Ab initio CORRELATION EFFECTS IN DENSITY FUNCTIONAL THEORIES: AN ELECTRON-DISTRIBUTION-BASED STUDY FOR NEON

Karol JANKOWSKI[a1,*], Ireneusz GRABOWSKI[a2], Krzysztof NOWAKOWSKI[a3] and Jan WASILEWSKI[b]

[a] *Institute of Physics, Nicolaus Copernicus University, 87-100 Toruń, Poland;*
e-mail: [1] karoljan@phys.uni.torun.pl, [2] ig@phys.uni.torun.pl, [3] binio@phys.uni.torun.pl
[b] *Department of Informatics, Nicolaus Copernicus University, 87-100 Toruń, Poland;*
e-mail: janwas@phys.uni.torun.pl

Received March 22, 2005
Accepted May 17, 2005

This work is dedicated to Professor Josef Paldus on the occasion of his 70th birthday, with our best wishes of many more years of excellent creativity so inspiring for the whole quantum chemical community.

We have briefly reviewed the idea of studies aiming at such a bridging of the methodological gap between *ab initio* methods (or wave function theory (WFT)) and density functional theory (DFT) that would afford carrying over results concerning details of the structure of correlation effects from one method to the other. Special attention is paid to the problem of coverage of the WFT correlation effects by the exchange-correlation functionals of DFT. A short survey of the concept of supplementing energy-based investigations in this field by electron-density-based studies is given and illustrated by results for the Ne atom. DFT densities are generated for representatives of all four generations of presently used exchange-correlation functionals, including the recently developed orbital-dependent one. These densities are compared with WFT densities calculated at the MP2, MP3, and Brueckner determinant levels. It is found that the exchange-only parts of the local, gradient-corrected, and hybrid functionals account for the bulk of WFT correlation effects. The impact of the associated correlation functionals is very small and their physical nature is not quite clear. The situation is different for the orbital-dependent functional for which the exchange-only functional provides an almost exact description of the Hartree–Fock density. Here, the correlation effects are entirely represented by the correlation functional. Attention is also paid to the suitability of Kohn–Sham orbitals for the description of WFT correlation effects and to their presumptive similarity with Brueckner orbitals.

Keywords: Electron correlation; *Ab initio* methods; DFT methods; Electron density distribution; Radial electron density; Brueckner coupled-cluster method; Brueckner orbitals; Kohn–Sham orbitals; Exchange-correlation functionals; Exchange-only functionals; Subspace similarity indices.

doi:10.1135/cccc20051157

During the last decade, the experts in both the main categories of contemporary many-electron theory – the *wave function theory* (WFT), based on the concept of the wave function, and the *density functional theory*[1–3] (DFT), based on the concept of electron density distribution have demonstrated an increasing tendency to join their efforts in overcoming problems related to the proper description of electron correlation effects. In WFT the problem consists in the lack of accurate post-Hartree–Fock methods that could be efficiently applied to larger systems, whereas in DFT, the difficulties arise from the lack of knowledge of the functionals correctly accounting for the effects of electron interaction on the electron distribution.

Further progress in many-electron theory would require intensification of the WFT-DFT collaboration both on the fundamental level, involving further studies on the mathematical and physical foundations of both methods, and on the practical (computational) level consisting in using methods of either of the two categories to improve the computational efficiency and/or reliability of the methods.

Among the well known examples of WFT-DFT collaboration on the computational level let us just mention: (i) Using accurate *ab initio* WFT energies, densities and other molecular properties in reliability studies (see, e.g., refs[4–6]) and for calibration of approximate density functionals (see refs[7,8]); (ii) Development of “third-generation-DFT” approaches[9–12] (“orbital dependent DFT”, “*ab initio* DFT”). The basic idea of this approach is to take an exchange-correlation energy expression derived in the *ab initio* WFT and use it as an explicitly orbital-dependent exchange correlation functional (xc-functional) in DFT. This universal and parameter-free methodology allows one to directly exploit knowledge from WFT and systematically improve xc-potentials in the Kohn–Sham (KS) DFT scheme. Moreover, the functionals obtained are free of self-interaction; (iii) Studies of the usefulness of Kohn–Sham orbitals (KSOs) for improving the performance of standard WFT methods in calculations of correlation energies. The outcome of these investigations is not unique. In addition to rather pessimistic opinions on the usefulness of KSOs (see, e.g., refs[13,14]), there are also several optimistic ones (see, e.g., refs[15,16]).

An interesting conjecture that KSOs may be close to Brueckner orbitals (BOs), which are well approximated by Brueckner coupled-cluster (BCC) orbitals[17–19], has been made by Heßelmann and Jansen in their article on intermolecular first-order interaction energies[20]. Inspired by this idea, Lindgren and Salomonson[21] have set up a new model referred to as the Brueckner–Kohn–Sham (BKS) scheme in which the electron correlation effects are accounted for by means of a *nonlocal* exchange correlation potential similar to that defining the BCC orbitals. These authors have argued that also the DFT orbitals from standard KS schemes are close to Brueckner orbitals. The usefulness of KSOs in the description of intramolecular correlation effects in calculations of first-order interaction energies has been independently confirmed by Misquitta and Szalewicz[22] and by Heßelmann and Jansen[23]. Both groups, however, have emphasized that the prerequisite for efficiency seems to be that the KS orbitals considered correspond to asymptotically correct xc-potentials, which might suggest that only some of the widely used KSOs resemble the BOs. This suggestion has been confirmed in recent studies of the present authors[24,25]. Let us mention that the interest in applying KSOs to the description of correlation effects in WFT approaches is stimulated by the prospects of enormous savings in the computational effort, e.g., it is much cheaper to obtain KSOs than BCC orbitals. It seems, however, that a prerequisite for purposeful applications of KSOs in *ab initio* approaches is a rather detailed understanding of the "physical reality" of *ab initio* correlation effects represented by the structure of orbitals corresponding to individual types of xc-potentials.

The identification of methodologically equivalent levels of description of correlation effects in WFT and DFT is a difficult task because these effects are differently defined in both theories. A very instructive discussion of these differences together with many references to the relevant literature can be found, e.g., in the articles by Gross et al.[26] and Filippi et al.[27] It is important to remember that exchange and correlation functionals were originally designed to describe all electron correlation effects (including Fermi correlation) in an electron system, but not to give an accurate separate account of exchange and correlation. However, to get a better comprehension of the way electron correlation is covered by DFT, correlation functionals (c-functionals) are often discussed separately.

