iSURF: a family of infinite-time surface flux methods

F Morales, T Bredtmann and S Patchkovskii

Max-Born-Institute, Max-Born-Strasse 2A, D-12489 Berlin, Germany

E-mail: sergei.patchkovskii@mbi-berlin.de

Received 17 June 2016, revised 24 October 2016
Accepted for publication 31 October 2016
Published 22 November 2016

Abstract

The computation and analysis of photoelectron spectra (PES) is a fundamental technique in atomic and molecular physics to study the structural and dynamical properties of a target system, and to gain insight into the process of its ionization. Since the first numerical solutions of the time-dependent Schrödinger equation (TDSE), numerous methods have been developed to extract PES from the calculated wave functions. However, most of these methods have severe limitations or are computationally very demanding. Here we present a new family of methods, based on the ideas of the so-called analytical Volkov continuation, or time-dependent surface flux (Ermolaev et al 1999 Phys. Rev. A 60 483145; Ermolaev and Selin 2000 Phys. Rev. A 62 015401; Tao and Scrinzi 2012 New J. Phys. 14 013021), that allows one to obtain fully-converged PES at the end of the laser pulse using either Volkov states or the exact scattering-states, and that has been implemented in the TDSE solver (Patchkovskii and Muller 2016 Comput. Phys. Commun. 199 153–69).

Keywords: photoelectron spectra, above threshold ionization, atomic physics, time dependent Schrödinger equation, ionization

(Some figures may appear in colour only in the online journal)

1. Introduction

Angle- and energy-resolved photoelectron spectroscopy is among the most accurate and popular techniques in atomic and molecular science [5]. The most basic method to analyze photoionized electrons is the time-of-flight spectroscopy, providing a high resolution in energy of the electron. State-of-the-art technologies, such as VMI (velocity map imaging, [6, 7]) and COLTRIMS (cold target recoil ion momentum spectroscopy [8]) yield both energy and angular resolved photoelectron spectra (PES). These experimental techniques have been successfully applied to study processes involving ionization, e.g., above threshold ionization (ATI) [9] or sequential and non-sequential double ionization of atoms [10–12], and facilitate advanced experimental methods such as time-resolved photoelectron holography [13], or the attoclock setup [14, 15]. In addition, PES underlay characterization of ultrashort laser pulses or pulse trains, using techniques such as RABITT (reconstruction of attosecond beating by interference of two-photon transition) [16] and the attosecond streak camera [17].

As the complexity and resolution of experimental PES has increased, calculation of highly accurate PES has become essential, triggering advances in theoretical methods both for solving the time-dependent Schrödinger equation (TDSE) (see for example [4, 18–28]) and extracting accurate PES. The commonly accepted formal definition of the PES for one-electron ionization is the projection of the solution of the TDSE onto asymptotic scattering states of the binding potential in the absence of the perturbation. Although asymptotic scattering states are known analytically for Coulomb potentials, numerically stable calculation of these states is not entirely trivial [29]. For a more general binding potential, the calculation of a large number of scattering states and the corresponding projections may become quite cumbersome, spurring the development of numerous alternative approaches to calculate PES.

Among the most popular techniques are:

• Window methods [30, 31]: this method uses a energy-dependent window function to project onto the real field-free Hamiltonian of the system. However this kind of methods are only able to extract the absolute value of the
amplitudes of the PES. Due to the use of the window function, the spectral resolution is limited, especially in the low-energy region where high Rydberg states need to be separated from the true continuum. The wavefunction needs to remain inside the simulation volume until the end of the ionizing laser pulse. Among the major advantages of the window methods is the correct handling of long-range potentials and norm conservation.

- Coordinate space masking + Fourier image: this commonly used method is equivalent to the projection onto a plane-wave continuum. It requires that the continuum and bound parts of the wavefunction are well-separated in coordinate space. Similar to the window methods, the wavefunction must remain within the simulation volume, in which case the technique is norm-conserving. For long-range potentials, the photoelectron energies are overestimated. Spurious interferences may also arise due to the mixing of contributions from different energies to the same plane wave \( k \) vector. Finally, artifacts due to the masking step are difficult to avoid.

- Numerical calculation of scattering states (see \([32–34]\) for recent examples): this method provides exact spectra, with the correct scattering phase, as long as the correct scattering states are known. For arbitrary potentials, calculating a numerical solution of these functions is a delicate task. However, this method is not norm conserving for a finite \( k \) grid. The wavefunction needs to remain within the simulation volume.

- Volkov-state continuation (also known as tSURFF) \([1–3, 35]\): this method is designed to relax the whole-wavefunction requirement, which might become prohibitively expensive for the case of an intense infrared laser field. This approach is particularly suitable in the strong-field, where the ponderomotive potential and the free-electron oscillation amplitude may become large. The projection onto a scattering state is replaced by a time integral of the outer-surface flux, thus allowing much smaller simulation volumes. In common with the scattering-state projection tSURFF is not norm-conserving. In common with the Fourier image approach, it is only rigorous for a short-range potential, and may introduce similar artifacts in the PES (see below). Calculation of converged PES may also require long field-free propagation after the end of the pulse, especially if the low-energy parts of the spectra are desired \([36]\) (see below).

