PHYSICAL REVIEW A **76**, 030701(R) (2007)

Two-photon double ionization of helium above and below the threshold for sequential ionization

D. A. Horner,[1] F. Morales,[2] T. N. Rescigno,[3] F. Martín,[2] and C. W. McCurdy[3,4]
[1]*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[2]*Departamento de Química C-9, Universidad Autónoma de Madrid, 28049 Madrid, Spain*
[3]*Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[4]*Department of Applied Science and Department of Chemistry, University of California, Davis, California 95616, USA*
(Received 26 April 2007; published 19 September 2007)

We present accurate cross sections for two-photon double ionization of helium at photon energies above and below the threshold for sequential double ionization. Above this threshold (54.4 eV), sequential ionization competes with nonsequential ionization. Remarkably, even below 54.4 eV, sequential ionization leaves a clear signature in the magnitude and shape of both the total and energy-sharing cross sections—even though at these energies it is only a virtual process.

DOI: 10.1103/PhysRevA.76.030701 PACS number(s): 32.80.Fb, 32.80.Rm, 34.10.+x

Double ionization of the helium atom by two extreme ultraviolet (xuv) photons in the range of 40 to 50 eV has recently become the subject of intense theoretical interest [1–10] as well as the target of new experiments with high-harmonic-generation sources [11] and experiments under way at the free-electron laser source (FLASH) in Hamburg. Even in the intensity regime where second-order perturbation theory is expected to be valid, recent calculated cross sections vary over more than an order of magnitude. We present accurate, time-independent calculations of this process well beyond the energy regimes of earlier treatments, using methods that have produced benchmark results for double ionization of atoms [12] and molecules [13]. These methods provide grid-based, numerical solutions of the Schrödinger equation with no appeal to approximate asymptotic forms nor to ansatz wave functions. We predict a rapid rise in the total cross section considerably below the threshold for sequential ionization, as well as dramatic changes in the shape of the singly differential cross section caused by this virtual process. These calculations should influence planned experiments on multiphoton ionization with new xuv sources.

The cross section for two-photon double ionization from lowest-order perturbation theory (LOPT) in the velocity gauge, differential in the energy sharing and angular dependence of the ejected photoelectrons, is given by the expression

$$\frac{d\sigma}{dE_1 d\Omega_1 d\Omega_2} = \frac{2\pi}{\hbar}\frac{(2\pi\alpha)^2}{m^2\omega^2} k_1 k_2 |f(\mathbf{k}_1,\mathbf{k}_2,\omega)|^2, \quad (1)$$

where $\mathbf{k}_1$ and $\mathbf{k}_2$ are the momenta of the photoelectrons, ω is the photon frequency, m is the electron mass, and α is the fine-structure constant. The amplitude $f(\mathbf{k}_1,\mathbf{k}_2,\omega)$ is in turn given by

$$f(\mathbf{k}_1,\mathbf{k}_2,\omega) = \langle \Psi^-_{\mathbf{k}_1,\mathbf{k}_2} | \mu (E_0 + \hbar\omega - H + i\eta)^{-1} \mu | \Phi_0 \rangle, \quad (2)$$

where H is the atomic Hamiltonian, Φ_0 is the initial state of the atom with corresponding energy E_0, $\Psi^-_{\mathbf{k}_1,\mathbf{k}_2}$ is the full momentum-normalized scattering wave function, with incoming boundary conditions corresponding to two free electrons, and the dipole operator μ is defined in terms of the momentum operators $\mathbf{p}_i$ for the two electrons, $\mu = \mu_1 + \mu_2 = \boldsymbol{\epsilon}\cdot\mathbf{p}_1 + \boldsymbol{\epsilon}\cdot\mathbf{p}_2$.

There are a number of obstacles associated with an accurate evaluation of the amplitude in Eq. (2). One of those is coping with the infinite sum over intermediate states that follows from making a spectral expansion of the resolvent operator $(E_0+\hbar\omega-H+i\eta)^{-1}$. However, the major obstacle is the calculation of the double-continuum state $\Psi^-_{\mathbf{k}_1,\mathbf{k}_2}$ and the difficult boundary conditions associated with three-body Coulomb breakup.

