iSURF: A family of infinite-time surface flux methods

F. Morales¹, T. Bredtmann, and S. Patchkovskii¹

¹Max-Born-Institute, Max-Born-Strasse 2A, D-12489 Berlin, Germany

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

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, 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 ([1, 2, 3]), 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 Time Dependent Schrödinger Equation (TDSE) solver [4].

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 photo-ionized 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 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, 11, 12], and facilitate advanced experimental methods such as time-resolved photoelectron holography [13], or the attoclock setup [14, 15]. In addition, photoelectron spectra 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 (see for example [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 4]) and extracting accurate photoelectron

spectra. The commonly accepted formal definition of the PES for 1-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]: This method uses a energy-dependent window function to project onto the real field-free Hamiltonian of the system. Here, only the absolute value of the PES amplitude is retrieved. 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 [31, 32, 33] for recent examples): This is an exact method that 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 any finite k grid. The wavefunction needs to remain within the simulation volume.
- Volkov-state continuation (also known as tSURFF)[1, 2, 34, 3]: This method is designed to remove the requisite of retaining the entire wavefunction remaining within the simulation volume, which might become prohibitively expensive for the case of an intense infrared laser field. In this approach, the ponderomotive potential and the free-electron oscillation amplitude are assumed to be large. Here, 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

introduces 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 [35] (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) ([36, 37, 38, 39, 40, 41, 42, 43]), making the Hamiltonian non-Hermitian. 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 the non-Hermiticity of the field-free 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 described above.

For simulation volumes large enough to contain the entire wavefunction at the end of the laser pulse, the 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. This method we refer to as the iSURFC method.

The rest of this paper is structured as follows: we start 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 the two implemented target functions (Volkov and Coulomb states) with a naive implementation of the original tSURFF method.

2. Theory

We begin by recapitulating the derivation of the surface-flux approach to calculate PES. The technique was originally developed by Ermolaev et al. [1, 2] and Serov et al. [34], and popularized by Tao et al. [3]. The discussion is this section closely follows Ref.[3].

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

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi. \tag{1}$$

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

$$i\hbar \frac{\partial}{\partial t}X = \hat{H}_S X,\tag{2}$$

or, equivalently:

$$-i\hbar \frac{\partial}{\partial t}X^* = X^*\hat{H_S}. \tag{3}$$

The projection of Ψ onto X is given by:

$$a_X(t_0) = \int d\vec{r} \{ X^*(\vec{r}, t_0) \Psi_S(\vec{r}, t_0) \}$$
(4)

For example, if X belongs the continuum part of the spectrum, a_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:

$$a(t_0) =_{t_0 \to \infty} \int d\vec{r} \{ X^*(\vec{r}, t_0) \hat{\Theta}_S \Psi(\vec{r}, t_0) \}, \tag{5}$$

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

$$\hat{\Theta}_S = \begin{cases} 0, & r < R_0 \\ 1, & r \ge R_0 \end{cases}$$
 (6)

If we further assume that at some initial time t_i the wavepacket Ψ is localized near the origin, so that:

$$\hat{\Theta}_S \Psi(\vec{r}, t_i) \equiv 0 \tag{7}$$

eq. 5 can be re-written as a time integral:

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

$$= \int_{t_i}^{t_0} dt \frac{\partial}{\partial t} \int dr \frac{i}{\hbar} X^* \{ \hat{H}_S \hat{\Theta}_S - \hat{\Theta}_S \hat{H} \} \Psi.$$
 (8)

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 eq. 8 becomes a commutator $[\hat{H}_S, \hat{\Theta}_S] \equiv [\hat{H}, \hat{\Theta}_S]$. 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:

$$\hat{H}_S = \frac{1}{2m}(\hat{p} - e\vec{A})^2 = \frac{1}{2m}(-i\hbar\hat{\nabla} - e\vec{A})^2,$$
(9)

the volume integral in eq. 8 becomes:

$$b(t) = \int dr X^* \frac{i}{\hbar} [\hat{H}_S, \Theta] \Psi$$

=
$$\int_{R_0} d\Omega_r r^2 \{ \frac{i\hbar}{2m} (\frac{\partial X^*}{\partial r} \Psi - X^* \frac{\partial \Psi}{\partial r}) - \frac{e}{m} A_r X^* \Psi \},$$
(10)

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 Ψ . This property makes it possible to directly calculate ionization amplitudes using an L^2 representation of Ψ .

