

Theoretical study on the dynamical correlation in Ar focusing on 3s excitation with outer-shell ionization due to electron impacts

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We investigate the energy-loss spectra of high-energy electrons incident on Ar atoms using linear density response theory with a self-interaction correction. The energy region of the spectra covers from 24.5 to 30.0 eV, where many *ns*, *np*, and *nd* autoionizing resonant states from the 3s orbital of Ar exist with the continuum background from the 3p orbital. We compare the calculated spectra to recent energy-loss spectra measurements and identify the observed autoionizing resonant states. We also discuss the dependence of the spectra on the scattering angles and their physical meanings.

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I. INTRODUCTION

The problem of how to treat electron correlation when electronic transitions are induced in an atom or molecule by an external field remains an important topic in contemporary physics [1]. In particular, atomic photoabsorption spectra of excited discrete states embedded in an ionization continuum have been studied extensively. Such problems have been investigated using energy-loss spectra from charged particles impacting atoms or ions [2–6]. These spectra not only show optically allowed transitions but also optically forbidden ones. By varying the scattering angle of incident charged particles, one can obtain information concerning the so-called dynamic correlation for both types of transitions. In addition to these energy-loss spectra studies, the existence and physical significance of resonant discrete states in the continuum background have been studied using various theoretical tools [1,7–9], such as configuration interaction [10], hyperspherical coordinates [11], close-coupling methods [12], and *R*-matrix theory [13]. Here, we only cite the most recent papers for each respective method. For a more detailed list, we refer the reader to a paper by Yuan *et al.* [14]. We note that most studies discuss the resonant energy positions and resonance widths, but do not pay attention to energy-loss spectra and their momentum-transfer dependence on the charged particles. Two important exceptions are an experimental study of the energy-loss spectra of electron incident on a He target [15] and a theoretical study of the same system using *R*-matrix theory [14].

In this paper, we present a calculation for the energy-loss spectra of an electron incident on an argon atom as a func-

tion of the scattering angle and the momentum transfer of the scattering electron. The method is based on linear density response theory using an optimized effective potential incorporating a self-interaction correction [16]. Argon, the target atom in the process we examined in this paper, has been a subject of a number of theoretical and experimental studies. Examples of the former include a study by Fano [1] on photoabsorption phenomena in Ar and an *R*-matrix theory calculation by Burke and Taylor [17] on the photoexcitation of the inner-valence 3s electron of Ar. Examples of the latter include studies by Madden *et al.* [6], Mitchell *et al.* [18], and Wu *et al.* [19]. Madden *et al.* [6] were the first to measure the photoabsorption spectra of Ar. Mitchell *et al.* [18,20] measured the energy-loss spectra for the first time on Ar and Ne targets using electron energy-loss methods. Wu *et al.* [19] measured the spectra of Ar in the excitation energy region around 25–31 eV and its momentum-transfer dependence. In this energy regime, excitations occur from the inner-shell 3s orbital to *np*, *nd*, and *ns* Rydberg states up to the ionization limit of the $3s3p^6\ ^2S$ state. Most recently, a Japan-China joint experimental group [21] measured the energy-loss spectra and obtained results compatible to those of Wu *et al.* Since these most recent experimental results cover a wide range of the momentum transfers or scattering angles, we compare our theoretical results to them and identify the autoionization states for both optically allowed and optically forbidden transitions.

II. THEORETICAL METHOD

Linear response theory [22–24] can be applied to various physical phenomena. The electron density-functional approach has extensively been used to study the dynamic correlation induced by photoionization processes. It takes the simplicity of the independent-particle approximation (IPA), while taking into account dynamic correlation effects. In an

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earlier paper [16], we applied linear density response theory to experiments involving autoionizing resonances in Ar induced by electron-impact ionization with small scattering angles (less than 3°). In this paper, we extend our research to a wide range of scattering angles and compare our results to recent experimental measurements. Since we provide a detailed explanation of the method in our earlier paper [16], we discuss it only briefly here.

