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***Ab initio* studies of the $4s4p^2\ ^4P$ state in Ca^-** C. Froese Fischer,¹ J.E. Hansen,² and H.W. van der Hart^{2,*}¹*Vanderbilt University, Box 1679B, Nashville, Tennessee 37235*²*Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, NL-1018 XE, Amsterdam, The Netherlands*

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Ab initio calculations of the position of the $4s4p^2\ ^4P$ term in Ca^- are described that take the interaction with the core into account in two different ways: one by means of a model potential using a spline basis and the other by an explicit multiconfiguration Hartree-Fock calculation. The calculated electron affinities relative to the $4s4p\ ^3P$ term are in good agreement but differ from experiment. The model potential result is in somewhat better agreement with experiment if the energy is interpreted relative to the Ca^{2+} ground state. Possible reasons for the discrepancy are discussed.

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I. INTRODUCTION

The Ca^- ion has turned out to be an interesting test case for theoretical calculations. The reason is the polarizability of the core which depends, in particular, rather strongly on the presence or absence of $3d$ electrons and even on the state of the $3d$ electron. Froese Fischer was the first to predict the stability of the Ca^- ground state, which predominantly has $4s^24p\ ^2P$ character [1], although correlation with $3d$ electrons is essential for the binding. This first calculation treated explicitly the correlation among the valence electrons, but not the effect of the polarizability of the core. A number of theoretical results followed (see [2] for a review and evaluation of the different effects included in the various calculations), some including corrections for the polarizability of the core, which also gave results in rather good agreement with the early observations [3]. However, recently different experimental techniques have been applied to measure the electron affinity (EA) of the Ca ground state and the result has been a substantial revision of the EA from a value of 43 meV to about 18 meV [4–7]. The smallness of the affinity, which is defined as the difference between the total energies of the ground state of Ca and the ground state of Ca^- and usually is calculated from the definition, shows that the theoretical determination will be of extreme difficulty. A comparison of the previous calculations with the new experimental results shows that the complexity of the problem is compounded by the necessity to include the interaction with the core.

II. A FEW ELECTRONS OUTSIDE A CORE

Atomic systems such as Ca are often thought of as two-electron systems and indeed, for qualitative descriptions,

many observations can be explained on this basis. To obtain quantitative results, Müller *et al.* [8] have shown that a number of effects need to be included.

(i) Valence correlation among the outer electrons is crucial for obtaining binding in negative atoms.

(ii) Intershell correlation between the valence electrons and the core, also referred to as core polarization, has already been mentioned. This effect consists of two parts in a two- (or three-) electron atom. The first electron may polarize the core considerably, but the polarization will often be reduced by the second electron since the two will try to avoid each other and prefer to be on opposite sides of the core. The latter effect is called dielectronic core polarization and is taken into account separately. In some cases the contribution from dielectronic polarization may increase the polarization. For instance, the sign of the exchange dielectronic polarization contribution depends on the total spin and for a pure sp^3P^o term dielectronic polarization increases the polarization [9] due to the presence of exchange.

(iii) Core rearrangement occurs because of the presence of one or more outer electrons and is particularly large if any of these penetrate the core. In the case of Ca^+ , the Hartree-Fock (HF) energy of the $3d\ ^2D$ state is 300 meV higher if computed in the fixed potential of the Ca^{2+} ion compared with a fully variational calculation.

(iv) Intracore exclusion effects, due to the presence of valence electrons, reduce the correlation of the core.

(v) Relativistic shift effects are particularly important for s electrons. In addition, relativistic effects will lift the degeneracy between different levels belonging to a particular term.

Model potential methods attempt to capture all but valence correlation in a potential so that calculations for calcium, for example, can proceed as though for a two-electron system. It has been known for a long time, however, [8,10] that the d series in Ca, in particular as mentioned already the $3d$ state, is difficult to describe in such a scheme.

