Construction and application of an accurate local spin-polarized Kohn-Sham potential with integer discontinuity: Exchange-only theory

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An accurate spin-polarized exchange-only Kohn-Sham (KS) potential is constructed from a consideration of the optimized-effective-potential (OEP) method. A detailed analysis of the OEP integral equation for the exchange-only case results in a set of conditions which are manifestly satisfied by the exact OEP; these conditions are employed to construct an approximate OEP, $V_{x\sigma}$, and therefore an approximate KS exchange-only potential as a functional of KS orbitals. Further, it is shown that this $V_{x\sigma}$ can be derived analytically based on a simple approximation of the Green's functions in the OEP integral equation. The constructed potential, although approximate, contains many of the key analytic features of the exact KS potential: it reduces to the exact KS result in the homogeneous-electron-gas limit, approaches $-1/r$ as $r \to \infty$, yields highest occupied-orbital energy eigenvalues $\varepsilon_{m\sigma}$ that satisfy Koopmans's theorem, 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. In addition $\varepsilon_{m\sigma}$ nearly exactly satisfies Janak's theorem. The approximate OEP is a simple but remarkably accurate representation of the exact, numerically derived exchange-only OEP. Detailed numerical results obtained by employing $V_{x\sigma}$ as the exchange-only potential for ten atoms with closed subshells yield total energies, Hartree potentials, single-particle expectation values, and ε_m 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. Similarly, the properties of alkali-metal atoms are 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. Finally, we demonstrate the accuracy of $V_{x\sigma}$ by calculating the total energy, $\varepsilon_{m\uparrow}$, and $\varepsilon_{m\downarrow}$ as a function of fractional filling f, of the highest occupied single-particle orbital for the magnesium atom ($Z=12$) from $N=9-12$ electrons and find excellent agreement with both spin-unrestricted OEP and HF results even when $\varepsilon_{m\sigma}$ is strongly dependent on f. In addition we display the integer discontinuity in $V_{x\sigma}$ when the highest-energy spin subshell begins to be filled.

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I. INTRODUCTION

The major problem in the implementation of the Hohenberg-Kohn [1], Kohn-Sham [2] (KS) density-functional theory for the calculation of the ground-state properties of interacting electrons subject to external potentials is in obtaining an accurate approximation to the exchange-correlation potential $V_{xc}([n],\mathbf{r})$, which is the functional derivative of the exchange-correlation energy functional $E_{xc}[n]$ with respect to the electron density $n(\mathbf{r})$. Unfortunately, although it has been shown that E_{xc} may be written as a functional of n only [1], no functional of n alone [or of the spin densities $n_\sigma(\mathbf{r})$ in a spin density theory [2,3]] has yet been proposed which results in accurate calculations of the total energy E, the maximum occupied orbital energy eigenvalue ε_m, which has been shown to equal the negative of the ionization energy of the system [4], and $n(\mathbf{r})$. Moreover, the likelihood of ever finding a $V_{xc}([n],\mathbf{r})$ that respects the principle of integer preference [4–6] has been considered doubtful. Such a V_{xc}, for a closed-subshell system, would be a

discontinuous function of N, the total number of electrons in the system. In such a system, the value of $V_{xc}(\mathbf{r})$ must essentially jump by a constant for finite $\mathbf{r}$ as the number of electrons is allowed to vary from $N-\delta$ to $N+\delta$ where δ is a positive infinitesimal [4–7]. Such a discontinuity is important not only to ensure that atoms that are far apart contain an integral number of electrons, but also makes a significant contribution to the calculation of energy band gaps in semiconductors and insulators [8,9].

Reasonably accurate results for E, ε_m, and $n(\mathbf{r})$ have been obtained by Perdew and Zunger [10], who employ an orbital-density-dependent self-interaction correction to the usual local-spin-density approximation (LSDSIC) for E_{xc}. This method lies outside the usual KS theory in that instead of each orbital with spin projection σ being acted on by the same exchange-correlation potential, $V_{xc\sigma}$, each orbital $\phi_{i\sigma}$ is acted on by an orbital-dependent potential, $v_{xc\sigma}^{(i)}$. The Perdew-Zunger method, however, effectively yields a discontinuity in the orbital potential for the highest occupied state when N is increased through integral occupancy and thus enables it to respect

the principle of integer preference [5,6]. Recently, Krieger and Li [11], extending an earlier physically motivated conjecture of Harbola and Sahni [12], have shown how any $\{v_{xc\sigma}^{(i)}\}$, including possibly SIC and gradient-expansion corrections, may be combined to calculate a single $V_{xc\sigma}$ for each σ which yields nearly the same results for E, $n_\sigma(\mathbf{r})$, and generally for the $\varepsilon_{m\sigma}$ as do the $\{v_{xc\sigma}^{(i)}\}$ for integral N [13]. However, the resultant $V_{xc\sigma}$ varies continuously as the number of electrons is varied continuously about integer occupancy.

In the present work we discuss the derivation and application of an accurate local spin-polarized Kohn-Sham potential for the exchange-only case by constructing an approximate solution of the integral equation for the optimized effective potential [14,15] V_σ^o. Here V_σ^o corresponds to the set of spin-polarized potentials whose eigenfunctions, when employed as elements in a Slater determinant, minimize the expectation value of the Hamiltonian of the system.

Section II is devoted to a discussion of some properties of the exact solution of $V_{x\sigma}^o$, which is the exchange potential obtained by subtracting the external potential and the Hartree potential from V_σ^o [14]. In particular we show that the expectation value of $V_{x\sigma}^o$ in the state $\psi_{m\sigma}^o$ corresponding to the occupied orbital having spin projection σ with maximum single-particle-energy eigenvalue $\varepsilon_{m\sigma}^o$ is identically equal to the expectation value of the Hartree-Fock (HF) orbital potential corresponding to this state. From this it follows that $\varepsilon_{m\sigma}^o$ is exactly equal to the expectation value of $h_{m\sigma}^{\mathrm{HF}}$, the single-particle HF Hamiltonian corresponding to the $m\sigma$ orbital, and thus Koopmans's theorem [16] is satisfied. In the uniform-electron-gas limit, we find that $V_{x\sigma}^o$ reduces to the usual local-spin-density result [2,3]. In addition, we show that $\varepsilon_{m\sigma}^o$ equals the rate of change of the total energy E^o, with respect to the fractional occupancy $f_{m\sigma}$ of the $m\sigma$ state, i.e., Janak's theorem [17] is valid for $E_x = E_x^{\mathrm{HF}}[\{\psi_{i\sigma}^o\}]$, but only for the highest occupied single-particle state of a given spin projection σ. Furthermore, we show that the exact $V_{x\sigma}^o$ must behave discontinuously when the number of electrons is increased to fill a complete spin subshell and a simple expression is derived for the size of this discontinuity. Finally, we derive the behavior of $V_{x\sigma}^o$ in any region in which one orbital dominates the density.

Using simple physical arguments together with the known behavior of $V_{x\sigma}^o$ in any region in which one orbital dominates the density, we derive in Sec. III a simplified integral equation for the approximate optimized effective potential (OEP) $V_{x\sigma}$. This equation is found to be identical to that obtained by making a simple approximation [14] to the single-particle Green's function in the exact OEP integral equation. The resulting $V_{x\sigma}$ is shown to preserve exactly all the properties satisfied by the exact $V_{x\sigma}^o$ discussed in Sec. II with the exception of the exact extension of Janak's theorem, which is now only approximately satisfied. In addition, the relation of $V_{x\sigma}$ to the Harbola-Sahni [12] exchange-only potential W_x is discussed. Finally, the exact solution of the integral equation for $V_{x\sigma}$ is derived and expressed as a functional of the occupied orbitals having spin projection σ.

Section IV is devoted to a detailed study of the accuracy of $V_{x\sigma}$, the approximate exchange-only potential, compared with numerical solutions of the HF equations and the exact OEP equation for atoms with closed subshells [18,19] as well as with results obtained employing the exact Slater exchange potential [20], the LSD exchange potential, and W_x [21]. We find that for the total energy our results are only 9 ppm above the OEP result [18] for Be, the overestimate decreasing to < 1 ppm for Xe, and are only $\approx \frac{1}{4}$ to $\frac{1}{3}$ a greater overestimate of the exact HF result [22] than that given by the OEP calculations. In addition, the calculated ε_m (for systems with closed subshells $\varepsilon_{i\uparrow} = \varepsilon_{i\downarrow}$) are very close to what is believed to be the essentially exact OEP [23] lying higher with an average difference of ≈ 0.002 Ry and a maximum difference of 0.003 Ry. The eigenvalues satisfy Janak's theorem to within 0.002 Ry on the average. The $V_{x\sigma}$ is shown to be a much better approximation to $V_{x\sigma}^o$ than is $V_{x\sigma}^{\mathrm{LSD}}$ or the exact Slater potential and the resulting Hartree potential, which is a measure of the accuracy of the calculated density, is nearly identical to that given by a numerical HF calculation. The electron density at the atomic nucleus is found to be within $\approx 0.3\%$ of the exact result and the expectation value of r^2, which is proportional to the diamagnetic susceptibility, is closer to the result of an exact calculation than similar calculations using other approximate exchange potentials. Furthermore, we find that the overlap integrals between the corresponding orbitals derived from the self-consistently calculated $V_{x\sigma}$ and those calculated using $V_{x\sigma}^o$ or calculated by solving the HF equations are ≥ 0.999 for all states in the ten atoms with closed subshells from Be to Xe.

In Sec. V, calculations using spin-polarized exchange potentials have been performed for alkali-metal atoms and compared with the results of spin-unrestricted Hartree-Fock (SUHF) [24] calculations as well as spin-polarized OEP results. We again find excellent agreement with the SUHF and OEP calculations for total energy, $\varepsilon_{m\uparrow}$ and $\varepsilon_{m\downarrow}$, the electron density and the spin density for each atom. The behavior of the $V_{x\sigma}$ for fractional occupancy of the highest occupied orbital is also discussed in Sec. V. We show analytically that $V_{x\sigma}$ changes discontinuously as a spin subshell is filled and also show that $V_{x\sigma} \to -f/r$ as $r \to \infty$ where f is the fractional occupancy of this state. A detailed numerical analysis is presented for Mg ($Z = 12$) as the number of electrons is increased from $N = 9$ to 12. We show that calculations employing $V_{x\sigma}$ closely approximate those given by the spin-polarized extension of the OEP method as well as by the SUHF method. In particular, we find that our results for the total energy are only a few ppm from the OEP calculations and closely approximate the SUHF results with a cusp in the E versus N curve at integer occupancy. In addition, the $V_{x\sigma}$ yield $\varepsilon_{m\sigma}$ for both σ as a function of N, which are discontinuous at integral occupancy and are nearly identical to those obtained from the OEP and SUHF calculations even when these eigenvalues are strongly N dependent. Furthermore, we show numerically the behavior of the discontinuity in $V_{x\sigma}$ as a function of f. In particular, we show that the discontinuity in the

exchange potential is a constant for $r < R$ where R becomes large compared with the size of the atom when $f \ll 1$. Finally, in Sec. VI we discuss the implications of our results concerning applications to other many-electron problems.

II. SPIN-POLARIZED OPTIMIZED EFFECTIVE EXCHANGE POTENTIAL: DERIVATION OF EQUATION AND PROPERTIES

In the usual spin-density-functional theory, the exchange-energy functional $E_x[\{n_\sigma\}]$ is assumed known. It then follows from minimizing the total energy E, with respect to arbitrary variations in the n_σ that preserve the total number of electrons in the system, that the KS orbitals satisfy the Schrödinger-like one-electron equations (in a.u.)

$$-\tfrac{1}{2}\nabla^2 \psi_{i\sigma}^{KS} + [V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{x\sigma}^{KS}(\mathbf{r})]\psi_{i\sigma}^{KS}$$
$$= \varepsilon_{i\sigma}^{KS}\psi_{i\sigma}^{KS} . \quad (1)$$

Here $V_{ext}(\mathbf{r})$ is the external potential, $V_H(\mathbf{r})$ is the usual Hartree potential of the electrons, and the exchange potential is given by

$$V_{x\sigma}^{KS}(\mathbf{r}) = \frac{\delta E_x[\{n_\sigma\}]}{\delta n_\sigma(\mathbf{r})} . \quad (2)$$

In practice, since $E_x[\{n_\sigma\}]$ is not known exactly, approximations to it must be employed, e.g., local-spin-density approximation, gradient corrections [25], and generalized gradient corrections [26].

If, however, we define the exact exchange-energy functional [27] as that given by the HF theory, i.e., $E_x \equiv E_x^{HF}[\{\psi_{i\sigma}\}]$, then it is no longer possible to simply calculate the corresponding exchange potential by employing Eq. (2) because the functional derivative of the $\{\psi_{i\sigma}\}$ with respect to n_σ is not known. An alternative procedure, which reduces to the KS result if $E_x = E_x[\{n_\sigma\}]$ is to find the spin-polarized optimized effective potentials V_σ^o, which, when employed in a single-particle Schrödinger equation, yield eigenfunctions whose Slater determinant minimizes the expectation value of the total Hamiltonian. Such a method was first proposed by Sharp and Horton [14] (for the unpolarized case) long before the advent of density-functional theory. It was their intention to investigate whether the Slater exchange potential [20] could be approximately obtained

from such an analysis. We shall have more to say about such a relationship in Sec. III. In this section we present the generalization of the derivation of the equation satisfied by the optimized potential to include the possibility of orbital fractional occupancy [5] for spin-polarized potentials corresponding to spin-unrestricted HF theory [24] and discuss some important properties of the exact solution of this equation.

The condition that the total energy $E[\{\psi_{i\sigma}\}]$ be minimized with respect to variations in the optimized effective potential V_σ^o may be expressed as

$$\frac{\delta E[\{\psi_{i\sigma}^o\}]}{\delta V_\sigma^o(\mathbf{r})} = \sum_{i,\sigma'}\int d\mathbf{r}' \frac{\delta E}{\delta \psi_{i\sigma'}^o(\mathbf{r}')}\frac{\delta \psi_{i\sigma'}^o(\mathbf{r}')}{\delta V_\sigma^o(\mathbf{r})} + c.c. = 0 \quad (3)$$

where the optimized orbitals satisfy an equation analogous to Eq. (1), i.e.,

$$h_\sigma \psi_{i\sigma}^o(\mathbf{r}) \equiv -\tfrac{1}{2}\nabla^2 \psi_{i\sigma}^o(\mathbf{r}) + V_\sigma^o(\mathbf{r})\psi_{i\sigma}^o(\mathbf{r}) = \varepsilon_{i\sigma}^o\psi_{i\sigma}^o(\mathbf{r}) . \quad (4)$$

Equation (3) is useful because it follows immediately from perturbation theory that, if $V_\sigma^o \rightarrow V_\sigma^o + \delta V_\sigma^o$ in Eq. (4) [5,14,15],

$$\delta \psi_{i\sigma}^o(\mathbf{r}') = -\int d\mathbf{r}'' G_{i\sigma}^o(\mathbf{r}',\mathbf{r}'')\psi_{i\sigma}^o(\mathbf{r}'')\delta V_\sigma^o(\mathbf{r}'') \quad (5)$$

where $G_{i\sigma}^o(\mathbf{r}',\mathbf{r}'')$ is the Green's function for noninteracting electrons moving in the potential $V_\sigma^o(\mathbf{r})$, i.e.,

$$G_{i\sigma}^o(\mathbf{r}',\mathbf{r}'') = \sum_j{}' \frac{\psi_{j\sigma}^o(\mathbf{r}')\psi_{j\sigma}^{o*}(\mathbf{r}'')}{\varepsilon_{j\sigma}^o - \varepsilon_{i\sigma}^o} \quad (6)$$

where the prime on the sum means the sum over j is restricted to states for which $\varepsilon_{j\sigma}^o \neq \varepsilon_{i\sigma}^o$.

Consequently,

$$\frac{\delta \psi_{i\sigma'}^o(\mathbf{r}')}{\delta V_\sigma^o(\mathbf{r})} = -G_{i\sigma}^o(\mathbf{r}',\mathbf{r})\psi_{i\sigma}^o(\mathbf{r})\delta_{\sigma\sigma'} . \quad (7)$$

Furthermore, in the exchange-only approximation we have

$$E[\{\psi_{i\sigma}^o\}] = \sum_{i,\sigma}f_{i\sigma}\int \psi_{i\sigma}^{o*}(-\tfrac{1}{2}\nabla^2)\psi_{i\sigma}^o d\mathbf{r}$$
$$+ \int V_{ext}(\mathbf{r})n^o(\mathbf{r})d\mathbf{r}$$
$$+ \tfrac{1}{2}\int\int \frac{n^o(\mathbf{r})n^o(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_x^{HF}[\{\psi_{i\sigma}^o\}] \quad (8)$$

where

$$E_x^{HF}[\{\psi_{i\sigma}^o\}] = -\tfrac{1}{2}\sum_\sigma\sum_{i,j}f_{i\sigma}f_{j\sigma}\int\int \frac{\psi_{i\sigma}^{o*}(\mathbf{r}')\psi_{j\sigma}^{o*}(\mathbf{r}')\psi_{i\sigma}^o(\mathbf{r})\psi_{j\sigma}^o(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' , \quad (9)$$

$$n^o(\mathbf{r}) = \sum_{i,\sigma}n_{i\sigma}^o(\mathbf{r}) ,$$

$$(10)$$

$$n_{i\sigma}^o(\mathbf{r}) = f_{i\sigma}\psi_{i\sigma}^{o*}(\mathbf{r})\psi_{i\sigma}^o(\mathbf{r}) ,$$

and $f_{i\sigma}$ is the fractional occupancy of the $i\sigma$ orbital. It follows from Eq. (8) that

$$\frac{\delta E[\{\psi^o_{i\sigma}\}]}{\delta \psi^o_{i\sigma}(\mathbf{r}')} = f_{i\sigma}\{-\tfrac{1}{2}\nabla^2 \psi^{o*}_{i\sigma}(\mathbf{r}')$$

$$+[V_{\text{ext}}(\mathbf{r}')+V_H(\mathbf{r}')+v_{i\sigma}(\mathbf{r}')]\}\psi^{o*}_{i\sigma}(\mathbf{r}') \qquad (11)$$

$$= f_{i\sigma}\{\varepsilon^o_{i\sigma} - V^o_{x\sigma}(\mathbf{r}')+v_{i\sigma}(\mathbf{r}')\}\psi^{o*}_{i\sigma}(\mathbf{r}') \qquad (12)$$

where we have defined (for $f_{i\sigma}\neq 0$)

$$v_{i\sigma}(\mathbf{r}) \equiv \frac{1}{f_{i\sigma}\psi^{o*}_{i\sigma}(\mathbf{r})}\frac{\delta E^{\text{HF}}_x}{\delta \psi^o_{i\sigma}(\mathbf{r})}$$

$$= -\sum_j f_{j\sigma}\int \frac{\psi^{o*}_{i\sigma}(\mathbf{r}')\psi^{o*}_{j\sigma}(\mathbf{r}')\psi^o_{j\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|\psi^{o*}_{i\sigma}(\mathbf{r})}d\mathbf{r}' , \qquad (13)$$

$$V^o_{x\sigma}(\mathbf{r}) \equiv V^o_{\sigma}(\mathbf{r})-V_{\text{ext}}(\mathbf{r})-V_H(\mathbf{r}) . \qquad (14)$$

$V_H(\mathbf{r})$ is the Hartree potential and we have used Eq. (4). Equation (13) is of course exactly the effective single-particle HF potential that appears in the HF equation for $\psi^{\text{HF}*}_{i\sigma}$ as can be seen by relaxing the condition that the $\{\psi^o_{i\sigma}\}$ satisfy Eq. (4) but instead minimizing E with respect to variations in the $\{\psi^o_{i\sigma}\}$ subject to the usual orthonormality condition between orbitals.

Substituting Eqs. (7) and (12) into Eq. (3) and using

$$\int \psi^{o*}_{i\sigma}(\mathbf{r}')G^o_{i\sigma}(\mathbf{r}',\mathbf{r})d\mathbf{r}'=0$$

we obtain for each σ

$$\sum_i f_{i\sigma}\int d\mathbf{r}'[V^o_{x\sigma}(\mathbf{r}')-v_{i\sigma}(\mathbf{r}')]$$

$$\times G^o_{i\sigma}(\mathbf{r}',\mathbf{r})\psi^{o*}_{i\sigma}(\mathbf{r}')\psi^o_{i\sigma}(\mathbf{r})+\text{c.c.}=0 \qquad (15)$$

which is the generalization of the original equation for the optimized effective exchange potential to the case of the spin-polarized potentials including fractional occupancy.

