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Nonlocal density functionals: Comparison with exact results for finite systems

A. C. Pedroza

Department of Theoretical Physics, University of Lund, Sölvegatan 14A, S-223 62 Lund, Sweden

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The performance of approximations to the Hohenberg-Kohn-Sham density functionals is tested by comparing with essentially exact results for light atoms (the He isoelectronic series, Be, and Ne). The approximation schemes considered here are the effective gradient schemes due to Langreth and Mehl (LM), and the "modified weighted-density" (MWD) approximation due to Gunnarsson and Jones. Compared to the local density approximation the LM schemes give markedly better exchange-correlation energies and a certain improvement in the density profiles, effective potentials, and orbital eigenvalues. The MWD scheme gives good improvements of the exchange-correlation energies but improves the densities, potentials, and eigenvalues only for the He isoelectronic series. The sensitivity of the MWD scheme with respect to the model pair correlation used, as well as some additional approximations used in practical applications of the MWD scheme, are also analyzed.

I. INTRODUCTION

The density-functional (DF) theory as formulated by Hohenberg, Kohn, and Sham[1,2] has, during the last 15 years, become one of the most widely used and successful tools for obtaining the ground-state properties of complex systems. The current interest in DF theory has resulted in several recent reviews.[3] In most applications the simplest so-called local density (LD) approximation is employed, which usually gives useful and rather accurate results. For systems of high symmetry, such as elemental perfect solids, the experimental and theoretical level is, however, sometimes high enough to motivate improvements beyond the LD approximation. The development of better approximations has proved to be a difficult task, and significant progress has been made only rather recently. The most promising development appears to be that due to Langreth, Perdew, and Mehl,[4-6] who focus on a description of exchange and correlation in reciprocal space. Important progress has also been made by Gunnarsson and co-workers, who concentrated on a description of the exchange-correlation hole in real space,[7] and found important sum rules.[8] These studies enabled Gunnarsson *et al.*[8,9] and Alonso and Girifalco[10] to design new approximations to the functionals which have been reported to give improvements in a number of test cases. Besides giving improved schemes, the works by Gunnarsson and Langreth and co-workers also shed light on the unexpected accuracy of the LD approximation.

The purpose of the present study is to test the performance of these new approximations to DF theory by applying them to systems where accurate solutions to the many-electron problem by other means are available. At present, accurate correlated wave functions are available only for a limited selection of light atoms[11] and, consequently, we choose these systems as our test cases. The aim of the present work is, however, to shed light on the general usefulness of different approximations to the density functional and not to study exchange and correlation in specific atoms. In recent years there has been a renewed interest[12] in the energy eigenvalues of the DF orbital equations.[2] Therefore, we compare not only ground-state properties such as the particle density and the total energy obtained using approximate density functionals with the corresponding "exact" quantities, but we also study approximations to the energy eigenvalues and effective one-particle potential of DF theory. (Essentially exact results for the latter quantities have been obtained by Almbladh and Pedroza[13] and by von Barth and Car.[14]) In the present work we also study the accuracy of some additional approximations used in practical applications[15,16] of the schemes due to Gunnarsson *et al.*[8,9] and Alonso and Girofalco.[10]

II. NONLOCAL DENSITY FUNCTIONALS

A. Formulations in real space

We here summarize approximations proposed by Gunnarsson *et al.* and by Alonso and Girifalco. The basic exchange-correlation functional $E_{\rm xc}[n]$ of DF theory can be written formally in terms of the exact pair-correlation function,[17]

$$E_{\rm xc}[n]=\frac{1}{2}\int d^3r\,d^3r'\,n(\mathbf{r})n(\mathbf{r}')[\tilde{g}(\mathbf{r},\mathbf{r}')-1]v(|\mathbf{r}-\mathbf{r}'|)\ . \tag{1}$$

Here, $n(\mathbf{r})$ is the electron density and $v(r)=1/r$ is the electron-electron interaction (we use atomic units such that $e^2=\hbar=m=1$). The quantity $\tilde{g}$ is defined in terms of the pair-correlation function $g_\lambda(\mathbf{r},\mathbf{r}';n)$ corresponding to a rescaled interaction $\lambda v(r)$ and a fixed-density profile $n(\mathbf{r})$:

$$\tilde{g}(\mathbf{r},\mathbf{r}')=\int_0^1 d\lambda\, g_\lambda(\mathbf{r},\mathbf{r}';n)\ . \tag{2}$$

When studying approximations for $\tilde{g}$, Gunnarsson found it essential to fulfill the sum rule that the exchange-correlation hole around an electron should contain exactly one electron. The exchange-correlation hole is described by the quantity

$$n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')=n(\mathbf{r}')[\tilde{g}(\mathbf{r},\mathbf{r}')-1]\;, \tag{3}$$

and the sum rule states

$$\int n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')d^3r'=-1\;. \tag{4}$$

Gunnarsson *et al.*[8] proposed two different approximation schemes which satisfy the sum rule in Eq. (4). We shall confine ourselves here to the "weighted-density" (WD) approximation, which was independently suggested also by Alonso and Girifalco.[10] In this scheme $\tilde{g}(\mathbf{r},\mathbf{r}')$ in Eq. (1) is approximated by its counterpart $\tilde{g}_h(\mathbf{r}-\mathbf{r}',\tilde{n})$ for a homogeneous system, where the effective density $\tilde{n}\equiv\tilde{n}(\mathbf{r})$ is chosen so as to fulfill the sum rule for the exchange-correlation hole [Eq. (4)].

In its original form, the WD approximation gives substantial improvement of the exchange energy of atoms, but the correlation energies are poor. To overcome this failure Gunnarsson and Jones[9] proposed a modified WD (MWD) scheme where the correlation function $\tilde{g}_h$ for the homogeneous electron gas is replaced by a simple analytic function $\bar{g}(r,n)$. This function is chosen to give the correct sum rule and the correct exchange-correlation energy $\epsilon_{\mathrm{xc}}(n)$ for a homogeneous system:

$$n\int[\bar{g}(r,n)-1]d^3r=-1\;, \tag{5}$$

$$\tfrac{1}{2}n\int v(r)[\bar{g}(r,n)-1]d^3r=\epsilon_{\mathrm{xc}}(n)\;. \tag{6}$$

