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# Direct versus sequential double ionization in atomic systems

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In view of recent papers on two-photon double ionization of helium, pertaining to a perceived anomaly in the behavior of the sequential process and its influence on the direct process, as well as the dependence of both on the laser pulse duration, we show that upon the proper formulation, the sequential is well defined and free of divergence, and that the dependence on pulse duration is considerably more intricate. We also argue that the apparent sharp rise of the cross section for the direct process, around 54.4 eV, is due to the unintended inclusion of the sequential process, which in any case is not properly describable in terms of a single cross section.

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Several recent papers [1–7] on the theory of two-photon double ionization (TPDI) of helium and in particular the value of the (generalized) cross section for direct double ionization (DDI) have injected new issues on the subject, in addition to the existing discrepancy between theoretical values obtained through various approaches. One has to do with whether the value of the cross section for DDI, as a function of photon energy, exhibits a sharp rise around 54.4 eV [2–4,7], and if so, what is the underlying physics. The second, in relation to the sequential double ionization (SDI), has to do with whether the relevant rate exhibits a divergence or else is ill defined [2,3]. Our purpose in this report is to offer a few, hopefully helpful clarifications, showing that the two are related and that there is neither a conceptual nor a computational difficulty in connection with SDI.

As long as the discussion refers, as it indeed does, to a cross section, for the notion and therefore the calculations to be meaningful, it is assumed that the relevant experiments are to be performed with radiation of intensity and pulse duration within the appropriate range. Since the relevant photon energies have to be within the range of about 40–80 eV, this means that the peak intensity should not exceed, say, $10^{17}$ W/cm$^2$ and the pulse duration not be shorter than about ten cycles of the field, which roughly speaking translates into more than about 0.5 fs. This is indeed the case for sources presently available or in the stage of development in the conceivable future. Under such conditions, the most unambiguous and conceptually straightforward approach to the problem is the calculation, in lowest (nonvanishing) order perturbation theory (LOPT), of the corresponding two-photon amplitude, the square of the absolute value of which, integrated over electron emission angles and energies, provides the value of the total direct cross section. After all, that is how its single-photon counterpart, known by now with great accuracy, has always been calculated. But at least in the present context, an unambiguous and conceptually straightforward approach is not necessarily the easiest to implement, although some approaches have in fact been implemented along such lines [1,6,8].

For reasons of computational convenience, however, a number of results have been obtained through the solution of the time-dependent Schrödinger equation (TDSE), which, for a given temporal pulse shape, duration, and peak intensity, provides the ionization yield ($Y_2$) at the end of the pulse. The cross section for the direct two-photon process ($\sigma_2$) can then be obtained from the yield, through the equation $Y_2(T) = \int_0^T dt\, \sigma_2(\omega) F^2(t)$, which relates the cross section to the yield [9–11]. In the above equation $F(t)$ is the photon flux while $T$ is the pulse duration. For the value thus obtained to be reliable, it is imperative for the TPDI yield $Y_2$, as extracted from the time-dependent calculation, to contain only the contribution of the direct two-photon process [channel (c) in Fig. 1]. Typically, this information is extracted by projecting the complete wave function of the atom (as it has evolved under the field), at the end of the pulse, on the double-continuum state reached by the absorption of two photons [4,10–12].

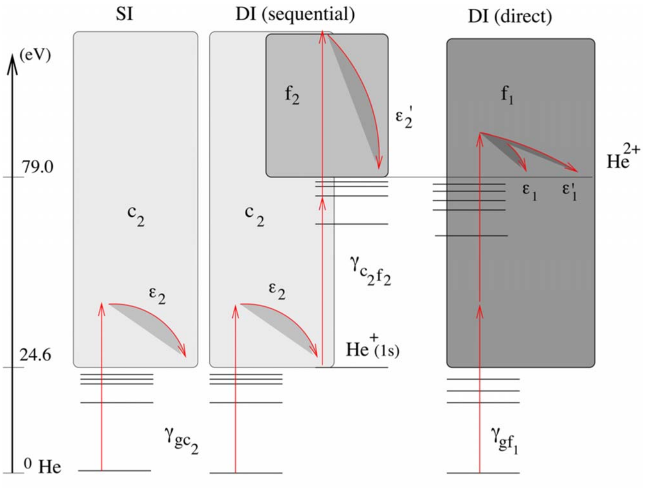

FIG. 1. (Color online) Schematic figure of the dominant channels involved in the ionization of helium atoms under a pulse in the energy window 40–54.4 eV. In the present case the direct channel is a two-photon channel (within LOPT), while the sequential channel is a three-photon channel.

