Effect of core-valence electron correlation in low-energy electron scattering with Ca atoms

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R-matrix calculations have been carried out to investigate the effect of core-valence electron correlation on the scattering of electrons with Ca atoms at low energies. While the major feature of the d-wave shape resonance with a peak near 1.3 eV in the total cross section can be reproduced by including only the correlation among the valence electrons, we show that the existence of a low-energy peak near 0.15 eV, which has also been observed experimentally, can be obtained only if the correlations between the valence and core electrons are considered. This low-energy peak is shown not caused by a shape resonance, but rather due to the rapid decrease of the s- and p-wave phase shifts with collision energies. The present result also indirectly supports the previous conclusion that core-valence electron correlation is responsible for bringing the electron affinity of Ca^- from 72 to 15 meV, i.e., to a value which is much closer to the experiment. [S1050-2947(98)11509-3]

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In the past two decades, both the electron scattering and the negative ions of alkaline-earth atoms have been extensively studied by many authors [1–24]. In particular, most of these works were carried out after the discovery of the existence of stable Ca^- ions [5,6]. For electron collisions with Ca atoms, the early theoretical study by Fabrikant [1] is a close-coupling calculation based on atomic wave functions generated from a model potential. In the work of Amusia *et al.* [4] and later of Gribakin *et al.* [12] and Dzuba, Flambaum, and Suskov [15], the Dyson equation was solved with the effective potential obtained by perturbation theory. Several kinds of model potentials have also been used by different authors [3,9]. In other calculations, the relativistic polarized orbital method was applied by Semytkowski and Sienkiewicz [16]. In a recent paper, Yuan and Fritsche [24] used the R-matrix method to study low-energy electron collisions with Ca atoms where the correlation between the valence electrons is fully considered. The R-matrix method was also used by Kim and Greene [8] earlier, but it was restricted to the p-wave phase shift and the binding energy of the negative ion only.

Many authors have investigated the binding energy of the Ca^- negative ion. The first theoretical prediction of stable Ca^- ions was based on a multiconfiguration-Hartree-Fock (MCHF) calculation [5], where the electron affinity was predicted to be 45 meV. In a later improved MCHF calculation, Fischer [7] arrived at an electron affinity of 70 meV without the relativistic corrections. This value was believed to be the correct limit if one only includes correlations among the valence electrons [7,8,21,22]. The first experimental observation of the stable Ca^- ions by Pegg *et al.* [6] gave the electron affinity to be 43 ± 7 meV. But later experiments [18–20] gave smaller values, in the range of 17.5–24.55 meV. Meanwhile, later calculations showed that the affinity of Ca^- is reduced considerably if the core-valence electron correlation is included [21–23]. According to the generalized quantum-defect theory [25], the quantum defect below the threshold is related to the phase shift above the threshold,

and the generalized quantum defect is smooth across the threshold. Therefore, if the core-valence correlation affects the binding energy of the negative ion significantly, it should have a considerable influence on the phase shifts as well as the cross sections near the elastic threshold. In this study, R-matrix calculations are carried out with the core-valence correlation included to show its effects on the electron scattering cross sections.

The R-matrix method for electron-atom collisions was discussed in great detail in Ref. [26]. The present calculations have been carried out using the R-matrix package of Berrington *et al.* [27]. In an R-matrix calculation, the wave function of the $(N+1)$-electron system is given as

$$\Psi_k(X_1,\ldots,X_{N+1}) = \sum_{ij} c_{ijk}\Phi_i(X_1,\ldots,X_N\hat{\mathbf{r}}_{N+1}\sigma_{N+1})$$
$$\times u_{ij}(r_{N+1})$$
$$+ \sum_j d_{jk}\phi_j(X_1,\ldots,X_{N+1}), \qquad (1)$$

where the basis functions under the first sum refer to the N-electron target bound states multiplied by continuum states, and those under the second sum are $(N+1)$-electron bound states. In Eq. (1), X stands for spin (σ) and spatial ($\vec{r}$) coordinates. Bound state orbitals are cast as linear combinations of Slater-type orbitals

$$P_{nl} = \sum_j C_{jnl}r^{I_{jnl}}\exp(-\xi_{jnl}r). \qquad (2)$$

The parameters ξ_{jnl} and I_{jnl}, and the coefficients C_{jnl} for $1s$ to $6s$, $2p$ to $6p$, $3d$ to $5d$, and $4f$ to $5f$ orbitals, which are used in the present calculations, are determined by using the CIV3 code of Hibbert [28] to optimize the ground-state energies of both the neutral atom and the negative ion.

