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Energies of metastable $^4S^o$ states in the alkaline-earth sequence

Hugo W. van der Hart
JILA and Department of Physics, Campus Box 440, University of Colorado, Boulder, Colorado 80309-0440

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Theoretical binding energies have been obtained for the metastable $np^3\,{}^4S^o$ states in the alkaline-earth sequence using a *B*-spline configuration-interaction approach. The results agree with available experimental and theoretical data within 5 meV for Be$^-$ and within 10 meV for Mg$^-$. The binding energies of the $p^3\,{}^4S^o$ state in Mg$^-$, Ca$^-$, and Sr$^-$ are larger than the one in Be$^-$ by roughly 250 meV due to the stronger interactions with the d^2p configurations. For Ca$^-$, the $^4S^o$ binding energy is determined to be 555.5 meV, including a contribution of -70 meV due to dielectronic core polarization. For Sr$^-$ the $^4S^o$ binding energy is 557.9 meV, including a decrease of only 6 meV due to dielectronic core polarization. This behavior for the $^4S^o$ states in Ca$^-$ and Sr$^-$ is ascribed to the different neutral-atom states to which the $^4S^o$ states are bound. [S1050-2947(99)02402-6]

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I. INTRODUCTION

Negative ions have been of special interest to theoretical and experimental physicists, since for many negative ions the ground state cannot be approximated adequately by a single configuration. The strength of the dielectronic repulsion compared to the nuclear attraction dramatically changes the electronic orbitals upon the binding of an additional electron to the neutral atom. Additionally, since the binding energy of the outer electron can be quite small, relativistic, core-core, and core-valence interactions have relatively large consequences. Accurate measurements and theoretical calculations are therefore important to indicate the strength of these less important interactions. For an overview of experimental and theoretical investigations on negative ions, the reader is referred to the review by Blondel [1].

For a long time, it was believed that no stable negative ion existed within the alkaline-earth sequence. The discovery of the existence of a stable bound Ca$^-$ state, both theoretically [2] and experimentally [3], was therefore very surprising. Since then many studies have been devoted to examine the properties of the negative-ion ground states within the alkaline-earth sequence (for a review of these studies see [4]), revealing that after the initial investigations our understanding was still rather limited. For example, subsequent experiments demonstrated that the binding energy of the outer electron in Ca$^-$ was substantially smaller than estimated earlier [5,6]. The continued development of spectroscopic techniques has allowed the determination of the binding energies for Ca$^-$ [7], Sr$^-$ [8,9], and Ba$^-$ [10] to within a fraction of a meV. Theoretical calculations only produce binding energies in agreement with experiment when the influence of core-valence interactions or core polarization is included in the calculations [11,12]. In addition, also core-core and relativistic interactions have a distinct influence on the binding energies [11,13–15].

Despite significant recent efforts to obtain highly accurate binding energies for the ground states of these ions, considerably less attention has been devoted to the metastable states. The predictions for the $4s4p^2\,{}^4P^e$ state in Ca$^-$ [16–18] have recently been found to agree very well with experiment [19], although only when the effects from dielectronic core polarization are included. The binding energies for the sublevels of the $5s5p^2\,{}^4P^e$ state in Sr$^-$ were determined as well in this experimental study [19]. A subsequent theoretical study obtained good agreement for its center-of-gravity binding energy [20].

The metastable $^4P^e$ states have also been investigated for the lighter ions in the sequence. Kristensen *et al.* [21] reported a binding energy for $2s2p^2\,{}^4P^e$ in Be$^-$ of 290.99 $\pm$0.10 meV, while theory has determined a binding energy of 289.1$\pm$1.0 meV using large-scale configuration interaction (CI) calculations including core excitations [22]. Also the theoretical and experimental fine-structure splittings agree to within 6%. For the $3s3p^2\,{}^4P^e$ state in Mg$^-$, theory has predicted a binding energy of 367.1 meV [23], using the CI with core excitations and relativistic corrections, and 379.8 meV [24], employing the multiconfiguration Hartree-Fock (MCHF) approach.

