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Reactions ($\gamma, 2e$) and ($e, 3e$) as probes of electronic correlations in atoms

M. Ya. AMUSIA

Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, U.S.A.
and
A.F. Ioffe Physical-Technical Institute, St. Petersburg 194021, Russia

Abstract: Cross sections of the ($\gamma, 2e$) and ($e, 3e$) reactions carry information on two vacancy energy spectrum and on electron pair correlations in initial and final states of the target atom. Physical pictures of these processes are presented for two- and many-electron atoms. Simplest mechanisms of them are discussed, demonstrating some features which are waiting for experimental confirmation. Attention is given to high photon energy and even to relativistic energy region of these reactions. The energy distribution of outgoing relativistic electrons is qualitatively different from what it is for the nonrelativistic case. Origin and types of corrections to the simplest mechanisms and possible means of their detection are discussed. Role of different resonances: shape, giant, autoionizational, and Feshbach-type are considered. Results of calculations are compared with experimental data, mainly on double photoionization cross sections. Different possible objects as targets for the reactions are mentioned, including negative ions, excited atoms, molecules and clusters. Modification of the type of these reactions due to rather probable emission of the photon is discussed. Future of the domain is outlined.

1. Introduction

By definition, ($\gamma, 2e$) and ($e, 3e$) are reactions, in which all final state electrons are observed in coincidence, their emission cross section as a function of angle and energy being measured. Therefore, the investigation of these processes give incomparably much more information than what can be obtained by photoabsorption, electron inelastic scattering, or (γ, e) and ($e, 2e$) reactions.

The more particles are registered in the final state, the more detailed information on the process is obtained and the more difficult it is to reach accurate theoretical description of the investigated process. So, for the theorists the beginning of extensive investigation of ($\gamma, 2e$) and ($e, 3e$) processes means a challenge: how to absorb and interpret all the information which could be obtained experimentally. It is necessary to have in mind, that while ($\gamma, 2e$) tells mainly upon the direct interaction between eliminating electrons, ($e, 3e$) is in this sense more complicated because the process is determined also by the interaction of the projectile with both of the eliminating electrons.

The interest to double electron ionization has a long history. It started more than 25 years ago with the measurements of total He double photoionization cross section [1] and the attempts of theoretical description of this process for He [2] and any other atoms [3]. Soon it became clear, that double electron photoionization is very sensitive to the detailed mechanisms of electron interaction inside the atom, but in order to obtain all that information coincidental experiments with observation of both outgoing electrons are desirable [4-5]. It takes close to fifteen years until the first $(\gamma, 2e)$ measurement was performed [6].

An incoming electron as a source of action upon the target atom is much richer, than a photon, mainly a dipole: the atomic reaction can be studied as a function of not only the transferred energy, but also the transferred momentum, linear and angular. It gives additional information, but makes not only observation, but also interpretation more complicated, than in the case of interaction with photons.

The story of $(e, 2e)$ development which shows its advantages and short-comings, as compared to (γ, e) , demonstrates, that studying of both reactions is fruitful and very interesting. This motivates the development of $(e, 3e)$, the first measurements of which were performed recently [7]. The investigation of $(e, 3e)$ is now strongly stimulated by the observation of the difference in double electron ionization of atoms, particularly He, by rather fast electrons and positively charged particles, positrons and protons [8], which is a clear manifestation of a strong interaction between the projectile and target.

In what follows we will present the physical pictures of $(e, 3e)$ and $(\gamma, 2e)$ processes, discussing which kind of information and under which conditions may be derived from these reactions. Different photon or electron energy ranges will be discussed: from almost near zero up to very high relativistic values. Some recommendation for experiment will be given and the results obtained will be presented.

2. Physical Picture of the $(\gamma, 2e)$ and $(e, 3e)$ Processes

Even for He (H^-) the reaction $(\gamma, 2e)$ is a three-, while $(e, 3e)$ is a four-body problem, to solve which one must be able to describe the two-(three)-electron motion in a Coulomb field of the nucleus. For all but He atom (or H^- negative ion) the other electrons, except those two which are ionized can play an important role. For these more complicated than He (H^-) targets, i.e. for multielectron atoms, the other electrons are participating in the considered processes by:

- a. Modifying the field acting upon the considered eliminating electrons as compared to the pure Coulomb field of the nucleus,
- b. Modifying the interaction between two eliminating electrons and the atomic electrons and the projectile due to virtual excitations of the atomic core, or, in other words, due to dynamical screening of the Coulomb interelectron interaction by other atomic electrons,
- c. Modifying the energy and momentum, transferred to the outgoing electrons, due to excitation or even elimination of another target electron.

