

Electron affinities of alkaline-earth-metal atoms

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The negative ions of the alkaline-earth-metal atoms (Be to Ba) have been studied by means of a pseudopotential model together with configuration-interaction and multiconfiguration self-consistent-field techniques. Only the heavier ions Sr^- and Ba^- have been predicted to be stable. For Ca atoms the situation is very complicated, and our calculations do not permit us to decide whether the negative ion is stable with respect to the neutral atom or not. The calculated electron affinities are very small and depend strongly on the correlation energy. It has been found that the core-valence correlation contribution to the electron affinities is important and reduces their values significantly.

INTRODUCTION

The theoretical study of negatively charged ions has been a difficult task for current methods. The correlation energy plays a very important role in the stabilization of the extra electron. Thus, one of the standard computational methods, the Hartree-Fock (HF) method, is not able to provide reliable results, except for some very special cases. It is also disappointing that, unlike positive ions and neutral species, solutions to the HF equations for negative ions may not exist. Some of the problems are connected with the diffuse character of the electronic cloud which makes necessary the use of large basis sets in large-scale configuration-interaction (CI) calculations to get reliable results. In the study of negative ions one of the primordial quantity to be evaluated is the electron affinity (EA) defined as the difference between the total energies of the ground states of the neutral atom and its negative ion. Its small value adds difficulty to the calculations. All those problems were first numerically investigated by Sasaki and Yoshimine¹ using very large basis sets and lengthy configuration expansions. Their calculations accounted for 95% of the correlation energy of the atoms of the first period, however, for EA's they give only 85% of the correlation contributions resulting in errors of 0.1–0.3 eV.

On the experimental side, the advent of tunable dye lasers had made possible the development of a negative ion spectroscopy. The laser photo detachment method permits to measure the detachment products of a sample of negative ions by energy analyzing the detached electrons. As a result, the knowledge of atomic EA's has improved considerably. The accuracy of the data is for some atoms very satisfactory, some EA's are now known to within 0.01 cm^{-1} . There are, however, other factors which sometimes limit the experimental resolution.²

It has been usually assumed that alkaline-earth-metal atoms are not able to bind an extra electron. It is known that Be^- (like He^-) exist only as a metastable state,³ and

any attempt to find a stable ground-state negative ion has failed. Theoretical calculations on Mg^- have also given evidence of the existence of a metastable state. Until very recently, the situation was very similar for the heavier alkaline-earth-metal atoms (Ca, Sr, and Ba) in that only metastable states were supposed to exist. However, the new works by Pegg *et al.*⁴ and Froese Fischer, Lagowski, and Vosko⁵ report some evidence, both experimental and theoretical, for the existence of a stable Ca^- ion formed in the bound $4s^2 4p^2 P$ state. Since those results were published new theoretical investigations have confirmed the stability of Ca^- and also of Sr^- , Ba^- , and Ra^- .^{6–9} However, not one of those works have properly taken into account the core valence correlation effects which, as we will show later on, are very important in calculating the EA's of the alkaline-earth-metal atoms.

In this work, the negatively charged alkaline-earth-metal atoms will be studied by means of configuration-interaction (CI) and multiconfiguration self-consistent-field (MCSCF) techniques. The problems originating from the increasing number of core electrons when going down the column of the periodic table is overcome using pseudopotentials. This allows us to study core-valence interaction and relativistic effects in a rather simple way. Furthermore, since in all calculations no more than two or three valence electrons are explicitly treated it is possible to employ relatively large basis sets and to perform full CI calculations in the valence space. In addition MCSCF calculations with different active spaces are performed and compared to the full CI results.

METHODS

The valence model Hamiltonian used in this work is

$$H = -\frac{1}{2} \sum_i \nabla^2 + \sum_i V(r_i) + \sum_{i,j} r_{ij}^{-1}, \quad (1)$$

where $V(r_i)$ is the semilocal pseudopotential of the form

$$V(r_i) = -\frac{Q}{r_i} + \sum_l B_l e^{-\beta_l r^2} \hat{P}_l, \quad (2)$$

$$\hat{P}_l = \sum_{l, m_l} |l m_l\rangle \langle l m_l|. \quad (3)$$

Q denotes the charge of the core, i and j are electron indices, and \hat{P}_l is the projection operator onto the Hilbert subspace with angular symmetry l .

