PHYSICAL REVIEW A VOLUME 5, NUMBER 1 JANUARY 1972

Autoionization States of Li^- and Na^- †

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(Received 17 May 1971)

A multiconfiguration Hartree-Fock method has been used to compute low-lying autoionization states of Li^- and Na^-. The electron-detachment potentials for these systems have also been computed and agree well with a similar calculation by Weiss. The present formulation permits a simple construction of projection operators used in determining autoionization states for e^-–alkali-atom systems. For Li^- three autoionization states have been found below the $1s^2 3p$ level and four below the $1s^2 3p$ level. Only one autoionization state is found for Na^-.

I. INTRODUCTION

The existence of states of compound nuclei made up of an excited target nucleus and an incident nucleon has long been known to give rise to the strong resonances found in nucleon-nucleus elastic scattering. Similar phenomena existing in atoms such as the sharp maxima in optical absorption and the resonant peaks of electron-atom scattering cross sections can be equally well explained by the compound or autoionization states in atoms. The calculation of energy levels of these states of the compound atom (relative to an absolute energy scale) is difficult since the accurate computation for the energy of systems with two or more electrons is known to be tedious. However, recently developed techniques for calculating the ionization potential (IP) and electron affinity (EA) of atoms can be used to compute these levels relative to the atomic energy levels.

The calculation of the EA itself used to be a difficult task, because the EA is the small difference between two comparatively large number, the atomic energy E_0 and the ion energy E_-. An accurate result can be obtained only if E_0 and E_- are computed with a high degree of precision or if E_0 and E_- are known to be computed with the same absolute error.

Weiss[1] has used a method of superposition of configurations (SOC) to calculate the detachment potentials for alkali ions and other atoms. The method consists of writing a trial function for the N-electron system as a linear superposition of terms which include the ground-state Hartree-Fock function and a number of virtual excited orbitals. The calculation of the energies is carried out in a manner which produces approximately the same error in both the N- and the $(N-1)$-electron systems. His results agree very well with experimental values.[2,3]

In the present work we calculate the energies of the N-electron and the $(N-1)$-electron systems in a manner similar to Weiss.[1] The $(N-1)$-electron system is described by a single configuration of orbitals obtained from an analytic Hartree-Fock description using a self-consistent V^{N-2} potential. The N-electron system is described by a fixed-core multiconfiguration Hartree-Fock wave function which uses the *same* orbitals obtained for the $(N-1)$-electron system. This formalism is briefly discussed in Sec. II. Section III gives the application of this formalism to obtain the electron-detachment potentials of Li^- and Na^-. In Sec. IV we apply a projection formalism to compute the autoionization states for the e^--Li and e^--Na systems. Conclusions and a brief discussion are given in Sec. V.

II. FORMALISM

The present formalism follows closely the analysis of Salmona and Seaton[4] which was applied there to scattering states of the electron–alkali-atom system. Before discussing how configurations of the $(N-1)$- and N-electron systems are constructed, we outline the method used to obtain the analytic single-particle states utilized in the mixing.

The single-particle states used here are determined by diagonalizing (self-consistently) the $(N-2)$ electron closed-shell Hartree-Fock Hamiltonian in the manner of Clementi[5]

$$\langle u_\sigma^\gamma(i)\,|h_{\mathrm{HF}}^{\mathrm{core}}(i)|\,u_{\sigma'}^{\gamma'}(i)\rangle = E_\gamma\,\delta_{\sigma\sigma'}\,\delta_{\gamma\gamma'} , \tag{1}$$

where the u_σ^γ are spin orbitals

$$u_\sigma^\gamma(i) = u^\gamma(i)\chi_\sigma(i) , \tag{2}$$

with spatial functions expanded in a set of Slater orbitals

$$u^\gamma(i) = Y_{l_\gamma m_\gamma}(i)\textstyle\sum_k b_{\gamma k} f_{\gamma k}(i) . \tag{3}$$

The lowest orbitals of the appropriate species are identified as core orbitals and are determined in a self-consistent fashion. We label the core spin-orbitals by a_i, $i=1,\ldots, N-2$. The Hartree-Fock Hamiltonian is then given by[6]

$$h_{\mathrm{HF}}^{\mathrm{core}} = -\nabla^2 - 2Z/r + V - W , \tag{4}$$

where

$$Vu_\sigma^\gamma(i)=\sum_{j=1}^{N-2} v(a_j,\, a_j)\, u_\sigma^\gamma(i) \quad , \tag{5}$$

$$Wu_\sigma^\gamma(i)=\sum_{j=1}^{N-2} v(a_j,\, u_\sigma^\gamma)\, a_j(i) \quad , \tag{6}$$

$$v(a_j,\, a_k)=2\int dr\, a_j^\dagger(\vec{r})\, a_k(\vec{r})/|\vec{r}-\vec{r}_i| \quad . \tag{7}$$

