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# Benchmark calculations for reduced density-matrix functional theory

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Reduced density-matrix functional theory (RDMFT) is a promising alternative approach to the problem of electron correlation. Like standard density functional theory, it contains an unknown exchange-correlation functional, for which several approximations have been proposed in the last years. In this article, we benchmark some of these functionals in an extended set of molecules with respect to total and atomization energies. Our results show that the most recent RDMFT functionals give very satisfactory results compared to standard quantum chemistry and density functional approaches. © 2008 American Institute of Physics. [DOI: 10.1063/1.2899328]

## I. INTRODUCTION

Reduced density-matrix functional theory (RDMFT) is based on Gilbert's theorem,<sup>1</sup> which guarantees that the expectation value of any observable of a system in its ground-state is a unique functional of the ground-state one-body reduced density matrix (1-RDM). Thus, the fundamental quantity in RDMFT is the 1-RDM instead of the electronic density upon which density functional theory (DFT) is built. Although this idea is relatively old, functionals of the 1-RDM have been exploited for practical applications only in the last decade.

The total energy of the ground state of a system of  $N$  electrons can be written in terms of the 1-RDM  $\gamma$  as

$$E_{\text{tot}}[\gamma] = \int d^3r \int d^3r' \delta(\mathbf{r} - \mathbf{r}') \left[ -\frac{1}{2} \nabla_r^2 \right] \gamma(\mathbf{r}, \mathbf{r}') + \int d^3r \int d^3r' \delta(\mathbf{r} - \mathbf{r}') v(\mathbf{r}) \gamma(\mathbf{r}, \mathbf{r}') + \frac{1}{2} \int d^3r \int d^3r' \frac{\gamma(\mathbf{r}, \mathbf{r}) \gamma(\mathbf{r}', \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[\gamma]. \quad (1)$$

The first term is the kinetic energy of the system. The second is the energy due to an external potential  $v(\mathbf{r})$  acting on the system. This external potential, which for simplicity is assumed to be local, is normally the ionic potential for atoms and molecules. The last two terms account for the electron-electron interaction that can be cast into a usual Coulomb part and the remainder, which in the DFT fashion we will call exchange-correlation term  $E_{\text{xc}}$ . This last part is the only term that is unknown and, for practical applications of the theory, needs to be approximated. A great advantage of RDMFT, compared to DFT, is that the kinetic energy term is an

explicit functional of the ground state  $\gamma$ . Another advantage is that  $\gamma$  is a nonlocal quantity and contains more information than the electronic density.

The knowledge of the exact, or of a reasonable approximation, of functional (1) allows for the minimization with respect to  $\gamma$  to determine the total energy and  $\gamma$  for the ground state. In basically all practical implementations of RDMFT, the minimization with respect to  $\gamma$  is replaced by a minimization with respect to its eigenvalues  $n_i$  and its eigenfunctions  $\varphi_i(\mathbf{r})$ , called, respectively, the occupation numbers and natural orbitals. In such a minimization, the  $N$ -representability conditions for the 1-RDM (Refs. 2 and 3) have to be enforced. These conditions are

$$\sum_i n_i = N, \quad 0 \leq n_i \leq 1. \quad (2)$$

The first represents particle number conservation, while the second reflects the Pauli antisymmetry principle. The first can be enforced through the minimization of the quantity

$$F = E_{\text{tot}} - \mu \left( \sum_i n_i - N \right), \quad (3)$$

instead of the total energy  $E_{\text{tot}}$ . The quantity  $\mu$  is the appropriate Lagrange multiplier. A dramatic consequence of the second condition is that it allows for occupation numbers being border minima, i.e., exactly equal to 1 or 0. We refer to the corresponding states as "pinned states." The fundamental difference between these states and those with fractional occupancy is that for the pinned states the derivative  $\partial F / \partial n_p \neq 0$ , where  $n_p$  is the occupation number of the pinned state. Thus,  $\delta F / \delta \gamma \neq 0$  at the minimizing  $\gamma$ . It has been demonstrated<sup>4</sup> that this is not an exceptional situation but rather the rule for several approximate functionals of the 1-RDM.

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The  $N$ -representability conditions warrant that the trial  $\gamma(\mathbf{r}, \mathbf{r}')$  corresponds to either a pure  $N$ -electron state or to an ensemble of  $N$ -electron states.<sup>3</sup> However, they do not warrant that the reconstructed two-body reduced density-matrix (2-RDM) is also  $N$ -representable.<sup>5</sup> The  $N$ -representability of the 2-RDM is a much more complex problem.

Most of the approximations to  $E_{xc}$  do not explicitly depend on  $\gamma$  but are written in terms of the natural orbitals and the occupation numbers. For this reason, RDMFT is also called natural orbital functional theory. The first functional was devised by Müller<sup>6</sup> in 1984, but it attracted little interest for almost 15 years. The situation changed due to the works of Goedecker and Umrigar<sup>7</sup> and Buijse and Baerends,<sup>8</sup> who demonstrated that correlation energies for small atomic and molecular systems calculated with the Müller functional (or simple modifications of it) were in good agreement with the exact ones. Since then, several promising new functionals have appeared in the literature.<sup>4,9–18</sup>

The real quality of an approximate functional comes from its ability to describe accurately electronic correlation and other properties of real systems. Ideally, the performance of a functional should also be uniform over a large class of systems. Furthermore, it is important to know the limitations of existing functionals, as that increases their reliability. In this respect, benchmarking has a fundamental role in the development of any approach to electronic correlation.