Apart from $^4P^e$ states, metastable $^4F^o$ and $^4S^o$ states have also been identified for negative ions in the alkaline-earth sequence. A $6s6p5d\,{}^4F^o$ state has been observed experimentally in Ba$^-$ [25], while in Sr$^-$ the $5s5p4d\,{}^4F^o$ state is found theoretically to lie very close to the first excited state of Sr [20]. The $np^3\,{}^4S^o$ state has been observed experimentally in Be$^-$ [21,25]. Recent theoretical investigations [22,24] have resulted in binding energies within 1 meV of experiment. For Mg$^-$, theoretical binding energies have been provided for the $^4S^o$ state [23,24], whereas experiment has not been fruitful yet [26,27].

Despite the increased interest in the negative ions of the heavier alkaline-earth atoms, the theoretical study of the $^4S^o$ state has not received the same amount of attention. Their study is nevertheless of interest for the fine tuning of the theoretical calculations. Furthermore, such a study provides information about the strength of core polarization and relativistic interactions in these heavier systems. For high-accuracy experiments, a good knowledge of the position of the $^4S^o$ states is beneficial since a smaller part of the spectrum may need to be investigated for a particular transition.

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In this paper, binding energies for the $^4S^o$ states in the alkaline-earth sequence will be presented and compared with the available data. The availability of high-quality results allows the testing of the numerical convergence of the present computations before attempting the heavier ions. After giving a brief description of the theoretical approach, we will also discuss the influence of core polarization on the calculated binding energies and illustrate some experimental consequences.

II. THEORETICAL APPROACH

The general difficulty in the theoretical description of a negative ion is that the orbitals in the neutral atom and the negative ion are quite different. In order to obtain a reliable estimate of the binding energy of the outermost electron, both the neutral atom and the negative ion must be described accurately using a similar basis set. This basis set must therefore be flexible enough to describe both tightly bound electrons and loosely bound electrons simultaneously.

The *B*-spline basis set is an example of a basis set that is well suited for the description of (quasi)bound states in negative ions as demonstrated by previous calculations for Ca^- and Sr^- [12,18,20]. In the application of *B* splines, the free negative ion is approximated by confining it within a box. This approximation is valid if the box is large enough to contain the entire wave function. For low-lying states of negative ions, this box must contain the loosely bound outermost electron. In the present studies, a box size of 80 a.u. has been chosen. This box is then subdivided into intervals, which are chosen according to the problem. In the present study of binding energies for metastable bound states, the intervals increase exponentially in length since bound-state wave functions oscillate more rapidly close to the nucleus. Twenty-five intervals have been chosen, which, after applying the boundary conditions that the wave functions vanish at the boundaries of the box, gives a total of 28 basis functions for each angular momentum.

The $^4S^o$ state is now approximated as a nonrelativistic three-electron state outside a closed-shell core. The potential arising from the nucleus and the closed-shell core is then approximated by a model potential for a single electron outside a closed-shell core. The Be^+ potential has been described by Bachau *et al.* [28], while the Mg^+ potential has been developed by Aymar *et al.* [29]. The Ca^+ potential for Ca^+ has been reported by Laughlin [30], while the Sr^+ potential has been given in [20]. The latter two potentials include a semiempirical term arising from the polarization of the closed-shell core, while no such term is included for the Be^+ and Mg^+ potentials. The increased influence of core polarization in Ca and Sr is mainly due to the smaller energy difference between the filled np^6 shell and the empty nd shell for alkaline-earth atoms beyond Ca. When core polarization for a valence electron is included in the Hamiltonian, for consistency also the interaction between two valence electrons has to be modified. A semiempirical dielectronic core polarization term has to be added to the dielectronic repulsion $1/r_{12}$ (see, e.g., [31]).

