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Systematic approximations to the optimized effective potential: Application to orbital-density-functional theory

J. B. Krieger and Yan Li
Physics Department, Brooklyn College, City University of New York, Brooklyn, New York 11210

G. J. Iafrate
U.S. Army Research Office, Research Triangle Park, North Carolina 22709-2211

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The integral equation originally derived by Sharp and Horton for the optimized effective potential (OEP) is exactly transformed into an equivalent form from which it is manifestly clear that the OEP, $V_{x\sigma}^0(\mathbf{r})$, is an implicit functional of only $\{n_{i\sigma}\}$, the orbital densities of the occupied states $\{\psi_{i\sigma}\}$, and the corresponding single-particle exchange potentials $\{v_{i\sigma}\}$. Furthermore, the transformed OEP has exactly the same form as one recently developed by the authors [Phys. Rev. A **45**, 101 (1992)] from a more heuristic approach, the only difference being that in the present work a term proportional to the gradient of $n_{i\sigma}$ is added to each $v_{i\sigma}$ whose average value when taken over the $i\sigma$ state is zero. This result leads to the natural development of an iterative approximation for $V_{x\sigma}^0$, with the zeroth approximation being given by our previous result. The application of this technique to the calculation of the total energy and highest-energy single-particle eigenvalue for selected atoms is presented. In addition, we note that our results are applicable to the calculation of the OEP for any assumed exchange-correlation functional $E_{\mathrm{xc}}[\{\psi_{i\sigma}\}]$, where $v_{i\sigma}$ is taken as the appropriate functional derivative of E_{xc}. In the case that E_{xc} is a functional of $\{n_{i\sigma}\}$ only, as in the case of the local-density approximation with self-interaction correction, the resulting $V_{\mathrm{xc}\sigma}^0$ is a functional of the $\{n_{i\sigma}\}$ only.

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I. INTRODUCTION

Recently, we [1] have proposed an approximate solution of the optimized effective potential (OEP) equation for the exchange-only case based on the utilization of certain conditions manifestly satisfied by the exact OEP, $V_{x\sigma}^0$. The resulting approximate solution $V_{x\sigma}(\mathbf{r})$ is identical to one that is analytically obtained [2] by making a simple approximation [3] in the Green's functions in the OEP integral equation [3,4].

The approximate potential $V_{x\sigma}$ maintains many of the fundamental properties of the exact potential $V_{x\sigma}^0$: It reduces to the exact Kohn-Sham [5] result in the homogeneous-electron-gas limit, approaches $-1/r$ as $r\rightarrow\infty$ [4], yields highest-occupied-orbital-energy eigenvalues $\varepsilon_{m\sigma}$ that satisfy Koopmans's theorem [6,7], and exhibits an integer discontinuity when considered as a function of fractional occupancy of the highest-energy occupied single-particle state of a given spin projection σ [8]. In addition, it very nearly satisfies Janak's theorem [9].

Previous detailed numerical results obtained by employing $V_{x\sigma}$ as the exchange-only potential for ten atoms with closed subshells have yielded total energies, Hartree potentials, single-particle expectation values, and $\varepsilon_{m\sigma}$ which are in excellent agreement with both exact OEP and Hartree-Fock (HF) results and represent a significant improvement over the results obtained by employing other exchange-only potentials [1]. Similarly, the properties of alkali-metal atoms have been calculated, including the separate spin-up and spin-down densities, to obtain results in excellent agreement with those of spin-unrestricted OEP and HF methods [1]. More recent work [10] on all atoms with $Z\leq 54$ gives further support to the conclusion that the approximate OEP is a simple, but remarkably accurate, representation of the exact, numerically derived exchange-only OEP.

Nevertheless, the construction of the approximate OEP poses some interesting questions with respect to the fundamental form of the exact OEP as well as limitations on the numerical accuracy of the approximate OEP. The equation satisfied by $V_{x\sigma}^0$ depends on the entire set of orbitals $\{\psi_{i\sigma}^0\}$ which are the eigenfunctions of a single-particle Hamiltonian, whereas $V_{x\sigma}$ depends only on the orbital densities of the occupied states (both $V_{x\sigma}^0$ and $V_{x\sigma}$ also depend on $\{v_{i\sigma}\}$, the single-particle exchange potentials corresponding to the occupied states): It is therefore natural to consider whether the equation for $V_{x\sigma}^0$ may be inverted to yield solutions which do not require the inclusion of unoccupied states.

Furthermore, the construction of $V_{x\sigma}$ is somewhat *ad hoc*, being obtained from the exact solution of an approximate OEP integral equation. This approximate integral equation is itself obtained by taking the orbital-density-weighted average of the single-particle exchange potentials $v_{i\sigma}$ shifted by orbital-dependent constants [11], chosen so as to satisfy explicitly some properties of the exact $V_{x\sigma}^0$ [7]. This equation is identical to one obtained by assuming all the energy denominators in the Green's functions appearing in the OEP integral equation are equal to the same constant [2,3]. However, the equivalence of the two procedures does not guarantee that either paradigm is valid. Moreover, the method of constructing $V_{x\sigma}$ does not lead to the possibility of any systematic way of improving the approximation. We address these issues in Sec. II. In particular, we show in general that the OEP integral equation may be transformed into an equation involving only the occupied single-particle densities and the $\{v_{i\sigma}\}$ [4]. Using this form of the OEP equation, we derive the properties of $V_{x\sigma}^0$ previously obtained by less rigorous arguments. More significantly, we show that the OEP integral equation may be further exactly transformed into an equation of the same form as that satisfied by $V_{x\sigma}$, the only difference being the addition of a term to each $v_{i\sigma}$ which is zero when averaged over the $i\sigma$ orbital. In addition, we discuss a simple approximation for this term.

