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Ground-state energies and highest occupied eigenvalues of atoms in exchange-only density-functional theory

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The exchange-correlation potential of the Kohn-Sham density-functional theory has recently been interpreted as the work required to move an electron against the electric field of its Fermi-Coulomb hole charge distribution. In this paper we present self-consistent results for ground-state total energies and highest occupied eigenvalues of closed subshell atoms as obtained by this formalism in the exchange-only approximation. The total energies, which are an upper bound, lie within 50 ppm of Hartree-Fock theory for atoms heavier than Be. The highest occupied eigenvalues, as a consequence of this interpretation, approximate well the experimental ionization potentials. In addition, the self-consistently calculated exchange potentials are very close to those of Talman and co-workers [J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976); K. Aashamar, T. M. Luke, and J. D. Talman, At. Data Nucl. Data Tables **22**, 443 (1978)].

In a recent paper, Harbola and Sahni[1] have provided a physical interpretation for the local many-body exchange-correlation potential of Hohenberg-Kohn-Sham[2] density-functional theory. As a consequence of their interpretation, the potential can be determined directly from the Fermi-Coulomb hole charge distribution of an electron in which all the many-body effects are incorporated. In the Kohn-Sham theory[2] this potential is derived by the application of the variational principle for the energy to be the functional derivative of a universal exchange-correlation energy functional. Neither the universal energy functional nor the Fermi-Coulomb hole charge distribution of interacting electron gas systems is known exactly. In the exchange-only approximation,[3] in which only Pauli correlations between the electrons are assumed in the wave function, the universal exchange-energy functional of the density of the Kohn-Sham theory is also unknown, and thus so is its functional derivative. However, the Fermi hole charge distribution of an electron is known precisely in terms of the orbitals which generate the electronic density, and consequently the local exchange potential can be determined. Furthermore, according to Harbola and Sahni,[1] the asymptotic structure of the exchange-correlation potential is that of the Pauli-correlated approximation, and thus also known. Now the highest occupied eigenenergy of the Kohn-Sham equation, which has the interpretation[4] of being the negative of the ionization potential, depends principally on the structure of the exchange-correlation potential in the region beyond the inner shells. Thus the highest occupied eigenenergies of Harbola-Sahni exchange-only theory should approximate well the nonrelativistic ionization potentials. In this paper we present results for ground-state total energies and highest occupied eigenvalues of atoms as obtained by the Harbola-Sahni formalism within the exchange-only approximation[3] of density-functional theory. We compare the energies with those of Hartree-Fock theory, and the eigenvalues with experimental ionization potentials.

According to Harbola and Sahni,[1] the exchange-correlation potential $W_{\mathrm{xc}}(\mathbf{r})$ is the work required to bring an electron from infinity to its final position against the electric field of its Fermi-Coulomb hole charge distribution. Consequently, the Kohn-Sham differential equation to be solved for the orbitals $\Psi_i(\mathbf{r})$, which leads to the density $\rho(\mathbf{r})=\sum_i \Psi_i^*(\mathbf{r})\Psi_i(\mathbf{r})$, is

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

where $V_{\mathrm{es}}(\mathbf{r})$, the Hartree electrostatic potential, includes the nuclear Coulomb potential. The potential $W_{\mathrm{xc}}(\mathbf{r})$ is

$$W_{\mathrm{xc}}(\mathbf{r})=-\int_{\infty}^{\mathbf{r}}\mathcal{E}_{\mathrm{xc}}\cdot dl ,$$

where the electric field $\mathcal{E}_{\mathrm{xc}}(\mathbf{r})$ due to the Fermi-Coulomb hole charge density $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ at $\mathbf{r}'$ for an electron at $\mathbf{r}$ is given by Coulomb's law as

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

The exchange-correlation energy is obtained as the energy of interaction between an electron and its Fermi-Coulomb hole.

