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Self-interaction correction: The transition-metal atoms

Pietro Cortona
Dipartimento di Fisica, Università degli Studi di Genova, I-16146 Genova, Italy
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The method that we have recently proposed to correct the local-density approximation of the density-functional theory for spurious self-interaction effects is used to calculate the interconfigurational energies and the ionization potentials of the transition-metal atoms. The results so obtained are compared with the corresponding quantities calculated by using the local-density approximation and the Perdew and Zunger self-interaction correction. In both cases we find very large improvements which are essentially due to a better description of the 3*d* electrons. The results of this paper show that the large local-density errors for these quantities are mainly due to the self-interaction terms. They also indicate that the latter are probably a major source of errors in the local-density calculations of the electronic properties of the transition-metal dimers and solids.

I. INTRODUCTION

The calculation of the transition-metal atoms interconfigurational energies (ICE's) by using approximate versions of the density-functional theory has been the object of a number of papers.

Some years ago it was shown[1-3] that the local-density approximation (LDA) reproduces remarkably well the trend of the ICE's $(3d)^{n-1}(4s)^1$-$(3d)^{n-2}(4s)^2$ and $(3d)^n$-$(3d)^{n-2}(4s)^2$, but that the numerical values of these energies are wrong for about 1 eV and 1.5 eV, respectively. It was also shown that these errors are not sensibly modified by using different local expressions of the correlation energy.[4]

The earlier calculations were performed without taking into account the multiplet structure contributions. This was done by Gunnarsson and Jones[5] by means of the method suggested by Ziegler, Rauk, and Baerends[6] and by von Barth.[7] It was found that the multiplet contributions are important in order to account for the small deviations from the trend of the experimental data, but that they are quite ineffective on the values of the discrepancies from these data. So, in order to study these discrepancies, it is about equivalent to include the multiplet structure effects into the theoretical calculations and to compare with the experimental data or to perform the usual central-field calculations and to compare with spherically averaged experimental results (obtained by taking a weighted average of the terms which have the same spin multiplicity as the lowest term corresponding to each configuration).

Nonlocal effects were considered by Gunnarsson and Jones[8] who calculated the ICE's by using their nonlocal exchange-correlation functional. Although these calculations were performed by introducing a shell partitioning in order to obtain the best performance of this method, only marginal improvements of the LDA results were found.

Hartree-Fock (HF) data for the ICE's were considered by Harris and Jones.[1] These authors used relativistic HF data by Kagawa[9] and they pointed out large discrepancies between the trends of the theoretical and of the experimental results. This conclusion was contradicted by Gunnarsson and Jones,[5] who reexamined the HF ICE's using HF data by Clementi and Roetti[10] and who found a better agreement between the trends of the experimental and of the theoretical results. The latter, however, presented some residual irregularities.

More recently Baroni[11] has performed HF calculations of ICE's. The trend of the Baroni results agrees very well with the experimental one and the discrepancies are of the same order of those obtained from LDA calculations including correlation. In the same paper Baroni has also considered the correlation contribution—as a first-order perturbation and using the LDA—to the ICE's. He found that this contribution brings the HF ICE's in a quite good agreement with the experimental ones. In particular, the sign of this correction is always such as to reduce the discrepancies between the theoretical and the experimental data.

ICE's calculations were also performed[3,12] by using the self-interaction-corrected LDA in the form proposed by Perdew and Zunger.[12] It was found that the errors of this approximation are of the same order of those of the LDA. This is quite different from what one obtains by treating the self-interaction terms by first-order perturbation theory. In this latter way, in fact, one finds errors greater than the LDA errors.[12] This is due to the important relaxation effects involved in these transitions,[13] effects which seem to be better taken into account by using the self-interaction correction than the too soft LDA. It should also be noted that in a later paper Harrison[14] has shown that a modified version of the Perdew and Zunger theory produces ICE's in better agreement with experiment.