The pseudopotential $V(r)$ takes into account the effects of the core electrons on the valence electrons in the frozen-core approximation. Since the alkaline-earth-metal atoms have easily polarizable cores, one may ask for the effect of the polarization of the cores due to the valence electrons. We account for this effect in some of our calculations by adding to $V(r)$ a polarization potential of the form¹⁰

$$V_{\text{pol}} = -\frac{1}{2} \alpha f^2, \quad (4)$$

$$f = \sum_i r_i^{-3} \mathbf{r}_i (1 - e^{-\delta r_i^2}), \quad (5)$$

where α is the dipole polarizability of the core and f is the electric field generated at the site of the core by the valence electrons. δ is a cutoff parameter to avoid divergences. The pseudopotential including the polarization potential is adjusted to reproduce the first experimental energy levels of the ions with one valence electron, whereas the pseudopotential without the polarization potential reproduces the eigenvalue of the Dirac-Fock (or Hartree-Fock) equation for the valence electron of the different ions. On this basis, it is possible to study, in an empirical way, the core polarization (for atoms, core-valence correlation) and the relativistic effects starting from the frozen-core Hartree-Fock model. Details of the fitting procedure and numerical values of the parameters can be found in Refs. 11 and 12. Since these pseudopotentials have been proven to yield very reliable results for a number of atomic properties, (i.e., ionization potentials and electric dipole polarizabilities),¹¹ and also for bonding properties of neutral and ionic hydrides,^{13,14} it seems quite natural to have some confidence in the reliability of this approach also for determining the EA of the alkaline-earth-metal atoms.

To take care of the valence correlation energy on which the EA's strongly depend different CI (Ref. 15) and MCSCF (Ref. 16) calculations were done. Full CI calculations in the restricted valence space were done for the atoms and the ions. For the latter, this means that all the triple excitations are included. To get further insight into the mechanism of stabilizing the extra electron, various MCSCF calculations with different active spaces were done. All configurations which are possible within that space were included [complete active space SCF (CASSCF) (Ref. 17)].

The calculations were done employing Gaussian basis sets. They were constructed starting from a $9s8p$ basis set optimized for the Be atom by Werner and Meyer.¹⁸ A set of four d functions taken from Ref. 10 augmented by a tight function of exponent 0.648 was added to the basis set. For the other atoms, the exponents were scaled ac-

ording to the inverse of the $\langle r^2 \rangle$ expectation values of the s valence electrons; the scaling factors are 2.410, 1.693, 0.853, and 0.693 for Be, Mg, Sr, and Ba, respectively. The reference basis set^{18,10} was optimized to calculate the atomic dipole polarizability. Thus, the resulting $9s8p5d$ basis sets should be sufficient to describe the electronic cloud of the neutral atoms as well as the extra electron in the anions. To check, in part, this statement, the ionization potentials were calculated. As an example, for Ca atom a value of 6.120 eV was obtained in good agreement with the experimental value of 6.115 eV. Nevertheless, the possible importance of f orbitals was investigated in some calculations, especially for the heavy atoms. For the Ca atom one f function of exponent 1.4 taken from Ref. 19 was used. For Ba, two f functions of exponents 0.103 and 0.092 were used.

All the calculations on the neutral atoms and the anions were done completely separate. Thus a full relaxation of the wave function was allowed. Since there are good evidence that the more stable state for the negative ion is a $ns^2np(^2P)$ one, almost all the calculations were done for this state.