The two- and three-electron problems are now solved including all allowed couplings involving partial waves up to $\ell=4$. For the three-electron problem, these couplings are given in Table I. Including all allowed configurations results in an expansion length on the order of 10^5, which is too large to be treated in a single diagonalization. Therefore, the basis set is truncated using the criteria indicated in Table I, which results in an expansion length suitable for diagonalization. After obtaining the eigenenergies and eigenfunctions in this reduced expansion, the effects of the excluded configurations are added using second-order perturbation theory. The magnitude of the second-order energy shift is checked after the calculations to examine whether important configurations have been inadvertently left out of the calculations. Typically, the total second-order shift is less than 10 meV and individual contributions do not exceed 0.15 meV.

TABLE I. Angular momentum expansions $\ell_1\ell_2\ell_3$ used for the three-electron systems. The $n_1\ell_1n_2\ell_2n_3\ell_3$ configurations are sorted on n, with $n_{low}\leqslant n_{mid}\leqslant n_{up}$. The configuration is included in the diagonalization if all three n values are at most the value indicated in the table. Where two values are given, the first value is for s and p electrons and the second is for d, f, and g electrons.

Atom	Maximum n_{low}	Maximum n_{mid}	Maximum n_{up}
Be	5	19	$19+\ell$
Mg	5	19	$19+\ell$
Ca	7,6	8,7	$22+\ell$
Sr	7,6	8,7	$22+\ell$
Symmetries	ppp, ddp, ffp, ggp, ddf, fff, ggf		

III. RESULTS AND DISCUSSION

A. Neutral-atom states

The first question to be addressed when a model potential for a single-electron system is employed for multielectron calculations is the quality of the energies for the two-electron system. This is a far more stringent test of the overlap of the different wave functions than the energies of the single-electron system since the dielectronic repulsion is quite sensitive to small deviations in the wave functions. For each alkaline-earth atom studied here, we have chosen to examine the accuracy of the energies for two states, the ground state and the lowest state for which an additional electron can create a $^4S^o$ state. A comparison between the theoretical results and the experimental values is given in Table II. The experimental data are obtained from [32] for Be, from [33] for Mg, from [34] for Ca, and from [35] for Sr.

The largest difference is observed for Sr, where the ground-state energy differs from the experimental binding energies by 29.6 meV, while the energy of the $^3P^e$ state differs from experiment by 53.3 meV. Also for the ground state of Be and the $^3D^o$ state of Ca, the present calculations and experiment differ by roughly 30 meV. All other differences are smaller than 20 meV. Although these discrepancies are not negligible, they are still sufficiently small to permit a reliable estimate of the $^4S^o$ binding energies. The largest errors are observed for Sr since for this atom a single-electron model potential equal for all angular momenta is employed. For heavier atoms, this description becomes poorer and use of ℓ-dependent potentials may improve on the present accuracy [29,30]. Also, the use of LS coupling

TABLE II. Binding energies of neutral-atom states in the alkaline-earth sequence to which the $^4S^o$ states are bound. Energies are given in eV with respect to the ground-state of the doubly charged species and compared to the experimental values from the data tables [31–34].

Atom	State	Present theory	Experiment
Be	$2s^2\,{}^1S^o$	−27.5621	−27.5339
Be	$2p^2\,{}^3P^o$	−20.1492	−20.1325
Mg	$3s^2\,{}^1S^o$	−22.6762	−22.6691
Mg	$3p^2\,{}^3P^o$	−15.4922	−15.5086
Ca	$4s^2\,{}^1S^o$	−17.9856	−17.9849
Ca	$4p3d\,{}^3D^o$	−13.2148	−13.2439
Sr	$5s^2\,{}^1S^o$	−16.7546	−16.7250
Sr	$5p^2\,{}^3P^e$	−12.3732	−12.3199

becomes a poorer approximation due to the increased strength of relativistic interactions, which have been neglected in the present calculations.

B. Binding energies for the $^4S^o$ states

The energies of the np^3 states of X^-(X=Be, Mg, Ca, and Sr) with respect to the X^{2+} ground state are given in Table III. Also the energies with respect to the lowest state in X, for which an additional electron may lead to a $^4S^o$ state, are given in Table III. For Ca$^-$ and Sr$^-$, binding energies are given when the contribution from dielectronic core polarization is both excluded and included. The preferred energies are those with dielectronic core polarization included.

