

## Fine structure of $\text{Ca}^-$ , $\text{Sr}^-$ , $\text{Ba}^-$ , and $\text{Ra}^-$ from the many-body theory calculation

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Atomic many-body theory methods are used to calculate the fine structure of negative ions formed by binding a  $p$  electron into an open shell,  $\text{Ca}^-$ ,  $\text{Sr}^-$ ,  $\text{Ba}^-$ , and  $\text{Ra}^-$ . This binding is due to a strong correlation potential acting between the electron and the neutral atom. Comparison with experimental data shows that the second order many-body perturbation theory calculation overestimates the correlation potential by 10% to 15%. Scaling factors are introduced in the correlation potential to reproduce experimental binding energies of the lower  $p_{1/2}$  components. This procedure yields fine-structure intervals in excellent agreement with experiment for  $\text{Ca}^-$ ,  $\text{Sr}^-$ , and  $\text{Ba}^-$ , and allows us to predict that in  $\text{Ra}^-$  the  $p_{1/2}$  state is bound by 100 meV, and  $p_{3/2}$  is a resonance at 16 meV in the continuum. [S1050-2947(97)06303-8]

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In 1987 the stability of the negative ion of  $\text{Ca}^- 4s^2 4p$  was demonstrated both theoretically [1] and experimentally [2], and the first values of its electron affinity were produced, 45 and  $43 \pm 7$  meV, respectively. These works opened up a whole new area in the physics of negative ions. Subsequently, a number of calculations of the weakly bound negative ions of Ca and heavier alkaline-earth atoms [3–8] were published. They reported the electron affinity of Ca to be close to or greater than the values quoted above, and predicted the increase of electron affinity for Sr and Ba. These ions are formed by binding an electron into the  $np$  state by closed shell  $ns^2$  atoms. The effect of binding is due to the large dipole polarizability of the corresponding atoms, which gives rise to a strong polarization potential acting between the atom and the electron. The relativistic many-body theory calculation for  $\text{Ca}^-$ ,  $\text{Sr}^-$ , and  $\text{Ba}^-$  [9,10] showed that the spin-orbit interaction has a pronounced effect on the negative ion binding, since the fine-structure splitting  $\Delta E_{\text{fs}}$  is comparable to the binding energies (for  $\text{Ra}^-$  it is even greater, so that the  $p_{3/2}$  state is a resonance in the continuum [11]).

Later experimental studies [12,13] suggested that the true binding energy of the  $4p$  electron in  $\text{Ca}^-$  is smaller, and probably around 20 meV. In a thorough multiconfiguration Hartree-Fock (MCHF) calculation [14] it was shown that core-valence correlations (i.e., correlations between the three valence electrons  $ns^2 np$  and the  $\text{Ca}^{2+}$  core) indeed reduce the binding energy (see Table I). Even smaller electron affinities were obtained in the configuration-interaction calculation [15] and the MCHF work [16], 17.7 and 7.2 meV, respectively. The latter calculation, which included single-electron excitations from the core, also produced the electron affinities of 16 and 113 meV for Sr and Ba, smaller than in earlier calculations. On the whole, the large scatter of the theoretical binding energy values shows that precise calculation of energy levels in strongly correlated systems is still beyond the capacity of even most sophisticated methods and

approaches. This is particularly true for negative ions where very high absolute precision is needed to obtain relatively accurate values of small electron affinities.

Recently a new experimental technique has been developed, and very accurate binding energies of both fine-structure components of the negative ions of Ba [17], Ca [18], and Sr [19] have been obtained (Table I). This puts an end to the uncertainty about electron binding to the alkaline-earth atoms. The absolute precision of 0.1 meV achieved in the experiments sets a very high standard for any future calculations. On the other hand, as was mentioned in [11], theoretical predictions of the  $np_{1/2} - np_{3/2}$  fine-structure intervals  $\Delta E_{\text{fs}}$  from fully relativistic calculations should be much more reliable than the binding energies. Indeed, the value we obtained for Ba,  $\Delta E_{\text{fs}} = 57$  meV [9,10], is in good agreement with the measured  $\Delta E_{\text{fs}} = 55.0$  meV [17]. However, for Sr and especially for Ca our predictions [9] are considerably greater than the experimental values. In all three cases the calculated binding energies are larger than the experimental values, as are the fine-structure intervals. Below we give a simple physical explanation of this situation.