Recently we have proposed[15] a new method of introducing a self-interaction correction into the LDA, which differs from the Perdew and Zunger one for the treatment of the intrashell exchange terms. In that paper (hereafter referred to as I) we have successfully tested our approximation by calculating a number of electronic properties of light atoms. The purpose of the present work is to investigate if that method reduces the large LDA errors also in the case of the ICE's of the transition metal atoms. This will be carried out in Sec. III, while in Sec. II we shall compare briefly the main features of our correction with those of the other more strictly related methods, and Sec. IV will be devoted to the conclusions of this work.

II. THE SELF-INTERACTION-CORRECTED LDA

A simple way to try to improve the LDA consists in introducing a self-interaction correction. Briefly, in this approach one treats exactly the self-exchange terms and one uses an approximate expression for the interelectron exchange and correlation. The one-electron equation which is obtained in this way is not a Kohn-Sham equation because the potential is orbital dependent. Nevertheless, it can be considered as an approximation of another exact one-electron equation—also proposed by Kohn and Sham[16]—which is obtained by separating the exchange from the correlation energy and by using for the first one its HF expression. It should be noted that the usual self-interaction-corrected LDA potentials, at large distance from a finite neutral system, decrease proportionally to $1/r$. This is a major difference from the LDA and its main consequence is that the energy eigenvalues are a better approximation of the electronic ionization potentials.

In a very comprehensive article on the self-interaction correction—we refer to this work for an extensive discussion of the theoretical aspect of this type of theory as well as for a review of the works on this subject up to 1981—Perdew and Zunger[12] have presented a large number of results obtained by using the following general prescription in order to deduce, from an arbitrary approximate expression E_{xc} of the exchange-correlation energy, a corresponding self-interaction free expression $E_{\text{xc}}^{\text{ie}}$:

$$E_{\text{xc}}^{\text{ie}}=E_{\text{xc}}[\rho_\uparrow,\rho_\downarrow]-\sum_{\alpha\sigma}E_{\text{xc}}[\rho_{\alpha\sigma},0]\ , \tag{1}$$

where α is the quantum number set characterizing (with σ) the one-particle states, ρ_σ is the total charge density of the electrons of spin σ, and $\rho_{\alpha\sigma}$ is the charge density of one electron in the state $\alpha\sigma$.

Perdew and Zunger justified this prescription essentially by the fact that the exchange-correlation energy of a system containing only one electron should be zero, and they verified that in a number of cases the results given by this method improved the LDA ones.

Two years later, Harrison[17] pointed out that the spherical average which is commonly used in the atomic calculations, can be performed in two nonequivalent ways. In the first one, which is the traditional procedure for the Hartree-like theories and which was used by Perdew and Zunger, one replaces the orbital charge densities in Eq. (1) with their spherical averages and one derives the potential from the resulting expression. In the second one, nonspherical orbital charge densities are used in Eq. (1). Then one derives the potential, which results to be spherically symmetric, but to depend from the quantum number m_l. Finally, the central-field approximation is obtained by taking the average of the potentials for the electrons which have identical quantum numbers, but different values of m_l. Following this second procedure one finds results which depend on the choice of the representation for the angular part of the orbitals. In particular, Harrison found that using spherical-harmonic or Cartesian representations in exchange-only calculations, one obtains lower energies in the first case, while the second choice produces results in better agreement with HF. For this latter reason Harrison decided to use Cartesian orbitals in his calculations, and in this way he found that the Perdew and Zunger results can be considerably improved.[18]

At about the same time, we pointed out[19] that the interelectron exchange energy E_σ^{xie} (for unit volume) of a homogeneous gas containing N_σ electrons of spin σ had been calculated by Rae[20] and that it can be written in the following form:

$$E_\sigma^{\text{xie}}=-\frac{3}{4}\left[\frac{6}{\pi}\right]^{1/3}\rho_\sigma^{4/3}\gamma(N_\sigma)=\gamma(N_\sigma)E_\sigma^{x}\ , \tag{2}$$

where E_σ^x is the total exchange energy of the homogeneous gas and $\gamma(N_\sigma)$ is a function of the number of electrons N_σ defined by the two equations:

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

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

In that paper we also used these equations in a simple way in order to approximate the interelectron exchange potential of the self-interaction-corrected one-electron equation and in this way we obtained some improvements with respect to LDA.