As mentioned above, for all energies presented here, relativistic interactions have been neglected. For the (meta)stable states of Ca$^-$, the binding energy was found to decrease by 6 meV (Ca$^-$) when relativistic interactions were included [36,18]. For Sr$^-$, the decrease was approximately a factor 3 larger [36]. Similar influences may exist for the $^4S^o$ states. It should be mentioned, however, that the semiempirical model potentials have been fitted to reproduce the energies of the Ca$^+$ and Sr$^+$ states. Single-electron relativistic interactions have thus been included implicitly for the effect on the center of gravity. Since there is only one level in the $^4S^o$ states, the change in binding energy due to relativistic interactions is expected to be smaller than the 6 meV and 18 meV for Ca$^-$ and Sr$^-$, respectively, estimated from previous calculations.

Table III shows a systematic trend in the behavior of the $^4S^o$ binding energies in the alkaline-earth sequence. The smallest value is found for Be$^-$, with a large increase in the binding energy of Mg$^-$. For the heavier systems in the sequence, smaller increases are observed for Ca$^-$ and Sr$^-$. This trend may be somewhat coincidental since for Ca$^-$ the $^4S^o$ state is bound with respect to the $^3D^o$ state instead of the $^3P^e$ state. The difference between the $^4S^o$ binding energy for Be$^-$ and the other negative ions is ascribed to the closer proximity of the d shell in Mg, Ca, and Sr. The increased flexibility to bind an additional electron due to the strong interaction between np^2 with nd^2 causes an increase in the $^4S^o$ binding energy of approximately 250 meV.

The contribution from dielectronic core polarization differs quantitatively for the binding energies of the $^4S^o$ states in Ca$^-$ and Sr$^-$. In Ca$^-$, the binding energy is reduced by 68.7 meV, while for Sr$^-$ the binding energy decreases by only 5.7 meV. The effect on the total binding energy of the $4p^3\,{}^4S^o$ state in Ca$^-$ and the $5p^3\,{}^4S^o$ state in Sr$^-$ is nevertheless very similar, a decrease of 77.5 meV and 106 meV, respectively. However, the shift of the respective threshold binding energies are very different, a decrease of 8.9 meV for the $4p3d\,{}^3D^o$ state in Ca compared to a decrease of 100 meV for the $5p^2\,{}^3P^e$ state in Sr. The main differences caused by dielectronic core polarization are therefore found in the neutral atom.

In order to explain the different behavior of the $^4S^o$ binding energies, we must examine the influence of dielectronic core polarization on the neutral-atom states. For the $5p^2$ state in Sr, the main effect of dielectronic core polarization is to decrease the interaction strength between the $5p^2$ and the $4d^2$ configurations. The same $5p^2 \leftrightarrow 4d^2$ interaction is also important for the $^4S^o$ state through the interaction between the $5p^3$ and $4d^2(^3P)5p$ configurations. Similar interactions are thus important for both the neutral atom and the negative ion, which may cause a large cancellation of the effects from dielectronic core polarization in the neutral atom and the negative ion.

For the $4p3d\,{}^3D^o$ state in Ca, almost no change due to dielectronic core polarization is observed. The reason for this is the same as has been discussed by Norcross and Seaton [38] for the small effect of dielectronic core polarization on the binding of the $2s2p\,{}^1P^o$ state in Be. Generally, dielectronic core polarization reduces the binding energy by decreasing the interaction strength between configurations. In

TABLE III. Binding energies in meV of the quasibound $np^3\,{}^4S^o$ states in the alkaline-earth sequence with respect to the $np^2\,{}^3P^e$ state for Sr$^-$, Mg$^-$, and Be$^-$ and the $np(n-1)d\,{}^3D^o$ state for Ca$^-$. DCP stands for dielectronic core polarization.

