Semiclassical Neutral Atom as a Reference System in Density Functional Theory

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We use the asymptotic expansions of the semiclassical neutral atom as a reference system in density functional theory to construct accurate generalized gradient approximations (GGAs) for the exchange-correlation and kinetic energies without any empiricism. These asymptotic functionals are among the most accurate GGAs for molecular systems, perform well for solid state, and overcome current GGA state of the art in frozen density embedding calculations. Our results also provide evidence for the conjointness conjecture between exchange and kinetic energies of atomic systems.

The Kohn-Sham (KS) ground-state density functional theory [1,2] is nowadays the most frequently used first-principles computational method to describe many-electron systems in condensed-matter physics and quantum chemistry. Although exact in principle, the KS method relies on approximations for the exchange-correlation (XC) energy, that includes all the many-body effects beyond the Hartree method. Different approximations for the XC energy have been developed based on reference systems and/or exact conditions (e.g., scaling relations, gradient expansions [2]). In solid-state physics the most important reference system is the homogeneous electron gas (HEG), from which the local density approximation (LDA) was constructed [1]. Most of the generalized gradient approximations (GGAs) [3–5] and meta-GGAs [6,7] are also built to recover this limit. In quantum chemistry instead, reference systems are often light atoms or small molecules and different (meta-)GGA functionals were proposed to achieve good chemical accuracy [3,6–9], even though some (e.g., BLYP [9]) do not even recover the correct correlation energy of the HEG. Recently, the non-relativistic semiclassical neutral atom (SCA) was proposed as a new paradigm for quantum chemistry and condensed-matter physics and used to explain why a GGA functional cannot be accurate for both atoms and solids [10]. This idea was the basis for the construction of new functionals (PBEsol [4], and revTPSS [7]).

With the development of density-based embedding theories [11–15] there is renewed interest in finding good approximations for the noninteracting kinetic energy (KE) [16,17], that enters the embedding potential through the nonadditive kinetic term. Even though fundamental differences between the exchange and KE densities [2] exist, the development of KE GGAs is often guided by the so called *conjointness conjecture* [18,19]

$$E_x[n] = \int d\mathbf{r} \epsilon_x^{\text{HEG}} F_x(s) \leftrightarrow T_s[n] = \int d\mathbf{r} \tau_s^{\text{HEG}} F_s(s),$$

where ϵ_x^{HEG} (τ_s^{HEG}) is the exchange (kinetic) energy density of the HEG [2], $s = |\nabla n|/\{2(3\pi^2)^{1/3} n^{4/3}\}$ is the dimensionless gradient, and the exchange and kinetic enhancement factors F_x and F_s are assumed to have the same functional form.

In this Letter we use the SCA reference system to construct accurate XC and KE GGAs for molecular systems and provide evidence for the validity of the conjointness conjecture. For many-electron neutral atoms the noninteracting KE (T_s) and the exchange energy (E_x) have the following asymptotic expansions

$$T_s = c_0 Z^{7/3} + c_1 Z^2 + c_2 Z^{5/3} + \dots, \qquad (1)$$

$$E_x \approx E_x^{\text{LDA}} + d_1 Z + d_2 Z^{2/3} + \dots, \qquad (2)$$

with Z the number of electrons. The kinetic coefficients were obtained analytically: $c_0 = 0.768745$ is given by the Thomas-Fermi theory [2], $c_1 = -0.5$ is the Scott correction due to the atomic inner core [20], and $c_2 = 0.2699$ accounts for quantum oscillations [21]; the exchange coefficients were instead derived after a careful numerical analysis [22]: $d_1 = -0.2240$ is an atomic inner core term, and $d_2 = 0.2467$ is related to atomic quantum oscillations as in the KE case. These asymptotic expansions are very accurate, even for small Z, with a typical error of order 0.5%–0.2% [22,23] for atoms of the periodic table.

The second-order gradient expansions (GE2s) [2]

$$F_x(s) = 1 + \mu_x^{\text{GE2}} s^2; \qquad F_s(s) = 1 + \mu_s^{\text{GE2}} s^2, \qquad (3)$$

cannot recover the asymptotic expansions (1) and (2) if $\mu_x^{\text{GE2}} = 5/27$ [2] and $\mu_s^{\text{GE2}} = 10/81$ [24], derived from small perturbations of HEG, are used. However, the *exact* c_1 and d_1 coefficients can be obtained by the modified second-order gradient expansions (MGE2s) [22,23] with

$$\mu_x^{\text{MGE2}} = 0.260, \qquad \mu_s^{\text{MGE2}} = 0.23889.$$

For c_2 and d_2 the gradient expansions are less useful because they are related to atomic quantum oscillations.