It is interesting to compare Eqs. (2)–(4) with the analogous quantities calculated by the Perdew and Zunger theory. Using the latter one obtains the following value of γ:

$$\gamma(N_\sigma)=1-(N_\sigma)^{-1/3}\ , \tag{5}$$

which shows that this theory does not reproduce Rae's correct result for this limiting case.

In paper I we have discussed in considerable more detail the problem of applying the Rae equations to the inhomogeneous case. We found that a reasonable way to do this consists in partitioning the total electron density of the inhomogeneous system in a number of pieces which have small overlaps. Equations (2)–(4) can then be used for the interelectron exchange of each single piece and the exchange interaction between the different pieces (which obviously does not contain self-interaction contributions) can be taken into account by the usual local expression of the exchange energy. In the case of an atomic system, for example, the natural units for partitioning the total charge density are the electronic shells. Assuming this type of partition, one obtains the following expression of the interelectron exchange potential $V_{nl\sigma}^{\text{xie}}$ for one electron belonging to the shell of quantum number nl:

$$V_{nl\sigma}^{\text{xie}}=-\left[\frac{6}{\pi}\rho_\sigma\right]^{1/3}+\left[\frac{6}{\pi}\rho_{nl\sigma}\right]^{1/3}N_{nl\sigma}^{1/3}[1-\gamma(N_{nl\sigma})] \tag{6}$$

and for the interelectron exchange energy E^{xie}:

$$E^{\text{xie}}=\frac{3}{4}\sum_{nl\sigma} N_{nl\sigma}\rho_{nl\sigma}V_{nl\sigma}^{\text{xie}} \ . \tag{7}$$

In these expressions $N_{nl\sigma}$ is the number of electrons of spin σ *present* in the shell *nl*. In paper I we replaced $N_{nl\sigma}$ in the coefficient $N_{nl\sigma}^{1/3}[1-\gamma(N_{nl\sigma})]$ of the potential with the degeneracy $(2l+1)$ of the same shell. This makes only a little difference on the total energies (only the electrons belonging to open shells are treated differently) and ensures a more effective compensation of the errors when one is concerned with total energy differences of two different systems.

We emphasize that the scheme just described is strictly *a local scheme,* except for the self-exchange terms which are treated exactly. In I we have indicated this method with *D*-SIC. We will adopt this notation in this paper as well and, following the common use, we will indicate with SIC the Perdew and Zunger correction.

III. THE TRANSITION-METAL ATOMS INTERCONFIGURATIONAL ENERGIES AND IONIZATION POTENTIALS

It is clear that a self-interaction correction can solve only in part the problems of the LDA and that for a number of properties one can expect only a partial improvement or, in some cases, no improvement at all. A typical quantity which cannot be better estimated by introducing the self-interaction correction is the spin-flip energy of the 4*s* electron in the $(3d)^{n-1}(4s)^1$ configuration of the transition-metal atoms. In fact, the self-interaction contributions to the total energies of the two configurations $(3d)^{n-1}(4s)_{\uparrow}$ and $(3d)^{n-1}(4s)_{\downarrow}$ are about the same, and they cancel out when one takes the difference. On the other hand, the spin-flip energy is entirely due to the interaction of the 4*s* electron with the electrons belonging to the more inner shells. This is a typical nonlocal interaction that cannot be correctly described by the LDA. So, it is quite natural to find large discrepancies between the LDA spin-flip energies and the experimental ones.[2] Unfortunately the self-interaction-corrected methods, as SIC and *D*-SIC, describe this interaction exactly in the same way as LDA and one expects to find—and this is indeed confirmed by the actual calculations—about the same results from the three approximations.

