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Atomic structure in the Pauli-correlated approximation

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In the approach proposed by Harbola and Sahni for the determination of electronic structure, the correlations between the interacting electrons are directly related to the local effective many-body potential in which they move by Coulomb's law. As such this potential is the work required to move an electron in the force field of its Fermi-Coulomb-hole-charge distribution. In this paper we have applied this approach within the Pauli-correlated approximation, in which only correlations between the electrons due to the Pauli exclusion principle are considered, to atoms from He ($Z=2$) to Rn ($Z=86$). For open-shell atoms the central-field model is assumed. The calculations are also spin restricted and nonrelativistic. The self-consistently-determined atomic properties presented are the total ground-state energy, the highest-occupied-orbital eigenvalue, and the expectation value of the single-particle operators r, r^2, r^{-1}, r^{-2}, and $\delta(\mathbf{r})$. The total ground-state energies and expectation values are essentially equivalent to those of Hartree-Fock theory, with the relative differences diminishing with increasing atomic number. The total ground-state energies lie above, as must be the case, and within parts per million of the Hartree-Fock theory results. By ^{9}F this difference is 50 ppm, by ^{35}Br 10 ppm, and by ^{72}Hf less than 5 ppm. The most remarkable results, however, are those for the highest-occupied-orbital eigenvalues. In the Harbola-Sahni approach, the asymptotic structure of the effective potential in the Pauli-correlated approximation is that of the fully correlated system, in which correlations between the electrons due to Coulomb repulsion are also considered. This is manifested by the fact that in comparison with Hartree-Fock theory, the highest-occupied-orbital eigenenergies for the majority of atoms are closer to the experimental ionization potentials. For the remaining atoms, the differences between the two theories are of the order of hundredths of a rydberg or less. Furthermore, we note that in the central-field model the density-functional-theory exchange-energy-potential sum rule due to Levy and Perdew is rigorously satisfied by the potentials and orbitals of this approach. For the present calculations this sum rule is satisfied numerically from six to eight significant figures, as is the virial theorem. Finally, the Harbola-Sahni approach in the Pauli-correlated approximation is contrasted to Hartree-Fock theory, and directions for future research to go beyond it within this framework are indicated.

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I. INTRODUCTION AND FORMALISM

The determination of nonrelativistic electronic structure requires knowledge of electron correlations which arise due to the Pauli exclusion principle and Coulomb's law. In Schrödinger theory the physics of these correlations is incorporated in the wave function. The effect of Pauli correlations is explicitly manifested by the requirement that the wave function be antisymmetric in an interchange of the coordinates (including spin) of any two electrons. However, closed-form analytical solutions of the Schrödinger equation for interacting systems do not exist, and the explicit dependence of the wave function on the coordinates of the electrons due to Coulomb repulsion is unknown. The wave function must therefore be approximated. The best approximate wave functions are determined by application of the variational principle for the energy. For each approximate wave function a rigorous upper bound to the true total ground-state energy is thereby obtained. Hartree-Fock theory provides the best wave functions when only Pauli correlations between the electrons are considered. This wave function is the Slater determinant of the solutions of the Hartree-Fock equations. The approximate effect of Coulomb correlations are usually determined by the use of correlated or configuration-interaction-type wave functions.

The physical consequence of the correlations between the electrons due to the Pauli exclusion principle and Coulomb's law is that there is a reduction in the quantum-mechanical probability of electrons approaching each other. This reduction in probability is the Fermi-Coulomb-hole-charge distribution surrounding each electron. The effect of electron correlations is therefore to lower the total energy of the system by the many-body (exchange-correlation) energy. Thus, physically the exchange-correlation energy E_{xc} is the energy of interaction between the charge density of the electrons and the Fermi-Coulomb-hole charge. As such it is given as

$$E_{\mathrm{xc}}=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' , \tag{1}$$

where $\rho(\mathbf{r})$ is the electronic density and $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ the Fermi-Coulomb-hole charge at $\mathbf{r}'$ for an electron at $\mathbf{r}$.

In recent work [1–9], Harbola and Sahni have proposed an approach for the determination of electronic structure that is based on the Fermi-Coulomb-hole-charge distribution in whose structure all correlations between the electrons are accounted for. According to Harbola and Sahni the *local* many-body effective potential seen by the interacting electrons is the work required to move an electron against this charge. However, in contrast to the electronic and external charge distributions, which are static, the Fermi-Coulomb-hole-charge distribution is a dynamic (nonlocal) distribution whose structure changes as a function of electron position. Thus, to account for this dynamic behavior in calculating the work required to move an electron, the force field due to its Fermi-Coulomb-hole charge must first be determined. This electric field $\mathcal{E}_{xc}(\mathbf{r})$ is given as

$$\mathcal{E}_{xc}(\mathbf{r})=\int \frac{\rho_{xc}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}d\mathbf{r}' , \tag{2}$$

and the local many-body potential $W_{xc}(\mathbf{r})$ in which the electrons move is then given by the line integral

$$W_{xc}(\mathbf{r})=-\int_{\infty}^{\mathbf{r}} \mathcal{E}_{xc}(\mathbf{r}')\cdot d\mathbf{l}' . \tag{3}$$

The differential equation to be solved for the determination of the properties of an interacting electronic system in the presence of some external potential (charge) is then

$$[-\tfrac{1}{2}\nabla^2+V_{es}(\mathbf{r})+W_{xc}(\mathbf{r})]\Phi_i(\mathbf{r})=\varepsilon_i\Phi_i(\mathbf{r}) , \tag{4}$$

where $V_{es}(\mathbf{r})$ is the Hartree electrostatic potential and where the orbitals $\Phi_i(\mathbf{r})$ lead to the density $\rho(\mathbf{r})=\sum_i|\Phi_i(\mathbf{r})|^2$. The work $W_{xc}(\mathbf{r})$ may also be written as the sum $W_x(\mathbf{r})+W_c(\mathbf{r})$, where $W_x(\mathbf{r})$ and $W_c(\mathbf{r})$ are the work done against the electric fields $\mathcal{E}_x(\mathbf{r})$ and $\mathcal{E}_c(\mathbf{r})$ due to the Fermi $[\rho_x(\mathbf{r},\mathbf{r}')]$ and Coulomb $[\rho_c(\mathbf{r},\mathbf{r}')]$ hole-charge distributions, respectively. The Fermi hole is a consequence of the Pauli principle, whereas the Coulomb hole arises due to Coulomb repulsion. The work $W_x(\mathbf{r})$ against the force field due to the Fermi hole charge can be determined *exactly* since the Fermi hole is known explicitly in terms of the orbitals $\Phi_i(\mathbf{r})$ as $\rho_x(\mathbf{r},\mathbf{r}')=|\gamma(\mathbf{r},\mathbf{r}')|^2/2\rho(\mathbf{r})$, where $\gamma(\mathbf{r},\mathbf{r}')=\sum_i\Phi_i^*(\mathbf{r})\Phi_i(\mathbf{r}')$ is the single-particle density matrix with the index i including spin. However, since the determination of the Coulomb-hole charge requires knowledge of the true wave function, its structure is unknown and must be approximated. Thus the work $W_c(\mathbf{r})$ is unknown and also to be approximated.

Implicit in the association of a force field with the Fermi-Coulomb-hole charge is that the work $W_{xc}(\mathbf{r})$ done is path independent or equivalently that the curl of the electric field vanishes in order that the potential be well defined. This is rigorously the case for symmetric systems [2,3] such as spherically symmetric atoms and jellium metal surfaces as well as open-shell atoms in the central-field model. For nonsymmetrical systems there is as yet [2,3] no rigorous proof of the path independence of the work $W_{xc}(\mathbf{r})$. In the literature, it has been shown [10] that for nonspherical densities as obtained from degenerate states of atoms within the central-field model, the curl of the electric field due to the Fermi hole is finite. This, however, does not constitute [11] a rigorous proof that the work $W_x(\mathbf{r})$ or more generally $W_{xc}(\mathbf{r})$ is path dependent for nonsymmetrical systems. The reason for this is that these calculations are non-self-consistent, and therefore intrinsically inconsistent with the fact that in a central potential the curl of the electric field must vanish. If for systems of arbitrary symmetry, the curl does not vanish, it has been proposed [2,3,7,8] that an approximation to the many-body potential be constructed from the irrotational component of the electric field. The applicability [8] of this approximation in a non-self-consistent calculation of the potential for nonsymmetric atoms has been demonstrated. It has been shown [9] that the solenoidal component of the electric field is negligible in comparison to the irrotational component and therefore the approximation is accurate. Further, what is observed [8] is that the difference between the potentials in different directions is small and occurs primarily in the intershell regions.