The exact analytic solution of Eq. (15) to yield $V^o_{x\sigma}$ as a functional of the $\{v_{i\sigma}\}$ and the $\{\psi^o_{i\sigma}\}$ is not known. We may, however, obtain some insight into the behavior of the exact $V^o_{x\sigma}$ by a careful analysis of Eq. (15) [28]. For simplicity, we assume that V_{ext}, and consequently V^o_σ, has a small symmetry breaking term so the solutions of Eq. (4) for a given σ are nondegenerate and therefore can be chosen as real. Let $f_{i\sigma}=0$, $i>m$, i.e., $\psi^o_{m\sigma}$ is the occupied orbital corresponding to the highest single-particle-energy eigenvalue $\varepsilon^o_{m\sigma}$ of a state having spin projection σ. Then, since $\psi^o_{m\sigma}$ approaches zero as $r\to\infty$ more slowly than does any other orbital, $R_{m\sigma}$ exists such that

$$|f_{i\sigma}\psi^o_{i\sigma}(\mathbf{r})/f_{m\sigma}\psi^o_{m\sigma}(\mathbf{r})|<\delta , \quad i<m$$

for $r>R_{m\sigma}$ where δ is arbitrarily small. Then dividing both sides of Eq. (15) by $f_{m\sigma}\psi^o_{m\sigma}(\mathbf{r})$ and dropping terms of $O(\delta)$ we obtain for $r>R_{m\sigma}$

$$\int d\mathbf{r}'[V^o_{x\sigma}(\mathbf{r}')-v_{m\sigma}(\mathbf{r}')]\psi^o_{m\sigma}(\mathbf{r}')G^o_{m\sigma}(\mathbf{r}',\mathbf{r})=0 . \qquad (16)$$

Operating on Eq. (16) with $\varepsilon^o_{m\sigma}-h_\sigma(\mathbf{r})$, where h_σ is defined in Eq. (4), and employing

$$[\varepsilon^o_{m\sigma}-h_\sigma(\mathbf{r})]G^o_{m\sigma}(\mathbf{r}',\mathbf{r})=-\sum_{i\neq m}\psi^o_{i\sigma}(\mathbf{r}')\psi^o_{i\sigma}(\mathbf{r})$$

$$=-[\delta(\mathbf{r}-\mathbf{r}')-\psi^o_{m\sigma}(\mathbf{r}')\psi^o_{m\sigma}(\mathbf{r})] \qquad (17)$$

for all $\mathbf{r}$ and $\mathbf{r}'$, and performing the indicated integration over $\mathbf{r}'$, we obtain for $r>R_{m\sigma}$

$$V^o_{x\sigma}(\mathbf{r})=v_{m\sigma}(\mathbf{r})+(\bar{V}^o_{x\sigma m}-\bar{v}^o_{m\sigma}) \qquad (18)$$

where the average values of $V^o_{x\sigma}$ and $v_{m\sigma}$ are both taken over the $m\sigma$ state, i.e.,

$$\bar{v}^o_{p\sigma} \equiv \int \psi^{o*}_{p\sigma}(\mathbf{r})\psi^o_{p\sigma}(\mathbf{r})v_{p\sigma}(\mathbf{r})d\mathbf{r} \qquad (19)$$

and similarly for $\bar{V}^o_{x\sigma m}$. Equation (18) has the same property possessed by Eq. (15) that if $V^o_{x\sigma}(\mathbf{r})$ is a solution so is $V^o_{x\sigma}(\mathbf{r})+C$ where C is an arbitrary constant. Choosing C such that $V^o_{x\sigma}(\mathbf{r})\to 0$ for $r\to\infty$ and using $v_{m\sigma}\to -f_{m\sigma}/r$ for $r\to\infty$ from Eq. (13) we obtain from Eq. (18)

$$\bar{V}^o_{x\sigma m}=\bar{v}^o_{m\sigma} \qquad (20)$$

and

$$V^o_{x\sigma}(\mathbf{r})\to -\frac{f_{m\sigma}}{r} , \quad r\to\infty \qquad (21)$$

for each σ. Equation (21) is the generalization for fractional occupancy of a previously derived result [15] for the case $f_{m\sigma}=1$ and is the same result as that obtained for the exact KS exchange-correlation potential [29].

It is also of interest to consider the behavior of $V^o_{x\sigma}(\mathbf{r})$ in a region of space in which one orbital other than $\psi^o_{m\sigma}$ dominates the density. Whereas $\psi^o_{m\sigma}$ will dominate the density for sufficiently large r, in any physical problem it may not be possible to find a region Ω_p for which $n^o_{p\sigma}(\mathbf{r})\gg n^o_{i\sigma}(\mathbf{r})$, $i\neq p$. Nevertheless, it will be useful to consider those cases in which such a condition exists. We may then divide Eq. (15) by $f_{p\sigma}\psi^o_{m\sigma}(\mathbf{r})$ and dropping terms of $O(f_{i\sigma}\psi^o_{i\sigma}(\mathbf{r})/f_{p\sigma}\psi^o_{p\sigma}(\mathbf{r}))$ for $\mathbf{r}$ in Ω_p we obtain the equation analogous to Eq. (16), i.e.,

$$\int d\mathbf{r}'[V^o_{x\sigma}(\mathbf{r}')-v_{p\sigma}(\mathbf{r}')]\psi^o_{p\sigma}(\mathbf{r}')G^o_{p\sigma}(\mathbf{r}',\mathbf{r})=0 \qquad (22)$$

for $\mathbf{r}$ in Ω_p. Operating on Eq. (22) with $[\varepsilon^o_{p\sigma}-h_\sigma(\mathbf{r})]$ and employing the equation analogous to Eq. (18) with m replaced by p we obtain [32] for any p provided $n^o_{i\sigma}(\mathbf{r})/n^o_{p\sigma}(\mathbf{r})\to 0$ for all $i\neq p$,

$$V^o_{x\sigma}(\mathbf{r})=v_{p\sigma}(\mathbf{r})+(\bar{V}^o_{x\sigma p}-\bar{v}^o_{p\sigma}) . \qquad (23)$$

The extension of the derivation of Eq. (18), and consequently of Eqs. (20)–(24), to the degenerate case with a choice of possibly complex orbitals is treated in Appendix A.

In the constant-density limit $V^o_{x\sigma}$ is clearly a constant. It then follows rigorously from Eq. (20) that in the homogeneous-electron-gas limit, the value of $V^o_{x\sigma}$ equals the value of the HF exchange potential at the Fermi ener-

gy, a result obtained by Kohn and Sham [2] by employing the local-density approximation; it is well known that this result is $\frac{2}{3}$ the value obtained by Slater by averaging the single-particle HF exchange potentials over all the occupied states. Furthermore, since

$$\varepsilon_{m\sigma}^o = \int \psi_{m\sigma}^{o*}(-\tfrac{1}{2}\nabla^2 + V_{\text{ext}} + V_H + V_{x\sigma}^o)\psi_{m\sigma}^o d\mathbf{r} \quad (24)$$

it follows from Eq. (20) that

$$\varepsilon_{m\sigma}^o = \int \psi_{m\sigma}^{o*}(-\tfrac{1}{2}\nabla^2 + V_{\text{ext}} + V_H + v_{m\sigma})\psi_{m\sigma}^o d\mathbf{r}$$
$$= \int \psi_{m\sigma}^{o*} h_{m\sigma}^{\text{HF}} \psi_{m\sigma}^o d\mathbf{r} \equiv \overline{\varepsilon}\,_{m\sigma}^{o\text{HF}} \quad (25)$$

where the HF single-particle Hamiltonian corresponding to the orbital $m\sigma$ is evaluated using the OEP orbitals $\{\psi_{i\sigma}^o\}$. [It should be noted that since Eq. (20) is valid only for the highest-energy occupied orbital of spin projection σ, the equation analogous to Eq. (25) will not in general be valid for $i \neq m$.] But since the right-hand side (rhs) of Eq. (25) is identical to the difference in the expectation values of the total energy for the N- and $(N-1)$-particle systems if a Slater determinant of the exact same unrelaxed orbitals is employed, it follows from Eq. (25) that

$$E^o(N) - E_u^o(N-1) = \varepsilon_{m\sigma}^o \quad (26)$$

where $E^o(M)$ is the expectation value of the total energy for the M-particle system; the subscript u indicates the value calculated using the same orbitals as employed in the N-particle calculation with the $m\sigma$ orbital missing. Thus, as in the HF calculation, Koopmans's theorem [16] is satisfied, but here only for the highest-energy occupied state of either spin projection.

We may also study the rate of change of the total energy E with respect to $f_{p\sigma}$, the fractional occupancy of the nondegenerate state with energy eigenvalue $\varepsilon_{p\sigma}^o$ by treating E as a functional of both $f_{p\sigma}$ and the $V_{\sigma'}^o$ [$\sigma' = (\uparrow, \downarrow)$] because the $\{\psi_{i\sigma}^o\}$ are functionals of V_σ^o from Eq. (4). In the following we take all $f_{i\sigma} = \text{const}$, $i \neq p$.

If $f_{p\sigma} \to f_{p\sigma} + \delta f_{p\sigma}$, which leads to a change in the self-consistent potentials from $V_{\sigma'}^o$ to $V_{\sigma'}^o + \delta V_{\sigma'}^o$ in order that the new total energy be minimized, then

$$\delta E^o = \frac{\partial E^o}{\partial f_{p\sigma}}\bigg|_{V_{\sigma'}^o} \delta f_{p\sigma} + \sum_{\sigma'} \int \frac{\delta E^o}{\delta V_{\sigma'}^o}\bigg|_{f_{p\sigma}} \delta V_{\sigma'}^o d\mathbf{r} . \quad (27)$$

But the condition satisfied by the $V_{\sigma'}^o$ is that E is minimized for fixed $\{f_{i\sigma'}\}$, i.e., Eq. (3) so it follows from Eqs. (3) and (27) that

$$\frac{dE^o}{df_{p\sigma}} = \frac{\partial E^o}{\partial f_{p\sigma}} . \quad (28)$$

The same result obtains in a density-functional theory in which E (or the exchange-correlation energy functional E_{xc}) is taken as a functional of the density $n(\mathbf{r})$ [17] or of the spin densities $n_\sigma(\mathbf{r})$, or in the HF theory in which the single-particle potentials $v_{i\sigma}$ are orbital dependent [10]. In each one of those cases, the right-hand side of Eq. (28) is shown to be equal to the expectation value of the single-particle Hamiltonian for which the $p\sigma$ state is an eigenfunction with eigenvalue $\varepsilon_{p\sigma}$, a result which is

known as Janak's theorem. However, in the present case, this is not always valid, i.e., by direct differentiation of E given by Eq. (8) where E and n_σ^o are given by Eqs. (9) and (10) we obtain the usual HF result, i.e.,

$$\frac{\partial E}{\partial f_{p\sigma}} = \int \psi_{p\sigma}^{o*} h_{p\sigma}^{\text{HF}} \psi_{p\sigma}^o d\mathbf{r} = \int \psi_{p\sigma}^o \frac{\delta E}{f_{p\sigma}\delta\psi_{p\sigma}^o} d\mathbf{r} . \quad (29)$$

But unlike the case where the $p\sigma$ states are eigenfunctions of $h_{p\sigma}^{\text{HF}}$ with eigenvalue $\varepsilon_{p\sigma}^{\text{HF}}$, the $\psi_{p\sigma}^o$ are eigenfunctions of h_σ given by Eq. (4) and the expectation value of $h_{p\sigma}^{\text{HF}}$ in the state $p\sigma$ will generally not be equal to $\varepsilon_{p\sigma}^o$ except in one case, i.e., if $p = m$ as shown in Eq. (25). Thus in general

$$\frac{dE^o}{df_{p\sigma}} = \int \psi_{p\sigma}^{o*} h_{p\sigma}^{\text{HF}} \psi_{p\sigma}^o d\mathbf{r} = \int \psi_{p\sigma}^o \frac{\delta E}{f_{p\sigma}\delta\psi_{p\sigma}^o} d\mathbf{r} \quad (30)$$

and for the highest-energy occupied state with spin σ

$$\frac{dE^o}{df_{m\sigma}} = \varepsilon_{m\sigma}^o(f_{m\sigma}) = \int \psi_{m\sigma}^o \frac{\delta E}{f_{m\sigma}\delta\psi_{m\sigma}^o} d\mathbf{r} . \quad (31)$$

In the homogeneous-electron-gas limit, the single-particle wave functions are plane waves and satisfy $\psi_{p\sigma}^o(\mathbf{r}) = \psi_{p\sigma}^{\text{HF}}(\mathbf{r})$ which results in $E^o = E^{\text{HF}}$ and it follows from Eq. (30) that

$$\frac{dE^o}{df_{p\sigma}} = \varepsilon_{p\sigma}^{\text{HF}} = \frac{k_{p\sigma}^2}{2m} + V_{x\sigma}^{\text{HF}}(k_{p\sigma}) \quad (32)$$

for all $p\sigma$ where $V_{x\sigma}^{\text{HF}}(k_{p\sigma})$ is the exact HF exchange potential for an electron with momentum $k_{p\sigma}$, which is the exact result for the ground state of the energy functional given by Eqs. (8) and (9). It is interesting to note that the result of employing Janak's theorem is

$$\frac{dE^{\text{KS}}}{df_{p\sigma}} = \varepsilon_{p\sigma}^{\text{KS}} = \frac{k_{p\sigma}^2}{2m} + V_{x\sigma}^{\text{HF}}(k_{m\sigma}) \neq \varepsilon_{p\sigma}^{\text{HF}} , \quad p \neq m \quad (33)$$

where $\varepsilon_{p\sigma}^{\text{KS}}$ is the KS eigenvalue, and $k_{m\sigma}$ is the Fermi momentum. Thus although $E^{\text{KS}} = E^{\text{HF}}$ if all states below the Fermi energy are filled, it is not possible to obtain the correct rate of change of E with respect to $f_{p\sigma}$ by merely replacing $n_{p\sigma}(\mathbf{r})$ by $f_{p\sigma}\psi_{p\sigma}^*\psi_{p\sigma}$ in the KS energy functional for states below the Fermi energy. It follows that although Janak's theorem is an exact consequence of extending the domain of the energy functional to include fractional occupancy in this simple way, this extension does not yield the HF total energy for fractional occupancy and thus the theorem is an identity satisfied by the self-consistent solutions of the KS equations without physical significance for $p \neq m$. On the other hand, the OEP result given by Eqs. (30) and (31) shows explicitly that only $\varepsilon_{m\sigma}^o$ has the significance of being equal to the rate of change of E^o with respect to fractional occupancy $f_{m\sigma}$ and that in general the rate of change of E^o with respect to the fractional occupancy of any state, $f_{p\sigma}$, is equal to the expectation value of the corresponding single-particle HF Hamiltonian $h_{p\sigma}^{\text{HF}}$, and not to the value of $\varepsilon_{p\sigma}^o$, the latter having no special significance for $p \neq m$.

Finally, it is possible to deduce from Eq. (20) that $V_{x\sigma}^o$ is discontinuous as the number of electrons with spin pro-

jection σ is increased from N_σ to $N_\sigma + f$ where N is the number necessary to completely fill a spin subshell. It is clear from Eq. (21) that $V_{x\sigma}^o(\mathbf{r}, N_\sigma) \rightarrow -1/r$ and $V_{x\sigma}^o(\mathbf{r}, N_\sigma + f) \rightarrow -f/r$ for $r \rightarrow \infty$ thereby showing that the asymptotic form of the exchange potential changes discontinuously when N_σ is increased infinitesimally beyond an integer. However, for sufficiently small f this change in the asymptotic value of the potential has a negligible effect on $\{\psi_{i\sigma}^o\}$, $i = 1, \ldots, m$, because it obtains only for $r > R$ corresponding to the region in which all $\psi_{i\sigma}^o \rightarrow 0$, $i = 1, \ldots, m$. Moreover, for $r < R$, corresponding to the region in which the additional fractionally occupied state makes a negligible contribution to the density, we expect the $\psi_{i\sigma}^o$ to be essentially unchanged in the limit $f \rightarrow 0$ so we may continue to approximate these wave functions by their value for $f = 0$. It then follows that a consistent solution of Eq. (15) for $V_{x\sigma}^o(\mathbf{r}, N_\sigma + f)$ is identical to $V_{x\sigma}^o(\mathbf{r}, N_\sigma)$ up to possibly an overall constant for $r < R \rightarrow \infty$ as $f \rightarrow 0$, i.e., [5]

$$V_{x\sigma}^o(\mathbf{r}, N_\sigma + f) - V_{x\sigma}^o(\mathbf{r}, N_\sigma) = C_{x\sigma}^o . \tag{34}$$

But in order that $V_{x\sigma}^o(r, N_\sigma + f) \rightarrow 0$ as $r \rightarrow \infty$ it follows from Eq. (20) that

$$\bar{V}_{x\sigma, m+1}^o(N_\sigma + f) = \bar{v}_{m+1,\sigma}^o \tag{35}$$

where it follows from Eq. (34) and the definition of $v_{i\sigma}$ given by Eq. (13) in the limit $f \rightarrow 0$, $\bar{v}_{m+1,\sigma}$ is identical to the result obtained by taking the exchange potential to be given by $V_{x\sigma}^o(\mathbf{r}, N_\sigma)$. Then, taking the expectation value of Eq. (34) in the $m+1,\sigma$ state and using Eq. (35) yields

$$C_{x\sigma}^o = \bar{v}_{m+1,\sigma}^o - \bar{V}_{x\sigma, m+1}^o(N_\sigma) \tag{36}$$

which in general will not be zero provided $\psi_{m+1,\sigma}^o$ is not trivially related to $\psi_{m\sigma}^o$. This is, of course, the case when N_σ electrons fill a complete spin subshell so the $m+1,\sigma$ state is not simply related to the $m\sigma$ state so that the satisfaction of Eq. (20) does not lead to a similar result for $m\sigma \rightarrow m+1,\sigma$. On the other hand, for a metal the $m+1$ state is only infinitesimally different from the m state which leads to $C_{x\sigma}^o = 0$ as given by Eq. (36).

In concluding this section it is useful to note the significance of Eq. (20). We have seen that this relationship immediately leads to the LSD approximation for $V_{x\sigma}^o$ in the homogeneous gas limit as well as to the result given by Eq. (25) that $\varepsilon_{m\sigma}^o$ equals the expectation value of $h_{m\sigma}^{HF}$, the HF single-particle Hamiltonian, and consequently to the satisfaction of Koopmans's theorem given by Eq. (26). Moreover, the extension of Janak's theorem given by Eq. (31) for the $m\sigma$ state follows directly from Eq. (20) as well as the size of the discontinuity in the exchange potential given by Eq. (36).

III. CONSTRUCTION OF AN APPROXIMATE OPTIMIZED EFFECTIVE POTENTIAL

The integral equation satisfied by $V_{x\sigma}^o$ given by Eq. (15) has no known analytic solution for $V_{x\sigma}^o$ as a functional of the $\{\psi_{i\sigma}^o\}$. Moreover, it is difficult to solve numerically,

with results having been published only for problems for which the potential is a function of a single variable, i.e., spherically symmetric atoms [15,18,19] and jellium surfaces [30]. It would be useful to obtain $V_{x\sigma}^o$ as an explicit functional of the $\{\psi_{i\sigma}^o\}$ since it could then be employed in the KS equations for the exchange potential just as any expression that is a functional of the n_σ or, as for the Harbola-Sahni exchange potential [12,21], which is a functional of the single-particle orbitals. We discuss such a construction below from two different points of view — one using simple physical arguments and a second employing an approximation to the Green's function in Eq. (15) first proposed by Sharp and Horton [14]. We find that both methods lead to the identical result and that this result yields a $V_{x\sigma}$ that maintains nearly all of the exact properties possessed by the exact $V_{x\sigma}^o$ as discussed in Sec. II.

The earliest approximation for a single local exchange potential that could be employed to obtain results similar to those from a HF calculation was given by Slater [20]. His result, generalized to the spin-polarized case, may be written

$$V_{x\sigma}^S(\mathbf{r}) = \frac{\sum_i n_{i\sigma}(\mathbf{r}) v_{i\sigma}(\mathbf{r})}{\sum_i n_{i\sigma}(\mathbf{r})} \tag{37}$$

where $v_{i\sigma}(\mathbf{r})$ is given by Eq. (13) and $n_{i\sigma}$ is given by Eq. (10) with, in both expressions, $\{\psi_{i\sigma}^o\}$ replaced by $\{\psi_{i\sigma}^S\}$, the self-consistently calculated orbitals, when $V_{x\sigma}^S$ is employed as the exchange potential. The potential given by Eq. (37) has the property that in the region in which $n_{p\sigma}(\mathbf{r})$ dominates $n_\sigma(\mathbf{r}) \equiv \sum_i n_{i\sigma}(\mathbf{r})$, $V_{x\sigma}^S \approx v_{p\sigma}$ so that one might anticipate that the resulting single-particle orbital $\psi_{p\sigma}^S \approx \psi_{p\sigma}^{HF}$, the HF single-particle orbital provided that the self-consistently calculated Hartree potential is close to that calculated using the HF electron density. However, it is clear from detailed numerical calculations [31], or by simply taking the local-spin-density approximation to Eq. (37), that $V_{x\sigma}^S$ is too deep, i.e., Eq. (37) results in an exchange potential that is too large in magnitude, and is a factor of $\frac{3}{2}$ larger than both the KS-LSD and the OEP results in the homogeneous-electron-gas limit as discussed in Sec. II.

