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Quantitative assessment of the many-body interactions in the M-shell photoionization of argon

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The individual effect of the ground-state configuration interaction and the final-state intershell and interchannel interactions to the photoionization of the $3s$ and $3p$ electrons is studied in the vicinity of their respective Cooper minima. Channels of configurations corresponding to these many-body interactions are included in our study by extending a recently developed theory of atomic transitions. Our calculation has successfully removed the quantitative disagreement between the experimental measurements and earlier theoretical estimates.

I. INTRODUCTION

Recent extensive theoretical studies of the many-body effects in the photoabsorption of free atoms have successfully accounted for the photoionization cross sections in energy regions where the ionization is dominated by one type of the many-body interaction. Perhaps the best known example is the photoionization of the $3p$ electrons of Ar up to about 20 eV above the ionization threshold. With modest computational effort, most of the existing many-body methods[1-5] are capable of yielding quantitatively reliable cross sections by including the dominating ground-state configuration interactions (or, equivalently, the ground-state correlation effect) between the $3p^6$ and $3p^4dd$ configurations.

However, when more than one many-body interaction of comparable importance contributes to a given transition, detailed theoretical estimation of each individual interaction would require enormous numerical efforts. This, in turn, severely reduces the effectiveness of most of the existing many-body methods. To carry out an efficient calculation, most of these methods would usually neglect the quantitative estimation and, consequently, the physical interpretation, of each individual many-body effect. In addition, to minimize the computational effort, approximations are sometimes made at the expense of quantitative accuracy. These difficulties are demonstrated in the theoretical studies of the photoionization of the $3s$ electron of Ar near its ionization threshold.[6-8] While the importance of the intershell interaction between the $3p$ and $3s$ electons in this transition is clearly established by these calculations, their detailed quantitative estimations differ significantly.[9]

To examine the relative importance of various many-body interactions in the photoionization of atomic systems, it is necessary to carry out a detailed calculation for each of the contributing interactions which are of comparable importance in a given energy region. In this paper, we report the result of such a calculation for the photoionization of the $3s$ and $3p$ electrons of Ar in the vicinity of their respective "Cooper" minima (i.e., with photon energy between 30 and 70 eV). The important many-body interactions in this energy region include (i) the ground-state configuration interactions associated with $3s^23p^6$, $3s^23p^4dd$, $3s^23p^4ss$ and $3p^6pp$ configurations, (ii) the intershell interaction between the $3s \rightarrow kp$ and $3p \rightarrow ks$ or kd transitions, and (iii) the interchannel interaction between the $3p \rightarrow ks$ and $3p \rightarrow kd$ transitions. We have studied each of these interactions individually by employing a recently reformulated many-body theory of atomic transition.[10,11] In Sec. II, we briefly outline the theoretical approach. The reliability of this approach is demonstrated by the excellent agreement between the present calculation and the available experimental measurements as shown in Secs. III and IV.

Perhaps of equal importance to the physical interpretation provided by this theoretical approach is its potential applicability to other problems of current interest. Among them, for instance, is the systematic compilation of the energy-research-related transition data of atomic ions which is experimentally inaccessible at the present time.

II. THEORY

For the ^1P transition of the M-shell electrons of Ar, the ground-state configuration interaction and the final-state intershell and interchannel interactions, as mentioned earlier, can be taken into account effectively by extending the theoretical procedure given in Refs. 10 and 11. The configurations relevant to the initial-state wave function include $3s^23p^6$, $3s^23p^4dd$, $3s^23p^4ss$ and $pp3p^6$, and their corresponding final-state configurations are $3s^23p^5kd$, $3s^23p^5ks$, and $3s3p^6k'p$.