Significant effort has been devoted to the assessment of the quality of existing exchange-correlation functionals of the 1-RDM. A few of the articles that proposed new functionals also presented example calculations, normally for atoms or small molecular systems.<sup>7–10,17–24</sup> Particular attention has been given to the performance of several functionals for the whole dissociation curve of dimers.<sup>17,22,25–27</sup> Besides atomic and molecular systems, RDMFT functionals have also been applied to the homogeneous electron gas (HEG).<sup>4,15,16,28</sup> This prototype metallic system has been proven quite useful in the evaluation and the development of 1-RDM functionals.<sup>4,16</sup> Apart from the correlation energy, other properties were also calculated like ionization potentials,<sup>19–21,29</sup> the chemical hardness and the fundamental gap,<sup>21,30</sup> dipole moments and static polarizabilities,<sup>18,21,23,31</sup> and vibrational frequencies.<sup>19</sup> Finally, effort has been recently devoted in the formulation of time dependent RDMFT.<sup>32,33</sup>

However, a thorough benchmark of the most used functionals for larger molecular systems is still lacking. In this article, we address this issue and present a systematic study of the most common exchange-correlation functionals within RDMFT for the G2/97 molecule set.<sup>34,35</sup> This set comprises 148 neutral molecules, including 29 radicals, 35 nonhydrogen systems, 22 hydrocarbons, 47 substituted hydrocarbons, and 15 inorganic hydrides. Furthermore, the molecules present in the G2/97 set are well known experimentally and theoretically, which allows us to compare the relative merits of current RDMFT functionals to other quantum chemistry approaches and standard DFT. We present both correlation and atomization energies.

The rest of this article is structured as follows. In Sec. II, we give an overview of the existing 1-RDM functionals with

a special emphasis on those we chose to include in our benchmark. Then, in Sec. III, we describe our numerical method and discuss our results. Finally, in Sec. IV, we conclude and give a brief outlook on the present status of RDMFT.

## II. FUNCTIONALS

In this section, we present some of the most known functionals of the 1-RDM that have been introduced to date. A number of these, including those of interest in the present work, can be cast into the form

$$E_{xc} = -\frac{1}{2} \sum_{j,k} \int d^3r \int d^3r' f(n_{j\sigma}, n_{k\sigma}) \times \frac{\varphi_{j\sigma}^*(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (4)$$

i.e., they have the form of the usual Hartree–Fock (HF) exchange modified by the function  $f(n_{j\sigma}, n_{k\sigma})$  of the occupation numbers. Functionals of this form are sometimes referred to as of  $J$ - $K$  type, as they only involve Coulomb ( $J$ )- and exchange ( $K$ )-type integrals over the natural orbitals. The symbol  $\sigma$  in Eq. (4) denotes the spin index and will be omitted in the following, i.e., we restrict the presentation of functionals to closed shell systems for simplicity. In that case, a factor of 2 should be introduced in expression (4). We refer to Refs. 21 and 24 for the generalization of the functionals to open shell systems.

The first approximation to  $E_{xc}$ , introduced by Müller in 1984,<sup>6</sup> corresponds to the simple formula,

$$f^{\text{Müller}}(n_j, n_k) = \sqrt{n_j n_k}. \quad (5)$$

In reality, Müller considered a more general form  $f = n_j^\alpha n_k^{1-\alpha}$ , but found that  $\alpha = 1/2$  was the optimal value. He showed that the probability of finding an electron at  $\mathbf{r}$  when a second one is at  $\mathbf{r}'$  becomes negative in the neighborhood of  $\mathbf{r}'$ . This unphysical negative value is minimized for  $\alpha = 1/2$ . Buijse and Baerends<sup>8</sup> arrived at the same formula for  $f$  by modeling the exchange and correlation hole. Interestingly, the reconstructed second density associated with this functional satisfies the sum rule relating the second and the first order densities. In addition, it yields the correct dissociation limit of dimers of open shell atoms such as  $\text{H}_2$ . Note that HF and also standard DFT functionals fail for these cases. However, the Müller functional substantially overestimates the correlation energy<sup>26,27</sup> of all systems it has been applied to (including the HEG<sup>4,15,28</sup>). It was recently shown by Frank *et al.*<sup>36</sup> that for two electron systems the Müller functional provides a lower bound for the total energy. They also showed that, for this functional, the total energy does not go to zero if the ionic potential is switched off but to the value  $-N/8$  a.u. They interpreted this value as an effective self-interaction (SI) error and proposed a correction to the Müller functional equal to  $N/8$  a.u.

