Threshold behavior of the M-shell photoionization of argon

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The multiconfiguration Hartree-Fock method, which has been extended to study photoionization of atoms, is applied to calculate the $3s \rightarrow kp$ photoionization cross section of argon. It has been shown that the interchannel interaction associated with the $3p \rightarrow kd$ transition, which is very strong in the $3s$ subshell photoionization cross section, can be very efficiently simulated by the bound-continuum channel interaction associated with the $3p \rightarrow 3d$ transition. The length and velocity forms of cross section agree very well throughout the range of energies considered. Our results compare well with other theoretical estimates and are in better agreement with experimental measurements.

I. INTRODUCTION

The photoionization of atoms is of fundamental importance in many branches of physics, such as plasma physics, atmospheric, space, and astrophysics, as well as in the area of radiation physics. In addition, it is important in many applications, particularly in the study of the transport of radiation in planetary and stellar atmospheres. Photoionization cross sections are used in determining the photoionization rates produced in the ionosphere owing to the interaction of the extreme ultraviolet radiation from the sun with the earth's atmosphere. Moreover, the theoretical analysis of stellar and laboratory spectra requires a knowledge of photoionization cross sections for a wide variety of transitions over a comprehensive range of energies.

The photoionization of atoms has received increasing attention from both experimentalists and theoreticians in the past few years as a rich source of information on detailed atomic structure and processes. On the experimental side, with the rapid advance of photoelectron spectroscopy and with the increasing availability of synchrotron radiation sources, many precision measurements of atomic photoionization are carried out over the whole spectral range from the visible to the x-ray region. The experiments have been directed towards the determination of both total and partial cross sections from individual subshells as a function of photon energy. Theoretically, many-body methods are being increasingly applied to make accurate predictions for the atomic system and to understand the dynamics of photoionization processes.

At the threshold where the new channel opens, photoionization cross sections show rapid variations as a function of photon energy. The properties of virtual bound states can give potential information about the cross section near the threshold. These bound states are stationary only within an independent-particle approximation. Interactions between the particles actually cause these bound states to autoionize into the continuum. Interchannel interaction always produces a readjustment of the results of an independent-particle calculation. It has been found by many investigators[1-4] that the interaction of the $3p \rightarrow kd$ channel with the $3s \rightarrow kp$ channel is very strong towards the partial photoionization cross section of the $3s$ subshell. The $ns \rightarrow kp$ partial photoionization cross section is very small compared to the total photoionization cross section of the outer shell of argon. Cooper and Manson[5] performed calculations on the photoionization cross section of $3s \rightarrow kp$ transition, using wave functions generated from the Herman-Skillman model potential. Kennedy and Manson[6] used Hartree-Fock wave functions to calculate a photoionization cross section of the same transition. Although both of these calculations disagree with experiments,[7-9] their results show the cross section to be small and to increase monotonically with energy near the threshold. Amusia *et al.*[1] carried out calculations of this transition with the random-phase approximation with exchange (RPAE), using the Hartree-Fock basis. They studied the influence of the $3p \rightarrow kd$ transition on the $3s \rightarrow kp$ photoionization cross section. Lin[2] used a simplified version of the random-phase approximation with exchange (SRPAE) to calculate numerically the cross section of the $3s \rightarrow kp$ transition of Ar, taking into account its coupling with the $3p \rightarrow kd$ transition. The results obtained by RPAE and SRPAE are very different from that obtained by an independent-particle approximation. Burke and Taylor[3] studied the photoionization cross section of $3s \rightarrow kp$ transition, using the R-matrix method. In this calculation both the initial bound state and the final atomic continuum state are expanded in terms of an R-matrix basis. Chang[4] used many-body perturbation theory to calculate the M-shell photoionization cross sections of argon. He studied the individual effect of the ground-state configuration interaction and the final-state intershell and interchannel interactions in the calculation.

