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Relativistic Calculations for Photoionization Cross Sections and the Spin Orientation of Photoejected Electrons from Potassium, Rubidium, and Cesium Atoms*

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By using relativistic Hartree-Fock equations which automatically take the spin-orbit interaction into account, we calculate the single-particle states for photoejected electrons from heavy alkali-metal atoms. We derive an expression for the perturbation function x. Our results are in fair agreement with the experiments, but more accurate calculations including electron correlations are desirable.

INTRODUCTION

Recently, there has been considerable interest in the spin-orbit interaction in alkali-metal atoms.[1-4] As pointed out by Weisheit and Dalgarno,[4] the spin-orbit interaction was used by Fermi[5] in 1930 to explain the anomalous ^2P line strength ratio in alkali-metal atoms. Seaton[6] mentioned that the nonzero minimum of the photoionization cross sections of alkali-metal atoms is due to the spin-orbit interaction. Fano[1] has shown that the spin-orbit interaction for the valence electron of the alkali metals leads to a spin orientation of photoelectrons ejected by circularly polarized light. This spin orientation has been confirmed experimentally by Kessler and Lorenz[2] and by Baum, Lubell, and Raith.[3]

As shown by Fano, the degree of spin orientation is given by

$$P=(1+2x)/(2+x^2)\ , \tag{1}$$

where

$$x=[2R(\epsilon,\tfrac{3}{2})+R(\epsilon,\tfrac{1}{2})]/[R(\epsilon,\tfrac{3}{2})-R(\epsilon,\tfrac{1}{2})] \tag{2}$$

and

$$R(\epsilon,j')=\int_0^\infty P(\epsilon pj';\ r)\,r\,P(ns\tfrac{1}{2};\ r)\,dr\ . \tag{3}$$

In the above equation, $P(\epsilon pj';\ r)$ is the radial part of the continuum wave function with energy ϵ, and $P(ns\frac{1}{2};\ r)$ is the radial wave function for the valence ns electron.

Weisheit and Dalgarno calculated x for potassium by including a core-polarization correction which they obtained semiempirically by multiplying the operator $\vec{r}$ with a function which contains the effective core radius r_c as an adjustable parameter. They also adopted the spin-orbit parameter $\xi(r)=17.33/r^3$. By choosing $r_c=4.22a_0$, where a_0 is the Bohr radius, their results for x are in excellent agreement with the experimental values. In this paper, we use relativistic Hartree-Fock (HF) equations to calculate the continuum wave functions and

TABLE I. Calculated photoionization data for potassium.

ϵ photoejected electron energy (in a.u.)	$\langle Q_{\epsilon\bar{p}} \vert P_{4s}\rangle$ ($\times 10^{-4}$)	$\langle P_{\epsilon\bar{p}} \vert Q_{4s}\rangle$ ($\times 10^{-4}$)	$\langle P_{\epsilon p} \vert Q_{4s}\rangle$ ($\times 10^{-4}$)	$I+\epsilon$[a] photon energy (in a.u.)	x perturbation function	P polarization parameter	σ (10^{-21} cm^2)
0.005	0.749	-0.756	-1.016	0.153 020	10.260	0.200	11.533
0.01	0.376	-0.379	-0.636	0.158 020	6.292	0.327	4.041
0.015	0.034	-0.034	-0.287	0.163 020	2.407	0.746	0.684
0.016	-0.030	0.031	-0.220	0.164 020	1.645	0.911	0.400
0.017	-0.094	0.095	-0.155	0.165 020	0.871	0.994	0.233
0.018	-0.157	0.159	-0.091	0.166 020	0.108	0.604	0.166
0.019	-0.218	0.221	-0.028	0.167 020	-0.652	-0.125	0.197
0.02	-0.279	0.283	0.033	0.168 020	-1.410	-0.456	0.318
0.03	-0.834	0.842	0.599	0.178 020	-8.805	-0.208	5.318
0.04	-1.306	1.318	1.081	0.188 020	-15.743	-0.122	14.416
0.05	-1.711	1.723	1.492	0.198 020	-22.019	-0.088	25.014
0.06	-2.059	2.071	1.844	0.208 020	-27.472	-0.071	35.676

[a] For the ionization energy I, we have used the relativistic HF single-particle energy. See Table V.

the wave functions for the ground state of the atom. We also obtain an expression for the perturbation parameter x for relativistic single-particle wave functions.

