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On different mechanisms of the two-electron atomic photoionization

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Abstract

We evaluate the partial contribution of different mechanisms leading to the single-photon two-electron atomic ionization processes: photoionization with excitation and double photoionization. We estimate the photon energy at which the shake-off mechanism becomes dominant over the two-step mechanism. We support our findings by scaling the photoionization cross-sections of neutral atomic species with the electron scattering cross-sections on the corresponding positive ions.

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The single-photon two-electron ionization processes, photoionization with excitation and double photoionization (DPI), are only possible due to many-electron correlations in the atomic target. That is why these processes attract so much attention, both experimentally and theoretically. Since the pioneering works by Carlson (1967) and Byron and Joachain (1967) it is well known that two different mechanisms can lead to a two-electron transition following absorption of a single photon. The shake-off mechanism (more precisely, shake-up in the case of ionization with excitation) is a single ionization followed by the removal or excitation of the remaining bound electron due to a sudden change of the atomic field. The two-step mechanism is a single ionization followed by inelastic scattering of the ejected electron on the positive ion. It is intuitively clear that the shake-off mechanism requires a certain excess energy above the ionization threshold which enables the first ejected electron to leave the atom quickly enough to produce a sudden change of the atomic field. For this reason one would not expect this mechanism to be dominant near the double ionization threshold. On the contrary, when the excess energy is large, the two ejected electrons leave the atom with a highly asymmetric energy sharing. In this case one can neglect the interaction of the fast ejected electron with the ion and the whole yield of the DPI process would be due to the shake-off.

There have been few attempts to substantiate these simple qualitative arguments by a direct numerical evaluation. The simplest estimate of the relative contribution of the shake-off and the two-step mechanisms can be made by evaluating the lowest order terms of the many-body perturbation theory (MBPT). Some ambiguity of this evaluation arises from the choice of the non-perturbed one-electron states. Most commonly the MBPT is built on the Coulomb basis. In this case, in addition to the shake-off and two-step terms, the lowest order MBPT contains an extra ground state correlation term which describes a virtual two-electron-two-hole excitation in the target prior to absorption of the photon. This extra term, however, would not have appeared had the correlated ground state been used. So the split between the shake-off and two-step terms is not so straightforward in the MBPT. Besides, the relative contribution of the three lowest MBPT terms depends very

strongly on the gauge of the electromagnetic operator.

Nevertheless, some indication of the dominance of the shake-off mechanism at large photon energies can be gained from the MBPT. Amusia *et al* (1975) used the electromagnetic operator in the velocity gauge and showed the shake-off to be the parametrically leading term at very high photon energies. Dalgarno and Sadeghpour (1992) reached the same conclusion by using the acceleration gauge and following the method of Dalgarno and Stewart (1960). They calculated the asymptotic ratio of the double-to-single photoionization cross-sections in the limit of infinite, but still non-relativistic, photon energy. In this calculation the two-step mechanism was completely ignored. However, the calculated ratio for helium was confirmed experimentally by Spielberger *et al* (1995) to a very high accuracy. At the same time, Dalgarno and Sadeghpour (1992) showed the shake-off and the two-step terms to be comparable in the length gauge. Hino *et al* (1993) investigated the partial contribution of the three lowest order MBPT terms over an extended range of photon energies. They showed that the shake-off becomes dominant at a few keV photon energy if the velocity or the acceleration gauges of the electromagnetic operator are chosen. In the length gauge the two-step term is always much greater than the shake-off term.

The interest to the problem of relative contribution of the two-step and shake-off mechanisms was renewed lately in the light of recent experiments on the double ionization of He in a superstrong electromagnetic field (Weber *et al* 2000). Keller (2000) used the lowest order MBPT terms to calculate the fully differential cross-section of the double photoionization of He. He concluded that the two-step mechanism made a dominant contribution at excess energy of 50 eV and a very asymmetric energy sharing of the two photoelectrons.