We may, however, generalize the Slater method of combining the separate $v_{i\sigma}$ to form $V_{x\sigma}$ by writing [32]

$$V_{x\sigma}(\mathbf{r}) = \frac{\sum_i n_{i\sigma}(\mathbf{r}) [v_{i\sigma}(\mathbf{r}) + C_{i\sigma}]}{\sum_i n_{i\sigma}(\mathbf{r})} \tag{38}$$

where the $\{C_{i\sigma}\}$ are a set of orbital-dependent constants. Equation (38) reduces to $V_{x\sigma} \approx v_{p\sigma} + C_{p\sigma}$ in the region in which $n_{p\sigma}(\mathbf{r})$ dominates $n_\sigma(\mathbf{r})$, which leads to a shift in the single-particle-energy eigenvalues, but continues to suggest that the single-particle eigenfunctions satisfy $\psi_{p\sigma} \cong \psi_{p\sigma}^{HF}$ provided the resulting V_H is close to V_H^{HF}.

The appropriate $\{C_{i\sigma}\}$ may be chosen by requiring that in the limit in which $n_{p\sigma}$ dominates n_σ, the potential given by Eq. (38) should be identical in form to the poten-

tial obtained from the OEP equation in the same limit. It then follows immediately from Eq. (23) that for each $C_{p\sigma}$,

$$C_{p\sigma} = \bar{V}_{x\sigma p} - \bar{v}_{p\sigma} \qquad (39)$$

where $\bar{v}_{p\sigma}$ is given by the analogous expression to Eq. (19) with $\psi_{p\sigma}^0$ replaced by the self-consistently obtained $\psi_{p\sigma}$.

Substituting Eq. (39) into Eq. (38) yields

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

$$= V_{x\sigma}^S(\mathbf{r}) + \sum_i \frac{n_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})}(\bar{V}_{x\sigma i} - \bar{v}_{i\sigma}) \qquad (40)$$

where we have used Eq. (37).

Equation (40) may also be derived from the OEP equation by employing an approximation to the Green's function $G_{i\sigma}^o(\mathbf{r}',\mathbf{r})$ first suggested by Sharp and Horton [14]. If we approximate $\varepsilon_{j\sigma}$ in Eq. (6) by some mean energy $\bar{\varepsilon}_{i\sigma}$, we obtain the approximation to $G_{i\sigma}^o$

$$G_{i\sigma}(\mathbf{r}',\mathbf{r}) \equiv (\bar{\varepsilon}_{i\sigma} - \varepsilon_{i\sigma})^{-1}\sum_j{}' \psi_{j\sigma}(\mathbf{r}')\psi_{j\sigma}^*(\mathbf{r})$$

$$= (\bar{\varepsilon}_{i\sigma} - \varepsilon_{i\sigma})^{-1}[\delta(\mathbf{r} - \mathbf{r}') - \psi_{i\sigma}(\mathbf{r}')\psi_{i\sigma}^*(\mathbf{r})] \qquad (41)$$

where the $\{\psi_{j\sigma}\}$ and $\varepsilon_{i\sigma}$ are the self-consistent solutions of Eq. (4) corresponding to employing $V_{x\sigma}$ as the exchange potential where $V_{x\sigma}$ is the solution of the OEP equation with $G_{i\sigma}^o$ replaced by $G_{i\sigma}$. Here we have assumed the energy level $\varepsilon_{i\sigma}$ is nondegenerate. The degenerate case will be treated in Appendix B. They then substituted Eq. (41) into Eq. (15) and neglected the terms arising from the contribution of the second term on the rhs of Eq. (41) (see footnote 4 of Ref. [14]). They found that if the further approximation is made that $\bar{\varepsilon}_{i\sigma} - \varepsilon_{i\sigma} \equiv \Delta\varepsilon_\sigma$ is independent of i, the resultant $V_{x\sigma}$ is identical to the then recently derived Slater exchange potential given by Eq. (37). However, if the nonlocal second term on the rhs of Eq. (41) is treated exactly and the only approximations made in evaluating $G_{i\sigma}$ are

$$\varepsilon_{j\sigma} = \bar{\varepsilon}_{i\sigma} \qquad (42)$$

independent of j, and

$$\bar{\varepsilon}_{i\sigma} - \varepsilon_{i\sigma} = \Delta\varepsilon_\sigma \qquad (43)$$

independent of i, then the substitution of Eq. (41) into Eq. (15) yields

$$\sum_i f_{i\sigma} \int d\mathbf{r}'[V_{x\sigma}(\mathbf{r}') - v_{i\sigma}(\mathbf{r}')]\psi_{i\sigma}^*(\mathbf{r}')$$

$$\times \psi_{i\sigma}(\mathbf{r})[\delta(\mathbf{r} - \mathbf{r}') - \psi_{i\sigma}(\mathbf{r}')\psi_{i\sigma}^*(\mathbf{r})] = 0 . \qquad (44)$$

Performing the indicated integration over $\mathbf{r}'$, we obtain

$$\sum_i f_{i\sigma}\{[V_{x\sigma}(\mathbf{r}) - v_{i\sigma}(\mathbf{r})]\psi_{i\sigma}^*(\mathbf{r})\psi_{i\sigma}(\mathbf{r})$$

$$- [\bar{V}_{x\sigma i} - \bar{v}_{i\sigma}]\psi_{i\sigma}^*(\mathbf{r})\psi_{i\sigma}(\mathbf{r})\} = 0 \qquad (45)$$

exactly.

Consequently,

$$V_{x\sigma}(\mathbf{r})\sum_i n_{i\sigma}(\mathbf{r}) - \sum_i n_{i\sigma}[v_{i\sigma}(\mathbf{r}) + (\bar{V}_{x\sigma i} - \bar{v}_{i\sigma})] = 0 . \qquad (46)$$

Solving Eq. (46) for $V_{x\sigma}(\mathbf{r})$ immediately yields Eq. (40) without further approximation as previously claimed [33]. Clearly, if the contribution arising from the inclusion of the second term on the rhs of Eq. (41) in $G_{i\sigma}$ is neglected, i.e., the term proportional to $(\bar{V}_{x\sigma i} - \bar{v}_{i\sigma})$ in Eq. (45), then the solution for $V_{x\sigma}$ is given by Eq. (37), i.e., by the Slater exchange potential [14]. However, we shall show below that including these terms leads to a significant improvement over the Slater expression and results in an exchange potential that more closely approximates $V_{x\sigma}^o$ than any other exchange potential previously proposed.

Unlike Eq. (37), which expresses the Slater exchange potential as a functional of the self-consistently derived orbitals, Eq. (40) is an integral equation for $V_{x\sigma}$ since the unknown expectation values, $\bar{V}_{x\sigma i}$, appear on the rhs. Before deriving the exact solution of this equation, it is useful to discuss the properties of this solution and to compare them with the properties of the exact $V_{x\sigma}^o$ as discussed in Sec. II.

As for the solution of the OEP equation given by Eq. (15), the solution of Eq. (40) is determined only up to a constant, i.e., if $V_{x\sigma}$ is a solution, so is $V_{x\sigma} + C$, since the eigenfunctions will be the same, which results in all $v_{i\sigma}$ being unchanged, and each $\bar{V}_{x\sigma i} \to \bar{V}_{x\sigma i} + C$. Consequently, the addition to the rhs of Eq. (40) is $\sum_i n_{i\sigma} C/n_\sigma = C$, so if $V_{x\sigma}$ is a solution so is $V_{x\sigma} + C$. Choosing this constant so that $V_{x\sigma} \to 0$ for $r \to \infty$ requires

$$\bar{V}_{x\sigma m} = \bar{v}_{m\sigma} \qquad (47)$$

because for a system with a finite number of electrons, $V_{x\sigma}^S(\mathbf{r}) \to -f_{m\sigma}/r$ for $r \to \infty$ and, using the same argument employed in the discussion of the asymptotic behavior of $V_{x\sigma}^o$ that for sufficiently large r, $n_{i\sigma}/n_\sigma \to 0$ $(i \neq m)$ the coefficient of $n_{m\sigma}/n_\sigma$ in Eq. (40) must be zero. Equation (47) is the analog of the condition satisfied by the exact solution of the OEP equation given by Eq. (20).

However, it is by no means obvious that if Eq. (47) is substituted into Eq. (40) the resulting equation

$$V_{x\sigma}(\mathbf{r}) = \frac{\sum_i n_{i\sigma}(\mathbf{r})v_{i\sigma}(\mathbf{r})}{\sum_i n_{i\sigma}(\mathbf{r})} + \sum_i{}' \frac{(\bar{V}_{x\sigma i} - \bar{v}_{i\sigma})n_{i\sigma}(\mathbf{r})}{\sum_i n_{i\sigma}(\mathbf{r})} \qquad (48)$$

(where the prime means sum over $i = 1, \ldots, m - 1$) has a solution such that Eq. (47) is satisfied, i.e., the value of $\bar{V}_{x\sigma m}$ does not even appear in Eq. (48) and there is no apparent a priori reason that Eq. (47) will be satisfied by the solution of Eq. (48). We can, however, show analytically that the solution of Eq. (48) satisfies Eq. (47) by multiplying both sides of Eq. (48) by $n_\sigma(\mathbf{r})$ and integrating over $\mathbf{r}$. The resulting equation is then

$$\sum_i f_{i\sigma}\overline{V}_{x\sigma i}=\sum_i f_{i\sigma}\overline{v}_{i\sigma}+\sum_i' f_{i\sigma}(\overline{V}_{x\sigma i}-\overline{v}_{i\sigma})$$

or

$$f_{m\sigma}\overline{V}_{x\sigma m}=f_{m\sigma}\overline{v}_{m\sigma}\;.$$

Thus for any $f_{m\sigma}>0$, Eq. (47) is exactly satisfied by the solution of Eq. (48).

As noted at the end of Sec. II, the fact that Eq. (20) is satisfied leads to several important relationships satisfied by the exact OEP results. Similarly, the fact that Eq. (47) is exactly satisfied by $V_{x\sigma}$ given by Eq. (48) leads to many of the analogous results that we now discuss.

First of all, it follows from Eq. (48) and the asymptotic behavior of $V_{x\sigma}^S$ that

$$V_{x\sigma}(\mathbf{r})\to-\frac{f_{m\sigma}}{r}\;,\quad r\to\infty \tag{49}$$

which is the analog of Eq. (21). The analog of Eq. (23) is also valid by our initial construction of $V_{x\sigma}$ given in Eq. (40).

In the uniform-electron-gas limit, $V_{x\sigma}$ is independent of $\mathbf{r}$ and thus equal to its value averaged over the $m\sigma$ orbital. But according to Eq. (47), this is equal to the average value of the HF single-particle exchange potential averaged over the $m\sigma$ orbital, i.e., equal to the exchange potential in the LSD approximation. Thus, in the homogeneous-electron-gas limit,

$$V_{x\sigma}\to V_{x\sigma}^{\mathrm{LSD}}=\tfrac{2}{3}V_{x\sigma}^S\;, \tag{50}$$

which is identical to the behavior of $V_{x\sigma}^o$ as discussed above Eq. (24). Therefore, not only are the corrections to $V_{x\sigma}^S$ given in Eq. (40) non-negligible, but they provide precisely the necessary terms so that $V_{x\sigma}$ reduces to the correct LSD and $V_{x\sigma}^o$ result in the uniform gas limit. In addition, in the other limit in which there is only one occupied orbital with spin projection σ, it follows from Eqs. (48) and (13) that

$$V_{x\sigma}(\mathbf{r})=v_{1\sigma}(\mathbf{r})=-\int\frac{n_\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \tag{51}$$

which cancels exactly the self-interaction term in the Hartree potential as it must and is identical to $V_{x\sigma}^o(\mathbf{r})$, as can be seen from Eq. (15) if only $f_{1\sigma}\neq0$.

Using the same arguments as in Sec. II, it follows immediately from Eq. (47) that the analog of Eq. (25) is valid, i.e.,

$$\varepsilon_{m\sigma}=\langle\psi_{m\sigma}|h_{m\sigma}^{\mathrm{HF}}|\psi_{m\sigma}\rangle\equiv\overline{\varepsilon}_{m\sigma}^{\mathrm{HF}} \tag{52}$$

where now the HF single-particle Hamiltonian corresponding to the $m\sigma$ orbital is evaluated using the orbitals $\{\psi_{i\sigma}\}$ that are obtained by taking $V_{x\sigma}$ rather than $V_{x\sigma}^o$ as the exchange potential. Furthermore, since the difference in the expectation value of the total Hamiltonian of the system with and without the $m\sigma$ orbital (all other orbitals held fixed) is given by the expectation value of the single-particle Hamiltonian $h_{m\sigma}^{\mathrm{HF}}$ in the $m\sigma$ state, it follows from Eq. (52) that

$$E(N)-E_u(N-1)=\varepsilon_{m\sigma}\;, \tag{53}$$

i.e., analogously to Eq. (26), Koopmans's theorem is satisfied.

It is, however, not possible to exactly derive the analogous equations to Eqs. (30) and (31), which were valid for the exact $V_{x\sigma}^o$ because we may not employ the conditions that $\delta E/\delta V_{x\sigma}=0$. Thus, although the equations corresponding to Eqs. (27) and (29) obtain, instead of Eqs. (30) and (31) we find

$$\frac{dE}{df_{p\sigma}}=\int\psi_{p\sigma}^*h_{p\sigma}^{\mathrm{HF}}\psi_{p\sigma}d\mathbf{r}+\sum_{\sigma'}\int\frac{\delta E}{\delta V_{\sigma'}}\bigg|_{f_{p\sigma}}\frac{\partial V_{\sigma'}}{\partial f_{p\sigma}}d\mathbf{r} \tag{54}$$

and

$$\frac{dE}{df_{m\sigma}}=\varepsilon_{m\sigma}(f_{m\sigma})+\sum_{\sigma'}\int\frac{\delta E}{\delta V_{\sigma'}}\bigg|_{f_{m\sigma}}\frac{\partial V_{\sigma'}}{\partial f_{m\sigma}}d\mathbf{r}\;. \tag{55}$$

Equation (55) can provide a useful self-consistency test for the accuracy of $V_{x\sigma}$, i.e., if $V_{x\sigma}$ were exact, then Eq. (31) would obtain. Thus a comparison of $dE/df_{m\sigma}$ and $\varepsilon_{m\sigma}(f_{m\sigma})$ will give an estimate of the accuracy of $\varepsilon_{m\sigma}(f_{m\sigma})$ because $dE/df_{m\sigma}$ should be very close to $dE^o/df_{m\sigma}$, since it follows from the variational principle that if $V_{x\sigma}$ is in error by $O(\delta)$, then E will be in error by $O(\delta^2)$. We shall illustrate this in Secs. IV and V. We note that in the homogeneous-electron-gas limit, $V_\sigma=V_\sigma^o$, so $\delta E/\delta V_\sigma=0$ and Eq. (54) reduces to the exact OEP result given by Eq. (32).

Furthermore, since the existence of a discontinuity in $V_{x\sigma}^o$ was derived solely on the basis that $V_{x\sigma}^o\to0$ as $r\to\infty$ and Eq. (20) is valid, it follows from Eqs. (47) and (49) that as $f\to0$, for finite r

$$V_{x\sigma}(\mathbf{r},N_\sigma+f)-V_{x\sigma}(\mathbf{r},N_\sigma)=C_{x\sigma} \tag{56}$$

where

$$C_{x\sigma}=\overline{v}_{m+1,\sigma}-\overline{V}_{x\sigma,m+1}(N_\sigma)\;. \tag{57}$$

It is easy to see how this result arises from Eq. (48). If a fractionally occupied orbital with $f_{m+1,\sigma}\ll1$ is added to the system, then as $f_{m+1,\sigma}\to0$, we expect the $n_{i\sigma}$ and $v_{i\sigma}$, $i=1,\ldots,m$, to be essentially unchanged for $r<R$, where R is such that $n_{i\sigma}(\mathbf{r})\gg n_{m+1,\sigma}(\mathbf{r})$ in this region. However, once the $m+1,\sigma$ orbital is added to the second term in Eq. (48), no matter how small the value of $f_{m+1,\sigma}$, as long as $f_{m+1,\sigma}>0$, in order for $V_{x\sigma}\to0$ as $r\to\infty$ instead of satisfying Eq. (47), the potential must now satisfy

$$\overline{V}_{x\sigma m+1}(N_\sigma+f)=\overline{v}_{m+1,\sigma}\;; \tag{58}$$

therefore

$$\overline{V}_{x\sigma m+1}(N_\sigma+f)-\overline{V}_{x\sigma m+1}(N_\sigma)$$
$$=\overline{v}_{m+1,\sigma}-\overline{V}_{x\sigma m+1}(N_\sigma)\equiv C_{x\sigma}\;. \tag{59}$$

Furthermore, since as $f_{m+1,\sigma}\to0$, all the $n_{i\sigma}$ and $v_{i\sigma}$ must remain unchanged, this implies that the potential itself changes only by a constant for $r<R$, and this constant must be equal to the average value of the difference $V_{x\sigma}(\mathbf{r},N_\sigma+f)-V_{x\sigma}(\mathbf{r},N_\sigma)$ in any orbital, e.g., the $m+1,\sigma$ orbital, so $C_{x\sigma}$ is this constant that yields Eq. (56) for $r<R$. We note that if each $\overline{V}_{x\sigma i}$ in Eq. (48) is

changed to $\bar{V}_{x\sigma i} + C_{x\sigma}$ and the sum is taken over $i = 1, \ldots, m$, then

$$V_{x\sigma}(\mathbf{r}, N_\sigma + f) = V_{x\sigma}(\mathbf{r}, N_\sigma) + C_{x\sigma}, \quad r < R$$

$$\rightarrow -\frac{f}{r}, \quad r \rightarrow \infty \tag{60}$$

so the argument is self-consistent.

Finally, in order solve the integral equation given by Eq. (48), we need to find the constants, $\bar{V}_{x\sigma i}$, $i = 1, \ldots, m-1$. This can be achieved by multiplying Eq. (48) by $n_{j\sigma}(\mathbf{r})$, $j = 1, \ldots, m-1$ and integrating over $\mathbf{r}$. Then

$$f_{j\sigma}\bar{V}_{x\sigma j} = f_{j\sigma}\bar{V}^s_{x\sigma j} + \sum_{i=1}^{m-1} M_{ji}^{(\sigma)}(\bar{V}_{x\sigma i} - \bar{v}_{i\sigma}),$$

$$j = 1, \ldots, m-1 \tag{61}$$

with

$$M_{ji}^{(\sigma)} \equiv \int \frac{n_{j\sigma}(\mathbf{r})n_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})} d\mathbf{r}, \quad i,j = 1, \ldots, m-1. \tag{62}$$

It then follows by dividing by $f_{j\sigma}$ and subtracting $\bar{v}_{j\sigma}$ from both sides of Eq. (61) that

$$\sum_{i=1}^{m-1} (\delta_{ji} - f_{j\sigma}^{-1} M_{ji}^{(\sigma)})(\bar{V}_{x\sigma i} - \bar{v}_{i\sigma}) = \bar{V}^S_{x\sigma j} - \bar{v}_{j\sigma}. \tag{63}$$

Then

$$\bar{V}_{x\sigma i} - \bar{v}_{i\sigma} = \sum_{j=1}^{m-1} (A_\sigma^{-1})_{ij}(\bar{V}^s_{x\sigma j} - \bar{v}_{j\sigma}), \quad i = 1, \ldots, m-1 \tag{64}$$

where

$$(A_\sigma)_{ji} \equiv \delta_{ji} - f_{j\sigma}^{-1} M_{ji}^{(\sigma)}. \tag{65}$$

[Equation (64) corrects a typographical error appearing in Eq. (17) of Ref. [33].] Substituting this result into Eq. (48) yields $V_{x\sigma}(\mathbf{r})$ as a functional of the $\{\psi_{i\sigma}\}$. In addition, since $n_{i\sigma}/n_\sigma \leq 1$ for all $\mathbf{r}$ and the integral of $n_{j\sigma}$ over all space equals $f_{j\sigma}$, it follows from Eq. (62) that $0 < f_{j\sigma}^{-1} M_{ji}^{(\sigma)} \leq 1$.

IV. APPLICATION OF APPROXIMATE OPTIMIZED EXCHANGE POTENTIAL TO ATOMS WITH CLOSED SUBSHELLS

In order to test the accuracy of the approximate OEP given by the solution of Eq. (48), we have performed self-consistent calculations for the ground state of the ten atoms with closed subshells from Be to Xe and have compared our results with those of the most accurate numerical solution of the OEP equation that has been published [18]. As noted in Sec. III, for a system with only one electron with a given spin projection, $V_{x\sigma}$ is identical to the exact HF exchange potential. Thus our results for He are identical to the HF results as well as to those of an exact OEP calculation and will not be further discussed here. The other ten atoms from Be to Xe then constitute all the remaining systems considered in Ref. [18]. For each one of these atoms, there is only a single exchange potential because states with opposite spin projection have the same occupancy.