These three complications, added to absolutely nontrivial three-(four)-body problem makes the situation very difficult and requires simplification in order to interpret the experimental data. This simplification can be achieved by choosing a simple target (like He or H⁻), a convenient energy region - high or low, or an aim of investigation, for instance to obtain data on atomic electron wave functions at short or long distances.

Let us start with high (but nonrelativistic) energies. In this case it is natural to substitute the knocked-out electrons wave function as well as that of the projectile by plane waves. Then it is easy to show, that ⁽¹⁾ the following relations hold:

$$\frac{d\sigma_{(\gamma,2e)}}{d\vec{p}_1 d\vec{p}_2} \sim |\Psi_{i_1 i_2}(\vec{p}_1 \vec{p}_2)|^2 \quad a)$$

$$|\vec{p}_1 + \vec{p}_2| \approx R^{-1} ; \quad p_1, p_2 \gg R^{-1} \quad (1)$$

$$\frac{d\sigma_{(e,3e)}}{d\vec{p}' d\vec{p}_1 d\vec{p}_2} \sim \frac{1}{q^4} |\Psi_{i_1 i_2}(\vec{p}_1 - \vec{q}, p_2)|^2 \quad b)$$

$$\vec{q} = \vec{p} - \vec{p}' ; \quad p, p' \gg R^{-1} .$$

Here $\vec{p}_1, \vec{p}_2$ are the momenta of the outgoing electrons with energies ε_1 and ε_2 , $\Psi_{i_1 i_2}(\vec{p}_1, \vec{p}_2)$ is the Fourier-image of their wave function in the initial state $i_1 i_2$, R is the atomic radius, $\vec{p}, \vec{p}'$ are the projectile momenta before and after the collision, respectively.

It is meaningful to compare (1) with corresponding formulae for (γ, e) and $(e, 2e)$ reactions derived under the same conditions as (1a) and (1b):

$$\frac{d\sigma_{(\gamma, e)}}{d\vec{p}_1} \sim |\varphi_i(p_1)|^2 , \quad a)$$

$$(2)$$

$$\frac{d\sigma_{(e, 2e)}}{d\vec{p}' d\vec{p}_1} \sim \frac{1}{q^4} |\varphi_i(\vec{p}_1 - \vec{q})|^2 , \quad b)$$

$$\vec{q} = \vec{p} - \vec{p}' .$$

Here p_1 is the ejected electron momentum, $\vec{p}, \vec{p}'$ are the momentum of the projectile before and after collision, the energies being ε and ε' respectively, and $\varphi_i(\vec{p}_1)$ is the Fourier image of the one-particle atomic electron wave function in its ground state.

So, it is seen, that studying of $(\gamma, 2e)$ and $(e, 3e)$ reaction can in principle give information on the energy and wave functions of electron pairs in their initial state. The energy of these states can be found considering the $(\gamma, 2e)$ and $(e, 3e)$ reactions cross sections as functions only of the energy, transferred to the residual ion: either $\omega - \varepsilon_1 - \varepsilon_2$ (for the $(\gamma, 2e)$) or $\varepsilon - \varepsilon' - \varepsilon_1 - \varepsilon_2$ (for $(e, 3e)$). Just as single vacancy states, the double vacancy ones will be accompanied by their satellites, which have at least one extra excited electron and a vacancy. The difference between reactions with photons - (1a), (2a) and electron scattering (1b), (2b) is essential: in the latter case the dependence upon the transferred momentum $\vec{q}$ appear. Formula (1), (2) are valid only if the action of the atomic field upon the outgoing electron and/or projectile is

⁽¹⁾Atomic system of units is used throughout this paper: $e = m_e = \hbar = 1$, e and m_e being the electron charge and mass.

negligible, i.e. at $p, p', p_1, p_2 \gg \sqrt{I}$, I being the target's ionizational potential. Usually this is not the case and corrections due to atomic field action upon the outgoing electron and projectile must be taken into account. For fast electrons, the eikonal approximation is sufficient, at least for $(e, 2e)$. The corresponding corrections permitted to derive the intensity of main and satellite lines, where an essential difference between the results coming from (γ, e) and $(e, 2e)$ reaction was observed and then explained [9]. Similar measurements, but for two-vacancy states and their satellites should be performed in $(\gamma, 2e)$ and $(e, 3e)$ reactions.