Finally, in Sec. III we apply this approximation to the calculation of the ground-state energy E, and ε_m of some selected atoms. We find that the correction term accounts for nearly all the small differences between $V_{x\sigma}^0$ and $V_{x\sigma}$ for atoms with $Z \leq 10$ yielding total energies which are within 0.0001 a.u. of the exact E for these atoms with ε_m that are generally closer to the OEP (and HF) results [1,10]. For heavier atoms, the fractional change in the energy using this approximation is less significant but always an improvement over the $V_{x\sigma}$ results yielding total energies that are less than 2 ppm above the exact OEP values with the ε_m values nearly unchanged, remaining only a few tenths of 1% from the OEP and HF results [1,10].

II. THE EQUATION FOR THE OPTIMIZED EFFECTIVE POTENTIAL AS A FUNCTIONAL OF THE OCCUPIED SINGLE-PARTICLE DENSITIES

The integral equation satisfied by the spin-unrestricted OEP, $V_{x\sigma}^0(\mathbf{r})$, in the exchange-only approximation, is [1]

$$\sum_i f_{i\sigma} \int d\tau' [V_{x\sigma}^0(\mathbf{r}') - v_{i\sigma}(\mathbf{r}')] G_{i\sigma}^0(\mathbf{r}',\mathbf{r}) \times \psi_{i\sigma}^{0*}(\mathbf{r}')\psi_{i\sigma}^0(\mathbf{r}) + \text{c.c.} = 0 , \tag{1}$$

where $f_{i\sigma}$ is the fractional occupancy of the state described by the wave function $\psi_{i\sigma}^0$. Here $\psi_{i\sigma}^0$ satisfies the single-particle Schrödinger-like equation

$$h_\sigma \psi_{i\sigma}^0(\mathbf{r}) \equiv -\tfrac{1}{2}\nabla^2\psi_{i\sigma}^0 + [V_{\text{ext}} + V_H + V_{x\sigma}^0]\psi_{i\sigma}^0 = \varepsilon_{i\sigma}^0 \psi_{i\sigma}^0 , \tag{2}$$

with $V_{\text{ext}}(\mathbf{r})$ and $V_H(\mathbf{r})$ the external potential and the Hartree potential, respectively, and

$$G_{i\sigma}^0(\mathbf{r};\mathbf{r}) \equiv \sum_j{}' \frac{\psi_{j\sigma}^0(\mathbf{r}')\psi_{j\sigma}^{0*}(\mathbf{r})}{\varepsilon_{j\sigma}^0 - \varepsilon_{i\sigma}^0} , \tag{3}$$

where the prime on the sum means the sum over j is restricted to states for which $\varepsilon_{j\sigma}^0 \neq \varepsilon_{i\sigma}^0$. The single-particle potentials $v_{i\sigma}$ appearing in Eq. (1) are given by (for $f_{i\sigma} \neq 0$)

$$v_{i\sigma}(\mathbf{r}) \equiv \frac{1}{f_{i\sigma}\psi_{i\sigma}^{0*}(\mathbf{r})} \frac{\delta E_x^{\text{HF}}[\{\psi_{i\sigma}^0\}]}{\delta\psi_{i\sigma}^0(\mathbf{r})} , \tag{4}$$

where E_x^{HF} is the usual Hartree-Fock exchange energy functional of the occupied orbitals.

For simplicity, we shall choose the $\psi_{i\sigma}^0$ as real. In that case

$$G_{i\sigma}^0(\mathbf{r}',\mathbf{r}) = G_{i\sigma}^0(\mathbf{r},\mathbf{r}') ,$$

and it then follows from Eqs. (2) and (3) that

$$(h_\sigma(\mathbf{r}) - \varepsilon_{i\sigma}^0) G_{i\sigma}^0(\mathbf{r},\mathbf{r}') = \sum_j{}' \psi_{j\sigma}^0(\mathbf{r})\psi_{j\sigma}^0(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') - \psi_{i\sigma}^0(\mathbf{r})\psi_{i\sigma}^0(\mathbf{r}') . \tag{5}$$

