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Electron affinities of the light atoms in self-interaction corrected LDA

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Résumé. — Nous présentons les valeurs des affinités électroniques des atomes légers ($Z < 36$) que nous avons calculées en utilisant l'approximation locale (LDA) à la théorie de la fonctionnelle de densité et deux façons différentes de corriger les effets de la self-interaction. Nous trouvons un bon accord entre nos valeurs et les meilleures données expérimentales disponibles dans le cas des ions négatifs obtenus en ajoutant un électron s ou p à un atome neutre, tandis que l'accord est mauvais lorsqu'il s'agit d'un électron d. Nous avons également comparé les valeurs obtenues par la méthode de correction de la self-interaction qui donne les meilleurs résultats avec des données très récentes, qui ont été calculées par la méthode Hartree-Fock et les plus évoluées des approximations non-locales à la fonctionnelle énergie de corrélation actuellement disponibles. Nous trouvons que dans de nombreux cas les premiers résultats sont plus précis que les seconds.

Abstract. — We report values for the electron affinities of the light atoms ($Z < 36$) calculated in the local-density approximation (LDA) to the density-functional theory with two different forms of the self-interaction correction. We obtain good agreement with the best available experimental values for the negative ions involving the addition of an s or a p electron to a neutral atom, while the agreement is not good for the negative ions involving the addition of a d electron to a transition metal atom. The values obtained with the form of the self-interaction correction giving better results are compared with very recent values obtained using the Hartree-Fock method and the best available approximations to the correlation energy functionals. Surprisingly the former values turn out to be more accurate than the latter in a number of cases.

Introduction.

The density-functional theory (DFT) [1, 2] states that the ground state charge density and total energy of an electronic system can be obtained exactly from the solutions of the Kohn and Sham one-electron equation

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{en}} + V_{\text{eff}} \right) \psi_i = \varepsilon_i \psi_i \quad (1)$$

where V_{en} is the electron-nucleus potential and V_{eff} is an effective potential which describes the electron-electron interactions. Generally V_{eff} is divided in two terms, V_{c} and V_{xc} , where the first one is the ordinary coulombic potential

$$V_{\text{c}} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (2)$$

and the second one, the exchange-correlation potential, contains all of the remaining electron interactions and is given by the functional derivative of the exchange-correlation ground state energy E_{xc} with respect to the electron density ρ :

$$V_{\text{xc}} = \frac{\delta E_{\text{xc}}}{\delta \rho}. \quad (3)$$

As the explicit form of the functional $E_{\text{xc}}[\rho]$ is unknown, one needs some approximation of it in order to use equation (1) in actual calculations. The most common one, the local-density approximation (LDA), consists in assuming that the dependence of E_{xc} from ρ is the same as for an homogeneous electronic gas.

The problem of correcting equation (1) for the electronic self-interaction effects arises because the coulombic potential (Eq. (2)) contains a non-physical self-interaction term. The Kohn and Sham theory, which is based on the use of an orbital independent effective potential, states that to cancel out explicitly this term is not necessary. This is accomplished implicitly by the exact effective potential which verifies the following three conditions : i) the « exchange-correlation hole » satisfies the « sum rule » [3], ii) V_{xc} reduces to $-V_{\text{c}}$ for a system containing only one electron, iii) at large distance from a neutral finite system $V_{\text{en}} + V_{\text{eff}}$ decreases proportionally to $1/r$ [4]. These properties, which are very natural on physical ground, are rigorously true for the exact Kohn and Sham potential. The first one, in particular, is considered of crucial importance for the success of any approximation to the exact theory. This is the case, for example, of the LDA [3], which, however, does not verify the other two properties. This drawback has a number of consequences, such as the instability of the negative ions, or the fact that the highest energy eigenvalue of an isolated finite system is only a bad approximation of the first ionization potential, while in the exact theory these two quantities should coincide [4].

A natural way of taking into account the self-interaction effects consists in separating the exchange from the correlation and in treating the first as in the Hartree-Fock (HF) theory. Also in this way, however, if one uses the LDA for the correlation potential, one has to do something like a self-interaction correction, because the expressions derived from the homogeneous gas theory fail to vanish in the case of a system containing only one electron. The main advantage of proceeding in this way is that one requires only an approximate description of the « correlation hole », which has a vanishing total charge. The obvious drawback is that one has to perform complicated HF-like calculations. For this latter reason one is interested, in general, in approximations of the exchange contribution as well.

