t-SURFF: fully differential two-electron photo-emission spectra

Armin Scrinzi
Ludwig Maximilians Universität, Theresienstrasse 37, 80333 Munich, Germany
E-mail: armin.scrinzi@lmu.de

New Journal of Physics 14 (2012) 085008 (17pp)
Received 16 February 2012
Published 1 August 2012
Online at http://www.njp.org/
doi:10.1088/1367-2630/14/8/085008

Abstract. The time-dependent surface flux (t-SURFF) method is extended to single and double ionization of two-electron systems. Fully differential double emission spectra by strong pulses at extreme UV and infrared wavelengths are calculated using simulation volumes that only accommodate the effective range of the atomic binding potential and the quiver radius of free electrons in the external field. For a model system, we found a pronounced dependence of shake-up and non-sequential double ionization on the phase and duration of the laser pulse. The extension to fully three-dimensional calculations is discussed.

Contents

1. Introduction 2
2. The time-dependent surface flux method for two-electron systems 3
   2.1. Single ionization into ionic ground and excited state channels 4
   2.2. Double-ionization spectra 6
   2.3. Computational remarks 8
3. Numerical demonstration of the method 9
   3.1. The one-dimensional two-electron model system 9
   3.2. Two-photon double ionization in the extreme ultraviolet 10
   3.3. Single ionization and shake-up by an infrared pulse 12
   3.4. Double-ionization spectra generated by an infrared pulse 13
4. Discussion and conclusions 15
Acknowledgments 16
References 16
1. Introduction

Differential double photo-electron spectra and the corresponding ionic recoil momentum spectra testify to dynamical correlation between the electrons. By sweeping extreme ultraviolet (XUV) photon energies from below to above the threshold for single-photon double ionization of the He atom, one probes correlation in the initial and final states. At wavelengths in the infrared (IR) range, momentum distributions of recoil ions provide evidence for the importance of re-collision processes \[1\], where first one electron is ionized, which is subsequently re-directed by the oscillating laser field into a collision with its parent ion, causing excitation and possibly detachment of the second electron. The observation of unexpectedly enhanced double ionization of helium in IR fields \[2\] is now generally ascribed to this mechanism. Experimental data on strong-field IR photo-ionization are also available for many other atomic and molecular systems, and it has even been proposed to utilize re-collision electron spectra for the analysis of the structure and dynamics of molecules \[3\].

For the XUV wavelength, theoretical and experimental questions have matured, even though still under debate (see, e.g., \[4\] for a recent contribution to the debate with ample reference to theory and experiment). At longer wavelengths, a large body of experimental data (see, e.g., \[5–9\] and references therein) and a somewhat smaller range of theoretical models mostly based on classical or semi-classical methods (see, e.g., \[10–13\]) are all plagued by the almost complete lack of reliable theoretical verification, with the notable exception of a few very-large-scale simulations of two-electron systems in strong fields \[14–16\], where, however, only in \[15\] is the full two-electron dynamics treated for a laser wavelength of 800 nm. There are many reasons for this striking absence of complete \textit{ab initio} simulations of ionization of two-electron systems. Firstly, even single ionization is non-trivial to compute if the external fields are non-perturbative. Roughly speaking, the effort at computing single ionization grows with the fourth power of the wavelength $\lambda^4$ owing to the growth of peak momenta $\propto \lambda$, quiver amplitude of the electron motion in the field $\propto \lambda^2$ and the growth of minimum pulse duration $\sim \lambda$ (see also the discussion in \[17\]). When the effect of the field is perturbative, the situation for single ionization relaxes somewhat, as basically one only needs to know the initial neutral state and the single-electron stationary scattering solutions in the energy range of interest. Although obtaining scattering solutions may be difficult, there are a well-defined procedure and the whole technology of electron–ion scattering theory available for approaching the problem. For double ionization, also in the perturbative regime the situation is more complex. The convenient partition into bound and singly ionized spectral eigenfunctions cannot be continued to above the double-ionization threshold: eigenfunctions above the double-ionization threshold will, in general, have both single- and double-ionization asymptotics. For distinguishing single from double ionization, we therefore invariably need the solutions at large distances. Even without the need for asymptotic analysis, scattering with open double-ionization channels is a challenging task.

Numerical simulations, in principle, can provide the full answer. The asymptotic analysis is usually done by propagating the wave function until after the end of the pulse and then analyzing its remote parts either in terms of momentum eigenfunctions, i.e. plane waves, or when the tails of the ionic Coulomb potentials are not considered negligible, in terms of two-body Coulomb scattering solutions. Three-body scattering solutions, which would obviate a purely asymptotic analysis, unfortunately, are not accessible. The by far largest part of the computational effort in these simulations goes into following the solution to large distances until the pulse is over and
analysis can begin. It may be irritating to think that large effort is made to simulate dynamics that
is known exactly in the case of finite-range potentials or approximately at sufficient distances
from all Coulomb centers: the free motion of one or two electrons in a laser field.

In a previous publication [17], we have shown how, by absorbing the wavefunction and
by recording flux before absorption, single-particle photo-electron spectra can be computed
using simulation volumes that only contain the relevant range of the atomic potential and the
electronic quiver motion in the field. In the so-called time-dependent surface flux (t-SURFF)
method, asymptotic information is accumulated during time propagation rather than drawn from
the full-wave function after the end of the pulse. The equivalence of both approaches was proven
in [17] mathematically and by comparing numerical results with the literature. Depending on
the system parameters and accuracy requirements, absorption radii for typical strong field setups
can be kept as small as 20 Bohr radii, and as few as 90 linear discretization coefficients for the
radial motion can give better than 1% accurate spectra over the complete spectral range. For
Coulomb systems, due to the long range interaction, larger radii of \( \sim 100 \) Bohr and 200–300
discretization points may be needed.

In this paper, we extend this approach to two-electron systems and multi-channel single-
ionization as well as double-ionization spectra. A numerical demonstration is provided using
a two times one-dimensional (1D) model system. As first physical results, we found the phase
and pulse-duration dependence of shake-up and double-ionization spectra, phenomena that are
consistent with the spatial asymmetry of very short laser pulses and the re-collision mechanism
for shake-up and non-sequential double ionization.

