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Numerical multiconfiguration self-consistent-field studies of atomic photoionization cross sections: Dynamical core-polarization effects in atomic potassium

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The numerical multiconfiguration self-consistent-field method is used to calculate photoionization cross sections of atomic potassium in its ground state for photoelectron energies ranging from 0.0 to 12 eV. The effects of core polarization, which are very important for this atom, are analyzed in detail and are taken into account effectively *ab initio* in both the initial and the final state, by the configuration-interaction procedure. It is found that the core-polarization effect is very strong in the photoionization cross section of potassium. Our results are found to be in good agreement with previous theoretical calculations throughout the energy region considered and also with experiment except at high energies.

I. INTRODUCTION

Interest in studying the photoionization of alkali-metal atoms has increased in recent years. This is due to the fact that theoretical calculations have not yet been able to reproduce the experimental results, on one hand, and to a desire to check the validity of new methods of calculations, on the other hand. Several theoretical analyses, based on different approaches, have been used to date to calculate photoionization cross sections of these atoms. The first really successful theoretical calculation of the total cross section was performed using many-body methods in an attempt to give a quantitative explanation of experimental observations. However, in all the many-body theories the results obtained do not lead directly to a very clear physical picture of the interactions being included in the calculation, or to an identification of the dominant excitations for the case being studied. Chang and Poe¹ have given a detailed treatment of photoabsorption by many-body perturbation theory. Similar applications have also been given by Kelly and co-workers.²⁻⁵ Chang⁶ obtained very good results for the photoionization cross section, particularly of sodium and potassium atoms, using the many-body theory. His investigation concentrates on the region where the photoelectron energy exceeds 2 eV. In the case of alkali-metal atoms the valence electron in the initial state and the photoelectron in the final state polarize the core. Chang⁶ included the effects of virtual excitations of the inner-shell electrons by calculating the lowest diagrammatic terms using orbitals obtained from a long-range polarization potential instead of evaluating the infinite sum of diagrams corresponding to virtual excitations of Hartree-Fock orbitals.

Weisheit and Dalgarno⁷ and Weisheit⁸ calculated the photoionization cross section of potassium and other alkali-metal atoms by including the spin-orbit interaction and the correction to the dipole matrix element due to the core polarization. They used a model potential to

study the effects of core polarization and the spin-orbit interaction potential to account for the spin-orbit interaction. Chichkov and Shevelko⁹ calculated the photoionization cross sections of alkali-metal atoms using the simple one-electron method, with allowance for polarization of the core. They described the influence of the core polarization on the photoionization cross sections by changing the one-electron operator $\langle \mathbf{r} \rangle$ to an operator $\langle \mathbf{r} - \mathbf{q} \rangle$, where $\mathbf{q}$ is the induced dipole moment of the core.

None of the above-mentioned theoretical calculations was able to reproduce the experimental results of Hudson and Carter¹⁰ and Marr and Creek.¹¹ Although the results obtained by Chang⁶ agree reasonably well above the minimum, experimental values are still higher than the calculated values.

In this paper we attempt to calculate the photoionization cross section of potassium atoms, starting from first principles, in order to reduce the lack of agreement between theory and experiment. Experience with the theoretical calculation of atomic photoionization leads to the conclusion that electron correlation and core polarization are very important to the photoionization process. All previous calculations included the core-polarization effects semiempirically. The multiconfiguration Hartree-Fock (MCHF) method has been used quite successfully to study the electron correlation and core-polarization effects in the calculation of energy levels and oscillator strengths in atoms. Thus we feel that it should be potentially very powerful in calculating cross sections in which these effects are important.

To study the nonrelativistic electron correlation effects in atomic photoionization systemically and rigorously, Saha, *et al.*^{12,13} extended the MCHF program¹⁴ for bound-state systems to include the case of a continuum function in a single open channel. In their code, an MCHF wave function for a continuum state can be expressed in terms of a correlated ionic core with an outer continuum electron and other bound-state contributors.

