Self-consistent approximation to the Kohn-Sham exchange potential

Oleg Gritsenko, Robert van Leeuwen, Erik van Lenthe, and Evert Jan Baerends

Afdeling Theoretische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

A scheme of approximation of the Kohn-Sham exchange potential v_x is proposed, making use of a partitioning of v_x into the long-range Slater v_S and the short-range response v_{resp} components. A model potential v_{resp}^{mod} has been derived from dimensional arguments. It possesses the proper short-range behavior and the atomic-shell stepped structure characteristic for v_{resp}. When combined with the accurate v_S, v_{resp}^{mod} provides an excellent approximation to the exchange potential of the optimized potential model v_x^{OPM}. With the generalized-gradient approximation to v_S v_{resp}^{mod} provides an efficient density-functional-theory approach that fits closely the form of the accurate exchange potential and yields reasonably accurate exchange and total energies as well as the energy of the highest occupied orbital.

I. INTRODUCTION

Efficient approximation of the Kohn-Sham exchange potential v_x remains one of the important problems of density-functional theory (DFT) [1–5]. v_x is defined in the DFT as a functional derivative of the exchange energy $E_x[\rho]$ with respect to the density $\rho(\mathbf{r})$

$$v_x(\mathbf{r}) = \frac{\delta E_x[\rho]}{\delta \rho(\mathbf{r})} . \tag{1}$$

In the one-electron Kohn-Sham equations (hartree atomic units will be used throughout the paper)

$$\{ -\tfrac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_x(\mathbf{r}) + v_C(\mathbf{r}) \} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \tag{2}$$

v_x represents the local effect of exchange, the dominant part of the electron correlation, while the external v_{ext} and hartree v_H potentials represent the electrostatic interaction and v_c is the effective potential of the electron Coulomb correlation.

Figure 1 illustrates the typical behavior of v_x with the exchange potential of the optimized potential model (OPM) [6–8] for Mg. v_x is finite at the nucleus position

$$v_x(r) = \text{const} \quad \text{for } r = 0 , \tag{3}$$

it has the Coulombic asymptotics [6,9,10]

$$v_x(\mathbf{r}) \rightarrow -\frac{1}{|\mathbf{r}|} \quad \text{for } |\mathbf{r}| \rightarrow \infty , \tag{4}$$

and it possesses shell structure, i.e., a nonmonotonous dependence on r with different slopes in different shells and small peaks in the regions between the atomic shells [1,6,11,12]. Taken together, these features of v_x present considerable difficulties for its efficient approximation.

Recent progress within DFT is due to the generalized-gradient approximation (GGA) [11,13–16], which gives a remarkable improvement to the exchange-correlation energies of the local-density approximation (LDA) [17–21]. It was shown [2,4,5,22–24], however, that the standard

GGA exchange potentials do not possess the proper asymptotic behavior and shell structure. The corresponding gradient corrections add little to the LDA exchange potential.

For the analysis [25] and approximation [1,5] of v_x it appears very useful to separate the Slater potential v_S [26]
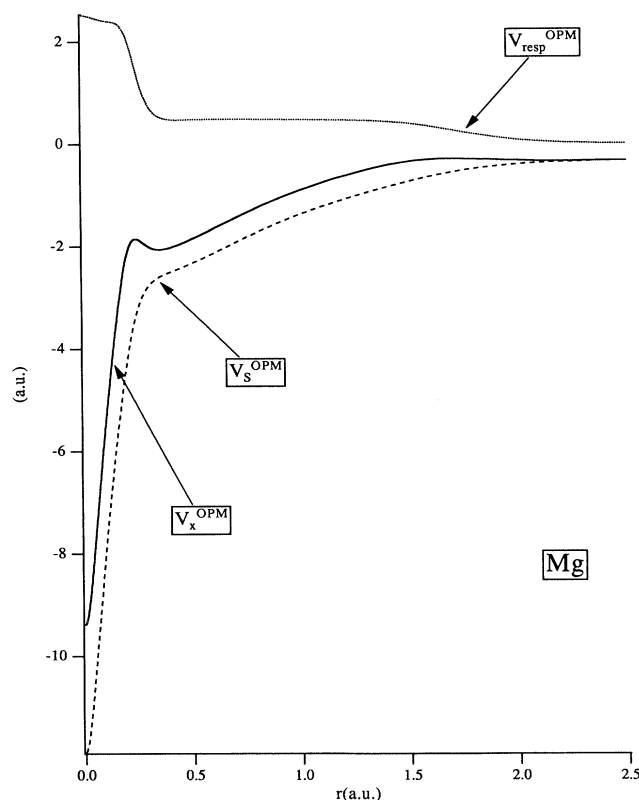

FIG. 1. OPM exchange potential and its components for Mg.

$$v_S(\mathbf{r}_1) = \int \frac{\rho(\mathbf{r}_2)\{g_x([\rho];\mathbf{r}_1,\mathbf{r}_2)-1\}}{|\mathbf{r}_1-\mathbf{r}_2|} d\mathbf{r}_2 \tag{5}$$

as an individual part of v_x. In (5) g_x is the exchange pair-correlation function, which can be expressed in terms of the occupied Kohn-Sham orbitals $\phi_i(\mathbf{r})$

$$g_x([\rho];\mathbf{r}_1,\mathbf{r}_2) = 1 - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{\phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_2)\phi_j^*(\mathbf{r}_1)\phi_j(\mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} . \tag{6}$$

The separation of v_S follows naturally from the expression of E_x in terms of v_S

$$E_x = \frac{1}{2}\int \rho(\mathbf{r})v_S(\mathbf{r})d\mathbf{r} . \tag{7}$$

Differentiation (1) of (7) with a proper account of (5) represents v_x as a sum of v_S and the additional potential v_{resp}, an integral of the linear "response" of g, $\delta g(\mathbf{r}_1,\mathbf{r}_2)/\delta \rho(\mathbf{r}_3)$ [27],

$$v_x(\mathbf{r}) = v_S(\mathbf{r}) + v_{\text{resp}}(\mathbf{r}) , \tag{8}$$

$$v_{\text{resp}}(\mathbf{r}_1) = \frac{1}{2}\int \rho(\mathbf{r}_2)d\mathbf{r}_2 \int \frac{\rho(\mathbf{r}_3)}{|\mathbf{r}_2-\mathbf{r}_3|}$$

$$\times \frac{[\delta g_x([\rho];\mathbf{r}_2,\mathbf{r}_3)]}{\delta\rho(\mathbf{r}_1)}d\mathbf{r}_3 . \tag{9}$$

The potentials v_S and v_{resp} have rather distinct, characteristic behavior [5,25] and Fig. 1 clearly illustrates this with the v_S^{OPM} and $v_{\text{resp}}^{\text{OPM}}$ components of the OPM exchange potential v_x^{OPM} [6–8]. v_S is an attractive potential, which embodies the Coulombic asymptotics (4) of the total potential v_x

$$v_S(\mathbf{r}) \rightarrow -\frac{1}{|\mathbf{r}|} \quad \text{for} \quad |\mathbf{r}| \rightarrow \infty . \tag{10}$$

It is rather smooth and does not display a very pronounced shell structure.