The choice of the V^{N-2} approximation for the single-particle states is made for two reasons. First we desire a reasonable single-configuration representation of the ground *and* excited states of the $(N-1)$-electron system and these are best represented by the V^{N-2} approximation. Further, as shown by Salmona and Seaton,[4] the formalism for describing the N-electron system is materially simplified if the single-particle orbitals diagonalize the core Hartree-Fock Hamiltonian.

The procedure used for choosing the Slater orbitals to be coupled in Eq. (3) is as follows. Although we self-consistently diagonalize in the V^{N-2} approximation, the set of Slater orbitals which we use is that set obtained by Clementi[5] in the V^{N-2} approximation, augmented with additional Slater orbitals to better represent the lowest-lying excited states of the valence electron. For those angular momentum species not included in the Clementi calculation we have simply chosen a reasonable basis set and in some cases have optimized parameters to obtain low-lying excited valence states of these angular momentum species. In the present calculation only states with symmetry $l=0$, 1, 2 have been included.

The ground state and lowest-lying excited states of the $(N-1)$ electron system are represented by the single configuration

$$\Psi^\gamma(N-1)=D_{N-1}(a_1a_2\cdots a_{N-2}\,u_\sigma^\gamma) \quad , \tag{8}$$

where D_{N-1} is a determinental function for $N-1$ electrons. Here the a_i are the core spin-orbitals and $u_\sigma^\gamma \neq a_i$ is the single-particle valence spin-orbital (e.g., for Li we have $a_1=1s\uparrow$, $a_2=1s\downarrow$, and $u_{\sigma=\uparrow}^\gamma=2s\uparrow,\ 2p\uparrow,\ 3s\uparrow,\ldots$) obtained as described above. The assumption that the excited states of the $(N-1)$-electron system can be represented by single-particle excitations of the valence electrons restricts the application to the lowest-lying excited states. The wave function Eq. (8) is an eigenstate of orbital angular momentum $L=l_\gamma$, $M=m_\gamma$, spin angular momentum $S=\frac{1}{2}$, $M_s=\sigma$, and parity $\pi=(-1)^L$.

We describe the N-electron system by a fixed closed core of $N-2$ electrons with the multiconfiguration mixing of states of the valence and binding electron

$$\Psi^\Gamma(N)=\mathfrak{N}\sum_{\gamma\nu} C_{\gamma\nu}\sum_\sigma C(\tfrac{1}{2}\tfrac{1}{2}\,S;\,\sigma-\sigma 0)$$
$$\times\sum_{m_\gamma m_\nu} C(l_\gamma l_\nu L;\, m_\gamma m_\nu M)$$
$$\times D_N(a_1a_2\cdots a_{N-2}\,u_\sigma^\gamma\, u_{-\sigma}^\nu) \quad . \tag{9}$$

Here $\mathfrak{N}$ is the normalization and the $C_{\gamma\nu}$ are mixing coefficients. The states chosen to be coupled are such that Ψ^Γ is an eigenstate of L, S, M, $M_s=0$ and $\pi=(-1)^L$. In addition we impose $u^\gamma\neq u^\nu$ for triplet states. Equation (9) can readily be made orthogonal to Hartree-Fock representations of the ground state and lowest-lying excited states of the $(N-1)$-electron system obtained above by simply restricting the summations over γ and ν to exclude those states desired. Thus we see one of the advantages of using the same single-particle states for both the $(N-1)$- and N-electron systems.

The calculation of the total energies of the $(N-1)$- and N-electron systems is carried out in a standard fashion, by evaluating $\langle\Psi^\gamma(N-1)|H(N-1)|\Psi^\gamma(N-1)\rangle$ and $\langle\Psi^\Gamma(N)|H(N)|\Psi^\Gamma(N)\rangle$, respectively.

III. EA's OF Li AND Na

The single-particle states generated from Eq. (1) diagonalize the Li⁺ Hartree-Fock Hamiltonian. The Slater basis functions of Eq. (3) take the form

$$f_{\gamma k}(r)=N_{\gamma k}\, r^{n_k-1}\, e^{-\chi_k r} \quad , \tag{10}$$

where $N_{\gamma k}$ is a normalization factor and the parameters n_k, χ_k for a given angular momentum species are listed in Table I. We have used 10(8, 5) or-

TABLE I. Parameters of the Slater basis functions.

	$l=0$		$l=1$		$l=2$	
	n_k	χ_k	n_k	χ_k	n_k	χ_k
Li⁻	1	4.70710	2	3.50000	3	2.50000
	1	3.50000	2	1.80000	3	1.20000
	1	2.48030	2	1.00000	3	0.60000
	2	1.73500	2	0.71109	3	0.33300
	2	1.00000	2	0.49782	3	0.10000
	2	0.66000	2	0.33300		
	2	0.35000	2	0.10000		
	2	0.10000	2	0.00100		
	2	0.05000				
	2	0.00100				
Na⁻	1	11.00000	2	5.50000	3	3.20000
	3	12.36850	4	8.39370	3	1.50000
	3	8.02540	4	5.42060	3	0.70000
	3	5.70590	4	3.56460	3	0.33300
	3	3.63100	4	2.28330	3	0.10000
	3	2.15370	4	1.00000		
	3	1.10810	4	0.50000		
	3	0.70830	4	0.33300		
	3	0.35000				
	3	0.10000				

TABLE II. Single-particle eigenvalues E_γ in the V^{N-2} approximation.

	Li$^-$	Na$^-$
1*s*	−5.584 72	−81.519 44
2*s*	−0.392 61	−6.147 36
3*s*	−0.146 93	−0.363 62
4*s*	−0.071 67	−0.140 11
5*s*	−0.032 50	−0.057 31
6*s*	−0.001 00	0.088 20
7*s*	0.165 67	1.661 61
8*s*	1.863 78	8.937 12
9*s*	10.014 69	36.207 18
10*s*	62.979 64	161.384 48
2*p*	−0.257 27	−3.594 37
3*p*	−0.113 02	−0.218 35
4*p*	−0.060 02	−0.100 45
5*p*	−0.001 00	0.003 03
6*p*	0.037 00	1.113 34
7*p*	0.604 14	5.907 55
8*p*	2.996 75	21.209 26
9*p*	16.215 37	79.891 23
3*d*	−0.111 12	−0.111 33
4*d*	−0.051 75	−0.051 45
5*d*	0.017 57	0.064 37
6*d*	0.846 10	1.288 19
7*d*	6.218 42	7.206 73

bitals for $s(p, d)$ species. The energy eigenvalues E_γ of Eq. (1) are given in Table II. The eigenvector associated with the lowest-energy *s* state is identified with the 1*s* orbital and is treated self-consistently. We label the eigenstates of Eq. (1) by 1*s*, 2*s*... 10*s*; 2*p*, 3*p*,... 9*p*; 3*d*, 4*d*,... 7*d* in order of increasing energies. However we note that only those states *nl* with $n \leqslant 4$ can be considered to be reasonable Hartree-Fock approximations to the hydrogenlike excited states of the valence electron. Although all eigenstates are localized, some have energies in the continuum. This is desirable because it is known that the mixing of continuumlike states is important to obtain good energies.

The Hartree-Fock energy for the $1s^2\,2s(^2S)$ configuration of Li is found to be −14.865 44 Ry. This is to be compared with the Weiss[1] value of −14.8654 Ry.

The energy of the ^1S ground state of Li$^-$ was computed using Eq. (9) with a mixing of 34 configurations for the outer two electrons which included

$$\gamma\nu(S) = 2s^2,\ 2s3s, \ldots\ 2s8s;\ 3s^2, \ldots\ 3s8s;\ 4s^2;\ 2p^2, \ldots\ 2p8p;\ 3p^2, \ldots\ 3p8p;\ 4p^2;\ 3d^2, \ldots\ 3d7d;\ 4d^2\ . \tag{11}$$

The energy computed in this manner was found to be −14.910 49 Ry. Taking the difference between this value and the Hartree-Fock energy of Li computed here, we obtain an electron affinity for Li of 0.045 05 Ry (0.613 eV) as compared to the value of 0.62 eV obtained by Weiss.[1]

TABLE III. Convergence of the electron affinity of Li.

n	Electron affinity (Ry)
1	−0.075 35
7	0.006 57
14	0.044 90
34	0.045 05

Subsidiary calculation were performed in which only some of the configurations listed in Eq. (11) were mixed. We give results for $n = 1(2s^2)$, $n = 7$ $(2s^2,\ 2s3s, \ldots\ 2s8s)$, $n = 14(2s^2, \ldots\ 2s8s;\ 2p^2, \ldots\ 2p8p)$, and $n = 34$. The results are presented in Table III. The contribution to the polarizability of Li from the 2*s* state is also calculated to check the goodness of our single-particle wave functions. The 2*s*-2*p* coupling gives 167.297 which agrees exactly with Karule and Peterkop.[7]

We have investigated the Li$^-$ system in the ^3S, $^{1,3}P$, and $^{1,3}D$ states and find that it does not bind.