In the case of the *s*-*d* promotion energies, the self-interaction contribution is not the same for the two configurations and does not cancel out in taking the difference. So, it is possible that introducing a self-interaction correction one finds improved values of these quantities. However, it is physically clear that purely nonlocal interactions, as those discussed for the spin-flip energies, should give an important contribution to the ICE's as well and that for this reason one can only expect a partial improvement of the LDA values.

In the following we shall give the results of self-consistent spin-polarized calculations. As in paper I we have taken into account the correlation contributions by using the Perdew and Zunger parametrization[12] of the Ceperley and Alder[21] Monte Carlo data for the correlation energy of the homogeneous gas and the small nonorthogonality effects by a Schmidt orthogonalization of the orbitals after each iteration.

In all the figures of this paper we report the differences between theoretical and experimental quantities. The latter, which have been deduced from Moore's spectroscopic data tables,[22] have been spherically averaged in order to obtain values which can be directly compared with the results of our central-field theoretical calculations.

In Figs. 1 and 2 we show the errors of the different approximations for the ICE's $(3d)^{n-1}(4s)^1$-$(3d)^{n-2}(4s)^2$ and $(3d)^n$-$(3d)^{n-2}(4s)^2$, respectively. As it was noted in previous works,[3,12] the LDA and SIC descriptions of these quantities are about equivalent and SIC is a little better in the second case. On the other hand, *D*-SIC introduces systematic improvements. In the case of Fig. 1 the errors are reduced for about 50% in the first half of the series and even more in the second half. It should also be noted that *D*-SIC gives the correct ground-state configuration in all cases, while SIC and LDA fail in the cases of Ti and of Co.[23]

The improvements are even more evident in Fig. 2. In this case, in fact, the errors of *D*-SIC are smaller than 0.5 eV (except for Ca), while LDA underestimate these ICE's for about 1.5 eV and the SIC errors are included between 0.8 and 1.9 eV. It is also interesting to note that the LDA does not predict the correct order of the configurations for Ni: indeed, in this case, the LDA ener-

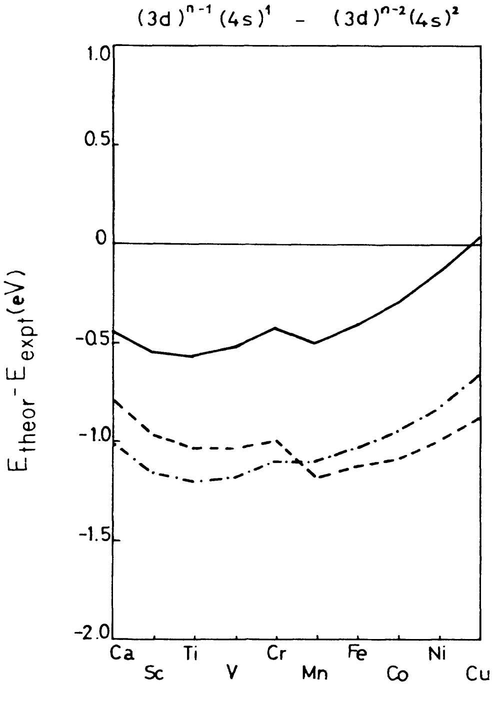

FIG. 1. Differences between the various theoretical values for the $(3d)^{n-1}(4s)^1$-$(3d)^{n-2}(4s)^2$ interconfigurational energies and the corresponding experimental data. ——, *D*-SIC; — — —, LDA; —·—·—, SIC.

