Separation and identification of dominant mechanisms in double photoionization

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(Dated: December 14, 2021)

Double photoionization by a single photon is often discussed in terms of two contributing mechanisms, knock-out (two-step-one) and shake-off with the latter being a pure quantum effect. It is shown that a quasi-classical description of knock-out and a simple quantum calculation of shake-off provides a clear separation of the mechanisms and facilitates their calculation considerably. The relevance of each mechanism at different photon energies is quantified for helium. Photoionization ratios, integral and singly differential cross sections obtained by us are in excellent agreement with benchmark experimental data and recent theoretical results.

PACS numbers: 3.65.Sq, 32.80.Fb, 34.80.Dp

Our understanding of dynamical processes often rests on isolating approximate mechanisms which leave characteristic traces in the measured or computed observables. A prime example is double photoionization. After the initial absorption of the photon by the primary electron the subsequent redistribution of the energy among the electrons is often discussed in terms of two mechanisms [1], knock-out (KO) (sometimes called ‘two-step-one’ [2]) and shake-off (SO) [3, 4, 5]. The first mechanism describes the correlated dynamics of the two electrons as they leave the nucleus where the primary electron has knocked out the secondary electron in an (e, 2e)-like process. The second mechanism accounts for the fact that absorption of the photon may lead to a sudden removal of the primary electron. This causes a change in the atomic field so that the secondary electron relaxes with a certain probability to an unbound state of the remaining He$^+$ ion, i.e., the secondary electron is shaken off.

Apart from general properties, e.g., the prevalence of shake-off at high photon energies, it is difficult to separate the processes. However, they are distinct with respect to their quantum nature: shake-off is a purely quantum mechanical phenomenon while knock-out dynamics occurs classically as well as quantum mechanically. This opens up the possibility to separate shake-off and knock-out by calculating the latter (quasi-)classically, provided that absorption of the photon may lead to a sudden removal of the primary electron. This causes a change in the atomic field so that the secondary electron relaxes with a certain probability to an unbound state of the remaining He$^+$ ion, i.e., the secondary electron is shaken off.

The two phases of double photoionization, initial absorption and redistribution of the energy, can be expressed by the relation

$$\sigma_X^{++} = \sigma_{\text{abs}} P_X^{++}$$

where X stands for either shake-off or knock-out. In the following, we evaluate $P_X^{++}$ for full fragmentation of the ground state and use the experimental data of Samson et al. [6] for $\sigma_{\text{abs}}$. We obtain the classical double escape probability for KO with a classical-trajectory Monte-Carlo (CTMC) phase space method. CTMC has been frequently used for particle impact induced fragmentation [1, 6, 7, 8, 9, 10] with implementations differing typically in the way the phase space distribution, $\rho(\Gamma)$, of the initial state is constructed. Details of our approach will be published elsewhere, here we summarize the important steps only.

Within our phase space approach the double escape probability $P_{K\!O}^{++}$ is formally given by

$$P_{K\!O}^{++} = \lim_{t\to\infty} \int \! d\Gamma P^{++} \exp((t - t_{\text{abs}})L_3) \rho(\Gamma),$$

with the classical Liouvillian $L_3$ for the full three-body Coulomb system propagated from the time $t_{\text{abs}}$ of photoabsorption. The projector $P^{++}$ indicates that we have to integrate only over those parts of phase space that lead to double escape (the asymptotic final energies of the two electrons, $\epsilon$ and $E - \epsilon$, are positive). The integral in Eq. (2) is evaluated with a standard Monte-Carlo technique which entails following classical trajectories in phase space.

The electrons are described immediately after absorption by the distribution

$$\rho(\Gamma) = \mathcal{N} \delta(\vec{r}_1) \rho_2(\vec{r}_2, \vec{p}_2)$$

where $\mathcal{N}$ is a normalization constant. The primary electron absorbs the photon which has an energy $\hbar \omega$. With $\delta(\vec{r}_1)$ we demand the absorption to occur at the nucleus, an approximation which becomes exact in the limit of high photon energy [11]. This approximation significantly reduces the initial phase space volume to be sampled. Regularized coordinates [12, 13] are used to avoid problems with electron trajectories starting at the nucleus ($\vec{r}_1 = 0$).

The function $\rho_2(\vec{r}_2, \vec{p}_2)$ describing the secondary electron in Eq. (3) is given by

$$\rho_2(\vec{r}_2, \vec{p}_2) = \mathcal{W}_0(\vec{r}_2, \vec{p}_2) \delta(c_2^{\text{fin}} - \epsilon_B).$$
It is obtained by calculating the Wigner distribution, \( W_\alpha(\vec{r}_1, \vec{r}_2) \), of the orbital \( \psi(\vec{r}_2) = \Psi_0(\vec{r}_1 = 0, \vec{r}_2) \) for a choice of initial wavefunction \( \Psi_0 \), and restricting the initial energy of the secondary electron, \( \varepsilon_B^{\text{p}} \), to an energy shell \( \varepsilon_B \). In the KO mechanism the initial state correlation is not important so we take the independent particle wavefunction \( \Psi_0(\vec{r}_1, \vec{r}_2) = (Z_{\text{eff}}^3/\pi) \exp(-2\varepsilon_B^{\text{p}}(\vec{r}_1 + \vec{r}_2)) \) with effective charge \( Z_{\text{eff}} = Z - 5/16 \). From this choice follows \( \varepsilon_B = -Z_{\text{eff}}^2/2 \) and \( \varepsilon_B^{\text{p}} = p_{\text{eff}}^2/2 - Z_{\text{eff}}/r_{\text{eff}} \).

