Application of the many-body theory of atomic transitions to the photoionization of neon and argon

T. N. Chang

Physics Department, The University of Southern California, Los Angeles, California 90007
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Results are presented of calculations on the photoionization of neon and argon based on a recently developed many-body theory of atomic transitions. The results of our calculation demonstrate that this approach is capable of providing a reliable theoretical estimation as well as studying the individual contributions of various many-body effects associated with the atomic transitions.

I. INTRODUCTION

A many-body theory of atomic transitions has been formulated recently as an extension of the ordinary theory of atomic spectra.[1,2] Starting from a joint Schrödinger equation for the initial and final states of an atomic transition of a given symmetry, a hierarchy of equations for the transition matrices is constructed. Subject to various truncations, these equations take a form similar to the ordinary Hartree-Fock equations and can be identified as equivalent to various forms of many-body theories (e.g., the random-phase approximation, the time-dependent Hartree-Fock approach, many-body perturbation theory, etc.).

Several distinct features in this approach provide the much needed flexibility and simplicity in any *realistic* many-body approach. First, in contrast to other many-body approaches which usually employ the quantum field theory technique, this approach takes a more conventional configuration-interaction point of view. By selecting only those important configurations associated with the relevant physical effects from the outset, one is able to concentrate his attention and computational efforts on the relative importance of each contributing physical effect. This, in turn, provides a more precise physical interpretation as well as a more efficient calculational procedure. Second, since the spin and the angular variables are treated explicitly from the outset, one has effec-

tively avoided the unnecessary complication in the evaluation of the angular factors. Third, within a single numerical calculation, this approach permits a detailed quantitative comparison of various many-body approaches which was made only approximately in other separate many-body calculations where different numerical procedures were used. In this paper, we report the result of an application of this new approach to the photoionization of Ne and Ar.

II. THEORY

Following the derivation of Ref. 1, with the (np^6) and $(np^4mlm'l)$ configurations (where $l = 0$ or 2) included in the ground state and $(np^5\epsilon l)$ configuration included in the final state, the dipole transition matrix element for the photoionization of the rare-gas atoms from its ground state is given by

$$[2(2l+1)]^{1/2} \begin{pmatrix} l & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} [(\chi_{np}|D|\psi_l) - (\phi_l|D|\chi_{np})] , \quad (1)$$

where D is the dipole operator and χ_{np} is the ground-state Hartree-Fock radial wave function for the outermost shell np. It was shown in Ref. 1 that by selecting those terms included in the random-phase approximation (RPAE) calculation of Amusia and his co-workers,[3] the single-particle radial functions ψ_l and ϕ_l satisfy a set of coupled equations

$$(H^{N-1}_{(np)l} - \epsilon_{np} - E)\psi_l(r) - \sum_k \left(\frac{2}{3}\delta_{k1} - \begin{Bmatrix} l & 1 & k \\ l & 1 & 1 \end{Bmatrix} \right)(l||V^k(\phi_l, \chi_{np}; r)||1)\chi_{np}(r) = 0 , \quad (2a)$$

$$(H^{N-1}_{(np)l} - \epsilon_{np} + E)\phi_l(r) - \sum_k \left(\frac{2}{3}\delta_{k1} - \begin{Bmatrix} l & 1 & k \\ l & 1 & 1 \end{Bmatrix} \right)(l||V^k(\psi_l, \chi_{np}; r)||1)\chi_{np}(r) = 0 , \quad (2b)$$

where the effective single-particle Hamiltonian $H^{N-1}_{(np)l}$ for the $^1P_0$ dipole transition is given by[4]

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

$$(l||V^k(a, b; r)||l') = (l||C^{[k]}||l')(l_a||C^{[k]}||l_b) \int_0^\infty dr' \, a(r')b(r') \frac{r^k_<}{r^{k+1}_>} . \quad (4)$$

The matrix elements of $C^{[k]}$ are standard[5] and H_l^N is the usual Hartree-Fock radial Hamiltonian.[6]

Based on Eqs. (2), three separate calculations can be reexamined within a single calculation.

