Direct Approximation of the Long- and Short-Range Components of the Exchange–Correlation Kohn–Sham Potential

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ABSTRACT

An approximation scheme was developed for the Kohn–Sham exchange–correlation potential \( v_{xc} \), making use of a partitioning of \( v_{xc} \) into a long-range screening \( v_{scr} \) and a short-range response \( v_{resp} \) component. For the response part, a model \( v_{mod}^{resp} \) was used, which represents \( v_{resp} \) as weighted orbital density contributions, the weights being determined by the orbital energies. \( v_{mod}^{resp} \) possesses the proper short-range behavior and the atomic-shell stepped structure characteristic for \( v_{resp} \). For the screening part, two model potentials \( v_{mod}^{scr} \) were used, one with the accurate Slater potential; the other one with the generalized gradient approximation (GGA) for the exchange part. Both use the GGA for the Coulomb correlation contribution to \( v_{scr} \). The scheme provides an adequate approximation to \( v_{xc} \) in the outer-valence region with both the proper asymptotics and a rather accurate estimate of the ionization potential from the highest one-electron energy and a reasonable estimate of atomic \( E_{xc} \) and total energies \( E_{tot} \). © 1997 John Wiley & Sons, Inc.

Introduction

Adequate approximation of the Kohn–Sham exchange–correlation potential \( v_{xc} \) remains an important problem of density functional theory (DFT) [1–8]. For the ground state of a given many-electron system, the component \( v_{xc}^{cor} \) of \( v_{xc} \) is defined in DFT as a functional derivative of the exchange–correlation energy \( E_{xc} \{ \rho \} \) with respect to the spin density \( \rho_s(r) \):

\[
v_{xc}^{cor}(r) = \frac{\delta E_{xc} \{ \rho \}}{\delta \rho_s(r)}, \quad (1)
\]

\[
\rho(r) = \rho_s(r) + \rho_p(r). \quad (2)
\]
In the one-electron Kohn–Sham equations [9] (Hartree atomic units will be used throughout the article)

\[ \left\{ +\frac{1}{2} \nabla^2 + v_{xc}(\mathbf{r}) \right\} \phi_{\alpha}(\mathbf{r}) = e_{\phi} \phi_{\alpha}(\mathbf{r}), \]

\[ v_{xc}(\mathbf{r}) = v_{xc}^{\text{ext}}(\mathbf{r}) + v_{H}(\mathbf{r}) + v_{xc}^{\text{tr}}(\mathbf{r}), \]

\( v_{xc}^{\text{tr}} \) represents the local effect of the electron exchange and Coulomb correlation on the Kohn–Sham potential \( v_{xc} \), while the external \( v_{xc}^{\text{ext}} \) and the Hartree \( v_{H} \) potentials represent the electrostatic interaction.

The physically significant properties of \( v_{xc} \) and \( v_{xc}^{\text{tr}} \) are the Coulombic long-range asymptotics of \( v_{xc}^{\text{tr}} \) for finite systems [10–12]:

\[ v_{xc}^{\text{tr}}(\mathbf{r}) \rightarrow -\frac{1}{|\mathbf{r}|}, \quad \text{for } |\mathbf{r}| \rightarrow \infty \]

and the eigenvalue \( \epsilon_{N\alpha} \) of the operator \((-\frac{1}{2}\nabla^2 + v_{xc}^{\text{tr}})\) for the highest occupied orbital \( \phi_{N\alpha} \), which equals the ionization energy \(-I_p\) of the system [1, 10, 11, 13]

\[ \epsilon_{N\alpha} = -I_p. \]

Examples of \( v_{xc} \) can be obtained via the procedures of [8, 12, 14–17], which use a given \( \rho \) (usually, \( \rho \) from ab initio calculations) to construct \( v_{xc} \). Hitherto, \( v_{xc} \) was obtained only for few-electron atomic systems and for the two-electron \( \text{H}_2 \) molecule; in the latter case, \( v_{xc} \) is calculated for a given \( \rho \) in a straightforward way [18].

In Figure 1, \( v_{xc} \) for the Ne atom is presented. It was constructed via the procedure [8] with \( \rho \) taken from configuration interaction (CI) calculations [9]

(here, the spin index is omitted because of identity of \( \alpha \) and \( \beta \) components for closed-shell systems). \( v_{xc} \) is finite at the position of the nucleus

\[ v_{xc}(r) = \text{const} \quad (r = 0), \]

and it reflects the atomic shell structure, i.e., it has a nonmonotonous dependence on \( r \) with different slopes in different shells and small peaks in the regions between the atomic shells. This form of the potential and the properties (5), (6), and (7) can serve as benchmarks for successful \( v_{xc} \) approximations. Recent progress of the DFT is due to the generalized gradient approximation (GGA) [20–23] that gives a remarkable improvement to the exchange–correlation energies of the local density approximation (LDA) [9, 24–28]. However, the standard GGA exchange–correlation potentials do not possess the proper asymptotic behavior (5) and are infinite at the nucleus. To illustrate this, in Figure 1, the self-consistent Becke–Perdew–Wang GGA potential \( v_{xc}^{\text{GGA}} \) is compared with the LDA one, \( v_{xc}^{\text{LDA}} \), and with the above-mentioned \( v_{xc} \) obtained from the correlated density [8]. \( v_{xc}^{\text{GGA}} \) is the functional derivative of the sum of the Becke exchange [21] and the Perdew–Wang correlation [23, 29–31] energy functionals, which are among the best GGA functionals for finite systems.

One can see from the Figure 1 that in the outer-valence region of Ne \( v_{xc}^{\text{GGA}} \) practically coincides with \( v_{xc}^{\text{LDA}} \). Both potentials are not sufficiently attractive in comparison with \( v_{xc} \) in this region and do not possess the accurate Coulombic asymptotics (5). Due to this, as will be shown in the fourth section, \( -\epsilon_N \) values of the GGA approach are typically 1.6–1.7 times as small as the corresponding \( I_p \) values in contradiction with (6). On the other hand, in the inner region, \( v_{xc}^{\text{GGA}} \) becomes overattractive and it diverges at the nucleus. Overall, \( v_{xc}^{\text{GGA}} \) can be considered as a more balanced approximation than is \( v_{xc}^{\text{LDA}} \); the latter potential is almost everywhere less attractive than is \( v_{xc} \). This means that in integrals with \( v_{xc}^{\text{GGA}} \) errors of the opposite sign from inner and outer regions can cancel each other, for instance, in the integral in the virial theorem relation [32–34]

\[ E_{xc} + T_c = \sum \int \left[ 3 \rho_{\alpha}(\mathbf{r}) + r \nabla \rho_{\alpha}(\mathbf{r}) \right] v_{xc}(\mathbf{r}) \, d\mathbf{r}, \]

where \( T_c \) is the kinetic contribution to the electron Coulomb correlation energy. However, locally and, especially, for the outer-valence region and near
the nucleus, the $\psi_{xc}^{GGA}$ form is not superior to that of $\psi_{xc}^{LDA}$, as Figure 1 demonstrates.