In order to see the accuracy of MGE2, in Fig. 1 we report $|\Delta E_x| = |E_x^{exact} - E_x^{approx}|/|E_x^{LDA}|$ and $|\Delta T_s| = |T_s^{exact} - T_s^{approx}|/T_s^{LDA}$ in the cases of LDA, GE2 and MGE2 for heavy nonrelativistic noble atoms, starting from Kr ($Z = 36$) to $Z = 2022$, and we interpolate every curve to $Z = \infty$. We use accurate exact-exchange orbitals and densities. In a heavy atom, the density is slowly varying over a Fermi wavelength in the entire atomic core, and MGE2 becomes remarkably accurate. The MGE2 provides thus a link between the KS method and the SCA since any reasonable enhancement factor that recovers μ_s^{MGE2} (μ_x^{MGE2}) in the slowly varying density limit will yield a reasonable asymptotic expansion (1) and (2).

In Fig. 2 we report $|\Delta E_x|$ and $|\Delta T_s|$ for the fictional noble atom with $Z = 1138$ [25]. We consider the simple PBE-like enhancement factor [3,26]

$$F(s) = 1 + \kappa - \kappa/(1 + \mu s^2/\kappa), \qquad (4)$$

that in the small-s limit behaves as $1 + \mu s^2$ and in the large-s limit $F \to 1 + \kappa$ which, although is not the correct limit for both the exchange and kinetic energies, can well account for valence properties [6]. We consider different values of μ and fix $\kappa = 0.804$ to satisfy the Lieb-Oxford bound for the exchange [3]. Figure 2 is very insightful. (i) The exchange error is indeed minimized for μ close to μ_x^{MGE2} ($Z = 2022$ fictional noble atom [25] gives similar results), while all the other conventional PBE-like exchange approximations yield worse performance. In particular the increased κ of revPBEx [8] with respect to PBEx, does not lead to any improvement. The *nonempirical* exchange functional with $\mu = \mu_x^{MGE2}$ and $\kappa = 0.804$ (APBEx) is thus the best one. (ii) The kinetic error is indeed minimized for μ close to μ_s^{MGE2}. In this case the LC94 GGA [17], that contains five empirical parameters fitted to atoms, performs very well. The *nonempirical* PBE-like kinetic functional with $\mu = \mu_s^{MGE2}$ and $\kappa = 0.804$ (APBEK) also shows excellent performance. We also found that for $\kappa = 0.7, 0.9,$ and 1.2 the KE error

increases (but still comparable to the meta-GGA [16]). Thus this large-Z atom shows that $\kappa = 0.804$ is a good choice for both exchange and KE. Note that the μ, κ parameters of the APBEK functional are thus close to the ones of Ref. [19], which were fitted to noble atoms of the periodic table. Here, the SCA provides a nonempirical derivation of an accurate KE functional. (iii) The APBEK enhancement factor can be also used for exchange, leading (see Fig. 2) to quite accurate results (better than B86x [26]), showing the strong link between exchange and kinetic energies of atoms [18,19,26]. Within the SCA model, this can be understood by observing the ratio

$$\mu_x^{MGE2}/\mu_s^{MGE2} = 1.09,$$

which provides a theoretical rationale for the *conjointness conjecture* [18]. Note that such a link will not work for extended systems, where $\mu_x^{GE2}/\mu_s^{GE2} = 0.67$ [4,10].

Now we make use of the SCA reference system to construct an accurate XC GGA that recovers the asymptotic expansion (2). This is named APBE (asymptotic PBE-like functional), uses the nonempirical APBEx, and is associated with a PBE-like correlation functional where the parameter $\beta = 3\mu/\pi^2$ is used, in order to ensure the correct LDA linear response [3]. This is the opposite of what was done in the PBE construction where β was fixed by the gradient expansion of the correlation energy and $\mu = \pi^2\beta/3$ fixed from the LDA linear response. Indeed, recent work [4,10] showed that the gradient expansion of the correlation energy is less important.

To test our APBE functional we calculate atomization energies (AEs) and equilibrium bond lengths (BLs) for a series of representative sets of molecules [25] (AE6 and MGBL19 for organic molecules, MCAE6 and MCBL6 for metal complexes, and TMAE4 and TMBL4 for transition metal dimers) as well as lattice constants and bulk moduli
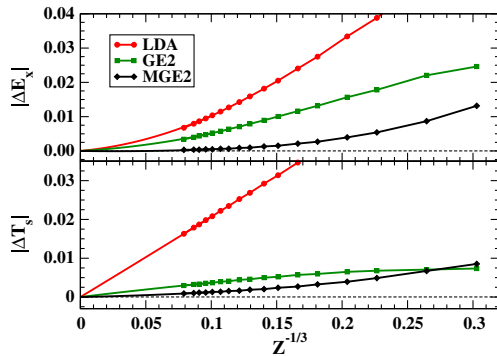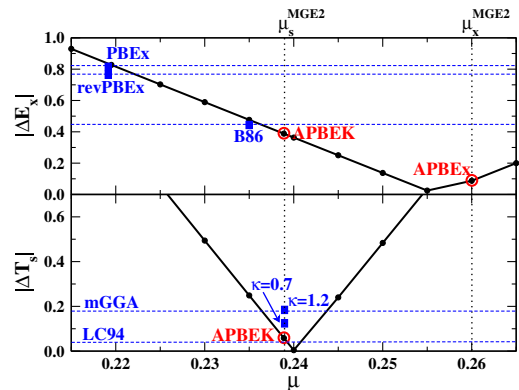

