A Combination of the Work Formalism for Exchange with an Optimized Correlation Energy Functional for Atoms

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Abstract. — The Harbola-Sahni formalism for the exchange potential of many-electron systems gives extremely accurate total energies for atoms (the energies are practically indistinguishable from the Hartree-Fock energies). We combine here this formalism with the usual density functional prescription for the correlation potential, using a recently developed optimized local correlation functional (Gritsenko O.V *et al*, *Phys Rev. A* **47** (1993) 1811). Numerical tests carried out for several closed shell atoms and ions indicate that the results preserve the accuracy of the exchange-only calculations. We expect the same behavior to hold true for large molecules and atomic clusters. However, similar tests for the He, Be and Ne isoelectronic series indicate that the optimized local correlation functional is not valid for highly ionized atoms

1. Introduction

The usual way to introduce the exchange-correlation potential in density functional theory (DFT) is through the variational derivative of the exchange-correlation energy functional [1,2] (Hartree atomic units will be used through the paper unless explicitly stated otherwise)

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \tag{1}$$

The main problem with this rigorous formulation is that the exact form of the energy functional $E_{xc}[\rho]$ is unknown, and in practice, one is bound to use simple approximations like the well known local density approximation (LDA) [1,2]. Another alternative, pioneered by Slater [3] has been to construct directly $V_{xc}(\mathbf{r})$ making use of the idea of the Fermi-Coulomb hole. A successful step in this direction has been taken via the Work-formalism developed by Harbola and Sahni (HS) [4–7]. In this formalism, $V_{xc}(\mathbf{r})$ is calculated as the work $W_{xc}(\mathbf{r})$ required to bring an electron from infinity to its position $\mathbf{r}$ against the force field $\mathbf{E}_{xc}(\mathbf{r})$ of its Fermi-Coulomb hole charge distribution

$$W_{xc}(\mathbf{r}) = -\int_{\infty}^{\mathbf{r}} \mathbf{E}_{xc}(\mathbf{r}') \cdot d\mathbf{l}, \tag{2}$$

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

In equation (3), $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ is the Fermi-Coulomb hole charge distribution surrounding an electron placed at $\mathbf{r}$. Of course, this method is useful only if one is able to evaluate, or at least set up an accurate approximation for $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$. This can be done in the exchange-only case. $\rho_{\mathrm{x}}(\mathbf{r},\mathbf{r}')$ can be evaluated exactly in this case, and all the applications of the formalism have been performed so far at the exchange-only level [4–7]. A consequence is that $W_{\mathrm{x}}(\mathbf{r})$ retains the correct asymptotic behavior $-\dfrac{1}{r}$ of the exchange potential in an atom, which is crucial for an accurate description of properties depending on the tail of the density.

Due to our lack of knowledge in constructing $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$, it is difficult to extend the Work-formalism beyond the exchange-only level. In principle, it is possible to study the exchange-correlation case within the Work formalism if one writes the wavefunction as an (infinite) linear combination of Slater determinants [8]. As an alternative, the procedure we explore in this paper is a combination of the Harbola-Sahni method for exchange with standard DFT for correlation. Returning to the exchange-correlation potential $V_{\mathrm{xc}}(\mathbf{r})$, we first separate this out in exchange and correlation parts

$$V_{\mathrm{xc}}(\mathbf{r}) = V_{\mathrm{x}}(\mathbf{r}) + V_{\mathrm{c}}(\mathbf{r}). \tag{4}$$

In this paper, $V_{\mathrm{x}}(\mathbf{r})$ is calculated according to the Harbola-Sahni prescription, that is $V_{\mathrm{x}}(\mathbf{r}) = W_{\mathrm{x}}(\mathbf{r})$. On the other hand, the DFT prescription $V_{\mathrm{c}}(\mathbf{r}) = \dfrac{\delta E_{\mathrm{c}}[\rho]}{\delta \rho(\mathbf{r})}$, where $E_{\mathrm{c}}[\rho]$ is the correlation-energy functional, is employed for $V_{\mathrm{c}}(\mathbf{r})$. This combination retains the full exchange-correlation potential local in character. In Section 2 we give some details of the method and indicate the approximation used for $E_{\mathrm{c}}[\rho]$. In Section 3 we present results for several free atoms, ions and isoelectronic series. Our applications are restricted to systems with closed electronic shells, because for those spherically symmetric systems one is absolutely sure that the work $W_{\mathrm{xc}}(\mathbf{r})$ of equation (2) is path-independent. For open shell systems, or for systems with arbitrary symmetry, there is no rigorous proof that the work W_{xc} is path independent. In such cases, Harbola and Sahni recommend to use an "approximate" potential obtained from the irrotational component of the field [7]. This approximation should also be very accurate because the solenoidal component of the electric field for non-spherical atoms is negligible in comparison to the irrotational component. Evidently the work is also path-independent for all atoms if we use the central field approximation. Section 4 contains our conclusions, as well as proposals for application of this method to interesting systems other than atoms.

