Density-Functional Calculations for Large Systems: Can GGA Functionals Be Competitive with Hybrid Functionals?

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Abstract: Two recently proposed correlation functionals, TCA and *Rev*TCA, belonging to the generalized-gradient approximation (GGA) class, are briefly presented and their performances are discussed. The emphasis is put on the comparison with hybrid functionals, which are often the preferred ones for applications to molecular (but not to solid-state) systems. We show that the TCA and *Rev*TCA performances are not far from those of hybrid functionals such as B3LYP or PBE0 when standard tests are performed and can be even better when less standard systems are considered. This is particularly interesting in view of applications to nano-scale systems or systems of biological interest, and, in general, in all the cases where the computer time requirements become an important constraint.

Key words: density-functional theory, correlation functionals, GGA functionals, hybrid functionals, atomization energies, activation energies for chemical reaction, hydrogen bond.

1   Introduction

To perform accurate calculations on very large systems remains a challenge in spite of the continuous increase of the computer power. A complete quantum mechanics treatment of systems of biological interest, for example, is impossible and some kind of approximate method must be used. The current approaches are based on a partition of the system. This is the case, for instance, of QM/MM methods, where a part of the system is treated by quantum mechanics and the remaining part by semi-empirical classical models. The basic idea is that many properties are determined by the "local" features of the system, thus a high level treatment of the overall system is unnecessary.

In a slightly different spirit, methods such as Yang's Divide-and-Conquer (Yang, 1991) or Cortona's subsystem formulation of the density-functional theory (Cortona, 1991) were proposed some years ago. In both cases the system is partitioned in subsystems which are individually treated by quantum mechanics as well as their mutual interactions. In both cases, the general treatment originally proposed can be simplified in order to obtain approximate methods adapted to specific

problems. From this point of view they constitute a bridge towards the QM/MM approaches. The method proposed by Cortona, for instance, was originally devised for completely self-consistent calculations, where all the subsystems are treated on the same footing. In such a way it was used for calculating structural and cohesive properties of various solids (Cortona, 1992, 2004 and 2005; Cortona and Villafiorita Monteleone, 1994 and 1996; Cortona *et al.*, 1995; Cortona and Masri, 1998). However, a current use of the method consists in partitioning the system in two subsystems and to freeze the electronic density of one of them obtaining, in such a way, an embedding method (Wesolowski and Warshel, 1993). This kind of approach was originally used in order to study solvent effects on chemical reactions and was further developed in several papers and applied in various different contexts.

In all these methods, quantum mechanics calculations of the electronic structure of at least a part of the system must be performed. These calculations can be done by traditional quantum chemistry techniques, which can be very accurate and adequate in some cases but, in general, they are too computer time consuming. Alternatively, they can be performed by density-functional theory (DFT). If this last approach is adopted, one has still to decide which exchange-

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correlation functional to use. This functional is in fact the only quantity which must be approximated in DFT and its choice determines the accuracy of the results. Once again, a compromise between accuracy and computer time requirements must be done: hybrid functionals, such as B3LYP (Becke, 1993; Stephens *et al.*, 1994) and PBE0 (Adamo and Barone, 1999; Ernzerhof and Scuseria, 1999) are in many cases highly successful, but they are much more expensive in terms of computer time than approximations of a lower level such as those belonging to the generalized-gradient approximation (GGA) or to the local functionals classes.

In the present paper, we will analyze the results obtained by two recently proposed GGA-like functionals (Tognetti *et al.*, 2008). In particular, we will show that their performances are competitive with those of hybrid functionals and, for some properties, even better.

2 The exchange-correlation functionals

The two functionals to be discussed here were devised in order to include density-gradient dependent contributions in the local correlation functional proposed by Ragot and Cortona (RC) (Ragot and Cortona, 2004). This functional, in its spin-polarized version, is given by:

$$E_c^{RC} = \int A(r_s(\vec{r}))C(\zeta(\vec{r}))d^3r \qquad (1)$$

where r_s is the Seitz radius, ζ is the relative spin-polarization and $C(\zeta)$ is the spin-polarization factor introduced by Wang and Perdew (Wang and Perdew, 1991). The function $A(r_s)$ can be written as:

$$A(r_s(\vec{r})) = \frac{3}{4\pi r_s^3}\varepsilon_c^{RC}(r_s(\vec{r})) \qquad (2)$$

where the correlation energy per electron ε_c^{RC} is given by:

$$\varepsilon_c^{RC} = \frac{-0.655868\arctan(4.888270+3.177037r_s)+0.897889}{r_s} \qquad (3)$$

Eq. (3) was determined (Ragot and Cortona, 2004) following an unusual way. At first, an expression for the correlation kinetic energy was derived by applying a Colle-Salvetti-like approach (Colle and Salvetti, 1975) to the homogeneous electron gas. Then, ε_c^{RC} was obtained by means of the density-functional virial theorem. The value of the only constant which enters in the Colle-Salvetti theory was fixed by looking at the behavior of the homogeneous electron gas in the high and low density limits.

