Many-Body Calculations of the Electron Affinity for Ca and Sr

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We have combined the quasiparticle method in many-body perturbation theory with methods used when solving the coupled-cluster equations in order to evaluate the proper self-energy potential beyond second order in perturbation theory. The method is used to calculate the affinities of Ca and Sr including second-order relativistic effects. The result is 19 meV for Ca^- $4p_{1/2}$ and 54 meV for Sr^- $5p_{1/2}$, which are in fair agreement with experiment. [S0031-9007(96)00040-3]

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Negative alkaline-earth ions pose a formidable challenge in atomic physics. They form a critical testing ground for atomic theory, and it is hard to make accurate measurements on them, since they are very fragile quantum systems. Specifically for Ca^- and Sr^- it has turned out to be very hard to acquire reliable data from both experiment and theoretical calculations. There is no long-range Coulomb field present outside the neutral atom, and the extra electron is bound solely through correlation with the other electrons. For both Ca^- and Sr^- the single-configuration Hartree-Fock (HF) model does not even produce a bound single-particle orbital for the extra electron.

In 1987 the stable negative Ca ion, in the state $4s^2 4p\ ^2P$, was both predicted [1] and observed [2]. The first theoretical prediction of the electron affinity by Froese-Fischer was 45 meV and in the first experiment, by Pegg and coworkers, the result 43 ± 7 meV was obtained. The discovery of Ca^- stimulated a large amount of theoretical work. Several theoretical results were published between 1987 and 1992, most of them in the range from 45 to 82 meV; see Refs. [1,3–9].

A few years ago, however, Walter and Peterson [10] measured a substantially smaller electron affinity for Ca, 18.4 ± 2.5 meV. Nadeau *et al.* [11] obtained the value 17.5^{+4}_{-2} meV in an independent measurement the same year. Very recently the affinity has also been measured in Aarhus [12], and their result is 24.55 ± 0.10 meV for $4p_{1/2}$ and 19.73 ± 0.10 meV for $4p_{3/2}$, resolving the fine structure for the first time.

The situation is similar for Sr^-. In a recent measurement by Berkovits *et al.* [13] an electron affinity of 48 ± 6 meV was obtained, while there are several theoretical results reported in the range from 93 to 160 meV [3–6,8,9,14].

Since there are large discrepancies between the measured affinities and most theoretical results for both Ca and Sr, it is of great interest to improve the theoretical methods to gain a deeper understanding of the correlation effects responsible for binding an extra electron to these neutral atoms.

In this Letter we report on calculations on Ca^- and Sr^- using a many-body perturbation-theory (MBPT) approach for evaluating the proper many-body self-energy (SE) potential to high orders. In previous calculations [5,6,9] using this proper self-energy potential (PSEP) approach only the lowest order [5] and restricted classes of higher-order contributions [6,9] to this potential were included, yielding poor agreement with experiment. To improve these calculations we found it necessary to include higher-order contributions to the potential systematically. This gives a significant improvement in the agreement between theory and experiment when compared to earlier MBPT results.

Ca^- and Sr^- have the same principal electron configuration, $(\text{core})ns^2np$. The two ns electrons and the np electron are loosely bound, and the systems are essentially effective three-body systems. Therefore, in our analysis we will refer to all three outer electrons as valence electrons. This separation between core and valence electrons is used to divide the correlation effects into valence correlation, core-valence correlation, and core correlation contributions.

Calculations including only valence correlation gives affinities between 73 and 75 meV for Ca [3,15]. By including only the valence correlation the binding force seems greatly overestimated. If the core-valence correlation is also taken into account, the affinity is reduced substantially [15,16]. Thus, the attractive valence correlation is to a large extent screened by the correlation with the core.

In order to introduce the PSEP method, we consider a negative ion having a single electron outside closed shells. Such systems can be treated in MBPT as effective one-body systems because the interaction between the single electron and the rest of the system can be described with a nonlocal, energy-dependent potential, the PSEP. This potential describes the correlation effects on the interaction between the attached electron and the neutral atom. The quasiparticle orbital $\varphi(\mathbf{r})$ of the outer electron satisfies the *quasiparticle equation*

$$h_0\varphi(\mathbf{r}_2) + \int \Sigma^\star(\mathbf{r}_2, \mathbf{r}_1, \varepsilon)\varphi(\mathbf{r}_1)d^3r_1 = \varepsilon\varphi(\mathbf{r}_2), \quad (1)$$

where h_0 is a zeroth-order single-particle Hamiltonian, for example, the HF Hamiltonian used in this work.

