Asymptotic Properties of the Optimized Effective Potential

T. Kreibich[a], S. Kurth[b], T. Grabo[a] and E.K.U. Gross[a]

[a] Institut für Theoretische Physik, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[b] Dept. of Physics, University of Antwerpen (RUCA), Groenenborgerlaan 171, 2020 Antwerpen, Belgium

Abstract

Rigorous properties of the optimized effective potential (OEP) are derived. We present a detailed analysis of the asymptotic form of the OEP, going beyond the leading term. Furthermore, the asymptotic properties of the approximate OEP scheme of Krieger, Li and Iafrate [Phys. Lett. A **146**, 256 (1990)] are analysed, showing that the leading asymptotic behavior is preserved by this approximation.

1 Introduction

Density Functional Theory (DFT) has become a powerful tool for ab-initio electronic structure calculations of atoms, molecules and solids [1, 2, 3]. The success of DFT relies on the availability of accurate approximations for the exchange-correlation (xc) energy functional E_{xc} or, equivalently, for the xc potential v_{xc}. Though these quantities are not known exactly, a number of properties of the exact xc potential $v_{\mathrm{xc}}(\mathbf{r})$ are well-known and may serve as valuable criteria for the investigation of approximate xc functionals. In this contribution, we want to focus on one particular property, namely the asymptotic behavior of the xc potential: For finite systems, the exact xc potential $v_{\mathrm{xc}}(\mathbf{r})$ is known to decrease like $-1/r$ as $r \to \infty$, reflecting also the proper cancellation of spurious self-interaction effects induced by the Hartree potential.

Most of the conventional xc functionals including the local density approximation (LDA) as well as more refined generalized gradient approximations (GGAs) fail to reproduce this asymptotic behavior correctly. As a consequence, these approximations yield rather poor results for properties where the asymptotic region of the xc potential is of crucial importance, e.g. for ionization potentials [4] or excitation energies [5] of atoms and molecules.

In recent years, a different type of approximate xc functionals has gained increasing interest: It was found that the correct asymptotic behavior can be obtained by employing xc functionals depending explicitly on the set of Kohn-Sham (KS) single-particle orbitals rather than the density [6]. The implementation of orbital functionals in the KS scheme is known as the optimized effective potential (OEP) method [7, 8]. It was recognized early on [9] that with the exact Hartree-Fock expression for the exchange energy functional, the OEP method is equivalent to the *exact* x-only implementation of KS theory. The fact that the correct asymptotics as well as other exact properties are reproduced within the OEP scheme turned out to be an important advantage over the conventional xc functionals beyond the x-only limit Consequently, approaches using orbital-dependent xc functionals have been shown to yield highly accurate results comparable to those of quantum chemical calculations [4].

The original proof [8] of the asymptotic behavior of the OEP was based on the asymptotic form of the Green's function which is easily accessible only in 1D. Considering the 3D Green's function, Krieger, Li and Iafrate [6] made it plausible that the statement holds true in the 3D case as well. An alternative proof was recently given [10] for the x-only case.

This proof uses the exact scaling behavior of the x-energy functional and can therefore not be extended to the correlation potential. The purpose of the present contribution is to provide a rigorous proof valid for both exchange and correlation. Our investigation confirms the statement of Ref. [6] for a particular well-defined class of orbital functionals for the correlation energy. Furthermore, we investigate how exactly the asymptotically leading term is approached. The paper is organized as follows: After a brief introduction to the OEP method in section 2.1, the asymptotic form of the OEP is investigated in detail in section 2.2. The central result is a lemma proven in section 2.2.1. In the final chapter 3, the analysis of section 2 is applied to the approximate OEP scheme of Krieger, Li and Iafrate (KLI) [6, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23].

2 The OEP method

2.1 Derivation of the OEP integral equation

In this section, we derive the OEP equations for the spin-dependent version of DFT [24, 25], where the basic variables are the spin-up and spin-down densities $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$, respectively. They are obtained by self-consistently solving the single-particle Schrödinger equations

$$\left(-\frac{\nabla^2}{2} + V_{S\sigma}[\rho_\uparrow, \rho_\downarrow](\mathbf{r})\right) \varphi_{j\sigma}(\mathbf{r}) = \varepsilon_{j\sigma}\varphi_{j\sigma}(\mathbf{r}) \qquad j = 1, \ldots, N_\sigma \qquad \sigma = \uparrow, \downarrow \tag{1}$$

where

$$\rho_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2. \tag{2}$$

For convenience we shall assume in the following that infinitesimal symmetry-breaking terms have been added to the external potential to remove any possible degeneracies. The KS orbitals can then be labeled such that

$$\varepsilon_{1\sigma} < \varepsilon_{2\sigma} < \ldots < \varepsilon_{N_\sigma\sigma} < \varepsilon_{(N_\sigma+1)\sigma} < \ldots \tag{3}$$

The Kohn-Sham potentials $V_{S\sigma}(\mathbf{r})$ may be written in the usual way as

$$V_{S\sigma}(\mathbf{r}) = v_0(\mathbf{r}) + \int d^3r' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\mathrm{xc}\sigma}(\mathbf{r}), \tag{4}$$

$$\rho(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \rho_\sigma(\mathbf{r}) \tag{5}$$

where $v_0(\mathbf{r})$ represents the external potential and $V_{\mathrm{xc}\sigma}(\mathbf{r})$ is a local exchange-correlation (xc) potential defined by the functional derivative of the xc energy:

$$V_{\mathrm{xc}\sigma}(\mathbf{r}) := \frac{\delta E_{\mathrm{xc}}\left[\rho_\uparrow, \rho_\downarrow\right]}{\delta \rho_\sigma(\mathbf{r})}. \tag{6}$$

At this point we want to emphasize that, by virtue of the Hohenberg-Kohn theorem applied to non-interacting systems, all single-particle orbitals are formally functionals of the densities, i.e.

$$\varphi_{j\sigma}(\mathbf{r}) = \varphi_{j\sigma}[\rho_\uparrow, \rho_\downarrow](\mathbf{r}) \, . \tag{7}$$

As a consequence, any orbital functional $E_{\rm xc}[\{\varphi_{j\tau}\}]$ is an (implicit) functional of $\rho_\uparrow$ and $\rho_\downarrow$, provided the orbitals come from a local potential. Having this in mind, we may equivalently start out with an approximation for the xc energy functional depending explicitly on the set of KS orbitals, i.e.

$$E_{\rm xc} = E_{\rm xc}[\{\varphi_{j\tau}\}] \tag{8}$$

rather than the conventional density-dependent approximations for $E_{\rm xc}$. However, the calculation of the corresponding xc potentials $v_{{\rm xc}\sigma}(\mathbf{r})$ becomes somewhat more complicated: For the case of orbital-dependent xc functionals $v_{{\rm xc}\sigma}(\mathbf{r})$ has to be determined by the solution of an integral equation, the so-called OEP integral equation. To demonstrate this, we may start out from the very definition of the local KS xc potential, Eq. (6), following a derivation first given by Görling and Levy [26]: In order to use Eq. (6) for orbital-dependent functionals, we employ the chain rule for functional derivatives, leading to

$$\begin{aligned} V^{\rm OEP}_{{\rm xc}\sigma}(\mathbf{r}) &= \frac{\delta E^{\rm OEP}_{\rm xc}\left[\{\varphi_{j\tau}\}\right]}{\delta\rho_\sigma(\mathbf{r})} \\ &= \sum_{\alpha=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha}\int d^3r'\,\frac{\delta E^{\rm OEP}_{\rm xc}\left[\{\varphi_{j\tau}\}\right]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta\rho_\sigma(\mathbf{r})} + c.c.\,. \end{aligned} \tag{9}$$

Here and in the following we assume that the xc functional $E_{\rm xc}[\{\varphi_{i\sigma}\}]$ only depends on the occupied KS orbitals. By applying the functional chain rule once more, we obtain

$$V^{\rm OEP}_{{\rm xc}\sigma}(\mathbf{r}) = \sum_{\alpha,\beta=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha}\int d^3r'\int d^3r''\left(\frac{\delta E^{\rm OEP}_{\rm xc}\left[\{\varphi_{j\tau}\}\right]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\beta}(\mathbf{r}'')} + c.c.\right)\frac{\delta V_{S\beta}(\mathbf{r}'')}{\delta\rho_\sigma(\mathbf{r})}\,. \tag{10}$$

The last term on the right-hand side is readily identified with the inverse $\chi_S^{-1}(\mathbf{r},\mathbf{r}')$ of the density response function of a system of non-interacting particles

$$\chi_{S\alpha,\beta}(\mathbf{r},\mathbf{r}') := \frac{\delta\rho_\alpha(\mathbf{r})}{\delta V_{S\beta}(\mathbf{r}')}. \tag{11}$$

This quantity is diagonal with respect to the spin variables so that Eq. (10) reduces to

$$V^{\rm OEP}_{{\rm xc}\sigma}(\mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha}\int d^3r'\int d^3r''\left(\frac{\delta E^{\rm OEP}_{\rm xc}\left[\{\varphi_{j\tau}\}\right]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r}'')} + c.c.\right)\chi^{-1}_{S\sigma}(\mathbf{r}'',\mathbf{r})\,. \tag{12}$$