Then, if we define $g_{i\sigma}^0(\mathbf{r},\mathbf{r}')$ by

$$G_{i\sigma}^0(\mathbf{r},\mathbf{r}') \equiv g_{i\sigma}^0(\mathbf{r},\mathbf{r}')\psi_{i\sigma}^0(\mathbf{r})\psi_{i\sigma}^0(\mathbf{r}') , \tag{6}$$

operating on Eq. (6) with $[h_\sigma(\mathbf{r}) - \varepsilon_{i\sigma}^0]$ and employing Eq. (2) yields

$$\tfrac{1}{2}\nabla\cdot(\tilde{n}_{i\sigma}^0(\mathbf{r})\nabla g_{i\sigma}^0(\mathbf{r},\mathbf{r}')) = -[\delta(\mathbf{r}-\mathbf{r}') - \tilde{n}_{i\sigma}^0(\mathbf{r})] , \tag{7}$$

where

$$\tilde{n}_{i\sigma}^0(\mathbf{r}) \equiv (\psi_{i\sigma}^0(\mathbf{r}))^2 , \tag{8}$$

i.e., the orbital density for a fully occupied $i\sigma$, and

$$g_{i\sigma}^0(\mathbf{r},\mathbf{r}') = g_{i\sigma}^0(\mathbf{r}',\mathbf{r}) .$$

In addition, it follows from the definition of $G_{i\sigma}^0$ in Eq. (3) and the definition of $g_{i\sigma}^0$ in Eq. (6) that for all $\mathbf{r}'$,

$$\int g_{i\sigma}^0(\mathbf{r},\mathbf{r}')\tilde{n}_{i\sigma}^0(\mathbf{r})d\tau = 0 , \tag{9}$$

which can be employed to fix the value of $g_{i\sigma}^0$ which is determined only up to an additive constant by Eq. (7).

Substituting the expression for $G_{i\sigma}^0$ given by Eq. (6) into Eq. (1) yields

$$\sum_i f_{i\sigma} \int d\tau' [V_{x\sigma}^0(\mathbf{r}') - v_{i\sigma}(\mathbf{r}')] g_{i\sigma}^0(\mathbf{r},\mathbf{r}') \times \tilde{n}_{i\sigma}^0(\mathbf{r}')\tilde{n}_{i\sigma}^0(\mathbf{r}) = 0 . \tag{10}$$

Then, since $g_{i\sigma}^0$ is a functional of $\tilde{n}_{i\sigma}^0$ only, the OEP integral equation for $V_{x\sigma}^0$ involves only the (at least partially) occupied orbital densities, i.e., those for which $f_{i\sigma} \neq 0$, and the single-particle potentials $v_{i\sigma}$ corresponding to these states which are also functionals of the occupied orbitals only.

Equation (10) may be significantly simplified by defining

$$p_{i\sigma}^0(\mathbf{r}) \equiv \int d\tau' [V_{x\sigma}^0(\mathbf{r}') - v_{i\sigma}(\mathbf{r}')] g_{i\sigma}^0(\mathbf{r},\mathbf{r}')\tilde{n}_{i\sigma}^0(\mathbf{r}') , \tag{11}$$

so that it may be written as

$$\sum_i p_{i\sigma}^0(\mathbf{r}) n_{i\sigma}^0(\mathbf{r}) = 0 , \tag{12}$$

where

$$n_{i\sigma}^0(\mathbf{r}) \equiv f_{i\sigma}(\psi_{i\sigma}^0(\mathbf{r}))^2 , \tag{13}$$

i.e., the orbital density of the $i\sigma$ state. The differential equation satisfied by $p_{i\sigma}^0$ is obtained by multiplying Eq. (7) by

$$f_{i\sigma}[V^0_{x\sigma}(\mathbf{r}')-v_{i\sigma}(\mathbf{r}')]\tilde{n}^0_{i\sigma}(\mathbf{r}')$$

and integrating over $\mathbf{r}'$, which yields

$$\tfrac{1}{2}\nabla\cdot[n^0_{i\sigma}(\mathbf{r})\nabla p^0_{i\sigma}(\mathbf{r})] = -n^0_{i\sigma}(\mathbf{r})[V^0_{x\sigma}(\mathbf{r})-v_{i\sigma}(\mathbf{r})-(\bar{V}^0_{x\sigma i}-\bar{v}^0_{i\sigma})] \,, \tag{14}$$

where $\bar{V}^0_{x\sigma i}$ and $\bar{v}^0_{i\sigma}$ are the expectation values of $V^0_{x\sigma}$ and $v_{i\sigma}$ averaged over the $i\sigma$ state. Finally, it follows from Eqs. (9) and (11) that

$$\int p^0_{i\sigma}(\mathbf{r})n^0_{i\sigma}(\mathbf{r})d\tau=0 \,, \tag{15}$$

which can be employed to determine the arbitrary additive constant left undetermined by Eq. (14).