Since the effective many-body potential $W_{xc}(\mathbf{r})$ is local, the Harbola-Sahni approach falls within the framework of Hohenberg-Kohn-Sham [12,13] density-functional theory. However, the Kohn-Sham and Harbola-Sahni potentials are not equivalent. The reason for this is that Kohn-Sham theory is a mathematical formalism based on the variational principle for the energy, whereas the Harbola-Sahni approach relates the quantum-mechanical correlations of the interacting electrons directly via Coulomb's law to the local effective potential in which they move. For a comparison between these approaches to the many-body problem, we refer the reader to the literature [1–11,14,15].

The Pauli-correlated approximation within the Harbola-Sahni approach is comprised of setting $W_c=0$ in Eq. (4) and calculating the work $W_x(\mathbf{r})$ exactly from the orbitals $\Psi_i(\mathbf{r})$ of the resulting differential equation. This approximation is thus the counterpart to Hartree-Fock theory for which the orbital-dependent potentials are also explicitly known in terms of the orbitals. A fundamental difference between Hartree-Fock theory and the Pauli-correlated approximation of the Harbola-Sahni approach, however, is that the former is derived via the variational principle for the energy, whereas the latter is based entirely on physical arguments. Furthermore, whereas the effects of Pauli correlation in Hartree-Fock theory are represented by an integral operator, the potential $W_x(\mathbf{r})$ is multiplicative. This locality of the many-body potential in the Harbola-Sahni approach makes calculations for atoms and jellium metal surfaces easier to perform, and in all probability this should also prove to be the case for more complex systems. The orbitals $\Psi_i(\mathbf{r})$, however, are not the Hartree-Fock theory orbitals because they are derived from a local potential. Thus the total ground-state energy, calculated with a Slater determinant of these orbitals, will be a rigorous upper bound to the Hartree-Fock-theory value.

Within the Pauli-correlated approximation, the highest-occupied-orbital eigenenergy of the Harbola-Sahni differential equation has important physical significance. This arises as a consequence of the fact that the asymptotic structure of the many-body potential

$W_{xc}(\mathbf{r})$ for the fully (Pauli and Coulomb) correlated system is known *exactly* and is that of the potential $W_x(\mathbf{r})$ alone. The reason for this is that the hole charge around each electron is the same in magnitude as that of the electron whether one considers only Pauli or both Pauli as well as Coulomb correlations. Since both the Fermi-Coulomb and Fermi holes satisfy the charge-conservation sum rule

$$\int \rho_{xc}(\mathbf{r},\mathbf{r}')d\mathbf{r}'=\int \rho_x(\mathbf{r},\mathbf{r}')d\mathbf{r}'=1 , \tag{5}$$

it follows that the total Coulomb-hole charge is zero. Thus the Coulomb hole contributes to the potential $W_c(\mathbf{r})$ for electron positions within or about this charge distribution. The asymptotic structure of the potential $W_{xc}(\mathbf{r})$ is determined entirely by the Fermi hole. Therefore, by solving the problem in the Pauli-correlated approximation, the asymptotic structure of the potential for the fully correlated system is automatically determined. As a consequence, the corresponding highest-occupied-orbital eigenvalue which depends principally on this asymptotic structure should approximate well the experimental ionization potential. On the other hand, the highest-occupied-orbital eigenvalue of Hartree-Fock theory can only be interpreted as a removal energy via Koopmans's theorem [16]. The highest-occupied-orbital eigenvalue of Hartree-Fock theory is the difference between the total ground-state energies of the neutral and singly ionized systems, with the latter energy being determined by the orbitals of the neutral system. Thus, if the true orbitals of the ionized system do not differ from those of the neutral system, as is the case for metals, then the Hartree-Fock highest-occupied-orbital eigenvalue can be interpreted as a removal energy. However, if there is a relaxation of the orbitals on ionization, as is the case for atoms, the interpretation of the highest-occupied-orbital eigenvalue as a removal energy is less rigorous.

The results of application of the Harbola-Sahni approach in the Pauli-correlated approximation to the inhomogeneous electronic systems at metallic surfaces [1,2,4,5] and atoms [1–3,6] with closed subshells confirm the above remarks on the total ground-state energy, the asymptotic structure of the potential, and the highest-occupied-orbital eigenvalues. It has been shown [2,4,5] that the asymptotic structure of the potential at a metal surface is the image potential, in agreement with the results of classical physics. The asymptotic structure of the potential in atoms [1–3,6] goes as $-(1/r)$, in agreement with both classical physics and Schrödinger theory. The total ground-state energies [6] of the atoms considered are upper bounds to and lie within 50 ppm of the Hartree-Fock-theory results [17] for atoms heavier than beryllium. The highest-occupied-orbital eigenvalues [6] are good approximations to the experimental ionization potentials [18], being closer to experiment than those of Hartree-Fock theory. More recently [19], employing the Harbola-Sahni approach, convergent self-consistent solutions for stable negative ions within the Pauli-correlated approximation have been achieved. In the past [20] such convergent solutions within the local-density approximation [12,13] have only been obtained by constraining the electrons with a fictitious spherical barrier. As is the case for neutral atoms the ground-state energies are essentially the same and lie above those of Hartree-Fock theory [21]. More significantly, the highest-occupied-orbital energies are closer to the experimental electron affinities [22] of the corresponding neutral atoms than those obtained by Hartree-Fock theory. In addition, Hartree-Fock quality values of the static dipole and quadrupole antishielding factors for negative ions have also been obtained [23].

In this paper we present the results of self-consistent calculations on atoms from He ($Z=2$) to Rn ($Z=86$) as performed via the Harbola-Sahni approach in the Pauli-correlated approximation. The central-field model is assumed for the open-shell atoms so that the effective exchange potential for all atoms is path independent. However, as noted previously, the noncentral part of the exchange potential for open-shell atoms is a small perturbation in the less significant intershell regions (see Fig. 4 of Ref. [8]), and thus the central-field approximation for these atoms is accurate. The calculations are also spin restricted and nonrelativistic. The results presented are the total ground-state energies, highest-occupied-orbital eigenvalues, and the expectation values of the single-particle operators r, r^2, r^{-1}, r^{-2}, and $\delta(\mathbf{r})$. (Results for total energies and highest-occupied-orbital eigenvalues for atoms with closed subshells up to Xe ($Z=54$) have been given previously [2,6].) All the results are compared with those of Hartree-Fock theory [17] within the central-field model of atoms. The highest-occupied-orbital eigenvalues are in addition compared to the experimental ionization potentials [18]. We reiterate, however, that in our calculations we have not incorporated either Coulomb-correlation or relativistic effects. Both these effects are important for the determination of electronic structure, with the latter being particularly significant for the heavier atoms ($Z>30$). Our purpose for comparing the highest-occupied-orbital eigenenergies with the experimental ionization potentials, however, is to demonstrate that it is the exchange potential $W_x(\mathbf{r})$ which corresponds to the total local effective potential in the asymptotic regions of the atom. We note that in contrast there is no such connection between the asymptotic structure of the orbital-dependent potentials of Hartree-Fock theory and the total effective potential.

In Sec. II we describe the central-field model of an atom as defined within the Harbola-Sahni approach. The results of application and their evaluation are given in Sec. III. Concluding remarks and directions for future research are given in Sec. IV.

