Coherences in the decay of autoionizing states in photoionization. I. Exchange effect between photo- and Auger electrons

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(Received 15 November 1993)

An interference effect on angular correlation patterns due to exchange of Auger and photoelectrons of the same energy is discussed. The detection in coincidence of the Auger and photoelectrons may reveal a striking angular correlation pattern when a synchrotron light source is tuned so that the Auger and photoelectron energies are nearly equal. This effect is present even when only one electron is detected, but is strongly reduced by the averaging over the direction of the undetected electron.

PACS number(s): 32.80.Fb, 32.80.Hd

I. INTRODUCTION

In both photoionization and electroionization the availability of incident beams with well defined energy makes the study of nearly monoenergetic ejected electrons possible. Then the effect of electron exchange between the directly ionized electron and another electron of about the same energy can be investigated. Many $(e,2e)$ experiments have been done in which both final electrons were detected at the same energy and analyzed with a model containing an antisymmetrized free electron-electron cross section as a factor.

Doering *et al.* [1] have reported a striking angular correlation between two electrons of equal energy resulting from the double ionization of argon by electron impact at threshold incident electron energies. The two 205-eV electrons are produced by the knockout of an argon $2p$ electron followed by 205-eV *LMM* Auger decay of the $2p$ vacancy. The two electrons are emitted preferentially at a large angle to each other. Since the energy of the knocked-out electron is the same as the Auger energy, the distinction between the two electrons is lost; thus due to the antisymmetry of the final-state wave function a relevant interference effect should occur in the angular correlation pattern [2]. If the spin-dependent interactions can be neglected and the two electrons participating in the Auger process are in a triplet state before the decay then the knocked-out and autoionized electrons are in a triplet state, too. In this case the orbital state must be antisymmetric and therefore the angular correlation between the two electrons expresses a strong enhancement for the electrons ejected antiparallel to each other.

This effect may explain the behavior of the angular correlation measured by Doering *et al.* [1], since the 205-eV Auger lines correspond to the decay of ^3P states [3]. To quantitatively compare with the experiment [1], the formalism of Berezhko and Kabachnik [4], which describes the angular correlation between the ejected and Auger electrons, may be used. This formalism [4] applies only if we add all terms which become relevant when the energies of the two electrons are nearly equal. The extension of the model of Berezhko and Kabachnik [4] is a rather involved task since there are a number of amplitudes which could give relevant contributions to the cross section. For that reason we examine the coherent addition of amplitudes for the simpler photoionization process.

The photoionization process followed by autoionization provides a good possibility to study the electron exchange effect. Both final electrons have sharp energy distributions and well defined orbital momenta. Generally the effect of electron exchange is negligible because, due to the sharp energy distributions of both electron peaks, the Auger electron and photoelectron can be distinguished. But if the photoelectron has approximately the same energy as the autoionized electron, pronounced electron exchange effects may appear. In this paper we consider the exchange effects in the final state of photoinduced reactions. We discuss the process within the framework of the time-independent description.

The width Γ (or the lifetime $\tau = \hbar/\Gamma$) of the autoionizing state is an important parameter of the effect. The indistinguishability of the two emitted electrons becomes relevant when the incident photon beam is tuned such that the energy of the photoelectron coincides with the energy of the Auger peak within the width Γ. To fulfill this condition photon beams consisting of wave packets having energy spreads smaller than or equal to Γ are needed. The energy spread of the Schrödinger wave corresponding to the photoelectron is thus less than or equal to Γ, which is the energy spread of the Auger electron. Owing to the time-energy uncertainty relation $\Gamma\Delta t \geq \hbar$, the wave packets for both the direct and Auger electrons overlap in the time domain and the time delay between the two emitted electrons does not distinguish them. Therefore, in principle, the interference pattern can be realized even in the case of a long-lived autoionizing state if photon wave packets having the required energy spread are used.

II. THE AMPLITUDE

To describe the amplitude of the Auger-electron emission following photoionization we use the treatment of Åberg and Howat [5]. Let β denote the quantum numbers of the final state with two continuum electrons and a doubly charged ion, while x_j, $j = 1, 2$ are the spin and momentum coordinates of the two continuum electrons. The quantization axis is chosen along the direction of the incident photon. Neglecting the nonresonant double-ionization contribution, the T matrix element of the transition induced by the $\hbar\omega$ photon with helicity λ absorbed by an atom being in its initial state α with ground-state energy E_α takes the form

$$T^\lambda_{\beta\alpha} = \int \frac{\langle \Psi_{\beta\varepsilon_1\varepsilon_2}(x_1, x_2)|H_{\rm el}|\phi_\tau\rangle\langle\phi_\tau, 0|H_{\rm int}|i, \hbar\omega, \lambda\rangle d\tau}{\varepsilon_1 + \varepsilon_2 - \varepsilon_r - \tau + i\frac{\Gamma}{2}}, \tag{1}$$

where ε_1 and ε_2 represent the kinetic energies of the outgoing electrons in the final state so that

$$\varepsilon_1 + \varepsilon_2 = \hbar\omega - (E_\beta - E_\alpha) \tag{2}$$

and $\varepsilon_r = E_r - E_\beta$. The complex energy $E_r - i\frac{\Gamma}{2}$ is the position and width of the resonance corresponding to the autoionizing state ϕ, and E_β refers to the double-ionization threshold for channel β. $H_{\rm int}$ and $H_{\rm el}$ are the operators of the photon-electron and electrostatic interactions, respectively, and ϕ_τ are the intermediate states.

If $\hbar\omega \gg E_\beta - E_\alpha$, it is reasonable to approximate [5] the intermediate state ϕ_τ by product wave functions $|nLJM\rangle|\tau\rangle$ where $nLJM$ are the quantum numbers of the autoionizing state ϕ and $|\tau\rangle$ describes the continuum electron. If the final state is approximated in the same way, then

$$\langle \Psi_{\beta\varepsilon_1\varepsilon_2}(x_1, x_2)|H_{\rm el}|\phi_\tau\rangle = \langle\varepsilon_2|\tau\rangle\langle\Psi_{\beta\varepsilon_1}|H_{\rm el}|nLJM\rangle. \tag{3}$$

When the wave functions $|\varepsilon_j\rangle$ and $|\tau\rangle$ are orthogonal we have $\langle\varepsilon_j|\tau\rangle = \delta(\varepsilon_j - \tau)$. This assumption involves neglect of postcollision interactions. In this case the integration over τ in (2) can be performed.

Let $J_f M_f$ be the angular momentum quantum numbers of the final state of the doubly ionized atom. Representing the continuum electrons by the momenta $\mathbf{k}_1$, $\mathbf{k}_2$ and the spin projections σ_1, σ_2, respectively, $T^\lambda_{\beta\alpha}$ is expressed as

$$T^\lambda_{\beta\alpha} = \frac{\langle \mathbf{k}_1\sigma_1 J_f M_f|H_{\rm el}|nLJM\rangle\langle \mathbf{k}_2\sigma_2 nLJM|H_{\rm int}|i, \hbar\omega, \lambda\rangle}{\varepsilon_1 - \varepsilon_r + i\frac{\Gamma}{2}}. \tag{4}$$

For the sake of simplicity we shall consider only the ionization of closed shell atoms. Using the dipole approximation and expanding the final state into partial waves, the amplitude of the photoionization can be written in the form

$$\langle \mathbf{k}_2\sigma_2 nLJM|H_{\rm int}|i, \hbar\omega, \lambda\rangle = \sum_{j_1\mu_1 l_1 m_1} (l_1 m_1 \tfrac{1}{2}\sigma_2|j_1\mu_1)(JMj_1\mu_1|1\lambda)Y_{l_1 m_1}(\Omega_2)\langle k_2 J(l\tfrac{1}{2})j; 1\|D\|0\rangle. \tag{5}$$

Here $j_1\mu_1$ and $l_1 m_1$ are the total and orbital angular momenta of the photoelectron, and the reduced matrix element $\langle k_2 J(l\frac{1}{2})j; 1\|D\|0\rangle$ is proportional to the dipole radial integral.

Using the partial-wave expansion, the amplitude of the Auger decay of the JM state reads

$$\langle \mathbf{k}_1\sigma_1 J_f M_f|H_{\rm el}|nLJM\rangle = \sum_{j_2\mu_2 l_2 m_2} (l_2 m_2 \tfrac{1}{2}\sigma_1|j_2\mu_2)(J_f M_f j_2\mu_2|JM)Y_{l_2 m_2}(\Omega_1)\langle k_1 J_f(l_2\tfrac{1}{2})j_2; J\|H_{\rm el}\|J\rangle. \tag{6}$$

$\langle k_1 J_f(l_2\frac{1}{2})j_2; J\|H_{\rm el}\|J\rangle$ is the reduced matrix element of the Auger decay from the initial state with a hole in the shell with total angular momentum J and orbital momentum L to a final state of the ion with total angular momentum J_f and a continuum electron with quantum numbers $l_2 j_2$ and momentum k_1.

III. THE AMPLITUDE WITH EXCHANGE

Now using the antisymmetry of the final two-electron wave function, the amplitude (1) is written as the difference between the direct and exchange amplitudes

$$T^\lambda_{\beta\alpha} = \frac{1}{\sqrt{2}}\left(\frac{\langle \mathbf{k}_1\sigma_1 J_f M_f|H_{\rm el}|nLJM\rangle\langle \mathbf{k}_2\sigma_2 nLJM|H_{\rm int}|i, \hbar\omega, \lambda\rangle}{\varepsilon_1 - \varepsilon_r + i\frac{\Gamma}{2}} - \frac{\langle \mathbf{k}_2\sigma_2 J_f M_f|H_{\rm el}|nLJM\rangle\langle \mathbf{k}_1\sigma_1 nLJM|H_{\rm int}|i, \hbar\omega, \lambda\rangle}{\varepsilon_2 - \varepsilon_r + i\frac{\Gamma}{2}}\right). \tag{7}$$

According to Eq. (7) the probability of a photoionization-autoionization process is large only if at least one of the energies ε_1 or ε_2 is close enough to ε_r. If ε_1 is fixed by this requirement, ε_2 is determined by (2),

$$\varepsilon_2 \approx \hbar\omega - (E_r - E_\alpha). \tag{8}$$

The second term of the amplitude (7) is of comparable magnitude when

$$\varepsilon_2 \approx \varepsilon_1 \approx \varepsilon_r. \tag{9}$$

Under these conditions the two amplitudes in Eq. (7)

add coherently. Condition (9) requires the tuning of the synchrotron light source to the frequency determined by relations (8) and (9) within the accuracy of the resonance width Γ.

IV. CROSS SECTIONS

For specifying the polarization of the incident light beam we use the density matrix of the photon beam which is expressed by the Stokes parameters S_1, S_2, and S_3 as follows:

$$\rho = \frac{1}{2}\begin{pmatrix} 1+S_3 & -S_1+iS_2 \\ -S_1-iS_2 & 1-S_3 \end{pmatrix}. \tag{10}$$

The cross section for the double-ionization process is given in terms of the density matrix ρ as

$$\sigma_{\beta\alpha} = T^{\lambda'+}_{\beta\alpha}\rho_{\lambda'\lambda}T^{\lambda}_{\beta\alpha}. \tag{11}$$

Cross sections obtained by substituting (7) into (11) are expressed in terms of the state multipoles $\rho_{kq}(1,1)$ (see, for example, the textbooks [6]). These dipole photon statistical tensors are defined by the elements of the density matrix ρ,

$$\rho_{kq}(1,1) = \sum_{\lambda\lambda'}(-1)^{1-\lambda'}(1\lambda 1-\lambda'|kq)\rho_{\lambda'\lambda}. \tag{12}$$

In our coordinate system where the quantization axis is chosen along the direction of the incident photon, $\rho_{kq}(1,1) = 0$ with $q = \pm 1$. Using Eqs. (10) and (12), for the nonvanishing components of $\rho_{kq}(1,1)$ we obtain

$$\rho_{00} = \frac{1}{\sqrt{3}},\quad \rho_{10} = \frac{S_3}{\sqrt{2}},\quad \rho_{20} = \frac{1}{\sqrt{6}},\quad \rho_{2\pm 2} = -\frac{S_1 \pm iS_2}{2}. \tag{13}$$