Eq. (1) is a local functional and its implementation in a DFT calculation program is similar to that of the usual local-spin-density approximation (LDA). The tests we have performed on atomic and molecular systems (Tognetti *et al.*, 2007) gave results which strongly improve the LDA ones. Thus, Eqs. (1-3) seem to be a good starting point in order to include gradient-dependent effects in the theory.

The first correlation functional considered here, which will be referred to as TCA, was proposed by Tognetti, Cortona and Adamo (Tognetti *et al.*, 2008) and is defined by:

$$E_c^{TCA} = \int A(r_s(\vec{r}))B(s(\vec{r}))C(\zeta(\vec{r}))d^3r \qquad (4)$$

where s is the reduced density gradient:

$$s = \left(\frac{3}{2\pi}\right)^{1/3}\left\|\vec{\nabla}r_s\right\| = \frac{\left\|\vec{\nabla}\rho\right\|}{2(3\pi^2)^{1/3}\rho^{4/3}} \qquad (5)$$

The function $B(s)$ was determined in order to satisfy the following two constraints:

$$B(0) = 1, \quad \lim_{s\to\infty}B(s) = 0 \qquad (6)$$

The first one means that Eq. (4) reduces to Eq. (1) for homogeneous systems. The second one accounts for the vanishing of the correlation energy in the high density gradient limit.

A very simple expression satisfying both these conditions is:

$$B(s(\vec{r})) = \frac{1}{1+\sigma s(\vec{r})^\alpha} \qquad (7)$$

The values of the two constants σ and α were determined (σ=1.43, α=2.30) by a mean gradient analysis (Zupan *et al.*, 1997).

The second correlation functional which will be considered (it will be referred to as RevTCA) was designed (Tognetti *et al.*, 2008) in order to correct the self-interaction error of the correlation energy functional for hydrogenoid ions. This is achieved by the following functional:

$$E_c^{RevTCA} = \int A[r_s]B[s]C[\zeta](1-D[r_s,s,\zeta])d^3r, \quad (8)$$

and choosing

$$D[r_s,s,\zeta] = \zeta^4\left(1 - \left\{Sinc\left(\frac{\pi s}{ar_s}\right)\right\}^2\right), \quad (9)$$

where $a = \left(\frac{4}{9\pi}\right)^{1/3}$.

This expression assures not only that the correlation energy vanishes for all the hydrogenoid ions in their exact ground state, but also that the RC and TCA limits are recovered in the homogeneous and non-spin-polarized cases, respectively.

In order to perform calculations, the correlation functionals must be combined with an exchange counterpart. In the RC case it is quite natural to use the Slater local exchange, but for the GGA-like functionals the choice is less obvious. We have combined the TCA correlation with the PBE (Perdew *et al.*, 1996) exchange, while in the *Rev*TCA case we have used a PBE exchange modified as described below[1].

The PBE exchange functional is given by:

$$E_x^{PBE} = \int e_x^{uniform}(r_s(\vec{r})) F_x^{PBE}(s(\vec{r})) d^3r \qquad (10)$$

where

$$F_x^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu}{\kappa}s^2} \qquad (11)$$

As it was discussed in details in (Tognetti *et al.*, 2008), the original PBE value of the μ parameter, which determines the exchange behavior at small gradients, does not need do be changed. On the contrary, the κ value becomes important for large gradients. It was fixed by PBE by requiring that the *local* Lieb-Oxford bound be satisfied everywhere. This is actually an unnecessary constraint: a greater value of κ can be chosen without violate the original *integral* Lieb-Oxford condition (Zhang and Yang, 1998). Taking $\kappa = 1.227$ the local Lieb-Oxford bound is satisfied in all the so-called "physical interval" ($s \in [0,3]$) and the integral condition is very likely verified for all the systems of physical interest.

3 Results

We will focus on some properties for which the new GGA functionals perform similarly or better than the hybrid ones. Before that, let us present the results of a standard test for this kind of functionals: the calculation of the atomization energies for the molecules of the G2 data set (Curtiss *et al.*, 1997). The results we have obtained for the reduced as well as for the extended data set (55 and 148 molecules, respectively) are gathered in Table 1. The comparison is done with the LDA, and with two functionals representative of the GGA and hybrid classes: PBE and B3LYP, respectively.