THEORY

Relativistic atomic calculations have been extensively reviewed by Grant.[7] Here we follow the notation of the 1961 paper of Ref. 7. The interaction between electron and photon is $e\vec{\alpha}\cdot\vec{A}$. If we assume right-circularly polarized photons and use the dipole approximation by putting $e^{i\vec{k}\cdot\vec{r}}=1$ in $\vec{A}$, then we have three matrix elements describing ns transitions to the continuum:

$$\langle \bar{p}_{1/2,1/2} | \alpha_+ | s_{1/2,-1/2}\rangle = i\sqrt{2}\langle Q_{\bar{p}} | P_s\rangle + i\tfrac{1}{3}\sqrt{2}\langle P_{\bar{p}} | Q_s\rangle , \quad (4)$$

$$\langle p_{3/2,1/2} | \alpha_+ | s_{1/2,-1/2}\rangle = -i\tfrac{2}{3}\langle P_p | Q_s\rangle , \quad (5)$$

$$\langle p_{3/2,3/2} | \alpha_+ | s_{1/2,1/2}\rangle = -i(2/\sqrt{3})\langle P_p | Q_s\rangle , \quad (6)$$

where $|s_{1/2,\pm 1/2}\rangle$ is the ns state with $j=\frac{1}{2}$ and $m_j=\pm\frac{1}{2}$; P_s and Q_s are the radial parts of the large and small components for the state ns, respectively. The states $\bar{p}$ and p are the continuum $l=1$ states with $j=\frac{1}{2}$ and $\frac{3}{2}$, respectively. The matrix $\alpha_+ = -(1/\sqrt{2})\times(\alpha_x + i\alpha_y)$, where α_x and α_y are the usual Dirac matrices.[7] The unexcited single-particle states which are taken as basis functions are calculated self-consistently[8] from the relativistic HF equations for the ground state of the atom. The excited p-electron continuum states are calculated from the relativistic HF equation by removing the valence s electron with a fixed core left. We integrate the equations repeatedly from the origin to the point where the basis functions are all zero to 10^{-6} until each exchange integral becomes stable. Then we pass to the asymptotic region and normalize[9] so that $\int \phi_\epsilon \phi_{\epsilon'} dv = \delta(\epsilon-\epsilon')$.

For alkali atoms, the photoionization cross section[10] which corresponds to the lowest-order contribution from many-body perturbation theory is

TABLE II. Calculated photoionization data for rubidum.

ϵ photoejected electron energy (in a.u.)	$\langle Q_{\epsilon\bar{p}} \vert P_{5s}\rangle$ ($\times 10^{-4}$)	$\langle P_{\epsilon\bar{p}} \vert Q_{5s}\rangle$ ($\times 10^{-4}$)	$\langle P_{\epsilon p} \vert Q_{5s}\rangle$ ($\times 10^{-4}$)	$I+\epsilon$[a] photon energy (in a.u.)	x perturbation function	P polarization parameter	σ (10^{-21} cm^2)
0.005	1.995	-1.997	-3.080	0.145 036	7.508	0.274	106.538
0.01	1.614	-1.606	-2.673	0.150 036	6.592	0.312	75.899
0.015	1.265	-1.249	-2.302	0.155 036	5.709	0.358	53.056
0.02	0.945	-0.923	-1.962	0.160 036	4.851	0.419	36.247
0.03	0.380	-0.350	-1.362	0.170 036	3.228	0.600	15.317
0.04	-0.101	0.134	-0.853	0.180 036	1.729	0.893	5.465
0.05	-0.514	0.543	-0.420	0.190 036	0.370	0.814	2.134
0.06	-0.870	0.891	-0.053	0.200 036	-0.826	-0.243	2.503
0.07	-1.192	1.213	+0.265	0.210 036	-1.870	-0.498	4.927

[a] For the ionization energy I, we have used the relativistic HF single-particle energy. See Table V.

TABLE III. Calculated photoionization data for cesium.

ϵ photoejected electron energy (in a.u.)	$\langle Q_{\epsilon\bar{p}} \vert P_{6s}\rangle$ ($\times 10^{-4}$)	$\langle P_{\epsilon\bar{p}} \vert Q_{6s}\rangle$ ($\times 10^{-4}$)	$\langle P_{\epsilon p} \vert Q_{6s}\rangle$ ($\times 10^{-4}$)	$I+\epsilon$[a] photon energy (in a.u.)	x perturbation function	P polarization parameter	σ (10^{-21} cm^2)
0.005	1.106	-1.103	-3.6996	0.133 236	3.282	0.592	144.513
0.02	0.129	-0.120	-2.601	0.148 230	2.162	0.798	61.530
0.045	-0.988	0.994	-1.328	0.173 236	0.722	0.970	17.478
0.06	-1.454	1.455	-0.739	0.188 236	0.011	0.511	11.456
0.07	-1.702	1.703	-0.492	0.198 236	-0.326	0.165	11.474
0.08	-1.914	1.910	-0.241	0.208 236	-0.665	-0.135	12.244