For the analysis [1, 35] and approximation [3–5, 36] of $\psi_{sca}$, it appears very useful to subdivide it into long- and short-range components. This subdivision of $\psi_{xc}$ follows naturally from the expression of $E_{xc}$ in terms of the exchange–correlation energy density per particle $\varepsilon_{xc}$:

$$E_{xc}[\rho] = \sum_{\sigma} \int \rho_{\sigma}(r) \varepsilon_{xc}(r) \, dr,$$  \hspace{1cm} (9)

the latter function being defined with the potential of the exchange-correlation hole or the screening potential $\varepsilon_{sca}$ [1, 35]:

$$\varepsilon_{sca}(r_1) = \frac{1}{2} \varepsilon_{sca}(r_1)$$

$$= \frac{1}{2} \sum_{\sigma_2} \int \rho_{\sigma_2}(r_2) \left[ g_{\sigma_1\sigma_2}(r_1, r_2) \right] \, dr_2.$$  \hspace{1cm} (10)

$\varepsilon_{sca}$ represents the screening of the interparticle Coulomb potential between electrons at $r_1$ and $r_2$ by exchange–correlation effects with a screening factor equal to $g_{\sigma_1\sigma_2}$; the latter function is the coupling constant $\lambda$ integral of the pair-correlation function $g_{\sigma_1\sigma_2}$ [37, 38]:

$$g_{\sigma_1\sigma_2}(r_1, r_2) = \int_{r_1}^{r_2} g_{\sigma_1\sigma_2}(r) \, dr.$$  \hspace{1cm} (11)

Functional differentiation (1) of (9) with a proper account of (10) represents $\psi_{sca}$ as a sum of $\psi_{sca}$ and the additional potential $\psi_{res}$. an integral of the linear “response” of $g_{\sigma_1\sigma_2}(r_1, r_2)$.

$$\psi_{sca}(r) = \psi_{sca}(r) + \psi_{res}(r),$$  \hspace{1cm} (12)

$$\psi_{res}(r_1) = \frac{1}{2} \sum_{\sigma_2} \int \rho_{\sigma_2}(r_2) \rho_{\sigma_1}(r_1)$$

$$\times \frac{\delta g_{\sigma_1\sigma_2}(r_1, r_2)}{\delta \rho_{\sigma_1}(r_1)} \, dr_2 \, dr_3.$$  \hspace{1cm} (13)

(Note that $\psi_{sca}$ and $\psi_{res}$ as defined here differ from those in [35] in that the present ones have built in the contributions of the kinetic potentials and their responses via the coupling constant integration. The potentials $\psi_{sca}$ and $\psi_{res}$ have a rather distinct, characteristic behavior: $\psi_{sca}$ is the long-range, attractive potential, which embodies the Coulombic asymptotics (5) of the total potential $\psi_{sca}$:

$$\psi_{sca}(r) \rightarrow -\frac{1}{|r|}, \hspace{1cm} \text{for} \hspace{1cm} |r| \rightarrow \infty.$$  \hspace{1cm} (14)

Contrary to this, $\psi_{res}$ is short-range and has a repulsive character [35].

This specialized behavior makes desirable the modeling of $\psi_{sca}$ with direct individual approximation of $\psi_{sca}$ and $\psi_{res}$In our previous work [36], we performed such a modeling at the exchange-only level, with $\psi_{res}$ being approximated by an orbital energy weighted average of orbital density contributions. In this article, the full exchange-correlation extension of this model is developed. The present model provides an adequate approximation to $\psi_{sca}$ in the outer-valence region with both the proper asymptotics and eigenvalue $\varepsilon_{n}$ of the one-electron potential and a reasonable estimate of the atomic exchange–correlation energy $E_{xc}$ and total energy $E_{tot}$.

### A Model Potential $\psi_{res}^{mod}$

To approximate $\psi_{res}$, we used a modification of our previous model $\psi_{res}^{mod}$ developed at the exchange-only level [36]. An exchange-only analog $\psi_{res}^{mod}$ of $\psi_{res}$ can be defined similarly to (13):

$$\psi_{res}^{mod}(r_1) = \frac{1}{2} \int \rho_{\sigma}(r_2) \rho_{\sigma}(r_3)$$

$$\times \frac{\delta g_{\sigma}(r_1, r_2, r_3)}{\delta \rho_{\sigma}(r_1)} \, dr_2 \, dr_3.$$  \hspace{1cm} (15)

with the exchange pair-correlation function $g_{\sigma}$, which can be expressed in terms of the occupied Kohn–Sham orbitals $\phi_{ij}$.

$$g_{\sigma}(r_1, r_2) = 1 - \frac{1}{2} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \frac{\phi_{ij}(r_1) \phi_{ij}^*(r_2) \phi_{ij}(r_1) \phi_{ij}(r_2)}{\rho_{\sigma}(r_1) \rho_{\sigma}(r_2)}.$$  \hspace{1cm} (16)

Figure 2 illustrates the typical behavior of $\psi_{res}^{mod}$ with the potential (15) for Ne obtained within the optimized potential model [40–42]. As was established in [35], the step-function behavior of $\psi_{res}^{mod}$
manifests itself in the shell structure of the Kohn–Sham potential. The steps of \( v_{\text{resp}} \) originate from the corresponding stepped structure of the “response” \( \delta g_{\text{xc}}(r_1, r_2) / \delta \rho_\sigma(r_3) \) as a function of \( r_3 \) [36].

A model of the form

\[
v^{\text{mod}}_{\text{resp}}(r) = K[\rho] \sum_{i=1}^{N} \sqrt{\epsilon_{N\sigma} - \epsilon_{i\sigma}} \frac{|\phi_{i\sigma}(r)|^2}{\rho_\sigma(r)} \tag{17}
\]

was proposed in [36], which reproduces the stepped structure of \( v_{\text{resp}} \) (see Fig. 2) using an average of orbital densities with weights or step heights \( \sqrt{\epsilon_{N\sigma} - \epsilon_{i\sigma}} \). The dimensionless numerical coefficient \( K[\rho] \) in (17) was determined from the homogeneous electron gas model and also via a self-consistent procedure based on the Levy–Perdew relation [34]. Model (17) possesses gauge invariance, proper scaling, and short-range behavior, and self-consistent calculations with this model yield rather accurate results at the exchange-only level [36].

Since exchange is the dominating effect of electron correlation, one can expect that \( v_{\text{resp}} \) has a form similar to that of its exchange-only analog \( v_{\text{xc}} \). Bearing this in mind, we propose to approximate \( v_{\text{resp}} \) of Eq. (13) by model (17) with the numerical coefficient \( K[\rho] \) determined from the available data on electron correlation and from the known properties of the exchange–correlation functionals.