Gunnarsson and Jones chose

$$\bar{g}(r,n)=1+C\{1-\exp[(-\lambda/r)^5]\}$$

(where C and λ depend on the density n), which reproduces the correct long-range behavior of the functional far outside a metal surface. However, to model the correct long-range behavior in other systems, one would need different analytic forms of $\bar{g}$. In order to test the sensitivity of the MWD scheme with respect to the choice of model for $\bar{g}$, we have studied a variety of other plausible analytic forms. We found it is essential to fulfill the condition that $\bar{g}(r,n)$ is non-negative everywhere for all densities in order to obtain good results. We have chosen the following two analytic forms for a more detailed study, namely

$$\bar{g}_1(r,n)=1+(a+br)\exp(-cr^2) \tag{7}$$

and

$$\bar{g}_2(r,n)=1+(a+br)\exp(-cr)\;, \tag{8}$$

which model a localized exchange-correlation hole and which properly tend to unity at far distances. The coefficients a, b, and c are functions of n chosen so as to fulfill Eqs. (5) and (6). In order to define the parameters uniquely, we also specified the value of $\bar{g}$ at zero particle separation. By choosing $\bar{g}(0,n)=\xi/(1+\gamma r_s)$ with $\xi=0.57$ and $\gamma=0.47$ for $\bar{g}_1$ and $\xi=1.0$ and $\gamma=0.8$ for $\bar{g}_2$, we obtained non-negative correlation functions. The exact $\tilde{g}(\mathbf{r},\mathbf{r}')$ at zero particle separation can take values only between 0 and $\frac{1}{2}$, a condition which is violated by $\bar{g}_1$ for very high densities [$\bar{g}_1(0,n)\rightarrow 0.57$ when $n\rightarrow\infty$].

As explained above, the MWD scheme approximates the exchange-correlation energy functional by

$$E_{\mathrm{xc}}[n]=\tfrac{1}{2}\int d^3r\,d^3r'n(\mathbf{r})n(\mathbf{r}')[\bar{g}(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))-1]\times v(|\mathbf{r}-\mathbf{r}'|)\;, \tag{9}$$

where $\bar{n}(\mathbf{r})$ is obtained from the sum rule

$$\int d^3r'n(\mathbf{r}')[\bar{g}(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))-1]=-1\;. \tag{10}$$

Thus $\bar{n}$ is a function of $\mathbf{r}$ and a functional of the density. The exchange-correlation potential $v_{\mathrm{xc}}(\mathbf{r})$, which is defined by

$$v_{\mathrm{xc}}(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})}\;, \tag{11}$$

becomes, in this approximation,

$$v_{\mathrm{xc}}(\mathbf{r})=v_1(\mathbf{r})+v_2(\mathbf{r})+v_3(\mathbf{r})\;, \tag{12}$$

where

$$\begin{aligned} v_1(\mathbf{r})&=\tfrac{1}{2}\int d^3r'n(\mathbf{r}')v(|\mathbf{r}-\mathbf{r}'|)[\bar{g}(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}))-1]\;,\\ v_2(\mathbf{r})&=\tfrac{1}{2}\int d^3r'n(\mathbf{r}')v(|\mathbf{r}-\mathbf{r}'|)[\bar{g}(|\mathbf{r}-\mathbf{r}'|,\bar{n}(\mathbf{r}'))-1]\;,\end{aligned} \tag{13}$$

$$v_3(r)=\tfrac{1}{2}\int d^3r'd^3r''n(\mathbf{r}')n(\mathbf{r}'')v(|\mathbf{r}'-\mathbf{r}''|)\times\frac{\partial\bar{g}(|\mathbf{r}'-\mathbf{r}''|,\bar{n})}{\partial\bar{n}(\mathbf{r}')}\frac{\delta\bar{n}(\mathbf{r}')}{\delta n(\mathbf{r})}\;.$$

Here, $\delta\bar{n}(\mathbf{r}')/\delta n(\mathbf{r})$ can be obtained from Eq. (10). We notice that $v_1(\mathbf{r})$ is different from $v_2(\mathbf{r})$. This is due to the fact that the WD and MWD schemes violate the symmetry property $\tilde{g}(\mathbf{r},\mathbf{r}')=\tilde{g}(\mathbf{r}',\mathbf{r})$ of the exact pair-correlation function. In practical applications using the MWD scheme,[15,16] $v_2(\mathbf{r})$ has been assumed to be equal $v_1(\mathbf{r})$, and $v_3(\mathbf{r})$ has either been neglected[15] or approximated by an expression valid for an electron gas.[16] In Sec. IV we will study the validity of these approximations for atoms.

B. Approximations based on formulations in reciprocal space

In the scheme due to Langreth, Perdew, and Mehl,[4–6] the exchange-correlation energy in Eq. (1) is rewritten as

$$E_{\mathrm{xc}}[n]=\int\frac{d^3k}{(2\pi)^3}E_{\mathrm{xc}}(\mathbf{k},n)\;, \tag{14}$$

where

$$E_{\mathrm{xc}}(\mathbf{k},n)=v(k)\tilde{S}(\mathbf{k},n)\;. \tag{15}$$

Here, $v(k)=4\pi/k^2$ is the Coulomb potential in Fourier space. The quantity $\tilde{S}$ is given by

$$\tilde{S}(\mathbf{k})=1+\tfrac{1}{2}\int n(\mathbf{r})n(\mathbf{r}')[\tilde{g}(\mathbf{r},\mathbf{r}')-1]\times\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')]d^3r\,d^3r'\;. \tag{16}$$

Instead of working with the pair-correlation function, Langreth and Mehl[6] (LM) write the wave-vector decomposition $E_{\mathrm{xc}}(\mathbf{k},n)$ of the exchange-correlation energy as

$$E_{\mathrm{xc}}(\mathbf{k},n)=E_{\mathrm{xc}}^{\mathrm{LD}}(\mathbf{k},n)+\frac{1}{2\pi k^2}\int d^3r\,K_F^2z_{\mathrm{xc}}(K_F,q;k)q^2\;, \tag{17}$$

which formally defines a function $z_{xc}(K_F,q;k)$. Here, E_{xc}^{LD} is the wave-vector decomposition of the LD energy functional, $K_F=[3\pi^2 n(\mathbf{r})]^{1/3}$ is the local Fermi wave vector, and $q(\mathbf{r})$ is equal to $|\nabla n(\mathbf{r})|/6n(\mathbf{r})$.

