VOLUME 71, NUMBER 10 PHYSICAL REVIEW LETTERS 6 SEPTEMBER 1993

Influence of Core Polarization on the Electron Affinity of Ca

Hugo W. van der Hart,[1] C. Laughlin,[2] and Jørgen E. Hansen[1]
[1]*van der Waals–Zeeman Laboratory, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands*
[2]*Department of Mathematics, University of Nottingham, Nottingham NG7 2RD, England*

(Received 27 April 1993)

We have developed a method, based on the use of B-spline basis sets and model potentials, for determining properties of systems with two or three electrons outside a polarizable closed-shell core. It is applied to the calculation of the electron affinity of Ca and the resulting value of 17.7 meV is in excellent agreement with the most recent experiments. It is found that the dielectronic core-valence interaction reduces the electron affinity by 39.5 meV.

PACS numbers: 31.15.+q, 31.20.Di

Negative ions are of fundamental importance in atomic physics. One significant aspect is that the additional electron is often bound by means of electron correlation, and so the structure and dynamics of negative ions form a critical testing ground for atomic theory. Ca^- has turned out to be one of the more elusive and challenging negative ions. A clear account of the tortuous path of the research into the structure of this ion has recently been given by Peterson [1]. In short, a few years ago, the existence of a stable negative Ca^- $4s^24p$ ^2P ion was predicted [2] and observed [3]. Since then, a large number of calculations have been devoted to the determination of the electron affinity (EA) of Ca [4–11]. In most of these calculations values in the range 45–82 meV were obtained [4,5,7,8,10,11] in general agreement with the observations of Pegg *et al.*, who used electron spectroscopy and fast ion beam techniques to determine an electron affinity of 43 ± 7 meV [3]. However, in one calculation an EA of 0 meV was obtained [9], while another deviating calculation reported a value of 22 meV [6].

Very recently Walter and Peterson [12] have measured a substantially smaller electron affinity for Ca, 18.4 ± 2.5 meV, in a tunable-laser photodetachment experiment. This latter result was subsequently verified by electric-field dissociation experiments [13] which resulted in an EA of 17.5 $^{+4}_{-2}$ meV. In addition, Haugen *et al.* recently reported [14] a decay time of 490 μs for the Ca^- ground state which was interpreted as due to photodetachment induced by blackbody radiation. Based on the expected blackbody spectrum, a lifetime of this magnitude supports the smaller values of the EA. Since the new experimental values are in disagreement with the original measurement of Pegg *et al.* [3] and with almost all of the previous theoretical results, there is renewed impetus for determining the binding energy of the ground state of Ca^-. In this Letter we report a new calculation, which is in agreement with the new experimental values, and discuss the physical interpretation of the differences between previous calculated values and the current one.

Accurate calculations on negative ions must go beyond the Hartree-Fock (HF) approximation since no binding is found in this, the best, single-particle model. Thus correlation is essential for obtaining binding. Correlation can be divided into several types. For Ca^- there will be correlation between the three valence electrons. This correlation can be accurately included for example in multiconfiguration HF calculations (MCHF). Another type, the correlation between the valence electrons and the core, is for three valence electrons very difficult to take into account. In fact most previous calculations for the Ca^- ground state have treated the valence correlation in detail while core-valence correlations have been treated less rigorously. It is thus reasonable to assume that the deficiencies in these approaches are due to inadequate descriptions of core-valence interaction. We include core-valence interaction via a model potential, which allows for the polarization of the core by the outer electron(s).

Froese Fischer has pointed out that it is easier to get too small a value for the EA, rather than one which is too large, because neglect of valence correlation reduces the binding. Thus a reliable method must reproduce the very elaborate valence-correlation results obtained in particular by Froese Fischer and co-workers [2,4,11]. It must also predict with high precision the binding energy of the neutral Ca ground state.