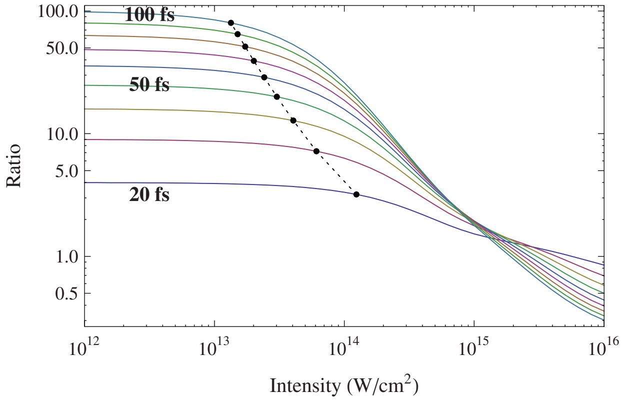

FIG. 2. (Color online) Yield dependence of the sequential on the pulse duration and as a function of the intensity for photon energy $\omega$=45 eV. The ratio of the sequential ionization yield for various pulse durations to the yield for a pulse of 10 fs duration is plotted. It is only for lower intensities that the ratio is quadratically dependent on the pulse duration $\sim T^2$.

Much of the ongoing discussion concerns the appropriate and/or acceptable form of this final state, which among other things may depend on the atomic basis employed in the calculation. There are arguments in the literature [2,4,10] in favor of projecting onto a product of two Coulomb functions with $Z$=2 and counterarguments [11,13] against such an approximation. We refrain from taking a position on this matter here, as it is beyond the scope of this paper. We assume from here on that, given a particular implementation of a time-dependent calculation, a projection to the appropriate final double continuum state is known and that, equally importantly, care has been taken for the double-ionization yield not to be inadvertently contaminated by single ionization; see, for example, the discussion in Ref. [11]. The problem we do wish to address here has to do with the sequential [channel (b) in Fig. 1]. Depending on the photon energy $\omega$, SDI represents a three- or two-photon process, the latter being the case for $\omega \geqslant 54.4$ eV. In any case and within the conditions of validity of LOPT, SDI represents a two-step process. Specifically, in the first step, the absorption of one photon leads to He$^+(1s)$ followed, in the second step, by a two-or one-photon ionization of the ion, leading to He$^{2+}$. The proper formal description of a two-step process requires a set of equations governing the evolution of the atomic and ionic species during the pulse. If it is only the dependence of the species populations on the laser peak intensity that is desired, the relevant rate equations can be found in Refs. [14,15]. The one- and/or two-photon ionization cross sections of He and He$^+$ entering the rate equations are unambiguously defined and in fact known [16]. For photon energies below 54.4 eV, the two-photon ionization cross section of the ion will exhibit peaks whenever the photon energy is on resonance with one intermediate ionic state. These are well-understood two-photon resonant cross sections, with no divergence, as the intermediate states have a nonzero width. If the intensity is sufficiently large to drive the transition to the intermediate state strongly, in the sense that the corresponding Rabi frequency is comparable to the ionization width, then the overall process becomes a three-step process. In that case, the most rigorous formulation is in terms of the density matrix [17]. The main point, however, is that there is no divergence, under any circumstances. Moreover, as the photon energy crosses the threshold of ~54.4 eV, where the two-photon ionization of the ion becomes one-photon ionization, again there is no divergence. The situation is analogous to the so-called channel closing in above-threshold ionization (ATI), where ionization of a particular order is suppressed, as the ionization potential moves upward with increasing intensity, due to the ponderomotive energy. No divergence exists there either. The difference here is that it is the photon frequency that changes and not the position of the ionization potential. At the risk of being overly redundant, it may be useful to point out that SDI represents a sequence of single ionizations governed by Fermi's golden rule, which is not known to lead to divergence. It is in obtaining a process within Fermi's golden rule through a time-dependent calculation that causes the apparent difficulty. Examples of calculations through such rate equations can be found in [18]. It is perhaps worth noting, in passing, that one significant conclusion that has emerged out of such calculations is that the intensity should not exceed a certain value (which depends on the frequency and the relative magnitude of the cross sections for the direct and sequential), because, above that intensity, the sequential dominates, hindering thus the observation of the direct. The rate equations can also help clarify the issue of the dependence of the direct and sequential yields on the pulse duration. A rather simple argument, advanced recently in Ref. [4], goes as follows: For direct ionization, the yield, as implied by $Y_2(T)=\int_0^T dt\,\sigma_2(\omega)F^2(t)$, would be proportional to the pulse duration, while sequential ionization, being the double integral over time of the product of two cross sections multiplied by the respective powers of the flux, would be proportional to the square of the time [see, e.g., Eq. (20) in Ref. [4]]. This argument would be valid if the population of the initial state did not change with time significantly and if, in addition, the population of He$^+(1s)$, formed in the first step of the sequential, did not change significantly with time either, as has indeed been the case for the conditions of the calculation in [4]. But clearly this cannot be the case in the generality implied by the above argument in [4], because the populations vary during the pulse in an intricate fashion. To illustrate the point, we present in Figs. 2 and 3 the results of calculations, for some typical cross sections, showing how the yields of the sequential and direct ionizations depend on pulse duration, as a function of the intensity. To facilitate inspection, we have plotted the respective ratios of the yield for various pulse durations to the yield for a pulse of 10 fs duration. Clearly, the $T^2$ for the SDI (Fig. 2) and $T$ (Fig. 3) for the DDI dependence on the pulse duration $T$ is valid only for low intensity, because then the population of the initial state has not changed much. As a guide to the eye, note that to the right of the line joining the dots, the ratios depart from the simple rule by more than 80%. Although we have chosen to use 10 fs as a reference point, the reader can verify that the dependence of the above ratios on pulse duration is fairly intricate. The curves would be different if, say, 50 fs was used as a reference. Therefore, the simple dependence on pulse duration would be valid very early in the pulse, or for a pulse sufficiently weak and/or short, so that the populations

