TPSSloc can correctly describe quantum effects at the edges of electronic systems), \( t = |\nabla n|/2k_F \phi \), \( k_s = (4k_F/\pi)^{1/2} \) being the Thomas-Fermi screening wave vector \( k_F = (3\pi^2 n)^{1/3} \), \( r_s = |3/(4\pi n)|^{1/3} \) being the local Seitz radius, and \( \phi = ((1 + \zeta)^{2/3} + (1 - \zeta)^{2/3})/2 \) being a spin-scaling factor. The TPSSloc correlation functional is very accurate for the description of correlation effects in the Hooke’s atom at all confinement regimes, has an accurate and realistic short-range correlation hole, and for this reason is more compatible with exact exchange than the TPSS13 or revTPSS13 correlation functionals. In a previous work, we used the TPSSloc correlation functional in combination with the revTPSS exchange, obtaining good results for systems where the exact XC hole is localized (atomization energies, kinetics and bond lengths of small molecules). This approach is however of limited general applicability because, since the TPSSloc correlation hole density is strongly localized around the electron, for broad applicability it needs to be paired with an exchange functional which performs (at least) as well as revTPSS exchange for problems displaying a reduced nonlocality, but also properly describes the missing nonlocality effects. Such an exchange functional should account for most of the tail XC hole effects, and the static correlation present in electronic systems near the equilibrium, which can be well captured by semilocal functionals. We recall that semilocal exchange functionals describe nonlocality effects through a proper shape of the enhancement factor, especially at medium and large values of the reduced gradient for exchange \( s = |\nabla n|/2k_F n \), also containing static correlation that scales as exchange under the uniform scaling of the density, which is essential for the description of electronic systems with more delocalized density.

In this article we consider this problem and we introduce a non-empirical meta-GGA exchange functional with balanced nonlocality contributions, that is fully compatible with the TPSSloc correlation functional. The resulting XC functional with balanced localization is named BLOC. Because of a better separation and proper balancing of exchange, dynamical correlation, and long-range XC effects, can achieve a good accuracy over a broad range of problems, correcting most of the XC TPSSloc limitations. In addition, to account for dispersion-related problems, which cannot be described by our localized correlation nor through the exchange nonlocality, we introduce a semiempirical disper-
sion correction\textsuperscript{22} to the functional, obtaining the BLOC-D3 functional.

\section{Theory}

As starting point of our construction we consider the TPSS and revTPSS exchange functionals, having the form

\[ E_x[n] = \int d\mathbf{r} \ n \ \epsilon_x^{LDA} F_x, \]

with \( \epsilon_x^{LDA} \) the LDA exchange energy per particle\textsuperscript{1} and \( F_x \) the exchange enhancement factor\textsuperscript{12}

\[ F_x = 1 + \kappa - \kappa/(1 + x/\kappa). \]

The parameter \( \kappa = 0.804 \) is fixed from the Lieb-Oxford bound\textsuperscript{22}, while

\[ x = \left( \frac{10}{81} + e \frac{z^f}{(1 + z^f)^2} \right) s^2 + \frac{146}{2025} s^2 - \frac{73}{405} \frac{q_0}{\kappa} \left( \frac{3}{5} z^2 \right)^2 + \frac{1}{2} s^4 + \frac{1}{\kappa} \frac{10}{81} s^4 + \frac{10}{81} \frac{5}{3} |\mathbf{\nabla} s|^2 + e \mu s^6 \right) / (1 + \sqrt{e} s^2)^2, \]