Our calculations are based on a many-body theory approach first applied to negative ions in the nonrelativistic version in [20] and later used in relativistic calculations [7,9,10]. The quasiparticle wave function of the outer electron in the negative ion is found from the exact single-particle (Dyson) equation,

$$H_0 \psi(\mathbf{r}) + \int \Sigma_E(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}' = E \psi(\mathbf{r}). \quad (1)$$

The interaction between this electron and the atomic core is described in terms of a nonlocal energy-dependent correlation potential  $\Sigma_E(\mathbf{r}, \mathbf{r}')$ , which is added to the zeroth-order Dirac-Fock Hamiltonian  $H_0$  of the neutral atom. The correlation potential can be presented as a perturbation theory expansion in terms of the residual electron-electron interaction. The terms of the series are best described using diagrams. The main contribution to  $\Sigma_E(\mathbf{r}, \mathbf{r}')$  is then given by the lowest (second-) order diagrams.

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TABLE I. Binding energies and fine-structure intervals of the alkaline-earth negative ions (in meV).

Ion	SO <sup>a</sup>	Present results			Other calculations		
		SF <sup>b</sup>	SSO <sup>c</sup>	Expt. <sup>d</sup>	MCHF <sup>e</sup>	MCDF <sup>f</sup>	MBPT <sup>g</sup>
Ca <sup>-</sup> 4 <i>p</i> <sub>1/2</sub>	63.5		24.53	24.55(10)	41.9	55.41	19
Ca <sup>-</sup> 4 <i>p</i> <sub>3/2</sub>	57.7	0.8957	19.58	19.73(10)	37.8	50.16	13
$\Delta E_{fs}$	5.8		4.95	4.82	4.1	5.25	6.2
Sr <sup>-</sup> 5 <i>p</i> <sub>1/2</sub>	105.9		52.11	52.12(5)		103.76	54
Sr <sup>-</sup> 5 <i>p</i> <sub>3/2</sub>	82.5	0.8665	32.22	32.236(20)		81.03	29
$\Delta E_{fs}$	23.4		19.89	19.88		22.73	25
Ba <sup>-</sup> 6 <i>p</i> <sub>1/2</sub>	212.5		144.61	144.62(6)		217.24	
Ba <sup>-</sup> 6 <i>p</i> <sub>3/2</sub>	150.5	0.8592	89.84	89.60(6)		161.87	
$\Delta E_{fs}$	62.0		54.77	55.02		55.37	
Ra <sup>-</sup> 7 <i>p</i> <sub>1/2</sub>	161.6		100.2				
Ra <sup>-</sup> 7 <i>p</i> <sub>3/2</sub>	18.7	0.86	16.0				
$\Delta E_{fs}$	142.9		116.2				

<sup>a</sup>Results obtained from the Dyson equation with the second-order correlation potential.

<sup>b</sup>Scaling factor (SF) for the second-order correlation potential chosen to reproduce the experimental binding energies of the  $np_{1/2}$  state in Ca<sup>-</sup>, Sr<sup>-</sup>, and Ba<sup>-</sup>. For Ra we use the SF close to that of Ba.

<sup>c</sup>Results obtained with the scaled second-order correlation potential.

<sup>d</sup>Precise binding energies obtained by the Aarhus group for Ca<sup>-</sup> [18], Sr<sup>-</sup> [19], and Ba<sup>-</sup> [17].

<sup>e</sup>Multiconfiguration Hartree-Fock calculations [14] with model core-polarization and dielectronic correction, relativistic shifts, and spin-orbit interactions.

<sup>f</sup>Multiconfiguration Dirac-Fock calculations [23] using GRASP2 package [24], core-valence correlations omitted.

<sup>g</sup>Dyson equation method of the many-body theory with higher-order diagrams included in the correlation potential by means of the coupled-cluster equations [22], fine structure intervals from the second-order calculation.