For Na we have proceeded in a manner similar to the Li calculation. The EA obtained is 0.039 41 Ry (0.536 eV), which agrees with the value of 0.54 eV by Weiss.[1]

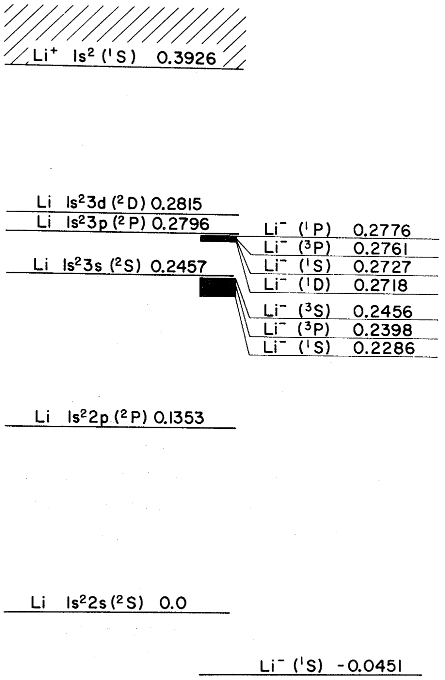

FIG. 1. Hartree-Fock energy levels for Li and the multiconfiguration Hartree-Fock ground state and metastable excited states of Li$^-$.

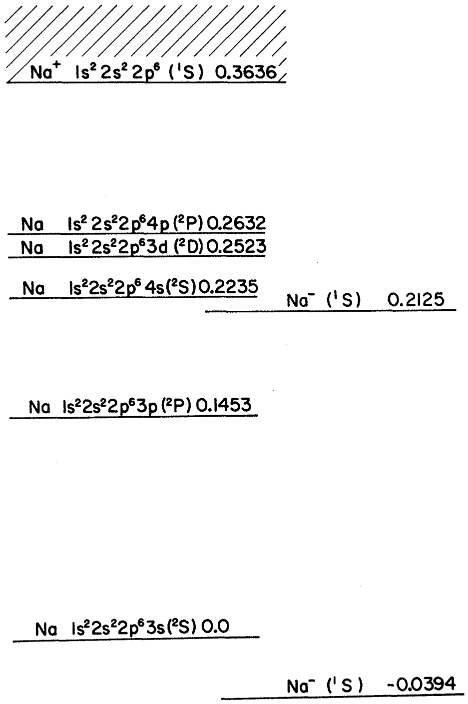

FIG. 2. Hartree-Fock energy levels for Na and the multiconfiguration Hartree-Fock ground state and metastable excited state of Na^-.

IV. AUTOIONIZATION STATES OF e^--Li AND e^--Na SYSTEMS

In the calculation of autoionization states, we use the approach developed by Feshbach,[8] and applied to atomic systems by several other authors.[9–11] The projection operator has the form

$$P=\sum\nolimits_{\gamma} | \Psi^{\gamma} \rangle \langle \Psi^{\gamma} | , \qquad (12)$$

where Ψ^{γ} are the atomic ground and excited states.

In Sec. II, we expressed the orbitals of the "binding" electron in terms of the single-particle orbitals obtained for the $(N-1)$-electron system. This makes the construction of the projection operator particularly convenient. By excluding any excited state from the sum, the "binding" state is made automatically orthogonal to that state.

Approximations to autoionization states of the e^--alkali-atom systems can be readily obtained in the formalism used here. The accuracy of the binding energy (relative to the energy of the excited valence state to which the additional electron binds) will be comparable to that obtained for the electron affinity. As described in Sec. II, single-configuration Hartree-Fock wave functions can be obtained for the low-lying excited states of Li and Na. Equation (9) can be used for the wave function of the autoionization state if the summation over γ and ν excludes the ground-state orbitals and other excited valence orbitals of energy lower than that of interest.