A modified form of the Müller functional was introduced independently by Goedecker and Umrigar (GU).<sup>7</sup> In the GU functional the SI terms are removed from the xc term of the Eq. (4) and the direct Coulomb term. The corresponding function  $f$  takes the form

$$f^{\text{GU}}(n_j, n_k) = \sqrt{n_j n_k} - \delta_{jk}(n_j - n_k^2). \quad (6)$$

Contrary to the functional of Müller, GU is not consistent with the sum rule relating the second and the first order densities.<sup>7</sup> Furthermore, it cannot be expressed as an explicit functional of  $\gamma$ . However, it yields much better correlation energies than the Müller functional for atoms and molecules at the equilibrium geometry. Unfortunately, it fails to reproduce the correct dissociation limit of small molecules.<sup>26,27</sup>

Csányi and Arias<sup>15</sup> devised a functional by considering a class of computationally feasible approximations of the two-body density matrix as a finite sum of tensor products of single-particle operators. They called their approximation corrected Hartree–Fock (CHF). It reads

$$f^{\text{CHF}} = n_j n_k + \sqrt{n_j(1-n_j)} \sqrt{n_k(1-n_k)}. \quad (7)$$

They applied CHF and the Müller functionals to the HEG (Ref. 15) and found that the two functionals coincide in the low density limit. As the density increases, however, CHF considerably undercorrelates and the solution quickly collapses to the HF idempotent solution. The same is found for a series of two-electron systems.<sup>25–27</sup> For example, CHF gives the idempotent solution for H<sub>2</sub> at equilibrium (but not for large distances).<sup>25,27</sup> Thus, the tendency to fall to the idempotent HF solution is a drawback of this functional, especially at the equilibrium geometries. We also found this behavior for most of the molecular systems we applied it to. For this reason, we did not consider this functional in our evaluation.

Noticing that, in the high density limit, CHF underestimates the correlation energy, while the Müller functional overcorrelates it considerably, Csányi, Goedecker, and Arias (CGA) introduced<sup>16</sup> a form for the function  $f$  which is an average between these two functionals,

$$f^{\text{CGA}} = \frac{1}{2} [n_j n_k + \sqrt{n_j(2-n_j)} \sqrt{n_k(2-n_k)}]. \quad (8)$$

This functional is very accurate in the high-density limit of the HEG (Ref. 16) and is comparable to common generalized-gradient approximations for atoms (albeit not as precise as the GU functional). Interestingly, it reproduces the correct dissociation limit for small molecules.<sup>26,27</sup>

We now turn our attention to the most recent functionals of the 1-RDM. A promising approach was recently put forth by Gritsenko *et al.*<sup>17</sup> They proposed three hierarchical corrections in order to treat the overcorrelation of the Müller functional: the BBC1, BBC2, and BBC3. For all these functionals, it is essential to divide the natural orbitals into strongly and weakly occupied. This distinction naturally appears for finite systems since usually in this case the natural orbitals have occupation numbers that are either close to 1 or to 0. We denote the set of strongly occupied orbitals as  $S$  and the set of the weakly occupied as  $W$ . For the BBC1, the function  $f(n_j, n_k)$  is

$$f^{\text{BBC1}}(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & \text{for } j \neq k \wedge \phi_j, \phi_k \in W \\ \sqrt{n_j n_k} & \text{otherwise,} \end{cases} \quad (9)$$

while for BBC2, we have

$$f^{\text{BBC2}}(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & \text{for } j \neq k \wedge \phi_j, \phi_k \in W \\ n_j n_k & \text{for } j \neq k \wedge \phi_j, \phi_k \in S \\ \sqrt{n_j n_k} & \text{otherwise.} \end{cases} \quad (10)$$

The symbol  $\wedge$  stands for the logical “and,” while  $\in$  means that the orbitals on the left belong to the set on the right. In other words, the BBC1 functional consists in a sign change of the function  $f$  of the Müller functional for orbitals  $i \neq j$  that are both weakly occupied, while the BBC2, in addition to BBC1 correction, restores the exchangelike form for orbitals  $i \neq j$  that are both strongly occupied. The reconstructed second order density associated with BBC1 and BBC2 is also consistent with the sum rule relating the second and first order densities.

Finally, in the BBC3 functional, there are corrections that apply only to the bonding and antibonding orbitals. An issue that emerges especially when BBC3 is applied to systems with large number of electrons is the possibility of degenerate bonding and antibonding orbitals. Selecting one of the degenerate orbitals as bonding or antibonding breaks the symmetry of the molecule. For this reason, in our treatment, we consider a modification that respects the degeneracies of bonding and/or antibonding orbitals. We subdivide further the set  $S$  into two subsets: the subset  $S_b$  for the degenerate bonding orbitals and the subset  $S_c$  for the rest. Accordingly, we subdivide the set  $W$  into the subset  $W_a$  of the degenerate antibonding orbitals and  $W_h$  of the rest weakly occupied orbitals. The function  $f$  for the BBC3 becomes

$$f^{\text{BBC3}}(n_j, n_k) = \begin{cases} -\sqrt{n_j n_k} & \text{for } j \neq k \wedge \phi_j, \phi_k \in W \\ n_j n_k & \text{for } j \neq k \wedge \phi_j, \phi_k \in S \\ n_j n_k & \text{for } (\phi_j \in S_c \wedge \phi_k \in W_a) \vee (\phi_k \in S_c \wedge \phi_j \in W_a) \\ n_j^2 & \text{for } j \neq k \wedge \phi_j, \phi_k \in S_c \cup W_h \\ \sqrt{n_j n_k} & \text{otherwise,} \end{cases} \quad (11)$$

where  $\cup$  stands for the union of two sets and  $\vee$  for the logical “or.” The first two cases in definition (11) represents the BBC1 and BBC2 corrections, and the third the inclusion of the antibonding orbitals in the BBC2 correction (unless they interact with bonding orbitals). Finally, the fourth case stands for the removal of the SI terms as in the GU functional for all orbitals apart from those belonging to the bonding or antibonding subsets. This final correction violates the sum rule between the second and first order densities.