In order to eliminate boundary reflections, most of the practical approaches to solve the TDSE include the use of a complex absorbing potential (CAP) \([37–44]\), substituting a non-Hermitian model Hamiltonian for the (Hermitian) physical Hamiltonian. This non-Hermiticity is often viewed as a necessary evil to keep the computation tractable. Here, we will demonstrate a new family of methods, complementary to the ideas of \([1, 2]\) and \([3]\), which uses non-Hermiticity of the field-free model Hamiltonian to analytically extend the tSURFF time integral to an infinite time. Used with the Volkov states, our approach allows calculation of fully-converged tSURFF spectra immediately at the end of the laser pulse (from here on referred as the iSURFV method). Apart from the time-integral convergence, this technique shares the advantages and shortcomings of the Volkov-state continuation approaches.

For simulation volumes large enough to contain the entire wavefunction at the end of the laser pulse, non-Hermiticity of the field-free Hamiltonian also allows calculation of the exact scattering-state projections. The knowledge of the asymptotic form of the target state is sufficient for the calculation of the projection. However, unlike the explicit projection methods \([32–34]\), a ‘perfect absorber’ \([40, 44]\) may be needed to avoid boundary-reflection artifacts. This method we refer to as the iSURF method.

We would like to emphasize that the use of methods as the ones in \([1–3]\) and the ones presented in this paper are independent of the technique chosen discretize the wavefunction, benefiting from all the advantages of radial basis sets (e.g. B-Splines \([45, 46]\), FEM-DVR \([47, 48]\)), but also allowing to obtain PES, while keeping the radial part small. It is also worth mentioning that the implementation of this family of methods does not rely on a particular choice of the TDSE solver.

The rest of this paper is structured as follows: we begin by restating the main expressions of the tSURFF approach. Then we introduce the analytical continuation to infinite time, and demonstrate its results in a series of examples, comparing two choices of the target functions (Volkov and Coulomb states) with a naïve implementation of the original tSURFF method.

### 2. Theory

We begin by sketching the derivation of the surface-flux approach to PES calculations. The technique was originally developed by Ermolaev et al \([1, 2]\) and Serov et al \([35]\), and then independently rediscovered and popularized by Tao et al \([3]\). The discussion is this section closely follows \([3]\).

We assume that the exact solutions \(\Psi(t)\) for the time-dependent Hamiltonian \(\hat{H}\) are known, and satisfy the TDSE:

\[
i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi,
\]

We are interested in expressing \(\Psi\) in terms of the solutions \(X(t)\) of a (possibly different) time-dependent Hamiltonian \(\hat{H}_X\). Functions \(X\) satisfy the corresponding TDSE:

\[
i\hbar \frac{\partial}{\partial t} X = \hat{H}_X X,
\]

or, equivalently:

\[-i\hbar \frac{\partial}{\partial t} X^* = X^* \hat{H}_X.\]

The projection of \(\Psi\) onto \(X\) is given by:

\[
a_X(t_0) = \int d^3r \{ X^*(\vec{r}, t_0) \Psi_{\Psi}(\vec{r}, t_0) \}.\]
For example, if $X$ belongs to the continuum part of the spectrum, $\alpha_X$ is the corresponding ionization amplitude.

For sufficiently large $t_0$, the projection (4) onto a continuum state is dominated by the part of space far away from the coordinate origin, and can be replaced by:

$$a(t_0) = t_0 \rightarrow \infty \int d\vec{r} \left\{ X^*(\vec{r}, t_0) \hat{\Theta}_S \Psi(\vec{r}, t_0) \right\},$$

with $\hat{\Theta}_S$ being the spherical Heaviside function of $r$:

$$\hat{\Theta}_S = \begin{cases} 0, & r < R_0, \\ 1, & r \geq R_0. \end{cases}$$

If we further assume that at some initial time $t_i$ the wave-packet $\Psi$ is localized near the origin, so that:

$$\hat{\Theta}_S \Psi(\vec{r}, t_i) \equiv 0$$

equation (5) can be re-written as a time integral:

$$a(t_0) = \int_{t_i}^{t_0} \frac{1}{\hbar} \frac{\partial}{\partial t} \int d\vec{r} X^*(\vec{r}, t) \hat{\Theta}_S \Psi(\vec{r}, t),$$

$$= \int_{t_i}^{t_0} \frac{1}{\hbar} \frac{\partial}{\partial t} \int d\vec{r} \frac{i}{\hbar} [\hat{H}_S, \hat{\Theta}_S \Psi] = [\hat{H}_S, \hat{\Theta}_S \Psi] (t_i)$$

Provided that the Hamiltonians $\hat{H}$ and $\hat{H}_S$ coincide outside of the central region ($r \geq R_0$), the term in the curly brackets in equation (8) becomes a commutator. This commutator is non-zero on the surface of the dividing sphere, and vanishes identically everywhere else. For the specific case of the dipole-approximation Volkov Hamiltonian in velocity gauge:

$$\hat{H}_S = \frac{1}{2m} (\vec{p} - e\vec{A})^2 - \frac{1}{2m} (-i\hbar \hat{\nabla} - e\vec{A})^2,$$

the volume integral in equation (8) becomes

$$b(t) = \int d\Omega \frac{1}{2m} \frac{\partial}{\partial r} \left\{ \frac{\partial X^*}{\partial r} - \frac{e}{m} A_r X^* \right\},$$

where $A_r(t)$ is the spherical radial component of the vector potential of the laser field $\vec{A}$. Note that this derivation does not require the target functions $X$ to be defined in the same Hilbert space as the wavepacket $\Psi$. This property makes it possible to directly calculate ionization amplitudes using an $L^2$ representation of $\Psi$.