A particular difficulty with calculations of negative ions is the diffuse character of the orbitals involved. This has the consequence that it is important to be able to span a large function space. We have employed a B-spline basis set in a model-potential approach. Our basis set consists of 22 B-splines of order 9 defined on an interval from 0 to 60 a.u. We have checked that a box size of 40 a.u. is too small with our approach while the results change insignificantly when the box size is increased to 80 a.u. The one-electron basis functions are determined by solving the Schrödinger equation for the Ca^+ ion with the Ca^{2+} core described by a local model potential:

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z_c}{r} + V(r)\right)\Psi_{n\ell}(r) = \epsilon_{n\ell}\Psi_{n\ell}, \tag{1}$$

with

$$V(r) = V_P(r) + V_{\mathrm{HF}} - \frac{N_c}{r} + U_\ell(r), \tag{2}$$

where

$$V_P(r) = -\frac{\alpha_d}{2r^4}W_6\left(\frac{r}{r_c}\right) - \frac{\alpha_q - 6\beta_1}{2r^6}W_8\left(\frac{r}{r_c}\right). \tag{3}$$

0031-9007/93/71(10)/1506(4)$06.00

This model potential, developed by Laughlin [15], consists of V_{HF}, the direct electrostatic repulsion of the outer electron by the core; V_P, the interaction between the valence electron and the dipole and quadrupole moments it induces in the Ca^{2+} core; and $U_\ell(r)$, an angular-momentum dependent fitting potential chosen to reproduce the bound Ca^+ spectrum (with an accuracy of a small fraction of 1 meV). The polarization terms are effectively cut off at $r = r_c$ by the $W_n(r)$ functions to account for the decrease in the polarization interactions when the outer electron penetrates into the core. Z_c is the net charge of the Ca^{2+} core and N_c is the number of core electrons. The accuracy of this potential for the one-electron problem was demonstrated by determining oscillator strengths for various transitions in Ca^+ [15]. The model potential includes in an approximate way [via $U_\ell(r)$] the effects of relativity on the Ca^+ valence-electron energies. For Ca and Ca^-, two-body relativistic effects are not so straightforward and they are not explicitly included in the present calculation. They have been found to be smaller than the one-body effects, which are calculated to be < 10 meV in magnitude [11], and most of the latter are included implicitly in our approach via the model potential.

When two active electrons are considered, a dielectronic polarization (DP) potential, V_{P12}, must be added to the electrostatic repulsion $\frac{1}{r_{12}}$ [16,17]:

$$V_{P12} = -\frac{\alpha_d}{r_1^2 r_2^2} W_3\left(\frac{r_1}{r_c}\right) W_3\left(\frac{r_2}{r_c}\right) P_1(\cos\theta_{12}) - \frac{\alpha_q}{r_1^3 r_2^3} W_4\left(\frac{r_1}{r_c}\right) W_4\left(\frac{r_2}{r_c}\right) P_2(\cos\theta_{12}). \tag{4}$$

To estimate the influence of core polarization on the EA, we have calculated the ground-state energies of both Ca and Ca^- in three different approximations: excluding V_P, V_{P12}, and U_ℓ terms (denoted A), excluding only V_{P12} terms (denoted B), and including all polarization terms (denoted C). The configuration interaction (CI) procedures developed for He-like systems [18] can readily be adapted to the Ca ground-state problem. In the current application, we include all physically allowed pairs of one-electron basis functions with angular momenta up to f^2.

As a check on our procedures we compare in Table I our values for the ground-state energy of Ca with the experimental and some other theoretical values. From MCHF calculations [4], we estimate that the core-polarization contribution to the energy is about 5700 cm^{-1} and, with this in mind, there is good agreement between the various approaches. We observe that our best calculation, which includes all polarization terms, differs from experiment by only 7 cm^{-1} and, as far as we know, this is the most accurate theoretical determination of the ground-state energy of Ca to date. The dipole term in Eq. (4) is dominant: including the dielectronic dipole term decreases the binding energy of Ca by 680 cm^{-1}, whereas the quadrupole term increases it by only 20 cm^{-1}. Higher-order core-valence interactions [17] would therefore appear to be negligible. Because the U_ℓ terms are omitted, calculation A gives a rather poor result for the Ca ground-state energy since it does not include any exchange interactions with the Ca^{2+} core and so it is not directly comparable to any of the other calculations in Table I.

TABLE I. Binding energies (in cm^{-1}) for the ground state of Ca relative to the Ca^{2+} ground state.