Thus bound-bound and bound-continuum interactions can be taken into account directly. Orbitals describing the bound states (but not the ionic core) can be determined variationally, which accounts for certain interactions with continuum functions. Thus, indirectly, relative to a fixed basis approach, some continuum-continuum interactions are also included. A basic restriction, however, is the single open channel.

The above approach is valid for cases in which the spin-orbit interaction can be ignored. For bound-bound transitions, the MCHF plus Breit-Pauli (BP) method has been found effective for systems in which relativistic effects (including spin-orbit interaction) can be treated as a correction within the Breit-Pauli approximation. In this approach, the MCHF method is used to determine a radial basis for a wave-function expansion obtained by diagonalizing the Breit-Pauli interaction matrix. These relativistic effects are ignored in the present paper.

Recently the multiconfiguration Hartree-Fock (MCHF) method was applied favorably to the calculation of photoionization cross sections of sodium atoms.^{12,13} In the present paper we report a similar study of core polarization effects in the photoionization cross section of potassium atoms. Our aim is to improve the accuracy of the wave functions describing the initial and the final states. Core polarization by the valence electron in the initial state and by the photoelectron in the final state is very important in determining the dynamics of photoionization of alkali-metal atoms. We include the core-polarization effects very efficiently *ab initio* using the multiconfiguration Hartree-Fock method. For the calculation we use a version of the MCHF program extended by Saha, *et al.*^{12,13} and later modified by Saha¹⁵ to compute the MCHF continuum wave functions. This program is capable of varying both the bound and the continuum orbitals simultaneously.

II. MCHF WAVE FUNCTION FOR A CONTINUUM STATE

The MCHF wave function for a continuum state may be expressed in terms of a single continuum orbital coupled to a wave function for an N -electron core and other bound, $(N+1)$ -electron configuration states.

Let

$$\psi(\gamma_c L_c S_c; N) = \sum_j^{m_c} a_j \Phi(\gamma_j L_c S_c; N) \quad (1)$$

be a wave function describing an N -electron core that is an eigenstate of L_c and S_c , in terms of N -electron bound configuration states $\Phi(\gamma_j L_c S_c; N)$ with configuration γ_j and term $L_c S_c$, mixing coefficients a_j , and total energy E_c . Let ϕ_{kl} be a one-electron, continuum orbital with orbital angular momentum l . Then an MCHF wave function for a continuum state with label γ , energy E , and term LS may be expressed in a series of the form

$$\begin{aligned} \psi(\gamma LS; N+1) = & \sum_{j=1}^{m_c} a_j \Phi(\gamma_j L_c S_c; N) \phi_{kl} \\ & + \sum_{i=1}^m c_i \Phi(\gamma_i LS, N+1), \end{aligned} \quad (2)$$

where

$$\Phi(\gamma_j L_c S_c; N) \phi_{kl}$$

represents the coupling of the N -electron configuration with a single electron to yield an antisymmetric configuration state for the $(N+1)$ -electron system with the designated final term value and configuration $\gamma_j kl$.

The above wave function is defined in terms of a set of radial functions, say, $P_i(r)$, $i=1$ to m . The MCHF method for continuum states assumes all the radial functions describing the core are fixed, along with the mixing coefficients a_j . Other bound-state radial functions may be determined variationally along with the radial function for the continuum electron. In the close-coupling approximation, all the radial functions are solutions of equations of the form

$$\begin{aligned} & \left[\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] P_i(r) \\ & = \frac{2}{r} [Y_i(r)P_i(r) + X_i(r) + I_i(r)] + \sum_{i'} \epsilon_{ii'} P_{i'}(r), \end{aligned} \quad (3)$$

where the off-diagonal energy parameters $\epsilon_{ii'}$ are related to Lagrange multipliers that insure orthogonality assumptions. Here $(2/r)Y_i(r)$ is part of the potential, $(2/r)X_i(r)$ is the exchange function, and $(2/r)I_i(r)$ represents terms arising from interactions between the configurations. The radial function for the continuum electron differs only in the boundary conditions it satisfies and the definition of the diagonal energy parameter. Bound radial functions satisfy the boundary conditions,