According to linear density response theory, the frequency-dependent electron-density change $\delta\rho(\mathbf{r}, \omega)$ induced by an external potential $V^{ext}(\mathbf{r}, \omega)$ is given by (atomic units $\hbar=m=e=1$ are used unless specified otherwise)

$$\delta\rho(\mathbf{r}, \omega) = \int \chi(\mathbf{r}, \mathbf{r}', \omega) V^{ext}(\mathbf{r}', \omega) d^3\mathbf{r}' \quad (1)$$

$$= \int \chi^{IPA}(\mathbf{r}, \mathbf{r}', \omega) V^{SCF}(\mathbf{r}', \omega) d\mathbf{r}', \quad (2)$$

where $\chi(\mathbf{r}, \mathbf{r}', \omega)$ is a full dynamical susceptibility or a response function, $\chi^{IPA}(\mathbf{r}, \mathbf{r}', \omega)$ is a dynamical susceptibility under the independent-particle approximation, and $V^{SCF}(\mathbf{r}, \omega)$ is the self-consistent field including both the external field and the field induced by the density change.

We use Eq. (2) to calculate the density changes instead of using Eq. (1) since it is difficult to calculate the full dynamical susceptibility. The susceptibility $\chi^{IPA}(\mathbf{r}, \mathbf{r}', \omega)$ is written as

$$\chi^{IPA}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i,j} (n_i - n_j) \frac{\psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_i(\mathbf{r}') \psi_j^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i\eta}, \quad (3)$$

with η a positive infinitesimal used to ensure the outgoing wave boundary conditions. $\{\psi_i(\mathbf{r})\}$ and $\{\epsilon_i\}$ are the eigenfunctions and eigenenergies of the single electron orbitals and n_i is the occupation number for a given orbital. $\{\psi_i(\mathbf{r})\}$ and $\{\epsilon_i\}$ are calculated from the Schrödinger equation

$$\left[-\frac{1}{2} \nabla^2 + V^{eff}(r) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (4)$$

where $V^{eff}(r)$ is an effective potential obtained from the optimized effective potential method [25]. The $V^{SCF}(\mathbf{r}, \omega)$ satisfies the equation

$$V^{SCF}(\mathbf{r}, \omega) = V^{ext}(\mathbf{r}, \omega) + \int \frac{\delta\rho(\mathbf{r}, \omega)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \left. \frac{\partial V_{xc}(\mathbf{r})}{\partial \rho(\mathbf{r})} \right|_{\rho_0(\mathbf{r})} \delta\rho(\mathbf{r}, \omega), \quad (5)$$

where $V_{xc}(\mathbf{r})$ is the exchange-correlation potential and $\rho_0(\mathbf{r})$ is the ground-state electron density.

For the electron-impact excitation or ionization under the Born-approximation, the external field is

$$V^{ext}(\mathbf{r}, \omega) = \exp[i\mathbf{K} \cdot \mathbf{r}] \quad (6)$$

and the generalized oscillator strength (GOS) is written as

$$f(\omega, K) = \frac{2\omega}{K^2} \left| \langle \Psi_f | \sum_j \exp[i\mathbf{K} \cdot \mathbf{r}_j] | \Psi_0 \rangle \right|^2 \delta(E_f - E_0 - \omega). \quad (7)$$

In the equation above, Ψ_0 and Ψ_f are the initial and final states of the target atom with energies E_0 and E_f , ω and \mathbf{K} are the impact electron energy loss and momentum transfer during the collision, and the summation j runs over all the electrons of the target atom.

Using the electron-density change $\delta\rho(\mathbf{r}, \omega)$ due to $V^{ext}(\mathbf{r}, \omega)$, the GOS is expressed as

$$f(\omega, K) = \frac{2\omega}{K^2} \text{Im} \int V^{ext}(\mathbf{r}, \omega) \delta\rho(\mathbf{r}, \omega) d\mathbf{r}. \quad (8)$$

Due to parity conservation and angular-momentum conservation, we can decompose each ℓ th pole contribution by replacing $V^{ext}(\mathbf{r}, \omega)$ with

$$V_\ell^{ext}(\mathbf{r}, \omega) = \sum_m 4\pi i^\ell j_\ell(Kr) Y_{\ell m}^*(\hat{\mathbf{K}}) Y_{\ell m}(\hat{\mathbf{r}}) \quad (9)$$

in Eqs. (2) and (5) and obtain the corresponding partial GOS labeled as $f^\ell(\omega, K)$. Thus, the total GOS can be rewritten as

$$f(\omega, K) = \sum_\ell f^\ell(\omega, K). \quad (10)$$

With the calculated GOS, the electron-impact excitation or ionization cross sections are obtained as

$$\sigma(\omega) = \frac{2\pi}{E_e} \frac{1}{\omega} \int_{K_{min}}^{K_{max}} \frac{f(\omega, K)}{K} d\mathbf{K}, \quad (11)$$

with E_e the incident electron kinetic energy and $K_{min}(K_{max})$ the minimum (maximum) momentum transfer.