Gritsenko *et al.*<sup>17</sup> applied the BBC functionals to diatomic molecules and showed that they give an accurate description of these molecules at both the equilibrium distance and at the dissociation limit. BBC1 and BBC2 were also applied to the HEG.<sup>4</sup> BBC3 involves single orbital type of corrections and for the HEG it coincides with BBC2.

Another functional that was recently introduced by Piris<sup>18</sup> uses the cumulant expansion to derive a reconstructed functional of the two matrix. Under further considerations, Piris arrived at the functional (which we will call PNOF0 from Piris natural orbital functional)

$$f^{\text{PNOF0}} = \Lambda_{jk}^{(0)} - \delta_{jk}(n_j - n_j^2), \quad (12)$$

with

$$\Lambda_{jk}^{(0)} = \left[ 1 - 2\theta\left(\frac{1}{2} - n_j\right)\theta\left(\frac{1}{2} - n_k\right) \right] \sqrt{n_j n_k}, \quad (13)$$

where  $\theta$  is the Heaviside step function. This approximation can be seen as a combination of the removal of the SI terms, as in the GU functional, applied on top of the BBC1 correction. In order to avoid the effect of state pinning, Piris modified  $\Lambda_{jk}$  by adding an extra term. We refer to this functional as Piris natural orbital functional (PNOF). It reads

$$f^{\text{PNOF}} = \Lambda_{jk} - \delta_{jk}(n_j - n_j^2), \quad (14)$$

with

$$\Lambda_{jk} = \Lambda_{jk}^{(0)} + \theta\left(n_j - \frac{1}{2}\right)\theta\left(n_k - \frac{1}{2}\right)\sqrt{(1 - n_j)(1 - n_k)}. \quad (15)$$

PNOF was applied to a set of 57 molecules by calculating the correlation energies and dipole moments and comparing to coupled cluster theory and experimental values.<sup>18</sup> It was also applied to the calculation of ionization potentials and vibrational frequencies.<sup>19–21</sup> Recently, a generalization of this functional to open shell systems was introduced<sup>21</sup> and applied to the calculation of correlation energies, ionization potentials, and electron affinities. Finally, a new ansatz based on PNOF (Ref. 22) has been introduced for the calculation of dispersion forces and applied to the calculation of helium dimer.

### III. RESULTS

#### A. Implementation

Our implementation of RDMFT for finite systems is based on an expansion of the natural orbitals on Gaussian basis sets. The total energy as well as its gradients with respect to the occupation numbers and the natural orbitals can then be written in terms of the so-called one- and two-electron integrals. Thus, the numerical treatment can be based on a HF implementation provided that the functional is of  $J$ - $K$  type. Note that all functionals we are concerned with

in this article are of this type. The required one- and two-electron integrals are inputs to our program. In the current implementation, we have been using the GAMESS program<sup>37</sup> for this task.

We minimize the total energy of Eq. (1) following two steps that are alternately repeated. In the first, we minimize with respect to the occupation numbers keeping the natural orbitals fixed. For this step, we use a sequential quadratic programming method.<sup>38</sup> For the second, we use a conjugate gradient method. We use appropriate energy gradients which respect the orbital orthonormality.<sup>25,39</sup> The gradients of the total energy with respect to the natural orbitals have the form

$$\frac{\delta E_{\text{tot}}}{\delta \phi_i^*} = F^{(i)} \phi_i, \quad (16)$$

where  $F^{(i)}$  is a generalization of the Fock matrix of HF theory that in RDMFT depends on the orbital  $i$ . Consequently, the problem does not reduce to a simple diagonalization, and the matrices  $F^{(i)}$  have to be updated very often in the minimization process. This turns out to be the most time-consuming part of our implementation since the calculation of  $F^{(i)}$  involves the summation over the two electron integrals. A possible workaround to the orbital minimization problem has been proposed by Pernal.<sup>40</sup> In this approach, all natural orbitals stem from the same nonlocal potential that is obtained from a procedure inspired by the optimized effective potential method of DFT.

We used two sets of calculations: The first set includes all molecules of the G2/97 set, calculated with the Cartesian 6-31G\* Gaussian basis set. In the second, we employed the significantly larger cc-pVDZ basis set but we considered a subset of the G2/97 set (G2-1) that includes 55 molecules. In this way, we could check the dependence of our findings on the choice of basis set. As reference, we used the coupled cluster method with singles, doubles, and perturbative triples [CCSD(T)],<sup>41</sup> employing the same basis sets.

Apart from the orbitals with occupancy close to 1, we included 40 extra natural orbitals in the minimization procedure. It has been shown that this number is sufficient to achieve convergence of the total energy.<sup>7,24</sup> For systems that are small enough and this number exceeds the size of the basis, we performed full variation, i.e., the number of the varied natural orbitals was equal to the size of the basis. For comparison, we computed the correlation energy using DFT with the Becke 3 parameter exchange-correlation functional<sup>42,43</sup> (B3LYP) and Møller-Plesset second-order perturbation theory (MP2). For these, as well as for the CCSD(T) calculations, we used the GAUSSIAN 98 program.<sup>44</sup> In all calculations, the geometries optimized with the MP2 method were used.

