Electron affinities of alkaline-earth atoms by means of different density functionals

Patricio Fuentealba

Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

Andreas Savin, Hermann Stoll, and Heinzwerner Preuss

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
7000 Stuttgart 80, Federal Republic of Germany

Various correlation energy density functionals have been used to evaluate the electron affinities of the alkaline-earth atoms. A related approach based on polarization potentials was also tested. The results give evidence for the existence of stable negative ions of the atoms Ca, Sr, and Ba. The various density functionals perform relatively well yielding qualitatively correct predictions.

Very recently two papers on the existence of a stable Ca$^-$ ion have been published.[1,2] One of them[1] gave experimental results for the electronic structure of the negatively charged ion, and the other one reported theoretical calculations of the electron affinity (EA) of the Ca atom. The concordance between the experimental EA and the theoretical one is very good. Furthermore, both works superseded early attempts to find a stable negative ion. Experimental investigation of the structure of Ca$^-$ was performed by Heinicke et al.[3] several years ago. They estimated a lifetime of about 10 ms for the ion, but were unable to identify whether it was a metastable or stable state. Now, Pegg et al.,[1] through photodetachment spectroscopy measurements, have shown that the Ca$^-$ ion is stably bound, being formed in the $4s^2 4p(^2P)$ state. From the theoretical side, *ab initio* configuration-interaction (CI) calculations by Jeung et al.[4] failed to predict a stable negative ion, whereas Bunge et al.[5] in a through search of negative ions did not look for ground-state Ca$^-$. Motivated by all those works, Hotop and Lineberger in their update review[6] suggested that the negative ions of the alkaline-earth atoms in the ground state are unstable. Only the new very sophisticated calculations by Froese Fischer et al.[2] yielded a positive value for the EA of the Ca atom.

After those investigations on the Ca atom, it is natural to reexamine the situation for the EA of the other elements of the IIA group. The $ns^2 np \to nsnp'(n-1)d$ type of excitations are increasingly important for Ca$^-$, Sr$^-$, and Ba$^-$. They contribute directly to the EA of the heavy ions.[7] Based on this qualitative argument one could expect an increasing EA going down the series. In this Brief Report we shall investigate the negatively charged ions of all the alkaline-earth atoms by means of various correlation energy density functionals and a related approach based on a polarization potential.

The theoretical determination of electron affinities is a rather difficult task. Hartree-Fock or limited CI calculations are not able to provide reliable results, except for some very special cases. Hartree-Fock, i.e., single-configuration self-consistent-field (SCF) calculations,

often fail to give an even qualitatively correct answer. In fact, the Hartree-Fock method predicts all the alkaline-earth negative ions to be unstable. Reliable results have been achieved so far only with the use of powerful computational methods like multiconfiguration self-consistent-field (MCSCF) and large-scale CI. It is therefore a challenge for relatively simple methods, like the density-functional (DF) method, to yield at least the qualitatively correct answer for the EA of the alkaline-earth atoms.

One of the difficulties for investigating some property for all the atoms of a group is the increasing number of electrons when going down the periodic table of elements. Thus it is rather difficult to achieve a similar accuracy for all atoms. In this work this problem has been solved using a pseudopotential which simulates the effect of the core electrons on the valence space. A pseudopotential of the following form has been used:

$$V(r) = -\frac{Q}{r} + \sum B_1 \exp(-\beta_1 r^2) P_1 , \qquad (1)$$

where Q is the closed-shell ion charge (for the alkaline-earth atoms $Q=2$). P_1 is a projection operator onto the subspace of angular symmetry 1. B_1 and β_1 are adjusted parameters. The whole pseudopotential is adjusted in such a way that it reproduces relativistic frozen-core all-electron results. That means it includes the most important relativistic effects. Details of the fitting procedure and numerical values of the parameters can be found in Refs. 8 and 9. Since these pseudopotentials have proven to yield very reliable results for atomic properties (i.e., ionization potentials, electric dipole polarizabilities),[8] and also for bonding properties of neutral and ionic hydrides,[10,11] it seems quite natural to have a great confidence in the reliability of this approach also for determining the electron affinity of the alkaline-earth atoms.