There have been many endeavors at finding connections between the widely used methods of describing electron correlation effects within the frameworks of DFT and WFT. Most of these attempts have been based on comparisons of various energy increments such as the exchange, correlation, and, first of all, the total energies (for details and many references, see, e.g., refs[8,28]). Much less attention has been paid to comparative investigations directly based on the electron density distributions, which seem to highlight additional aspects of the electron correlation problem than do the energy-based studies.

Such expectations are based on the fact that, when using the language of the configuration interaction method, the role of the individual configurations for densities is different than for the energy contributions. As was found by H. Meyer et al.[29], when going from the correlation energy to the correlation density, the dominating role of the double excitations is reduced from ≈90–95% to ≈20–50%, whereas the importance of single excitations is strongly enhanced, from ≈1% to ≈30–60%. Another demonstration of the dominating effect of single excitations on correlated densities, closely related to the present research, is the finding by van Heusden et al.[30] These authors have shown that the densities corresponding to the BOs represented by BCC orbitals, i.e., the total densities corresponding to the Brueckner determinants, are qualitatively similar to the response densities obtained at the Brueckner-coupled-cluster level, which means that they include the majority of effects important for correlated densities.

Taking into account the different perspectives of energy- and density-based approaches, comparison of the DFT results for density distributions with their WFT counterparts should provide a valuable insight into physical consequences of using various functionals and, possibly, provide information helpful for the systematic improvement of DFT functionals. Such investigations were pioneered by Krijn and Feil[31] who studied the impact of various standard approximations to exchange and correlation functionals on the electron density distribution. For atoms they found that, unlike the energies, the response of the electron density to correlation is only qualitatively reproduced by the functionals considered. The effect of various DFT methods on the electron charge distribution in molecules and atoms (treated within the *atoms-in-molecules* approach) was afterwards studied by Laidig[32]. Recently, the potentiality inherent in density distribution studies of the correlation effects accounted for by DFT functionals has been successfully exploited by Cremer, Kraka, and He[33,34]. For several molecules, these authors have undertaken very comprehensive studies comparing the densities obtained for a number of exchange-correlation and exchange-only functionals with their WFT counterparts obtained by means of several purposely chosen methods including the highly correlated fourth-order Møller–Plesset[35] and the coupled-cluster (see, e.g., ref.[36]) CCSD, and CCSD(T) approaches. Their findings are of significance both from the practical and methodological points of view.

Among the methodological aspects addressed by Cremer et al., of special interest are their extensive studies of the fundamental problem concerning the ability of DFT to cover the dynamic and non-dynamic correlation effects defined in *ab initio* approaches. A very comprehensive attempt of linking the WFT definitions of non-dynamic and dynamic correlation with the understanding of electron correlation effects in DFT has been undertaken by Neumann, Nobes and Handy[8]. These studies were essentially concerned with defining an optimum exchange functional for the purpose of understanding uniquely the content of the exchange-correlation and correlation functionals and included an examination of various properties of exchange-correlation potentials and calculations of energies and geometrical parameters of various molecules. These authors have argued that the correlation functionals should include only dynamic correlation effects, whereas exchange functionals should include the non-dynamic correlation effects, i.e., they should give predictions which are close to the CASSCF[37] ones. To achieve such a situation, it has been suggested to model good exchange functionals on a system for which there is effectively no non-dynamic correlation such as the Ne atom.

In turn, the conclusions by Cremer et al.[33,34], made in density distribution studies involving many of the commonly used exchange-correlation and exchange-only functionals, are that the latter functionals include lower-order WFT correlation effects while the correlation ones represent the higher-order correlation effects. The authors also suggest that, in currently used DFT functionals, the non-dynamic correlation effects are simulated in an unspecified way by the exchange correlation functionals. To improve the situation they suggest developing properly self-interaction-corrected (SIC) functionals (for recent results and references see, Cremer et al.[38]).

Let us just mention that an approach not based on comparison of energy increments has been very recently[24,25] used by the present authors in their attempts to compare several KSOs (which are considered to account for correlation effects) with BOs and HF orbitals. Our approach is based on a direct comparison of various subspaces spanned by these orbitals.

The main aim of this paper is to present some results of our studies on the efficiency of several types of KSOs in carrying over to the WFT information about the structure of correlation effects that are useful for the improvement of the efficiency of *ab initio* approaches. These results are based on calculations for the Ne atom. This system appears to be especially suited for our studies for several reasons: First, Ne is one of the few systems whose correlation effects are almost entirely dynamic[8,39]. Hence, from the point of view of WFT, we have to deal with the simplest structure of correlation effects. Second, for noble gas atoms presumably exchange and correlation effects are almost independent. Such findings have been made both in energy-based (see, e.g., ref.[8]) and density-distribution-based[31] studies. Third, since we have to deal with an S state, we do not face the angular symmetry problems arising for states with $L > 0$, recently studied by Fertig and Kohn[40]. Fourth, due to the symmetry just mentioned, a comparison of density distributions can be made in one dimension and is far simpler than for molecules where comparisons are predominantly based on density difference maps.

We will base our studies on the analysis of difference radial electron densities defined with respect to the Hartree–Fock (HF) radial density. Within the DFT approach, we consider densities for exchange-correlation and exchange-only potentials, which are selected to represent all the presently used types of functionals, including the recently developed orbital-dependent functionals. These results are compared with WFT density distributions represented by MP2 and MP3 response densities and the density corresponding to the Brueckner determinant, which, as we have mentioned above, is expected to be close to the accurate one. This comparison should be helpful in getting more insight into the role of exchange and correlation functionals in simulating dynamic correlation effects.

These density-based considerations will be supplemented by a discussion of the structure of the KSOs corresponding to the functionals considered in terms of indices characterizing their similarity to Brueckner and HF orbital which have been defined in our recent studies[24,25].