In this paper, we intend to apply the multiconfiguration Hartree-Fock (MCHF) method to the M-shell photoionization of argon. The MCHF method extended to compute continuum wave function has been

successfully applied to the photoionization of sodium atoms and photodetachment of negative hydrogen ions. Although the present method of calculation at the moment has the limitation of dealing with a single continuum channel, it can simulate very effectively the effect of so-called interchannel interaction with the bound-continuum channel interaction. This paper reports results which are comparable with other theoretical results and even in better agreement with experiment than other theoretical results. In this paper we see how the cross section of the $3s \rightarrow kp$ photoionizing transition in Ar is changed mostly by the channel coupling with the $3p \rightarrow 3d$ transition. The addition of the bound channel coupling to the direct transition changes the threshold behavior of $3s \rightarrow kp$ completely. The inclusion of the bound-continuum interaction is equivalent to the removal of a $3s$ electron through an intermediate virtual excitation of the $3p$ subshell, i.e., through a transition $3s^2 3p^6 \rightarrow 3s^2 3p^5 3d \rightarrow 3s 3p^6 kp$. It is known from the earlier investigations[1-4] that configurations generated by the two-electron excitations into the $3d$ shell are particularly important in the case of argon. Accordingly, we select all the configurations generated by one- and two-electron excitations into the $3d$ shell in the initial- and the final-state configurations, in order to obtain accurate wave functions for both the states. The reliability of the MCHF approach is demonstrated by the excellent agreement between the present calculation and the available experimental measurements.[7-9]

II. THEORY

A. MCHF theory of photoionization

The calculation of photoionization cross sections requires wave functions of the initial bound state and the final state of the electron-plus-ion system. In the dipole approximation the photoionization cross section is given by

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

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

$$T=T_L=\sum_{j=1}^{n} Z_j \quad \text{in the length form}$$

and

$$T=T_V=\sum_{j=1}^{n} \frac{\nabla_j^z}{i\omega} \quad \text{in the velocity form} .$$

The matrix elements are evaluated in atomic units. a_0 is the Bohr radius, α is the fine-structure constant, and ω is the photon energy in atomic units. Ψ_i and Ψ_f are, respectively, the initial- and the final-state wave functions and the sums run over final configurations and all magnetic quantum numbers. The summation over j extends over all the electrons in the atom.

B. MCHF wave function for the final continuum state

Briefly, the final MCHF wave function for the continuum state with label γ, energy E, and the term LS is expanded in a series of the form

$$\Psi(\gamma LS;N+1)=\sum_{j=1}^{m_c} a_j \Phi(\gamma_j L_C S_C;N)\phi_{kl} + \sum_{i=1}^{m} C_i \Phi(\gamma_i LS;N+1) , \tag{1}$$

where the first term represents an N-electron case 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, coupled with a continuum orbital ϕ_{kl} of angular momentum l to yield an antisymmetric configuration state for the $(N+1)$-electron system with the designated final term value and configuration, whereas the second term is the sum of $(N+1)$-electron bound-state configurations which are eigenstates with the same L and S and which are included to allow for electron correlation and the core polarization. A set of radial functions $P_i(r)$, $i=1,\ldots,m$, which defines the above MCHF wave function, is a solution of the coupled integro-differential equations of the form

$$\left[\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l(l+1)}{r^2}\right]P_i(r) = \frac{2}{r}[Y_i(r)P_i(r)+X_i(r)+I_i(r)]+\sum_{i'}\varepsilon_{ii'}P_{i'}(r) . \tag{2}$$

The off-diagonal energy parameters $\varepsilon_{ii'}$ are related to Lagrange multipliers to ensure orthogonality assumptions. (For an explanation of the terms in the equation, see Ref. 10.) In the MCHF method for the continuum state, all the radial functions describing the core are assumed to be fixed along with the mixing coefficients a_j. Other bound-state radial functions are determined variationally along with the radial function for the continuum electron.

Bound radial functions satisfy the boundary conditions,

$$P_i(r) \underset{r\rightarrow 0}{\sim} r^{l+1} \quad \text{and} \quad P_i(r) \underset{r\rightarrow \infty}{\sim} 0 . \tag{3}$$

In this case the diagonal energy parameter ε_{ii} is an eigenvalue of the integro-differential equation and hence needs to be determined. The radial functions for the continuum orbital satisfy the conditions

$$P_i(r) \underset{r\rightarrow 0}{\sim} r^{l+1} ,$$
$$P_i(r) \underset{r\rightarrow \infty}{\sim} \left[\frac{2}{\pi k}\right]^{1/2} \sin\left[kr-\frac{l\pi}{2}+\frac{q}{k}\ln(2kr)+\sigma_l+\delta_l\right] , \tag{4}$$

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 $\varepsilon_{ii} = -k^2$, k^2 being the kinetic energy of the continuum electron.