For the valence correlation energy, on which the electron affinity sensitively depends, various density functionals have been used. Let us start with the correlation energy functional in the usual local approximation

$$E_c[n_a,n_b] = \int d\mathbf{r}\, n(r)\epsilon(n_a(r),n_b(r)) . \qquad (2)$$

Here the function ϵ, which depends on the spin densities n_a and n_b ($n = n_a + n_b$), is taken from homogeneous electron-gas calculations. The function has been accurately parametrized by Vosko, Wilk, and Nusair.[12] The results obtained with their parametrization will be denoted by VWN.

One way to improve the local approximation is through a gradient expansion:

$$E_c[n_a,n_b] = \int d\mathbf{r}\, n\epsilon + \int d\mathbf{r}\, B(n_a,n_b)|\nabla n|^2 + \cdots , \qquad (3)$$

where the function $B(n_a,n_b)$ must be determined. In this work, two different gradient-corrected expansions have been used. The functional determined by Perdew[13] will be denoted as GCP, and the one proposed by Langreth and Mehl[14] will be denoted as GCL (following the notation in Ref. 15).

Another way to correct the local approximation is taking into account the self-interaction energy. The correction published by Stoll, Pavlidou, and Preuss[16] (SPP) has been used. They proposed the following correlation energy density functional:

$$E_c[n_a,n_b] \int d\mathbf{r}[n\epsilon(n_a,n_b) - n_a\epsilon(n_a,0) - n_b\epsilon(0,n_b)] . \qquad (4)$$

In this approach, the one-electron systems have vanishing correlation energy, which is not the case in the VWN, GCP, or GCL approximations.

A more heuristic approximation was also used. Very recently, Fuentealba, Stoll, and Savin[17] (FSS) proposed to replace, in Eq. (2), the functional ϵ by a correlation potential which might be considered as a functional of the density. In a very simple approach, the potential was chosen to be a polarization potential. In this case, one can directly calculate correlation energy differences. Two different forms for it have been proposed in Ref. 17. Since the results are in both cases very similar, we will only show here the results obtained using the following formula [Eqs. (4) and (6) of Ref. 17]:

$$\Delta E_c = \int d\mathbf{r}\, n_0(r)\frac{\alpha}{2r^4}[1 - \exp(-r^2/r_0^2)]^4 , \qquad (5)$$

where α is the electric dipole polarizability of the $(N-1)$-electron system and r_0 is a cutoff parameter chosen to be the square root of the expectation value $\langle r^2 \rangle$ of the outermost orbital of the $(N-1)$-electron system; $n_0(r)$ is the density of the outermost orbital of the N-electron system. To evaluate the correlation energy contribution to the electron affinity of the alkaline-earth atoms using Eq. (5) it is necessary to know α and $\langle r^2 \rangle$ for all the corresponding neutral atoms. They are shown in Table I.

To implement the different methods the exact ground-state electron density should be known. It is customary to approximate it by the Hartree-Fock density. However, in the cases under consideration, the extra electron goes into an np orbital which in the Hartree-Fock approximation is not bound, producing a meaningless densi-

TABLE I. Parameters to be used in the polarization potential [Eq. (5)]: the cutoff parameter $r_0 = \langle r^2 \rangle^{1/2}$, and the electric dipole polarizability α, in a.u.

	r_0 [a]	α [b]
Be	2.90	36.3
Mg	3.52	70.7
Ca	4.51	157
Sr	4.88	200
Ba	5.15	280

[a] For Be to Sr the $\langle r^2 \rangle$ values have been taken from Ref. 21. For Ba the result of Ref. 22 was used.
[b] Values from Ref. 8.

ty (if the basis set is flexible enough the np orbital should go to the continuum). One way to overcome this problem is to employ a better approximation than the Hartree-Fock approximation. In this work small MCSCF calculations were done to obtain the densities (details of those and other CI calculations will be published elsewhere.[7]) Once the densities are obtained the integrals of Eqs. (2)–(5) are solved numerically. Separate calculations for the atoms and the ions have been done to evaluate the EA using the VWN, SPP, GCL, and GCP functionals. For the FSS approximation it is necessary to perform only one atomic calculation using the atomic density because it yields the EA directly as an energy difference.