Acting with the response operator (11) on both sides of Eq. (12) one obtains

$$\int d^3r'\,V^{\rm OEP}_{{\rm xc}\sigma}(\mathbf{r}')\chi_{S\sigma}(\mathbf{r}',\mathbf{r}) = \sum_{\alpha=\uparrow,\downarrow}\sum_{i=1}^{N_\alpha}\int d^3r'\,\frac{\delta E^{\rm OEP}_{\rm xc}\left[\{\varphi_{j\tau}\}\right]}{\delta\varphi_{i\alpha}(\mathbf{r}')}\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r})} + c.c.. \tag{13}$$

The second functional derivative on the right-hand side of Eq. (13) is calculated using first-order perturbation theory. This yields

$$\frac{\delta\varphi_{i\alpha}(\mathbf{r}')}{\delta V_{S\sigma}(\mathbf{r})} = \delta_{\alpha,\sigma}\sum_{\substack{k=1\\k\neq i}}^{\infty}\frac{\varphi_{k\sigma}(\mathbf{r}')\varphi^*_{k\sigma}(\mathbf{r})}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}}\varphi_{i\sigma}(\mathbf{r}). \tag{14}$$

Using this equation, the response function

$$\chi_{S\alpha,\beta}(\mathbf{r},\mathbf{r}') = \frac{\delta}{\delta V_{S\beta}(\mathbf{r}')}\left(\sum_{i=1}^{N_\alpha}\varphi^*_{i\alpha}(\mathbf{r})\varphi_{i\alpha}(\mathbf{r})\right) \tag{15}$$

is readily expressed in terms of the orbitals as

$$\chi_{S\sigma}\left(\mathbf{r},\mathbf{r}'\right) = \sum_{i=1}^{N_\sigma}\sum_{\substack{k=1\\k\neq i}}^{\infty} \frac{\varphi^*_{i\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r})\varphi^*_{k\sigma}(\mathbf{r}')\varphi_{i\sigma}(\mathbf{r}')}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}} + c.c.. \tag{16}$$

Inserting (14) and (16) in Eq. (13), we obtain the standard form of the OEP integral equation:

$$\sum_{i=1}^{N_\sigma}\int d^3r' \left(V^{\mathrm{OEP}}_{\mathrm{xc}\sigma}(\mathbf{r}') - u_{\mathrm{xc}i\sigma}(\mathbf{r}')\right) G_{Si\sigma}\left(\mathbf{r}',\mathbf{r}\right)\varphi_{i\sigma}(\mathbf{r})\varphi^*_{i\sigma}(\mathbf{r}') + c.c. = 0 \tag{17}$$

where

$$u_{\mathrm{xc}i\sigma}(\mathbf{r}) := \frac{1}{\varphi^*_{i\sigma}(\mathbf{r})}\frac{\delta E^{\mathrm{OEP}}_{\mathrm{xc}}\left[\{\varphi_{j\tau}\}\right]}{\delta\varphi_{i\sigma}(\mathbf{r})}. \tag{18}$$

The quantity $G_{Si\sigma}(\mathbf{r}',\mathbf{r})$, given by

$$G_{Si\sigma}\left(\mathbf{r}',\mathbf{r}\right) := \sum_{\substack{k=1\\k\neq i}}^{\infty}\frac{\varphi_{k\sigma}(\mathbf{r}')\varphi^*_{k\sigma}(\mathbf{r})}{\varepsilon_{i\sigma}-\varepsilon_{k\sigma}}, \tag{19}$$

represents the Green's function of the KS equation projected onto the subspace orthogonal to $\varphi_{i\sigma}(\mathbf{r})$, i.e., it satisfies the equation

$$\left(\hat{h}_{S\sigma}(\mathbf{r}) - \varepsilon_{i\sigma}\right) G_{Si\sigma}(\mathbf{r}',\mathbf{r}) = -\left(\delta(\mathbf{r}'-\mathbf{r}) - \varphi_{i\sigma}(\mathbf{r}')\varphi^*_{i\sigma}(\mathbf{r})\right) \tag{20}$$

where $\hat{h}_{S\sigma}(\mathbf{r})$ is a short-hand notation for the KS Hamiltonian

$$\hat{h}_{S\sigma}(\mathbf{r}) := -\frac{\nabla^2}{2} + V_{S\sigma}[\rho_\uparrow,\rho_\downarrow](\mathbf{r}). \tag{21}$$

Now, the OEP scheme is complete: The integral equation (17), determining the local xc potential $v_{\mathrm{xc}}(\mathbf{r})$ corresponding to an orbital-dependent approximation of E_{xc}, has to be solved self-consistently with the KS equation (1) and the differential equation for $G_{Si\sigma}(\mathbf{r}',\mathbf{r})$, Eq. (20).

The main advantage of such an approach is that it allows for greater flexibility in the choice of appropriate xc functionals. In particular, the OEP method can be used for the treatment of the exact exchange energy functional, defined by inserting KS orbitals in the Fock term, i.e.

$$E^{\mathrm{exact}}_{\mathrm{x}}[\rho] = -\frac{1}{2}\sum_{\sigma=\uparrow,\downarrow}\sum_{j,k=1}^{N_\sigma}\int d^3r\int d^3r'\,\frac{\varphi^*_{j\sigma}(\mathbf{r})\varphi^*_{k\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{22}$$

2.2 Asymptotic properties of the OEP

In this section a number of rigorous statements on the optimized effective potential for finite systems will be derived. For this purpose, the exchange-only potential and the correlation potential have to be treated separately within the OEP scheme. The exact exchange potential of DFT is defined as

$$V_{x\sigma}[\rho_\uparrow, \rho_\downarrow](\mathbf{r}) = \frac{\delta E_x^{\text{exact}}}{\delta \rho_\sigma(\mathbf{r})}\,, \qquad \sigma = \uparrow, \downarrow \tag{23}$$

where the exact exchange-energy functional is given by Eq. (22). In an ordinary OEP calculation, one only determines the potential $V_{x\sigma}[\rho_{\uparrow 0}, \rho_{\downarrow 0}](\mathbf{r})$ corresponding to the self-consistent ground-state spin densities $(\rho_{\uparrow 0}, \rho_{\downarrow 0})$ of the system considered. If one were to calculate $V_{x\sigma}[\rho_\uparrow, \rho_\downarrow]$ *for an arbitrary given set* $(\rho_\uparrow, \rho_\downarrow)$ *of spin densities* one would have to perform the following three steps:

1. Determine the unique potentials $V_{S\sigma}[\rho_\uparrow, \rho_\downarrow](\mathbf{r}), \sigma = \uparrow, \downarrow$, corresponding to the given spin densities $(\rho_\uparrow, \rho_\downarrow)$

2. Solve the Schrödinger equation (1) for the spin-up and spin-down orbitals with the potentials of step (1)

3. Plug the orbitals obtained in step (2) into the OEP integral equation

$$\sum_{i=1}^{N_\sigma} \int d^3r' \, (V_{x\sigma}(\mathbf{r}') - u_{xi\sigma}(\mathbf{r}')) G_{Si\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \varphi^*_{i\sigma}(\mathbf{r}') + c.c. = 0 \tag{24}$$

   and solve this equation for $V_{x\sigma}$ keeping the orbitals of step (2) fixed.

In this way Filippi, Umrigar and Gonze [27] have recently calculated the exchange potentials corresponding to the *exact* (not the x-only) densities of some atoms where the exact densities were determined in a quantum Monte-Carlo calculation. Likewise, for any given approximate functional $E_c[\{\varphi_{i\sigma}\}]$, the corresponding correlation potential

$$V_{c\sigma}[\rho_\uparrow, \rho_\downarrow](\mathbf{r}) = \frac{\delta E_c}{\delta \rho_\sigma(\mathbf{r})} \tag{25}$$

is obtained by the above steps (1) and (2), and step (3) replaced by the solution of

$$\sum_{i=1}^{N_\sigma} \int d^3r' \, (V_{c\sigma}(\mathbf{r}') - u_{ci\sigma}(\mathbf{r}')) G_{Si\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \varphi^*_{i\sigma}(\mathbf{r}') + c.c. = 0\,. \tag{26}$$

Whenever, in the following derivations, the OEP equations (24) and (26) are used or transformed it is understood that the orbitals $\{\varphi_{i\sigma}\}$ are kept fixed so that they always correspond to a unique fixed set $(\rho_\uparrow, \rho_\downarrow)$ of spin densities.

