

that has the same general shape as the observed cross section in the energy region ± 100 meV around the 2P threshold and predicts a sharp drop of approximately a factor of 2 within 8 meV near the 2P thresholds. This result suggests that the spin-orbit interaction of the atomic electron is more important than that of the detached electron, but that both are negligible except in the region of the doublet.

Such calculations have also been done for Cs, using solutions of three-state ($6s-6p-5d$) coupled-equation expansion for both the initial and final states. The $^1P^\circ$ elastic-scattering phase shift was found to resonate strongly just below the $6p$ excitation threshold, rising by over $\pi/2$ in the last 150 meV, yielding a very sharp minimum in the photodetachment cross section near threshold. The final-state wave function was found to be dominated by the configuration $6p7s$ in this region with a strong admixture of $6p5d$, perhaps explaining the failure of the resonance to appear in earlier two-state ($6s-6p$) calculations.⁸ This assignment is supported by detailed study of the total photodetachment matrix element, which reveals that the maximum in the sum of the elements connecting the ground state with the configuration $6p7s$ is associated with the zero in the sum of the remaining elements, in accord with the theory of Fano.⁶ Similar calculations are underway for Rb^- , but, based on the Cs^- results, we make the tentative assignment $5p6s$ to the observed Rb^- resonances.

In summary we have measured the electron

affinities of all of the alkalis using laser photo-detachment techniques and have observed strong resonances resulting from autoionizing states in the heavy alkalis. These resonances are by far the narrowest ever observed in electron-atom system. The electron-affinity results are summarized in Table I.

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Application of Scattering Theory to the Calculation of Alkali Negative-Ion Bound States*

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Binding energies of the ground 1S states of the alkali negative ions are calculated using the coupled equations of scattering theory, based on semiempirical effective potentials for the neutral atoms. An additional true bound state with configuration 3P lying just below the first excited state of the neutral atom is predicted for every species except Li^- .

A number of calculations have been made of the electron affinities of the alkali atoms, both *ab initio*¹⁻³ and based on semiempirical potentials for the neutral atom,⁴⁻⁶ using both single-configuration^{1,4} and multiconfiguration^{2,3,5,6} negative-ion wave functions. Of these several sets of

results, those of Weiss² and Schwarz⁵ are in the best overall agreement with recent experimental results.⁷ There has not yet been a calculation in good agreement with experiment for Cs^- . None of these calculations has predicted more than one true bound state (as opposed to autoionizing

states) of the alkali negative ions.

This work demonstrated that the intrashell correlation energy is large for all the alkali negative ions, i.e., that some sort of multiconfiguration treatment of the two outer electrons is essential. The intershell correlation energy was assumed to be less important,² particularly for the lighter species in which the core polarization is smaller. The magnitude of the effect has not, however, been specifically investigated.

The method to be described here differs from any previously used in one important respect. The coupled-equations formalism usually applied to electron scattering by the N -electron (neutral alkali, in this case) system is used with all channels closed to define an eigenvalue problem for the $(N+1)$ -electron system. This technique has been previously used to obtain the unshifted positions of Feshbach resonances in electron-He⁺ scattering,⁸ and to calculate bound-state energies for neutral atoms and positive ions.⁹ To our knowledge, it has never before been applied to negative ions, nor applied to any system using the effective-potential method. Successful application to negative ions, however, might appear unlikely, considering the very large number of terms required in earlier multiconfiguration calculations. This is not necessarily the case, as will be seen.

$$\left[\frac{d^2}{dr^2} - \frac{l_2(l_2+1)}{r^2} + V(r) + k_a^2 \right] F_{\gamma'\gamma''}(r) = \sum_{\gamma''} [V_{\gamma'\gamma''}(r) + W_{\gamma'\gamma''}(r)] F_{\gamma''\gamma}(r), \quad (3)$$

where $V_{\gamma'\gamma''}$ and $W_{\gamma'\gamma''}$ are the direct and exchange matrix operators resulting from the electrostatic interaction $(\vec{r}_1 - \vec{r}_2)^{-1}$ between the two outer electrons, k_a^2 is a diagonal matrix of energies of the second electron relative to the atomic states, and the $F_{\gamma'\gamma}(r)$ are the radial parts of $\varphi_{\gamma'\gamma}(\vec{X})$. This is the usual infinite set of coupled integro-differential equations of scattering theory, and $F_{\gamma'\gamma}(r)$ is usually thought of as the radial wave function for the scattered electron in channel $\gamma' = a'l_2'$ for the incident electron in channel $\gamma = al_2$.