[a] For the ionization energy I, we have used the relativistic HF single-particle energy. See Table V.

$$\sigma=(2\pi)^2\alpha\frac{\hbar^2c^2}{\hbar\omega}\frac{1}{2}\Big(\left|\langle \bar{p}_{1/2,1/2}|\,\alpha_+|\,s_{1/2,-1/2}\rangle\right|^2 + \left|\langle p_{3/2,1/2}|\,\alpha_+|\,s_{1/2,-1/2}\rangle\right|^2 + \left|\langle p_{3/2,3/2}|\,\alpha_+|\,s_{1/2,1/2}\rangle\right|^2\Big)\,, \tag{7}$$

where α is the fine-structure constant. The factor $\frac{1}{2}$ in Eq. (7) comes from averaging over initial states $|s_{1/2,1/2}\rangle$ and $|s_{1/2,-1/2}\rangle$.

In calculating spin orientation, with the final state $|1,\ \frac{1}{2},\ m_l',\ m_s'\rangle$ in the uncoupled scheme, the desired matrix element is

$$\langle 1,\ \tfrac{1}{2},\ m_l',\ m_s'|\,\alpha_+|\,\phi_{k_1m_1}\rangle = \sum_{k_2m_2}\langle 1,\ \tfrac{1}{2},\ m_l',\ m_s'|\,\phi_{k_2m_2}\rangle\langle\phi_{k_2m_2}|\,\alpha_+|\,\phi_{k_1m_1}\rangle\,, \tag{8}$$

where ϕ_{km} is a relativistic single-particle wave function, and $\langle 1,\ \frac{1}{2},\ m_l',\ m_s'|\,\phi_{k_2m_2}\rangle$ is a Clebsch-Gordan coefficient. After writing the matrix corresponding to Eq. (3) in Ref. 1, we can see that $\langle p_{3/2,3/2}|\,\alpha_+|\,s_{1/2,1/2}\rangle$ plays the same role as iR_3 in Ref. 1. Similarly, $\langle p_{3/2,1/2}|\,\alpha_+|\,s_{1/2,-1/2}\rangle$ replaces $i(1/\sqrt{3})R_3$, and $\langle\bar{p}_{1/2,1/2}|\,\alpha_+|\,s_{1/2,-1/2}\rangle$ replaces $i(\frac{2}{3})^{1/2}R_1$. By simple substitution for $x=(2R_3+R_1)/(R_3-R_1)$, we obtain the perturbation parameter

$$x=\frac{4\langle P_p|\,Q_s\rangle-(3\langle Q_{\bar{p}}|\,P_s\rangle+\langle P_{\bar{p}}\,|\,Q_s\rangle)}{2\langle P_p|\,Q_s\rangle+(3\langle Q_{\bar{p}}\,|P_s\rangle+\langle P_{\bar{p}}\,|Q_s\rangle)}\,. \tag{9}$$

The degree of spin orientation of photoejected electrons is still given by Eq. (1).

RESULTS AND DISCUSSION

For lithium and sodium, we found that the photoionization cross-section curves are nearly the same as calculated from the nonrelativistic HF orbitals by using the velocity form. We estimate that the spin polarization for sodium may become appreciable in an approximate interval 0.001 a.u. near the energy 0.035 a.u. for the photoejected electron. Since this interval is quite small, it will be more difficult to measure this effect for sodium than for the higher alkali metals.

For potassium, rubidium, and cesium, the absolute values of $\langle Q_{\bar{p}}|P_s\rangle$ and $\langle P_{\bar{p}}|\,Q_s\rangle$ are almost the same, but different from that of $\langle P_p|\,Q_s\rangle$, and they come to zero at different energies. This results in a nonzero minimum photoionization cross section.

