Quasiclassical double photoionization from the $2^{1,3}S$ excited states of helium including shakeoff

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Abstract

We account for the different symmetries of the $2^{1,3}S$ helium excited states in a quasiclassical description of the knockout mechanism augmented by a quantum shakeoff contribution. We are thus able to formulate the separate contribution of the knockout and shakeoff mechanisms for double photoionization for any excess energy from the $2^{1,3}S$ states. Photoionization ratios and singly differential cross sections calculated for the $2^{1,3}S$ excited states of helium are found to be in very good agreement with recent theoretical results.

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A two electron transition in an atom after the absorption of a single photon is only possible due to electron-electron correlations. The study of two electron transitions in helium, the simplest atomic target with two electrons, probes the role of electron-electron correlations in their purest form. As a result, there has been an extensive amount of experimental and theoretical studies of double photoionization from the ground state of the helium atom.

In addition to the role of electron-electron correlations, the study of two electron escape by a single photon absorption from the singlet, $2^1S$, and triplet, $2^3S$, excited states of helium probes the role of symmetry in the two electron dynamics. This is particularly important for quasiclassical approximations where symmetries and quantum interferences are difficult to include. With the exception of a few earlier studies in the high energy limit [1, 2], it is only recently that the study of double photoionization from the $2^{1,3}S$ excited states of helium has attracted considerable theoretical interest. Experimental measurements of photon absorption cross sections from the helium excited states still remain a challenge. In these recent studies sophisticated fully numerical ab-initio methods namely the R-matrix method [3] and the convergent close-coupling method [4] are used to compute integral double ionization cross sections, double to single ratios, and only very recently, single and triple differential cross sections as well [5]. However, due to the numerical nature of these sophisticated ab-initio calculations approximate methods are also essential in uncovering the underlying mechanism of the two electron dynamics in the double escape process. Such approximate methods have been successfully developed for the double photoionization from the helium ground state [6, 7]. The current work focuses on an approximate method to describe double photoionization from the helium excited states.

In the double photoionization process the redistribution of the energy, following the photon absorption, is often discussed in terms of two mechanisms, that is, knockout and shakeoff dominant in the low and high energy limit, respectively. In the knockout mechanism one electron, the primary, absorbs the photon and undergoes a hard collision with the secondary electron, thus, knocking it out of the atom. The knockout mechanism dominates at low energies where the interaction time of the two electrons is large and can be described classically [6, 8]. For knockout, electron correlations are essential in the final continuum state. On the other hand, in the shakeoff mechanism the primary electron absorbs the photon and leaves the atom very fast without undergoing a direct interaction with the secondary electron. The secondary electron feels the sudden change in the atomic field and relaxes in
one of the bound or continuum eigenstates of the remaining ion. The shakeoff mechanism is quantum mechanical in nature and prevails at high energies where the interaction time of the two electrons is short. For shakeoff, electron correlations are important in the initial state before the photon is absorbed.

In the following, we formulate the explicit but separate contribution of both mechanisms for double photoionization from the $2^1S$ helium excited states for *any* excess energy by extending the model developed to separate the contribution of both mechanisms for the helium ground state in ref. [8]. The separation is achieved by a *quasiclassical* formulation of the knockout process. By construction it is free from any shakeoff contribution which is purely *quantum mechanical*. This separation not only facilitates the calculation of double photoionization but offers considerable insight into the process concerning for example the similarity with electron impact ionization of $He^+$. Compared to the ground state, formulating the separate contribution of both mechanisms from the helium excited states is a much harder problem since the different symmetry of the $2^1S$ states has to be accounted for in the model.

We express the two steps of the double photoionization process from the helium excited states, absorption of the photon and afterwards redistribution of the energy, as

$$\sigma_+^+ = \sigma_{abs} P_{+}^+, \quad (1)$$

where $X$ stands for either knockout or shakeoff and $P_{+}^+$ is the double electron ionization probability. In what follows we discuss how to obtain $P_{+}^{+KO}$ and then $P_{+}^{+SO}$ for the $2^1S$ helium states.