Guided by exact results for small $\mathbf{k}$ and using some rather subtle arguments, LM arrived at the following approximations for the exchange (z_x) and correlation (z_c) part of z_{xc}:

$$z_x(K_F,q;k)\simeq z_x(K_F,0;k) ,$$

$$z_c(K_F,q;k)\simeq z_c(K_F,0;k)\Theta(k-k_c) ,$$

where $k_c=6fq$ and where f is a parameter close to $\frac{1}{6}$. The quantity $z_c(K_F,0;k)$ was calculated in the random-phase approximation (RPA) parametrized form. Using these results together with Eqs. (14) and (17), LM found

$$E_{xc}[n]=E_{xc}^{LD}(n)+a\int d^3r\,|\nabla n|^2 n^{-4/3}(2e^{-F}-\tfrac{7}{9}) , \tag{18}$$

where

$$F=b\,|\nabla n(\mathbf{r})|\,[n(\mathbf{r})]^{-7/6}$$

and where E_{xc}^{LD} is the LD energy functional. The values of the constants a and b in atomic units are $a=\pi/[16(3\pi^2)^{4/3}]$ and $b=(9\pi)^{1/6}f$. Since the second term in Eq. (18) has been obtained using the RPA, it is important that electron-gas data obtained from the RPA are used also in the first term E_{xc}^{LD} in order to have the error in the LD term cancelled out by the gradient term. The potential v_{xc} can be obtained by using Eqs. (11) and (18) (for details, see Ref. 6).

For finite systems Langreth and Mehl[6] suggested a scheme which treats the exchange part exactly:

$$E_{xc}[n]=E_x+E_c^{LD}+a\int d^3r\,|\nabla n|^2 n^{-4/3}(2e^{-F}+18f^2) . \tag{19}$$

Here, E_x was represented by a functional due to Talman and Shadwick,[18] which, at least for atoms, is extremely close to the exact density functional for exchange effects only. In this work we choose for E_x the exact density functional for exchange effects, and for $v_x(\mathbf{r})=\delta E_x/\delta n(\mathbf{r})$ the exact exchange potential, which was first obtained by von Barth and Car[14] (the construction of the exact functionals will be briefly explained in Sec. III). It should be noted that the scheme in Eq. (19) does not follow from a straightforward division of $z_{xc}(K_F,q;k)$ in Eq. (17) in an exchange and a correlation part, and that it is valid only for finite systems.

III. NOTES ON THE DF EFFECTIVE-ORBITAL SCHEMES

As is well known, DF theory leads to simple Hartree-like equations,[2]

$$[-\tfrac{1}{2}\nabla^2+w(\mathbf{r})+V_H(\mathbf{r})+v_{xc}(\mathbf{r})]\phi_i(\mathbf{r})=e_i\phi_i(\mathbf{r}) , \tag{20}$$

whose solutions give the density according to

$$n(\mathbf{r})=\sum_1^N|\phi_i(\mathbf{r})|^2 . \tag{21}$$

[In Eq. (20), w and V_H are, respectively, the "external" potential from the nuclei and the electrostatic potential due to the electronic ground-state density $n(\mathbf{r})$]. The orbital eigenvalues $\{e_i\}$ are, in general, just auxiliary mathematical parameters, but are often, in practice, regarded as approximations to excitation energies.

Recently, a renewed interest in the physical interpretation of these eigenvalues has taken place, initiated mainly by Williams and von Barth,[12] which has resulted in a number of new results. Thus, it has been shown that the uppermost occupied eigenvalue e_N always gives the exact ionization potential I of the system regardless of its size,[19]

$$e_N=-I . \tag{22}$$

For metallic systems this result was obtained already in the pioneering paper by Kohn and Sham.[2] An excellent demonstration may be found in the recent review by Kohn and Vashista.[20] An earlier, approximate result by Perdew *et al.*[21] for finite systems gave

$$\epsilon_N\le -I+v_{xc}(\infty) ,$$

with $v_{xc}\ge 0$. The quantity $v_{xc}(\infty)$ was estimated to be small but nonzero by Perdew and Norman.[22] (This paper referred to the then forthcoming letter by Perdew *et al.*[21]) The work by Almbladh and von Barth shows that both inequalities above can actually be replaced by equalities.

Yet another somewhat unexpected recent result is that the fundamental band gap in an insulator is *not* given by the exact DF eigenvalues, despite the fact that it can be related to differences in ground-state energies.[23] Owing to the current interest in the DF eigenvalues, here we will compare the eigenvalues and the effective one-electron potential

$$v_{xc}(\mathbf{r})=\delta E_{xc}[n]/\delta n(\mathbf{r})$$

corresponding to approximate functionals with their exact counterparts.

The exact potential $v_{xc}(\mathbf{r})$ and the DF eigenvalues were obtained by the following method used by Almbladh and Pedroza[13] and by von Barth and Car.[14] The uniqueness theorem by Hohenberg and Kohn[1] implies that the effective potential of a set of one-electron orbital equations is uniquely determined by the density it produces via Eq. (21). Thus, by finding the effective potential that produces the exact density profile of a given system, one obtains the exact exchange-correlation potential v_{xc} without resorting to its definition as a variational derivative, and the exact DF eigenvalues. The v_{xc} (or v_x) potential was found by using a trial potential in Eq. (20), involving some 25 parameters, which was varied until the density computed from the orbitals agreed with the given correlated (or Hartree-Fock) reference density to within a prescribed accuracy (usually 0.01%). Since one has access to a reference density only in a finite (but large) region in space, the fitting procedure only gives the DF potential and eigenvalues to within a constant. This constant is uniquely determined by the eigenvalue theorem in Eq. (22) (or its counterpart in the DF theory for exchange), and thus one finally obtains the potential and eigenvalues on an absolute energy scale. For further details the reader is referred to Refs. 13 and 14.

TABLE I. Total energies as given by different schemes. The essentially exact correlated values are also given. Energies in eV. The relative errors in percent are given within parentheses.

Atom	$-E$ MWD	LD	LMxc	LMc	HF	Exact
H^-		14.0(2.8)		14.6(1.4)	13.3(7.6)	14.4[a]
He	80.98(2.5)	77.15(2.4)	79.21(0.2)	79.10(0.1)	77.88(1.5)	79.02[a]
Li^+	200.8(1.4)	194.4(1.9)	197.8(0.2)	197.8(0.2)	196.9(0.6)	198.1[a]
Be^{2+}	374.84(0.8)	365.86(1.6)	371.77(0.2)	370.65(0.3)	370.38(0.4)	371.85[a]
Be	402.00(0.7)	393.13(1.5)	397.94(0.3)	398.95(0.04)	396.56(0.6)	399.11[a]
Ne	3506.5(0.05)	3489.4(0.5)	3503.0(0.2)	3507.9(0.01)	3498.1(0.3)	3508.4[b]

[a] See Ref. 25.

[b] Reference 26.

IV. RESULTS

Here we compare self-consistent results obtained using the nonlocal functionals discussed in Sec. II with essentially exact results for a number of light atoms. For the two-electron atoms H^-, He, Li^+, and Be^{2+}, and for the neutral Be atom, we have access to correlated densities,[24] whereas for the Ne atom we have access only to the Hartree-Fock (HF) density.