A possible option to generate \( K[\rho] \) is to use the above-mentioned “exact” potentials \( v_{\text{xc}} \) and Kohn–Sham orbitals \( \phi_{i\sigma} \) obtained from the correlated densities \( \rho_\sigma \). One can insert \( v_{\text{xc}} \) and the model response potential (17), built from \( \phi_{i\sigma}, \epsilon_{i\sigma} \), and \( \rho_\sigma \), into expression (12) to obtain for \( v_{\text{scr\sigma}} \)

\[
v_{\text{scr\sigma}}(r) = v_{\text{xc\sigma}}(r) - K[\rho] \times \sum_{i=1}^{N} \sqrt{\epsilon_{N\sigma} - \epsilon_{i\sigma}} \frac{|\phi_{i\sigma}(r)|^2}{\rho_\sigma(r)}. \tag{18}
\]

With (18), \( K[\rho] \) can be “fitted” using the requirement that [according to Eqs. (9) and (10)], the integral of \( v_{\text{scr\sigma}} \) of Eq. (18) should reproduce \( E_{\text{xc}[\rho]} \):}

\[
\frac{1}{2} \sum_{\sigma} \rho_\sigma(r) v_{\text{scr\sigma}}(r) \, dr = E_{\text{xc}[\rho]} \tag{19}
\]

In this article, to obtain \( K[\rho] \), we use the correlated density \( \rho \) [19] for Ne and the corresponding \( v_{\text{xc}} \) (see Fig. 1) constructed via the procedure in [8]. \( E_{\text{xc}[\rho]} \) in (19) is approximated with a sum of the OPM exchange energy [42] and an empirical estimate of the Coulomb correlation energy [44] for Ne. From (18) and (19), the value \( K[\rho] = 0.470 \) is obtained, which is somewhat larger than the exchange-only value \( K[\rho] = 0.382 \) derived from the homogeneous electron gas model in our previous work [36].

Another option is to determine \( K[\rho] \) for a particular system within the SCF procedure. In this case, model \( v^{\text{mod}}_{\text{resp}} \) of Eq. (17) is combined with some suitable approximation to \( v^{\text{mod}}_{\text{scr\sigma}} \) to form the model exchange–correlation potential \( v^{\text{mod}}_{\text{scr\sigma}} \):

\[
v^{\text{mod}}_{\text{scr\sigma}}(r) = v^{\text{mod}}_{\text{xc\sigma}}(r) + K_{\text{xc}}[\rho] \times \sum_{i=1}^{N} \sqrt{\epsilon_{N\sigma} - \epsilon_{i\sigma}} \frac{|\phi_{i\sigma}(r)|^2}{\rho_\sigma(r)}. \tag{20}
\]

One can define \( K_{\text{xc}}[\rho] \) from the requirement that the virial theorem relation (8) with the potential (20) should yield the same value of \( E_{\text{xc}} \) as do Eqs. (9) and (10) with the potential \( v^{\text{mod}}_{\text{scr\sigma}} \):

\[
E_{\text{xc}} = \sum_{\sigma} \int \left[ 3 \rho_\sigma(r) + r \nabla \rho_\sigma(r) \right] \times \left[ v^{\text{mod}}_{\text{scr\sigma}}(r) + K_{\text{scr\sigma}}[\rho] R_\sigma(r) \right] \, dr - T_c
\]

\[
= \frac{1}{2} \sum_{\sigma} \rho_\sigma(r) v^{\text{mod}}_{\text{scr\sigma}}(r) \, dr,
\tag{21}\]

\[
R_\sigma(r) = \sum_{i=1}^{N} \sqrt{\epsilon_{N\sigma} - \epsilon_{i\sigma}} \frac{|\phi_{i\sigma}(r)|^2}{\rho_\sigma(r)}.
\tag{22}
\]
From requirement (21) follows the expression for \( K_{sc\sigma}[\rho] \):

\[
K_{sc\sigma}[\rho] = -\frac{I_{1\sigma}}{I_{2\sigma}},
\]

\( I_{1\sigma} = \int \left( \frac{5}{2} \rho_\sigma(r) + r \nabla \rho_\sigma(r) \right) \psi_{sc\sigma} \)

\( -\rho_\sigma(r) t_{cs\sigma}(r) \) \( dr \), \( (24) \)

\( I_{2\sigma} = \int \left[ 3 \rho_\sigma(r) + r \nabla \rho_\sigma(r) \right] R_\sigma(r) \) \( dr \), \( (25) \)

with \( t_{cs\sigma} \) being the energy density of \( T_{cs\sigma} \) per particle.

\[
T_{cs\sigma} = \int \rho_\sigma(r) t_{cs\sigma}(r) \) \( dr \).
\( (26) \)

We performed self-consistent Kohn–Sham calculations with both variants of \( v^{\text{mod}}_{sc\sigma} \), i.e., with \( K_{1} \) and \( K_{2\sigma} \), in combination with approximations to \( v^{\text{mod}}_{sc\sigma} \), which will be presented in the next section.

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**Model Potentials \( v^{\text{mod}}_{sc\sigma} \) and Self-Consistent Calculations with \( v^{\text{mod}}_{sc\sigma} \) and \( v^{\text{mod}}_{resp} \)**

To approximate \( v_{sc\sigma} \), we subdivide it into the exchange and Coulomb correlation parts:

\[
v_{sc\sigma}(r) = v_{5\sigma}(r) + v_{cs\sigma}(r),
\]

\( (27) \)

The exchange part of \( v_{sc\sigma} \), the Slater potential \( v_{5\sigma} \), is defined analogous to (10):

\[
v_{5\sigma}(r_1) = \int \rho_\sigma(r_2) \left[ g_{5\sigma}[\rho]; r_1, r_2 \right] - 1] \right) \frac{d r_2}{|r_1 - r_2|}
\]

\( (28) \)

via the exchange pair-correlation function \( g_{5\sigma} \) [Eq. (16)]. According to (10), partitioning (27) can be equivalently rewritten in terms of the exchange \( e_{5\sigma} \) and Coulomb correlation \( e_{cs\sigma} \) energy densities per particle:

\[
v_{sc\sigma}(r) = 2 e_{5\sigma}(r) + 2 e_{cs\sigma}(r). \]

(29)

To approximate \( v_{5\sigma} \), we adopted the same two options as in our previous work [36] at the exchange-only level: We used the accurate expression (28) with \( g_{5\sigma} \) [Eq. (16)] built from the occupied Kohn–Sham orbitals and we also approximate \( v_{5\sigma} \) with the GGA exchange energy density function \( e_{x\sigma}^{\text{GGA}} \) of Becke [21]:

\[
v_{5\sigma}^{\text{GGA}}(r) = 2 e_{x\sigma}^{\text{GGA}}(r), \]

\( (30) \)

\[
e_{x\sigma}^{\text{GGA}}(r) = -\rho_\sigma^{1/3}(r)
\]

\[
\times \left\{ \frac{3}{2} \left[ 3 \left( \frac{3}{4} \right)^{1/3} + \frac{b x_\sigma^2}{1 + 6 b x_\sigma \sinh^{-1} x_\sigma^2} \right] \right\}
\]

\( b = 0.0042, \)

\( (31) \)

\[
x_\sigma = \frac{|\nabla \rho_\sigma(r)|}{\rho_\sigma^{1/3}(r)}.
\]

(32)

To approximate \( v_{cs\sigma} \), we used the GGA Coulomb correlation energy density function \( \varepsilon_{x\sigma}^{\text{PW}}(r_\sigma, \xi, x) \) of Perdew and Wang [23, 29–31]:

\[
v_{cs\sigma}^{\text{GGA}}(r) = 2 \varepsilon_{x\sigma}^{\text{PW}}(r_\sigma, \xi, x; r).
\]