Even with eikonal corrections expressions (1), (2) are valid only if the outgoing electrons energy is much bigger than their ionization potential, i.e. if $\epsilon, \epsilon', \epsilon_1, \epsilon_2 \gg I$. It means that $(\gamma, 2e)$ and (γ, e) give information on the wave function at short interelectron distances and short electron-nucleus distances, respectively (p_1, p_2 are big), while $(e, 3e)$ and $(e, 2e)$ can supply information on the long (atomic range) distances also, if being studied as a function of q , because (1b) and (2b) are valid for any $\bar{p}_1 - \bar{q}$, even small.

Of interest is the outgoing particles energy region, where one of them is slow and thus strongly interacting with the core: it bears information on the correlations of this electron with that of the core.

Rather specific is the energy region, where two outgoing electrons are very slow. There the energy and angular distribution of both of them is completely determined by their Coulomb repulsion, which leads to a decrease of the near threshold cross section [10].

$$\sigma^{++}(\omega) \sim (\omega - I^{++})^{1.056} \quad (3)$$

as compared to the first power for the case when the interaction between outgoing particles is of finite range ⁽²⁾. Here I^{++} is the double electron ionization potential. According to Wannier [10] the outgoing electrons have rather strong angular correlation, being directed oppositely. It is still unclear, however what is the real range of validity of (3) (see, for example, [11]), although a number of accurate measurements have been performed, claiming confirmation of (3) in 1 eV region above threshold [12].

Rather interesting and challenging is the near threshold region in $(e, 3e)$ where all three particles in the final state are slow.

3. Attempt to Calculate the Cross Sections - Simplest Version

We will start the discussion here by applying a perturbative in interelectron interaction approach, which can give at least an insight on what and where is important. Using the many-body diagrammatical technique, adjusted to atomic physics problems [13] one can present the amplitude of $(\gamma, 2e)$ reaction in the lowest order in the interelectron interaction by four following diagrams:

⁽²⁾The exponent 1.056 is for double ionization of neutral targets.

In (4) a line with an arrow to the right (left) denotes an electron at an excited level or in the continuous spectrum (vacancy), the wavy line represents the Coulomb interelectron potential, while the dashed line stands for incoming photon. It is implied, that the one-electron (vacancy) wave function is calculated in the self consistent field of the ion. Having in mind, that time in the ionization process depicted in (4) is assumed to increase from the left to the right, it is said usually, that (4a) and (4b) describes final while (4c) and (4d) initial state correlations.

If energy conservation permits the vacancy j to decay into $i_1 i_2 \epsilon$ state, (4a) is an amplitude of a two step process, the first being the inner vacancy j creation then followed by its Auger decay. If $j = i_1$ (or i_2), (4a) is the lowest order matrix element of a shake-off process, in which the instantly created vacancy j eliminates another electron creating another vacancy i_2 .

It is essential, that the ratio $\sigma^{++}(\omega)/\sigma^+(\omega)$ has a limit, which is for ionizing s-electrons a constant [2]:

$$\eta(\omega) = \frac{\sigma^{++}(\omega)}{\sigma^+(\omega)} \xrightarrow{\omega \rightarrow \infty} \text{const.} \quad (5)$$

The calculations, performed in "velocity" dipole form for high photon energies ω permit to disclose where which diagram (4) is most important. The results [4] are collected in Table [1]:

Table 1

Double-electron photoionization cross section

Diagram (4)	$p_1 \gg p_2$	$p_1 \sim p_2$	$p_1 \ll p_2$
a)	$\omega^{-7/2}$	$\omega^{-17/2}$	$\omega^{-13/2}$
b)	$\omega^{-9/2}, m \sim p_{1,2}^{(3)}$	$\omega^{-9/2}, m \sim R^{-1}$	$\omega^{-13/2}, \text{ any } m$
c)	$\omega^{-7/2}, m \sim R^{-1}$	$\omega^{-9/2}, m \sim P_1$	$\omega^{-13/2}, m \sim R^{-1}$
d)	$\omega^{-13/2}$	$\omega^{-9/2}$	$\omega^{-13/2}$

⁽³⁾Here m is the intermediate state ϵ' (see (4b, c)) momentum.

The dimensionless quantity in table 1 is $(I^{++}/\omega) \ll 1$. It is seen that in the "velocity" form the main contribution to σ^{++} is coming from (4a) and (4c), with one fast and the second slow electrons. Note, that the contribution of the ground state correlational two electron wave function, here represented by (4c), is at $p_1 \sim p_2$ by a factor $(I^{++}/\omega) \ll 1$ smaller. It must be kept in mind that the same order term is coming also from the final state correlations - (4b). It means, that $(\gamma, 2e)$ in $p_1 \sim p_2$ region gives more complicated information about the atom than the two-electron ground state correlated wave function.

Note, that the suppression of contribution of the region $p_1 \sim p_2$ to the absolute cross section is due to the fact, that if $p_1, p_2 \gg R^{-1}$, two considered electrons becomes unbound and cannot absorb a dipole photon. It is of interest to trace therefore how this feature is altering with increase of frequency, where the dipole approximation start to be violated and spin interaction of the photon, which distinguish spin "up" and "down" electron becomes important. This leads to increase of the cross section σ^{++} in the $p_1 \sim p_2$ region, where both electrons absorb a photon as a pair of almost free particles.

It is of interest to present data on the energy distribution of the two outgoing electrons[4], which are collected in Table 2. It is seen, that for relativistic photon energies $\omega \geq c^2$ the double ionization cross section becomes almost as big as σ^+ [15], mainly due to the increase of the middle region contribution.

Table 2

Contribution of Different Spectral Regions to $d\sigma^{++}/d\epsilon$ and σ^{++}

Spectral Region	Contribution to $d\sigma^{++}/d\epsilon$	Contribution to σ^{++}
$\epsilon_1 \sim \omega, \epsilon_2 \sim I^{++}$ "Edge" region	$\sim \sigma^+/I^{++}$	$\sim \sigma^+$ (0.092 σ^+/Z^2) (4)
$\epsilon_{1,2} \gg I^{++}$ $ \epsilon_1 - \epsilon_2 \leq (\omega + cR^{-1})(\omega/c^2)^{1/2}$ "Middle" region	a) $\omega \ll cR^{-1}$ $\sim (\sigma^+/\omega)(I^{++}/\omega)^{1/2}$ b) $\omega \geq c^2$ $\sim \sigma^+/\omega$	$\sim \sigma^+(I^{++}/\omega)$ $\sim \sigma^+$ (0.59 σ^+/Z^2)

This is illustrated by the Fig. 1, where the curve $d\sigma^{++}/dE$ at high frequencies acquire a powerful maxima in the "middle" region.

The angular distributions are also quite different in the "edge" and "middle" regions. At the edge, the fast electron has the same angular distribution as in single ionization, while the second tend to be isotropic. The "middle" region electrons are moving as unbound particles after absorbing the photon energy and momentum. It means, that it is a strong angular correlations between two outgoing electrons. In high photon energy region it is of interest to study the photoelectrons spin orientation: that which belong to the "middle" region must have mostly parallel spin.

(4)Z is the nucleus charge for Helium like ions.

Fig. 1. Differential in energy double-electron photoionization cross section $d\sigma^{++}/d\varepsilon$:
a) $\omega = 20 I^+$; b) $\omega = 137 I^+$; c) $\omega = 1000 I^+$.

The simplest description of the $(e,3e)$ reaction can be achieved by limiting ourself with the same diagrams as that in (4). However instead of a real photon, a virtual one connects the projectile and target, which is illustrated by (6a):

It is obvious, that (6a) is similar to (4a). However comparatively big values of transferred momentum $\vec{q} = \vec{p} - \vec{p}'$ as compared to that of photon with the same energy makes the situation more complicated. On the other hand, a pair of free electrons can have, for example, a quadrupole moment, it can be turned into motion by an incoming electron, thus increasing the yield in the "middle" region.

Until recently it was almost a general feeling that corrections (6b) to the amplitude of (e,3e) similar to (4) are unimportant. To a large extent it was supported by the fact that single electron ionization with fast electrons and protons at same velocities has almost the same cross section. It appeared, however, that this is not the case [8] even for rather high velocities so that the theoretical description of (e,3e) require to include the ionization by two-step collision (6b) even in the perturbative approach.

4. Corrections to the Simplest Approach

In the low and intermediate energy region the picture of the process given by (4) and (6) is insufficient and more complicated interactions or correlations must be taken into account.