It can be seen that the new functionals reduce the errors with respect to functionals belonging to the same class: RC improves LDA by a factor of about 3, and TCA and *Rev*TCA improve PBE: for the large G2 set the mean absolute error (MAE) is almost divided by 2 using TCA and by 3 using *Rev*TCA. The comparison with B3LYP shows that the gap in accuracy is strongly reduced: the performances of *Rev*TCA, in particular, are nearer to those of B3LYP than to those of PBE. Similar remarks can be done for the activation barriers

[1] See (Tognetti *et al.*, 2008) for a detailed discussion of these choices.

Table 1   Mean absolute errors (MAE, kcal/mole) and maximum absolute errors (Max, kcal/mole) for the atomization energies of the two G2 sets.

	G2-1 (55 molecules)		G2 (148 molecules)	
	MAE	Max	MAE	Max
LDA	39.7	93.8 (CO_2)	91.4	228.7 (C_6H_6)
RC	14.6	51.1 (CO_2)	26.3	123.6 (C_2F_4)
PBE	8.1	29.1 (F_2)	17.0	50.6 (C_2F_4)
TCA	6.7	27.7 (ClF)	9.0	33.2 (C_2F_4)
*Rev*TCA	4.4	14.4 (NO)	5.9	31.3 (SiF_4)
B3LYP	2.3	9.9 (HOCl)	3.1	20.0 (SiF_4)

of some class of chemical reactions. We have performed calculations for standard benchmark sets[2] and we have found that RC improves LDA and TCA and RevTCA improve PBE reducing the performance gap with respect to B3LYP. A first example of property for which the GGA functionals work better than B3LYP is the bond lengths of some class of molecules (Tognetti *et al.*, 2008). We have considered three benchmark sets: G2-32, G2-M and C2. The first one is a subset of the reduced G2 set; the second one is a set of ten representative metal complexes; the last one includes twelve diatomic molecules containing a monochalcogenic atom. The results we have obtained are gathered in Table 2.

Table 2   Mean absolute errors (and absolute maximal deviations) in Å for the bond lengths of the G2-32, G2-M and C2 sets.

Method	G2-32	G2-M	C2
PBE	0.013 (0.067)	0.014 (0.036)	0.012 (0.026)
TCA	0.012 (0.067)	0.015 (0.040)	0.012 (0.024)
*Rev*TCA	0.014 (0.080)	0.019 (0.059)	0.010 (0.018)
B3LYP	0.007 (0.057)	0.016 (0.043)	0.024 (0.040)

For the bond lengths, the new functionals don't improve PBE: the accuracy is approximately the same. Comparing with B3LYP it can be noticed that the latter is better for the G2-32 set. This could be expected because B3LYP is an empirical functional containing several parameters some of which were determined in order to optimize the performances for a variety a properties (including the bond lengths) of the molecules of the G2 set. This explains why its performances degrade when one consider other sets of molecules: this appears already for the G2-M set (the B3LYP accuracy is similar to that of the GGA functionals) but it is much more evident for the C2 set. This latter remark allows one to conclude that, when the system contains heavy atoms,

[2] We have considered (Tognetti *et al.*, 2008) hydrogen transfer (HT), heavy atom transfer (HAT), nucleophilic substitution (NS), unimolecular and association (UA), and proton transfer (PT) reactions.

a parameter-free GGA functional is probably a better choice than B3LYP, which was optimized for systems containing light atoms.

A second example is given by hydrogen-bonded complexes (Tognetti *et al.*, 2008). We have performed calculations for the benchmark set proposed by Boese and Martin (2004) obtaining the results reported in Table 3 and in Table 4.

Here the comparison is done with PBE0, a hybrid functional which works very well for these systems. The comparison shows that the TCA and PBE0 results have

approximately the same accuracy. For these systems TCA strongly improves with respect to PBE.

A last example is offered by the activation enthalpies of the 1, 3-dipolar cycloaddition reactions (Tognetti *et al.*, 2009). The calculation of these quantities must be performed very carefully, paying care to the use of a sufficiently large basis set (Grimme *et al.*, 2006). We have calculated the activation enthalpies for 18 reactions using the 6-311G(d, p) basis set recommended by Grimme *et al.* The results we have obtained are collected in Table 5.