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III. MODEL POTENTIALS FOR Ca AND Ca⁻

Recently calculations using a B -spline basis set and a model potential to describe the interaction with the core [11] have been successful in reproducing the new experimental values for the Ca affinity. The model potential $V(r)$, developed by Laughlin [12], consists of several parts: $V(r) = V_{\text{HF}}(r) - N_c/r + U_l(r) + V_P(r) + V_{P12}(r)$, where $V_{\text{HF}}(r)$ is the direct electrostatic repulsion of the outer electron by the core while N_c/r is the nuclear attraction, N_c being the number of electrons in the core [the attraction due to the net charge of the core Ca^{2+} is included in the Schrödinger equation together with $V(r)$]; $U_l(r)$ is an angular-momentum-dependent fitting potential chosen to reproduce the observed Ca^+ spectrum (with an accuracy of a small fraction of 1 meV); $V_P(r)$ takes the interaction between the valence electron and the dipole and quadrupole moments it induces in the Ca^{2+} core into account, while $V_{P12}(r)$ represents the dielectronic polarization potential [13]. The dipole and quadrupole moments used are obtained from the observed Ca^+ spectrum using the fitting procedure described by Edlén [14] and the value for the dipole moment, $3.30a_0^3$, is consistent with the value derived from experiment by Öpik [15] ($3.26a_0^3$) as well as being close to the theoretical value obtained by Johnson *et al.* [16] ($3.254a_0^3$), which has been used in other recent applications of model potential methods to the Ca I and Ca II spectra [17,18]. The quadrupole moment has a much smaller effect so that the influence of higher moments is expected to be negligible [11]. It should be mentioned that already Öpik [15] commented on the small size of the *sum* of the quadrupole and higher-order terms. Finally a cutoff radius equal to $2.70a_0$ is used to remove the singularity of the potential. Physically the cutoff compensates for the penetration of the core by the valence electron. The cutoff radius used here is larger than some values found in the literature [17,18]. However, another cutoff function was used in these references. The present potential gave excellent agreement for the Ca ground state [11]. The potential was then used to calculate the lowest 2P term in Ca^- and excellent agreement was found with the new experimental results for the Ca affinity. The reason for the difference to older calculations was the introduction of the dielectronic polarization term $V_{P12}(r)$, which has a large effect in this case, combined with the completeness of the B -spline basis. In this paper a further test of the potential is made by calculating another Ca^- term.

Only one other term is known in Ca^- . This is $4s4p^2\ ^4P$, first predicted by Bunge *et al.* [19]. Much less theoretical work has been done on this term. Experimentally one level was established by Hanstorp *et al.* [20] in 1989. They interpreted their experiment as being the observation of the $J = 5/2$ level mainly based on an analogy with the $1s2s2p\ ^4P$ term in He^- as well as on the excellent agreement with the energy predicted by Bunge *et al.* [19]. More recently, the interpretation of the J value has been questioned. Brage and Froese Fischer [21] showed that the $J = 5/2$ and $3/2$ levels have very short

lifetimes for autodetachment, while later Miecznik *et al.* [22] found that the $J = 1/2$ level has a longer lifetime due to destructive interference. Still their calculated lifetime is much shorter than that observed, but they concluded that if the $4s4p^2\ ^4P$ term “really forms a metastable component it should be attributed to the $J = 1/2$ level,” an interpretation which has been endorsed by Peterson [23], who also points out that the new value of the Ca^- ground state energy, which makes photodetachment due to blackbody radiation possible from this term [6], means that a reevaluation of the experimental results is required [24]. The other fine-structure levels are not known.