For the following analysis we find it more convenient not to work with the standard form (17), but with a transformed representation of the OEP integral equation. Following KLI [18] we define

$$\begin{aligned}\psi^*_{i\sigma}(\mathbf{r}) \;&:=\; \sum_{\substack{k=1\\k\neq i}}^{\infty} \frac{\int d^3r' \varphi^*_{i\sigma}(\mathbf{r}') \left(V^{\text{OEP}}_{xc\sigma}(\mathbf{r}') - u_{xci\sigma}(\mathbf{r}')\right) \varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} \varphi^*_{k\sigma}(\mathbf{r}) \\ &=\; \int d^3r' \varphi^*_{i\sigma}(\mathbf{r}') \left(V^{\text{OEP}}_{xc\sigma}(\mathbf{r}') - u_{xci\sigma}(\mathbf{r}')\right) G_{Si\sigma}(\mathbf{r}', \mathbf{r})\,. \end{aligned} \tag{27}$$

With this abbreviation, the OEP integral equation (17) can be rewritten in the simple form:

$$\sum_{i=1}^{N_\sigma} \psi^*_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) + c.c. \;=\; 0\,. \tag{28}$$

Now, the defining equation for $G_{Si\sigma}(\mathbf{r}',\mathbf{r})$ enables us to deduce a differential equation satisfied by the newly defined quantity $\psi^*_{i\sigma}(\mathbf{r})$: Acting with the operator $(\hat{h}_{S\sigma} - \varepsilon_{i\sigma})$ on Eq. (27) readily leads to

$$\left(\hat{h}_{S\sigma}(\mathbf{r}) - \varepsilon_{i\sigma}\right)\psi^*_{i\sigma}(\mathbf{r}) = -\left[V^{\mathrm{OEP}}_{\mathrm{xc}\sigma}(\mathbf{r}) - u_{\mathrm{xc}i\sigma}(\mathbf{r}) - (\bar{V}_{\mathrm{xc}i\sigma} - \bar{u}_{\mathrm{xc}i\sigma})\right]\varphi^*_{i\sigma}(\mathbf{r}) \tag{29}$$

where $\bar{V}_{\mathrm{xc}i\sigma}$ denotes the average of $V_{\mathrm{xc}\sigma}(\mathbf{r})$ with respect to the ith orbital, i.e.

$$\bar{V}_{\mathrm{xc}i\sigma} := \int d^3r\, \varphi^*_{i\sigma}(\mathbf{r})V^{\mathrm{OEP}}_{\mathrm{xc}\sigma}(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) \tag{30}$$

and

$$\bar{u}_{\mathrm{xc}i\sigma} := \int d^3r\, \varphi^*_{i\sigma}(\mathbf{r})u_{\mathrm{xc}i\sigma}(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}). \tag{31}$$

The differential equation (29) will serve as the starting point of the analysis below.

Before doing this, we discuss some properties of the quantity $\psi^*_{i\sigma}(\mathbf{r})$. First, since the KS orbitals $\{\varphi_{i\sigma}\}$ span an orthonormal set, we readily conclude from Eq. (27) that the function $\psi_{i\sigma}(\mathbf{r})$ is orthogonal to $\varphi_{i\sigma}(\mathbf{r})$:

$$\int d^3r\, \psi^*_{i\sigma}(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) = 0\,. \tag{32}$$

Secondly, we note that Eq. (29), having the structure of a KS equation with an additional inhomogeneity term, plus the boundary condition that $\psi^*_{i\sigma}(\mathbf{r})$ tends to zero as $r \to \infty$ uniquely determines $\psi^*_{i\sigma}(\mathbf{r})$. We can prove this statement by assuming that there are two independent solutions $\psi^*_{i\sigma,1}(\mathbf{r})$ and $\psi^*_{i\sigma,2}(\mathbf{r})$ of Eq. (29). Then the difference between these two solutions, $\Psi^*_{i\sigma}(\mathbf{r}) := \psi^*_{i\sigma,1}(\mathbf{r}) - \psi^*_{i\sigma,2}(\mathbf{r})$, satisfies the homogeneous KS equation

$$(\hat{h}_{S\sigma} - \varepsilon_{i\sigma})\Psi^*_{i\sigma}(\mathbf{r}) = 0, \tag{33}$$

which has a unique solution

$$\Psi^*_{i\sigma}(\mathbf{r}) = \varphi^*_{i\sigma}(\mathbf{r}), \tag{34}$$

if the above boundary condition is fulfilled. However, this solution leads to a contradiction with the orthogonality relation (32) so that $\Psi^*_{i\sigma}(r)$ can only be the trivial solution of Eq. (33),

$$\Psi^*_{i\sigma}(\mathbf{r}) \equiv 0\,. \tag{35}$$

This completes the proof.

Finally, it seems useful at this point to attach some physical meaning to the quantity $\psi_{i\sigma}$: From Eq. (27) it is obvious that $\psi_{i\sigma}$ is the usual first-order shift in the wave function caused by the perturbing potential $\delta V_{i\sigma} = V^{OEP}_{\mathrm{xc}\sigma} - u_{\mathrm{xc}i\sigma}$. This fact also motivates the boundary condition assumed above. In x-only theory, $u_{\mathrm{x}i\sigma}$ is the local, orbital-dependent HF exchange potential so that $-\psi_{i\sigma}$ is the first order shift of the KS wave function towards the HF wave function. One has to realize, however, that the first-order change of the orbital dependent potential $u_{\mathrm{x}i\sigma}[\{\varphi_{i\sigma}\}]$ has been neglected. This change can be expected to be small compared to $\delta V_{i\sigma}$ [18].

2.2.1 An important lemma

We now first prove an important *lemma* concerning the constants defined by Eqs. (30) and (31). The lemma states that

(i)

$$\bar{u}_{\mathrm{x}N_\sigma\sigma} = \bar{V}_{\mathrm{x}N_\sigma\sigma}$$

is satisfied for

$$u_{\mathrm{x}i\sigma}(\mathbf{r}) = \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})}\frac{\delta E_{\mathrm{x}}^{\mathrm{exact}}}{\delta\varphi_{i\sigma}(\mathbf{r})} \tag{36}$$

with the exact exchange-energy functional;

(ii)

$$\bar{u}_{\mathrm{c}N_\sigma\sigma} = \bar{V}_{\mathrm{c}N_\sigma\sigma}$$

is satisfied for any approximate correlation energy functional $E_{\mathrm{c}}[\{\varphi_{i\sigma}\}]$ *having the property*

$$u_{\mathrm{c}i\sigma}(\mathbf{r}) = \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})}\frac{\delta E_{\mathrm{c}}}{\delta\varphi_{i\sigma}(\mathbf{r})} \stackrel{r\to\infty}{\longrightarrow} \mathrm{const}\ , i = 1...N_\sigma\ . \tag{37}$$

We begin with the proof of statement (ii). To this end we use Eq. (29) for the correlation part only:

$$\left(-\frac{\nabla^2}{2} + V_{S\sigma}(\mathbf{r}) - \varepsilon_{i\sigma}\right)\psi_{i\sigma}^*(\mathbf{r}) = \left(V_{\mathrm{c}\sigma}(\mathbf{r}) - u_{\mathrm{c}i\sigma}(\mathbf{r}) - C_{i\sigma}\right)\varphi_{i\sigma}^*(\mathbf{r}) \tag{38}$$

where we have introduced the abbreviation

$$C_{i\sigma} = \bar{V}_{\mathrm{c}i\sigma} - \bar{u}_{\mathrm{c}i\sigma}\ . \tag{39}$$

If Eq. (38) is satisfied with potentials $V_{S\sigma}(\mathbf{r})$, $V_{\mathrm{c}\sigma}(\mathbf{r})$ and $u_{\mathrm{c}i\sigma}(\mathbf{r})$ it will also be satisfied with the constantly shifted potentials

$$\begin{aligned} \tilde{V}_{S\sigma}(\mathbf{r}) &:= V_{S\sigma}(\mathbf{r}) + B_{S\sigma} && (40)\\ \tilde{V}_{\mathrm{c}\sigma}(\mathbf{r}) &:= V_{\mathrm{c}\sigma}(\mathbf{r}) + B_{\mathrm{c}\sigma} && (41)\\ \tilde{u}_{\mathrm{c}i\sigma}(\mathbf{r}) &:= u_{\mathrm{c}i\sigma}(\mathbf{r}) + B_{i\sigma} && (42) \end{aligned}$$

and the corresponding eigenvalues $\tilde{\varepsilon}_{i\sigma}$ and the constants $\bar{\tilde{V}}_{\mathrm{c}i\sigma}$, $\bar{\tilde{u}}_{\mathrm{c}i\sigma}$, reflecting the fact that the eigenvalues as well as the various potentials are only determined up to an arbitrary constant. The constants $B_{S\sigma}$, $B_{\mathrm{c}\sigma}$, $B_{i\sigma}$ cancel out in Eq. (38) because the eigenvalues $\tilde{\varepsilon}_{i\sigma}$ resulting from solving the Schrödinger equation (1) with the potential (40) are given by

$$\tilde{\varepsilon}_{i\sigma} = \varepsilon_{i\sigma} + B_{S\sigma} \tag{43}$$

and the constants $\bar{\tilde{V}}_{\mathrm{c}\sigma}$, $\bar{\tilde{u}}_{\mathrm{c}i\sigma}$ obtained from the correlation parts of Eqs. (30), (31) with the potentials (41), (42) are

$$\begin{aligned} \bar{\tilde{V}}_{\mathrm{c}i\sigma} &= \bar{V}_{\mathrm{c}i\sigma} + B_{\mathrm{c}\sigma} && (44)\\ \bar{\tilde{u}}_{\mathrm{c}i\sigma} &= \bar{u}_{\mathrm{c}i\sigma} + B_{i\sigma}\ . && (45) \end{aligned}$$