METHOD AND COMPUTATIONAL ASPECTS

We shall consider the difference radial charge densities (DRCD), $d_{\omega}^{\mathrm{A}}(r)$, defined for a given subshell or shell of electrons, denoted by ω with respect to the corresponding Hartree–Fock densities as

$$d_{\omega}^{\mathrm{A}}(r) = D_{\omega}^{\mathrm{A}}(r) - D_{\omega}^{\mathrm{HF}}(r) \qquad (1)$$

where $D_{\omega}^{\mathrm{A}}(r)$ denotes the radial charge density obtained within the approach "A", i.e.,

$$D_{\omega}^{\mathrm{A}}(r) = 4\pi r^{2}\,\overline{\rho}_{\omega}^{\mathrm{A}}(r) \qquad (2)$$

and $\overline{\rho}_{\omega}^{\mathrm{A}}(r)$ stands for the spherical average of the electronic charge density $\rho_{\omega}^{\mathrm{A}}(\mathbf{r})$. The $D_{\omega}^{\mathrm{A}}(r)$ functions have been frequently used in atomic shell structure studies (for references, see, e.g., refs[41,42]). For each method considered, the use of $d_{\omega}^{\mathrm{A}}(r)$ allows for a direct monitoring of the changes with respect to the HF densities, which is helpful in the discussion of the impact of the correlation effects accounted for by this method. For the DFT methods we calculate the densities from the KSOs, which makes it possible to consider both orbital and total densities. The WFT densities are represented by the

MP2 and MP3 response densities and by the BO densities. Notice that only in the latter case we can obtain orbital densities.

We have calculated radial densities for sets of KSOs corresponding to various exchange-correlation and exchange-only potentials and for the set of BOs. We consider the KSOs generated for the following standard xc-functionals (the acronyms are identical with those employed in Gaussian 98 and in the literature): (i) at the local potential level we use the SVWN5 xc-functional consisting of the Slater approximation of the exchange energy[43] and the correlation energy formulas of Vosko, Wilk and Nusair[44] (SVWN5); (ii) at the gradient-corrected level we consider the BLYP functional (Dirac's exchange with Becke's (B88) gradient correction[7] plus the Lee–Yang–Parr (LYP) correlation[45]) functional); (iii) the hybrid functionals are represented[46] by the B3LYP functional which is a mixture of 20% of the exact exchange functional and the SVWN5 and BLYP xc-functionals. We also consider the BHandHLYP potential (as defined in the Gaussian 98 [47] documentation) containing a mixture of the exact, Slater, and B88 exchange functionals and the LYP correlation term. We have also employed the exchange-only functionals referred to as B3ex and BHHex functionals which are obtained from the B3LYP and BHandHLYP ones, respectively, by omitting the correlation terms. The set of KSOs corresponding to widely used functionals is complemented by the orbital sets representing the very recently developed *ab initio* DFT approaches. On the exchange-only level, the orbitals correspond to the optimized orbital potentials (OEP), first considered within the framework of WFT half a century ago[48,49], which have been implemented into the DFT during the last decade (see, e.g., refs[50–53]). In turn on the exchange-correlation level, we are concerned with KSOs representing the recent developments in DFT based on the orbital-dependent exchange and correlation functionals (see, e.g., refs[9–12]). In this work we use the one of the functionals of the OEP-MBPT(2) approach developed by Grabowski et al.[12], viz. the OEP-MBPT(2)-f version described in detail by Bartlett et al.[54] All orbitals, except the KSOs corresponding to orbital-dependent functionals, have been generated by means of the Gaussian 98 system of programs[47]. The latter orbitals have been obtained when using the ACES II suite of programs[55]. In all calculations, we employed an uncontracted ROOS-ATZP basis[56] consisting of 95 Gaussian primitives.

For comparing the KS, HF, and BO orbital sets considered, we have employed indices characterizing distances between pairs of equidimensional subspaces spanned by these orbitals (for details, see refs[24,25]). These indices are defined in terms of the magnitudes of the determinant of the mixed-overlap matrices as

$$D = \sqrt{2(1 - P)} \tag{3}$$

where $P = |\det \mathbf{M}|$, with $(\mathbf{M})_{ij} = \langle \psi_i | \varphi_i \rangle$ where ψ_i and φ_j are members of the basis sets spanning the subspaces of the pair.

It is convenient to scale the index defined in Eq. (*3*) with respect to the reference distance representing the distance between the subspaces spanned by the HF orbitals and the BOs. These distances are referred to as *relative distances*. Moreover, since the similarity of BOs and KSOs has been attributed to their ability to describe some correlation effects, we have also calculated the indices for the distances of the KS and HF orbital subspaces. The indices for the KSO–BO (KSO–HF) pairs are labeled by "B" (or "H"). For the BO–HF pair we use the label "B–H".

For the individual levels of comparison we use the notation (the tilde denotes relative indices):

1. On the level of individual orbitals labeled by κ:

$$\tilde{d}_\kappa^{\mathrm{B}} = \frac{d_\kappa^{\mathrm{B}}}{d_\kappa^{\mathrm{B-H}}} , \qquad \tilde{d}_\kappa^{\mathrm{H}} = \frac{d_\kappa^{\mathrm{H}}}{d_\kappa^{\mathrm{B-H}}} . \tag{4}$$

2. On the level of subspaces spanned by the subsets of orbitals of the symmetry specification ω:

$$\tilde{D}_\omega^{\mathrm{B}} = \frac{D_\omega^{\mathrm{B}}}{D_\omega^{\mathrm{B-H}}} , \qquad \tilde{D}_\omega^{\mathrm{H}} = \frac{D_\omega^{\mathrm{H}}}{D_\omega^{\mathrm{B-H}}} . \tag{5}$$

3. On the level of determinants constructed from doubly occupied orbitals:

$$\tilde{X}^{\mathrm{B}} = \frac{X^{\mathrm{B}}}{X^{\mathrm{B-H}}} , \qquad \tilde{X}^{\mathrm{H}} = \frac{X^{\mathrm{H}}}{X^{\mathrm{B-H}}} . \tag{6}$$

For the convenience of discussion, we include in the table just the KSO–BO distances and their ratios to the KSO–HF distances:

$$k_\kappa = \frac{\tilde{d}_\kappa^{\mathrm{B}}}{\tilde{d}_\kappa^{\mathrm{H}}} , \qquad k_\omega^{\mathrm{D}} = \frac{\tilde{D}_\omega^{\mathrm{B}}}{\tilde{D}_\omega^{\mathrm{H}}} , \qquad k_X = \frac{\tilde{X}^{\mathrm{B}}}{\tilde{X}^{\mathrm{H}}} . \tag{7}$$

If these ratios are smaller than unity, it is reasonable to consider the sets of KS orbitals to be more similar to the BOs than to the HF orbitals.