Atom	DCP	Neutral-atom state	E (eV)	Negative-ion state	E (eV)	Binding energy (meV)
Be	no	$2p^2\,{}^3P^e$	−20.1492	$2p^3\,{}^4S^o$	−20.4406	291.4
Mg	no	$3p^2\,{}^3P^e$	−15.4922	$3p^3\,{}^4S^o$	−16.0336	541.4
Ca	yes	$4p3d\,{}^3D^o$	−13.2148	$4p^3\,{}^4S^o$	−13.7703	555.5
Ca	no	$4p3d\,{}^3D^o$	−13.2236	$4p^3\,{}^4S^o$	−13.8478	624.2
Sr	yes	$5p^2\,{}^3P^e$	−12.3732	$5p^3\,{}^4S^o$	−12.9310	557.8
Sr	no	$5p^2\,{}^3P^e$	−12.4729	$5p^3\,{}^4S^o$	−13.0366	563.7

the $^3D^o$ case, however, there is an additional term allowed within a single configuration, arising from the exchange of the two electrons. Since exchange core polarization works opposite to the exchange Coulomb repulsion, exchange core polarization decreases the strength of the Coulomb exchange interaction. For the $4p3d\,^3D^o$ state, the Coulomb exchange term decreases the binding and the addition of the (counteracting) exchange core polarization term therefore increases the binding. The effects of the off-diagonal and diagonal terms in the dielectronic core polarization are therefore opposite and for the $4p3d\,^3D^o$ state these two contributions approximately cancel each other.

No core polarization has been included in the potentials for Be$^+$ and Mg$^+$ and the importance of dielectronic core polarization can therefore only be estimated. The single-electron core polarization effects are taken into account directly, through the model potential, since it has been fitted to reproduce the experimental spectrum. The dielectronic core polarization has not been accounted for. On the other hand, the calculations for Or$^-$ show that for a $p^3\,^4S^o$ state bound with respect to a $p^2\,^3P^e$ state, dielectronic core polarization effects are minor. This is therefore also expected to be the case for the binding energies of the $2p^3\,^4S^o$ state in Be$^-$ and the $3p^3$ state in Mg$^-$ and a reduction in the binding energy is not expected to exceed 3 meV.

Similar estimates for the influence of dielectronic core polarization can be obtained from other calculations. Olsen *et al.* [37] estimated that the effect of core-valence interactions for the $^4S^o$ state in Be$^-$ is to reduce the binding energy by 7 meV. Core-core interactions, which are neglected in the present approach, were estimated to reduce the binding energy by an additional 7 meV. These calculations were performed by including single excitations from the $1s^2$ core and included both monoelectronic and dielectronic core polarization terms. In addition, Olson *et al.* estimated the effect of core valence interactions through a model potential. Only the monoelectronic term was included and this term reduces the binding energy by 6 meV. Comparing this model potential result with the results obtained using core excitations, we can make a very rough estimate of the influence of dielectronic core polarization. Dielectronic core polarization approximately reduces the binding energy of the $2p^3\,^4S^o$ state in Be$^-$ by 1 meV.

A comparison of the present data with other theoretical and experimental binding energies is given in Table IV. Most available results have been obtained for Be$^-$. The most sophisticated calculations have given binding energies within 0.7 meV of the experimental results, using an extensive CI calculation including core excitations [22]. The present binding energies differ from these results by 4 meV. Bearing in mind the simplicity of the Be$^+$ potential employed and the present neglect of core excitations, this is quite good agreement. Since the approximations in the Ca$^-$ and Sr$^-$ potentials are expected to yield similar uncertainties in the binding energies, this agreement shows that the present method is well suited for determining the $^4S^o$ binding energies.

Also for Mg$^-$, the present results agree well with the available theoretical values. The present results agree with the nonrelativistic CI results of Beck [23] within 2.5 meV, although they differ with the extensive outer correlation MCHF results of Froese Fischer [24] by 10.4 meV. In both these studies, relativistic corrections have been evaluated as well. Surprisingly, in the CI calculations, these corrections are estimated to decrease the electron affinity by 3 meV, while in the MCHF approach they are estimated to decrease the electron affinity by only 0.1 meV. The reasons for these differences are unclear.