In the exchange-only approximation,[3] the work $W_{\mathrm{xc}}(\mathbf{r})$ is replaced in the differential equation by W_x, the work done against the force field of the Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$. The Fermi hole can be explicitly defined in terms of the orbitals as $\rho_x(\mathbf{r},\mathbf{r}')=|\gamma(\mathbf{r},\mathbf{r}')|^2/2\rho(\mathbf{r})$, where $\gamma(\mathbf{r},\mathbf{r}')=\sum_i\Psi_i^*(\mathbf{r})\Psi_i(\mathbf{r}')$ is the single-particle density matrix. The corresponding exchange energy $E_x[\rho]$, obtained from these orbitals as the interaction energy between an electron and its Fermi hole satisfies the scaling law

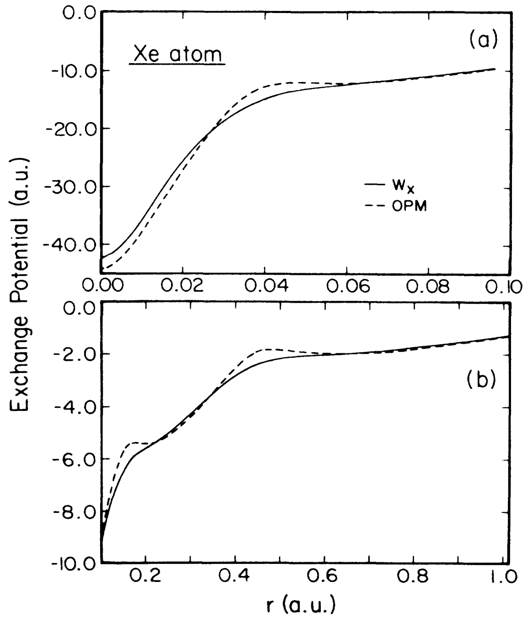

FIG. 1. The W_x and optimized potential method (OPM) exchange potentials for the xenon atom in the interior of the atom.

$E_x[\rho_\lambda]=\lambda E_x[\rho]$, where $\Psi_{i,\lambda}(\mathbf{r})=\lambda^{3/2}\Psi_i(\lambda\mathbf{r})$, so that $\rho_\lambda(\mathbf{r})=\lambda^3\rho(\lambda\mathbf{r})$. The local exchange potential W_x when substituted for the functional derivative $\mu_x\{\rho(\mathbf{r})\}=\delta E_x[\rho]/\delta\rho$, has also been shown[1] to satisfy the virial-theorem-based sum rule[5]

$$E_x[\Psi_i]=\frac{1}{2}\sum_{\substack{i,j\\ \text{(parallel spins)}}}\int\int\frac{\Psi_i^*(\mathbf{r})\Psi_j^*(\mathbf{r}')\Psi_i(\mathbf{r}')\Psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}$$

$$=-\int\rho(\mathbf{r})\mathbf{r}\cdot\nabla\mu_x\{\rho(\mathbf{r})\}d\mathbf{r}\ .$$

Since the exchange-correlation energy functional may be written as a sum of its exchange and correlation energy components, we may similarly think of the Fermi-Coulomb hole as being comprised of its Fermi and Coulomb hole charge distributions. However, as both the Fermi-Coulomb and Fermi hole charges are the same[6,7] in magnitude as that of the electron, the total Coulomb hole charge is zero. Thus the contribution of the Coulomb hole charge distribution to the electric field and potential for electron positions asymptotically far from the nucleus vanishes. Therefore the asymptotic structure of the potential $W_{xc}(\mathbf{r})$ for the fully correlated atom is that of $W_x(\mathbf{r})$ alone and precisely determinable. As such, the highest occupied eigenenergy values obtained by solution in the exchange-only approximation should constitute a significant fraction of the nonrelativistic ionization potential which is the maximum eigenvalue in the fully correlated case. We note that the asymptotic structure of the potential W_x in atoms has been shown[1] to be $-1/r$ as is the case, and at metallic surfaces[8] to be the image potential $-1/4x$, in agreement with classical electrostatics.