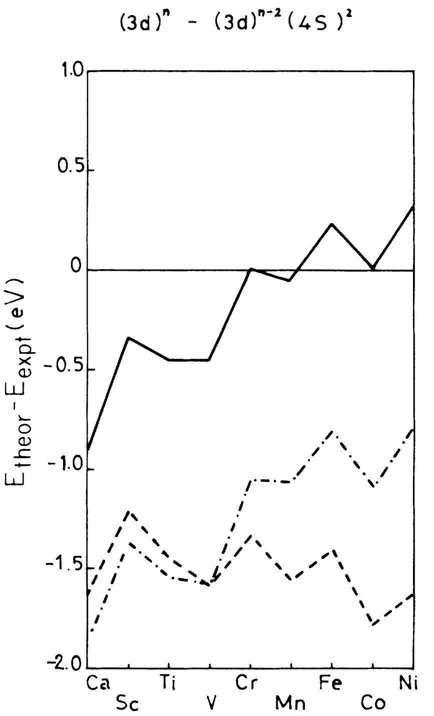

FIG. 2. Differences between the various theoretical values for the $(3d)^n$-$(3d)^{n-2}(4s)^2$ interconfigurational energies and the corresponding experimental data. ——, *D*-SIC; — — —, LDA; —·—·—·, SIC.

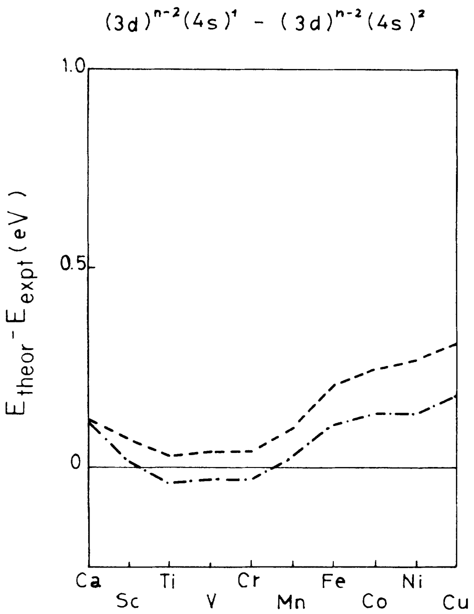

FIG. 3. Differences between the various theoretical values for the $(3d)^{n-2}(4s)^1$-$(3d)^{n-2}(4s)^2$ ionization potentials and the corresponding experimental data. — — —, LDA and D-SIC; —·—·—·, SIC.

gy of the $(3d)^n$ configuration is lower than that of the $(3d)^{n-2}(4s)^2$ one.

More information about the nature of the improvements introduced by using *D*-SIC can be obtained by analyzing the ionization potentials (IP's). These quantities are generally studied by considering the energy differences between the various ionic configurations and the $(3d)^{n-2}(4s)^2$ atomic configuration or, alternatively, the differences between the energies of the ionic and the atomic ground states, ignoring the (possible) differences in the ground-state configurations given by self-consistent calculations and by experiment. Proceeding in these ways, however, a part of the discrepancies is due to the errors in the *s*-*d* promotion energies, which have been separately examined. We are instead interested in the energy required to take away a 4*s* or a 3*d* electron from an atom without having to transfer at the same time any electron between these two shells. It is then possible, for example, to consider the $(3d)^{n-1}(4s)^1$-$(3d)^{n-2}(4s)^2$ ICE as the difference between the $(3d)^{n-2}(4s)^1$-$(3d)^{n-2}(4s)^2$ and the $(3d)^{n-2}(4s)^1$-$(3d)^{n-1}(4s)^1$ IP's.

All the possible IP's which do not involve electron transfers between the 4*s* and 3*d* shells are reported in Figs. 3–7. In Fig. 3 the *D*-SIC data are not shown because they are practically indistinguishable from the LDA ones.