$$P_i(r) \rightarrow r^{l+1} \text{ as } r \rightarrow 0 \text{ and } P_i(r) \rightarrow 0 \text{ as } r \rightarrow \infty,$$

in which case the diagonal energy parameter ϵ_{ii} must be an eigenvalue of the integrodifferential equation for non-trivial solutions to exist, and hence needs to be determined. The radial functions for the continuum orbital satisfy the conditions

$$\begin{aligned} & P_i(r) \rightarrow r^{l+1} \text{ as } r \rightarrow 0, \\ & P_i(r) \rightarrow \left[\frac{2}{\pi k} \right]^{1/2} \sin \left[kr - \frac{l\pi}{2} + \frac{q}{k} \ln 2kr + \delta_l + \sigma_l \right] \\ & \text{as } r \rightarrow \infty, \end{aligned} \quad (4)$$

where $\sigma_l = \arg[\Gamma(l+1-iq/k)]$ is the Coulomb phase shift, δ_l is the residual phase shift, $q = Z - N$ is the net charge of the ion, and $\epsilon_{ii} = -k^2$. Thus the multiconfiguration self-consistent-field procedures can be applied to this system as well, except that the continuum function is obtained by outward integration only, there being no exponentially decaying "tail" region. The same numerical procedures were used for bound radial functions, except that, at larger values of r , outward integration proceeded at half the usual step length with functions $Y_i(r)$, $X_i(r)$, and $I_i(r)$ interpolated at the midpoint. These functions are essentially "bound" in nature and vary smoothly as $r \rightarrow \infty$. In this way, some additional accuracy was acquired for the outward integration, and the logarithmic mesh could be retained. The continuum ra-

dial function was normalized by fitting the computed values at two adjacent points to the regular and irregular Coulomb function as soon as the Coulomb region was reached, which may be at considerably smaller values of r than the asymptotic form given by the boundary condition of Eq. (4).

In a bound-state problem the MCHF mixing coefficients are eigenvectors of an interaction matrix. In the present approximation, only the coefficients c_i need to be determined, and they are solutions of the system of equations derived from the condition that $\langle \psi | H - E | \psi \rangle$ be stationary with respect to variations in the coefficients, where H is the Hamiltonian for the $(N+1)$ -electron system and $E = E_c + k^2/2$ (in atomic units). Let

$$\Phi_j \equiv \Phi(\gamma_j L_c S_c; N) \cdot \phi_{kl}, \quad j = 1, \dots, m_c$$

and

$$\Phi_i \equiv \Phi(\gamma_i L S; N+1), \quad i = 1, \dots, m.$$

Then the coefficients c_i are solutions of the system of equations

$$\sum_{i'=1}^m \langle \Phi_i | H - E | \Phi_{i'} \rangle c_{i'} + \sum_{j=1}^{m_c} \langle \Phi_i | H - E | \Phi_j \rangle a_j = 0, \quad i = 1, \dots, m.$$

III. MCHF THEORY OF PHOTOIONIZATION

The MCHF theory of bound-bound transitions can be extended to describe atomic photoionization processes. In the present paper we will be concerned mainly with low-energy ionization, so that we may restrict our attention to dipole contributions from the $4s$ shell to the photoionization amplitude. In the dipole approximation the total photoionization cross section is given by

$$\sigma(\omega) = 4\pi^2 \alpha a_0^2 \omega \sum_{f,m} |\langle \psi_f | T | \psi_i \rangle|^2.$$

The operator T is the dipole transition operator, which is given by

$$T = T_L = \sum_{j=1}^n Z_j,$$

in the length form, and

$$T = T_V = \sum_{j=1}^n \frac{\nabla_j^Z}{i\omega},$$

in the velocity form. The matrix elements

$$M = \langle \psi_f | T | \psi_i \rangle$$

are evaluated in atomic units; ω is the incident photon energy in atomic units; α is the fine structure constant; a_0 is the Bohr radius of the hydrogen atom. ψ_i and ψ_f are the initial and final states, respectively, and the sums run over final configurations and all magnetic quantum numbers m . The length and velocity forms of the cross section will be identical when ψ_i and ψ_f are exact solutions of the same Hamiltonian equations.