The photoionization cross sections for the $nl_i \to kl$ transition in the dipole-velocity and dipole-length approximations are

$$\sigma^V = (16\pi\alpha/k)(k^2+\epsilon_I)^{-1}(5.29\times10^{-9})^2|D^V|^2 \text{ cm}^2 \quad (1)$$

and

$$\sigma^L = (4\pi\alpha/k)(k^2+\epsilon_I)(5.29\times10^{-9})^2|D^L|^2 \text{ cm}^2, \quad (2)$$

where ϵ_I is the ionization energy of the nl_i electron in the rydberg unit, α is the fine-structure constant, and k is the photoelectron momentum. The transition amplitude D in Eqs. (1) and (2) is given by

$$D = D_{sp} + D_{pd} + D_{ps} \quad (3)$$

and

$$D_{l_i l} = (\tfrac{2}{3})^{1/2}(-1)^l[(2l+1)(2l_i+1)]^{1/2}\begin{pmatrix} l_i & 1 & l \\ 0 & 0 & 0 \end{pmatrix} \times [(x_{nl_i}|d|\psi_l) - (\phi_l|d|x_{nl_i})], \quad (4)$$

where d stands for the dipole operator and x_{nl_i} represents the ground-state single-particle Hartree-Fock radial wave functions for the $3s(n=3,\ l_i=0)$ and $3p(n=3,\ l_i=1)$ electrons. The indices s, p, and d in Eq. (3) represent states of orbital angular momentum quantum number l (or l_i) equal to 0, 1, and 2, respectively.

The single-particle radial functions ψ_l and ϕ_l satisfy a set of coupled differential equations,

$$[H^{N-1}_{(3p)d}(r) - (\epsilon_{3p}+E)]\psi_d(r) = f_d(\phi_d, \psi_p, \phi_p, \psi_s, \phi_s; r), \quad (5a)$$

$$[H^{N-1}_{(3p)d}(r) - (\epsilon_{3p}-E)]\phi_d(r) = f_d(\psi_d, \phi_p, \psi_p, \phi_s, \psi_s; r), \quad (5b)$$

$$[H^{N-1}_{(3p)s}(r) - (\epsilon_{3p}+E)]\psi_s(r) = f_s(\phi_s, \psi_p, \phi_p, \psi_d, \phi_d; r), \quad (5c)$$

$$[H^{N-1}_{(3p)s}(r) - (\epsilon_{3p}-E)]\phi_s(r) = f_s(\psi_s, \phi_p, \psi_p, \phi_d, \psi_d; r), \quad (5d)$$

$$[H^{N-1}_{(3s)p}(r) - (\epsilon_{3s}+E)]\psi_p(r) = f_p(\phi_p, \psi_d, \phi_d, \psi_s, \phi_s; r), \quad (5e)$$

$$[H^{N-1}_{(3s)p}(r) - (\epsilon_{3s}-E)]\phi_p(r) = f_p(\psi_p, \phi_d, \psi_d, \phi_s, \psi_s; r), \quad (5f)$$

where ϵ_{3s} and ϵ_{3p} are the energy eigenvalues of the single-particle Hartree-Fock orbitals $3s$ and $3p$ of Ar, and E is the photon energy.

The effective single-particle radial Hamiltonian H^{N-1} for the ^1P dipole transition from nl_i to kl is given by

$$H^{N-1}_{(nl_i)l}(r)f_l(r) = H^N_l(r)f_l(r) - (1-P_l)\left(\tfrac{2}{3}(l||V^1(x_{nl_i}, f_l; r)||l_i)x_{nl_i}(r) + \sum_k (-1)^k \begin{Bmatrix} l & k & l \\ l_i & 1 & l_i \end{Bmatrix}(l||V^k(x_{nl_i}, x_{nl_i}; r)||l)f_l(r)\right), \quad (6)$$

where

$$(l||V^k(a,b;r)||l') = (l||C^{[k]}||l')(l_a||C^{[k]}||l_b) \times \int_0^\infty dr' a(r')b(r')\frac{r_<^k}{r_>^{k+1}}, \quad (7)$$

and P_l is the projection operator, i.e.,

$$P_0 = |1s\rangle\langle 1s| + |2s\rangle\langle 2s| + |3s\rangle\langle 3s|, \quad (8a)$$

$$P_1 = |2p\rangle\langle 2p| + |3p\rangle\langle 3p|, \quad (8b)$$

and

$$P_2 = 0. \quad (8c)$$

The matrix elements of $C^{[k]}$ are standard[12] and H^N_l is the usual Hartree-Fock radial Hamiltonian.[13]

For the s and d states, the coupling function on the right-hand side of Eqs. (5a)–(5d) takes the form

