PHYSICAL REVIEW A VOLUME 34, NUMBER 2 AUGUST 1986

New self-interaction-corrected local-density approximation to the density-functional theory

Pietro Cortona
Laboratoire de Physique des Solides, Université de Paris—Sud, F-91405 Orsay, France;
Dipartimento di Fisica, Università degli Studi di Genova, I-16146 Genova, Italy;
and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, I-16146 Genova, Italy
(Received 30 December 1985)

A self-interaction-corrected local-density approximation to the exchange part of the exchange-correlation functional is proposed. The method is based on the Rae exchange energy of an N-electron homogeneous gas and it gives rise to a one-electron equation where the exchange potential is a function of the number of electrons present in each shell. The results of the calculations of usual atomic properties, such as total and one-electron energies, electron affinities, and ionization potentials, are also presented, as well as the comparison with other approximations. In general, a very good agreement is found between the results of the method of this paper and the Hartree-Fock values and, when it is combined with a standard expression for correlation, with the experimental results.

INTRODUCTION

The main problem in the application of the density-functional theory[1–4] (DFT) to the calculation of the electronic structure of real systems is to find a good approximation to the exchange-correlation energy functional.

The more simple and more generally used method is the local-density approximation (LDA), which was proposed originally by Kohn and Sham[2] by similarity to the Thomas-Fermi theory and to the Slater[5] approximation to the Hartree-Fock (HF) theory. This approximation gave excellent results also for very inhomogeneous systems, as atoms or molecules, where one did not expect to find good results.[6]

This success is partly due to error compensation. Quantities which are calculated by differences, such as ionization potentials, binding energies of molecules or solids, and hyperfine fields, are generally very well predicted by LDA in spite of the not very good agreement between experimental and calculated total energies and the fact that charge densities near the nucleus are not very well described by this approximation.

But error compensation is not all. Other quantities, such as overall charge densities, are reasonably well reproduced by LDA, showing that some other argument, for example, the respect of the "sum rule,"[7] must be invoked to explain this success.

Nevertheless, it is well known that LDA fails on some questions. For example, in atomic physics, bound states are not predicted for some negative ions and total energies are systematically too high; in solids, the gap of insulators is greatly underestimated.

We do not want to list all the problems which are not correctly solved by LDA. We want only to point out that perhaps the most serious deficiency is given by the bad approximation that the LDA eigenvalues represent for the removal energies.

Recently, it was proved[8,9] that the one-electron energy of the more external electron of a finite system is, in the exact DFT, the ionization potential of this electron. The estimate of this eigenvalue given by LDA is very bad and this shows how different the LDA and the exact DF potentials are.

Improvement to LDA can be obtained using nonlocal approximations. Some general, nonlocal functionals exist[10–12] and have begun to be used in calculations of the electronic properties of atoms and solids. However, a simpler way to try to improve LDA is provided by the fact that the local approximation to the exchange-correlation functional does not compensate exactly the self-interaction in the Coulomb energy and potential. If one divides exchange and correlation into an exchange part, defined by the usual HF expression, and a correlation term, this spurious interaction is compensated by the self-exchange. So one can hope to obtain better results treating the self-exchange exactly and taking a local approximation of the interelectron exchange and of the correlation.

By its definition, correlation is self-interaction-free. Unfortunately, the expressions of the correlation energy obtained from the theory of the infinite homogeneous electronic gas do not give the correct result for a one-electron system. This justifies the introduction in the last few years of some self-interaction-corrected expressions of the correlation energy.[13–15] These expressions reduce remarkably the error of LDA and encouraged some authors[13,15–17] to treat exactly the exchange term and to use the local approximation for correlation only, as proposed originally by Kohn and Sham.[2]

For applications to systems such as large molecules and solids, where HF calculations are still not possible, we think that an accurate self-interaction-corrected local expression for the exchange energy is interesting.

In our first paper on this subject[18] (hereafter referred to as I) we used for that the Rae expression of the exchange energy.[19] This expression, which gives the interelectron exchange energy of a homogeneous gas of N electrons, reads as the classical expression for the infinite gas, multiplied by a factor γ which is a function of the number of electrons in the system.

The main problem in applying the Rae expression to inhomogeneous systems is to decide the number of electrons to use to determine γ. In the earlier paper we used the total number of electrons of the system. We obtained, from self-consistent calculations on atoms and ions, charge densities and eigenvalues in good agreement with HF. However, the zero of the energy, in that method, was not well defined. This was a consequence of the fact that adding an electron at large distance to a system changed the value of γ but not the physical properties of the system, and it made the total energies insignificant.