Hence we can assume *without restriction* that

$$V_{S\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} 0 \tag{46}$$

$$V_{c\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} 0 \tag{47}$$

$$u_{ci\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} 0\,. \tag{48}$$

In the following we shall investigate the asymptotic behavior of the KS orbitals $\varphi_{i\sigma}(\mathbf{r})$ and of the quantities $\psi_{i\sigma}(\mathbf{r})$ defined by Eq. (38). As a shorthand we write

$$\varphi_{i\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} \Phi_{i\sigma}(r) f_{i\sigma}(\Omega) \tag{49}$$

$$\psi_{i\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} \Psi_{i\sigma}(r) g_{i\sigma}(\Omega)\,. \tag{50}$$

The aim is to determine the asymptotically dominant functions $\Phi_{i\sigma}(r)$ and $\Psi_{i\sigma}(r)$. The angular parts $f_{i\sigma}(\Omega)$ and $g_{i\sigma}(\Omega)$ are not of interest in the present context. Using the fact that the KS potential of finite neutral systems behaves asymptotically as [28]

$$V_{S\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} -\frac{1}{r} \tag{51}$$

the KS equation (1) leads to the following asymptotic equation

$$\left(-\frac{1}{2}\frac{1}{r}\frac{d^2}{dr^2}r - \frac{1}{r} - \varepsilon_{i\sigma}\right)\Phi_{i\sigma}(r) = 0\,. \tag{52}$$

The asymptotic form of $\Phi_{i\sigma}(r)$ is easily found to be

$$\Phi_{i\sigma}(r) \stackrel{r\to\infty}{\longrightarrow} r^{1/\beta_{i\sigma}}\,\frac{\mathrm{e}^{-\beta_{i\sigma}r}}{r} \tag{53}$$

with

$$\beta_{i\sigma} := \sqrt{-2\varepsilon_{i\sigma}}\,. \tag{54}$$

By virtue of Eqs. (38) and (53), $\Psi_{i\sigma}(r)$ must satisfy the asymptotic equation

$$\left(-\frac{1}{2}\frac{1}{r}\frac{d^2}{dr^2}r - \frac{1}{r} - \varepsilon_{i\sigma}\right)\Psi_{i\sigma}(r) = \left(W_{i\sigma}(r) - C_{i\sigma}\right) r^{1/\beta_{i\sigma}}\,\frac{\mathrm{e}^{-\beta_{i\sigma}r}}{r} \tag{55}$$

where we have introduced the quantity $W_{i\sigma}(r)$ defined by

$$\Big(V_{c\sigma}(\mathbf{r}) - u_{ci\sigma}(\mathbf{r})\Big) \stackrel{r\to\infty}{\longrightarrow} W_{i\sigma}(r) w_{i\sigma}(\Omega)\,. \tag{56}$$

From Eqs. (47) and (48) we know that

$$W_{i\sigma}(r) \stackrel{r\to\infty}{\longrightarrow} 0\,. \tag{57}$$

Inserting the ansatz

$$\Psi_{i\sigma}(r) = p_{i\sigma}(r)\frac{\mathrm{e}^{-\beta_{i\sigma}r}}{r} \tag{58}$$

in Eq. (55) we find that the function $p_{i\sigma}(r)$ must satisfy the equation

$$\frac{1}{2}p''_{i\sigma} - \beta_{i\sigma}p'_{i\sigma} + \frac{p_{i\sigma}}{r} = C_{i\sigma}r^{1/\beta_{i\sigma}} \qquad \text{if} \quad C_{i\sigma} \neq 0 \tag{59}$$

and

$$\frac{1}{2}p_{i\sigma}'' - \beta_{i\sigma}p_{i\sigma}' + \frac{p_{i\sigma}}{r} = -W_{i\sigma}(r)r^{1/\beta_{i\sigma}} \qquad \text{if} \quad C_{i\sigma} = 0\,. \tag{60}$$

The asymptotic solution of Eq. (59) is immediately recognized as

$$p_{i\sigma}(r) \overset{r\to\infty}{\longrightarrow} -\frac{C_{i\sigma}}{\beta_{i\sigma}}\,r^{(1/\beta_{i\sigma}+1)} \tag{61}$$

so that

$$\Psi_{i\sigma}(r) = -\frac{C_{i\sigma}}{\beta_{i\sigma}}\,r^{1/\beta_{i\sigma}}\mathrm{e}^{-\beta_{i\sigma}r} \qquad \text{if} \quad C_{i\sigma} \neq 0\,. \tag{62}$$

Writing

$$p_{i\sigma}(r) = F_{i\sigma}(r)r^{1/\beta_{i\sigma}+1} \qquad \text{if} \quad C_{i\sigma} = 0 \tag{63}$$

one readily verifies by insertion in Eq. (60) that

$$F_{i\sigma}(r) \overset{r\to\infty}{\longrightarrow} 0 \tag{64}$$

as a consequence of (57).

We now prove statement (ii) of the lemma by reductio ad absurdum: Assume that $C_{N_\sigma\sigma} \neq 0$. Then the asymptotic form of $\Psi_{N_\sigma\sigma}(r)$ is given by (62) and we conclude that

$$\psi^*_{N_\sigma\sigma}(\mathbf{r})\varphi_{N_\sigma\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} -\frac{C_{N_\sigma\sigma}}{\beta_{N_\sigma\sigma}}r^{\left(\frac{2}{\beta_{N_\sigma\sigma}}-1\right)}\mathrm{e}^{-2\beta_{N_\sigma\sigma}r}\cdot g^*_{N_\sigma\sigma}(\Omega)f_{N_\sigma\sigma}(\Omega)\,. \tag{65}$$

For $i \neq N_\sigma$, on the other hand, we obtain

$$\psi^*_{i\sigma}(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} G_{i\sigma}(r)r^{\left(\frac{2}{\beta_{i\sigma}}-1\right)}\mathrm{e}^{-2\beta_{i\sigma}r}\cdot g^*_{i\sigma}(\Omega)f_{i\sigma}(\Omega) \tag{66}$$

where

$$G_{i\sigma}(r) = \begin{cases} -C_{i\sigma}/\beta_{i\sigma} & \text{if} \quad C_{i\sigma} \neq 0 \\ F_{i\sigma}(r) \overset{r\to\infty}{\longrightarrow} 0 & \text{if} \quad C_{i\sigma} = 0 \end{cases}\,. \tag{67}$$

From this we conclude that the OEP integral equation

$$\psi^*_{N_\sigma\sigma}(\mathbf{r})\varphi_{N_\sigma\sigma}(\mathbf{r}) + \sum_{i=1}^{N_\sigma-1}\psi^*_{i\sigma}(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) + c.c. \equiv 0 \tag{68}$$

is not satisfied for $r \to \infty$ because the dominant term given by (65) cannot be canceled by any of the other contributions (66) which all fall off more rapidly (cf. Eq. (3)). Consequently the $\psi_{j\sigma}$ cannot be solutions of the OEP equation which is the desired contradiction. This implies that $C_{N_\sigma\sigma} = 0$ which completes the proof of statement (ii).

In order to prove statement (i) of the lemma we first investigate the asymptotic form of the quantities $u_{\mathrm{x}i\sigma}(\mathbf{r})$. Employing the exact exchange-energy functional (22) we find

$$u_{\mathrm{x}i\sigma}(\mathbf{r}) = -\sum_{j=1}^{N_\sigma}\frac{\varphi^*_{j\sigma}(\mathbf{r})}{\varphi^*_{i\sigma}(\mathbf{r})}K_{ji\sigma}(\mathbf{r}) \tag{69}$$

with

$$K_{ji\sigma}(\mathbf{r}) := \int d^3r' \, \frac{\varphi_{j\sigma}(\mathbf{r}')\varphi^*_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \,. \tag{70}$$

Performing a multipole expansion of $K_{ji\sigma}(\mathbf{r})$ and using the orthonormality of the KS orbitals we find

$$K_{ii\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} \frac{1}{r} \tag{71}$$

$$K_{ji\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} \frac{1}{r^m} k_{ji\sigma}(\Omega) \qquad i \neq j \tag{72}$$

with some integer $m \geq 2$ that depends on i and j. Hence the sum in Eq. (69) must be dominated asymptotically by the $j = N_\sigma$ term:

$$u_{\mathrm{x}i\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} -\frac{\varphi^*_{N_\sigma\sigma}(\mathbf{r})}{\varphi^*_{i\sigma}(\mathbf{r})} K_{N_\sigma i\sigma}(\mathbf{r}) \,. \tag{73}$$

Using Eqs. (71), (72) and the asymptotic behavior (53) of the KS orbitals we obtain

$$u_{\mathrm{x}N_\sigma\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} -\frac{1}{r} \tag{74}$$

and

$$u_{\mathrm{x}i\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} -r^{\left(\frac{1}{\beta_{N_\sigma\sigma}} - \frac{1}{\beta_{i\sigma}} - m\right)} \mathrm{e}^{(\beta_{i\sigma} - \beta_{N_\sigma\sigma})r} \omega_{i\sigma}(\Omega) \,. \tag{75}$$