A. Single-particle approach

By setting $\phi_l = 0$ in Eqs. (2) (i.e., by neglecting the ground-state correlation effects introduced by the configuration mixing of np^6 with $np^4 m l m' l$), the single-particle calculation of Kennedy and Manson[7] is obtained as the first step of our calculation. The dipole matrix element (1) becomes

$$[2(2l+1)]^{1/2} \begin{pmatrix} l & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix} (\chi_{np} | D | \psi_l) , \tag{5}$$

where ψ_l satisfies the single-particle equation

$$(H_{(np)l}^{N-1} - \epsilon_{np} - E)\psi_l(r) = 0 . \tag{6}$$

This step will be referred to as I.

B. Many-body perturbation theory

It was shown in Ref. 1 that by dropping the coupling term

$$(l \| V^k(\phi_l, \chi_{np}; r) \| 1)\chi_{np}(r) \tag{7}$$

from Eq. (2a), the dipole matrix element (1) can be identified as to include the dominant many-body effects corresponding to diagrams 1(a)-1(f) with $p = q = r = np$ in the calculation of Kelly and Simons.[8] In the second step of our calculation, we have obtained this same result by solving the semicoupled Eqs. (6) and (2b). (An alternative calculation, with identical physical effects included, has been carried out recently by Swanson and Armstrong[9] using a multiconfiguration Hartree-Fock approach.) One should, however, point out that Kelly and Simons have also included the contributions from the excitation of $3s$ electron such as those represented by Fig. 1(a)-1(f) with $p = r = 3p$ and $q = 3s$ in their Ar calculation.[8] These effects are not present in Eqs. (2) but can be included in our derivation by adding additional configurations which are relevant to the $ns^2 np^6 \to nsnp^6 \epsilon p$ transition. This step will be referred to as II.

C. Random-phase approximation

The last step of our calculation is to solve the full coupled equations (2). As mentioned earlier, the dipole matrix element (1) has been shown in Ref. 1 to be equivalent to that calculated by Amusia and his co-workers.[3] We should point out here that the coupled equations (2) can also be derived from the time-dependent Hartree-Fock approach[10] by neglecting the couplings between the excitations of different shells and subshells. This step will be referred to as III.
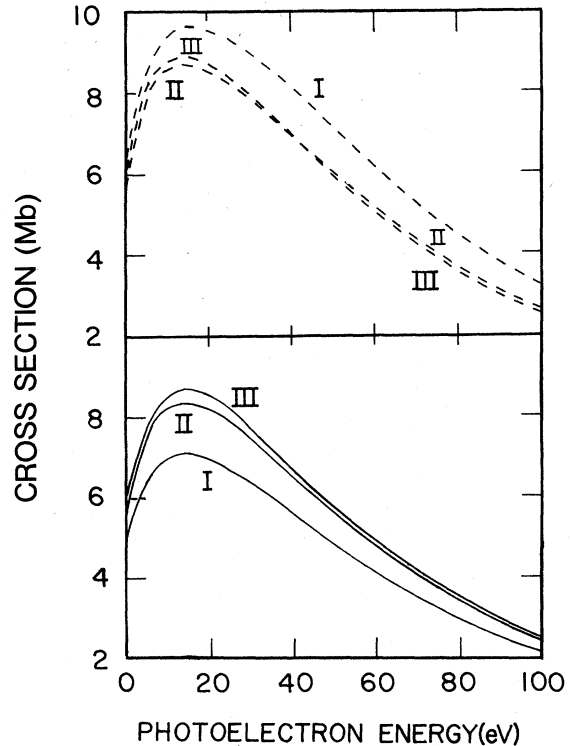

FIG. 1. Combined photoionization cross sections for the $2p \to \epsilon d$ and $2p \to \epsilon s$ transitions in neon. The solid lines are the velocity results and the dashed lines are the length results.