We address these problems by beginning with the coupled (Dalgarno-Lewis) driven equations that describe two-photon absorption in LOPT,

$$(E_0 + \hbar\omega - H)\Psi_1^{sc}(\mathbf{r}_1,\mathbf{r}_2) = \mu\Phi_0, \quad (3)$$

$$(E_0 + 2\hbar\omega - H)\Psi_2^{sc}(\mathbf{r}_1,\mathbf{r}_2) = \mu\Psi_1^{sc}, \quad (4)$$

both of which must be solved with purely outgoing-wave boundary conditions, and the second of which describes two-photon absorption. We then choose a large (in the present case six-dimensional) but finite volume beyond which the electron-electron interaction can be safely ignored and solve Eqs. (3) and (4) on that finite volume to arbitrary accuracy. The problem of the boundary conditions for both of these equations is addressed in our approach by making use of the method of *exterior complex scaling* (ECS) [14], which scales the electron coordinates by a phase factor, but only outside our chosen finite volume, thereby inducing an exponential falloff in the outgoing-wave part of the continuum wave function beyond the finite volume. By expanding Ψ_1^{sc} and Ψ_2^{sc} in a truncated product basis of spherical harmonics, Eqs. (3) and (4) can be converted into a set of coupled two-dimensional radial equations that can be solved on parallel computers with sparse matrix methods.

Having solved the coupled equations, we must devise a strategy for calculating the amplitude for double ionization, which is formally contained (to within an overall phase) in the asymptotic behavior of the solution for Ψ_2^{sc},

$$\Psi_2^{sc} \underset{\rho\to\infty}{\sim} \sqrt{2\pi i}\left(\frac{K^3}{\rho^5}\right)^{1/2} e^{iK\rho+\zeta \ln 2K\rho} f(k_1\hat{\mathbf{r}}_1, k_2\hat{\mathbf{r}}_2, \omega) \quad (5)$$

where $\rho=\sqrt{r_1^2+r_2^2}$, the energy shared by the outgoing electrons is $K^2/2=k_1^2/2+k_2^2/2$, and the angle-dependent coefficient of the logarithmic phase is $\zeta=Z/k_1+Z/k_2-1/|\mathbf{k}_1-\mathbf{k}_2|$. As we have previously shown [14], in the contexts of both double photoionization and electron impact ionization, the amplitude can be extracted (to within an irrelevant volume-dependent overall phase) using a surface integral that involves a pair of testing functions $\psi_{\mathbf{k}}^-(\mathbf{r})$, which are momentum-normalized, one-electron Coulomb functions with nuclear charge $Z=2$, in the case of helium:

$$f(\mathbf{k}_1,\mathbf{k}_2,\omega) = \frac{1}{2}\int [\psi_{\mathbf{k}_1}^{-*}(\mathbf{r}_1)\psi_{\mathbf{k}_2}^{-*}(\mathbf{r}_2)\,\nabla\,\Psi_2^{sc}(\mathbf{r}_1,\mathbf{r}_2) - \Psi_2^{sc}(\mathbf{r}_1,\mathbf{r}_2)\,\nabla\,\psi_{\mathbf{k}_1}^{-*}(\mathbf{r}_1)\psi_{\mathbf{k}_2}^{-*}(\mathbf{r}_2)]\cdot d\mathbf{S}. \quad (6)$$

We must emphasize that the functions $\psi_{\mathbf{k}_1}^-(\mathbf{r}_1)$ and $\psi_{\mathbf{k}_2}^-(\mathbf{r}_2)$ do *not* describe the final state of the system, but are merely the testing functions that extract the necessary amplitude from Ψ_2^{sc}. No ansatz has been made concerning the final state, and electron correlation is treated completely in the final outgoing wave function Ψ_2^{sc} as well as in the initial state Φ_0 in this approach.