Application of the MCHF procedure described in the previous papers^{12,13} proceeds in the following manner. First, the MCHF method is used to determine a set of radial functions. Using these radial functions, the dipole matrix element is calculated, and hence the photoionization cross section. The important polarization of the $3s^2 3p^6$ core by the valence electron for potassium is included in the original wave functions computed by the MCHF technique.

IV. DESCRIPTION OF THE APPROXIMATIONS

In our calculation we consider the process

$$\hbar\omega + K(1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 S) \rightarrow K^+(1s^2 2s^2 2p^6 3s^2 3p^6 {}^1S) + e^-(kp),$$

where the final state is ${}^2P^\circ$. The core polarization so important in potassium is nothing more than the distortion of the core orbitals due to the electric field produced by the valence electron or the photoelectron. This distortion is of course different for different kinetic energies of the photoelectron. Moreover, different degrees of polarization, e.g., dipole, quadrupole, and other multipole, are important for different kinds of core. The polarization of each kind can be taken into account by adding configurations generated by the replacement of core orbitals to produce dipole, quadrupole, and multipole effects. The polarization, which is different for each kinetic energy of the photoelectron, can be considered adequately by varying both bound and continuum orbitals simultaneously at each kinetic energy of the photoelectron. The procedure followed in the present calculation considers all the configurations sufficient to account for the polarizations of all kinds of the potassium ion core explicitly. It then provides a scheme for varying the bound and the continuum electron wave functions simultaneously at each kinetic energy of the photoelectron. In this way the dynamical core-polarization effects are taken into account very accurately. The resulting large set of coupled second-order integrodifferential equations is solved numerically by an iterative method which varies both the bound and the continuum orbitals simultaneously at each kinetic energy of the photoelectron.

We performed two sets of calculations in order to isolate the effects of core polarization by the valence electron in the initial state and by the continuum electron in the final state. In the first, called "HF," both initial and final states are represented as a single configuration. In the second, called "correlated," all configurations which contribute to the core polarization are included. For the $ns^2 np^6$ core the polarization effect can be taken into account very well by including configurations involving the single replacement of the core orbitals according to $ns \rightarrow n'p$ and $np \rightarrow n'd$ and $n's$, and then varying the bound $n'p$, $n'd$, $n's$, and continuum orbitals simultaneously. The $1s$, $2s$, $2p$, $3s$, and $3p$ wave functions are obtained from the HF calculation of $3s^2 3p^6 4s^2 S$ ground state.

A. Ground-state configuration $3s^2 3p^6 4s^2 {}^2S$

The initial ground-state wave function is calculated by the MCHF wave function expansion over the set of 52 configuration states coupled to form a 2S term:

$$\begin{aligned} &\{3s^2 3p^6 4s, 3s 3p^6 4s^2, 3s^2 3p^5 4s 4p, 3s 3p^6 3d 4d, \\ &3s 3p^6 3d^2, 3s 3p^6 4d^2, 3s 3p^6 4f^2, 3s^2 3p^5 3d 4p, \\ &3s^2 3p^5 3d 4f, 3s^2 3p^5 4p 4d, 3s^2 3p^5 4d 4f, 3s 3p^6 4s 5s, \\ &3s^2 3p^6 5s, 3s 3p^6 5s^2, 3s^2 3p^5 4p 5s, 3s^2 3p^5 4s 5p, \\ &3s 3p^6 3d 5d, 3s 3p^6 4d 5d, 3s 3p^6 5p^2, 3s 3p^6 5d^2, \\ &3s^2 3p^5 3d 5p, 3s^2 3p^5 4p 5d, 3s^2 3p^5 4d 5p, \\ &3s^2 3p^5 4f 5d, 3s^2 3p^5 5s 5p, 3s^2 3p^5 5p 5d, \\ &3s 3p^6 4s 6s, 3s 3p^6 6s^2, 3s^2 3p^5 4p 6s, 3s^2 3p^5 5p 6s, \\ &3s^2 3p^6 6s, 3s 3p^6 5s 6s\} {}^2S. \end{aligned}$$