We would like to emphasize that up to this point, we have simply recapitulated the formalism described in [1, 3] (see [2] for an extension to the eikonal-Volkov Hamiltonian).

### 2.1. Analytical continuation of the time integral

Calculation of ionization amplitudes using equations (8)–(10) require that the entire continuum part of the wavefunction passes through the dividing surface $S$. This may require that the simulation continues long after the pulse is over, especially if low final momenta are of interest. However, any wavepacket within a finite, discretized simulation volume can be trivially expanded over the eigenfunctions of the field-free Hamiltonian, giving its evolution at all future times analytically. We emphasize that the derivation below is neither mathematically rigorous nor applicable in a more general case: in particular, it assumes without proof that the discretization of $\hat{H}$ is not defective and that $(\hat{H} - \epsilon \hat{1})^{-1}$ exists for all positive real $\epsilon$. For a detailed analysis of the general case see [49] and references therein.

Using the same non-Hermitian spherical-coordinate representation as in [4]:

$$\Psi(t) = \frac{1}{r} \sum_{L,M,j} f_{LMj}(r) Y_{LM}(\Omega_r) \exp \left( -\frac{i}{\hbar} \mathcal{E}_{LMj}(t - t_i) \right),$$

$$\mathcal{E}_{LMj} = E_{LMj} - \frac{1}{2} \Gamma_{LMj},$$

$$f_{LMj} = \int d\Omega Y_{LM}^*(\Omega_r) \Phi_{LMj}(r)(t) \Psi(t_i),$$

where $t_r$ is an arbitrary time after the end of the laser pulse, and $\Phi_{LMj}$ and $\Phi_{LMj}$ are, respectively, the right and left eigenvector of the model field-free Hamiltonian, associated with the complex energy $\mathcal{E}_{LMj}$, $E_{LMj}$ and $\Gamma_{LMj}$ are the energy and the lifetime of the state $LMj$. The imaginary part $\Gamma$ arises due to the presence of the absorbing boundary, as it is discussed in detail in [40, 44]. Due to the presence of the boundary, the eigenstates $\Phi_{LMj}^R(y) Y_{LM}(\Omega_r)$ are not expected to coincide with the eigenstates of the Hermitian physical Hamiltonian. We do however expect that the absorber is ‘perfect’ [40, 44], so that the wavepacket dynamics in the inner region is the same for the model and physical Hamiltonians. This assumption is made (explicitly or tacitly) in most practical applications of TDSE to strong-field ionization dynamics, and can be satisfied to any desired degree in practice [44].

Finally, $L$ and $M$ are the usual orbital quantum numbers and $j$ is the ordinal number of the state within each $L, M$ channel boundary. Equation (11) is applicable for all $t \geq t_r$.

The decomposition in equation (11) is well-defined within the finite-dimensional Hilbert space used to propagate the time-dependent wave-function. The formal condition for the existence of such decomposition is that the field-free Hamiltonian matrix is not defective [50]. Although we have no formal proof of this property for the model Hamiltonian of [4], all Hamiltonian matrices we have encountered in practice do possess the full set of eigenvectors numerically.

Substituting equation (11) into equations (8)–(10), we readily obtain:

$$a(\infty) - a(t_i) = \int_{t_i}^{\infty} \sum_{LMj} g_{LMj} \exp \left( -\frac{i}{\hbar} (\mathcal{E}_{LMj}(t - t_i)) \right) dt,$$

$$g_{LMj} = \int d\Omega X^*(\vec{r}, t_i) \frac{i}{\hbar} [\hat{H}_S, \Theta] \frac{1}{r} f_{LMj}(r) Y_{LM}(\Omega_r),$$

where $\epsilon$ is the energy of the target state $X$ and the quantities $g_{LMj}$ are time-independent. The time integral in equation (14) converges, provided that $\Gamma_{LMj} > 0$ for all $L, M, j$ (state in the continuum) or the corresponding amplitude $f_{LMj}$ vanishes (bound state), yielding the final expression:
\[ a(\infty) - a(t_s) = \sum_{LM} \frac{\hbar R_{LM}}{(\varepsilon - E_{LM})^4 + \frac{1}{2} G_{LM}}. \]  

Note that equation (16) defines the overall amplitude as a coherent sum of Lorentzian line profiles, each associated with an eigenstate of the non-Hermitian field-free model Hamiltonian of the system.

If \( \hat{\mathcal{H}} - \varepsilon \) is a solution, equation (16) is formally equivalent to:

\[ a(\infty) - a(t_s) = \langle X | [\hat{\mathcal{H}}_S, \Theta] (\hat{\mathcal{H}} - \varepsilon)^{-1} | \Psi(t_s) \rangle \]

which makes an explicit connection between the work of [32, 51] and this work.

Equations (16) and (17) offer several possibilities for a practical implementation. For spherical-symmetric systems, considered presently, full diagonalization of the field-free model Hamiltonian is almost always a trivial task. Then, direct application of equations (15) and (16), which yields the ionization amplitude for any desired \( k, L, M \) with \( O(N_{\text{radial}}) \) additional effort, is computationally preferable. \( (N_{\text{radial}} \text{ is the dimensionality of the radial Hamiltonian within each } L, M \text{ channel}) \)

The preparatory steps in this approach require \( O(L_{\text{max}} N_{\text{radial}}^2) + O(L_{\text{max}} (M_{\text{max}} - M_{\text{min}} + 1) N_{\text{radial}}) \), respectively, for the diagonalization and eigenstate decomposition steps. This is the approach taken in the present work.