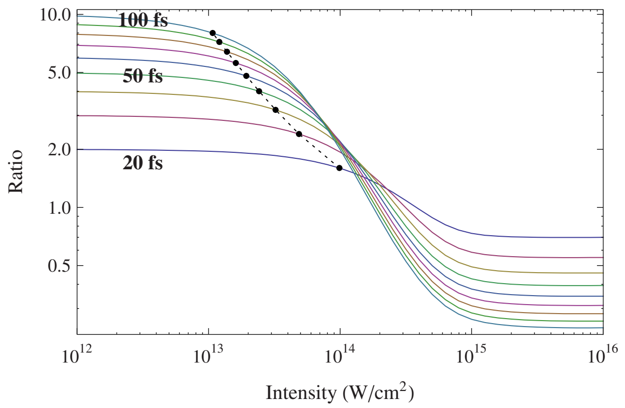

FIG. 3. (Color online) The same plot as in Fig. 2, but for the direct channel. It is only for the lower intensities that the ratio is linearly dependent on the pulse duration $\sim T$.

do not have the chance to change much. Needless to add here that, for a sufficiently long pulse, the ground states of the atom and the ion are eventually depleted. This has nothing to do with the breakdown of LOPT, in contrast to what has been argued in Refs. [2,3]. LOPT leads to a cross section and an associated rate for the "decay" of the initial state. And given enough time, the state will be depleted no matter how weak the intensity is.