The "shake-off versus two-step" problem was addressed recently from an entirely different prospective by Kheifets *et al* (2000) who examined the proportionality between the double-to-single photoionization cross-section ratio of the ground state and metastable He atom and the electron impact ionization cross-section of the He^+ ion:

$$\frac{\sigma^{2+}(E)}{\sigma^{+}(E)} \simeq \frac{\sigma^{e+}(E)}{\pi r^2} \tag{1}$$

Here E is the excess energy above the double ionization threshold of the He atom in the case of the DPI, and the electron energy above the single ionization threshold of the He^+ ion in the case of the electron impact ionization. This proportionality was first established experimentally by Samson and collaborators (Samson 1990, Samson *et al* 1992) in a number of atomic species (He, N, O, and Ne). The fitting parameter r was interpreted as the electron radius of the singly charged ion. As the shake-off mechanism contributes to σ^{2+}, but not to σ^{e+}, the proportionality (1) might indicate the smallness of this contribution. Once the shake-off becomes significant, the double photoionization term of (1) should deviate from the electron impact ionization term.

This departure from the proportionality relation (1) was indeed observed both experimentally (Samson 1990, Samson *et al* 1992) and theoretically (Kheifets *et al* 2000). In the latter case the cross-sections σ^{2+} and σ^{e+} were obtained from the convergent close-coupling (CCC) calculations. A graphical representation of the CCC model is shown in Fig. 1. The ground state correlation is displayed as a superposition of (diagonal) two-electron configurations obtained either by the multiconfiguration Hartree-Fock (MCHF) method or by the Legendre polynomial expansion of the Hylleraas ground state. Non-correlated final state is represented by a Coulomb wave $\boldsymbol{k}$ and a discrete pseudostate nl. The latter is obtained by diagonalizing the target Hamiltonian on the Laguerre basis. The negative energy pseudostates form the single ionization channels, whereas the positive energy pseudostates contribute to the double ionization. The final state correlation is represented by the half-off-shell T-matrix $\langle \boldsymbol{k}'\, n'l'|\, T\, |nl\, \boldsymbol{k}\rangle$ which includes the interelectron interaction to all orders of the perturbation theory. The sum over the intermediate discrete states $n'l'$ and the integral over the continuum $\boldsymbol{k}'$ is assumed.

In the CCC model, the "bare" shake-off process is calculated as a product of the one-electron dipole matrix element and the direct overlap of the (nonorthogonal) one-electron orbitals in the initial and final states (Fig. 1a). However, some part of the integral term (Fig. 1b) can be incorporated into the shake-off. Indeed, the continuous orbitals $\boldsymbol{k}$ in the CCC model are Coulomb waves and the elastic electron scattering on the ion has to be

included to account for the distorting potential of the remaining bound electron. The sum of diagram (a) and the diagonal part $n'l' = nl$ of diagram (b) can be absorbed into diagram (c) in which the photoelectron state is distorted by the field of the positive ion. Despite this distortion, the shake-off process (c) can be described by a final state with uncorrelated atomic electrons whereas diagram (b) implies such correlation.

The remaining part of diagram (b) which contains a nondiagonal T-matrix $\langle \boldsymbol{k}'\, n'l' |\, T\, | nl\, \boldsymbol{k} \rangle$ contributes to the two-step process. This non-diagonal T-matrix also determines the cross-section of the inelastic electron scattering on the singly ionized atom which leaves the ion in the excited or doubly charged states.

This simple separation of the shake-off and the two-step mechanisms allows one to turn them on and off at will in the CCC model. In this Letter we present the full CCC calculation of the two-electron photoionization of He which includes both the diagonal and non-diagonal terms in the T-matrix. This calculation contains contribution from both the shake-off and the two-step processes. In addition we perform a CCC calculation with the diagonal T-matrix only which amounts to neglecting the two-step mechanism.

The full T-matrix calculations of the two-electron photoionization were reported elsewhere for the ground state He, Li^+ and H^- by Kheifets and Bray (1998), and for the metastable He by Kheifets *et al* (2000). In brief, the 20-term Hylleraas expansions were used to describe the ground state of He, Li^+ and H^-. The metastable $1s2s\,^{1,3}S$ helium was described by the 14- and 10-term MCHF expansions for the singlet and triplet states, respectively. The final singly or doubly ionized state of the target was represented by a $(17-l)$, $l = 0 \ldots 2$ pseudostates making a total of 48 s, p and d pseudostates. The projectile continuum was treated using around 70 k-grid points with orbital momentum $l = 0 \ldots 4$. There were also up to 9 projectile bound states included for every l. The accuracy of the initial and final states was monitored by a close convergence (better then 5% with the Hylleraas ground state) between calculations performed in three gauges of the electromagnetic interaction - length, velocity and acceleration.