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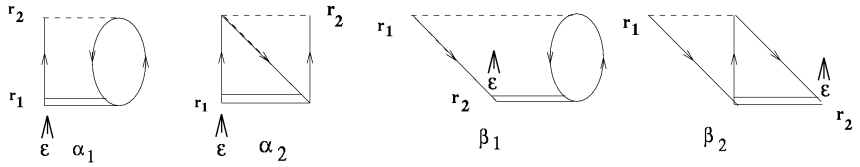

FIG. 1. The second-order skeletons contributing to the PSEP using the HF potential in h_0. The solid lines with an arrow are electron lines and the dashed lines denote the Coulomb interaction. Electron lines pointing downwards denote core electrons, and lines pointing upwards denote virtual electrons. The horizontal double lines represent the effective Coulomb interaction including the pair-correlation effects discussed in connection with Fig. 2. The energy dependence of the PSEP is denoted by ε.

$\Sigma^\star(\mathbf{r}_2, \mathbf{r}_1, \varepsilon)$ is the PSEP, which accounts for the correlation effects beyond the single-particle model described by h_0. For large distances, the total potential for the outer electron approaches the local dipole polarization potential, proportional to r^{-4}. The application of this approach to negative ions was first done by Chernysheva *et al.* [17] on He^- and Pd^-.

In this work we have used the HF model of the closed-shell neutral atom to define the zeroth-order approximation, h_0. This means that all electrons in the negative ion feel the direct and exchange interaction with the atomic electrons described by atomic HF orbitals. Having calculated the PSEP to some level of approximation, it is added to h_0, and the quasiparticle equation is solved in the same way as the zeroth-order equation. Since $\Sigma^\star$ is energy dependent, the equation has to be solved self-consistently with respect to ε.

The PSEP can be expanded in terms of the Coulomb interaction using ordinary perturbation theory. With the HF model, the first nonvanishing contributions are given by the four second-order Goldstone diagrams in Fig. 1 (with the first-order approximation of the effective Coulomb interaction). In third order with our choice of h_0 there are 52 independent diagrams contributing to the PSEP. All second-order and third-order contributions can be described as two-body correlation effects. In fourth order the number of Goldstone diagrams is more than a factor of 10 larger and also true three-particle effects contribute. Therefore a complete order-by-order calculation beyond third order is presently unfeasible.

A systematic inclusion of higher-order contributions to the PSEP can be accomplished by combining the quasiparticle method with all-order MBPT methods used to solve the coupled-cluster equations [18–20].

In order to go beyond the second-order approximation of the PSEP, we solve equations for the one- and two-body cluster operators S_1 and S_2. We follow closely the method described in Ref. [20] but with modifications to achieve the PSEP instead of the corresponding SE denoted by W_1. In this work only linear terms have been included in the cluster equations. The equations solved are

$$[S_1, H_0] = Q(V_2 S_2)_{1,c}\,,$$
$$[S_2, H_0] = Q(V_2 + V_2 S_2)_{2,c}\,, \qquad (2)$$

where V_2 is the two-body part of the Coulomb interaction, Q is the projection operator onto excited states, and the subscript c denotes that only connected diagrams are retained. The diagrammatic representation of the cluster equations, Eq. (2), is shown in Fig. 2. These cluster equations are solved self-consistently by iterative methods, thereby including pair-correlation effects to all orders. The truncation used for evaluating the proper SE $W_1^\star$ (corresponding to the PSEP) is

$$W_1^\star = P[V_2 S_2 + (S_2^\dagger V_2 S_2)_r + V_2 S_1 + S_1^\dagger V_2]_{1,c}\,, \qquad (3)$$

where the projection operator P is equal to $1 - Q$. This truncation for $W_1^\star$ is of Hermitian form [21]. The subscript r on the term $(S_2^\dagger V_2 S_2)_r$ denotes that restrictions are imposed in order to avoid double counting. Using the first- and second-order approximations of the clusters S_1 and S_2 a complete third-order proper SE can be evaluated. The self-consistent solutions for S_1 and S_2 will yield a proper SE which is complete to third order and contains systematically a large class of effects to all orders. The relation between the proper SE, $W_1^\star$, and the PSEP, $\Sigma^\star(\varepsilon)$, is $W_1^\star = \langle\varphi_0|\Sigma^\star|\varphi_0\rangle$ where φ_0 is the zeroth-order orbital for the outermost electron. The total SE, on the other hand, can be evaluated as $W_1 = \langle\varphi|\Sigma^\star|\varphi\rangle$ where φ is the quasiparticle orbital from Eq. (1).