Here it will be discuss which are these corrections, modifying the simplest theoretical picture presented in the previous section. Let us consider perturbative type corrections, starting from diagrams (4), which assume that the atomic electrons and vacancies wave function are calculated in the Hartree-Fock approximation. In general, following corrections are of importance:

- If the transferred energy either to the atom or between the outgoing electrons is close to the ionization potential of a multielectron atomic shell, its virtual excitations in the frame of the Random Phase Approximation with Exchange (RPAE) must be taken into account,
- If one of the outgoing electrons is slow, its Coulomb interaction with vacancies must be included nonperturbatively, by solving a Hartree-Fock equation of the residual ion, where the presence of a vacancy or vacancies is explicitly taken into account,
- If the relative velocity of the outgoing electrons is small, their wave function must be corrected by including the Coulomb interaction of the considered electrons, or by deriving the three-body wave function which describes the motion of two electrons in the field of the residual ion.

The case a) is exemplified by two diagrams, modifying (4c):

The corrections of the type (7a) are of importance if either i_2 or i'' belongs to a multielectron shell or the considered transferred energy $E_2 + I_{i_2}$ is in the region of i'' subshell ionization potential. For multielectron shells such corrections must be taken into account nonperturbatively by solving RPAE equations (see [13]).

The corrections similar to that depicted in (7a) are decisively important if ω is close to the multielectron atomic subshell ionization potential. It can increase the total double charged ion yield considerably.

The case b) is exemplified by the following diagram

which is a modification of (4a) accounting for the fact, that starting from the moment of the inner j vacancy Auger-decay into the state $i_1 i_2 \epsilon_2$, the electron ϵ_1 is moving in the field of $i_1 i_2$ instead of j . As a result the amplitude acquire a factor $(\epsilon' / \tilde{\epsilon}_1)$ i.e. an overlap integral which is different from $\delta(\epsilon' - \epsilon_1)$ because ϵ' and ϵ_1 are calculated in different fields, namely that of vacancy j and $i_1 i_2$, respectively. This instant change of the field due to Auger decay of vacancy is called in literature Post Collision Interaction (PCI). It leads to modification of the spectrum of electrons ϵ_1 , ϵ_2 , their angular distributions and, perhaps, electron spin polarization.

Rather specific is the case when the final state, presented in (8), is formed close to the inner shell threshold j by an incoming electron which loose almost all its energy, exiting the intermediate state $j\epsilon'$. In this case the problem becomes excitingly interesting, but also rather complex, because the interaction of two outgoing slow electrons must be also taken into account. This two electron PCI is presented by a diagram:

The account of this diagram, which has two overlap integrals $(\epsilon''' / \tilde{\epsilon}_1)$ and $(\epsilon'' / \tilde{\epsilon}_1)$ instead of one in (8) modifies the energy and angular distribution of all three final state electrons. Of course, for two slow electrons their mutual interaction is of importance thus leading to the following classical formula for the energy shift of the Auger-electron line ϵ_2 :

$$\Delta\varepsilon_2 = \left[\frac{1}{v_1} + \frac{1}{v'} - \frac{1}{|\vec{v}_1 - \vec{v}'|} \right] \Gamma_j, \quad (10)$$

where Γ_j is the total Auger width of the vacancy j . Note, that this energy shift depends upon the angle between $\vec{v}_1$ and $\vec{v}'$ and its relative value, transforming into an ordinary expression for PCI shift if either v_1 or v' are much bigger than the other: $\Delta\varepsilon_2 = \Gamma/v'$ or Γ/v_1 .

In the case c) of small relative velocity of two outgoing electrons the direct interaction between them must be taken into account, which is essential mainly far off the target atom. It means, that this kind of corrections is almost insensitive to the inner structure of the atom. Thus the study of the $(e,3e)$ or $(\gamma,2e)$ reaction with two very slow electrons in the final state informs mainly on the Coulomb three - (four) - body problem, being sensitive only to the asymptotics of the wave function in distance. But for $\varepsilon_1, \varepsilon_2 \geq 1$ eV, the distances of the order of atomic radius R start to be important [16].

The inclusion of interaction of outgoing electrons ε_1 and ε_2 at big separations is difficult to perform numerically due to long range nature of the Coulomb force. Now most common is an attempt to use for the final state the so-called Redmond wave function [17], which is precise only asymptotically. Therefore in some cases the Redmond correction of the wave function makes the results even worse. So, a two electron wave function $\Psi_{\varepsilon_1\varepsilon_2}(\vec{r}_1, \vec{r}_2)$ must be constructed as a combination of a numerically calculated at $r_1, r_2 \lesssim R$ function and its analytical asymptotics $\Psi_{\varepsilon_1\varepsilon_2}^{(Red)}$.