TABLE IV. Binding energies for the metastable $np^3\,^4S^o$ states in the alkaline-earth sequence. Available theoretical and experimental data are presented for comparison. CV stands for core-valence corrections, CVCC for core-valence and core-core corrections, CPP for core polarization potential, and RC for relativistic corrections.

Method	Atom	Binding energy (meV)
	Be	
Present results		291.4
Valence CI [a]		262
Valence MCHF approach [b]		300.0±5
Valence MCHF approach with CV [b]		293.0±5
Valence MCHF approach with CVCC [b]		286.0±5
CI with CPP [b]		294.0±5
Outer correlation MCHF approach [c].		300.8
CI with core polarization [c]		295.0±0.7
Experiment [d]		295.72±0.11
Experiment [e]		295.49±0.25
	Mg	
Present results		541.4
CI with core excitations and RC [f]		539
Outer correlation MCHF approach [c]		551.8
	Ca	
Present results		555.5
Valence CI [a]		592.1
	Sr	
Present results		557.9

[a] Reference [16].
[b] Reference [37].
[c] Reference [24].
[d] Reference [25].
[e] Reference [21].
[f] Reference [23].

Several experiments have attempted to evaluate the binding energy of the $^4S^o$ state in Mg$^-$ by measuring the frequency of the transition between the $3s3p^2\,^4P^e$ state and the $3p^3\,^4S^o$ state [26,27]. These attempts have not been fruitful. The difficulties were associated with the low production rate of the $^4S^o$ state of Mg$^-$ through Mg$^+$-foil collisions, while the radiative transition may also have been obscured by the more intense $2p^53s3p^2\,^5P_3 \leftrightarrow 2p^53s3p4s\,^5D_4$ transition [26,27].

The comparison with other data is more difficult for Ca$^-$. Only one result [16] has been presented previously, reporting a binding energy of 592.1 meV. The present result differs by 36.6 meV from the previous calculation. This difference can be assigned to two main sources. A larger basis set is employed in the present calculations, adding 30 meV to the binding energy. Furthermore, the present calculations include dielectronic core polarization, which reduces the binding energies by 68.7 meV. These differences are consistent with the differences observed previously for the $^4P^e$ state [18], where model potential and MCHF results gave a binding of 10 meV larger than the results by Bunge *et al.* [16] when dielectronic core polarization was excluded and 40 meV smaller when it was included.

The present results help to establish the most likely energies of the $^4S^o$ states, which should be useful for experimentalists. Threshold spectroscopy, for example, gives binding energies with very high accuracy, but a good estimate of the binding energy is needed to reduce the time required to search for the threshold. The present results can also be employed to find the frequencies of the radiative transition between the $^4P^e$ state and the $^4S^o$ state in Ca^- and Sr^-. These transitions are allowed and their frequencies are determined to be 22 698 cm^{-1} in Ca^- and 20 621 cm^{-1} in Sr^-. These frequencies are obtained from the experimental binding energy for the $^4P^e$ state [19], the experimental energy differences between the thresholds [34,35], and the present theoretical values for the $^4S^o$ binding energy.

The energy position of the $^4S^o$ state in Ca^- also has some other experimental implications. In one of the earliest experiments on Ca^-, Hanstorp *et al.* [39] observed a threshold photo-electron spectrum in the frequency range around 20 700 cm^{-1} with the threshold energy determined as 20 704 cm^{-1}. At first, this threshold spectrum was assigned to the photodetachment of the $4s4p^2\,^4P^e$ state and its lifetime was given as 290 ± 100 μs.