IV. B-SPLINE BASIS CALCULATIONS

With only minor changes, the computer programs used to study the bound ground state of Ca^- [11] can be used to calculate the metastable $4s4p^2\ ^4P$ state. In this calculation we have used a basis set consisting of 22 B splines of order 9 for $l = 0, 1, 2$, and 3 defined in a cavity of size 60 a.u. A major problem with calculations of negative ions is the diffuse character of the valence orbitals, but we have checked that this box size is sufficient. If all possible combinations of basis states are included a configuration-interaction (CI) calculation becomes very large and in the final CI expansion some combinations of basis states are neglected. To determine the optimum size of the CI expansion, a number of CI calculations were performed and the neglected basis states taken into account as a second-order perturbation. In the latter calculation, configurations with a significant energy contribution were monitored in order to spot possible flaws in the choice of included configurations. Subsequently, the CI expansion was adjusted so as to limit the magnitude of the second-order energy shift. The final CI expansion included 3104 states with the angular couplings and expansion sizes reported in Table I. The CI expansion is smaller than that for the $4s^24p\ ^2P$ ground state because the quartet spin state restricts the coupling of the first two electrons to a triplet spin state, while in the ground state the first two electrons in addition can couple to a singlet state.

In the calculation for the Ca affinity the introduction of dielectronic core polarization was found to be essential for obtaining the correct affinity. The influence of $V_{P12}(r)$ is also large in the present case. The total contribution to the 4P term is about 150 meV. When this

TABLE I. Configurations included in the CI expansion of $\text{Ca}^- 4s4p^2\ ^4P$ in the B -spline approach. All allowed intermediate triplet couplings are included for the indicated configurations. Configurations are reordered to $n\ell n'\ell' n''\ell''$ with $n \leq n' \leq n''$ and the maximum allowed values of n, n' , and n'' are specified. In addition, configurations of the types *ppd* and *pfd* that have one $6p$ orbital, one $6d$ or $6f$ orbital, and one orbital with a higher n value are excluded.

Angular momenta	<i>pps, ppd, dds</i>
	<i>ddd, ffs, pfd</i>
maximum allowed n	5 ($\ell \geq 2$), 6 ($\ell \leq 1$)
maximum allowed n'	7
maximum allowed n''	17

term is excluded, we find a binding energy with respect to the center of gravity of $4s4p\ ^3P$ equal to 564 meV (see Table II), which is reduced to 516 meV when dielectronic core polarization is included (for both terms). In both cases the second-order energy shift is about 4 meV. This means that without the dielectronic term, the difference with experiment is 9 meV, while the difference increases to 40 meV when $V_{P12}(r)$ is included. However, since all other energies in the B -spline approach have been determined with respect to the Ca^{2+} ground state, the same is done here and somewhat better agreement with experiment is obtained. Table II reports the results both without and with the dielectronic core polarization term. Experimental values are included for comparison. The wave function corresponding to the $4s4p^2\ ^4P$ term consists for more than 92% of $nsnp^2$ states with fractions of about 1% in np^2nd basis states and slightly more than 3% in $nsnd^2$ configurations.

In most applications of model potentials, interest has focused on the computed value for the affinity with no assurance that the approach is valid for the individual states. However, in [11] it was established that the model potential gave extremely good agreement for the Ca ground state energy relative to the Ca^{2+} ground state. Since the ground state of the neutral atom primarily consists of contributions of s and p character (less than 1% of the eigenvector involves d character and higher angular momenta give negligible contributions) this indicates that both s and p electrons, as well as their mutual interaction, are well described by the present model potential. As mentioned above, the $4s4p^2\ ^4P$ term has less than 5% contribution of d character, but an error relative to the Ca^{2+} ground state of 180 cm^{-1} (22 meV) which seems rather large for a term with so little d character (see later).

V. MCHF CALCULATIONS

Variational calculations including core polarization are problematic for the $4s^24p\ ^2P$ ground state of Ca^- in

TABLE II. Energies of the $4s4p^2\ ^4P$ state in Ca^- (a) relative to the $4s4p\ ^3P$ state and (b) relative to the Ca^{2+} ground state obtained in B -spline calculations without and with the V_{P12} term in the model potential included. In the case of the 4P and 3P terms the calculated energies are for the center of gravity of the term. The observed value in (a) is the distance between the $^4P_{1/2}$ level and the center of gravity of the 3P term (see text). The observed value was originally given relative to the $4s4p\ ^3P_2$ level.