The above expansion represents the set of configurations whose contribution towards the dipole matrix element is appreciable. The initial-state radial wave functions were obtained by MCHF calculation varying nine bound orbitals simultaneously.

B. The final-state configuration $3s^2 3p^6 k p {}^2P^\circ$

The final MCHF wave function expansion was over the set of 40 configuration states of the ${}^2P^\circ$ term:

$$\begin{aligned} &\{3s^2 3p^6 k p_1, 3s^2 3p^5 4p_2 ({}^1S), 3s 3p^6 3d 4p_2, \\ &3s 3p^6 4p_2 ({}^1P) 5s, 3s^2 3p^5 4p_2 ({}^1D, {}^3P), \\ &3s 3p^6 4p_2 ({}^3D) 4f, 3s 3p^6 3d ({}^1D) 4f, 3s 3p^6 3d ({}^1D) 5p_2, \\ &3s 3p^6 4s 5p_2, 3s 3p^6 5s 5p_2, 3s^2 3p^5 3d 4s, \\ &3s^2 3p^5 3d ({}^1P) 4d, 3s^2 3p^5 3d 5s, \\ &3s^2 3p^5 3d ({}^1P, {}^1F, {}^3P, {}^3F) 5d, 3s^2 3p^5 4s 4d, \\ &3s^2 3p^5 4s 5s, 3s^2 3p^5 4s 5d, 3s^2 3p^5 4d 5s, \\ &3s^2 3p^5 5s 5d, 3s^2 3p^5 3d^2, 3s^2 3p^5 4s^2, 3s^2 3p^5 5s^2\} {}^2P^\circ. \end{aligned}$$

The core radial functions $1s, 2s, 2p, 3s$ and $3p$ were kept fixed at their ground-state $3s^2 3p^6 4s^2 {}^2S$ values. The above expansion was selected after a series of tests had been performed and represents the set of configurations which contributes most strongly to the dipole matrix element. The final-state radial functions were obtained by varying six bound and one continuum orbital simultaneously.

V. RESULTS

The calculated photoionization threshold energy is 4.381 eV, which is very accurate compared to the experimental value of 4.339 eV. In all of the cross-section calculations we used the experimental ionization energy.

In Fig. 1 we present our "HF" and "correlated" results for the photoionization cross section of potassium calculated in the dipole length and dipole velocity approximations as a function of photoelectron energy ranging from

FIG. 1. Photoionization cross section of the potassium atom vs photoelectron energy. E , experimental results of Hudson and Carter; CL, present correlated (length) results; CV, present correlated (velocity) results; PL, results (length) obtained by Chang; PV, results (velocity) obtained by Chang; W , results of Weisheit, and Dalgarno, and Weisheit; HL, present Hartree-Fock length results; and HV, present Hartree-Fock velocity results.

0.0 to 12.0 eV. Our results are also compared with the experimental results of Hudson and Carter.¹⁰ Our HF length results decrease from threshold to a minimum at about 0.8 eV, then increase to a maximum at about 6 eV, and, following that, decrease slowly. The HF velocity results also decrease from threshold, reach a minimum at about 0.4 eV, then increase to a maximum at about 6 eV, and finally decrease slowly with the increase of photoelectron energy. At an energy less than the minimum of the velocity results, the length results are higher than the corresponding velocity results; after the minimum, the velocity results are higher than the length. Below the minimum both length and velocity results are higher than the experimental values of Hudson and Carter.¹⁰ The velocity results are closer to the experimental results than the length results. After the minimum the experimental results increase sharply with an increase in photoelectron energy, becoming too high compared to both the HF length and velocity results.