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TABLE I. The minimum and maximum numbers of electrons that are allowed in each valence orbital when a $3p$ electron is removed from the filled core level. This restriction limits the number of configurations that can be included in the treatment of core-valence electron correlation.

Orbital	$3p$	$4s$	$4p$	$3d$	$5s$	$5p$	$4d$	$4f$	$6s$	$6p$	$5d$	$5f$
Minimum	5	1	0	0	0	0	0	0	0	0	0	0
Maximum	5	2	3	3	2	2	2	1	0	1	1	0

We use the widely accepted definition for the core and valence orbitals, i.e. $1s$, $2s$, $2p$, $3s$, and $3p$ are the so-called core orbitals for the present system, and all the other orbitals are the valence orbitals. Thus in the ground configuration we have two valence electrons for the neutral atom and three valence electrons for the negative ion and the electron-Ca collision system. In this calculation, valence correlation is included by allowing all possible excitations of the valence electrons into any of the valence orbitals, excluding the possibility of having more than one electrons in the f orbitals. In order to control the number of configurations to a manageable value, the core-valence correlation is included with restricted excitations. When a $3p$ electron is excited to one of the valence orbitals, the allowed minimum and maximum occupation number of electrons in each of the valence orbitals are given in Table I. This rule is applied to the calculations of the atomic energy levels of Ca as well as to the electron-Ca system.

The atomic energy levels obtained with and without the inclusion of core-valence correlation are presented in Table II, where we also compare the excitation energies to the experimental values [29]. One notes that without the inclusion of core-valence correlation, the order among the $^3D^e$, $^1D^e$, and $^1P^o$ levels is incorrect. With the limited core-valence correlation included in the present calculation, the energy levels of $^3P^o$ and $^1P^o$ are reasonable, but the energy levels of $^3D^e$ and $^1D^e$ still have large errors. As the core-valence correlation is more significant for the ground state than for the excited states, the calculated excitation energies are slightly larger than those obtained without the core-valence correlation. No attempt was made to improve the represen-

TABLE II. Calculated relative positions of the ground state and the first four excited states of Ca. The calculated total energy for the ground state is -676.78668 a.u. without core-valence correlation, and -676.80213 a.u. with the core-valence correlation. The excitation energies are compared to the experimental values [29].

State	Energy (eV)		
	a	b	expt.
$^1S^e$	0.0	0.0	0.0
$^3P^o$	1.6896	2.0305	1.8924
$^3D^e$	2.8806	3.0444	2.5239
$^1D^e$	2.8722	3.1370	2.7090
$^1P^o$	2.8692	3.1764	2.9325

[a]Including valence-electron correlation only.
[b]Including both valence-electron and core-valence electron correlation.

tation of the $^3D^e$ and $^1D^e$ states since they do not play a major role in collisions at low energies, and any attempt to improve them would make the calculation too large to handle.

The present R-matrix calculations are carried out using the five target atomic states listed in Table II. For the continuum orbitals [u_{ij} of Eq. (1)] we include five angular momentum quantum numbers ($l=0$–4) to construct the orbitals, and for each l we have 25 numerical basis functions. For the ($N+1$)-electron correlation terms in Eq. (1), 541 bound states were included for $^2S^e$ symmetry to 1639 bound states for $^2D^e$ symmetry. Both the continuum scattering states and bound states of the negative ion are calculated by the R-matrix method. The negative-ion bound state is calculated by matching the exponentially decaying function in the asymptotic region to the inside solution at the R-matrix boundary ($=60$ a.u.). The negative-ion state can also be calculated by the configuration-interaction method. This means that only the second term on the right-hand side of Eq. (1) is retained in the construction of the negative-ion wave function. Nevertheless, it is found that the first term in the R-matrix expansion is very important for obtaining an accurate electron binding energy, in particular, when the core-valence correlation is included. The binding energies of Ca^- obtained by the configuration-interaction calculation are 61 and 0.9 meV, respectively, without and with the core-valence correlation, while the corresponding R-matrix results are 72 and 15 meV. These numbers are, respectively, quite close to the calculations which include valence electrons only [7,8,10,21,22], and to those including core-valence correlations also [22,23]. Our result of 72 meV obtained including only valence-electron correlation implies that valence correlation has been fully accounted for in the present R-matrix calculation. The value of 15 meV agrees very well with the recent experiments [18–20]. It also agrees with the findings of Ref. [23] that the correlation between the valence electrons and the $3p$ shell accounts for the major improvement.