is constructed to recover the fourth-order gradient expansion (GE4) of the exchange energy\textsuperscript{14}, for a slowly-varying density. Here, \( z = \tau^W/\tau \) (0 \( z \leq 1 \)) is the meta-GGA ingredient\textsuperscript{13} that distinguishes the iso-orbital regions (when \( z \to 1 \)) and the slowly-varying regime (when \( z \to 0 \)), with \( \tau^W = |\nabla n|^2/(8n) \) being the von Weizsäcker kinetic energy density; \( s \) is the reduced gradient for exchange; and \( q_0 = (9/20)(\alpha - 1)/\sqrt{1 + 0.4\alpha(\alpha - 1) + 2s^2/3} \) mimics the reduced Laplacian of the density \( q = \nabla n^2/(4\pi n^2)^2/3n^{5/3} \), with \( \alpha = (\tau - \tau^W)/\tau_{\text{nuc}} \) (5/3)\( s^2(1/z - 1) \). The parameters \( c \) and \( e \) were fixed from the constraint that the exchange potential should be finite near the nucleus (where \( z = 1 \) and \( s \approx 0.4 \)) and by fitting the exchange energy of the hydrogen atom (where \( z = 1 \))\textsuperscript{13,14}. The parameter \( \mu \) dictates the behavior of the functional at large \( s \) (\( s \geq 2 \)), i.e. in valence and tail regions. In TPSS \( \mu = 0.21951 \) which represents the non-empirical PBE value, whereas in revTPSS \( \mu = 0.14 \) was set from semi-empirical considerations. Finally, the parameter \( f \) controls the slowly-varying behavior of the meta-GGA: when \( f \) is small (e.g. \( f = 2 \) in TPSS) the functional recovers GE4 only when \( s \) is very small (\( s \leq 0.1 \)); when \( f \) is larger (e.g. \( f = 3 \) in revTPSS) the functional recovers GE4 over a broader range of \( s \) values (\( s \leq 0.3 \)), and thus gains improved accuracy for bulk solids\textsuperscript{14}.

Due to many successful applications of TPSS and revTPSS, the ansatz of Eq. \textsuperscript{15} has been proved to be very robust in its general form. Thus, it provides an ideal starting point for building our new meta-GGA functional through selected modifications and improvements. We recall that this is a common practice in functional development, so for example the TPSS meta-GGA was developed on the skeleton of the PKZB meta-GGA precursor\textsuperscript{13}, whereas revTPSS is just a judicious modification to TPSS, which brings new physical ideas. We also acknowledge the very recent work\textsuperscript{16} into the direction of simplifying Eq. \textsuperscript{15} and solving the order of limits problem. However, this new development, despite its conceptual importance, does not appear, at present, to improve considerably for practical molecular applications. Therefore, it will not be considered in the present work.

We build our exchange functional using Eqs. \textsuperscript{22}, \textsuperscript{23}, and \textsuperscript{45}, and we fix the \( \mu \) parameter to its non-empirical PBE and TPSS value of 0.21951. In this way the good TPSS description at large \( s \) values, i.e. in the outer-valence and tail regions, is recovered. Moreover, imposing the known meta-GGA constraints\textsuperscript{13} for the hydrogen atom, we also have \( c = 1.59096 \) and \( e = 1.537 \). Note that these parameters are fixed only by constraints implying \( z = 1 \), and thus they cannot optimize the functional for the slowly- and moderately- varying density regimes, i.e. for short- and partially long- ranges effects. This behavior is instead controlled by the value of \( f \), which determines how fast, for \( s \to 0 \), GE4 is recovered\textsuperscript{11}, and also the behavior of the functional in the valence regions where \( 0.6 \leq z < 1 \) and \( s \) is moderately large. Thus, a proper choice of \( f \) is crucial for the compatibility between exchange and correlation parts, being able to modulate both short- and long-range effects.

In our construction we adopt therefore a flexible choice for \( f \) and generalize it to be a linear function of \( z \) (i.e. \( f(z) = az + b \)). Note that \( z \) is always finite (0 \( z \leq 1 \)), and it is a good indicator for iso-orbital regions (where \( z \approx 1 \)) as well as for the slowly-varying regime (where \( z \approx 5s^2/3 \ll 1 \)). We specify the following properties:

(i) \( f(z) \geq 3 \) for \( z \leq 0.3 \); this condition ensures the recovery of GE4 over a wide range of \( s \) values, and thus the functional can be accurate for bulk solids\textsuperscript{14}, granting a good description of short-range effects. Note that \( z \leq 0.3 \) in most of the bulk solids, where the density is slowly-varying.