II. CENTRAL-FIELD MODEL OF ATOMS

In the central-field model of atoms, the electrons are assumed to move in a central potential so that the electronic wave functions are separable and may be written as

$$\Psi_{nlm}(\mathbf{r})=R_{nl}(r)Y_{lm}(\theta,\phi) , \tag{6}$$

where $R_{nl}(r)$ is the radial part of the wave function and $Y_{lm}(\theta,\phi)$, the angular part, is the spherical harmonic of order (l,m). In the Harbola-Sahni approach within the Pauli-correlated approximation, the central-field model is comprised of spherically averaging the single-particle density matrix $\gamma(\mathbf{r},\mathbf{r}')$ over the coordinates of the electrons of a given orbital-angular-momentum quantum number. For open-shell atoms this is equivalent to spherically averaging the radial component of the electric field due to the Fermi hole so that the resulting field and potential are spherically symmetric. For closed-subshell atoms, this is automatically the case. The spherical average of the radial component of the electric field defined by Eq. (2) is

$$\mathscr{E}_{\mathrm{x},r}(r)=-\frac{1}{4\pi}\int \rho_{\mathrm{x}}(\mathbf{r},\mathbf{r}')\frac{\partial}{\partial r}\frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'d\Omega_{\mathbf{r}}\ , \tag{7}$$

and the expression for the Fermi hole $\rho_{\mathrm{x}}(\mathbf{r},\mathbf{r}')$ to be substituted into it is

$$\begin{aligned}\rho_{\mathrm{x}}(\mathbf{r},\mathbf{r}')&=-\frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{2\rho(\mathbf{r})}\\ &=-\frac{2}{\rho(r)}\sum_{\substack{n,l,m\\ n',l',m'}} R_{nl}(r)R_{nl}(r')R_{n'l'}(r)R_{n'l'}(r')\\ &\qquad\times Y^*_{lm}(\Omega)Y_{lm}(\Omega')\\ &\qquad\times Y_{l'm'}(\Omega)Y^*_{l'm'}(\Omega')\ ,\end{aligned} \tag{8}$$

where the density $\rho(r)$ is

$$\rho(r)=\frac{1}{2\pi}\sum_{n,l}(2l+1)R^2_{nl}(r)\ . \tag{9}$$

Employing the expansion

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|}=4\pi\sum_{l'',m''}\frac{1}{2l''+1}Y^*_{l''m''}(\Omega)Y_{l''m''}(\Omega')\frac{r^{l''}_<}{r^{l''+1}_>}\ , \tag{10}$$

where $r_<$ $(r_>)$ is the smaller (larger) of $|\mathbf{r}|$ and $|\mathbf{r}'|$, the expression for the electric field becomes

$$\begin{aligned}\mathscr{E}_{\mathrm{x},r}(r)=\frac{2}{\rho(r)}\int\sum_{\substack{n,l,m\\ n',l',m'\\ l'',m''}}\frac{1}{(2l''+1)}R_{nl}(r)R_{nl}(r')R_{n'l'}(r)R_{n'l'}(r')\left[\frac{\partial}{\partial r}\frac{r^{l''}_<}{r^{l''+1}_>}\right]r'^2dr'\\ \times\int Y^*_{lm}(\Omega)Y_{l'm'}(\Omega)Y^*_{l''m''}(\Omega)d\Omega\int Y_{lm}(\Omega')Y^*_{l'm'}(\Omega')Y_{l''m''}(\Omega')d\Omega'\ .\end{aligned} \tag{11}$$

Using the orthonormality condition [24], and the coupling rule [24] for spherical harmonics, which is

$$Y_{l_1m_1}(\Omega)Y_{l_2m_2}(\Omega)=\sum_l\left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}\right]^{1/2}C(l_1l_2l;m_1m_2)C(l_1l_2l;000)Y_{l,m_1+m_2}(\Omega)\ , \tag{12}$$

where C are the Clebsch-Gordan [24,25] coefficients, the integrals over the solid angles in Eq. (11) which are complex conjugates of each other are

$$\int Y^*_{l_3m_3}(\Omega)Y_{l_2m_2}(\Omega)Y_{l_1m_1}(\Omega)d\Omega=\left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}\right]^{1/2}C(l_1l_2l_3;m_1m_2m_3)C(l_1l_2l_3;000)\delta_{m_3,m_1+m_2}\ . \tag{13}$$

Substituting for these integrals, the expression for the spherically averaged field becomes

$$\begin{aligned}\mathscr{E}_{\mathrm{x},r}(r)=\frac{1}{2\pi\rho(r)}\int\sum_{\substack{n,l,m\\ n',l',m'\\ l''}}R_{nl}(r)R_{nl}(r')R_{n'l'}(r)R_{n'l'}(r')\left[\frac{\partial}{\partial r}\frac{r^{l''}_<}{r^{l''+1}_>}\right]r'^2dr'\frac{(2l+1)}{(2l'+1)}\\ \times C^2(ll''l';m,m'-m,m')C^2(ll''l';000)\ .\end{aligned} \tag{14}$$

The above expression Eq. (14) for the electric field has been derived for closed-subshell atoms so that an occupancy of $(2l+1)$ has been assumed. For open subshells a partial occupancy of $N_l/(2l+1)$, where N_l is the number of electrons in the subshell, should be used. Since the curl of this electric field vanishes, the spherically symmetric local exchange potential $W_{\mathrm{x}}(r)$ is given by the integral

$$W_{\mathrm{x}}(r)=-\int_\infty^r\mathscr{E}_{\mathrm{x},r}(r')dr'\ . \tag{15}$$

With this local potential, the resulting radial differential equation [see Eq. (4)] is then solved to self-consistency following Madelung's law [26] for the configuration of atoms. According to this law, the electron shells for consecutive atoms are filled in the order of the sum of the quantum numbers $(n+l)$, and shells with equal $(n+l)$ numbers are filled in the order of the quantum number n. (The configurations assumed in Fischer's Hartree-Fock-theory calculations are those of Madelung's law.) The total ground-state energy is then the sum of the kinetic E_k, electrostatic E_{es}, and exchange E_{x} energies, where

$$E_k = -\tfrac{1}{2}\sum_i \int \Psi_i^*(\mathbf{r})\nabla^2\Psi_i(\mathbf{r})d\mathbf{r} \ ,$$

$$E_{\text{es}} = \tfrac{1}{2}\int \rho(\mathbf{r})V_{\text{es}}(\mathbf{r})d\mathbf{r} \ , \tag{16}$$

$$E_{\text{x}} = \tfrac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho_{\text{x}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \ .$$

[Note that the sum of the expressions of Eq. (16) is equivalent to the expectation value of the nonrelativistic Hamiltonian taken with a Slater determinant of the orbitals.]

III. RESULTS

In this section we present and analyze the results for ground-state energies, highest-occupied-orbital eigenvalues, and various single-particle operator expectation values of atoms as obtained in the central-field model described in the preceding section. However, prior to discussing the results we make the following general remarks. A sensitive indicator of the accuracy of numerical computations such as these involving local potentials is the degree to which the virial theorem based exchange-energy-potential sum rule of density-functional theory due to Levy and Perdew [27] is satisfied. (The satisfaction of the sum rule is also an indicator of the accuracy of different formalisms.) The sum rule is an integral relationship between the exchange potential μ_{x} of Kohn-Sham theory, which is the functional derivative of the exchange energy functional, and the exchange energy, and is given as

$$E_{\text{x}}[\Phi_i] = -\int d\mathbf{r}\,\rho(\mathbf{r})\mathbf{r}\cdot\nabla\mu_{\text{x}}(\rho(\mathbf{r});\mathbf{r}) \ . \tag{17}$$

It has been shown analytically [1,8] that for orbitals generated from a field whose curl vanishes the potentials (and the orbitals) satisfy this sum rule. In our calculations, the self-consistently-determined orbitals and exchange potentials satisfy this sum rule from six to eight significant figures. We refer the reader to Ref. [6] on closed-subshell atoms for a comparison of the accuracy of the exchange energy as obtained from the orbitals and from the local exchange potential. The orbitals generated also satisfy the virial theorem to the same degree. The structure of the local exchange potential is as described in our previous work [1–3,6]. The slope of the potential is always positive, there being a distinct change in the slope in the intershell regions. This indicates that work must always be done against the attractive force of the Fermi hole in order to remove an electron from the atom. For asymptotic positions of the electron, the effective potential is $-(1/r)$, and is that of the exchange potential alone. Lastly, as is implicit in the Harbola-Sahni approach, all the results for the He atom are the same as those of the Hartree-Fock theory. For purposes of completeness we also include here results for the closed-subshell atoms given previously [6]. We next discuss the specific results.

