

Ab initio dynamic correlation effects in density functional theories: a density based study for argon

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Received: 20 May 2009 / Accepted: 9 September 2009 / Published online: 4 October 2009
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Abstract In an attempt to get more insight into the links between the coverage of dynamic electron correlation effects defined in traditional wave function theories (WFT) by density functional theories (DFT) we have performed comprehensive studies for the Ar atom, for which the dynamic correlation effects play the dominant role. A density-based approach directly hinged on difference radial density (DRD) distributions defined with respect the Hartree-Fock radial density has been employed for analyzing the impact of dynamic correlation effects on the density. The DRD-distributions calculated by ab initio methods have been compared with their DFT counterparts generated for representatives of several generations of broadly used exchange-correlation functionals and for the recently developed orbital-dependent OEP2 exchange-correlation functional (Bartlett et al. in *J Chem Phys* 122:034104, 2005). For the local, generalized-gradient, and hybrid functionals it has been found that the dynamic WFT correlation effects on the density are to a significant extent accounted for by densities resulting from exchange-only calculations. It has been shown that the removal of self-interaction errors does not change this result. It has been demonstrated that the VWN5 and LYP correlation functionals do not represent any substantial dynamical correlation effects on the electron density, whereas these effects

are well represented by the orbital-dependent OEP2 correlation functional. Critical comparison of the results of the present investigations with various published results obtained for more complex many-electron systems has been made. Attention has been paid to bringing into sharper relief the differences between the conclusions reached when using energy- or density-based criteria.

Keywords Electron correlation · Radial density · Density functional theory · Ab initio densities

1 Introduction

To satisfy the hard-to-meet requirement for quantum-mechanical theories describing in a reliable way many-electron systems of increasing sizes and complexity is the central problem of both main categories of contemporary many-electron-theory methods: the traditional ab initio or wave function theory (WFT) methods, which are more or less directly grounded on the concept of the wave function, and the density functional theory (DFT) [26, 32], essentially based on the concept of electron density. WFT methods offer, in principle, better instruments of controlling the ways of increasing the accuracy of results but become prohibitively expensive for larger systems, whereas the much cheaper, most widely used DFT approaches still suffer various reliability problems primarily caused by the lack of knowledge of the exact form of the functionals for exchange and correlation.

To overcome the reliability problems of these approaches, enormous efforts have been invested in the search for possibly realistic representations of the unknown exchange and correlation functionals (to get some flavor of this important problem see, e.g., the discussion in Ref. [51]).

Dedicated to Professor Sandor Suhai on the occasion of his 65th birthday and published as part of the Suhai Festschrift Issue.

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An important role among the procedures for the design and selection of new functionals has so far been played by methods employing for their calibration accurate WFT energies or other properties (see Refs. [3, 45]). It is essential for the reliability of the outcome of these procedures that the parametrization of exchange and correlation functionals is done in such a way that the analytical formulas are adjusted to represent the WFT exchange and correlation effects in the DFT formalism. The satisfaction of this requirement is a very difficult task because these effects are distinctly defined in both theories (see, e.g., Refs. [1, 13, 38]). These difficulties become even more severe if one is interested in the separation of the non-dynamic and dynamic components of the correlation effects, which has become an unavoidable requirement towards construction of reliable exchange-correlation (XC) functionals [59]. In the present decade there is an increasing interest in investigations of the details of covering the dynamical and non-dynamical WFT correlation effects by various types of exchange and correlation functionals (for details and references, see, e.g., Refs. [7, 21]). These investigations are certainly in the spirit of the *due diligence* requirement of good science, which, according to Perdew et al. [51], demand some understanding of what the approximations involved in a given DFT approach are and how they are constructed.

An important factor which gives impetus to studies of the coverage of correlation effects defined in WFT by the exchange and correlation functionals is due to the fact that in recent years there has been an increasing interest in the search for ways of blending the expensive WFT approaches with the much cheaper DFT ones in order to efficiently exploit the advantages offered by both categories. Let us mention just a few examples of such blended WFT-DFT approaches: There have been several attempts to apply Kohn–Sham (KS) orbitals in WFT calculation, e.g., within the coupled-cluster (CC) method [20, 2]. Misquitta et al. [42] employed in WFT calculations of the dispersion energy at finite intermolecular separations frequency-dependent density susceptibilities of the monomers calculated by means of time-dependent DFT. Unfortunately, at present, little is known about the “physical reality” of ab initio correlation effects represented by the structure of KS orbitals corresponding to individual types of XC potentials, which is a prerequisite for purposeful applications of these orbitals in WFT calculations. Similarly, at present, the blended methods are still formulated at the *trial-and-error* level. Therefore, devising of effective blended WFT-DFT approaches or, at least, a purposeful carrying over of some results from one approach to the other, will require a better understanding of details concerning the coverage of the WFT dynamical and non-dynamical correlation effects by the DFT functionals.

Since the beginning of the KS-DFT, there have been many attempts at finding connections between the ways of describing electron correlation effects and electron exchange in DFT and WFT. Almost all of them have been based on comparisons of the results of calculations of various energy-related quantities (for details and many references see, e.g., Refs. [21, 30]). Until recently, little attention has been paid to studies based on the direct comparisons of electron density distributions. It might be anticipated that such an approach may provide information complementary to the findings of the energy-based approaches. These expectations are based on the fact that in WFT calculations it was found (see, e.g., [41]) that when using the language of the configuration interaction method, the impact of various types of configurations on density distributions and energy-related quantities is considerably different. The dominating effect of single excitations on correlated electron densities, closely related to the present research, is manifested by the result of van Heusden et al. [60] that the total density obtained for the single determinant constructed from approximate *Brueckner orbitals* (BO) [44], generated in Brueckner-coupled-cluster with doubles (BCCD) [23] calculations, is qualitatively similar to the response density calculated at the highly correlated BCCD level. This finding means that these approximate BOs describe the bulk of effects important for correlated densities. In this way we have a possibility of approximately probing how the WFT correlation effects modify individual orbitals defined at the “uncorrelated” HF level.