2. Method

Neglecting Coulomb correlation in the Work formalism, equations (2) and (3) are replaced by

$$W_{\mathrm{x}}(\mathbf{r}) \quad = \quad - \int_{\infty}^{\mathbf{r}} \mathbf{E}_{\mathrm{x}}(\mathbf{r}') \cdot \mathrm{d}\mathbf{l}, \tag{5}$$

$$\mathbf{E}_{\mathrm{x}}(\mathbf{r}) \quad = \quad \int \frac{\rho_{\mathrm{x}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{3}} \left(\mathbf{r} - \mathbf{r}' \right) \mathrm{d}\mathbf{r}'. \tag{6}$$

The properties of the system are then obtained by solving the single-particle differential equations

$$\left[-\frac{1}{2}\nabla^{2} + V_{\mathrm{es}}(\mathbf{r}) + W_{\mathrm{x}}(\mathbf{r}) \right] \psi_{\imath}(\mathbf{r}) = \varepsilon_{\imath}\psi_{\imath}(\mathbf{r}), \tag{7}$$

where
$$V_{\mathrm{es}}(\mathbf{r}) = v_n(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}' \tag{8}$$

is the electrostatic potential seen by the electrons. This is the sum of the external nuclear potential and the classical Coulomb potential of the electrons.

The Fermi hole charge $\rho_{\mathrm{x}}(\mathbf{r}, \mathbf{r}')$ can be rigorously expressed in terms of the one electron orbitals of equation (7) as

$$\rho_{\mathrm{x}}(\mathbf{r}, \mathbf{r}') = \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{2\rho(\mathbf{r})}. \tag{9}$$

Here $\gamma(\mathbf{r}, \mathbf{r}') = \sum_i \psi_i^*(\mathbf{r})\, \psi_i(\mathbf{r}')$ is the single-particle density matrix and the electron density $\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$ is just the diagonal part of $\gamma(\mathbf{r}, \mathbf{r}')$. These summations are extended over the occupied single-particle states. The total energy of the system is easily computed as

$$
\begin{aligned}
E \;=\; & \sum_i \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{r})\, \mathrm{d}\mathbf{r} + \int v_n(\mathbf{r})\, \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} \\
& + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\,\rho_{\mathrm{x}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'.
\end{aligned}
\tag{10}
$$

Equation (9) indicates that $\rho_{\mathrm{x}}(\mathbf{r}, \mathbf{r}')$ is constructed exactly in this exchange-only theory. As a consequence of this fact, extremely accurate total ground state energies have been obtained for neutral atoms by this approach [5,6]. Those energies are virtually identical to the Hartree-Fock ones. The results for excited states are also very encouraging [9]

As stated in the Introduction, we are interested in adding Coulomb correlation into the formalism in the way indicated after equation (4). The usual LDA suggests itself as a possible approximation for $E_{\mathrm{c}}[\rho]$, although it is well known that LDA correlation energies based on homogeneous electron gas data give poor results for atoms (roughly a factor of two larger) [10]. Among other possible alternatives [10–14], we have chosen a recently developed "optimized local approximation" (OLA) [10,14] which has been successfully tested for free atoms [10,14] and positive ions [15]. The OLA is based on an explicit modelling of the correlation hole arising from the Coulomb repulsion between electrons. Fulfillment of the sum rule for the normalization of this hole (zero charge) is required, in addition to the high density limit and to some exact conditions at zero interelectronic separation. Within this approximation, we express the Coulomb correlation energy as:

$$E_{\mathrm{c}}[\rho] = \int \rho(\mathbf{r})\varepsilon_{\mathrm{c}}(\rho(\mathbf{r}))\mathrm{d}\mathbf{r} \tag{11}$$