Solution of the set of equations (3) for some channels open (some $k^2 \geq 0$) results in the usual scattering matrix as a function of k^2 . If all channels are closed (all $k^2 < 0$), however, all the functions $F_{\gamma'\gamma}(r)$ are bounded at large radial distance, and (3) becomes a matrix eigenvalue problem, having solutions only for certain values of k^2 which are eigenenergies of the two-electron system. The method is obviously very flexible, in

As in all other model-potential calculations, we consider the alkali negative ions as two-electron systems, and represent the interaction between the outer electrons and closed-shell core electrons in an approximate manner. The total wave function for the two-electron system is written as a partial-wave expansion in LS coupling over functions of the type

$$\Phi_{\gamma}(LSM_L M_S | \vec{X}_1 \vec{X}_2) = \sum_{\gamma'} c_{\gamma'\gamma} \psi_{a'}(\vec{X}_1) \varphi_{\gamma'}(\vec{X}_2), \quad (1)$$

where \vec{X}_1 and \vec{X}_2 represent all space and spin coordinates of the two electrons, the $\psi_a(\vec{X}_1)$ are valence-electron wave functions of the neutral atom, the $\varphi_{\gamma'}(\vec{X}_2)$ are expansion coefficients which are functions of the coordinates of the second electron, and $c_{\gamma'\gamma}$ represents the appropriate antisymmetrization and vector-coupling operations. The functions ψ have radial parts P which satisfy

$$\left[\frac{d^2}{dr^2} - \frac{l_1(l_1+1)}{r^2} + V(r) + \epsilon_a \right] P_a(r) = 0, \quad (2)$$

where $-\epsilon_a$ is the ionization energy of state $a = nl_1$ of the neutral atom and $V(r)$ is some effective central potential representing the interaction of the valence electron with the atomic nucleus and closed-shell core.

Putting (1) into the variational expression for the total energy, and using (2), we obtain

addition to being variational, and has the added advantage that wave functions are obtained in a form that is extremely convenient for subsequent photodetachment calculations.

We take for the effective potential

$$V(r) = V(\lambda, r) + V_p(r), \quad (4)$$

the first term of which is the scaled Thomas-Fermi statistical-model potential with limiting forms

$$\lim_{r \rightarrow 0} V(\lambda, r) \sim 2Z/r, \quad \lim_{r \rightarrow \infty} V(\lambda, r) \sim 2/r, \quad (5)$$

where λ is an adjustable parameter which specifies the potential at intermediate distances, and Z is the nuclear charge. The potential $V_p(r)$ represents the effect of induced core moments on the valence electron, and is taken to be

$$V_p(r) = \alpha_d r^{-4} W_8(r_c, r) + \alpha_q r^{-6} W_{10}(r_c, r), \quad (6)$$

where α_d and α_q are the dipole and effective-quadrupole polarizabilities of the core, respectively, and the $W_m(r_c, r)$ are cutoff functions of the form

$$W_m(r_c, r) = 1 - \exp[-(r/r_c)^m]. \quad (7)$$

In specifying the effective potentials for the alkali atoms, the best available value of α_d was adopted, and the remaining parameters λ , r_c , and α_q were adjusted to give the best possible agreement between calculated and experimental values of ϵ_γ in (2). Additional flexibility was introduced by allowing the cutoff radius r_c to be a function of l . We note that although the method

is semiempirical, it does have the distinct advantage of providing a representation of core polarization through $V_p(r)$ in both (2) and (3). Any attempt to take account of this effect in an *ab initio* calculation would require a much more elaborate calculation than has yet been attempted for the alkalis. The solutions of (2) have $n-l-1$ nodes, in contrast to pseudopotential technique,^{4,5} in which the eigenfunction of the valence-electron ground state is nodeless.

In addition to the first-order correction for core polarization through $V_p(r)$ in (2) and (3), we may also include a correction for polarization correlation. This is the so-called "dielectric term" first introduced by Chisholm and Öpik.¹⁰ This term amounts to augmenting $(\vec{r}_1 - \vec{r}_2)^{-1}$ by

$$V_p(r_1 r_2) = -\frac{\alpha_d}{r_1^2 r_2^2} W_6(r_c, r_1) W_6(r_c, r_2) P_1(\cos\theta_{12}) - \frac{\alpha_q}{r_1^3 r_2^3} W_{10}(r_c, r_1) W_{10}(r_c, r_2) P_2(\cos\theta_{12}), \quad (8)$$

where θ_{12} is the angle between the two electrons. For the sake of completeness we have introduced the quadrupole correction not included in earlier work,¹⁰ although its effect was found to be small. Terms similar to $V_p(r)$ and $V_p(r_1 r_2)$ were included in a recent calculation⁶ for Li^- . In other model-potential calculations^{4,5} the effect of core polarization was not represented by a term such as (6) with the correct asymptotic form, but rather through the empirical adjustment of the short-range part of $V(r)$, and no dielectric correction was included in the two-electron problem.