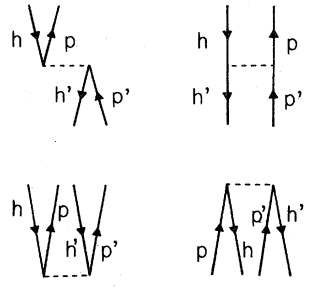

FIG. 1. Elementary interactions included in the coupling functions f_l in Eqs. (9) and (10).

$$f_l(g1_l, g2_{l'}, g3_{l''}, g4_{l'''}, g5_{l''''}; r) = (1-P_l)\Big[\sum_k \Big(\tfrac{2}{3}\delta_{k1} - \begin{Bmatrix} l & k & 1 \\ l & 1 & 1 \end{Bmatrix}\Big)(l||V^k(g1_l, x_{3p}; r)||1)x_{3p}(r)$$
$$+\tfrac{2}{3}(l||V^1(x_{3s}, g2_{l'}; r)||1)x_{3p}(r) - \begin{Bmatrix} l & 1 & l' \\ 0 & 1 & 1 \end{Bmatrix}(l||V^1(x_{3s}, x_{3p}; r)||l')g2_{l'}(r)$$
$$+\tfrac{2}{3}(l||V^1(g3_{l''}, x_{3s}; r)||1)x_{3p}(r) + \begin{Bmatrix} l & l & 0 \\ l' & 1 & 1 \end{Bmatrix}(l||V^l(g3_{l''}, x_{3p}; r)||0)x_{3s}(r)$$
$$+\tfrac{2}{3}(l||V^1(x_{3p}, g4_{l'''}; r)||1)x_{3p}(r)$$
$$+\sum_k \begin{Bmatrix} l & k & l'' \\ 1 & 1 & 1 \end{Bmatrix}(l||V^k(x_{3p}, x_{3p}; r)||l'')g4_{l'''}(r)$$
$$+\Big(\tfrac{2}{3} - \begin{Bmatrix} l & 1 & 1 \\ l'' & 1 & 1 \end{Bmatrix}\Big)(l||V^1(g5_{l''''}, x_{3p}; r)||1)x_{3p}(r)\Big]. \tag{9}$$

For the p state, the coupling function in Eqs. (5e) and (5f) is given by

$$f_p(g1_p, g2_d, g3_d, g4_s, g5_s; r) = (1-P_1)\Big[\Big(\tfrac{2}{3} - \begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \end{Bmatrix}\Big)(1||V^1(g^1_p, x_{3s}; r)||0)x_{3s}(r)$$
$$+\tfrac{2}{3}(1||V^1(x_{3p}, g2_d; r)||0)x_{3s}(r) - \begin{Bmatrix} 1 & 1 & 2 \\ 1 & 1 & 0 \end{Bmatrix}(1||V^1(x_{3p}, x_{3s}; r)||2)g2_d(r)$$
$$+\tfrac{2}{3}(1||V^1(g3_d, x_{3p}; r)||0)x_{3s}(r) + \begin{Bmatrix} 1 & 2 & 1 \\ 2 & 1 & 0 \end{Bmatrix}(1||V^2(g3_d, x_{3s}; r)||1)x_{3p}(r)$$
$$+\tfrac{2}{3}(1||V^1(x_{3p}, g4_s; r)||0)x_{3s}(r) - \begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \end{Bmatrix}(1||V^1(x_{3p}, x_{3s}; r)||0)g4_s(r)$$
$$+\tfrac{2}{3}(1||V^1(g5_s, x_{3p}; r)||0)x_{3s}(r) + \begin{Bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \end{Bmatrix}(1||V^0(g5_s, x_{3s}; r)||1)x_{3p}(r)\Big]. \tag{10}$$

Each individual coupling term in Eqs. (9) and (10) can be identified with one of the four elementary interactions which are represented diagrammatically in Fig. 1. The dotted line represents the Coulomb interaction, h and h' represent the occupied orbits in the initial state (i.e., $3s$ or $3p$ Hartree-Fock orbit), and p and p' represent those states described by the radial functions ψ_l or ϕ_l. A more detailed description of similar interactions is given in Ref. 10. The coupling functions f_s, f_p, and f_d include all interactions pertaining to a ^1P transition with $h, h' = 3s$ or $3p$ and $p, p' = \psi_l$ or ϕ_l. However, they do not include those with $h = h'$ and $p = p'$, which have already been included in the H^{N-1} Hamiltonian.[10] A straightforward expansion of Eqs. (5a)–(5f) leads to an infinite series of perturbation expansion terms with multiple applications of these four elementary interactions to infinite order.