(33)

The explicit expression of \( \varepsilon_{x\sigma}^{\text{PW}}(r_\sigma, \xi, x) \) as a function of the Wigner radius parameter \( r_\sigma \)

\[
r_\sigma = \left[ \frac{4}{3} \pi \rho(r) \right]^{-1/3},
\]

(34)

the local sp-polarization \( \xi \),

\[
\xi(r) = \frac{\rho_\sigma(r) - \rho_\sigma(r)}{\rho(r)},
\]

(35)

and the density gradient parameter \( x \),

\[
x = \frac{||\nabla \rho(r)||}{\rho^{1/3}(r)}
\]

(36)

is rather lengthy, so we do not present it in the text and refer to the corresponding formulas in [23]. Note that the resultant model potential \( v_{sc\sigma}^{\text{mod}} \)

\[
v_{sc\sigma}^{\text{mod}}(r) = v_{5\sigma}(r) + v_{cs\sigma}^{\text{GGA}}(r), \]

(37)

possesses the correct properties (7) and (14), for both accurate \( v_{5\sigma} \) of Eqs. (16) and (28) and its approximation \( v_{5\sigma}^{\text{GGA}} \) (30).

The individual approximation of the screening and response components presented above enabled us to use the resulting model exchange–correlation potential

\[
v_{x\sigma}^{\text{mod}}(r) = v_{5\sigma}(r) + v_{cs\sigma}^{\text{GGA}}(r) + K[\rho] R_\sigma(r)
\]

(38)

within the Kohn–Sham self-consistent scheme. According to this scheme, the one-electron
Kohn–Sham Eqs. (3) are solved with the exchange–correlation potential (38). The resulting Kohn–Sham orbitals are used to calculate the total energy, with the exchange–correlation energy being calculated from (9) and (10) with the self-consistent potential \( v_{\text{scr}}^{\text{mod}} \).

\[
E_{xc}(\rho) = \frac{1}{2} \sum_{\sigma} \int \rho_\sigma(r) v_{\text{scr}}^{\text{mod}}(r) \, dr.
\]

In (38), either \( K_r = 0.470 \) or \( K_{scr} \) from Eq. (23) can be chosen. According to (24) and (26), the latter option requires calculation of the kinetic energy density \( t_c \). To do this, we used the expression of Görling, Levy, and Perdew [45, 46]:

\[
t_c(r) = -\varepsilon_c(r) r_e \frac{\partial}{\partial r_e} \left[ \frac{\varepsilon_c^{\text{PW}}(r_e, \xi, x; r)}{\varepsilon_c(r)} \right] = -r_e \frac{\partial \varepsilon_c^{\text{PW}}}{\partial r_e} - \varepsilon_c^{\text{PW}},
\]

\[
\varepsilon_c(r_e) = -\frac{0.45817}{r_e},
\]

relating the kinetic energy density to the partial derivative of \( \varepsilon_c^{\text{PW}}(r_e, \xi, x) \) with respect to \( r_e \). The results of self-consistent calculations within the proposed scheme are discussed in the next section.

A Comparison of the Self-consistent Potentials and One-electron Energies \( \varepsilon_N \)

To test the proposed self-consistent scheme, comparative calculations were been performed for eight light spherical closed- and open-shell atoms He, Be, N, Ne, Na, Mg, P, and Ar. Light atoms were chosen, because for those atoms, accurate empirical estimates of the Coulomb correlation energies are available [44, 47, 48]. The potentials \( v_{\text{scr}}^{\text{mod}(S)} \) and \( v_{\text{scr}}^{\text{mod}(GGA)} \) are tested, the former being model (38) with the full Slater potential \( v_S \) of Eqs. (16) and (28), while the latter is the same model, but with the GGA approximation \( v_{\text{GGA}} \) [Eq. (30)].

In both \( v_{\text{scr}}^{\text{mod}(S)} \) and \( v_{\text{scr}}^{\text{mod}(GGA)} \), the response part is calculated in both variants, i.e., with \( K_r \) and \( K_{scr} \). For the correlation part, the GGA approximation \( v_{\text{GGA}}^{\text{mod}(GGA)}(r) = 2 \varepsilon_c^{\text{PW}}(r) \) is always used.

The results of the calculations are compared with those of the standard Becke–Perdew–Wang GGA [21, 23] with the potential \( v_{\text{xc}}^{\text{GGA}} \), which can be expressed in a form similar to Eq. (38):

\[
v_{\text{xc}}^{GGA}(r) = \frac{\delta E_{xc}^{GGA}}{\delta \rho(r)} = v_{\text{xc}}^{GGA}(r) + v_{\text{xc}}^{\text{GGA}}(r)
\]

\[
+ v_{\text{resp}}^{\text{GGA}}(r)
\]

with the response part \( v_{\text{resp}}^{\text{GGA}} \) being defined through the functional derivatives of the GGA functions \( \varepsilon_{\sigma}^{\text{GGA}} \) [Eq. (31)] and \( \varepsilon_{\sigma}^{\text{PW}}(r_e, \xi, x) \):

\[
v_{\text{resp}}^{\text{GGA}}(r) = \int \rho_\sigma(r') \frac{\delta \varepsilon_{\sigma}^{\text{GGA}}(r')}{\delta \rho_\sigma(r)} \, dr'
\]

\[
+ \int \rho(r) \frac{\delta \varepsilon_{\sigma}^{\text{PW}}(r_e, \xi, x; r')}{\delta \rho_\sigma(r)} \, dr' - \varepsilon_{\sigma}^{\text{GGA}}(r) - \varepsilon_{\sigma}^{\text{PW}}(r_e, \xi, x; r).
\]

By construction, the model \( v_{\text{xc}}^{\text{mod}(GGA)} \) has the same screening part as that of \( v_{\text{xc}}^{\text{GGA}} \) and differs from the latter potential only in its response part (17). To study the effect of the response potential, calculations were also performed with complete neglect of the response potential in (43), i.e., with just the GGA screening potential,

\[
v_{\text{scr}}^{\text{GGA}}(r) = v_{\text{xc}}^{\text{GGA}}(r) + v_{\text{xc}}^{\text{GGA}}(r),
\]

being used as the exchange–correlation potential within the Kohn–Sham equations.

In Figure 3, the reference \( v_{\text{xc}} \) obtained from the correlated density via the procedure of [8] can be compared with our self-consistent model potentials \( v_{\text{xc}}^{\text{mod}(S)} \) and \( v_{\text{xc}}^{\text{mod}(GGA)} \) calculated for Ne with \( K_r \). The GGA exchange–correlation potential \( v_{\text{xc}}^{\text{GGA}} \).
and the bare GGA screening potential \( v_{\text{scr}}^{\text{GGA}} \) are also displayed.