2. The time-dependent surface flux method for two-electron systems

We will first briefly summarize t-SURFF for the single-particle case. The basic requirement is
that there is some radius \( R_c \) beyond which the Hamiltonian reduces to an asymptotic one with
known solutions. Let \( H(t) \) denote the time-dependent Hamiltonian of our system, and assume
that there exists an exactly solvable \( H_v(t) \) that at large distances agrees with \( H(t) \):

\[
H_v(t) = H(t) \quad \text{for} \quad |\vec{r}| > R_c \quad \text{and} \quad \forall t. \tag{1}
\]

For a single particle in a laser field described in velocity gauge and a short-range potential
\( V(\vec{r}) = 0 \) for \( |\vec{r}| > R_c \), \( H_v(t) \) is the Hamiltonian for free motion in the laser field

\[
H_v(t) = \frac{1}{2} [-i\vec{\nabla} - \vec{A}(t)]^2, \tag{2}
\]

where \( \vec{A}(t) = -\int_{-\infty}^{t} \vec{E}(t')dt' \) for an electric dipole field \( \vec{E}(t) \). Here and throughout, we use
atomic units \( \hbar = m_e = e^2 = 1 \) unless indicated otherwise (\( m_e \) and \( e \) denote the electron mass and
unit charge, respectively; the unit of length is the Bohr radius). The time-dependent Schrödinger
equation (TDSE) with \( H_v(t) \) has the Volkov solutions

\[
\chi_k(\vec{r}, t) = (2\pi)^{-3/2} e^{-i\Phi(\vec{k}, t)} e^{i\vec{k} \cdot \vec{r}}, \tag{3}
\]

i.e. plane waves times the well-known Volkov phase

\[
\Phi(\vec{k}, t) = \frac{1}{2} \int_{-\infty}^{t} dt' [\vec{k} - \vec{A}(t')]^2. \tag{4}
\]
Scattering describes the behavior of the time-dependent wave function $\Psi(\vec{r}, T)$ at long times $T$ and large distances $|\vec{r}| > R_c$. We choose $T$ and $R_c$ large enough such that at $T$ the pulse is over

$$H_v(t) = -\frac{1}{2}\Delta \quad \text{for } t > T$$

and the wave function has split into its bound and scattering parts

$$\Psi(\vec{r}, T) = \Psi_b(\vec{r}, T) + \Psi_s(\vec{r}, T)$$

with the properties

$$\Psi_b(\vec{r}, T) \approx 0 \quad \text{for } |\vec{r}| \geq R_c$$

$$\Psi_s(\vec{r}, T) \approx 0 \quad \text{for } |\vec{r}| \leq R_c.$$  

The approximate sign in (7) refers to the tails of any bound state function, which decay exponentially with increasing $R_c$. The approximate sign in (8) refers to the fact that electrons with very low energies $\vec{k}^2/2 \sim 0$ may not have passed $R_c$ at time $T$. We only need to analyze $\Psi_s(\vec{r}, T)$ in terms of asymptotic functions $\chi(\vec{r}, T)$. As $\Psi_s(\vec{r}, T)$ vanishes inside the radius $R_c$, we can multiply the full $\Psi(\vec{r}, T)$ by the function

$$\theta(\vec{r}, R_c) = \begin{cases} 0 & \text{for } |\vec{r}| < R_c, \\ 1 & \text{for } |\vec{r}| \geq R_c, \end{cases}$$

and write the emission amplitude for the photo-electron momentum $\vec{k}$ as

$$b(\vec{k}, T) = \langle \chi_{\vec{k}}(T)|\theta(R_c)|\Psi(T)\rangle.$$  

To obtain a time integral over a surface flux, we write (10) as an integral of the time derivative and use the fact that on the support of $\theta(R_c)$ both $\chi_{\vec{k}}(\vec{r}, t)$ and $\Psi(\vec{r}, t)$ evolve by the same Hamiltonian $H_v(t)$. We obtain that

$$\langle \chi_{\vec{k}}(T)|\theta(R_c)|\Psi(T)\rangle = i \int_0^T dt \langle \chi_{\vec{k}}(t)|[H_v(t), \theta(R_c)]|\Psi(t)\rangle.$$

The commutator vanishes everywhere except on $|\vec{r}| = R_c$: the asymptotic information is obtained by integrating the time-dependent flux through a surface at finite distance $R_c$. For further discussion of the single-particle case and numerical examples with short-range and Coulomb potentials, see [17].

2.1. Single ionization into ionic ground and excited state channels

The simplest extension of the single-electron method is for the computation of single ionization into ground and excited state ionic channels. A complication is that in the presence of a strong field the ionic state can differ from the field-free ionic state due to polarization, and one must make sure to count flux passing through the surface into the correct ionic channel. In this section, we consider only the lowest ionic states that remain bound and do not contribute to double ionization.

For decomposing the coordinate space into bound and asymptotic regions, we define on both the coordinates $\vec{r}_1$ and $\vec{r}_2$ the projector functions $\theta_1(\vec{r}_1, R_c)$ and $\theta_2(\vec{r}_2, R_c)$, respectively, as in the single-particle case (9). Again picking sufficiently large times $T$ and a sufficiently large...
Figure 1. Partitioning of the coordinate space into bound (B), singly ionized (S, \( \bar{S} \)) and doubly ionized D regions. Single and double photo-electron spectra are obtained by integrating the flux across the boundaries between the regions.

surface radius \( R_c \), we can partition the wave function \( \Psi(T) \) into its bound, singly ionized and doubly ionized parts (see figure 1)

\[
\Psi(T) = (1 - \theta_1)(1 - \theta_2)\Psi(T) + \theta_1(1 - \theta_2)\Psi(T) + (1 - \theta_1)\theta_2\Psi(T) + \theta_1\theta_2\Psi(T)
\]

(12)

\[
:= \Psi_b(T) + \Psi_s(T) + \Psi_{\bar{s}}(T) + \Psi_d(T).
\]

(13)

Here and in the following, we suppress the arguments \( \vec{r}_1, \vec{r}_2 \) and \( R_c \) of \( \theta_1 \) and \( \theta_2 \). Note that the assignment of singly and doubly ionized character to the different regions is asymptotically exact: the error can be made arbitrarily small for any specific solution \( \Psi(T) \) by choosing sufficiently large \( T \) and \( R_c \).