Contrary to this, v_{resp} is repulsive and short ranged. Remarkably enough, it exhibits step-function behavior [25]. As has been shown in [28], the steps of v_{resp} originate from the corresponding stepped structure of the response $\delta g(\mathbf{r}_1,\mathbf{r}_2)/\delta \rho(\mathbf{r}_3)$ as a function of $\mathbf{r}_3$. One can see from Fig. 1 that the above-mentioned small intershell peaks of v_x are evidently built in by the superposition of the stepped form of v_{resp} on the smooth v_S.

This special behavior makes desirable the modeling of v_x with individual approximations of v_S and v_{resp}. In this paper a model $v_{\text{resp}}^{\text{mod}}$ is derived, using dimensional arguments, which represents v_{resp} as the statistical average of orbital energy contributions. $v_{\text{resp}}^{\text{mod}}$ possesses the properties and closely reproduces the behavior of the accurate potential. When combined with the exact v_S obtained from Eqs. (5) and (6), $v_{\text{resp}}^{\text{mod}}$ provides an excellent approximation to v_x^{OPM}. A more practical approximation is obtained with $v_{\text{resp}}^{\text{mod}}$ and using the GGA [14] for the exchange energy density $\epsilon_x(\mathbf{r})$ to obtain v_S [cf. (7)]. Contrary to the standard GGA schemes, the latter combination provides both the proper form and eigenvalues of the

one-electron potential and a reasonable estimate of atomic exchange and total energies E_x and E_{tot}.

II. MODEL POTENTIAL $v_{\text{resp}}^{\text{mod}}$

As a starting point for our model we use an approximate equation of Krieger, Li, and Iafrate (KLI) [1] for the OPM exchange potential v_x^{OPM}. OPM neglects the electron Coulomb correlation and its Kohn-Sham equations have the form [6]

$$\{-\tfrac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_x(\mathbf{r})\}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) . \tag{11}$$

The ground-state OPM wave function is the Slater determinant of the eigenfunctions ϕ_i of (11), so that the components v_S^{OPM} and $v_{\text{resp}}^{\text{OPM}}$ of v_x^{OPM} have the form (5) and (9) with g_x built from these functions. In [1] a very accurate approximation to v_x^{OPM} was defined with the equation

$$v_x^{\text{KLI}}(\mathbf{r}) = v_S(\mathbf{r}) + \sum_{i=1}^{N}w_i\frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} . \tag{12}$$

In (12) v_S is the exact functional (5) and (6) and the second term is the statistical average of orbital contributions w_i, the latter being the difference between the expectation values of the potential (12) and the Hartree-Fock exchange operator v_{xi} for the orbital ϕ_i

$$w_i = \int |\phi_i(\mathbf{r})|^2[v_x^{\text{OPM}}(\mathbf{r}) - v_{xi}(\mathbf{r})]d\mathbf{r} , \tag{13}$$

$$v_{xi}(\mathbf{r}_1) = -\frac{1}{\phi_i(\mathbf{r}_1)}\sum_{j=1}^{N}\phi_j^*(\mathbf{r}_1)\int\frac{\phi_i^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_2 . \tag{14}$$

Note that for the highest occupied orbital ϕ_N the expectation values of v_x^{OPM} and v_{xi} are equal [1], making the corresponding parameter w_N vanish

$$w_N = 0 . \tag{15}$$

The second term of (12) offers a promising form for the model $v_{\text{resp}}^{\text{mod}}$. Because of the integral kernel (14), straightforward evaluation (13) requires laborious calculation of the two-electron integrals with the orbitals ϕ_i. However, with some suitable approximation for w_i one can develop an efficient model

$$v_{\text{resp}}^{\text{mod}}(\mathbf{r}) = \sum_{i=1}^{N}w_i\frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} . \tag{16}$$

w_i can be calculated, for example, as the orbital expectation values of some local potential v_w

$$w_i = \int |\phi_i(\mathbf{r})|^2 v_w(\mathbf{r})d\mathbf{r} , \tag{17}$$

chosen as the best local approximation of the difference $[v_x(\mathbf{r}) - v_{xi}(\mathbf{r})]$.

In this paper an alternative approach is presented. We propose to use the model (16) with the orbital contributions w_i being approximated by a function of the orbital energies of Eq. (2). The form of this function is chosen to provide gauge invariance, proper scaling, and the short-range behavior of $v_{\text{resp}}^{\text{mod}}$.

According to the gauge invariance requirement, shift-

ing the external potential by a constant, which leads to addition of a constant to the eigenvalues ϵ_i, should not alter the w_i values. To satisfy this requirement, we choose w_i to be a function of the difference $(\mu - \epsilon_i)$

$$w_i = f(\mu - \epsilon_i) , \tag{18}$$

where μ is the Fermi level of a given system, which is equal to the one-electron energy of the highest occupied orbital $\mu = \epsilon_N$.

The exchange potential (1) and its components v_S and v_{resp} have the scaling property

$$v_x([\rho_\lambda];\mathbf{r}) = \lambda v_x([\rho];\lambda\mathbf{r}) , \tag{19}$$

where

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda\mathbf{r}) , \tag{20}$$

while ϵ_i has the scaling property

$$\epsilon_i[\rho_\lambda] = \lambda^2 \epsilon_i[\rho(\mathbf{r})] . \tag{21}$$

To provide (19), the function f from Eq. (24) should scale as

$$f(\lambda^2(\mu - \epsilon_i)) = \lambda f(\mu - \epsilon_i) \tag{22}$$

and so we find the square root of $(\mu - \epsilon_i)$ to be the properly scaling function f

$$w_i = f(\mu - \epsilon_i) = K[\rho]\sqrt{\mu - \epsilon_i} . \tag{23}$$

By definition, (23) satisfies the condition (15). Owing to this, the highest occupied orbital ϕ_N does not contribute to the numerator of (16), thus providing the short-range behavior of v_{resp}^{mod}

$$v_{resp}^{mod}(\mathbf{r}) = K[\rho] \sum_{i=1}^{N} \sqrt{\mu - \epsilon_i} \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} . \tag{24}$$

As a result, our model potential (24) possesses the required gauge invariance, proper scaling, and short-range behavior.

$K[\rho]$ in (24) is a numerical coefficient, which can be determined from the homogeneous electron gas model. For the gas of density ρ the exact v_{resp} of Eq. (9) has the form

$$v_{resp} = \frac{k_F}{2\pi} , \tag{25}$$

where k_F is the Fermi wave vector

$$k_F = (3\pi^2\rho)^{1/3} . \tag{26}$$

Setting v_{resp}^{mod} of Eq. (24) equal to (25), one can calculate $K_g[\rho]$. For the homogeneous electron gas the Kohn-Sham orbitals and eigenvalues of Eq. (2) are given by

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} , \tag{27}$$

where V is the volume of the system and

$$\epsilon_{\mathbf{k}} = \frac{k^2}{2} + v_x[\rho] + v_c[\rho] . \tag{28}$$

The Fermi level is given by

$$\mu = \frac{k_F^2}{2} + v_x[\rho] + v_c[\rho] . \tag{29}$$

Inserting the above expression in (24), we obtain

$$v_{resp}^{mod} = \frac{K_g[\rho]}{\sqrt{2}\rho V} \sum_{|\mathbf{k}| < k_F} \sqrt{k_F^2 - k^2} . \tag{30}$$

A replacement of the sum in (30) by an integral yields

$$v_{resp}^{mod}(\mathbf{r}) = \frac{K_g[\rho]}{\sqrt{2}(2\pi)^3\rho} \int_0^{k_F} \sqrt{k_F^2 - k^2} \, 4\pi k^2 dk$$

$$= \frac{K_g[\rho]k_F^4}{2\sqrt{2}(2\pi)^2\rho} \int_0^1 \sqrt{1-x^2} x^2 dx = \frac{3\pi K_g}{16\sqrt{2}} k_F . \tag{31}$$

From (25) and (31) the $K_g[\rho]$ value is defined by

$$K_g[\rho] = K_g = \frac{8\sqrt{2}}{3\pi^2} \approx 0.382 , \tag{32}$$

which is valid for the homogeneous electron gas of an arbitrary density, i.e., in this case $K_g[\rho]$ does not depend on ρ.