For the open shell systems, our implementation<sup>24</sup> assumes spin dependent occupation numbers but spin independent natural orbitals. Furthermore, in the minimization with respect to the spin dependent occupation numbers, both spin-up and spin-down total numbers of electrons were kept fixed. One can show that in this formulation the  $S_z$  component of the total spin of the system is preserved. Moreover, this approach is very efficient numerically, as the number of orbitals included in the variation process is half the number

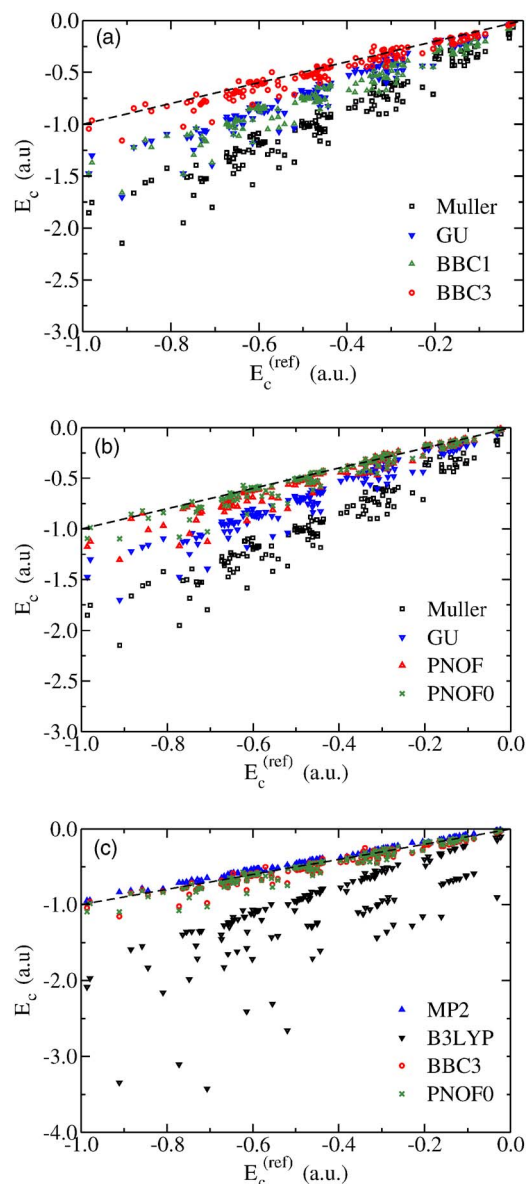


FIG. 1. (Color online) Correlation energy calculated by a variety of methods vs reference values ( $E_c^{(\text{ref})}$ ) obtained with CCSD(T). The dashed line corresponds to  $E_c = E_c^{(\text{ref})}$ .

for the full unrestricted case. We should mention that there is not a unique way to generalize 1-RDM functionals to the case of open shell systems. For example, a generalization, alternative to the one used in this work, was recently introduced for the PNOF functional.<sup>21</sup>

## B. Total energy

In Fig. 1, we plot the correlation energy obtained with various methods versus the reference values. The dashed lines correspond to the perfect agreement with the reference energies calculated with the CCSD(T) method. The complete set of our results can be found in the supplementary material to this article.<sup>45</sup> It can be easily seen from the figure that the Müller functional overcorrelates substantially all systems. This is in complete agreement with previous calculations for finite systems and for the HEG and supports the idea that this functional could be a lower bound for the total energy.<sup>36</sup> In

Figs. 1(a) and 1(b), we show the improvement over the Müller and GU functionals which is provided by the BBCs and Piris functionals, respectively. In Fig. 1(c), we compare the results obtained with the more accurate functionals, i.e., PNOF0 and BBC3, with MP2 and B3LYP values. Note that we define correlation energy as  $E_c = E_{\text{tot}} - E_{\text{HF}}$ , where  $E_{\text{HF}}$  is the HF total energy. In DFT, both exchange and correlation are approximated, and therefore, the above definition includes also the error in using the approximate exchange. In other words, it can be misleading to use the above formula to obtain absolute correlation energies with DFT methods, such as B3LYP, and compare with wave-function methods. However, for the sake of completeness, we included B3LYP results in Tables I and II and in Fig. 1.

In Tables I and II, we show a few quantities that measure the deviation from the reference values. The meaning of the columns is the following:

$$\bar{\Delta} = \sqrt{\sum (E_c - E_c^{(\text{ref})})^2 / N_{\text{mol}}}, \quad (17a)$$

$$\Delta_{\text{max}} = \max |E_c - E_c^{(\text{ref})}|, \quad (17b)$$

$$\bar{\delta} = 100 \sqrt{\sum [(E_c - E_c^{(\text{ref})}) / E_c^{(\text{ref})}]^2 / N_{\text{mol}}}, \quad (17c)$$

$$\delta_{\text{max}} = 100 \times \max |(E_c - E_c^{(\text{ref})}) / E_c^{(\text{ref})}|, \quad (17d)$$

$$\bar{\delta}_e = \sum |E_c - E_c^{(\text{ref})}| / (N \times N_{\text{mol}}), \quad (17e)$$

where  $N_{\text{mol}}$  is the number of molecules in the test set and  $N$  is the number of electrons in the molecule.