We recognize that $u_{\mathrm{x}i\sigma}(\mathbf{r})$ diverges exponentionally to $-\infty$ for $i < N_\sigma$. In the x-only case, the quantities $\psi_{i\sigma}(\mathbf{r})$ satisfy the equation

$$\left(-\frac{\nabla^2}{2} + V_{S\sigma}(\mathbf{r}) - \varepsilon_{i\sigma}\right) \psi^*_{i\sigma}(\mathbf{r}) = \left(V_{\mathrm{x}\sigma}(\mathbf{r}) - u_{\mathrm{x}i\sigma}(\mathbf{r}) - C_{i\sigma}\right) \varphi^*_{i\sigma}(\mathbf{r}) \tag{76}$$

where

$$C_{i\sigma} = \bar{V}_{\mathrm{x}i\sigma} - \bar{u}_{\mathrm{x}i\sigma} \,. \tag{77}$$

In the following we prove statement (i) of the lemma by reductio ad absurdum: Assume that $C_{N_\sigma\sigma} \neq 0$. Then, by Eq. (74), the right-hand side of Eq. (76) for $i = N_\sigma$ is asymptotically dominated by $-C_{N_\sigma\sigma}\varphi^*_{N_\sigma\sigma}(\mathbf{r})$ and we obtain, in complete analogy to the correlation-only case:

$$\Psi_{N_\sigma\sigma}(r) = -\frac{C_{N_\sigma\sigma}}{\beta_{N_\sigma\sigma}} r^{1/\beta_{N_\sigma\sigma}} \mathrm{e}^{-\beta_{N_\sigma\sigma} r} \qquad \text{for} \quad C_{N_\sigma\sigma} \neq 0 \,. \tag{78}$$

For $i < N_\sigma$, the right-hand side of Eq.(76) is dominated by $-u_{\mathrm{x}i\sigma}(\mathbf{r})\varphi^*_{i\sigma}(\mathbf{r})$. Using Eqs. (53) and (75) $\Psi_{i\sigma(r)}$ satisfies the asymptotic differential equation

$$\left(-\frac{1}{2}\frac{1}{r}\frac{d^2}{dr^2}r - \frac{1}{r} - \varepsilon_{i\sigma}\right) \Psi_{i\sigma}(r) = r^{\left(\frac{1}{\beta_{N_\sigma\sigma}} - 1 - m\right)} \mathrm{e}^{-\beta_{N_\sigma\sigma} r} \,. \tag{79}$$

From this equation one readily concludes that

$$\Psi_{i\sigma}(r) \overset{r\to\infty}{\longrightarrow} \frac{1}{\varepsilon_{N_\sigma\sigma} - \varepsilon_{i\sigma}} r^{\left(\frac{1}{\beta_{N_\sigma\sigma}} - 1 - m\right)} \mathrm{e}^{-\beta_{N_\sigma\sigma} r} \,, \qquad i < N_\sigma \,. \tag{80}$$

We note in passing that all the functions $\psi_{i\sigma}$, $i = 1...N_\sigma$, have the *same* exponential decay, $\mathrm{e}^{-\beta_{N_\sigma\sigma} r}$, determined by the highest occupied orbital energy $\beta_{N_\sigma\sigma} = \sqrt{-2\varepsilon_{N_\sigma\sigma}}$. This fact further supports the interpretation of the quantities $\psi_{i\sigma}$ (in the x-only case) as a shift from the KS orbitals towards the HF orbitals: The HF orbitals $\varphi_{i\sigma}^{\mathrm{HF}}$ are known [29] to be asymptotically dominated by the exponential decay $\mathrm{e}^{-\beta_{N_\sigma\sigma} r}$ of the highest occupied orbital. The same holds true for the shifted KS orbitals $(\varphi_{i\sigma} + \psi_{i\sigma})$.

From Eqs. (53), (78) and (80) we obtain

$$\psi^*_{N_\sigma\sigma}(\mathbf{r})\varphi_{N_\sigma\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} -\frac{C_{N_\sigma\sigma}}{\beta_{N_\sigma\sigma}} r^{\left(\frac{2}{\beta_{N_\sigma\sigma}}-1\right)} \mathrm{e}^{-2\beta_{N_\sigma\sigma} r} \cdot g^*_{N_\sigma\sigma}(\Omega) f_{N_\sigma\sigma}(\Omega) \, . \tag{81}$$

and

$$\psi^*_{i\sigma}(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} \frac{1}{\varepsilon_{N_\sigma\sigma} - \varepsilon_{i\sigma}} r^{\left(\frac{1}{\beta_{N_\sigma\sigma}}+\frac{1}{\beta_{i\sigma}}-2-m\right)} \mathrm{e}^{-(\beta_{N_\sigma\sigma}+\beta_{i\sigma})r} \cdot g^*_{i\sigma}(\Omega) f_{i\sigma}(\Omega) \, , \quad i < N_\sigma \, . \tag{82}$$

Once again we conclude that in the OEP equation (68) the asymptotically dominant term (81) cannot be canceled by any of the other terms (82), leading to the contradiction that the $\psi_{j\sigma}(\mathbf{r})$ are not solutions of the OEP integral equation. Hence we conclude that $C_{N_\sigma\sigma} = 0$ which completes the proof of the lemma.

Görling and Levy [10] recently gave a proof of statement (i) of the above lemma. This proof is based on the scaling properties of the exchange-energy functional and can therefore not be generalized to the case of correlation. The proof presented above for the correlation part of the OEP (statement (ii) of the lemma) is valid for all correlation energy functionals leading to asymptotically bounded functions $u_{\mathrm{c}i\sigma}(\mathbf{r})$. For asymptotically diverging $u_{\mathrm{c}i\sigma}(\mathbf{r})$ the lemma might still be valid. In particular, if the divergence is the same as the one (Eq.(75)) found in the exchange case, the proof of statement (i) carries over. This lemma will be used in the subsequent section in the derivation of the asymptotic form of the OEP.

2.2.2 Asymptotic form of the OEP

In this section we shall investigate the asymptotic form of the exchange and correlation potentials. It will be shown that $V_{\mathrm{x}\sigma}(\mathbf{r})$ and $u_{\mathrm{x}N_\sigma\sigma}(\mathbf{r})$ approach each other exponentially fast for $r \to \infty$, and that the difference between $V_{\mathrm{c}\sigma}(\mathbf{r})$ and $u_{\mathrm{c}N_\sigma\sigma}(\mathbf{r})$ decays exponentially as well. Using the notation of the last section the detailed statements read as follows:

Theorem 1:

$$V_{\mathrm{x}\sigma}(\mathbf{r}) - u_{\mathrm{x}N_\sigma\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} r^{\left(\frac{1}{\beta_{(N_\sigma-1)\sigma}}-\frac{1}{\beta_{N_\sigma\sigma}}-m\right)} \mathrm{e}^{-(\beta_{(N_\sigma-1)\sigma}-\beta_{N_\sigma\sigma})r} \tag{83}$$

where m is an integer satisfying $m \geq 2$.

Theorem 2: *If the constant $C_{(N_\sigma-1)\sigma}$ defined by Eq. (39) does not vanish then*

$$V_{c\sigma}(\mathbf{r}) - u_{cN_\sigma\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} C_{(N_\sigma-1)\sigma} r^{\left(\frac{2}{\beta_{(N_\sigma-1)\sigma}} - \frac{2}{\beta_{N_\sigma\sigma}} + 1\right)} \mathrm{e}^{-2(\beta_{(N_\sigma-1)\sigma} - \beta_{N_\sigma\sigma})r}. \quad (84)$$

If $C_{(N_\sigma-1)\sigma} = 0$ the right-hand side of (84) is an upper bound of $|V_{c\sigma}(\mathbf{r}) - u_{cN_\sigma\sigma}(\mathbf{r})|$ for $r \to \infty$, i.e. for $C_{(N_\sigma-1)\sigma} = 0$, $V_{c\sigma}(\mathbf{r})$ and $u_{cN_\sigma\sigma}(\mathbf{r})$ approach each other even faster than given by the right-hand side of Eq. (84).