But there is another problem that must be addressed before we can proceed. For photon energies greater than the first ionization potential of the atom, Ψ_1^{sc}, the solution of Eq. (3), will have single-ionization terms that behave, at large *real* values of the electron coordinates, as the (symmetrized) product of a bound state of He^+ times an undamped outgoing wave in the other electron coordinate. This fact means that $\mu\Psi_1^{sc}$, which is the driving term for Eq. (4), will not vanish as $r_1, r_2 \to \infty$ along the real axis. Since the dipole operator μ is a one-body operator, Eq. (4) will be ill conditioned, irrespective of the gauge being used, and the ionization amplitudes extracted from Ψ_2^{sc} will not converge with increasing volume. We can circumvent this problem by adding a small, positive imaginary part to ω in Eq. (3) only, which will produce a solution Ψ_1^{sc} with an exponential falloff for real r values. With this procedure, we have a valid driving term for the solution of Eq. (4), which can then be solved directly under ECS for real ω. As we will see, this procedure yields convergent amplitudes that can then be numerically extrapolated to purely real photon energies.

For the present calculations, we used partial waves up to $l=4$ to expand the initial state and up to $l=5$ in the intermediate and final states, including all product pairs allowed by symmetry. The coupled Dalgarno-Lewis equations were solved using our finite-element discrete-variable representation (DVR) method [15]. We used a 15th-order Gauss-Lobatto DVR with the first element boundary at 5.0 bohr and subsequent element boundaries spaced 10.0 bohr apart. Calculations were performed with different real grids ranging from 85.0 to 255.0 bohr on a side; the complex portion of the grid was always 30.0 bohr in length. We computed the singly differential cross section (SDCS), which is the quantity defined in Eq. (1) integrated over the angles Ω_1 and Ω_2,

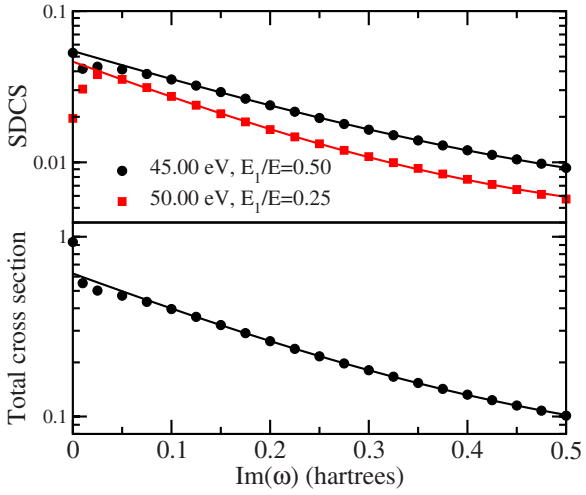

FIG. 1. (Color online) Upper panel: Dependence of the SDCS at 45 and 50 eV and 25% and 50% energy sharing, respectively, on the imaginary part of ω used in solving Eq. (3). Lower panel: Dependence of the total cross section at 45 eV photon energy on Im(ω). SDCS in units of 10^{-52} cm^4 s eV^{-1}; total cross section in units of 10^{-52} cm^4 s.

over a range of complex photon energies in Eq. (3) and extrapolated the results to real photon energies, i.e., to Im(ω) $=0$.

The SDCS is a relatively flat function of energy sharing for photon energies between 40 and 50 eV. In this energy range, we can integrate the SDCS over energy sharing and then extrapolate the results to get the total cross section. The upper panel of Fig. 1 shows the dependence of the SDCS on Im(ω) at two different photon energies and energy sharings, while the lower panel shows the corresponding dependence for the total cross section at 45 eV. Above 51 eV, where the SDCS begins to rise at the extremes of energy sharing, i.e., near $E_1/E=0.0$ and 1.0, a pointwise extrapolation of the SDCS is needed to compute total cross sections. Above 54.4 eV, which is the threshold for sequential double ionization (SI) (see Fig. 2), the SDCS has clearly defined peaks at $E_1=\hbar\omega-54.4$ eV and $E_1=\hbar\omega-24.6$ eV, as seen in Fig. 3. Before we can discuss these results, it is important to under-