Investigations of the quality of various approximate forms of the exchange-correlation potential from the density-based perspective were pioneered by Pedroza [49] and Krijn and Feil [36]. These authors found that, unlike the energies, the response of the electron density to correlation is only qualitatively reproduced by the functionals considered. The idea that the density-based methods can, in principle, be used to develop and parametrize DFT functionals was suggested by Wang et al. [62].

In the present decade very comprehensive density-based studies aimed at understanding of the relationship between the WFT and DFT ways of describing exchange and correlation effects have been undertaken in the group of Cremer (for details see Refs. [7, 17, 25]). In their earlier papers, Cremer et al. have reported results based on comparison of molecular densities obtained for a number of exchange-only (X-only) and XC functionals with WFT densities generated by means of several methods, purposely chosen to take into account various types of correlation effects including the highly correlated fourth-order Möller-Plesset [43] as well as the coupled-cluster CCSD (see, e.g., Ref. [48]) methods. Of special interest are the results concerning the important problem of the ability of the DFT functionals to cover the dynamic and non-dynamic

correlation effects defined in WFT approaches studied for the first time in density-based investigations. Cremer et al. found that widely used DFT exchange functionals account for lower-order WFT correlation effects, including both the dynamic [53] and non-dynamic correlation effects [7, 25] whereas the correlation functionals represent the higher-order electron correlation effects that represent couplings between the lower-order ones. In several papers (see, e.g., Refs. [7, 53]) these authors have argued that the mimicking of correlation effects by the exchange functionals is to a large extent caused by the self-interaction errors associated with the XC functionals considered.

Comparison of these density-based results with the findings of alternative energy-based investigations indicate the existence of some differences. Consider, for example, the extensive studies by Handy and collaborators (for details and references see [21, 22, 45]), which were concentrated on the construction of optimal exchange functionals, e.g., the OPTX exchange functional [21], for the purpose of uniquely understanding the content of the XC and correlation functionals. The exchange functionals were modeled on closed-shell atoms, for which there is effectively no non-dynamic correlation. Unlike Cremer et al., these authors concluded that their exchange functionals include just the non-dynamic correlation effects, i.e., they should give predictions which are close to the CASSCF [54] ones, whereas the correlation functionals should include the entire dynamic correlation effects. The same point of view has been represented by Seidle et al. [55]. Mention should be made that so far nobody has succeeded in constructing an explicitly density-dependent exchange functional not covering any electron correlation effects, and, as it has been recently demonstrated by the present authors in Ref. [29] (referred to as JNGW), Handy's OPTX exchange functional includes in fact the bulk of dynamical correlation effects on the electron density.

It seems to the present authors that this discord of the conclusions reached from the energy- and density-based perspectives may be caused by the fact that both groups have been concerned with applications to many-electron systems for which dynamic and non-dynamic effects appear simultaneously in a difficult-to-control proportion. Therefore, we have revisited in the JNGW article the problem of linking the WFT and DFT descriptions of correlation effects for the ground state of the Ne atom, for which the WFT correlation effects are almost entirely dynamic [28, 45].

The main aim of the present study is to establish whether our interesting findings for the Ne atom are also valid for larger closed-shell atoms. We have chosen for our analysis the ground state of the Ar atom, which in comparison with the Ne atom, has a more complex electronic structure caused by the additional presence of the two subshells of the M shell. Although this structure is simpler

than for molecules, we already have to deal with regions of significant density differences. For the Ar atom one would expect that the non-dynamic correlation effects are slightly larger than for Ne. Although the correlation effects of the Ar atom are almost entirely dynamic, the structure of these effects is by no means trivial because we do not have to deal exclusively with radial correlation effects, as stated sometimes in the literature (see, e.g., Ref. [12]), but also with angular correlation. For this atom one can take advantage of the fact that, since we consider an S state, we do not face the angular symmetry problems arising for states with $L > 0$ recently studied by Fertig and Kohn [11]. Moreover, due to the spherical symmetry, comparison of density distributions can be made just in one dimension, which is by far simpler than for molecules.

Like in JNGW, the present studies of the impact of electron correlation effects on the electron density are based on an analysis of graphical representations of difference radial-density (DRD) distributions defined with respect to the Hartree-Fock (HF) radial density. Such a graphical representation provides a global impression of the electron correlation effects that is more informative than the analysis of a set of values of molecular properties, e.g., energies, density moments, etc. We compare DRD distributions for DFT approaches representing all types of broadly used exchange and correlation functionals generated at the X-only and XC functional levels with WFT density distributions calculated by means of several WFT approaches. Our studies have also included the recently developed orbital-dependent DFT functionals [15, 16, 27]. Since the effect of electron correlation on WFT electron densities is sometimes considered to be less important than the incomplete-basis-set effect (see Ref. [8]), we have paid special attention to the choice of adequate basis sets. We have also discussed the impact of the self interaction error (SIE) on our results. To visualize the differences between the conclusions reached when using energy- or density-based criteria, we find it convenient to use the DRD distributions obtained for the B88 and OPTX exchange functionals.

2 Methodological and computational details

2.1 Difference radial-density (DRD) distributions

Taking advantage of the spherical symmetry of closed-shell atoms, we shall employ the radial charge densities defined as

$$D^A(r) = 4\pi r^2 \rho^A(r), \quad (1)$$

where $\rho^A(r)$ denotes the electron density at the distance r from the nucleus calculated by means of the method A. The $D^A(r)$ functions have been frequently used in atomic

shell structure studies (for references, see, e.g., Refs. [33, 40]).

Since the differences between the curves of the individual total radial densities are barely distinguishable, we follow the practice (see, e.g., Refs. [7, 25, 29]) of using in comparative studies of both WFT and DFT results the *difference radial-density (DRD) distributions* defined with respect to the HF radial-density distribution,

$$d^A(r) = D^A(r) - D^{\text{HF}}(r), \quad (2)$$

This choice of the reference density turns out to be convenient for several reasons. First, for more-than-four electron atoms there is still no access to “almost exact” ab initio WFT densities which have been used as references for two- or even four-electron systems. Moreover, the basis sets used in our studies yield high quality HF as well as post-HF and DFT densities. Second, in WFT, the electron correlation effects on the density are defined with respect to the HF density, which alleviates the discussion of the links with the DFT counterparts of these effects.