**Knockout mechanism** - After the photon absorption by the primary electron, we describe the subsequent evolution of the two electrons using the classical-trajectory Monte Carlo (CTMC) phase space method. CTMC has been successfully used to describe charged particle impact processes [9, 10, 11, 12, 13]. We model the initial phase space of the trajectories quantum mechanically using a Wigner distribution [14]. To do so, we first find the initial two-electron wavefunction. Since electron correlations are not important in the initial state of the knockout mechanism, we choose our initial state as the independent electron wavefunction

$$\Psi_0(r_1, r_2) = \phi_{1s}^{Z_1s}(r_1)\phi_{2s}^{Z_2s}(r_2), \quad (2)$$

where $\phi_{1s}^{Z_1s}(r_1) = (Z_{1s}^3/\pi)^{1/2}e^{-Z_{1s}r_1}$ and $\phi_{2s}^{Z_2s}(r_2) = (Z_{2s}^3/(8\pi))^{1/2}(1 - Z_{2s}r_2/2)e^{-Z_{2s}r_2/2}$ are hydrogenic $1s$ and $2s$ orbitals with effective charges $Z_{1s}$ and $Z_{2s}$, respectively. $\Psi_0(r_1, r_2)$
given by Eq. (2) is not a symmetrized wavefunction, thus, we do not yet account for the
different symmetries of the triplet \( 2^3S \) and the singlet \( 2^1S \) helium excited states. To find
the effective charges \( Z_{1s} \) and \( Z_{2s} \) we use the two-electron ionization energies \( I_{2^1S/2^3S}^{++} \approx 2.146/2.175 \) for the \( 2^1S/2^3S \) states given in ref. [2], and the ionization energies of the \( 1s \) and
\( 2s \) orbitals as follows. The energy needed to remove the \( 1s \) electron after the \( 2s \) electron has
been ionized is 2 a.u. and thus from \( I_{1s} = Z_{1s}^2/2 = 2 \) we find \( Z_{1s} = 2 \) for both the triplet
and the singlet states. From \( I_{2^1S/2^3S}^{++} - I_{1s} = I_{2s} = Z_{2s}^2/8 \) we find \( Z_{2s} \approx 1.081/1.184 \) for the
\( 2^1S/2^3S \) states, respectively. Atomic units are used throughout this paper unless otherwise
indicated.

While, for the \( 1s^2 \) helium ground state the photon is necessarily absorbed by a \( 1s \) electron,
for the \( 1s2s \) configuration of the \( 2^{1,3}S \) helium states the photon can be absorbed by a \( 1s \) or a
\( 2s \) electron. For the values of the effective charges given above, one can show that the cross
section is much larger for photon absorption from a \( 1s \) electron rather than a \( 2s \) electron
using the independent electron picture [16]. Therefore, we take the primary electron to be
the one on the \( 1s \) orbital. With the PEAK approximation, exact in the high photon energy
limit [13], we assume that the photon absorption happens directly at the nucleus. This
significantly reduces the initial phase space to be sampled by the CTMC method.

The initial phase space distribution, \( \rho(\Gamma) \), is the two electron density immediately after
the photon absorption given by

\[
\rho(\Gamma) = N\delta(r_1)\rho_2(r_2, p_2),
\]

where \( N \) is a normalization constant. The initial distribution of the primary electron is \( \delta(r_1) \)
(PEAK approximation) while that of the secondary electron is given by

\[
\rho_2(r_2, p_2) = W_\psi(r_2, p_2)\delta(\epsilon_2^{in} - \epsilon_B),
\]

where \( W_\psi(r_2, p_2) \) is the Wigner distribution function of the two electron wavefunction with
the primary electron at the nucleus, \( r_1 = 0 \),

\[
\psi(r_2) = \Psi_0(r_1 = 0, r_2)(\langle \Psi_0(r_1 = 0, r_2) | \Psi_0(r_1 = 0, r_2) \rangle)^{-1/2}.
\]

In Eq. (1), we take the energy of the secondary electron immediately after photon absorption,
\( \epsilon_2^{in} \), to be fixed on the \( 2s \) energy shell \( \epsilon_B = -Z_{2s}^2/8 \). From Eq. (2), it follows that \( \epsilon_2^{in} = p_2^2/2 - Z_{2s}/r_2 \). The excess energy available to the two electron system after photon absorption
is determined by the photon energy to be

\[ E = \omega - I_{21}^{++}, \quad E = \omega - I_{23}^{++} \]  