The differential equations (5a)–(5f) are solved with the boundary conditions

$$\phi_l(r) \text{ and } \psi_l(r) \xrightarrow[r\to 0]{} r^{l+1}, \tag{11a}$$
$$\phi_l(r) \xrightarrow[r\to\infty]{} 0, \tag{11b}$$

and

$$\psi_l(r) \xrightarrow[r\to\infty]{} A_l \sin[kr + (q/k)\ln(2kr) - \tfrac{1}{2}l\pi + \delta_l], \tag{11c}$$

where the potential in which ψ_l is calculated is q/r as r approaches infinity. The solution is normalized such that the coefficient A_l equals unity for the transition $nl_i \to kl$. For a more realistic description of the final state of the transition, the energy values $\epsilon_{3p} + E$ and $\epsilon_{3s} + E$ in Eqs. (5a), (5c), and (5e) are replaced by k^2_{3p} and k^2_{3s}, respectively. The photoelectron momenta k_{3p} and k_{3s} of the ionized electrons from the $3p$ and $3s$ subshells are related by the equation

$$k^2_{3p} - k^2_{3s} = \epsilon_{3p} - \epsilon_{3s}, \tag{12}$$

where ϵ_{3p} (= 15.76 eV) and ϵ_{3s} (= 29.24 eV) are the

ionization energies of the $3p$ and $3s$ subshell, respectively. The numerical procedures employed in the present calculation are given elsewhere,[3,14]

With this theoretical approach, the effect of each individual many-body interaction to the photoionization can be examined by including the relevant configurations in the initial and final state of the transition at separate steps in a series of calculations. The effect on the wave function can be studied by comparing the radial function ψ_l at each of these steps. The effect on the transition amplitude can be determined by examining the individual contribution from terms given in Eqs. (3) and (4). Finally, we should point out that unlike other multiconfigurational calculations where configurations of a given principal quantum number are included individually, the infinite number of configurations with the same orbital angular momentum quantum number are included in the present approach as a single channel of configurations.

III. PHOTOIONIZATION OF THE $3s$ ELECTRON OF ARGON

In a single-particle Hartree-Fock calculation, the partial photoionization cross section for the $3s$ electron of Ar shows a smooth rise from the ionization threshold. After it reaches a broad maximum at about 60 eV, it levels off at higher energies. However, when the intershell interaction associated with the $3p \rightarrow kd$ transition is taken into account, the qualitative feature of the cross section near the threshold is completely reversed. The cross section, in fact, decreases from the threshold to a Cooper minimum at about 41 eV. This drastic change of the qualitative feature was first pointed out by Amusia *et al.*[6] in a RPAE calculation and was subsequently confirmed by experimental measurements[9,15,16] as well as other theoretical calculations.[7,8]

While the qualitative features of these theoretical calculations are similar, their detailed quantitative estimations differ significantly. Furthermore, these calculations agree quantitatively with the experimental measurements only in limited energy regions. This quantitative difficulty, however, is not totally unexpected. The presence of the Cooper minimum strongly suggests that the transition amplitude is determined by the large cancellation of contributions from more than one many-body interaction of comparable importance in this energy region. To resolve this difficulty, we have carried out a calculation following the theoretical procedure given in Sec. II.

To estimate the relative importance of each individual many-body interaction, we have separated our calculation into three steps. First, Eqs. (5a)–(5f) are solved by setting ψ_d, ψ_s, ϕ_d, and ϕ_s equal to zero. This is equivalent to a calculation which includes only one configuration, $3s3p^6kp$, in the final state and two configurations, $3s^23p^6$ and $pp3p^6$, in the initial state. The difference between the length and velocity calculation is found to be small. Curve $L1$ in Fig. 2 gives the result of the length calculation. In the energy region of our interest, this cross section does not differ much from the single-particle Hartree-Fock calculation. We conclude that the effect of the ground-state configuration interaction is minimal in this transition.