In the following, we shall show how one can use the Rae expression in self-consistent calculations, fixing the γ coefficient by the number of electrons present in each shell. The scheme obtained will be naturally free of the zero-energy problem.

THE SELF-INTERACTION-CORRECTED LOCAL-SPIN-DENSITY APPROXIMATION

Let us review the Rae theory of the exchange energy of a homogeneous gas of N electrons. The exchange energy, in atomic units, of N_σ electrons of spin σ in a box of volume V with periodic boundary conditions is given by

$$E_\sigma^x = -\frac{1}{2V}\sum_{\substack{i,j=1\\ i\neq j}}^{N_\sigma} \frac{4\pi}{|\mathbf{k}_i-\mathbf{k}_j|^2} . \tag{1}$$

This expression is usually evaluated by transforming it into the integral

$$E_\sigma^x = -\frac{1}{2V}\left[\frac{V}{8\pi^3}\right]^2 \int_{k_2<k_F}\int_{k_1<k_F} \frac{4\pi}{|\mathbf{k}_1-\mathbf{k}_2|^2} d^3k_1\, d^3k_2 , \tag{2}$$

where k_F is the Fermi momentum.

To do that the $i\neq j$ condition is disregarded, and this implies the inclusion of the self-interaction terms. To take in account this condition Rae[19] proposed to eliminate from the integration region in Eq. (2) a small volume around $|\mathbf{k}_1-\mathbf{k}_2|=0$. This volume is defined by the condition that it contains N_σ states

$$N_\sigma = \left[\frac{V}{8\pi^3}\right]^2 \int\int_{|\mathbf{k}_1-\mathbf{k}_2|\leq \beta k_F} d^3k_1\, d^3k_2 . \tag{3}$$

One obtains

$$N_\sigma^{-1} = \beta^3 - \tfrac{9}{16}\beta^4 + \tfrac{1}{32}\beta^6 . \tag{4}$$

This equation determines β as a function of N_σ.[20] One can now calculate the integral (2) with the condition $|\mathbf{k}_1-\mathbf{k}_2| > \beta k_F$. The result is

$$\frac{E_\sigma^x}{V} = -\frac{3}{4}\left[\frac{6}{\pi}\right]^{1/3}\left[\frac{N_\sigma}{V}\right]^{4/3}\gamma(N_\sigma), \tag{5}$$

where

$$\gamma(N_\sigma) = 1 - \tfrac{4}{3}\beta + \tfrac{1}{2}\beta^2 - \tfrac{1}{48}\beta^4 . \tag{6}$$

Thus the self-interaction-corrected exchange energy of a homogeneous gas of N_σ electrons of spin σ is given by the classical expression for the infinite gas, multiplied for a factor γ which is a function of N_σ. As $N_\sigma=1$, one obtains $\beta=2$ and $\gamma=0$; as $N_\sigma\rightarrow\infty$, one obtains $\beta=0$ and $\gamma=1$. So Eqs. (4)–(6) give the correct results for the limiting cases.

Suppose now that there is an external potential $V_{\text{ext}}(\mathbf{r})$. DFT says that, if one knows the functional dependence of the exchange-correlation energy from the spin-up and spin-down charge densities ρ_σ, one can obtain, in principle exactly, the ground-state charge density by

$$\rho_\sigma(\mathbf{r}) = \sum_i \rho_{i\sigma}(\mathbf{r}) = \sum_i u_{i\sigma}^*(\mathbf{r})u_{i\sigma}(\mathbf{r}) , \tag{7}$$

where $u_{i\sigma}(\mathbf{r})$ are the solutions of the one-electron equation

$$(-\tfrac{1}{2}\nabla^2 + V_{\text{ext}} + V^C + V_\sigma^{\text{xc}})u_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma}u_{i\sigma}(\mathbf{r}) , \tag{8}$$

V^C is the electrostatic interaction between the electrons

$$V^C(\mathbf{r}) = \sum_{k,\sigma}\int \frac{u_{k\sigma}^*(\mathbf{r}')u_{k\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' , \tag{9}$$

and $V_\sigma^{\text{xc}} = \delta E^{\text{xc}}/\delta\rho_\sigma$ is the functional derivative of the exchange-correlation energy. Disregarding correlation, V_σ^x is approximated in LDA by the expression for the infinite homogeneous gas

$$V_\sigma^x = -\left[\frac{6}{\pi}\rho_\sigma\right]^{1/3} \tag{10}$$

while the self-interaction-corrected theories prefer an orbital-dependent expression:

$$V_{i\sigma}^x(\mathbf{r}) = -\int \frac{u_{i\sigma}^*(\mathbf{r}')u_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + V_{i\sigma}^{\text{xie}} . \tag{11}$$