If it is the angle-integrated photoelectron energy spectrum (PES) that is desired, a set of equations in terms of amplitudes (instead of populations), including the direct process, is more appropriate. An example of the relevant equations can be found in Refs. [19,20], where multiphoton double ionization of atomic carbon and TPDI of atomic Mg are examined, respectively. In the case where $N$-ionic states can be reached in the first step of the sequential path, the amplitude equations are as follows:

$$\dot{u}_g(t) = -(1/2)\left[\gamma_{gf_1} + \sum_{q=2}^{N+1} \gamma_{gc_q}\right] u_g(t), \tag{1a}$$

$$\dot{u}_{f_1}(t) = -i\Delta E_1 u_{f_1}(t) - iD_{f_1 g} u_g(t), \tag{1b}$$

$$\dot{u}_{c_q}(t) = \left[\Delta\bar{E}_q - i(\gamma_{c_q f_q}/2)\right] u_{c_q}(t) - iD_{c_q g} u_g(t), \tag{1c}$$

$$\dot{u}_{f_q}(t) = -i\Delta E_q u_{f_q}(t) - iD_{f_q c_q} u_{c_q}(t), \tag{1d}$$

with $q=2, 3, \ldots, N+1$ and $D$ the electric-dipole operator. In the above equations, $u_{f_q}(t) \equiv u_{f_q}(\epsilon_q, \epsilon'_q, t)$ represent the amplitudes as a function of time of the double-continuum channels reached from the direct ($q=1$) and sequential ionizations through the ionic stages represented as $u_{c_q}(t) \equiv u_{c_q}(\epsilon_q, t)$. The detunings are given as $\Delta E_q = \epsilon_q + \epsilon'_q - [E_g + (n_q + N_q)\omega]$ and $\Delta\bar{E}_q = E_q + \epsilon_q - (E_g + N_q\omega)$, with $\epsilon_q$ and $\epsilon'_q$ being the kinetic energies of the ejected electrons associated with the final continua reached from the direct or sequential ionization through the ionic stage $q$. $E_g$ and $E_q$ are the energies of the neutral and $q$th ionic stage, respectively, while $n_q$ and $N_q$ are the number of photons absorbed in the first and second steps of the sequential path $q$, respectively. In the present case of the TPDI of helium we set $N=1$, $n_q=1$, $q=1,2$, and $N_1=1$. The ionization widths $\gamma_{gf_1}$, $\gamma_{gc_q}$, and $\gamma_{c_q f_q}$ into the final continua (as labeled by the subscripts), reached via the direct or the sequential channels, correspond to single- and multiple-photon transition matrix elements according to the order of the process. More specifically, the ionization widths are given by $\gamma_{gf_1} = 2\pi \int d\epsilon_1 d\epsilon'_1 |D_{gf_1}^{(n_1+N_1)}(\epsilon_1, \epsilon'_1)|^2$, $\gamma_{gc_q} = 2\pi |D_{gc_q}^{(n_q)}|^2$, and $\gamma_{c_q f_q} = 2\pi |D_{c_q f_q}^{(N_q)}|^2$. In the present case where $N_1=1$ and $n_1=1$ it holds that $\gamma_{gf_2} = \sigma_2$. Solving the above system of equations in time, with the appropriate temporal pulse shape, we can calculate the PES, at the end of the pulse, associated with the double continuum as

$$\frac{dP_q}{d\epsilon_q} = \int d\epsilon'_q |u_{f_q}(\epsilon_q, \epsilon'_q, t \to \infty)|^2 \quad (q = 1, 2, \ldots, N+1)$$

and the PES associated with the single continuum as

$$\frac{d\bar{P}_q}{d\epsilon_q} = |u_{c_q}(\epsilon_q, t \to \infty)|^2 \quad (q = 2, 3, \ldots, N+1).$$

It should be underscored here that the presence of the widths in Eqs. (1) is essential, as they account for the nonzero width of the respective photoelectron spectral lines. They appear naturally through the rigorous derivation of Eqs. (1) and preclude any divergence. The effective width of these spectral lines, obtained automatically through the solution of the differential equations, results from the combined influence of the Fourier bandwidth of the pulsed laser and the ionization widths appearing in the above equations. The illustrative example of such a spectrum in Fig. 3 of Ref. [20] for atomic magnesium represents a situation slightly more complicated than helium, because it involves sequential peaks sitting on top of the continuous spectrum of the direct. Nevertheless, no divergence appears in the calculation. To forestall possible misunderstanding due to terminology, note that solving the above system of differential equations is very different from solving the TDSE. Here, it is understood that the values of the cross sections (including the direct) entering the equations have been obtained beforehand, the aim of the above treatment being to evaluate the contributions of the direct and sequential ionizations to the PES.

Although as emphasized above sequential ionization is a two-step process, a semiquantitative description of its basic features, showing the positions of the energy peaks and approximate widths, can be obtained in terms of a single equation—i.e., a single-transition probability. The proper expression can be derived, for example, through the resolvent operator and provides what is called the spectrum of final states, the end result being (for $N=1$)

$$|u_{f_1}(\epsilon_1, \epsilon'_1, t \to \infty)|^2 = \frac{\gamma_1/2\pi}{[\Delta E_1^2 + \gamma_1^2/4]} \frac{\gamma_2/2\pi}{[\Delta\bar{E}_1^2 + \gamma_2^2/4]}, \tag{2}$$

where $\Delta E_1 = \epsilon_1 + \epsilon'_1 - (E_{1s^2} + 2\omega)$ and $\Delta\bar{E}_1 = \epsilon_1 - E_{1s} - N_2\omega$ with $E_{1s^2}$, $E_{1s}$ and $\gamma_1, \gamma_2$ being the energies and the total ionization widths of the neutral and the singly ionized helium, respectively. The details of its derivation can be found in Refs. [21,22]. Note that it also contains, as it should, the ionization widths of the ground states of the neutral and ionized helium, as discussed above in connection with Eqs. (1). In spirit, it is the analog of the expression given in Eq. (8) of Ref. [3], from which, however, the widths are missing, with the consequence of an apparent divergence. The photoelectron energy spectral shapes, obtained from the above expression, have been given in Ref. [22] and are identical to Fig. 1 of Ref. [3]. It bears repeating that, being a single-transition amplitude approximation to a two-step process, it does not contain either the effect of the pulse width or the depletion of populations; it should therefore be viewed only as a semiquantitative expression. Be that as it may, there is no divergence in this expression either.

Care should also be taken in interpreting results for direct ionization, obtained for different pulse durations, through time-dependent approaches. A case in point is the result in Fig. 9 of Ref. [4], in which direct ionization extracted from the shorter pulse does not exhibit nearly as sharp a rise, as it does for the longer pulse. This is perfectly compatible with the peaked behavior of sequential ionization around the two-photon threshold. Two effects come into play here: (a) The shorter pulse has a larger bandwidth, as a result of which the influence of the peak of the sequential is diminished (smoothed out). (b) The two processes have a different dependence on the photon flux. Yet in extracting the cross section from the yield, a linear dependence on the photon flux is assumed, which is an oversimplification if the sequential contribution is contained in the yield. This is also related to the different dependence of the SDI and DDI on pulse duration, as discussed above. It goes without saying that, for extremely short pulses of bandwidth comparable to the energy separation of the two peaks of the SDI, the distinction between sequential and direct ionizations is not meaningful. In that case, only time-dependent calculations of the yields are appropriate, and of course the cross section is no longer meaningful [5].

In conclusion, we have shown that, in TPDI within LOPT, the direct and sequential processes are well defined and, in the theoretical treatment, spectrally separable. There are no divergences, as there is also no apparent reason for the cross section of direct ionization to exhibit a sharp rise at the threshold of the two-photon sequential ionization ($\sim$54.4 eV). It appears that such a rise in the direct ionization, as reported in Refs. [2–4], is most likely due to the unintended inclusion of sequential ionization as well, which in any case is not properly describable by a single cross section.

Finally, in the interest of keeping the focus on the essence of the issue discussed herein, we have ignored an additional sequential channel. It consists of two-photon absorption (ATI) from the ground state of the neutral helium, known to leave the ion preferentially in excited states, which then ionize by single-photon absorption, leading to $\mathrm{He}^{2+}$ [15]. This being an overall three-photon process would not be of importance above 54.4 eV. Below that threshold, it is not negligible, as it is of the same order as the one discussed above. Its inclusion is straightforward along the same lines, at the cost of more equations. It is not expected to change things significantly, but its precise contribution needs to be evaluated when it comes to the theoretical interpretation of experimental results.

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