with

$$
\begin{aligned}
\varepsilon_{\mathrm{c}}(\rho(\mathbf{r})) = \;& \left[1 - \frac{I_2^u}{I_3^u}\ln\left(1 + \frac{I_3^u}{I_2^u}\right)\right] \frac{\mathrm{e}^x Ei(-x)}{\pi b^u} \\
& + \left[\frac{I_2^u}{I_3^u} - \left(\frac{I_2^u}{I_3^u}\right)^2 \ln\left(1 + \frac{I_3^u}{I_2^u}\right)\right] \left[\frac{1}{\pi^{1/2} k b^u} - \frac{\mathrm{e}^x[1 - \Phi(x^{1/2})]}{(b^u)^{3/2}\, \rho^{1/2}(\mathbf{r})}\right] \\
& + \left[1 - \frac{2I_2^v}{I_3^v}\ln\left(1 + \frac{I_3^v}{2I_2^v}\right)\right] \left[\frac{\mathrm{e}^y Ei(-y)}{\pi b^v} - \frac{\mathrm{e}^z Ei(-z)}{\pi b^v}\right] \\
& + \left[\frac{I_2^v}{I_3^v} - \frac{1}{2}\left(\frac{2I_2^v}{I_3^v}\right)^2 \ln\left(1 + \frac{I_3^v}{2I_2^v}\right)\right]
\end{aligned}
$$

$$\times \left[\frac{1}{\pi^{1/2}kb^v} - \frac{e^y[1-\Phi(y^{1/2})]}{(b^v)^{3/2}\,\rho^{1/2}(\mathbf{r})} - \frac{1}{\pi^{1/2}kb^v z^{1/2}} + \frac{e^z[1-\Phi(z^{1/2})]}{(b^v)^{3/2}\,\rho^{1/2}(\mathbf{r})} \right] , \quad (12)$$

where x, y, z, I_n^u, I_n^v, b^u and b^v are functions of the local density $\rho(\mathbf{r})$ and a parameter k (the interested reader is referred to [14] for details about the derivation of this functional and the precise form of x, y, z, I_n^u, I_n^v, b^u and b^v). The value $k = 0.196$ of this empirical parameter was optimized in [14] by a global fit to the empirical correlation energies of small closed shell atoms. Evidently, when we introduce correlation, $W_x(\mathbf{r})$ in equation (7) has to be substituted by $W_x(\mathbf{r}) + V_c^{OLA}(\mathbf{r})$ and the correlation energy term, $E_c^{OLA}[\rho]$ has to be added to the total energy in equation (10).

The fitting of the parameter k was done using for the exchange energy the non-local Weighted Density Approximation (WDA) [14, 16, 17]. Since calculations using the WDA for exchange will be also presented in this paper for comparative purposes, we briefly describe the WDA functional. The exchange energy is expressed as

$$E_x^{WDA}[\rho] = -\frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')g_x^{WDA}(|\mathbf{r}-\mathbf{r}'|;r_x(\mathbf{r}))}{|\mathbf{r}-\mathbf{r}'|} \; d\mathbf{r}\; d\mathbf{r}' \qquad (13)$$

This energy can be interpreted as the electrostatic interaction between two charge distributions: one is the usual electron density $\rho(\mathbf{r})$, and the other, $\{\rho(\mathbf{r}')g_x^{WDA}(|\mathbf{r}-\mathbf{r}'|;r_x(\mathbf{r}))\}$, is a non-local charge density representing the Fermi hole around an electron placed at $\mathbf{r}$. The WDA form for the pair correlation function $g_x(\mathbf{r_1},\mathbf{r_2})$ is chosen as

$$g_x^{WDA}(|\mathbf{r}-\mathbf{r}'|;r_x(\mathbf{r})) = -\frac{1}{2}\exp\left\{ - \left[\frac{|\mathbf{r}-\mathbf{r}'|}{r_x(\mathbf{r})} \right]^{3/2} \right\} \qquad (14)$$

where $r_x(\mathbf{r})$, which can be interpreted as the effective radius of the Fermi hole, is fixed by the sum rule giving the exact charge of this hole:

$$\int \rho(\mathbf{r}')g_x^{WDA}(|\mathbf{r}-\mathbf{r}'|;r_x(\mathbf{r})) \; d\mathbf{r}' = -1 , \qquad (15)$$

so that the WDA exchange energy functional is completely free of parameters. Equation (15) indicates that $r_x(\mathbf{r})$ depends in a nonlocal way on the electron density.