(ii) \( f(z) \leq 2 \) for \( z \geq 0.6 \); this constraint dictates the behavior of the functional in rapidly-varying regions, giving \( E_x \geq ET_{\text{PPSS}} \) in valence and tail regions.

(iii) as for the TPSSloc correlation, we take the jellium surfaces as reference system. Thus, we require the exchange functional to complement the TPSSloc correlation in such a way to be in agreement with diffusion Monte Carlo (DMC) estimates\textsuperscript{31,32} of jellium surface XC energies (i.e. \( \sigma_{\text{XC}} \approx \sigma_{\text{DMC}} \)). We consider the benchmark \( \sigma_{\text{DMC}} \) given by Eq. (5) of Ref. \textsuperscript{32}.

Conditions (i)-(iii) are satisfied by the simple form

\[ f(z) = 4 - 3.3z, \]

which completes the construction of the desired exchange meta-GGA functional (BLOC exchange). We note that
Thus, we expect it to work similarly as the TPSSloc XC relation. For condition (i). For change may recall the recently proposed VT
\{\text{factor is slightly greater than TPSS, fulfilling condition (iii)}\). Nevertheless, this exchange functional preserves, and even improves, the performance of the TPSSloc functional for the Hooke’s atom, especially in the tightly-bounded region, outperforming all the reported meta-GGAs (TPSS, revTPSS, and M06-L\textsuppresse{14}). We recall that the Hooke’s atom\textsuppresse{19} represents two interacting electrons in an isotropic harmonic potential. Thus, a good description of both two-electron exchange and correlation is required. This model system provides deep physical inside into strongly-correlated and tightly-bounded regimes, being an important and hard test for density functionals.

Additionally, Fig. 2 shows that the BLOC XC functional preserves, and even improves, the performance of the TPSSloc functional for the Hooke’s atom, especially in the tightly-bounded region, outperforming all the reported meta-GGAs (TPSS, revTPSS, and M06-L\textsuppresse{14}). We recall that the Hooke’s atom\textsuppresse{19} represents two interacting electrons in an isotropic harmonic potential. Thus, a good description of both two-electron exchange and correlation is required. This model system provides deep physical inside into strongly-correlated and tightly-bounded regimes, being an important and hard test for density functionals.

Finally, in Fig. 3 we show a comparison of the TPSS, revTPSS and BLOC exchange (upper panel) and XC (lower panel) energy densities, at a jellium surface of bulk parameter \(r_s = 2\). The BLOC exchange energy density
program packages. The two programs were used for

 We considered a set of representative and widely used
tests (including overall more than 300 systems), which
were divided into seven groups:

- **Atomization energies and proton affinities of**
  **organic molecules**, which includes the W4444
  and PA1245,46 test sets. Moreover, the AE6 test47
  for atomization energies was also chosen, because
  this small representative test is often used to bench-
  mark quantum chemistry methods and provides
  therefore a direct comparison with many other
  works. Finally, the W4-MR test48 of molecules
  with non-single-reference character, was considered
  for completeness.

- **Reaction energies and kinetics**, including
  representative tests for organic reaction energies
  (OMRE45), barrier heights (BH642) and both
  (K949).

- **Other** tests, which are relevant for assessing den-
  sity functionals: ionization potentials (IP1350),
  isomerization energies (ISOL653), difficult cases for
  DFT (DC9/1252), and absolute atomic energies
  (AE1753).

- **Non-covalent interactions**, comprising tests for
  hydrogen bonds (HB642), dipole-dipole interactions
  (DI653), π–π stacking (PPS553), and the S22
  test45,46, which includes a broad selection of non-
  covalent interactions.

- **Structural properties** of organic molecules. This
  group includes a test of optimized bond lengths
  (MGBL1955) and one test of harmonic vibrational
  frequencies (F3855).