Clearly, the least performing approximation is the Müller functional. On average, it overestimates the correlation energy by more than 100%, while in the worst case, the error exceeds 400%. The GU, CGA, BBC1, and BBC2 functionals significantly improve with errors of the order of 45%–90% for both sets of calculations. Finally, BBC3 and the Piris functionals are the most accurate. Their performance is quite remarkable, with average errors in the range of 17%–20% which are by merely a factor of 1.5 larger than the average error of MP2. They correct 85% of the error of the Müller functional. Interestingly, PNOF0, i.e., the Piris functional without the additional term which keeps the occupations fractional, is slightly better in performance than BBC3 or PNOF and is the most accurate as far as correlation energies are concerned.

As we see in Fig. 1(a), all 1-RDM functionals we tested tend to overcorrelate compared to CCSD(T). This trend is the same for both sets of calculations. For the first set, BBC3, PNOF, and PNOF0 give total energies lower than CCSD(T) for 120, 126, and 104 systems, respectively, out of the 148 of the G2 set. The other 1-RDM functionals overcorrelate for nearly all the cases.

Note that the performance of the functionals for the two sets of calculations is quite similar (see Tables I and II). This indicates that the convergence rate of the correlation energies obtained with 1-RDM functionals is similar to MP2 or CCSD(T). Note that it is well known that DFT functionals converge fast with respect to the basis set.<sup>46,47</sup>

TABLE I. Error in the correlation energies calculated with a variety of methods for the first set of calculations (whole G2/97 set, 6-31G\* basis). The reference energies ( $E_c^{\text{ref}}$ ) were obtained with CCSD(T). The values in the first, second, and last columns are in a.u.

| Method | $\bar{\Delta}$ | $\Delta_{\text{max}}$                  | $\bar{\delta}$ (%) | $\delta_{\text{max}}$ (%) | $\bar{\delta}_e$ |
|--------|----------------|--|--------------------|---------------------------|------------------|
| Müller | 0.55           | 1.23 (C <sub>2</sub> Cl <sub>4</sub> ) | 135.7              | 438.3 (Na <sub>2</sub> )  | 0.0193           |
| GU     | 0.26           | 0.79 (C <sub>2</sub> Cl <sub>4</sub> ) | 51.63              | 114.2 (Si <sub>2</sub> )  | 0.0072           |
| CGA    | 0.22           | 0.55 (C <sub>2</sub> Cl <sub>4</sub> ) | 69.11              | 331.9 (Na <sub>2</sub> )  | 0.0077           |
| BBC1   | 0.29           | 0.75 (C <sub>2</sub> Cl <sub>4</sub> ) | 69.91              | 159.1 (Na <sub>2</sub> )  | 0.0098           |
| BBC2   | 0.18           | 0.50 (C <sub>2</sub> Cl <sub>4</sub> ) | 45.02              | 125.0 (Na <sub>2</sub> )  | 0.0058           |
| BBC3   | 0.068          | 0.27 (SiCl <sub>4</sub> )              | 18.37              | 50.8 (SiH <sub>2</sub> )  | 0.0017           |
| PNOF   | 0.102          | 0.42 (SiCl <sub>4</sub> )              | 20.84              | 59.1 (SiCl <sub>4</sub> ) | 0.0021           |
| PNOF0  | 0.072          | 0.32 (SiCl <sub>4</sub> )              | 17.11              | 46.0 (Cl <sub>2</sub> )   | 0.0015           |
| MP2    | 0.040          | 0.074(C <sub>2</sub> Cl <sub>4</sub> ) | 11.86              | 35.7 (Li <sub>2</sub> )   | 0.0015           |
| B3LYP  | 0.75           | 2.72 (SiCl <sub>4</sub> )              | 305.0              | 2803.7 (Li <sub>2</sub> ) | 0.022            |

In the last column of Tables I and II, we show the average error  $\bar{\delta}_e$  of the correlation energy per electron. The largest value is for the Müller functional, 0.019 a.u., and is one order of magnitude smaller than the correction of 1/8 a.u. per electron proposed by Frank *et al.*<sup>36</sup> Thus, it is clear that this correction is rather unrealistic leading to very high total energies.

We now turn our attention to the quality of the minimization  $\gamma$ . We have already mentioned that most of the functionals considered in this work (all except PNOF) produce pinned states for all systems except those with only two electrons. The presence of a pinned state means that the particular natural orbital is present in all determinants of the full configuration-interaction expansion with nonzero coefficients. This situation is rather unlikely for the systems included in the present benchmark. Nevertheless, we would not consider it necessarily as a serious drawback. Pinned states are usually core states with occupation extremely close to 1 also in the exact  $\gamma$ . Moreover, these core states do not significantly affect many important quantities based on total energy differences.

A quantity which is a measure, although still not absolute, of the quality of the occupation numbers produced by the 1-RDM functionals is the total charge  $q_w$  occupying the weakly occupied states of the set  $W$ . The quantity  $q_w$  shows

how much the calculated  $\gamma$  differs from an idempotent matrix, i.e., it is a measure of the degree of correlation of the system. We calculated this quantity for a few representative molecules using the 1-RDM functionals. The results are in the Table III where we have also included the values obtained with coupled cluster with double excitations (CCD).<sup>48</sup> For the CCD calculations, we used the GAUSSIAN 98 program employing the same basis set as above. The overcorrelation of the Müller functional is again obvious, overestimating  $q_w$  by a factor of 4. The rest of the functionals significantly improve as far as this quantity is concerned, with BBC3 being the most accurate, with an error of only 15%. The second best is the PNOF0 functional with an error of 17%.