3. Results

As a test of the Work+OLA method, we have performed nonrelativistic calculations for some closed shell atoms and positive and negative ions in their ground state. The correlation energies obtained in this way are given in Table I. These are very close to the empirical correlation energies (obtained by subtracting from the total experimental energy, the Hartree-Fock energy and relativistic corrections excluding the Lamb shift) [13, 18]. For comparison, we include the correlation energies obtained from a DFT calculation in which exchange effects are treated by the WDA of equations (13,14) and correlation is treated with the OLA functional of equations (11,12). There is a very satisfactory agreement between the two sets of theoretical correlation energies, a fact that indicates that the electron densities obtained in both methods are very similar. The comparison with the empirical correlation energies is also satisfactory, although one cannot expect our DFT Coulomb correlation energies to exactly agree with the empirical values from references [13, 18]. The reason is that the DFT correlation energies include a small contribution from the difference between the kinetic energy of independent and

Table I. — *Calculated correlation energies (in atomic units) compared to empirical values. Exchange was treated by the weighted density approximation (WDA) and Harbola-Sahni (HS) formalisms and the OLA functional was used for correlation in both cases. Errors (calculated energy − empirical energy) are given in brackets.*

Ion	WDA	HS	Empirical [13, 18]
He	−0.045 (−0.003)	−0.045 (−0.003)	−0.042
Li⁺	−0.061 (−0.018)	−0.061 (−0.018)	−0.043
Li⁻	—	−0.082 (−0.010)	−0.072
Be	−0.094 (0.000)	−0.094 (0.000)	−0.094
B⁺	−0.113 (−0.003)	−0.113 (−0.003)	−0.110
F⁻	—	−0.327 (0.064)	−0.391
Na⁺	−0.396 (−0.017)	−0.398 (−0.019)	−0.379
Na⁻	—	−0.407 (0.003)	−0.410
Ne	−0.362 (0.018)	−0.366 (0.015)	−0.381
Mg	−0.443 (−0.015)	−0 445 (−0.017)	−0.428
Al⁺	−0.476 (−0.034)	−0.477 (−0.035)	−0.442
Cl⁻	—	−0.694 (−0.012)	−0.706
Ar	−0.732 (0.000)	−0.735 (−0.003)	−0.732
Ca	−0.818	−0.820	—
Zn	−1.454	−1.461	—
Kr	−1.816	−1.821	—
Cd	−2.584	−2.590	—
Xe	−2.958	−2.963	—
Pt	−4.773	−4.799	—
Hg	−4 932	−4.938	—
Rn	−5.343	−5.348	—

interacting electrons [19], usually called correlation kinetic energy, whereas the empirical correlation energies of the last column of the Table correspond to the usual quantum chemical definition, which uses as a reference a Hartree-Fock calculation.

The empirical correlation energies given in Table I have not been corrected for the Lamb shift. The reason is that this correction was not taken into account in the process of fitting the free parameter k in reference [14]. Only data for atoms with low atomic number were used for that fitting and in those cases the Lamb shift correction is small (at least generally not larger than the errors made in the fitting). However, the Lamb shift correction becomes important for medium Z and especially for large Z atoms. In this paper we have just tried to be consistent with the prescription used in our previous work [14], but a new determination of the parameter k should be done using empirical correlation energies corrected for the Lamb shift (this is in our plans).

The total ground state energies of closed shell neutral atoms are compared in Table II with empirical values (experimental energy minus relativistic contributions excluding Lamb shift).

The HS energies are very accurate. The errors of the WDA calculation are also small, though larger than the errors in the HS calculation. We ascribe this to the WDA exchange potential, which is less accurate than $W_x(\mathbf{r})$.