Alternatively, one can evaluate equation (17) by solving an auxiliary system of linear equations:

\[ (\hat{\mathcal{H}} - \varepsilon) |Z\rangle = |\Psi(t_s)\rangle, \]

\[ a(\infty) - a(t_s) = \langle X | [\hat{\mathcal{H}}_S, \Theta] |Z\rangle. \]

Equation (18) must be solved for each target energy \( \varepsilon \), at the cost of at least \( O(L_{\text{max}} (M_{\text{max}} - M_{\text{min}} + 1) N_{\text{radial}}) \) or more if \( \hat{\mathcal{H}} - \varepsilon \) cannot be evaluated in linear time. No preparatory steps are necessary in this case. If only a few energies are desired, or low symmetry of the problem precludes full diagonalization, this implementation becomes preferable. This is the approach taken by [32].

Finally, equation (17) can also be evaluated by applying the operator to the left instead:

\[ (\hat{\mathcal{H}} - \varepsilon) |Y\rangle = -i [\hat{\mathcal{H}}, \Theta] |X\rangle, \]

\[ a(\infty) - a(t_s) = \langle X | [\hat{\mathcal{H}}_S, \Theta] |Y\rangle, \]

where we assumed that \( \hat{\mathcal{H}}_S \) is Hermitian. Equation (20) needs to be solved for each \( L, M, \varepsilon \). Unless quantities \( |Y\rangle \) can be simplified or precomputed and stored (implying a small number of desired final photoelectron amplitudes), equation (20) is less numerically efficient than equation (18).

Equations (20) and (21) are reminiscent of the approach taken by [51], which simplifies evaluation of equation (20) by using Volkov states and physically-motivated approximations.

So far, equation (16) does not assume any particular form of the long-range Hamiltonian \( \hat{\mathcal{H}}_S \) or the associated functions \( X \). If we choose \( \hat{\mathcal{H}}_S \) to be the Volkov Hamiltonian, implying that the functions \( X \) are plane waves, we obtain an infinite-time correction to the surface-flux integral (equation (8)) of [1, 3]. Coherently combining this correction term with the time integral of equation (8), we obtain the ‘iSURFV’ method. It is applicable to small simulation volumes, where the wavepacket reaches the boundary before the end of the pulse. The result is obtained immediately after the end of the pulse, with no additional wavepacket propagation needed. However, similar to iSURF, for long-range potentials iSURFV may introduce artifacts if the final PES (see section 3 below).

On the other hand, if \( \hat{\mathcal{H}}_S \) is given by the Coulomb Hamiltonian and thus \( X \) are the Coulomb scattering functions, equation (16) yields corrections to the exact ionization amplitudes in the presence of a long-range potential. Unfortunately, no useful analytical solution is available for the Coulomb–Volkov Hamiltonian. These solutions could be evaluated numerically, but the required effort for a single final \( L, M, \varepsilon \) is comparable to the cost of numerically solving the TDSE for a central potential in a large, absorption-free simulation volume. For low-symmetry, molecular cases, it may be advantageous to combine a molecular calculation in a small volume with numerically-evaluated Coulomb–Volkov functions in equation (8). For the spherical-symmetric case considered here, we instead require that a simulation targeting Coulomb scattering functions uses a sufficiently large box, so that no absorption occurs by the end of the pulse \( t_s \) and the contribution from equation (8) vanishes. (Note that, somewhat counter-intuitively, we still require that a ‘perfect’ absorbing boundary is present, even though no absorption occurs.) This is the ‘iSURF’ method.

The following section gives some examples, illustrating applications of both techniques. The technical details of the implementation in the SCID-TDSE code [4] given in appendices A and B.

### 3. Illustration examples

#### 3.1. Few-photon ionization of the hydrogen atom ground state

We consider the hydrogen atom in its 1s ground state. The laser field is a linearly-polarized Gaussian pulse along the Cartesian Z direction, with a peak intensity of \( 4.0 \times 10^{12} \) W cm\(^{-2} \), a duration of 1.45 fs (FWHM), and a sine electric-field carrier. The central photon energy is 1 Hartree (27.2 eV).