RESULTS AND DISCUSSION

Radial Density Distributions for Ne

We shall show the results of our calculations in graphical form. In Fig. 1 we present the total radial density distribution, $D_{\text{tot}}^{\text{HF}}(r)$, for Ne calculated for the uncontracted ROOS-ATZP basis. This density distribution provides reference values for all the difference radial electron density distributions, Eq. (*1*), displayed in Figs 2–5. The maxima of the K and L shell radial densities are at $r = 0.105$ and 0.650 a.u., respectively. The position of the minimum, at $r = 0.307$ a.u., provides a partitioning into core and valence regions. Let us notice that this position is the same for all the densities calculated in these studies.

For a discussion of the charge redistribution (with respect to the HF reference) for the individual methods considered, we define in each case three or four regions limited by r-values corresponding to zeros of the DRCD distributions, d_{ω}^{A}. Region I ranges from $r = 0$ to $r \simeq 0.14$ a.u. and strongly overlaps with the K shell region including the area defining the maximum of the K shell. Region II ranges from $r \simeq 0.14$ to $r \simeq 0.5$ a.u. and includes, almost in the middle, the core-valence partitioning point. Therefore, it might be considered as approximately representing the intershell region. Region III ranges from $r \simeq 0.5$ to $r \simeq 1.5$ a.u. and includes the maximum of the L shell distribution. We refer to this region as the inner-valence-shell region.

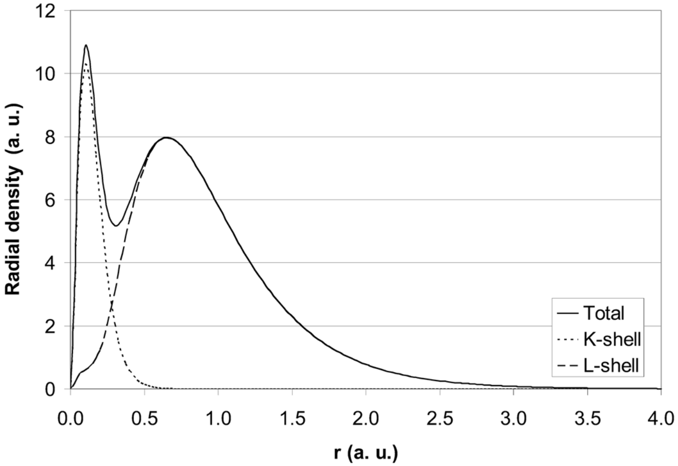

FIG. 1
Radial charge density distribution for Ne, $D_{\text{tot}}^{\text{HF}}(r)$, calculated for the Hartree–Fock determinant

Region IV ranges from $r \simeq 1.5$ a.u. to infinity and is referred to as the outer-valence-shell region.

The difference radial total charge densities defined by Eq. (*1*), obtained for the WFT ($d_{\text{tot}}^{\text{BO}}(r)$, $d_{\text{tot}}^{\text{MP2}}(r)$, $d_{\text{tot}}^{\text{MP3}}(r)$) and for the DFT $d_{\text{tot}}^{\text{xc}}(r)$ methods (where "xc" indicates that the complete xc-potential has been used) are displayed in Fig. 2. We find significant differences in the overall shape of the curves. A comparison of our WFT density distributions with the results of Meyer et al.[57], who studied the impact of electron correlation on radial electron densities using the MRCI-SD method in very large basis sets, shows a close similarity to the MP3 distribution.

Note that all curves representing WFT densities are inside the DFT curves. The best *ab initio* representation of all the DFT densities is provided by the MP2 one. The closest resemblance is found for the MP2 and the OEP-MBPT(2)-f curves. The similarity is almost as close as for the MP2 and

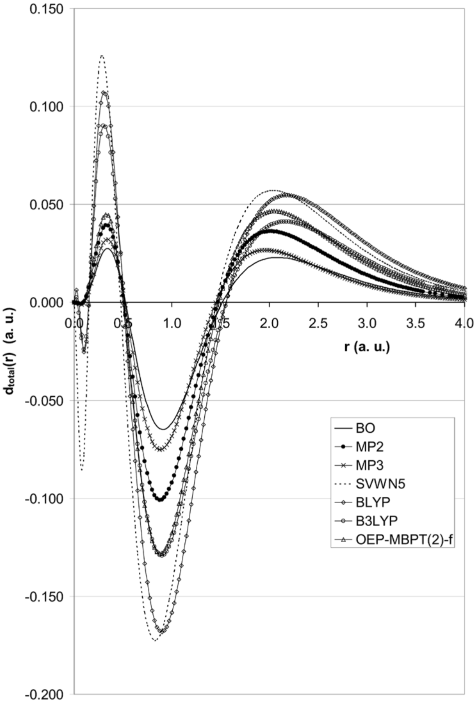

FIG. 2

Difference radial charge density distributions for Ne, $d_{\text{tot}}^{\text{A}}(r)$, for the MP2, MP3, and Brueckner-determinant WFT methods and for the Kohn–Sham orbitals corresponding to the SVWN5, BLYP, B3LYP, and OEP-MBPT(2)-f exchange-correlation functionals

B3LYP curves, in which case the larger disagreement is noticed in the intershell region. The disagreement between the MP2 and DFT curves is most pronounced for the SVWN5 and BLYP densities. Our experience with the structure of electron correlation in Ne makes us to believe that the relative density curve would be between the MP3 and MP2 density curves. Therefore, our assessment of the relative ability of the various DFT exchange correlation functionals to mimic WFT correlation effects seems to be reliable.