$V_{i\sigma}^{\text{xie}}$ is some approximation of the interelectron exchange potential. For example, Lindgren[21] and Perdew and Zunger[14] assumed

$$V_{i\sigma}^{\text{xie}} = -\left[\frac{6}{\pi}\rho_\sigma\right]^{1/3} + \left[\frac{6}{\pi}\rho_{i\sigma}\right]^{1/3} . \tag{12}$$

Let us now show how the Rae expression can be used to obtain an approximation for $V_{i\sigma}^{\text{xie}}$. Consider a system of N_σ electrons of charge density $\rho_\sigma(\mathbf{r})$ and exchange-per-volume unit $\mathscr{E}_\sigma^x(\rho_\sigma)$. Suppose now we divide $\rho_\sigma(\mathbf{r})$ in two *arbitrary* groups containing $N_{a\sigma}$ and $N_{b\sigma}$ electrons and let $\rho_{a\sigma}(\mathbf{r})$ and $\rho_{b\sigma}(\mathbf{r})$ be their densities. Then one can write

$$\begin{aligned}\mathscr{E}_\sigma^x(\rho_\sigma) &= [\mathscr{E}_\sigma^x(\rho_\sigma) - \mathscr{E}_\sigma^x(\rho_{a\sigma}) - \mathscr{E}_\sigma^x(\rho_{b\sigma})] \\ &\quad + \mathscr{E}_\sigma^x(\rho_{a\sigma}) + \mathscr{E}_\sigma^x(\rho_{b\sigma}) ,\end{aligned} \tag{13}$$

where the value within parentheses is the "intergroups" exchange. Taking now the local approximation and using Eq. (5) to obtain a self-interaction-free expression, one has

$$\begin{aligned}\mathscr{E}_\sigma^{\text{xie}} &= -\frac{3}{4}\left[\frac{6}{\pi}\right]^{1/3}(\rho_\sigma^{4/3} - \rho_{a\sigma}^{4/3} - \rho_{b\sigma}^{4/3}) \\ &\quad -\frac{3}{4}\left[\frac{6}{\pi}\right]^{1/3}[\gamma(N_{a\sigma})\rho_{a\sigma}^{4/3} + \gamma(N_{b\sigma})\rho_{b\sigma}^{4/3}]\end{aligned} \tag{14}$$

because there is no self-interaction in the intergroups term. So, the interelectron exchange potential for an electron of the group a is given by

$$V^{\mathrm{xie}}_{a\sigma}=-\left[\frac{6}{\pi}\rho_\sigma\right]^{1/3}+\left[\frac{6}{\pi}\rho_{a\sigma}\right]^{1/3}[1-\gamma(N_{a\sigma})]\;. \quad (15)$$

In the homogeneous-gas case there is no reason to divide the electrons into groups. All the electrons are equivalent, in the sense that their densities are identical. A consequence of this is that Eqs. (14) and (5) are consistent only if $N_{a\sigma}=N_\sigma$ and $N_{b\sigma}=0$.

Suppose now that $\rho_{a\sigma}$ and $\rho_{b\sigma}$ are two densities such that their overlap integral is zero. Then the total exchange is the sum of the exchange energies of the two distributions, and using the Rae result for both these densities one obtains the second term in the second member of Eq. (14). The intergroups exchange must be zero and this is correctly given by the first term in the second member of Eq. (14). In conclusion, Eq. (14) is the correct LDA for the interelectron exchange of this system.

We think that many inhomogeneous systems can be treated using these limiting cases. In an atom, for example, electrons in the same shell (identified by the same values of n and l) have identical densities in spherical average and we think that one can apply to them the Rae expression. On the other hand, electrons in different shells and slightly overlapping, for example $1s$ and $3s$, can be well described by Eq. (14). There are, naturally, intermediate cases, such as $2s$ and $2p$, that one cannot easily classify as one group or two different groups.

We *assume* that one can divide the electrons shell by shell and treat them by Eq. (14). The intermediate cases will be a source of errors which add to those due to the local approximation.