We would like to close the discussion on the occupation numbers by mentioning a minor problem of the BBC3 functional. This functional introduces orbital specific corrections involving the bonding and antibonding orbitals. These corrections are repulsive, i.e., they reduce (in absolute value) the correlation energy. Consequently, the tendency in the minimization process is to lower the occupation of these states and in that way counteract the effect of the repulsive correction. In several cases, the impact of this counteraction is so strong that the occupation number of some of the antibonding orbitals gets equal to zero (pinned at zero). One remedy that we tried for this problem was to update, during the

TABLE II. Error in the correlation energies calculated with a variety of methods for the second set of calculations (G2-1 set, cc-pVDZ basis). The reference energies ( $E_c^{\text{ref}}$ ) were obtained with CCSD(T). The values in the first, second, and last columns are in a.u.

| Method | $\bar{\Delta}$ | $\Delta_{\text{max}}$                  | $\bar{\delta}$ (%) | $\delta_{\text{max}}$ (%) | $\bar{\delta}_e$ |
|--------|----------------|--|--------------------|---------------------------|------------------|
| Müller | 0.34           | 0.56 (Cl <sub>2</sub> )                | 154.7              | 438.8(Na <sub>2</sub> )   | 0.0191           |
| GU     | 0.12           | 0.28 (Cl <sub>2</sub> )                | 45.59              | 120.4(Na <sub>2</sub> )   | 0.0049           |
| CGA    | 0.16           | 0.33 (Si <sub>2</sub> )                | 89.23              | 330.9(Na <sub>2</sub> )   | 0.0085           |
| BBC1   | 0.18           | 0.36 (ClO)                             | 75.48              | 180.8(Na <sub>2</sub> )   | 0.0096           |
| BBC2   | 0.10           | 0.23 (Cl <sub>2</sub> )                | 49.10              | 144.6(Na <sub>2</sub> )   | 0.0055           |
| BBC3   | 0.043          | 0.14 (Cl <sub>2</sub> )                | 19.98              | 68.9(Na <sub>2</sub> )    | 0.0018           |
| PNOF   | 0.046          | 0.16 (Cl <sub>2</sub> )                | 18.36              | 49.5 (Cl <sub>2</sub> )   | 0.0017           |
| PNOF0  | 0.040          | 0.14 (Cl <sub>2</sub> )                | 16.84              | 44.6(Na <sub>2</sub> )    | 0.0016           |
| MP2    | 0.026          | 0.057(Si <sub>2</sub> H <sub>6</sub> ) | 14.55              | 34.1 (Li <sub>2</sub> )   | 0.0016           |
| B3LYP  | 0.51           | 1.117 (Cl <sub>2</sub> )               | 423.5              | 2642.5(Na <sub>2</sub> )  | 0.023            |

TABLE III. Total charge  $q_w$  (electrons per spin) occupying weakly occupied natural orbitals for a few representative molecules compared to the result of CCD.

| Molecule           | Müller | GU    | CGA   | BBC1  | BBC2  | BBC3  | PNOF  | PNOF0 | CCD   |
|--------------------|--------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ammonia            | 0.246  | 0.080 | 0.219 | 0.153 | 0.126 | 0.071 | 0.053 | 0.052 | 0.061 |
| Ethane             | 0.379  | 0.183 | 0.309 | 0.126 | 0.154 | 0.093 | 0.106 | 0.095 | 0.112 |
| CO <sub>2</sub>    | 0.560  | 0.276 | 0.520 | 0.329 | 0.229 | 0.149 | 0.167 | 0.154 | 0.131 |
| H <sub>2</sub> O   | 0.220  | 0.066 | 0.200 | 0.148 | 0.114 | 0.065 | 0.047 | 0.048 | 0.055 |
| Acetylene          | 0.447  | 0.183 | 0.435 | 0.239 | 0.191 | 0.108 | 0.088 | 0.087 | 0.115 |
| $\bar{\delta}$ (%) | 293    | 65    | 258   | 132   | 82    | 15    | 18    | 17    |       |

variation, the grouping of the orbitals into the four sets mentioned in the previous section. This involves a mechanism that repeatedly finds the antibonding orbitals, for example, according to their occupation. However, this process adds a nonanalytic behavior to the total energy as a function of the occupation numbers. For this reason, it was not possible to converge the calculation for several molecules, which lead us to abandon this path. Thus, the version of BBC3 functional that we used for all our calculations is the one of Eq. (11), with the grouping of the orbitals into the four different sets defined at the beginning from the HF initial guess. However, it is very common that some of the orbitals chosen as antibonding are left with zero or almost zero occupation for the optimal  $\gamma$ .

### C. Atomization energies

It is clear from Tables I and II that all 1-RDM functionals give a better account for the correlation energy than B3LYP (which strongly overcorrelates). However, for methods that are not variational, such as RDMFT or DFT, one should not fall in the temptation of using the quality of the calculated correlation energy as the only criterion to assess the performance of functionals. In fact, quantities that are total energy differences are usually much more important than the correlation energy. For this reason, we also included atomization energies in our benchmark.