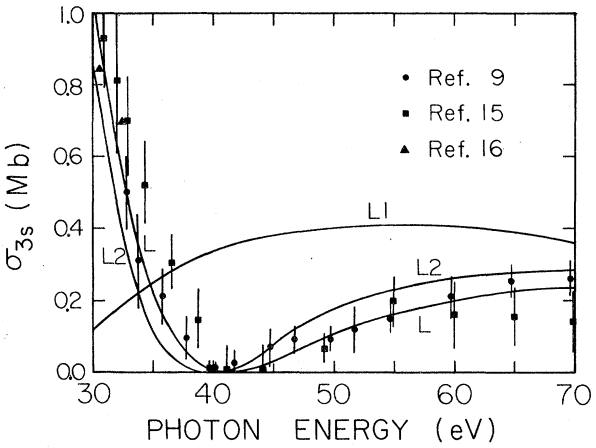

FIG. 2. Partial photoionization cross section of the $3s$ electrons.

In the second step, only ψ_s and ϕ_s are set equal to zero. Thus by including additional configurations, $3s^23p^5kd$ in the final state and $3s^23p^4dd$ in the initial state, our calculation is, in fact, equivalent to the RPAE calculation of Amusia *et al.*[6] The result of the length calculation is given by the curve $L2$ in Fig. 2. As expected, it is in excellent agreement with that of Amusia *et al.* Although our calculation shows that the effect of the intershell interaction associated with the $3p \rightarrow kd$ transition to the radial function ψ_p is negligible, its contribution to the transition amplitude has completely changed its qualitative feature. Near the threshold, the value of D_{pd}, with an opposite sign to that of D_{sp}, is several times larger than that of D_{sp}. As photon energy increases, the cancellation between D_{sp} and D_{pd} becomes more complete and eventually the transition amplitude reaches zero at about 40 eV. At even higher energy, the effect of the intershell interaction from the $3p \rightarrow kd$ transition diminishes as energy increases.

Finally, we solve the complete set of coupled equations (5a)–(5f) without any approximation.

Curve L in Fig. 2 gives the result of the length calculation. The addition of the intershell interaction from $3p \rightarrow ks$ transition has successfully removed the quantitative disagreement between the earlier theoretical estimations and the experimental measurements. Our calculation also shows that the contribution from this intershell interaction is significant at all energies of interest.

IV. PHOTOIONIZATION OF THE 3p ELECTRON OF ARGON

The photoionization of the $3p$ electrons has long been viewed as a testing ground for new theoretical approach to the atomic transition. The partial photoionization cross section for the $3p \rightarrow kd$ transition is strongly affected by the ground-state configuration interaction between the Hartree-Fock configuration ($3s^2 3p^6$) and a channel of doubly excited configurations ($3s^2 3p^4 dd$). The detailed analysis of this interaction based on the present theoretical approach was reported earlier.[4] In the present calculation, we have limited our attention to the photon energy in the vicinity of the Cooper minimum (from 40 to 70 eV).

The nature of the Cooper minimum in the $3p \rightarrow kd$ transition is quite different from that of the $3s \rightarrow kp$ transition. Instead of the cancellation between contributions from D_{sp} and D_{pd}, as in the $3s \rightarrow kp$ transition, the Cooper minimum in the $3p \rightarrow kd$ transition results from the direct sign reversal of the transition amplitude D_{pd}. This change of sign is due to the shift of the first node of the radial function ψ_d to a smaller radius as energy increases. This is shown in Fig. 3, where the radial functions ψ_d are plotted at two photoelectron momenta $k = 1.073$ and 2.057. The radial wave function of the Hartree-Fock $3p$ orbit (dotted line) is also given as reference.