III. SELF-CONSISTENT SCHEME WITH v_{resp}^{mod}

We propose to use the model (24) within a self-consistent scheme, in which the Kohn-Sham equations (11) are solved with the approximate exchange potential

$$v_x^{mod}(\mathbf{r}) = v_S(\mathbf{r}) + v_{resp}^{mod}(K, \mathbf{r}) , \tag{33}$$

where v_S is the Slater potential (5) or a suitable approximation. The resulting Kohn-Sham orbitals are used to calculate the total energy, with the exchange energy being calculated from (7) with the self-consistent potential v_S. The electron-gas value K_g of (32) can be chosen as the universal parameter of v_{resp}^{mod} for all systems. Another option is to determine K self-consistently from the requirement that the Levy-Perdew relation [29]

$$E_x = \int [3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})]v_x^{mod}(\mathbf{r})d\mathbf{r} \tag{34}$$

should yield the same value of E_x as in Eq. (7) with the potential v_S

$$E_x = \int [3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})][v_S(\mathbf{r}) + K_{sc}[\rho]R(\mathbf{r})]d\mathbf{r}$$

$$= \frac{1}{2} \int \rho(\mathbf{r})v_S(\mathbf{r})d\mathbf{r} , \tag{35}$$

$$R(\mathbf{r}) = \sum_{i=1}^{N} \sqrt{\mu - \epsilon_i} \frac{|\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} . \tag{36}$$

From requirement (35) follows an expression for $K[\rho]$

$$K_{sc}[\rho] = -\frac{I_1}{I_2} , \tag{37}$$

$$I_1 = \int [\tfrac{5}{2}\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})]v_S d\mathbf{r} , \tag{38}$$

$$I_2 = \int [3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})]R(\mathbf{r})d\mathbf{r} . \tag{39}$$

We will give examples of the use of our model response potential together with the exact v_S of Eq. (5), but in order to develop an efficient DFT scheme with (33), an appropriate approximation to v_S is needed. One can use, for example, the weighted-density approximation [30–32] for the pair-correlation function g_x, which guarantees the correct asymptotics (10) of v_S. In this paper we use a more practical model of v_S, which is obtained from the GGA of Becke [14,5]. In [14] the exchange energy density $\epsilon_x(\rho;\mathbf{r})$

$$E_x = \int \epsilon_x(\rho;\mathbf{r})d\mathbf{r} , \tag{40}$$

to the second order of the gradient expansion

$$\epsilon_x^{\text{approx}}(\rho;\mathbf{r}) = -\rho^{4/3}(\mathbf{r})\left[\frac{3}{2}\left[\frac{3}{8\pi}\right]^{1/3} + a_0\xi\right] , \tag{41}$$

$$\xi = 2^{2/3}\left[\frac{\nabla\cdot\rho(\mathbf{r})}{\rho^{4/3}(\mathbf{r})}\right]^2 , \tag{42}$$

is modified with the correction function f of the argument $\xi^{1/2}\sinh^{-1}\xi^{1/2}$

$$\epsilon_x^{\text{GGA}}(\rho;\mathbf{r})$$
$$= -\rho^{4/3}(\mathbf{r})\left[\frac{3}{2}\left[\frac{3}{8\pi}\right]^{1/3} + a_0 f(\xi^{1/2}\sinh^{-1}\xi^{1/2})\xi\right] , \tag{43}$$

$$f(\xi^{1/2}\sinh^{-1}\xi^{1/2}) = \frac{1}{1+6a_0\xi^{1/2}\sinh^{-1}\xi^{1/2}} . \tag{44}$$

Using (7) and (40), one can derive from (43) the corresponding approximation for v_S

$$v_S^{\text{GGA}}(\mathbf{r}) = \frac{2\epsilon_x^{\text{GGA}}(\rho;\mathbf{r})}{\rho(\mathbf{r})}$$
$$= -\rho^{1/3}(\mathbf{r})\left[3\left[\frac{3}{8\pi}\right]^{1/3}\right.$$
$$\left. + 2a_0 f(\xi^{1/2}\sinh^{-1}\xi^{1/2})\xi\right] . \tag{45}$$

This potential has the proper scaling (19), the correct asymptotics (10), and for the fitted value $a_0 = 0.0042$ it yields a rather accurate estimate of E_x via the integral (7). The results of self-consistent calculations within the proposed scheme will be discussed in the following sections.

IV. COMPARISON OF THE SELF-CONSISTENT POTENTIALS

In order to test the proposed self-consistent scheme, comparative exchange-only atomic calculations have been performed for the closed-shell atoms Be, Ne, Mg, Ar, Ca, Zn, Kr, Sr, Cd, and Xe. The exchange potentials v_x to be compared can be subdivided into two groups, depending on whether the accurate function $v_S(5)$ or its GGA $v_S^{\text{GGA}}(45)$ is used as the Slater potential in (33). The first group includes the bare v_S [i.e., in this case v_{resp} is

neglected in (33)] $v_x^{\text{mod}(S)}$, which is a sum of v_S and $v_{\text{resp}}^{\text{mod}}$ calculated with either K_{sc} or K_g, and the full v_x^{OPM}. The second group includes the bare v_S^{GGA}, $v_x^{\text{mod}(\text{GGA})}$, which is a sum of v_S^{GGA} and $v_{\text{resp}}^{\text{mod}}$ calculated with either K_{sc} or K_g, and the total exchange potential v_x^{GGA} of the standard GGA [22,14], obtained as the functional derivative of E_x^{GGA}. The response part of v_x^{GGA} is defined by Eq. (45) and the equality

$$v_x^{\text{GGA}}(\mathbf{r}) = \delta E_x^{\text{GGA}}/\delta\rho(\mathbf{r}) = v_S^{\text{GGA}}(\mathbf{r}) + v_{\text{resp}}^{\text{GGA}} . \tag{46}$$

The results will also be compared with those obtained with the KLI potential (12).

To investigate the quality of the GGA to v_S locally, in Fig. 2 v_S^{GGA} [Eq. (45)] is compared to v_S^{OPM} [Eqs. (5) and (6)]. The orbitals and densities have been obtained self-consistently in GGA and OPM calculations, respectively, for Ne and Mg. There are appreciable local deviations of v_S^{GGA} from v_S^{OPM}. For both Ne and Mg the former is more attractive than the latter within the regions of $1s$ and $2s$ shells and less attractive in the intershell region. At longer distances (not shown here) all the potentials presented have the same Coulombic asymptotics (10). The differences between v_S^{GGA} and v_S^{OPM} originate from the different expressions, Eqs. (45) and (5), respectively, and not from differences in the self-consistent densities and orbitals. Even the change in self-consistent orbitals and densities resulting from neglect of the response part of the exchange potential during the self-consistency iterations, which leads to $\bar{v}_S^{\text{GGA}}$ and $\bar{v}_S^{\text{OPM}}$, has little effect. v_S^{OPM} and $\bar{v}_S^{\text{OPM}}$ are hardly distinguishable from each other on the scale presented. The neglect of $v_{\text{resp}}^{\text{GGA}}$ makes $\bar{v}_S^{\text{GGA}}$ slightly more attractive than v_S^{GGA}.