With this assumption, introducing an index of shell s and using $\rho_{s\sigma}$ for the density of one electron with spin σ in the s shell and $N_{s\sigma}$ for the number of electrons with spin σ in this shell, from Eqs. (15) and (14) one respectively obtains

$$V^{\mathrm{xie}}_{s\sigma}=-\left[\frac{6}{\pi}\rho_\sigma\right]^{1/3}+\left[\frac{6}{\pi}\rho_{s\sigma}\right]^{1/3}N_{s\sigma}^{1/3}[1-\gamma(N_{s\sigma})]\,, \quad (16)$$

$$\mathcal{E}^{\mathrm{xie}}_{\sigma}=-\frac{3}{4}\left[\frac{6}{\pi}\right]^{1/3}\left[\rho_\sigma^{4/3}-\sum_s N_{s\sigma}^{4/3}[1-\gamma(N_{s\sigma})]\rho_{s\sigma}^{4/3}\right]$$
$$=\frac{3}{4}\sum_s N_{s\sigma}\rho_{s\sigma}V^{\mathrm{xie}}_{s\sigma}\;. \quad (17)$$

We remark that this scheme is free of the zero-energy problem because an electron added at large distance to the system belongs necessarily to a different shell and it does not affect the γ's pertaining to the other shells.

We point out that Eqs. (16) and (17) were already used for self-consistent calculations in two limiting cases. In paper I we considered all the electrons of spin σ as a group and we calculated γ using the total number of electrons. The opposite approximation, where each electron is itself a group, coincides with the self-interaction correction (exchange only) proposed by Perdew and Zunger.[14] Their method, usually referred to as SIC, if applied to the homogeneous gas, does not give the Rae expression. For the reasons explained above, we believe that our approximation, consisting in the intermediate choice of fixing the γ coefficient by the number of electrons present in each shell is more consistent with the homogeneous-gas theory and, as we shall see, can give better results.

Finally, we want to point out that, in spite of the fact that one can look at SIC as a limiting case of our approximation, a different conception underlies the two theories. The Perdew and Zunger method is a general method to correct *any* non-self-interaction-free expression of the exchange-correlation energy. It is not dependent on the particular form of this expression. Our method gives a *special* approximation for the exchange energy based on the nonrelativistic theory of the homogeneous gas. It cannot be extended without further work. In the following we refer to the method described in this section as N-SIC (N-dependent self-interaction correction).

RESULTS AND DISCUSSION

In this section we show the results of self-consistent spin-polarized calculations on atoms and ions of the first two rows of the Periodic Table. Some elements of the third row (K, Se, Br) will also be considered.

With a view to testing our approximation for the exchange energy, we compare our calculations with the HF results, which we consider the "exact" values. Comparison will also be done with the results of the Kohn and Sham (KS) local-density approximation and with the self-interaction-corrected local-density approximation of Perdew and Zunger.

Calculations including correlation will also be reported to show that our approximation of the exchange, combined with a well-known correlation expression, agrees very well with the experimental values.

Apart from the results in the HF approximation taken from Ref. 22, all the results in this paper were obtained using a predictor-corrector program to solve the radial Schrödinger equation. The small nonorthogonality effects, due to the use of a Hartree-type equation, were taken into account by a Schmidt orthogonalization after each iteration.[23]

Before beginning the discussion of the results, we must note that quantities such as ionization potentials (IP) and electron affinities (EA) cannot be accurately obtained if there is not a compensation of errors in the atomic and ionic calculations. This cannot happen in the N-SIC approximation since it uses coefficients which depend on the number of electrons in each shell. The errors in the contribution of the more external electrons to the exchange energy have a different weight. For this reason, we *arbitrarily* decide to fix the γ coefficient by the degeneracy $(2l+1)$ of each shell. Of course there is a difference only if there are open shells in the system. We will refer to this method as D-SIC.

We remark that quantities which are not calculated as differences are generally better reproduced by N-SIC. Consider, for example, Ar. The total energy of atomic Ar is 1053.635 Ry in HF approximation and 1053.208 Ry both in N-SIC and in D-SIC. The energy of the ion Ar^+

TABLE I. Hartree-Fock (HF) total energies and the differences between the total energies calculated by the KS, SIC, and *D*-SIC approximations and the HF values (Ry).

	HF (Ry)	KS (Ry)	SIC (Ry)	*D*-SIC (Ry)
Li	−14.865	0.478	−0.003	−0.003
Be	−29.146	0.699	−0.010	−0.010
B	−49.058	0.931	−0.040	0.007
C	−75.377	1.153	−0.113	0.007
N	−108.802	1.383	−0.211	0.008
O	−149.619	1.635	−0.307	0.029
F	−198.819	1.870	−0.453	0.025
Ne	−257.094	2.111	−0.625	0.021
Na	−323.718	2.428	−0.718	0.056
Mg	−399.229	2.730	−0.828	0.071
Al	−483.753	3.039	−0.931	0.120
Si	−577.709	3.343	−1.049	0.168
P	−681.437	3.657	−1.164	0.231
S	−795.010	3.969	−1.290	0.293
Cl	−918.964	4.274	−1.433	0.350
Ar	−1053.635	4.597	−1.568	0.427

is 1052.549, 1052.169, and 1052.131 Ry in HF, *N*-SIC, and *D*-SIC, respectively; as one can see there is a small difference between *N*-SIC and *D*-SIC (only the $3p$ electrons "spin down" are treated differently) and the total-energy *N*-SIC is slightly better than *D*-SIC. However, the IP is 14.78, 14.14, and 14.66 eV in HF, *N*-SIC, and *D*-SIC, respectively.