Method	Energy	
	(a) (meV)	(b) (cm^{-1})
Theory (B splines)		
potential = $V(r) - V_{P12}(r)$	564.3	135329
potential = $V(r)$ (full core polarization)	515.8	134093
Experiment		
photodetachment [20]	555 ± 5	134273 ± 40

that variational procedures can only be applied to bound systems and for this state the binding energy is very small. In the case of $4s4p^2\ ^4P$, the extra electron is sufficiently bound that multiconfiguration Hartree-Fock (MCHF) calculations could be performed that include valence correlation, core polarization, some core rearrangement, and non-fine-structure relativistic effects explicitly. The polarization of the $3s^2$ and $3p^6$ shells has been taken into account, while the remaining core rearrangement and intracore correlation could not be estimated. However, changes in these effects are expected to be negligible for the addition of an extra p electron to $4s4p\ ^3P$. In fact, in the calculation already the effect of the $3s^2$ shell is much smaller than the effect due to $3p^6$ and the same has been reported by Sundholm and Olsen [25] for the Ca^- ground state. Thus accurate energy differences are expected. In contrast, accuracy relative to the Ca^{2+} ground state is harder to obtain in this approach.

A systematic series of MCHF calculations was undertaken where the orbital basis increases at each stage. The notation $n = 5$, for example, is used to indicate that the orbital set contains all orbitals with $n \leq 5$ except that, for convenience, the nd orbital is included in the $(n+1)l$ set of orbitals since, in the MCHF methodology, the principal quantum number plays no significant role and in this way the $n = 4$ set contains one active orbital of each symmetry in addition to the core orbitals. The expansion is a complete active space (CAS) expansion over the set of all possible configuration state functions (CSFs) with a $3s^23p^6$ core in the case of outer (or valence) correlation. In the core-polarization calculations, at most one electron is excited from the $3s$ or $3p$ shell, thus CSFs with a $3s^23p^5$ or $3s3p^6$ core represent core polarization. By allowing the $3s$ and $3p$ orbitals to vary, some core rearrangement is included. Sundholm and Olsen [25] in their calculation for the Ca^- ground state also allowed only one electron to be excited from the $3s$ or $3p$ shell, although they did not allow the $3s$ and $3p$ orbitals to relax. For the core-polarization calculation the CAS expansions became too long after the $n = 5$ stage and techniques were employed to constrain the size of the problem. For the higher n values, CSFs with expansion coefficients less than 0.00005 were deleted from the calculation for the previous n and CSFs containing new orbitals added incrementally according to the scheme given in Table III. The largest wave function expansion includes 21 922 configuration states. For the valence correlation calculation, core orbitals were determined from the $n = 4$ calculation; tests were performed to confirm that results did not depend on whether orbitals were from the 3P or 4P calculation. In the case of the calculation with core polarization, the orbitals $1s, 2s, 2p$ were determined from 3P and all others optimized independently for the two states. For some of the larger expansions, the relativistic shift (mass velocity correction, one- and two-body Darwin terms, and spin-spin contact) is computed.

Table IV summarizes the electron affinities, computed as a difference of the total energies, that are obtained from these calculations. It shows the very important effect of core polarization and also a significant relativistic contribution. Two different electron affinities are re-

TABLE III. Details of the MCHF expansions including core polarization explicitly. The active set of orbitals is designated by the maximum principal quantum numbers, with $l \leq 4$. The calculations for $n = 4$ and $n = 5$ have a complete active space expansion. For the higher n values small eigenvector contributions were deleted, as explained in the text, and CSFs containing new orbitals added, as shown below, where $\{n, n'\}^N$ signifies that N electrons are distributed over the n and n' shells. The notation implies that the added configurations have at least one electron with principal quantum number n .