The local deviations of v_S^{GGA} from the accurate v_S clearly manifest themselves in Table I where the atomic K_{sc} values for $v_x^{\text{mod}(S)}$ and $v_x^{\text{mod}(\text{GGA})}$ are presented (we drop in the remainder the superscript OPM on v_S and there is no need to distinguish between v_S^{OPM} and $\bar{v}_S^{\text{OPM}}$). For all atoms (with the exception of the lightest Be and Ne) K_{sc} values obtained with the accurate functional (5) are rather close to the electron-gas constant $K_g = 0.382$. However, replacement of v_S by v_S^{GGA} leads to a great overestimation of the integral I_1 of (38). As a result, the

TABLE I. Values of the parameter K_{sc} obtained within the self-consistent scheme for potentials $v_x^{\text{mod}(S)}$ and $v_x^{\text{mod}(\text{GGA})}$.

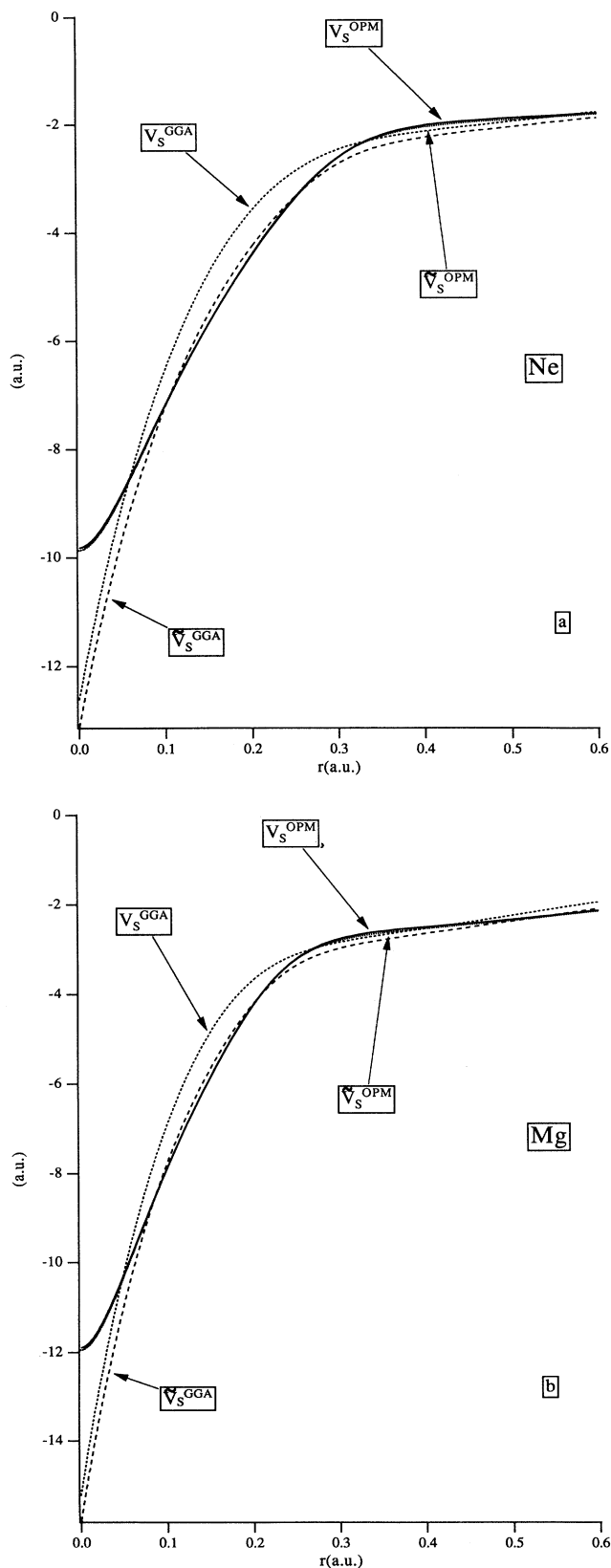| Atom	$v_x^{\text{mod}(S)}$	$v_x^{\text{mod}(\text{GGA})}$
Be	0.305	0.803
Ne	0.342	0.518
Mg	0.384	0.536
Ar	0.365	0.463
Ca	0.389	0.478
Zn	0.381	0.440
Kr	0.381	0.440
Sr	0.397	0.453
Cd	0.388	0.432
Xe	0.386	0.428

FIG. 2. Slater potentials calculated self-consistently as the parts of the OPM and GGA exchange potentials and also obtained with the neglect of v_{resp}. (a) Ne and (b) Mg.

K_{sc} value for Be calculated with v_S^{GGA} is 2.6 times as large as that calculated with v_S. The overestimation decreases rapidly with increasing atomic number. Still, even for Xe, K_{sc} for v_S^{GGA} is about 1.1 times as large as that for v_S.

The analysis of the contributions to I_1 shows that the major part of the above-mentioned overestimation comes from the region close to the nucleus where v_S^{GGA} exhibits the largest deviations from v_S (see Fig. 2). The success of the GGA for the exchange energy is due to the fact that the exchange energy integrals (7) with v_S^{GGA} are very close to those with v_S; the typical error is only about 0.1% [14]. However, our results show that it is not a high local quality of the GGA, but an incredibly precise cancellation of local errors when v_S^{GGA} is integrated against $\rho(\mathbf{r})$ [Eq. (7)] that provides this success. For the integrals of the type (38) associated with the Levy-Perdew relation this balance is destroyed, which leads to the overestimated K_{sc} values (see Table I). We refer to Refs. [23,24,5] for detailed discussions of the local deficiencies of the total GGA potential and its components (Slater and response respectively).

To analyze the local quality of the proposed model (24) for the response potential, $v_{\text{resp}}^{\text{mod}(S)}$ with the parameter K_{sc} and $v_{\text{resp}}^{\text{mod}(\text{GGA})}$ with K_g are compared for Ne and Mg in Fig. 3 with $v_{\text{resp}}^{\text{OPM}}$ and $v_{\text{resp}}^{\text{KLI}}$ with the parameters w_i from (13) and also with the corresponding potential $v_{\text{resp}}^{\text{GGA}}$, the latter being obtained from the total exchange potential v_x^{GGA} of the GGA [22,14] by the subtraction of its Slater part v_S^{GGA} [Eq. (45)]. In this case the GGA gives a considerably worse approximation than in the case of the Slater potentials discussed above. Due to the inclusion of the uncompensated Laplacian terms, $v_{\text{resp}}^{\text{GGA}}$ has incorrect Coulombic divergence at the nucleus, being proportional to $-1/r$ [4,22]. At large distances it has incorrect Coulombic decay, being proportional to $1/r$. Furthermore, $v_{\text{resp}}^{\text{GGA}}$ does not display the shell structure at intermediate distances, thus exhibiting large local deviations from $v_{\text{resp}}^{\text{OPM}}$.