A comparison of the results of employing our approximate $V_{x\sigma}$ for the calculation of the energy given by Eq. (8) with those obtained by using other standard approximate exchange potentials is presented in Table I. For each comparison, we have tabulated, in mRy, the energy by which each approximation overestimates the OEP result, the latter representing the lowest possible energy calculated by employing a Slater determinant constructed from orbitals that are eigenfunctions of a single local potential. In addition, we have also tabulated the difference between the OEP and HF results, the latter representing the lowest possible energy calculated by employing any Slater determinant, to put into perspective the magnitude of these overestimates. The HF total energies are tabulated in order to compare the size of these overestimates with the total energy.

We see immediately that the results of employing $V_{x\sigma}$ given by Eq. (48) yield the smallest overestimate of the OEP energy compared with the results obtained by employing any other approximate exchange potential, being at most only < 10 ppm above the OEP result for Be with the fractional overestimate decreasing to < 1 ppm for Xe. They are only $\approx \frac{1}{4}$ to $\frac{1}{3}$ greater overestimates of the exact HF results than those given by the OEP calculations.

TABLE I. Comparison of overestimates of the OEP total energy E^o, calculated in various approximations compared with the overestimate of the Hartree-Fock total energy by E^o (in mRy) for ten atoms with closed subshells. [E_{calc} was calculated using $V_{x\sigma}$ given by Eq. (48).]

Atom	$-E^{HF}$ (Ref. [22]) (Ry)	E^o (Ref. [18]) $-E^{HF}$	$E_{\text{calc}} - E^o$	E^{HS} (Ref. [21]) $-E^o$	$E^{LSD} - E^o$	$E^S - E^o$
Be	29.1460	1.1	0.3	2.0	8.7	22.1
Ne	257.0942	3.4	1.1	6.9	35.7	89.4
Mg	399.2292	6.0	1.8	10.6	28.5	157.2
Ar	1 053.6350	10.6	3.4	15.8	34.4	218.3
Ca	1 353.5164	12.6	4.4	18.6	32.2	291.5
Zn	3 555.6962	27.5	7.3	29.5	101.6	516.1
Kr	5 504.1100	24.1	6.3	26.9	64.3	574.0
Sr	6 263.0914	24.5	7.1	28.3	58.5	648.5
Cd	10 930.2662	37.4	12.0	43.4	88.7	837.8
Xe	14 464.2768	35.0	12.1	39.9	68.0	897.5

This overestimate of the OEP results is on the average only $\approx \frac{1}{10}$ of that obtained if the KS-LSD approximation is employed and is about a factor of 100 smaller than that provided by the Slater approximation. The Slater-LSD approximation (not tabulated) results in total energies that are even higher.

A significant improvement over the KS-LSD result is obtained if W_x, the potential conjectured by Harbola and Sahni [12], is employed [21]. They pointed out that Slater's original arguments tacitly assumed that the exchange hole is static, whereas a more careful derivation should include the fact that it is dynamic, i.e., that the exchange potential arises from an exchange hole that changes as the electron on which it acts changes its position. W_x is then the work done by an external force in moving an electron from infinity to r in the presence of the electric field of the dynamic Fermi hole. Unlike the Slater potential, W_x reduces to the KS-LSD potential, i.e., to the exact $V_{x\sigma}^0$, in the homogeneous-electron-gas limit [18], has the correct asymptotic behavior, and exactly satisfies the virial-based Levy-Perdew theorem [27] analytically, which must be satisfied by the exact OEP [18]. This theorem, which states that the exact OEP should yield $\{\psi_{i\sigma}^0\}$ such that

$$E_x^{HF}\{\psi_{i\sigma}^0\} = -\int n^0(\mathbf{r})\mathbf{r}\cdot\nabla V_x^0(\mathbf{r})d\mathbf{r} \qquad (66)$$

is satisfied to $\approx 1\%$ by our $V_{x\sigma}$ results, although the calculated $E_x^{HF}[\{\psi_{i\sigma}\}]$ equals the numerically calculated $E_x^{HF}[\{\psi_{i\sigma}^0\}]$ to within a part per thousand.

It is interesting to note that W_x may be derived by making a simple approximation in Eq. (40) as shown in Appendix C. However, the resulting W_x no longer satisfies Eq. (47) and consequently does not satisfy Koopmans's theorem nor does it exhibit an integer discontinuity. Most significantly, its application results in the overestimate of the OEP energy, which is more than a factor of 3 larger than that provided by employing $V_{x\sigma}$, the exact solution of Eq. (48). Recently, Sahni and Harbola [34] have noted the fact [21] that the single-particle-energy eigenvalues ε_m, calculated by employing W_x as the exchange potential, are generally closer to minus the ionization energy than ε_m^{HF} suggesting that W_x should not be considered as an approximation to the exchange-only OEP but rather as a separate method that somehow incorporates some of the effects beyond those of exchange. We shall therefore forgo making any further detailed comparisons of the Harbola-Sahni potential calculations with the results of the other approximations appearing in Table I.

The result that the total energy calculated by employing $V_{x\sigma}$ is significantly closer to the OEP result than the LSD or Slater results suggests that $V_{x\sigma}$ more closely approximates $V_{x\sigma}^0$ than the other exchange-only approximations. This is in fact the case, as displayed in Fig. 1 for Ne, the lightest element in Table I for which the last complete subshell has p electrons, and in Fig. 2 for Cd, the heaviest element in Table I for which the last complete subshell has s electrons. We see that in both cases the Slater potential is much too strong and is significantly
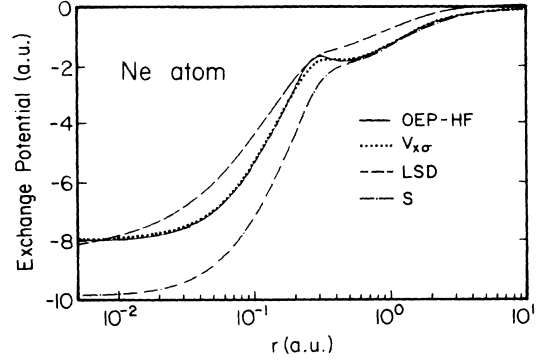

FIG. 1. Exchange potential (in a.u.) vs distance from the nucleus (in a.u.) for neon. The OEP refers to the exact Kohn-Sham result as calculated using a modification of the computer code in Ref. [19]. $V_{x\sigma}$ refers to the results obtained by employing Eq. (48): LSD refers to the local-spin-density exchange-only potential [3]: and S refers to the exact Slater potential given by Eq. (37).

deeper than is the OEP. However, when the second term on the rhs of Eq. (48) is added to $V_{x\sigma}^s$, the resulting $V_{x\sigma}$ is an excellent approximation to $V_{x\sigma}^0$, particularly in the regions between the bumps in $V_{x\sigma}^0$, which correspond to the electron shells, i.e, for the regions in space in which $n_{i\sigma} \gg n_{j\sigma}$ for $i \neq j$, $V_{x\sigma}$ is nearly identical to $V_{x\sigma}^0$, which is to be expected on the basis of the construction of $V_{x\sigma}$ discussed above Eq. (40). Moreover, $V_{x\sigma}$ is not merely an interpolation formula connecting these regions but clearly mimics the behavior of $V_{x\sigma}^0$ even in the vicinity of the bumps that appear in the intershell regions. In addition, we see that the exchange potential corresponding to the LSD approximation is generally too weak nearly everywhere in space and becomes a better approximation to $V_{x\sigma}^0$ for Cd, the atom with the higher atomic number. All of the above observations are valid for all atoms listed in Table I, including the result that the LSD result tends to improve as Z increases, although it never approximates $V_{x\sigma}^0$ as well as $V_{x\sigma}$ does.

In order for an approximate exchange potential to yield results close to those of the OEP, it must result in a
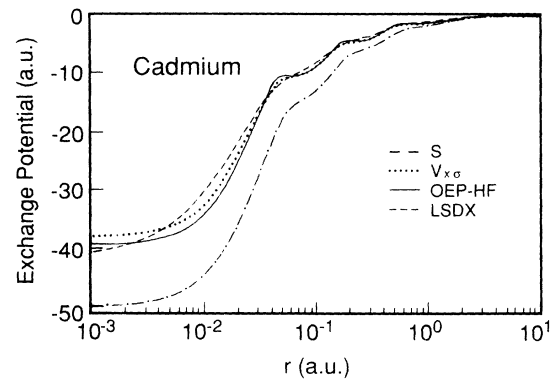

FIG. 2. Exchange potential (in a.u.) vs distance from the nucleus (in a.u.) for cadmium. The curves denoted OEP, $V_{x\sigma}$, LSD, and S refer to the same potentials described in Fig. 1.

Hartree potential that is a good approximation to the V_H calculated by employing $V_{x\sigma}^o$ as the exchange potential. This follows from the fact that the Hartree energy is a significant term in the expression for $E[\{\psi_{i\sigma}\}]$ as well as the fact that $\varepsilon_{m\sigma}$ is the eigenvalue of a Schrödinger-like equation that includes V_H. Figures 3 and 4 display the difference between the calculated Hartree potential and V_H^{HF}, the Hartree potential calculated using the density obtained from the solutions of the appropriate single-particle HF equations. We see that in both cases the V_H calculated using the OEP density is very close to the exact HF result, corresponding to the fact that n^o is nearly identical to n^{HF}, and the V_H obtained by employing $V_{x\sigma}$ as the exchange potential is an excellent approximation to the V_H^{HF} as well. In both cases, the result of employing $V_{x\sigma}^S$ leads to a Hartree potential that is significantly too large. This follows from the fact, as already seen in Figs. 1 and 2, that this exchange potential is too deep and thus leads to electrons being too localized near the nucleus. On the other hand, the V_H in the LSD approximation is too small, which follows from the fact that the corresponding exchange potential was too weak. Similar results obtain for all atoms in Table I, including the fact that the relative error in V_H in the LSD approximation becomes smaller for increasing atomic number.

We may also compare the accuracy of various exchange potentials by examining the expectation values of various one-electron operators. Of particular interest are $n(0)$, the value of the density at the origin, and $\langle r^2 \rangle$, which is proportional to the diamagnetic susceptibility, this latter expectation value being sensitive to the behavior of the density far from the nucleus.

Table II is a compilation of the values of $n(0)$ calculated by employing the exact HF results and those obtained from the OEP and the other approximate exchange potentials for the atoms listed in Table I. We find that the OEP result is nearly identical to that of HF, the two being the same through at least five significant figures except for Ne, which agrees through four. The $V_{x\sigma}$ results are systematically too low (except for Be) and are always within 2.5 parts per thousand of the HF and OEP results, with the discrepancy decreasing to ≈ 1 part per

thousand for large atomic number. The discrepancy between the OEP and the LSD results varies from being a factor of 3 larger than the $V_{x\sigma}$ discrepancy for light atoms to a factor of 2 for the heavy atoms, with the LSD results also being systematically too low, as expected. Finally, we see that the Slater result is systematically too large, as expected, with a discrepancy with the OEP result that is slightly larger than that for the LSD. If the LSD approximation is made on the Slater potential, the results (not tabulated) have an even larger discrepancy. Thus, for all atoms, the density at the origin obtained from employing $V_{x\sigma}$ is closer to both the HF and the OEP results than those obtained from either the LSD or the Slater approximations.

Similarly, we see from Table III that the OEP and HF results for $\langle r^2 \rangle$ are nearly identical for the ten atoms with a difference of < 1 part per thousand. Moreover, for every atom, the use of $V_{x\sigma}$ yields results that are closer to the OEP results than those provided by employing the LSD or Slater exchange potentials. The $V_{x\sigma}$ results for the noble gases are particularly accurate, being less than 1 part per thousand from the OEP and HF values. The largest discrepancy exists for Zn and Cd, for which the differences from the OEP values are 1.7% and 1.2%, respectively. This is undoubtedly due to the strong exchange interaction of the s states in the last filled subshell of these atoms with the filled d states immediately below them, which makes their precise description difficult. Similar difficulties arise in calculating properties sensitive to the precise description of the outer electron states of these atoms when the self-interaction correction is made to the LSD [35]. In addition, we find that the discrepancy in the LSD results is usually several times that of the $V_{x\sigma}$ results, with the values for the noble-gas atoms always above those of OEP and the results for the other atoms lying below the OEP values with the exception of Be. However, the results obtained by employing $V_{x\sigma}^S$ are always too small, as expected, with errors of 5–8 % for the noble-gas atoms and $> 15\%$ for the others.

The accuracy of the various approximations in describing the electron density in the interior of the atom may be discussed in terms of the calculated values of $\langle 1/r \rangle$. We

FIG. 3. The difference between the Hartree potential $V_H(\mathbf{r})$ calculated by employing different expressions for the exchange potential and the Hartree potential calculated using the HF density $V_H^{HF}(\mathbf{r})$ vs the distance from the nucleus for neon.
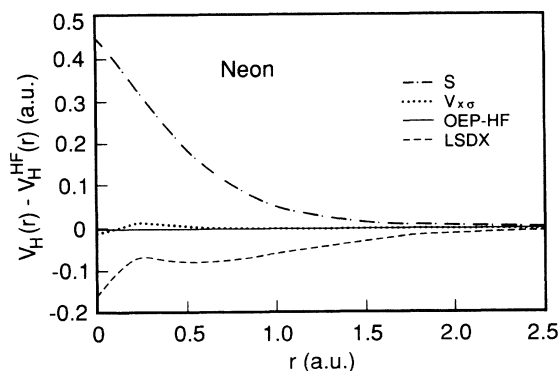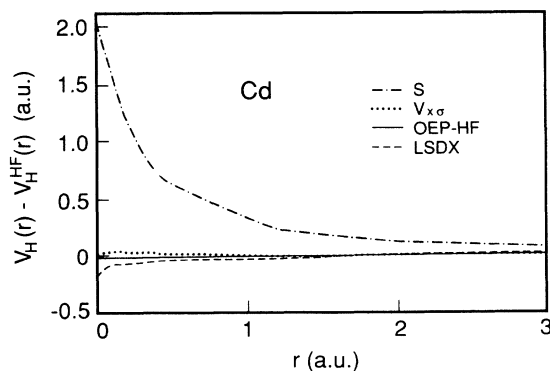
FIG. 4. The difference between the Hartree potential $V_H(\mathbf{r})$ calculated by employing different expressions for the exchange potential and the Hartree potential calculated using the HF density $V_H^{HF}(\mathbf{r})$ vs the distance from the nucleus for cadmium.

TABLE II. Values of $n(0)$, the electron density at the origin, for ten atoms with closed subshells calculated by employing various exchange-only approximations (in a.u.).

Atom	HF	OEP[a]	$V_{x\sigma}$[b]	LSD	Slater
Be	35.3877	35.3877	35.4426	34.7001	36.0089
Ne	619.922	619.930	618.310	614.230	625.820
Mg	1 093.72	1 093.73	1 091.15	1 085.12	1 104.09
Ar	3 839.78	3 839.78	3 832.60	3 818.69	3 864.60
Ca	5 319.61	5 319.64	5 310.47	5 293.06	5 352.63
Zn	18 447.7	18 447.6	18 421.7	18 387.2	18 526.2
Kr	32 235.9	32 235.9	32 194.1	32 144.3	32 351.3
Sr	38 042.8	38 043.0	37 995.1	37 939.7	38 175.4
Cd	77 641.6	77 641.7	77 561.0	77 475.6	77 859.1
Xe	111 219.4	111 219.6	111 112.7	111 003.7	111 496.5

[a]Calculated using a modified computer code of Ref. [19].
[b]Calculated using $V_{x\sigma}$ given by Eq. (48).

find that in this case the HF and OEP results are different by $\lesssim$ one part in one hundred thousand for all atoms listed in Table I. The values obtained by employing $V_{x\sigma}$ as the exchange potential are different from these results by less than one part in a thousand for Be, with the deviation decreasing for increasing atomic number to one part in ten thousand for large Z. The LSD results for $\langle 1/r \rangle$ are always too low, with a discrepancy at least ten times larger than those obtained by employing $V_{x\sigma}$. Furthermore, the results obtained by using $V_{x\sigma}^S$ lie above the OEP results, with a discrepancy that is larger than that of LSD and that unlike the other approximations, does not significantly improve for large Z.

The most interesting single-particle property and also the one that has been most difficult to accurately calculate using various approximate exchange functions is ε_m, which, as we have seen in Sec. II, has particular significance.

In Table IV, we present our results for the calculation of ε_m, $\bar{\varepsilon}_m^{HF}$ [defined in Eq. (25)], and of dE/df_m for the OEP [using a modification of Talman's code [19], denoted OEP[b]]; for our approximation to the OEP, $V_{x\sigma}$, discussed in Sec. III; and for the LSD and Slater exchange potentials for the ten atoms listed in Table I. The values of dE/df_m were obtained by calculating $\Delta E/\Delta f_m$ for small

variations (± 0.05) in the occupancy of the highest occupied atomic subshell. These results were checked by repeating the calculation by varying the occupancy of only one spin subshell in a spin-polarized calculation. In addition, we also list ε_m and $\bar{\varepsilon}_m^{HF}$ [23], using the same numerically calculated $V_{x\sigma}^o$ as in Wang et al. [18] [denoted OEP[a]]. The results for dE/df_m, using an extension of this code to include fractional occupancy, are not available. The HF eigenvalues ε_m^{HF} are listed for comparison.

We note that if the OEP calculations were the exact numerical solutions, then according to Eq. (31), the two numbers in the OEP[a] column and the three in the OEP[b] column should all be identical. The fact that they differ slightly arises from the difficulty in precisely solving the integral equation. It should be noted that for a given numerical solution of the OEP equation, the estimated accuracies of ε_m, $\bar{\varepsilon}_m^{HF}$, and dE/df_m are not the same. This follows from the fact that if the numerically calculated solution of the OEP equation is in error by $O(\delta)$, then the eigenvalue calculated from this potential, ε_m, can be expected to be in error by $O(\delta)$, whereas the total energy will be in error by $O(\delta^2)$. This is consistent with the fact that both OEP calculations for the energy are the same to 1×10^{-4} Ry, the precision of the results given in Ref. [18] (corresponding to differences of less than 1 ppm) but the

TABLE III. Values of $\langle r^2 \rangle$, for ten atoms with closed subshells calculated by employing various exchange-only approximations (in a.u.).

Atom	HF	OEP[a]	$V_{x\sigma}$[b]	LSD	Slater
Be	4.3297	4.3316	4.3255	4.4809	3.9064
Ne	0.9372	0.9372	0.9367	1.0036	0.8918
Mg	2.4676	2.4693	2.4610	2.4575	2.0538
Ar	1.4464	1.4465	1.4467	1.4889	1.3511
Ca	2.8283	2.8282	2.8174	2.7503	2.3348
Zn	1.1660	1.1648	1.1453	1.1392	0.9716
Kr	1.0981	1.0980	1.0985	1.1196	1.0162
Sr	2.0016	2.0006	1.9923	1.9294	1.6500
Cd	1.1325	1.1312	1.1180	1.1065	0.9685
Xe	1.1602	1.1600	1.1607	1.1716	1.0743

[a]Calculated using a modified computer code of Ref. [19].
[b]Calculated using $V_{x\sigma}$ given by Eq. (48).

ε_m calculated by employing these potentials may be different by as much as a few parts per thousand. On the other hand, the fact that E is in error by $O(\delta^2)$ implies that dE/df_m is in error by $O(\delta^2)$. The estimated accuracy of $\bar{\varepsilon}_m^{HF}$ generally lies between these limits, as can be seen from the following argument.

Whereas the value of ε_m^o depends explicitly on $V_{x\sigma}^o$, the value of $\bar{\varepsilon}_m^{oHF}$ depends only implicitly on $V_{x\sigma}^o$ through the value of the $\{\psi_{i\sigma}\}$ that must be employed in constructing $v_{m\sigma}\{\psi_{i\sigma}\}$ [as well as the value of $V_H(r)$, which is common to both calculations]. The value of $\bar{\varepsilon}_m^{oHF}$ can thus be expected to change at a slower rate than does ε_m^o as $V_{x\sigma}^o$ is varied about its exact value. We have studied this variation numerically by calculating ε_m^o and $\bar{\varepsilon}_m^{oHF}$ for the ex-

change potential given by $\lambda V_{x\sigma}^o$ where $V_{x\sigma}^o$ is the numerically calculated OEP and λ is nearly unity. We find that $\bar{\varepsilon}_m^{oHF}$ changes approximately one-third as rapidly as ε_m^o does. Thus we conclude that the most accurate value of ε_m^o is given by dE/df_m followed by $\bar{\varepsilon}_m^{HF}$, with the least accurate value given by the direct calculation of the eigenvalue, ε_m.

It follows from the above analysis that the most accurate approximation to ε_m^o is given by the value of dE/df_m calculated using our modification of Talman's code, appearing as the third entry for each atom in Table IV in the column denoted OEP[b]. These results are in each case within 0.0001 Ry of the corresponding OEP[b] calculation of $\bar{\varepsilon}_m^{HF}$ providing further support for the self-

TABLE IV. Values of ε_m, the single-particle eigenvalue corresponding to the highest-energy occupied state $\bar{\varepsilon}_m^{HF}$, defined by Eq. (25), and $dE/df_{m\sigma}$, calculated by employing various exchange-only approximations (in Ry) for ten atoms with closed subshells.