Figures 3 and 4 show that the LDA and *D*-SIC values of the IP's for the 4*s* electrons are quite similar, while SIC gives a little better results. There is some analogy between these results and what is found for the average radius of the 3*d* and 4*s* orbitals. Indeed, in the case of the $(3d)^{n-2}(4s)^2$ configuration, the LDA and *D*-SIC radius agree generally better than 1%, while SIC gives values which are smaller for the 3*d* electrons and greater for the 4*s*. Of course this cannot be considered the reason for the

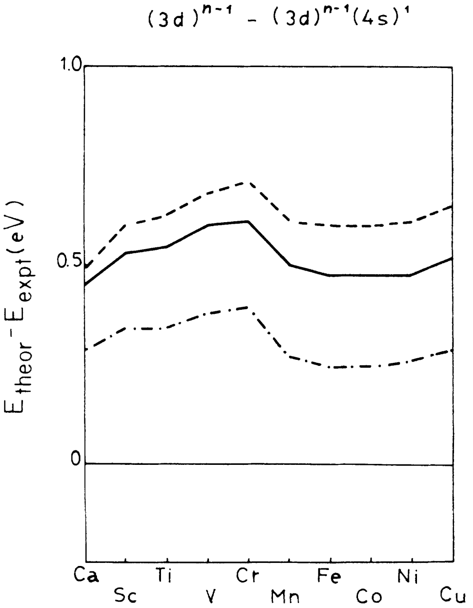

FIG. 4. Differences between the various theoretical values for the $(3d)^{n-1}$-$(3d)^{n-1}(4s)^1$ ionization potentials and the corresponding experimental data. ——, *D*-SIC; — — —, LDA; —·—·—·, SIC.

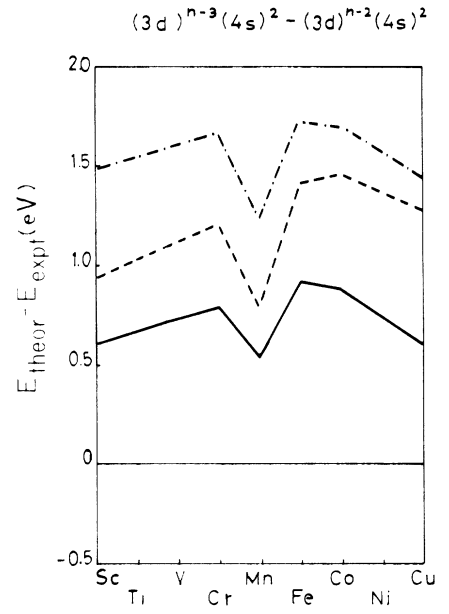

FIG. 5. Differences between the various theoretical values for the $(3d)^{n-3}(4s)^2$-$(3d)^{n-2}(4s)^2$ ionization potentials and the corresponding experimental data. ——, *D*-SIC, — — —, LDA; —·—·—·, SIC.

FIG. 7. Differences between the various theoretical values for the $(3d)^{n-1}$-$(3d)^n$ ionization potentials and the corresponding experimental data. ——, *D*-SIC; — — —, LDA; —·—·—·, SIC.

similarity of the LDA and *D*-SIC IP's, which indeed seems rather casual.[24] It is only another indication of the rough equivalence of the descriptions of the 4*s* electrons given by these two approximations.

Coming back now to the analysis of Figs. 3 and 4, it can be noted that the error on the IP's increases with the number of 3*d* electrons of the same spin as the 4*s* electron concerned in the ionization, while this error is roughly constant in that part of the series where the number of 3*d* electrons of opposite spin is increasing. So it is quite natural to attribute this effect to the exchange interaction between the 4*s* and the 3*d* electrons, interaction which seems to be, in particular, the main source of errors in the case of the $(3d)^{n-2}(4s)^2$ configuration.