The binding energies of the  $np_{1/2,3/2}$  electron obtained with the second-order (SO) correlation potential are shown in Table I. Note that they are slightly different from those we obtained in [9,10], since we have improved the numerical accuracy in the present calculation. The calculated binding energies are considerably larger than the experimental ones. Greater binding of the outer  $p$  electron means that its wave function is more compact than the true one. By means of the normalization condition, it has larger magnitude at small distances. Since the relativistic spin-orbit interaction is strongest in the vicinity of the nucleus, the fine-structure interval corresponding to the calculated wave function is also greater than the experimental one. One can see from the table that the largest relative error for  $\Delta E_{fs}$  is for Ca, where the  $p_{1/2}$  binding energy is overestimated by a factor of 2.5.

Obviously, the approximation based of the SO diagrams overestimates the true strength of the correlation potential. There are ways of including dominating series of higher-order diagrams [21] which significantly improve the accuracy of the correlation potential method for neutral atoms. However, to investigate the relation between the binding energy and the fine-structure interval, in the present work we use the following semiempirical procedure. A numerical factor is introduced before the SO correlation potential. Its value is chosen to reproduce the experimental binding energy of the lower  $p_{1/2}$  negative ion state. This factor is then used to calculate the binding energy of the  $p_{3/2}$  state, and the fine-structure splitting is calculated. This enables us to estimate the size of the higher-order contribution in  $\Sigma_E(\mathbf{r}, \mathbf{r}')$ , and check the consistency of the experimental and theoretical data on the fine-structure intervals.

The results obtained with the scaled correlation potential

are shown in the 4th column of Table I. Figure 1 shows the radial quasiparticle wave function of the  $4p_{1/2}$  state in Ca<sup>-</sup>. It is obvious that in agreement with the discussion above, the reduction of the correlation potential gives rise to smaller electron densities at small distances, and hence, smaller fine-structure intervals. The values of the scaling factor show that higher-order diagrams must give a 10% to 15% reduction on the SO correlation potential. The fine-structure intervals ob-

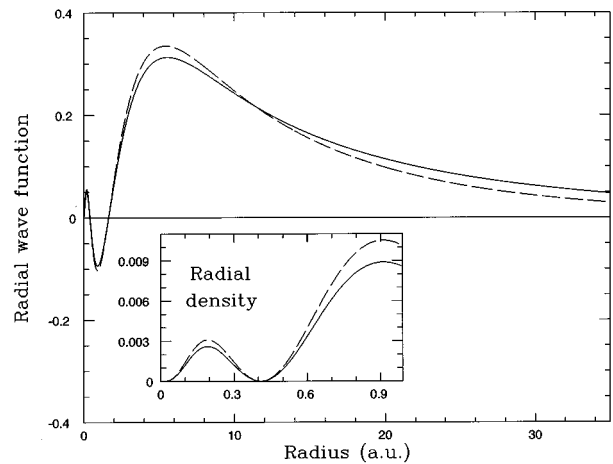


FIG. 1. Quasiparticle wave function of the Ca<sup>-</sup> 4*p*<sub>1/2</sub> state obtained using the second-order correlation potential ( $E = -63.5$  meV, dashed curve), and the scaled second-order correlation potential ( $E = -24.2$  meV, solid curve). Shown on the inset are radial densities of the  $4p_{1/2}$  electron at small distances. The decrease of the radial density in the latter calculation corresponds to a 20% reduction of the corresponding fine-structure interval.

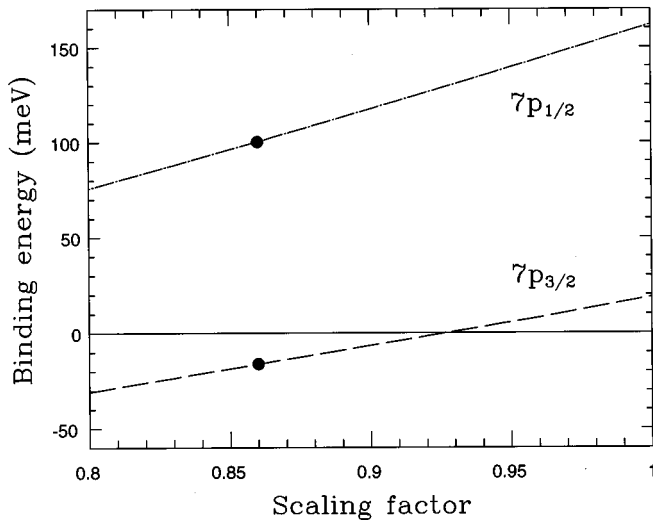


FIG. 2. Dependence of the binding energies of the  $7p_{1/2}$  and  $7p_{3/2}$  states of  $\text{Ra}^-$  on the magnitude of the scaling factor for the second-order correlation potential. Solid circles show our predictions obtained with the scaling factor of 0.86 inferred from the calculation of  $\text{Ba}^-$ .