Atom		HF	OEP[a]	OEP[b]	$V_{x\sigma}$[c]	LSD	Slater
Be	$-\varepsilon_m$	0.6185	0.6182	0.6184	0.6177	0.3401	0.6529
	$-\bar{\varepsilon}_m^{HF}$	0.6185	0.6185	0.6185	0.6177	0.6246	0.5868
	$-dE/df_{m\sigma}$	0.6186		0.6185	0.6184	0.6149	0.6295
Ne	$-\varepsilon_m$	1.7008	1.6971	1.7014	1.6988	0.8861	1.8240
	$-\bar{\varepsilon}_m^{HF}$	1.7008	1.7016	1.7014	1.6988	1.7921	1.5202
	$-dE/df_{m\sigma}$	1.7009		1.7015	1.7021	1.6696	1.7109
Mg	$-\varepsilon_m$	0.5061	0.5059	0.5060	0.5048	0.2843	0.5681
	$-\bar{\varepsilon}_m^{HF}$	0.5061	0.5061	0.5060	0.5048	0.5085	0.4314
	$-dE/df_{m\sigma}$	0.5061		0.5061	0.5061	0.5080	0.5368
Ar	$-\varepsilon_m$	1.1820	1.1770	1.1815	1.1786	0.6676	1.2763
	$-\bar{\varepsilon}_m^{HF}$	1.1820	1.1817	1.1816	1.1786	1.2059	1.0163
	$-dE/df_{m\sigma}$	1.1821		1.1815	1.1817	1.1708	1.1990
Ca	$-\varepsilon_m$	0.3911	0.3908	0.3912	0.3901	0.2227	0.4491
	$-\bar{\varepsilon}_m^{HF}$	0.3911	0.3911	0.3913	0.3901	0.3880	0.3137
	$-dE/df_{m\sigma}$	0.3911		0.3913	0.3913	0.3954	0.4274
Zn	$-\varepsilon_m$	0.5850	0.5847	0.5855	0.5837	0.3707	0.5425
	$-\bar{\varepsilon}_m^{HF}$	0.5850	0.5858	0.5855	0.5837	0.6062	0.4610
	$-dE/df_{m\sigma}$	0.5850		0.5856	0.5856	0.5902	0.6476
Kr	$-\varepsilon_m$	1.0484	1.0424	1.0478	1.0440	0.5997	1.1347
	$-\bar{\varepsilon}_m^{HF}$	1.0484	1.0472	1.0468	1.0440	1.0645	0.8486
	$-dE/df_{m\sigma}$	1.0484		1.0468	1.0466	1.0390	1.0759
Sr	$-\varepsilon_m$	0.3569	0.3572	0.3572	0.3564	0.2055	0.4173
	$-\bar{\varepsilon}_m^{HF}$	0.3569	0.3575	0.3573	0.3564	0.3522	0.2700
	$-dE/df_{m\sigma}$	0.3569		0.3573	0.3574	0.3623	0.3970
Cd	$-\varepsilon_m$	0.5297	0.5307	0.5310	0.5301	0.3357	0.6588
	$-\bar{\varepsilon}_m^{HF}$	0.5297	0.5314	0.5310	0.5301	0.5401	0.3822
	$-dE/df_{m\sigma}$	0.5297		0.5311	0.5313	0.5381	0.5915
Xe	$-\varepsilon_m$	0.9146	0.9085	0.9145	0.9109	0.5314	0.9927
	$-\bar{\varepsilon}_m^{HF}$	0.9146	0.9133	0.9129	0.9109	0.9176	0.6905
	$-dE/df_{m\sigma}$	0.9145		0.9128	0.9126	0.9083	0.9454

[a]Reference [23].
[b]Calculated using a modified computer code of Ref. [19].
[c]Calculated using $V_{x\sigma}$ given by Eq. (48).

consistency of these calculations and are on average only 0.0002 Ry from the corresponding OEP^a calculation of $\bar{\varepsilon}_m^{HF}$. The high precision of the OEP^b results is consistent with the fact that these calculations satisfy the Levy-Perdew theorem to within 1 part in 10^4.

The major problem in calculating the eigenvalues ε_m^o is ensuring that the calculated $V_{x\sigma}^o \to 0$ as $r \to \infty$. This is usually accomplished by adding a constant to the potential so that it satisfies Eq. (21) at some large value of $r \equiv R$ and then employing Eq. (21) as the potential for $r > R$. Typically R is obtained from the solution of $R \psi_{m\sigma}^o(R) = 0.0001$ which yields R of order 10 a.u. However, even if the exact $V_{x\sigma}^o$ is different from the asymptotic value given by Eq. (21) by 1%, this procedure results in a constant shift of order 0.001 a.u. (0.002 Ry) from the exact value of the potential which leads to an error of this magnitude in the calculation of ε_m^o as found in the OEP^a eigenvalues for the noble-gas atoms. We have avoided this problem by employing Eq. (18) [with Eq. (20)] to give the exchange potential for $r > R$. Whereas Eqs. (18) and (21) yield the same result in the large-r limit, Eq. (18) is valid when $n_{m\sigma}(r)$ is the dominant contribution to $n_\sigma(r)$, a condition that is satisfied for smaller r than that given by Eq. (21). We find that our OEP^b calculations of ε_m are unchanged through five significant figures for s states when Eq. (18) is employed rather than Eq. (21) for $r > R$, but the ε_m corresponding to p states are ≈ 0.003–0.004 Ry deeper.

The resulting OEP^b eigenvalues, when Eq. (18) is employed, are listed in Table IV and are nearly identical to $\bar{\varepsilon}_m^{HF}$ and dE/df_m except for Kr and Xe which are nevertheless a significant improvement over the OEP^a calculation. We note that the values of $\bar{\varepsilon}_m^{HF}$ (as well as dE/df_m) are independent of the addition of a constant to the potential, which explains the excellent agreement between the values of $\bar{\varepsilon}_m^{HF}$ calculated by the OEP^a and OEP^b procedures, even though the ε_m calculated by the OEP^a are considerably different for p states. Finally, we observe that the best approximation to ε_m^o is very close to $\bar{\varepsilon}_m^{HF}$, as would be expected on the basis of Eq. (25), with the difference generally increasing in magnitude with increasing Z.

We now consider the accuracy of the approximate exchange potentials in calculating ε_m, $\bar{\varepsilon}_m^{HF}$, and dE/df_m. First of all, we note that unlike the OEP^a and OEP^b calculations, the results of employing $V_{x\sigma}$ given by Eqs. (48) and (64) are pairs of ε_m and $\bar{\varepsilon}_m^{HF}$ that satisfy Eq. (52) exactly as they should. The reason is that in this case, $V_{x\sigma}$ is given as an explicit functional of the $\{\psi_{i\sigma}\}$, which makes it much simpler to calculate this exchange potential with higher precision than is possible in numerically solving the OEP integral equation. Secondly, we note that, in agreement with the observation that dE/df_m is in error by $O(\delta^2)$, their calculated values, using this approximate $V_{x\sigma}$, are nearly identical to those calculated by the OEP^b method, being within 0.0002 Ry for all atoms except Ne, for which the difference is only ≈ 1 part in 3000. Finally, and most significantly, the direct calculations of the eigenvalues ε_m are remarkably accurate, being at most 0.4% from the best estimate of ε_m^o and of ε_m^{HF}

as well. Furthermore, these values of ε_m for the noble-gas atoms are even closer to ε_m^o than the direct calculation provided by the OEP^a procedure.

In comparing the $V_{x\sigma}$ results with those of LSD and $V_{x\sigma}^S$, we see that, as expected, the values of dE/df_m give the best approximation to ε_m^o but the deviation from the exact result is at least 20 times that of the results of the $V_{x\sigma}$ calculation. In addition, we note that although the $V_{x\sigma}^S$ results for the direct calculation of ε_m are too deep by approximately 10%, the LSD eigenvalues, as is well known, are too shallow by $\approx 40\%$. This is due to the fact that the LSD exchange potential has the wrong asymptotic form, approaching zero like $n^{1/3}$ as $r \to \infty$ instead of becoming equal to the correct result given by $v_{m\sigma}(\mathbf{r})$, as is the case for $V_{x\sigma}^S$. Finally, we observe that despite this fact, the values of $\bar{\varepsilon}_m^{HF}$ calculated in the LSD approximation are much closer to ε_m^o than are those calculated by employing $V_{x\sigma}^S$, the latter being consistently too shallow.

This result may be understood as follows. Suppose the set of orthornormal functions $\{\phi_{i\sigma}\}$ is a one-to-one approximation to $\{\psi_{i\sigma}^{HF}\}$. Then

$$\phi_{i\sigma} = \psi_{i\sigma}^{HF} + \delta\psi_{i\sigma} \tag{67}$$

so

$$\bar{\varepsilon}_{i\sigma}^{HF} \equiv \langle \phi_{i\sigma} | h_{i\sigma}^{HF} \{\phi_{j\sigma}\} | \phi_{i\sigma} \rangle$$

$$= \langle \psi_{i\sigma}^{HF} + \delta\psi_{i\sigma} | h_{i\sigma}^{HF} \{\psi_{i\sigma}^{HF}\} + \delta V_H + \delta v_{i\sigma} | \psi_{i\sigma}^{HF} + \delta\psi_{i\sigma} \rangle$$

$$= \varepsilon_{i\sigma}^{HF} + \langle \phi_{i\sigma} | \delta V_H + \delta v_{i\sigma} | \phi_{i\sigma} \rangle + O(\delta^2) \tag{68}$$

where δV_H and $\delta v_{i\sigma}$ are the changes in V_H and $v_{i\sigma}$ when these functionals are evaluated with $\{\phi_{i\sigma}\}$ instead of $\{\psi_{i\sigma}^{HF}\}$. Generally, if the $\{\phi_{i\sigma}\}$ are eigenfunctions of a single potential, V_σ, then the more attractive this potential is, the more localized will be the $\{\phi_{i\sigma}\}$. For sufficiently attractive V_σ, this results in the exchange potential $v_{i\sigma}$ being more negative than $v_{i\sigma}^{HF}$, i.e., $\delta v_{i\sigma} < 0$, and the resulting V_H becomes larger, i.e., $\delta V_H > 0$. Generally, $v_{i\sigma}$ varies more slowly than V_H does when the wave functions are varied, so although there is some cancellation, $\delta V_H + \delta v_{i\sigma}$ will usually have the same sign as δV_H and be of the same order of magnitude.

When $V_{x\sigma}^S$ is employed as the approximate exchange potential, the resulting potential is too attractive, leading to a Hartree potential that is too large for each atom, as illustrated in Figs. 3 and 4. Consequently, it follows from Eq. (68) that in the Slater approximation, $\bar{\varepsilon}_m^{HF}$ always lies above ε_m^{HF}, as seen in Table IV, even though in this approximation, ε_m lies below ε_m^{HF}. Similarly, when the LSD approximation is employed, the exchange potential is generally too weak, although a much better approximation than is $V_{x\sigma}^S$. The resultant δV_H is negative, as illustrated in Figs. 3 and 4, but much smaller in magnitude than in the Slater approximation. Thus, in the LSD approximation, $\bar{\varepsilon}_m^{HF}$ is much closer to ε_m^{HF} than in the case where $V_{x\sigma}^S$ is employed and generally lies below ε_m^{HF}, except in two cases (Ca and Sr), where the two are $< 5 \times 10^{-3}$ Ry apart.

The above analysis also provides some insight into the behavior of the ε_m when $V_{x\sigma}$ is employed. Since Eq. (52) is satisfied by our numerical procedures to within 10^{-6} Ry, it suffices to consider $\bar{\varepsilon}_m^{HF}$ given by Eq. (68). Then, since V_H is positive and much smaller in magnitude than in the LSD case, $\bar{\varepsilon}_m^{HF}$ will be closer to ε_m^{HF} than the LSD result and will generally be above ε_m^{HF}. The last remark is true for all atoms in Table IV except Cd, for which ε_m in the $V_{x\sigma}$ approximation lies deeper than ε_m^{HF} by only 4×10^{-4} Ry, but lies above ε_m^o. Thus the fact that Eq. (52) is satisfied, along with the result that $V_{x\sigma}$ results in $n(r)$ very close to $n^{HF}(r)$ and thus to small δV_H essentially guarantees that the eigenvalues ε_m obtained will be very close to the ε_m^{HF}. Similarly, using the same argument when the exact $V_{x\sigma}^o$ is employed, we conclude that the exact ε_m^o should be very close to ε_m^{HF}, which is indeed the case.

In addition, we note that since Eq. (68) is valid for all i it follows that if the $\{\phi_{i\sigma}\}$ is a good approximation to $\{\psi_{i\sigma}^{HF}\}$, then $\bar{\varepsilon}_{i\sigma}^{HF}$ will be very close to $\varepsilon_{i\sigma}^{HF}$, i.e., we could obtain an accurate approximation to $\varepsilon_{i\sigma}^{HF}$ for each i without the necessity of solving the nonlocal HF single-particle equations. As discussed at the beginning of Sec.

III, our construction of the equation satisfied by $V_{x\sigma}$ was based on an attempt to obtain an exchange potential that would result in single-particle eigenfunctions that closely approximated the corresponding HF single-particle orbitals.

In order to test how accurately the single-particle eigenfunctions approximate the HF orbitals when $V_{x\sigma}$ is employed as the exchange potential, we have calculated the overlap integral $\langle\psi_i^{HF}|\psi_i\rangle$ of corresponding orbitals. These overlap integrals for the two highest-energy occupied states for the atoms listed in Table I are tabulated in Table V. The value of the overlap integral for all lower-lying states is $>0.999\,955$. In addition, for purposes of comparison, we have also calculated the overlap integrals of both the KS-LSD eigenfunctions, $\langle\psi_i^{HF}|\psi_i^{LSD}\rangle$, and the Slater eigenfunctions, $\langle\psi_i^{HF}|\psi_i^S\rangle$, with the HF orbitals. The value of the overlap integral for all lower states for the KS-LSD and Slater orbitals is >0.9997 and 0.9977, respectively. We see that in all cases these overlap integrals are remarkably close to unity with the $V_{x\sigma}$ results yielding the largest overlap and the LSD results being larger than the Slater results for atoms heavier than Ne.

In order to make a more quantitative comparison, we

TABLE V. Comparison of overlap integrals calculated by employing various exchange-only approximations for the two highest occupied states with the corresponding Hartree-Fock orbitals for ten atoms with closed subshells.

Atom	$\langle\psi_i^{HF}|\psi_i\ ^a\rangle$	$\langle\psi_i^{HF}|\psi_i^{LSD}\rangle$	$\langle\psi_i^{HF}|\psi_i^S\rangle$	$\langle\psi_i^{OEP\ b}|\psi_i\ ^a\rangle$
Be(1s)	0.999 984	0.999 716	0.999 971	1.000 000
Be(2s)	0.999 970	0.999 723	0.997 660	0.999 991
Ne(2s)	0.999 986	0.999 810	0.999 969	0.999 997
Ne(2p)	0.999 996	0.999 423	0.999 536	0.999 998
Mg(2p)	0.999 989	0.999 835	0.999 578	0.999 999
Mg(3s)	0.999 907	0.999 737	0.990 436	0.999 975
Ar(3s)	0.999 980	0.999 917	0.999 287	0.999 997
Ar(3p)	0.999 980	0.999 675	0.998 761	0.999 994
Ca(3p)	0.999 968	0.999 879	0.998 782	0.999 993
Ca(4s)	0.999 875	0.999 341	0.985 430	0.999 964
Zn(3d)	0.999 809	0.998 946	0.999 251	0.999 985
Zn(4s)	0.998 962	0.997 503	0.985 321	0.999 698
Kr(4s)	0.999 859	0.999 749	0.999 677	0.999 989
Kr(4p)	0.999 972	0.999 718	0.998 308	0.999 993
Sr(4p)	0.999 951	0.999 885	0.998 261	0.999 992
Sr(5s)	0.999 851	0.998 852	0.981 459	0.999 954
Cd(4d)	0.999 845	0.999 403	0.998 913	0.999 983
Cd(5s)	0.999 087	0.997 597	0.983 821	0.999 712
Xe(5s)	0.999 794	0.999 624	0.996 768	0.999 987
Xe(5p)	0.999 974	0.999 805	0.997 952	0.999 993

[a] Calculated using $V_{x\sigma}$ given by Eq. (48).
[b] Calculated using a modified computer code of Ref. [19].

note that for normalized ϕ_i

$$1-|\langle \psi_i^{HF}|\phi_i\rangle|^2 = \sum_{j\neq i}^{\infty} |\langle \psi_j^{HF}|\phi_i\rangle|^2 \qquad (69)$$

so the value of the left-hand side of Eq. (69) is a measure of the deviation of ϕ_i from the corresponding ψ_i^{HF}. Applying this criterion, we find, using the results presented in Table V, that for the highest occupied state (except Ne), the LSD results have a deviation from HF that is $< \frac{1}{10}$ that of the Slater result. For lower-lying states, the LSD results are usually, but not always, an improvement over the Slater results. More significantly, the results of employing $V_{x\sigma}$ as the exchange potential yield deviations for the highest occupied state that are always smaller than those of LSD and $\approx \frac{1}{100}$ those obtained by using the Slater exchange approximation. Since $\langle \psi_i^{HF}|\psi_i\rangle > 0.999\,955$ for all lower-lying states when $V_{x\sigma}$ is employed, we conclude that this exchange potential results in eigenfunctions that are an excellent approximation to the HF orbitals for all states of these ten atoms. Moreover, we also see that employing our approximate OEP exchange potential results in eigenfunctions that are even closer to the OEP orbitals than they are to those of HF for the two highest occupied orbitals for all ten atoms considered. In addition, for all lower-lying states of these atoms, $\langle \psi_i^o|\psi_i\rangle \geq 0.999\,993$, which is another demonstration of how well $V_{x\sigma}$ approximates $V_{x\sigma}^o$ and suggests that the $\bar{\varepsilon}_{i\sigma}^{HF}$ calculated by employing these orbitals should not only closely approximate $\varepsilon_{i\sigma}^{HF}$ but closely approximate $\bar{\varepsilon}_{i\sigma}^{oHF}$ as well.

Table VI is a comparison of ε_i^{HF} with $\bar{\varepsilon}_{i\sigma}^{HF}$ calculated by employing our modification of Talman's OEP code, $V_{x\sigma}$, the KS-LSD approximation, and $V_{x\sigma}^S$, as well as the results of the direct eigenvalue calculation ε_i for each approximation for Zn. Zinc is chosen because in one sense it is the worst case for $V_{x\sigma}$ since, according to Table V, its 4s state has the smallest overlap integral with both the HF and the OEP 4s state. We find that for each i, ε_i^o is

significantly closer to the corresponding value calculated by employing $V_{x\sigma}$ than that obtained from either the LSD or the Slater approximations, which provides further support that $V_{x\sigma}$ more accurately approximates $V_{x\sigma}^o$ than the other exchange potentials. It is interesting to note that ε_i^S is always closer to ε_i^{HF} than is calculated by the other methods, including the OEP for all i except $i=m$. This is generally the case for the other atoms as well because $V_{x\sigma}^S$ reduces to $v_{i\sigma}$ in the limit in which $n_{i\sigma}$ dominates the density, whereas this is not true for the other approximations, except in the case $i=m$ for both $V_{x\sigma}^o$ and $V_{x\sigma}$. However, as we have seen in Sec. II, the physically meaningful quantity is $\bar{\varepsilon}_{i\sigma}^{oHF}$ since this quantity is equal to the rate of change of the total OEP energy with respect to the fractional occupation of the $i\sigma$ state (generalization of Janak's theorem) and is also equal to the difference of the total ground-state energy and the total unrelaxed energy with the $i\sigma$ state unoccupied (Koopmans's theorem). Similar statements are true for $\varepsilon_{i\sigma}^{HF}$ if the HF approximation is employed.

Comparing the calculated values of $\bar{\varepsilon}_i^{HF}$ for each approximation with $\bar{\varepsilon}_i^{oHF}$, we see that the LSD results are a significant improvement over those obtained from $V_{x\sigma}^S$, which are systematically too deep compared with $\bar{\varepsilon}_i^{HF}$ or $\bar{\varepsilon}_i^{oHF}$ by $\approx \frac{1}{10}$ the energy that $\bar{\varepsilon}_i^{SHF}$ underestimates the magnitude of these quantities. More significantly, we find that the $V_{x\sigma}$ results, $\bar{\varepsilon}_i^{HF}$, are a substantial improvement over the LSD results, with energy differences from $\bar{\varepsilon}_i^{oHF}$ from $\approx \frac{1}{10}$ to $\frac{1}{100}$ of those obtained from the latter approximation. In fact, the $V_{x\sigma}$ results for $\bar{\varepsilon}_i^{HF}$ are on the average even closer to ε_i^{HF} than are the calculated $\bar{\varepsilon}_i^{oHF}$, having a mean difference of 0.005 Ry from the HF result, which suggests that a more precise OEP calculation would bring $\bar{\varepsilon}_i^{oHF}$ even closer to ε_i^{HF} for all i, which, as we have seen from our discussion of Table II, must be true for $i=m$. Similarly, for all atoms in Table I, we find that the LSD is a significant improvement over $V_{x\sigma}^S$ in calculating accurate values of $\bar{\varepsilon}_i^{HF}$ and that the $V_{x\sigma}$ results are

TABLE VI. Comparison of ε_i^{HF} with $\bar{\varepsilon}_i^{HF}$ calculated in various exchange-only approximations for Zn (in Ry). Also listed are the values of the single-particle eigenvalues (ε_i) calculated in the same approximations.