The coupled integro-differential equations are solved numerically by the iterative method. The multiconfiguration (MC) self-consistent-field (SCF) procedure is applied to compute both the bound and the continuum wave functions. The same numerical procedures are used for both the bound and the continuum wave functions. The bound radial functions are essentially bound in nature and vary smoothly as $r \to \infty$. The continuum radial function is obtained by outward integration only, there being no exponentially decaying "tail" region. The continuum radial function was normalized by fitting the computed values at two adjacent points to the regular and irregular Coulomb functions as soon as the Coulomb region is reached. The coefficients C_i are solutions of the system of equations

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

$$i = 1, \ldots, m ,$$

where

$$\Phi_j \equiv \Phi(\gamma_j L_C S_C; N)\phi_{kl}, \quad j = 1, \ldots, m_C$$

and

$$\Phi_i \equiv \Phi(\gamma_i LS; N+1), \quad i = 1, \ldots, m .$$

H is the Hamiltonian for the $(N+1)$-electron system and $E = E_C + k^2/2$ (in a.u.).

We consider the process

$$\hbar\omega + \mathrm{Ar}(1s^2 2s^2 2p^6 3s^2 3p^6\, {}^1S) \to \mathrm{Ar}^+(1s^2 2s^2 2p^6 3s 3p^6) + e^-(kp) ,$$

where the final state is $^1P^0$.

The ground-state configuration interaction and the final-state configuration interaction can be taken into account effectively by following the same procedure given in Refs. 10 and 11. The initial ground-state wave function is calculated by the MCHF wave function expansion over the following configurations coupled to form ^1S term:

$$\{3s^2 3p^6, 3s^2 3p^4 3d^2, 3p^6 3d^2\}\, {}^1S .$$

The MCHF method has been used to compute all the bound orbitals. In this calculation all the bound orbitals including $1s$, $2s$, and $2p$ were varied simultaneously to obtain accurate wave functions. The final-state configuration interaction was taken into account by the following expansion of the $^1P^0$ term:

$$\{3s 3p^6 kp, 3s^2 3p^5 3d, 3s 3p^5 3d^2, 3p^5 3d^3, 3s^2 3p^3 3d^3\}\, {}^1P^0 .$$

The MCHF method described above has been used to compute the continuum wave function. In this calculation the bound orbitals including $3d$ are kept the same as the ground-state wave function. The interaction between the bound configuration $3s^2 3p^5 3d$ and the continuum configuration $3s 3p^6 kp$ is found to be very strong at low photon energies. As the photon energy increases, the coefficient C_1 [in Eq. (1)] of the bound configuration $3s^2 3p^5 3d$ slowly decreases. This indicates a continual decrease in the interaction between the bound $3s^2 3p^5 3d$ and the continuum $3s 3p^6 kp$ configurations with the increase of the photon energies.

At low photon energies the positive contribution of the dipole matrix element between the initial $3s^2 3p^6$ and the final $3s^2 3p^5 3d$ configurations is much larger than the corresponding negative contribution between the initial $3s^2 3p^6$ and the final $3s 3p^6 kp$ configurations. With the increase in photon energy the positive contribution of the dipole matrix element for the transition $3p \to 3d$ gradually decreases and the corresponding negative contribution for the transition $3s \to kp$ slowly increases. At Cooper minimum these two contributions become nearly equal. With a further increase in photon energies, contribution from the $3s \to kp$ transition dominates and finally at high photon energies the $3s \to kp$ transition is found to be the main contribution.

III. NUMERICAL RESULTS FOR THE Ar $3s \to kp$ PHOTOIONIZATION CROSS SECTION

We calculated photoionization cross section of Ar from the $3s$ subshell, taking into consideration the electron correlation effects in both the initial- and the final-state wave functions through the configuration-interaction procedure. The results of this calculation provide a most sensitive test of the present MCHF theory of photoionization, since they depend on accuracy of the approximation methods. We used experimental ionization energy for this calculation.

We present our results of the $3s \to kp$ photoionization cross section of argon in the dipole length and dipole velocity approximations in Fig. 1, along with the experimental results of Samson and Gardner,[7] Houlgate *et al.*,[8] and Marr.[9] The figure shows the cross section as a function of photoelectron energy. The present length and velocity cross sections agree very well. The length cross section decreases sharply from near threshold, goes to a minimum of zero at about 0.9 Ry (photoelectron energy), then increases as the photoelectron energy increases up to 2.5 Ry, then decreases a little up to 3.0 Ry, and then increases a little and becomes flat for higher energies. The velocity result is slightly lower than the length result below the minimum. It goes to a minimum at about 0.8 Ry and then shows behavior similar to the length result at higher energies. Our results agree very well, within the errors, with experiment.