Table III gives an analysis of the errors in the HS calculation. The last column of this Table

Table II. — *Calculated total energies (in atomic units) compared to empirical values. Exchange was treated by the weighted density approximation (WDA) and Harbola-Sahni (HS) formalisms and the OLA functional was used for correlation in both cases. Errors (calculated energy − empirical energy) are given in brackets.*

Atom	WDA	HS	Empirical [18]
He	−2.909 (−0.005)	−2.906 (−0.002)	−2.904
Be	−14.605 (0.061)	−14.665 (0.001)	−14.666
Ne	−128.914 (0.011)	−128.906 (0.019)	−128.925
Mg	−200.108 (−0.065)	−200.049 (−0 006)	−200.043
Ar	− 527.680 (−0.138)	−527.537 (0 005)	−527.542
Ca	− 677.786	−677.560	—
Zn	−1779.670	−1779.276	—
Kr	−2753.855	−2753.854	—
Cd	−5467.183	−5467.717	—
Xe	−7234.101	−7235.160	—
Pt	−17332.748	−17337.294	—
Hg	−18410.690	−18415.554	—
Rn	−21868.225	−21874.815	—

Table III. — *Analysis of the errors of the HS calculation. Error-c are the correlation energy errors from Table I, and error-xc are the total energy errors from Table II. Error-x are the total energy errors from an exchange-only HS calculation performed by Harbola and Sahni [7]. Errors are in a.u.*

Atom	error-x	error-c	error-x + error-c	error-xc
He	0.000	−0.003	−0.003	−0.002
Be	0.002	0.000	0.002	0.001
Ne	0.005	0.015	0.020	0.019
Mg	0.009	−0.017	−0.008	−0.006
Ar	0.014	−0.003	0.011	0.005

gives the error in the total energy, labelled "error-xc", taken from Table II. The first column, labelled "error-x", gives the total energy error from exchange-only HS calculations performed by Harbola and Sahni [7], and the second column, labelled "error-c", gives the correlation energy error of Table I. Then we observe that error-xc is approximately equal to the sum of error-x and error-c. On the other hand, the correlation errors are of the same order of magnitude as the total energy errors of the exchange-only HS calculation. This indicates that inclusion of correlation through the OLA functional preserves the extreme accuracy of the total energies.

We present in Tables IV, V and VI the results for the ions of the He, Be and Ne isoelectronic series. The first column gives the atomic number of the ion. The empirical non-relativistic total energy is given in column 2 and the empirical correlation energy in column 3. In columns

Table IV. — *Energy differences (in a.u.) between the self-consistent DFT results and the non-relativistic empirical values (from Ref. [20]) for the He isoelectronic series.* E_{tot}^{emp} *and* E_c^{emp} *are empirical total and correlation energies.* $\Delta E_{tot} = E_{tot}^{DFT} - E_{tot}^{emp}$, $\Delta E_c = E_c^{DFT} - E_c^{emp}$.

Z	$-E_{tot}^{emp}$	$-E_c^{emp}$	WDA		HS	
			ΔE_{tot}	ΔE_c	ΔE_{tot}	ΔE_c
2	2.9037	0.0420	−0.0049	−0.0025	−0.0024	−0.0025
3	7.2799	0.0435	−0.0218	−0.0178	−0.0177	−0.0178
4	13.6556	0.0443	−0.0352	−0.0298	−0.0298	−0.0298
5	22.0310	0.0447	−0.0467	−0.0397	−0 0396	−0.0397
6	32.4062	0.0451	−0.0565	−0.0480	−0.0477	−0.0479
7	44.7814	0.0453	−0.0648	−0.0551	−0.0550	−0.0551
8	59.1566	0.0455	−0.0724	−0.0614	−0.0610	−0.0614
9	75.5317	0.0456	−0.0796	−0.0670	−0.0667	−0.0670
10	93.9068	0.0457	−0.0865	−0.0721	−0 0718	−0.0721
11	114.2819	0.0458	−0.0929	−0.0768	−0 0765	−0.0767
12	136 6569	0.0459	−0.0988	−0.0810	−0.0807	−0.0810
13	161.0320	0.0459	−0.1041	−0 0849	−0.0847	−0.0849
14	187.4071	0.0460	−0.1088	−0.0886	−0 0885	−0.0886
15	215.7821	0.0460	−0.1133	−0.0920	−0.0919	−0.0920
16	246.1571	0 0461	−0.1173	−0.0952	−0.0950	−0.0952
17	278.5322	0.0461	−0.1212	−0.0982	−0.0982	−0.0982
18	312.9072	0.0461	−0.1248	−0.1010	−0.1009	−0.1010
19	349.2822	0.0462	−0.1288	−0.1037	−0.1037	−0.1037
20	387.6572	0.0462	−0.1324	−0.1063	−0.1063	−0.1063