Results of the full T-matrix calculations of the two-electron photoionization of the ground

state helium are presented in Fig. 2. This calculation is essentially gauge insensitive and only the velocity gauge results are plotted. We show cross-sections of the ground state photoionization σ_1, photoionization with excitation σ_n, $n = 2 \ldots 5$ and double photoionization σ^{2+}. On the same figure we also show results of the diagonal T-matrix calculation (also only the velocity gauge) which neglects the two-step mechanism. We see that the full and diagonal T-matrix calculations are almost identical for the ion $n = 1$ ground state. The difference between the full and diagonal T-matrix calculations becomes noticeable for $n = 3$ at few tens of eV above the double ionization threshold. This differences increases at $n = 4, 5$ and becomes large for the double photoionization. However, at about 100 eV away from the threshold, both the full and diagonal T-matrix calculations are hardly distinguishable. This indicates the complete take over of the shake-off mechanism.

Another indication of this takeover can be seen in Fig. 3 where we plot the cross-sections of the inelastic electron scattering on the He^+ ion derived from the full T-matrix CCC calculation. The electron impact ionization cross-section σ^{e+} is scaled, to the best visual fit, to the double-to-single photoionization ratio σ^{2+}/σ^{+} (bottom right panel of Fig. 3). The same scaling constant is applied to the inelastic electron scattering cross-sections $\sigma^e_n, n = 2 \ldots 5$ which are shown together with excited-to-ground state photoionization cross-sections ratios σ_n/σ_1. The plots of Figs. 2 and 3 complement each other. Deviation of the electron scattering cross-sections from the corresponding photoionization ratios occurs at about the same energy where the full and the diagonal T-matrix calculations merge together and were, we presume, the shake-off mechanism becomes dominant.

In conclusion, we performed the calculations of the two-electron photoionization of helium using the CCC method with both the full and diagonal T-matrices. The latter calculation contains contribution of the shake-off process only, whereas the former includes both the shake-off and the two-step mechanisms. The velocity gauge calculation clearly indicates gradual takeover of the shake-off mechanism which is complete at about 100 eV above the double ionization threshold. At about the same energy the excited-to-ground and the double-to-single photoionization cross-section rations start to deviate from the corresponding

inelastic electron scattering cross-sections. This again can be interpreted as the take-over of the shake-off mechanism. Qualitatively similar behaviour was observed in other two-electron targets, H^- and Li^+.

The diagonal T-matrix calculation show a strong gauge dependence and only the velocity gauge calculation shown in Fig. 2 can be interpreted in this simple way. On the other hand, the proportionality relation (1), illustrated in Fig. 3, is gauge independent. Deviation from this proportionality can be interpreted as some indication of the cross-over from correlated to uncorrelated double ionization regime.

Results of the present study can simplify significantly calculation of the two-electron photoionization on more complex atomic targets. As is seen from Fig. 2, the shake-off process alone, when calculated with an accurate ground state wave function and correct distorted waves, can describe the two-electron ionization in a very broad photon energy range starting from only 100 eV above the double ionization threshold. In contrast, when simple Coulomb states are used, the shake-off contribution becomes dominant at excess energy as high as few keV (Hino *et al* 1993).

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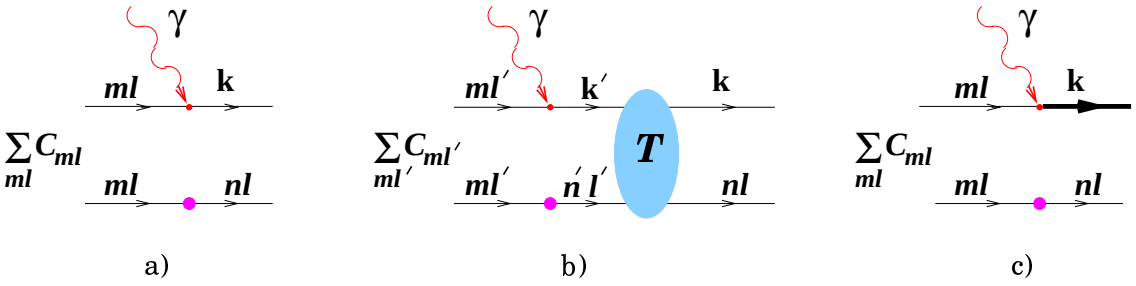

FIG. 1. Graphical representation of the shake-off (a) and the two-step (b) mechanisms of the two-electron atomic ionization. A thin straight line with an arrow indicates an electron state in the Coulomb field of the nucleus, the wavy line shows a photon. The filled oval represents the inter-electron interaction in all orders of the perturbation theory (the T-matrix). The ground state correlation is shown as a superposition of various diagonal two-electron configurations. The dot indicates an overlap of the non-orthogonal one-electron orbitals of the initial and final states of the target. Diagram (a) and a diagonal part $n'l' = nl$ of diagram (b) can be absorbed into diagram (c) in which the thick line shows the electron state in the field of the positive ion with the bound electron nl.

