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Baerends, E.J.; van Leeuwen, R.

published in

Physical Review A. Atomic, Molecular and Optical Physics
1994

DOI (link to publisher)

[10.1103/PhysRevA.49.2421](https://doi.org/10.1103/PhysRevA.49.2421)

document version

Publisher's PDF, also known as Version of record

[Link to publication in VU Research Portal](#)

citation for published version (APA)

Baerends, E. J., & van Leeuwen, R. (1994). Exchange-correlation potential with correct asymptotic behavior. *Physical Review A. Atomic, Molecular and Optical Physics*, 49(4), 2421-2431.
<https://doi.org/10.1103/PhysRevA.49.2421>

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Exchange-correlation potential with correct asymptotic behavior

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(Received 8 June 1993)

In this work we analyze the properties of the exchange-correlation potential in the Kohn-Sham form of density-functional theory, which leads to requirements for approximate potentials. Fulfilment of these requirements is checked for existing gradient-corrected potentials. In order to examine the behavior of approximate potentials over all space we compare these potentials with exact Kohn-Sham potentials calculated from correlated densities using a newly developed iterative procedure. The main failures in the existing gradient-corrected potentials arise in the asymptotic region of the atom where these potentials decay too fast and at the atomic nucleus where the potentials exhibit a Coulomb-like singular behavior. We show that the main errors can be corrected by a simple potential in terms of the density and its gradients leading to considerably improved one-electron energies compared to the local-density approximation. For Be and Ne it is shown that the electron density is improved in the outer region.

PACS number(s): 31.20.Sy

I. INTRODUCTION

In the past few years there has been considerable progress within density-functional theory [1] in the calculation of properties of electronic systems ranging from solids to atoms and molecules. This progress is due to the introduction of gradient-corrected density functionals [2–5] that give an overall improvement to the exchange-correlation energies of the local-density approximation (LDA). For instance, the atomization energies of a standard set of molecules are improved by an order of magnitude compared to LDA [6], thereby correcting the overbinding of LDA. There are also successful applications of nonlocal corrections in transition metal chemistry [7] and solid-state and surface physics [8]. (Although the gradient-corrected potentials are still local, we follow the conventional nomenclature of “nonlocal corrections” to distinguish from the LDA.) However, several other features are not improved by the present day nonlocal corrections. This is especially the case for properties that are sensitively dependent on the behavior of the exchange-correlation potential. One can, for instance, prove rigorously [9,10] that the eigenvalue of the highest occupied Kohn-Sham orbital represents the ionization energy of the system. However, typical errors in LDA for this quantity are 5 eV. This same error prevents the calculations of bound state solutions for negative ions as LDA gives an unbound outer electron with positive eigenvalue. The origin of this error can be traced to the incorrect asymptotic decay of the LDA exchange-correlation potential. This potential has an exponential decay into the vacuum as can directly be seen from the exponential decay of the density itself. On physical grounds, however, (see for a proof [9]), the outer electron should experience the mean field of the ion it leaves behind, i.e., a potential that decays Coulombically like $-1/r$. The LDA electron is therefore too weakly bound and for negative ions even unbound. This breakdown of LDA in the outer region of the atom or molecule is also

reflected in the exchange-correlation energy per particle $\epsilon_{xc}(r)$ which can equivalently be seen as the potential due to the exchange-correlation hole and which has an asymptotic decay like $-1/2r$. The LDA in this case gives again an exponential decay. In the electron gas this quantity ϵ_{xc} is usually expressed in terms of the Wigner-Seitz radius r_s , representing the mean electronic distance which is proportional to $\rho^{-1/3}$. If the local-density approximation is applied to the outer regions of atoms and molecules r_s grows exponentially and loses its meaning as a mean interelectronic distance which should grow linearly. If one believes (for intuitive physical reasons) that the mean electronic distance determines ϵ_{xc} then the bad representation of this quantity by LDA explains the failure of LDA in this region.

One might now wonder if the present day nonlocal gradient corrections give any improvement for this asymptotic failure of LDA. Somewhat surprisingly, this is not the case. Although they give large improvements in energies they give little improvement in the asymptotic behavior of the exchange-correlation potential. This is immediately apparent from the fact, undoubtedly noted by many density-functional theory (DFT) practitioners, that the gradient-corrected potentials yield almost no improvement in the LDA eigenvalues, which are generally in error by 5–6 eV. In this paper we discuss, apart from the fairly well-known asymptotic behavior, other requirements which are to be fulfilled by the exact exchange or exchange-correlation potential. Those requirements apply to limiting or special situations ($r \rightarrow \infty, r \downarrow 0$), transition regions from one atomic shell to the next, limit of homogeneous electron gas) and also comprise invariance conditions (translational, rotational). They are useful in constructing approximate Kohn-Sham potentials. In Sec. III we use the formulated requirements to examine some of the presently used nonlocal functionals, in particular, the Becke correction for exchange and the Perdew correction for correlation. In order to investigate the potentials at arbitrary r , we need the exact Kohn-Sham po-

tential over all space. In Sec. IV we discuss a general procedure to construct the Kohn-Sham exchange-correlation potential from a given electron density ρ . The procedure is simple and is applicable to both atoms and molecules and to systems with an arbitrary number of electrons. This procedure is used to generate exact Kohn-Sham potentials from very accurate (highly correlated) densities of Be and Ne. This affords detailed insight into the strengths and weaknesses of existing approximations. As a first step towards improved potentials, we propose in Sec. V a model Kohn-Sham potential which exhibits the correct asymptotic behavior and also displays atomic-shell structure. This potential gives a large improvement over the LDA eigenvalues and is in fact capable of yielding good ionization energies as determined from the highest occupied Kohn-Sham orbital energy. It also improves the asymptotic decay of the electron density. In Sec. VI we present a summary and conclusions.

II. NONLOCAL EXCHANGE-CORRELATION POTENTIALS: REQUIREMENTS

In this section we will discuss some of the requirements that approximate exchange-correlation potentials have to satisfy. In connection with this we shall demonstrate in the next section which of these requirements are lacking with some of the presently used nonlocal potentials.

Scaling. The exchange energy within density-functional theory may be defined as [11]

$$E_x[\rho] = \int \rho(\mathbf{r}) \epsilon_x(\mathbf{r}) d\mathbf{r}, \quad (1)$$

in which the potential of the exchange hole $\epsilon_x(\mathbf{r})$ or equivalently the exchange energy density per electron is defined as

$$\epsilon_x(\mathbf{r}) = -\frac{1}{2\rho(\mathbf{r})} \int \frac{|\gamma_s(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2)$$

Here γ_s is the Kohn-Sham one-particle density matrix, constructed from a determinant of Kohn-Sham orbitals. The exchange functional of Eq. (1) is a functional of the density as the Kohn-Sham orbitals of which the one-particle density matrix γ_s is composed are uniquely determined by the density (an explicit scheme for doing this is presented in Sec. IV). The exchange functional satisfies the following *scaling* relation [12]:

$$E_x[\rho_\lambda] = \lambda E_x[\rho], \quad (3)$$

in which ρ_λ is the following scaled density:

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r}). \quad (4)$$

The exchange potential which is defined as the functional derivative of the exchange functional satisfies the following scaling relation [11,12]:

$$v_x([\rho_\lambda]; \mathbf{r}) = \lambda v_x([\rho]; \lambda \mathbf{r}). \quad (5)$$

Using the scaling relation (3) one can prove the Levy-Perdew relation [12]:

$$E_x[\rho] = - \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_x(\mathbf{r}) d\mathbf{r}. \quad (6)$$

Any approximate exchange potential should satisfy Eq. (5). It is then possible to define an approximate exchange energy using the Levy-Perdew relation (6). We will return to this relation between potential and energy below.