In Fig. 1 we show the Hartree-Fock spectrum of the low-lying states of Li with configuration $1s^2 nl$. Autoionization states below the $1s^2 3s$ state, for example, can be obtained by excluding the orbitals $1s$, $2s$, $2p$ from the summation in Eq. (9). In this manner we have obtained several shallow autoionization states below the $1s^2 3s$ and $1s^2 3p$ levels. Elastic scattering calculations by Karule and Peterkop[12] in the strong-coupling ($2s$-$2p$) approximation have detected no resonances below the $2p$ excitation threshold, in agreement with the present results. However, since they have not coupled higher excited states the resonances associated with the autoionization states obtained here were not included. The experimental results[13] for the elastic scattering of electrons from Li are suggestive of the resonances near the $1s^2 3p$ threshold, but the data are insufficient to be conclusive.

The same method has been used to search for autoionization states of the e^--Na system. We show in Fig. 2 the only state found for this case, but it is difficult to say whether this is due to weaker interactions or due to the smaller number of single-particle states with large spatial extent that are include in the mixing.

V. CONCLUSIONS

We have formulated an analytic multiconfiguration Hartree-Fock method of determining accurate values for the electron affinity of alkali atoms. This allows for a simple application of the projection techniques necessary for the determination of the autoionization states for the e^--alkali system and the location of these states, relative to the atomic excited states, can be found with essentially the same degree of accuracy as the electron-affinity calculation. The detection of these autoionization states depends on the widths of the levels, and we have not attempted to determine values of these widths in this work.

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†Research supported in part by the U. S. Office of Naval Research under Contract No. N00014-69-A-0211-0004.

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PHYSICAL REVIEW A VOLUME 5, NUMBER 1 JANUARY 1972

Eigenvalues of the $2p3p\ ^3P$ and $2p3d\ ^{1,3}D$ Bound States of the Helium Isoelectronic Sequence

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(Received 9 August 1971)

The $1/Z$ expansion method is used to calculate the eigenvalues of the $2p3p\ ^3P$ and $2p3d\ ^{1,3}D$ states of the helium isoelectronic sequence. The results are compared to variational calculations for neutral helium. Wavelengths are predicted for a number of transitions originating in doubly excited states of the heliumlike ions up to Fe XXV. The results for neutral helium are compared to recent beam-foil experiments and alternative line identifications are made. The predicted wavelength for the $2p3d\ ^3D$–$2p^2\ ^3P$ transition is 3014 Å, in close agreement with the line observed by Berry *et al.* at 3012 ± 2 Å.

I. INTRODUCTION

The existence of doubly excited states in neutral helium has been known for many years through studies of the helium arc spectrum[1,2] and the energy-loss spectrum in electron-helium scattering.[3] States such as the $2pnl\ ^{1,3}L$ sequence give rise to sharp spectral lines since they are prevented from autoionizing by parity and angular-momentum selection rules. Recent studies of these states by the trapped-electron method[4] and beam-foil spectroscopy[5,6] emphasize the need for accurate calculations of their positions and radiative lifetimes. In addition, lines involving doubly excited states of the heliumlike ions have been observed in solar flares[7] and the solar corona.[8]

The $2p^2\ ^3P$ state has been studied by several authors.[9–12] The most extensive calculations by Aashamar,[10] including mass polarization and relativistic effects, predict a $2p^2\ ^3P$–$1s2p\ ^3P$ transition frequency of 312 217 cm^{-1} in slight disagreement with the old experimental value, 312 118 cm^{-1},[2] but in agreement with the new value of 312 214 cm^{-1}.[13] The $2p3p\ ^1P$ states of the helium sequence have been studied by Drake and Dalgarno.[11]

In this paper, the $1/Z$ expansion perturbation method is applied to the bound $2p3d\ ^{1,3}D$ and $2p3p\ ^3P$ states of the helium sequence. Wavelengths are predicted for transitions originating from the doubly excited states for the heliumlike ions with $Z \leq 26$ (Fe XXV). Variational calculations for neutral helium are presented as a check on the accuracy of the perturbation expansion. The results suggest that the line observed by Berry *et al.* at 306 ± 1 Å is the $2p3d\ ^1D$–$1s3d\ ^1D$ transition ($\lambda = 305.4$ Å).

II. 1/Z EXPANSION METHOD

An accurate and efficient method of generating wave functions for the entire helium isoelectronic sequence is provided by the Hylleraas-Scherr-Knight variation-perturbation procedure.[14] The Schrödinger equation to be solved is

$$(H - E)\Psi = 0 \ , \tag{1}$$

where

$$H = H_0 + Z^{-1} V_{12} \ , \tag{2}$$

$$H_0 = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 \ , \tag{3}$$

$$V_{12} = 1/r_{12} \ . \tag{4}$$

The unit of energy is Z^2 a.u., and the unit of length is $Z^{-1}\, a_0$. Introducing the perturbation expansions