Equations (14) and (15) completely determine $p^0_{i\sigma}(\mathbf{r})$ once the terms on the right-hand side (rhs) of Eq. (14) are assumed known and it is assumed that $n^0_{i\sigma}(\mathbf{r})$ decays exponentially to zero as $r\to\infty$. This follows from the fact that $v_{i\sigma}(\mathbf{r})\to 0$ for $r\to\infty$ and since $V^0_{x\sigma}$ is determined only up to a constant by Eq. (1), we can take $V^0_{x\sigma}\to 0$ as $r\to\infty$. Then it follows from Eq. (14) that $\nabla p^0_{i\sigma}(\mathbf{r})$ converges as $r\to\infty$. Now suppose there are two solutions of Eq. (14) corresponding to the same rhs. Then the equation satisfied by the difference between these two solutions, $q^0_{i\sigma}$, is

$$\nabla\cdot[n^0_{i\sigma}(\mathbf{r})\nabla q^0_{i\sigma}(\mathbf{r})]=0 \,. \tag{16}$$

Multiplying Eq. (16) by $q^0_{i\sigma}$, integrating over a large sphere of radius R, and taking the limit as $R\to\infty$ yields

$$\int |\nabla q^0_{i\sigma}|^2 n^0_{i\sigma}(\mathbf{r})d\tau=0 \,, \tag{17}$$

where the contributions from the surface integral vanish because $n^0_{i\sigma}\to 0$ exponentially rapidly. It follows from Eq. (17) that the two solutions of Eq. (14) differ by a constant. Equation (15) then determines the value of this additive constant.

The OEP equation given by Eq. (12) enables us to easily obtain the asymptotic behavior of $V^0_{x\sigma}(\mathbf{r})$. Dividing Eq. (12) by $n^0_{m\sigma}(\mathbf{r})$, the orbital density of the highest (partially) occupied state, we have

$$p^0_{m\sigma}(\mathbf{r})+\sum_{i=1}^{m=1}(n^0_{i\sigma}/n^0_{m\sigma})p^0_{i\sigma}=0 \,. \tag{18}$$

For sufficiently large r, $n^0_{i\sigma}/n^0_{m\sigma}\to 0$ exponentially fast, and since $\nabla p^0_{i\sigma}$ converges in this limit, it follows that each term in the sum in Eq. (18) approaches zero exponentially fast as $r\to\infty$. (Here for simplicity we are assuming $\psi^0_{i\sigma}$ is nondegenerate for a given $i\sigma$ [1].)

Then, operating on Eq. (18) with

$$[-2n^0_{m\sigma}(\mathbf{r})]^{-1}\nabla\cdot[n^0_{m\sigma}(\mathbf{r})\nabla]$$

and employing Eq. (14) yields

$$[V^0_{x\sigma}(\mathbf{r})-v_{m\sigma}(\mathbf{r})-(\bar{V}^0_{x\sigma m}-\bar{v}^0_{m\sigma})]\to 0$$

exponentially fast as $r\to\infty$. Thus,

$$V^0_{x\sigma}(\mathbf{r})\to v_{m\sigma}(\mathbf{r})+(\bar{V}^0_{x\sigma m}-\bar{v}^0_{m\sigma}),\quad r\to\infty \tag{19}$$

so that if we require that $V^0_{x\sigma}(\mathbf{r})\to 0$ as $r\to\infty$, since

$$v_{m\sigma}(\mathbf{r})\to -f_{m\sigma}/r \quad \text{as } r\to\infty \,,$$

then

$$V^0_{x\sigma}(\mathbf{r})\to -f_{m\sigma}/r \tag{20}$$

and

$$\bar{V}^0_{x\sigma m}=\bar{v}^0_{m\sigma} \,. \tag{21}$$

Similarly, if there is some region Ω_j in space in which the $j\sigma$ orbital dominates the density, i.e., $n^0_{i\sigma}(\mathbf{r})/n^0_{j\sigma}(\mathbf{r})\ll 1$ for $i\neq j$, then dividing Eq. (12) by $n^0_{j\sigma}$ and performing the same operations as described above with i replacing m, we obtain, after dropping terms of $0(n^0_{i\sigma}/n^0_{j\sigma})$, the analogous result to Eq. (19), i.e., in Ω_j,

$$V^0_{x\sigma}(\mathbf{r})\to v_{j\sigma}(\mathbf{r})+(\bar{V}^0_{x\sigma j}-\bar{v}^0_{j\sigma}) \,. \tag{22}$$

Equations (19)–(22) are identical to results previously obtained by less rigorous arguments [1].

We may further transform Eq. (12) to explicitly display $V^0_{x\sigma}$ by operating on it with ∇^2. Then,

$$\sum_i \nabla\cdot[n^0_{i\sigma}(\mathbf{r})\nabla p^0_{i\sigma}(\mathbf{r})]+\nabla\cdot[p^0_{i\sigma}(\mathbf{r})\nabla n^0_{i\sigma}(\mathbf{r})]=0 \,. \tag{23}$$

Employing Eq. (14) to evaluate the first term in Eq. (23), we obtain, after some rearrangement, the exact relation

$$V^0_{x\sigma}(\mathbf{r})=\frac{\sum_i n^0_{i\sigma}[v_{i\sigma}+(\bar{V}^0_{x\sigma i}-\bar{v}^0_{i\sigma})]}{\sum_i n^0_{i\sigma}} + \frac{1}{2}\frac{\sum_i \nabla\cdot(p^0_{i\sigma}\nabla n^0_{i\sigma})}{\sum_i n^0_{i\sigma}} \,. \tag{24}$$

Equation (24) is still an integral equation but, unlike Eq. (1), leads naturally to a method of successive approximations, i.e., to lowest order, we can take all $p^0_{i\sigma}=0$ [which satisfies Eqs. (12) and (15)] and obtain

$$V_{x\sigma}(\mathbf{r})=\frac{\sum_i n_{i\sigma}[v_{i\sigma}+(\bar{V}_{x\sigma i}-\bar{v}_{i\sigma})]}{\sum_i n_{i\sigma}} \,, \tag{25}$$

where we drop the superscript 0 because the self-consistent solutions for the $\{\psi_{i\sigma}\}$ obtained by using this approximation to the OEP will not yield the exact optimized $\{\psi^0_{i\sigma}\}$.