- **Transition metals**. In this group we collected
  a set of tests involving transition metal complexes
  (TM10AE25 for atomization energies and TMBL26
  for bond lengths) and gold clusters (AunAE25,26
  for atomization energies and AuBL626 for bond
  lengths).

- **Bulk solids**. This group includes the tests of the
  equilibrium lattice constants (LC12), bulk mod-
  uli (BM12), and cohesive energies (COH12) of 12
  bulk solids: Li, Na, Al (simple metals); Cu, Ag,
  Pd (transition metals); Si, Ge, GaAs (semiconduc-
  tors); NaCl, NaF, MgO (ionic solids). The reference
data were taken from Ref. 42.

  To assess the performance of different functionals for
each group of tests we consider, beside the individual
mean absolute error (MAE) for each test, an overall MAE
relative to TPSS (RMAE), defined as

\[
RMAE = \frac{1}{M} \sum_{i}^{M} \frac{MAE_i}{MAE_{TPSS}}.
\]
where the sum runs over all tests (M) within a group and MAE$^{\text{TPSS}}_i$ is the MAE of TPSS for the $i$-th test. The RMAE provides an indication of whether any method is better (RMAE < 1) or worse (RMAE > 1) than TPSS for a given problem. Thus, it allows a fair global assessment of all the results.

Finally, in addition to the tests listed above we considered two special cases which are known to be difficult for semilocal density functionals, namely the description of the bending potential of the silver trimer$^{59,60}$ and the dimensional crossover of gold anionic clusters$^{61,62}$.

**IV. RESULTS**

The results of all tests are summarized in Tab. I where we report the MAEs and RMAEs for different tests and groups as resulting from different functionals. The TPSS and revTPSS results are considered for direct comparison with parent non-empirical functionals. The M06-L results are also reported, to have a reference of a widely used and highly parameterized meta-GGA functional.

Inspection of the Tab. I shows that BLOC performs better than both revTPSS and TPSS in more than 60% of the tests. On the other hand, it compares also relatively well with the “benchmark” M06-L results, yielding lower MAEs in 30% of the cases and giving significantly worse results only in two cases (atomic energies and barrier heights). Even though this performance may not appear to be outstanding at first sight, we remind the reader of the difficulty of outperforming highly parameterized meta-GGA functionals without resorting to higher non-empirical rungs of the DFT Jacob’s ladder$^{63}$. At the same time, the comparison of BLOC, TPSS, and revTPSS results shows how difficult it is to reach a good accuracy at meta-GGA level, for a broad range of properties, without introducing a high level of empiricism. In this sense, the good performance of BLOC is quite satisfactory, and its rather systematic improvement over TPSS and revTPSS indicates that the functional captures well the essential physics of a wide selection of electronic systems at the simple semilocal level. Thus, the balanced description of different regimes and the physical concepts included in exchange and correlation parts of the BLOC functional are relevant.

In particular, we underline here the good performance of the BLOC functional for the structural properties of molecules, atomization energies/proton affinities, and all the properties of transition metal systems. On the other hand, in only three cases (BH6, IP13, S22) BLOC is worse than both revTPSS and TPSS (still being very close to the TPSS). Moreover, at least two of these tests (BH6, S22) can hardly be accurate for non-empirical semilocal functionals. We also remark that HF+TPSSloc is extremely good for BH6 (see Table I of Ref. 22), and thus we expect that a hybrid of BLOC functional can be rather accurate for barrier heights.

Overall BLOC has the second best RMAE (0.92) for chemical properties and the best RMAE for bulk solids (0.92). Note that the M06-L functional is the best for molecular properties, but it is modest for solids. The more recent M11-L functional$^{29}$ improves lattice constants, but not solid-state cohesive energies$^{66}$. In fact, even revTPSS improves over TPSS for lattice constants, but worsens both bulk moduli and cohesive energies (see Tab. I and also Ref. 67). On the other hand, BLOC gives a very good balance for all solid-state properties.