Some forms of the self-interaction correction.

Before examining some possible ways of performing the self-interaction correction in the case of inhomogeneous systems, let us recall a result of the theory of the homogeneous electronic gas.

Let us consider N_{σ} electrons of spin σ in a box of volume $V = 1$ with periodic boundary

conditions. The interelectron exchange energy $E_{x\sigma}^{\text{ie}}$ has been calculated by Rae [5] and is given by :

$$E_{x\sigma}^{\text{ie}} = -\frac{3}{4} \left(\frac{6}{\pi} \right)^{1/3} \rho_{\sigma}^{4/3} \gamma(N_{\sigma}) = \gamma(N_{\sigma}) E_{x\sigma} \quad (4)$$

where $E_{x\sigma}$ is the total exchange energy (including self-interaction) of the homogeneous gas and $\gamma(N_{\sigma})$ is a function of N_{σ} defined by the two equations :

$$N_{\sigma}^{-1} = \beta^3 - \frac{9}{16} \beta^4 + \frac{1}{32} \beta^6 \quad (5)$$

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

We note that if $N_{\sigma} = 1$, $\beta = 2$ and $\gamma = 0$; and that if $N_{\sigma} \rightarrow \infty$, $\beta = 0$ and $\gamma = 1$. So equation (4) takes the correct values in these limiting cases.

Historically the first self-interaction corrections were due to Hartree and to Fermi and Amaldi. As is well known, in the Hartree theory each electron interacts with an *orbital dependent* potential which is given by the coulombic term (Eq. (2)) minus the contribution to this potential due to the electron itself. Fermi and Amaldi proposed [6], in the context of the Thomas-Fermi theory, subtracting to the coulombic energy $E_c[\rho]$ an *average self-interaction* of the electrons given by :

$$E_c^{\text{si}} = N E_c \left[\frac{\rho}{N} \right] \quad (7)$$

where N is the number of electrons in the system.

Starting from these two basic ideas many versions of the self-interaction correction were elaborated. In particular, the Fermi-Amaldi correction can be easily generalized in order to derive an expression for the interelectron exchange and correlation. Indicating by $E_{x\sigma}[\rho_{\sigma}]$ and by $E_{\text{corr}}[\rho_{\uparrow}, \rho_{\downarrow}]$ the total exchange and the total correlation of the homogeneous gas and with $E_{x\sigma}^{\text{ie}}$ and $E_{\text{corr}}^{\text{ie}}$ the corresponding interelectron parts, one obtains :

$$E_{x\sigma}^{\text{ie}} = E_{x\sigma} - N_{\sigma} E_{x\sigma} \left[\frac{\rho_{\sigma}}{N_{\sigma}} \right] \quad (8)$$

$$E_{\text{corr}}^{\text{ie}} = E_{\text{corr}} - \sum_{\sigma} N_{\sigma} E_{\text{corr}} \left[\frac{\rho_{\sigma}}{N_{\sigma}}, 0 \right]. \quad (9)$$

These two expressions have been recently used in self-consistent calculations of atomic properties. The first one by Cedillo *et al.* [7], who performed exchange-only calculations where the average coulombic self-interaction was cancelled out by using equation (7). The second one by Vosko and Wilk [8] and by Lagowski and Vosko [9], who used equation (9) in order to include the correlation into Hartree-Fock-like calculations.

The use of the Rae equations in the context of the DFT was first considered by Böbel and Cortona [10] who, assuming that equation (4) could be used to approximate the interelectron exchange of an inhomogeneous system, derived a self-interaction-free one-electron equation. Also in this case, as in the Fermi-Amaldi-like theories, an explicit dependence from the *total* number of electrons is introduced in the theory.