There are no known scaling relations for the correlation energy functional defined as

$$E_c[\rho] = E_{xc}[\rho] - E_x[\rho], \quad (7)$$

in which E_{xc} is the Kohn-Sham exchange-correlation energy which can be defined, for instance, using the coupling strength integration method [13–16].

Asymptotic behavior. An approximate functional or potential also has to satisfy some requirements with respect to asymptotic behavior. First of all it follows from Eq. (2) using the sum rule property of the one-particle density matrix γ_s , that

$$\epsilon_x(\mathbf{r}) \sim -\frac{1}{2r} \quad (r \rightarrow \infty). \quad (8)$$

Thus the potential of the exchange hole has a Coulombic asymptotic behavior. The exchange potential has to fulfill a similar type of relation [17,18]:

$$v_x(\mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty). \quad (9)$$

The asymptotic behavior of the potential due to the (coupling strength integrated) Coulomb hole is not known. We can only say that the correlation potential must decay faster than a Coulombic potential at infinity. This follows from the asymptotic $-1/r$ decay of the total Kohn-Sham potential [19,10]:

$$v_{xc}(\mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty) \quad (10)$$

and the similar behavior of the exchange potential of Eq. (9). This result is consistent with the fact that the Coulomb hole of the coupling strength integrated two-particle density matrix integrates to zero electrons.

Weak inhomogeneity. Further known properties of the exchange functional follow from the gradient expansion of the weakly varying electron gas [20] or from the semiclassical expansion of the Kohn-Sham one-particle density matrix [21]. This gives the following approximate nonlocal correction to the exchange energy (for the spin unpolarized case):

$$E_x[\rho] = -\beta \int \frac{(\nabla \rho)^2}{\rho^{4/3}} d\mathbf{r}. \quad (11)$$

This is the nonlocal correction used in the $X\alpha\beta$ approximation [22]. For weakly varying densities there is a known gradient expansion for the correlation energy. The nonlocal correction is (up to second order) given by

$$E_c[\rho] = \int C(\rho) \frac{(\nabla \rho)^2}{\rho^{4/3}} d\mathbf{r}, \quad (12)$$

in which $C(\rho)$ is a local function of the electron density [23].

Translational and rotational invariance. Two requirements which must be fulfilled by any density functional representing a physical quantity are translational and ro-

tational invariance. The question of translational invariance, for instance, arises naturally in the discussion of the asymptotic $-1/r$ behavior of the energy densities and the exchange or exchange-correlation potentials, where r should not refer to the distance from the arbitrary origin of the coordinate system. Denoting a physical quantity by A , translational invariance means

$$A[\rho'] = A[\rho], \quad (13)$$

with

$$\rho'(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R}), \quad (14)$$

in which \mathbf{R} is an arbitrary translation vector. This means physically that A should not change when we translate our coordinate system. If we define

$$a([\rho]; \mathbf{r}) = \frac{\delta A}{\delta \rho(\mathbf{r})}[\rho] \quad (15)$$

then it follows that

$$a([\rho']; \mathbf{r}) = a([\rho]; \mathbf{r} + \mathbf{R}). \quad (16)$$

This does not hold for arbitrary $a([\rho]; \mathbf{r})$ but it does hold if a is the functional derivative of a translational invariant functional A . This equation is easily proved if one uses

$$\begin{aligned} \delta A[\rho] &= \int \delta \rho(\mathbf{r}) a([\rho]; \mathbf{r}) d\mathbf{r} \\ &= \int \delta \rho(\mathbf{r} + \mathbf{R}) a([\rho]; \mathbf{r} + \mathbf{R}) d\mathbf{r} \\ &= \int \delta \rho'(\mathbf{r}) a([\rho]; \mathbf{r} + \mathbf{R}) d\mathbf{r}. \end{aligned} \quad (17)$$

Comparing this equation with

$$\delta A[\rho'] = \int \delta \rho'(\mathbf{r}) a([\rho']; \mathbf{r}) d\mathbf{r} \quad (18)$$

yields Eq. (16) as both variations should be equal for any variation $\delta \rho'(\mathbf{r}) = \delta \rho(\mathbf{r} + \mathbf{R})$. We will now take $A = E_x$ and $a = v_x$. Noting the explicit \mathbf{r} dependence in the Levy-Perdew relation between E_x and v_x one might wonder whether this relation is translationally invariant. The exact exchange potential of course satisfies the translational invariance equation (16). Then it follows from the Levy-Perdew relation (6), if we insert ρ' , that

$$E_x[\rho'] = E_x[\rho] + \mathbf{R} \cdot \int \rho(\mathbf{r}) \nabla v_x([\rho]; \mathbf{r}) d\mathbf{r}. \quad (19)$$

Translational invariance requires the last term in this equation to be zero. As this should be true for any vector \mathbf{R} we obtain (after carrying out a partial integration)

$$\int v_x(\mathbf{r}) \nabla \rho(\mathbf{r}) d\mathbf{r} = 0. \quad (20)$$

Translational invariance thus gives an additional condition on the potential. The above formula is a special case of a more general result which follows directly from Eq. (13):

$$\begin{aligned} A[\rho] &= A[\rho'] \\ &= A[\rho + \mathbf{R} \cdot \nabla \rho + O(R^2)] \\ &= A[\rho] + \int \frac{\delta A}{\delta \rho(\mathbf{r})} \mathbf{R} \cdot \nabla \rho(\mathbf{r}) d\mathbf{r} + O(R^2). \end{aligned} \quad (21)$$

As this equation should be valid for any translation vector \mathbf{R} it follows that

$$\int \frac{\delta A}{\delta \rho(\mathbf{r})} \nabla \rho(\mathbf{r}) d\mathbf{r} = 0. \quad (22)$$

This equation has also been noted without proof in Ref. [11]. Equation (20) is then obtained by taking $A = E_x$ in the last equation. In particular, for $A = E_{xc}$ we obtain

$$\int v_{xc}(\mathbf{r}) \nabla \rho(\mathbf{r}) d\mathbf{r} = 0. \quad (23)$$

For the case of rotational invariance we require Eq. (13) to be valid for

$$\rho'(\mathbf{r}) = \rho(R\mathbf{r}), \quad (24)$$

in which R is a rotation operation within three-dimensional coordinate space. For the functional derivative of A we then have

$$a([\rho']; \mathbf{r}) = a([\rho]; R\mathbf{r}). \quad (25)$$

This equation is proven in the same way as Eq. (16). If we take $a = v_x$ and use Eq. (25) we see that the Levy-Perdew equation (6) is already rotationally invariant. In general rotational invariance gives the following constraint on the functional derivative of A :

$$\int \frac{\delta A}{\delta \rho(\mathbf{r})} \mathbf{r} \times \nabla \rho(\mathbf{r}) d\mathbf{r} = 0, \quad (26)$$

which can be proved by performing an infinitesimal rotation instead of a translation in Eq. (21). This gives

$$\int v_{xc}(\mathbf{r}) \mathbf{r} \times \nabla \rho(\mathbf{r}) d\mathbf{r} = 0. \quad (27)$$

We have now summarized some properties of the exact exchange-correlation potential, which are at the same time requirements to be fulfilled by approximate potentials. We will concentrate in the remainder of this paper on the potential rather than on the energy. One of the reasons is that the potential, being a unique, local function of the position \mathbf{r} , is more easily obtained, analyzed, and modeled (see below). Of course, even if one has obtained a good model potential that very closely approximates the exact Kohn-Sham potential, the exchange-correlation energy still has to be determined. This problem will be addressed in a subsequent paper.