The differential cross section of an electron with energy loss ω at scattering angle Ω is given by

$$\frac{d\sigma(\omega)}{d\Omega} = \frac{d\sigma(\omega)}{d\hat{K}} \frac{d\hat{K}}{d\Omega} \propto \sum_\ell f^\ell(\omega, K). \quad (12)$$

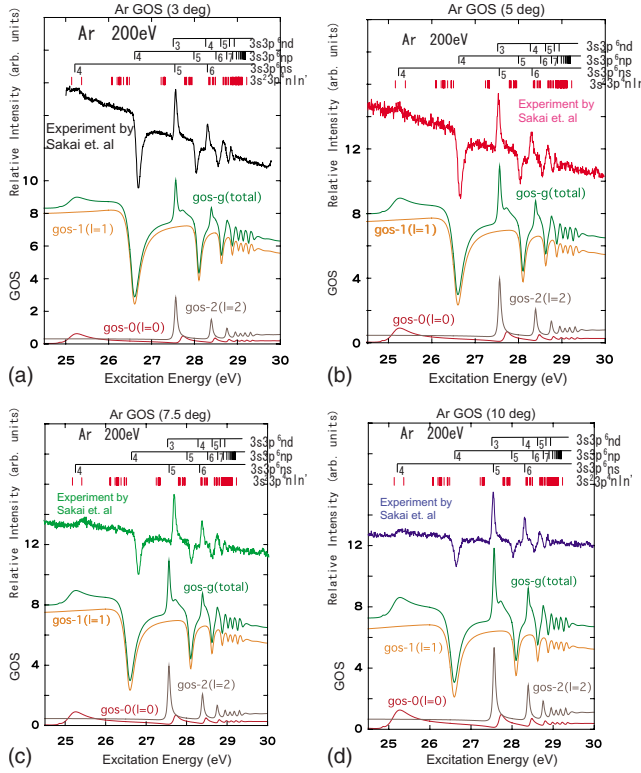
The scattering angle θ and the momentum transfer K are related by the following equation as

$$K^2 = k_i^2 + k_f^2 - 2k_i k_f \cos \theta, \quad (13)$$

with k_i, k_f are the incident electron momenta before and after the collision. The equations derived above are for a paired spin system, but these equations can be extended to the case of an unpaired spin system in a straightforward manner [26].

III. RESULTS AND DISCUSSION

Using Eq. (12), we calculated the impact electron energy-loss spectra when argon's $3s$ electron is excited to some resonant states or its $3p$ electron is ionized. The energy-loss spectra from 24.5 to 30.0 eV were calculated in 0.01 eV intervals. In the present calculation, we took into account monopole, dipole, and quadrupole contributions, but ignored higher multipole contributions because their effects are negligible for an incident energy of 200 eV. Since we already showed in



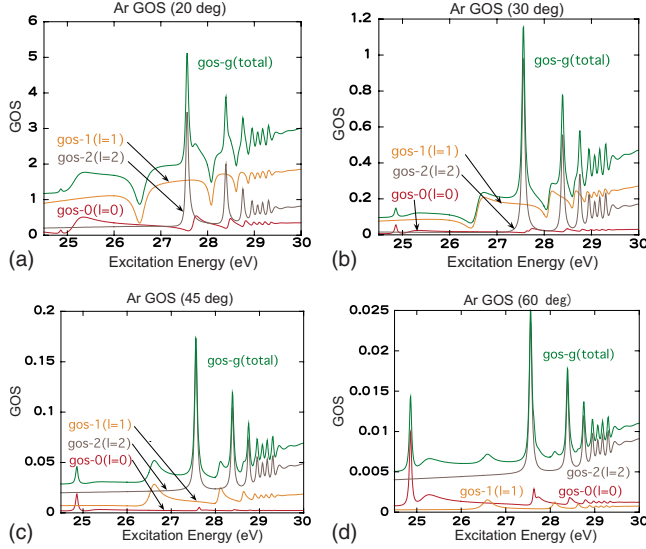


FIG. 2. (Color online) The same as Fig. 1 for the large scattering angles as (a) $\theta=20^\circ$, (b) $\theta=30^\circ$, (c) $\theta=45^\circ$, and (d) $\theta=60^\circ$.

parameter, we must note that the resonance line profile, the absorption cross section per unit energy $d\sigma/dE$ which is embedded in the ionization continuum $f_c(E)$, can be expressed in terms of excitation energy E , the energy of resonant level E_r , and resonance line width Γ as

$$\frac{d\sigma}{dE} = f_a \left(\frac{(q + \epsilon)^2}{1 + \epsilon^2} - 1 \right) + f_c(E), \quad (14)$$

where

$$\epsilon = \frac{E - E_r}{\Gamma/2}.$$

In short, Fano's q parameter characterizes the line shape of the resonant absorption.