4 and 5 we show the deviations of the WDA-OLA results from the empirical values, while the last two columns present the same comparison for the HS-OLA formalism. We see again, as in Table I, that the correlation energies are nearly the same for both methods (WDA-OLA and HS-OLA) For the three isoelectronic series, the errors of the correlation energy increase with Z. Those errors remain not large for the Be series, but for the Ne series, and especially for the He series, ΔE_c becomes unacceptably large as Z increases. The OLA is unable to reproduce the near-constancy of E_c in each of these two series. The reason for this failure seems to be rooted on the fact that the "free parameter" k in the OLA functional has been fixed by a global fit to the correlation energies of some closed-shell "neutral" atoms, and is not adequate for highly charged ions. Its use is then not recommended in the case of highly charged ions. An obvious observation from those three Tables is that the total energy error of the HS-OLA calculation is exclusively due to correlation.

A characteristic of the exchange-only HS calculations for neutral atoms is that the energy eigenvalues of the highest occupied orbitals ($-\epsilon_{HOMO}$) are consistently closer to the experimental ionization potentials (IP) than the corresponding Hartree-Fock eigenvalues [5, 6]. Our results from non-relativistic HS calculations with OLA correlation for closed-shell neutral atoms and positive ions are given in Table VII, and corroborate the fact that $-\epsilon_{HOMO}$ gives a good approximation to IP(exp). This can be substantiated by the ionization potential theorem which states that in exact DFT (in other words, if $V_{xc}(\mathbf{r})$ were exactly known), then $-\epsilon_{HOMO}$ gives the ionization potential exactly [22]. The interpretation of the results in Table VII (where the

Table V. — *Energy differences (in a.u.) between the self-consistent DFT results and the non-relativistic empirical values (from Ref. [20]) for the Be isoelectronic series. E_{tot}^{emp} and E_c^{emp} are empirical total and correlation energies.* $\Delta E_{tot} = E_{tot}^{DFT} - E_{tot}^{emp}$, $\Delta E_c = E_c^{DFT} - E_c^{emp}$.

			WDA		HS	
Z	$-E_{tot}^{emp}$	$-E_c^{emp}$	ΔE_{tot}	ΔE_c	ΔE_{tot}	ΔE_c
4	14.6674	0.0943	0.0625	0.0006	0.0021	0.0001
5	24.3489	0.1114	0.0751	−0.0015	0.0003	−0.0018
6	36.5349	0.1264	0.0878	−0.0026	−0.0007	−0.0028
7	51.2228	0.1405	0.1019	−0.0024	−0.0005	−0.0026
8	68.4117	0.1540	0.1161	−0.0013	0 0007	−0.0014
9	88.1011	0.1671	0.1301	0.0008	0.0027	0.0006
10	110.2909	0.1799	0.1448	0.0036	0.0055	0.0035
11	134.9809	0.1925	0.1605	0.0071	0.0090	0.0069
12	162.1711	0.2050	0.1773	0.0111	0.0141	0.0110
13	191.8614	0.2174	0.1953	0.0157	0.0185	0.0156
14	224.0517	0.2296	0.2141	0.0207	0.0234	0.0206
15	258.7421	0.2418	0 2331	0.0261	0.0287	0.0260
16	295.9326	0.2540	0.2523	0.0319	0.0383	0 0318
17	335.6231	0.2660	0.2714	0.0380	0 0403	0.0379
18	377.8136	0.2781	0.2904	0.0444	0 0466	0.0443
19	422.5042	0.2901	0.3094	0.0510	0.0538	0.0509
20	469.6947	0.3021	0.3284	0.0579	0.0605	0.0578

Table VI. — *Energy differences (in a.u.) between the self-consistent DFT results and the non-relativistic empirical values (from Ref. [20]) for the Ne isoelectronic series. E_{tot}^{emp} and E_c^{emp} are empirical total and correlation energies.* $\Delta E_{tot} = E_{tot}^{DFT} - E_{tot}^{emp}$, $\Delta E_c = E_c^{DFT} - E_c^{emp}$.