III. THE NONLOCAL EXCHANGE AND CORRELATION POTENTIALS OF BECKE AND PERDEW

Using the conditions formulated in the preceding section we shall now discuss some of the currently used exchange-correlation functionals and potentials that include nonlocal corrections. These are the potentials derived from Becke's nonlocal exchange functional [2] and Perdew's nonlocal correlation functional [3]. First we discuss Becke's nonlocal exchange functional [2] which in spin polarized form is given by

$$E_x[\rho_\sigma] = \sum_\sigma \int \rho_\sigma^{4/3}(\mathbf{r}) f(x_\sigma(\mathbf{r})) d\mathbf{r}, \quad (28)$$

in which $x_\sigma = |\nabla \rho_\sigma| / \rho_\sigma^{4/3}$ is a dimensionless quantity and

σ is a spin index. The function f is given by

$$f(x) = -\beta \frac{x^2}{1 + 6\beta x \sinh^{-1}(x)}. \quad (29)$$

The form of Eq. (28) is chosen such that the exchange functional satisfies the scaling relation (3). The function f is chosen such that the potential of the exchange hole $\epsilon_x(\mathbf{r})$ or equivalently the exchange energy density per electron behaves asymptotically as $-1/2r$ [Eq. (8)]. To enforce relation (8) the function f in Eq. (28) must satisfy the following asymptotic relation:

$$f(x) \sim -\frac{1}{6} \frac{x}{\ln(x)} \quad (r \rightarrow \infty \Rightarrow x \rightarrow \infty), \quad (30)$$

which is easily verified if exponentially decaying densities are inserted. If one also wants to obtain the gradient expansion result of Eq. (11) for slowly varying densities f must satisfy

$$f(x) \sim -\beta x^2 \quad (x \downarrow 0). \quad (31)$$

The form chosen by Becke is one of the simplest interpolations of f between these two limits and therefore his energy functional satisfies the important requirements of correct $r \rightarrow \infty$ and $x \rightarrow 0$ behavior as well as translational and rotational invariance. However, the potential of the Becke energy expression decays asymptotically as [24,18]

$$v_x^{\text{Becke}}(\mathbf{r}) \sim \frac{k}{r^2} \quad (r \rightarrow \infty), \quad (32)$$

in which k is some constant instead of the exact [17,18]:

$$v_x(\mathbf{r}) \sim -\frac{1}{r}. \quad (33)$$

In the following we will prove that any functional of the form of Eq. (28) satisfying the asymptotic relation (30) will not satisfy asymptotic relation (33). Such a proof has also been given by Engel *et al.* [18] and is only presented here for reason of clarity and completeness. We will, however, also use the following short proof to make some statements about the behavior of the exchange potential near the atomic nucleus for exchange functions of the form of Eq. (28).

For simplicity we use the spin unpolarized form but everything goes exactly through for the spin polarized case by just adding a spin index everywhere in the derivation. This is due to the fact that the exchange energy in the spin polarized case is just a simple sum of contributions of α and β spins in which both contributions have the same structure. We will take the functional of the form

$$E_x[\rho] = \int \rho^{4/3}(\mathbf{r}) f(x(\mathbf{r})) d\mathbf{r}, \quad (34)$$

with

$$x = \frac{|\nabla\rho|}{\rho^{4/3}}. \quad (35)$$

The second derivative of the function f is assumed to exist. The functional derivative of E_x of (34) is then given by

$$\begin{aligned} \frac{\delta E_x}{\delta \rho(\mathbf{r})} = v_x(\mathbf{r}) = & \frac{4}{3} \rho^{1/3} \left[f - x \frac{df}{dx} + x^2 \frac{d^2 f}{dx^2} \right] \\ & + \sum_{i,j} \frac{\partial_i \rho \partial_j \rho}{|\nabla\rho|^3} \left[\frac{df}{dx} - x \frac{d^2 f}{dx^2} \right] \\ & - \frac{\nabla^2 \rho}{|\nabla\rho|} \frac{df}{dx}. \end{aligned} \quad (36)$$

We insert for the density the exponential $\rho(\mathbf{r}) = Ne^{-\alpha r}$. This exponential is exact in two regions of the atom: near the atomic nucleus where we have $\alpha = 2Z$ with Z the nuclear charge and for the outer asymptotic region where $\alpha = 2\sqrt{-2\mu}$ with μ the chemical potential (negative of the ionization energy). This gives

$$v_x(\mathbf{r}) = \frac{4}{3} \rho^{1/3} \left[f - x \frac{df}{dx} + x^2 \frac{d^2 f}{dx^2} \right] - \alpha x \frac{d^2 f}{dx^2} + \frac{2}{r} \frac{df}{dx}. \quad (37)$$

In order to satisfy the asymptotic behavior of ϵ_x [Eq. (8)] f must satisfy the asymptotic relation (30). If we now insert the large x behavior of f [Eq. (30)] into Eq. (37) we get, retaining only the terms of lowest order in $1/\ln x$,

$$v_x(\mathbf{r}) \sim -\frac{1}{3r} \frac{1}{\ln x} \sim -\frac{1}{3r} \frac{1}{\ln \alpha \rho^{-1/3}} \sim -\frac{1}{\alpha} \frac{1}{r^2} \quad (r \rightarrow \infty). \quad (38)$$

We thus see that the exchange potential has a $-\alpha^{-1}/r^2$ behavior instead of a Coulombic behavior. Hence it follows that the requirements of correct asymptotic behavior of ϵ_x [relation (8)] and of v_x [relation (33)] are incompatible for exchange functionals of the form (34).

From Eq. (37) we can also draw the following conclusion concerning the behavior for $r \rightarrow 0$: If $df/dx|_{x=x(0)} \neq 0$ then

$$v_x(\mathbf{r}) \sim \frac{k}{r} \quad (r \downarrow 0), \quad (39)$$

in which the constant k is given by

$$k = 2 \frac{df}{dx} \Big|_{x=x(0)}. \quad (40)$$

This is an unphysical behavior of the exchange potential near the nucleus. In practice, however (that is, for the Becke functional), the constant k is very small compared to the nuclear charge (a typical value for k is 0.02 for the noble gases).