To study the impact of the correlation effects represented by the correlation functional C on a radial density distribution we define the response radial distributions $\delta^{C/X}(r)$ as the difference of DRD distributions calculated for an XC functional, X^C , $d^{X^C}(r)$, including the correlation functional C , and for the corresponding X-only functional $d^X(r)$, i.e.,

$$\delta^{C/X}(r) = d^{X^C}(r) - d^X(r). \quad (3)$$

For better relating the calculated correlation effects on the density with details of the electronic structure of Ar, the total HF radial charge density distribution $D^{\text{HF}}(r)$ calculated for the uncontracted ROOS-ATZP basis [64] is given in Fig. 1. This density distribution provides reference values for all the DRD distributions discussed in this article. The $D^{\text{HF}}(r)$ curve is additionally decomposed into the contributions of the K-, L- and M-shells. The maxima of the K, L, and M shell radial densities (denoted as A, C, and E) are at $r = 0.059$ a.u., $r = 0.293$, and $r = 1.238$, respectively, whereas the positions of the minima (denoted as B and D) are at $r = 0.141$ a.u. and $r = 0.795$ a.u., respectively. Although there is no generally accepted method of partitioning of the charge density into shell contributions (for details on the problem and references see, e.g., Ref. [56]) the maxima and minima of the $D^{\text{HF}}(r)$ are useful in defining reasonable shell and intershell regions and, in providing a partitioning into core and valence regions. We have tentatively partitioned the K and L shells by the KL intershell region ranging from $r = 0.1$ a.u. to $r = 0.225$ a.u. and the L and M shells by the LM intershell region ranging from $r = 0.55$ a.u. to $r = 1.04$ a.u.

Within the core- and valence-shell regions, the values of the DRD distributions are very small in comparison with the values of the total HF radial charge densities. This fact has

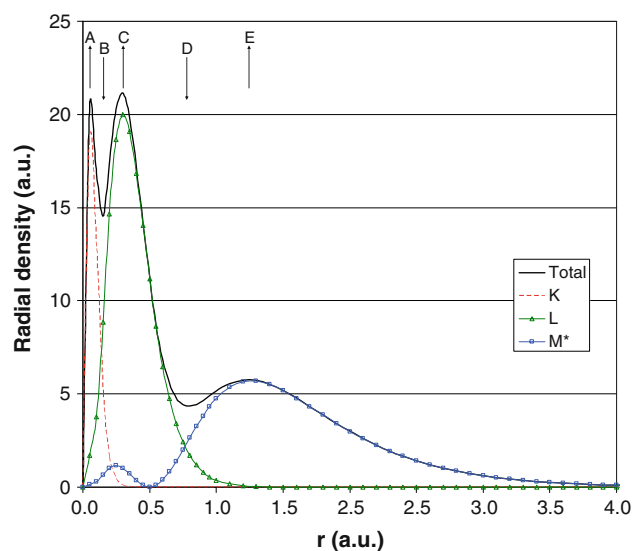


Fig. 1 Radial charge density distribution $D^{\text{HF}}(r)$ for Ar, calculated for the HF determinant. The arrows indicate: A, C, and E—the maxima of the K-, L-, and M-shell densities, respectively; B and D—the intershell densities

given rise to opinions that the correlation effects on the electron density in atoms are of smaller importance as compared to the effect associated to basis set extension (see, e.g., Ref. [8]). Therefore, to assess the reliability of our results, we have carefully studied the dependence of the shape of calculated DRD profiles on the structure of the Gaussian basis sets. We have performed test calculations for the WFT methods and for all but the OEP2-f DFT approaches using the following bases: the Dunning’s [9] correlation-consistent basis sets cc-pVxZ and aug-cc-pVxZ ($x = \text{D, T, Q, and } 5$), and the ROOS-ATZP basis set [64] consisting of 95 Gaussian primitives. Details of these studies are presented in Ref. [46]. For the DFT densities we have found that a reasonable representation of the correlation effects on the electron distribution can be obtained for all, but the smallest, basis sets considered. In particular, the DRD distributions for the most extensive basis sets considered differ little from the distribution for the uncontracted ROOS-ATZP basis. Since for the OEP procedure [2] to correctly represent the OEP potential we need uncontracted basis sets, to preserve uniformity at the basis set level, all DFT densities discussed in this paper are calculated for the uncontracted ROOS-ATZP basis set. For the WFT densities the differences between curves obtained for the largest basis sets and the ROOS-ATZP one are non-negligible. Therefore, we use for comparison with the DFT results the curves obtained for the most extensive basis set. Our present studies for Ar have confirmed the finding of JNGW that the basis-set-effect on the density is very similar for the LDA, GGA, and hybrid functionals, which is in discord with the conclusion of Ref. [63] that this effect is stronger for the LDA than for the GGA functionals.

All calculations, except those corresponding to the orbital-dependent functionals, have been based on the Gaussian 03 system of programs [14]. In the orbital-dependent case, the ACES II suite of programs [57] has been used.