An interesting feature of the curves in Fig. 2 is that all of them define the main charge shift (relative the HF charge distribution) from the inner-valence-shell region (III) either to the outer-valence-shell (IV) or to the intershell (II) regions. For the DFT methods there is also a minor charge displacement from the core (I). A quantitative description of the charge shifts is given in Table I. One sees from that table that the displacement from region III is larger for the DFT densities than for the WFT ones. The largest shifts of about 0.1e correspond to the local and gradient-corrected functionals. The shifts are smaller for the hybrid and orbital-dependent functionals. It might be of some interest to note from Table I that, irrespective of the magnitude of the charge shifted from region III, about 80% goes to region IV. Hence, all our WFT and DFT density distributions confirm the

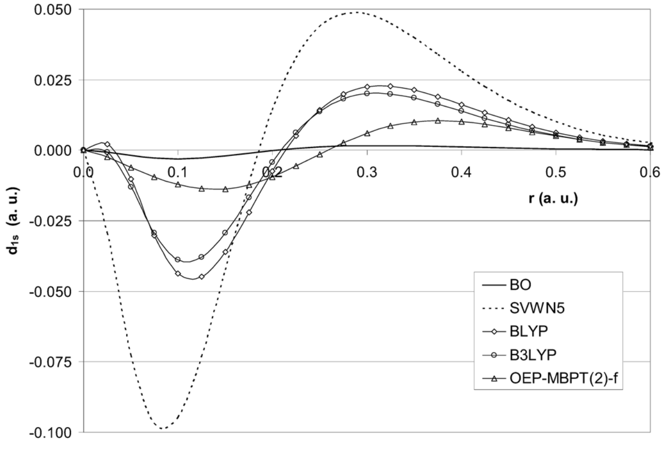

FIG. 3
Difference radial charge density distributions for the 1s-shell of Ne, $d_{1s}^{A}(r)$, the Brueckner orbitals and for the Kohn–Sham orbitals generated for the SVWN5, BLYP, B3LYP, and OEP-MBPT(2)-f exchange-correlation functionals

exceptional behavior found by Meyer et al.[57] that for N and Ne, unlike for other second row atoms, inclusion of electron correlation entails an increase in the atomic size. The present results do not seem to confirm the findings of de Proft and Geerlings[58] 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 intershell region.

To get a more detailed insight into the charge distribution in the core region, we illustrate in Fig. 3 the relative radial charge distribution for the 1s electrons, $d_{1s}(r)$. In this case the only WFT density available is the BO 1s-density, which differs only slightly from the HF one. We find significant differences between these orbital densities. By far the largest deviation from the HF density is found for the SVWN5 approach, which explains the relatively large charge displacement from the core region indicated in Table I. The density profiles obtained for the BLYP and B3LYP functionals are similar and deviate significantly from the OEP-MBPT(2)-f one.

To gain a better understanding of how the *ab initio* correlation effects are simulated by the exchange and correlation functionals, we have calculated the DRCD curves for DFT densities for exchange-only functionals, $d_{\text{tot}}^{\text{x}}$, corresponding to the xc-functionals discussed above. These curves are displayed in Fig. 4 together with the WFT curves already shown in Fig. 2. For the Slater (S), B88, and B3ex exchange-only potentials, the curves resemble strongly the corresponding xc-potential curves given in Fig. 2. In both cases we have to deal with the same regions of charge depletion and accumulation. The main difference consists in the magnitudes of the charge displaced from region III to region IV, which is slightly larger for the B88 and B3ex potentials and significantly larger for the S potential. These results

TABLE I

Electron charge displacements relative the HF charge distribution (in a.u.)

Region[a]	BD	MP2	MP3	SVWN5	BLYP	B3LYP	OEP-MBPT(2)-f
I	–	–	–	–0.008	–0.001	–0.002	–
II	0.007	0.010	0.008	0.026	0.024	0.021	0.011
III	–0.038	–0.057	–0.041	–0.100	–0.103	–0.048	–0.075
IV	0.031	0.048	0.034	0.082	0.081	0.060	0.064

[a] Regions are defined as follows: I, vicinity of the nucleus; II, intershell; III, inner-valence-shell; IV, outer-valence-shell.

clearly indicate that the densities obtained for representatives of the widely used local, gradient-corrected, and hybrid exchange-only potentials account for the bulk of WFT correlation effects.

The situation is radically different for the OEP exchange-only (OEPX) potential, where the $d^{\mathrm{x}}_{\mathrm{tot}}$ curve is extremely close to the abscissa, which is a consequence of using the optimized exchange potential designed to closely simulate the HF exchange potential[48,49].

To answer some questions concerning the role of the c-functionals in covering the WFT correlation effects, we show in Fig. 5 plots representing the effect of these functionals on the density distributions. The curve for the LYP functional represents the difference of the charge distributions for the BLYP and B88 functionals. Mention must be made that almost identical curves have been obtained for the SLYP – S as well as for the BHandHLYP – BHHex differences, which confirms the belief (see, e.g., ref.[8]) that exchange

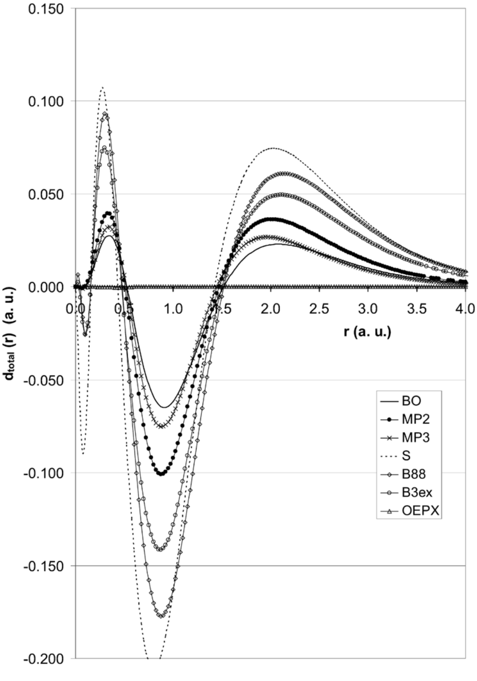

FIG. 4
Difference radial charge density distributions for Ne, $d^{\mathrm{A}}_{\mathrm{tot}}(r)$, for the MP2, MP3, and Brueckner-determinant WFT methods and for the Kohn–Sham orbitals generated for the SVWN5, BLYP, B3LYP, and OEPX exchange-only functionals

and correlation effects for closed-shell atoms are almost independent. The plot representing the LYP correlation effects shows that for Ne these effects are rather small and lead to an enhanced density in the inner-valence-shell region, which is not in line with the findings by Cremer et al.[33,34] who in their molecular studies ascribed this enhancement to the core region. It is apparent from Fig. 5 that the plot representing the impact of the LYP potential is completely different from the MP2 and MP3 plots, which might suggest that the LYP correlation functional represents higher-order correlation effects, as postulated by Cremer[34] in the discussion of molecular results. Taking into account the way the LYP functional has been derived, it is difficult for the present authors to accept this suggestion for the closed-shell Ne atom.