The single-ionization Hamiltonian

\[
H_s(t) = H_s(t) \otimes 1 + 1 \otimes H_{\text{ion}}(t)
\]

agrees with the exact Hamiltonian on the support of \( \theta_1(1 - \theta_2) \) (region S in figure 1). The corresponding Hamiltonian on \( \bar{S} \) is obtained by particle exchange. Channel solutions \( \chi_{c,\vec{k}}(\vec{r}_1, \vec{r}_2, t) \) for the TDSE on S

\[
\frac{i}{\hbar}\frac{d}{dt}\chi_{c}(\vec{r}_1, \vec{r}_2, t) = H_s(t)\chi_{c}(\vec{r}_1, \vec{r}_2, t)
\]

(15)

have the form

\[
\chi_{c,\vec{k}}(\vec{r}_1, \vec{r}_2, t) = (2\pi)^{-3/2}e^{-i\Phi(t)}e^{i\vec{k}\vec{r}_1} \otimes \phi_c(\vec{r}_2, t).
\]

(16)

Here \( \phi_c(\vec{r}_2, t) \) solves the ionic TDSE

\[
\frac{i}{\hbar}\frac{d}{dt}\phi_c(\vec{r}_2, t) = H_{\text{ion}}(t)\phi_c(\vec{r}_2, t).
\]

(17)

Rather than an initial we use a final condition that \( \phi_c(\vec{r}_2, t) \) for \( t > T \) should be the desired final ion state (we need to solve the TDSE backward in time). The channel solution on the support \( \bar{S} \) of the particle exchanged projector \( (1 - \theta_1)\theta_2 \) is

\[
\bar{\chi}_{c,\vec{k}}(\vec{r}_1, \vec{r}_2, t) = \chi_{c,\vec{k}}(\vec{r}_2, \vec{r}_1, t).
\]
With the spectral amplitude
\[ b(\vec{k}, c, T) = \langle \chi_{\vec{k},c}(T) | \theta_1(1 - \theta_2) | \Psi_s(T) \rangle, \]  
(18)
the probability density for finding at time \( T \) an electron with momentum \( \vec{k} \) in the ionic channel \( c \) is
\[ \sigma(\vec{k}, c, T) = 2 |b(\vec{k}, c, T)|^2. \]  
(19)
Factor 2 arises from adding the two identical exchange symmetric contributions. For converting this integral into a time integral over a surface we make the simplifying assumption that the ionic solution never leaves the bound area
\[ \phi_c(\vec{r}_2, t) \approx 0 \quad \text{for} \quad |\vec{r}| > R_c \quad \text{and} \quad \forall t. \]  
(20)
This is a precise version of the assumption that the ionic states considered do not get further ionized. The approximate sign refers to the fact that again there is always an exponential tail reaching arbitrary distances and further that interaction with any pulse will lead to a small amount of ionization. Using (20) we neglect the flux between the singly ionized regions \( S, \bar{S} \) and the doubly ionized region \( D \) at all times. Then, using the same procedure as for a single particle, we obtain
\[ b(\vec{k}, c, T) = i \int_{-\infty}^{T} dt \langle \chi_{\vec{k}}(t) | [H_v(t), \theta_1] | \psi_c(t) \rangle, \]  
(21)
where \( \psi_c(\vec{r}_1, t) \) is the channel projected wave function
\[ \psi_c(\vec{r}_1, t) := \int d^3r_2 \phi_c^*(\vec{r}_2, t) \Psi(\vec{r}_1, \vec{r}_2, t). \]  
(22)
For evaluating the integral (21), we only need to know values and radial derivatives of \( \psi_c \) on the surface \( |\vec{r}| = R_c \).

For the computation it means solving the full two-electron problem up to time \( T \) and up to radius \( R_c \). Beyond \( R_c \) one can absorb all amplitudes. In addition, for each channel \( c \), we need to solve one single-electron problem up to the same time and radius (which is usually a much simpler task).

2.2. **Double-ionization spectra**

When double ionization occurs, flux passes from the bound region \( B \) through the singly ionized regions \( S \) or \( \bar{S} \) into the doubly ionized region \( D \). Our naming of the areas is suggestive but does not imply any bias as to an actual state that the electrons occupy within any of these areas. It is insubstantial for the present discussion whether some intermediate ionic bound state is occupied by one of the electrons in \( S \) or \( \bar{S} \) (sequential ionization) or whether both electrons must be considered unbound. The sole purpose of the partitioning is to have well-defined surfaces outside the ranges of the respective potentials where we will integrate fluxes.

For double ionization there is one obvious limitation of the discussion so far: on the line \( |\vec{r}_1 - \vec{r}_2| = a \) the electron–electron interaction is constant and not negligible for small \( a \). This problem is not related to the long-range Coulomb potential, rather it is a general problem for any multi-particle breakup, which is why break-up processes are more complex than single-particle scattering. Within the framework of the present approach the problem can be solved for short-range electron–electron repulsion without making approximations, which will be discussed.
below. A pragmatic solution has been effectively employed in many earlier publications, which is to neglect electron–electron repulsion at large distances from the nucleus. This is what using any projection onto products of single-electron states implies, be it Coulomb scattering waves or plane waves (both approaches are discussed, for example, in [18]). Sensitivity to this approximation can be tested by varying the distance from the nucleus where the projection starts.

As the pragmatic solution was found to work well in many cases, we make this approximation explicit in the present paper by smoothly turning off all potentials including the electron–electron interaction before the surface radius \( R_c \). In that case we can always use the free (Volkov) Hamiltonian \( H_v(t) \) beyond \( R_c \).