Contrary to this, the simple model (24) provides a good fit to $v_{\text{resp}}^{\text{OPM}}$ and to the more complicated approximation $v_{\text{resp}}^{\text{KLI}}$. Both potentials $v_{\text{resp}}^{\text{mod}(S)}$ and $v_{\text{resp}}^{\text{mod}(\text{GGA})}$ have the proper short-range behavior and they reproduce well the height and the width of the individual shell steps of $v_{\text{resp}}^{\text{OPM}}$, the largest differences being constants within the $1s$ shell.

In Fig. 4 various self-consistent approximate exchange potentials are compared with v_x^{OPM}. The bare Slater potential v_S is everywhere more attractive than v_x^{OPM} (the response part of the exchange potential is positive) and the v_S can be considered as a satisfactory approximation to v_x only at larger distances where both potentials have the same Coulombic asymptotics. At $r < 1$ a.u. the neglect of the repulsive potential v_{resp} leads to a substantial overestimation of the exchange effect.

The GGA [14] offers a more balanced approximation to v_x, though the above-mentioned defects of its components v_S^{GGA} and $v_{\text{resp}}^{\text{GGA}}$ clearly manifest themselves in the total potential v_x^{GGA}. In particular, it has incorrect long-range asymptotics $-1/r^2$ and it is not attractive enough in the outer region. However, due to the diver-
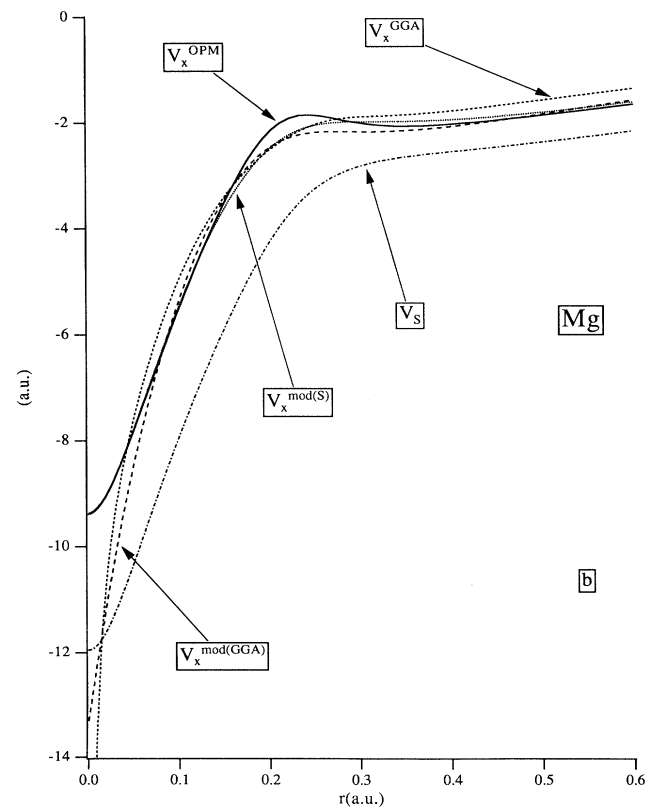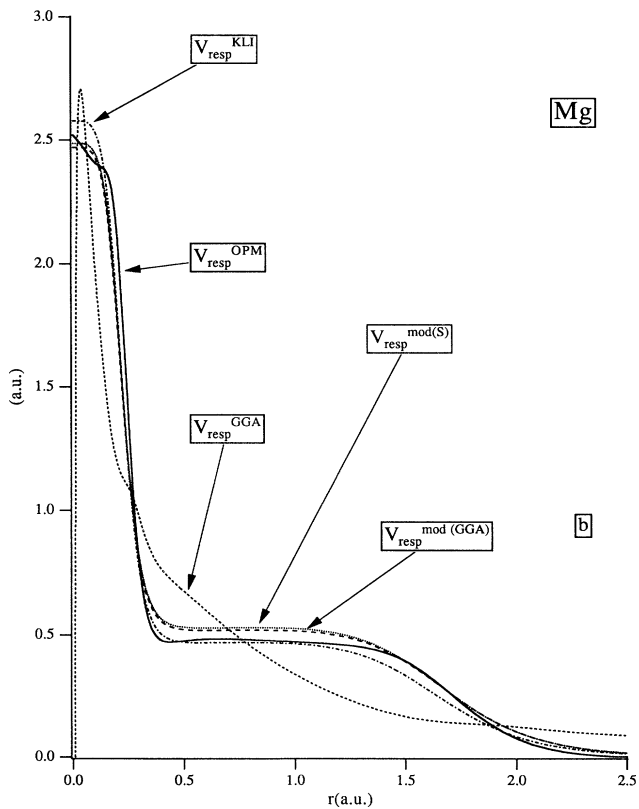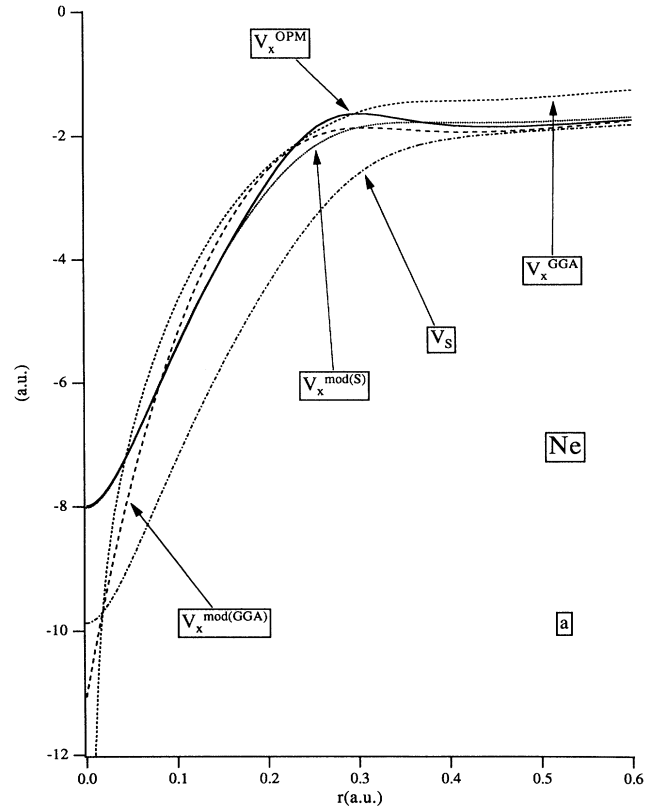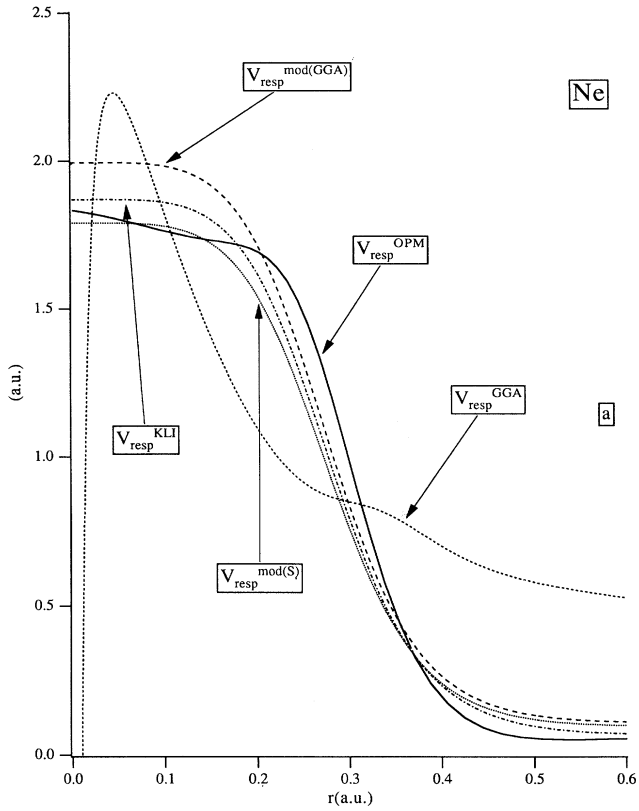
FIG. 3. Comparison of v_{resp}^{OPM} with various approximate response potentials. (a) Ne and (b) Mg.