The double-to-single ratio in the absence of the SO mechanism is simply given by

\[
R_{\text{KO}} = P_{\text{KO}}^{++}/(1 - P_{\text{KO}}^{+}).
\]

In Fig. 1 we show \( R_{\text{KO}} \) as a function of the excess energy \( E \) (dashed line). The shape is characteristic of an impact ionization process \cite{14}. For high energies the primary electron moves away so quickly that there is no time to transfer energy to the secondary electron, \( R_{\text{KO}} \) thus drops to zero as expected. The non-zero asymptotic ratio (indicated by an arrow in Fig. 1) is due to SO which we describe next.

In contrast to KO the shake mechanism is inherently non-classical in nature. Moreover, initial state correlations are important for shake-off. As a generalization of the standard formula for SO \cite{4}, Åberg gave an expression for the probability to find the shake electron in state \( \phi_\alpha \) at any excess energy \( \varepsilon \):

\[
P_\alpha^{\nu} = |\langle \phi_\alpha | \nu^{\nu} \rangle|^2/\langle \nu^{\nu}| \nu^{\nu} \rangle,
\]

with

\[
\nu^{\nu}(\vec{r}_2) = \int d^3r_1 \nu^{\nu}(\vec{r}_1) \Psi_0(\vec{r}_1, \vec{r}_2),
\]

where \( \nu(\vec{r}_1) \) is the wavefunction of the primary electron after it has left the atom. If it was in an \( s \)-state before the absorption it is in a \( p \)-state afterwards. The secondary (shake) electron does not change its angular momentum. It can be found with probability \( P_\alpha^{\nu} \) in an hydrogenic eigenstate of the bare nucleus, being either bound \( (\alpha = n_2) \), or in the continuum \( (\alpha = \varepsilon) \). As for KO we assume that the primary electron absorbs the photon at the nucleus. In this situation we do not need to know \( \nu(\vec{r}_1) \) but can simply replace \( \nu^{\nu}(\vec{r}_2) \) by \( \Psi_0(\vec{r}_1 = 0, \vec{r}_2) \) in Eq. (7).

We may further simplify the calculation of shake-off for practical applications in two-electron atoms by taking for \( \Psi_0(\vec{r}_1 = 0, \vec{r}_2) \) a normalized hydrogenic wavefunction \( \phi_{s_{\text{absorbed}}}^{Z_{\text{absorbed}}}(\vec{r}_2) \) where the correlations have been ‘absorbed’ into an effective shake charge \( Z_{\text{SO}} \). For \( Z_{\text{SO}} \approx 2 - 0.51 \) the exact asymptotic ratio \( R_\infty = 0.01645 \) \cite{16, 17} is reproduced. We have found little difference for the shake probability as a function of excess energy between this simple ansatz and a fully correlated Hylleraas wavefunction \cite{18} for \( \Psi_0 \).

The shake-off probability of Eq. (7) reduces now to

\[
P_\alpha = |\langle \phi_\alpha | \phi_{Z_{\text{SO}}} \rangle|^2.
\]

The total double ionization probability from shake-off at finite energies \( E \) is given by integrating expression (8) over the energy \( \varepsilon \) of the shake electron in the continuum \( \alpha \equiv \varepsilon \):

\[
P_{\text{SO}}^{++}(E) = \int_0^E d\varepsilon P_\varepsilon.
\]

The photoionization ratio when only the SO mechanism is taken into account (same as Eq. (8) but for SO) is shown in Fig. 1 (chained line). The ratio rises slower than the KO mechanism result up to an energy of around 100 eV where the KO ratio reaches its maximum value. The SO ratio continues to rise until at a couple of hundred eV it moves more slowly up toward the asymptotic value. An interesting feature of the plot is where the KO and SO results cross at an excess energy of \( \sim 350 \) eV.
To obtain more insight into the two mechanisms we calculate the differential probabilities $dP^{++}_{X}/d\varepsilon$, where $X$ stands for either SO or KO. In our classical model of the KO mechanism we divide the interval of values for $\varepsilon$ which corresponds to double escape ($0 \leq \varepsilon \leq E$) into $N$ equally sized bins (we take $N=21$) and work out the differential probability by finding the trajectories which fall into the bins. For the SO mechanism the probability per energy unit, $P_\varepsilon$ in Eq. (4), already gives the differential probability. Since the electrons are indistinguishable the differential probabilities must be symmetrized about the equal energy sharing point ($\varepsilon = E - \varepsilon = E/2$),

$$\left.\frac{dP^{++}_X}{d\varepsilon}\right|_{\text{sym}} = \frac{1}{2} \left( \frac{dP^{++}_X(\varepsilon, E)}{d\varepsilon} + \frac{dP^{++}_X(E - \varepsilon, E)}{d\varepsilon} \right).$$

In the case of low excess energy (6 eV) we find a slightly concave shape for the KO distribution, see Fig. 2(b). This implies a preference for equal energy sharing, the typical behavior close to threshold \[12\]. The SO result in contrast displays a slightly convex shape which becomes flat as $E \to +0$. Unequal energy sharing is always preferred by SO since the photoelectron is fast with respect to the secondary electron. For all higher excess energies shown both mechanisms display a convex form.