We remark also that notably these results can be in general obtained with a small error compensation for situations where the XC hole is reasonably localized (e.g. for the AE6 test), because of the higher compatibility of the TPSSloc correlation with exact exchange$^{22}$. In these cases in fact TPSSloc and BLOC correctly yield very close results. On the other hand, for systems characterized by delocalized electrons and/or static correlation, our balanced exchange functional proves to be capable to compensate well for the missing long-tail behavior of the TPSSloc correlation, so that good results can be finally obtained using the BLOC XC functional (see e.g. W4-MR, DC9/12, AmAE, and COH12).

The results of Tab. I show (second last column) that a small further improvement can be achieved by complementing the BLOC functional with semiempirical dispersion corrections. In fact, dispersion cannot be described by the localized TPSSloc correlation nor can it be included in the exchange part. We implemented this correction through the DFT-D3 semiempirical model$^{22}$, fixing the two free parameters of the model by fitting to the MAE of the S22 test. The resulting parameters are $s_{r,6} = 1.104$ and $s_8 = 0.888$, slightly smaller than the TPSS values. We see that the BLOC-D3 functional of course strongly improves the performance for dispersion-dominated tests (e.g., S22, PPS5) but, at the same time, also preserves the accuracy for all tests, even slightly improving the MAE in some cases (e.g. structural properties, W4, OMRE). Thus, the semiempirical DFT-D3 correction appears to integrate well with our construction, and as a result the BLOC-D3 functional yields a very good performance for chemistry-related tests (RMAE=0.87).

**A. Silver trimer**

As additional test for our assessment of the BLOC functional we consider a particularly difficult case for DFT: the description of the potential energy related to the bending of the Ag$_3$ cluster$^{59,60}$. For this case in fact high-level methods indicate the existence of a single minimum at a bond angle of $\theta \approx 70^\circ$, whereas all PBE-based functionals yield two almost degenerate minima at $\theta \approx 70^\circ$ and at $\theta \approx 140^\circ$,$^{22}$, and all LYP-based functionals yield only the wrong 140$^\circ$ minimum. The results reported in Fig. 3 show indeed that the popular PBE and even the meta-GGA TPSS or the hybrid PBE0 functionals yield a poor quantitative description of the problem,