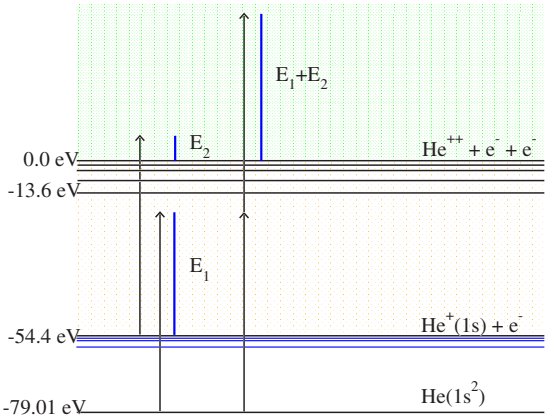

FIG. 2. (Color online) Schematic represention of sequential and nonsequential two-photon double ionization of He.

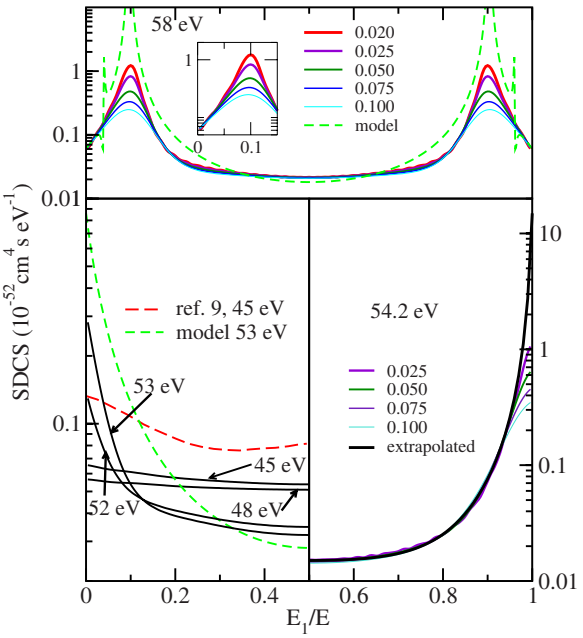

FIG. 3. (Color online) Upper panel: SDCS at 58 eV; solid curves labeled by minumum Im(ω) used in extrapolating the data; short-dashed curve, results of the simplified model. Lower left panel: Extrapolated SDCSs at energies below the SI threshold along with results of Ref. [9] at 45 eV and the simplified model at 53 eV. Lower right panel: Extrapolation of SDCS at 54.2 eV with curves labeled by minumum Im(ω) used.

stand the origin of the peaks and their consequences for the extrapolations near the sequential ionization threshold.

We can understand the origin of the peaks in the SDCS using a simple model that ignores both correlation and screening in the final and intermediate states, following the logic of Proulx, Pont, and Shakeshaft [10]. We begin with the exact spectral representation of the Green's function in the definition of the amplitude in Eq. (2),

$$\langle \Psi^-_{\mathbf{k}_1,\mathbf{k}_2}|\mu(E_0+\hbar\omega-H+i\eta)^{-1}\mu|\Phi_0\rangle = \sum\!\!\!\!\!\!\int_v \frac{\langle \Psi^-_{\mathbf{k}_1,\mathbf{k}_2}|\mu|v\rangle\langle v|\mu|\Phi_0\rangle}{E_0+\hbar\omega-E_v+i\eta}. \quad (7)$$

We first make the approximation that the sum and integral over intermediate states $|v\rangle$ includes only the integral over the lowest singly ionized continuum $|\psi^-_{\mathbf{k},1s}\rangle$ of the helium atom. To approximate $\langle \Psi^-_{\mathbf{k}_1,\mathbf{k}_2}|\mu|\psi^-_{\mathbf{k},1s}\rangle$, we then ignore screening and correlation in both the intermediate and properly symmetrized final states by using Coulomb functions with $Z=2$ for all free electrons.