Details concerning the correlated wave functions are given in Ref. 25. Here we just mention that our correlated wave functions give 98% or more of the actual correlation energy, corrected for relativistic and mass-polarization effects, and that they give a charge density at the nucleus and low-order moments $\int r^n \rho(r) d^3r$ in good agreement with the best available literature data.

There is a partial overlap between our results and those by Langreth and Mehl.[6] We show them again, either because they have been obtained in a different manner (e.g., for different values of the parameter f) or because more details are given.

In Table I we give total energies as calculated using the different schemes. The LD approximation was evaluated using electron-gas data by Ceperley and co-workers,[27] and the LM schemes were evaluated using $f = 0.17$. By "exact" we mean results obtained from the correlated wave functions.[24] From Table I we see that the LM nonlocal schemes, "LMxc" for both exchange and correlation and "LMc" for only the correlation effects, give much better total energies than the HF and LD approximations. For Li^+ and Be^{2+} one could, in the LMc scheme, improve the results by choosing $f = 0.14$, but since the functionals are universal, one should not regard f as a system-dependent parameter. The MWD scheme also gives good results, especially for atoms with valence shells.

In Table II we show the exchange-correlation energies for which we observe the same trends as in the preceding table. The LMxc scheme gives results very close to the exact values for all systems tested.

In Table III we give the correlation energies obtained using the LMc scheme, which treats the exchange effects exactly [cf. Eq. (19)]. For the He, Be, and Ne atoms this scheme gives correlation energies accurate to 10% or better. For systems with no valence electrons (Li^+, Be^{2+}) and for the somewhat special case of the H^- ion, the accuracy of the LMc is not as good, but it is, anyhow, much better than the accuracy of the LD approximation, which usually overestimates the correlation energy by a factor of 2 or more. In the case of the Li^+ and Be^{2+} ions we would have obtained a better accuracy of the LMc scheme by instead choosing the value $f = 0.14$ of the parameter in Eq. (11) (giving 0.041 a.u. for Li^+ and 0.029 a.u. for Be^{2+}). However, in general, $f = 0.17$ gives better results and is thus the preferred value.

The properties discussed so far mainly probe the accuracy of the exchange-correlation *functional* E_{xc} rather than its functional derivative, the exchange-correlation potential v_{xc}. We now turn to properties like density profiles and DF eigenvalues which more directly test the accuracy of v_{xc}. In Figs. 1–3 we show the relative charge-

TABLE II. Exchange-correlation energies as given by different schemes compared with exact values. Energies in eV. Relative errors in percent are given within parentheses.

Atom	$-E_{xc}$ MWD	LD	LMxc	Exact
He	31.3(7.9)	26.4(9.0)	28.8(0.5)	29.0[a]
Li^+	49.0(6.3)	41.6(9.8)	45.4(1.5)	46.1[a]
Be^{2+}	66.4(5.1)	56.6(10.4)	62.0(1.9)	63.2[a]
Be	77.8(3.2)	68.6(9.0)	73.7(2.3)	75.4[a]
Ne	335.5(1.3)	318.7(6.2)	332.8(2.1)	339.9[b]

[a] See Ref. 13.

[b] $E_{xc} = E_x^{DF} + E_c$.

TABLE III. Correlation energies as given by different schemes compared with exact values. Energies in eV. Relative errors in percent are given within parentheses.

Atom	$-E_c$ LD	LMc	Exact
H^-	1.91(75)[a]	1.39(28)	1.09[b]
He	3.05(168)	1.25(9.7)	1.14[b]
Li^+	3.65(212)	0.82(30)	1.17[b]
Be^{2+}	4.08(240)	0.27(78)	1.20[b]
Be	6.12(139)	2.39(7)	2.56[b]
Ne	20.1(90)	10.3(3)	10.6[c]

[a] Finite atom (see text).

[b] Reference 13.

[c] See Ref. 26.

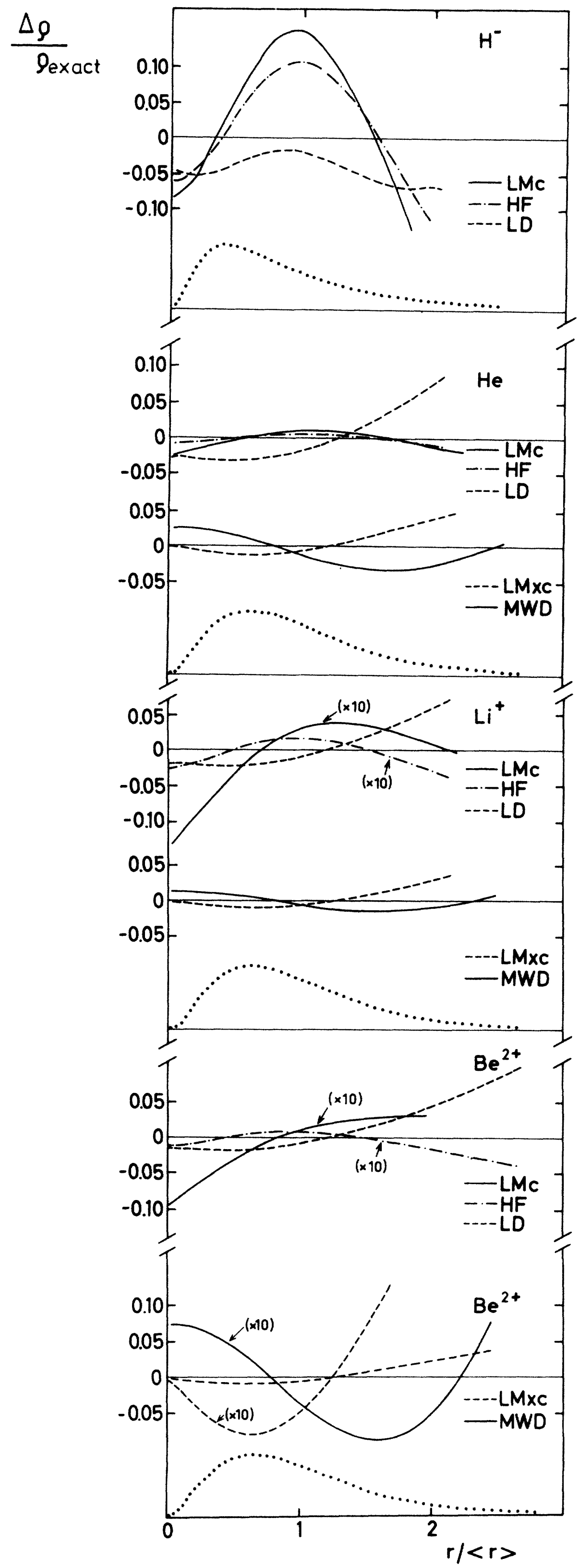

FIG. 1. Relative charge-density differences $\Delta\rho/\rho_{\text{exact}}$ for H^-, He, Li^+, and Be^{2+} as given by different schemes. The variable $r/\langle r\rangle$ is used, where $\langle r\rangle$ is given in the last column of Table IV. The radial charge density $4\pi\rho r^2$ (dotted line) is also given.

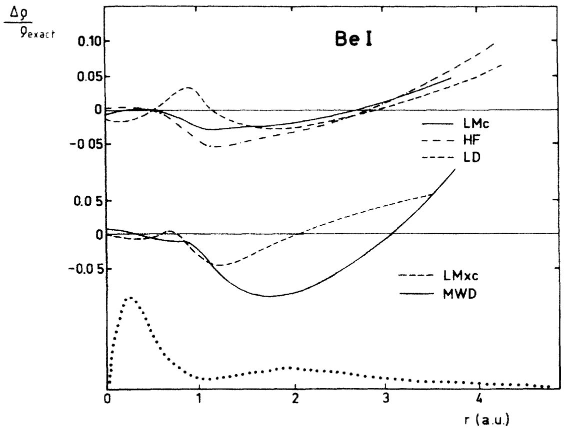

FIG. 2. Relative charge-density differences $\Delta\rho/\rho_{\text{exact}}$ for the neutral Be, as given by different schemes. The radial charge density $4\pi\rho r^2$ (dotted line) is also given.

density differences between exact densities and densities from the various approximations used. For comparison, we also present the HF and LD differences already published.[25]

For the case of the H^- ion, which is unstable in the LD approximation,[28] we obtained an LD density profile by confining the system within a finite but large sphere as described in Ref. 25. The reason why the LD approximation fails to describe H^- properly (and presumably other negative ions as well) is due to the fact that the LD potential tends exponentially to zero, whereas the exact v_{xc} tends to $-1/r$ far away from the system,[19] and therefore the LD potential is not attractive enough to give a solution with a negative eigenvalue for the H^- system. We were also unable to obtain proper solutions for H^- using the MWD and the LMxc schemes. We notice in Fig. 1 that whereas the LMc scheme properly describes H^- as a bound system, it gives a somewhat poor density.

We see in Figs. 1 and 2 that within the 1*s* shell the HF approximation gives the most accurate densities, followed by, in order of decreasing accuracy, the LMc, LMxc, MWD, and LD approximations. The LMc densities are

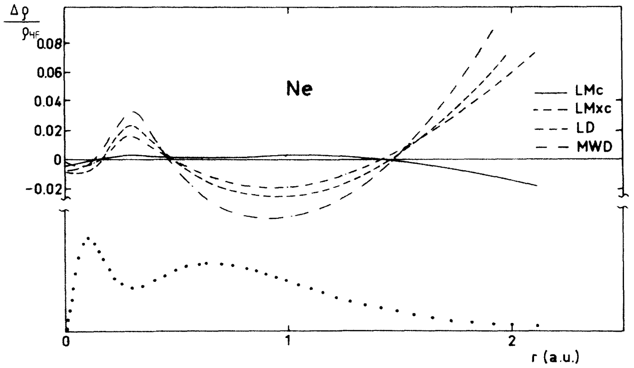

FIG. 3. Relative charge-density differences $\Delta\rho/\rho_{\text{HF}}$ for the neutral Ne, as given by different schemes. The radial charge density $4\pi\rho r^2$ (dotted line) is also given.

TABLE IV. Orbital eigenvalues (e_i), charge densities at the nucleus [$n(0)$], and expectation values of r ($\langle r \rangle$), as given by different schemes, compared to exact results. Atomic units are used, except for energies, which are given in eV.

Atom		MWD	LD	LMxc	LMc	HF	Exact
H^-	$-e_{1s}$		(0)		2.28	1.36	0.76[a]
	$n(0)$		0.314		0.301	0.309	0.328[b]
	$\langle r \rangle$				2.39	2.50	2.71[b]
He	$-e_{1s}$	15.81	15.51	15.78	26.12	26.12	24.59[a]
	$n(0)$	3.72	3.56	3.62	3.53	3.60	3.63[b]
	$\langle r \rangle$	0.929	0.959	0.939	0.927	0.927	0.929[b]
Li^+	$-e_{1s}$	60.08	59.59	60.41	77.01	75.92	75.65[a]
	$n(0)$	13.88	13.44	13.69	13.52	13.67	13.71[b]
	$\langle r \rangle$	0.573	0.585	0.577	0.574	0.572	0.573[b]
Be^{2+}	$-e_{1s}$	131.3	130.9	132.0	155.1	154.3	153.9[a]
	$n(0)$	34.65	35.43	34.38	34.07	34.36	34.40[b]
	$\langle r \rangle$	0.414	0.421	0.417	0.415	0.414	0.414[b]
Be	$-e_{1s}$	110.36	105.04	105.85	113.20	128.71	115.10[a]
	$-e_{2s}$	5.53	5.71	5.99	9.52	8.44	9.32[a]
	$n(0)$	35.59	34.86	35.39	35.12	35.39	35.37[b]
	$\langle r \rangle$	1.572	1.522	1.505	1.513	1.532	1.494[b]
Ne	$-e_{1s}$	837.4	824.8	827.2	838.7	891.7	838.7[c]
	$-e_{2s}$	35.8	35.9	36.5	48.4	52.5	46.8[c]
	$-e_{2p}$	13.7	13.6	13.6	24.8	23.1	23.1[c]
	$n(0)$	615.70	614.52	617.80	617.84	619.92	
	$\langle r \rangle$	0.810	0.802	0.798	0.787	0.789	

[a] Reference 13.
[b] Reference 25.
[c] DF theory for exchange only.

almost as accurate as the HF ones within the $1s$ shell. Turning to the valence-electron region, we see that in the Be $2s$ shell the LMc scheme gives the best density, followed by, in order of decreasing accuracy, the LMxc, LD, HF, and MWD approximations. Actually, the LD and LMxc results are of comparable accuracies, the LD result being better in the intershell region and the LMxc scheme being better further out in the atom. In the case of the Be atom, the correlation effects are unusually strong, as evidenced by the relatively large difference between the HF and the "exact" density. This is not expected to be the case of Ne discussed below. The MWD density for Be, finally, is quite accurate in the $1s$ shell but not as good in the valence-electron region.

In case of the Ne atom we can only make a comparison with the HF density which, however, is expected to be rather close to the exact one (Fig. 3). We observe the same trends as before. The LMc density is everywhere very close to the HF one, followed by the LMxc and LD densities. The MWD scheme is quite accurate in the $1s$ shell but inferior to the LD approximation in the valence shell. The lower accuracy of the MWD densities for the multishell systems Be and Ne is probably due to an inaccurate representation of the intershell correlation as pointed out by Gunnarsson *et al.*[8] To improve the performance of the WD and MWD schemes, these workers have proposed a somewhat *ad hoc* procedure of "shell partitioning" where the WD scheme is used only for obtaining the intrashell exchange-correlation energy and where the remaining intershell part is estimated using the LD approximation. The corresponding potential has not yet been worked out. We notice, however, that one would need the variational derivatives $\delta\phi_i(\mathbf{r})/\delta n(\mathbf{r}')$ of the DF orbitals with respect to density variations. These derivatives involve the Green's function of the orbital equation and are quite difficult to compute.

TABLE V. The MWD approximation to the exchange-correlation energy $E_{\rm xc}$ evaluated using two different models for the pair correlation [see Eqs. (7) and (8)]. Energies in eV. Relative errors in percent are given within parentheses.

		$-E_{\rm xc}$	
Atom	g_1	g_2	Exact
H^-	12.60(9.6)	12.35(7.8)	11.51[a]
He	30.99(6.8)	30.91(6.5)	29.03[a]
Li^+	48.82(5.9)	49.04(6.4)	46.11[a]
Be^{2+}	66.40(5.0)	66.97(5.9)	63.25[a]
Be	77.93(3.4)	74.78(0.8)	75.36[a]
Ne	337.1(0.8)	314.0(7.6)	339.9[b]

[a] Reference 13.
[b] $E_{\rm xc} = E_x^{\rm DF} + E_c$.

In Table IV we give $n(0)$, the charge density at the nucleus, and the moment

$$\langle r \rangle = \int r n(\mathbf{r}) d^3 r \Big/ \int n(\mathbf{r}) d^3 r \ .$$

We notice that the MWD scheme gives very accurate values of $\langle r \rangle$ for the He isoelectronic series, and that the LMxc scheme gives a density at the nucleus which is slightly better than that obtained from the LMc scheme.

As far as eigenvalues are concerned (Table IV), only the LMc scheme gives a substantial improvement compared to the LD approximation. The accuracy of the LMc eigenvalues is a consequence of the fact that v_x, the major part in v_{xc}, is treated exactly.

The results on charge-density differences can be understood by looking at the exchange-correlation potentials in Figs. 4 and 5 and the exact exchange potential for Ne in Fig. 6. The LMxc potentials show some exact features, like the large negative value for small r and the peaks at the intershell regions, but they diverge faster than the exact potentials for small r and are inaccurate for very low densities far out.[6] The MWD potentials are close to those in the LMxc scheme, but it does not reproduce the structure in the intershell region. The LMxc and MWD schemes give a reasonable representation of v_{xc} for the two-electron systems, but are unable to reproduce the finer details. In Figs. 7 and 8 we show the difference between approximate and exact exchange-correlation potentials. We see that in the LMxc scheme this difference is more constant than in LD scheme, which explains the better accuracies of the LMxc density profiles.

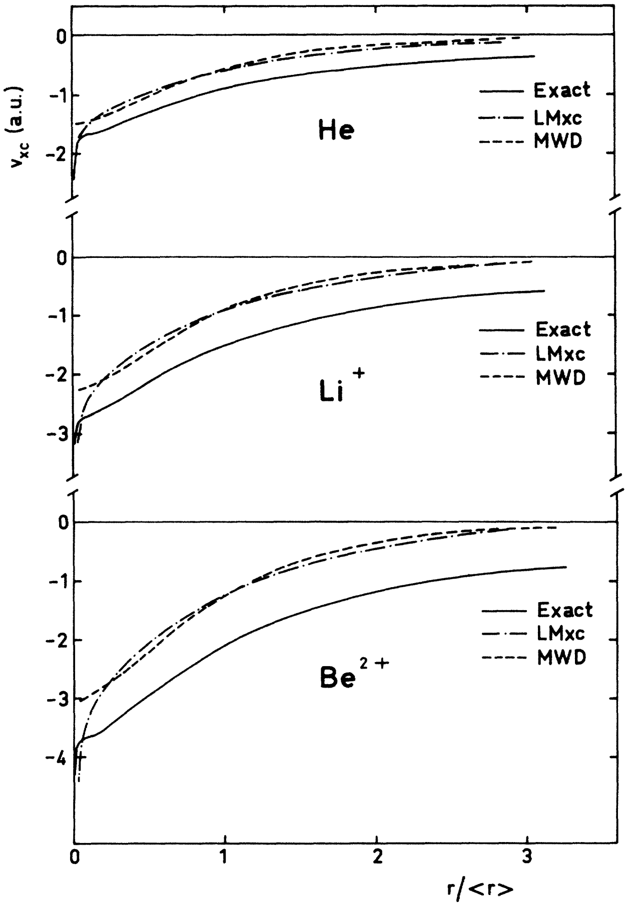

FIG. 4. Approximations to the exchange-correlation potential $v_{xc}(r)$ compared to exact results for He, Li$^+$, and Be^{2+}. The variable $r/\langle r \rangle$ is used and the potentials are given in atomic (Hartree) units.

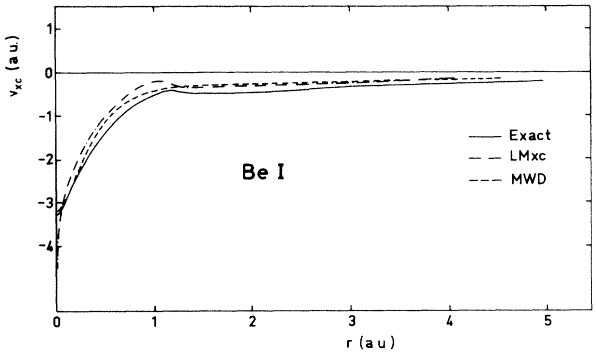

FIG. 5. Approximate and exact results for exchange-correlation potential $v_{xc}(r)$ for the case of neutral Be. Units are a.u.

In Fig. 9 we compare the exact correlation potential $v_c = v_{xc} - v_x$ with the correlation potential in the LMc scheme. For the two-electron systems the LMc correlation correction to the effective potential does not bring it closer to the exact potential, despite the fact that the LMc correlation correction to the *energy* is remarkably accurate. For neutral Be, Fig. 10, we notice that the LMc correlation potential (except for small r) is in reasonable agreement with the exact one, particularly in the 2s-shell region. As a consequence the LMc scheme significantly improves the charge density compared to HF theory in this case.