TABLE IV. The average ( $\bar{\delta}$ ) and the maximum ( $\delta_{\max}$ ) errors defined in Eqs. (17c) and (17d) for the atomization energies calculated with different methods for the two sets of calculations. Reference values are the atomization energies calculated with CCSD(T) method.

|        | Set 1              |                        | Set 2              |                        |
|--------|--------------------|------------------------|--------------------|------------------------|
|        | $\bar{\delta}$ (%) | $\delta_{\max}$ (%)    | $\bar{\delta}$ (%) | $\delta_{\max}$ (%)    |
| R(O)HF | 42.4               | 195 (F <sub>2</sub> )  | 53.8               | 233 (F <sub>2</sub> )  |
| MP2    | 6.24               | 34 (Na <sub>2</sub> )  | 7.94               | 35(Na <sub>2</sub> )   |
| B3LYP  | 11.7               | 40(BeH)                | 12.1               | 38 (F <sub>2</sub> )   |
| Müller | 32.7               | 138 (Na <sub>2</sub> ) | 40.6               | 130(Na <sub>2</sub> )  |
| GU     | 43.7               | 239(ClF <sub>3</sub> ) | 50.4               | 180 (F <sub>2</sub> )  |
| CGA    | 42.5               | 116(ClF <sub>3</sub> ) | 47.4               | 115 (F <sub>2</sub> )  |
| BBC1   | 31.0               | 107(ClF <sub>3</sub> ) | 34.8               | 75 (O <sub>2</sub> )   |
| BBC2   | 26.9               | 142 (ClO)              | 40.1               | 142 (F <sub>2</sub> )  |
| BBC3   | 18.0               | 117 (Li <sub>2</sub> ) | 25.6               | 103 (Li <sub>2</sub> ) |
| PNOF0  | 17.5               | 76 (Li <sub>2</sub> )  | 23.9               | 73 (Cl <sub>2</sub> )  |
| PNOF   | 25.5               | 161(ClF <sub>3</sub> ) | 30.4               | 127 (F <sub>2</sub> )  |

For this task, we calculated the energies of the atoms with the same functionals and basis sets used for the molecules [supplementary material (Ref. 45)]. The large majority of the atoms involved are open shell systems. Like in the case of the open shell systems of the G2/97 set, we employed the open shell generalization introduced in Ref. 24. Clearly, the performance of the functionals in the calculation of the atomization energies is also affected by this choice.

Tables with atomization energies of all functionals are included in the supplementary material to this article.<sup>45</sup> The performance of all the methods is summarized in Table IV. As in the case of total energies, the latest generation functionals, i.e., BBC3 and Piris functionals, perform better compared to their predecessors. Again, in this case, PNOF0 slightly gives better results than BBC3 and PNOF. Even if the performance of the Piris and BBC3 functionals is quite satisfactory, they still do not provide the accuracy of MP2 or even B3LYP. The error of PNOF0 is 1.5 times the error of B3LYP and about three times the error of MP2. Furthermore, the BBC3 functional yields a negative atomization energy (unbound system) for Li<sub>2</sub>. This is probably due to a size-inconsistency problem of the open shell treatment. It is a question whether the sum of the total energies of the atoms consisting a molecule equals the total energy of the stretched molecule obtained by a single closed-shell calculation. Li<sub>2</sub> is an extreme case, which is also enhanced by the very small value of its atomization energy. However, more atomization energies might deviate from the exact values due to this inconsistency. It would be interesting to investigate if different open shell schemes, for example, that of Ref. 21, improve the results of RDMFT on the atomization energies.

### IV. CONCLUSIONS

We presented benchmark calculations on an extended set of molecules for a series of exchange-correlation functionals proposed within RDMFT. We assessed the accuracy of these functionals concerning both the correlation and the atomization energies.

RDMFT functionals fared quite well in the total energy test and the latest ones reproduce the correlation energies of most of the systems quite accurately. More specifically, the oldest of the approximations, the functional of Müller, substantially overcorrelates. The GU and CGA significantly improve compared to the functional of Müller. Finally, the BBC3 functional of Gritsenko *et al.*, and the functional of Piris are the most successful in correcting the error of the Müller functional. PNOF0, i.e., the Piris functional *without*



the term which prevents pinned states, performs better than all the functionals we considered, with a precision already comparable to MP2 theory.

For the atomization energies, 1-RDM functionals are also satisfactory, yielding, however, a somewhat lower accuracy than B3LYP. The best 1-RDM functional for this quantity is again PNOF0, with an average error 1.5 times larger than B3LYP. We found that the treatment of open shell atoms introduces a size inconsistency which significantly affects the accuracy of the atomization energies.

We also report a problem in the behavior of BBC3 functional which comes from the orbital-specific corrections introduced in this functional. More specifically, we observed a counteraction to the repulsive correction that leads to zero occupation for some of the antibonding orbitals. In spite of this problem, BBC3, as well as the Piris functional, was found very accurate in reproducing the total charge that occupies the weakly occupied states.

It is clear from our results that the available functionals already have enough precision to be used in many problems of theoretical material science. The hope is that RDMFT in its present status or with further functional development could give answers for problems where DFT results deviate from experiment. Furthermore, it is still a young field, and it is reasonable to expect fast advances in the construction of new functionals, with increased precision and range of applicability. However, one big problem still remains to be solved: the efficiency of the minimization of the total energy with respect to the 1-RDM. In addition, up to now, the existing RDMFT codes are research codes, relatively slow, and of limited availability. We hope that the results present in this paper will motivate developers of mainstream quantum chemistry codes to include RDMFT in their set of methods, bringing, therefore, this very promising approach to a much wider public.

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