To prove theorem 1 we write

$$\Psi_{N_\sigma\sigma}(r) = q(r)\frac{\mathrm{e}^{-\beta_{N_\sigma\sigma}r}}{r} \quad . \quad (85)$$

Using the lemma of the last section ensuring that $C_{N_\sigma\sigma} = 0$, $q(r)$ must satisfy the following asymptotic differential equation:

$$-\frac{1}{2}r^{-\frac{1}{\beta_{N_\sigma\sigma}}} q''(r) + \beta_{N_\sigma\sigma} r^{-\frac{1}{\beta_{N_\sigma\sigma}}} q'(r) - r^{-\left(\frac{1}{\beta_{N_\sigma\sigma}}+1\right)} q(r) = V_{x\sigma}(\mathbf{r}) - u_{xN_\sigma\sigma}(\mathbf{r}) \quad . \quad (86)$$

This is readily verified by inserting (51), (53) and (85) in Eq. (76). By virtue of Eqs. (3) and (82) the sum

$$\sum_{i=1}^{N_\sigma-1} \psi_{i\sigma}^*(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) \quad (87)$$

must be asymptotically dominated by the $i = (N_\sigma - 1)$ term which decays as

$$\psi_{(N_\sigma-1)\sigma}^*(\mathbf{r})\varphi_{(N_\sigma-1)\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} \frac{1}{\varepsilon_{N_\sigma\sigma} - \varepsilon_{(N_\sigma-1)\sigma}} r^{\left(\frac{1}{\beta_{N_\sigma\sigma}} + \frac{1}{\beta_{(N_\sigma-1)\sigma}} - 2 - m\right)} \mathrm{e}^{-(\beta_{N_\sigma\sigma} + \beta_{(N_\sigma-1)\sigma})r} \, . \quad (88)$$

This term cannot be canceled by any other term of the sum (87). Hence, for the OEP equation (28) to be asymptotically satisfied, the expression (88) must be canceled by the $i = N_\sigma$ term which behaves as

$$\psi_{N_\sigma\sigma}^*(\mathbf{r})\varphi_{N_\sigma\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} q(r) r^{\left(\frac{1}{\beta_{N_\sigma\sigma}} - 2\right)} \mathrm{e}^{-2\beta_{N_\sigma\sigma}r} \quad . \quad (89)$$

Equating the right-hand side of Eqs. (88) and (89), the function $q(r)$ is readily determined to be

$$q(r) = \frac{1}{\varepsilon_{N_\sigma\sigma} - \varepsilon_{(N_\sigma-1)\sigma}} r^{\left(\frac{1}{\beta_{(N_\sigma-1)\sigma}} - m\right)} \mathrm{e}^{-(\beta_{(N_\sigma-1)\sigma} - \beta_{N_\sigma\sigma})r} \quad . \quad (90)$$

Finally, by inserting this result in the left-hand side of Eq. (86), we confirm that the right-hand side of this equation decays asymptotically as stated in theorem 1.

To prove theorem 2 we write for the correlation-only case

$$\Psi_{N_\sigma\sigma}(r) = p(r)\frac{\mathrm{e}^{-\beta_{N_\sigma\sigma}r}}{r} \quad . \quad (91)$$

Since $C_{N_\sigma\sigma} = 0$, $p(r)$ must satisfy the following asymptotic differential equation (cf. Eq. (60)):

$$-\frac{1}{2}r^{-\frac{1}{\beta_{N_\sigma\sigma}}}p''(r) + \beta_{N_\sigma\sigma}r^{-\frac{1}{\beta_{N_\sigma\sigma}}}p'(r) - r^{-\left(\frac{1}{\beta_{N_\sigma\sigma}}+1\right)}p(r) = V_{\mathrm{c}\sigma}(\mathbf{r}) - u_{\mathrm{c}N_\sigma\sigma}(\mathbf{r}) \ . \tag{92}$$

If $C_{(N_\sigma-1)\sigma} \neq 0$, the sum

$$\sum_{i=1}^{N_\sigma-1} \psi_{i\sigma}^*(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) \tag{93}$$

is asymptotically dominated by the $i = (N_\sigma - 1)$ term which, according to Eqs. (66) and (67), decays as

$$\begin{aligned}&\psi_{(N_\sigma-1)\sigma}^*(\mathbf{r})\varphi_{(N_\sigma-1)\sigma}(\mathbf{r}) \\ &\qquad \overset{r\to\infty}{\longrightarrow} -\frac{C_{(N_\sigma-1)\sigma}}{\beta_{(N_\sigma-1)\sigma}} r^{\left(\frac{2}{\beta_{(N_\sigma-1)\sigma}}-1\right)} \mathrm{e}^{-2\beta_{(N_\sigma-1)\sigma}r} \ .\end{aligned} \tag{94}$$

Once again this term cannot be canceled by any other term of the sum (93). Hence it must be canceled asymptotically by the $i = N_\sigma$ term which behaves as

$$\psi_{N_\sigma\sigma}^*(\mathbf{r})\varphi_{N_\sigma\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} p(r) r^{\left(\frac{1}{\beta_{N_\sigma\sigma}}-2\right)} \mathrm{e}^{-2\beta_{N_\sigma\sigma}r} \ . \tag{95}$$

Equating the right-hand sides of Eqs. (94) and (95) we can identify the asymptotic form of $p(r)$:

$$p(r) = -\frac{C_{(N_\sigma-1)\sigma}}{\beta_{(N_\sigma-1)\sigma}} r^{\left(\frac{2}{\beta_{(N_\sigma-1)\sigma}}-\frac{1}{\beta_{N_\sigma\sigma}}+1\right)} \mathrm{e}^{-2(\beta_{(N_\sigma-1)\sigma}-\beta_{N_\sigma\sigma})r} \ . \tag{96}$$

Insertion of this expression in the left-hand side of Eq. (92) proves Eq. (84) for the case $C_{(N_\sigma-1)\sigma} \neq 0$. If $C_{(N_\sigma-1)\sigma} = 0$ the asymptotic form of $V_{\mathrm{c}\sigma}(\mathbf{r}) - u_{\mathrm{c}N_\sigma\sigma}(\mathbf{r})$ cannot be stated explicitly. It is clear, however, that the $i = N_\sigma$ term (95) must be canceled asymptotically by some contribution to the sum (93). Since, by Eqs. (66) and (67), *all* contributions to the sum (93) fall off more rapidly than the right-hand side of (94), $p(r)$ must decay more rapidly than the right-hand side of (96). Hence, by Eq. (92), the right-hand side of (84) provides an upper bound of $|V_{\mathrm{c}\sigma}(\mathbf{r}) - u_{\mathrm{c}N_\sigma\sigma}(\mathbf{r})|$ for $r \to \infty$ if $C_{(N_\sigma-1)\sigma} = 0$. This completes the proof.

Since the asymptotic form of $u_{\mathrm{x}N_\sigma\sigma}(\mathbf{r})$, as derived in Eq. (74), is $-\frac{1}{r}$, theorem 1 immediately implies that

$$V_{\mathrm{x}\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} -\frac{1}{r} \ . \tag{97}$$

This is a well-known result that has been obtained in several different ways [8, 30, 28, 31, 32] The exact correlation potential of DFT is known [28] to fall off as $-\alpha/(2r^4)$ for atoms with spherical N and $(N-1)$-electron ground states, with α being the static polarizability of the $(N-1)$-electron ground state. Theorem 2 provides a simple way of checking how the OEP correlation-only potential $V_{\mathrm{c}\sigma}(\mathbf{r})$ falls off for a given approximate orbital functional $E_{\mathrm{c}}^{\mathrm{approx}}[\{\varphi_{i\sigma}\}]$: One only needs to determine the asymptotic decay of $u_{\mathrm{c}N_\sigma\sigma}(\mathbf{r})$.

3 Approximation of Krieger, Li and Iafrate

3.1 Derivation of the KLI approximation

The OEP method, discussed in the preceding paragraph, opens up a way for using orbital-dependent functionals within the KS scheme. However, as a price to pay, one has to solve an integral equation self-consistently with the KS equation. Due to the rather large computational effort involved in this scheme, it has not been used extensively. Indeed, the solution of the OEP integral equation has been achieved so far only for systems of high symmetry such as spherical atoms [6, 8, 16, 17, 33] and for solids within the linear muffin tin orbitals atomic sphere approximation [13, 34, 35, 36]. Therefore, practical applications of the OEP scheme to a greater variety of systems require some simplification.

Krieger, Li and Iafrate have suggested an approximation leading to a highly accurate but numerically tractable scheme preserving many important properties of the exact OEP method [6, 11, 13, 14, 15, 16, 17, 18, 19]. It is most easily derived by replacing the energy denominator of the Green's function (19) by a single constant, i.e.

$$G_{Si\sigma}(\mathbf{r}',\mathbf{r}) \approx \frac{1}{\Delta\varepsilon}\left(\delta(\mathbf{r}'-\mathbf{r}) - \varphi_{i\sigma}(\mathbf{r}')\varphi^*_{i\sigma}(\mathbf{r})\right) . \tag{98}$$