The present R-matrix results for low-energy electron scattering with Ca atoms are shown in Fig. 1. In Fig. 1(a), the calculated total cross sections are compared to the experiments of Romanyuk et al. [17]. There are two sets of measurements by this group [2,17]. In their earlier measurement, the absolute cross sections were obtained, but the position of the main maximum appears at a lower energy, around 0.7 eV. In the later experiment, a hypocycloidal electron spectrometer was used, and only the relative values of the elastic cross sections were obtained by integrating over a specified range of scattering angles. The main peak in the latter experiment was observed at 1.2 eV, but another peak was found below 0.7 eV. We plotted their new data in Fig. 1(a) by normalizing the experimental data to our calculated value at 1.3 eV, which is close to the peak of the second maximum. Results from two separate R-matrix calculations are shown. The full calculations including core-valence interactions are given by the solid lines, and the calculations neglecting the core-valence interactions are shown as dashed lines. The full calculations are in good agreement with the experimental data. In particular, the position of the second peak, the rise of a cross section below 0.7 eV, and the appearance of a third peak near 2.2–2.4 eV in the experimental data are all well reproduced. In the meanwhile the positions of the minima
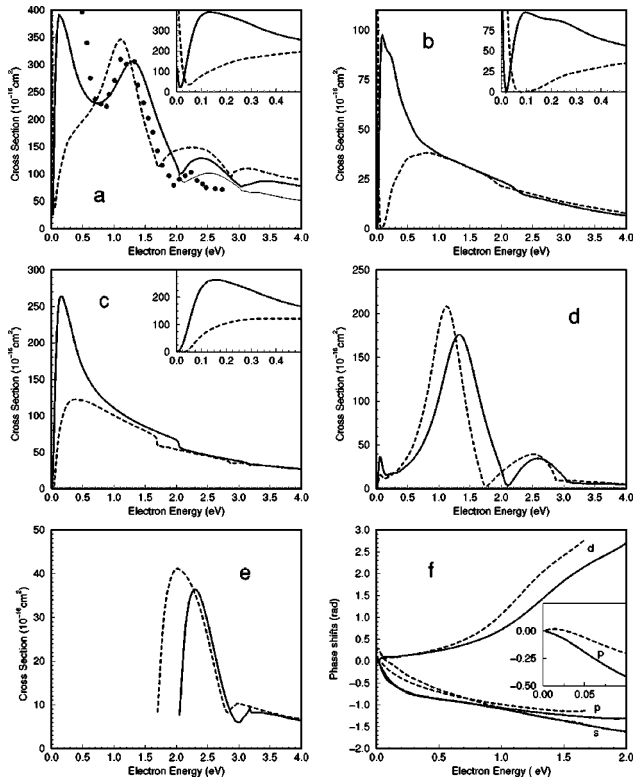
FIG. 1. Cross sections of electron scattering from Ca atoms. (a) The total cross section. (b) The elastic $^2S^e$ partial cross section. (c) The elastic $^2P^o$ partial cross section. (d) The elastic $^2D^e$ partial cross section. (e) The total inelastic excitation cross section to the first excited state. (f) The elastic-scattering phase shifts of the first three partial waves. In the figures, the solid lines represent the results with the core-valence correlation included, and dashed lines the results without the core-valence correlation. The thin solid line in (a) is the elastic cross section above the first excitation threshold, and the filled circles are the experimental data [17].

near 0.8 and 1.9 eV are also predicted by the calculation when the core-valence interactions are included. We note that if the core-valence interaction is neglected, the resulting structures in the higher-energy domain are still similar, but the positions are shifted toward the lower energies. This shift is partly due to the inaccuracy in the theoretical excitation energies. Note that the cross section varies rapidly with collision energies near the threshold. The inset gives an expanded view of the calculated cross sections below 0.5 eV. We did not present earlier theoretical results [1,3,4,9,12,15,16]. Most of them predicted a rather smooth cross section in the energy domain covered, and reproduced only the middle peak seen in the experiment. Although a much sharper structure around 0.1 eV was predicted as due to a p-wave shape resonance in the calculations of Kurtz and Jordan [3] and Amusia *et al.*, the predicted p-wave shape resonance is not consistent with the well-known fact that Ca has one single stable negative ion in the ^2P state. We comment that a 0.5-eV retarding potential was used in the experiment [17] which rendered experimental data not reliable below 0.5 eV.