The pulse has a finite duration of 4.6 fs \((t_1 = 70 \text{ au}[t]; t_2 = 95 \text{ au}[t])\); see equations (71) and (72) of [4]. We use a non-uniform grid, consisting of 10 points with a grid spacing of 0.0364 \( a_0 \) (\( a_0 \) is the Bohr radius) at the origin, followed by a 25-point logarithmic grid with a scaling parameter of 1.1, starting at 0.4 \( a_0 \) and a 965-point uniform grid with a spacing of 0.4 \( a_0 \) starting at 4.34 \( a_0 \). A transmission-free CAP [41] \((k_{\text{min}} = 0.2, \delta = 0.2)\) starts 357.9 \( a_0 \) from the origin and has a width of 32.8 \( a_0 \). The energy of the initial ground state calculated on this grid is \(-0.499988\) Hartree. We use a time step of 0.01 au\([t]\). The simulation includes angular channels with \( L \leq 4 \), and is converged to machine accuracy with respect to the angular momentum and the time step. The Coulomb potential was not modified.
The dividing surface is placed 347.9 \( a_0 \) away from the origin, 10 \( a_0 \) before the start of the absorber. By the end of the pulse, the entire population is still contained within the dividing surface. Therefore, we only calculate the infinite-time contributions to the iSURF PES. The total probability of ionization is 0.132\%, with the 1-, 2-, and 3-photon ionization peaks clearly visible in the spectra. The PES is cylindrically symmetric around the laser polarization direction. The XZ section of the PES is shown in figure 1. The iSURFV and iSURFC spectra are barely distinguishable on this scale. The lineouts of the spectra along the positive \( k \) direction are shown in figure 2. For final momenta exceeding \( \approx 0.3a_0/au[t] \) (kinetic energy of \( \approx 1.2 \) eV) the cross-sections (but not the phases, data not shown) calculated using the Volkov and Coulomb-state projection are virtually identical. However, careful examination of the low-energy part of the spectrum shows that the iSURFC spectrum goes smoothly to the expected cusp at zero energy. The Volkov projections, on the other hand, broadly follow the correct cross-sections, but show an increasingly oscillatory pattern when approaching zero momentum. This defect is expected: plane waves are an increasingly poor approximation to the Coulomb scattering wave for low final momenta. In principle, the range of \( k \) magnitudes where substantial distortions occur can be reduced by increasing the simulation volume. However, this procedure converges very slowly (as \( O(R_{\text{max}}^{-1/2}) \)). Alternatively, the problem could also be alleviated by using eikonal-Volkov states [2]. However, since eikonal-Volkov states are only approximately orthonormal [52], they potentially introduce other, hard to control, artifacts in the PES.

### 3.2. Strong-field ionization of the hydrogen atom ground state

Again, we start with the hydrogen atom in its 1s ground state. The structure of the radial grid and the parameters of the absorbing boundary are the same as in the previous example (section 3.1). The laser field is a linearly-polarized Gaussian pulse along the Cartesian \( Z \) direction, with a peak intensity of \( 1.0 \times 10^{13} \) W cm\(^{-2} \), a duration of 4.84 fs (FWHM), and a sine electric-field carrier. The central photon energy is 0.05695 Hartree (800 nm; 1.55 eV). The pulse has a finite duration of 11.9 fs \( (t_1 = 170 \text{ au}[t]; t_2 = 245 \text{ au}[t] \) [4]), comprising approximately five cycles. The simulations used a time step of 0.0025 au[t] and \( L_{\text{max}} = 60 \).

We start by calculating the PES using a large, \( R_{\text{max}} = 870 \text{ au} \) simulation box. This box is sufficient to contain the entire wavefunction at the end of the laser pulse. The resulting angle-resolved spectra are shown in figure 3.
All the expected features of a strong-field PES are clearly visible, including the multiple re-scattering rings, the holographic 'fingers', the ATI rings, the low-energy structures, etc. In the angle-integrated ATI spectrum (figure 3(c)), the \(2U_p\) and \(10U_p\) cut-offs and the low-energy structure are clearly visible. At final photoelectron momenta \(\geq 0.3\, \text{a}_0/\text{au}[t]\), the iSURFV and iSURFC spectra are visually indistinguishable. Zooming into the low-energy structure region, (figure 4), we see that all qualitative features of the LES are present in the iSURFV spectrum. However, these features are superimposed into the artefactual interferences due to the plane-wave final states, and may be difficult to discern without referring to the (exact) iSURFC spectrum.

The spectra in figures 3 and 4 are obtained using the final-time analysis of the total wavefunction, which remains entirely within the simulation box. The iSURFV spectrum is equivalent to the infinite-time limit of the tSURFF method. It is therefore instructive to examine the convergence of the tSURFF spectrum with the simulation time. The calculated cuts of the tSURFF spectra along the \(K_x = K_y = 0\) direction are shown in figure 5. Evaluating the tSURFF amplitudes immediately after the end of the laser pulse (the green curve) does not result in a useful spectrum. After additional 2000 au [t] \(\approx 50\, \text{fs}\); magenta curve), the spectra are converged in the plateau region \(0.5 \leq K_z \leq 1.3\, \text{a}_0/\text{au}[t]\). Fully converging the spectrum within the second plateau region \(K_z \leq 2.1\, \text{a}_0/\text{au}[t]\) requires the simulation to continue for \(10^7\, \text{au}[t]\) \((2.5\, \text{ps};\ \text{brown curve})\). At shorter simulation times, the spectrum may appear to converge in some regions, but remains unconverged for similar momenta in the opposite direction \((10^4\, \text{au}[t])\), gold curve). Remarkably, coherently adding the iSURFV correction at the end of the laser pulse to the tSURFF spectrum (blue line) results in an essentially converged simulation, at the negligible additional cost compared to the tSURFF simulation alone (green line). We note that an ad-hoc technique for accelerating convergence of the tSURFF time integral has also been proposed in [36].

None of the tSURFF and iSURFV simulations converge to the correct result in the low-energy region (figure 5 insert). The level of artifacts in the LES region decreases with an increasing radius of the matching sphere; however, the convergence is extremely slow.

### 3.3. Strong-field ionization of the ‘argon’ \(3p_{-1}\) state in a circularly polarized field

Our final example involves calculation of the photoelectron spectrum of the \(3p_{-1}\) state of the ‘argon 2P’ effective potential, fitted to reproduce valence and Rydberg one-
Figure 5. Photoionization probabilities for $K_i = K_f = 0$, calculated with the tSURFF method for different time delays. Pulse parameters are the same as in figure 3. The dividing surface is taken at 266 $a_0$, with the interaction potential truncated smoothly to zero between 240 and 260 $a_0$. Photoelectron spectra sections calculated with the iSURFV and iSURFC (using dividing surface at 828 $a_0$), and iSURFV spectra with dividing surface at 266 $a_0$ are shown for comparison. The inset shows the PES convergence in the low-energy region for the iSURFC, iSURFV, and tSURFF calculations.