Other corrections avoid this kind of dependence. This is the case, for example, of the method proposed by Lindgren [11]. Lindgren started from an *approximate* expression of the interelectron exchange energy of the homogeneous gas. This expression can be derived from

equations (4-6) by neglecting the higher powers of β in equation (5) and in equation (6) to obtain

$$\beta = N_{\sigma}^{-1/3} \quad (10)$$

and

$$\gamma(N_{\sigma}) = 1 - \frac{4}{3} N_{\sigma}^{-1/3} \quad (11)$$

and then replacing this latter equation with the following

$$\gamma(N_{\sigma}) = 1 - N_{\sigma}^{-1/3} \quad (12)$$

in order to obtain an exchange energy which vanishes when $N_{\sigma} = 1$.

The resulting expression is, in fact, still given by equation (8). Lindgren noted, however, that this equation coincides, in the particular case of the homogeneous gas, with another natural expression for the interelectron exchange energy :

$$E_{x\sigma}^{\text{ie}} = E_{x\sigma} - \sum_i E_{x\sigma}[\rho_{i\sigma}] \quad (13)$$

where i indicates the quantum numbers of the occupied orbitals, and he proposed using this expression in the inhomogeneous case.

The Lindgren approach was then generalized by Perdew and Zunger [12], who included the correlation by assuming the following equation

$$E_{xc}^{\text{ie}} = E_{xc} - \sum_{i\sigma} E_{xc}[\rho_{i\sigma}, 0] \quad (14)$$

as the base of their theory (E_{xc} = exchange-correlation energy). Perdew and Zunger made extensive tests of this method finding, for a number of properties, important improvements with respect to the corresponding LDA results.

Further progress in this method was done by Harrison [13] who focused on the way of performing the spherical average in atomic calculations. A well known characteristic of an orbital dependent scheme is, in fact, the non-invariance under unitary transformation of the orbitals. In the case of equation (14), performing the usual spherical average of the orbital charge densities one has no problem because the results become orbital-independent. But, using non-spherical orbital charge densities in equation (14) and then performing the spherical average, one gets different results for different choices of the orbitals. It was suggested that the optimum choice is given by the orbitals which minimize the total energy of the system [12]. Harrison showed that these orbitals *are not* those which give the best results : in atomic calculations, spherical-harmonic orbitals give a total energy lower than cartesian orbitals, but the latter produce considerably better results, for example for the interconfigurational energies of the transition metal atoms [14].

In a recent paper, Cortona [15] has re-analyzed the use of equation (4) in the inhomogeneous case. In fact, it is not obvious that N_{σ} should be identified with the total number of electrons in the system. For example, in the case of a system composed of two well separated groups of electrons $\gamma(N_{1\sigma}) E_{x\sigma}[\rho_{1\sigma}] + \gamma(N_{2\sigma}) E_{x\sigma}[\rho_{2\sigma}]$ is certainly a better approximation for $E_{x\sigma}^{\text{ie}}$ than $\gamma(N_{1\sigma} + N_{2\sigma}) E_{x\sigma}[\rho_{1\sigma} + \rho_{2\sigma}]$. On the other hand, the latter should be better than the first one when there is a large overlap between the two charge densities. So, for an inhomogeneous system, one shall partition the total charge density in parts having a small overlap and one shall apply equation (4) separately to each part. For

example, in the case of atomic calculations, it was suggested that the electronic shells are the natural units to do this partition. Furthermore, to neglect completely the intergroups exchange is too rough an approximation : it seems better to treat it by using the LDA and to include in the interelectron exchange energy a term similar to equation (13), but with $\rho_{i\sigma}$ replaced by the density of each group. This gives the following expression :

$$E_{x\sigma}^{\text{ic}} = E_{x\sigma} - \sum_s E_{x\sigma} [\rho_{s\sigma}] + \sum_s \gamma (N_{s\sigma}) E_{x\sigma} [\rho_{s\sigma}] \quad (15)$$

where s indicates the different groups of electrons.

About the equation above some remarks are in order. First of all, the intergroups exchange energy does not contain self-interaction. So to use for it the usual LDA does not contrast with the use of equation (4) for the intragroups exchange. Second, in the case of groups localized very far apart, the intergroups exchange correctly vanishes, leaving a sum of terms of the type of equation (4). Third, the intergroups exchange is, for its nature, nonlocal. A local approximation to it is necessarily very rough, and one can expect bad results for all the properties which are essentially determined from it. Finally, equation (13) is a particular case of equation (15) : the two expressions coincide if all the electrons are localized in well separated regions of space. If this is not the case, equation (15) takes into account more completely the results of the homogeneous gas theory, and, for this reason, we believe that it is the natural *local* expression for the interelectron exchange of an inhomogeneous system.