III. RESULTS AND DISCUSSION

In Figs. 1 and 2, we present the combined photoionization cross sections for the $np^6 \to np^5 \epsilon d$ and $np^6 \to np^5 \epsilon s$ transitions of Ne ($n = 2$) and Ar ($n = 3$), respectively. Curves I give the results of the single-particle calculation (step I in the present
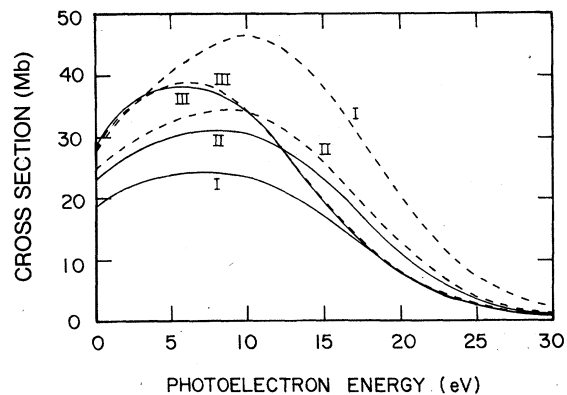

FIG. 2. Combined photoionization cross sections for the $3p \to \epsilon d$ and $3p \to \epsilon s$ transitions in argon. The solid lines are the velocity results and the dashed lines are the length results.

calculation) which are identical to the results of other previous calculations.[3,8,9] Curves II give the results which include the dominant ground-state correlation effects (step II). For Ne, our results are identical to our previous many-body perturbation calculation[11] and agree very well with the equivalent calculation of Swanson and Armstrong.[9] The detailed comparison with the calculation of Kelly and Simons[8] is difficult due to the additional effects included in their calculation. However, we should point out that while at higher energies the present calculation seems to agree well with that of Kelly and Simons,[8] a discrepancy of up to 10% can be seen at lower energy side. Curves III (step III) give the results which are in excellent agreement with the RPAE calculation of Amusia and his co-workers.[3] (Although it is expected that in a *complete* RPAE calculation, the length and velocity results should be identical, the present calculation, however, has neglected the interchannel interactions between the excitations of different shells and subshells and the effect of this approximation can be seen in the small difference between the length and velocity calculations.) Our calculations also agree well with the results of a recent R-matrix calculation.[12]

While both step II and step III in our calculation have greatly improved the theoretical calculation, a substantial difference exists between these two calculations. In particular, a maximum of up to 30% difference is seen in the Ar results. The existence of this difference suggests that the ef-
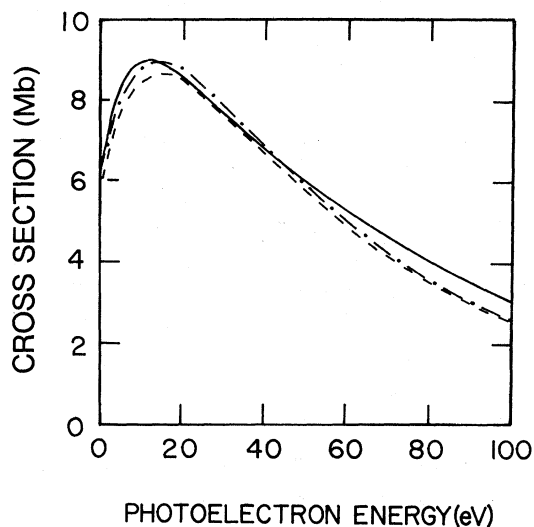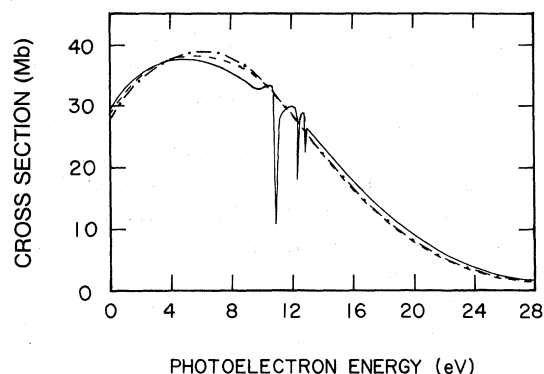

PHOTOELECTRON ENERGY (eV)

FIG. 4. Comparison of the present calculation (step III) and the experimental results in argon. The solid line gives the experimental results. The dashed line gives the velocity results and the dashed-dotted line gives the length results.

fect of the coupling term (7), which represents the correction to the single-particle wave function ψ_l of the outgoing photoelectron due to the ground-state configuration mixing, is significant. This large difference is actually within our expectation in view of the large correction to the transition matrix by the ground-state configuration mixing in Ar.