Concerning the asymptotic behavior, we note that in the outer-valence region \( v_{\text{xc}}^{\text{GGA}} \) has an over-repulsive character and \( v_{\text{xc}}^{\text{GGA}} \) is overattractive. \( v_{\text{xc}}^{\text{mod(GGA)}} \) and \( v_{\text{xc}}^{\text{mod}} \) approximate \( v_{\text{xc}} \) more closely in this region. The approximations, \( v_{\text{xc}}^{\text{mod}} \) and \( v_{\text{xc}}^{\text{mod(GGA)}} \), have the correct Coulombic asymptotics (5), as does the bare \( v_{\text{scr}}^{\text{GGA}} \), but the latter can be considered as a satisfactory approximation to \( v_{\text{xc}} \) only at longer distances \( r > 1 \) au. At shorter distances, the neglect of the repulsive potential \( v_{\text{resp}} \) leads to a much too attractive potential.

Concerning the peak of \( v_{\text{xc}} \) between the 1s and 2s, 2p shells, we note that this is virtually lacking in both \( v_{\text{scr}}^{\text{GGA}} \) and \( v_{\text{xc}}^{\text{GGA}} \). \( v_{\text{scr}}^{\text{GGA}} \) is a monotonous function of \( r \), and adding the GGA response potential evidently builds only a small and displaced peak in \( v_{\text{xc}}^{\text{GGA}} \). In contrast, the presence of our model response potential in \( v_{\text{xc}}^{\text{mod}} \) and \( v_{\text{xc}}^{\text{mod(GGA)}} \) evidently creates clear intershell peaks, although in the latter case, the peak is also somewhat displaced and a bit exaggerated.

Considering the behavior of the potentials within the regions of the 1s and 2s shells, we make the following observation: Both \( v_{\text{xc}}^{\text{mod}} \) and \( v_{\text{xc}}^{\text{mod(GGA)}} \) include the same functionals \( v_{\text{scr}}^{\text{mod}} \) and \( v_{\text{resp}}^{\text{mod}} \), which appear to be not too sensitive to differences between the Kohn–Sham orbitals and eigenvalues that are generated in the respective self-consistent calculations. Because of this, comparison of \( v_{\text{xc}}^{\text{mod}} \) and \( v_{\text{xc}}^{\text{mod(GGA)}} \) in Figure 3 reveals, mainly, the difference between their exchange parts \( v_{\text{xc}}^{\text{sc}} \) and \( v_{\text{xc}}^{\text{GGA}} \). As has already been mentioned in our previous work at the exchange-only level [36], the latter is more attractive than is the former within the regions of 1s and 2s shells, leading to analogous differences between \( v_{\text{xc}}^{\text{GGA}} \) and \( v_{\text{xc}}^{\text{mod}} \).

The region close to the nucleus shows important differences between the various potentials. The erroneous Coulombic singularity in the GGA potential \( v_{\text{xc}}^{\text{GGA}} \) for \( r < 0 \) is well known [6, 8]. The replacement of \( v_{\text{resp}}^{\text{GGA}} \) of Eq. (43) by model (17) removes this error and provides a finite value of \( v_{\text{xc}}^{\text{mod(GGA)}} \) at the nucleus. One might expect that \( v_{\text{xc}}^{\text{mod(GGA)}} \) should go closer to \( v_{\text{xc}} \) than does \( v_{\text{xc}}^{\text{mod}} \), because the former includes the accurate Slater potential [Eqs. (16) and (28)], while the latter includes its GGA approximation [Eq. (30)]. This is actually true for some \( r \)-values, e.g., the interval 0.1 au < \( r < 0.8 \) au, but definitely not near the nucleus. The somewhat shallow bell-like form of \( v_{\text{xc}}^{\text{mod}} \) reflects the shape of the accurate \( v_{\text{xc}} \) and is in agreement with the potential of the exchange-only OPM model. However, the analysis performed in [14, 35] to extract and characterize \( v_{\text{xc}} \) shows that it has a sharp negative peak at the nucleus and this peak of \( v_{\text{xc}} \) introduces a peaked form of \( v_{\text{xc}} \). It is clear from the results of [36] that the exchange energy density approximation \( 2 \varepsilon_{e} \) of the GGA model, which enters our potential \( v_{\text{xc}}^{\text{mod(GGA)}} \) as the \( v_{\text{GGA}} \) part, does not, in fact, reproduce the exchange-only behavior, but has, for \( r < 0 \), a shape more similar to the \( v_{\text{xc}}^{\text{mod}} \)-derived cusp of the total \( v_{\text{xc}} \). So, the peaked form of \( v_{\text{xc}}^{\text{mod(GGA)}} \) is caused by its part \( v_{\text{GGA}} \) or, more precisely, by peak at the nucleus of the LDA part \(-3[3/(8\pi)]^{1/3} 1/3 \) of \( v_{\text{GGA}}^{\text{GGA}} \). We note that the correlation-induced peaked form of \( v_{\text{xc}} \) close to the nucleus is not built in by the GGA Coulomb correlation energy density \( \varepsilon_{\text{xc}}^{\text{PW}(r, \xi, x)} \), which is a rather shallow function of \( r \). In \( v_{\text{xc}}^{\text{mod}} \), other parts, \( v_{\text{xc}} \) and \( v_{\text{resp}}^{\text{mod}} \), have, respectively, a shallow bell-like and a flat stepped function at small \( r \) values. Taken together, these features provide the observed shallow form of the total \( v_{\text{xc}}^{\text{mod}} \). So, the GGA exchange functional simulates also the effect of Coulomb correlation. In this case, the simulation exaggerates the correlation effect and the peak of \( v_{\text{xc}}^{\text{mod}} \) appears to be larger than that of \( v_{\text{xc}} \), although the value of \( v_{\text{xc}}^{\text{mod(GGA)}} \) at the nucleus is closer to that of \( v_{\text{xc}} \) than is the corresponding \( v_{\text{xc}}^{\text{mod}} \) value (see Fig. 3).

The local differences between \( v_{\text{xc}}^{\text{mod}} \) and \( v_{\text{xc}}^{\text{mod(GGA)}} \) (mostly between \( v_{\text{sc}} \) and \( v_{\text{GGA}}^{\text{GGA}} \)) clearly manifest themselves in Table I, where the atomic \( K_{\text{sc}} \) values for the potentials \( v_{\text{xc}}^{\text{mod}} \) and \( v_{\text{xc}}^{\text{mod(GGA)}} \) are presented. For all atoms, \( K_{\text{sc}} \) values calculated from Eqs. (23)–(25) with the sum \( v_{\text{sc}}^{\text{mod}} + v_{\text{GGA}}^{\text{GGA}} \) as the screening potential are smaller than \( K_{\text{f}} \). On the other hand, all \( K_{\text{sc}} \) calculated with the sum \( v_{\text{sc}}^{\text{GGA}} + v_{\text{GGA}}^{\text{GGA}} \) are larger than \( K_{\text{f}} \).

Analysis of the contributions to \( K_{\text{sc}} \) shows that in all cases the source of this difference is the integral \( I_{1\sigma} \) of (24) and that within \( I_{1\sigma} \) it originates from the region close to the nucleus. These results indicate that the picture presented in Figure 3 for Ne is also typical for other atoms. The model \( v_{\text{xc}}^{\text{mod(GGA)}} \) overestimates the exchange–correlation effect near the nucleus, thus producing overestimated \( K_{\text{sc}} \) values. On the other hand, \( v_{\text{xc}}^{\text{mod}} \) yields underestimated \( K_{\text{sc}} \) values because of the underestimation of the exchange–correlation in this region. One can argue then that the unknown single optimal \( K \) value is placed in
between the two sets of $K_{\text{scr}}$ values and it should be close to $K_f = 0.470$. This argumentation justifies using $K_f$ obtained for Ne as the universal parameter for all systems.