Equation (25) is precisely the same potential employed in Ref. [1] to approximate $V^0_{x\sigma}$ by constructing the simplest possible expression that would reduce to Eqs. (19) and (22) in the appropriate limits, but here derived as the leading term in an expansion of $V^0_{x\sigma}$. Moreover, we can write Eq. (24) in the same form as that given by Eq. (25), i.e.,

$$V^0_{x\sigma}(\mathbf{r})=\frac{\sum_i n^0_{i\sigma}[v'_{i\sigma}+(\bar{V}^0_{x\sigma i}-\bar{v}'^0_{i\sigma})]}{\sum_i n^0_{i\sigma}} \,, \tag{26}$$

where

$$v'_{i\sigma} \equiv v_{i\sigma} + \frac{1}{2n^0_{i\sigma}} \nabla \cdot (p^0_{i\sigma} \nabla n^0_{i\sigma}) \tag{27}$$

and

$$\bar{v}'^0_{i\sigma} = \bar{v}^0_{i\sigma} \ , \tag{28}$$

because the correction to $v_{i\sigma}$ given in Eq. (27) has zero average value over the $i\sigma$ state, i.e., when this term is multiplied by $(\psi^0_{i\sigma})^2$, the integral can be evaluated by the divergence theorem and the integrand in the resulting surface integral approaches zero exponentially fast in the large-r limit so the contribution from the surface integral at infinity vanishes.

It is therefore now apparent why Eq. (25) yields $V_{x\sigma}$ which is close to the exact $V^0_{x\sigma}$, i.e., the difference between the approximate equation (25) and the exact equation (26) is completely accounted for by the differences in $v_{i\sigma}$ and $v'_{i\sigma}$ which corresponds to terms whose value averaged over the $i\sigma$ orbital is zero. Furthermore, if we make the approximation in Eq. (14) that Eq. (22) is valid everywhere, then the solution $p_{i\sigma}=0$ for all $i\sigma$ uniquely satisfies both Eqs. (14) and (15) so that Eq. (26) reduces to Eq. (25), in this approximation. It is interesting to note that if the same approximation is employed in Eq. (25), we have shown that the Harbola-Sahni [12] potential may be derived as an approximation to $V_{x\sigma}$ [1]. We also note that in the homogeneous-electron-gas limit, $V^0_{x\sigma}$ and $v_{i\sigma}$ are constants so the rhs of Eq. (14) is zero which yields $p^0_{i\sigma}=0$. Thus, Eq. (25) can be considered an approximation to Eq. (26) in the slowly varying density limit.

In addition, it follows from Eq. (18) that $p^0_{m\sigma} \rightarrow 0$ as $r \rightarrow \infty$ exponentially fast and consequently so does $\nabla p^0_{m\sigma}$. Thus, from Eqs. (26)–(28) we find that in the large-r limit, where $n_{i\sigma}/n_{m\sigma} \rightarrow 0$, $i \neq m$,

$$V^0_{x\sigma}(\mathbf{r}) \rightarrow v'_{m\sigma} + (\bar{V}^0_{x\sigma m} - \bar{v}'^0_{m\sigma}) = v_{m\sigma}(\mathbf{r}) + (\bar{V}^0_{x\sigma m} - \bar{v}^0_{m\sigma}) \ ,$$

in agreement with Eq. (19), and consequently Eq. (26) yields Eqs. (20) and (21), as it must since it is derived from Eq. (12) without approximation. Moreover, it is clear that the addition to $v_{i\sigma}$ in Eq. (27) may be significant in the region near the nodes of $n^0_{i\sigma}$ since in this region $n^0_{i\sigma} \sim (r-r_0)^2$, which leads to a term $\sim p^0_{i\sigma}(r-r_0)^{-2}$, whereas it follows from Eq. (4) that near a node of $\psi^0_{i\sigma}$, $v_{i\sigma} \sim (r-r_0)^{-1}$. The fact that these terms are weighted by $n^0_{i\sigma}$ in Eq. (26) leads to a finite, nonzero contribution to the sum at the nodes of $n^0_{i\sigma}$ and results in pronounced bumps in the exact $V^0_{x\sigma}$ in the intershell region in atoms, whereas the approximate $V_{x\sigma}$, which lacks this additional term given by Eq. (25), leads to either a significantly smaller bump or a plateau in this region.