Figure 6. Magnitudes of the ionization amplitudes for the "argon 2P" $3p_{-1}$ in a 0.73 fs, circularly polarized (XY plane) field with a peak intensity of $2 \times 10^{14}$ W cm$^{-2}$ and a central photon energy of 4.08 eV. (a) Amplitude isosurface for the counter-rotating field; (b) Amplitude isosurface for the co-rotating field. The isosurfaces are at the 0.04 (au[t]/$a_0$)$^{-3/2}$ level; (c) $K_x$, $K_y$ section of the (a)–(b) difference. The color scheme is logarithmic. The radial box extent is 455 $a_0$. The matching sphere is at 413 $a_0$.

The laser field is a Gaussian pulse, circularly-polarized within the Cartesian XY plane. The pulse has a peak intensity of $2 \times 10^{14}$ W cm$^{-2}$, a duration of 0.73 fs (FWHM), and sine (X axis) and cosine (Y axis) carrier–envelope phases. The central photon energy is 0.15 Hartree (4.08 eV; 304 nm). The pulse has a finite duration of 4.6 fs ($t_1 = 70$ au[t]; $t_2 = 95$ au[t]; see equations (71) and (72) of [4]). We use a non-uniform grid, consisting of 50 points with a grid spacing of 0.0392 $a_0$ at the origin, followed by a 104-point logarithmic grid with the scaling parameter of 1.02, starting at 15.4 $a_0$.

Particle states of the argon atom:

$$v_{2p} (r) = -\frac{1}{r} \left( 1 + 7.625195 e^{-1.02557r} - \frac{124.55}{1 + e^{10(r-0.37110)}} \right)$$  \hspace{1cm} (22)

The simulation includes angular channels with $L \leq 18$, and is converged to machine accuracy with respect to the angular momentum and the time step.

The iSURFC PES in the large, 455 $a_0$ simulation box are shown in figure 6. For the laser field co-rotating with the initial state, absorption of the IR photons leads to an increase in the photoelectron angular momentum, following the usual selection rules. This results in the pronounced ‘doughnut’ structure in the 3D spectrum (panel b). The counter-rotating field, on the other hand (panel a) can populate states with $L = 0$, filling out the spectrum at low final momenta. In both cases, the peak of the ionization probability is found at $\approx 0.54a_0$/au[t], close to where the first ATI peak would be expected in a CW field of the same intensity and frequency ($\approx 0.4a_0$/au[t]). Subtraction of the counter- and co-rotating PES (panel c) reveals a clear ATI progression on one of the
sides of the distribution, where the two sub-cycle bursts found in the counter-rotating case interfere. In the opposite direction, a smooth, featureless spectrum is seen, with a strong energy dependence in the final emission direction for the two fields.

Next, we examine the convergence of the iSURFV result with respect to the position of the matching sphere. In order to guarantee that the physical Hamiltonian coincides with the Volkov Hamiltonian outside of the matching sphere \( R_0 \), we truncate the long-range part of the potential by applying the transformation:

\[
\begin{align*}
\psi_{\text{cut}}(r) &= (v(r) + v_{\text{shift}}) f_{\text{mask}}(r), \\
f_{\text{mask}} &= \begin{cases} 
1, & r \leq R_0, \\
\frac{1}{2} - \frac{1}{2} f_B \left( f_B \left( 2 \frac{r - R_0}{r - R_X} - 1 \right) \right), & R_0 \leq r \leq R_X, \\
0, & r \geq R_X,
\end{cases}
\end{align*}
\]

In equation (23), \( f_B \) is the Becke’s switching function \([54]\). The resulting shifted and masked potential \( \psi_{\text{cut}} \) is smooth to \( O(r^3) \). The masking radii \( R_0 \) and \( R_X \) are chosen 22 and 2 \( a_0 \) before the matching sphere. The vertical shifts are 9.3, 4.89, and 3.28 mH, respectively, for the simulation boxes of 155, 255, and 355 \( a_0 \).

The cuts in the calculated photoionization probabilities along the \( K_x = K_z = 0 \) direction are collected in figure 7. The Volkov-state projection calculated with the smallest matching sphere radius (155 \( a_0 \), green line) agrees well with the ‘exact’
iSURFC spectrum for final momenta between 0.3 and 1.0 $a_0$/au. Matching further away from the origin (255 $a_0$, magenta line) leads to a virtually converged spectrum for $0.2 \leq |K| \leq 2.4$ $a_0$/au. Finally, Volkov projection at 355 $a_0$ (gold line) is identical to the exact result for $|K| \geq 0.2$, and is limited by the numerical accuracy of the underlying type.