(6)

for the \(2^1S\) and \(2^3S\) states, respectively. Due to the PEAK approximation the primary electron can have any energy necessary so that together with the initial energy \(e_2^{in}\) of the secondary electron it adds up to the excess energy \(E\) in Eq.(6). After modelling the initial phase space distribution, we propagate the electron trajectories using the classical equations of motion (CTMC). Regularized coordinates \[17\] are used for the propagation of the electron trajectories to avoid problems with trajectories starting at the nucleus \(r_1 = 0\). Doubly ionized are those trajectories that end with the asymptotic energies of both electrons being positive. To evaluate the double electron escape probability each trajectory is weighted by the initial phase space Wigner distribution.

So far we have treated the two electrons as distinguishable particles, that is, we distinguish between the primary and the secondary electron. To account for the singlet and triplet symmetries we have to symmetrize the probability amplitude (differential probability) \(dP_{K0}^{++}/d\epsilon\) with respect to the two identical particles,

\[ \frac{dP_{K0}^{++}}{d\epsilon} = \frac{1}{2} \left( \sqrt{\frac{dP_{K0}^{++}(\epsilon, E)}{d\epsilon}} \pm \sqrt{\frac{dP_{K0}^{++}(E - \epsilon, E)}{d\epsilon}} \right)^2. \] 

(7)

In Eq.(7), \(dP_{K0}^{++}(\epsilon, E)/d\epsilon\) is the probability for both electrons to escape when the primary electron is ejected with energy \(\epsilon\), where \(0 \leq \epsilon \leq E\), and the secondary electron is ejected with energy \(E - \epsilon\). To evaluate \(dP_{K0}^{++}(\epsilon, E)/d\epsilon\) we divide the energy interval \([0, \epsilon]\) into \(N\) equally sized bins and find the doubly ionized trajectories which fall into the bins. In our calculations we take \(N = 21\) for excess energies up to 80 eV and \(N = 27\) for higher excess energies. The double ionization probability \(P_{K0}^{++}\) is obtained by integrating over all possible energies that an electron can be ejected with, that is

\[ P_{K0}^{++} = \int_0^E \frac{dP_{K0}^{++}}{d\epsilon} d\epsilon. \] 

(8)

Note that for the case of the helium ground state the double ionization probability \(P_{K0}^{++}\) is worked out without using the differential probabilities \[9\].

\- **Shakeoff mechanism**- Assuming that the primary electron is suddenly removed from the atom, Aberg \[18\] found that the probability for the shaken (secondary) electron to relax on
a hydrogenic eigenstate of the remaining ion for any excess energy is

\[ P_\alpha = \frac{|\langle \phi_\alpha | \psi' \rangle|^2}{\langle \psi' | \phi_\alpha \rangle}, \]  

(9)

where \( \psi'(r_2) = \int d^3r_1 \nu'(r_1)\Psi_0(r_1, r_2) \) and \( \nu(r_1) \) is the primary electron wavefunction after it has left the atom. The primary electron is in an s state before the photon absorption and in a p state afterwards. \( \Psi_0(r_1, r_2) \) is the initial state wavefunction of the 2^1S helium excited states and \( \phi_\alpha \) is a hydrogenic eigenstate of the bare nucleus (\( Z = 2 \)) that is either a bound (\( \alpha = n \)) or a continuum state (\( \alpha = \epsilon \)). Aberg [18] has further shown that when the primary electron leaves the atom with very high energy (\( \nu(r_1) = (2\pi)^{-3/2}e^{-ikr_1} \)) Eq.\((9)\) takes the simplified form

\[ P_\alpha = \frac{|\langle \phi_\alpha | \Psi_0(r_1 = 0, r_2) \rangle|^2}{\langle \Psi_0(r_1 = 0, r_2) | \Psi_0(r_1 = 0, r_2) \rangle}. \]  

(10)

Eq.\((10)\) reveals the quantum mechanical nature of the shakeoff process since it is expressed as an overlap of the initial bound state wavefunction and the final continuum state wavefunction.