In summary, the properties which directly probe the quality of the exchange-correlation potential give a partly different picture of the performance of the approximate functionals than does the total energy. Thus, whereas the MWD scheme gives energies which are much better than the LD energies, it does not, in general, give correspond-

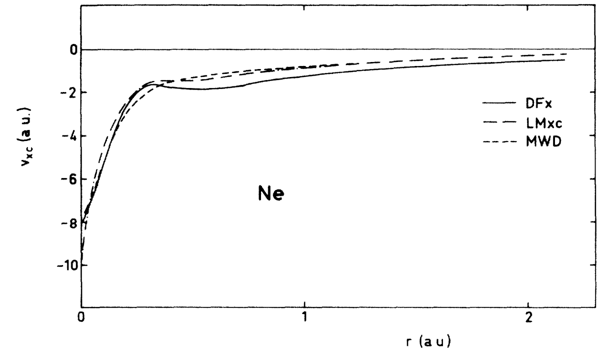

FIG. 6. Approximate exchange-correlation potentials $v_{xc}(r)$ as compared to the exact exchange-only potential (DFx) for Ne. Units are a.u.

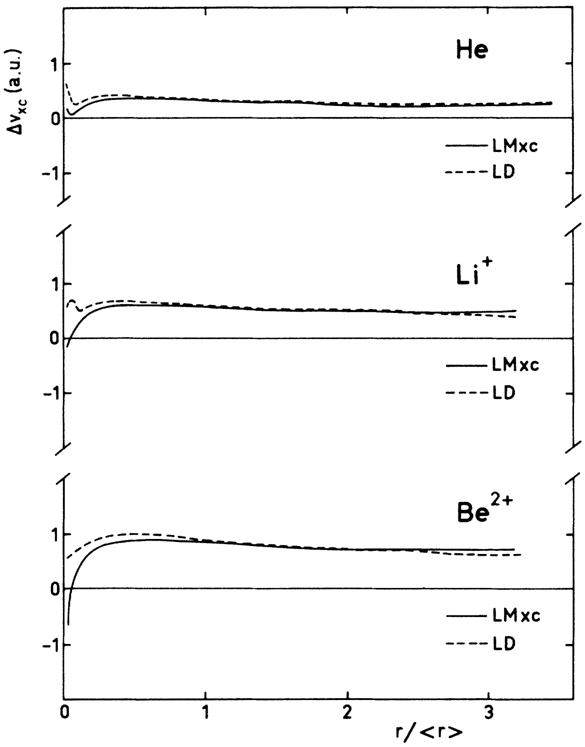

FIG. 7. Differences $\Delta v_{xc}=v_{xc}^{\mathrm{LD,LMxc}}-v_{xc}$ for He, Li$^+$, and Be^{2+}. Units are a.u.

ing improvements of densities and potentials. Also, the LMxc scheme gives very good energies, but they give potentials and densities which are usually only moderately better than their LD counterparts. As remarked by Williams and von Barth,[12] the functional differentiation used to constructed v_{xc} probes fine details in the functional $E_{xc}[n]$, which seems to enhance inaccuracies inherent in approximate schemes.

Finally, in the rest of this section we will discuss some aspects related to the MWD scheme. We show in Table V the MWD approximation to exchange-correlation energy E_{xc} as calculated with $\bar{g}_1$ and $\bar{g}_2$ [Eqs. (7) and (8), respectively] and the HF density profile. For the He isoelectronic series the results from $\bar{g}_1$ and from $\bar{g}_2$ agree within 1% or less, except for H$^-$, where the difference is about 2%. For the multishell systems Be and Ne, however, the MWD results are more sensitive to the model pair correlation used. This may be due to an inaccurate representation of intershell exchange and correlation effects. A second aspect is illustrated by Figs. 11, 12, and 13, where the potentials $v_1(\mathbf{r})$, $v_2(\mathbf{r})$, and $v_3(\mathbf{r})$, defined by Eq. (13), are shown. We notice that the lack of symmetry in the pair-correlation function with respect to $\mathbf{r}$ and $\mathbf{r}'$ produces a term $v_2(\mathbf{r})$ different from $v_1(\mathbf{r})$, contrary to the exact re-

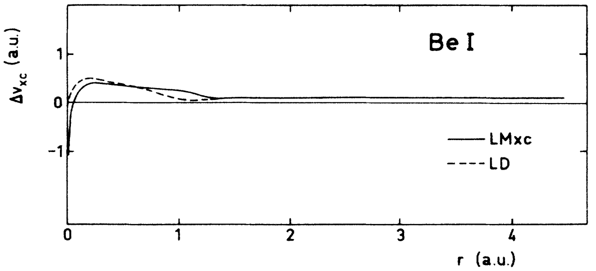

FIG. 8. Differences $\Delta v_{xc}=v_{xc}^{\mathrm{LD,LMxc}}-v_{xc}$ for neutral Be. Units are a.u.

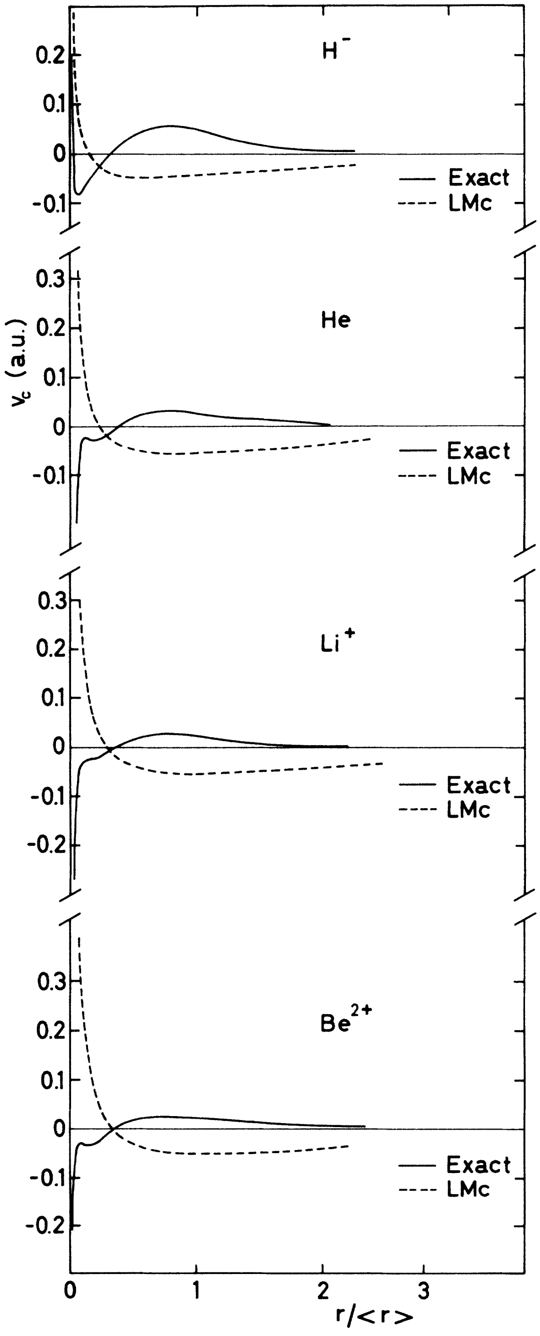

FIG. 9. Exact correlation potential v_c (solid line) and the corresponding potential as given by the LMc scheme for the He isoelectronic series. Units are a.u.