Basis	$4s4p^3P$ of Ca	$4s4p^2^4P$ of Ca^-
$n = 6$	$\{3\}^7\{3, 4, 5\}\{4, 5, 6\}^2$	$\{3\}^7\{3, 4, 5\}^2\{4, 5, 6\}^2$
$n = 7$	$\{3\}^7\{3, 4, 5\}\{4, 5, 6, 7\}^2$	$\{3\}^7\{3, 4, 5\}^2\{4, 5, 6, 7\}^2$
$n = 8$	$\{3\}^7\{3, 4\}\{4, 5, 6, 7, 8\}^2$	$\{3\}^7\{3, 4\}^2\{4, 5, 6, 7, 8\}^2$
$n = 9$	$\{3\}^7\{3, 4\}\{4, 5, 6, 7, 8, 9\}^2$	$\{3\}^7\{3, 4\}^2\{4, 5, 6, 7, 8, 9\}^2$

ported: (a) those where the orbitals of the anion were used to compute both energies and (b) those where each is computed from the independently optimized orbitals. As expected, the EA for the latter is smaller. For the simpler, valence correlation calculation, as the orbital basis increases, calculations (a) and (b) both approach the value of 553 meV, which is reduced by 6 meV when the relativistic shift is included. For the more difficult calculation including core polarization, the two sets of values appear not to be converging to the same limit, though (a) is somewhat better converged. Since different $3s$ and $3p$ orbitals were used for the two states, calculations for the neutral atom were also performed with these orbitals fixed to those of the anion: the effect was small, increasing the EA by 2 meV. From these results, it would appear that the nonrelativistic EA is in the range 530–518 meV. The computational model favors the neutral atom, so the EA may indeed be larger than the value in the low end of the range, obtained from the independently optimized calculations.

The non-fine-structure relativistic effect reduces the electron affinity. The early stages of the core-valence calculations reported in Table IV exhibited a considerable reduction, though this decreased with the size of the orbital basis. Because of the large expansions involved, the calculation of the relativistic shift for this approximation was abandoned. Instead corrections were obtained from

a calculation including only core polarization with $3p^6$: the EA's were similar, but the relativistic correction more stable, converging to approximately 7 meV. Assuming a nonrelativistic electron affinity of 524 meV, reduced by 7 meV due to relativistic effects, we estimate the electron affinity to be 517 ± 10 meV as reported in Table V.

As just mentioned, another series of calculations was made in which only the core polarization associated with the $3p^6$ shell was taken into account. These calculations converged faster and the final result was very close to the value reported in Table IV. This means that the polarization due to the $3s^2$ shell has a small effect on the binding. A similar result has been reported by Sundholm and Olsen [25], who calculated that the correlation due to the $3s$ shell is about 6 times smaller than the effect due to $3p$.

VI. COMPARISON WITH OTHER THEORY AND EXPERIMENT

The amount of work reported for $4s4p^2^4P$ is rather small in comparison with the effort lavished on the Ca^- ground state. Bunge *et al.* [19] predicted a value of 550 meV for the electron affinity relative to $4s4p^3P$; core polarization was not included and this value is in good agreement with the MCHF value at the same level of approximation. Cowan and Wilson [26], using a relativistic Hartree-Fock program and a free-electron approximation for correlation including core polarization, obtained a value of 512 meV, which is in good agreement with our values including core polarization. Cowan and Wilson [26] reported only a value relative to $4s4p^3P$. These results are presented in Table V according to the type of calculation — valence correlation only or valence correlation and core polarization. There is good agreement among the different valence correlation results and also among the results including core polarization. However, the latter, which from a theoretical standpoint are the most accurate, deviate substantially from experiment [20]. If the model potential energy relative to Ca^{2+} is combined with the observed energy for the $4s4p^3P$ state, the binding would be 532.9 meV, still about 20 meV smaller than the observed value. Given the complexity of the calculation, it is tempting to see the theory as the main source of the disagreement, but the close agree-

TABLE IV. Electron affinities from MCHF calculations (in meV) for $4s4p^2^4P$ of Ca^- relative to $4s4p^3P$ of Ca as a function of the active set used. In calculations (a), the orbitals of Ca^- were used to compute also the energy of Ca; in (b) the orbitals were independently optimized for the two systems. The basis set expansions are shown in Table III and discussed in the text.