One can also see in Fig. 5 that the curve representing the impact of the OEP-MBPT(2)-f correlation functional, obtained as the difference of the OEP-MBPT(2)-f and OEPX density distributions, fairly resembles the MP2 distribution. Hence, charging the correlation functional with the task of complete representation of dynamic correlation effects would require designing of exchange functionals providing an extremely accurate description of the exchange-correlation (Fermi) hole. This point of view is in line

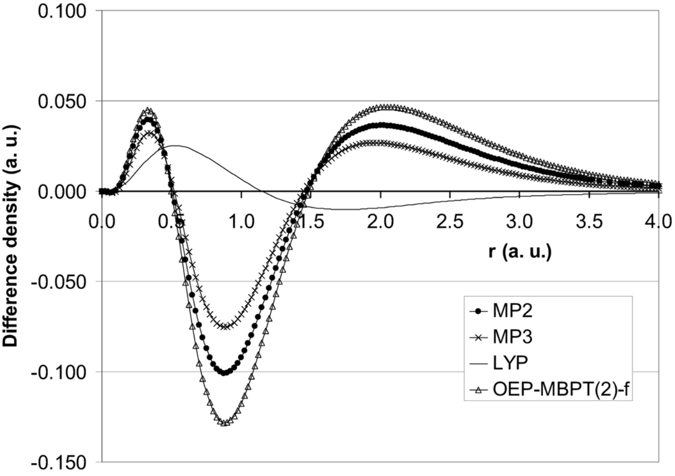

FIG. 5

Comparison of difference radial charge density distributions, $d^{\mathrm{A}}_{\mathrm{tot}}(r)$, for the MP2 and MP3 methods with the differences $\Delta_{\mathrm{LYP}} \equiv d^{\mathrm{BLYP}}_{\mathrm{tot}}(r) - d^{\mathrm{B88}}_{\mathrm{tot}}(r)$ and $\Delta_{\mathrm{OEP}} \equiv d^{\mathrm{OEP\text{-}MBPT(2)\text{-}f}}_{\mathrm{tot}}(r) - d^{\mathrm{OEPX}}_{\mathrm{tot}}(r)$ representing the impact of the LYP and OEP-MBPT(2)-f correlation functionals with the reasoning of Neumann, Nobes and Handy[8] who designated for this role the Becke–Roussel[59] exchange functional.

Comparison of Kohn–Sham and Brueckner Orbitals

The similarity indices characterizing the distances of subspaces spanned by the KSOs, BOs, and HF orbitals are displayed in Table II. The table includes only potentials that differ in the exchange part because we have demonstrated in ref.[24] that for potentials that differ only in the correlation part, the indices take close values.

The KSOs, BOs, and HF orbitals corresponding to the lowest energy are practically indistinguishable, which is consistent with the difference densities shown in Fig. 3. This closeness causes that the BO–HF reference distance is extremely small and the corresponding indices might be considerably affected by numerical errors. Therefore, the table does not include the 1s indices. Let us just mention that the relative magnitudes of the $\tilde{d}_{1s}^{B}$ indices are consistent with the density differences displayed in Fig. 2. For the

TABLE II
Comparison of the indices[a] characterizing distances of subspaces defined by various Kohn–Sham orbitals from corresponding subspaces defined by Brueckner and by Hartree–Fock orbitals generated for the Ne atom

Functional	$\tilde{d}_{2s}^{B}$	k_{2s}	$\tilde{D}_{s}^{B}$	k_{s}^{D}	$\tilde{d}_{2p}^{B}$	k_{2p}	$\tilde{X}^{B}$	k_x
SVWN5	2.71	0.77	2.96	0.79	1.55	0.61	1.68	0.64
S	3.20	0.79	2.42	0.71	2.33	0.70	2.42	0.71
BLYP	1.68	0.64	1.83	0.66	1.88	0.66	1.88	0.66
B88	1.87	0.66	2.15	0.69	2.16	0.69	2.15	0.69
B3LYP	1.15	0.55	1.29	0.59	1.13	0.54	1.15	0.54
B3ex	1.41	0.60	1.52	0.63	1.46	0.60	1.47	0.60
BHandHLYP	0.23	0.19	0.45	0.35	0.32	0.25	0.33	0.26
BHex	0.53	0.37	0.59	0.41	0.47	0.33	0.48	0.33
OEP-MBPT(2)-f	0.96	0.50	1.06	0.53	0.97	0.49	0.98	0.50
Reference values for the BO–HF pair	0.004833		0.004846		0.010361		0.026301	

[a] The indices $\tilde{d}_{\kappa}^{B}$ (κ = 2s, 2p), $\tilde{D}_{s}^{B}$, and $\tilde{X}^{B}$ are defined by Eqs (*4*), (*5*), and (*6*), respectively. All *k*-ratios are defined by Eq. (*7*).

remaining orbitals, we find that $\tilde{d}_{\kappa}^{\mathrm{B}} \leq 3.2$. These indices take the largest values for the local and the gradient-corrected potentials, decreasing when proceeding to the hybrid potentials. The minimum of the KSO–BO orbital distances is attained for the BHandHLYP xc-potential for which this distance is much smaller than for the B3LYP hybrid potential.

On all levels of comparison, the KSO–BO distances for the local and gradient-corrected potentials are considerably larger than the corresponding BO–HF reference distances, i.e., the KSOs differ more from the BOs than do the HF orbitals. To a smaller extent, such a situation takes place even for the B3LYP hybrid potentials. Only for the BHandHLYP potential we find that the KSOs are significantly closer than the HF orbitals to the BOs, which indicates that the increase in the admixture of the exact exchange from 20% to 50% results in a strong modification of the form of the KSOs.