Equation (26) could in principle be employed to obtain the exact numerical solution for $V^0_{x\sigma}$ by first calculating the self-consistent solution of Eq. (25) and then iterating Eq. (26) with $p^0_{i\sigma}$ obtained by solving Eq. (14) in terms of these calculated quantities. This method is practical only at most for one-dimensional problems, in which case Eq. (14) may be reduced to an ordinary differential equation. However, in such a case the highly accurate numerical solution of Eq. (1) may be easily found by more direct methods. The principal use of Eq. (26) is in generating a better approximation to $V^0_{x\sigma}$ than that given by Eq. (25) by approximating $p^0_{i\sigma}$ by a functional of the orbitals. We may then solve for the approximate $\bar{V}^0_{x\sigma i} - \bar{v}'^0_{i\sigma}$ in Eq. (26) in exactly the same way as in Ref. [1].

If we treat Eq. (25) as the lowest approximation to Eq. (26), i.e., Eq. (25) can be obtained from Eq. (26) by taking $p^0_{i\sigma}=0$ for all i, then the next approximation is to take $p^0_{i\sigma}$ as that functional which would yield Eq. (25) if substituted into the OEP equation given by Eq. (12), i.e.,

$$p_{i\sigma}(\mathbf{r}) = b_\sigma [V_{x\sigma}(\mathbf{r}) - v_{i\sigma}(\mathbf{r}) - (\bar{V}_{x\sigma i} - \bar{v}_{i\sigma})] \ , \tag{29}$$

where b_σ is a constant independent of i. Equation (29) is exactly the same result as obtained from Eq. (1) if all the energy denominators in the expression for $G^0_{i\sigma}$ given by Eq. (3) are set equal to a constant independent of i [2], i.e., b_σ^{-1}. For consistency, the $V_{x\sigma}$ in Eq. (29) is given by the functional expressed by Eq. (25) and is therefore in principle known as a functional of the orbital densities $\{n_{i\sigma}\}$ and the $\{v_{i\sigma}\}$ since Eq. (25) may be solved exactly for $V_{x\sigma}$ in terms of these quantities. The constant b_σ may be determined by multiplying both sides of Eq. (14) by $p^0_{i\sigma}$, integrating over all space, and summing over the occupied orbitals to obtain the exact result

$$\begin{aligned} \tfrac{1}{2} \sum_i \int |\nabla p^0_{i\sigma}|^2 n^0_{i\sigma}(\mathbf{r}) d\tau &= \sum_i \int n^0_{i\sigma}(\mathbf{r}) p^0_{i\sigma}(\mathbf{r}) [V^0_{x\sigma}(\mathbf{r}) - v_{i\sigma}(\mathbf{r}) \\ &\quad - (\bar{V}^0_{x\sigma i} - \bar{v}^0_{i\sigma})] d\tau \ . \end{aligned} \tag{30}$$

Then, substituting $p_{i\sigma}$ given by Eq. (29) into this expression (and approximating $V^0_{x\sigma}$, etc., by the solution of Eq. (25), i.e., by the $V_{x\sigma}$ corresponding to the approximation $p^0_{i\sigma}=0$), we obtain

$$b_\sigma = \frac{2 \sum_i \int n_{i\sigma}(\mathbf{r}) [V_{x\sigma}(\mathbf{r}) - v_{i\sigma}(\mathbf{r}) - (\bar{V}_{x\sigma i} - \bar{v}_{i\sigma})]^2 d\tau}{\sum_i \int n_{i\sigma}(\mathbf{r}) |\nabla [V_{x\sigma}(\mathbf{r}) - v_{i\sigma}(\mathbf{r})]|^2 d\tau} \ . \tag{31}$$

Approximating $p^0_{i\sigma}$ by $p_{i\sigma}$ given by Eq. (29) with b_σ given by Eq. (31), we can solve Eq. (26) for $\bar{V}^0_{x\sigma i} - \bar{v}'^0_{i\sigma}$ as an explicit functional of the $\{n_{i\sigma}\}$ and $\{v_{i\sigma}\}$, i.e. [1],

$$\bar{V}^0_{x\sigma i} - \bar{v}'^0_{i\sigma} = \sum_{j=1}^{m-1} (A_\sigma^{-1})_{ij} (\bar{V}^s_{x\sigma j} - \bar{v}'_{j\sigma}) \ , \qquad i=1,\ldots,m=1 \tag{32}$$

where

$$(A_\sigma)_{ji} = \delta_{ji} - f_{j\sigma}^{-1} M^{(\sigma)}_{ji} \ , \tag{33}$$

$$M^{(\sigma)}_{ji} \equiv \int \frac{n_{j\sigma}(\mathbf{r}) n_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})} d\tau, \quad i,j=1,\ldots,m-1 \tag{34}$$

and $V^s_{x\sigma}$ is the Slater potential [13] given by

$$V^{s}_{x\sigma} \equiv \frac{\sum_i n_{i\sigma} v_{i\sigma}}{\sum_i n_{i\sigma}} \; . \tag{35}$$

Here $\{n_{i\sigma}\}$ are the self-consistently determined single-particle densities in this approximation and $V_{x\sigma}$ appearing in Eq. (31) is obtained from Eq. (25) with $\bar{V}_{x\sigma i} - \bar{v}_{i\sigma}$ given by Eq. (32) with $\{v'_{j\sigma}\}$ replaced by $\{v_{j\sigma}\}$.