In order to compare with previous calculations, we have first evaluated the PSEP to second order both nonrelativistically and relativistically (only Coulomb interaction), using the numerical finite basis-set method as described in Ref. [19]. The radial coordinate is discretized with $r = e^x/Z$, where the grid points are equidistantly distributed

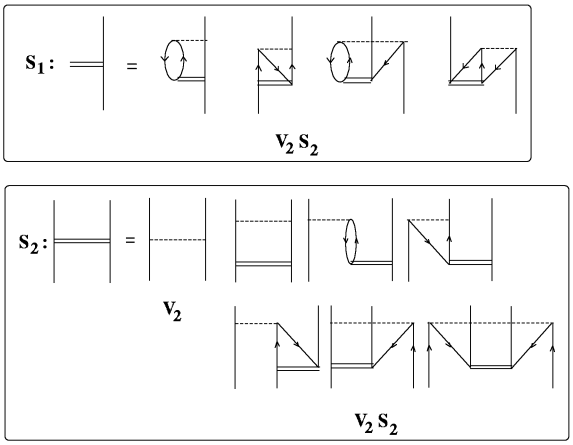

FIG. 2. Diagrammatic representation of the one-body, S_1, and two-body, S_2, cluster equations solved in this work.

TABLE I. Second-order binding energies for Ca^- $4p$ and Sr^- $5p$. Active core: $3s^2 3p^6 4s^2$ and $3d^{10}4s^2 4p^6 5s^2$, respectively. $\Delta^r np_j$ are the relativistic shifts for the states np_j. Units meV.

Ca^-	$4p$	$4p_{1/2}$	$4p_{3/2}$	$\Delta^r 4p_{1/2}$	$\Delta^r 4p_{3/2}$	$\Delta E_{\rm fs}$
$l \le 4$[a]	−50.6	−45.8	−39.9	4.8	10.7	5.9
$l \le 8$[a]	−62.1	−57.3	−51.1	4.8	11.0	6.2
Johnson[b]		−56.6				
Dzuba[c]		−56	−49			6.9
Sr^-	$5p$	$5p_{1/2}$	$5p_{3/2}$	$\Delta^r 5p_{1/2}$	$\Delta^r 5p_{3/2}$	$\Delta E_{\rm fs}$
$l \le 4$[a]	−104	−87	−64	17	40	23
$l \le 8$[a]	−119	−101	−76	18	43	25
Johnson[b]		−93				
Dzuba[c]		−102	−80			22

[a]This work.
[b]Johnson, Sapirstein, and Blundell [5], $|\kappa| \le 9$, $3d^{10}$ not active in Sr^-.
[c]Dzuba *et al.* [9], $3s^2$ not active in Ca^-, active core unknown for Sr^-.

in x from $x_{\rm min} = -6.0$ to $x_{\rm max} = 8.0$, corresponding to $R_{\rm max} \approx 150$ a.u. for Ca^-. In Table I we compare our results with those of Johnson, Sapirstein, and Blundell [5] and Dzuba *et al.* [9]. In the relativistic calculation by Johnson, Sapirstein, and Blundell only the second-order contributions to the PSEP were retained. By using virtual core-excited states calculated in the presence of a core hole, Dzuba *et al.* included a certain class of effects beyond second order. In addition, a class of polarization effects beyond second order was added. The agreement with both Johnson, Sapirstein, and Blundell and the second-order results of Dzuba *et al.* is good. The small difference can be explained by different truncation for the angular momenta and different size of the box.