SO may be viewed as an additional quantum contribution to the quasi-classically calculated double photoionization given by KO. This means that the full result is given by

$$\frac{d\sigma^{++}}{d\varepsilon} = \sigma_{\text{abs}} \left[ \frac{dP^{++}_{SO}}{d\varepsilon} + \frac{dP^{++}_{KO}}{d\varepsilon} \right].$$

Integration over $\varepsilon$ yields the total double ionization cross section,

$$\sigma^{++} = \sigma_{\text{abs}}(P^{++}_{SO} + P^{++}_{KO}) = \sigma_{\text{abs}}^{++} + \sigma_{\text{SO}}^{++}. \quad (12)$$

FIG. 3: Singly differential cross sections normalized to 1 for $\varepsilon = 0$. Solid lines: our complete theoretical results at excess energies of (a) 6 eV, (b) 21 eV, (c) 41 eV. Dashed lines: new results of Colgan et al. \[21\] at excess energies of (a) 4 eV, (b) 20 eV and 25 eV, (c) 40 eV.

The single ionization cross section is $\sigma^+ = \sigma_{\text{abs}} - \sigma^{++}$ and the double-to-single ratio is given by $R = \sigma^{++}/\sigma^+ = P^{++}/(1 - P^{++})$, where $P^{++} = P^{++}_{SO} + P^{++}_{KO}$.

In Fig. 1 we compare the ratio $R$ (solid line) to the experimental data of Samson et al. \[20\]. For excess energies up to 200 eV we find an excellent agreement. In the energy regime where the two contributions are of the same size there is a deviation between experiment and our result (at worst 8%). Exactly in this situation any interference which exists between SO and KO would show its largest effect. The deviation we find may be due to such an interference which we cannot account for since we determine KO quasi-classically. At higher energies the difference decreases again (already visible in the plot) until at very high energies our result reproduces the asymptotic ratio.

Knowing that the differential probabilities for KO and SO enter the full ionization probability with the same weight we can assess the relative importance of both contributions at different energies. From Fig. 2 one sees that at 110 eV SO has become more important than KO for highly unequal energy sharings. As energy is increased to 450 eV SO begins to dominate regions of unequal energy sharing. On the other hand, KO is higher at equal energy sharing for all excess energies $E$.

FIG. 4: Absolute singly differential cross sections. Solid lines: our theoretical results at excess energies of (a) 6 eV, (b) 11 eV, (c) 21 eV, (d) 31 eV, (e) 41 eV. Circles: recalibrated (see text) experimental data of Wehlitz et al. \[22\] at the same excess energies apart from (a) which is at 5 eV. The triangles in (e) additionally show the Wehlitz data renormalized to the $\sigma^{++}(41 \text{ eV})$ of Samson \[20\].
excess energies below 20 eV. This is in disagreement with our results which are convex down to 6 eV. In Fig. 4 we compare our absolute SDCS to the experimental data of Wehlitz et al. [22] which has been recalibrated using the values of the photoabsorption cross section of Samson et al. [24]. In their original work Wehlitz et al. normalized their SDCS using a photoabsorption cross section which is now known to overestimate the 5-41 eV range by 9 to 16%. In addition, the photoionization ratio they measured at 41 eV is \( \sim 17\% \) higher than the Samson et al. [20] data and so we renormalize Fig. 4(e) to take this into account.

Our approach not only facilitates the calculation of double photoionization, it also offers considerable insight into the physical process, e.g., concerning the similarity with electron impact ionization of He\(^+\) [24]. Indeed, we can show that impact ionization may be viewed as the KO part of double photoionization (Fig. 2). The only difference is that impact ionization sees a He\(^+\) hydrogenic target electron with binding energy \( E_B = -Z^2/2, Z = 2 \), while the KO process involves a bound electron with energy \( E_B' = -Z_{\text{eff}}^2/2 \). One may thus say that both processes differ only slightly, namely in the energy scale set by the respective bound electron.

We conclude that the separate formulation and calculation of knock-out and shake-off offers an accurate description of double photoionization. In principle this approach can be extended to describe angular differential cross sections. We have used a description in terms of the simplest wavefunctions possible having in mind to tackle three electron problems in a similar way.

It is a pleasure to thank R. Wehlitz and J. Colgan for providing us with their results. T.S. thanks Andreas Becker and Thomas Pattard for valuable discussions. Financial support by the DFG within the Gerhard Hess-program is gratefully acknowledged.

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