With these approximations a pair of momentum-conserving δ functions pick out two terms in the integral over intermediate states that correspond to the sequential process. Ignoring the phases of $\langle \psi^-_{\mathbf{k},1s}|\mu|\Phi_0\rangle$ and $\langle \Psi^-_{\mathbf{k}_1,\mathbf{k}_2}|\mu|\psi^-_{\mathbf{k},1s}\rangle$, substituting the result into Eq. (1), and integrating over the ejection directions $d\Omega_1$ and $d\Omega_2$ allows us to write an approximate expression for the SDCS in terms of the single-photoionization cross sections of He and He$^+$,

$$\frac{d\sigma^{\mathrm{seq}}}{dE_1} \approx \frac{\hbar}{4\pi}\left(\frac{\sqrt{\sigma^{\mathrm{He}^+}(E_2)\sigma^{\mathrm{He}}(E_1)}}{E_0+\hbar\omega-\epsilon_{1s}-E_1}+\frac{\sqrt{\sigma^{\mathrm{He}^+}(E_1)\sigma^{\mathrm{He}}(E_2)}}{E_0+\hbar\omega-\epsilon_{1s}-E_2}\right)^2, \quad (8)$$

with $E_1+E_2=K^2/2$. In Eq. (8) $\sigma^{\mathrm{He}}(E)$ is the single-photoionization cross section of the neutral helium atom, and $\sigma^{\mathrm{He}^+}(E)$ is the single-photoionization cross section of He$^+$. The singularities in Eq. (8) corresponding to the SI process are separated in the SDCS by the difference between the ionization potential of He$^+$ and the first ionization potential of He. We believe these singularities to be a fundamental feature of LOPT and not the consequence of the simplifying approximations made in deriving Eq. (8).

The lower left panel of Fig. 3 shows the calculated SDCS, extrapolated to real ω, for several energies between 45 and 53 eV. Results from the simple model at 53 eV (using single-photoionization cross sections from an earlier calculation [16]) are also plotted for comparison. One sees that, by 52 eV, the SDCS already begins to develop wings near extreme energy sharing, showing the signature of the sequential process whose energy threshold is at 54.4 eV. At 54.2 eV, as shown in the lower right panel of Fig. 3, the extrapolation scheme becomes unreliable at extreme energy sharing, where the SDCS shows a residual dependence on the smallest value of Im(ω) used in the extrapolation. The final estimate of the SDCS shown in the figure was therefore obtained by extrapolating the calculated SDCS using a functional form that included singularities as in Eq. (8).

The upper panel of Fig. 3 shows results for calculations at 58 eV, along with the simple model prediction. The calculations show that the extrapolated peaks in the SCDS at energies corresponding to sequential ionization increase with decreasing Im(ω). These peaks would become singularities in the limit of an infinite-size box. In the model results, there are sharp peaks outside the singularities which arise from the contribution of the first doubly excited ($2s2p$, ^1P) state of He* in σ^{He}. It is worth noting that the *ab initio* SDCS data for 58 eV photon energy do show a slight asymmetry about the sequential peaks, with a modest broadening in the regions corresponding to excitation of doubly excited states (see Fig. 3 inset). One would expect postcollision interaction to significantly broaden such states, but whether these states are causing the asymmetry in the peaks is difficult to say.

Figure 4 shows our total cross sections, along with the results of earlier studies. The cross sections have been obtained (i) by extrapolating the total cross section, as in Fig. 1(b) (open circles from 40 to 51 eV) and (ii) by extrapolating the SDCS as shown in the lower right panel of Fig. 3 and then integrating (solid squares from 50 to 54.4 eV), yielding identical results at 50 and 51 eV. We note that, at lower energies, where we can compare with the results of other calculations, our cross sections compare favorably with the results of several other methods, but are significantly smaller than the most recent studies published by Foumouo *et al.* [3] and by Nikolopoulos and Lambropoulos [1,8]. The inflection in the total cross section at about 49 eV can be understood from the behavior of the SDCS in Fig. 3 as follows. As the nonsequential background portion of the SDCS begins to