For potassium, the values of $\langle Q_{\bar{p}}|\,P_s\rangle$ and $\langle P_{\bar{p}}|\,Q_s\rangle$ change sign near the energy 0.015 a.u. for the photoejected electron, but that of $\langle P_p|\,Q_s\rangle$ changes sign near 0.019 a.u. for the photoejected electron as shown in Table I. Our calculated nonzero minimum photoionization cross section for potassium is 1.6×10^{-22} cm^2 as compared with 2.2×10^{-22} cm^2 calculated by Weisheit and Dalgarno[4] and with $4\pm2\times10^{-21}$ cm^2 observed by Marr and Creek.[11] For rubidium, the values of $\langle Q_{\bar{p}}|\,P_s\rangle$ and $\langle P_{\bar{p}}|\,Q_s\rangle$ change sign near the energy 0.03 a.u. for the photoejected electron, but that of $\langle P_p|\,Q_s\rangle$ changes sign near an energy 0.06

TABLE IV. Cross sections for minima in the photoionization curves of the alkali-metal atoms.[a]

Atom	$\sigma_{\rm min}$(calc.) (10^{-18} cm^2)	$\lambda_{\rm min}$(calc.) (Å)	$\sigma_{\rm min}$(obs.) (10^{-18} cm^2)	$\lambda_{\rm min}$(obs.) (Å)[b]
K	1.6×10^{-4}	2710	$4\pm2\times10^{-3}$	2725 ± 15
Rb	2×10^{-3}	2400	$8\pm3\times10^{-3}$	2480 ± 25
Cs	1.1×10^{-2}	2450	$6\pm1\times10^{-2}$	2650 ± 25

[a] For the ionization energies, we have used the relativistic Hartree-Fock single-particle energies. See Table V.

[b] Observed values are from Marr and Creek, Ref. 12.

TABLE V. Ionization potentials.

Atom	I_1(eV)[a]	I_2(eV)[b]
K	4.032	4.32
Rb	3.810	4.159
Cs	3.489	3.87

[a] Calculated relativistic Hartree-Fock single-particle energy.

[b] Experimental ionization energy, taken from Ref. 13.

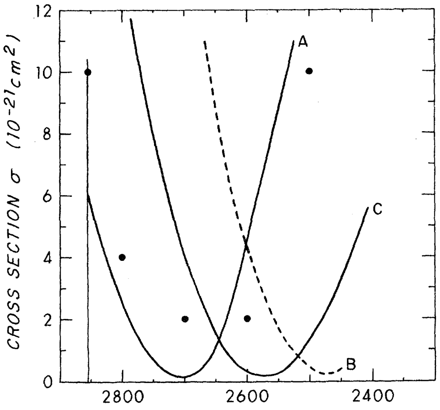

FIG. 1. Photoionization cross section σ of potassium. The circles are measurements by Hudson and Carter (Ref. 12); A and B, calculations by Weisheit and Dalgarno (Ref. 4), with and without a core-polarization correction, respectively; C, this paper.

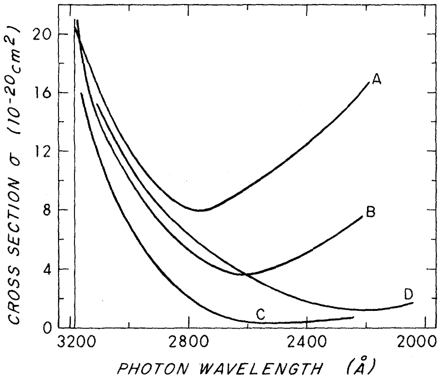

FIG. 3. Photoionization cross section σ of cesium: A, experiment by Braddick and Ditchburn (1934) (Ref. 14); B, by Mohler and Boeckner (1929) (Ref. 15); C, by Lawrence and Edlefsen (1929) (Ref. 16); D, this paper.

a.u. for the photoejected electron as shown in Table II. Our calculated nonzero minimum photoionization cross section for rubidium is 2.1×10^{-21} cm^2 as compared with $8\pm3\times10^{-21}$ cm^2 observed by Marr and Creek.[11] For cesium, the values of $\langle Q_{\bar{p}} | P_s \rangle$ and $\langle P_{\bar{p}} | Q_s \rangle$ change sign near the energy 0.02 a.u. for the photoejected electron, but that of $\langle P_p | Q_s \rangle$ changes sign near 0.08 a.u. for the photoejected electron as shown in Table III. Our calculated nonzero minimum photoionization cross section for cesium is 1.1×10^{-20} cm^2 as compared with $6\pm1\times10^{-20}$ cm^2 observed by Marr and Creek[11] as shown in Table IV.

There are two ways to choose the incoming photon energy, $\hbar\omega = I+\epsilon$, in our calculation. The ionization energy I could be chosen from the relativistic HF calculation or from experiment. The energy of the photoejected electron is ϵ. In Tables I, II, and III, the values of the photoionization cross sections are calculated by using the relativistic HF single-particle energy. Photoionization cross-section curve C in Fig. 1, curve B in Fig. 2, and curve D in Fig. 3 were obtained using the experimental values[13] for the ionization energies. In all cases, our calculated cross sections fall considerably below the experimental cross sections[11,14–16] for energies above the energy for the nonzero minimum. The effect of electric quadrupole and magnetic dipole transitions was evaluated for potassium and found to be very small as expected. These contributions are not included in our final results.