We fit the calculated GOS to the above formula to obtain the q values. Figure 3 shows the q values as a function of K^2 , the square of the momentum transfer, for optically allowed transitions to the $3s3p^63p\ ^1P$ state [Fig. 3(a)] and optically forbidden transitions to the $3s3p^63d\ ^1D$ state. Overall, our calculated q values are in reasonable agreement with the corresponding values computed experimental measurements.

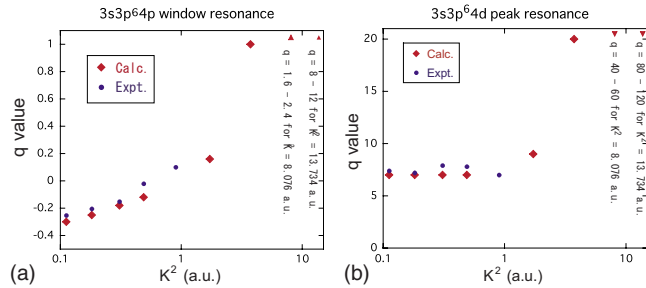


FIG. 3. (Color online) The q parameter of $3s3p^6np$ window resonance (left panel) and $2s3p^6nd$ sharp resonance (right panel) as a function of K^2 in logarithmic scale. Experimental values are by Sakai *et al.* [21] and Zhu *et al.* [27].

For optically allowed transitions, the q value starts from a negative value and increases as K^2 increases. The q value reaches zero at $K^2 \approx 0.2$. The positive and negative q values indicate different asymmetrical line profiles. To study the physical origins of the line profile changes, let us go back to the definition of the q value. The q value is defined as

$$q = \frac{\langle \psi_i | T | \psi_r \rangle}{\langle \psi_i | T | \psi_c \rangle}, \quad (15)$$

where ψ_i is the initial-state wave function and ψ_r and ψ_c the wave functions of the resonant state and the final continuum, respectively. In general, T may be any kind of electronic transition operator. For the present case, however, T is approximated as $\exp[i\mathbf{K} \cdot \mathbf{r}]/|\mathbf{K}|$, where \mathbf{K} is momentum transferred to the scattered electron and \mathbf{r} the electronic coordinate of the electron to be excited.

In 1980, Mitchell *et al.* [18] reported the GOSs of Ar, but they did not measure the spectra for the whole excitation energy region but instead measured precise spectra of resonance peaks and windows using electron-impact spectroscopy. They also measured the spectra impact energy dependence for small scattering angles and its angular scattering dependence for low-impact energies. Though they focused their attention on obtaining resonance profiles rather than the entire energy-loss spectra, we were able to compare their data results to our high-impact energy and small scattering angle results and determined that the two are consistent.

To compare the results of Mitchell *et al.* [18] to our results, we needed to obtain a relation between the parameter D that Mitchell *et al.* introduced in their analysis and our calculated q values. To obtain this relation, it is useful to introduce two new parameters η and μ for ϵ and q in Eq. (14), where $\epsilon = -\cot \eta$ ($0 \leq \eta < \pi$) and $q = -\cot \mu$ ($0 \leq \mu < \pi$). With these new parameters, we can write

$$1 + \epsilon^2 = \frac{\sin^2 \eta + \cos^2 \eta}{\sin^2 \eta} = \frac{1}{\sin^2 \eta},$$

$$(\epsilon + q)^2 = (-\cot \eta - \cot \mu)^2 = \frac{(\sin \eta \cos \mu + \cos \eta \sin \mu)^2}{(\sin \eta \sin \mu)^2}.$$

It also follows that

$$\frac{d\sigma}{dE} = f_a \left(\frac{1 + \epsilon^2}{(\epsilon + q)^2} - 1 \right) + f_c(E) = f_a \left(\frac{\sin^2(\eta + \mu)}{\sin^2 \mu} - 1 \right) + f_c(E).$$

As the energy ϵ changes from $-\infty$ to ∞ , η changes from 0 to π . This means that when $q = -\infty$, $\mu = 0$, when $q = 0$, $\mu = \pi/2$, and when $q = +\infty$, $\mu = \pi$. Given a background wave function ψ_c and a resonant state wave function ψ_r , a coupled state can be expressed as $\psi_0 = \cos \eta \psi_c + \sin \eta \psi_r$. The total spectrum is given by $|\langle \psi_0 | T | \psi_f \rangle|^2 \propto \sin^2(\eta + \mu)$.