We emphasize that our choice to calculate γ for open shells using the degeneracy, is completely arbitrary and one can obtain better results for the energy differences with "*ad hoc*" choices as, for example, the numbers of the electrons in the atomic or in the ionic shell, or intermediate numbers. In the following we will report only the *D*-SIC results.

Let us first consider the total energies. In Table I we report the HF total energies of all the atoms of the first two rows of the Periodic Table and the differences, with respect to HF, of the total energies calculated by the different approximations. In all cases (including positive and negative ions which are not reported in the table) the *D*-SIC error is smaller than 0.04%. Furthermore, *D*-SIC improves SIC (excepted Li and Be, where the two approximations coincide) and KS by a factor varying between 3 and 30 and between 10 and 170, respectively.

Similar conclusions can be obtained by comparing the exchange energies (self-exchange plus interelectron exchange), that we report in Table II for the rare-gas atoms Ne, Ar, and Kr. The error of *D*-SIC is 0.6, 1.0, and 1.5%, respectively, and *D*-SIC improves SIC by about a factor of 2 and KS by at least a factor of 4.

We remark finally that the total and the exchange energies in the *D*-SIC approximation are generally higher than the HF values, while the SIC values are systematically lower.

In Table III we show the one-electron energies for a neutral atom and for a positive and a negative ion. It is known that while the HF eigenvalues have the meaning of nonrelaxed IP's, in the DFT, only the one-electron energy of the more external electron can be interpreted, in the exact theory, as its relaxed IP. The comparison between this eigenvalue and the IP will be done in Tables V and VI. However, we think that some remarks about the structure of the eigenvalue set can be interesting. The energy differences between the last level with principal quantum number n and the first level with principal quantum number $n+1$ are about the same in HF, SIC, and *D*-SIC and are very different with respect to KS. So this difference seems determined by the self-exchange term, whereas the interelectron exchange seems uninfluential. This is reasonable because orbitals with different principal quantum number have a small overlap. On the other hand, the splitting of two levels with the same value of the principal quantum number is more similar in SIC, *D*-SIC, and KS than in HF. This shows that this splitting is essentially determined by the interelectron exchange. There is not much difference between SIC and *D*-SIC. Curiously, the first is a better approximation of HF for p states, whereas the latter is better for s states.

We have briefly studied the total charge densities by calculating their Fourier transforms for the values of $\sin\theta/\lambda$ between 0.05 and 1.50 Å^{-1}, with a step of 0.05 Å^{-1}. We report in Table IV, for all the atoms of the first and second row, the average percent errors of each method with respect to HF. As one can see, SIC and *D*-

TABLE II. Total exchange energies (self-exchange + interelectron exchange) for some rare-gas atoms from HF, KS, SIC, and *D*-SIC calculations (eV).

	HF (eV)	KS (eV)	SIC (eV)	*D*-SIC (eV)
Ne	−329.5	−297.6	−337.6	−327.5
Ar	−821.3	−755.8	−841.6	−812.8
Kr	−2561.9	−2407.5	−2630.8	−2523.4

TABLE III. One-electron energies for Cl^-, Ar, and K^+ by the HF method and the KS, SIC, and *D*-SIC approximations (Ry).

		HF (Ry)	KS (Ry)	SIC (Ry)	*D*-SIC (Ry)
Cl^-	1*s*	209.010		208.467	208.640
	2*s*	20.458		19.082	19.181
	2*p*	15.391		15.089	14.855
	3*s*	1.466		1.167	1.214
	3*p*	0.300		0.252	0.215
Ar	1*s*	237.221	227.433	236.606	236.765
	2*s*	24.644	21.460	23.145	23.232
	2*p*	19.143	16.756	18.786	18.513
	3*s*	2.555	1.666	2.161	2.196
	3*p*	1.182	0.668	1.098	1.040
K^+	1*s*	267.507	257.102	266.825	266.977
	2*s*	29.418	25.989	27.803	27.884
	2*p*	23.478	20.876	23.073	22.767
	3*s*	3.929	2.902	3.457	3.487
	3*p*	2.342	1.726	2.231	2.157

SIC describe very well the charge densities, their average error being always smaller than 0.5% (except *N* for SIC). *D*-SIC is slightly better than SIC for the atoms of the first line, whereas the two methods are about equivalent for the atoms of the second line. KS, which has an average error smaller than 1% beginning from C, is clearly worse than SIC and *D*-SIC for the first line, whereas it is equivalent to *D*-SIC for the second line. It can be also interesting to remark that the maximum error of *D*-SIC is 1.06% for Li while in all the other cases it is smaller than 1%. Furthermore, the maximum error of *D*-SIC is always smaller than the maximum error of SIC (except Ar) and of KS (except P).