tained with the scaled correlation potential are in excellent agreement with experiment. The scaling factors are still close to unity, which means that the radial dependence of the SO correlation potential  $\Sigma_E(\mathbf{r}, \mathbf{r}')$  is basically correct.

The scaling factors for Sr and Ba are close, and we can assume that the value of 0.86 can be used to correct the SO correlation potential for Ra. After this, the upper  $7p_{3/2}$  component becomes unbound, and thus represents a  $p_{3/2}$ -wave resonance in the electron-atom continuum at 16 meV. Our prediction for the binding energy of the  $\text{Ra}^-7p_{1/2}$  state is 100 meV. In Fig. 2 we show the dependence of the binding energies of the  $7p_{1/2}$  and  $7p_{3/2}$  states on the value of the scaling factor. As expected for the low-lying states with  $l > 0$  [25], the dependence of the energies on the strength of the potential is close to linear throughout the whole near-threshold region. Figure 2 shows that a 1% error in the scaling factor converts into a few percent error in the energy of the  $7p_{1/2}$  state, and 10% error in the energy of the  $7p_{3/2}$  resonance. Given the closeness of the scaling factors for Sr and Ba, we estimate this to be the accuracy of our prediction.

The interesting feature one observes in the electron affinities of the alkaline-earth atoms is the reversal of the trend of

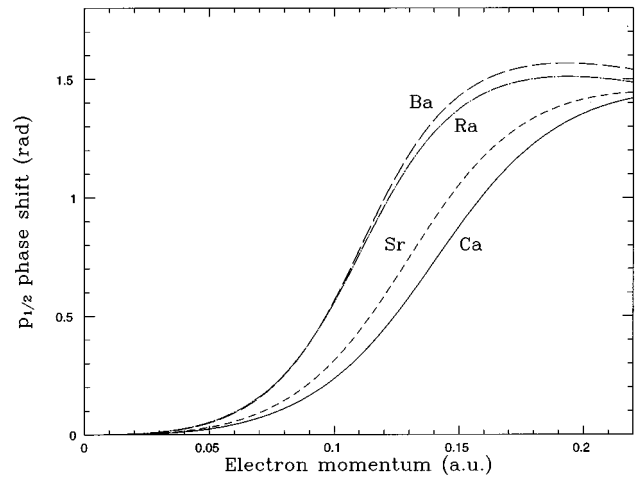


FIG. 3. The  $p_{1/2}$  phase shifts for the electron in the static Dirac-Fock potential of the ground state Ca, Sr, Ba, and Ra.

its increase when going from Ba to Ra. It can also be seen in the atomic ionization potentials (6.11, 5.69, 5.21, and 5.27 eV for Ca, Sr, Ba, and Ra, respectively), energies of the  $ns^2 - nsnp$  atomic excitations, and atomic dipole polarizabilities (170, 186, 270, and 260 for Ca through to Ra [26]). We believe that this is mostly a relativistic effect. To illustrate this we plot in Fig. 3 the Dirac-Fock  $p_{1/2}$  phase shifts for the electron in the field of the atom in the ground state. In the absence of the correlation potential they have a resonant behavior [3,8]. The shapes of the curves tell us that the static Dirac-Fock potential acting on the  $p_{1/2}$  electron is slightly weaker in Ra than in Ba. Combined with a smaller dipole polarizability, and consequently, a slightly weaker correlation potential, this leads to the smaller  $p_{1/2}$  binding of the Ra negative ion. On the other hand, there are no reasons to suspect that the contribution of higher-order diagrams to the correlation potential in Ra should be much different from those in Sr or Ba. Thus, the scaling factor of 0.86 must give reliable estimates of the  $7p$  energies in  $\text{Ra}^-$ .

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