III. NUMERICAL RESULTS

We have performed self-consistent calculations for $V^{(1)}_{x\sigma}$, the potential obtained from Eq. (26) by approximating $p^0_{i\sigma}$ by Eq. (29) with b_σ given by Eq. (31) for selected atoms. We find that the inclusion of this correction term results in $V^{(1)}_{x\sigma}$ being significantly closer to the exact numerical solution of the OEP equation in the region near the bump in the OEP potential between maxima in the electron density corresponding to the $n=1$ and $n=2$ states. Figure 1 displays the results for neon. We see that the result previously obtained [1], i.e., using Eq. (25), yields $V_{x\sigma}$, which closely approximates $V^0_{x\sigma}$, the exact OEP, everywhere except near the potential bump. However, $V^{(1)}_{x\sigma}$ is clearly a much better approximation with a potential bump of almost exactly the correct size slightly shifted to lower r. Figure 2, which displays the difference between the various approximate potentials and the exact OEP, clearly shows the significant improvement of $V^{(1)}_{x\sigma}$ over $V_{x\sigma}$ for $r < 1$ a.u. and also exhibits the result that the LSD approximation significantly underestimates the strength of the exchange potential by ≈ 0.5 a.u. in the region in which the p-state density peaks, which explains why the LSD single-particle energy eigenvalue ε_{2p} is significantly too small in magnitude. For heavier atoms we find similar results obtain, i.e., $V^{(1)}_{x\sigma}$ makes a significant improvement over $V_{x\sigma}$ in the region from $r=0$ through the first bump in the OEP potential corresponding to the intershell region between the $n=1$ and $n=2$ states. For larger r, $V^{(1)}_{x\sigma}$ is very close to $V_{x\sigma}$, both potentials closely approximating $V^0_{x\sigma}$.

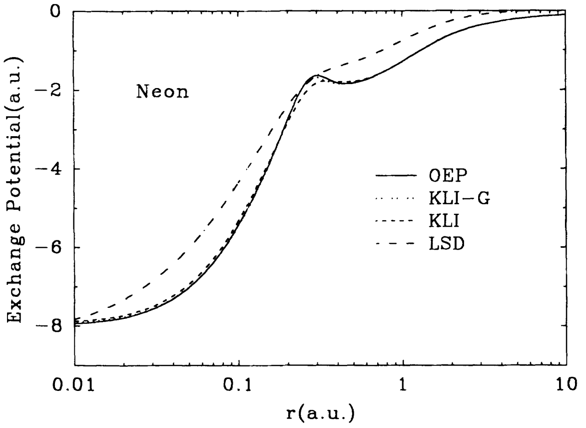

FIG. 1. Exchange potential (in a.u.) vs distance from nucleus (in a.u.) for a neon atom. Included are the results for the optimized effective potential (OEP), the potential given by the solution of Eq. (25) (KLI), the potential given by the solution of Eq. (26) with the approximation for the gradient term given by Eq. (29) (KLI-G), and the exchange potential in the local-spin-density approximation (LSD).

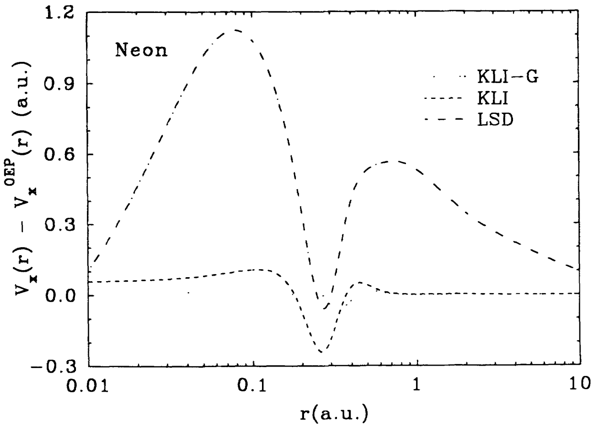

FIG. 2. The difference in the approximate exchange potential, $V_{x\sigma}(r)$, and the optimized effective potential $V^0_{x\sigma}(r)$ (in a.u.) for neon, vs r, the distance from the nucleus (in a.u.). The approximate potentials are the same as those given in Fig. 1.

As a consequence of this behavior, the total energy for atoms with $Z \le 10$, calculated by employing a Slater determinant whose elements are states that satisfy Eq. (2) with $V^{(1)}_{x\sigma}$ replacing $V_{x\sigma}$, is very close to E^0, the result obtained by employing the exact $V^0_{x\sigma}$. More specifically, Table I shows that the result of employing $V^{(1)}_{x\sigma}$ yields an overestimate of the exact E^0 which is ≤ 0.0001 a.u. for atoms with $Z \le 10$, corresponding to a small fraction of the overestimate of E^{HF} provided by E^0. For heavier atoms, the improvement becomes a smaller fraction of the overestimate of E^0, being approximately 50% for Ar and decreasing to 20% for Xe. From Ca to Xe the de-

TABLE I. Comparison of overestimates of the OEP total energy E^0, calculated in various approximations, compared with the overestimate of the spin-unrestricted Hartree-Fock total energy by E^0 (in ma.u.) for selected atoms. Here, E corresponds to the result obtained by employing $V_{x\sigma}$ given by Eq. (25), and $E^{(1)}$ corresponds to the results obtained by employing $V^{(1)}_{x\sigma}$. The latter is obtained from Eq. (26) with $p_{i\sigma}$ given by Eq. (29).