Atomic state	HF	OEP[a]	$V_{x\sigma}$ [b]	LSD	Slater
1s	-706.609	-706.600	-706.611	-706.888	-704.028
		(-691.519)	(-691.103)	(-689.772)	(-700.618)
2s	-88.723	-88.708	-88.710	-88.951	-86.923
		(-83.431)	(-83.366)	(-82.942)	(-85.883)
2p	-77.850	-77.842	-77.849	-78.098	-75.958
		(-73.487)	(-73.505)	(-73.173)	(-76.313)
3s	-11.276	-11.268	-11.277	-11.468	-10.437
		(-9.591)	(-9.518)	(-9.040)	(-10.017)
3p	-7.679	-7.673	-7.681	-7.863	-6.856
		(-6.421)	(-6.372)	(-5.939)	(-6.892)
3d	-1.565	-1.556	-1.560	-1.703	-0.829
		(-1.076)	(-1.050)	(-0.696)	(-1.513)
4s	-0.5850	-0.5855	-0.5837	-0.6062	-0.4395
		(-0.5855)	(-0.5837)	(-0.3707)	(-0.7135)

[a]Calculated using a modified computer code of Ref. [19].
[b]Calculated using $V_{x\sigma}$ given by Eq. (48).

a significant improvement over the LSD results, with the maximum difference between $\bar{\epsilon}_i^{HF}$ and ϵ_i^{HF} or $\bar{\epsilon}_i^{oHF}$ being a few hundredths of a Rydberg even though the eigenvalue ϵ_i calculated in the $V_{x\sigma}$ approximation may be different by as much as tens of Ry.

V. APPLICATION OF APPROXIMATE OPTIMIZED EFFECTIVE POTENTIAL TO SPIN-POLARIZED SYSTEMS

Our discussion of the results of employing $V_{x\sigma}$ as the approximate exchange potential in Sec. IV was limited to atoms with closed subshells. Consequently, there is only a single exchange potential, i.e., $V_{x\uparrow} = V_{x\downarrow}$, for these systems. In this section, we investigate the accuracy of employing the spin-polarized potentials $V_{x\uparrow}$ and $V_{x\downarrow}$ for the simplest open-shell atoms, i.e., Li, Na, and K, as well as study the accuracy of employing $V_{x\sigma}$ to approximate the exchange potential as a function of fractional occupancy of the highest-energy occupied state. Finally, we demonstrate numerically the existence of the integer discontinuity in $V_{x\sigma}$ as a spin subshell is completely filled.

Table VII is analogous to Table I and presents the results for the total energy for Li, Na, and K obtained by performing a spin-unrestricted Hartree-Fock (SUHF) calculation for each atom. In addition, we tabulate (in mRy) the overestimate of this energy by the energy calculated using the spin-polarized generalization of our modification of Talman's code for the pair of OEP potentials, $V_{x\sigma}^o$. Finally, we tabulate the overestimate of the OEP energy by the results obtained by employing $V_{x\sigma}$ given by the solutions of Eq. (48) and by the LSD approximation. (The results obtained by employing $V_{x\sigma}^S$ provide significantly larger overestimates of the energy as found in Sec. IV and will not be further discussed.)

We find that the trends displayed by the results tabulated in Table I are evident here as well, i.e., the fractional overestimate of the energy calculated by employing the OEP, $V_{x\sigma}$, or the LSD approximation significantly decreases with increasing Z, the results of employing $V_{x\sigma}$ overestimate the OEP result by only $\approx \frac{1}{3}$ of the OEP overestimate of the SUHF result, and, most significantly, the overestimate of the OEP total energy by the LSD results is at least eight times larger than the overestimate provided by the $V_{x\sigma}$ results.

Further evidence supporting the conclusion that the pair of spin-polarized $V_{x\sigma}$ closely approximate the corresponding OEP potentials is presented in Figs. 5 and 6.

We see that for potassium (where we have assigned the unpaired electron to the $4s\uparrow$ state), both $V_{x\uparrow}$ and $V_{x\downarrow}$ are an excellent approximation to the corresponding OEP results except possibly at the bumps in the latter, which occur in the intershell regions. We find that the major difference between the spin-up and spin-down OEP potentials is the small bump that appears in the spin-up potential near $r \approx 2$ a.u. corresponding to the intershell region between $n = 3$ and 4, which is missing in the spin-down potential because the $n = 4$ spin-down states are all unoccupied. It is clear that $V_{x\sigma}$ accurately accounts for this difference and is nearly identical to $V_{x\sigma}^o$ for $r > 1$ a.u. We also observe, as in the previous discussion concerning atoms with closed subshells, that the LSD approximation is nearly everywhere too weak and approaches zero too rapidly because $V_{x\sigma}^{LSD} \sim n_\sigma^{1/3}$, which $\rightarrow 0$ exponentially fast as $r \rightarrow \infty$ instead of approaching zero like $-1/r$. This is more evident in the graph of the spin-down potential because the exponential decay of the spin-down density is much faster, depending essentially on the more tightly bound $3p\downarrow$ state than the density of the $4s\uparrow$ state, which determines the decay of the LSD·spin-up exchange potential.

It is also interesting to compare the calculated $\epsilon_{m\sigma}$ with $\bar{\epsilon}_{m\sigma}^{HF}$ and $dE/df_{m\sigma}$ for each spin projection, which should be equal to each other in an exact OEP or SUHF calculation, as discussed in Sec. II. In addition, $\epsilon_{m\sigma} = \bar{\epsilon}_{m\sigma}^{HF}$ if the exact $V_{x\sigma}$ given by Eq. (48) is employed. We observe from Table VIII that Eq. (31) is almost exactly satisfied by the OEP results for the most weakly bound electron, i.e., spin up, for each atom. In all cases, for both spin up and spin down, the value of $dE^o/df_{m\sigma}$, which we believe is the most accurate estimate of the exact $\epsilon_{m\sigma}^o$, is very close to the value of $\bar{\epsilon}_{m\sigma}^{HF}$. The value of the direct calculation of the energy eigenvalue, which we believe is the least accurate estimate, is within 0.05% of these results.

In considering the accuracy of the $V_{x\sigma}$ calculations, we note that, as in the unpolarized case, the condition that $\epsilon_{m\sigma} = \bar{\epsilon}_{m\sigma}^{HF}$ is exactly satisfied to the precision of the tabulation and is in fact satisfied to 1×10^{-6} Ry by our numerical procedures. In addition, the calculated $\epsilon_{m\uparrow}$ is within 0.0002 Ry of the best estimate of $\epsilon_{m\uparrow}^o$ and $\epsilon_{m\downarrow}$ is within 0.3% of the best estimate of $\epsilon_{m\downarrow}^o$ and the values of $dE/df_{m\sigma}$ are within one part in 3000 of the values of $dE^o/df_{m\sigma}$. On the other hand, the LSD results for the direct calculation of $\epsilon_{m\sigma}$ are too shallow by at least 40% for $\sigma = \uparrow$ and at least 25% too shallow for $\sigma = \downarrow$ (both re-

TABLE VII. Comparison of overestimates of the spin-polarized OEP total energy E^o calculated in various spin-polarized approximations compared with the overestimate of the spin-unrestricted Hartree-Fock (SUHF) total energy by E^o (in mRy) for three alkali atoms.

Atom	$-E^{SUHF}$ (Ry)	$E^{oa} - E^{SUHF}$	$E^b - E^o$	$E^{LSD} - E^o$
Li	14.865050	0.51	0.12	7.74
Na	323.7159	4.6	1.4	30.6
K	1198.3297	11.6	3.9	32.7

[a]Calculated using a spin-polarized extension of the computer code of Ref. [19].
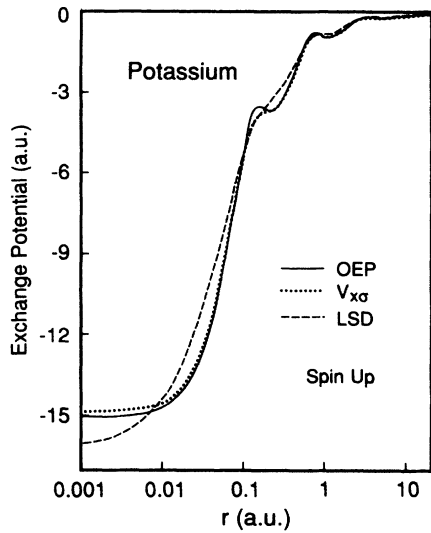[b]Calculated using $V_{x\sigma}$ given by Eq. (48).

FIG. 5. Exchange potential for spin up for potassium vs the distance from the nucleus. The OEP, $V_{x\sigma}$, and LSD refer to the same potentials as described in Fig. 1.
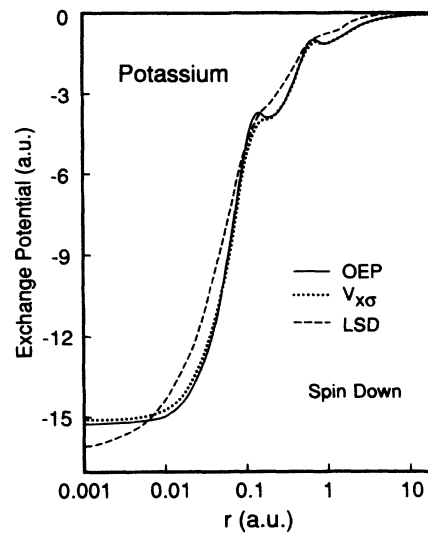

FIG. 6. Exchange potential for spin down for potassium vs the distance from the nucleus. The OEP, $V_{x\sigma}$, and LSD refer to the same potentials as described in Fig. 1.

sults arising from the observation that this potential is a poor approximation to $V_{x\sigma}^o$ for large r). The fact that these LSD eigenvalues are not close to a self-consistent OEP calculation is further demonstrated by the large differences between $\varepsilon_{m\sigma}$ and $\bar{\varepsilon}_{m\sigma}^{HF}$ evaluated in this approximation. As expected, the values of $\bar{\varepsilon}_{m\sigma}^{HF}$ are a much better approximation to the exact OEP results, but are

still not consistently as close to the exact result as the direct eigenvalue calculation when $V_{x\sigma}$ is employed.

We may also test the accuracy of any approximate exchange potential by comparing the separate spin densities with those calculated by SUHF as well as by the $V_{x\sigma}^o$. The values of $n_{\uparrow}(0)$, $n_{\downarrow}(0)$, and the resultant spin density at the nucleus, $m(0) \equiv n_{\uparrow}(0) - n_{\downarrow}(0)$, are presented in

TABLE VIII. Values of $\varepsilon_{m\sigma}$, $\bar{\varepsilon}_{m\sigma}^{HF}$, and $dE/df_{m\sigma}$ for $\sigma = \uparrow$ and $\sigma = \downarrow$ calculated by employing various spin-polarized exchange-only approximations (in Ry) for three alkali-metal atoms.

Atom (electron state)		SUHF	OEP[a]	$V_{x\sigma}$ [b]	LSD
Li(2s ↑)	$-\varepsilon_{m\sigma}$	0.3927	0.3926	0.3924	0.2009
	$-\bar{\varepsilon}_{m\sigma}^{HF}$	0.3927	0.3926	0.3924	0.3944
	$-dE/df_{m\sigma}$	0.3927	0.3926	0.3925	0.3895
Li(1s ↓)	$-\varepsilon_{m\sigma}$	4.9374	4.9377	4.9343	3.6092
	$-\bar{\varepsilon}_{m\sigma}^{HF}$	4.9374	4.9377	4.9343	4.9801
	$-dE/df_{m\sigma}$	4.9375	4.9378	4.9379	4.9068
Na(3s ↑)	$-\varepsilon_{m\sigma}$	0.3644	0.3641	0.3640	0.1934
	$-\bar{\varepsilon}_{m\sigma}^{HF}$	0.3644	0.3642	0.3640	0.3686
	$-dE/df_{m\sigma}$	0.3644	0.3642	0.3642	0.3667
Na(2p ↓)	$-\varepsilon_{m\sigma}$	3.0341	3.0339	3.0311	1.9940
	$-\bar{\varepsilon}_{m\sigma}^{HF}$	3.0341	3.0354	3.0311	3.1041
	$-dE/df_{m\sigma}$	3.0342	3.0355	3.0361	3.0152
K(4s ↑)	$-\varepsilon_{m\sigma}$	0.2953	0.2954	0.2954	0.1609
	$-\bar{\varepsilon}_{m\sigma}^{HF}$	0.2953	0.2954	0.2954	0.2975
	$-dE/df_{m\sigma}$	0.2953	0.2954	0.2955	0.3002
K(3p ↓)	$-\varepsilon_{m\sigma}$	1.9070	1.9066	1.9012	1.2811
	$-\bar{\varepsilon}_{m\sigma}^{HF}$	1.9070	1.9069	1.9012	1.9109
	$-dE/df_{m\sigma}$	1.9070	1.9069	1.9071	1.9013

[a]Calculated using a spin-polarized extension of the computer code of Ref. [19].
[b]Calculated using $V_{x\sigma}$ given by Eq. (48).

Table IX for Li, Na, and K. First of all, we note that the SUHF and OEP results are almost identical for the separate spin densities, with differences of less than 15 ppm for Li and decreasing to only 4 ppm for K. The $V_{x\sigma}$ results for $n_\uparrow(0)$ and $n_\downarrow(0)$ are within 0.2% of the OEP results and the deviation of the LSD results is about three times larger, which is similar to the discrepancy in $n(0)$ for the atoms with closed subshells. The resulting values of $m(0)$ for both SUHF and OEP calculations are nearly identical, with differences of at most $\approx 1\%$ for K. However, because $m(0)$ is a very small fraction of the separate spin densities, $n_\uparrow(0)$ and $n_\downarrow(0)$, small percent deviations in the latter lead to much larger deviations in the former. In fact, the deviations in the separate spin densities are much larger in magnitude than $m(0)$. More detailed analysis reveals that the contribution to $m(0)$ from the highest-energy s state, which for these atoms is unpaired, is $\approx 90\%$ of the total OEP, $V_{x\sigma}$, and LSD result, with reasonable accuracy, while the contribution of the inner subshells in both the $V_{x\sigma}$ and LSD approximations is very small with large percent errors compared with the OEP results. Thus the deviation in the LSD result for $m(0)$ from the OEP value is $\approx 10\%$ for Li, and increases to $\approx 15\%$ for Na and K, while the deviation in the $V_{x\sigma}$ values is approximately $\frac{2}{3}$ as large. For larger values of r, the values of $m(r)$ tend to decrease with the $V_{x\sigma}$ results more closely approximating the SUHF and OEP values than those of LSD as depicted in Fig. 7 for K.

We have also studied the accuracy of the above exchange-only potentials in calculating the properties of N, P, and As, each of which has a highest-energy spin subshell with three spin-polarized p electrons, and Mn, whose highest occupied states are two $4s$ electrons that lie above five spin-polarized $3d$ electrons. We find that in each case the spin-polarized $V_{x\sigma}$ results for the energy are again only $\approx \frac{1}{3}$ as large an overestimate of the OEP result as the OEP result is above the SUHF value. In addition, the $V_{x\sigma}$ results for $\varepsilon_{m\sigma}$ are within 0.004 Ry of the best estimate of the OEP values for both spin-up and spin-down states, whereas the LSD results for the highest $\varepsilon_{m\sigma}$ deviate from the OEP results by more than 40%. Moreover, the separate spin densities $n_\uparrow(0)$ and $n_\downarrow(0)$ ob-
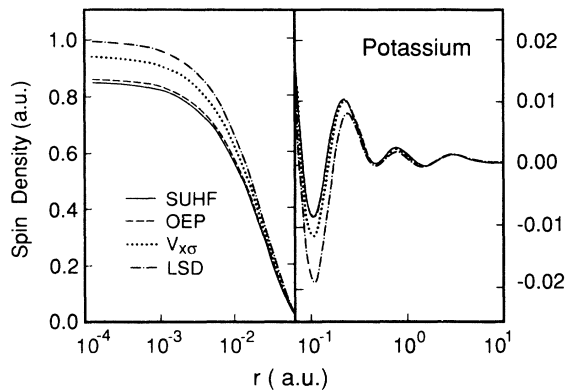

FIG. 7. The net spin density $m(r)$ (in a.u.) for potassium vs the distance from the nucleus (in a.u.). The OEP, $V_{x\sigma}$, and LSD refer to the same potentials as described in Fig. 1. SUHF refers to spin-unrestricted Hartree-Fock calculation.

tained from the OEP calculation are again only a few ppm from the SUHF result and the deviation of the $V_{x\sigma}$ values is less than four parts per thousand, which is about half the deviation in the LSD results. However, unlike the situation for the alkali-metal atoms, there are no unpaired s electrons that make the dominant contribution to $m(0)$. Instead, $m(0)$ arises from the polarization of these pairs by the subshell occupied by totally polarized p or d states with more than one s subshell making a significant contribution to $m(0)$. Moreover, for a given atom, these separate s subshell contributions have possibly different signs so there is a considerable amount of cancellation and, in addition, as in the case of the alkali-metal atoms, the OEP contributions from these separate s subshells containing electrons of opposite spin are not always well approximated by the $V_{x\sigma}$ or LSD calculations. Consequently, the values of $m(0)$ calculated in these approximations are unreliable and may even have the wrong sign. However, it should be noted that as r increases, the contributions to $m(r)$ from the totally spin-polarized highest-energy occupied p states (for N, P, and As) and d states (for Mn) rapidly dominate the contributions of the other subshells and the $V_{x\sigma}$ and LSD approx-

TABLE IX. Spin densities at the origin, $n_\sigma(0)$, and net spin density at the origin, $m(0)=n_\uparrow(0)-n_\downarrow(0)$, for three alkali-metal atoms calculated in various spin-polarized exchange-only approximations (in a.u.).

Atom		SUHF	OEP[a]	$V_{x\sigma}$[b]	LSD
Li	$n_\uparrow(0)$	7.019 75	7.019 84	7.032 03	6.837 59
	$n_\downarrow(0)$	6.795 06	6.794 96	6.793 39	6.635 99
	$m(0)$	0.224 68	0.224 88	0.238 64	0.201 60
Na	$n_\uparrow(0)$	417.203 3	417.206 5	416.189 6	413.679 4
	$n_\downarrow(0)$	416.555 9	416.561 5	415.465 9	412.946 3
	$m(0)$	0.647 4	0.645 0	0.723 7	0.733 1
K	$n_\uparrow(0)$	2269.756 3	2269.766 7	2265.715 8	2257.920 9
	$n_\downarrow(0)$	2268.902 9	2268.906 8	2264.773 0	2256.923 2
	$m(0)$	0.853 4	0.859 9	0.942 8	0.997 7

[a]Calculated using a spin-polarized extension of the computer code of Ref. [19].
[b]Calculated using $V_{x\sigma}$ given by Eq. (48).

imations yield values for $m(r)$ that are very close to both the SUHF and the OEP results for $r \gtrsim 0.2$ a.u., for those cases in which these approximations do not give the correct sign for $m(0)$. Consequently, the deviations in the calculated spin density are significant only within a small fraction of the volume of these atoms in which the value of $m(r)$ is relatively small and in the region of space in which $m(r)$ reaches its maximum value, the spin density is accurately approximated by both the $V_{x\sigma}$ and LSD results.

Thus far, our analysis has been restricted to testing the accuracy of $V_{x\sigma}$ for integral occupancy of the individual orbitals. However, the full implications of the KS theory are best understood by treating systems in which the particle number is allowed to vary so that the highest-energy occupied state has a fractional occupancy [4–7] $0 < f_{m\sigma} \leq 1$.