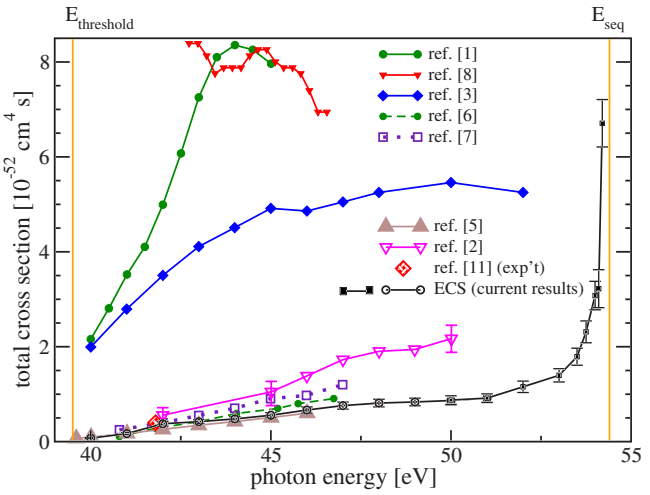

FIG. 4. (Color online) Calculated two-photon double-ionization total cross sections compared with those of previous calculations. The vertical lines label the DI and SI thresholds.

decrease, the contribution from the wings due to the energetically closed sequential process increases, and the total cross section again begins to increase.

In summary, we have carried out accurate calculations of two-photon double ionization in LOPT for the helium atom. Since these calculations treat electron correlation in the initial, virtual intermediate, and final states essentially exactly, our results show that the large degree by which previous theoretical calculations disagree is not necessarily due to the various levels at which correlation was previously treated. Rather, it appears that numerical approximations made using either time-independent or time-dependent descriptions of this process are to blame. We have shown that, below the threshold for the sequential process, the signature of SI is prominently revealed in the singly differential cross section, even at energies where it is less apparent in the total cross section. Above the threshold for sequential ionization, that process competes with nonsequential double ionization and both processes appear in LOPT. Although the SDCS is well defined at all energies, its apparently singular behavior at the sequential double-ionization peaks means that the *total* cross section is not well defined in LOPT above that threshold.

This work was performed under the auspices of the U.S. DOE and was partially supported by the U.S. DOE OBES, Division of Chemical Sciences, the DGI Project No. FIS2006-00298 (Spain), and the COST Action No. D26/0002/02. C.W.M. acknowledges support from the NSF (Grant No. PHY-0604628). Computations were carried out at the Institutional Computing (Los Alamos), NERSC (Berkeley), and Mare Nostrum (Spain) computer centers.

[1] L. A. A. Nikolopoulos and P. Lambropoulos, J. Phys. B **40**, 1347 (2007).
[2] I. A. Ivanov and A. S. Kheifets, Phys. Rev. A **75**, 033411 (2007).
[3] E. Foumouo, G. L. Kamta, G. Edah, and B. Piraux, Phys. Rev. A **74**, 063409 (2006).
[4] A. S. Kheifets and I. A. Ivanov, J. Phys. B **39**, 1731 (2006).
[5] S. X. Hu, J. Colgan, and L. A. Collins, J. Phys. B **38**, L35 (2005).
[6] L. Feng and H. W. van der Hart, J. Phys. B **36**, L1 (2003).
[7] B. Piraux, J. Bauer, S. Laulan, and H. Bachau, Eur. Phys. J. D **26**, 7 (2003).
[8] L. A. A. Nikolopoulos and P. Lambropoulos, J. Phys. B **34**, 545 (2001).
[9] J. Colgan and M. S. Pindzola, Phys. Rev. Lett. **88**, 173002 (2002).
[10] D. Proulx, M. Pont, and R. Shakeshaft, Phys. Rev. A **49**, 1208 (1994).
[11] H. Hasegawa, E. J. Takahashi, Y. Nabekawa, K. L. Ishikawa, and K. Midorikawa, Phys. Rev. A **71**, 023407 (2005).
[12] C. W. McCurdy, D. A. Horner, T. N. Rescigno, and F. Martín, Phys. Rev. A **69**, 032707 (2004).
[13] W. Vanroose, F. Martín, T. N. Rescigno, and C. W. McCurdy, Science **310**, 1787 (2005).
[14] C. W. McCurdy, M. Baertschy, and T. N. Rescigno, J. Phys. B **37**, R137 (2004).
[15] T. N. Rescigno and C. W. McCurdy, Phys. Rev. A **62**, 032706 (2000).
[16] C. W. McCurdy and F. Martín, J. Phys. B **37**, 917 (2002).