In the final nonrelativistic calculations we have also included effects beyond second order in the PSEP as indicated above. A pure second-order plus third-order PSEP does *not* yield a bound $4p$ state in Ca^-, demonstrating how sensitive the problem is to correlation. The size of the contributions to the PSEP can be estimated by calculating the SE, W_1, using a quasiparticle orbital with the experimental binding energy. By doing so we have found that the size of the second-order effects is ~ -320 meV (giving the binding energy ~ -60 meV) and the total third-order SE contributes with $\sim +70$ meV (leading to a nonbound result). Out of the 52 independent third-order diagrams 10 are *larger* in size than 70 meV, 21 of them are in the range between 20 and 70 meV, and only 4 are less than 2 meV. Clearly the PSEP has not converged in third order. To calculate the binding energy accurately, one needs to include even higher-order effects systematically in the PSEP, and this has been done by solving the cluster equations, Eq. (2), iteratively to self-consistency.

In Table II the calculated second-order and self-consistent binding energies for Ca^- are given for different angular momentum truncations. As seen from the table, the l convergence shows quite a different behavior for the two results.

The results for different choices of active core in Ca^- are given in Table III. Also here the behavior of the second-order and self-consistent binding energies are different. For the self-consistent values the valence correlation has a strong binding effect but the binding energy is significantly reduced by the correlation with the $3p$ shell. The influence of the other shells in the core is much smaller. Our result including only valence correlation, −39.0 meV, differs from the results by Froese-Fisher, −73.0 meV, and by Sundholm and Olsen, −74.9 meV. This indicates that there are still important valence-correlation effects left out in our calculation. The valence correlation is, however, screened by the correlation with the core. Our nonrelativistic result, including also correlation with and within the core, is −23.6 meV, which is close to the later experiments. This indicates that the missing valence correlation effects (true three-particle effects and coupled-cluster effects) to a large extent are canceled by corresponding effects involving the core that have been neglected.

In Table IV our final results are given for both Ca^- and Sr^-. The binding energies given are the nonrelativistic self-consistent energies, −23.6 meV for Ca^- and −72.4 meV for Sr^-, plus the relativistic effects from

TABLE II. Binding energy for $4p$ in Ca^-. Dependence on angular momentum truncation. Active core: $3s^2 3p^6 4s^2$. Units meV.

$l_{\rm max}$	4	6	8	10
Second order	−50.6	−59.7	−62.2	−63.2
Self-consistent	−23.73	−23.67	−23.64	−23.63

TABLE III. Binding energy for $4p$ in Ca^-. Dependence on the choice of active core denoted in the table by the lowest active core shell. Angular momenta $l \le 4$ are included. Units meV.

Act. core	$4s$	$3p$	$3s$	$2p$	$2s$	$1s$
Second order	−18.1	−49.1	−50.6	−52.4	−52.8	−52.9
Self-cons	−39.0	−23.4	−23.7	−23.1	−23.6	−23.6

TABLE IV. Final results for Ca^- $4p$ and Sr^- $5p$. Active core: $3s^2 3p^6 4s^2$ and $3d^{10}4s^2 4p^6 5s^2$, respectively. Angular momenta $l \leq 8$ are included. Units meV.

	Ca^-			Sr^-		
	$4p_{1/2}$	$4p_{3/2}$	ΔE_{fs}	$5p_{1/2}$	$5p_{3/2}$	ΔE_{fs}
This work	−19	−13	6.2	−54	−29	25
Expt.	−24.55[a]	−19.73[a]	4.8[a]	−48 ± 6[d]		26 ± 7[d]
	−18.4[b]					
	−17.5[c]					

[a]Petrunin *et al.* [12].
[b]Walter and Peterson [10].
[c]Nadeau *et al.* [11].
[d]Berkovits *et al.* [13].

second order given in Table I. The fine-structure interval ΔE_{fs} given in Tables I and IV are deduced from the pure second-order calculations and can be improved by implementing the iterative method for evaluating the PSEP also relativistically.

In summary, by combining the quasiparticle method with methods used when solving the coupled-cluster equations in MBPT, we have evaluated the PSEP in a systematic way beyond second order. The potential is complete to third order and contains large classes of effects to all orders. By doing so we have succeeded in calculating the binding energies for the $4p_{1/2}$ state in Ca^- and the $5p_{1/2}$ state in Sr^- with significantly improved accuracy when compared to previous MBPT calculations [5,6,9]. We have found that a low-order approximation of the PSEP is definitely not sufficient to obtain accurate binding energies for these systems.

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