A. Angular correlation

Now we substitute the expressions of the amplitude given in (7) and the matrix elements (5) and (6) into formula (11). At the derivation of (11) we summed up the product of Clebsch-Gordan coefficients and spherical harmonics by using vector coupling coefficient relations from [7]. Introducing the shorthand notations

$$\begin{aligned} H_{l_2 j_2} &\equiv \hat{l}_2\hat{j}_2\langle k_r J_f(l_2\tfrac{1}{2})j_2; J\|H_{\rm el}\|J\rangle, \\ D_{l_1 j_1} &\equiv \hat{l}_1\hat{j}_1\langle k_r J(l_1\tfrac{1}{2})j_1; 1\|D\|0\rangle, \end{aligned} \tag{14}$$

where $\hat{a} \equiv \sqrt{2a+1}$, we obtain

$$\frac{d\sigma}{d\varepsilon_1 d\Omega_1 d\Omega_2} = \frac{3(2J+1)}{4\pi}C\sum_{k_1k_2\kappa}\left\{\frac{B(k_1k_2\kappa)}{(\varepsilon_2-\varepsilon_r)^2+\frac{\Gamma^2}{4}} + \frac{(-1)^\kappa B(k_2k_1\kappa)}{(\varepsilon_1-\varepsilon_r)^2+\frac{\Gamma^2}{4}}\right\}\mathcal{A}_{k_1k_2\kappa}(\Omega_1\Omega_2)$$

$$-2\,\mathrm{Re}\left\{\frac{B_{\rm int}(k_1k_2\kappa)}{(\varepsilon_1-\varepsilon_r+i\frac{\Gamma}{2})(\varepsilon_2-\varepsilon_r-i\frac{\Gamma}{2})}\mathcal{A}_{k_1k_2\kappa}(\Omega_1\Omega_2)\right\}, \tag{15}$$

where $\mathcal{A}_{k_1k_2\kappa}(\Omega_1\Omega_2)$ is a sum of the products of bipolar spherical harmonics and state multipoles

$$\mathcal{A}_{k_1k_2\kappa}(\Omega_1\Omega_2) = \sum_q [Y_{k_1}(\Omega_1)\times Y_{k_2}(\Omega_2)]^\kappa_q\rho_{\kappa q}(1,1) \tag{16}$$

and the bipolar spherical harmonics are defined as usual (see, for example, in [7]):

$$[Y_{k_1}(\Omega_1)\times Y_{k_2}(\Omega_2)]^\kappa_q = \sum_{q_1q_2}(k_1q_1k_2q_2|\kappa q)Y_{k_1q_1}(\Omega_1)Y_{k_2q_2}(\Omega_2). \tag{17}$$

The coefficients $B(k_1k_2\kappa)$ and $B_{\rm int}(k_1k_2\kappa)$ depend upon geometrical factors and the dynamics of the double-ionization process. The first two terms in (15) with $B(k_1k_2\kappa)$ give the sum of the photoelectron and Auger-electron intensities in the absence of interference. $B(k_1k_2\kappa)$ is represented in the form

$$B(k_1k_2\kappa) = \sum_{j_1l_1j_1'l_1'}\sum_{j_2l_2j_2'l_2'}(-1)^{j_1+k_2+J_f+J}H_{l_2j_2}H^*_{l_2'j_2'}D_{l_1j_1}D^*_{l_1'j_1'}(l_10l_1'0|k_10)(l_20l_2'0|k_20)$$

$$\times\begin{Bmatrix} J_f & j_2 & J \\ k_2 & J & j_2' \end{Bmatrix}\begin{Bmatrix} l_1 & \frac{1}{2} & j_1 \\ j_1' & k_1 & l_1' \end{Bmatrix}\begin{Bmatrix} l_2 & \frac{1}{2} & j_2 \\ j_2' & k_2 & l_2' \end{Bmatrix}\begin{Bmatrix} j_1 & J & 1 \\ j_1' & J & 1 \\ k_1 & k_2 & \kappa \end{Bmatrix}. \tag{18}$$