A. Total ground-state energies

In Table I we present our results for the total ground-state energies in atomic units together with those of Hartree-Fock theory. The latter calculations are also performed [17] in the central-field model of an atom. The negative values of the energies in atomic units are quoted. Observe that since the energies are obtained from orbitals generated from a local potential, they all lie above those of Hartree-Fock theory, as they must. However, the two sets of results are essentially equivalent. In Table II we quote the differences in parts per million between the energies obtained by us and those of Hartree-Fock theory. Note that as the number of electrons in the atoms increases, these differences diminish. For the lighter atoms, ^{3}Li to ^{8}O, the differences lie between 137 and 53 ppm. By ^{9}F these differences are down to 50 ppm, by ^{35}Br they are down to 10 ppm, and by ^{72}Hf they are less than 5 ppm. For ^{86}Rn, our result differs from that of Hartree-Fock theory by 2 ppm.

B. Highest-occupied-orbital eigenvalues

As noted in the Introduction, the asymptotic structure of the potential $W_{\text{x}}(\mathbf{r})$ is that of the fully correlated system. Consequently, it is meaningful to compare the self-consistently-determined highest-occupied-orbital eigenvalues obtained within the Pauli-correlated approximation to the experimental ionization potentials. In Table III we present the Harbola-Sahni (HS) approach results for the highest-occupied-orbital eigenvalues together with the experimental ionization potentials and those of Hartree-Fock (HF) theory. The negative values of the eigenenergies are quoted. In the table the atoms are grouped together on the basis of the commonality of chemical properties. The atomic configurations according to Madelung's law [26] are also given.

We summarize the results for all the atoms by plotting in Figs. 1 and 2 the magnitude of the difference between the experimental ionization potential and the highest-occupied-orbital eigenvalues as obtained via Hartree-Fock theory and the Harbola-Sahni approach. Panels (a) of these figures correspond to those atoms for which the HS results are closer to the experimental ionization potentials than those due to HF, and panels (b) for the cases where the reverse is true. Note that whereas the scales of Figs. 1(a) and 2(a) are the same, those for Figs. 1(b) and 2(b) are different. It is evident from these figures that for the majority of atoms considered, the HS results lie closer to experiment. Furthermore, for those atoms for which the HF results are closer, the differences between the two theories [see Figs. 1(b) and 2(b)] are of the order of a few hundredths of a rydberg. For atoms with $Z < 55$ the HS highest-occupied-orbital eigenvalues lie within 0.05 of the experimental ionization potentials and for the heavier atoms within 0.1. These results clearly demonstrate that in the outer regions of an atom, the potential $W_{\text{x}}(r)$ is in fact the exact effective potential. The differences between the HS results and experiment of course arise because both correlation and relativistic effects are not accounted for in the present calculations.

We also note that the observed structure of certain

TABLE I. Total ground-state energy of atoms in the central-field model as obtained by the Harbola-Sahni approach in the Pauli-correlated approximation. The corresponding Hartree-Fock-theory results are also given. The negative values of the energies in atomic units are quoted.

Atomic number	Atom	Hartree-Fock[a]	Harbola-Sahni	Atomic number	Atom	Hartree-Fock[a]	Harbola-Sahni
2	He	2.862	2.862	45	Rh	4 685.801	4 685.762
3	Li	7.433	7.432	46	Pd	4 937.783	4 937.744
4	Be	14.573	14.571	47	Ag	5 197.518	5 197.479
5	B	24.529	24.526	48	Cd	5 465.133	5 465.093
6	C	37.689	37.685	49	In	5 740.169	5 740.130
7	N	54.401	54.396	50	Sn	6 022.932	6 022.893
8	O	74.809	74.805	51	Sb	6 313.485	6 313.447
9	F	99.409	99.405	52	Te	6 611.784	6 611.746
10	Ne	128.547	128.542	53	I	6 917.981	6 917.944
11	Na	161.860	161.851	54	Xe	7 232.138	7 232.101
12	Mg	199.615	199.606	55	Cs	7 553.934	7 553.895
13	Al	241.877	241.868	56	Ba	7 883.544	7 883.506
14	Si	288.854	288.844	57	La	8 221.064	8 221.021
15	P	340.719	340.707	58	Ce	8 566.920	8 566.871
16	S	397.505	397.493	59	Pr	8 921.181	8 921.125
17	Cl	459.482	459.470	60	Nd	9 283.883	9 283.822
18	Ar	526.818	526.804	61	Pm	9 655.099	9 655.034
19	K	599.165	599.149	62	Sm	10 034.953	10 034.883
20	Ca	676.758	676.743	63	Eu	10 423.543	10 423.466
21	Sc	759.736	759.717	64	Gd	10 820.617	10 820.546
22	Ti	848.406	848.382	65	Tb	11 226.568	11 226.500
23	V	942.884	942.858	66	Dy	11 641.453	11 641.385
24	Cr	1 043.310	1 043.280	67	Ho	12 065.290	12 065.223
25	Mn	1 149.866	1 149.833	68	Er	12 498.153	12 498.087
26	Fe	1 262.444	1 262.414	69	Tm	12 940.174	12 940.109
27	Co	1 381.415	1 381.386	70	Yb	13 391.456	13 391.389
28	Ni	1 506.871	1 506.843	71	Lu	13 851.808	13 851.745
29	Cu	1 638.950	1 638.922	72	Hf	14 321.250	14 321.187
30	Zn	1 777.848	1 777.820	73	Ta	14 799.813	14 799.750
31	Ga	1 923.261	1 923.235	74	W	15 287.546	15 287.484
32	Ge	2 075.360	2 075.334	75	Re	15 784.533	15 784.469
33	As	2 234.239	2 234.212	76	Os	16 290.649	16 290.588
34	Se	2 399.868	2 399.842	77	Ir	16 806.113	16 806.054
35	Br	2 572.441	2 572.416	78	Pt	17 330.949	17 330.891
36	Kr	2 752.055	2 752.030	79	Au	17 865.212	17 865.153
37	Rb	2 938.357	2 938.330	80	Hg	18 408.991	18 408.932
38	Sr	3 131.546	3 131.519	81	Tl	18 961.825	18 961.768
39	Y	3 331.684	3 331.656	82	Pb	19 524.008	19 523.953
40	Zr	3 538.995	3 538.963	83	Bi	20 095.586	20 095.532
41	Nb	3 753.552	3 753.517	84	Po	20 676.501	20 676.448
42	Mo	3 975.443	3 975.405	85	At	21 266.882	21 266.830
43	Tc	4 204.789	4 204.747	86	Rn	21 866.772	21 866.721
44	Ru	4 441.487	4 441.448				

[a] See Reference [17].

atoms differs from that of Madelung's law. These atoms and their observed structures are ^{24}Cr ([Ar]$3d^5 4s^1$), ^{29}Cu ([Ar]$3d^{10} 4s^1$), ^{45}Rh ([Kr]$4d^8 5s^1$), ^{46}Pd ([Kr]$4d^{10}$), ^{47}Ag ([Kr]$4d^{10} 5s^1$), ^{57}La ([Xe]$5d^1 6s^2$), ^{64}Gd ([Xe]$4f^7 5d^1 6s^2$), and ^{79}Au ([Xe]$4f^{14} 5d^{10} 6s^1$). However, we expect that the difference in configuration cannot affect to any degree the results quoted since the energy separation between the last d and s shells or d and f shells is small.

C. Expectation values

In Table IV we present our results for the expectation value of the single-particle operators r, r^2, r^{-1}, r^{-2}, and $\delta(\mathbf{r})$ in atomic units. These expectation values sample both the exterior and interior of atoms as well as determine its size. They are also related to various atomic properties [28] such as the diamagnetic susceptibility

TABLE II. Total ground-state energy differences in parts per million between the results of the Hartree-Fock theory and Harbola-Sahni approach.

Atoms	Differences (ppm)
^{2}He	0
^{3}Li, ^{4}Be	137
^{5}B	122
^{6}C	106
^{7}N	92
^{8}O	53
^{9}F–^{34}Se	50–10
^{35}Br–^{71}Lu	10–5
^{72}Hf–^{86}Rn	<5

($\langle r^2 \rangle$), nuclear magnetic shielding ($\langle r^{-1} \rangle$), and the Fermi contact term ($\langle \delta(\mathbf{r}) \rangle$). Since Fischer's [17] calculations are performed in the central-field approximation with a single-configuration wave function, the expectation values of these operators taken with the resulting Hartree-Fock-theory wave functions are, according to Brillouin's theorem [29], correct to second order in the error of the wave function. Thus, for purposes of comparison we also include in Table IV these expectations as determined via Hartree-Fock theory.