We will now discuss some properties of the Perdew nonlocal correlation functional which is of the form [3]

$$E_c[\rho] = \int f(\rho_\alpha, \rho_\beta) e^{-g(\rho)|\nabla\rho|} \frac{(\nabla\rho)^2}{\rho^{4/3}} d\mathbf{r}. \quad (41)$$

In this formula f is a local function of ρ_α and ρ_β , which are spin densities, and g is a local function of the total density. The form of this functional is adapted from the correlation part of the Langreth-Mehl functional in such a way that the functional reduces to the gradient expansion expression of Eq. (12) for slowly varying densities.

The corresponding potential decays exponentially to infinity. This is not a bad feature as the correlation potential should decay faster than Coulombically although maybe one should expect a correlation potential decaying as $-\alpha/r^4$ in which α is the polarizability of the system. This term occurs in the exact exchange-correlation potential [19] and describes the polarization of the system by an asymptotic electron, which is clearly a correlation effect.

Near the nucleus the Perdew potential also has a Coulombic singular behavior. The origin of this unphysical singularity can be traced, as in the Becke potential, to terms in the potential that contain the Laplacian of the density, which due to the Slater-like behavior of the atomic density near the nucleus leads to a Coulomb potential. These terms also occur in potentials of other nonlocal-density functionals such as the one from Langreth and Mehl [5] and in the generalized gradient approximation (GGA) of Perdew and Wang [25]. These functionals consequently also suffer from this same deficiency.

IV. CONSTRUCTING THE POTENTIAL FROM THE DENSITY

We have demonstrated that the most widely used gradient-corrected exchange and correlation potentials suffer from incorrect asymptotic behavior at $r \rightarrow 0$ and $r \rightarrow \infty$. In order to investigate these potentials over the whole r range one needs the exact Kohn-Sham potential at arbitrary position. In this section we present an iterative scheme of obtaining the Kohn-Sham potential from a given electron density ρ . This scheme is different from most other schemes used thus far [26,19,27] and in particular is not limited to two-electron systems but is applicable to systems with any number of electrons. Recently during the writing of this paper we have noticed that work along similar lines has been carried out [28]. However, our procedure is somewhat simpler and as we tested has the same convergence rate. In contrast to Ref. [28], in which calculations within a basis set were performed, we use a completely numerical approach, obtaining a basis-set-free representation of the potential.

We start from the Kohn-Sham equations

$$[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (42)$$

in which v_s is the Kohn-Sham potential. The Kohn-Sham orbitals are required to satisfy

$$\sum_i^N |\phi_i(\mathbf{r})|^2 = \rho(\mathbf{r}), \quad (43)$$

where N is the number of electrons in the system. Multiplying Eq. (42) by ϕ_i^* and summing over i gives, after dividing by ρ ,

$$v_s(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_i^N \frac{1}{2} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) + \epsilon_i |\phi_i(\mathbf{r})|^2. \quad (44)$$

We now define an iterative scheme using this equation. We want to calculate the potential corresponding to the density ρ . Suppose that at some stage in the iteration we

have calculated orbitals ϕ_i^o with eigenvalues ϵ_i^o and density ρ^o and potential v^o . In the next step we define the new potential

$$\begin{aligned} v^n(\mathbf{r}) &= \frac{1}{\rho(\mathbf{r})} \sum_i^N \frac{1}{2} \phi_i^{o*}(\mathbf{r}) \nabla^2 \phi_i^o(\mathbf{r}) + \epsilon_i^o |\phi_i^o(\mathbf{r})|^2 \\ &= \frac{\rho^o(\mathbf{r})}{\rho(\mathbf{r})} v^o(\mathbf{r}). \end{aligned} \quad (45)$$

Using this potential we calculate new orbitals and a new density and define in the same way a new potential. This procedure is continued until the density calculated from the orbitals is the same as the given density. We use this procedure until

$$\max_{\mathbf{r}} \left| 1 - \frac{\rho^o(\mathbf{r})}{\rho(\mathbf{r})} \right| < \epsilon, \quad (46)$$

with ϵ a given threshold. To achieve convergence one should take care to keep the prefactor in the last term of Eq. (45) in each iteration within an acceptable range:

$$1 - \delta < \frac{\rho^o(\mathbf{r})}{\rho(\mathbf{r})} < 1 + \delta, \quad (47)$$

for example, with $\delta=0.05$. We noticed in the application of this procedure that one has to make sure that the potential is set to zero in infinity, otherwise one might fail to converge. This is due to the fact that one can add an arbitrary constant to both the potential and the one-electron eigenvalues without changing the density. This may also play a role in the practical application of the procedure of Ref. [28] where explicit use is made of the one-electron eigenvalues in the potential construction procedure. The fixing of the potential in infinity is, however, easily carried out in our program, in which differential equations are solved numerically. In that case boundary conditions at infinity and at the nucleus immediately fix the solution.

The scheme is not guaranteed to converge as there are densities which are not noninteracting v representable (however, many densities which are not v representable by one determinant are v representable by a linear combination of determinants [29] which can be accomplished in our scheme by using fractional occupation numbers). However, if the procedure converges then its limit is unique as guaranteed by the Hohenberg-Kohn theorem applied to a noninteracting electron system [20].

We have calculated exact potentials for the beryllium and the neon atoms as for these atoms accurate densities from configuration-interaction calculations are available. Both densities have been published by Bunge and Esquivel [30,31] in a large basis of Slater functions. The use of Slater functions is advantageous because they give a much better representation of the density tail in the outer regions of the atom than, for instance, Gaussian functions do. For the calculation of the potentials from these densities we used a modification of the Herman-Skilman atomic program [32] based on numerical integration. For the results of Table I we have used our atomic and molecular density-functional package based on Slater-Type orbitals (STO's) with which it is possible to carry out self-consistent calculations using the Becke-Perdew potential.

In the local-density approximation we use for the correlation potential the Vosko-Wilk-Nusair parametrization of the electron-gas data [33]. For the open shell atoms discussed in this article we performed spherically averaged spin polarized calculations. The exact exchange-correlation potentials are displayed in Figs. 1(a) and 2(a) for Be and Ne, respectively, and r times these potentials in Figs. 1(c) and 2(c). Both potentials have the same structure, a characteristic peak between the atomic shells (in our case between the K and the L shell) and a Coulombic asymptotic behavior. These features are most clearly displayed in the plots of rV . The appearance of the intershell peak has been observed before [19,27] and can be understood from the work of Buijse, Baerends, and Snijders [34]. In Ref. [34] it has been observed that an important contribution to the Kohn-Sham potential is the so-called kinetic potential V_{kin} defined in terms of the conditional amplitude Φ :

$$\Phi(x_2, \dots, x_N | x_1) = \frac{\Psi(x_1, \dots, x_N)}{\sqrt{\rho(x_1)/N}}, \quad (48)$$

$$V_{\text{kin}}(x_1) = \int \Phi^* \left(-\frac{1}{2} \nabla_1^2\right) \Phi dx_2 \cdots dx_N \\ = +\frac{1}{2} \int |\nabla_1 \Phi|^2 dx_2 \cdots dx_N. \quad (49)$$

TABLE I. Ionization energies and electron affinities from the highest occupied Kohn-Sham orbital.