In Fig. 2, we compare our length results with the experimental result of Samson and Gardner,[7] Houlgate *et al.*,[8] and Marr[9] and with the Hartree-Fock calculations of Kennedy and Manson,[6] the RPAE calculations of Amusia *et al.*,[1] the SRPAE calculations of Lin,[2] the R-matrix calculations of Burke and Taylor,[3] and the many-body perturbation calculations of Chang.[4] In the independent-particle Hartree-Fock approximation, the

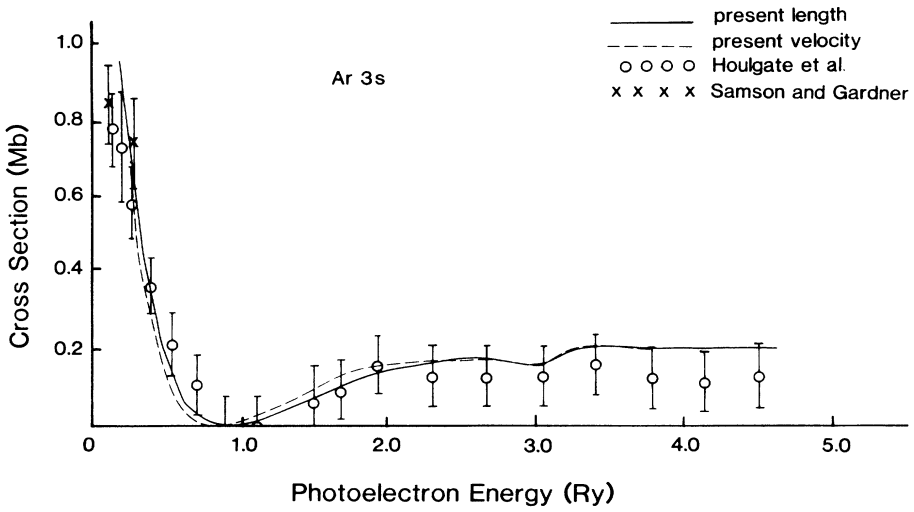

FIG. 1. 3*s* subshell photoionization cross section of argon as a function of photoelectron energy. ——, present length results; — — —, present velocity results; ○, experimental results of Houlgate *et al.* (Ref. 8); and ×, experimental results of Samson and Gardner (Ref. 7).

partial photoionization cross section for the 3*s* electron of Ar shows a smooth rise from the ionization threshold. After it reaches a broad maximum, it levels off at higher energies. On the other hand, in the present calculation, the effect of bound channel interaction associated mainly with the transition $3p \rightarrow 3d$ changes completely the qualitative feature of the $3s \rightarrow kp$ cross section near threshold. The cross section, instead of rising smoothly from the threshold, as predicted by the Hartree-Fock approximation, decreases sharply from the threshold to a Cooper minimum at about 0.9 Ry. The existence of a dip and rapid variations with energy was first pointed out by Amusia *et al.*[1] in a RPAE calculation and was subsequently confirmed by experimental measurements[7–9] as well as other theoretical calculations.[1–4] Interference between the slow electron ejected from the 3*s* subshell and the electron excited from the outer 3*p* subshell is responsible for this drastic change of the qualitative feature of the cross section. The presence of the Cooper minimum strongly suggests that the transition amplitude is determined by the large cancellation of contributions from more than one transition amplitude of comparable impor-