As an example, we consider the magnesium atom $(Z = 12)$ as the number of electrons is continuously increased from $N = 9$ to 12. Figure 8 is a graph of the total SUHF energy as well as the energy calculated using the spin-polarized $V_{x\sigma}$ potentials, both as a function of N, the number of electrons in the system. The $V_{x\sigma}$ results overestimate the SUHF total energy by less than 0.008 Ry for all N. The results of the spin-polarized OEP calculations (not shown) lie above the SUHF results by $\lesssim 0.006$ Ry and lie below the $V_{x\sigma}$ total energy by less than 0.002 Ry. We note that there are cusps in the E versus N curves at integer values of N as expected, and the values of the slopes, i.e., $dE/df_{m\sigma}$, on both sides of each cusp are within 0.3% of the eigenvalues $\varepsilon_{m\sigma}$ calculated by employing $V_{x\sigma}$ as the exchange potential. In an exact SUHF or OEP calculation, these quantities are of course exactly equal according to Eq. (31).
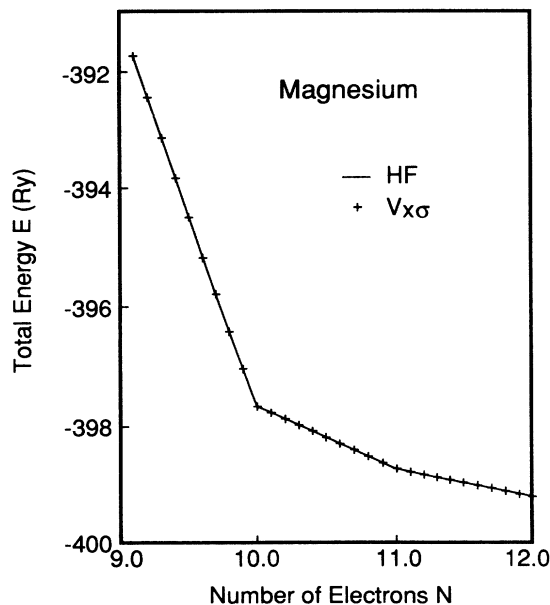
Moreover, the eigenvalues of the highest occupied spin-up and spin-down single-particle states calculated by employing $V_{x\sigma}$ are in excellent agreement with those obtained from the SUHF, not merely at integral values of N but for $9 < N < 12$, as shown in Fig. 9. Here the lower-energy state is completely filled and the higher-energy state is fractionally occupied when N is nonintegral. We see from the figure that $\varepsilon_{m\uparrow}$ and $\varepsilon_{m\downarrow}$ are both very close to the corresponding values of $\varepsilon_{m\uparrow}^{HF}$ and $\varepsilon_{m\downarrow}^{HF}$ even when these eigenvalues significantly change as the occupancy of the highest occupied energy state is increased. Thus for $9 < N < 10$, the value of $\varepsilon_{2p\downarrow}^{HF}$ gradually rises as the $2p\uparrow$ spin subshell is filled from a total occupancy greater than two to an occupancy of three electrons. At $N = 10$, the $2p\uparrow$ and $2p\downarrow$ subshells are filled, so $\varepsilon_{2p\uparrow}^{HF} = \varepsilon_{2p\downarrow}^{HF}$. The strong dependence of $\varepsilon_{2p\downarrow}^{HF}$ on the fractional occupancy of the highest occupied level can be attributed mainly to the increase in the Hartree potential as the $2p\uparrow$ subshell is filled. Similarly, in the ranges $10 < N < 11$ and $11 < N < 12$, the single-particle eigenvalues corresponding to the filled $2p\uparrow$ and $3s\downarrow$ subshells, respectively, also rise with increasing fractional occupancy of the highest-energy occupied subshell for the same reason. On the other hand, as the $3s$ spin subshells are filled, these highest occupied states have $\varepsilon_{3s\sigma}$ almost independent of fractional occupancy, as would be expected for the highest occupied state in a theory that included correlation effects [4]. In view of this fact, the dependence of $\varepsilon_{2p\uparrow}$ on fractional filling of this level for $9 < N < 10$ and the related slight bowing of the E versus N curve in this interval is an artifact of the SUHF theory, i.e., an exact calculation including correlation would yield E versus N as a series of straight lines with cusps at integral values of N. It then follows that $\varepsilon_{m\sigma} = dE/df_{m\sigma}$ would be independent of $f_{m\sigma}$ with $m\sigma$ being the highest occupied state. Nevertheless, it should be noted that the $V_{x\sigma}$ results for $\varepsilon_{m\sigma}$ for both spin projections are as close to the values of the corresponding values of $\varepsilon_{m\sigma}^{HF}$ and $\varepsilon_{m\sigma}^{o}$ (not

FIG. 8. The total energy E (in Ry) for magnesium vs the number of electrons N. HF refers to spin-unrestricted Hartree-Fock calculations and $V_{x\sigma}$ is described in Fig. 1.
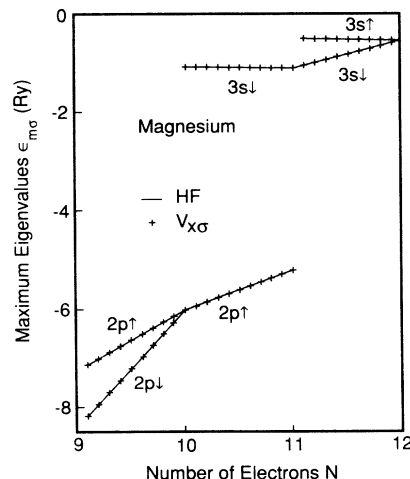

FIG. 9. The maximum energy eigenvalues $\varepsilon_{m\sigma}$ (in Ry) for spin up and spin down for magnesium vs the number of electrons N. HF refers to spin-unrestricted Hartree-Fock calculations and $V_{x\sigma}$ is described in Fig. 1.

shown) for fractional N as they are for integral N, while the LSD results (not shown) remain 25–40 % too small in magnitude.

Finally, it is interesting to examine how the exchange potential changes discontinuously when an unoccupied spin subshell begins to be filled. Figure 10 displays the self-consistent solutions of Eq. (48) for $V_{x\uparrow}$ for magnesium with $N = 11$ electrons, i.e., a filled $3s\downarrow$ and an empty $3s\uparrow$ subshell, and $V_{x\uparrow}$ for $N = 11 + f$, where $f = 10^{-6}$, i.e., a filled $3s\downarrow$ and a partially filled $3s\uparrow$ subshell. In agreement with our discussion in Sec. III, we see from Fig. 11 that for $f = 10^{-6}$, the discontinuity in the potential is almost exactly constant for $r < 5$ a.u. with the difference $\sim -1/r$ in the large-r limit. In addition, we see that the size of this discontinuity is ≈ 1 Ry, which is nearly identical to that required to yield the correct value of $\varepsilon_{3s\uparrow}$ when $V_{x\uparrow}^{(N=11)}(r)$ was the exchange potential that resulted in the correct value of $\varepsilon_{2p\uparrow}$ when the $3s\uparrow$ state was empty (see Fig. 9). We also note from Fig. 11 that for much smaller fractional occupancy, i.e., $f = 10^{-15}$, the region of constant discontinuity extends further in space but maintains the same value. The extension to larger r follows from the fact that the asymptotic form of the potential given by Eq. (49) becomes valid only in the limit in which $n_{m\sigma} \gg n_{i\sigma}$ for all $i < m$, which requires larger r if f is decreased. The reason the size of the constant discontinuity remains essentially unchanged is that for $f = 10^{-6}$, the region for which the constant discontinuity obtains is so large it contains almost the entire $3s\uparrow$ state, so Eq. (47) remains satisfied without any additional change in the size of $V_{x\uparrow}$ in this region [note that it follows from Eq. (13) that $v_{m\sigma}$ is essentially independent of $f_{m\sigma}$ for $f_{m\sigma} \ll 1$]. However, if the fractional occupancy of the $3s\uparrow$ state is increased to $f = 10^{-2}$, then the region of constant discontinuity is reduced to one that is sufficiently small that it no longer contains nearly the entire $3s\uparrow$ state. Consequently, in order that Eq. (47) remain valid, $V_{x\uparrow}$ must increase by a slightly larger constant when the value of f is increased from 10^{-6} to 10^{-2}. These results concerning the range of the constant discontinuity as a function of f as well as the size of the
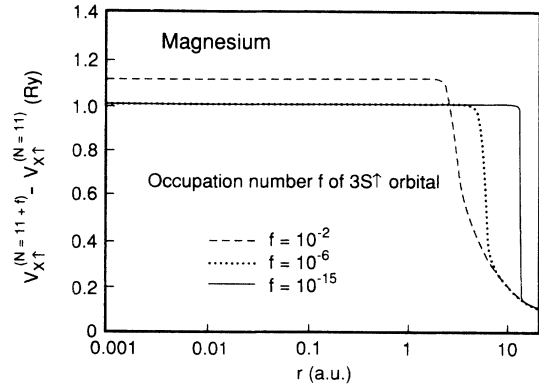
FIG. 11. The difference in the spin-up exchange potential for Mg^+ with fractional occupancy f of the $3s\uparrow$ state, $V_{x\uparrow}^{(N=11+f)}$, and the spin-up exchange potential for $f = 0$, $V_{x\uparrow}^{(N=11)}$ (in Ry) vs the distance from the nucleus (in a.u.) for three values of f.

discontinuity are in excellent agreement with numerical results obtained from directly solving the OEP integral equation. However, accurate $V_{x\sigma}$ results are much easier to obtain due to instabilities in the OEP equation for small f [7].

VI. CONCLUDING REMARKS

The exchange potential $V_{x\sigma}$, derived in Sec. III as a functional of the occupied orbitals $\{\psi_{i\sigma}\}$, is an excellent approximation to the exact $V_{x\sigma}^{o}$; $V_{x\sigma}$ exhibits many of the analytic properties of the exact OEP and yields results for E, $\varepsilon_{m\sigma}$, and $n_\sigma(r)$ as well as the integer discontinuity in the potential that are in excellent agreement with the $V_{x\sigma}^{o}$ results. In addition, these results are in much better agreement with the exact OEP values than those given by the LSD or Slater approximations.

Moreover, the numerical results presented in Secs. IV and V demonstrate that the OEP values for E, $\varepsilon_{m\sigma}$, and $n_\sigma(r)$ are all very close to the corresponding HF or SUHF results. Consequently, in addition to closely approximating the OEP, the $V_{x\sigma}$ results may be used to serve as an excellent approximation to HF and SUHF results as well.

Furthermore, the agreement between the calculated values of E and $\varepsilon_{m\sigma}$ for both spin polarizations calculated by employing the spin-polarized $V_{x\sigma}$ are remarkably close to both the corresponding HF and OEP as a function of fractional filling f of the highest-energy single-particle state even when the $\varepsilon_{m\sigma}$ are strongly dependent on f. The fact that the valence electron states are so accurately described, as determined by the accuracy of the $\varepsilon_{m\sigma}$, the values of $\langle r^2 \rangle$, or the fact that the overlap integral with either the corresponding HF or OEP wave function is so close to unity, supports the contention that this method, especially when extended to include correlation effects, will provide an accurate procedure for molecular calculations. In addition, for the first time, an explicit functional of the orbitals has been given that displays the integer discontinuity that is known to exist in the KS potential and that is important for maintaining the prin-
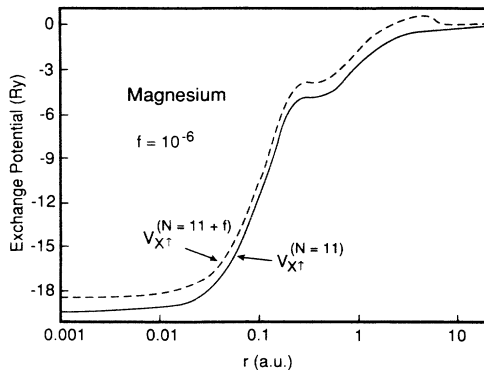

FIG. 10. Spin-up exchange potentials $V_{x\uparrow}$ (in Ry), for Mg^+ for filled $2p$ subshells and empty $3s\uparrow$ subshell (lower curve) and for partially filled $3s\uparrow$ state with $f_{3s\uparrow} = 10^{-6}$ plotted as a function of the distance from the nucleus (in a.u.).

ciple of integer preference in molecules, as well as being crucial for the accurate calculation of electron energy bands in solids. We note that the value of this discontinuity in Mg is ≈ 1 Ry, which is the same order as the underestimate the LSD approximation makes in calculating the band gaps of noble-gas solids.

In completing this discussion on the accuracy of various quantities calculated by employing $V_{x\sigma}$ as the exchange potential, we compare our results with those obtained from the exchange-only local-spin-density approximation with self-interaction correction [10] (LSDSIC). Although this approximation lies outside the usual KS theory because it employs a different orbital-density-dependent potential for each state, it has proved to be a useful method for correcting some of the problems inherent in the LSD. In the following discussion, we shall refer to the work of Li [35], who performed LSDSIC calculations for the ten atoms listed in Table I. We find that for the atoms heavier than Be, the LSDSIC values of E, given by Eq. (8) with $\psi_{i\sigma}^o$ replaced by the LSDSIC $\psi_{i\sigma}$, not only lie above the $V_{x\sigma}$ result but lie above those obtained by employing the Harbola-Sahni potential [21]. (The LSDSIC results for the energy for Be are lower than E^o, reflecting the fact that these orbitals, for a given σ, are not eigenfunctions of a single Hamiltonian and therefore E^o is not a lower bound to the LSDSIC energy.) In addition, although the LSDSIC method makes a significant improvement over the LSD in correctly calculating ε_m, the results for the p states are still in error by an average of 8% and in all cases the ε_m for the ten atoms listed in Table I calculated by employing $V_{x\sigma}$ are much closer to both the HF and the OEP results. Furthermore, the LSDSIC density and, consequently, Hartree potential do not approximate the HF results as well as the corresponding $V_{x\sigma}$ results, nor are the overlap integrals with corresponding HF orbitals as large. We thus conclude that although the individual LSDSIC single-particle potentials are expected to mimic the HF $v_{i\sigma}$, the results of employing the single $V_{x\sigma}$ given by Eq. (48) lie closer to the HF values.

Finally, in order to perform realistic calculations on atoms, molecules, and solids, it is necessary to include the effects of electron correlation. In principle, the correlation energy functional may be written as a functional of the spin densities n_σ, i.e., $E_c[\{n_\sigma\}]$. If such a functional could be found, then it could be added to the expression for the Hartree energy in Eq. (8) and would lead to an additional contribution to the Hartree potential given by $v_{c\sigma}(\mathbf{r}) = \delta E_c/\delta n_\sigma(\mathbf{r})$, with the OEP exchange potential still given by the solution of Eq. (15). In practice, however, it is difficult to construct such a functional that includes the self-interaction correction, and functionals that depend on orbital densities, i.e., LSDSIC [10], have been employed.

In this regard we note that the OEP method is not limited to the exchange-only case [6,7] but can be applied to

any possible $E_{xc}[\{\psi_{i\sigma}\}]$ by merely replacing $E_x[\{\psi_{i\sigma}\}]$ by $E_{xc}[\{\psi_{i\sigma}\}]$ in Eqs. (8) and (13) and replacing $V_{x\sigma}$ by $V_{xc\sigma}$. It is then possible to generalize many of the results obtained in Sec. II to the case in which both exchange and correlation effects are treated as well as to extend the derivation of Eq. (48) with $v_{i\sigma}$ now given by the generalization of Eq. (13). In future work, we intend to extend the generalization of Secs. II and III to include correlation effects. We also plan to test the accuracy of various exchange-correlation energy functionals in predicting the properties of atoms with both open and closed subshells as well as to demonstrate that our results satisfy the principle of integer preference.

ACKNOWLEDGMENTS

APPENDIX A: DERIVATION OF ANALYTIC PROPERTIES OF THE OPTIMIZED EFFECTIVE POTENTIAL FOR SYSTEMS WITH DEGENERATE STATES

The derivation of the integral equation satisfied by $V_{x\sigma}^o$ given by Eq. (15) did not assume that the single-particle states were nondegenerate [note that the sum in Eq. (6) is restricted to $\varepsilon_{j\sigma}^o \neq \varepsilon_{i\sigma}^o$, so is well defined even if the $i\sigma$ state is degenerate] and is applicable to systems with degenerate states.

In the following we give a brief description of how the results of Sec. II may be generalized to the degenerate case. We shall denote $\psi_{i\sigma}^{o(\beta)}$, $\beta = 1, \ldots, \beta_{i\sigma}$ as the set of degenerate OEP states with single-particle-energy eigenvalue $\varepsilon_{i\sigma}^o$. Then from the definition of the Green's function in Eq. (6), $G_{i\sigma}^{o(\beta)} = G_{i\sigma}^o$ independent of β. Equation (15) may then be written for $r > R_{m\sigma}$ as

$$\sum_\beta f_{m\sigma}^{(\beta)} \int d\mathbf{r}' [V_{x\sigma}^o(\mathbf{r}') - v_{m\sigma}^{(\beta)}(\mathbf{r}')]$$

$$\times G_{m\sigma}^o(\mathbf{r}',\mathbf{r}) \psi_{m\sigma}^{o(\beta)*}(\mathbf{r}') \psi_{m\sigma}^{o(\beta)}(\mathbf{r}) + \text{c.c.} = 0 . \quad \text{(A1)}$$

For sufficiently large r the wave functions take the asymptotic form

$$\psi_{m\sigma}^{o(\beta)}(\mathbf{r}) \to g_{m\sigma}^{(\beta)}(\theta,\phi) R_{m\sigma}(r) . \quad \text{(A2)}$$

Dividing both sides of Eq. (A1) by $R_{m\sigma}(r)$, operating on the resultant equation with $[\varepsilon_{m\sigma}^o - h_\sigma(\mathbf{r})]$, neglecting terms proportional to $\nabla g_{m\sigma}^{(\beta)}(\theta,\phi) \sim 1/r$ and $\nabla^2 g_{m\sigma}^{(\beta)}(\theta,\phi) \sim 1/r^2$, and multiplying the resulting equation by $R_{m\sigma}(r)$, we obtain

$$\sum_\beta f_{m\sigma}^{(\beta)} \int d\mathbf{r}' [V_{x\sigma}^o(\mathbf{r}') - v_{m\sigma}^{o(\beta)}(\mathbf{r}')]\{[\varepsilon_{m\sigma}^o - h_\sigma(\mathbf{r})]G_{m\sigma}^o(\mathbf{r}',\mathbf{r})\} \psi_{m\sigma}^{o(\beta)*}(\mathbf{r}') \psi_{m\sigma}^{o(\beta)}(\mathbf{r}) + \text{c.c.} = 0 . \quad \text{(A3)}$$

But

$$[\varepsilon_{m\sigma}^{o}-h_{\sigma}(\mathbf{r})]G_{m\sigma}^{o}(\mathbf{r}',\mathbf{r})= - \sum_{\varepsilon_{j\sigma}^{o}\neq\varepsilon_{m\sigma}^{o}} \psi_{j\sigma}^{o}(\mathbf{r}')\psi_{j\sigma}^{o*}(\mathbf{r})$$

$$= -[\delta(\mathbf{r}-\mathbf{r}')$$

$$-\sum_{\gamma}\psi_{m\sigma}^{o(\gamma)}(\mathbf{r}')\psi_{m\sigma}^{o(\gamma)*}(\mathbf{r})]$$

(A4)

which is the generalization of Eq. (17). Substituting Eq. (A4) into Eq. (A3) and, as is customary in degenerate perturbation theory, taking the $\{\psi_{m\sigma}^{o(\beta)}\}$ such that the off-diagonal matrix elements of $(V_{x\sigma}^{o}-\hat{v})$ (where $\hat{v}$ is the HF exchange operator) are zero, we obtain for large r

$$\sum_{\beta}\{[V_{x\sigma}^{o}(\mathbf{r})-v_{m\sigma}^{(\beta)}(\mathbf{r})]-(\overline{V}_{x\sigma m}^{o(\beta)}-\overline{v}_{m\sigma}^{o(\beta)})\}$$

$$\times n_{m\sigma}^{o(\beta)}(\mathbf{r})+\text{c.c.}=0 ,\quad\text{(A5)}$$

whose solution is

$$V_{x\sigma}^{o}(\mathbf{r})=\frac{\sum_{\beta}[v_{m\sigma}^{(\beta)}(\mathbf{r})+(\overline{V}_{x\sigma m}^{o(\beta)}-\overline{v}_{m\sigma}^{o(\beta)})]n_{m\sigma}^{o(\beta)}(\mathbf{r})}{\sum_{\beta}n_{m\sigma}^{o(\beta)}(\mathbf{r})}$$

(A6)

which is the generalization of Eq. (18) to the degenerate case, including the use of possibly complex wave functions. In the above, we have taken $v_{m\sigma}^{(\beta)}(\mathbf{r})$ as real since in the large-r limit, $v_{m\sigma}^{(\beta)}(\mathbf{r})\to -f_{m\sigma}^{(\beta)}/r$.

Since the angular dependence of different $n_{m\sigma}^{o(\beta)}(\mathbf{r})$ will in general be different, the condition that $V_{x\sigma}^{o}(\mathbf{r})\to 0$ for $r\to\infty$ independent of θ,ϕ will require

$$\overline{V}_{x\sigma m}^{o(\beta)}=\overline{v}_{m\sigma}^{o(\beta)}$$

(A7)

for each β, which is the generalization of Eq. (20).