Atom	HF	LDA	NL(BP)	Model	Expt.
H	0.500	0.234	0.280	0.440	0.500
He	0.918	0.571	0.585	0.851	0.903
Be	0.309	0.206	0.209	0.321	0.343
Ne	0.850	0.490	0.496	0.788	0.792
Ar	0.591	0.381	0.380	0.577	0.579
Kr	0.524	0.346	0.344	0.529	0.517
Xe	0.457	0.310	0.308	0.474	0.446

Ion	HF	LDA	NL(BP)	Model	Expt.
F ⁻		-0.097	-0.099	0.128	0.125
Cl ⁻		-0.022	-0.023	0.140	0.133
Br ⁻		-0.008	-0.009	0.140	0.124
I ⁻		+0.005	+0.004	0.139	0.112

Molecule	HF	LDA	NL(BP)	Model	Expt.
N ₂	0.622	0.328	0.322	0.557	0.573
F ₂		0.339	0.334	0.607	0.582
CO	0.551	0.334	0.336	0.529	0.515

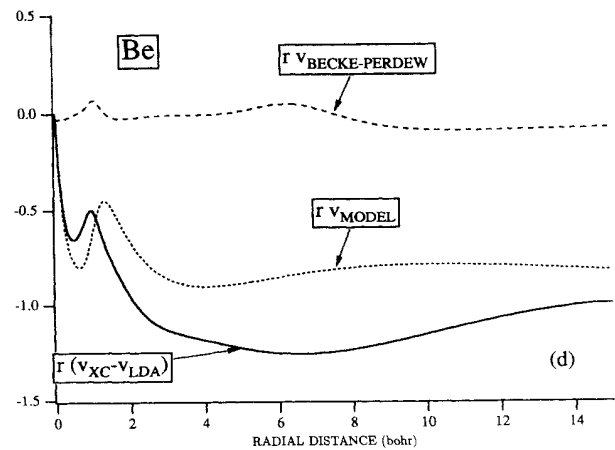
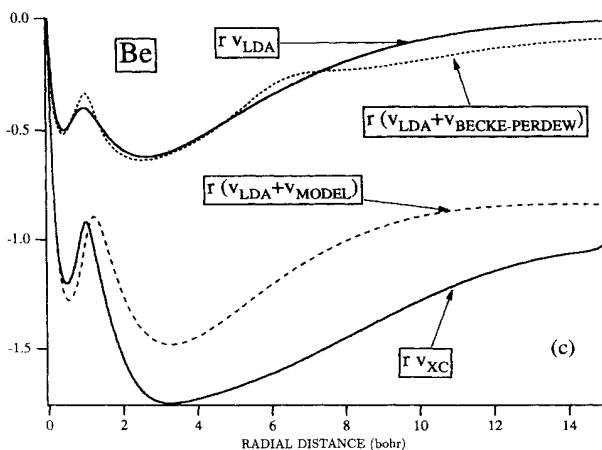
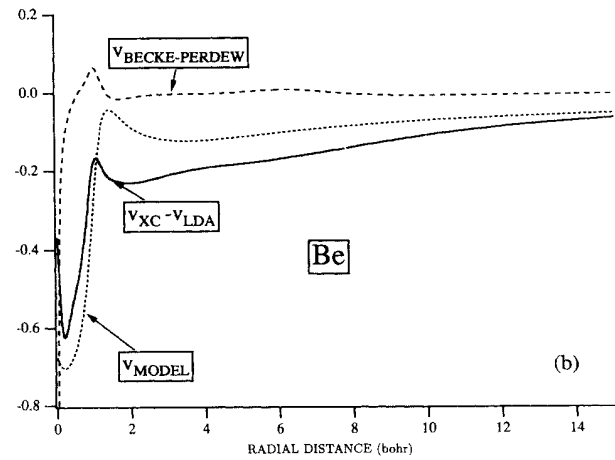
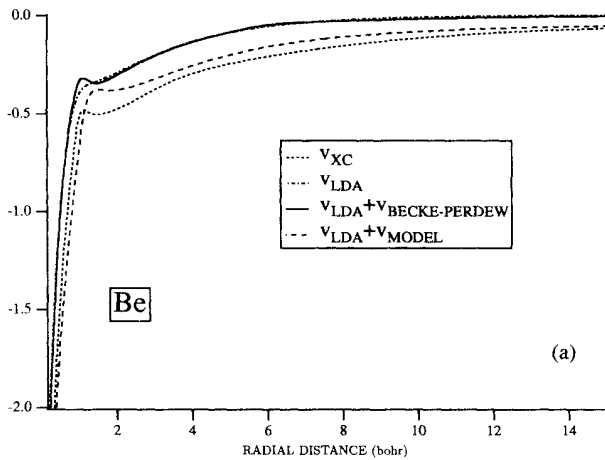


FIG. 1. Exchange-correlation potentials of the beryllium atom.

The conditional amplitude $\Phi(x_2, \dots, x_N | x_1)$ describes the system of $N-1$ electrons with positions x_2, \dots, x_N when one electron is known to be at position x_1 and is the amplitude connected with the conditional probability of finding the other electrons when one electron is known to be at x_1 . V_{kin} makes a significant (positive) contribution to the effective potential v_{eff} in the Schrödinger equation for the square root of the density at those positions x_1 of the reference electron where the conditional amplitude changes rapidly, so that $\nabla_1 \Phi$ is large. As discussed in Ref. [34], this is the case when x_1 crosses the border region between two atomic shells, since the exchange hole is localized within one atomic shell if the reference position is in that shell but “jumps” to the next shell when the reference position crosses the border (see Refs. [35–37]). The intershell peaks of V_{xc} , which are less pronounced than those in v_{eff} , also originate from relatively strong changes in the pair correlation function at shell boundaries [38]. It is obvious from the figures that the LDA potentials almost completely lack this important feature of the exact potential. This is particularly clear from the pronounced appearance of peaks in the difference plots of $(V_{\text{xc}} - V_{\text{LDA}})$ and $r(V_{\text{xc}} - V_{\text{LDA}})$ in Figs. 1(b) and 1(d) and 2(b) and 2(d). The LDA potential also has a wrong asymptotic behavior for $r \rightarrow \infty$, as is

evident from the fact that rV_{LDA} does not go to -1 but to 0 . The exact potential has a much improved asymptotic behavior. However, the quality of the exact potential we generate depends on the quality of the correlated wave function and density on which it is based. The asymptotic region is notoriously difficult to describe accurately, since wave functions are almost invariably obtained from energy optimization algorithms which have a strong bias towards improving the energetically important inner region. In the case of neon we observe that for large r ($r \geq 3$ bohrs) there is a spurious minimum in the curve for the exact V_{xc} [Fig. 2(c)] which we ascribe to inaccuracy of the correlated density at such large r . It is nevertheless clear that the “exact” rV_{xc} approaches -1 much better than the LDA potential does. For Be it is not evident that the calculated “exact” V_{xc} suffers from poor accuracy of the asymptotic behavior of the configuration-interaction (CI) density, but we do feel that some suspicion is warranted concerning the (too?) slow approach by rV_{xc} to the limiting value of -1 [Fig. 1(c)]. This suspicion is aggravated by the strange minimum between 6 and 8 bohrs in the curve of $r(V_{\text{xc}} - V_{\text{LDA}})$ in Fig. 1(d).