TABLE IV. Average percent deviations in the interval $0.05 \leq \sin\theta/\lambda \leq 1.5$ Å^{-1} of the charge-density Fourier transforms with respect to the HF values.

	KS (%)	SIC (%)	*D*-SIC (%)
Li	2.49	0.30	0.30
Be	1.74	0.39	0.39
B	1.24	0.38	0.37
C	0.89	0.48	0.34
N	0.71	0.59	0.37
O	0.60	0.44	0.36
F	0.55	0.43	0.40
Ne	0.54	0.49	0.45
Na	0.44	0.48	0.44
Mg	0.41	0.46	0.42
Al	0.34	0.39	0.35
Si	0.31	0.33	0.31
P	0.27	0.29	0.27
S	0.26	0.22	0.26
Cl	0.25	0.19	0.25
Ar	0.25	0.17	0.26

The first ionization potentials of all the atoms of the first two lines of the Periodic Table and the electron affinities of some elements are shown respectively in Tables V and VI. We have evaluated them both as total-energy differences (method usually referred to as ΔSCF) and taking the negative of the eigenvalue concerned (value within parentheses). From this test, one can obtain much information about a self-interaction-corrected theory, because the results are determined both by the quality of the functional and by its ability of compensating the errors. It is for this latter property that the KS results for the IP (ΔSCF) are very good, better than the SIC values. *D*-SIC removes this drawback of SIC, giving IP often better than KS. Furthermore, it reduces greatly the large error (≈ 1 eV) of SIC for some elements (C—Ne). Similar conclusions can be obtained from the EA of Table VI.

Essentially *D*-SIC is better than SIC when a *p* electron is concerned (exception: Al and P), while the two methods are about equivalent when an *s* electron is concerned.

The examination of IP and EA as determined by the eigenvalues gives rise to different remarks. First, one can see that SIC and *D*-SIC are clearly better than KS, which gives wrong values. Second, in all the cases where the relaxation effects are important, the SIC or *D*-SIC eigenvalues are a better approximation of the IP or of the EA obtained by ΔSCF-HF rather than the HF eigenvalue itself. This means that the quality of both functionals is sufficiently good to permit one to see a part of the relaxation effects included in the exact theory. This does not happen in KS. Comparison with ΔSCF-HF shows a better agreement with *D*-SIC for the EA and some IP, with SIC for the majority of the IP.

No contribution is given in this paper to the correlation study. So, to compare with experiment, we will use an existing expression for the correlation energy. Without comparing the different possibilities, we choose to use the

TABLE V. Ionization potentials, in eV, from exchange-only calculations. The first value is the IP calculated as difference of total energies; the value within parentheses is the IP obtained from the negative of the one-electron energy.

	HF (eV)	KS (eV)	SIC (eV)	*D*-SIC (eV)
Li	5.34 (5.34)	5.03 (2.73)	5.38 (5.31)	5.38 (5.31)
Be	8.04 (8.42)	7.64 (4.63)	8.13 (8.38)	8.13 (8.38)
B	7.93 (8.43)	7.55 (3.27)	8.30 (7.93)	7.67 (7.08)
C	10.79 (11.79)	10.77 (5.33)	11.59 (11.24)	10.90 (10.28)
N	13.96 (15.44)	14.01 (7.52)	14.87 (14.60)	14.12 (13.54)
O	11.88 (17.19)	11.87 (5.70)	12.59 (13.06)	11.91 (12.04)
F	15.72 (19.86)	16.26 (8.87)	17.02 (17.56)	16.28 (16.42)
Ne	19.84 (23.14)	20.51 (12.05)	21.29 (21.96)	20.49 (20.72)
Na	4.95 (4.95)	4.87 (2.63)	5.18 (5.06)	5.22 (5.09)
Mg	6.61 (6.88)	6.48 (3.87)	6.87 (6.96)	6.90 (6.99)
Al	5.51 (5.71)	5.16 (2.35)	5.57 (5.21)	5.18 (4.70)
Si	7.66 (8.08)	7.44 (3.91)	7.91 (7.47)	7.49 (6.90)
P	10.04 (10.66)	9.69 (5.53)	10.23 (9.74)	9.77 (9.10)
S	9.03 (11.90)	8.82 (4.69)	9.41 (9.34)	8.95 (8.69)
Cl	11.79 (13.78)	11.71 (6.92)	12.36 (12.16)	11.86 (11.44)
Ar	14.78 (16.08)	14.49 (9.08)	15.18 (14.94)	14.66 (14.15)

TABLE VI. Electron affinities, in eV, from exchange-only calculations. The first value is the EA calculated as the difference of total energies; the value within parentheses is the EA obtained from the negative of the one-electron energy.