FIG. 1 (color online). Comparison of the exchange (upper panel) and kinetic (lower panel) relative errors of LDA, GE2 and MGE2 for heavy noble atoms.

FIG. 2 (color online). $|\Delta E_x|$ and $|\Delta T_s|$ as functions of μ ($\kappa = 0.804$) for the noble atom with $Z = 1138$. Reference values are shown as horizontal dashed lines. Minima corresponding to $\kappa = 0.7$ and $\kappa = 1.2$ at $\mu = 0.23889$ are also shown.

TABLE I. Mean absolute errors (MAEs) of various properties of selected molecular and solid-state test sets. Smallest (largest) errors denoted by bold (underlined) style.

Test set	PBE	APBE	revPBE	BLYP
Atomization energies (kcal/mol)				
Organic molecules	<u>14.50</u>	7.98	8.85	**6.85**
Metal complexes	<u>10.52</u>	7.39	**6.33**	9.02
Transition metals	6.26	**6.05**	<u>7.85</u>	6.64
Overall MAE	<u>10.95</u>	**7.28**	7.66	7.61
Bond lengths (mÅ)				
Organic molecules	**9.27**	9.44	11.44	<u>12.34</u>
Metal complexes	9.19	**8.24**	<u>16.51</u>	15.63
Transition metals	**52.8**	57.3	<u>62.2</u>	57.2
Overall MAE [a]	8.70	**8.68**	11.77	<u>12.11</u>
Solid-state systems				
Lattice constants (mÅ)	**71**	90	130	<u>151</u>
Bulk moduli (GPa)	**10.3**	15.0	15.8	<u>23.1</u>
Surface XC energy (erg/cm^2)	**42**	50	62	<u>279</u>

[a]Considers 1/10 of transition metals values.

for seven solids [25], and jellium surface XC energies for different values of the bulk parameter r_s. All results are summarized in Table I along with results from PBE, revPBE [8], and BLYP [9], the most used GGAs.

The APBE GGA is overall the best functional for molecular systems for both AEs and BLs and the second best (close to PBE) for extended systems, where indeed the underlying theory [i.e., Eqs. (1) and (2)] is not expected to work exactly. In particular, for the AE6 test, APBE reduces the error to about one half and it is also superior to revPBE, which was empirically optimized to atoms and molecules. The APBE functional works very well and gives the best mean absolute error (MAE) for atomization energies of transition metals and for BLs of metal complexes. In all other cases it gives the second best results, thus providing a realistic balance between AEs and BLs (revPBE and BLYP perform badly for BLs, solids and surfaces).

These results indicate the robustness of the construction of the APBE functional for molecular systems. This traces back to the choice of the parameters that were derived from a well defined and accurate theoretical model with no empiricism. To further investigate how the derived values of μ and κ fulfill the requirement of a well balanced and accurate description of energy and geometry in a wide range of (molecular) systems, we study the variation of the MAE of atomization energies and bond lengths for different classes of systems. We vary either μ or κ around their actual value, keeping for the correlation $\beta = 3\mu/\pi^2$. The results are shown in Fig. 3. The pair of values $\mu = 0.26$ and $\kappa = 0.804$ corresponds approximately to a local minimum for the AE6, TMAE4 and MCBL6 curves. Indeed, for these systems APBE is the best PBE-like functional in Table I. All GGA methods overestimate atomization energies [25] of transition metal complexes (MCAE6): better agreement can be obtained with increased nonlocality due to an error cancellation with

the overestimated bond lengths (see MCBL6 curve). Others curves (MGBL19 and TMBL4) display a linear trend, due to the limited range in the plot. We note that for all classes of systems investigated here, an increase of the bond length is obtained for high values of κ, which explains the poor performance of revPBE (and BLYP) for this property. From these findings we may state that APBE provides overall the best compromise for all systems and properties considered and the nonempirical parameters $\kappa = 0.804$ and $\mu = \mu_x^{\mathrm{MGE2}}$ can hardly be improved for molecules. This implies the validity of the SCA as a reference system for molecules.