In two recent papers [15, 16], Cortona has applied equation (15) in self-consistent calculations of atomic properties. The method gave general improvement of both the local-spin-density and the Perdew and Zunger approximations for all the properties that were studied. In particular, remarkably good results were obtained for the total energies (errors < 0.04 %) and for the interconfigurational energies of the transition metals (errors reduced by 50 % or more).

In the following section we will extend this analysis by giving a complete discussion of the electron affinities of the light atoms ($Z < 36$) which are known to have stable negative ions. Calculations of electron affinities of these elements have previously been reported by Cole and Perdew [17], who used the Perdew and Zunger method (Eq. (14)), and by Lagowski and Vosko [9], whose work will be briefly discussed later on.

The electron affinities of the light atoms.

Equation (15), when applied to the atomic case, takes the form :

$$E_{x\sigma}^{\text{ic}} = \frac{3}{4} \sum_{nl} N_{nl\sigma} \rho_{nl\sigma} V_{x, nl\sigma}^{\text{ic}} \quad (16)$$

where $V_{x, nl\sigma}^{\text{ic}}$, the orbital dependent exchange potential, is given by

$$V_{x, nl\sigma}^{\text{ic}} = - \left(\frac{6}{\pi} \rho_{nl\sigma} \right)^{1/3} + \left(\frac{6}{\pi} \rho_{nl\sigma} \right)^{1/3} N_{nl\sigma}^{1/3} [1 - \gamma (N_{nl\sigma})]. \quad (17)$$

In these expressions $\rho_{nl\sigma}$ is the density of the shell of quantum numbers $nl\sigma$ normalized to 1 and $N_{nl\sigma}$ is the number of electrons in this shell. The coefficient $N_{nl\sigma}^{1/3} [1 - \gamma (N_{nl\sigma})]$, which enters in the effective potential, characterizes the approximation and distinguishes it, in practice, from the Perdew and Zunger one. This coefficient is, in principle, a function of the occupation number $N_{nl\sigma}$. However, with minimum changes of the total energies and with a more effective compensation of the errors (see Ref. [15] for a discussion of this point)

$N_{nl\sigma}$ can be replaced by the degeneracy $D_\ell = (2\ell + 1)$ of the shell. The effective interelectron exchange potential takes then the form

$$V_{x,nl\sigma}^{\text{ic}} = - \left(\frac{6}{\pi} \rho_\sigma \right)^{1/3} + \left(\frac{6}{\pi} \rho_{nl\sigma} \right)^{1/3} D_\ell^{1/3} [1 - \gamma(D_\ell)] \quad (18)$$

where the coefficient $D_\ell^{1/3} [1 - \gamma(D_\ell)]$ is equal to 1 for s electrons, to 1.130153 for p electrons and to 1.167141 for d electrons. The method based on equations (16) and (18) was called D-SIC. We shall use this notation and we shall indicate the Perdew and Zunger method by its usual name SIC.

All the results that we present in this paper have been obtained by self-consistent spin polarized calculations. As in the preceding papers, we have included the correlation contributions by using the Perdew and Zunger [12] parametrization of the Ceperley and Alder [18] Monte Carlo data for the homogeneous gas, that we have corrected for the self-interaction effects using the Perdew and Zunger method. Furthermore, we have taken into account the non-orthogonality of the orbitals by performing a Schmidt orthogonalization after each iteration.

In table I we show the differences between the calculated electron affinities (EA) and the experimental ones ⁽¹⁾. The theoretical values have been obtained as differences of total energies (Δ SCF method), while the experimental data are the « recommended » values given by Hotop and Lineberger [20]. The precision of these latter data is generally very good (except in a few cases, such as Ga and Ge) and, in any case, quite sufficient for our purposes.