2.2 DFT functionals studied

Our investigations of the description of correlation effects in the Ar atom are based on the DRD distributions generated for a number of widely used exchange and correlation functionals. We shall present typical examples for each of the four classes of functionals. Whenever possible, the acronyms are identical with those employed in Gaussian03 [14]. At the X-only level of computations, our presentation includes the following functionals: (a) for the LDA class—the Dirac-Slater functional (S); (b) for the GGA class we have considered two functionals: (1) Becke’s original exchange functional, B88X, consisting of the Dirac-Slater functional and Becke’s gradient correction [3] and (2) the *optimized exchange potential* OPTX functional of Handy and Cohen [4]; (c) for the hybrid functionals—the functional obtained from the B3LYP functional [4] by omitting the correlation term (referred to as B3ex); (d) for the orbital dependent class [10, 34, 37]—the optimized effective potential (OEP) for exchange first considered within the framework of WFT, where it was designed to closely simulate the HF exchange potential, [58] (referred to as OEPX). In the XC case, we present the DRD distribution curves for the following functionals: (a) for the LDA class—the SVWN5 functional consisting of the S functional plus the Vosko, Wilk and Nusair (VWN5) correlation functional [61]; (b) for the GGA class—we consider two functionals: (1) the BLYP functional consisting of the B88X exchange functional plus the Lee-Yang-Parr (LYP) correlation functional [39] and (2) the OLYP functional constructed from the OPTX functional plus the LYP functional; (c) for the hybrid functional class—the complete B3LYP, i.e., B3ex plus the correlation part; (d) for the orbital dependent class—the OEP2-f functional developed by Bartlett et al. [2], where the orbital-dependent correlation functional, OEPC, takes the form of the second-order Many-Body-Perturbation-Theory (MBPT-2) energy.

The reason why we present the results for two GGA type exchange functionals, B88X and OPTX, is to bring into sharper relief the differences between the energy- and density-based perspectives of studying the coverage of correlation effects in DFT approaches.

2.3 Impact of electron correlation on WFT densities

To show the effect of various WFT methods of accounting for electron correlation effects, we have generated the

response density distributions for the following methods: MP2, MP4(SDQ) (MP4 without contributions from triply-excited configurations), and CCSD. The corresponding DRD distributions for MP2 and CCSD are displayed in Fig. 2, but without MP4(SDQ) plot which is almost identical with CCSD one. Our DRD distribution curve for the CCSD method is very similar to the MR-SDCI curve obtained by Mayer [40]. We also display the distribution for the approximate Brueckner determinant (BD).

From Fig. 2 one can also see that the strongest impact of the correlation effect on the density is observed for the MP2 method, which introduces electron pair correlation effects for individual electron pairs. When proceeding to CCSD method, which includes both orbital relaxation and infinite pair correlation effects, we observe a decrease of the correlation effects on the density which is considerably smaller than that found in JNGW for Ne. The above-mentioned closeness of the CCSD and MP4(SDQ) densities has also been found for Ne but has not been observed

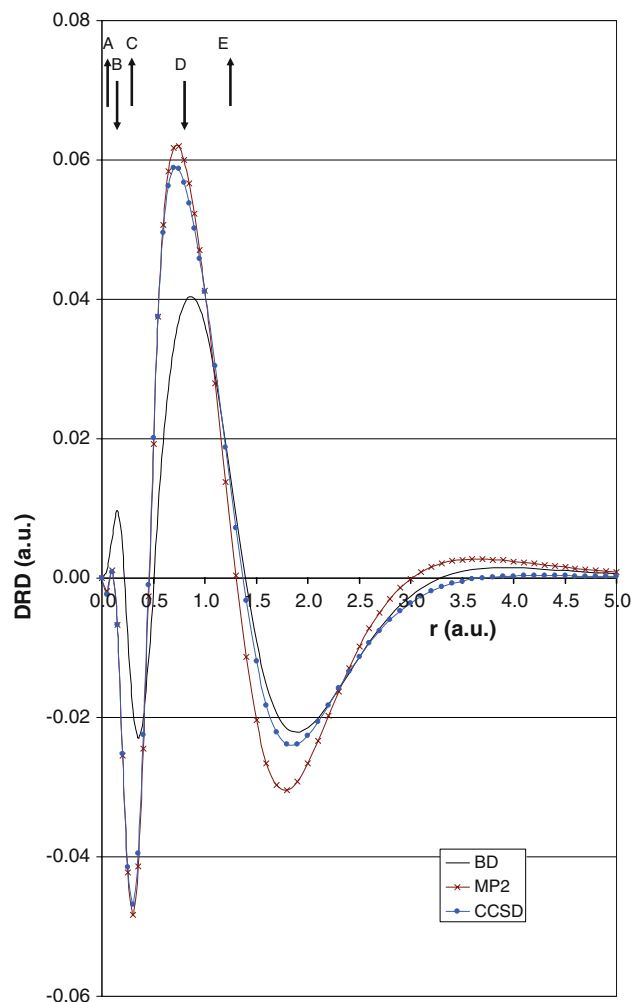


Fig. 2 Difference radial density (*DRD*) distributions $d^A(r)$ for Ar generated by means of WFT methods. *Arrows* defined in Fig. 1

by He et al. [25]. Let us note that the DRD distribution for the approximate BD given in this figure reflects all essential features of the CCSD curve, although the associated charge shifts are less pronounced. This behavior provides support to the previously mentioned finding of van Heusden et al. [60].

An interesting feature of the DRD distribution curves for the WFT methods considered is that the largest charge shift takes place from the outer-valence-shell region to the intershell LM region. A much smaller shift is observed from the region of maximum L-shell density to the intershell KL region. The depletion of density in the neighborhood of the M-shell maximum entails a very small decrease of the atomic size. Let us mention that in JNGW we have observed for the Ne atom that the dominant charge shift takes also place from the outer-valence region. But in that case the charge is shifted towards larger r -values which causes a small increase of the atomic size. The present results do not confirm the findings of de Proft and Geerlings [8] that introducing electron correlation leads to an increase in the number of electrons in the core region. In the light of Fig. 2, we would rather attribute this increase to the inter-shell LM region.

Comparison of the magnitudes of the electron density shifts for Ar and Ne shows that these shifts are smaller for the former atom, e.g., for the CCSD method, one obtains from Table I of JNGW for Ne the total shift of 0.045 a.u., whereas in this work for Ar we have found the value of 0.034 a.u. Hence, we have obtained a somewhat unexpected result that for two closed shell atoms of similar structure of the correlation effects the impact of electron correlation on the density decreases with the increase of the number of electrons.

3 Results and discussion

In this section we would like to discuss the structure of the DRD distributions for the DFT functionals listed in Sect. 2.2 with special emphasis on their ability to reflect the dynamic correlation effects of the WFT methods.