This indicates that μ is the position when the interaction with the resonance level starts and that the interaction ends when $\eta = \pi$. The maximum value of the spectrum is $f_a/(1/\sin^2 \eta - 1) + f_c(E)$, occurs at $\eta + \mu = \pi/2$, and the minimum value is $f_c(E) - f_a$, occurs at $\eta + \mu = 0$ or π . The value of D which was defined by Mitchell *et al.* $\sin^2 \mu$ for $\pi/2$

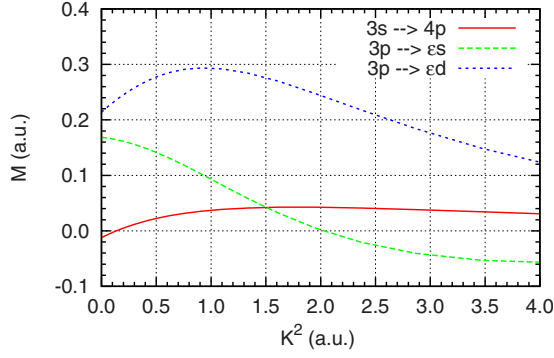


FIG. 4. (Color online) The transition matrix elements of $M = \langle \psi_i | j_1(Kr) Y_1(\hat{K}\hat{r}) | \psi_f \rangle / K$ defined in Eq. (15) for the transitions of $3s \rightarrow 4p$, $3p \rightarrow \epsilon s$, and $3p \rightarrow \epsilon d$.

$\leq \mu < \pi$. A variable D is cut at $D = \pm 1 (q=0)$ and in the present treatment, a branch cut is set at $\mu = n\pi (n=0, 1) (q = \mp \infty)$ as Fano defined q in Ref. [1].

Figure 4 shows the matrix elements $M = \langle \psi_i | j_1(Kr) Y_1(\hat{K}\hat{r}) | \psi_f \rangle / K$ as a function of K^2 . The wave functions used in our calculation are obtained from Eq. (4). We see that the $3s \rightarrow 4p$ matrix element changes its sign around $K^2 \approx 0.2$. This means that a sign change in the q value is associated with change in shape of the resonance structure. For example, as the q value changes from negative to positive, a resonance structure having a profile similar to a sine function over one full cycle (0 to 2π) will change to the structure having a profile similar to the sine function reflected about the x axis. In other words, as the q value changes from negative to positive, the positive hump of the profile will become a negative hump and vice versa. Admittedly, this is only a qualitative observation, but it does provide some insight into the physical meaning of the q value. It should be noted that the resonant state interacts with two continuum states. Although the transition matrix of $3p \rightarrow \epsilon s$ changes its sign at $K^2 = 2.0$ while that of $3p \rightarrow \epsilon d$ does not,

the q value does not undergo a sign change because the magnitude of the former transition matrix is small.

V. SUMMARY AND CONCLUSIONS

In the former paper [16], we studied the energy-loss spectra of charged particles incident on an Ar atom as a function of excitation energies for the case of small scattering angles (below 3°) by calculating the GOS using linear-response theory together with a optimized effective potential incorporating a self-interaction correction. In this paper, we extended the method to treat the case of larger electron-scattering angles (from 3° to 60°) with an impact energy of 200 eV. The results of our calculations showed good agreement with the results of recent experiments. Finally, it should be noted that the data calculated for a particle having a given incident energy and a large scattering angle can be compared directly to a case having a higher incident energy and smaller scattering angle. This is because Eq. (11) does not depend on the electron incident energy explicitly. In other words, our results can be used to study cases where the incident particle's energies are much larger than 200 eV. For example, the case of an electron having an incident energy of 200 eV and a scattering angle of 60° ($K^2 = 13.7$ a.u.) corresponds to the case in which an electron has an incident energy of 200 KeV and a scattering angle of 2.5° .

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