Basis	Valence correlation			With core polarization		
	Nonrelativistic		Relativistic	Nonrelativistic		Relativistic
	(a)	(b)		(a)	(b)	
$n = 4$	745.7	460.8		732.4	379.1	
$n = 5$	568.4	544.7		696.5	376.3	
$n = 6$	554.4	552.1	546.7	588.0	479.5	
$n = 7$	553.3	553.0	547.4	537.2	511.8	504.6
$n = 8$				533.1	515.8	509.1
$n = 9$				531.7	516.9	

TABLE V. Experimental and theoretical energies (in meV) of the $4s4p^2\ ^4P$ term in Ca^- relative to the center of gravity of the $4s4p\ ^3P$ state in Ca. The experimental value is believed to be for the $J = 1/2$ level of the 4P term while the theoretical values are for the center of gravity of the two terms. MCHF results predict the fine-structure splitting between $J = 1/2$ and $J = 5/2$ to be 11.4 meV. Thus the experimental value is roughly 5 meV larger than the distance between the center of gravity of the two terms. CP stands for core polarization.

Method	Valence correlation	With CP – $V_{P12}(r)$	With full CP
	Theory		
B splines (present)		564.3	515.8
MCHF (present)	547.4		517±10
CI [19]	550		
HFR [26]			512
	Experiment		
Photodetachment [20]			555±5

ment between the explicit (model potential) and the implicit (MCHF) inclusion of core polarization does make it worthwhile to reexamine the experimental results also. An argument pointing in the same direction is that the error in the $4s4p\ ^3P$ energy in the B -spline calculation is less than 17 meV [27], while the error in the $4s4p^2\ ^4P$ energy is 40 meV relative to $4s4p\ ^3P$. This means that the extra loosely bound $4p$ electron introduces an error of about 25 meV, which seems rather large for a state with so little d character. We note that the largest deviation in the Ca spectrum [27] is 61 meV for the $4s3d\ ^3D$ term, which obviously is closely connected with the $3d$ character of this state, while all other deviations are less than 32 meV and all errors of this size correspond to terms with much more d character than $4s4p^2\ ^4P$ has. There is a possible counterargument insofar as all three $4p^2$ terms in Ca have errors of the order of 30 meV, but all three terms have much larger d components than $4s4p^2\ ^4P$, which makes this comparison less relevant. This follows because the addition of $4s$, which is an inner electron, can be expected to have a larger effect on $4p^2\ ^3P$ than the addition of the “outer” $4p$ electron has on $4s4p\ ^3P$. Sundholm and Olsen [25] have estimated that a 10–15 meV error in their calculation for the Ca^- ground state is due to core-core correlation. Core-core correlation can be expected to be larger for the Ca^- ground state than for the metastable state so that also this effect seems too small to explain the discrepancy. In addition we think that by allowing the $3s$ and $3p$ orbitals to vary we have included a part of what Sundholm and Olsen call core-core correlation.

Finally, it should be kept in mind that the identification of the observed feature cannot be said to be defini-

tively settled as mentioned in the Introduction. The lifetime calculated by Miecznik *et al.* [22] for the $J = 1/2$ level, even though longer than the lifetimes predicted for $J = 5/2$ and $3/2$, is still more than a factor of 2000 shorter than the value observed by Hanstorp *et al.* [20]. Even though the calculation is difficult (as well as the experiment) and might be in error by an appreciable amount, the discrepancy is worrisome. To check that the discrepancy is not due to the level identification a Breit-Pauli calculation based on the MCHF results for $4s4p^2\ ^4P$ was performed, omitting interactions with the 2P , 2D , and 2S terms in the $4s4p^2$ configuration. The predicted splitting of the $J = 1/2$ and $J = 5/2$ levels was 11.4 meV, which does not explain the discrepancy. As a check, the splitting of the $J = 0$ and $J = 2$ levels of the $4s4p\ ^3P$ term was calculated using the same approximations. The result is 21.2 meV, comparable with the observed value of 19.6 meV.

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