Figure 3 compares the final results of the present calculation (step III) with the experimental values[13-15] of the total photoabsorption cross sections of Ne. The seemingly large discrepancy at higher energies results from the absence in our calculation of the contributions from the $ns^2 \rightarrow ns\epsilon p$ transition and the double ionization. These contributions account for about 5–20% of the total absorption cross section in that energy region.[15]
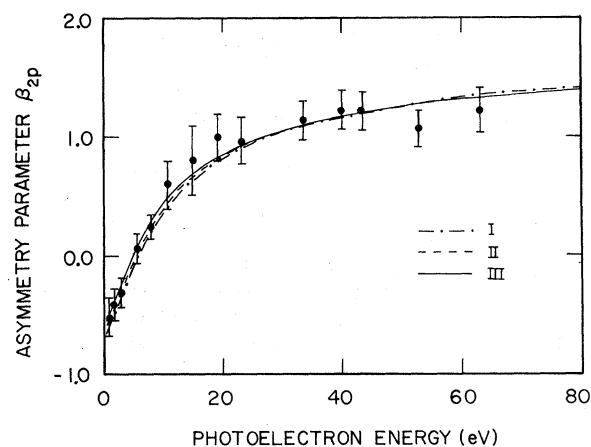

PHOTOELECTRON ENERGY(eV)

FIG. 3. Comparison of the present calculation (step III) and the experimental results in neon. The solid line gives the experimental results. The dashed line gives the velocity results and the dashed-dotted line gives the length results.

PHOTOELECTRON ENERGY (eV)

FIG. 5. Comparison of the calculated asymmetry parameters β with their observed values ($\dagger$, Ref. 18) for neon. Only velocity results are given here.

In fact, when we include the contributions from those two transitions,[11] an excellent agreement between the calculation and the experimental result is obtained. Figure 4 compares the results of our Ar calculation (step III) with the experimental measurements[13,14,16] of the total photo-absorption cross sections. The calculated angular distributions of the outgoing photoelectron, represented by the asymmetry parameter β,[7,17] are compared with their observed values[18] in Figs. 5 and 6 for Ne and Ar, respectively. Since the phase shifts used in our calculation are obtained from the solutions of Eq. (2a) rather than that of Eq. (6), curves III in Figs. 5 and 6 are slightly different from the calculation of Amusia *et al.*[19]

In conclusion, our calculation has demonstrated that the present approach, with its much simplified calculational procedure, is capable of retaining the dominant many-body effects as well as providing the reliable theoretical results. More important, with the dominant physical effects explicitly included, this approach can be used as the zeroth order approximation in a more refined investigation where other minor many-body interactions can be included either by treating them as perturbations or by adding the relevant configurations
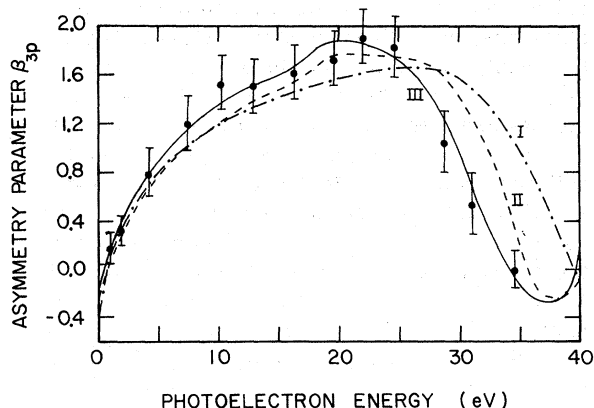

PHOTOELECTRON ENERGY (eV)

FIG. 6. Comparison of the calculated asymmetry parameters β with their observed values (, Ref. 18) for argon. Only length results are given here.

in the joint Schrödinger equation [Eq. (1) of Ref. 1] for the transition of our interest. Such an extension to include the additional many-body effects such as the interchannel interactions among the $ns^2np^6 \rightarrow ns^2np^5\epsilon d$, $ns^2np^6 \rightarrow ns^2np^5\epsilon s$, and $ns^2np^6 \rightarrow nsnp^6\epsilon p$ transitions is currently in progress.

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