	HF (eV)	SIC (eV)	*D*-SIC (eV)
${}_{3}$Li	−0.12 (0.40)	−0.08 (0.40)	−0.08 (0.40)
${}_{8}$O	−0.54 (3.52)	0.70 (1.73)	0.37 (1.13)
${}_{9}$F	1.36 (4.92)	2.78 (4.35)	2.38 (3.65)
${}_{11}$Na	−0.12 (0.34)	−0.02 (0.38)	−0.01 (0.38)
${}_{16}$S	0.91 (2.92)	1.56 (1.82)	1.28 (1.39)
${}_{17}$Cl	2.58 (4.08)	3.14 (3.43)	2.82 (2.93)
${}_{19}$K	−0.08 (0.28)	0.03 (0.03)	0.02 (0.03)
${}_{34}$Se	1.04 (2.75)	1.59 (1.76)	1.32 (1.36)
${}_{35}$Br	2.58 (3.78)	3.00 (3.14)	2.70 (2.69)

TABLE VII. Ionization potentials, in eV, from KS, SIC, and *D*-SIC calculations including correlation. The values were obtained as differences of total energies. The experimental results (Ref. 25) are given in the first column.

	Expt. (eV)	KS (eV)	SIC (eV)	*D*-SIC (eV)
Li	5.39	5.47	5.44	5.44
Be	9.32	9.04	9.11	9.11
B	8.30	8.56	8.87	8.24
C	11.26	11.72	12.07	11.37
N	14.53	14.94	15.30	14.56
O	13.62	13.99	14.24	13.54
F	17.42	18.11	18.37	17.61
Ne	21.56	22.19	22.44	21.64
Na	5.14	5.36	5.30	5.34
Mg	7.65	7.74	7.74	7.77
Al	5.99	5.99	6.03	5.63
Si	8.15	8.25	8.33	7.90
P	10.49	10.50	10.62	10.16
S	10.36	10.62	10.78	10.32
Cl	12.97	13.29	13.50	12.99
Ar	15.76	15.95	16.19	15.65

TABLE VIII. Electron affinities, in eV, from SIC and *D*-SIC calculations including correlation. The values were obtained as differences of total energies. The experimental results (Ref. 26) are given in the first column.

	Expt. (eV)	SIC (eV)	*D*-SIC (eV)
$_{3}$Li	0.62	0.56	0.56
$_{8}$O	1.46	1.81	1.46
$_{9}$F	3.40	3.75	3.34
$_{11}$Na	0.55	0.59	0.59
$_{16}$S	2.08	2.53	2.23
$_{17}$Cl	3.62	4.01	3.66
$_{19}$K	0.50	0.56	0.56
$_{34}$Se	2.02	2.51	2.24
$_{35}$Br	3.36	3.83	3.52

Perdew and Zunger[14] parametrization of the Ceperley-Alder[24] precise data for the homogeneous gas and to correct the self-interaction effects in it by the SIC method.

There is not much to learn when examining the total energies. It is well known that correlation expressions derived from the homogeneous-gas theory overestimate the correlation energy in an atomic case for about a factor of 2 and that the self-interaction correction reduces greatly this error.[14]

It is more interesting to examine the IP and EA reported, respectively, in Tables VII and VIII. In these tables we compare the experimental values, with KS, SIC, and *D*-SIC. We remark that in KS we used a non-self-interaction-corrected correlation, whereas the difference between the SIC and *D*-SIC results is entirely due to the exchange term. The comparison with the corresponding Tables V and VI points out that the agreement of *D*-SIC including correlation with experiment is better than the agreement of the same method (exchange only) with HF. This reveals a (causal) mechanism of compensation of errors which works very well even in cases where the errors of the correlation and exchange contributions are large. In most cases the self-interaction-corrected correlation is satisfactory enough and it gives a contribution to the IP and to the EA that brings their values close to the correct experimental ones. This does not happen for the non-self-interaction-corrected KS expression which generally gives a too-large contribution to the IP.