By our assumptions, in the region \( |\vec{r}_1| \geq R_c \), the Hamiltonian is identical to \( H_v(t) \), equation (14), which motivates the ansatz

\[
\theta_1 \Psi(\vec{r}_1, \vec{r}_2, t) = \int d^3 k \sum_n \chi^*_n(\vec{r}_1, t) \xi_n(\vec{r}_2) b'(\vec{k}, n, t), \tag{23}
\]

with the Volkov solutions \( \chi^*_n(\vec{r}_1, t) \) on the coordinate \( \vec{r}_1 \) and an expansion into a time-independent, complete but otherwise arbitrary set of functions \( \xi_n(\vec{r}_2) \) on \( \vec{r}_2 \). Using orthogonal projection onto the expansion functions \( \chi^*_n \) and \( \xi_n \), the coefficients \( b'(\vec{k}, n, t) \) are obtained as

\[
b'(\vec{k}, n, t) = \int d^3 k' q_0(\vec{k}, k', t) b(\vec{k}', n, t) \tag{24}
\]

with

\[
b(\vec{k}, n, t) = \int_{R^3} d^3 r_1 \chi^*_n(\vec{r}_1, t) \theta_1 \int_{R^3} d^3 r_2 \xi_n(\vec{r}_2) \Psi(\vec{r}_1, \vec{r}_2, t). \tag{25}
\]

The integral (24) over \( q_0 \) accounts for the fact that the plane waves are not \( \delta \)-orthonormal when the integration is restricted by \( \theta_1 \); the inverse overlap is defined by

\[
\int d^3 k' q_0(\vec{k}, \vec{k}', t) \langle \chi^*_n, t | \theta_1 | \chi^*_n, t \rangle = \delta^{(3)}(\vec{k} - \vec{k}'). \tag{26}
\]

For notational brevity, we assume here that the basis functions \( \xi_n \) are orthonormal. The time derivative of the \( b(\vec{k}, n, t) \) is

\[
i \frac{d}{dt} b(\vec{k}, n, t) = \langle \chi^*_n(t) | \theta_1 | \xi_n | H_{\text{ion}}(t) | \Psi(t) \rangle - \langle \chi^*_n(t) | \theta_1 | \xi_n | \Psi(t) \rangle. \tag{27}
\]

By the double right bracket \( ) \) we emphasize that integration is over both coordinates \( \vec{r}_1 \) and \( \vec{r}_2 \). Inserting the representation (23) into the first term, we obtain an inhomogeneous equation for the \( b(\vec{k}, n, t) \):

\[
i \frac{d}{dt} b(\vec{k}, n, t) = \sum_m \langle \xi_m | H_{\text{ion}}(t) | \xi_m \rangle b(\vec{k}, m, t) - \langle \chi^*_n(t) | \theta_1 | \xi_n | \Psi(t) \rangle. \tag{28}
\]

where we have used (26). The inhomogeneity is the flux through the surface \( |\vec{r}_1| = R_c \).

Initial conditions are \( b(\vec{k}, n) \equiv 0 \), i.e. no electrons outside \( R_c \). We write the double-ionization amplitude

\[
b(\vec{k}_1, \vec{k}_2, T) = \langle \chi^*_n(T) | \theta_2 | \Psi(T) \rangle, \tag{29}
\]
and use one more time the conversion into integrals over the surface flux
\[ b(\vec{k}_1, \vec{k}_2, T) = \langle \chi_{k_1}(T) | \langle \chi_{k_1}(T) | \theta_2 | \Psi(T) \rangle \rangle \]
\[ = \int^T_0 \frac{d}{dt} \langle \chi_{k_1}(t) | \langle \chi_{k_1}(t) | \theta_2 | \Psi(t) \rangle \rangle \]
\[ = : i \int^T_0 dt [ B(\vec{k}_1, \vec{k}_2, t) + \tilde{B}(\vec{k}_1, \vec{k}_2, t) ]. \]  
(30)  
(31)  
(32)

The two terms \( B \) and \( \tilde{B} \) are related by exchange symmetry
\[ B(\vec{k}_1, \vec{k}_2, t) = \tilde{B}(\vec{k}_2, \vec{k}_1, t) = \langle \chi_{k_2}(t) | \langle \chi_{k_2}(t) | H_r(t), \theta_2 | \Psi(t) \rangle \rangle. \]  
(33)

For computing \( B \), we only need to know \( \theta_1 \Psi(t) \), for which we insert the representation (23) to obtain
\[ B(\vec{k}_1, \vec{k}_2, t) = \sum_m \langle \chi_{k_1}(t) | [H_r(t), \theta_2] | \xi_m \rangle b(\vec{k}_2, m, t). \]  
(34)

The inverse overlap \( q_0(\vec{k}_1, \vec{k}_1') \), (26), cancels with the overlap integrals and never needs to be evaluated explicitly.

\( B(\vec{k}_1, \vec{k}_2, t) \) is the contribution to the double-ionization spectrum passing at time \( t \) through the surface \( \vec{r}_2 = R_c \) from region \( S \) into \( D \). In \( S \), the first electron is already detached and has a fixed canonical momentum \( \vec{k}_1 \) that is carried into the double-ionized region \( D \). \( \tilde{B}(\vec{k}_1, \vec{k}_2, t) \) is the alternative contribution going through region \( \tilde{S} \).

2.3. Computational remarks

The substantial gain of the method is that, rather than computing the full solution in region \( D \) and then analyzing it, we only need to integrate the flux through the surface separating \( S \) from \( D \). In the direction parallel to that surface the wave function is represented in terms of the free solutions \( \chi_{k_1}(\vec{r}_1, t) \), where we do not need to expand the wave function completely, but can restrict propagation to the momenta \( \vec{k}_1 \) that we are interested in. For each \( \vec{k}_1 \) we need to solve equation (28), which is anionic TDSE with an additional source term (the flux entering \( S \) from the bound region \( B \)). Although the derivation may appear complex, the implementation of the procedure can be done by the following simple algorithm:

- Set up \( b(\vec{k}_1, n, t) \) on a \( \vec{k}_1 \) grid of the desired density and initialize to 0.
- Get time grid points \( t_i \) with a time step that resolves the fastest amplitude oscillations for the desired energy range \( \Delta t < 2\pi/E_{\text{max}} \).
- In a loop through all times \( t_i \), get the surface terms from file or from a simultaneous calculation of \( |\Psi(t_i)\rangle \) and use (28) to advance to \( b(\vec{k}_1, n, t_i) \).
- Add the contribution from region \( S \) to the spectral amplitude
\[ s(\vec{k}_1, \vec{k}_2, t_i) = s(\vec{k}_1, \vec{k}_2, t_{i-1}) + \Delta t B(\vec{k}_1, \vec{k}_2, t). \]  
(35)

The contribution \( \delta \) from region \( \tilde{S} \) is obtained from \( s \) by particle exchange. The total spectral amplitude is the sum of both contributions
\[ b(\vec{k}_1, \vec{k}_2, T) = s(\vec{k}_1, \vec{k}_2, T) + \delta(\vec{k}_1, \vec{k}_2, T) = s(\vec{k}_1, \vec{k}_2, T) + s(\vec{k}_2, \vec{k}_1, T). \]  
(36)
The asymptotic value—the spectral amplitude—is attained at times $T$ when the flux through the surfaces becomes negligible.