3.1 DRD distributions for exchange-only functionals

The total DRD distributions, defined by Eq. 2, generated for the X-only functionals presented in Sect. 2.2 are presented in Fig. 3. To show how these functionals mimic the dynamic correlation effects defined within WFT, we also include the $d^{\text{MP2}}(r)$ and $d^{\text{CCSD}}(r)$ curves.

Notice that the $d^{\text{OEPX}}(r)$ curve has a shape completely different from all the remaining ones, which is a consequence of the fact that for Ar the OEPX functional closely simulates the HF exchange. The small oscillations

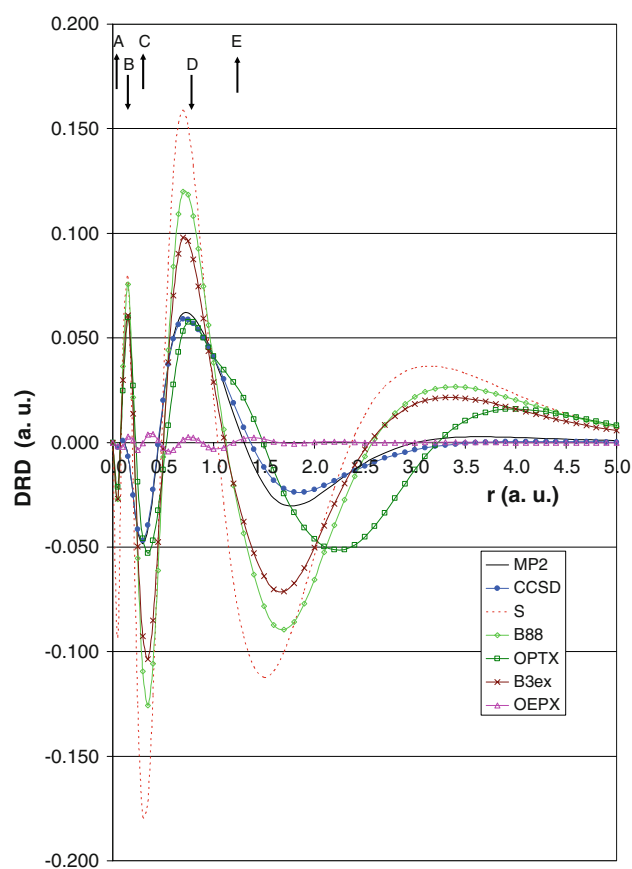


Fig. 3 Difference radial density (*DRD*) distributions for Ar generated for X-only functionals: $d^{\text{S}}(r)$, $d^{\text{B88}}(r)$, $d^{\text{OPTX}}(r)$, $d^{\text{B3ex}}(r)$, and $d^{\text{OEPX}}(r)$. The WFT distributions $d^{\text{MP2}}(r)$ and $d^{\text{CCSD}}(r)$ are also given. Arrows defined in Fig. 1

observed for this curve for $r < 2.0$ are results of some numerical instabilities and do not represent any physical effects.

Concentrating on collating the remaining DFT curves, one can see that although they differ significantly among themselves, they disclose the common feature of defining charge shifts (relative the HF charge distribution) from similar regions of the atom. This similarity is especially visible for the S, B88, and B3ex functionals for which the main charge shift takes place from the outer-valence shell both to the intershell LM region and to the farther-out region. A minor charge shift takes also place from the L-shell region to the intershell regions KL and LM. One can see from Fig. 3. that the regions of charge depletions associated with these three exchange functionals are almost identical with such regions found for the correlated WFT densities. The situation is different for the OPTX functional, for which the main region of depletion is significantly shifted towards larger r -values.

Although the regions of charge depletion are similar for the WFT-correlated densities and the densities generated

for the four X-only functionals, the magnitudes of the charge shifted are considerably larger in the DFT case, which is evident from Fig. 3 where the WFT curves are always located “inside” of the DFT ones in such a way that the MP2 curve runs closer to the DFT curves than the CCSD one. A common feature of the DRD curves for the four functionals considered is the shift of a relatively large portion of charge to the large- r region which does not take place in the WFT case. The disagreement between the MP2 and DFT curves is most pronounced for the $d^S(r)$ curve. A relatively large difference with the WFT densities is also found in all regions of the atom for the B88 functional. In turn, the DRD distribution obtained for the OPTX functional differs considerably both from the WFT and B88 curves. The latter dissimilarity is rather unexpected, because both the OPTX and B88 functionals were designed to represent accurate exchange functionals and were carefully parametrized for atomic systems by means of energy-based criteria. Indeed, from the results in Table 1 of Ref. [21] we can evaluate the DFT exchange energies for the B88 and OPTX functionals to amount to -29.4125 a.u. and -29.4146 a.u., respectively, i.e., their difference amounts just to 0.007% of the value directly calculated from the HF and Hartree energies which is equal to -29.4304 a.u. Hence, we have shown that exchange functionals which are very close in terms of energy-based criteria differ considerably if density-based criteria are applied. An identical situation has been found in JNGW for the Ne atom. These results provide a demonstration of the different perspectives of density- and energy-based criteria.

The present density-based results indicate that the LDA, GGA, and hybrid exchange functionals considered represent not only the exchange effects but also give rise to correlation effects on the density resembling those caused in WFT by accounting for dynamic correlation effects. The latter effects are even more pronounced than the correlation effects found in WFT. Hence, we have to deal with simulating of dynamic correlation effects by functionals designed to represent the exchange energy. Let us notice that the present findings resemble to a large extent the results found in density-based studies for the Ne atom reported in JNGW. The tendency of widely used exchange functionals to emulate the role attributed in WFT to electron correlation effects has been observed for a relatively long time in various atomic and molecular calculations, first for energy-type results (for an early example see, e.g., Ref. [24]) and quite recently for density distributions [7, 25]. Among the attempts to explain this additional role of the widely used exchange functionals prevail arguments (see, e.g., Refs. [7, 17, 53]) relating the mimicking of correlation effects to the self-interaction errors resulting from the incomplete cancellation of the unphysical self-interactions contained in these functionals (for details and

references see, e.g., Refs. [5, 18, 52]). This conviction would have serious consequences because it means that a controlled way of description of correlation effects in DFT approaches would require eliminating the SIE from the XC functionals, i.e., proceeding to self-interaction corrected (SIC) functionals.