The situation however changes if one considers angular-resolved distributions. In figure 8 we show constant-momentum cuts of the ionization probability in the $K_z = 0$ plane. Because the three tSURFF/iSURF simulations use slightly different potential shifts (see above), the cuts are taken at slightly different $|K|$ values, corresponding to absorption of the same energy from the laser field. Because the photoelectron distributions in this range of $K$ are smooth, the exact position of the $K$ cut does not materially affect the discussion. The maximum and minimum of the ‘exact’ distribution are found at, respectively, 145.5° and 26.5° with respect to the laboratory $X$ axis direction. For the smallest (155 $a_0$) matching sphere, the Volkov projection leads to the maximum appearing at 148.0°, with the minimum at 26.0°. More importantly the shape of the angular dependence is substantially different. Increasing the size of the matching sphere moves the position of the maximum to 144.0 for both 255 and 355 $a_0$ spheres. The minimum is found at 26.0° for both spheres. While a 1.0° deviation in the position of the maximum does not appear to be critical, for 1.6 μm driving field, for example, this would correspond to a 15-attosecond error in an attoclock measurement [14]—comparable to the measured time delays [55]. Furthermore, the convergence of the tSURFF and iSURF angular distributions with the matching-sphere radius appears to be extremely slow.

4. Conclusions

We show that the surface-flux approach for calculation of PES [1–3, 35] allows natural, analytical continuation to infinite time. For large-box simulations, where the entire wavefunction remains within the simulation volume at the end of the pulse, the infinite-time form can be used to evaluate the ‘exact’ ionization probabilities and phases for both long- and short-range potentials (the iSURFC approach). The knowledge of the asymptotic form of the scattering solutions is sufficient for these calculations; it is not necessary to evaluate scattering states in the vicinity of the origin.

For small simulation volumes, where parts of the electron probability reach the absorber while the laser field is still on, it is no longer possible to evaluate the projection onto the exact scattering states. However, the infinite-time continuation can still be applied to the Volkov states (becoming plane waves in the absence of the laser field). This correction can be combined coherently with the Volkov-state continuation (‘tSURFF’), yielding the iSURF approach. This technique produces the same, well-documented artifacts [3] as the ‘tSURFF’ approach. However, it affords the fully-converged projection onto the Volkov states immediately after the end of the laser pulse, without the need for tedious field-free propagation.

Acknowledgments

We would like to thank Armin Scrinzi for inspiring discussions and for his helpful advice. We would also like to thank Misha Ivanov for his support and encouragement, and Maria Richter for her suggestions and corrections. We would like to acknowledge support from the Deutsche Forschungsgemeinschaft project SM 292/2-3.

Appendix A. Implementation of tSURFF and iSURFV

In SCID-TDSE, the time-dependent wavefunction has the form:

$$\Psi(\vec{r}, t) = \frac{1}{\pi} \sum_{LM} \Psi_{LM}^{\gamma}(\vec{r}, t) Y_{LM}(\Omega_r).$$  \hspace{1cm} (A.1)

The Volkov functions are given by

$$X = \frac{1}{(2\pi)^{2/3}} \exp(\vec{K}\vec{r}) \exp\left(-\frac{1}{2m} \int_0^t (\vec{K}^2 - e\vec{A})^2 dt\right).$$ \hspace{1cm} (A.2)

where the plane wave term can be expressed in a spherical harmonics expansion (see [56], section 5.17, formula 165)

$$\exp(\vec{K} \cdot \vec{r}) = 4\pi \sum_{LM} \vec{H}_{LM} Y_{LM}(\Omega_r) Y^*_{LM}(\Omega_r),$$ \hspace{1cm} (A.3)

where $j_L(kr)$ are the spherical Bessel functions.

Then, the integral in equation (10) becomes

$$\int d\Omega_r^\gamma \frac{1}{\hbar} [\hat{H}_\gamma, \Theta] \Psi = \sum_{LM} \left\{ F_{LM} \Psi^\gamma_{LM} + G_{LM} \frac{\partial}{\partial \Omega} \Psi^\gamma_{LM} \right\},$$  \hspace{1cm} (A.4)

where

$$F_{LM} = c\frac{\gamma^*}{m} (-i)^{L+1} \frac{k}{2} Y_{LM}(\Omega_k) \frac{1}{2L+1} (Lj_{L+1}(kr)$$

$$- (L+1)j_{L-1}(kr)) + eA_z (C_{LM} Y_{L-1,M}(\Omega_k)j_{L-1}(kr)$$

$$- C_{L+1,M} Y_{L+1,M}(\Omega_k)j_{L+1}(kr)) \},$$  \hspace{1cm} (A.5)

$$G_{LM} = \frac{c^*}{m} \frac{\gamma^*}{2} \frac{L^2 - M^2}{2L + 1} Y_{LM}(\Omega_k)j_L(kr),$$ \hspace{1cm} (A.6)

$$C_{LM} = \left( \frac{L^2 - M^2}{4L^2 - 1} \right)^{1/2},$$ \hspace{1cm} (A.7)

$$c^* = \frac{4\pi}{(2\pi)^{1/2}} \exp\left(\frac{i}{2m} \int_0^t (\vec{K}^2 - e\vec{A})^2 dt\right).$$  \hspace{1cm} (A.8)
Appendix B. Implementation of iSURFC

For the Coulomb-state projection in equations (15) and (16), it is convenient to work with the outgoing Coulomb spherical waves. A numerically accurate implementation of the Coulomb spherical waves and their derivatives is available in [29]. The surface integral in equation (15) can then be evaluated directly as written.