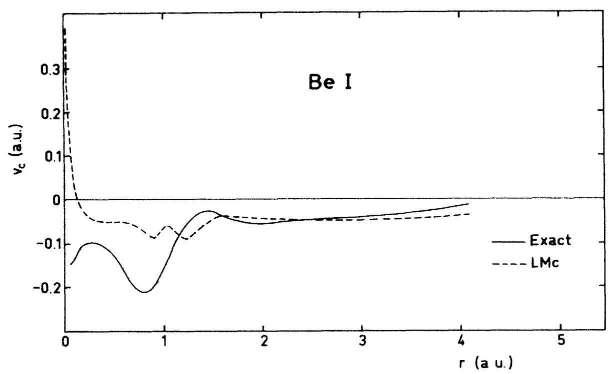

FIG. 10. Exact correlation potential v_c (solid line) and the corresponding potential as given by the LMc scheme for the neutral Be. Units are a.u.

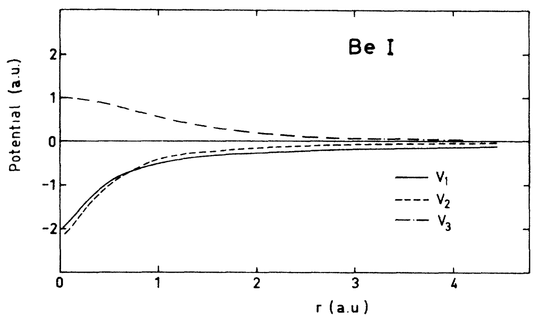

FIG. 12. Different parts (see text) of the exchange-correlation potential $v_{xc}(r)$ in the MWD scheme for neutral Be. Units are a.u.

sult. A third aspect, also evident in Figs. 11—13, is the size of $v_3(\mathbf{r})$ compared with $v_1(\mathbf{r})$. It is clear that $v_3(\mathbf{r})$ is appreciable, although it has shorter range than $v_1(\mathbf{r})$. Thus, at least for atoms, it is not justified to neglect this term. This is also inappropriate in the homogeneous limit, as pointed out by von Barth[3] and others. Thus, the approximation used by Kerker[15] to neglect v_3 appears to be questionable. The approximation[15,16] to replace v_1+v_2 by $2v_1$ seems less severe, judging from the results in Figs. 11—13.

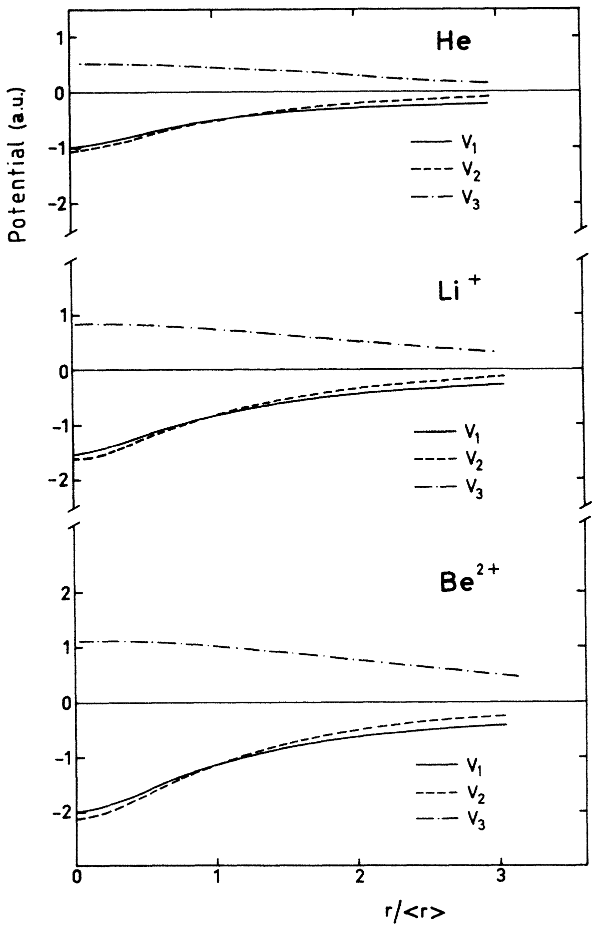

FIG. 11. Different parts [see text, Eq. (13)] of the exchange-correlation potential $v_{xc}(r)$ in the MWD scheme for He, Li$^+$, and Be^{2+}. Units are a.u.

V. CONCLUSIONS

In this work we have compared results obtained using the approximate LD, LM, and MWD density functionals with essentially exact results for light atoms. We have found that the LM schemes give results which are markedly better than those obtained using the LD approximation. The "LMc" scheme, which treats the exchange potential exactly, was found to give particularly good results.

In a recent work the LMc scheme has been applied to molecules and has been found to give a substantial improvement over the LD approximation also in that case.[29] Also, the MWD scheme was found to give significant improvements beyond the LD approximation for total energies, but gave improvement for the effective potential (v_{xc}) or the energy eigenvalues only for the case of two-electron systems. In fact, a general finding is that approximate functionals usually give better results for total energies than they do for effective potentials, eigenvalues, and density profiles.

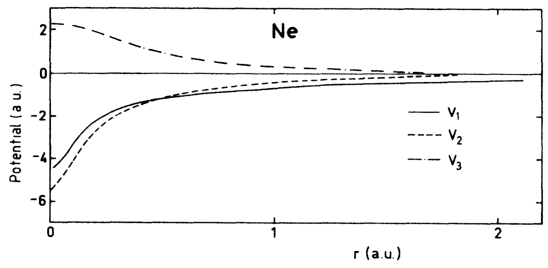

FIG. 13. Different parts (see text) of the exchange-correlation potential $v_{xc}(r)$ in the MWD scheme for neutral Ne. Units are a.u.

We have also tested the sensitivity of the MWD approximation to the model pair correlation used. We have found it essential to fulfill the requirement that the pair correlation should be non-negative. The MWD results were then found to be unsensitive to the model pair correlation for atoms with one single shell but more sensitive for multishell atoms. Finally, we have tested some additional approximations used in applications of the MWD scheme. We have found it essential to keep that term in v_{xc} which arises from the functional derivative of the pair-correlation function.

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