The electron interaction effects caused by exchange-SIE can be visualized by comparing the density distribution curves obtained in SIC-exchange-only and ordinary X-only calculations. We have made such comparison for the S and SIC-S functionals. The latter functional has been obtained by an approach based on the Perdew and Zunger [52] method of removing the SIE contained in the exchange functionals implemented with the OEP method [58] employing the Krieger–Li–Iafrate approximation [34, 35]. The calculations have been performed by means of the NWChem 5.1 system of programs [6] using the version *sic.oep* in which the OEP is built in each step of the self-consistent process. The plot of the DRD distribution generated for the SIC-S is displayed in Fig. 4 together with the plots for the original S functional and the charge distributions for the correlated WFT densities. A comparison of the density plot for the S functional with the plot for the SIC-S one indicates that the latter plot resembles only slightly more the WFT plots than the former one. It should be mentioned that a similar result has been reported in JNGW for the Ne atom. Hence, the SIC version of the exchange functional is still mimicking of correlation effects and our results do not provide arguments in support of the widespread opinion that the simulation of correlation effects by exchange functionals is a result of SIE.

3.2 Results for exchange-correlation functionals

In Fig. 5 we compare the DRD distributions calculated for all XC functionals presented in Sect. 2.2 together with their

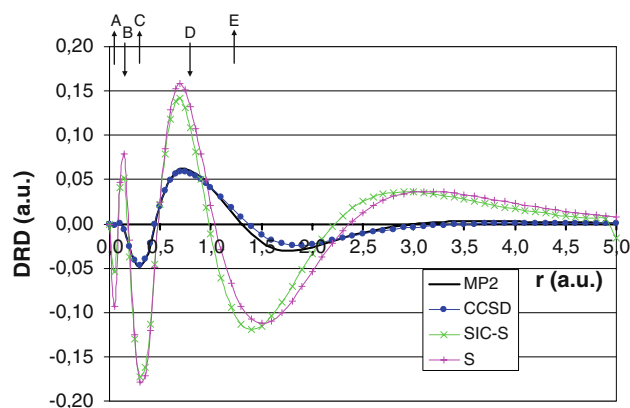


Fig. 4 Difference radial density (*DRD*) distributions for Ar generated for the SIC-S and S functionals. The WFT distributions $d^{\text{MP2}}(r)$ and $d^{\text{CCSD}}(r)$ are also given. Arrows defined in Fig. 1

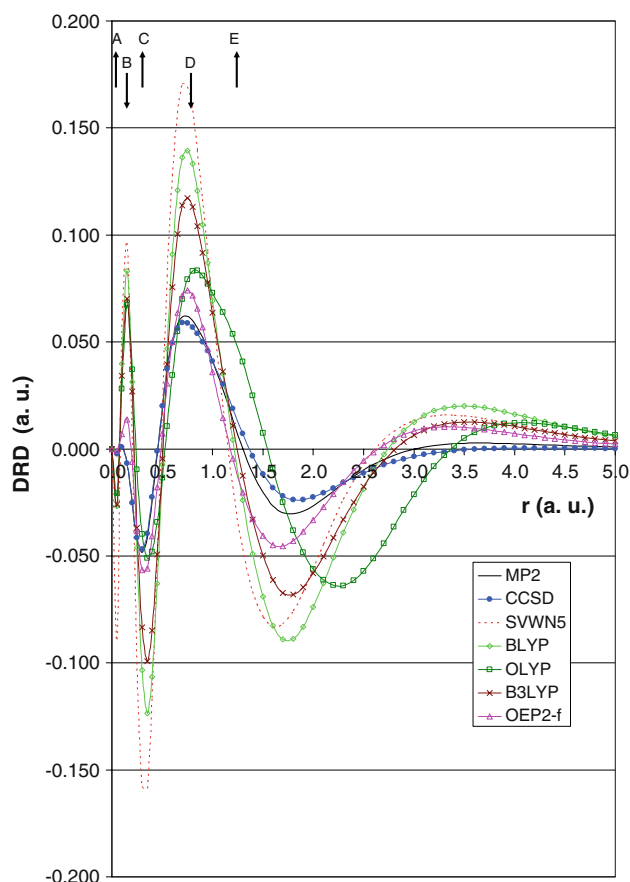


Fig. 5 Difference radial density (*DRD*) distributions for Ar generated for XC functionals: $d^{\text{SVWN5}}(r)$, $d^{\text{BLYP}}(r)$, $d^{\text{OLYP}}(r)$, $d^{\text{B3LYP}}(r)$, and $d^{\text{OEP2-f}}(r)$. The WFT distributions $d^{\text{MP2}}(r)$ and $d^{\text{CCSD}}(r)$ are also given. Arrows defined in Fig. 1

WFT counterparts generated for the MP2 and CCSD methods. As expected, the strongest effect of supplementing the X functional by the correlation one can be observed for the OEP2-f orbital-dependent functional. As one can see in the figure, for this functional the DRD distribution curve shows the strongest similarity with the WFT curves. For the SVWN5, BLYP, OLYP, and B3LYP functionals, we can notice that, despite the inclusion of the correlation effects by means of the correlation functionals, the DFT curves still resemble very much the curves obtained within the X-only approach and exhibited in Fig. 3. One can see that we have to deal with almost the same charge-shift characteristic, and again, except for the OLYP functional, the WFT curves are situated “inside” all DFT curves. We can also see that the DFT curves are closer to the MP2 curve than to the CCSD one. This result is in discord with the conclusions of He et al. [25] that DFT results cover correlation effects only covered by CC methods, and therefore comparison with MP2 methods is unjustified. Consequently, we cannot confirm the opinion presented in Ref. [7] that the special composition of the B3LYP

functional guarantees that both higher-order pair-pair coupling effects are mimicked.