The results are given in Table I. The atomic eigenstates included in the expansion (1) are indicated ($n_0 l$ denotes the lowest valence-electron bound state for the given l), as is the extent to which $V_p(r_1 r_2)$ is included. In the work performed to date $V_p(r_1 r_2)$ has been included explicitly only in $V_{\gamma\gamma}(r)$; the results in row *c* were obtained by evaluating the effect of $V_p(r_1 r_2)$ in $W_{\gamma\gamma}(r)$ as a perturbation. It is clearly more important to include the dielectric core-polarization correction than to include a large number of atomic eigenstates in (1), even for Li^- . The total core-polarization effect also includes the effect of $V_p(r)$, of course, which contributes in a sense opposite to $V_p(r_1 r_2)$.

The effect of adding additional states might be considered surprisingly small, in view of the requirements of other multiconfiguration methods. The Na^- results of Weiss,² for example, show that configurations in addition to $3s^2$ and $3p^2$ contribute over 100 meV to the affinity, whereas the combined effect of adding the $4s$ and $3d$ states in the present work is less than 4 meV. Part of the

explanation is the $3s^2$ Hartree-Fock configuration with which Weiss started, but we also note that the present two-state solutions could in principle be decomposed by Schmidt orthogonalization into the infinite set ($3sns$, $3pnp$) for $n=3, \dots, \infty$.

As a check on the sensitivity of the results to the form of the cutoff functions used in $V_p(r_1 r_2)$, the forms W_3 and W_5 were substituted for W_6 and W_{10} , respectively, and the two-state calculations, row *c*, repeated. The maximum change in the dielectric correction was 10%.

TABLE I. Electron affinities, in eV.

	Li	Na	K	Rb	Cs
1_S state					
a) $n_0 s n_0 p$ without $V_p(r_1 r_2)$.618	.547	.528	.521	.511
b) $n_0 s n_0 p$ with $V_p(r_1 r_2)$ in $V_{\gamma\gamma}$.614	.538	.501	.487	.467
c) as (b) with $V_p(r_1 r_2)$ in $W_{\gamma\gamma}$.612	.534	.493	.478	.455
d) as (b) + $n_0 d$.615	.540	.506	.497	.481
e) as (b) + $n_1 s$.615	.539	.502	.488	.467
3_P state					
f) $n_0 p n_0 d$ without $V_p(r_1 r_2)$	none	.063	.126	.153	.183
g) $n_0 p n_0 d$ with $V_p(r_1 r_2)$ in $V_{\gamma\gamma}$	none	.062	.119	.144	.166

TABLE II. Electron affinities, in eV for the 1S state.

Ref. No.	Li	Na	K	Rb	Cs
2 (calc.)	0.616	0.539	0.472	0.42 ^a	0.39 ^a
5 (calc.)	0.62	0.54	0.51	0.48	
6 (calc.)	0.591				
This work	0.614	0.538	0.498	0.490	0.470
7 (meas.) ^b		0.543 ± 0.010	0.5012 ± 0.0005	0.4859 ± 0.0015	0.472 ± 0.003
7 (meas.) ^c	0.620 ± 0.007	0.548 ± 0.004		0.486 ± 0.003	0.470 ± 0.003

^aExtrapolated.^bPhotodetachment thresholds.^cPhotoelectron spectroscopy.

That we obtain true bound states with configuration $n_0p^2\ ^3P$ is consistent with the prediction of a similar state ($2p^2\ ^3P$) in H^- ,¹¹ with binding energy relative to the $2p$ state of 0.0095 eV (the affinities given in the table for the 3P states are relative to the first excited state of the neutral alkali). It is, however, curious that the state is not found in Li^- , as one might expect some smooth behavior from H^- to Cs^- , as happens for the 1S states. The cause might be inadequate convergence of the two-state expansion for the 3P states, although the contribution to the polarizability of the $2p$ state from the second ($4d$) state is only 4% of that from the first ($3d$) state.

The present results for the 1S states are shown in Table II, along with experimental results⁷ and representative results of earlier calculations. The entries for the present work are estimates of the exact solutions of the model problem, obtained by adding the effects of the n_1s and n_0d states to the results in row *c* of Table I. One might conclude that the difference between the result of Weiss² for K^- and experiment is due to the neglect of core polarization.

Given the magnitudes of the dielectric corrections obtained here, the good agreement of the pseudopotential results of Schwarz⁵ with experiment for the heavier alkalis must be judged fortuitous. Recent elaborate pseudopotential calculations by Bardsley and colleagues¹² support this conclusion. They also neglect the dielectric correction, and obtain results larger than the measured values by amounts comparable to the magnitudes of the dielectric corrections obtained here.

The reason for the difference between the present result and that of Victor and Laughlin⁶ for Li^- is not understood, since very similar effective potentials were employed, and the above argument suggests that the present method should

be equivalent to a large multiconfiguration expansion. The different forms of $V_p(r_1r_2)$ used do not appear to be responsible, as the sensitivity test mentioned above resulted in a change of less than 0.2 meV, and the change when the cutoff radius due to Victor and Laughlin (about half that used in the present work) was used in $V_p(r_1r_2)$ with either set of cutoff functions was less than 0.5 meV.

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