In panels (a) and (c) of Figs. 1 and 2 we have also added Becke’s gradient-corrected exchange potential [2] and

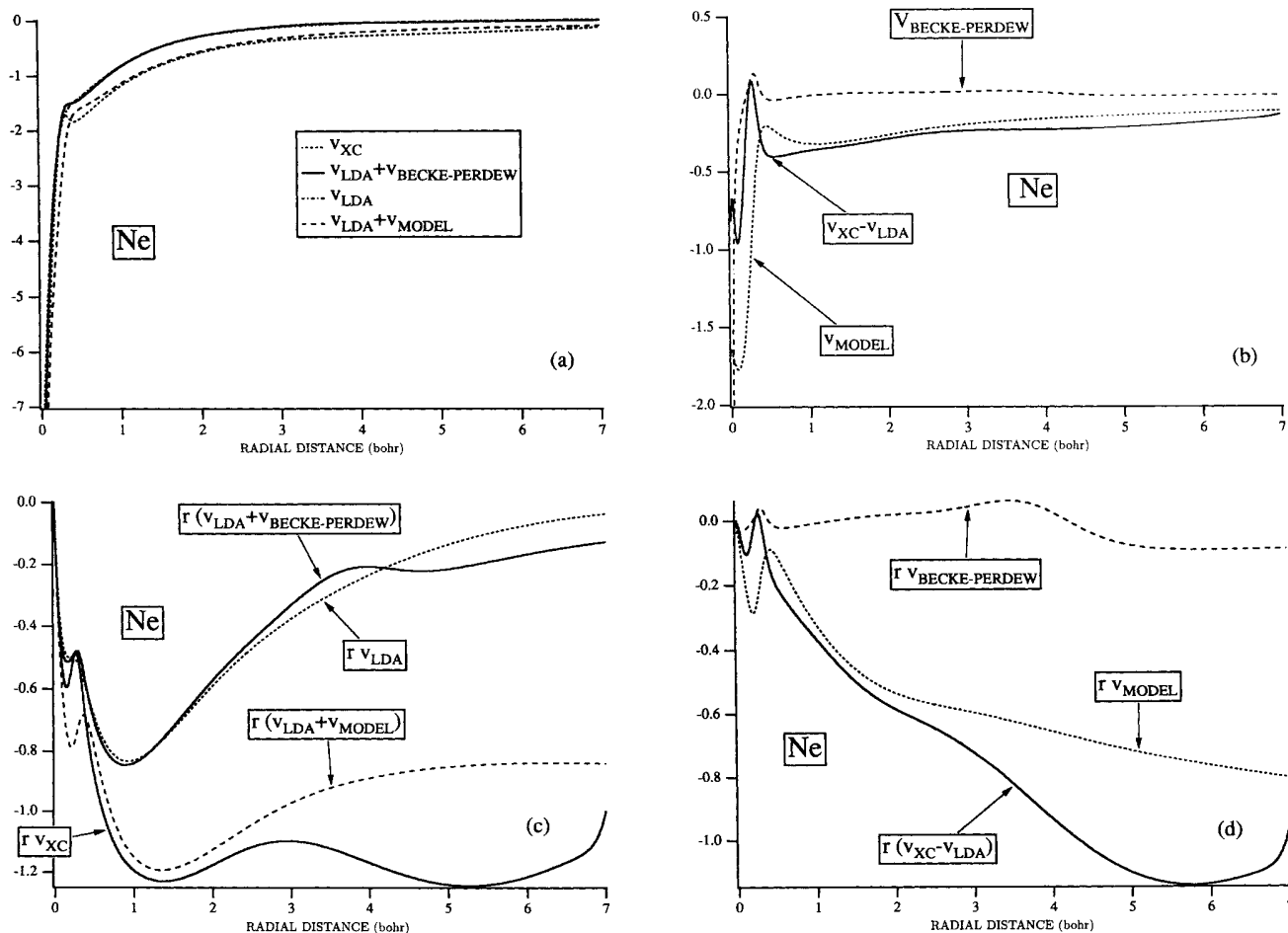


FIG. 2. Exchange-correlation potentials of the neon atom.

Perdew's correlation potential [3] to the LDA potential. The plots demonstrate that these potentials make rather small corrections to the LDA potential. This makes it understandable that the one-electron energies shown in Table I, which are rather poor for LDA when compared to the experimental ionization energies, do not improve when the Becke-Perdew nonlocal corrections are included in the self-consistent-field (SCF) calculation. Panels (b) and (d) of the figures display directly the comparison between the nonlocal corrections to the potential and the difference ($V_{xc} - V_{LDA}$) to which they should be equal. It can be seen that the nonlocal Becke-Perdew potential behaves singularly near the atomic nucleus. This potential has in this region the Coulombic singular behavior discussed earlier. At somewhat larger distances it crosses the horizontal axis and gives a small positive peak which is located at the right spot in the intershell region. For Be this does not lead to good agreement with ($V_{xc} - V_{LDA}$) in the intershell region, but for Ne $V_{Becke-Perdew}$ quite nicely approximates ($V_{xc} - V_{LDA}$) just at the position of the intershell peak. At larger distances the Becke-Perdew potential is almost zero and there is no correction to the LDA potential, in agreement with the failure to give improvement of the LDA eigenvalues. The large deviation in the asymptotic region between the Becke-Perdew potential and the exact nonlocal potential is most clearly exhibited in panels (a): the exact nonlocal corrections correctly tend to a constant which approximates -1 , whereas the Becke-Perdew potential tends to zero. The panels (d) also demonstrate that the Becke-Perdew potential multiplied by the radial distance does not tend to zero at the atomic nucleus but to a finite value, indicating the Coulombic behavior of this potential in this region.

V. A MODEL POTENTIAL

In this section we will make a first step towards the construction of model potentials that more closely resemble the exact Kohn-Sham potential. The advantage in modeling potentials instead of energy expressions is the fact that potentials are uniquely defined by the exact density. The quality of model potentials can therefore be judged by comparing to exact potentials calculated from accurate densities.