The decrease in the KSO–BO distance indices when proceeding from the local to the hybrid potentials has been rationalized[24] by the reduction of the errors in the asymptotic of these potentials. Instead of an exponential vanishing for the local potentials, we have to deal with an $1/nr$ ($n > 1$) vanishing for the hybrid ones, which is the closest to the $1/r$ decrease in the exact potential. However, the indices corresponding to the asymptotically correct OEP-MBPT(2)-f are larger than for the BHandHLYP potential. This fact indicates that the asymptotic correctness of the KS potential is not a sufficient condition for the similarity of the KSOs and BOs.

A comparison of the indices for KSOs generated for each of the exchange-correlation potentials with their counterparts obtained for the exchange-only potentials reveals in all cases an increase in the latter ones. The relative increase is most pronounced for the BHandHLYP potential. This increase, however, does not modify the differences found at the xc-potential level for various generations of potentials. Hence, the structure of the KSO is essentially defined by the exchange-only functional. Inclusion of the correlation potential modifies the shape of the KSOs to a limited extent, moving them closer to the BOs. Hence, the BOs represent, on the WFT level, correlation effects described on the DFT level by both the exchange and correlation potentials. An improvement of the similarity of KSOs and BOs should be, first of all, achieved by improving the exchange potential, by adjusting it to a reliable description of the exchange hole.

In closing this discussion, we would like to emphasize that on all the levels of comparison, we can see in Table II that the k-indices take values smaller than unity, i.e., the KSO–BO distances are smaller than the KSO–HF ones. They reach their minima for the BHandHLYP potential.

CONCLUSIONS

The efforts of bridging the methodological gap between the wave function theory (WFT) and density functional theory (DFT) that would afford carrying over some intermediate results are shortly reviewed. Special attention is paid to the problem of coverage of the WFT correlation effects by the exchange-correlation functionals of DFT. A short survey of the concept of supplementing energy-based investigations in this field by electron-density based studies is given and illustrated by results of calculations of the radial density distribution for the Ne atom.

We have calculated DFT radial electron density distributions for representatives of all four generations of presently used exchange-correlation functionals, including the recently developed orbital-dependent OEP-MBPT(2)-f functional[12]. These density distributions have been compared with WFT densities calculated at the MP2, MP3, and Brueckner determinant levels.

The present results indicate that the exchange-only parts of the widely used local, gradient-corrected, and hybrid functionals account for the bulk of WFT correlation effects. The impact of the associated correlation functionals on the density distributions is rather marginal, and an understanding of the physical content of these functionals requires further studies.

A different behavior has been disclosed for the orbital-dependent functional, for which the exchange-only component yields an almost exact Hartree–Fock density. Now, the correlation effects are entirely represented by the correlation functional and there is a clear understanding of its physical content.

We have also been concerned with a continuation of our recent studies[24] on the efficiency of Kohn–Sham orbitals (KSOs) in carrying over to WFT the information on the structure of correlation effects. This efficiency has been related to the presumptive similarity of KSOs and Brueckner orbitals[21] (BOs). It is found that BOs like KSOs describe mainly the correlation effects that are accounted for in DFT by the exchange-only functionals. Hence, BOs represent “correlation effects” in a more general sense than considered in quantum chemistry.

We realize that electron-density-distribution based investigations for molecules provide a more comprehensive insight into details that are of interest for DFT practitioners than studies limited to atomic systems. However, a large variety of details, the necessity of using a more-than-one-dimensional representation of the density distributions, and the basis set effects seem to be obstacles preventing the identification of the requirements to be made for the DFT functionals to obtain a well defined representation of the most important WFT correlation effects. Therefore, noble-gas atoms, for which these obstacles are reduced to a minimum, seem to be better suited than molecules at early stages of systematic searches for new generations of functionals enabling the transfer of intermediate results between WFT and DFT.

We hope that the present preliminary results will contribute to recognition of the potentiality of electron-density-distribution studies for closed-shell atoms as a means helpful in the search for effective and transparent methods of describing *ab initio* correlation effects in DFT.

This work was supported in part by the Committee for Scientific Research (KBN) through grant No. 4 T09A 187 25.

REFERENCES

1. Hohenberg P., Kohn W.: *Phys. Rev.* **1964**, *136*, B864.
2. Parr R. G., Yang W.: *Density-Functional Theory*. Oxford University Press, New York 1989.
3. Dreizler R. M., Gross E. K. U.: *Density Functional Theory – An Approach to the Quantum Many-Body Problem*. Springer, Berlin 1990.
4. Chakravorty S. J., Gwaltney S. R., Davidson E. R.: *Phys. Rev. A* **1993**, *47*, 3649.
5. Andrae D., Brodbeck R., Hinze J.: *Int. J. Quantum Chem.* **2001**, *82*, 227.
6. Jankowski K., Nowakowski K., Słupski R., Flores J. R.: *Int. J. Quantum Chem.* **2004**, *99*, 277.
7. Becke A. D.: *Phys. Rev. A* **1988**, *38*, 3098.
8. Neumann R., Nobes R. H., Handy N. C.: *Mol. Phys.* **1996**, *87*, 1.
9. Görling A.: *Phys. Rev. Lett.* **1999**, *83*, 5459.
10. Ivanov S., Hirata S., Bartlett R. J.: *Phys. Rev. Lett.* **1999**, *83*, 5455.
11. Grabo T., Kreibich T., Kuth S., Gross E. K. U. in: *Strong Coulomb Correlations in Electronic Structure Calculations* (V. I. Anisimov, Ed.). Gordon and Breach, London 1999.
12. Grabowski I., Hirata S., Ivanov S., Bartlett R. J.: *J. Chem. Phys.* **2002**, *116*, 4415.
13. Warken M.: *Chem . Phys. Lett.* **1995**, *237*, 256.
14. Jankowski K., Gryniaków J., Rubiniec K.: *Int. J. Quantum Chem.* **1998**, *67*, 221.
15. Hupp T., Engels G. B., Della Sala F., Görling A.: *Chem. Phys. Lett.* **2002**, *360*, 175.
16. Gutle C., Heully J. L., Krieger J., Savin A.: *Phys. Rev. A* **2002**, *66*, 012504.
17. Čížek J., Paldus J., Šroubková L.: *Int. J. Quantum Chem.* **1969**, *3*, 149.
18. Bartlett R. J., Purvis G. D.: *Int. J. Quantum Chem.* **1978**, *14*, 561.
19. Chiles R. A., Dykstra C. E.: *J. Chem. Phys.* **1981**, *74*, 4544.
20. Heßelmann A., Jansen G.: *J. Chem. Phys.* **2000**, *112*, 6949.
21. Lindgren I., Salomonson S.: *Int. J. Quantum Chem.* **2002**, *90*, 294.
22. Misquitta A. J., Szalewicz K.: *Chem. Phys. Lett.* **2002**, *357*, 301.
23. Heßelmann A., Jansen G.: *Chem. Phys. Lett.* **2002**, *362*, 319.
24. Jankowski K., Nowakowski K., Wasilewski J.: *Chem. Phys. Lett.* **2004**, *389*, 393.
25. Wasilewski J., Nowakowski K., Jankowski K.: *Struct. Chem.* **2004**, *15*, 437.