RESULTS AND DISCUSSION

For the Ca atom, the EA has been investigated using various configuration lengths. The results obtained by different choices of the active space in MCSCF calculations are presented in Table I. An active space formed by only one orbital of each symmetry s , p , and d is clearly insufficient for stabilizing the negative ion. Since the p orbital in the ion is already occupied with one electron it is necessary to include at least two p orbitals in the active space. The active space ($1s2p1d$) formed still yields a negative EA which is, however, 0.1 eV better than the former one and very similar to the SDCI value (-0.059 eV). A positive EA is first found after the inclusion of a second s orbital to the active space ($2s2p1d$) allowing for a better description of the radial correlation. A further significant improvement is obtained using a $2s2p2d$ active space. The latter choice implies a configuration lengths of 242 configurations for the negative ions, and it was considered good enough to be used for investigating the other atoms. A more extensive calculation employing $3s3p3d$ orbitals to build the active space yields an EA in good agreement with the experimental value⁴ (0.043 ± 0.007 eV). However, as will be shown later on, the excellent concordance breaks down by considering the core-valence correlation contributions to the EA's. Note that the MCSCF calculation with an $3s3p3d$ active space predicts the same EA as the full valence space CI

TABLE I. MCSCF values for the EA of the Ca atom.

Active space	EA (eV)
$1s1p1d$	-0.140
$1s2p1d$	-0.046
$2s2p1d$	0.014
$2s2p2d$	0.035
$3s3p3d$	0.048

TABLE II. Most important expansion coefficients of the MCSCF wave functions of Ca and Ca⁻.

Ca		Ca ⁻	
Configuration	c_i	Configuration	c_i
4s ²	0.957	4s ² 4p	0.851
4p ²	0.109	4s ² 5p	0.380
4p5p	0.078	4p5p ²	0.130
5p ²	0.056	4s4p3d	0.076

calculation (see Table IV) performed with the same basis set. In Table II some of the more important expansion coefficients of the MCSCF wave functions using an 2s2p3d active space are shown. One can see from them, that the inclusion of a second *p* orbital in the active space is much more effective for the negative ion than for the neutral atom in line with its important role in the EA calculations.

Before passing to the other atoms the possible importance of a *f* function in the basis set was investigated. Adding one *f* function to both, the basis set and the active space did not give any improvement to the calculated EA. The *f* function on the Ca atom seems to be only necessary to correlate the core electrons¹⁹ which, in this work, are incorporated into the pseudopotential. Other test calculations on the Ca⁻ ion were performed to search for a stable ²D state. A MCSCF calculation using a 2s2p2d active space did not give any evidence for the existence of a stable ²D state confirming the density-functional results of Froese Fischer, Lagowski, and Vosko.⁵ Concluding, for the Ca⁻ ion, including only valence correlation, our best calculation gives an EA of 0.048 eV, which must be compared to the best calculation of Froese Fischer⁸ (EA of 0.062 eV, see Table VI). Our value is too low in 0.014 eV, possibly because of the basis-set expansion or the lack of core relaxation.

The 2s2p2d active space was used to perform MCSCF calculations on all of the alkaline-earth-metal atoms (ground state) and their negative ions (²P states). The calculated valence energies and EA's are shown in Table III. Be⁻ and Mg⁻ were found to be unstable with respect to the neutral atoms. From Ca down the column of the Periodic Table the EA's are positive and of increas-

TABLE III. MCSCF valence energies and EA's for alkaline-earth-metal atoms.

	Valence energies (a.u.)	EA (eV)
Be	-1.010 484	
Be ⁻	-0.997 068	-0.365
Mg	-0.820 090	
Mg ⁻	-0.811 628	-0.230
Ca	-0.637 064	
Ca ⁻	-0.638 365	0.035
Sr	-0.586 751	
Sr ⁻	-0.590 062	0.090
Ba	-0.527 718	
Ba ⁻	-0.535 106	0.201

ing magnitude. This trend can be explained with the decrease of the ¹S→^{1,3}D excitation energy of the neutral atoms going down the column.²⁰ Thus, for the heavier atoms, it is easier to stabilize the extra electron through excitations of the type *ns*²*np*→*nsnp'*(*n*-1)*d*. Note that in the neutral atoms the corresponding excitations are not allowed. Therefore they contribute directly to the EA's. Moreover, the experimental data for ¹S→^{1,3}D excitation energies show a slightly decrease going from Ca to Sr but a much lower value for Ba (experimental values for ¹S→¹D excitation energies are 20 335.4 cm⁻¹, 18 159.1 cm⁻¹ and 9034.0 cm⁻¹ for Ca, Sr, and Ba respectively),²⁰ which could explain the marked increase in the calculated EA for the Ba atom.

Since the evaluated EA's are very small and sensitive numbers it seemed to be necessary to study them in more detail. More expensive calculations and the incorporation of the core-valence correlation effects were, however, restricted to the heavy atoms Ca, Sr, and Ba, for which positive EA's were already found. For Ba, two *f* functions were added to the basis set. With the obtained 9s8p5d2*f* basis set a MCSCF calculation with an 2s2p2d1*f* active space was performed. It yields an EA of 0.211 eV, only 0.01 eV better than the results without *f* functions. Having proved, for Ca and Ba, the insensitivity of our calculations to the inclusion of *f* functions we have ruled them out for all other calculations.

Using pseudopotentials only two or three electrons are explicitly considered. That enables us to do full CI calculations in the space spanned by the basis set. The results are displayed in Table IV. The obtained EA's are almost the same as the MCSCF ones. That shows the reliability of the active space chosen for the MCSCF calculations. Moreover, the valence energies change by less than 1 mhartree, showing that the agreement is not a compensation effect. In calculating the valence correlation energy with pseudoorbitals a small error is made because of the nodeless nature of them.^{10,11} For the alkaline-earth-metal atoms the errors are of about 1 mhartree.¹⁰ However, in doing energy differences, one would expect a much smaller error. After having investigated the correctness of the calculated valence correlation energies the core-valence correlation contributions to the EA's were studied. That was done by adding to the pseudopotential the polarization potential of Eq. (4) and performing a full CI calculation again. The polarization energies and their contributions to the EA's of Ca, Sr, and Ba are shown in Table V. The effect is destabilizing and by no means negligible. It reduces the calculated EA's by a great amount. This

TABLE IV. CI valence energies and EA's for Ca, Sr, and Ba.

	Valence energies (a.u.)	EA (eV)
Ca	-0.637 301	
Ca ⁻	-0.639 080	0.048
Sr	-0.587 003	
Sr ⁻	-0.590 666	0.100
Ba	-0.528 245	
Ba ⁻	-0.535 601	0.200

TABLE V. Polarization energies and their contributions to the EA's of Ca, Sr, and Ba.

	Polarization energies (a.u.)	Δ EA (eV)	EA (eV)
Ca	-0.023 867		
Ca ⁻	-0.022 106	-0.048	0.00
Sr	-0.027 797		
Sr ⁻	-0.025 362	-0.066	0.044
Ba	-0.031 164		
Ba ⁻	-0.027 853	-0.090	0.110

strong destabilizing effect is surprising at first sight. One could try to rationalize it in the following way. The contraction of the valence density due to core polarization is stronger for the *s* electrons than for the extra electron in a *p* orbital because the latter is much more diffuse. As a result, the screening of the nuclear charge due to the *s* electrons augment reducing the binding energy of the *p* electron and thus also the EA's. Nevertheless, more detailed studies are necessary to elucidate this point. Note that for the EA of Ca atom the *ab initio* all-electron CI calculations of Froese Fischer, Lagowski, and Vosko⁵ and Froese Fischer⁸ which showed good agreement with the experimental result did not take into account for the core valence correlation. The eigenchannel *R*-matrix calculations performed by Kim and Greene⁹ using a model Hamiltonian include only part of the polarization potential. They have disregarded the two-electron term of the potential which tends to keep electrons apart, increasing the mean radius and raising the energy.¹⁰ This could explain in part the somewhat large EA values informed by Kim and Greene.⁹