In modeling the potentials one should incorporate the general features of atomic-shell structure and asymptotic Coulomb behavior. One might also wish the potential to satisfy some scaling properties. To incorporate the shell structure we use for our model potential the dimensionless parameter $x = |\nabla\rho|/\rho^{4/3}$. This parameter is proportional to the length of the gradient of the local Wigner-Seitz radius and can be interpreted as the change in mean electronic distance (at least in regions with slowly varying density where $r_s \sim \rho^{-1/3}$ is meaningful, i.e., in the regions where LDA is applicable). As an illustration of the behavior of this parameter we display both this parameter and $r^2\rho(r)$ in Fig. 3 for the krypton atom. Whereas the electron density $\rho(r)$ is monotonically decreasing in an atom, $r^2\rho(r)$ exhibits the shell structure. We observe

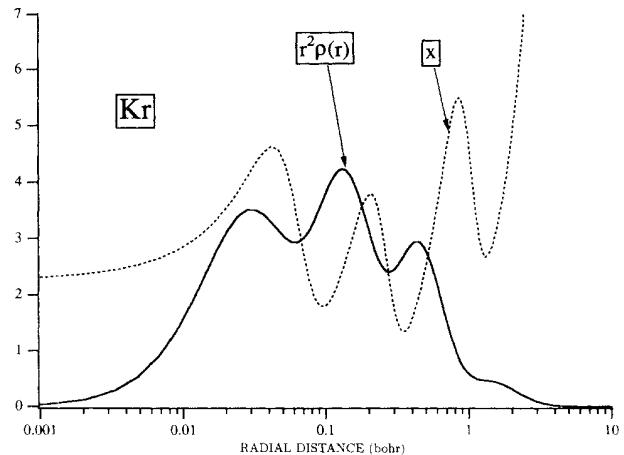


FIG. 3. The electron density times the radial distance squared and the parameter $x = |\nabla\rho|/\rho^{4/3}$ for the krypton atom.

that x also oscillates with the atomic shells, with maxima approximately at the inflection points of $r^2\rho(r)$, and thus seems a suitable parameter to model the shell structure of the exact potential. For the asymptotic behavior of the potential we then have to take into account that x behaves for an exponentially decaying density $\rho \sim e^{-ar}$ asymptotically as $\alpha\rho^{-1/3}$, i.e., increases exponentially (see Fig. 3). We thus choose our nonlocal correction to the LDA potential of the form

$$v_{xc}(\mathbf{r}) = \rho^{1/3}(\mathbf{r})f(x(\mathbf{r})). \quad (50)$$

This form of the potential scales like an exchange potential [12,11]:

$$v_{xc}([\rho_\lambda]; \mathbf{r}) = \lambda v_{xc}([\rho]; \lambda \mathbf{r}). \quad (51)$$

We do not know the scaling behavior of the correlation part of the potential but as the major part of the potential comes from the exchange we take the above form as an approximation. For systems with small density variations (small values of x) we want the nonlocal correction potential also to be small. We therefore require $f(0)=0$. We further know that [9,10]

$$v_{xc}(\mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty). \quad (52)$$

This means that f must asymptotically satisfy

$$f(x) \sim -\frac{1}{3} \frac{x}{\ln(x)} \quad (x \rightarrow \infty). \quad (53)$$

Our problem of finding a smooth interpolation between these limiting situations is similar to the one that Becke faced for the exchange energy density. Inspired by his solution we take

$$f(x) = -\beta \frac{x^2}{1 + 3\beta x \sinh^{-1}(x)}. \quad (54)$$

This gives the final form of our model potential for the nonlocal corrections. In spin polarized form

$$v_{xc}^\sigma(\mathbf{r}) = -\beta \rho_\sigma^{1/3}(\mathbf{r}) \frac{x_\sigma^2}{1 + 3\beta x_\sigma \sinh^{-1}(x_\sigma)}. \quad (55)$$

In order to check if with this potential we have captured the main features of the Kohn-Sham potential which the LDA potential is lacking, i.e., shell structure and a Coulombic asymptotic behavior, we compare to exact potentials in Figs. 1 and 2. The parameter β in our model potential was fitted in such a way that our model potential resembled as closely as possible the difference between the exact and the LDA potential for the beryllium atom. For this procedure we choose the beryllium atom instead of the neon atom because its density appears to be the most accurate of the two. This leads to a value of β of 0.05. The model potential for neon in Fig. 2 uses the same parameter β . The model potentials in Figs. 1 and 2 have been calculated self-consistently using our density-functional program package.

As can be seen from Fig. 1 for the beryllium atom our potential is in reasonable agreement with the exact potential. In particular, Figs. 1(c) and 1(d) show that the inter-shell peak is fairly well represented and the asymptotic behavior is essentially correct in that $r(V_{\text{LDA}} + V_{\text{model}})$ approaches -1 . Concerning the remaining difference, there is obviously room for improvement, although we suspect that part of the difference between our model potential and the exact potential in the asymptotic region is due to the possible inaccuracy in the latter mentioned before. The model potential does clearly improve upon the Becke-Perdew potential. For the neon atom (Fig. 2) the asymptotic behavior of the model potential appears to be quite good (assuming that the minimum of the "exact" potential between 5 and 6 bohrs is incorrect). However, in the inner region of the neon atom the model potential is not so well behaved. Although it does exhibit an inter-shell peak, the approximation of this feature to the true inter-shell peak is rather poor. As a matter of fact, the Becke-Perdew potential gives a better approximation to the exact nonlocal potential precisely at the inter-shell peak. Nevertheless, considering the whole r range we can say that for both the beryllium and the neon atom our simple model potential gives a considerable improvement of the LDA potential, especially in the asymptotic region where the Becke-Perdew potential gives almost no correction.

We might now ask whether these improvements are reflected in the quality of the eigenvalues. In order to investigate this question we calculated for several atoms and molecules the eigenvalue of the highest occupied Kohn-Sham orbital. This eigenvalue should be equal to the ionization energy of the system (or electron affinity for negative ions). We have done this for both LDA, LDA with the Becke-Perdew potential added, and for LDA with our potential ($\beta=0.05$) added. The results for H and a number of atoms with noble gas configurations

TABLE II. Expectation values of $\langle r \rangle$ and $\langle r^2 \rangle$ for the highest occupied orbitals with corresponding eigenvalue.

Atom	LDA			Model			Expt. ϵ
	$\langle r \rangle$	$\langle r^2 \rangle$	ϵ	$\langle r \rangle$	$\langle r^2 \rangle$	ϵ	
Li(2s)	3.822	17.345	0.12	3.815	17.410	0.19	0.20
Na(3s)	3.995	18.753	0.11	3.703	16.256	0.21	0.19
K(4s)	4.839	26.962	0.10	4.428	22.739	0.18	0.16
Rb(5s)	5.125	30.041	0.09	4.664	25.036	0.18	0.15
Cs(6s)	5.674	36.481	0.08	5.170	30.475	0.16	0.14
Be(2s)	2.621	8.263	0.20	2.595	8.118	0.32	0.34
Mg(3s)	3.137	11.572	0.17	2.985	10.528	0.29	0.28
Ca(4s)	3.991	18.304	0.14	3.771	16.437	0.24	0.22
Sr(5s)	4.339	21.468	0.13	4.079	19.066	0.23	0.21
Ba(6s)	4.880	26.909	0.12	4.588	23.897	0.21	0.19