FIG. 4. Comparison of v_x^{OPM} with various approximate exchange potentials. (a) Ne and (b) Mg.

gence of its component $v_{\text{resp}}^{\text{GGA}}$ at the nucleus and the overattractive character of v_S^{GGA} in the region close to the nucleus, v_x^{GGA} strongly overestimates the exchange effect in this region. At intermediate distances v_x^{GGA} smooths away the clear shell structure of v_x^{OPM}.

The self-consistent scheme of Sec. III produces potentials with a higher local quality of approximation to v_x^{OPM}. One can see from Fig. 4 that $v_x^{\text{mod}(S)}$, with the components v_S and $v_{\text{resp}}^{\text{mod}}$, is an excellent approximation to v_x^{OPM}. $v_x^{\text{mod}(S)}$ is very close to v_x^{OPM} at any distance and in the major intervals they are even hardly distinguishable from each other. The main difference is that the approximation (24) smooths away the small intershell peaks of v_x^{OPM}. However, this difference does not seem to be an important one since these peaks appear to be a minor detail of the stepped shell structure of v_x^{OPM} (see Figs. 1 and 4).

$v_x^{\text{mod(GGA)}}$ with the components v_S^{GGA} and $v_{\text{resp}}^{\text{mod}}$ shows a worse local quality of approximation, mainly due to the defects of v_S^{GGA} discussed above. Nevertheless, the replacement of $v_{\text{resp}}^{\text{GGA}}$ by $v_{\text{resp}}^{\text{mod}}$ improves the short- and long-range asymptotics of the approximate potential and makes more clear its shell structure. As a result, $v_x^{\text{mod(GGA)}}$ is, in contrast to v_x^{GGA}, finite at the nucleus and has the proper Coulombic asymptotics at longer distances (see Fig. 4).

V. CALCULATIONS
WITH THE ACCURATE SLATER POTENTIAL

Tables II and III present the total E_{tot} and exchange E_x atomic energies calculated self-consistently with v_S and various potentials v_{resp}, namely, with $v_{\text{resp}}^{\text{OPM}}$, $v_{\text{resp}}^{\text{KLI}}$, and $v_{\text{resp}}^{\text{mod}}$ (calculated with K_{sc} and K_g), and also with the neglect of v_{resp}. In all these approaches the energies are calculated with the same functional (5)–(7), so that the corresponding energy differences are caused exclusively by the differences in orbitals and densities generated with various exchange potentials. It is of no surprise that the OPM E_{tot} values [33,23] are always the lowest ones presented in Table II. The OPM potential is defined

within the variational method and so it provides the true minimum of E_{tot} calculated within the one-determinantal approach with the exchange functional (5)–(7). The inclusion of the proper v_{resp} is of importance for the quality of the calculated E_{tot}. Neglect of v_{resp} leads to considerable errors; the error in E_{tot} obtained with the bare v_S increases with increasing atomic number and reaches 0.45 a.u. for Xe.

One can see from Table II that the model (24) provides an excellent approximation to $v_{\text{resp}}^{\text{OPM}}$ as regards the total energy. It is not too sensitive to variations of the parameter K and calculations with either K_{sc} or K_g yield virtually the same energies as with the more complicated KLI approximation. E_{tot} values obtained with v_S and $v_{\text{resp}}^{\text{mod}}$ are only by a few millihartrees higher than those of the OPM. The corresponding error increases (though non-monotonously) with increasing atomic number, but even for Xe it is only about 0.01 a.u. It means that the addition of (24) considerably improves the quality of the Kohn-Sham orbitals and density, which come very close to those of the rigorous OPM.

Because of the attractive character of v_S, calculations with the neglect of the repulsive v_{resp} yield contracted orbitals and too negative E_x (see Table III). The addition of the approximate repulsive potentials v_{resp} brings the self-consistent E_x values much closer to E_x^{OPM} [8], but it overcompensates and makes them more positive than E_x^{OPM} (the only exception is E_x for Be obtained with $v_{\text{resp}}^{\text{KLI}}$). A comparison of Tables II and III reveals another type of compensation. In all cases the errors of E_x are compensated with those of the opposite sign in other parts of the total energy, so that E_{tot} errors are much smaller than those of E_x. In most cases the E_x errors of the model (24) are somewhat larger (though of comparable magnitude) than those of KLI.

The most important one-electron energetical characteristic of the Kohn-Sham theory is the energy ϵ_N of the highest occupied orbital ϕ_N. For the exact Kohn-Sham potential ϵ_N is equal to minus the ionization energy I_p of the system [34] and in the exchange-only case ϵ_N has the same meaning through Koopmans's theorem [35,1].

TABLE II. Comparison of differences (in mhartree) of the total energies calculated self-consistently with the exact potential v_S and various approximations to v_{resp}, with the OPM total energies $E_{\text{tot}}^{\text{OPM}}$ [33,23] (the latter are given in hartrees and are always more negative).

Atom	$-E_{\text{tot}}^{\text{OPM}}$	$v_{\text{KLI}}^{\text{resp}}$	$v_{\text{mod}}^{\text{resp}}(K_{\text{sc}})$	$v_{\text{mod}}^{\text{resp}}(K_g)$	Neglect of v_{resp}
Be	14.572	0	0	0	11
Ne	128.545	0	1	0	44
Mg	199.612	1	2	2	79
Ar	526.812	2	3	4	109
Ca	676.752	2	4	4	146
Zn	1777.834	4	6	6	258
Kr	2752.043	4	5	5	288
Sr	3131.533	4	7	7	324
Cd	5465.114	6	6	6	419
Xe	7232.121	7	12	11	450

TABLE III. Comparison of differences (in mhartree) of the OPM exchange energies E_x^{OPM} [8] (the latter are given in hartrees) and those calculated self-consistently with the exact potential v_S and various approximations to v_{resp}.

Atom	$-E_x^{\text{OPM}}$	$v_{\text{KLI}}^{\text{resp}}$	$v_{\text{mod}}^{\text{resp}}(K_{\text{sc}})$	$v_{\text{mode}}^{\text{resp}}(K_g)$	Neglect of v_{resp}
Be	2.666	-1	2	14	-49
Ne	12.107	9	5	30	-200
Mg	15.992	10	11	9	-305
Ar	30.182	8	41	63	-436
Ca	35.209	5	40	30	-525
Zn	69.647	78	55	60	-1030
Kr	92.875	65	88	90	-1101
Sr	101.974	58	59	14	-1177
Cd	148.963	123	150	123	-1536
Xe	179.173	119	218	199	-1591

Table IV represents ϵ_N values obtained with v_S and various v_{resp}. It follows from the table that in the case of the orbital energies ϵ_N, the qualitative trends are the same as in the case of the exchange energies discussed above. In spite of its correct asymptotics (10), the bare v_S always has too negative ϵ_N values. The addition of v_{resp} compensates this error. By construction, both $v_{\text{resp}}^{\text{KLI}}$ and $v_{\text{resp}}^{\text{mod}}$ decay exponentially in the region of ϕ_N, because ϕ_N does not contribute to the numerators of (24) and the second term of (12), while contributing to the density ρ in the denominators. The resulting exponential tails of $v_{\text{resp}}^{\text{mod}}$ and $v_{\text{resp}}^{\text{KLI}}$ produce the compensating repulsive contribution to ϵ_N. The addition of $v_{\text{resp}}^{\text{mod}}$ even has an overcompensating effect because the approximation (24) always (with the only exception of Zn) overestimates the value of the parameter w_{N-1} for ϕ_{N-1}, the next to the highest occupied orbital. As a result, $v_{\text{resp}}^{\text{mod}}$ becomes more positive than $v_{\text{resp}}^{\text{KLI}}$ in the outer valence region (see Fig. 3) and yields more positive ϵ_N values than those of KLI (the only exception is ϵ_N of Zn); the latter are virtually the same as the OPM ϵ_N. However, the corresponding errors are not large and vary within 0.01–0.03 a.u. in both variants (K_{sc}

and K_g).

The present results show that the self-consistent scheme with v_S and $v_{\text{resp}}^{\text{mod}}$ can be used as a very good approach to the OPM. The variants with K_{sc} and K_g yield results of the same quality, so one can use a more simple variant with the universal electron-gas parameter K_g for all systems. When the exact functional v_S is used, the scheme requires calculation of the two-electron integrals with the orbitals ϕ_i and the required computational time per iteration is approximately the same as in the case of KLI. However, replacement of $v_{\text{resp}}^{\text{KLI}}$ by $v_{\text{resp}}^{\text{mod}}$ greatly accelerates the convergence of the self-consistent procedure. The ratio of iterations needed to reach convergence in KLI and in the present scheme varies within 6–12 for the noble-gas atoms from Ar to Xe and within 12–18 for the alkaline-earth atoms from Mg to Sr. As a result, the proposed scheme takes about an order of magnitude less computational time than KLI.

Still, to develop a practical DFT scheme, one should approximate not only v_{resp}, but also v_S. The results of calculations with the GGA to v_S will be presented in the next section.

TABLE IV. Comparison of differences between the OPM values for the highest occupied orbital energy ϵ_N^{OPM} (in mhartree) [33,23] and those calculated self-consistently with the exact potential v_S and various approximations to v_{resp}.

Atom	$-\epsilon_N^{\text{OPM}}$	$v_{\text{KLI}}^{\text{resp}}$	$v_{\text{mod}}^{\text{resp}}(K_{\text{sc}})$	$v_{\text{mod}}^{\text{resp}}(K_g)$	Neglect of v_{resp}
Be	309	0	1	6	-17
Ne	851	2	21	30	-61
Mg	253	1	5	5	-31
Ar	591	2	18	21	-47
Ca	196	1	10	10	-29
Zn	293	1	-14	-14	-64
Kr	523	1	20	20	-44
Sr	179	1	12	10	-30
Cd	265	0	2	1	-65
Xe	456	1	23	22	-40

TABLE V. Comparison of differences (in mhartrees) between the OPM total energies $E_{\text{tot}}^{\text{OPM}}$ [33,23] and the GGA total energies, calculated self-consistently with v_S^{GGA} and various approximations to v_{resp}.

Atom	$-E_{\text{tot}}^{\text{OPM}}$	$v_{\text{GGA}}^{\text{resp}}$	$v_{\text{mod}}^{\text{resp}}(K_{\text{sc}})$	$v_{\text{mod}}^{\text{resp}}(K_g)$	Neglect of v_{resp}
Be	14.572	6	34	12	21
Ne	128.545	−45	−30	−29	35
Mg	199.612	−21	3	−5	78
Ar	526.812	11	33	26	141
Ca	676.752	−2	27	15	149
Zn	1777.834	−287	−272	−268	33
Kr	2752.043	−60	−39	−41	269
Sr	3131.533	−48	−19	−23	298
Cd	5465.114	−79	57	60	364
Xe	7232.121	2	35	25	463

VI. CALCULATIONS WITH THE GGA TO v_S

Tables V and VI represent E_{tot} and E_x values obtained with the GGA (45) to v_S, with and without the response potentials $v_{\text{resp}}^{\text{GGA}}$ and $v_{\text{resp}}^{\text{mod}}$ being used in the self-consistent field (SCF). These energies are given as differences with respect to $E_{\text{tot}}^{\text{OPM}}$, but it should be noted that, since they are calculated with the GGA energy functional, these energies reflect both the effect of changes in the SCF density and orbitals due to the use of different potentials and the effect of using a different energy expression. Engel and Vosko [24] have investigated both the substitution of self-consistent OPM densities into LDA and GGA energy functionals and the substitution of self-consistent LDA and GGA orbitals and densities into $E_{\text{tot}}^{\text{OPM}}$. The latter procedure gives energies that are typically only a few centihartrees too high, where the variational stability of $E_{\text{tot}}^{\text{OPM}}$ has to be kept in mind. The effect of switching to the GGA energy functional is of the order of 0.1%. Using OPM densities, the differences with $E_{\text{tot}}^{\text{OPM}}$ are again usually a few centihartrees (but occasionally a few tenths of a hartree) both positive and negative because $E_{\text{tot}}^{\text{OPM}}$ does not represent a lower bound for $E_{\text{tot}}^{\text{GGA}}$. Using the full GGA potential in the SCF calculation, including $v_{\text{resp}}^{\text{GGA}}$ derived from the functional derivative of E_x^{GGA}, yields the minimal $E_{\text{tot}}^{\text{GGA}}$ and Table V demonstrates that the differences with $E_{\text{tot}}^{\text{OPM}}$ are of the same order of mag-

nitude as with OPM densities substituted into $E_{\text{tot}}^{\text{GGA}}$, but now the energies are more consistently too negative. Note the exceptionally large error of −0.3 a.u. for Zn. The main message of Table V is that again calculations with the neglect of v_{resp} yield too positive E_{tot} values. The upward shift in the energies as a result of omission of v_{resp} is very similar to (in general, some 30–40 mhartree higher than) the one found in the calculations with the accurate v_S; cf. Table II. Compared to $E_{\text{tot}}^{\text{OPM}}$ the error is much larger than with the use of $v_{\text{resp}}^{\text{GGA}}$, except for Zn where it becomes fortuitously small due to adding a positive shift to the exceptionally large negative deviation of the $v_{\text{resp}}^{\text{GGA}}$ result. Inclusion of $v_{\text{resp}}^{\text{mod}}$ leads to results more similar to those of $v_{\text{resp}}^{\text{GGA}}$. E_{tot} for Be obtained with K_g is much closer to $E_{\text{tot}}^{\text{OPM}}$ than that obtained with K_{sc}, because of the overestimation of K_{sc} in the GGA discussed above. In general, however, both variants yield very similar E_{tot} values. The considerable local deviations of $v_{\text{resp}}^{\text{GGA}}$ from the model potentials $v_{\text{resp}}^{\text{mod}}$ show up in differences in the energy. These differences are of course positive with respect to the optimized GGA energy resulting from the use of $v_{\text{resp}}^{\text{GGA}}$ and indeed constitute an improvement with respect to $E_{\text{tot}}^{\text{OPM}}$ in the 6 out of 10 cases where $v_{\text{resp}}^{\text{GGA}}$ leads to a significant negative deviation. This improvement, which is not very significant, is thus understandable and cannot simply be related to the fact that the $v_{\text{resp}}^{\text{mod}}$ are actually much closer to the accurate step po-

TABLE VI. Comparison of differences (in mhartrees) between the OPM exchange energies E_x^{OPM} [8] and those calculated self-consistently with v_S^{GGA} and various approximations to v_{resp}.

Atom	$-E_x^{\text{OPM}}$	$v_{\text{GGA}}^{\text{resp}}$	$v_{\text{mod}}^{\text{resp}}(K_{\text{sc}})$	$v_{\text{mod}}^{\text{resp}}(K_g)$	Neglect of v_{resp}
Be	2.666	14	44	−10	−73
Ne	12.107	20	−36	−122	−359
Mg	15.992	20	25	−92	−406
Ar	30.182	59	93	−13	−520
Ca	35.209	27	97	−39	−606
Zn	69.646	−76	−138	−303	−1375
Kr	93.876	76	95	−83	−1277
Sr	101.974	61	91	−128	−1332
Cd	148.963	126	189	−27	−1688
Xe	179.174	167	314	100	−1714

TABLE VII. Comparison of differences of the OPM energies of the highest occupied orbital ϵ_N^{OPM} (in mhartrees) [33,23] and those calculated self-consistently with v_S^{GGA} and various approximations to v_{resp}.

Atom	$-\epsilon_N^{OPM}$	v_{GGA}^{resp}	$v_{mod}^{resp}(K_{sc})$	$v_{mod}^{resp}(K_g)$	Neglect of v_{resp}
Be	309	128	29	8	-15
Ne	851	396	128	98	9
Mg	253	104	19	6	-30
Ar	591	249	57	43	-23
Ca	196	80	15	6	-34
Zn	293	102	-19	-25	-74
Kr	523	218	42	33	-31
Sr	179	72	12	5	-38
Cd	265	95	-6	-13	-82
Xe	456	187	35	28	-34

tential v_{resp}^{OPM} (cf. Fig. 3) than is v_{resp}^{GGA}.

In complete analogy with the case of v_S, calculations with the bare v_S^{GGA} yield too negative E_x values (see Table VI). The addition of the approximate v_{resp} considerably compensates the corresponding error. In the case of v_{resp}^{GGA} and v_{resp}^{mod} with K_{sc} this leads even to overcompensation and for most atoms E_x are too positive, while in the case of v_{resp}^{mod} with K_g the compensation is not enough, thus producing too negative E_x (the only exception in the latter case is Xe). In general, all the schemes with the approximate v_{resp} yield E_x values of comparable accuracy.

The self-consistent scheme with v_S^{GGA} and v_{resp}^{mod} shows a definite advantage over the standard GGA in calculation of ϵ_N (see Table VII). As indicated in [2,4] and as one can see from Table VII, the GGA greatly underestimates the absolute magnitude of ϵ_N. Due to the incorrect asymptotics of its response parts (see Fig. 3), $|\epsilon_N|$ values of v_x^{GGA} are about twice as small as compared with the OPM values and are very close to the LDA ones [4]. On the other hand, the bare v_S^{GGA} overestimates $|\epsilon_N|$ (the only exception is Ne), though the corresponding errors are considerably smaller. The addition of v_{resp}^{mod} with K_{sc} to v_S^{GGA} overcompensates this effect and produces comparable errors of the opposite sign. The ϵ_N values of the potential $(v_S^{GGA}+v_{resp}^{mod})$ obtained with K_g are in most cases the best approximate ones and the closest to ϵ_N^{OPM}.

It follows from the above analysis that the self-consistent scheme with v_S^{GGA} and v_{resp}^{mod} provides the same accuracy for the total and exchange energies as the standard GGA scheme [14] and considerably improves the form and the eigenvalue ϵ_N of the one-electron potential. Bearing in mind the high quality of the presented results, we propose v_x^{mod} with the components v_S^{GGA} and v_{resp}^{mod} as an efficient approximation to v_x. The variant with K_g provides a better fit to the accurate v_{resp} and it is also simpler than that with K_{sc}, so the electron-gas value K_g can be recommended as the universal parameter for the many-electron calculations.

VII. CONCLUSIONS

In this paper a scheme of approximation of the Kohn-Sham exchange potential v_x has been proposed, making

use of a partitioning of v_x into Slater and response potentials. A model potential v_{resp}^{mod} has been derived from dimensional arguments that possesses the proper short-range behavior and the characteristic atomic-shell stepped structure. When combined with the accurate v_S, v_{resp}^{mod} provides an excellent approximation to v_x^{OPM}. With the GGA approximation to v_S, v_{resp}^{mod} provides an efficient DFT approach which possesses the three desirable properties of fitting closely the form of the accurate exchange potential, yielding reasonably accurate exchange and total energies and giving a reasonably accurate orbital energy of the highest occupied orbital.

Still, we have to mention appreciable errors, which are introduced with the GGA to v_S. In particular, the present GGA approximation shows considerable deviations from the accurate v_S in the region close to the nucleus. In spite of such local deficiencies in v_S^{GGA}, the error in the GGA to E_x is relatively small due to very precise cancellation of local errors in the integrand of Eq. (7). Nonetheless, the typical error of the calculated total energies is in the order of centihartrees with the replacement of v_S by v_S^{GGA}. So, in order to provide a better practical DFT scheme, one should improve, first of all, the quality of the applied v_S approximation. A promising way of obtaining an improved model Slater potential v_S^{mod} is to construct it not as a function of ρ and $\nabla\rho$, but as some function of the orbital densities $|\phi_i|^2$ and their gradients.

To test the quality of the developed v_x^{mod} approximation, exchange-only atomic calculations have been performed in this work. Our main goal, however, is to apply this approximation for full exchange-correlation molecular calculations. For this purpose one can use v_x^{mod} either as an independent exchange part of the approximate exchange-correlation Kohn-Sham potential v_{xc}^{appr} or as the basic functional form for approximation of the total v_{xc}. Within the former approach v_x^{mod} is inserted in the Kohn-Sham equations (2) together with some approximation for the Coulomb correlation potential v_c; the latter is to be constructed independently. Then the exchange energy is calculated via (7) with the self-consistent density and v_S^{mod}, while the correlation energy is calculated with the independent functional, which corresponds to v_c.

An alternative approach is based on the fact that v_x is the dominant part of v_{xc} and the exchange energy density

ϵ_x is the dominant part of ϵ_{xc}. To approximate the total v_{xc} and ϵ_{xc}, one can use the same models v_S^{mod} and v_{resp}^{mod} with other parameters chosen to fit the available accurate exchange-correlation Kohn-Sham potentials [4,10,36–38]. Work along both above-mentioned lines is in progress.

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