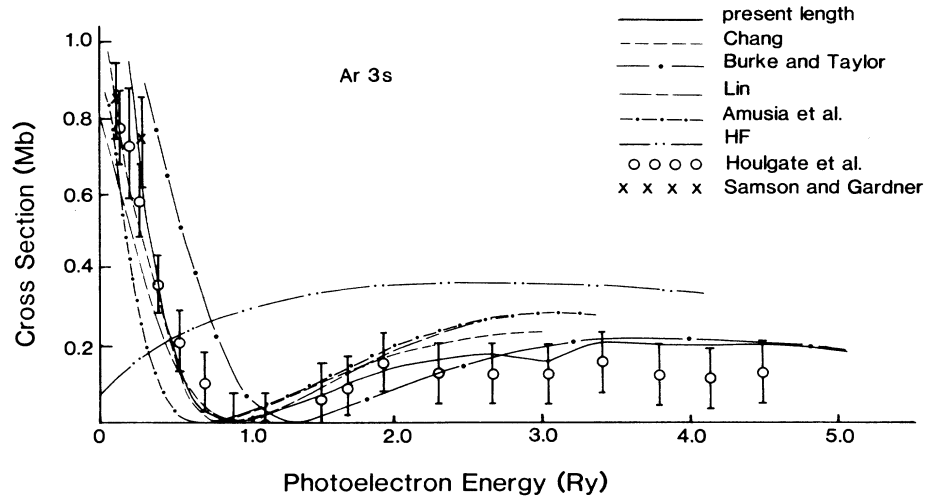

FIG. 2. 3*s* subshell photoionization cross section of argon as a function of photoelectron energy. ——, present length results; — — —, results obtained by Chang (Ref. 4); —·—·—·, results obtained by Burke and Taylor (Ref. 3); — - — -, results obtained by Lin (Ref. 2); ·-·-·-, results obtained by Amusia *et al.* (Ref. 1); —··—, Hartree-Fock results obtained by Kennedy and Manson (Ref. 6); ○, experimental results of Houlgate *et al.* (Ref. 8); and ×, experimental results of Samson and Gardner (Ref. 7).

tance in this energy region. Near the threshold, the contribution of the $3p \rightarrow 3d$ transition amplitude with an opposite sign to that of the $3s \rightarrow kp$ transition amplitude is several times larger than that of the $3s \rightarrow kp$ transition amplitude. With the increase of photoelectron energy, the cancellation between these two contributions becomes more complete and eventually the minimum occurs at 0.9 Ry, when the two contributions are approximately equal but with opposite sign. With the further rise of energy, the effect of the bound channel interaction from the $3p \rightarrow 3d$ transition diminishes as energy increases. The contributions from the other bound channel configurations are small, but they remove the quantitative disagreement between the length and the velocity cross sections.

Amusia *et al.*[1] used the RPAE approximation to calculate the $3s \rightarrow kp$ photoionization cross section of argon. They found the strong influence of the $3p \rightarrow kd$ transition on the $3s \rightarrow kp$ photoionization cross section. Their results agree qualitatively with the present results. Their results are lower than the present results below the minimum but higher above the minimum. Their minimum is obtained at lower photoelectron energy. Lin[2] calculated the photoionization cross section for this transition using simplified random-phase approximation with exchange. His calculation considers the effect of interchannel coupling with the $3p \rightarrow kd$ transition. Close to threshold, his result is lower than the present results; with the increase of energy his results become closer to the present results up to the minimum, then becomes higher as the energy increases. The energy at which the present result and the results obtained by Lin[2] show the vanishing cross section, is nearly the same. Burke and Taylor[3] applied R-matrix method to obtain photoionization cross section of $3s \rightarrow kp$ transition. The qualitative features of their theoretical calculations are similar. Their results are higher than the present result below the minimum. Their minimum has been shifted towards the higher energy. Above the minimum, their results are lower than ours up to 2.7 Ry, then become closer with the increase of energy. Chang[4] obtained the $3s \rightarrow kp$ photoionization cross section of argon by many-body perturbation theory. He took into account the final-state intershell and interchannel interactions into his calculations. His results are a little lower than the present results close to the threshold, with the increase of energy they become closer up to the minimum, then become higher than the present results above the minimum. The overall agreement of the theoretical data[1-4] obtained by various methods of approximation is reasonably satisfactory. The remaining discrepancy between the different theoretical results is probably due to the differences in the approximation methods. Comparison shows that the present results compare well with other theoretical results and are in slightly better agreement with experiment than the other theoretical results.

IV. CONCLUSION

The calculations presented in this paper for the $3s \rightarrow kp$ photoionization cross section of argon show that the MCHF method can give quantitative agreement with experiment similar to other accurate methods. We studied the effect of interactions between the bound and the continuum channels upon the $3s \rightarrow kp$ photoionization cross sections. We have found that bound-continuum interactions can simulate very well the effect of the interchannel interactions considered by many authors.[1-4] The results of the present calculation show that the bound-continuum interaction similar to the interchannel interaction is so strong that the $3s \rightarrow kp$ photoionization cross section is dominated near threshold, not by the direct transition process but by coupling with the $3p \rightarrow 3d$ transition similar to the $3p \rightarrow kd$ transition. It is found that the present results are in slightly better agreement with experiment than the other theoretical results. Finally, we conclude that the present calculations, which depend more on the accuracy of the approximation method, give us confidence in using the MCHF method to yield reliable quantitative atomic transition data.

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