Here the values of k_1 and k_2 are even due to parity conservation in photoionization and Auger decay. In (15) the term with $B_{\rm int}$ is the interference term which is the product of the direct and exchange amplitudes from Eq. (7). It is given by

$$B_{\rm int}(k_1k_2\kappa)=\sum_{j_1l_1j_1'l_1'}\sum_{j_2l_2j_2'l_2'}(-1)^{J+J_f+j_1+j_1'-j_2+k_1}H_{l_2j_2}H^*_{l_2'j_2'}D_{l_1j_1}D^*_{l_1'j_1'}(l_20l_1'0|k_20)(l_10l_2'0|k_10)$$
$$\times\begin{Bmatrix} l_1 & \frac{1}{2} & j_1\\ j_2' & k_1 & l_2'\end{Bmatrix}\begin{Bmatrix} l_1' & \frac{1}{2} & j_1'\\ j_2 & k_2 & l_2\end{Bmatrix}\sum_x \hat{x}^2\begin{Bmatrix} J & 1 & x\\ \kappa & j_1' & 1\end{Bmatrix}\begin{Bmatrix} j_2 & k_1 & x\\ \kappa & j_1' & k_2\end{Bmatrix}\begin{Bmatrix} j_1 & j_2' & k_1\\ J & J_f & j_2\\ 1 & J & x\end{Bmatrix}. \quad (19)$$

C is a normalization constant which is chosen so that the photoionization cross section in the absence of exchange is expressed as

$$\frac{d\sigma}{d\Omega}=C\frac{3(2J+1)\sum_{kq}B(k0k)Y_{kq}(\hat{\mathbf{k}})\rho_{kq}(1,1)}{\sum_{lj}|\langle k_rJ_f(l\tfrac{1}{2})j;J\|H_{\rm el}\|J\rangle|^2}. \quad (20)$$

Considering that in the cross section formula (15) the energy dependence of the radial matrix elements is small compared to those of the Lorentzian denominators, the radial matrix elements of the Auger decay and photoionization are approximated by their values taken at momentum k_r corresponding to the resonance energy ε_r, see Eqs. (14).

When the participating Auger electrons are in subshells of the same parity before the Auger decay the indices k_1 and k_2 in $B_{\rm int}(k_1k_2\kappa)$ are odd, owing to the opposite parities of the Auger and photoelectron partial waves. The angular correlation pattern is asymmetric, owing to the mixture of even and odd spherical harmonics. If the condition (9) does not hold, the interference term is negligible and formula (15) becomes identical to Eq. (6) of formalism [8].

As the cross section formula (15) shows, the relevant parameter of the exchange effect is the width of the autoionizing state. If Γ is narrow then the interference pattern is restricted to a narrow region of the incident photon energy $\hbar\omega$, see Eqs. (2) and (15). If $|\varepsilon_b-\varepsilon_r|$ becomes larger than Γ then the indistinguishability of electron b and electron a with energy $\varepsilon_a\approx\varepsilon_r$ becomes irrelevant since we can assume that now b is the photoelectron and a is the Auger electron.

B. Angular distributions

Now we consider the angular distribution of one of the two electrons when the second one is not detected. The fixed energy of the photoelectron defines only the sum of energies of the Auger electron and the doubly ionized final state of the target atom. In a noncoincidence arrangement we measure the incoherent sum of contributions corresponding to doubly ionized final states of different energies.

If we calculate the contribution to the cross section where $\varepsilon_2\approx\varepsilon_1\approx\varepsilon_r$, after squaring the amplitude (7) we integrate over the angles of the second electron. One obtains a nonvanishing interference term in the cross section only if the equivelocity Auger and photoelectron partial waves have the same parity. This happens if the electrons participating in the Auger process are in subshells of opposite parities before the decay. The branching ratio for these channels may be rather small. Therefore the electron exchange for noncoincidence measurements may result in only a slight effect.