Our calculation has shown that the effect of the ground-state configuration interaction to the radial function ψ_d is also significant. For instance, at $k = 1.073$, in a single-particle Hartree-Fock calculation [i.e., except for ψ_d, setting all ψ_l and ϕ_l in Eqs. (5a)–(5f) equal to zero], the first node of ψ_d is located at $r = 3.6a_0$. When the ground-state configuration interaction is included [i.e., solving the coupled equations (5a) and (5b) by setting all other ψ_l and ϕ_l equal to zero], the first node of ψ_d is shifted to $r = 3.2a_0$. This shift of ψ_d also leads to a large change of the transition amplitude in the length calculation. However, in the velocity calculation, the change in the matrix element $(x_{3p}|d|\psi_d)$ is almost totally compensated by the contribution from the matrix element $(\phi_d|d|x_{3p})$. The net change of the transition amplitude in the velocity calculation is

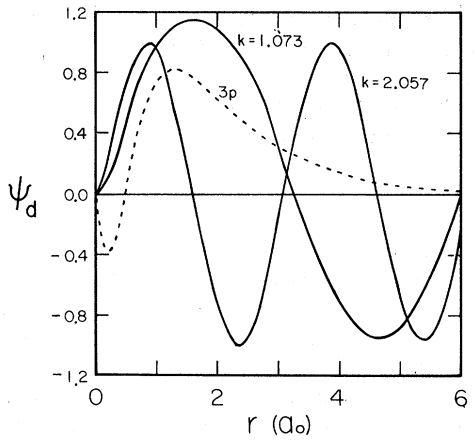

FIG. 3. Radial function ψ_d at $k = 1.073$ and $k = 2.057$.

small. The effect of the intershell and interchannel interactions is, in general, less than 5% in this energy region.

The final result of our calculation for the $3p \rightarrow kd$ transition is given in Fig. 4. The solid curves L and V represent the length and velocity calculation, respectively. The dotted curves $L1$ and $V1$ are the result of the single-particle Hartree-Fock calculation.

In the $3p \rightarrow ks$ transition, the effect of the ground-state configuration interaction between the configurations $3s^2 3p^6$ and $3s^2 3p^4 ss$ is small. The effects due to the intershell interaction associated with the $3s \rightarrow kp$ transition and the interchannel interaction associated with the $3p \rightarrow kd$ transition are small but noticeable. The transition amplitude is increased by about 5%–8% due to each of these two interactions. The net effect is about a 20%–25% increase in the ionization cross section in the energy region of our interest. The effect

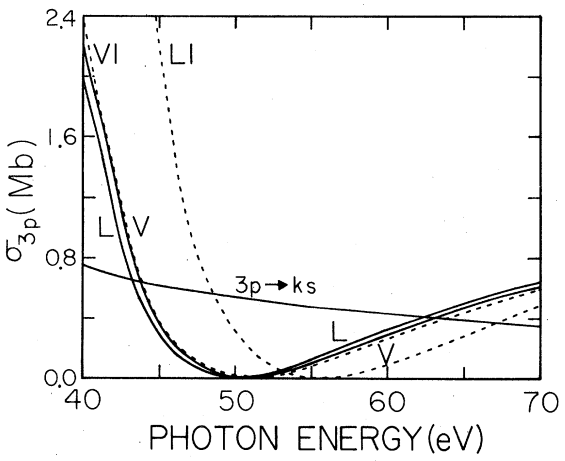

FIG. 4. Partial photoionization cross sections of the $3p$ electrons.

on the radial function ψ_s due to any of these interactions is negligible. The final result of our calculation is also given in Fig. 4. The difference between the length and velocity result on this scale is indistinguishable.

V. CONCLUDING REMARKS

The present calculation has clearly demonstrated the effectiveness of the many-body theoretical approach which we developed in Refs. 10 and 11. On the fundamental side, this approach provides an unambiguous quantitative interpretation of each individual many-body interaction in a complicated atomic transition. On the practical side, this approach is capable of yielding reliable quantitative atomic transition data. With its much improved computational efficiency, this approach can be extended readily to include additional interactions as appropriate in a more complicated physical process. Finally, from the close resemblance between Eqs. (5a)–(5f) and the Hartree-Fock equation in the well-established self-consistency Hartree-Fock procedure, we suggest that the present theoretical approach, perhaps, can also be established as a convenient procedure for a quantitative estimation of an atomic transition, particularly for those nonspecialists who are not familiar with the usual many-body theoretical methods.

ACKNOWLEDGMENT

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