Perhaps the most interesting feature of the model potentials $\vmod$ is that they reproduce very well the experimental ionization potentials $I_p$ [48–50]. In Table II, the energies of the highest occupied orbital $\epsilon_{\text{N}_e}$ calculated with various approximate exchange–correlation potentials are compared with $I_p$ values and also with $\epsilon_{\text{N}_e}$ of the exchange-only OPM potential [51]. Note that by construction (17) $\vmod$ vanishes for an arbitrary two-electron closed-shell system, so that for He model (38) reduces to the bare screening potential. The worst results are obtained with potential (43) of the standard GGA. Its $\epsilon_{\text{N}_e}$ are 1.6–1.7 times as small as the corresponding $I_p$. The replacement of the response potential (44) of the standard GGA by model (17) has a dramatic effect on the quality of the $\epsilon_{\text{N}_e}$. Model (38) with $\vmod$ and $K_f$ provides the best estimate of $I_p$, with the corresponding average error being only 12 mHartrees. It is essential that the exchange–correlation model improves the results of OPM in six cases out of eight, thus representing properly the effect of Coulomb correlation on orbital energies. With $\vmod$ and $K_f$, model (38) yields slightly worse $\epsilon_{\text{N}_e}$s with an average error of 20 mHartrees. This worsening appears, probably, because the errors of the approximation $\vmod$ in the outer-variance region manifest themselves in the latter case, while in the case of $\vmod$, they are canceled by errors of the opposite sign in $\vmod$.

With $K_{\text{scr}}$, model (38) yields slightly worse results than those for $K_f$, with the average error being about 25 mHartrees for both $\vmod$ and $\vmod$. The inclusion of the proper $\vresp$ appears to be essential for the quality of $\epsilon_{\text{N}_e}$. The average error of calculations with the neglect of the response potential, i.e., with potential (45), amounts to 50 mHartrees.

### Calculations of $E_{\text{tot}}$ and $E_{\text{xc}}$

In Table III, the total atomic energies $E_{\text{tot}}$ calculated self-consistently with the above-mentioned approaches are compared with the sum $E'_{\text{tot}}$:

$$E'_{\text{tot}} = E^{\text{OPM}}_{\text{tot}} + E'_{\text{xc}},$$

### TABLE I

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### TABLE II

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<th>$\v^{\text{mod}(S)}(K_f)$</th>
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EXCHANGE–CORRELATION KOHN–SHAM POTENTIAL

TABLE III
Comparison of differences (in mHartrees) between the total energies calculated with various approximate exchange–correlation potentials and the accurate empirical estimate $E_{tot}^e$.

<table>
<thead>
<tr>
<th>Atom</th>
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<th>$v_{xc}^{OPM}$</th>
<th>$v_{xc}^{GGA}$</th>
<th>$v_{xc}^{mod(GGA)}(K_{sc})$</th>
<th>$v_{xc}^{mod}(GGA)(K_f)$</th>
<th>$v_{xc}^{mod(GGA)}(K_f)$</th>
<th>$v_{xc}^{mod(S)}(K_{sc})$</th>
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<td>6</td>
<td>6</td>
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<td>28</td>
<td>57</td>
<td>55</td>
<td>189</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a*The entries in this column are by construction equal to the empirical estimates of the correlation energy $E_{xc}^e$ (see text).

of the OPM total energy $E_{tot}^{OPM}$ [51] and an empirical estimate of the Coulomb correlation energy $E_{xc}^e$ [44, 47, 48]. One can expect that $E_{tot}^e$ should be close to the unknown exact nonrelativistic total energy. To demonstrate the correlation effect, $E_{xc}^e$ values are presented in the third column of Table III as the error of the exchange-only OPM approach. It increases monotonously with increasing atomic number from 42 mHartrees for He to 792 mHartrees for Ar.

With the accurate potential $v_{xc}^{S}$ [Eqs. (16) and (28)] as the Slater part of $v_{xc}^{resp}$, giving the model potential $v_{xc}^{mod(S)}$ in the Kohn–Sham equations, the proposed self-consistent scheme provides the best agreement between calculated $E_{tot}^e$ values and energies (46). Variants with the parameters $K_f$ and $K_{sc}$ in the response part of $v_{xc}^{mod(S)}$ produce, of course, different orbitals and densities. However, the effect of these differences on the common energy functional (39) is small and both variants have the same average $E_{tot}^e$ error of only 9 mHartrees.

In all other approaches considered, $E_{tot}^e$ are calculated self-consistently with the GGA screening potential $v_{xc}^{GGA}$ and various response potentials, namely, with $v_{xc}^{GGA}$ and $v_{xc}^{resp}$ (calculated with $K_f$ and $K_{sc}$), and also with complete neglect of $v_{xc}^{resp}$. Again, in these approaches, the exchange–correlation energies are calculated with the same functional (39), $E_{xc} = (1/2) \rho v_{xc}^{mod} dr$, where $v_{xc}^{mod} = 2 e_g^0 + 2 e_r^{PW}$, so this is simply the GGA energy functional. The energy differences are caused exclusively by the differences in orbitals and densities generated with various exchange–correlation potentials.

Use of either $v_{xc}^{GGA}$ or $v_{xc}^{resp}$ provides a high quality of $E_{tot}^e$ values calculated with the GGA energy functional. The standard GGA potential with the variationally derived $v_{xc}^{resp}$ of Eq. (44) delivers the minimum of this functional. In all cases (with the exception of Be and Ar), the corresponding $E_{tot}^e$ values are too negative and the average absolute error, still small, amounts to 18 mHartrees. Since we are using the GGA energy functional, so that the total energy is stable with respect to small variations of the density around $\rho = \rho_{GGA}^e$, the use of improved potentials cannot be expected to lead to much improvement in the total energy, if any. The model $v_{xc}^{mod(GGA)}$ yields more positive energy values, slightly reducing the average error to 14 mHartrees in the variant with $K_f$ and slightly enlargening it to 20 mHartrees in the variant with $K_{sc}$. Only in the approach with the bare $v_{xc}^{GGA}$ increases with increasing atomic number and reaches 189 mHartrees for Ar.