The approach can only be successful when absorption does not significantly distort the solution at the integration surfaces. The ‘infinite range exterior complex scaling’ (irECS) absorber was shown in [17, 19] to provide traceless absorption over a very wide energy range at low computational cost. It outperforms standard complex absorbing potentials by several orders of magnitude in accuracy. If needed, irECS can be pushed to full machine precision using not more than 20 discretization coefficients per coordinate in the absorbing region $|\vec{r}| > A_0$. Absorption can begin at any $A_0 \geq R_c$. More mathematical and numerical details and ample numerical examples using irECS can be found in [17, 19].

In general, discretization errors for two electrons are similar to those for a single-electron system with the same ionization potential. This has the practical advantage that a suitable discretization can be determined from the single-electron problem. Only a few consistency checks on specific two-electron observables need to be performed for the computationally heavier two-electron calculation.

2.3.1. General single-ionization spectra. Once we have obtained the $b(\vec{k}_1, n, T)$ we can reconstruct the wave function for $|\vec{r}_1| > R_c$. In particular, the amplitude for single-ionization spectra for any ionic state $\phi_c$ is

$$b(\vec{k}, c) = \sum_n b(\vec{k}, n, T)a_n^{(c)}, \quad (37)$$

where $a_n^{(c)}$ are the expansion coefficients of $\phi_c$ with respect to the basis functions $\xi_n$:

$$\phi_c(\vec{r}) = \sum_n \xi_n(\vec{r})a_n^{(c)}. \quad (38)$$

This approach is not limited to non-ionizing $\phi_c$, as it analyzes the ionic population at time $T$ after the end of the pulse. For non-ionizing $\phi_c$, it is a substitute for the above single-ionization procedure. Note that here we need to solve the inhomogeneous ionic problem (28) for each photo-electron momentum $\vec{k}$. The total spectrum is a linear combination of the individual contributions of each $n$. Where applicable, the advantage of the single-ionization procedure of section 2.1 is twofold: firstly, for each final $\phi_c$ one needs to solve only one ionic TDSE and compute the values and derivatives of the channel surface function $\psi_c$. The complete spectrum can be obtained by time integration with little numerical effort. Secondly, as one directly obtains the channel spectrum without intermediate decomposition and final resummation of the wave function, the results are in general more robust numerically.

3. Numerical demonstration of the method

3.1. The one-dimensional two-electron model system

As even with the simplifications by $t$-SURFF the solution to the full 3D two-electron problem remains a very-large-scale computational task, we use for demonstration purposes the standard 1D two-electron model Hamiltonian

$$H(t) = \sum_{\alpha=1,2} \frac{1}{2} \left[ -i \frac{\partial}{\partial x_\alpha} - A(t) \right]^2 - \frac{2M(x_\alpha)}{\sqrt{x_\alpha^2 + 1/2}} + \frac{M(x_1)M(x_2)}{\sqrt{(x_1 - x_2)^2 + 0.3}}. \quad (39)$$

New Journal of Physics 14 (2012) 085008 (http://www.njp.org/)
For making all potentials strictly finite range, we have chosen a ‘truncation radius’ $C_p$ and a truncation function $M(x)$ that is $\equiv 1$ up to $|x_\alpha| = C_p - 5$ and goes differentiably smoothly to 0 at $|x_\alpha| = C_p$. Where not indicated otherwise, we use $C_p = 20$. The screening factor of $1/2$ in the ionic potential was chosen for esthetic reasons, as then the exact ionic ground state (without potential truncation) is $E_0 = -2$. The first ionic excited state occurs at $E_1 = -0.93$, substantially more strongly bound than the first excited He$^+$ energy of $-1/2$. With the electron–electron screening of 0.3, one obtains an ionization potential of 0.88, which we consider as a fair approximation of the actual He ionization potential of 0.90.

For all computations, we use a finite elements discretization where orders between 8 and 20 were used for convergence studies. For the present purposes, we found order 8 or 10 sufficient. A detailed discussion of the finite-element method for irECS calculations can be found in [19]. The irECS radius $A_0$, which marks the beginning of absorption, was varied between 20 and 100 au. The results do not depend on $A_0$ at the level of accuracy shown.

In all the calculations below, we use $\cos^2$ pulse shapes defined in terms of the vector potential

$$A(t) = \frac{E_0}{\omega} \cos^2 \left( \frac{\pi t}{2T_{\text{FWHM}}} \right) \sin(\omega t + \phi_{\text{CEO}}),$$

where $T_{\text{FWHM}}$ is the full-width at half-maximum of the envelope of the vector potential, $\omega$ is the laser central photon energy and $\phi_{\text{CEO}}$ the carrier-envelope offset phase. The peak field amplitude $E_0$ is related to the pulse peak intensity $I$ by $E_0 = \sqrt{2I}$. By construction, the electric field $E(t) = -\frac{d}{dt}A(t)$ has no zero-frequency component, which is important when studying the effects of $\phi_{\text{CEO}}$ with very short pulses. For a ‘cosine pulse’ $\phi_{\text{CEO}} = 0$ the peak of the electric field approximately coincides with the maximum of the pulse envelope with minor deviations due to the derivative of the envelope.