Since the initial state was not identified in this experiment, the reasons for assigning the initial state were the angular momentum of the outgoing electron, a p wave, and the transition frequency. For both the $^2P^o$ ground state of Ca^- and the $4s4p^2\,^4P^e$ state, a Ca threshold is reached with a photon having a frequency close to 20 704 cm^{-1}, namely, the $3d4s\,^3D^e$ threshold at 20 529 cm^{-1} for the $4s^24p\,^2P^o$ state and the $4s5s\,^1S^e$ threshold at 20 485 cm^{-1} for the $4s4p^2\,^4P^e$ state. After photoionization of the $^2P^o$ ground state the former threshold can only be excited after emission of even-parity electrons and was therefore excluded as the state observed experimentally. After photoionization of the $^4P^e$ state the latter threshold can be excited after emission of odd-parity electrons and the observed photoionization was therefore ascribed to negative ions initially in the $^4P^e$ state.

The binding energy of the $^4P^e$ state was in good agreement with the best calculations available at the time. Subsequent lifetime calculations, however, indicated difficulties with this assignment since the predicted lifetime was only in the order of 0.1 μs [40,41]. Improved theoretical calculations [18] later demonstrated a difference of 50 meV with the previous calculations and the experimental assignment was reinvestigated. Recent experiments confirmed the theoretical binding energy, so that now a consistent description of the $4s4p^2\,^4P^e$ state has been obtained [19].

This leaves the question of what was actually observed in the original experiment by Hanstorp *et al.* [39]. The $^4S^o$ state has not received any attention in the analysis, although there is a $3d4d\,^3P^e$ state in Ca, lying 20 544 cm^{-1} above the predicted energy of the $^4S^o$ state of Ca^-. Since the difference in threshold frequency between the one observed by Hanstorp *et al.* [39] and the present theory is 160 cm^{-1}, or 20 meV, which is comparable to the expected accuracy of the theoretical calculations, a photodetachment signal may originate from the $^4S^o$ state. However, after excitation of the $3d4d\,^3P^e$ state the outgoing electrons are again restricted to have an even parity, whereas the observations by Hanstorp *et al.* [39] indicate a p wave. The present calculations therefore do not provide an explanation of the observed threshold electrons. This nevertheless provides an indication that there are many pairs of Ca and Ca^- states, which may have a transition frequency close to one experimentally observed. A good spectrum in a wide frequency range is essential for an unambiguous assignment of the initial state.

IV. CONCLUSION

A *B*-spline basis set configuration interaction approach has been applied to study the $^4S^o$ binding energies in the alkaline-earth sequence. A binding energy of 291.4 meV has been found for Be^-, while for Mg^-, Ca^-, and Sr^- the binding energies are roughly 250 meV larger, 541.4 meV, 555.5 meV, and 557.9 meV, respectively. This difference is ascribed to the proximity of the d shell in the heavier systems, leading to stronger mixing with the d^2p configurations.

Good agreement with other theoretical and experimental results has been observed for Be^- and Mg^-. The differences with both theory and experiment amount to roughly 4 meV for Be^-, whereas the differences with other calculations amount to at most 10 meV for Mg^-. For Ca^-, a binding energy has been obtained that is smaller by 40 meV compared to the previous result. This difference has been ascribed to the increased size of the basis set in combination with the influence of dielectronic core polarization.

Dielectronic core polarization reduces the binding energy of the $^4S^o$ state in Ca^- by nearly 70 meV, whereas it reduces the binding energy of the $^4S^o$ state in Sr^- by only 6 meV. This small shift originates from a cancellation of shifts in the negative ion and the neutral atom due to dielectronic core polarization. Since the $p^3\,^4S^o$ state in Mg^- and Be^- is, similar to Sr^-, also bound with respect to the $p^2\,^3P^e$ state, also for these ions a small change in the $^4S^o$ binding energy due to dielectronic core polarization should be expected.

The $^4S^o$ state can in principle be excited from the metastable $^4P^e$ state and the transition frequencies for Ca^- and Sr^- are predicted to be 22 698 cm^{-1} and 20 621 cm^{-1}, respectively. It is hoped that the continuing development of spectroscopic techniques will allow an accurate determination of these wavelengths in order to establish the quality of the present theoretical description and the influence of small interactions on the binding energy.

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