Although Eq.\((10)\) was derived in the high energy limit we assume that the primary electron absorbs the photon on the nucleus for all excess energies, that is, we adopt the PEAK approximation as in the knockout case. To find the double escape probability \( P_{SO}^{++} \) we then integrate over all possible energies of the shaken electron in the continuum

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

(11)

We further simplify the evaluation of the shakeoff probability in Eqs.\((11)\), \((13)\) by taking the initial state to be the symmetrized wavefunction

\[ \Psi_0(r_1, r_2) = N_1 \left( \phi_{1s}^{Z_{SO}^1}(r_1)\phi_{2s}^{Z_{SO}^2}(r_2) \pm \phi_{1s}^{Z_{SO}^2}(r_2)\phi_{2s}^{Z_{SO}^1}(r_1) \right) \]  

(12)

for the singlet and triplet states, respectively, with \( N_1 \) a normalization constant. The initial state correlations are accounted for only through the effective charges. We next assign the same set of effective charges \( Z_{SO}^1 \) and \( Z_{SO}^2 \) for both the triplet and the singlet states as follows. The asymptotic ratio (high energy limit) of double to single ionization is found very accurately in ref.\([2]\) to be \( R_\infty = 0.009033/0.003118 \) for the singlet/triplet states where in our model \( R_\infty \) is given by

\[ R_\infty = P_{SO}^{++}(E \to \infty)/(1 - P_{SO}^{++}(E \to \infty)), \]  

(13)
and

\[ P_{SO}^{++}(E \rightarrow \infty) = \int_0^\infty P_\epsilon d\epsilon = 1 - \sum_n P_n. \]  

(14)

Using Eqs.(13), (14) and the symmetrized wavefunctions in Eq.(12) we find the sets of charges that match both asymptotic ratios \( R_\infty \) for the singlet and the triplet states. We then select that set of charges for which the shakeoff double ionization probability as a function of the excess energy, obtained using the simple wavefunctions given in Eq.(12), is closest to the one obtained using the fully correlated Hylleraas wavefunctions given in ref.[19].

The set of charges thus found is \( Z_{SO}^1 \approx 1.757 \) and \( Z_{SO}^2 \approx 1.728 \). The reason we do not use the Hylleraas wavefunctions given in ref.[19] is that they do not reproduce the accurate asymptotic ratios obtained in ref.[2] using highly accurate Pekeris-type wavefunctions. We emphasise though that one does not need to use the approximate wavefunctions in Eq.(12) to compute the double ionization probability; highly accurate wavefunctions that reproduce the correct asymptotic ratios could be used instead.

For the shakeoff probability, \( P_\epsilon \) in Eq.(10) already gives the differential double ionization probability. Despite the symmetrization in Eq.(12) we have lost the indistinguishability of the electrons by identifying one electron as the primary one which absorbs the photon. Thus we need to symmetrize again in the final state with respect to the equal energy sharing point \( \epsilon = E - \epsilon = E/2 \). That is,

\[ \frac{dP_{SO}^{++}}{d\epsilon} = \frac{1}{2} \left( \frac{dP_\epsilon}{d\epsilon} + \frac{dP_{E-\epsilon}}{d\epsilon} \right). \]  

(15)

- Photoionization ratios-. According to Eq.(11) \( \sigma^{++} = \sigma_{abs}(P_{K\bar{O}}^{++} + P_{SO}^{++}) \) and \( \sigma^+ = \sigma_{abs} - \sigma^{++} \). Thus, the double to single ionization ratio is given by

\[ \frac{\sigma^{++}}{\sigma^+} = \frac{P^{++}}{(1 - P^{++})}, \]  

(16)

where \( P^{++} = P_{K\bar{O}}^{++} + P_{SO}^{++} \). In figure (1) we compare the double to single ratio for the \( ^2S_1 \) helium excited states with the results obtained by Kheifets et al.[4] using the convergent close-coupling method and show that there is a very good agreement. The agreement is better for the \( ^2S_1 \) state. We find that the deviation occurs, particularly for the \( ^2S_1 \) state, at photon energies where the contribution of knockout and shakeoff mechanisms is comparable. At these energies any interference effect between the knockout and shakeoff mechanism would have its largest effect. So, it may be that the deviations we see are due to that interference effect that we do not account for in our calculation, since we add the knockout and shakeoff
contributions incoherently. For the $2^1S$ state a maximum of $\approx 2.84\%$ is reached at $14\text{ eV}$ above the double ionization threshold of the $2^1S$ state. For the $2^3S$ state a maximum of $\approx 0.69\%$ is reached at $60\text{ eV}$ above the ionization threshold of the $2^3S$ state. In figure (1) we see that at high energies the knockout contribution goes to zero as expected and the shakeoff contribution dominates and reaches the asymptotic limit of $0.009033/0.003118$ for the singlet/triplet states. Stronger correlation effects for the singlet symmetry ($r_1 = r_2$ is not forbidden as is the case for the triplet) result in a much higher double to single ionization ratio compared to the triplet case. From figure (1), for the $2^{1,3}S$ states, and ref. [6], for the helium ground state $^1S$, we see that as we go from $^1S \rightarrow 2^1S \rightarrow 2^3S$ the shakeoff mechanism overtakes the knockout mechanism at smaller energies. The reason is that the electron-electron correlation becomes smaller, thus diminishing the knockout contribution and favouring the shakeoff mechanism at even smaller energies.