	Binding energy
B-spline method A	122 519
B-spline method B	145 710
B-spline method C	145 051
Fuentealba *et al.* [9] without pol. terms	139 870
Fuentealba *et al.* [9] with pol. terms	145 107
Kim and Greene [5]	146 100
MCHF [4] val. corr. with rel. terms	139 335
Observed [19]	145 057.83

For the three-electron Ca^- problem we adopt a similar CI approach and expand the wave function in terms of products of one-electron basis functions. However, it is not feasible to include all (> 10^5) possible configurations which may be constructed from the set of basis functions. We used 6343 configurations in the CI expansion, and afterwards included others as a second-order perturbation. The configurations included are shown in Table II. We have performed several calculations with different configurations in the CI expansion in order to check that the results are independent of the initial expansion. Intermediate results can differ by up to 10 meV, but on addition of the second-order correction this difference almost disappears. The remaining uncertainty is estimated to be about 2 meV. The results are shown in Table III.

We first discuss calculation A which, despite its neglect of exchange, should provide an EA comparable to those of previous calculations which include an equivalent static core potential V_{HF} [Eq. (2)], since we expect strong cancellation between the valence-core exchange interactions in Ca and Ca^-. Specifically, we compare with calcula-

TABLE II. Configurations included in the CI expansion for Ca^-. Except when otherwise indicated, all intermediate couplings are included. Configurations are reordered to $n\ell n'\ell' n''\ell''$ with the maximum allowed values for n, n', and n'' as specified. Configurations of the type ddp, sdp, and ffp which have a $6p$, $6d$, or $6f$ orbital and an orbital with a higher n value are excluded.

Angular momenta	ssp, sdp, ddp ppp, sdf, ppf $ff(^{1,3}S)p$, $dd(^{1,3}D)f$
Maximum allowed n	5 ($\ell \geq 2$) , 6 ($\ell \leq 1$)
Maximum allowed n'	8
Maximum allowed n''	14

TABLE III. Electron affinities in meV for Ca.

	Electron affinity
Experiment	
Pegg *et al.* [3]	43 ± 7
Walter and Peterson [12]	18.4 ± 2.5
Nadeau *et al.* [13]	$17.5\ ^{+4}_{-2}$
Theory	
MCHF incl. rel. [4]	62
MCHF incl. rel. [11]	63.1
MCHF incl. rel. with pol. [11]	41.9
R-matrix [5]	70
Second-order CI [6]	22
MBPT [7]	57
MBPT [8]	58
CI without pol. [9]	48
CI with pol. [9]	0
Pseudorelativistic HF [10]	82
This work	
B-spline A	67.0
B-spline B	57.2
B-spline C	17.7

TABLE IV. Wave-function compositions for the ground state of Ca$^-$. For the B-spline CI calculations all configurations with a contribution > 1% are included. For the MCHF calculation the six largest expansion coefficients are given.

Term	MCHF [4]	B-spline A	B-spline C
$4s^2 4p$	61.7%	38.2%	34.2%
$4s^2 5p$	23.7%	28.3%	29.1%
$4s^2 6p$		6.9%	10.2%
$4s^2 7p$		1.7%	4.1%
$4s5s(^1S)4p$		9.7%	7.7%
$4s5s(^1S)5p$	2.3%	1.8%	2.0%
$4s3d(^3D)4p$	5.1%	2.9%	1.4%
$4s4d(^3D)4p$		1.2%	1.9%
$4p^3$	3.5%	2.6%	2.0%
$4p^2(^1S)5p$	1.9%	2.0%	1.9%

tions using a HF [2,4,11] and a Dirac-Fock [9] potential for the core. Our result, 67 meV, is in good agreement with the latest relativistic MCHF values, 62 and 63 meV, of Froese Fischer and co-workers [4,11]. We note that the basis sets used in the MCHF calculations included g orbitals whose contribution we have neglected, but estimated to be small, and that core relaxation contributed only 1 meV [11].

Our calculation A value of 67 meV is significantly higher than the 48 meV obtained by Fuentealba *et al.* [9] in a calculation omitting polarization terms. In addition to s, p, and d orbitals, these authors included only one f orbital in their basis and noted that it did not appreciably alter the electron affinity. In our calculation, f orbitals contribute 19.9 meV to the EA, a result consistent with a recent estimate of 23 meV by Froese Fischer and Brage [11]. It is thus reasonable to suppose that our more extensive expansions are primarily responsible for the disagreement with the result of Fuentealba *et al.* [9], though the possibility that part of the difference is due to the neglect of exchange with the Ca^{2+} core in calculation A cannot be excluded.

Examination of the wave-function compositions in Table IV shows that more Ca$^-$ configurations have a contribution larger than 1% in our approach than in the MCHF method so that, as expected, the MCHF approach provides a more compact wave-function expansion. The MCHF compositions quoted in Table IV were obtained from a calculation with an active set consisting of $4s, 5s, 6s, 4p, 5p, 6p, 3d, 4d, 5d, 4f, 5f$, and $5g$ orbitals [4]. The six largest eigenvector components in an expansion consisting of 116 configuration states are shown. Since the basis functions used in the MCHF and the B-spline approaches are very different, wave functions are best compared by examining the distribution over the different angular couplings such as ssp and spd. Such a comparison between the wave function from the latter MCHF set and the wave function from the B-spline CI method A reveals good agreement.

Next, the electron affinity obtained when the U_ℓ and V_P terms are included (B-spline B) is 57.2 meV (Table III). This result is very close to the values obtained by Johnson *et al.* [7] and Gribakin *et al.* [8], 56.6 meV and 58 meV, respectively. Both groups applied many-body perturbation theory and emphasized the importance of dipole polarizability in negative ion binding, so comparisons with calculation B are valid and the good agreement here is most encouraging.

Kim and Greene [5] used an R-matrix approach comparable to ours when we neglect the DP terms, and calculated an electron affinity 13 meV larger than ours. A possible explanation for this discrepancy may be that the value of their Ca ground-state energy is approximately 400 cm^{-1} (50 meV) lower than our equivalent (B-spline B) value (Table I). Kim and Greene seem to have used a value for $\alpha_d = 8.0$ a.u. [20] which is much larger than our value, $\alpha_d = 3.3$ a.u. The latter is determined solely from the properties of Ca$^+$ and is consistent with values obtained by other workers [21,22]. We believe that this difference is the origin of the discrepancy in EA between the two calculations.

Cowan and Wilson [10] added an approximate correlation potential, based on the correlation energy for a free-electron gas, to a pseudorelativistic Hartree-Fock Hamiltonian. Their procedure yields only the monoelectronic polarization terms and the predicted binding energy is somewhat larger than the other results.

Finally, inclusion of the DP terms in the two-electron interactions (method C) significantly reduces the binding energy of Ca$^-$ and results in an electron affinity of 17.7 meV (see Table III), in excellent agreement with the recent experimental values of 18.4 meV [12] and 17.5 meV [13]. Thus the effect of the DP terms is to decrease the electron affinity of Ca by 39.5 meV. Since, from Table I, the DP terms change the ground-state energy of neutral Ca by 81.7 meV, it follows that the additional DP contribution from the extra electron in Ca^- is almost 50% of the dielectronic polarization of Ca.

Fuentealba *et al.* [9] estimated the effect of polarization on the electron affinity to be 48 meV in good agreement with our value of 49.3 meV. Neglecting f orbitals in calculation C raises the ground-state energies of Ca and Ca^- by, respectively, 4 and 19 meV, thereby lowering the EA to only 2.7 meV, very close to the zero result predicted by Fuentealba *et al.* We also note the relatively close agreement between the results of calculation C and Ref. [9] for the Ca ground state and thus we are strongly reinforced in our opinion that the difference between the two calculations is primarily the inadequate description of configurations containing one or more f electrons in Ref. [9].

Froese Fischer and Brage [11] have recently considered the inclusion of core polarization in an MCHF calculation via a model potential. However, Table III shows that the reduction they obtain in the EA is considerably smaller than obtained by us or by Fuentealba *et al.* [9] and they note that use of the latter value (or ours) in conjunction with their value for the outer correlation would lead to agreement with the latest experimental values.

Fuentealba *et al.* [9] also reported EAs for Sr and Ba which are substantially smaller than previous calculations. It would be interesting to see how important the DP terms are in these atoms. Since the difference between the results of Froese Fischer [4] and Fuentealba *et al.* [9] decrease slightly with increasing Z, there is an indication that the DP terms are less important for the heavier atoms although part of the reduction could be due to relativistic effects. We estimate electron affinities of the order of 50 meV for Sr and 110 meV for Ba. However, we note that alkali-atom EAs decrease with increasing Z so any extrapolation must be treated with caution.

The only theoretical value for Ca which is at all close to our final value with all polarization terms included is obtained by Bauschlicher *et al.* [6]. They did not take polarization terms into account and, therefore, such close agreement would seem to be fortuitous and is probably due to an inadequate description of valence correlation.

In summary, we have developed a model-potential method for determining properties of systems with two or three electrons outside a closed-shell core with polarization effects included, using a B-spline basis set. It is used to predict the binding energy of the stable negative Ca^- ion and we obtain an electron affinity of 17.7 meV for Ca, in complete accord with recent experiments. To estimate the accuracy of our approach, we have carried out calculations without the dielectronic polarization terms and have obtained good agreement with other theoretical calculations. It is found that an accurate estimate of the polarization is needed for a reliable prediction of small electron affinities. As the heavy alkaline-earth atoms have large dipole polarizabilities, it is of great interest to determine experimentally their electron affinities. Our results show that the role played by core-valence interactions in these heavier atoms and their negative ions requires further investigation.

We would like to thank Professor C. Froese Fischer for spirited discussions. This work was sponsored by the Stichting Nationale computerfaciliteiten (National Computing Facilities Foundation, NCF) for the use of supercomputer facilities, with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for Scientific Research, NWO). A visitors grant from NWO for C.L. is acknowledged.

[1] J. R. Peterson, Aust. J. Phys. **45**, 293 (1992).
[2] C. Froese Fischer, J. B. Lagowski, and S. H. Vosko, Phys. Rev. Lett. **50**, 2263 (1987).
[3] D. J. Pegg, J. S. Thompson, R. N. Compton, and G. D. Alton, Phys. Rev. Lett. **59**, 2267 (1987).
[4] C. Froese Fischer, Phys. Rev. A **39**, 963 (1989).
[5] L. Kim and C. H. Greene, J. Phys. B **22**, L175 (1989).
[6] C. W. Bauschlicher, S. R. Langhoff, and P. R. Taylor, Chem. Phys. Lett. **158**, 245 (1989).
[7] W. R. Johnson, J. Sapirstein, and S. A. Blundell, J. Phys. B **22**, 2341 (1989).
[8] G. F. Gribakin, B. V. Gul'tsev, V. K. Ivanov, and M. Yu. Kuchiev, J. Phys. B **23**, 4505 (1990).
[9] P. Fuentealba, A. Savin, H. Stoll, and H. Preuss, Phys. Rev. A **41**, 1238 (1990).
[10] R. D. Cowan and M. Wilson, Phys. Scr. **43**, 244 (1991).
[11] C. Froese Fischer and T. Brage, Can. J. Phys. (to be published).
[12] C. W. Walter and J. R. Peterson, Phys. Rev. Lett. **68**, 2281 (1992).
[13] M. J. Nadeau, X. L. Zhao, M. A. Garwan, and A. E. Litherland, Phys. Rev. A **46**, R3588 (1992).
[14] H. K. Haugen *et al.*, Phys. Rev. A **46**, R1 (1992).
[15] C. Laughlin, Phys. Scr. **45**, 238 (1992).
[16] C. D. H. Chisholm and U. Öpik, Proc. Phys. Soc. **83**, 541 (1964).
[17] G. Peach, in *Atoms in Astrophysics*, edited by P. G. Burke, W. B. Eissner, D. G. Hummer, and I. C. Percival (Plenum Press, New York and London, 1983).
[18] H. W. van der Hart and J. E. Hansen, J. Phys. B **25**, 41 (1992).
[19] J. Sugar and C. Corliss, Phys. Chem. Ref. Data **8**, 865 (1979).
[20] C. H. Greene and L. Kim, Phys. Rev. A **36**, 2706 (1987).
[21] B. Edlén and P. Risberg, Arkiv Fysik **10**, 553 (1956).
[22] W. R. Johnson, D. Kolb, and K.-N. Huang, At. Data Nucl. Data Tables **28**, 333 (1983).