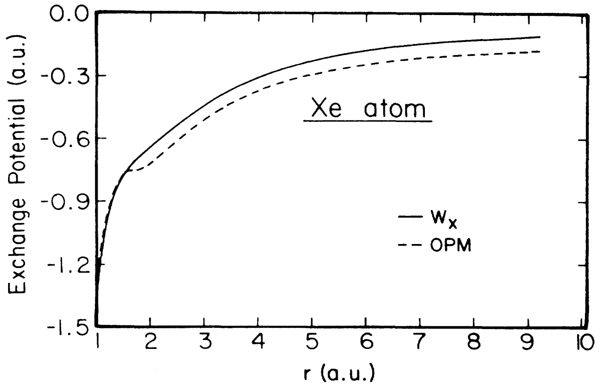

FIG. 2. The W_x and optimized potential method (OPM) exchange potentials for the xenon atom in the region exterior to the shells.

In Figs. 1 and 2 we plot the self-consistently determined local exchange potential W_x for the Xe atom. Figure 1 corresponds to the interior region of the atom up to the last subshell, and Fig. 2 corresponds to the region beyond as well as to the asymptotic region. Observe that the curve is monotonic with the shell structure of the atom clearly evident. Asymptotically (see Fig. 2), the potential varies as $-1/r$ due to the fact[1] that the Fermi hole stabilizes for these positions of the electron. The graph is typical of all the other atoms considered in this paper.

In Table I we present results for the ground-state energies of the first ten atoms of the Periodic Table that have closed subshells, together with the Hartree-Fock values.[9] With the exception of the Be atom, for which the W_x formalism value differs by 0.014%, the results for the remaining atoms lie within 50 ppm of those of Hartree Fock theory. For Kr and the heavier atoms, these differences are less than 10 ppm. Observe that the energies consistently lie above those of Hatree-Fock theory as they must.[3] The self-consistency procedure for the determination of the local potential W_x is also numerically easier than that for the orbital-dependent potentials of Hartree-Fock theory.

TABLE I. Ground-state atomic energies in the Pauli-correlated approximation. The negative values of the energies in atomic units are quoted.

Atom	Hartree-Fock[a]	Harbola-Sahni
Be	14.573	14.571
Ne	128.547	128.542
Mg	199.615	199.606
Ar	526.818	526.804
Ca	676.758	676.743
Zn	1777.848	1777.820
Kr	2752.055	2752.030
Sr	3131.546	3131.519
Cd	5465.133	5465.093
Xe	7232.138	7232.101

[a] See Ref. 9.

TABLE II. Highest occupied eigenvalues of atoms in the Pauli-correlated approximation and experimental ionization potentials. The negative values of the energies in rydbergs are quoted.

Atom	Hartree-Fock[a]	Harbola-Sahni	Expt.[b]
Be	0.619	0.626	0.685
Mg	0.506	0.521	0.562
Ca	0.391	0.402	0.449
Zn	0.585	0.646	0.690
Sr	0.357	0.369	0.419
Cd	0.530	0.583	0.661
Ne	1.701	1.713	1.585
Ar	1.182	1.178	1.158
Kr	1.048	1.035	1.029
Xe	0.915	0.899	0.892

[a] See Ref. 9.

[b] See Ref. 10.

In Table II we present our results for the highest occupied eigenenergies together with those of Hartree-Fock theory[9] as well as the experimental[10] ionization potentials. We group those atoms whose last closed subshell is an *s* subshell separately from the noble-gas atoms. The reason for the separation is that the experimental ionization potentials for the former group lie below those of Hartree-Fock theory, whereas for the latter they lie above. Observe that with the exception of Ne, the W_x formalism eigenvalues also lie above those of Hartree-Fock theory for the noble-gas atoms, and below those of Hartree-Fock theory for the others, so that they more closely approximate the experimental ionization potentials. Of course, the experimental values include relativistic contributions, but these are unknown. Also, the highest occupied eigenenergies of Hartree-Fock theory do not have the physical significance of being removal energies since Koopman's theorem[11] is valid[12] only for extended orbitals. Nevertheless, the above comparison implies that since the eigenenergies of the present work are a fair approximation to experiment, the local exchange potential W_x is physically accurate not only asymptotically but also in regions much closer to the atom. Certainly, the comparison with experiment demonstrates how principal the contributions of Pauli correlation are.