Substituting this into the OEP integral equation (17) leads to an approximate equation, known as the KLI approximation:

$$V^{\mathrm{KLI}}_{\mathrm{xc}\sigma}(\mathbf{r}) = \frac{1}{2\rho_\sigma(\mathbf{r})}\sum_{i=1}^{N_\sigma}|\varphi_{i\sigma}(\mathbf{r})|^2\left[u_{\mathrm{xc}i\sigma}(\mathbf{r}) + (\bar{V}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} - \bar{u}_{\mathrm{xc}i\sigma})\right] + c.c. \tag{99}$$

where $\bar{V}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma}$ is defined in analogy to Eq. (30). In contrast to the full OEP equation (17), the KLI equation, still being an integral equation, can be solved explicitly in terms of the orbitals $\{\varphi_{i\sigma}\}$: Multiplying Eq. (99) by $|\varphi_{j\sigma}(\mathbf{r})|^2$ and integrating over space yields

$$\bar{V}^{\mathrm{KLI}}_{\mathrm{xc}j\sigma} = \bar{V}^{S}_{\mathrm{xc}j\sigma} + \sum_{i=1}^{N_\sigma-1} M_{ji\sigma}\left(\bar{V}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} - \frac{1}{2}\left(\bar{u}_{\mathrm{xc}i\sigma} + \bar{u}^*_{\mathrm{xc}i\sigma}\right)\right) , \tag{100}$$

where

$$\bar{V}^{S}_{\mathrm{xc}j\sigma} := \int d^3r\,\frac{|\varphi_{j\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})}\sum_{i=1}^{N_\sigma}|\varphi_{i\sigma}(\mathbf{r})|^2\frac{1}{2}\left(u_{\mathrm{xc}i\sigma}(\mathbf{r}) + u^*_{\mathrm{xc}i\sigma}(\mathbf{r})\right) \tag{101}$$

and

$$M_{ji\sigma} := \int d^3r\,\frac{|\varphi_{j\sigma}(\mathbf{r})|^2|\varphi_{i\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})}. \tag{102}$$

The term corresponding to the highest occupied orbital $\varphi_{N_\sigma\sigma}$ has been excluded from the sum in Eq. (100) because $\bar{V}^{\mathrm{KLI}}_{\mathrm{xc}N_\sigma\sigma} = \bar{u}_{\mathrm{xc}N_\sigma\sigma}$, which will be proven in the next section. The remaining unknown constants $(\bar{V}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} - \bar{u}_{\mathrm{xc}i\sigma})$ are determined by the linear equation

$$\sum_{i=1}^{N_\sigma-1}(\delta_{ji} - M_{ji\sigma})\left(\bar{V}^{\mathrm{KLI}}_{\mathrm{xc}i\sigma} - \frac{1}{2}\left(\bar{u}_{\mathrm{xc}i\sigma} + \bar{u}^*_{\mathrm{xc}i\sigma}\right)\right) = \left(\bar{V}^{S}_{\mathrm{xc}j\sigma} - \frac{1}{2}\left(\bar{u}_{\mathrm{xc}j\sigma} + \bar{u}^*_{\mathrm{xc}j\sigma}\right)\right) , \tag{103}$$

with $j = 1, \ldots N_\sigma - 1$. Solving Eq. (103) and substituting the result into Eq. (99), we obtain an explicitly orbital dependent functional. The approximation 98 might appear rather crude. However, it can be justified by a much more rigorous derivation, showing that the KLI equation can be interpreted as a mean-field type approximation [6, 18].

3.2 Asymptotic properties of the KLI potential

In this section we shall demonstrate that the above rigorous properties of the full OEP discussed above are preserved by the KLI approximation. As for the OEP equation, we first write the KLI approximation (99) separately for the exchange and correlation potentials:

$$\sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \left(V_{\mathrm{x}\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{\mathrm{x}i\sigma}(\mathbf{r}) - \left(\bar{V}_{\mathrm{x}i\sigma}^{\mathrm{KLI}} - \bar{U}_{\mathrm{x}i\sigma} \right) \right) = 0 \tag{104}$$

$$\sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \left(V_{\mathrm{c}\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{\mathrm{c}i\sigma}(\mathbf{r}) - \left(\bar{V}_{\mathrm{c}i\sigma}^{\mathrm{KLI}} - \bar{U}_{\mathrm{c}i\sigma} \right) \right) = 0 \, . \tag{105}$$

where, for convenience, we have introduced

$$U_{\mathrm{x}i\sigma}(\mathbf{r}) = \frac{1}{2} \left(u_{\mathrm{x}i\sigma}(\mathbf{r}) + u_{\mathrm{x}i\sigma}^{*}(\mathbf{r}) \right) \tag{106}$$

and

$$U_{\mathrm{c}i\sigma}(\mathbf{r}) = \frac{1}{2} \left(u_{\mathrm{c}i\sigma}(\mathbf{r}) + u_{\mathrm{c}i\sigma}^{*}(\mathbf{r}) \right) \tag{107}$$

in order to deal with real-valued quantities only. Following the argument given in the beginning of section 2.2.1 (Eqs. (40) - (48)) we can assume *without restriction* that

$$V_{\mathrm{x}\sigma}^{\mathrm{KLI}}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} 0 \tag{108}$$

$$V_{\mathrm{c}\sigma}^{\mathrm{KLI}}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} 0 \tag{109}$$

$$U_{\mathrm{c}i\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} 0 \, . \tag{110}$$

This is because the structure of Eqs. (104) and (105) is again such that an additive constant in the potentials (108) - (110) cancels out. Of course, Eq. (110) is valid only for those approximate orbital functionals $E_{\mathrm{c}}[\{\varphi_{j\sigma}\}]$ leading to bounded functions $u_{\mathrm{c}i\sigma}(\mathbf{r})$ for $r \to \infty$ (cf. condition (37)).

In order to determine the asymptotic form of the KLI-x-only potential $V_{\mathrm{x}\sigma}^{\mathrm{KLI}}(\mathbf{r})$, we first investigate the asymptotic behavior of the term $\sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \cdot u_{\mathrm{x}i\sigma}(\mathbf{r})$ appearing in the KLI equation (104): By Eqs. (69) and (70) the expression

$$|\varphi_{N_\sigma\sigma}(\mathbf{r})|^2 u_{\mathrm{x}N_\sigma\sigma}(\mathbf{r}) + \sum_{i=1}^{N_\sigma - 1} |\varphi_{i\sigma}(\mathbf{r})|^2 u_{\mathrm{x}i\sigma}(\mathbf{r})$$

can be written as

$$= |\varphi_{N_\sigma\sigma}(\mathbf{r})|^2 u_{\mathrm{x}N_\sigma\sigma}(\mathbf{r}) + \sum_{i=1}^{N_\sigma-1} \sum_{j=1}^{N_\sigma} \varphi_{i\sigma}(\mathbf{r}) \varphi_{j\sigma}^{*}(\mathbf{r}) K_{ji\sigma}(\mathbf{r})$$

$$= |\varphi_{N_\sigma\sigma}(\mathbf{r})|^2 \left(u_{\mathrm{x}N_\sigma\sigma}(\mathbf{r}) + \sum_{i=1}^{N_\sigma-1} \sum_{j=1}^{N_\sigma} \left(\frac{\varphi_{i\sigma}(\mathbf{r})}{\varphi_{N_\sigma\sigma}(\mathbf{r})} \right) \left(\frac{\varphi_{j\sigma}^{*}(\mathbf{r})}{\varphi_{N_\sigma\sigma}^{*}(\mathbf{r})} \right) K_{ji\sigma}(\mathbf{r}) \right) \, .$$

Since $K_{ji\sigma}(\mathbf{r})$ decays as an inverse power the double sum over i and j must be asymptotically dominated by the term with $i = N_\sigma - 1$, $j = N_\sigma$ so that

$$\stackrel{r\to\infty}{\longrightarrow} |\varphi_{N_\sigma\sigma}(\mathbf{r})|^2 \left(u_{\mathrm{x}N_\sigma\sigma}(\mathbf{r}) + \frac{\varphi_{(N\sigma-1)\sigma}(\mathbf{r})}{\varphi_{N_\sigma\sigma}(\mathbf{r})} K_{N_\sigma(N_\sigma-1)\sigma}(\mathbf{r}) \right) \, .$$

The KLI equation (104) then yields

$$
\begin{aligned}
&\sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \left[V_{x\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{xi\sigma}(\mathbf{r}) - \left(\bar{V}_{xi\sigma}^{\mathrm{KLI}} - \bar{U}_{xi\sigma} \right) \right] \\
&\overset{r\to\infty}{\longrightarrow} \quad |\varphi_{N_\sigma\sigma}(\mathbf{r})|^2 \left[V_{x\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{xN_\sigma\sigma}(\mathbf{r}) - \left(\bar{V}_{xN_\sigma\sigma}^{\mathrm{KLI}} - \bar{U}_{xN_\sigma\sigma} \right) \right. \\
&\qquad + \left(\frac{\varphi_{(N\sigma-1)\sigma}(\mathbf{r})}{\varphi_{N_\sigma\sigma}(\mathbf{r})} K_{N_\sigma(N_\sigma-1)\sigma}(\mathbf{r}) + c.c. \right) \\
&\qquad \left. + \sum_{i=1}^{N_\sigma-1} \frac{|\varphi_{i\sigma}(\mathbf{r})|^2}{|\varphi_{N_\sigma\sigma}(\mathbf{r})|^2} \left(V_{x\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{xi\sigma}(\mathbf{r}) - \left(\bar{V}_{xi\sigma}^{\mathrm{KLI}} - \bar{U}_{xi\sigma} \right) \right) \right] \equiv 0 \, .
\end{aligned}
\tag{111}
$$