We next identify the origin of the structures in Fig. 1(a). The partial cross sections for the $^2S^e$ and $^2P^o$ symmetries are shown in Figs. 1(b) and 1(c), respectively. Clearly the first calculated peak in Fig. 1(a) below 0.7 eV is due to

contributions from these two partial waves. The ''peak'' in each partial wave cannot be identified with any resonances. In Fig. 1(f) the elastic phase shifts below the first excitation threshold are shown. One can observe that the structure is due to the rapid change of s- and p-wave phase shifts at low energies. In fact, the phase shift for an s wave passes through zero at about 0.025 eV, where the partial-wave cross section goes to zero [see the inset in Fig. 1(b)] to produce a Ramsauer-Townsend minimum, and the p-wave phase shift drops rapidly [see the inset in Fig. 1(f)] to produce a sharply rising p-wave scattering cross section [see the inset in Fig. 1(c)]. The sum of these two partial waves produces the sharp feature in the first peak. In contrast, in earlier calculations, for example, by Kurtz and Jordan [3], the p-wave phase shift displays a very sharp increase through $\pi/2$ at 0.06 eV, and thus they predicted a p-wave resonance.

The $^2D^e$ partial cross sections are shown in Fig. 1(d). The first structure is very small and will be neglected. The two outer peaks are responsible for the second and third maxima in Fig. 1(a). In Fig. 1(d), these two peaks can be approximately identified as the $4s^23d$ $^2D^e$ and $4s4p^2$ $^2D^e$ states. They are interpreted as shape resonances. In particular, the phase shift of the first peak indeed changes nearly by π, as seen in Fig. 1(f). The near-zero background phase shift also gives this shape resonance a Lorentzian profile. It appears that the second structure also resembles a shape resonance, and may be attributable to the strong coupling between $4s^23d$ $^2D^e$ and $4s4p^2$ $^2D^e$ states. In Fig. 1(e) we also show the inelastic excitation cross sections above the first excitation threshold. The peak originates predominantly from the $^2D^e$ partial cross sections, i.e., from the second shape resonance of Fig. 1(d).

In the figures above we also show the results from calculations without including the core-valence interaction. In such calculations the excitation thresholds are not well reproduced with respect to the experimental values, and thus the resulting cross sections are shifted. We note in particular that the first peak does not appear if the core-valence correlation is not included. From Table II, we note that the experimental $^3P^o$ excitation threshold is 1.8924 eV, but calculations with and without core-valence correlation give 2.0305 and 1.6896 eV, respectively. The discrepancy in the threshold energies mostly accounts for the differences in the two calculations and the experimental results, as can be seen in Fig. 1(a) and in Fig. 1(d). The R-matrix code [27] used in the present calculation provides the facility of using the experimental experimental excitation thresholds in the calculation of cross sections. Nevertheless, when a strong resonance structure occurs near the threshold, as in the present case around 2.0 eV, an artificial change of the threshold energy may cause changes in the strength or even in the characteristics of the resonance. In the present calculation we do not use experimental threshold energies, and the results presented are completely from *ab initio* calculations.

In summary, core-valence correlation effect in electron scattering from Ca atoms and in the binding energy of Ca$^-$ ions were studied by the R-matrix method. The inclusion of core-valence correlation is shown to be essential for obtaining the correct electron affinity of Ca$^-$. The core-valence interaction is also shown to be very important for predicting cross sections for electron collisions with Ca atoms at low

energies. This interaction gives an additional peak of the cross section just above the elastic threshold. The electron affinity as well as the electron-scattering cross sections obtained are in reasonable good agreement with experimental values when core-valence interactions are accounted for.

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