### 3.2. Two-photon double ionization in the extreme ultraviolet

In [4], perturbative two-photon double ionization of He by short XUV pulses with photon energies between the two- and single-photon ionization thresholds was investigated and a remarkable universal description of the process was found. The findings were confirmed by numerical solutions of the fully 3D two-electron TDSE. Pulse durations of $T = 4.5$ fs and photon energies $\omega$ between 42 and 80 eV were used. The perturbative regime at $\omega = 42$ eV extends up to intensities near $I = 10^{16}$ W cm$^{-2}$, where one first observes sizable deviations from the perturbative scaling $\propto I$ at the single-photon single-ionization peak and $\propto I^2$ for shake-up and double ionization.

As an example, figure 2 shows the two-electron spectrum for photon energy $\omega = 70$ eV at peak intensity $10^{16}$ W cm$^{-2}$. Three two-electron ridges at energies $|E_1| + |E_2| = n\omega + E_0$ are clearly visible. With ground state energy $E_0 = -2.88$ au $\approx -78$ eV, the first peak appears for $n = 2$-photon ionization. The ridges parallel to the energy axes are artifacts of the method: there is significant shake-up and the exponential tail of the excited ionic states reaches into region $D$. Note, however, that with the choice of $R_c = 40$ for the present calculation, the ridges are suppressed by at least a factor of $10^{-6}$ relative to the surrounding signal. Even stronger suppression can be obtained by further increasing $R_c$ or, alternatively and with a slower convergence rate, by propagating to longer times. If the ionic states are known accurately, their effect can completely be removed by projection (for a detailed discussion of the procedure, see [17]).

New Journal of Physics 14 (2012) 085008 (http://www.njp.org/)
Double electron emission by a 4.5 fs XUV pulse at a photon energy $\omega = 70$ eV with a peak intensity $10^{16}$ W cm$^{-2}$. Negative energies indicate emission to $(-\infty, -R_c]$. Straight lines at $45^\circ$ with constant $E_1 \pm E_2$ indicate correlated processes. The first three double-electron ridges are visible. Lines parallel to the energy axes are artifacts due to exponential tails of excited ionic bound states that reach beyond $R_c = 40$. Their peak values lie below $\lesssim 10^{-6}$ of the peak signal. Black color ($\leq 10^{-10}$) approximately indicates numerical noise.

Two-photon double ionization for photon energies 42, 54, 58, 70 and 80 eV. Lineouts are taken at the respective lowest-energy ridges with total energies $|E_1| + |E_2| = 6, 18, 30, 38, 62$ and 82 eV, respectively. Curves are normalized to 1 at $E_1 - E_2 = 0$.

In figure 3, we show lineouts of the two-photon two-electron energy ridges for photon energies between 42 and 80 eV. The curves are converged within the resolution of the plots with respect to $T$, $R_c$ and spatial discretization. Although the general characteristics are determined by the single-excitation resonances as in [4], for the present system we do not reproduce the universal behavior found there for the angle-integrated spectra. The likely reasons are shake-up interferences that also modify the angular distributions in the 3D case [4].

New Journal of Physics 14 (2012) 085008 (http://www.njp.org/)
Even at the present benign, nearly perturbative parameters, photo-electrons with energies of $E_\phi \sim 3 \text{ au} \approx 80 \text{ eV}$ travel to a distance $r_{\text{max}} \sim 2T_{\text{FWHM}}\sqrt{2E_\phi/m_e} \approx 900 \text{ au}$ during the duration of the pulse. To correctly represent the corresponding momenta, one needs a grid spacing of $\Delta r \lesssim 2\pi/\sqrt{2E_{\text{max}}} \approx 2.5$, which results in at least about 400 radial discretization points in a numerical calculation. In practice, finer grid spacings need to be used with a correspondingly larger number of discretization points. In addition, for the asymptotic analysis of the wave function, one may need to propagate further for a certain period of time after the pulse, leading to further increase of the required box radius $r_{\text{max}}$.

For comparison, using $t$-SURFF we obtain converged results using only 49 discretization coefficients on the positive half-axis $[0, \infty)$. The total number of discretization points per coordinate is twice as large because of the negative half-axis, which would correspond to a different angular direction in a 3D calculation. Of the 49 points, 32 were used in the interval $[0, 20]$, i.e. an effective grid spacing of $\sim 20/32 = 0.625$, which sets a theoretical limit for the maximum photo-electron energy of $\lesssim 50 \text{ au} \approx 1300 \text{ eV}$. The remaining 17 points were used for irECS absorption. The $t$-SURFF simulation volume radius $R_c$ is independent of pulse duration.

3.3. Single ionization and shake-up by an infrared pulse

Possibly the most elementary correlated process is shake-up: after forcefully removing a single electron, the remaining electrons rearrange not exclusively into the ionic ground state, but a fraction goes into excited states. The exact distribution of excited states strongly depends on system parameters. Shake-up by very strong, short IR pulses has recently been observed using ‘attosecond transient absorption spectroscopy’ \cite{20}, which can monitor the time evolution of an excited ionic state after IR ionization.

Within the present simplified model we can only demonstrate basic qualitative features of shake-up in IR ionization. We have studied the dependence on the carrier-envelope offset phase $\phi_{\text{CEO}}$ and on pulse duration. We use an intensity of $2 \times 10^{14} \text{ W cm}^{-2}$ and $\omega = 0.057 \text{ au}$ (corresponding to the wave length 800 nm). Converged results were obtained using the same discretization parameters as in the XUV case discussed above.

In figure 4, photo-electron spectra for the ground and first excited states calculated by formula (21), (smooth line) and, alternatively, by equation (37), (coarser energy grid) for a single-cycle cosine pulse: $T = 2\pi/\omega$ and $\phi_{\text{CEO}} = 0$. The spectra show some generic short-pulse features: pronounced asymmetry and absence of individual photo-electron peaks at energies where emission occurs only during a single laser half-cycle. Emission to the left is lower, as the field amplitude to the left is smaller.