$$\theta \approx 59.60$$

$$\theta \approx 70^\circ$$
| Test set                              | TPSS  | revTPSS | TPSSloc | BLOC  | BLOC-D3 | M06-L |
|--------------------------------------|-------|---------|---------|-------|---------|-------|
| **Atomization energies and proton affinities (kcal/mol)** |       |         |         |       |         |       |
| organic molecules (AE6)              | 5.4   | 6.6     | 3.9     | 3.6   | 3.6     | 3.4   |
| organic molecules (W4-NMR)           | 4.7   | 5.2     | 5.5     | 4.6   | 4.4     | 5.4   |
| static correlation (W4-MR)           | 8.8   | 9.4     | 14.0    | 8.9   | 9.1     | 5.9   |
| proton affinities (PA12)             | 4.7   | 4.8     | 3.8     | 3.7   | 3.8     | 4.5   |
| **RMAE**                             | **1.00** | **1.10** | **1.07** | **0.86** | **0.86** | **0.85** |
| **Reaction energies and kinetics (kcal/mol)** |       |         |         |       |         |       |
| organic molecules (OMRE)             | 8.0   | 10.2    | 7.9     | 7.1   | 6.0     | 5.3   |
| kinetics (K9)                        | 7.0   | 7.2     | 6.5     | 6.3   | 6.4     | 4.2   |
| barrier height (BH6)                 | 8.3   | 7.4     | 8.6     | 8.9   | 8.9     | 4.3   |
| **RMAE**                             | **1.00** | **1.07** | **0.98** | **0.95** | **0.91** | **0.59** |
| **Other (kcal/mol)**                 |       |         |         |       |         |       |
| ionization pot. (IP13)               | 3.1   | 2.9     | 3.0     | 3.3   | 3.3     | 3.1   |
| isomerization (ISOL6)                | 3.6   | 4.0     | 2.7     | 3.5   | 3.0     | 2.8   |
| difficult cases (DC9/12)             | 18.2  | 21.7    | 29.6    | 20.1  | 19.4    | 22.3  |
| atomic energies (AE17)               | 22.6  | 41.8    | 42.4    | 26.8  | 26.8    | 3.9   |
| **RMAE**                             | **1.00** | **1.27** | **1.31** | **1.08** | **1.04** | **0.79** |
| **Non-covalent interactions (kcal/mol)** |       |         |         |       |         |       |
| hydrogen bonding (HB6)               | 0.6   | 0.6     | 0.6     | 0.6   | 0.8     | 0.6   |
| dipole bonding (DI6)                 | 0.6   | 0.5     | 0.5     | 0.5   | 0.8     | 0.4   |
| π – π stacking (PPS5)                | 2.8   | 2.5     | 2.7     | 2.8   | 0.1     | 0.8   |
| various non-covalent (S22)           | 3.2   | 2.8     | 2.6     | 3.3   | 0.5     | 0.6   |
| **RMAE**                             | **1.00** | **0.90** | **0.90** | **0.97** | **0.71** | **0.53** |
| **Structural properties (mÅ and cm⁻¹)** |       |         |         |       |         |       |
| bond lengths (MGBL19)                | 6.9   | 7.4     | 6.8     | 5.9   | 5.7     | 3.0   |
| vibrations (F38)                     | 44.1  | 43.7    | 41.9    | 39.0  | 40.0    | 41.5  |
| **RMAE**                             | **1.00** | **1.03** | **0.97** | **0.87** | **0.87** | **0.69** |
| **Transition metals (mÅ, kcal/mol (TM10AE), and kcal/mol/atom (AUnAE)** |       |         |         |       |         |       |
| transition-metal energies (TM10AE)   | 10.8  | 11.1    | 10.3    | **11.1** | 11.0    | 7.9   |
| gold cluster energies (AUnAE )       | 0.6   | 1.6     | 4.4     | 0.3   | 0.4     | 1.4   |
| transition-metal geom. (TMBL)        | 12.7  | 11.6    | 17.7    | **11.2** | 11.3    | 10.9  |
| gold cluster geom. (AuBL6)           | 30.8  | 21.9    | 35.3    | 23.3  | 19.6    | 33.9  |
| **RMAE**                             | **1.00** | **1.33** | **2.71** | **0.79** | **0.80** | **1.26** |
| **Global assessment for chemical properties** |       |         |         |       |         |       |
| Average RMAE                         | **1.00** | **1.12** | **1.32** | **0.92** | **0.87** | **0.79** |

where the relative energy of the global minimum is underestimated, and only by the inclusion of exact exchange can the second minimum at \( \theta \approx 140^\circ \) be turned into a shoulder. On the other hand, revTPPS yields a good relative energy for the minimum at \( \theta \approx 70^\circ \), but still displays a small second minimum at \( \theta \approx 140^\circ \), due to a hill at \( \approx 100^\circ \). The BLOC functional instead gives a very good description of the bending potential of the Ag₃.
cluster in good agreement with CCSD(T) calculations\cite{ref60}, transforming the hill at \(\approx 100^\circ\) into a shoulder. We note finally, that for this problem highly empirical meta-GGAs (as M06-L) are also rather inaccurate (as shown in Fig. 4).

![Graph showing relative energy with respect to the linear structure of Ag\(_3\) as a function of the Ag-Ag-Ag bond angle \(\theta\) for several functionals.](image)

**FIG. 4:** Relative energy (in mHa) with respect to the linear structure of Ag\(_3\) (\(\Delta E = E(\theta) - E(180^\circ)\)) as a function of the Ag-Ag-Ag bond angle \(\theta\) (in degrees) for several functionals. CCSD(T) and MP2 values are taken from Ref. \cite{ref60}.