Finally, employing (A7) and the asymptotic behavior of $v_{m\sigma}^{(\beta)}$, it follows from (A6) that if some or all of the degenerate $m\sigma$ states have $f_{m\sigma}^{(\beta)}=f_{m\sigma}$ independent of β with the remaining $f_{m\sigma}^{(\beta)}=0$, then

$$V_{x\sigma}^{o}(\mathbf{r})\to -f_{m\sigma}/r ,\quad r\to\infty$$

(A8)

which generalizes Eq. (21).

Moreover, even for degenerate states, it is possible to derive the analog of Eq. (23). This follows from the fact that in such a case there can be regions in which one $\psi_{p\sigma}^{o(\beta)}(\mathbf{r})$ is much larger than the wave functions of other states with which it is degenerate, e.g., for states with angular momentum $l=1$, we may choose the $\{\psi_{p\sigma}^{o(\beta)}\}$ to be proportional to x, y, or z, in which case only one of them is nonzero along each coordinate axis. If we assume that this is in general the case, i.e., along some lines or in some regions of space, different real $f_{p\sigma}^{(\beta)}\psi_{p\sigma}^{o(\beta)}$ dominate the sum in Eq. (15), we can neglect the contributions of all other orbitals in the sum, which yields Eq. (22). It then follows in the same way as in the nondegenerate case that Eq. (23) is valid under these conditions. In addition, it follows from (A7), Eqs. (24) and (25), that

$$\varepsilon_{m\sigma}^{o}=\overline{\varepsilon}_{m\sigma}^{o(\beta)\text{HF}}$$

(A9)

and that consequently, Eq. (26), i.e., Koopmans's theorem, is also valid for the degenerate case as well.

Finally, we may extend Eqs. (30) and (31) to the degenerate case by noting that if $\{f_{p\sigma}^{(\beta)}\}\to\{f_{p\sigma}^{(\beta)}+\delta f_{p\partial}^{(\beta)}\}$, which leads to a change in the self-consistent potentials from $V_{\sigma'}^{o}$ to $V_{\sigma'}^{o}+\delta V_{\sigma'}^{o}$, then the change in the minimized energy is given by the generalization of Eq. (27), i.e.,

$$\delta E^{o}=\sum_{\beta}\frac{\partial E^{o}}{\partial f_{p\sigma}^{(\beta)}}\delta f_{p\sigma}^{(\beta)}$$

(A10)

where we have used Eq. (3).

It follows from Eqs. (8) and (9) that

$$\frac{\partial E^{o}}{\partial f_{p\sigma}^{(\beta)}}=\int \psi_{p\sigma}^{o(\beta)*}h_{p\sigma}^{(\beta)\text{HF}}\psi_{p\sigma}^{o(\beta)}d\mathbf{r}\equiv\overline{\varepsilon}_{p\sigma}^{o(\beta)\text{HF}} .$$

(A11)

For simplicity, we shall assume that $\overline{\varepsilon}_{p\sigma}^{o(\beta)\text{HF}}$ is also independent of β for all p and not merely for $p=m$, as already shown in Eq. (A9), i.e., by hypothesis $\varepsilon_{p\sigma}^{o}$ is degenerate and therefore independent of β; we are assuming that the corresponding $\overline{\varepsilon}_{p\sigma}^{o(\beta)\text{HF}}$ is also independent of β, which is certainly the case for all systems we have treated.

It then follows from Eqs. (A10) and (A11) that

$$\frac{dE^{o}}{df_{p\sigma}}=\overline{\varepsilon}_{p\sigma}^{o\text{HF}}$$

(A12)

where $f_{p\sigma}$ is the total number of electrons in the degenerate states. Moreover, it follows from Eqs. (A9) and (A10) that for $p=m$

$$\frac{dE^{o}}{df_{m\sigma}}=\varepsilon_{m\sigma}^{o}=\overline{\varepsilon}_{m\sigma}^{o\text{HF}} .$$

(A13)

Equations (A12) and (A13) are the generalizations of Eqs. (30) and (31) for the degenerate case.

In closing this appendix we observe that the result given by Eq. (A6) for the asymptotic behavior of the exact solution of the OEP equation gives support for the ad hoc weighting of the single-particle potentials employed in constructing the approximate solution given by Eq. (38).

APPENDIX B: DERIVATION OF APPROXIMATE OPTIMIZED EFFECTIVE POTENTIAL FOR SYSTEMS WITH DEGENERATE STATES

The arguments leading from Eq. (38) to Eq. (40) are applicable to systems with degenerate states once the generalization of Eq. (23) is employed for the determination of $C_{p\sigma}$ given by Eq. (39).

We consider here how Eq. (40) may also be obtained by making the approximations given by Eqs. (42) and (43) in the Green's functions for systems with degenerate states.

If we make the approximation for $\varepsilon_{j\sigma}$ given by Eq. (42) in $G_{i\sigma}^{o}$, then instead of Eq. (41) we obtain for the approximate Green's function

$$G_{i\sigma}(\mathbf{r'},\mathbf{r})=(\tilde{\varepsilon}_{i\sigma}-\varepsilon_{i\sigma})^{-1}\sum_{\varepsilon_{j\sigma}\neq\varepsilon_{i\sigma}}\psi_{j\sigma}(\mathbf{r'})\psi_{j\sigma}^{*}(\mathbf{r})$$

$$=(\tilde{\varepsilon}_{i\sigma}-\varepsilon_{i\sigma})^{-1}[\delta(\mathbf{r}-\mathbf{r'})-\sum_{\gamma}\psi_{i\sigma}^{(\gamma)}(\mathbf{r'})\psi_{i\sigma}^{(\gamma)*}(\mathbf{r})]\ .$$

$$(B1)$$

$$\sum_{i,\beta}f_{i\sigma}^{(\beta)}\int d\mathbf{r'}\ \left[[V_{x\sigma}(\mathbf{r'})-v_{i\sigma}^{(\beta)}(\mathbf{r'})]\left[\delta(\mathbf{r}-\mathbf{r'})-\sum_{\gamma}\psi_{i\sigma}^{(\gamma)}(\mathbf{r'})\psi_{i\sigma}^{(\gamma)*}(\mathbf{r})\right][\psi_{i\sigma}^{(\beta)*}(\mathbf{r'})\psi_{i\sigma}^{(\beta)}(\mathbf{r})]\right]+\mathrm{c.c.}=0\ . \qquad (B2)$$

Performing the indicated integration over $\mathbf{r'}$, we obtain

$$\sum_{i,\beta}f_{i\sigma}^{(\beta)}\{[V_{x\sigma}(\mathbf{r})-v_{i\sigma}^{(\beta)}(\mathbf{r})]-[\overline{V}_{x\sigma i}^{(\beta)}-\overline{v}_{i\sigma}^{(\beta)}]\}$$

$$\times\psi_{i\sigma}^{(\beta)}(\mathbf{r})\psi_{i\sigma}^{(\beta)*}(\mathbf{r})+\mathrm{c.c.}=0 \quad (B3)$$

where we have chosen the $\{\psi_{i\sigma}^{(\beta)}\}$ so that the off-diagonal elements of $[V_{x\sigma}-\hat{v}]$ between degenerate states is zero, as done in Appendix A.

The solution of (B3) for $V_{x\sigma}$ is then

$$V_{x\sigma}(\mathbf{r})=\frac{\displaystyle\sum_{i,\beta}n_{i\sigma}^{(\beta)}(\mathbf{r})[v_{i\sigma}^{(\beta)}(\mathbf{r})+(\overline{V}_{x\sigma i}^{(\beta)}-\overline{v}_{i\sigma}^{(\beta)})]}{\displaystyle\sum_{i,\beta}n_{i\sigma}^{(\beta)}(\mathbf{r})} \quad (B4)$$

where we have used the fact that it follows from Eqs. (13) and (37) that for any $\{f_{i\sigma}\}$ and $\{\psi_{i\sigma}\}$, $V_{x\sigma}^{S}$ is real. Equation (B4) is the generalization of Eq. (40) for complex and possibly degenerate $\{\psi_{i\sigma}^{(\beta)}\}$ and is identical to the previous result for real nondegenerate eigenfunctions, given by Eq. (40).

It follows from (B4) that the asymptotic behavior of $V_{x\sigma}(\mathbf{r})$ for large r has the same form as given by (A6). Thus, requiring that $V_{x\sigma}(\mathbf{r})\to 0$ as $r\to\infty$ results in results analogous to those given by Eqs. (A7)–(A9), i.e.,

$$\overline{V}_{x\sigma m}^{(\beta)}=\overline{v}_{m\sigma}^{(\beta)}\ , \quad (B5)$$

$$V_{x\sigma}(\mathbf{r})\to-\frac{f_{m\sigma}}{r}\ ,\quad r\to\infty \quad (B6)$$

where, as in Appendix A, we assume that if $f_{m\sigma}^{(\beta)}\neq 0$ then $f_{m\sigma}^{(\beta)}=f_{m\sigma}$ independent of β, and

$$\varepsilon_{m\sigma}=\overline{\varepsilon}_{m\sigma}^{(\beta)\mathrm{HF}} \quad (B7)$$

so that Koopmans's theorem is still valid in this approximation. Equations (B5)–(B7) are the generalizations of Eqs. (47), (49), and (52), which were derived for eigenfunctions that were real and nondegenerate. Finally, using the same reasoning that led to Eqs. (54) and (55), we find that if the fractional occupancy of the $p\sigma$ states changes, i.e., $\{f_{p\sigma}^{(\beta)}\to f_{p\sigma}^{(\beta)}+\delta f_{p\sigma}^{(\beta)}\}$, then

$$\delta E=\sum_{\beta}\frac{\partial E}{\partial f_{p\sigma}^{(\beta)}}\delta f_{p\sigma}^{(\beta)}+\sum_{\sigma'}\int\frac{\delta E}{\delta V_{\sigma'}}\sum_{\beta}\frac{\partial V_{\sigma'}}{\partial f_{p\sigma}^{(\beta)}}d\mathbf{r}\,\delta f_{p\sigma}^{(\beta)}\ . \quad (B8)$$

Then if we use the analog of Eq. (29) and take $\delta f_{p\sigma}^{(\beta)}$ independent of β, i.e., the fractional occupancy of each of the fractionally occupied states is changed by the same amount, then

Substituting this approximation for $G_{i\sigma}^{o}$ into Eq. (15) and making the further approximation given by Eq. (43), we obtain the integral equation for the approximate $V_{x\sigma}$, i.e.,

$$\frac{dE}{df_{p\sigma}}=\overline{\varepsilon}_{p\sigma}^{\mathrm{HF}}+\sum_{\sigma'}\int\frac{\delta E}{\delta V_{\sigma'}}\left\langle\frac{\partial V_{\sigma'}}{\partial f_{p\sigma}^{(\beta)}}\right\rangle d\mathbf{r} \quad (B9)$$

where $f_{p\sigma}$ is the total occupancy of the p states, $\langle\ \rangle$ denotes the value averaged over all β for fixed $p\sigma$, and we have assumed, as in Appendix A, that the degenerate $p\sigma$ also have the same $\overline{\varepsilon}_{p\sigma}^{\mathrm{HF}}$, which is true for all systems we have studied. Taking $p=m$ and using Eq. (B7), we obtain

$$\frac{dE}{df_{m\sigma}}=\varepsilon_{m\sigma}+\sum_{\sigma'}\int\frac{\delta E}{\delta V_{\sigma'}}\left\langle\frac{\partial V_{\sigma'}}{\partial f_{m\sigma}^{(\beta)}}\right\rangle d\mathbf{r}\ . \quad (B10)$$

Equations (B9) and (B10) are the generalizations of Eqs. (54) and (55) for the degenerate case.

The excellent agreement between $\varepsilon_{m\sigma}$ and $dE/df_{m\sigma}$ for atoms given in Table IV with differences of only $<0.3\%$ on average and with maximum difference of $<0.4\%$ supports the conclusion drawn from Table I that $\delta E/\delta V_{\sigma}\approx 0$. In addition, the results presented for zinc in Table VI demonstrate that the $\{\overline{\varepsilon}_{p\sigma}^{\mathrm{HF}}\}$ generally closely approximate both the $\{\overline{\varepsilon}_{p\sigma}^{o\mathrm{HF}}\}$ for the inner electrons as well as the $\{\varepsilon_{p\sigma}^{\mathrm{HF}}\}$. Similar results obtain for the other atoms considered in Table IV.

Finally, we note that if $\overline{v}_{i\sigma}^{(\beta)}$ is independent of β, and $f_{p\sigma}=f_{p\sigma}$, i.e., degenerate states have equal fractional occupancy, then it follows from Eq. (13) that $V_{x\sigma}$ given by Eq. (B4) is invariant under a unitary transformation of the degenerate states, which is a condition satisfied by the exact OEP, $V_{x\sigma}^{o}$. In addition, it is easy to show that $V_{x\sigma}$ given by Eq. (B4) satisfies the usual coordinate scaling properties of the exact Kohn-Sham exchange-only potential [36].

APPENDIX C: RELATION OF HARBOLA-SAHNI POTENTIAL TO $V_{x\sigma}$

In the following, we show that the spin-polarized extension of the Harbola-Sahni potential, $W_{x\sigma}$, may be derived directly from the expression for $V_{x\sigma}$ given by Eq. (40) by employing one further approximation. For simplicity, we assume that the $\{\psi_{i\sigma}\}$ have been chosen as real so the $\{v_{i\sigma}\}$ are all real.

We make use of the identity

$$\sum_{i}(\overline{V}_{x\sigma i}-\overline{v}_{i\sigma})\frac{n_{i\sigma}(\mathbf{r})}{n_{\sigma}(\mathbf{r})}=\sum_{i}\int_{\infty}^{\mathbf{r}}(\overline{V}_{x\sigma i}-\overline{v}_{i\sigma})\nabla\left[\frac{n_{i\sigma}(\mathbf{r})}{n_{\sigma}(\mathbf{r})}\right]\cdot d\mathbf{l}$$

$$(C1)$$

where the integral, which is independent of path, is taken over any path from ∞ to r. [Note we are assuming that Eq. (47) is satisfied so there is no contribution to the integral when evaluated at the lower limit.]

We now make the assumption that Eq. (23) is approximately satisfied for all r and not merely in the region in which one orbital dominates $n_\sigma(\mathbf{r})$, so

$$(\bar{V}_{x\sigma i} - \bar{v}_{i\sigma}) \cong [V_{x\sigma}(\mathbf{r}) - v_{i\sigma}(\mathbf{r})] \ . \tag{C2}$$

Then substituting Eq. (C2) into Eq. (C1) and using

$$\sum_i \int_\infty^{\mathbf{r}} V_{x\sigma}(\mathbf{r}) \boldsymbol{\nabla}\left[\frac{n_{i\sigma}}{n_\sigma}\right] \cdot d\mathbf{l} = \int_\infty^{\mathbf{r}} V_{x\sigma}(\mathbf{r}) \boldsymbol{\nabla}\left[\frac{\sum_i n_{i\sigma}}{n_\sigma}\right] \cdot d\mathbf{l} = 0 \tag{C3}$$

yields

$$\sum_i (\bar{V}_{x\sigma i} - \bar{v}_{i\sigma}) \frac{n_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})} \cong -\sum_i \int_\infty^{\mathbf{r}} v_{i\sigma}(\mathbf{r}) \boldsymbol{\nabla}\left[\frac{n_{i\sigma}}{n_\sigma}\right] \cdot d\mathbf{l} \ . \tag{C4}$$

Substituting Eq. (C4) into Eq. (40) and integrating by parts results, without any further approximation, in

$$V_{x\sigma}(\mathbf{r}) \cong \sum_i \int_\infty^{\mathbf{r}} \frac{n_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})} \boldsymbol{\nabla} v_{i\sigma}(\mathbf{r}) \cdot d\mathbf{l} \ . \tag{C5}$$

[Parenthetically, we note that the result given by Eq. (C5) is identical to one conjectured by Krieger and Li [11] for the construction of a single KS potential from the individual $v_{i\sigma}$ obtained from any E_x or E_{xc} as, for example, from the LSDSIC approximation.]

In the present case, employing the $\{v_{i\sigma}\}$ given by Eq. (13) for real $\{\psi_{i\sigma}\}$, we find

$$\frac{\sum_i n_{i\sigma}(\mathbf{r})\boldsymbol{\nabla} v_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})} = -\frac{1}{n_\sigma(\mathbf{r})}\left[\sum_{i,j} f_{i\sigma} f_{j\sigma}\psi_{i\sigma}(\mathbf{r})\psi_{j\sigma}(\mathbf{r}) \int \psi_{i\sigma}(\mathbf{r}')\psi_{j\sigma}(\mathbf{r}')\boldsymbol{\nabla}\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right] d\mathbf{r}'\right] + \mathbf{Q}(\mathbf{r}) \tag{C6}$$

where

$$\mathbf{Q}(\mathbf{r}) \equiv -\frac{1}{n_\sigma(\mathbf{r})}\sum_{i,j} f_{i\sigma} f_{j\sigma} \int \frac{\psi_{i\sigma}(\mathbf{r}')\psi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$
$$\times [\psi_{i\sigma}(\mathbf{r})\boldsymbol{\nabla}\psi_{j\sigma}(\mathbf{r})$$
$$-\psi_{j\sigma}(\mathbf{r})\boldsymbol{\nabla}\psi_{i\sigma}(\mathbf{r})]$$
$$= 0 \tag{C7}$$

because i,j are dummy indices being summed over, and interchanging i and j results in $\mathbf{Q}$ changing sign.

Finally, substituting Eqs. (C6) and (C7) into Eq. (C5), we obtain

$$V_{x\sigma}(\mathbf{r}) \cong -\int_\infty^{\mathbf{r}} \boldsymbol{\mathscr{E}}_{x\sigma}(\mathbf{r}) \cdot d\mathbf{l} \equiv W_{x\sigma}(\mathbf{r}) \tag{C8}$$

where

$$\boldsymbol{\mathscr{E}}_{x\sigma}(\mathbf{r}) = -\int \rho_{x\sigma}(\mathbf{r},\mathbf{r}') \boldsymbol{\nabla}\frac{1}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \tag{C9}$$

is the effective electric field due to the Fermi hole charge density given by

$$\rho_{x\sigma}(\mathbf{r},\mathbf{r}') = \frac{1}{n_\sigma(\mathbf{r})} n_\sigma^2(\mathbf{r},\mathbf{r}') \tag{C10}$$

with

$$n_\sigma(\mathbf{r},\mathbf{r}') = \sum_i f_{i\sigma}\psi_{i\sigma}(\mathbf{r})\psi_{i\sigma}(\mathbf{r}') \tag{C11}$$

for real $\{\psi_{i\sigma}\}$. Equation (C8), together with the defining Eqs. (C9)–(C11), is the spin-polarized, fractional-occupancy extension of the exchange-only potential first proposed by Harbola and Sahni [12], based on significantly different considerations.

Although the above arguments demonstrate that $W_{x\sigma}$

may be derived as an approximation to $V_{x\sigma}$, and thus to $V_{x\sigma}^o$, it lacks certain important properties possessed by the latter two potentials. First of all, $W_{x\sigma}$ does not satisfy Eq. (47) and consequently does not satisfy Koopmans's theorem, nor does it possess a discontinuity at integer filling of the highest occupied spin subshell for a given σ. Furthermore, although the integral given by Eq. (C1) is independent of path, the one appearing in Eq. (C4) and consequently in Eq. (C8) may conceivably be path dependent once the approximation given by Eq. (C2) is made because the curl of the integrand in Eqs. (C4) and (C8) is not manifestly zero except for systems in which the potential is a function of only r, i.e., spherically symmetric atoms, or only of x, i.e., jellium bounded by a surface in the yz plane [18]. On the other hand, the calculation of the potential $V_{x\sigma}$ does not require any path integrals and thus is well defined for any system.

As discussed in Sec. IV, the application of $W_{x\sigma}$ as an approximate $V_{x\sigma}^o$ yields total energy E, which is a significant improvement over the LSD results for atoms listed in Table I. However, the $V_{x\sigma}$ results obtained by employing Eq. (48) were significantly closer to those obtained by employing the OEP. Similarly, for the same ten atoms, the single-particle-energy eigenvalues of the highest occupied states, calculated by Li et al. [21] by employing W_x, are within $\approx 3\%$ of ε_m^{HF} and ε_m^o (with the exception of Zn and Cd), whereas the ε_m obtained by employing $V_{x\sigma}$ deviate on the average from the HF and OEP results by approximately an order of magnitude less. For Zn and Cd, the W_x calculations yield ε_m which are $\approx 10\%$ deeper than either the corresponding HF or the OEP results, whereas the energy eigenvalues obtained for these atoms by employing $V_{x\sigma}$ have a deviation of only $\approx 0.2\%$. A similar difficulty in the accurate calculation of ε_m for Zn and Cd exists when the LSDSIC exchange-only approximation is employed [35], which is probably

due to a significant overestimate of the exchange interaction with the lower-lying filled d states.

Thus we find that $W_{x\sigma}$, considered as an approximation to $V_{x\sigma}$ or $V_{x\sigma}^o$, is a good approximation for integral occupancy, except in those cases in which the next lowest-lying orbitals are d states. A different interpretation of the physical significance of $W_{x\sigma}$ has been given by Sahni and Harbola [34].

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