Clearly, the spectral structure is highly sensitive to $\phi_{\text{CEO}}$. However, also the total shake-up yield is strongly $\phi_{\text{CEO}}$ dependent. Table 1 lists the yields in the ground and first excited ionic states for different phases and pulse durations. While shake-up is strongly suppressed for a single cycle cosine pulse, it increases to a sizeable $\sim 10\%$ of the ground state ionic channel for $\phi_{\text{CEO}} = 3\pi/4$. We tentatively ascribe this fact to a recollision mechanism for shake-up. The fact that longer pulses with 2 and 3 optical cycles in general have shake-up fractions comparable to the $\phi_{\text{CEO}} = 3\pi/4$ is consistent with this hypothesis. We abstain from a more detailed analysis of the phenomenon for the present model, as due to the absence of transverse wave-packet spreading, recollision effects are greatly exaggerated in 1D models.
Figure 4. Single-photo-electron emission spectra in the lowest four ionic channels. Negative energies indicate emission to \((-\infty, -R_c]\). Spectra are calculated using equation (37). In addition, for the ground and first excited ion channels, curves computed by equation (21) are shown (black lines). The curves are scaled for better visibility.

Table 1. Shake-up as a function of \(\phi_{\text{CEO}}\). The total yield in the ionic ground \(Y_0\) and first excited \(Y_1\) states and the ratio \(Y_0/Y_1\) are also shown.

| \(T_{\text{FWHM}}\) | \(\phi_{\text{CEO}}\) | \(Y_0\)    | \(Y_1\)    | \(Y_1/Y_0\) |
|-----------------|-----------------|-----------|-----------|-------------|
| 1 opt.cyc.      | 0               | \(2.26 \times 10^{-7}\) | \(6.27 \times 10^{-10}\) | \(2.77 \times 10^{-3}\) |
|                 | \(\pi/4\)       | \(2.18 \times 10^{-7}\) | \(1.35 \times 10^{-8}\) | \(6.19 \times 10^{-2}\) |
|                 | \(\pi/2\)       | \(8.88 \times 10^{-8}\) | \(1.35 \times 10^{-8}\) | \(1.15 \times 10^{-1}\) |
|                 | \(3\pi/4\)      | \(1.38 \times 10^{-7}\) | \(2.60 \times 10^{-9}\) | \(1.88 \times 10^{-2}\) |
| 2 opt.cyc.      | 0               | \(2.36 \times 10^{-7}\) | \(1.16 \times 10^{-8}\) | \(4.91 \times 10^{-2}\) |
| 3 opt.cyc.      | 0               | \(1.44 \times 10^{-7}\) | \(3.18 \times 10^{-9}\) | \(2.21 \times 10^{-2}\) |

3.4. Double-ionization spectra generated by an infrared pulse

Figure 5 gives an overview of doubly differential photoemission spectra obtained for different \(\phi_{\text{CEO}}\) and pulse durations up to three optical cycles \(T_{\text{FWHM}} = 6\pi/\omega\) au \(\approx 7.5\) fs. The calculations were performed using a slightly more accurate discretization with 60 points on the half-axis \([0, \infty)\).

As is to be expected, we see pronounced asymmetries and strong effects of \(\phi_{\text{CEO}}\) for the shortest pulses. While the single-cycle cosine pulse essentially shows only weak and unidirectional emission of both electrons, backward emission and significantly higher yields arise at \(\phi_{\text{CEO}} = 3\pi/4\). Most probably, the mechanism responsible is re-collision. However, due to the limitations of the 1D model, we defer a more detailed discussion of the effects to a future fully 3D calculation.

3.4.1. Dependence on the potential cutoff. By truncating all potentials at \(C_p = 20\) au, the Volkov Hamiltonian \(H_v(t)\) is exact outside \(R_c\) and all errors of \(r\)-SURFF are either due to
Figure 5. Overview of double-ionization spectra for a laser wavelength 800 nm and a peak intensity $2 \times 10^{14}$ W cm$^{-2}$. Upper row pulse duration $T = 1$ optical cycle with $\phi_{\text{CEO}} = 0$ (left) and $3\pi/4$ (right). Lower row: $\phi_{\text{CEO}} = 0$ with $T = 2$ (left) and 3 (right). Negative energies indicate emission to $(-\infty, -R_c]$. Discretization or absorption. As a pragmatic approach such a truncation is very appealing, but the truncation error must be controlled. For our simple model, we performed a series of calculations for truncation radii up to $C_p = 100$. Figure 6 shows the single photo-emission spectrum for the first excited ionic channel, a diagonal lineout $E_1 = E_2$ of the double-emission spectrum and two lineouts where one energy is fixed at $E_1 = 0.1$ au (2.7 eV) and $E_1 = 0.5$ au (13.6 eV). The single-electron spectra are hardly affected by the truncation. The strongest effect, as is to be expected, is along the line $E_1 = E_2$. With $C_p = 20$ qualitative differences in the two-electron plots can be observed, while good qualitative agreement can be found for $C_p = 50$. The values $C_p$ at which the results are acceptable must be chosen based on the system and on the accuracy requirements. In our case, the on-diagonal spectra are still incorrect up to $C_p = 50$. In contrast, convergence for larger momentum differences appears to be quite acceptable at $C_p \approx 50$.

As an alternative to increasing $C_p$, one may use a different arrangement of surfaces, where an additional surface is placed at $|\vec{r}_1 + \vec{r}_2| = R_c$ (see figure 7). In scaled center-of-mass and interparticle coordinates $\vec{r}_\pm := (\vec{r}_1 + \vec{r}_2)/\sqrt{2}$ the asymptotic Hamiltonian $H_D(t)$ in region $D$ separates into the center-of-mass motion with a Volkov solution and field-free relative motion in the repulsive potential of the electrons

$$H_D(t) = \frac{i}{2} \left[ -i \nabla_+ - \sqrt{2} A(t) \right]^2 - \frac{i}{2} \Delta_- + V_{ee}(\sqrt{2}|\vec{r}_-|),$$  \hspace{1cm} (41)

where $\nabla_+$ and $\Delta_-$ denote the Nabla and Laplace operators in the coordinates $\vec{r}_+$ and $\vec{r}_-$, respectively. Thus the asymptotic problem reduces to field-free potential scattering and free motion in the laser field. The contribution going from region $B$ directly into $D$ can be conveniently expanded in this form. We leave the technical discussion and numerical demonstration of this procedure for future work.
Figure 6. Dependence of spectra on the potential cutoff $C_p = 20, 50, 80$ and 100 for a 800 nm single-cycle cosine pulse with peak intensity $2 \times 10^{14}$ W cm$^{-2}$. Top left: single ionization in the first shake-up channel $\sigma_1(E)$, top right: double ionization with equal energies $\sigma(E, E)$, bottom: lineouts of the double-ionization signal $\sigma(E, E_1)$ for energies $E_1 = 3$ eV (left) and 13 eV (right).