As a consequence of the fact that the operator r^{-1} appears in the Hamiltonian, its expectation value as calculated from wave functions obtained by application of the variational principle for the energy is particularly accu-

TABLE III. Highest-occupied-orbital eigenvalues of atoms in the central-field model as obtained by the Harbola-Sahni approach in the Pauli-correlated approximation. The corresponding Hartree-Fock-theory results as well as the experimental ionization potentials are also given. The negative values of the eigenenergies in rydbergs are quoted.

Atom	Structure		Hartree-Fock[a]	Harbola-Sahni	Experiment[b]
Atoms with last closed subshell an s subshell					
^{2}He	$2s^2$		1.836	1.836	1.807
^{4}Be	[He]$2s^2$		0.619	0.626	0.685
^{12}Mg	[Ne]$3s^2$		0.506	0.521	0.562
^{20}Ca	[Ar]$4s^2$		0.391	0.402	0.449
^{30}Zn	[Ar]$3d^{10}4s^2$		0.585	0.646	0.690
^{38}Sr	[Ar]$3d^{10}4p^6 5s^2$		0.357	0.369	0.419
^{48}Cd	[Kr]$4d^{10}5s^2$		0.530	0.583	0.661
^{56}Ba	[Xe]$6s^2$		0.315	0.325	0.383
^{70}Yb	[Xe]$4f^{14}6s^2$		0.365	0.383	0.460
^{80}Hg	[Xe]$4f^{14}5d^{10}6s^2$		0.522	0.580	0.767
Noble-gas atoms					
^{10}Ne	[He]$2s^2 2p^6$		1.701	1.713	1.585
^{18}Ar	[Ne]$3s^2 3p^6$		1.182	1.178	1.158
^{36}Kr	[Ar]$3d^{10}4s^2 4p^6$		1.048	1.035	1.029
^{54}Xe	[Kr]$4d^{10}5s^2 5p^6$		0.915	0.899	0.892
^{86}Rn	[Xe]$4f^{14}5d^{10}6s^2 6p^6$		0.856	0.838	0.790
First transition group					
^{21}Sc	[Ar]$3d^n 4s^2$	$n=1$	0.420	0.446 ($4s$) 0.415 ($3d$)	0.481
^{22}Ti		$n=2$	0.442	0.478	0.501
^{23}V		$n=3$	0.461	0.505	0.495
^{24}Cr		$n=4$	0.479	0.529	0.497
^{25}Mn		$n=5$	0.496	0.552	0.546
^{26}Fe		$n=6$	0.516	0.571	0.578
^{27}Co		$n=7$	0.535	0.591	0.578
^{28}Ni		$n=8$	0.553	0.610	0.561
Second transition group					
^{39}Y	[Kr]$4d^n 5s^2$	$n=1$	0.392	0.423 ($5s$) 0.337 ($4d$)	0.469
^{40}Zr		$n=2$	0.415	0.458 ($5s$) 0.438 ($4d$)	0.503
^{41}Nb		$n=3$	0.433	0.484	0.506
^{42}Mo		$n=4$	0.449	0.504	0.522

TABLE III (*Continued*).

Atom	Structure		Hartree-Fock[a]	Harbola-Sahni	Experiment[b]
		Second transition group			
^{43}Tc		$n=5$	0.463	0.523	0.535
^{44}Ru		$n=6$	0.480	0.536	0.542
^{45}Rh		$n=7$	0.494	0.548	0.548
^{46}Pd		$n=8$	0.507	0.560	0.613
		Third transition group			
^{72}Hf	[Xe]$4f^{14}5d^{n}6s^{2}$	$n=2$	0.418	0.470 ($6s$) 0.426 ($5d$)	0.515
^{73}Ta		$n=3$	0.435	0.494	0.580
^{74}W		$n=4$	0.450	0.513	0.587
^{75}Re		$n=5$	0.461	0.531	0.579
^{76}Os		$n=6$	0.478	0.540	0.639
^{77}Ir		$n=7$	0.491	0.551	0.669
^{78}Pt		$n=8$	0.503	0.561	0.662
		Rare earths			
^{58}Ce	[Xe]$4f^{n}6s^{2}$	$n=2$	0.324	0.338	0.402
^{59}Pr		$n=3$	0.328	0.342	0.398
^{60}Nd		$n=4$	0.332	0.347	0.404
^{61}Pm		$n=5$	0.335	0.351	0.408
^{62}Sm		$n=6$	0.339	0.355	0.414
^{63}Eu		$n=7$	0.342	0.359	0.417
^{64}Gd		$n=8$	0.346	0.362	0.451
^{65}Tb		$n=9$	0.349	0.366	0.430
^{66}Dy		$n=10$	0.352	0.369	0.436
^{67}Ho		$n=11$	0.356	0.373	0.442
^{68}Er		$n=12$	0.359	0.376	0.448
^{69}Tm		$n=13$	0.362	0.380	0.454
^{70}Yb		$n=14$	0.365	0.383	0.460
^{57}La		$n=1$	0.320	0.332 ($6s$) 0.267 ($4f$)	0.410
^{71}Lu	[Xe]$4f^{14}5d^{1}6s^{2}$		0.398	0.435 ($6s$) 0.330 ($5d$)	0.399
		Alkali metals			
^{3}Li	[He]$2s^{1}$		0.393	0.405	0.396
^{11}Na	[Ne]$3s^{1}$		0.364	0.390	0.378
^{19}K	[Ar]$4s^{1}$		0.295	0.317	0.319
^{37}Rb	[Kr]$5s^{1}$		0.276	0.299	0.307
^{55}Cs	[Xe]$6s^{1}$		0.247	0.268	0.286
		Halogens			
^{9}F	[He]$2s^{2}2p^{5}$		1.460	1.464	1.281
^{17}Cl	[Ne]$3s^{2}3p^{5}$		1.013	1.006	0.953
^{35}Br	[Ar]$3d^{10}4s^{2}4p^{5}$		0.914	0.900	0.868
^{53}I	[Kr]$4d^{10}5s^{2}5p^{5}$		0.806	0.791	0.768
^{85}At	[Xe]$4f^{14}5d^{10}6s^{2}6p^{5}$		0.760	0.743	0.708
		Atoms with less than half filled p subshells			
^{5}B	[He]$2s^{2}2p^{1}$		0.620	0.581	0.610
^{6}C	[He]$2s^{2}2p^{2}$		0.867	0.818	0.828
^{13}Al	[Ne]$3s^{2}3p^{1}$		0.420	0.406	0.440
^{14}Si	[Ne]$3s^{2}3p^{2}$		0.594	0.571	0.599

TABLE III. (*Continued*).

Atom	Structure	Hartree-Fock[a]	Harbola-Sahni	Experiment[b]
Atoms with less than half filled p subshells				
^{31}Ga	[Ar]$3d^{10}4s^{2}4p^{1}$	0.417	0.410	0.441
^{32}Ge	[Ar]$3d^{10}4s^{2}4p^{2}$	0.575	0.556	0.581
^{49}In	[Kr]$4d^{10}5s^{2}5p^{1}$	0.395	0.387	0.425
^{50}Sn	[Kr]$4d^{10}5s^{2}5p^{2}$	0.530	0.511	0.540
^{81}Tl	[Xe]$4f^{14}5d^{10}6s^{2}6p^{1}$	0.385	0.378	0.449
^{82}Pb	[Xe]$4f^{14}5d^{10}6s^{2}6p^{2}$	0.511	0.494	0.545
Atoms with half and two-thirds filled p subshells				
^{7}N	[He]$2s^{2}2p^{3}$	1.135	1.078	1.068
^{8}O	[He]$2s^{2}2p^{4}$	1.264	1.249	1.001
^{15}P	[Ne]$3s^{2}3p^{3}$	0.783	0.754	0.771
^{16}S	[Ne]$3s^{2}3p^{4}$	0.875	0.861	0.761
^{33}As	[Ar]$3d^{10}4s^{2}4p^{3}$	0.739	0.712	0.721
^{34}Se	[Ar]$3d^{10}4s^{2}4p^{4}$	0.806	0.789	0.717
^{51}Sb	[Kr]$4d^{10}5s^{2}5p^{3}$	0.669	0.644	0.635
^{52}Te	[Kr]$4d^{10}5s^{2}5p^{4}$	0.720	0.702	0.662
^{83}Bi	[Xe]$4f^{14}5d^{10}6s^{2}6p^{3}$	0.640	0.616	0.536
^{84}Po	[Xe]$4f^{14}5d^{10}6s^{2}6p^{4}$	0.683	0.665	0.619
Noble-metal atoms				
^{29}Cu	[Ar]$3d^{9}4s^{2}$	0.569	0.628	0.568
^{47}Ag	[Kr]$4d^{9}5s^{2}$	0.519	0.572	0.557
^{79}Au	[Xe]$4f^{14}5d^{9}6s^{2}$	0.513	0.570	0.678

[a] See Reference [17].