Since the KLI equation must be satisfied in the asymptotic region, the expression in square brackets on the right-hand side of Eq. (111) must vanish identically for $r \to \infty$. The term involving $\varphi_{(N_\sigma-1)\sigma}(\mathbf{r})/\varphi_{N_\sigma\sigma}(\mathbf{r})$ cannot be canceled by any of the terms involving $|\varphi_{i\sigma}(\mathbf{r})|^2/|\varphi_{N_\sigma\sigma}(\mathbf{r})|^2$ because the latter decay more rapidly. From this we conclude that

$$
\begin{aligned}
&V_{x\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{xN_\sigma\sigma}(\mathbf{r}) - \left(\bar{V}_{xN_\sigma\sigma}^{\mathrm{KLI}} - \bar{U}_{xN_\sigma\sigma} \right) \\
&\overset{r\to\infty}{\longrightarrow} \quad -\frac{\varphi_{(N\sigma-1)\sigma}(\mathbf{r})}{\varphi_{N_\sigma\sigma}(\mathbf{r})} K_{N_\sigma(N_\sigma-1)\sigma}(\mathbf{r}) + c.c. \\
&\overset{r\to\infty}{\longrightarrow} \quad -r^{\left(\frac{1}{\beta_{(N_\sigma-1)\sigma}} - \frac{1}{\beta_{N_\sigma\sigma}} - m\right)} \mathrm{e}^{-(\beta_{(N_\sigma-1)\sigma} - \beta_{N_\sigma\sigma})r}
\end{aligned}
\tag{112}
$$

where, in the second step, we have used Eqs. (53) and (72). $U_{xN_\sigma\sigma}(\mathbf{r})$ goes to zero asymptotically (cf. Eq. (74)) and the arbitrary additive constant in $V_{x\sigma}^{\mathrm{KLI}}(\mathbf{r})$ had been fixed in such a way that $V_{x\sigma}^{\mathrm{KLI}}(\mathbf{r})$ vanishes asymptotically (cf. Eq. (108)). Hence Eq. (112) immediately implies that

$$
\bar{V}_{xN_\sigma\sigma}^{\mathrm{KLI}} = \bar{U}_{xN_\sigma\sigma}
\tag{113}
$$

and thereby

$$
V_{x\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{xN_\sigma\sigma}(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} -r^{\left(\frac{1}{\beta_{(N_\sigma-1)\sigma}} - \frac{1}{\beta_{N_\sigma\sigma}} - m\right)} \mathrm{e}^{-(\beta_{(N_\sigma-1)\sigma} - \beta_{N_\sigma\sigma})r} \, .
\tag{114}
$$

We thus conclude that both the lemma of section 2.2.1 and the theorem 1 in section 2.2.2 are preserved in the KLI approximation. Once again, Eqs. (74) and (114) immediately imply that [6, 15, 16]

$$
V_{x\sigma}^{\mathrm{KLI}} \overset{r\to\infty}{\longrightarrow} -\frac{1}{r} \, .
\tag{115}
$$

For the correlation potential $V_{c\sigma}^{\mathrm{KLI}}(\mathbf{r})$ the considerations are even simpler. Dividing the KLI equation by $|\varphi_{N_\sigma\sigma}(\mathbf{r})|^2$ we find:

$$
0 \equiv V_{c\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{cN_\sigma\sigma}(\mathbf{r}) - C_{N_\sigma\sigma} + \sum_{i=1}^{N_\sigma-1} \frac{|\varphi_{i\sigma}(\mathbf{r})|^2}{|\varphi_{N_\sigma\sigma}(\mathbf{r})|^2} \left(V_{c\sigma}^{\mathrm{KLI}}(\mathbf{r}) - U_{ci\sigma}(\mathbf{r}) - C_{i\sigma} \right)
\tag{116}
$$

where

$$
C_{i\sigma} := \bar{V}_{ci\sigma}^{\mathrm{KLI}} - \bar{U}_{ci\sigma} \, .
\tag{117}
$$

By Eqs. (53), (109) and (110) all the r-dependent functions in (116) vanish asymptotically. Since the KLI equation (116) must be satisfied for $r \to \infty$ as well we readily conclude that

$$C_{N_\sigma \sigma} = 0 \tag{118}$$

so that

$$V_{c\sigma}^{\rm KLI}(\mathbf{r}) - U_{cN_\sigma\sigma}(\mathbf{r}) = \sum_{i=1}^{N_\sigma - 1} \frac{|\varphi_{i\sigma}(\mathbf{r})|^2}{|\varphi_{N_\sigma\sigma}(\mathbf{r})|^2} \left(C_{i\sigma} - V_{c\sigma}(\mathbf{r}) + U_{ci\sigma}^{\rm KLI}(\mathbf{r}) \right) . \tag{119}$$

If $C_{(N_\sigma - 1)\sigma} \neq 0$, the right-hand side of (119) is asymptotically dominated by the $i = (N_\sigma - 1)$ term and we obtain

$$V_{c\sigma}^{\rm KLI}(\mathbf{r}) - U_{cN_\sigma\sigma}(\mathbf{r}) \stackrel{r\to\infty}{\longrightarrow} C_{(N_\sigma-1)\sigma} r^{\left(\frac{2}{\beta_{(N_\sigma-1)\sigma}} - \frac{2}{\beta_{N_\sigma\sigma}}\right)} \mathrm{e}^{-2(\beta_{(N_\sigma-1)\sigma} - \beta_{N_\sigma\sigma})r} \tag{120}$$

If $C_{(N_\sigma-1)\sigma} = 0$, the right-hand side of (120) is an upper bound of $|V_{c\sigma}^{\rm KLI}(\mathbf{r}) - U_{cN_\sigma\sigma}(\mathbf{r})|$ for $r \to \infty$. We note that $V_{c\sigma}^{\rm KLI}(\mathbf{r})$ and $U_{cN_\sigma\sigma}(\mathbf{r})$ approach each other exponentially fast for $r \to \infty$ with the same exponential function as theorem 2 predicts for the full OEP. However, the power of r multiplying the exponential function in (120) differs by 1 from the power in theorem 2.

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References

[1] *Density Functional Theory*, Vol. 337 of *NATO ASI Series B*, edited by E.K.U. Gross and R.M. Dreizler (Plenum Press, New York, 1995).

[2] R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).

[3] R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[4] T. Grabo and E.K.U. Gross, Chem. Phys. Lett. **240**, 141 (1995).

[5] M. Petersilka, U.J. Gossmann, and E.K.U Gross, Phys. Rev. Lett. **76**, 1212 (1996).

[6] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **45**, 101 (1992).

[7] R.T. Sharp and G.K. Horton, Phys. Rev. **90**, 317 (1953).

[8] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[9] J.P. Perdew and M.R. Norman, Phys. Rev. B **26**, 5445 (1982).

[10] M. Levy and A. Görling, Phys. Rev. A **53**, 3140 (1996).

[11] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Lett. A **146**, 256 (1990).

[12] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Lett. A **148**, 470 (1990).

[13] J.B. Krieger, Y. Li, M.R. Norman, and G.J. Iafrate, Phys. Rev. B **44**, 10437 (1991).

[14] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **46**, 5453 (1992).

[15] J.B. Krieger, Y. Li, and G.J. Iafrate, Int. J. Quantum Chem. **41**, 489 (1992).

[16] Y. Li, J.B. Krieger, and G.J. Iafrate, Chem. Phys. Lett. **191**, 38 (1992).

[17] Y. Li, J.B. Krieger, and G.J. Iafrate, Phys. Rev. A **47**, 165 (1993).

[18] J.B. Krieger, Y. Li, and G.J. Iafrate, in *Density Functional Theory*, edited by R.M. Dreizler and E.K.U. Gross (Plenum Press, New York, 1995).

[19] J.B. Krieger, J. Chen, Y. Li, and G.J. Iafrate, Int. J. Quantum Chem. Symp. **29**, 79 (1995).

[20] J.B. Krieger, J. Chen, and G.J. Iafrate, Bull. Am. Phys. Soc. **41**, 748 (1996).

[21] J. Chen, J.B. Krieger, and G.J. Iafrate, Bull. Am. Phys. Soc. **41**, 748 (1996).

[22] J. Chen, J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **54**, 3939 (1996).

[23] J.B. Krieger, Y. Li, Y. Liu, and G.J. Iafrate, Int. J. Quantum Chem. **61**, 273 (1997).

[24] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[25] M.M. Pant and A.K. Rajagopal, Sol. State Commun. **10**, 1157 (1972).

[26] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).

[27] C. Filippi, C.J. Umrigar, and X. Gonze, Phys. Rev. A (1996), (submitted).

[28] C.O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).

[29] N.C. Handy, M.T. Marron, and H.J. Silverstone, Phys. Rev. **180**, 45 (1969).

[30] L. Sham, Phys. Rev. B **32**, 3876 (1985).

[31] M. K. Harbola and V. Sahni, Phys. Rev. Lett. **62**, 489 (1989).

[32] E. Engel, J.A. Chevary, L.D. Macdonald, and S.H. Vosko, Z. Phys. D **23**, 7 (1992).

[33] E. Engel and S.H. Vosko, Phys. Rev. A **47**, 2800 (1993).

[34] T. Kotani, Phys. Rev. B **50**, 14816 (1994), and Erratum (submitted).

[35] T. Kotani, Phys. Rev. Lett. **74**, 2989 (1995).

[36] T. Kotani and H. Akai, Phys. Rev. B **52**, 17153 (1995).