We also compare our results with the theoretical results obtained by Chang.⁶ Using many-body diagrammatic theory to include various electronic correlation effects, he investigated the photoionization cross section of potassium in the region beyond the minimum. He included the effects of virtual excitations of the inner-shell electrons by calculating the lowest-order diagrams which take into account the short-range correlation effects. As the direct evaluation of the diagrams which represent the dominant long-range polarization effect of the ionic core

on the outgoing photoelectron wave function and the similar effect on the valence electron wave function was extremely difficult, he included an additional long-range adiabatic polarization potential to obtain the valence and the photoelectron wave functions. The HF length and velocity results obtained by Chang agree very well with our corresponding HF results.

Again looking at Fig. 1 we note that our correlated length results also decrease from threshold to a minimum at 0.2 eV and then increase sharply with the increase of photoelectron energy. The correlated velocity results show a similar behavior. The correlated velocity results are slightly higher than the corresponding length results below the minimum, which is opposite the behavior of corresponding HF results. After the minimum, the correlated length results are higher than the correlated velocity results. Below the minimum, our correlated results agree very well with the experimental results of Hudson and Carter. After the minimum, our length results are closer to the experimental results of Hudson and Carter.

The present correlated calculation agrees well with the experimental results of Hudson and Carter, although there is a significant discrepancy between the length and velocity results. The agreement between the results obtained by Chang and the experimental results of Hudson and Carter is also fairly satisfactory, except for a similar discrepancy between the length and the velocity calculation. Chang's correlated results agree very well with the present correlated results. His results agree better with the experiment¹⁰ than do ours after 2 eV. Comparison between our correlated results and Chang's correlated results is not possible below 2 eV, as Chang's results are not available in that region. The slight difference between the results obtained by Chang and our results may be due to adiabatic approximation used by Chang in describing the long-range core-polarization effect. This approximation becomes less reliable at higher energies. It should be mentioned here that the adiabatic polarization potential used by Chang is independent of the kinetic energy of the photoelectron and hence does not adequately take into account the dynamical core-polarization effects. The difference between the present HF and correlated results is a measure of the core-polarization effect. The core-polarization effect is very strong in the case of potassium.

In Fig. 1 we also plotted the results obtained by Weisheit and Dalgarno⁷ and Weisheit⁸ for comparison. As mentioned earlier, they treated the polarization effect as a perturbation of the core wave function by the valence electron or the photoelectron. To study the effects of core polarization and the spin-orbit interaction they used a model potential and the spin-orbit interaction potential. Their results decrease slowly from threshold to a minimum at 0.2 eV, then increase to a maximum at 4.9 eV, and finally decrease. Their results agree well with experimental values from threshold through the region of the cross-section minimum. At higher energies their cross section is very low compared to measurement. Our correlated length and velocity results agree well with their results from threshold to 1.2 eV, except exactly at the minimum. Beyond 1.2 eV, their results are too low

compared to present correlated length and velocity results. Our results agree better with the experiment than theirs above 1.2 eV.

In Fig. 2 we compare the present calculated results with other theoretical and experimental results in an expanded diagram as a function of photoelectron energy in the region from 0.0 to 2.0 eV. This figure shows clearly the differences between the theoretical and the experimental results at very low energies. Comparison with Chang's results was not possible, as his results were not available in this energy region. It is seen from the figure that the present correlated velocity results from 0.0 to 0.85 eV near the minimum are in excellent agreement with the experimental results of Hudson and Carter.¹⁰ Above 0.85 eV the present correlated length results agree very well with the experiment. Below the minimum the results obtained by Weisheit and Dalgarno are nearly the same as our correlated length results and are in very good agreement with the experiment. Above the minimum, up to 1.0 eV, their results are very close to the present correlated velocity results and also agree very well with the experiment.