In compiling the table we have distinguished if the electron added to the atom is a s , p or d electron. We have done this in order to emphasize the different accuracy in the description of these electrons given by the two theoretical methods. The s electrons are treated by SIC and D-SIC exactly in the same way. The small differences in the EA are due to the differences in the core charge densities which can only produce minor effects owing to the large spatial separation between the core electrons and the electron which is concerned in the EA. As one can see in table I, the EA predicted by SIC and D-SIC for s electrons are about the same and they are quite accurate, with errors of some hundredths of eV.

Larger differences between the two methods are obtained for p electrons. D-SIC gives EA with an average error of 0.09 eV, while the corresponding error of SIC is about four times greater. In particular, we note that the accuracy of D-SIC is about the same as for the s electrons.

The case of the d electrons is more difficult. The intershells interactions, that the two theoretical methods treat by the local approximation, have an important role and they can be expected to introduce large errors in the calculated EA. That this is indeed the case can be seen in table I, even though, in analyzing these data, one should consider that the relativistic effects are not included in our calculations. These effects are practically negligible in all the cases of interest in this paper except for the d states of the transition metal atoms [9, 17]. In this case, in fact, they reduce the EA roughly by 0.2 eV thus reducing also the differences between calculated and experimental values (except for the D-SIC EA of Fe). Finally, we note that for the d electrons as well, D-SIC gives EA considerably better than SIC.

⁽¹⁾ We have performed corresponding calculations for Ca and Sc but these do not give stability for the pertinent negative ions which have a « peculiar » electronic structure with a delocalized $4p$ electron. Configuration interaction calculations and Hartree-Fock calculations with the full LDA correlation (with no self-interaction correction) do, instead, give stability for both the ions [19].

Table I. — *Experimental electron affinities and the differences between the theoretical and the experimental values (in eV). The calculated electron affinities are obtained as differences of total energies.*

	exp	D-SIC	SIC
s states			
H	0.75	-0.03	-0.03
Li	0.62	-0.06	-0.06
Na	0.55	0.04	0.04
K	0.50	0.06	0.06
Cr	0.67	-0.07	-0.13
Cu	1.23	0.15	0.05
p states			
B	0.28	0.09	0.37
C	1.26	0.04	0.40
O	1.46	0.00	0.35
F	3.40	-0.06	0.35
Al	0.44	-0.01	0.18
Si	1.39	-0.07	0.18
P	0.75	0.10	0.35
S	2.08	0.15	0.45
Cl	3.62	0.05	0.39
Ga	0.30	0.08	0.26
Ge	1.20	0.08	0.32
As	0.81	0.13	0.37
Se	2.02	0.22	0.49
Br	3.36	0.16	0.47
d states			
Ti	0.08	0.44	0.99
V	0.53	0.75	1.33
Fe	0.16	0.04	0.58
Co	0.66	0.46	1.01
Ni	1.16	0.84	1.41

An alternative way of evaluating the EA consists in taking the negative of the highest one-electron energy of every negative ion. The results of this procedure are reported in table II for s and p electrons and in table III for transition metal atoms. The analysis of table II is straightforward and quite similar to that of table I : D-SIC and SIC give similar results for s electrons, while D-SIC is better for p electrons. The accuracy of D-SIC is quite good and the errors are of the same order of magnitude as in the Δ SCF calculations (except for H, O and F).

Table III requires some more comments. In fact, by comparing the theoretical EA with the experimental ones (column exp 1), we find that the calculated EA not only are often far from the correct values, but also they fail to reproduce the trend of the EA with the atomic

Table II. — *Experimental electron affinities and the differences between the theoretical and the experimental values (in eV). The calculated electron affinities are obtained by taking the negative of the highest eigenvalue of every negative ion.*

	exp	D-SIC	SIC
s states			
H	0.75	0.95	0.95
Li	0.62	0.06	0.06
Na	0.55	0.12	0.12
K	0.50	0.07	0.07
p states			
B	0.28	0.12	0.47
C	1.26	0.17	0.69
O	1.46	0.68	1.30
F	3.40	0.97	1.69
Al	0.44	- 0.12	0.10
Si	1.39	- 0.27	0.07
P	0.75	0.03	0.41
S	2.08	0.08	0.54
Cl	3.62	- 0.04	0.48
Ga	0.30	- 0.01	0.20
Ge	1.20	- 0.13	0.19
As	0.81	0.03	0.39
Se	2.02	0.07	0.49
Br	3.36	- 0.04	0.43