Ion	LDA			Model			Expt. ϵ
	$\langle r \rangle$	$\langle r^2 \rangle$	ϵ	$\langle r \rangle$	$\langle r^2 \rangle$	ϵ	
Li ⁺ (1s)	0.585	0.468	2.19	0.576	0.453	2.65	2.78
Na ⁺ (2p)	0.803	0.839	1.34	0.795	0.821	1.70	1.74
K ⁺ (3p)	1.428	2.421	0.92	1.430	2.428	1.15	1.16
Rb ⁺ (4p)	1.720	3.428	0.80	1.713	3.404	1.01	1.00
Cs ⁺ (5p)	2.087	4.959	0.69	2.078	4.920	0.88	0.85
Be ²⁺ (1s)	0.421	0.240	4.81	0.417	0.235	5.45	5.66
Mg ²⁺ (2p)	0.684	0.599	2.46	0.681	0.592	2.88	2.95
Ca ²⁺ (3p)	1.260	1.866	1.58	1.263	1.879	1.85	1.87
Sr ²⁺ (4p)	1.555	2.775	1.34	1.553	2.772	1.58	1.60
Ba ²⁺ (5p)	1.912	4.129	1.14	1.909	4.123	1.35	1.35

are presented in Table I. In this table we also compare with the self-interaction free eigenvalues of the Hartree-Fock approximation. From the table we can see that the LDA eigenvalues have a large discrepancy with experiment, with a mean absolute error of 5.40 eV. We can also see that these values are not improved by inclusion of the Becke-Perdew potential. The model potential, on the other hand, gives a considerable improvement compared to the LDA eigenvalues, with a mean absolute error of 0.56 eV. A nice feature of the model potential is also that it yields bound state solutions for the negative ions. We see that the improvements are not restricted to atoms but also occur for molecules. Table II shows results for the alkali-metal and alkaline-earth-metal atoms and ions. The same quality is obtained as for the noble gas atoms and ions.

Does the improvement of the asymptotic behavior achieved by the model potential, apart from showing up clearly in the one-electron energies, also have observable consequences for the density? In Tables II–IV we investigate a number of moments of orbital and total densities. Table II demonstrates that the radial extent of the

TABLE III. Density moments for the beryllium atom.

	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$	$\langle r^5 \rangle$
HF	57.618	8.409	6.129	17.319	63.151	270.656	1325.49
LDA	56.766	8.339	6.091	17.019	61.475	261.641	1276.385
Model	57.837	8.446	6.022	16.704	59.796	250.937	1198.763
Exact	57.597	8.427	5.975	16.284	56.946	233.167	1085.87

TABLE IV. Density moments for the neon atom.

	$\langle r^{-2} \rangle$	$\langle r^{-1} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$	$\langle r^5 \rangle$
HF	414.890	31.113	7.891	9.372			
LDA	411.916	30.998	8.016	9.853	15.967	32.500	80.692
Model	416.406	31.275	7.895	9.477	14.799	28.576	66.239
Exact	414.967	31.110	7.935	9.545	14.941	29.006	67.904

highest occupied orbital in the alkali-metal and alkaline-earth-metal atoms is significantly affected by the asymptotic correction introduced by the model potential. Maximum errors of the LDA potential amount to 9% and 18% for $\langle r \rangle$ and $\langle r^2 \rangle$, respectively, of the alkali metals and 6% and 13% for the alkaline earth metals. The first members of the two series, Li and Be, show comparatively small errors of 0.2% and 0.3% for Li and 1% and 2% for Be. The errors are much smaller for the ions, probably since they possess very tight closed shells. Although the effects are rather small for Be, making this atom perhaps not a good test case, we happen to have a very accurate CI density available for this atom and therefore we compare in Table III for Be the moments of the total density as obtained from various calculations. Also the Hartree-Fock data are shown in this table, in order to see how much of the effect of correlation is taken into account by the LDA or model potential. Judging by this example, for $\langle r^p \rangle$ with p positive the LDA potential corrects the Hartree-Fock result in spite of the wrong asymptotic behavior of this potential, the model potential gives improvement over LDA but in general only something like 50% of the difference between Hartree-Fock and exact is covered by the model potential. For $\langle r^{-1} \rangle$ and $\langle r^{-2} \rangle$ there is no improvement over the Hartree-Fock results.

For neon (Table IV) it is seen that for $\langle r^p \rangle$ with p positive the model potential considerably improves the LDA result. With respect to the difference with Hartree-Fock the picture is different from that for Be: the LDA potential does not correct the Hartree-Fock results but gives as expected a too diffuse density. For $\langle r^{-1} \rangle$ and $\langle r^{-2} \rangle$ there is again no improvement over the Hartree-Fock results. The LDA potential appears to give a too diffuse, the model potential a too contracted density in the inner region.

VI. SUMMARY AND CONCLUSIONS

In this work we have formulated a number of conditions for approximate exchange-correlation potentials. Potentials of gradient-corrected density functionals that are currently used with much success to calculate atomic exchange and correlation energies as well as bond energies of molecules do not obey some of these conditions. In order to make comparisons over all space to (almost) exact Kohn-Sham potentials we devised an iterative scheme to obtain the corresponding Kohn-Sham potential from a given density. The scheme is applicable to both atoms and molecules and is not limited to systems with few electrons. In this paper highly accurate CI den-

sities for Be and Ne have been used to generate accurate Kohn-Sham potentials. Comparison to potentials derived from existing gradient-corrected functionals demonstrated that these potentials cover only a small part of the difference between the LDA potential and the exact one. This is at first sight a little surprising: how can we have large improvements in energies and almost no improvement in the potential? Several explanations may be advanced. First of all, the approximate nonlocal functional might "oscillate" around the exact functional, giving a good approximation of the energies but a bad approximation of its functional derivative. Other deficiencies are inherent to the derivation of the functionals. For instance, both the nonlocal exchange-correlation functional of Langreth and Mehl [5] and the Perdew-Wang generalized gradient expansion [25] use a long-range cutoff of the exchange-correlation energy density. Langreth and Mehl use a low- k (large distance) cutoff in the momentum distribution of the exchange-correlation energy and Perdew and Wang perform a real-space cutoff in the exchange-correlation hole. This neglect of this asymptotic region reflects itself in the potential which thereby loses its asymptotic Coulombic behavior. However, the Becke functional shows that even a correct behavior of the exchange hole potential does not guarantee a good behavior of the exchange potential.

A model potential has been presented which corrects some of the deficiencies of the current potentials, notably the asymptotic behavior. The improved asymptotic behavior shows up very clearly in the one-electron energies. The error in the highest occupied LDA eigenvalue (which should represent in the exact case the ionization energy) is reduced by almost an order of magnitude by using the model potential. The model potential also significantly corrects the higher moments of the density, notably for diffuse outer orbitals. Because of this correction of the highest occupied orbitals, the model potential may be useful in the calculation of highly excited diffuse states and in general for density-dependent properties such as dipole and quadrupole moments and derivatives thereof (infrared intensities).

In spite of some success, the present model potential is clearly deficient in some respects, notably the behavior in the atomic intershell region. It will therefore require further improvement. This problem will be addressed in a subsequent paper of this series. We feel that the most significant success of the nonlocal corrections to LDA applies to bond energies of molecules. In particular, the potential derived from the Becke gradient correction to the exchange energy density displays very interesting structure in molecules [39] that may explain the success

of the Becke energy expression for bond energies. We feel that further modeling of exchange-correlation potentials should not only try to optimize the potential for atoms but should take into account the special effects of chemical bonding.

ACKNOWLEDGMENT

We would like to thank Gijsbert Wiesenekker for his help in the programming of the iterative scheme of Sec. IV.

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