As may be seen in Fig. 5., some small differences between the XC and X-only DRD distributions appear in the magnitudes of the charge displaced from the outer-valence shell region, which is slightly smaller for the BLYP and B3LYP functionals and significantly smaller for the SVWN5 functional than for the B88, B3ex, and S functionals, respectively. As a result, the charge shifts are almost identical for the SVWN5 and BLYP functionals. It is also apparent from this figure that all WFT density distributions are quite different from the BLYP one. Hence, we cannot confirm the conclusions of Cremer et al. [7] that the BLYP functional generates a density distribution similar to that of MP2 but different from that of CCSD.

The present results clearly indicate that the densities obtained for the representatives of the broadly used local, gradient-corrected, and hybrid exchange functionals account for the bulk of WFT dynamical correlation effects and that adding of the correlation functionals has a rather small effect.

3.3 On the role of correlation functionals

To better understand the role of the correlation functionals in covering the WFT dynamic correlation effects, we have examined the plots for $\delta^{C/X}(r)$, defined by Eq. 3, representing response of the DRD distributions obtained in several X-only calculations, comprising also those for the nonlocal *exact exchange* functional— X_{exact} , to taking into account the widely used VWN5 and LYP correlation functionals. One can see in Fig. 6 that the plots for $\delta^{\text{VWN5}/X_{\text{exact}}}(r)$ and $\delta^{\text{VWN5}/S}(r)$ representing the response of the DRD distributions for the exchange functionals X_{exact}

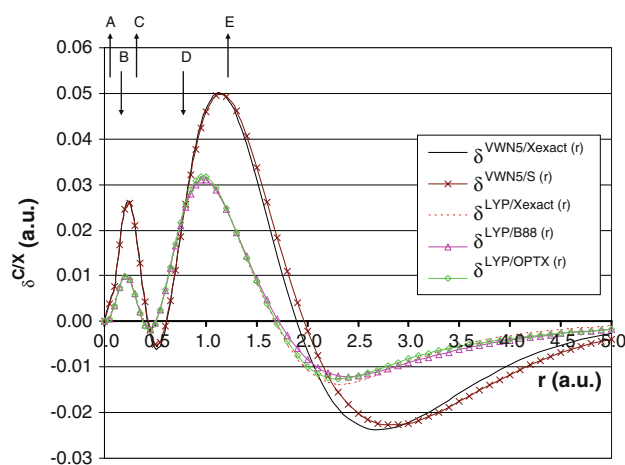


Fig. 6 Impact— $\delta^{C/X}(r)$ (defined by Eq. 3)—of the correlation functionals C (=VWN5, LYP) on the DRD distributions for X-only calculations, where X = X_{exact} , S, B88, OPTX. Arrows defined in Fig. 1

and S to the adding of the VWN5 functional are very similar. A remarkable similarity is also disclosed for the curves: $\delta^{\text{LYP}/X_{\text{exact}}}(r)$, $\delta^{\text{LYP}/\text{B88}}(r)$, and $\delta^{\text{LYP}/\text{OPTX}}(r)$ representing the response to the taking into account of the LYP functional. One can see from Fig. 6. that the response to the VWN5 functional is considerably stronger than to the LYP functional.

Hence, for both the LDA and GGA correlation functionals we have to deal with a very weak dependence of the response of density distribution on the form of the exchange functional used. This finding agrees with the observation made by Krijn and Feil [36] in studies of some predecessors of the presently used exchange and correlation functionals. The weakness of the impact of the exchange functional on the response to the correlation functional might also be helpful in rationalizing the observation of Ortiz-Henarejos and San-Fabian [47], that unlike the one- and two-electron energy contributions, the correlation energies calculated from the LYP functional for various densities were almost insensitive to the structure of these densities.

The very weak dependence of the density response to the inclusion of the correlation functionals on the type of functionals used at the X-only level gives rise to some difficulties with the understanding of the role played by the former functionals in the description of electron correlation effects. Consider for example the impact of the LYP (or the VWN5) functional on the densities obtained for the X_{exact} (i.e., the HF functional) and for the B88 (or the S) functional. In the first case, the LYP (or the VWN5) functional has to represent the entire WFT dynamic correlation effects because the X_{exact} functional does not include such effects. In turn, in the second case, the LYP (or the VWN5) functional should stand just for the small part of the WFT correlation effects not described by the B88 (or S) functional. These different roles of the LYP (or VWN5) functional with its almost identical impact on the X_{exact} and B88 (or S) density distributions can only be reconciled if one assumes that the LYP and VWN5 correlation functionals do not represent any considerable dynamic correlation effects. This assumption disagrees with the opinion of several researchers who argue that widely used correlation functionals represents dynamic correlation effects, see, e.g., Refs. [19, 21, 55]. Notice that the quasi-independence of the density response to the inclusion of correlation functionals on the form of the exchange functionals used at the X-only level contradicts the quite common opinion that the role of the correlation functionals consists in some compensation of errors caused by the form of the exchange functionals (see, e.g., Ref. [31]).

Pursuing our attempts to understand the role of the correlation functionals in representing WFT dynamic correlation effects, we compare in Fig. 7 the response curves

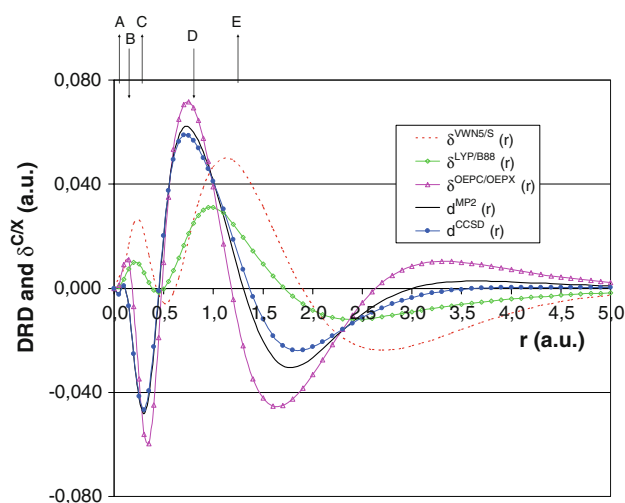


Fig. 7 Comparison of difference radial density (DRD) distributions, $d^{\text{MP2}}(r)$ and $d^{\text{CCSD}}(r)$ with the impact $\delta^{C/X}(r)$ of the correlation functionals C (=VWN5, LYP, OEPC) on the DRD distributions for the exchange functionals x (=S, B88, and OEPC). Arrows defined in Fig. 1