Table III. — *Experimental and theoretical electron affinities (in eV). In the column labelled exp 2 the experimental electron affinities are referred to the $(3d)^{n-1}(4s)^1$ configuration of the neutral atom. The theoretical values are obtained by taking the negative of the highest eigenvalue of every negative ion.*

	exp 1	exp 2	D-SIC	SIC
Ti	0.08	0.89	0.67	0.56
V	0.53	0.79	0.56	0.49
Cr	0.67	0.67	0.48	0.43
Fe	0.16	1.02	0.93	0.84
Co	0.66	1.09	1.05	0.97
Ni	1.16	1.19	1.17	1.08
Cu	1.23	1.23	1.28	1.19

number. The reason of this is that for all these ions the highest eigenvalue corresponds to a 4s electron. Taking off this electron leaves a neutral atom in the configuration $(3d)^{n-1}(4s)^1$ which is not the experimental ground state except in the case of Cr and Cu. So the natural quantities to compare with the theoretical values are not the experimental EA but the sums of the latter and the experimental [21] interconfigurational energies $(3d)^{n-1}(4s)^1 - (3d)^{n-2}(4s)^2$. This is the meaning of the data labelled as exp 2, which agree better with the calculated values.

Recently, Lagowski and Vosko (LV) [9] have calculated a number of ionization potentials (IP) and of EA in order to test the nonlocal correlation functionals proposed by Hu and Langreth (HL) [22] and by Perdew (P) [23]. These functionals are based on a modification of the gradient correction suggested by the analysis of this approximation performed by Langreth and Perdew [24, 25], and they have been used by LV in order to calculate the correlation contribution to the IP and to the EA to be added to the corresponding HF

Table IV. — *Experimental electron affinities and the differences between the theoretical and the experimental values (in eV). The calculated electron affinities are obtained as differences of total energies. The D-SIC values differ from those of table I for the addition of relativistic contributions. HL and P indicate results of Lagowski and Vosko [9] obtained including in Hartree-Fock-like calculations the nonlocal correlation functionals proposed by Hu and Langreth [22] and by Perdew [23].*

	exp	D-SIC	HL	P
s states				
Li	0.62	-0.06	0.21	-0.01
Na	0.55	0.04	0.29	0.02
K	0.50	0.06	0.27	0.02
Cr	0.67	-0.09	0.01	-0.34
Cu	1.23	0.18	-0.18	-0.52
p states				
B	0.28	0.08	0.37	-0.02
C	1.26	0.04	0.31	-0.13
O	1.46	-0.01	-0.28	-0.83
F	3.40	-0.07	-0.41	-0.96
Al	0.44	-0.02	0.42	0.06
Si	1.39	-0.08	0.51	0.11
P	0.75	0.09	0.33	-0.09
S	2.08	0.13	0.38	-0.07
Cl	3.62	0.03	0.47	0.00
d states				
Ti	0.08	0.29	-0.21	-0.52
V	0.53	0.57	-0.39	-0.70
Fe	0.16	-0.22	-0.96	-1.40
Co	0.66	0.16	-1.20	-1.63
Ni	1.16	0.49	-1.48	-1.88

quantities. We note that the HL and P functionals are the most sophisticated correlation functionals at present in use and that to combine them with the HF method gives the most accurate approximation that one can conceive in the context of the DFT for atomic calculations.

We report the LV results in table IV together with our D-SIC EA. In order to directly compare the three sets of data we have added to the D-SIC EA the relativistic contributions, which were calculated by a perturbative method by LV and which are included in their HL and P results. The comparison is quite surprising and reveals that D-SIC is generally the more accurate of the three methods. More in detail, the accuracy of the D-SIC and P results is about the same for most of the s electrons and p electrons, while D-SIC is better for O, F, and for all the transition metal atoms. On the other hand, the HL functional, which is based on the random phase approximation and which makes no use of the Monte Carlo results for the homogeneous gas, is often less accurate than the other two methods.

It is difficult to rationalize these results : the D-SIC exchange is approximated, while in HL and in P the exchange is exact ; D-SIC is a local method, while in HL and in P the nonlocal corrections are taken into account ; on the other hand the self-correlation is cancelled out in D-SIC but not in HL and in P. Perhaps the more important factor is the use of similar approximations for the exchange and for the correlation functionals. In any case we believe that table IV illustrates one more time the difficulty of going really beyond the local-density approximation.

Conclusions.

We have used a recently proposed method (D-SIC) of correcting the LDA for the self-interaction effects in order to calculate the EA of light atoms. We have found that this method reproduces the experimental values with a precision of roughly 0.1 eV for the EA of negative ions obtained by adding an s or a p electron to a neutral atom (except the cases of H, O and F if the EA are computed by taking the negative of the highest eigenvalue), while the errors are considerably greater in the case of the addition of a d electron to a transition metal atom.

We have compared the results of D-SIC with the analogous quantities calculated by using the self-interaction correction proposed by Perdew and Zunger (SIC). We have found that D-SIC gives clearly better results in all the cases where appreciable differences between the two methods could be expected. This is analogous to the findings of preceding papers [15, 16] for total and exchange energies, ionization potentials and interconfigurational energies.

We have also compared the D-SIC EA with values calculated [9] by using the best nonlocal correlation functionals presently available and the HF method. Also in this case D-SIC turns out to be generally the more accurate method. This is quite surprising, in particular in the case of d electrons : these have important nonlocal contributions to the EA and yet the nonlocal methods discussed give rather inaccurate results.

References

- [1] HOHENBERG P. and KOHN W., *Phys. Rev.* **136** (1964) B864.
- [2] KOHN W. and SHAM L. J., *Phys. Rev.* **140** (1965) A1133.
- [3] GUNNARSSON O. and LUNDQVIST B. I., *Phys. Rev. B* **13** (1976) 4274.
- [4] ALMBLADH C. O. and VON BARTH U., *Phys. Rev. B* **31** (1985) 3231.
- [5] RAE A. I. M., *Mol. Phys.* **29** (1975) 467.
- [6] FERMI E. and AMALDI E., *Mem. Accad. Italia* **6** (1934) 119.

- [7] CEDILLO A., ORTIZ E., GAZQUEZ J. L. and ROBLES J., *J. Chem. Phys.* **85** (1986) 7188.
- [8] VOSKO S. H. and WILK L., *J. Phys. B* **16** (1983) 3687.
- [9] LAGOWSKI J. B. and VOSKO S. H., *J. Phys. B* **21** (1988) 203.
- [10] BÖBEL G. and CORTONA P., *J. Phys. B* **16** (1983) 349.
- [11] LINDGREN I., *Int. J. Quantum Chem.* **S 5** (1971) 411.
- [12] PERDEW J. P. and ZUNGER A., *Phys. Rev. B* **23** (1981) 5048.
- [13] HARRISON J. G., *J. Chem. Phys.* **78** (1983) 4562.
- [14] HARRISON J. G., *J. Chem. Phys.* **79** (1983) 2265.
- [15] CORTONA P., *Phys. Rev. A* **34** (1986) 769.
- [16] CORTONA P., *Phys. Rev. A* **38** (1988) 3850.
- [17] COLE L. A. and PERDEW J. P., *Phys. Rev. A* **25** (1982) 1265.
- [18] CEPERLEY D. M. and ALDER B. J., *Phys. Rev. Lett.* **45** (1980) 566.
- [19] FROESE-FISCHER C., LAGOWSKI J. B. and VOSKO S. H., *Phys. Rev. Lett.* **59** (1987) 2263.
- [20] HOTOP H. and LINEBERGER W. C., *J. Phys. Chem. Ref. Data* **14** (1985) 731.
- [21] MOORE C. E., Atomic Energy Levels, Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C.) 1949 and 1952, Vols. I and II.
- [22] HU C. D. and LANGRETH D. C., *Phys. Scr.* **32** (1985) 391.
- [23] PERDEW J. P., *Phys. Rev. B* **33** (1986) 8822.
- [24] LANGRETH D. C. and PERDEW J. P., *Solid State Commun.* **31** (1979) 567.
- [25] LANGRETH D. C. and PERDEW J. P., *Phys. Rev. B* **21** (1980) 5469.