			WDA		HS	
Z	$-E_{tot}^{emp}$	$-E_c^{emp}$	ΔE_{tot}	ΔE_c	ΔE_{tot}	ΔE_c
10	128.939	0.392	0.025	0.030	0.033	0.026
11	162.069	0.392	0.029	−0 004	0 000	−0.007
12	199.224	0.394	0.029	−0.031	−0.027	−0.033
13	240.397	0.396	0.030	−0.055	−0.049	−0.057
14	285.579	0.398	0.029	−0.077	−0 071	−0.078
15	334.770	0.400	0.028	−0.096	−0 090	−0.098
16	387.967	0.402	0.026	−0.114	−0.107	−0.115
17	445.168	0.404	0.023	−0.131	−0.124	−0.132
18	506.373	0.405	0.019	−0.147	−0.139	−0.148
19	571.581	0.406	0.016	−0.162	−0.154	−0.163
20	640.792	0.407	0.015	−0.176	−0.168	−0.177

Table VII. — *Energy eigenvalue of the highest occupied atomic orbital obtained with the HS-OLA functional (in eV) compared to experimental ionization potentials (IP) [21].*

Ion	$-\epsilon_{HOMO}$	Experimental IP
He	25.64	24 59
Li^+	76.93	75 64
Be	8.83	9.32
Be^{2+}	155 36	153 89
B^+	24.42	25 15
B^{3+}	260.96	259.37
C^{2+}	46.92	47.89
C^{4+}	393 74	392.08
N^{3+}	76.28	77.47
N^{5+}	553.72	552.06
O^{4+}	112.45	113.90
F^{5+}	155.44	157 16
Ne	24.01	21 56
Na^+	50 21	47.29
Mg	7.34	7.65
Mg^{2+}	83.54	80 14
Al^+	18.42	18.83
Al^{3+}	123.83	119.99
Si^{4+}	171 04	166.77
P^{5+}	225.12	220.43
Ar	16.57	15 76
K^+	32.61	31.63
Ca	5.68	6.11
Sc^+	13.77	12.80
Zn	9.11	9.39
Ga^+	20 12	20.51
Kr	14 57	14.00
Rb^+	27.95	27.28
Cd	8.24	8.99
In^+	17.77	18.87
Xe	12 67	12.13
Cs^+	23.74	25.10
Pt	9.36	9.00
Au^+	21.77	20 50
Hg	8.19	10 44
Tl^+	17.25	20.43
Rn	11.83	10.75

mean absolute error with respect to experimental IP's is 4.7%) is then that $W_x(\mathbf{r}) + V_c(\mathbf{r})$ is already a good approximation to the exact exchange-correlation potential of DFT. A crucial component of the success is the correct asymptotic behavior of $V_{xc}(\mathbf{r})$ induced by $W_x(\mathbf{r})$. This

Table VIII. — *Energy eigenvalue of the highest occupied atomic orbital of the anion obtained with the HS-OLA functional (in eV) compared to experimental electron affinities (EA) [25].*

Atom	$-\epsilon_{HOMO}$ (anion)	Experimental EA
H	1.47	0.75
Li	0.37	0.62
F	5.33	3.40
Na	0.47	0.55
Cl	4.30	3.61
K	0.36	0.50
Cu	1 15	1.23
Br	3.90	3.36
Ag	1.02	1 30
I	3.59	3.06
Au	1.13	2.31
At	3.41	2.80

result can be useful in the study of molecules and clusters. The results for the electron affinities (EA), which should be equal to $-\epsilon_{HOMO}$ for the negative ion, are less accurate within the HS formalism [23, 24]. The values of $-\epsilon_{HOMO}$(anion) presented in Table VIII (notice that these anions have closed shells) have a mean absolute error of 32% with respect to experimental EA's. So they can only be considered as a rough estimation of the electron affinities.

4. Conclusions and Comments

In summary, we have explored a combination of the Harbola-Sahni formalism for the exchange potential with the usual density functional prescription for the correlation potential. Correlation has been treated using an optimized local-like functional. Calculations for closed shell atoms and ions show promising results, except in the case of highly ionized atoms. The reason is that the "free parameter" in the correlation energy functional was optimized only for neutral atoms. Work for open-shell systems is now under progress. To our knowledge, the HS method has been only applied to atoms (or ions) and to the jellium model of a metal surface [26]. Although the applicability of the HS method is certainly restricted, very large metal clusters provide examples of systems where the HS method could be useful. The electronic structure of those clusters is a topic of debate [27] and a central field approximation is enough for most purposes. The fact that the HS method preserves the correct asymptotic behavior of V_x constitutes a crucial improvement over the LDA and a key ingredient in favor of this method. Of course, correlation should be added, using the OLA functional or any other available. The OLA functional has only been tested for atoms and for molecules [28], but not for the valence elctrons in large metallic clusters. So, care should be taken in using the OLA for these systems.

Acknowledgments

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