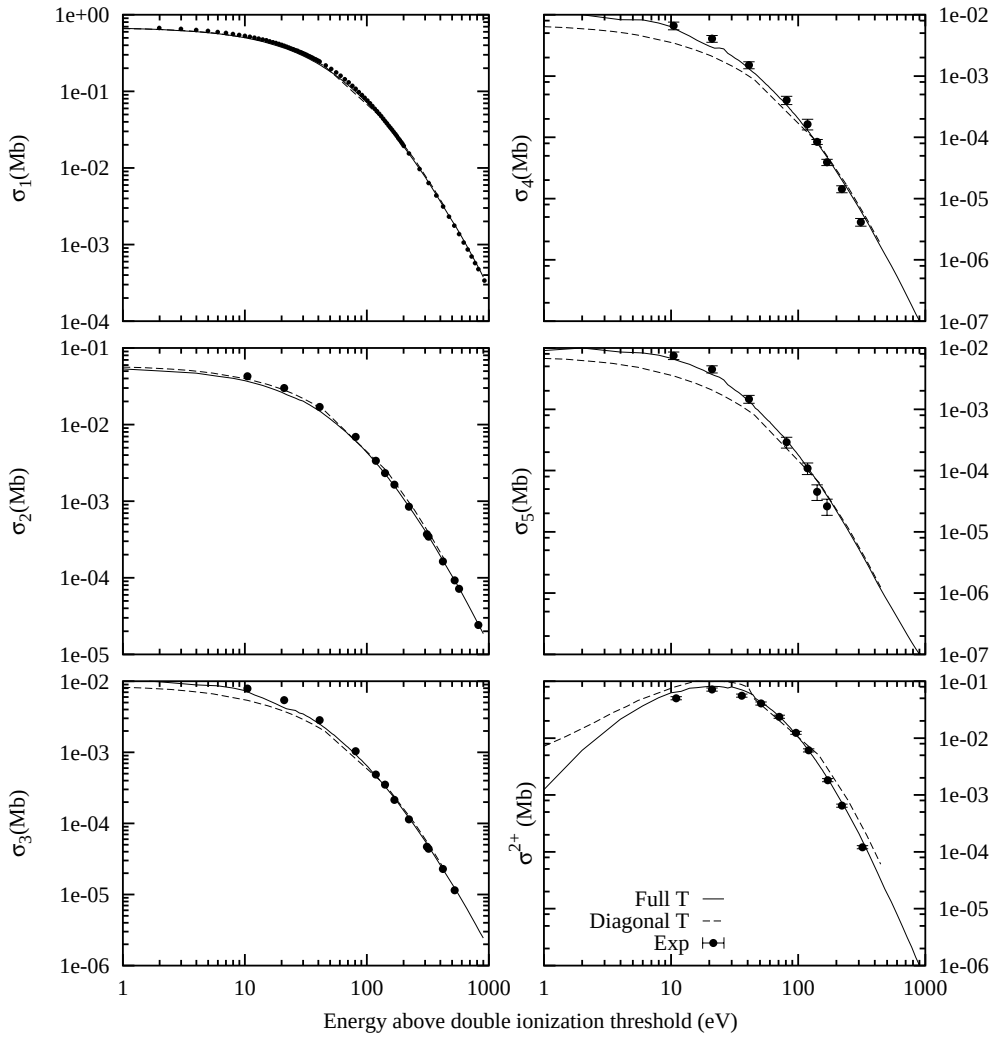

FIG. 2. Cross-sections of the ground state photoionization σ_1, photoionization with excitation σ_n, $n = 2 \ldots 5$ and double photoionization σ^{2+} in He. The solid line is the full T-matrix calculation (all three gauges coincide) which includes both the shake-off and the two-step processes. The dashed line is the diagonal T-matrix calculation (velocity gauge only) which takes into account just the shake-off process. The experimental data for ground state ionization are by Samson *et al* (1994), ionization-excitation by Wehlitz *et al* (1997), and for the double photoionization by Dörner *et al* (1998)