Figure 7. Integrating the flux for non-vanishing electron–electron interactions.

4. Discussion and conclusions

With the reduction of the simulation volume afforded by $\tau$-SURFF, fully dimensional calculations of double photo-ionization for a broad range of wavelengths and intensities have come within reach. Scaling to three dimensions depends on the laser frequency: in the perturbative regime, the number of angular momenta required may remain as low as 3 [18], which, in linear polarization, scales the problem size by $\sim 3^3 = 27$. In that case the computational effort is less than one order of magnitude larger than the calculations presented in section 3.2 if one considers that the positive and negative half-axes of the 1D model lead to a fourfold scaling of the problem compared to a radial problem. At IR wavelength, the complete angular phase space becomes activated. At a 800 nm wavelength and intensities of $\sim 2 \times 10^{14}$ W cm$^{-2}$, $\approx 30$ angular momenta are needed for full convergence of electron spectra.
For two-electron spectra, this entails an increase in problem size by \( \sim 30^3/4 \approx 7000 \) compared to the present calculation if we keep the same standards of accuracy. Considering that a typical solution to our problems takes 2 h on a single CPU, one sees that 3D calculations are quite feasible on a moderate-sized parallel computer. In addition, in 3D the fraction of the phase space where electron repulsion is important is much smaller than in 1D. This may possibly be exploited for further reduction of the problem size.

The development of \( r \)-SURFF is motivated by the photo-ionization problem. What is special about that problem is that in the dipole approximation the time-dependent field affects the whole wave function, including the asymptotic region and therefore final momenta cannot be determined before the end of the pulse, unless one uses knowledge of the time dependence of the asymptotic solution. However, also in situations without time dependence of the asymptotic Hamiltonian, the method may turn out to be useful in obtaining fully differential momentum spectra. All it requires is a reliable absorption method and knowledge of the solution in the asymptotic region. Among the candidates for further application are reactive scattering and chemical break-up processes.

Acknowledgments

This work was supported by the ‘Munich Advanced Photonics—MAP’ excellence cluster.

References

[1] Corkum P B 1993 Plasma perspective on strong-field multiphoton ionization Phys. Rev. Lett. 71 1994
[2] Chaloupka J L, Rudati J, Lafon R, Agostini P, Kulander K C and DiMauro L F 2003 Observation of a transition in the dynamics of strong-field double ionization Phys. Rev. Lett. 90 043003
[3] Meckel M et al 2008 Laser-induced electron tunneling and diffraction Science 320 1478–82
[4] Pazourek R, Feist J, Nagele S, Persson E, Schneider B, Collins L and Burgdörfer J 2011 Universal features in sequential and nonsequential two-photon double ionization of helium Phys. Rev. A 83 1–11
[5] l’Huillier A, Lompre L A, Mainfray G and Manus C 1983 Multiply charged ions induced by multiphoton absorption in rare gases at 0.53 \( \mu \)m Phys. Rev. A 27 2503–12
[6] Augst S, Talebpour A, Chin S L, Beaudoin Y and Chaker M 1995 Nonsequential triple ionization of argon atoms in a high-intensity laser field Phys. Rev. A 52 R917–9
[7] Moshammer R et al 2000 Momentum distributions of Ne\(^{++}\) ions created by an intense ultrashort laser pulse Phys. Rev. Lett. 84 447–50
[8] Rudenko A, Zrost K, Feuerstein B, de Jesus V L B, Schröter C D, Moshammer R and Ullrich J 2004 Correlated multielectron dynamics in ultrafast laser pulse interactions with atoms Phys. Rev. Lett. 93 253001
[9] Liu Y et al 2010 Multiphoton double ionization of ar and ne close to threshold Phys. Rev. Lett. 104 173002
[10] Becker A, Dörner R and Moshammer R 2005 Multiple fragmentation of atoms in femtosecond laser pulses J. Phys. B: At. Mol. Opt. Phys. 38 S753
[11] Ye D F, Liu X and Liu J 2008 Classical trajectory diagnosis of a fingerlike pattern in the correlated electron momentum distribution in strong field double ionization of helium Phys. Rev. Lett. 101 233003
[12] Shvetsov-Shilovski N I, Sayler A M, Rathje T and Paulus G G 2011 Momentum distributions of sequential ionization generated by an intense laser pulse Phys. Rev. A 83 033401
[13] Emmanouilidou A 2011 Prevalence of different double ionization pathways and traces of three-body interactions in strongly driven helium Phys. Rev. A 83 023403
[14] Awasthi M, Vanne Y V and Saenz A 2005 Non-perturbative solution of the time-dependent Schrödinger equation describing H$_2$ in intense short laser pulses *J. Phys. B: At. Mol. Opt. Phys.* **38** 3973–85

[15] Parker J S, Doherty B J S, Taylor K T, Schultz K D, Blaga C I and DiMauro L F 2006 High-energy cutoff in the spectrum of strong-field nonsequential double ionization *Phys. Rev. Lett.* **96** 133001

[16] van der Hart H W 2006 Ionization rates for He, Ne and Ar subjected to laser light with wavelengths between 248.6 and 390 nm *Phys. Rev. A* **73** 023417

[17] Tao L and Scrinzi A 2012 Photo-electron momentum spectra from minimal volumes: the time-dependent surface flux method *New J. Phys.* **14** 013021

[18] Feist J, Nagele S, Pazourek R, Persson E, Schneider B I, Collins L A and Burgdörfer J 2008 Nonsequential two-photon double ionization of helium *Phys. Rev. A* **77** 043420

[19] Scrinzi A 2010 Infinite-range exterior complex scaling as a perfect absorber in time-dependent problems *Phys. Rev. A* **81** 053845

[20] Goulielmakis E *et al* 2010 Real-time observation of valence electron motion *Nature* **466** 739–U7