[b] See Reference [18].

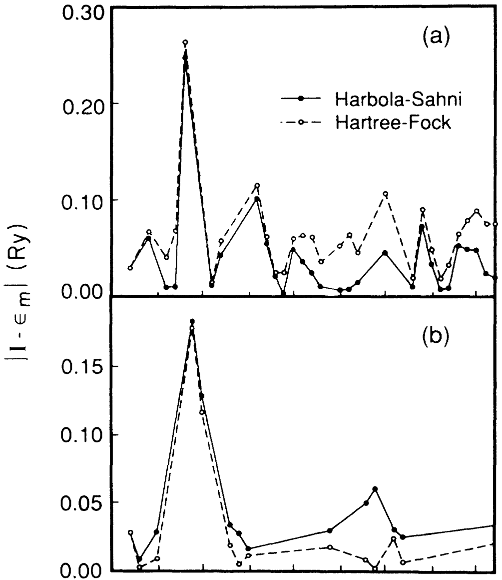

FIG. 1. The magnitude of the difference (in Ry) between the experimental ionization potential I and the highest-occupied-orbital eigenvalue ε_m as obtained in Hartree-Fock theory and the Harbola-Sahni approach within the Pauli-correlated approximation as a function of the atomic number Z for $Z=2$–42. Panel (a) corresponds to atoms for which the Harbola-Sahni results are closer to experiment than those of Hartree-Fock theory, and panel (b) to atoms for which the reverse is the case.

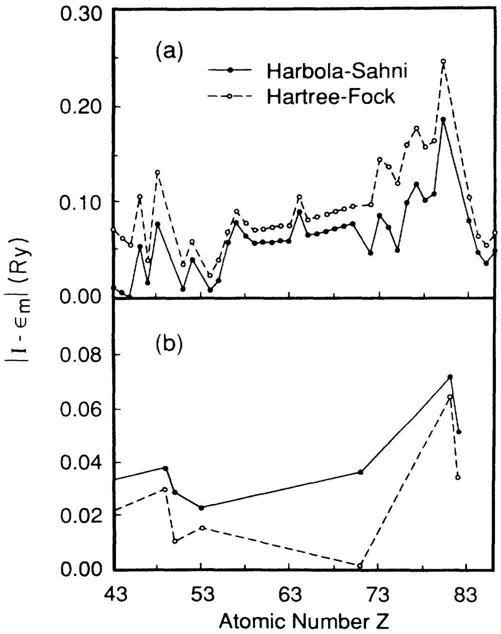

FIG. 2. The figure caption is the same as that of Fig. 1 with the exception that the atomic number Z ranges from $Z=42$–86.

TABLE IV. The expectation value of the single-particle operators r, r^2, r^{-1}, r^{-2}, and $\delta(\mathbf{r})$ for atoms in the central-field model as obtained by the Harbola-Sahni (HS) approach in the Pauli-correlated approximation. The corresponding Hartree-Fock (HF) theory (Ref. [17]) results are also given. The expectation values quoted are in atomic units.

Z	Atom		$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^{-1} \rangle$	$\langle r^{-2} \rangle$	$\langle \delta(\mathbf{r}) \rangle$
2	He	HS	0.9273	1.1848	1.6873	5.9955	3.5959
		HF	0.9273	1.1848	1.6873	5.9955	3.5959
3	Li	HS	1.6320	5.8541	1.9073	10.0624	13.8014
		HF	1.6733	6.2107	1.9052	10.0706	13.8148
4	Be	HS	1.5140	4.2211	2.1040	14.3918	35.3514
		HF	1.5322	4.3297	2.1022	14.4045	35.3877
5	B	HS	1.3525	3.1391	2.2779	18.6997	71.7560
		HF	1.3621	3.1702	2.2760	18.7310	71.9214
6	C	HS	1.1854	2.2892	2.4502	23.0792	127.0741
		HF	1.1908	2.2987	2.4482	23.1273	127.4580
7	N	HS	1.0468	1.7234	2.6212	27.5369	205.2651
		HF	1.0500	1.7261	2.6194	27.6000	205.9683
8	O	HS	0.9466	1.3851	2.7847	32.0602	310.2906
		HF	0.9512	1.3961	2.7824	32.1529	311.6609
9	F	HS	0.8597	1.1260	2.9490	36.6658	446.1298
		HF	0.8642	1.1371	2.9465	36.7818	448.3222
10	Ne	HS	0.7852	0.9280	3.1138	41.3537	616.7369
		HF	0.7891	0.9372	3.1113	41.4890	619.9221
11	Na	HS	0.9594	2.2373	3.2241	46.1839	829.9235
		HF	0.9858	2.4687	3.2209	46.3181	833.7575
12	Mg	HS	1.0051	2.3549	3.3294	51.1017	1 089.0796
		HF	1.0215	2.4676	3.3267	51.2379	1 093.7178
13	Al	HS	1.0444	2.5191	3.4255	56.0418	1 397.2025
		HF	1.0551	2.5751	3.4231	56.1829	1 402.8456
14	Si	HS	1.0265	2.2729	3.5197	61.0165	1 758.8655
		HF	1.0343	2.3043	3.5174	61.1619	1 765.6069
15	P	HS	0.9920	1.9968	3.6120	66.0241	2 178.3614
		HF	0.9982	2.0183	3.6099	66.1736	2 186.3141
16	S	HS	0.9616	1.8021	3.7009	71.0606	2 660.0332
		HF	0.9673	1.8227	3.6988	71.2166	2 669.4696
17	Cl	HS	0.9257	1.6081	3.7887	76.1275	3 208.1531
		HF	0.9307	1.6255	3.7869	76.2892	3 219.1902
18	Ar	HS	0.8885	1.4322	3.8755	81.2239	3 827.0091
		HF	0.8928	1.4464	3.8736	81.3908	3 839.7817
19	K	HS	1.0028	2.4780	3.9439	86.3706	4 524.3597
		HF	1.0237	2.6964	3.9417	86.5382	4 538.6539
20	Ca	HS	1.0484	2.7114	4.0100	91.5533	5 303.5527
		HF	1.0623	2.8283	4.0080	91.7232	5 319.6070
21	Sc	HS	1.0099	2.4179	4.0831	96.7001	6 164.4231
		HF	1.0227	2.5317	4.0814	96.8718	6 182.3042

TABLE IV. (*Continued*).