The results are presented in Table II. A negative value of the EA means only that the charged atom is not stable. They are displayed only to show whether the different functionals yield the qualitatively correct trend. Some of them (VWN, GCP, and FSS) perform relatively well, predicting the Ca⁻ ion as the lightest stable anion of the series. The self-interaction correction of Stoll et al.[16] yields a negative value of the EA for the Ca atom, whereas the gradient correction of Langreth and Mehl[14] predicts a stable Mg⁻ ion. The failure of the SPP functional is likely due to the neglect of the parallel spin correlation which is usually small[18] but of vital importance for the stabilization of the extra electron in the alkaline-earth anions. The GCL functional yields, in general, slightly too high values of the EA. This is in line with the results obtained by Savin et al.[19,20] using the GCL functional.

Experimentally, only the negatively charged Ca atom has been observed. Pegg et al.[1] measured an electron affinity of 0.0434 ± 0.007 eV. Since the value is so small, accurate calculations are a very difficult task and out of the scope of the DF method at the present stage. Nevertheless, some functionals yield good results. It is rather

TABLE II. Electron affinity for alkaline-earth atoms (in eV).

	VWN	SPP	GCL	GCP	FSS
Be	−0.07	−0.37	−0.04	−0.19	−0.11
Mg	−0.05	−0.28	0.09	−0.10	−0.15
Ca	0.12	−0.11	0.33	0.09	0.08
Sr	0.54	0.28	0.64	0.56	0.47
Ba	0.54	0.15	0.69	0.43	0.59

amazing that the naive approach of setting up a polarization potential (FSS) gives good results, repeating the success obtained for the two-, three-, and four-electron atom series.[17]

Froese Fischer et al.[2] have done DF calculations using the VWN parametrization for the Ca^- ion. They obtained an EA of 0.17 eV, which is greater than our value. However, their calculations are not directly comparable with ours: They introduced a correlation potential (the functional derivative of $E_c[n_a, n_b]$) into the Hartree-Fock equations; furthermore, they evaluated the all-electron correlation energy, whereas in this work only the valence correlation energy has been used. Thus slightly different results are expected.

Another important point to discuss is the variation of the EA in going from Sr to Ba. The SPP and GCP functionals show a decrease of the EA. The VWN approximation gives exactly the same value and the GCL functional shows a very slight increase. A marked increase is obtained by the unconventional FSS approximation only. It is worthwhile to mention that exhaustive MCSCF and CI calculations do not support a smaller EA for Ba than Sr.[7] So, this seems to be an artifact of the density functionals which can be related to the underestimation of the interpair correlation energy found by Savin et al.[20] using a correlation energy functional; this underestimation is most severe for the diffuse Ba orbitals.

There are some effects which have not been taken into account in this Brief Report (especially the core-valence correlation energy). We will deal with them in a forthcoming publication where more sophisticated methods have been used.[7] However, the qualitative trends discussed here will not be altered.

In conclusion, further evidence of the stable Ca^- ion has been obtained and the existence of stable anions of Sr and Ba has been predicted. Different correlation energy density functionals have been tested in calculating the EA of the alkaline-earth atoms. In spite of the fact that the electron affinities are small and sensitive values, the various functionals performed satisfactorily. However, the errors can still be too large for accurate predictions. In comparison to the other functionals, the very simple approach denoted FSS yields results of the same quality.

Note added. Since this work was finished, a similar work by Vosko et al.[23] was published. They also came to the conclusion that Sr^- and Ba^- would be stable.

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