In Table IV, the exchange–correlation parts $E_{xc}$ of $E_{tot}^e$ calculated within various approaches are compared with the sum $E_{xc}^e$ of the OPM exchange energy $E_{xc}^{OPM}$ [51] and $E_{xc}^e$ [44, 47, 48]. One can see from this table that the model $v_{xc}^{mod(S)}$ with $K_{sc}$ always yields lower $E_{xc}$ values than that with $K_f$. The reason for this trend is the inequality $K_f > K_{sc}$ valid for this model (see Table I and the discussion in the fourth section). Since $K[\rho]$ is the proportionality coefficient of the repulsive response component (17), $v_{xc}^{mod(S)}$ with smaller $K = K_{sc}$ is a more attractive potential, which generates more contracted density than that with $K = K_f$, and, as a result, yields lower (more negative, larger in an absolute sense) $E_{xc}$ values. The average absolute error in $E_{xc}$ is 31 mHartrees for $K = K_f$ and it is
23 mHartrees for $K = K_{sc}$. Analogously, because of the attractive character of the bare $v_{GGA}^{\text{mod}}$ (see Fig. 3), calculations with the neglect of $v_{\text{resp}}$ yield contracted densities and far too negative $E_{xc}$. The error in $E_{xc}$ increases with increasing atomic number and reaches −592 mHartrees for Ar. Addition of any one of the approximate repulsive potentials $v_{\text{resp}}$ brings the self-consistent $E_{xc}$ values much closer to $E_{xc}$. The corresponding average absolute error is 69 mHartrees for $v_{\text{mod(GGA)}}^{\text{scr}}$ with $K_{sr}$; it reduces to 38 mHartrees for $v_{\text{mod(GGA)}}^{\text{mod}}$ with $K_{sc}$ and it is only 12 mHartrees for the $v_{\text{mod(GGA)}}^{\text{GGA}}$ of Eq. (43). Although, in general, the accuracy of $E_{xc}$ values obtained with a self-consistent density generated with one of our model exchange–correlation potentials is lower than that of the GGA [21, 23], it can be considered as quite reasonable. This holds true in particular for total energy calculations. While errors in $E_{xc}$ produced with the bare $v_{\text{GGA}}^{\text{scr}}$ give rise to considerable errors in $E_{tot}$, $E_{xc}$ errors of the model potentials including a response part are effectively compensated within the self-consistent procedure with errors of the opposite sign in other parts of the total energy, thus providing the above-mentioned high quality of calculated $E_{tot}$ values (see Table III).

It is clear that our model potentials are not yet in perfect agreement with the accurate $v_{xc}$, notably not close to the nucleus. One may wonder how exactly the self-consistent density compares to, for instance, the GGA one. Since the GGA potential $v_{\text{GGA}}^{\text{xc}}$ deviates more from the accurate $v_{xc}$ than $v_{\text{mod(GGA)}}^{\text{mod}}$, the small error in $E_{xc}$ obtained with $v_{\text{GGA}}^{\text{scr}}$ may be a result of cancellation of a larger positive error coming from integration (9) in the outer-valence region (where $v_{\text{GGA}}^{\text{xc}}$ is overrepulsive) and a negative error from the inner region where $v_{\text{GGA}}^{\text{xc}}$ is overattractive (see Fig. 3). Rather than by displaying densities directly, we can check this supposition by calculating radial integrals $D(r_{1}, r_{2})$ where we use the energy density for importance weighting:

$$D(r_{1}, r_{2}) = \frac{1}{2} \int_{r_{1}}^{r_{2}} \left[ \rho_{\text{appr}}(r) v_{\text{GGA}}^{\text{GGA}}(\rho_{\text{appr}}), r \right] - \rho_{\text{acc}}(r) v_{\text{GGA}}^{\text{GGA}}(\rho_{\text{acc}}), r \right] 4\pi r^{2} dr. \quad (47)$$

We apply (47) for the case of Ne, $\rho_{\text{acc}}$ being the accurate correlated density [19], which has been used in the first section to construct $v_{xc}$, and $\rho_{\text{appr}}$ is the density obtained with some approximate exchange–correlation potential. $D(r_{1}, r_{2})$ is a contribution to the difference $E_{xc}^{\text{GGA}}[\rho_{\text{appr}}] - E_{xc}^{\text{GGA}}[\rho_{\text{acc}}]$ from the spherical shell within the radial interval $r_{1} < r < r_{2}$. Since the total value $E_{xc}^{\text{GGA}}[\rho_{\text{acc}}] = −12.504$ Hartrees calculated for Ne with $\rho_{\text{acc}}$ is only 4 mHartrees off the accurate estimate $E_{xc} = −12.504$ Hartrees (see Table IV), $v_{\text{GGA}}^{\text{GGA}}(\rho)$ is a sensible weighting function and $D(r_{1}, r_{2})$ may be taken to represent an error in $E_{xc}^{\text{GGA}}[\rho_{\text{appr}}]$ coming from the region $r_{1} < r < r_{2}$. For the density $\rho_{\text{GGA}}$ generated with $v_{\text{GGA}}^{\text{GGA}}$ of Eq. (43) as $\rho_{\text{appr}}$ and for $r_{d} = 0.65$ au as a division point between the outer-valence and inner regions (the inner sphere with $r < r_{d}$ is populated with about four electrons), an error from the outer region is $D(\infty, r_{d}) = 29$ mHartrees and that from the inner region is $D(0, r_{d}) = −11$ mHartrees. When summing up, the former error is partially compensated by the latter, and in accord with our supposition, the smaller total error $E_{xc}^{\text{GGA}}[\rho_{\text{GGA}}] - E_{xc}^{\text{GGA}}[\rho_{\text{acc}}] = 18$ mHartrees is produced.

It is interesting to compare these data with those for the density $\rho_{\text{mod(GGA)}}$ obtained with $v_{\text{mod(GGA)}}^{\text{GGA}}$ and $K = K_{sr}$, because the latter potential

**TABLE IV**

Comparison of differences (in mHartrees) between the exchange–correlation energies calculated with various approximate exchange–correlation potentials and the accurate empirical estimate $E_{xc}^{*}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>−$E_{xc}^{*}$</th>
<th>$v_{xc}^{GGA}$</th>
<th>$v_{xc}^{\text{mod}(S)}(K_{sc})$</th>
<th>$v_{xc}^{\text{mod}(S)}(K_{sr})$</th>
<th>$v_{xc}^{\text{mod}(GGA)}(K_{sc})$</th>
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<td>32</td>
<td>−592</td>
</tr>
</tbody>
</table>
produces for Ne the largest error in $E_{xc}$ among all other atoms and all variants of model (38) (see Table IV). For $\rho_{\text{mod}(\text{GGA})}^\sigma$, we obtain an error from the outer region $D(r_d, \infty) = -22$ mHartrees, of opposite sign and, in fact, somewhat smaller than for $\rho_{\text{GGA}}^\sigma$. This fits in what would be expected from the better asymptotic behavior of $v_{xc}^{\text{mod}(\text{GGA})}$.

From the inner region, however, the error is larger: $D(0, r_d) = -95$ mHartrees, producing the total error $E_{xc}^{\text{GGA}}[\rho_{\text{mod}(\text{GGA})}^\sigma] - E_{xc}^{\text{GGA}}[\rho_{\text{acc}}^\sigma] = 117$ mHartrees. Thus, from the point of view of criterion (47), $v_{xc}^{\text{mod}(\text{GGA})}$ with $K_f$ provides a better description for the outer region, which is also in agreement with the excellent estimate of the ionization potentials $I_p$ obtained within this model (see Table II), but the inner part needs further improvement (see next section).

Bearing in mind the overall good quality of the presented results, we propose $v_{xc}^{\text{mod}}$ of Eq. (38) as an efficient approximation to $v_{xc\sigma}$. The model with the potential $v_{\text{Sc}}$ [Eqs. (16) and (28)] is, to our best knowledge, the first approximate full exchange–correlation Kohn–Sham potential with the accurate Slater functional. Previously, the accurate $v_{\text{Sc}}$ was used exclusively as a part of the exchange-only approximate potential [51, 52]. All exchange–correlation approaches reported before are based on the Kohn–Sham equations with some effective DFT model of $v_{\text{Sc}}$ or on the Hartree–Fock–like equations with the nonlocal state-dependent exchange part [53, 54]. Although more complicated than the standard DFT schemes, model (38) with $v_{\text{Sc}}$ provides a reasonable approximation to $v_{xc\sigma}$, providing good Kohn–Sham one-electron energies (ionization potentials) and an excellent estimate of $E_{\text{tot}}$ for the light spherical atoms considered. A more practical DFT approximation to $v_{xc\sigma}$, which also represents correlation-induced features such as the cusp at the nucleus better, is model (38) with $v_{\text{Sc}}^{\text{GGA}}$ [Eq. (30)]. The variant with $K_{\text{sc}}$ provides better $E_{xc}$ values, while that with $K_f$ is simpler and it also yields a very good estimate of the ionization potentials, so that $K_f$ can be used as the universal parameter for many-electron calculations.

### Conclusions

In this article, a scheme of approximation of the Kohn–Sham exchange–correlation potential $v_{xc\sigma}$ was developed, making use of a partitioning of $v_{xc\sigma}$ into a long-range screening and a short-range response potential. For the response part, a modification of the model $v_{\text{resp}}^{\text{mod}}$ developed previously at the exchange-only level [36] was used. The screening part is identical to the exchange–correlation energy density and we represented the screening potential with the most promising exchange–correlation functionals among those available in the literature. The combined model (38) provides an adequate approximation to $v_{xc\sigma}$ in the outer valence region with proper asymptotics of the one-electron potential and, therefore, accurate eigenvalue $\epsilon_N$, and a reasonable estimate of atomic $E_{xc}$ and total energies $E_{\text{tot}}$. The variant with the potential $v_{\text{Sc}}$ [Eqs. (16) and (28)] represents the first example of an approximate full exchange–correlation Kohn–Sham potential with the accurate Slater potential for the exchange part. The variant with $v_{\text{Sc}}^{\text{GGA}}$ [Eq. (30)] provides an efficient and reasonably accurate DFT approximation to $v_{xc\sigma}$.

It appears that our model for the response potential is adequate and the errors of model (38) discussed in the fourth and fifth sections are caused mainly by the local deviations of the GGA potentials $v_{\text{Sc}}^{\text{GGA}}$ and $v_{\text{Sc\sigma}}^{\text{GGA}}$ from the corresponding accurate potentials. The most noticeable among these deviations is that near the nucleus, which manifests itself in the overattractive character of the model potential $v_{xc\sigma}^{\text{mod}(\text{GGA})}$ in this region (see Fig. 3). The main source of this error appears to be the overestimation of the electron exchange near the nucleus within the LDA, while both the nonlocal correction in $v_{\text{Sc}}^{\text{GGA}}$ and $v_{\text{Sc\sigma}}^{\text{GGA}}$ bring additional attractive contributions. Therefore, to further improve the local quality of $v_{xc\sigma}^{\text{mod}(\text{GGA})}$, at this point, attention should be turned to the screening potentials. It is clear that a repulsive term should be added to $v_{\text{Sc\sigma}}^{\text{GGA}}$ in the region close to the nucleus.

Improvement of the screening part of the potential, which implies improvement of the energy density and thus of the exchange–correlation energy, is outside the scope of this article. In closing, however, we just show an example of a model potential $v_{\text{Sc\sigma}}^{\text{mod}}$ with a better local behavior. Let us add to $v_{\text{Sc\sigma}}^{\text{GGA}}$ the repulsive term $\epsilon \rho_{\sigma}^{1/3}/x_{\sigma}$:

$$v_{\text{Sc\sigma}}^{\text{mod}}(r) = v_{\text{Sc\sigma}}^{\text{GGA}}(r) + v_{\text{Sc\sigma}}^{\text{GGA}}(r) + \frac{\epsilon \rho_{\sigma}^{1/3}(r)}{x_{\sigma}},$$

which depends on the reciprocal gradient argument $x_{\sigma}$ of Eq. (32), while retaining the model response part (17) with $K_f$ in the resulting total.
exchange–correlation potential:

\[ v_{xc}^{\text{mod}}(r) = v_{s\sigma}^{\text{GGA}}(r) + v_{xc\sigma}^{\text{GGA}}(r) + \frac{c \rho_{\sigma}^{1/3}(r)}{\chi_{\sigma}} + 0.47R_{\sigma}(r). \]  

The repulsive term has a sharp maximum at the nucleus, it is decaying exponentially at longer distances, and for atoms, it is everywhere finite, because, usually, \( \chi_{\sigma} \) is never too close to zero for the neutral atomic systems. Potential (49) has the proper scaling and asymptotics (5) and (7). We also modify in (48) the parameter \( b \) of the potential \( v_{xc}^{\text{GGA}} \) [Eqs. (30) and (31)] from its standard value \( b = 0.0042 \). A new value \( b = 0.0085 \) and the proportionality coefficient of the repulsive term \( c = 1.865 \) were obtained from least-squares fitting of the approximate potential (49) to the above-mentioned accurate potential \( v_{xc} \) for Ne constructed from the correlated density.

In Figure 4, the self-consistent potential (49) for Ne is compared with \( v_{xc} \). One can see from this figure that the above-mentioned deviation between the model and the accurate potential is almost completely removed by the addition of the repulsive term. The model exhibits slight oscillations around \( v_{xc} \), and, in general, goes rather close to the accurate potential. The values of \( E_{tot} \), \( E_{xc} \), and \( I_p \) for Ne obtained with (48) and (49) are the best among all other approximations considered with the corresponding errors \( \Delta E_{tot} = 5 \) mHartrees, \( \Delta E_{xc} = 11 \) mHartrees, and \( \Delta I_p = -8 \) mHartrees. However, model (49) does not provide a general solution of the problem; the quality of the results deteriorates rapidly if one goes from Ne either to the lighter or to the heavier atoms. Nevertheless, this example shows that the development of approximate screening potentials of a better form is a promising way to improve the quality of the proposed model (38).

In this work, the scheme of [36] with a direct approximation of the screening and response components of \( v_{xc} \) is extended to the full exchange–correlation level and is tested for atoms. Our model response potential appears to be very well suited to build in atomic shell effects. Such effects are extraneous to the electron gas and we feel that separate modeling is warranted, if not necessary. When the GGA energy densities are used for the screening potentials, quite satisfactory accuracy is achieved. The logical next step seems to be to improve upon the GGA representation for the screening potentials, which should at the same time improve the exchange–correlation energy, to which they are directly linked. This is certainly possible—see above. However, we feel that, first, typical molecular effects should be taken into account. The established feature of the molecular \( v_{xc} \) is a peak at the bond midpoint due to the left–right electron correlation [18, 55] and a successful model \( v_{xc}^{\text{mod}} \) should take this into account properly. Analysis and modeling of such features of the molecular \( v_{xc} \) within the proposed scheme is in progress.

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References