The circles and crosses in Fig. 4 are calculations for the function x of potassium by Weisheit and Dalgarno[4] with semiempirical core-polarization corrections; the triangles in Fig. 4 are their calculations without core-polarization corrections.

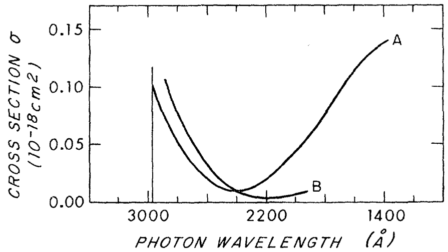

FIG. 2. Photoionization cross section σ of rubidium: A, experiment by Marr and Creek (Ref. 11); B, this paper.

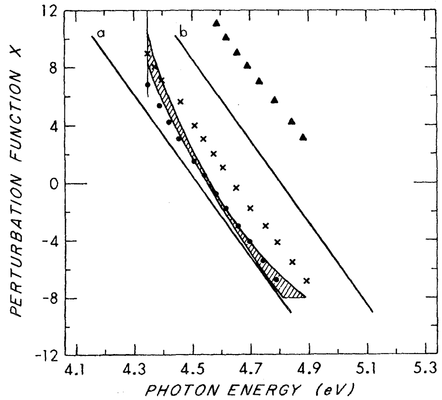

FIG. 4. Perturbation function x for potassium. The shaded area indicates the values measured by Baum, Lubell, and Raith (Ref. 3); the circles and crosses are calculations with core-polarization corrections by Weisheit and Dalgarno (Ref. 4); and the triangles represent calculations by Weisheit and Dalgarno (Ref. 4.) without the core-polarization correction. (a) and (b) are calculated relativistic Hartree-Fock values in this paper using the relativistic HF single-particle energy and the experimental ionization energy, respectively.

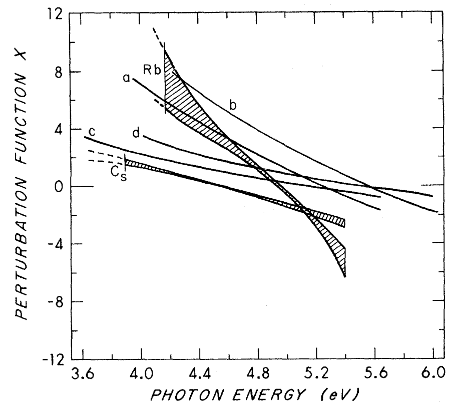

FIG. 5. Perturbation function x for rubidium and cesium. The shaded areas are measurements by Baum, Lubell, and Raith (Ref. 3); (a) and (b) are calculated values for Rb in this paper using the relativistic HF single-particle energies and the experimental ionization energies, respectively. Curves (c) and (d) are calculated values for Cs using relativistic HF single-particle energies and experimental ionization energies, respectively.

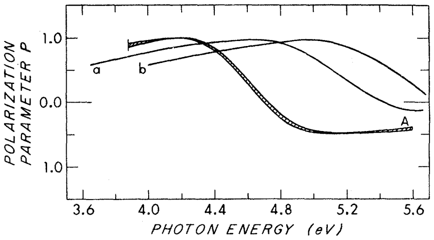

FIG. 6. Polarization parameter P for cesium: A, experiment by Baum, Lubell and Raith (Ref. 3); (a) and (b) are calculated values in this paper using the relativistic HF single-particle energy and the experimental ionization energy, respectively.

The curves labeled a and b in Fig. 4 are our calculations for the perturbation function of potassium by using the relativistic 4s HF single-particle energy and the experimental ionization energy, respectively. The curves labeled a and b in Fig. 5 are our calculations for the perturbation function x of rubidium by using the relativistic 5s HF single-particle energy and the experimental ionization energy, respectively. The curves labeled c and d are our calculations for the perturbation function x of cesium by using the relativistic 6s HF single-particle energy and the experimental ionization energy, respectively. In Fig. 6, our computed values for the polarization parameter P of cesium are compared with the experimental values by Baum, Lubell, and Raith.[3] The full spin selection with $P \cong 1$ for cesium occurs approximately at 4.2-eV photon energy from experiment and at 4.6 eV in our calculation.

We attribute our disagreement with the experiment to neglect of electron correlations. We note that Weisheit and Dalgarno[4] obtain considerable improvement in the agreement of their calculations with experiment by including effects of electron correlations. We plan to use many-body perturbation theory with spin-orbit effect included to see whether this will improve our results.

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