Z	Atom		$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^{-1} \rangle$	$\langle r^{-2} \rangle$	$\langle \delta(\mathbf{r}) \rangle$
22	Ti	HS	0.9686	2.1585	4.1569	101.8553	7 113.4939
		HF	0.9815	2.2798	4.1555	102.0276	7 133.2301
23	V	HS	0.9295	1.9439	4.2306	107.0212	8 155.1872
		HF	0.9426	2.0659	4.2293	107.1951	8 176.9552
24	Cr	HS	0.8929	1.7627	4.3041	112.1992	9 293.8828
		HF	0.9061	1.8820	4.3028	112.3751	9 317.8305
25	Mn	HS	0.8582	1.6042	4.3776	117.3902	10 533.938
		HF	0.8715	1.7229	4.3764	117.5669	10 560.077
26	Fe	HS	0.8284	1.4793	4.4497	122.5926	11 879.715
		HF	0.8407	1.5822	4.4483	122.7760	11 908.704
27	Co	HS	0.7997	1.3656	4.5218	127.8085	13 335.544
		HF	0.8114	1.4588	4.5203	127.9967	13 367.382
28	Ni	HS	0.7727	1.2645	4.5938	133.0376	14 905.764
		HF	0.7839	1.3497	4.5921	133.2301	14 940.568
29	Cu	HS	0.7473	1.1742	4.6655	138.2798	16 594.700
		HF	0.7579	1.2526	4.6638	138.4765	16 632.599
30	Zn	HS	0.7230	1.0920	4.7372	143.5356	18 406.677
		HF	0.7334	1.1660	4.7355	143.7352	18 447.675
31	Ga	HS	0.7467	1.2722	4.7969	148.8447	20 352.768
		HF	0.7548	1.3219	4.7952	149.0477	20 397.202
32	Ge	HS	0.7502	1.2703	4.8557	154.1725	22 432.300
		HF	0.7563	1.3005	4.8540	154.3779	22 480.118
33	As	HS	0.7461	1.2235	4.9136	159.5176	24 649.641
		HF	0.7509	1.2444	4.9119	159.7251	24 700.939
34	Se	HS	0.7430	1.1940	4.9699	164.8775	27 009.198
		HF	0.7472	1.2110	4.9683	165.0882	27 064.393
35	Br	HS	0.7356	1.1443	5.0256	170.2531	29 515.406
		HF	0.7392	1.1577	5.0240	170.4667	29 574.567
36	Kr	HS	0.7258	1.0875	5.0807	175.6439	32 172.660
		HF	0.7289	1.0981	5.0792	175.8599	32 235.890
37	Rb	HS	0.7927	1.7051	5.1281	181.0577	34 990.627
		HF	0.8055	1.8447	5.1264	181.2747	35 057.626
38	Sr	HS	0.8279	1.9179	5.1745	186.4894	37 971.637
		HF	0.8372	2.0016	5.1729	186.7082	38 042.812
39	Y	HS	0.8229	1.8176	5.2226	191.9137	41 114.120
		HF	0.8298	1.8818	5.2212	192.1329	41 189.282
40	Zr	HS	0.8102	1.6916	5.2710	197.3434	44 425.160
		HF	0.8173	1.7611	5.2698	197.5623	44 504.257
41	Nb	HS	0.7962	1.5807	5.3193	202.7793	47 909.362
		HF	0.8036	1.6536	5.3182	202.9982	47 992.582
42	Mo	HS	0.7818	1.4828	5.3674	208.2219	51 571.257
		HF	0.7895	1.5569	5.3663	208.4409	51 658.750
43	Tc	HS	0.7668	1.3921	5.4154	213.6716	55 415.360
		HF	0.7750	1.4693	5.4143	213.8903	55 507.100

(*Continued*). TABLE IV.

Z	Atom		$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^{-1} \rangle$	$\langle r^{-2} \rangle$	$\langle \delta(\mathbf{r}) \rangle$
44	Ru	HS	0.7542	1.3239	5.4627	219.1275	59 446.034
		HF	0.7616	1.3903	5.4616	219.3482	59 542.829
45	Rh	HS	0.7409	1.2570	5.5098	224.5906	63 667.865
		HF	0.7480	1.3177	5.5087	224.8126	63 769.628
46	Pd	HS	0.7277	1.1946	5.5568	230.0607	68 085.261
		HF	0.7345	1.2509	5.5557	230.2839	68 192.073
47	Ag	HS	0.7147	1.1365	5.6035	235.5378	72 702.656
		HF	0.7212	1.1893	5.6024	235.7619	72 814.609
48	Cd	HS	0.7016	1.0813	5.6502	241.0218	77 524.497
		HF	0.7081	1.1325	5.6490	241.2466	77 641.557
49	In	HS	0.7195	1.2188	5.6909	246.5312	82 563.142
		HF	0.7248	1.2552	5.6898	246.7584	82 686.163
50	Sn	HS	0.7253	1.2374	5.7313	252.0496	87 816.418
		HF	0.7294	1.2609	5.7301	252.2786	87 945.278
51	Sb	HS	0.7259	1.2197	5.7713	257.5767	93 288.803
		HF	0.7294	1.2366	5.7701	257.8074	93 423.567
52	Te	HS	0.7271	1.2129	5.8104	263.1115	98 984.739
		HF	0.7301	1.2261	5.8093	263.3444	99 125.883
53	I	HS	0.7252	1.1872	5.8492	268.6545	104 908.79
		HF	0.7277	1.1973	5.8481	268.8893	105 056.34
54	Xe	HS	0.7212	1.1524	5.8876	274.2056	111 065.41
		HF	0.7233	1.1602	5.8866	274.4421	111 219.44
55	Cs	HS	0.7721	1.6646	5.9220	279.7693	117 465.26
		HF	0.7816	1.7796	5.9208	280.0067	117 625.45
56	Ba	HS	0.8015	1.8685	5.9558	285.3428	124 109.98
		HF	0.8085	1.9399	5.9547	285.5817	124 276.86
57	La	HS	0.7891	1.7915	5.9952	290.8814	130 987.12
		HF	0.7956	1.8627	5.9943	291.1199	131 160.11
58	Ce	HS	0.7762	1.7195	6.0350	296.4212	138 113.04
		HF	0.7825	1.7913	6.0343	296.6589	138 292.14
59	Pr	HS	0.7634	1.6526	6.0749	301.9633	145 492.49
		HF	0.7696	1.7248	6.0744	302.2001	145 677.79
60	Nd	HS	0.7508	1.5906	6.1149	307.5081	153 130.05
		HF	0.7569	1.6622	6.1145	307.7447	153 321.83
61	Pm	HS	0.7386	1.5327	6.1548	313.0560	161 030.21
		HF	0.7446	1.6034	6.1545	313.2926	161 228.74
62	Sm	HS	0.7266	1.4782	6.1948	318.6072	169 197.52
		HF	0.7326	1.5481	6.1945	318.8437	169 402.77
63	Eu	HS	0.7149	1.4265	6.2347	324.1620	177 636.42
		HF	0.7209	1.4960	6.2346	324.3977	177 848.32
64	Gd	HS	0.7039	1.3793	6.2744	329.7198	186 351.40
		HF	0.7098	1.4460	6.2742	329.9579	186 571.24
65	Tb	HS	0.6931	1.3342	6.3141	335.2813	195 346.93
		HF	0.6989	1.3988	6.3138	335.5210	195 574.58

TABLE IV. (*Continued*).

Z	Atom		$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^{-1} \rangle$	$\langle r^{-2} \rangle$	$\langle \delta(\mathbf{r}) \rangle$
66	Dy	HS	0.6826	1.2912	6.3537	340.8466	204 627.47
		HF	0.6883	1.3541	6.3535	341.0874	204 862.90
67	Ho	HS	0.6723	1.2505	6.3933	346.4155	214 197.48
		HF	0.6779	1.3117	6.3931	346.6576	214 440.88
68	Er	HS	0.6624	1.2119	6.4329	351.9881	224 061.42
		HF	0.6679	1.2713	6.4326	352.2316	224 312.96
69	Tm	HS	0.6527	1.1750	6.4724	357.5645	234 223.74
		HF	0.6581	1.2330	6.4721	357.8089	234 483.40
70	Yb	HS	0.6432	1.1396	6.5119	363.1448	244 688.89
		HF	0.6485	1.1965	6.5116	363.3897	244 956.57
71	Lu	HS	0.6427	1.1189	6.5470	368.7549	255 475.02
		HF	0.6468	1.1609	6.5466	369.0013	255 751.36
72	Hf	HS	0.6384	1.0756	6.5820	374.3710	266 574.60
		HF	0.6426	1.1186	6.5815	374.6179	266 859.03
73	Ta	HS	0.6335	1.0349	6.6167	379.9924	277 991.90
		HF	0.6378	1.0790	6.6162	380.2400	278 284.59
74	W	HS	0.6281	0.9971	6.6511	385.6192	289 731.46
		HF	0.6326	1.0416	6.6505	385.8672	290 032.49
75	Re	HS	0.6223	0.9597	6.6853	391.2511	301 797.83
		HF	0.6271	1.0061	6.6847	391.4992	302 107.03
76	Os	HS	0.6178	0.9340	6.7191	396.8873	314 195.08
		HF	0.6221	0.9738	6.7184	397.1367	314 513.80
77	Ir	HS	0.6127	0.9064	6.7526	402.5284	326 928.18
		HF	0.6168	0.9426	6.7520	402.7788	327 256.11
78	Pt	HS	0.6075	0.8794	6.7860	408.1742	340 001.48
		HF	0.6113	0.9130	6.7853	408.4253	340 338.64
79	Au	HS	0.6021	0.8532	6.8193	413.8246	353 419.47
		HF	0.6057	0.8847	6.8186	414.0762	353 765.87
80	Hg	HS	0.5964	0.8270	6.8524	419.4795	367 186.65
		HF	0.6001	0.8578	6.8516	419.7314	367 542.13
81	Tl	HS	0.6093	0.9241	6.8824	425.1479	381 318.41
		HF	0.6126	0.9480	6.8816	425.4016	381 684.67
82	Pb	HS	0.6153	0.9496	6.9122	430.8217	395 809.60
		HF	0.6180	0.9658	6.9114	431.0767	396 186.26
83	Bi	HS	0.6182	0.9508	6.9418	436.5006	410 664.66
		HF	0.6204	0.9628	6.9410	436.7569	411 051.72
84	Po	HS	0.6214	0.9586	6.9709	442.1842	425 888.02
		HF	0.6234	0.9680	6.9701	442.4420	426 286.07
85	At	HS	0.6226	0.9525	6.9998	447.8727	441 484.32
		HF	0.6243	0.9597	6.9991	448.1319	441 893.32
86	Rn	HS	0.6224	0.9391	7.0286	453.5661	457 458.02
		HF	0.6239	0.9447	7.0278	453.8265	457 878.01