With regard to the cross-section minimum, it should be mentioned that we performed a nonrelativistic calculation in *LS* coupling. As expected, we obtained a zero minimum. The finite minimum which is found experimentally¹⁰ in the cross section of potassium is attributed to spin-orbit perturbation of the continuum electron wave function. This gives two slightly different wave functions: kp_j for the two final j values ($\frac{1}{2}$ and $\frac{3}{2}$), with corresponding matrix elements $M_{1/2}$ and $M_{3/2}$. The

FIG. 2. Photoionization cross section of potassium atom vs photoelectron energy. *E*, experimental results of Hudson and Carter; *CL*, present correlated (length) results; *CV*, present correlated (velocity) results; *W*, results of Weisheit and Dalgarno, and Weisheit; *HL*, present Hartree-Fock length results; and *HV*, present Hartree-Fock velocity results.

quantity M^2 in the cross section will then be replaced by $\frac{1}{3}(2M_{3/2}^2 + M_{1/2}^2)$ which will give a nonzero minimum, as $M_{1/2}$ and $M_{3/2}$ are not zero for the same photon energy. Fermi¹⁶ showed that this spin-orbit perturbation of valence-electron wave functions is responsible for the anomalous 2P line strength ratio in alkali-metal atoms. Fano¹⁷ also demonstrated that this spin-orbit perturbation causes photoelectrons produced by the ionization of unpolarized alkali-metal atoms by circularly polarized light at wavelengths near the cross-section minimum to be strongly polarized. Seaton,¹⁸ following the perturbation theory of Fermi and using the one-electron wave function of Bates¹⁹ and Mishra,²⁰ obtained the minimum to be 0.0003 Mb at 2700 Å.

Our length and velocity results at threshold are 0.006 and 0.01 Mb, respectively, which compare well with the experimental result of 0.01 Mb measured by Hudson and Carter¹⁰ and the theoretical result of 0.006 Mb calculated by Weisheit and Dalgarno.⁷ We obtain the zero-minimum cross section at 0.2 eV, instead of the nonzero minimum of 0.00022 Mb obtained by Weisheit and Dalgarno and 0.0003 Mb obtained by Seaton.¹⁸ The experimental result¹⁰ is 0.002 Mb. The energy at which the present minimum occurs compares very well with experiment and other theoretical results.

VI. CONCLUSION

We have applied the multiconfiguration Hartree-Fock method to calculate the photoionization cross section of the potassium atom at several photon energies from threshold to 12 eV. The core-polarization effect, which is very strong in the case of photoionization of potassium, has been taken very efficiently *ab initio* by a detailed and extensive calculation using the multiconfiguration self-consistent-field method through the configuration-interaction procedure. The agreement of our results with the many-body calculation of Chang⁶ above the minimum is good. Below the minimum our results agree very well with the results obtained by Weisheit and Dalgarno.⁷

The overall agreement of our results with experiment is good. Our results, as do all other theoretical results, differ from the experimental cross section at the higher energies. Chang's results are in better agreement with experiment above 2 eV. We obtained good agreement with the experimental ionization potential, which supports the accuracy of the initial-state wave function.

We do not consider the effects of spin-orbit splitting of the final-state continuum wave function in our calculation. That is why we obtain a zero minimum in the cross section instead of the finite minimum found by experiment¹⁰ and the theoretical calculation by Weisheit and Dalgarno,⁷ who included the spin-orbit interaction by a model potential. Spin-orbit interaction will not change the total photoionization cross-section results very much except at the minimum. Although we obtained reasonably good agreement with experiment throughout the energy region we explored, discrepancy still remains at the higher energies. However, Chang⁶ has pointed out that a possible explanation of the discrepancy between theory and experiment at the higher photon energies could be the presence of a small fraction of potassium molecules. These have a cross section almost two orders of magnitude larger than the atomic cross section and could account for the higher experimental value. Thus further experimental work on potassium, with particular care to eliminate all molecular absorption, would be helpful in clarifying the situation.

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