The main contribution to the double photoionization cross section is coming from (4c) at small ε_2 and ε' . Therefore in this region the correct wave function for two slow electrons is important. However this type of corrections may be taken into account by using for the initial state of the ionizing atom the ground state correlated function. Most simple to do this is for He of H^- . Because low ε' and ε_2 correspond to long distances off the atom the function used must have good long distance behavior.

5. Resonances in $(\gamma,2e)$ and $(e,3e)$ Reactions

Until this point we do not pay attention to the possible influence of atomic resonances upon the reaction cross sections. However, these are of great importance and must manifest themselves in a number of ways. We will start with shape resonances, which are able to affect the outgoing electron continuum wave functions ϕ_{ε_1} and ϕ_{ε_2} . These resonances, acting in a given partial wave, can increase considerably its contribution thus modifying the energy and angular distribution of outgoing particles in a rather broad energy region. Such resonances for electrons in the ion field are of interest. Rather important must be the Feshbach-type resonances which are due to the virtual excitation of core electrons by the ionized ones: ε_1 and ε_2 . They appear at energies ε_1 or ε_2 close to the creation of ion discrete excited state which is diagrammatically represented by (11), where n_2, n_1 are forming together with vacancy j_1 a discrete excitation $n_1 n_2 j_1$. These resonances appear in a given partial wave and rather specifically affect the energy and angular distribution.

Resonance behavior of the photoabsorption amplitude affects the $(\gamma, 2e)$ and dipole channel of $(e, 3e)$ reactions cross section when correction of the type (7b) are taken into account. Giant resonances in photoabsorption cross section alter mainly the total yield of the

doubly charged ions rather than any energy or angular distribution. Here a good example is the Xe atom, in which the cross section $\sigma^{++}(\omega)$ increases dramatically while the frequency

while the frequency ω approaches $4d^{10}$ subshell ionization threshold: even well below threshold σ^{++} starts to increase and the ratio σ^{++}/σ^+ becomes there as big as 0.8.

It is of importance to understand the role of discrete excited states and corresponding autoionizational resonances. Suppose, that ϵ^* in (7a) or (7b) is a discrete excited level. In its vicinity cross sections of $(\gamma, 2e)$ as functions of ϵ_2 or ω have Fano-type profiles, with their characteristics being determined by the interaction of a discrete excitation with either one electron continuum (see (7a)) or two-electron continuum (7b). Particularly interesting are cases, for which the decay into a "one electron-one vacancy" continuum is forbidden or strongly suppressed, so that only the decay into $\epsilon_1 \epsilon_2 i_1 i_2$ states becomes the source of width of the discrete "one electron- one vacancy" excitation.

Recently it became clear, that autoionizational decay of discrete excited states contributes considerably even to the total double photoionization cross section. It was observed [18], that in a rather broad frequency region ω about 30 + 40% of Ar^{++} ions are coming via satellite formation after $3s$ photoionization. This process is illustrated by the following diagram:

This diagram is specified for the Ar case. The dashed-dotted intermediate state includes a satellite $np\ 3p^{-1}$ to the main line $3s^{-1}$. This satellite decays autoionizationally into $\epsilon_2 3p^{-1}$ continuum, with emitting a slow electron ϵ_2 . The diagram (12) is of the next order in interelectron interaction as compared to (4), but is a resonance one which considerably increases its contribution.

The emission of two electrons via a resonance gives information on a rather important kind of correlations, connecting discrete and continuous spectrum states.

6. Results of Calculations

Quite a few calculations were performed of the reactions $(e,3e)$ and $(\gamma,2e)$ differential cross sections (see [19] and some references therein). Even the total double electron photoionization cross section was calculated only in several papers using only rather crude approximation. Mainly the diagrams (4) were taken into account, and some corrections, such as the interaction between ionizing electrons in initial and in a simplified version in the final state were added. The ratio of double-to single photoionization cross section at high energy is a constant (see (5)), which for He was calculated in a number of papers and recently measured. The results of calculations slightly change from one theoretical paper to another within the limits $1.6 \pm 2.3\%$ [2, 4, 21, 22], and agree with the experimental value 1.6% [20].