We now turn to analyze the accuracy of the APBEK for molecules. In Table II we report the kinetic atomization energies of a set of 12 small molecules (12 M) [16,25,27]. The APBEK is more accurate than the highly empirical
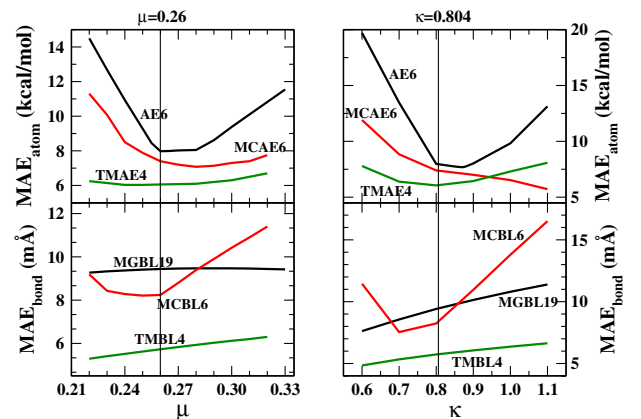
FIG. 3 (color online). Mean average error of the atomization energy (top) and bond length (bottom) for different molecular tests sets as a function of μ and κ. In each plot only one parameter is varied, the other is fixed to its APBE value. The TMBL4 values are divided by 10.

TABLE II. Mean absolute errors of atomization KE (ΔT_s in kcal/mol), KSCED valence densities (ξ_v), and KSCED total energies (ΔE in kcal/mol). Smallest errors are denoted in bold style. Results for ξ and ΔE are given for a monomolecular basis set (m) and for a supermolecular basis set (s).

	GE2	APBEK	revAPBEK	LC94
ΔT_s (12 M)	197	**152**	159	159
ξ_v (m)	2.01	**1.65**	1.71	1.69
ξ_v (s)	1.87	**1.49**	1.55	1.54
ΔE (m)	3.00	0.66	**0.23**	0.35
ΔE (s)	3.15	0.54	**0.20**	0.33

LC94. This test is one of the most difficult tests for KE approximations, because the local TF functional performs better than most (meta)-GGAs (MAE = 111 kcal/mol) [16]. In contrast, the exchange atomization energies are improved at the GGA level with respect to LDA. We also employed the APBEK functional in KS equations with constrained electron density (KSCED) [12] calculations with freeze-and-thaw cycles [14,15]. We considered eight weakly interacting test systems [25]. In this case we observed that a larger nonlocality (higher values of κ) favors accurate KSCED total energies. Therefore, we introduced a variant of the APBEK functional (named revAPBEK) with empirical $\kappa = \kappa^{\text{revPBE}} = 1.245$. The revAPBEK performs slightly worse than the APBEK functional for large atoms (see Fig. 2) and molecules (see Table II), but provides improved surface kinetic energies (MAE-APBEK = 56 erg/cm^2, MAE-revAPBEK = 41 erg/cm^2) and especially good embedding energies. The results of KSCED calculations are summarized in Table II for a monomolecular (m) and supermolecular (s) basis set [25]. The error on the embedding density (ξ) was computed as $\xi = \frac{1000}{N} \int |n^{\text{KSCED}}(\mathbf{r}) - n^{\text{KS}}(\mathbf{r})| d\mathbf{r}$, with N the number of electrons, $n^{\text{KSCED}}(\mathbf{r})$ and $n^{\text{KS}}(\mathbf{r})$ are the densities from KSCED and conventional supermolecular Kohn-Sham calculations, respectively. In Table II we reported the ξ values restricted to the valence density (ξ_v), as the core density is not relevant for chemical purposes. Similar results are obtained using the full density [25]. The error on total energy was defined as $\Delta E = E^{\text{KSCED}} - E^{\text{KS}}$. The APBEK, revAPBEK and LC94 functionals all provide similar KSCED densities, with a slightly improved performance of APBEK. Larger differences are observed for the energies. The revAPBEK functional, which contains only one parameter, is the best one and clearly outperforms LC94 (with five parameters), which is considered one the most accurate KE approximations for KSCED calculations.

In conclusion, we have used the SCA as a reference system to build accurate XC and KE functionals. The SCA-derived XC GGA (APBE) contains no empirical parameters, provides very accurate results for molecules and metal complexes, can be easily implemented in quantum-chemistry and solid-state codes, and thus appears a very promising approximation for applications in different fields. In addition, the revAPBEK is to our knowledge the most accurate GGA kinetic functional for the partition theory of weakly bounded molecular systems. Thus our results show that for atoms and molecules the MGE2 is as important as GE2 for solids [4]. Finally, we gave a simple, theoretical explanation of the conjointness conjecture in density functional theory based on the SCA.

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