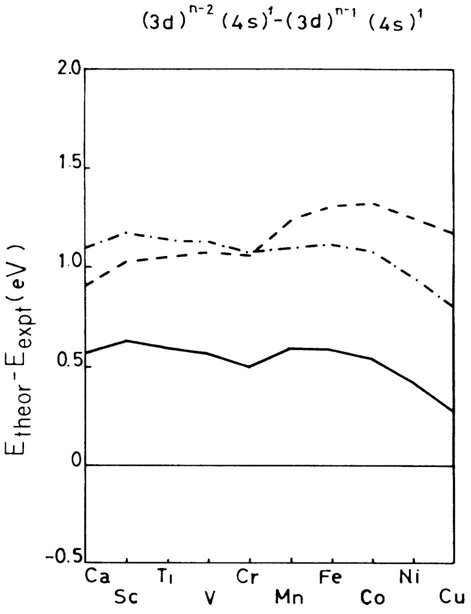

FIG. 6. Differences between the various theoretical values for the $(3d)^{n-2}(4s)^1$-$(3d)^{n-1}(4s)^1$ ionization potentials and the corresponding experimental data. ——, *D*-SIC; — — —, LDA; —·—·—·, SIC.

Completely different is the analysis of the 3*d* electron IP's (Figs. 5–7). In all the three possible cases *D*-SIC systematically improves LDA as well as SIC. On the other hand, the quality of the results obtained by these latter two approximations are about equivalent. LDA is better for the IP's of the 4*s* electron rich configuration (Fig. 5), while SIC is to be preferred in the opposite case (Fig. 7). Finally the two approximations are about equivalent in the intermediate case (Fig. 6).

In conclusion, the better description of the 3*d* IP's given by *D*-SIC seems to be the origin of the improvements that we have found for the ICE's.

IV. CONCLUSIONS

This work shows that *D*-SIC is successful not only in describing the electronic properties of the atoms of the two first rows of the Periodic Table, but also in the case of the third row transition metal atoms. In particular, we have shown that *D*-SIC gives ICE's and IP's (for *d* electrons) which agree considerably better with experiment than those calculated by using LDA or SIC. This last point confirms that the use of the self-interaction correction permits one to better take into account the relaxation contributions to these quantities and, besides, that *D*-SIC gives an improved description of the interelectron exchange terms inside each shell. Nevertheless, the errors of *D*-SIC are still important. They originate from interactions which are essentially nonlocal and that *D*-SIC treats in the same way as LDA. For these interactions, and particularly for the intershells ones, which are probably the main cause of the residual errors, appropriate approximations should be elaborated.

This work shows also that an orbital dependent scheme can be very useful in order to obtain approximations which accurately describe the chemical bond. It should be pointed out, however, that the Kohn and Sham theory states that this type of approach is not necessary: In principle, one can obtain exact results by using a unique effective potential for all the electrons. Of course, the difficulty is to find a good approximation of this potential, but, in the last few years, some important progress has been made in this field.[25–28] These new nonlocal functionals have not yet been tested by calculating critical properties such as the ICE's and it will be interesting to compare their results with those reported in this paper. In any case, an orbital dependent scheme has a greater flexibility, which permits not only the use of the self-interaction correction, but also, for example, a different treatment of the inter- and intra-shells nonlocal contributions. This last point, in our opinion, could be quite important in order to formulate approximate functionals which take into account the different physical features of these interactions.

Finally, we would like to point out that some methods for applying the self-interaction correction to solid state,[29] molecular,[30] and cluster[31] calculations have been recently elaborated and that in all these cases the utility of this type of correction has been proved. It would be interesting to apply the correction used in this paper to molecular and to band-structure calculations: The results we have reported seem indicate that in this way one could eliminate a part of the anomalies of the LDA results for the transition dimers and metals.

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[24] Indeed, the almost identical IP's for the $(3d)^{n-2}(4s)^2$ configuration derive from the sum of contributions, due to the different components of the total energy (kinetic, electron-nucleus, electron-electron Coulombic energy, etc.), which have rather different values in the two approximations.

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