CONCLUSIONS

The use of the Rae expression for the exchange energy of a homogeneous gas of N electrons permitted us to introduce a new method for a self-interaction correction in the LDA. We obtained a scheme where the exchange-energy density and the exchange potential are dependent from the number of electrons in each shell.

The calculation of the properties of atoms and ions of the first two rows of the periodic system gave results which agreed very well with HF and, combined with the Perdew and Zunger correlation, with experimental results. In particular, the total and exchange energies were very close to HF and clearly better than the corresponding KS and SIC values. Improvements were also obtained for the charge densities, the ionization potentials, and the electron affinities. The eigenvalue set structure was typically that of the self-interaction-corrected methods and the one-electron energy of the more external electron was a good approximation of the first ionization potential.

We think that this paper confirms the idea that simple considerations based on the homogeneous-gas theory permit, in many cases, a satisfying description even of very inhomogeneous systems. We believe that the use of this method can be useful for complex systems, where HF calculations with local correlation are still not available. In particular it would be interesting to apply it to the band calculations of semiconductors and insulators, hoping to obtain better values of the gap between the conduction and the valence bands.

ACKNOWLEDGMENTS

This work was supported in part by a grant of the Italian Research Council (Consiglio Nazionale delle Ricerche) under the French-Italian scientific collaboration agreement. The computer resources were provided in part by the Scientific Commitee of CCVR (Centre de Calcul Vectoriel pour la Recherche), Palaiseau, France. Stimulating discussions with G. Böbel, F. G. Fumi, and C. Sommers are gratefully acknowledged.

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[3] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[4] A. K. Rajagopal and J. Callaway, Phys. Rev. B **7**, 1912 (1973).

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

[6] The more important applications of the density-functional theory are reviewed by A. R. Williams and U. von Barth, in *Theory of the Inhomogeneous Electron Gas*, edited by N. H. March and S. Lundqvist (Plenum, New York, 1983). In the same book one can find a review of the theory by W. Kohn and P. Vashista. A more recent review is given by J. Callaway and N. H. March, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1984), Vol. 38, p. 135.

[7] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[8] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).

[9] C. O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).

[10] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Lett. **59A**, 177 (1976); Solid State Commun. **24**, 765 (1977); Phys. Rev. B **20**, 3136 (1979).

[11] J. A. Alonso and L. A. Girifalco, Phys. Rev. B **17**, 3735 (1978).

[12] D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. **47**, 446 (1981).

[13] H. Stoll, C. M. E. Pavlidou, and H. Preuss, Theor. Chim. Acta **149**, 143 (1978).

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

[15] S. H. Vosko and L. Wilk, J. Phys. B **16**, 3687 (1983).

[16] S. Baroni and E. Tuncel, J. Chem. Phys. **79**, 6140 (1983).

[17] S. Baroni, J. Chem. Phys. **80**, 5703 (1984).

[18] G. Böbel and P. Cortona, J. Phys. B **16**, 349 (1983).

[19] A. I. M. Rae, Mol. Phys. **29**, 467 (1975).

[20] Equation (4) can be easily solved by a recursion method. However, in the formulation of the self-interaction-correction given in this paper, one must know the solution for a few values of N_σ only. One obtains $\beta=2$ for $N_\sigma=1$; $\beta=1.033\,25$ for $N_\sigma=2$, $\beta=0.851\,209$ for $N_\sigma=3$; $\beta=0.750\,692$ for $N_\sigma=4$; $\beta=0.683\,876$ for $N_\sigma=5$.

[21] I. Lindgren, Int. J. Quantum Chem. **5**, 411 (1971).

[22] We took the HF data in E. Clementi and C. Roetti, At. Data Nucl. Data Tables **43**, 261 (1977) (total and one-electron energies, ionization potentials, and electron affinities); the exchange energies were given by J. C. Slater and J. H. Wood, Int. J. Quantum Chem. **4**, 3 (1971); finally the Fourier transforms of the charge densities were calculated using the analytical parametrization of D. T. Cromer and J. B. Mann, Acta Crystallogr. Sec. A **24**, 321 (1968).

[23] Comparison between orthogonalized and nonorthogonalized calculations can be found, for example, in Ref. 14 and also in V. Selvaraj and M. S. Gopinathan, J. Phys. B **18**, 3043 (1985).

[24] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[25] *Handbook of Chemistry and Physics (1983–84)*, 64th ed., edited by R. C. Weast (Chemical Rubber Company, Boca Raton, Florida, 1984).

[26] H. Hotop and W. C. Lineberger, J. Chem. Phys. Ref. Data **4**, 539 (1975).