Finally, we compare our results with those of Talman and co-workers[13] as determined within the framework of the optimized potential method.[13,14] The Talman and co-workers[13] ground-state energies are superior to those of the present work; they also lie above Hartree-Fock theory, but differ from it by approximately half the difference between the present and Hartree-Fock values. However, the optimized exchange potential as published[13] does not satisfy[1] the sum rule given above. The Talman highest occupied eigenvalues also generally approximate well the Hartree-Fock results, but their differences are random in sign. For the purposes of comparison, we plot in Figs. 1 and 2 the optimized exchange potential. Observe (see Fig. 1) that the two curves are essentially equivalent in the shell regions of the atom and differ only in the intershell regions where the optimized potential possesses bumps. These bumps have yet to be interpreted physically. Asymptotically (see Fig. 2), the optimized potential approaches $-1/r$ much more slowly than the W_x potential, which explains why the W_x formalism eigenvalues are superior to those of the optimized potential method. With the current definition[3] of the exchange energy of density-functional theory, the optimized potential should, in *principle,*[5] satisfy the virial-theorem-based sum rule. The fact that it does not[1] is a reflection of the numerical complexity of the formalism. The *exact* optimized potential is thus yet unknown. On the other hand, the potential W_x is the only physically derived potential known to satisfy[1] the sum rule *analytically.* It also satisfies[1] the sum rule numerically, thus demonstrating the numerical ease of these calculations. To show this we compare in Table III the exchange energies $E_x[\psi_i]$ as determined from the orbitals ψ_i with those obtained from the potential W_x employing the expression from the right-hand side of the virial theorem sum rule. Observe that the sum rule is satisfied to 6–8 significant figures. Thus, even if the potential W_x were not the exact functional derivative of the exchange energy functional, the results for the total energies and highest occupied eigenvalues presented, nevertheless, clearly demonstrate the high accuracy of this potential.

We conclude by noting that the Hartree-Fock, Kohn-Sham, and optimized-potential-method theories are all founded in the variational principle for the energy. The Harbola-Sahni formalism, on the other hand, is formulated entirely on the basis of physical considerations. The accuracy of the results presented in this paper and those for metallic surfaces given elsewhere,[8] together with the fact that the exchange-only potential W_x satisfies the virial-theorem sum rule, is all the more remarkable in light of this difference.

Work towards the determination of properties of nonspherical atoms is in progress and is planned to be presented elsewhere.

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TABLE III. Comparison of the exchange energies $E_x[\psi_i]$ in atomic units as determined from the orbitals ψ_i with those obtained from the potential W_x as given by the expression on the right-hand side of the virial theorem sum rule.

Atom	$-E_x[\psi_i]$	$+\int \rho(\mathbf{r})\mathbf{r}\cdot\nabla W_x d\mathbf{r}$
Be	2.666 468 3	2.666 467 9
Ne	12.121 832 2	12.121 831 3
Mg	16.003 442 4	16.003 441 3
Ar	30.188 792 1	30.188 790 5
Ca	35.214 000 2	35.213 998 4
Zn	69.621 831 4	69.621 828 6
Kr	93.863 478 6	93.863 475 1
Sr	101.961 127 6	101.961 124 0
Cd	148.879 953 6	148.879 949 7
Xe	179.092 056 4	179.092 052 3

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

[2] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[3] V. Sahni, J. Gruenebaum, and J. P. Perdew Phys. Rev. B **26**, 4371 (1982); V. Sahni and M. Levy, *ibid.* B **33**, 3869 (1986).

[4] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982); M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).

[5] M. Levy and J. P. Perdew, Phys. Rev. B **32**, 2010 (1985).

[6] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976); D. C. Langreth and J. P. Perdew, *ibid.* **15**, 2884 (1977).

[7] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[8] M. K. Harbola and V. Sahni, Phys. Rev. B **39**, 10437 (1989); V. Sahni, Surf. Sci, **213**, 226 (1989).

[9] C. F. Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

[10] C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra,* Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.), (U. S. GPO, Washington, D. C., 1970), Vol. 34.

[11] T. Koopmans, Physica **1**, 104 (1933).

[12] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[13] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976); K. Aashamar, T. M. Luke, and J. D. Talman, At. Data Nucl. Data Tables **22**, 443 (1978).

[14] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 3876 (1953).