-Single differentials- To compute the single differential probabilities for the helium excited states we use

$$\frac{dP^{++}}{d\epsilon} = \frac{dP^{++}_{KO}}{d\epsilon} + \frac{dP^{++}_{SO}}{d\epsilon}$$  \hspace{1cm} (17)$$

In addition we compute the single differential cross sections using

$$\frac{d\sigma^{++}}{d\epsilon} = \sigma_{abs} \left( \frac{dP^{++}_{KO}}{d\epsilon} + \frac{dP^{++}_{SO}}{d\epsilon} \right)$$  \hspace{1cm} (18)$$

where for $\sigma_{abs}$ we use the results for the total-photoionization cross section for the $2^1S$ and the $2^3S$ states given in ref. [4]. In figure (2) we compare our results for $d\sigma^{++}/d\epsilon$ with the results obtained very recently by Colgan et al [5] using the convergent close-coupling method for four values of the excess energy. We see that our results for the single differential cross section as a function of the ejected electron energy normalized by the excess energy are smaller for the $2^1S$ state while there is an excellent agreement for the $2^3S$ state. Again as we go from $^1S \rightarrow 2^1S \rightarrow 2^3S$ the single differential cross sections are more U-shaped for the same excess energy. The reason is again that the electron-electron correlation decreases thus favouring the ejection of one fast and one slow electron, that is favouring unequal energy sharing.

In figure (3) we show the separate contribution of knockout and shakeoff to the single differential probabilities for the $2^{1,3}S$ helium states for excess energies $10\text{ eV}, 40\text{ eV}$ and $160\text{ eV}$. For the singlet state the knockout contribution dominates at small excess energies, $10\text{ eV}$ and $40\text{ eV}$, while as the excess energy is increased to $160\text{ eV}$ the shakeoff contribution begins
to dominate regions of unequal energy sharing. For the triplet case the shakeoff mechanism is already significant at small excess energies. Note, that the knockout contribution for the triplet case is zero at the equal energy sharing point, \( \epsilon = E - \epsilon \), because of the symmetrization with respect to the two identical electrons, see Eq. (7).

In conclusion we have shown that the double ionization from the \( 2^{1,3}\)S states can be accurately described by a separate formulation and calculation of the knockout and shakeoff mechanism at any excess energy. In comparison to the helium ground state \( [6] \) this is a harder problem because we have to account for the different symmetries of the singlet and triplet states. The success of this simple model to describe double ionization from the helium ground state as well as the helium excited states is proof for its validity. In the future, we plan to use this simple model to describe triple photoionization cross sections.

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• Figure 1. Double to single ionization ratio as a function of the photon energy. Dots/open circles indicate the results of Kheifets et al. in the velocity/acceleration gauge. For the triplet state Kheifets results in both gauges are indistinguishable to the scale of the figure. Our results are indicated by a solid line for the total, by a dashed line for the knockout and by a dashed-dot line for the shakeoff double to single ratio.

• Figure 2. Absolute single differential cross sections as a function of the electron ejected energy scaled by the excess energy. The dashed lines are the results by Colgan et al. Our results are indicated by solid lines.

• Figure 3. Absolute single differential probabilities as a function of the ejected electron energy. The knockout contribution is indicated by dashed lines while the shakeoff by solid lines. The top panel is for the $2^1S$ state while the bottom is for the $2^3S$ state.
FIG. 1:

FIG. 2:
FIG. 3: