

**Bound states of Ca<sup>-</sup>**

Sy-Sang Liaw\*

*Department of Physics, National Chung-Hsing University, 250 Guo-Kwang Road, Taichung, Taiwan 40227, Republic of China*  
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We study the bound states of Ca<sup>-</sup> based on the Brueckner approximation. We use the *B*-spline method to solve the Brueckner equation self-consistently. At the first iteration we obtain the energy levels of *4p* states of Ca<sup>-</sup> which are close to those obtained by previous similar theoretical calculations. However, the bound states disappear after the first iteration in our calculation. This suggests that the existence of the bound states of Ca<sup>-</sup> is more subtle than previously thought.

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The discovery of bound states of negative ions Ca<sup>-</sup> offers a critical test for atomic theory. A theoretical work that predicted the existence of stable states [1] gave the electron affinity 45 meV, which is very close to the experimental value 43 meV obtained by Pegg and co-workers [2] in 1987. Since then, many theoretical works using different methods obtained electron affinity of Ca<sup>-</sup> mostly ranging from 45 to 82 meV. See Ref. [3] for a detailed list. There are also relativistic calculations [4,5] based on the Dyson equation that produced 56 meV for *4p*<sub>1/2</sub> and 49 meV for *4p*<sub>3/2</sub>. Recent experiments [3,6,7], however, obtain values about 20 meV for the electron affinity of Ca<sup>-</sup>. It is thus of importance to reexamine the bound states of Ca<sup>-</sup> from the theoretical side. A model-potential calculation has been carried out by van der Hart, Laughlin, and Hansen [8] to produce 17.7 meV. Recently, Jauregui and Bunge [9] used the configuration-interaction (CI) method with very large numbers of configurations to calculate the electron affinity. Their results is 12.8 meV. In this article we solve the Brueckner equation, which is obtained from Green's-function formalism in the second "order" approximation [10,11], to

search for the bound states of Ca<sup>-</sup>. Since relativistic effects are not negligible for Ca<sup>-</sup>, we solve the Dirac-type equation instead of the Schrödinger-type equation.

In Green's-function formalism, one starts from the ground state of neutral calcium which has *N*=20 electrons and tries to solve for orbitals of states with *N*+1 or *N*-1 electrons. We call states with *N*+1 electrons one-particle states, or simply particle states, and states with *N*-1 electrons hole states. Both particle states and hole states satisfy the same equation in each order of approximation. The equation is nothing but the Dirac-Fock (DF) equation in the first-order approximation [12], and the Brueckner equation in the second order. These two equations are given, respectively, by

$$(\epsilon_n^{DF} - H_0)|n\rangle = \Sigma^{(1)}|n\rangle, \tag{1}$$

$$(\epsilon_n^{Br} - H_0)|n\rangle = (\Sigma^{(1)} + \Sigma^{(2)})|n\rangle, \tag{2}$$

where *H*<sub>0</sub> is relativistic hydrogenlike Hamiltonian. The expectation values of the first- and second-order self-energy are given by

$$\langle n|\Sigma^{(1)}|n\rangle = \sum_a [\langle an|V|an\rangle], \tag{3}$$

$$\langle n|\Sigma^{(2)}|n\rangle = \sum_{a,i,j} \frac{1/2}{\epsilon_n + \epsilon_a - \epsilon_i - \epsilon_j} [\langle an|V|ij\rangle][\langle ij|V|an\rangle] + \sum_{a,b,i} \frac{1/2}{\epsilon_n + \epsilon_i - \epsilon_a - \epsilon_b} [\langle in|V|ab\rangle][\langle ab|V|in\rangle], \tag{4}$$

where *V* is the electron-electron interaction and  $\langle mn|V|st\rangle$  is defined as

$$\langle mn|V|st\rangle = \int \psi_m^\dagger(\mathbf{r}')\psi_n^\dagger(\mathbf{r}'') \times V(\mathbf{r}' - \mathbf{r}'')\psi_s(\mathbf{r}')\psi_t(\mathbf{r}'')d\mathbf{r}'d\mathbf{r}'' . \tag{5}$$

The bracket [ ] in Eqs. (3) and (4) denotes antisymmetrization, i.e.,

$$[\langle mn|V|st\rangle] \equiv \langle mn|V|st\rangle - \langle mn|V|ts\rangle . \tag{6}$$

In Eqs. (3) and (4), the indices *a* and *b* stand for hole

states; their corresponding sums range over the core. The indices *i* and *j* stand for particle states; their corresponding sums range over all positive states outside the core. The eigenvalues of these equations are the energy differences between (*N*±1)-electron states and the ground state,

$$\epsilon_n = \pm(E_n^{N\pm 1} - E_0^N) . \tag{7}$$

For hole states, the energies are negative. The energy  $\epsilon_n$  of a particle state is negative only when it is a bound state.

This has to be compared with some other methods such as the multiconfiguration Hartree-Fock method (MCHF) [1,13] in calculating the electron affinity of Ca<sup>-</sup>. In MCHF, one tries to solve for *E*<sub>*n*</sub><sup>*N*+1</sup> and *E*<sub>0</sub><sup>*N*</sup> separately.

\*Electronic address: liaw@phys.nchu.tw.edu

The electron affinity is determined by taking the difference of these two values. The ground energy is about 680 eV while the experimental value for the electron affinity is a few tens of meV. This means one has to solve both for  $E_0^N$  and  $E_n^{N+1}$  with an accuracy of 0.001% level. In addition, the relativistic effect, which is at least of the order of meV [13], has to be included by some estimation method.

Since we solve for  $\epsilon_n$  directly, a negative eigenvalue for a particle state means the state is a bound state. Because all the hole and particle states (bounded or not) satisfy the same equation, we can solve it using the  $B$ -spline method [14]. The solution of the  $B$ -spline method is a pseudocomplete set of wave functions which are known to have the following two properties: (i) there are a few wave functions in this set of solutions matching the exact low-lying bound states of the system very well; (ii) the whole set of solutions can be considered as a good approximation to the exact complete set of states. From the experience that we solved either the DF equation or Brueckner equation for alkaline atoms [10], we know that in addition to energies of hole states, the lowest few energies of particle states also match the exact values very well if the number of  $B$ -spline bases is 30 or larger. We therefore solve the Brueckner equation for  $\text{Ca}^-$  using the  $B$ -spline method with the number of bases equal to 30 and the size of the box equal to 40 a.u. We expect to see negative-energy solutions for hole states:  $1s$ ,  $2s$ ,  $3s$ ,  $4s$ ,  $2p_{1/2}$ ,  $3p_{1/2}$ ,  $2p_{3/2}$ , and  $3p_{3/2}$ , and for particle states  $4p_{1/2}$  and  $4p_{3/2}$  if they exist under the Brueckner approximation. We therefore look for a negative-energy solution in the spectrum with angular momentum  $l=1$ . We first solve the DF equation and list the first ten eigenvalues of the solutions for both  $p_{1/2}$  and  $p_{3/2}$  in the second column of Table I. There is no negative-energy solution other than the hole states  $2p_{1/2}$ ,  $3p_{1/2}$ ,  $2p_{3/2}$ , and  $3p_{3/2}$ . It is well known that there is no bound state of  $\text{Ca}^-$  under the DF approximation.

We then continue to solve the Brueckner equation. The second-order self-energy  $\Sigma^{(2)}$  that appears in the Brueckner equation has an essential difference from the first-order self-energy  $\Sigma^{(1)}$ . First,  $\Sigma^{(1)}$  depends on hole states only while  $\Sigma^{(2)}$  depends on both hole and particle states. For the DF equation, which does not include  $\Sigma^{(2)}$ , one can solve the coupled equation for hole states self-consistently to a high accuracy, and then use these hole state solutions to generate the whole spectrum. For the Brueckner equation we have to solve all orbitals simultaneously. Second,  $\Sigma^{(1)}$  is energy independent while  $\Sigma^{(2)}$  depends on the eigenvalue  $\epsilon_n$  itself. Thus we can generate the whole spectrum once and for all in the DF case, but we have to use some kind of method to eliminate the energy dependence in  $\Sigma^{(2)}$  in order to be able to solve the whole spectrum by iteration. For the present we use an approximation that we used in the cases of alkaline atoms [10] and boron [11]. Namely, we fix  $\epsilon_n$  in the denominator of  $\Sigma^{(2)}$ . The criterion of using this approximation is described in Ref. [11] and numerical examples are presented in Refs. [10] and [11].

Under this approximation we are able to iterate the process of solving the Brueckner equation. We start from

TABLE I. First ten eigenvalues of  $p_{1/2}$  and  $p_{3/2}$  of the first three iterations in solving the Brueckner equation using the  $B$ -spline method.

Label	DF	First iteration	Second iteration
$l=1, j=1/2$			
$2p_{1/2}$	-13.7311	-13.6826	-13.6486
$3p_{1/2}$	-1.3493	-1.4050	-1.3905
$(4p_{1/2})$	0.0023	-0.0020	0.0004
	0.0063	0.0026	0.0029
	0.0114	0.0078	0.0081
	0.0193	0.0156	0.0160
	0.0384	0.0330	0.0337
	0.0548	0.0539	0.0540
	0.0624	0.0602	0.0605
	0.1403	0.1229	0.1256
$l=1, j=3/2$			
$2p_{3/2}$	-13.5921	-13.5441	-13.5101
$3p_{3/2}$	-1.3337	-1.3893	-1.3748
$(4p_{3/2})$	0.0023	-0.0018	0.0006
	0.0064	0.0027	0.0030
	0.0117	0.0080	0.0084
	0.0201	0.0162	0.0166
	0.0399	0.0346	0.0354
	0.0545	0.0534	0.0536
	0.0650	0.0626	0.0629
	0.1492	0.1320	0.1347

the DF wave functions. Namely, for the first iteration we use the pseudocomplete set of DF wave functions obtained from the  $B$ -spline method to calculate the right-hand side of Eq. (2). The solutions of the first iteration are listed in the third column of Table I. Again, only the first ten eigenvalues for both  $p_{1/2}$  and  $p_{3/2}$  are listed. Notice that there is one more negative eigenvalue than the DF energies (column 2) for each of  $p_{1/2}$  and  $p_{3/2}$  spectra. We accordingly assign them as  $4p_{1/2}$  and  $4p_{3/2}$ , respectively. These two eigenvalues,  $-0.0020$  a.u. (54 meV) and  $-0.0018$  a.u. (49 meV), are very close to the results of Johnson, Sapirstein, and Blundell [4] and Dzuba *et al.* [5]. This is what we expected since both Johnson, Sapirstein, and Blundell and Dzuba *et al.* actually solve the same equation as Eq. (2) using the DF wave functions. However, the Brueckner equation has to be solved self-consistently. Thus we take this set of solutions to calculate the right side of Eq. (2) once again and then obtain solutions of the second iteration. The resultant spectrum, listed in column 4 of Table I, nevertheless, shows no bound particle states. With more iterations, the eigenvalues of potential bound states  $4p_{1/2}$  and  $4p_{3/2}$  stay as positive values. We have also increased the number of bases to 40 and the size of the box to 60 a.u. Still, no bound particle states are found. We therefore conclude that there are no bound states for  $\text{Ca}^-$  under the Brueckner approximation.

The conclusion may not be too surprising. In Green's-function formalism, we consider  $\text{Ca}^-$  as a core ( $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ ) plus one electron. Because this core is "soft," namely, it is a closed subshell rather than a

closed shell, the correlation between hole states and particle states is expected to be large. The order by order calculation based on the many-body perturbation theory (MBPT) is certainly no good. Here in Green's-function formalism we do have summed a subset of all order contributions in each "order" of approximation [15]. The eigenvalue of interest may or may not converge fast enough. In the case of boron which also has a soft core ( $1s^2 2s^2$ ), the results of the Brueckner approximation are pretty good [11]. However, there is no guarantee that the Brueckner approximation works well for other systems with a "soft" core. Our calculation for  $\text{Ca}^-$  shows that the Brueckner approximation is not adequate. That the bound states appear in the first iteration during the process of solving the Brueckner equation is fortuitous.

A better way to study  $\text{Ca}^-$  is to regard  $\text{Ca}^-$  as a system with a "hard" core ( $1s^2 2s^2 2p^6 3s^2 3p^6$ ) plus three valence electrons. One can first freeze the "hard" core and solve the three-electron system and then relax the core to include core-polarization effects. This picture should work better because the dominant correlations (the valence-valence interactions) are accounted for completely in the first step. The core polarization is much smaller and can be calculated by some approximation method. The Green's-function formalism can indeed be generalized to deal with systems with a core plus two or three electrons. The generalization for two-electron sys-

tems had been explicitly constructed by Liaw, Feldman, and Fulton [16]. For three-electron systems, one has to start from the three-particle Green's function. Detailed work still waits to be done. On the other hand, one can use configuration-interaction or MCHF methods to solve three-electron systems to a very high accuracy [1,8]. The core polarization then is not to be included in a perturbative way as in the Green's-function formalism, van der Hart, Laughlin, and Hansen [8] use a model potential to account for the core-polarization effects and obtain a very accurate ground-state energy of Ca.

In conclusion, we found that the bound states of  $\text{Ca}^-$  are still elusive on the theoretical side. So far there is no satisfactory relativistic *ab initio* calculation that can produce the electron affinity close to recent experiments. And perturbation theory of any kind seems unable to obtain converging bound states. On the other hand, the MCHF or CI calculations are nonrelativistic and their results do not agree with each other. The best theoretical value that agrees with recent experiments is the model-potential calculation done by van der Hart, Laughlin, and Hansen [8].

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