Table 3 Differences (in Å) between the calculated hydrogen bond lengths for some hydrogen-bonded complexes and the reference values (Boese and Martin, 2004). PBE and PBE0 values are taken from (Vydrov and Scuseria, 2006).

| Complex	Reference	PBE	TCA	PBE0
$(H_2O)_2$	1.954	−0.030	0.002	−0.024
$(H_3O^+)(H_2O)$	1.195	0.016	0.016	0.001
$(H_2O)(NH_3)$	1.978	−0.059	−0.036	−0.041
$(NH_3)_2$	2.302	−0.053	0.001	−0.034
$(FH)(NH_3)$	1.697	−0.070	−0.060	−0.051
$(ClH)(NH_3)$	1.793	−0.196	−0.161	−0.153
$(HF)_2$	1.823	−0.037	−0.007	−0.025
$(HCl)_2$	2.559	−0.122	−0.032	−0.067
$(CO)(HF)$	2.072	−0.001	0.042	−0.001
$(OC)(HF)$	2.081	−0.111	−0.085	−0.069
MSE[a]	–	−0.066	−0.032	−0.046
MAE[b]	–	0.070	0.044	0.047

[a]Mean signed error; [b]Mean absolute error.

Table 4 Differences (in kcal/mol) for the dissociation energies of hydrogen-bonded complexes between calculated and reference values (Boese and Martin, 2004). PBE and PBE0 values are taken from (Vydrov and Scuseria, 2006).

| Complex	Reference	PBE	TCA	PBE0
$(H_2O)_2$	4.98	0.12	−0.28	−0.01
$(H_3O^+)(H_2O)$	33.74	3.29	2.56	2.52
$(H_2O)(NH_3)$	6.41	0.57	0.05	0.26
$(NH_3)_2$	3.13	0.01	−0.36	−0.16
$(FH)(NH_3)$	12.45	1.84	1.22	1.21
$(ClH)(NH_3)$	8.34	2.50	1.53	1.57
$(HF)_2$	4.57	0.29	−0.04	0.13
$(HCl)_2$	2.01	0.07	−0.33	−0.23
$(CO)(HF)$	1.69	−0.07	−0.20	−0.09
$(OC)(HF)$	3.53	1.05	0.61	0.52
MSE[a]	–	0.97	0.48	0.57
MAE[b]	–	0.98	0.72	0.67

[a]Mean signed error; [b]Mean absolute error.

Table 5 Computed activation enthalpies ΔH_{0K} (in kcal/mol) and mean signed and absolute errors for 18 1, 3-dipolar cycloaddition reactions using various exchange-correlation functionals. Reference values from (Ess and Houk, 2005).

										MSE	MAE
Ref.	27.9	20.3	14.6	13.0	7.2	5.9	13.8	6.6	0.9	–	–
PBE	21.0	14.5	11.5	8.8	4.3	4.0	9.0	2.6	−0.2	−3.8	4.3
TCA	23.0	16.7	13.7	10.7	6.3	6.2	11.3	5.1	2.1	−1.7	2.0
*Rev*TCA	27.8	21.5	17.8	14.3	10.3	10.2	16.0	9.8	6.3	2.7	2.7
B3LYP	28.6	21.9	18.5	15.7	10.2	10.1	15.6	9.1	5.0	2.7	3.1

										MSE	MAE
Ref.	27.9	20.1	15.2	14.1	8.5	7.4	14.0	8.1	1.5	–	–
PBE	20.3	13.8	11.6	9.4	5.1	5.1	8.6	4.2	0.3	−4.3	4.3
TCA	22.1	15.8	13.7	11.2	7.0	7.2	10.9	6.5	2.4	−2.2	2.4
*Rev*TCA	26.8	20.4	17.5	14.6	10.8	11.0	15.4	10.9	6.3	1.9	2.1
B3LYP	28.0	21.2	18.4	16.3	10.9	11.0	15.3	10.2	5.2	2.2	2.2

For these reactions, the accuracy of TCA and *Rev*TCA is similar. Both divide the PBE MAE approximately by 2 and both improves the results with respect to B3LYP. This remark is quite surprising because, even though these reactions were not used for optimizing the parameters of the B3LYP functional, nevertheless all the atoms composing the reacting molecules are light atoms.

4 Conclusions

We have shown that GGA functionals are competitive with hybrid functionals. The performances of two recently proposed GGA functionals, TCA and *Rev*TCA, are not far from those of B3LYP for standard test properties such as the atomization energies of the G2 data set and can be even better for less standard systems, as we have shown in the cases of the activation enthalpies of the 1, 3-dipolar cycloaddition reactions or the bond lengths of the C2 data set. It is important to recall that TCA and *Rev*TCA as others (but not all) functionals of the GGA class such as PBE, are parameter-free, in the sense that all the constants entering in their analytical expression are determined on fundamental ground. This probably assures more systematic performances than parametrized functionals such as B3LYP.

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