### B. The dimensional transition of anionic gold clusters problem

Finally, we consider the problem of the 2-dimensional to 3-dimensional (2D \(\rightarrow\) 3D) transition in gold cluster anions which attracted great interest over the last several years\cite{ref61,ref64,ref68,ref69}. A joint electron diffraction and DFT study\cite{ref61} showed in fact that the 2D \(\rightarrow\) 3D transition occurs for Au\(_n^-\) clusters at \(n = 12\), where a 2D and a 3D structure are almost isoenergetic, while planar (2D) and 3D structures characterize the experimental spectrum for \(n = 11\) and \(n = 13\), respectively. However, most DFT functionals are unable to reproduce this outcome\cite{ref61,ref68,ref69}.

In Tab. II we show the relative energies of several 2D and 3D gold clusters as obtained from several meta-GGA functionals. The TPSS functional erroneously predicts the 2D structure to be favorable at \(n = 12\) (as most other GGA functionals, including PBE\cite{ref3,ref57}). The other meta-GGAs (revTPSS, TPSSloc, BLOC, and M06-L), on the other hand, correctly solve the dimensional crossover of anionic gold clusters. However, only the revTPSS and BLOC meta-GGAs predict almost isoenergetic structures for Au\(_{12}^-\)-I and Au\(_{12}^-\)-II, in better agreement with experiment\cite{ref43}, and with the M06 hybrid functional\cite{ref68}.

| System dim\(^a\) | TPSS  | revTPSS | TPSSloc | BLOC  | M06-L |
|-----------------|-------|---------|---------|-------|-------|
| Au\(_{11}^-\)-I | 2D    | 0       | 0       | 0     | 0     |
| Au\(_{11}^-\)-II| 3D    | 190     | 159     | 121   | 190   | 60    |
| Au\(_{11}^-\)-III| 3D   | 270     | 337     | 419   | 310   | 250   |
| Au\(_{12}^-\)-I | 3D    | 0       | 0       | 0     | 0     |
| Au\(_{12}^-\)-II| 2D    | -170    | 79      | 343   | 37    | 400   |
| Au\(_{13}^-\)-I | 3D    | 0       | 0       | 0     | 0     |
| Au\(_{13}^-\)-II| 3D    | 10      | 39      | 65    | 29    | 110   |
| Au\(_{13}^-\)-III| 2D   | 230     | 467     | 766   | 426   | 930   |

\(^a\) Dimensionality.

\(^b\) Data from Ref. \cite{ref68}.

### V. CONCLUSIONS

In conclusion, we constructed an accurate, non-empirical and physically motivated meta-GGA XC functional. Its dynamical correlation part is strongly localized, showing a realistic short-range correlation, and being more compatible with exact exchange than other popular correlation functionals\cite{ref22}. The exchange part was constructed to balance nonlocality effects at the semilocal exchange level, so to have a good description of different density regimes in different systems. Additional inclusion of dispersion effects can be efficiently obtained via semiempirical corrections.

Nowadays, highly-empirical functionals are optimized against a large set of data and chemical properties\cite{ref19}, and thus they become very attractive for many electronic structure calculations. However, due to their empirical nature, they may show unexpected failures for specific or exotic problems. On the other hand, the non-empirical functionals, constructed from exact quantum mechanics conditions and from model systems, show a reasonable accuracy for most of applications, due to the physics which they incorporate. The BLOC meta-GGA improves over, or is in line with, state-of-the-art TPSS and revTPSS for many energetic and structural properties of organic molecules, transition metal complexes and clusters, jellium surfaces, Hooke’s atom, and bulk solids, can correctly solve difficult problems as bending potential of the silver trimer and the dimensional crossover in gold anionic clusters, and thus can become a non-empirical workhorse tool in quantum chemistry and condensed matter.
VI. ACKNOWLEDGEMENT

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