Another effect worth of investigating is the spin-orbit coupling. For Ba, Silberbach²² has calculated its contribution to the EA using a quasirelativistic pseudopotential model.²³ It yields a small positive contribution of around 0.054 eV. To get an estimate of the spin-orbit contribution to the EA of the Ca atom one can assume that the atomic spin-orbit splitting quotient between the Ca and Ba atom will be preserved for the corresponding EA's. This way, a small stabilizing contribution of around 0.01 eV was estimated for the Ca atom. All other important relativistic effects are, in an empirical way, included in our method because the pseudopotential has been adjusted to reproduce either Dirac-Fock or experimental energy values. The relativistic contributions to the EA's were

also estimated by Froese Fischer⁸ and Vosko, Lagowski, and Mayer,⁷ who calculated that relativistic effects lower the EA's. However, for Ba⁻ Froese Fischer gave a too large contribution which seems to be a typographic error. Vosko, Lagowski, and Meyer⁷ calculated relativistic contributions to the EA's of 0.011, 0.033, and 0.065 eV, for Ca, Sr, and Ba, respectively, whereas Froese Fischer reported 0.008, 0.012, and 0.129 eV for Ca, Sr, and Ba, respectively. Clearly, the correction for the Ba atom is out of range. The atomic spin-orbit splitting quotient between Ca and Ba is around 5.4 which corresponds roughly to the ratio calculated from the values of Vosko, Lagowski, and Meyer.⁷ Using a ratio of 5.4, and the Froese Fischer EA value for Ca, the corrected EA and Ba should be around 0.234 eV, in much better agreement with our CI value.

In Table VI, the EA of the alkaline-earth-metal atoms calculated with different theoretical methods are displayed. Some of them, especially the MCHF results of Froese Fischer,⁸ have been already discussed. The density-functional values have been discussed in a previous work⁶ and should be seen as more approximate values, but much easier to obtain, than the CI ones. A rather different method of calculation, the eigenchannel *R*-matrix approximation, was used by Kim and Greene.⁹ The comparison is not obvious, especially for the heavy atoms, because of the incomplete polarization potential they have used. Nevertheless, for Be and Mg our MCSCF values agree very well with their calculated resonant states.

For the Ra atom, Vosko, Lagowski, and Meyer⁷ and Kim and Greene⁹ have predicted a smaller EA than for Ba atom. This can also be explained with the trend of the ¹S → ¹D excitation energies of the neutral atoms. For the Ra atom the ¹S → ¹D excitation energy is greater than for Ba.

Neither of those works have correctly taken into account for the core valence correlation which, as we have shown, is very important in reducing the calculated EA's.

CONCLUSIONS

Starting with a pseudopotential to implicitly account for the core electrons exhaustive CI calculations in the valence space were done. For the valence correlation contributions to the EA's, the possible errors due to incompleteness of the basis sets and the use of nodeless pseudoorbitals should be small. Thus, at this level of approximation the results are very reliable. However, the

TABLE VI. EA's of alkaline-earth-metal atoms (in eV).

Method	Ref.	Be	Mg	Ca	Sr	Ba
DF	Vosko <i>et al.</i> (Ref. 7)			0.13	0.16	0.20
DF	Fuentealba <i>et al.</i> (Ref. 6)	-0.19	-0.10	0.09	0.56	0.43
MCHF	Froese Fischer (Ref. 8)			0.062	0.106	0.148
<i>R</i> matrix	Kim and Greene (Ref. 9)	-0.25	-0.16	0.070	0.108	0.176
MCSCF	this work	-0.37	-0.23	0.035	0.090	0.201
CI	this work			0.048	0.100	0.200
CI + V _{pol}	this work			0.00	0.044	0.110

EA's are very small and sensitive numbers making core-valence correlation effects very important. Their inclusion through a polarization potential reduce the calculated EA's by a great amount. It turns out to be impossible to decide whether the Ca^- ion is stable or not. Therefore, most sophisticated calculations, perhaps all-electron methods, are necessary to elucidate this point.

The global trend found in a previous work employing density functionals was confirmed. The lighter anions Be^- and Mg^- are predicted to be unstable with respect to the neutral atoms and the heavier ones Sr^- and Ba^- are certainly bounded.

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