For the total double electron photoionization cross section of He the results of calculations are in reasonable quantitative agreement with experiment in a rather broad frequency region: from several eV above threshold up to keV and even higher (see [23] and references therein), which is illustrated by Fig. 2.

Fig. 2. Ratio $\sigma^{2+}(\omega)/\sigma^+(\omega)$ for He as a function of photon energy ω (compiled from [23]).

There are some data on other noble gases but in a much narrower frequency range. In almost all cases the calculations are performed mainly within the framework of diagrams (4). For other than He atoms (e.g. Ar and Xe), the ratio $\sigma^{2+}(\omega)/\sigma^+(\omega)$ increases rather fast from the threshold and reaches values of about $30 \pm 80\%$.

For low ω the energy distribution in ϵ_1 and ϵ_2 is almost flat and one of the emitted electrons is predominantly an s-, while the other is a p-wave. The main contribution is coming from the (4b) diagram so that the entire process may be presented as a two step with initial single photoionization and subsequent inelastic scattering of a photoelectron upon an ion [24,25], leading to the following expression

$$\sigma^{++}(\omega) \equiv \sigma_{\text{RPAE}}(\omega) [1 - \exp(-2 \text{Im} \delta_{\text{ph}}(\epsilon))], \quad (13)$$

where $\sigma_{\text{RPAE}}(\omega)$ is the one-electron photoionization cross section calculated in RPAE, $\text{Im} \delta_{\text{ph}}(\epsilon)$ is the imaginary part of the elastic scattering phase shift of the photoelectron with energy ϵ . Eq. (13) describes $\sigma^{++}(\omega)$ reasonably good, while the rest presents rather accurately the real single ionization in the same frequency region:

$$\sigma^+(\omega) \equiv \sigma_{\text{RPAE}}(\omega) \exp(-2 \text{Im} \delta_{\text{ph}}(\epsilon)), \quad (14)$$

It deserves to be mentioned, that at least for noble gases Ne, Ar and Xe a correspondence exists between the experimental cross section $\sigma_{\gamma^{++}}(\omega)$ and the calculated one in RPAE frame for the photoionization of ns subvalent subshells, if the calculation is performed using all theoretical, i.e. Hartree - Fock ionization thresholds. This is illustrated by Fig. 3, and it seems that doubly charged ion formation process looks like a realization of an energy forbidden ns-vacancy Auger-decay.

Fig. 3 Cross section of double ionization:
Solid lines: experiment, Ar and Xe,
Dashed lines: theoretical RPAE photoionization cross section of $3s^2$ (Ar) and $5s^2$ (Xe) with Hartree-Fock thresholds.

There is a simple theoretical prediction which could be checked using $(\gamma, 2e)$ reaction instead of σ^{++} measurement. Indeed, equation (5) holds only if s-electrons are ionized, while for p-electrons $\sigma^+(\omega)$ decreases at high frequencies as $\omega^{-9/2}$. The cross section $\sigma^{++}(\omega)$ for ionization of two p-electrons however still decreases as $\omega^{-7/2}$ with ω growth, because the intermediate states in (4a) - j and (4c) - ϵ' can be always s-states which determines the $\omega^{-7/2}$ behavior. Thus the ratio $\sigma^{++}(\omega)/\sigma^+(\omega)$ for p-electrons must increase as ω with ω growth.

7. Targets for (e,3e) and (γ ,2e) Reactions

The simplest target to study these reactions is He atom and H^- negative ion. Of course, for double electron processes He is just as important as Hydrogen for the single electron ones. So the desire to understand this object perfectly is quite reasonable. However more important and stronger are the correlations in multielectron atoms where the interaction between two ionized electrons can be considerably modified at short (of about the inner shell radius), intermediate and long (outer shell radius) distances. For this reason heavy noble gases seems to be very convenient.

Correlations are relatively stronger, when the role of central self-consistent field is as small as possible, which is achieved for negative ions and shells with high principal quantum numbers.

It is desirable therefore to study He-like sequence, i.e. Be, Ca etc. in order to see how the differential cross-section for ns^2 electrons is affected by increase of the ionized electron shell radius and by virtual excitation of the core $(n-1)p^6$. Of interest would be to compare these data with that obtained for atoms with $(n-1)d^{10} ns^2$ outer subshells.

Of specific interest would be the results of these reactions for excited atoms, starting with the simplest ones, such as He is $1s2s^3S$. The considerable change of the ionization potential, ground state wave function symmetry and atomic radius will affect essentially the reactions cross section.

As it was in (γ ,2e) or (e,2e) studies, the investigation of (γ ,2e) and (e,3e) should not limit itself to isolated atoms. More natural is to consider molecules and solid bodies as possible objects for investigation of the electron correlations role. Of interest are new atom-like objects - metallic clusters and fullness - there one has really multielectron and easily polarizable shells, which considerably modify the interaction of a pair of outgoing electrons. The combination of finite size, nonzero temperature and high polarizabilities with intensive inner shell discrete excitations makes them extraordinary interesting, because all correlational corrections: polarization of the core by emitted electrons, modification of the interelectron interaction, effect of autoionizational and shape resonances are presented in these objects to a very high extent.

8. Modification of (γ ,2e) and (e,3e): ($\gamma, A^{++}\gamma'$), ($\gamma, e\gamma'$), (e,2e γ') and ($e^+, 2ee^+$) Reactions

Particularly for He, of great interest is the observation of a secondary photon in coincidence with the double charged ion; i.e. the ($\gamma, A^{++}\gamma'$) reaction. If the difference between the incoming and secondary photon energies is close to the double ionization potential of the target, the reaction ($\gamma, A^{++}\gamma'$) gives information on the role of final state interaction between two outgoing electrons. In principle, very close to threshold Wannier-type corrections [10] may be observed, but with the difference, that in ($\gamma, A^{++}\gamma'$) for He the final electron state is an S-one with a bigger statistical weight than the P-state in photoionization. The cross section in the soft γ' region shows how essential is the change of only the angular momentum of one of the outgoing electrons. By studying the dependence of the cross section upon $\omega - \omega'$ for different ω literally the x-ray picture of the two electron wave function in initial, intermediate and final states could be done.

Recent experimental data on double ionization of He [26] and subsequent discussion [27] demonstrated the important role played by Compton effect in the frequency region above 5-6 keV. There is no doubt, that the single ionization is due to Compton-effect, which is absolutely dominating at $\omega \approx 10$ keV and higher. Therefore, the experimentally observed constant ratio σ^{++}/σ^+ which is equal to $1.5 \div 1.6\%$ in a very broad frequency region - from about 1 keV to 12 keV of the primary photon-means that the ratio is the same (or almost the same) for ionization accompanied by photon emission also. Qualitatively it is understandable: the main contribution to the cross section is coming from high energy photon emission by the fast outgoing electron, namely by ε_1 in (4a) and (4c). All other possible mechanisms require big energy transfer via Coulomb interaction, leading to smallness of the corresponding matrix element and to high virtuality of intermediate states. As for (4a) and (4c), the emission of high energy photon does not alter the ratio σ^{++}/σ^+ . Apart from this main feature, the very fact that $(\gamma, e\gamma)$ contributes much more than (γ, e) require careful investigation of $(\gamma, e\gamma)$, its energy, angular distribution and, perhaps, polarization. The $(\gamma, e\gamma)$ cross section just as that of $(\gamma, 2e)$ is affected by electron correlations.

The role of secondary photons emission can be important also in double ionization by fast electrons. Therefore the reaction $(e, 2e\gamma)$ deserves investigation. It is not much more complicated than $(e, 3e)$, at least for high ω' .

Along with $(e, 3e)$ the reaction $(e^+, 2ee^+)$ must be studied. Positron as a projectile has no exchange with atomic electrons. Being of opposite charge, it interacts with atomic target differently than an electron, thus giving information on non-Born effects in the process.

9. Concluding Remarks

The investigation of $(\gamma, 2e)$ and $(e, 3e)$ reactions was initiated and motivated to a large extent by the desire to obtain two-electron wave functions in the atomic ground state almost directly from experiment. Although it appeared that the reality is not that simple, a number of correlational effects, both in the initial and final state affecting the one-electron and two-electron wave functions are reflected in the reactions cross sections.

These reactions permit to study the long range purely Coulombic correlations and the modification of them due to short- and intermediate range interaction with core electrons. The reactions are able to give information on different resonance effects which can in principle alter the respective cross sections considerably.

Being among the most challenging experiments in atomic physics, the $(\gamma, 2e)$ and $(e, 3e)$ reactions require adequate theoretical support and interpretation: to my mind this is a case where close cooperation is absolutely important for success.

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