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On the density-functional description of the electron affinities of Ca and Sc

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Résumé. — Nous discutons la stabilité des ions négatifs du Ca et du Sc dans le contexte de la théorie de la fonctionnelle de densité et, à ce propos, nous examinons en particulier le rôle de la self-interaction comprise dans l'énergie de corrélation. Nous concluons que les approximations à la théorie qui sont couramment utilisées ne décrivent pas d'une façon satisfaisante les interactions d'échange et de corrélation inter-couches.

Abstract. — The stability of the negative Ca and Sc ions is discussed in the framework of the density functional theory, and the role of a self-interaction correction for the correlation energy is examined. We conclude that the approximations currently in use do not accurately describe the intershell exchange and correlation.

In a recent paper [1] we have presented a complete report on the electron affinities (EA) of the light atoms calculated using the D-SIC method proposed by one of us [2]. This method is essentially a way to eliminate the effects of the electron self-interaction from the local approximation (LDA) to the density functional theory (DFT) ⁽¹⁾. The method uses the theory of the homogeneous and finite electron gas [3] to obtain an expression of the exchange energy free from self-interaction which is then used in the non-homogeneous case together with the Coulomb interaction treated as in the Hartree theory, while the expression of the correlation energy is taken from the theory of Perdew and Zunger [4].

Until now the method has been used in atomic calculations and has produced a general improvement [1, 2, 5] of the results obtained with the LDA and with the self-interaction correction by Perdew and Zunger [4]. In reference [1] we have found, in particular, that the EA of the light atoms computed by D-SIC compare favourably with those computed by the method of Perdew and Zunger as well as with those obtained with the most sophisticated nonlocal correlation functionals presently available. Specifically the comparison has been made with the results by Lagowski and Vosko [6] who have included the correlation in a Hartree-Fock (HF) calculation through the nonclonal functionals by Hu and Langreth

⁽¹⁾ As is well known, the LDA does not give stable negative ions in the majority of cases.

Table I. — Average error of the EA of the light atoms (in eV) computed by various DFT approximations.

	D-SIC ^a	HL ^b	P ^b	KS ^b	VW ^b	SPP ^b
<i>s</i> and <i>p</i> states	0.07	0.32	0.23	0.21	0.25	0.43
<i>d</i> states	0.35	0.85	1.23	1.05	1.29	1.55

- a) Local-density-approximation with degeneracy-dependent self-interaction correction [1].
 b) Hartree-Fock calculations including correlation in different ways [6] :

HL nonlocal method by Hu and Langreth [7],

P nonlocal method by Perdew [8],

KS local-density-approximation without self-interaction correction,

VW local-density-approximation with the self-interaction correction by Vosko and Wilk [9],

SPP local-density-approximation with the self-interaction correction by Stoll, Pavlidou and Preuss [10].

(HL) [7] and by Perdew (P) [8]. The results of the comparison are summarized in table I, which reports the average errors of the various methods in the calculation of EA for all the stable negative ions from Li to Cu, with the only exception of Ca⁻ and Sc⁻ to be discussed in this paper. The values for the individual atoms can be found in references [1, 6]. The three columns denoted by KS, VW and SPP complete the comparison with the results by Lagowski and Vosko and refer to HF calculations with the LDA correlation not corrected for self-interaction (KS) or corrected by the method of Vosko and Wilk (VW) [9] or of Stoll, Pavlidou and Preuss (SPP) [10]. In table I we have separated from the others the five ions for which the EA concerns a 3d electron : for these ions the errors are greater and D-SIC is the only method to give positive EA (all the others methods give negative EA with the only exception of V⁻ in the HL approximation).

In reference [1] we have noted that D-SIC calculations for Ca⁻ and Sc⁻ do not give bound states for these ions, while experimentally it is known that they are stable [11] with the ground state configurations [Ar]4s²4p¹ and [Ar]3d¹4s²4p¹ and EA of 0.043 eV and 0.189 eV, respectively. The stability has also been confirmed by multiconfiguration HF calculations [12, 13] which give an EA of 0.062 eV for Ca and of 0.152 for Sc. A first DFT calculation has been performed by Froese-Fischer *et al.* [12] with the KS method (EA of 0.171 eV for Ca and of 0.452 eV for Sc) and the analysis has been later completed by Vosko *et al.* [14] who have calculated the EA of Ca and of the other alkaline-earth atoms by the HL, P, VW and SPP methods. All these methods (except SPP) give a stable negative ion for Ca. One has thus the problem to understand why the D-SIC method does not give stability for Ca⁻ and Sc⁻.

A first remark could be that the two EA are fairly small and practically within the error limits of the method : in fact the maximum error of D-SIC for *s* and *p* electrons is 0.18 eV. However, in reference [1] we hinted that the lack of bound states for these two ions could be related to their « peculiar » electronic structure with a 4p delocalized electron. To understand better the nature of the binding of the 4p electron to the ion, we have performed a calculation of the electronic structure of the Ca⁻ ion in the [Ar]4s²4p¹ configuration using the *entire* LDA correlation — as in the first DFT calculation of Froese-Fischer *et al.* [12] — together

with the D-SIC exchange. We have found that in such an approximation the ion is bound with an EA of 0.113 eV ⁽²⁾. Furthermore, the mean radius for the 4p electron is 12.4 Å — to be compared with a mean radius of 2.1 Å for the 4s electron. This last result further clarifies the « peculiar » nature of the electronic structure of the ion. While the mean radius is certainly quite sensitive to the approximation used — and the use of the HF exchange in place of the D-SIC exchange could considerably modify this value — it is clear that the 4p electron is strongly delocalized. This makes it very difficult to decide whether the correlation should be corrected for self-interaction or not. In fact the inclusion of the self-correlation gives a fictitious attractive potential which has an essential role in binding an electron as delocalized as the 4p electron of Ca⁻ — at least this is so in our calculation. The 4p electron of Ca⁻ is clearly bound by correlation effects which are intrinsically nonlocal — in the HF approximation Ca⁻ is not bound [12]. Obviously these nonlocal effects cannot be well described by essentially local methods as D-SIC, KS, VW and SPP. Indeed D-SIC and SPP, which cancel completely the self-interaction of the 4p electron, do not give bound states, while KS largely overestimates the EA. VW, which cancels a self-interaction *averaged* over all the electrons, leaves a weak attractive potential on the 4p electron and this may bind or not the electron, depending on the type of exchange used. The results of the HL and P methods are more difficult to analyze. In fact these methods correct in part the local approximation for the effects of the non-homogeneity of the system, as they are based on modifications of the gradient approximation. However, they include the self-correlation and thus their description of the binding of the 4p electron is not very different from the description given by KS. This is confirmed by the value 0.131 eV for the EA of Ca⁻ determined by Vosko *et al.* [14] with the P method : the value of EA in the HL method is not reported in reference [14], but one expects a value larger than that given by the P method on the basis of the results for all the other light atoms [6].

We feel, in conclusion, that the study of Ca⁻ and Sc⁻ reveals the inadequacy of the approximations to the DFT currently in use to describe the intershell exchange and correlations ⁽³⁾. This point was already discussed in reference [5] where it was noted that the errors found in the spin-flip energies and in the ionization potentials of the transition-metal atoms can be attributed in part to these interactions. Fortunately these effects are not important in the majority of cases, and this explains the good results obtained by these approximations for many properties.

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⁽²⁾ This value does not include the relativistic effects : these should reduce the EA by about 0.008-0.010 eV according to the estimates made in references [12-14].

⁽³⁾ See also the pertinent discussion by Gunnarsson *et al.* in reference [15].

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