26. Gross E. K. U., Petersilka M., Grabo T. in: *Density Functional Methods in Chemistry* (T. Ziegler, Ed.). ACP, Washington 1996.
27. Filippi C., Umrigar C. J., Gonze X.: *Phys. Rev. A* **1996**, *54*, 4810.
28. Johnson B. G., Gill P. M. W., Pople J. A.: *J. Chem. Phys.* **1993**, *98*, 5612.
29. Meyer H., Schweig A., Zittlau W.: *Chem. Phys. Lett.* **1982**, *92*, 637.
30. van Heusden C. M., Kobayashi R., Amos R. D., Handy N. C.: *Theor. Chim. Acta* **1993**, *86*, 25.
31. Krijn M. P. C. M., Feil D.: *Chem. Phys. Lett.* **1988**, *150*, 45.
32. Laidig K. E.: *Chem. Phys. Lett.* **1994**, *225*, 285.
33. He Y., Gräfenstein J., Kraka E., Cremer D.: *Mol. Phys.* **2000**, *98*, 1639.
34. Cremer D.: *Mol. Phys.* **2001**, *99*, 1899.
35. Møller C., Plesset M. S.: *Phys. Rev.* **1934**, *36*, 618.
36. Paldus J. in: *Handbook of Molecular Physics and Quantum Chemistry* (S. Wilson, Ed.). Wiley, Chichester 2003.
37. Roos B. O., Tylor P. R., Siegbahn P. E. M.: *Chem. Phys.* **1980**, *48*, 157.
38. Cremer D., Filatov M., Polo V., Kraka E., Shaik S.: *Int. J. Mol. Sci.* **2002**, *3*, 604.
39. Jankowski K., Malinowski P., Polasik M.: *Phys. Rev. A* **1980**, *22*, 51.
40. Fertig H., Kohn W.: *Phys. Rev. A* **2000**, *62*, 052511.
41. Sen K. D., Slamet M., Sahni V.: *Chem. Phys. Lett.* **1993**, *205*, 313.
42. Kohout M., Savin A.: *Int. J. Quantum Chem.* **1996**, *60*, 875.
43. Slater J. C.: *Quantum Theory of Molecules and Solids*, Vol. 4. McGraw–Hill, New York 1974.
44. Vosko S. H., Wilk L., Nusair M.: *Can. J. Phys.* **1980**, *58*, 1200.
45. Lee C., Yang W., Parr R. G.: *Phys. Rev. B* **1988**, *37*, 785.
46. Becke A. D.: *J. Chem. Phys.* **1993**, *98*, 5648.
47. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Zakrzewski V. G., Montgomery J. A., Jr., Stratmann R. E., Burant J. C., Dapprich S., Millam J. M., Daniels A. D., Kudin K. N., Strain M. C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford S., Ochterski J., Petersson G. A., Ayala P. Y., Cui Q., Morokuma K., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Cioslowski J., Ortiz J. V., Baboul A. G., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts R., Martin R. L., Fox D. J., Keith T., Al–Laham M. A., Peng C. Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Andres J. L., Gonzalez C., Head-Gordon M., Replogle E. S., Pople J. A.: *Gaussian 98*, Revision A.7. Gaussian Inc., Pittsburgh (PA) 1998.
48. Sharp R. T., Horton G. K.: *Phys. Rev.* **1953**, *90*, 317.
49. Talman J. D., Shadwick W. F.: *Phys. Rev. A* **1976**, *14*, 36.
50. Krieger J. B., Lie Y., Iafrate G. J.: *Phys. Rev. A* **1992**, *45*, 101.
51. Engel E., Vosko S. H.: *Phys. Rev. A* **1993**, *47*, 2800.
52. Niquet Y. M., Fuchs M., Gonze X.: *J. Phys. Chem.* **2003**, *118*, 9504.
53. Kümmel S., Perdew J. P.: *Phys. Rev. B* **2003**, *68*, 035103.
54. Bartlett R. J., Grabowski I., Hirata S., Ivanov S.: *J. Chem. Phys.* **2005**, *122*, 034104.
55. Stanton J. F., Gauss J., Watts J. D., Nooijen M., Oliphant N., Perera S. A., Szalay P., Lauderdale W. J., Kucharski S., Gwaltney S., Beck S., Balková A., Bernholdt D. E., Baeck K. K., Rozyczko P., Sekino H., Hober C., Bartlett R. J.: Integral packages included are VMOL (J. Almlf and P. R. Taylor); VPROPS (P. Taylor); ABACUS (T. Helgaker, H. J. Aa.

Jensen, P. Jörgensen, J. Olsen and P.R. Taylor): *ACES II*, Quantum Theory Project. Gainesville, Florida.

56. Widmark P. O., Malmqvist P. A., Roos B.: *Theor. Chim. Acta* **1990**, *77*, 291.
57. Meyer H., Müller T., Schweig A.: *J. Mol. Struct.* **1996**, *360*, 55.
58. de Proft F., Geerlings P.: *Chem. Phys. Lett.* **1994**, *220*, 405.
59. Becke A. D., Roussel M. E.: *Phys. Rev. A* **1989**, *39*, 3761.