V. RESULTS

In an experimental study of the exchange effect Schwarzkopf, Kämmerling, and Schmidt [9] have reported preliminary results on the two-step double photoionization in xenon. At photon energy 97.5 eV in $4d_{5/2}$ photoionization followed by N_5-$O_{23}O_{23}$ $^1S_0$ Auger decay the emitted electrons have about the same energies, 30 eV. Since the exchange effect predicts a strong asymmetry between the parallel and antiparallel ejections, the relative angle of the electron analyzers was 180°, that is,

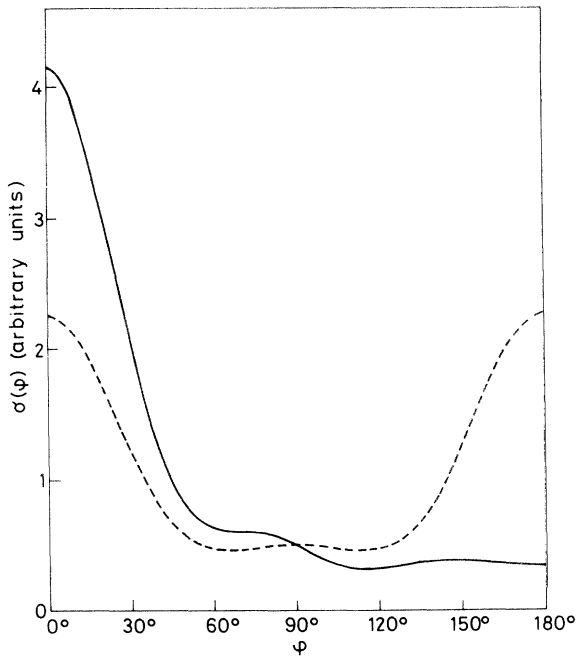

FIG. 1. Calculated angular correlation (solid line) between the two equivelocity electrons produced in $4d_{5/2}$ photoionization followed by N_5-$O_{23}O_{23}$ $^1S_0$ Auger decay for xenon at incident photon energy 97.5 eV. The broken line shows the same without exchange. According to the geometry of Schwarzkopf, Kämmerling, and Schmidt [9], electrons are emitted perpendicular to the direction of the photon beam and one electron is emitted along the line of the linear polarization, φ is the azimuth angle of the second electron. The state of the incident photon beam is characterized by the Stokes parameters $S_1=0.66$, $S_2=S_3=0.0$.

the two electrons were ejected antiparallel to each other.

In order to realistically compare with the experiment, we have calculated the angular correlation in the presence of the exchange term. Figure 1 shows the calculated cross section for the geometry of [9]. The photoionization dipole matrix elements were taken from [10]. Since the final state of the residual doubly ionized atom is $J_f = 0$, there is only one allowed channel for the Auger decay and the square of the Auger-decay matrix element $|H_{25/2}|^2$, taken to be unity here, is factorized out of the cross section formula (15). The two electrons are emitted perpendicular to the direction of the photon beam and one electron moves along the line of the linear polarization. The state of the incident photon beam in [9] is characterized by the Stokes parameters $S_1 = 0.66$, $S_2 = 0.0$. As Fig. 1 shows, the presence of an interference term leads to a strong enhancement for parallel ejection of the two electrons. The small, but nonvanishing, cross section at 180° reflects that here the interactions have some small dependences on the electron spins.

In the measurement [9] the energy resolution was too poor to detect the effect. The evaluation of the improved measurements is in preparation [12].

It can, however, be expected [11] that for parallel ejection the Coulomb interaction between the electrons may lead to a strong reduction of the coincident angular distribution pattern owing to electron-electron repulsion in the final state not included in our calculations. Therefore decays to triplet states of the doubly charged ion are better candidates to observe the exchange effect since the enhancement occurs for electrons with antiparallel momenta in this case. Final-state interaction effects are strongly reduced when electrons are ejected at relative angles of 180°.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. PHY-8918713 and by the Hungarian OTKA Foundation under Contract No. 3011. We thank R. L. Becker for his participation in the early stage of this work.

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