For comparison to experimental angle- and energy-resolved spectra it is then necessary to project the outgoing spherical Coulomb wavepacket onto a Rutherford scattering state [57]. The Coulomb wavepacket with the radial wavevector $k$ is given by:

$$
\Psi_k(r) = \frac{1}{2} \sum_{LM} a_{LM} Y_L^M(\Omega_r) F_{LM}(r),
$$

where $F_{LM}(r)$ are Coulomb spherical waves. $F_{LM}$ are normalized to $\delta(k - k')$. At large $r$, it is given by [57]:

$$
F_{LM} \rightarrow 2\sin \left( kr + \frac{1}{2} \log(2kr) - \frac{\pi L}{2} + \varphi_L \right),
$$

where

$$
\varphi_L = \arg \left( i \left( L + 1 - \frac{i}{k} \right) \right).
$$

The Rutherford scattering solution (the ‘Coulomb plane wave’) normalized $\delta(k - k')$, is asymptotically given by [57]:

$$
w(k) = \sqrt{\frac{2}{\pi}} \frac{1}{k} \sum_{L'} \int_{L'} \exp(i\varphi_{L'}) \sin \left( k'r + \frac{1}{2} \log(2k'r) - \frac{\pi L'}{2} + \varphi_{L'} \right) \times Y_{L'}^*(\Omega_k) Y_L^M(\Omega_r) \text{d}L'.
$$

Calculating an overlap between $\Psi_k$ and $w(k)$, we immediately obtain amplitudes $b_L$ of the Rutherford states:

$$
b_L = \sum_{LM} \frac{1}{2\pi k} \frac{1}{L} (-i)^L \exp(-i\varphi_L) Y_L^M(\Omega_k) a_{LM}.
$$

Appendix C. Evaluation of spherical harmonics

Calculation of photoelectron spectrum requires the repeated evaluation of spherical harmonics $Y_{LM}$, potentially for high values of angular momenta $L$ and $M$ ($L \leq 5000$). We find that the following recurrence formulae are fast and numerically stable for large $L$ and $M$:

$$
Y_{L0} = \frac{1}{\sqrt{4\pi}},
$$

$$
Y_{L,1,0} = 1 \sqrt{\frac{2L+1}{2L}} \exp(i\varphi \sin(\theta)),
$$

$$
Y_{L,-1,0} = -i \sqrt{\frac{2L+1}{2L}} \exp(-i\varphi \sin(\theta)),
$$

and finally:

$$
Y_{LM} = i^{(L' - 1)/2} \sqrt{\frac{2L+1}{2L}} \sqrt{\frac{L' - 1}{L' - 2}} \frac{L - 1}{2L - 3} \frac{L - M}{L' - M} Y_{L',M'},
$$

These recurrences formulae allow for the calculation of a range of $L$ values for a fixed $M$, without having to evaluate all intermediate $M$.

References

[1] Ermolaev A M, Puzyrin I V, Selin A V and Vinitsky S I 1999 Phys. Rev. A 60 4831–45
[2] Ermolaev A M and Selin A V 2000 Phys. Rev. A 62 015401
[3] Tao L and Scriinzi A 2012 New J. Phys. 14 013021
[4] Patchkovskii S and Muller H 2016 Comput. Phys. Commun. 199 153–69
[5] Wu G, Hockett P and Stolow A 2011 Phys. Chem. Chem. Phys. 13 18447–67
[6] Chandler D W and Houston P L 1987 J. Chem. Phys. 87 1445–7
[7] Bordas C, Paulig F, Helm H and Huestis D L 1996 Rev. Sci. Instrum. 67 2257–68
[8] Dörner R, Merkel V, Jagutzki O, Ullrich J, Moshammer R and Schmidt-Böcking H 2000 Phys. Rep. 330 95–192
[9] Agostini P, Fabre F, Mainfray G, Petie G and Rahman N K 1979 Phys. Rev. Lett. 42 1127–30
[10] Weber T, Giessen H, Weckenbrock M, Urbasch G, Staudte A, Spielerberger L, Jagutzki O, Merkel V, Vollmer M and Dörner R 2000 Nature 405 658–61
[11] Moshammer R et al 2000 Phys. Rev. Lett. 84 447–50
[12] Feuerstein B et al 2001 Phys. Rev. Lett. 87 043003
[13] Huisman Y et al 2011 Science 331 61–4
[14] Eckle P, Smolarski M, Schlup P, Biegert J, Staudte A, Schöffler M, Muller H G, Dörner R and Keller U 2008 Nat. Phys. 4 565–70
[15] Torlina L et al 2015 Nat. Phys. 11 503–8
[16] Paul P M, Toma E, Breger P, Mullot G, Augé F, Balcou P, Muller H G and Agostini P 2001 Science 292 1689–92
[17] Itatani J, Quéré F, Yudin G L, Ivanov M Y, Krausz F and Corkum P B 2002 Phys. Rev. Lett. 88 173903
[18] Tong X M and Chu S I 1997 Chem. Phys. 217 119–30
[19] Nurudina M and Faisal P H M 1999 Phys. Rev. A 60 3125–33
[20] Muller H G 1999 Laser Phys. 9 138–48
[21] Borisov A G 2001 J. Chem. Phys. 114 7770–7
[22] Bauer D and Koval P 2006 Comput. Phys. Commun. 174 396–421
[23] Guan X, Noble C J, Zatsarinny O, Bartschat K and Schneider B I 2006 Comput. Phys. Commun. 174 396–421
[24] Sorevik T, Birkeland T and Okša G 2009 J. Comput. Appl. Math. 225 56–67
[25] Tong X M and Toshima N 2011 Comput. Phys. Commun. 182 21–3
[26] Dziubak T and Matulewski J 2012 Comput. Phys. Commun. 183 800–12