Atom	$-E^{\mathrm{SUHF}}$ (a.u.)	$E^0 - E^{\mathrm{HF}}$	$E - E^0$	$E^{(1)} - E^0$
Li	7.432 75	0.25	0.07	0.03
Be	14.573 02	0.59	0.15	0.08
B	24.529 31	0.97	0.23	0.10
C	37.690 00	1.09	0.26	0.07
N	54.404 55	1.15	0.36	0.07
O	74.813 63	1.55	0.41	0.09
F	99.410 84	1.62	0.47	0.04
Ne	128.5471	1.7	0.6	0.04
Na	161.8590	2.3	0.7	0.14
Mg	199.6146	3.0	0.9	0.25
Ar	526.8175	5.3	1.7	0.85
Ca	676.7582	6.3	2.2	1.2
Xe	7232.1384	17.3	6.0	4.8

crease in the overestimate of E^0 remains nearly constant, varying from 0.0010 to 0.0012 a.u. For all atoms we find that our overestimate of the exact E^0 is less than the larger of 0.0001 a.u. or 2 ppm. Similarly, as can be seen from Table II, the highest-occupied single-particle eigenvalues ε_m are generally closer to the ε_m^0 (and to $\varepsilon_m^{\mathrm{HF}}$) when $V_{x\sigma}^{(1)}$ is employed, as compared with the results obtained using $V_{x\sigma}$. As in the case of the total energy, the most significant changes occur for $Z \leq 10$, with the changes in ε_m for heavier atoms being a small fraction of the difference between these eigenvalues and ε_m^0 (or $\varepsilon_m^{\mathrm{HF}}$).

Finally, we note that although this analysis was originally motivated by studying the exchange-only case, all the analytic results are directly applicable to finding the optimized effective potential $V_{\mathrm{xc}\sigma}^0$ corresponding to any exchange-correlation energy functional $E_{\mathrm{xc}}[\{\psi_{i\sigma}\}]$ [14,15]. This follows from the fact that for any E_{xc}, Eq. (1) is the correct equation for the optimized effective potential if $V_{x\sigma}^0$ is replaced by $V_{\mathrm{xc}\sigma}^0$ and $v_{i\sigma}$ is defined by the generalization of Eq. (4), i.e.,

$$v_{i\sigma} \equiv \frac{1}{f_{i\sigma}\psi_{i\sigma}^{0*}(\mathbf{r})} \frac{\delta F_{\mathrm{xc}}[\{\psi_{i\sigma}^0\}]}{\delta\psi_{i\sigma}^0(\mathbf{r})} \; .$$

Thus, the entire analysis may be repeated provided only that $v_{m\sigma} \rightarrow 0$ as $r \rightarrow \infty$. If, in addition, $v_{m\sigma} \rightarrow -f_{m\sigma}/r$ as $r \rightarrow \infty$, then all the results obtained for the exchange-only case also obtain for $E_{\mathrm{xc}}[\{\psi_{i\sigma}\}]$. This result is of considerable practical importance because it is much simpler to obtain accurate exchange-correlation functionals which depend on $\{\psi_{i\sigma}^0\}$ rather than simply on n_σ, as required in a spin-density-functional theory. Moreover, if E_{xc} is approximated by a functional only of the $\{n_{i\sigma}^0\}$, as is the case in the local (or gradient expansion) spin-density approximation with self-interaction correction, then it follows from Eq. (26) that $V_{\mathrm{xc}\sigma}^0$ can also be written as a functional of $\{n_{i\sigma}^0\}$ with Eq. (25) providing a highly accurate approximation to the exact result.

TABLE II. Values of $\varepsilon_{m\sigma}$ (in Ry), the single-particle eigenvalue corresponding to the highest-energy occupied state calculated by employing various exchange-only approximations as described in Table I for selected atoms.

Atom	SUHF	OEP	$V_{x\sigma}$	$V_{x\sigma}^{(1)}$
Li	0.3927	0.3926	0.3924	0.3925
Be	0.6185	0.6185	0.6177	0.6181
B	0.6219	0.6194	0.6191	0.6185
C	0.8711	0.8705	0.8698	0.8698
N	1.1418	1.1423	1.1409	1.1416
O	1.0187	1.0153	1.0138	1.0129
F	1.3475	1.3469	1.3449	1.3455
Ne	1.7008	1.7014	1.6988	1.7001
Na	0.3644	0.3642	0.3640	0.3641
Mg	0.5061	0.5061	0.5048	0.5049
Ar	1.1820	1.1815	1.1786	1.1788
Ca	0.3911	0.3913	0.3901	0.3902
Xe	0.9146	0.9128	0.9109	0.9109

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