rate. For the He atom, for example, the Hartree-Fock-theory result for $\langle r^{-1} \rangle$ differs from that of Pekeris's [30] result by only 0.06%, whereas for the expectation $\langle r^2 \rangle$ the error is 0.7%, an order of magnitude greater. The HS values of $\langle r^{-1} \rangle$ are greater but the same as those of HF to at least three, and for many of the heavier atoms ($Z > 47$) to four significant figures. For the heavier atoms the differences between the two are at most one part per ten thousand.

For the lighter atoms ($Z < 25$), the HS and HF results for $\langle r^{-2} \rangle$ are the same to two significant figures and for the heavier atoms to three significant figures. The difference for the heavier atoms is one part per thousand or less, and diminishes with increasing atomic number.

Since the HF total energies lie below those of the HS formalism, we expect the HF electron density at the nucleus $\langle \delta(\mathbf{r}) \rangle$ to be better. However, the HS results are the same to two significant figures for the lighter atoms ($Z < 25$) and to three significant figures for the heavier ones. The differences for the heavier atoms are a maximum of only two parts per thousand, and once again this difference diminishes with increasing atomic number.

The HS results for $\langle r \rangle$ and $\langle r^2 \rangle$ are consistently smaller but in general the same as HF to two significant figures. For $\langle r^2 \rangle$ the difference between the two theories is greatest for those atoms for which the outermost shell is comprised of *s* electrons. However, since the HS highest-occupied-orbital eigenvalues are in general closer to the experimental ionization potentials, we expect these HS expectation values to be better.

It is evident from a study of Table IV and the above analysis that the HS and HF orbitals are essentially equivalent; the expectations are essentially the same and all trends in the various expectations are equally reproduced. For example, the monotonic decrease in $\langle r \rangle$ as all *p*, *d*, and *f* subshells are filled with the exception of the 6*p* subshell for which it increases, the increase in $\langle r \rangle$ as all *s* subshells are filled with the exception of the 2*s* subshell, the dramatic increase in $\langle r^2 \rangle$ for *s* subshells following the filling of a *p* subshell, etc., are exactly the same in both formalisms.

IV. CONCLUSION

In this work we have applied the Harbola-Sahni approach to the theory of the inhomogeneous electron gas for the determination of the electronic structure of atoms within the nonrelativistic Pauli-correlated approximation. In these calculations the central-field model is assumed for open-shell atoms, so that the effective many-body potential is path-independent for all atoms considered. This assumption is justified since the noncentral part of the exchange potential for these atoms constitutes a small perturbation [8]. In both the Harbola-Sahni approach in the Pauli-correlated approximation, as well as in Hartree-Fock theory, only correlations between the electrons due to the Pauli exclusion principle are considered. In Hartree-Fock theory the absolute minimum of the total ground-state energy is guaranteed by the variational principle for the energy, and the accuracy of the single-particle operator expectation values by Brillouin's theorem [29]. An examination of the present results indicates that for properties such as the total ground-state energy and various single-particle operator expectation values, they are essentially equivalent to those of Hartree-Fock theory with the differences diminishing with increasing atomic number. The total ground-state energies, of course, lie above those of Hartree-Fock theory as they must. However, for the more significant and sensitive property of the removal energy, the corresponding highest-coupled-orbital eigenvalues for the majority of atoms considered are closer than those of Hartree-Fock theory when compared with experimental ionization potentials. For the remaining few atoms, the results for the highest-occupied-orbital eigenvalues of the two theories are equivalent.

For external potentials that vanish at infinity, the orbitals [31] of Hartree-Fock theory *all* have the *same* asymptotic structure $\phi_i(r) \underset{r\to\infty}{\sim} \exp(-\sqrt{2\varepsilon_m}\, r)$, where ε_m is the corresponding highest-occupied-orbital eigenvalue. Thus, in Hartree-Fock theory, all the orbitals, rather than just the highest occupied orbital as physically is the case, contribute to the asymptotic structure of the density. As such the relationship between the highest-occupied-orbital eigenvalue of Hartree-Fock theory and the experimental ionization potential has meaning only within the context of Koopmans's theorem [16].

In contrast to Hartree-Fock theory, the Harbola-Sahni approach to the many-electron problem is based entirely on physical arguments founded in Coulomb's law. Thus the equivalence of the results for the ground-state energy and expectation values to those of Hartree-Fock theory is indicative of the correctness of this physical interpretation of the local effective many-body potential. Further, the fact that the highest-occupied-orbital eigenvalues are good approximations to the experimental ionization potentials clearly demonstrates that the asymptotic structure of the Harbola-Sahni potential is that of the exact total effective potential.

Hartree-Fock theory may, of course, also be interpreted physically as described by Slater [32]. In this description each electron moves in an independent exchange potential which is due to a nonlocal orbital-dependent Fermi hole charge distribution $\rho_{x,i}(\mathbf{r},\mathbf{r}')$. Although this picture is appealing, the orbital-dependent Fermi holes cannot be interpreted in terms of quantum-mechanical probabilities since in fact they can be negative [5,33]. Furthermore, the orbital-dependent Fermi holes and consequently the potentials are singular at the nodes of the orbitals. Within this interpretation of Hartree-Fock theory, the single-particle potentials are obtained by treating the orbital-dependent holes as if they were static charge distributions. If the dynamic nature of these holes is explicitly taken into consideration by first calculating the electric fields, and then determining the total field by summing the weighted average of these fields weighted by the probability of occupation of each state, then the Harbola-Sahni potential $W_x(\mathbf{r})$ of the Pauli-correlated approximation is recovered [34].

As noted in the Introduction, the Harbola-Sahni approach to the many-electron problem falls within Kohn-Sham density-functional theory. However, whereas the potential W_x is physically derived, the exchange-only Kohn-Sham potential is *defined* [35] as that potential whose orbitals minimize the Hartree-Fock energy. Thus within exchange-only [35] Kohn-Sham theory, the Harbola-Sahni potential W_x and the Kohn-Sham potential μ_x are not the same. For atoms, the exchange-only Kohn-Sham potential is obtained via the variational principle by the optimized potential method [36,37]. As noted in our previous work [3,6], the total ground-state energies [15,37] of atoms obtained within the optimized potential method are closer to Hartree-Fock energies by approximately half the difference of those of the present work. Further, the highest-occupied-orbital energies [15,37] in this method have the same meaning as those of Hartree-Fock, and can be interpreted [38] as the removal energies only via Koopmans's theorem [16].

Finally, although the highest-occupied-orbital eigenvalues in our calculations within the Pauli-correlated approximation are good approximations to the experimental ionization potentials, the differences are in general greater for the heavier atoms. This, as noted previously, is primarily due to the neglect of relativistic effects. Thus, in future research we first propose to incorporate these effects within the Pauli-correlated approximation. We then propose to go beyond this approximation by also incorporating the effects of Coulomb correlations via the random-phase approximation and by the use of correlated wave functions.

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