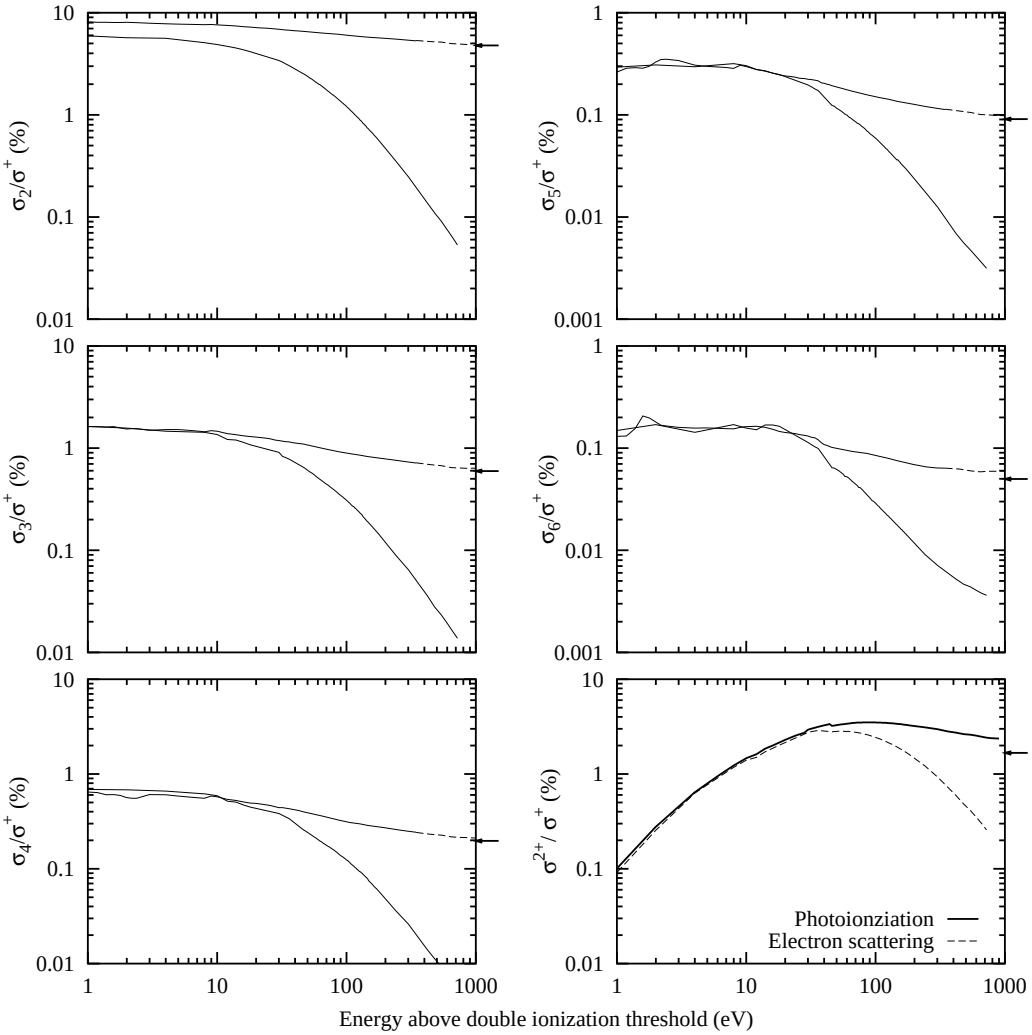

FIG. 3. The photoionization cross-section ratios of He $\sigma_n/\sigma_1, n = 1 \ldots 5$ scaled versus the inelastic electron scattering cross-sections of He^+ σ_n^e. The bottom right panel - double-to-single photoionization ratio σ^{2+}/σ^+ scaled versus the electron impact ionization cross-section σ^{e+}. The solid line is the full T-matrix photoionization calculation. The dashed line is the electron scattering calculation. All the electron scattering cross-sections are scaled to the corresponding photoionization ratios with the same constant. The arrows indicate the asymptotic photoionization ratios in the limit of infinite photon energy.