for $\delta^{\text{SVWN5}/S}(r)$, $\delta^{\text{LYP}/\text{B88}}(r)$, and $\delta^{\text{OEPC}/\text{OEPC}}(r)$, representing the impact of inclusion of the correlation functionals on the density distributions obtained at the X-only level, with the curves $d^{\text{MP2}}(r)$ and $d^{\text{CCSD}}(r)$ representing WFT correlation effects. One can see in this figure that the plot obtained for the orbital-dependent OEPC correlation functional fairly well resembles the MP2 and CCSD distributions, which is a consequence of the fact that correlation effects are not mimicked in X-only calculations defined by the OEPC functional. A completely different situation takes place in Fig. 7 for the curves corresponding to the VWN5 and the LYP correlation functionals, where the $\delta^{\text{LYP}/\text{B88}}(r)$ and $\delta^{\text{SVWN5}/S}(r)$ plots do not show any similarity with the $d^{\text{MP2}}(r)$ and $d^{\text{CCSD}}(r)$ ones. This disagreement may also be explained by the fact that the LYP and VWN5 correlation functionals do not represent any considerable dynamic correlation effects.

Let us also mention, that, as one can see from Fig. 7, the inclusion of the VWN5 and LYP functionals leads to a lower density in the outer-valence region and to an enhanced density in the inter-shell LM region, which is not in line with the findings by Cremer et al. [7, 25] who ascribed this enhancement to the core region.

Summarizing this section, the quasi-independence of the density response to the correlation functional on the form of the functional used at the X-only level as well as the strong disagreement of the density response to the inclusion of correlation functionals with the density changes caused by WFT methods of description of correlation effects leads us to the conclusion that the VWN5 or LYP correlation functionals do not represent any substantial dynamical correlation effects on the electron density. Since

LYP is by construction free of self-correlation (see, e.g., [7, 39, 50]), the findings of this subsection cannot be considered as a result of self-interaction errors. It should be emphasized that the results given here for the Ar atom confirm our previous results reported in JNGW for the Ne atom.

4 Concluding remarks

We have performed systematic studies concentrated on the problem of linking the dynamic electron correlation effects defined by traditional WFT with the structure of popular exchange-correlation (XC) functionals as well as the recently developed orbital-dependent OEP2-f functional [2]. We have concentrated our attention on the still open problem of representing the dynamic correlation effects by the exchange-correlation functionals. This work is a continuation of the first systematic studies of this problem recently completed [29] (referred to as JNGW) for the ground state of the Ne atom, which is the simplest non-trivial (larger than two to four electron) model for studying dynamic correlation. Now we have chosen for our investigations the Ar atom, for which the non-dynamic correlation effects play still a marginal role. The more complex electronic structure of Ar provides a demanding testing ground for the findings of our Ne studies. Like in these studies, special attention is paid to the avoiding of errors caused by the structure of primitive basis sets used in the calculations. The correlation effects accounted for by various DFT functionals have been graphically investigated by comparing the *difference radial densities* (DRD) with those calculated by means of WFT methods that cover the well-defined correlation effects. As a result, a global characteristics of the electron correlation effects are obtained that seem to be more informative than results of analyzing single values of selected atomic properties.

We have confirmed the finding of JNGW that (a) although the impact of correlation effects on the electron density is relatively weak, the DRD distribution curves provide a reliable description of the impact of these effects both at the WFT and DFT levels, and (b) the shapes of these curves are very sensitive to the form of the functionals considered, which causes that the DRD curves provide clearly distinct characteristics for functionals that are very close according to energy-based criteria. When comparing the global impact of the correlation effects on the DRD distributions for Ne and Ar, we have found that this impact is stronger for the former system.

We have found for the Ar atom that at the exchange-only (X-only) level of DFT the DRD distribution curves generated for the LDA, GGA, and hybrid functionals disclose a general resemblance to the correlated WFT curves,

which provides another clear demonstration of the fact that the widely used exchange functionals, in addition to their nominal role, represent dynamic correlation effects. We have also shown that the removal of self-interaction errors does not eliminate the representation of correlation effects by exchange functionals. The present investigations of the response of the DRD distribution curves obtained in X-only calculations to the inclusion of the VWN5 and LYP correlation functionals have confirmed the conclusions from JNGW that these correlation functionals do not represent any substantial dynamic correlation effects on the electron density, whereas the correlation functional defined in the OEP2-f orbital dependent approach represents in a reliable way the WFT correlation effects.

In various sections of this article we have compared our results with their counterparts reported in the literature, which should be helpful for developing methods of studying the links between the WFT and DFT coverage of the correlation effects for more complex systems. The present study affords further examples of the different perspectives of energy- and density-based approaches to the electron correlation problem, which strengthens our opinion about the usefulness of density-based criteria in reliability studies of new functionals.

Although, so far, we have been concerned with the Ne and Ar atoms, we are convinced that some of our results concerning the links between the WFT and DFT methods of description of dynamic correlation effects will be useful in the difficult endeavor of searching for new broadly applicable functionals. In particular, we believe that our demonstration of the reliability and usefulness of the DRD distribution curves will encourage their use as a complement to the energy-based criteria. Of special methodological importance should be the search for exchange functionals that provide simultaneously reasonable approximations to the exchange energies and the HF electron densities. For such endeavors we would like to recommend that Ne and Ar atoms be employed as essential testing systems.

Acknowledgments Dedicated to Professor Sandor Suhai on the occasion of his 65th birthday and published as part of the Suhai Festschrift issue. This work has been supported during the years 2006–2009 by the Polish Ministry of Higher Education as the research projects No. N204 126 31/2930 and NN204 074 633. We also thank Andrew Teale for the generation of accurate CCSD electron densities.

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