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

2.1. Analytical continuation of the time integral

Calculation of ionization amplitudes using eqs. 8-10 requires 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 can be trivially expanded over the eigenfunctions of the field-free Hamiltonian, giving its evolution at all future times analytically. Using the same non-Hermitian spherical-coordinate representation as in Ref. [4]:

$$\Psi(t) = \frac{1}{r} \sum_{LMj} f_{LMj} \Phi_{LMj}^{R}(r) Y_{LM}(\Omega_r) \exp\left(-\frac{\mathbf{i}}{\hbar} \mathcal{E}_{LMj}(t - t_x)\right), \tag{11}$$

$$\mathcal{E}_{LMj} = E_{LMj} - \frac{\mathbf{i}}{2} \Gamma_{LMj}, \tag{12}$$

$$f_{LMj} = \int dr \int d\Omega_r Y_{LM}^* (\Omega_r) \Phi_{LMj}^L (r) \Psi(t_x), \qquad (13)$$

where Φ_{LMj}^R and Φ_{LMj}^L are respectively the right and left eigenvector of the field-free Hamiltonian, associated with the complex energy \mathcal{E}_{LMj} . E_{LMj} and Γ_{LMj} are the energy and the lifetime of the state LMj. Finally, L and M are the usual orbital quantum numbers and j is the ordinal number of the state within each L, M channel. The finite lifetimes $\Gamma_{LMj} > 0$ are the consequence of the population being absorbed by the boundary. Eq. 11 is applicable for all $t \geq t_x$.

Substituting eq. 11 into eqs. 8–10, we readily obtain:

$$a\left(\infty\right) - a\left(t_{x}\right) = \int_{t_{x}}^{\infty} \sum_{LMj} g_{LMj} \exp\left(\frac{\mathbf{i}}{\hbar} \left(\epsilon - \mathcal{E}_{LMj}\right) \left(t - t_{x}\right)\right) dt, \tag{14}$$

$$g_{LMj} = \int dr X^*(r, t_x) \frac{i}{\hbar} [\hat{H}_S, \Theta] \frac{1}{r} f_{LMj} \Phi_{LMj}^R(r) Y_{LM}(\Omega_r), \qquad (15)$$

where ϵ is the energy of the target state X and the quantities g_{LMj} are time-independent. The time integral in eq. 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:

$$a\left(\infty\right) - a\left(t_{x}\right) = \mathbf{i} \sum_{LMj} \frac{\hbar g_{LMj}}{\left(\epsilon - E_{LMj}\right) + \frac{\mathbf{i}}{2} \Gamma_{LMj}}.$$
(16)

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

So far, eq. 16 does not assume any particular form of the long-range Hamiltonian \hat{H}_S or the associated functions X. If we choose \hat{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 (eq. 8) of Refs. [1, 3]. This is the "iSURFV" method.

On the other hand, if H_S is given by the Coulomb Hamiltonian and thus X are the Coulomb scattering functions, eq. 16 yields *exact* ionization amplitudes in the presence of a long-range potential. This is the "iSURFC" 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 4.0×10^{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 eqs. 71-72 of Ref. [4]). We use a non-uniform grid, consisting of 10 points with a grid spacing of 0.0364 Bohr at the the origin, followed by a 25-point logarithmic grid with a scaling parameter of 1.1, starting at 0.4 Bohr, and a 965-point uniform grid with a spacing of 0.4 Bohr starting at 4.34 Bohr. A transmission-free complex absorbing potential[40] $(k_{min} = 0.2, \delta = 0.2)$ starts 357.9 Bohr from the origin and has a width of 32.8 Bohr. 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 Bohr away from the origin, 10 Bohr 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 photoelectron spectra. 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_z direction are shown in Fig. 2. For final momenta exceeding ≈ 0.3 Bohr/jiffy (kinetic energy of ≈ 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 [44], they

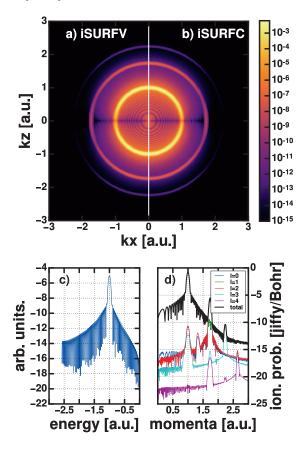


Figure 1. Angle-resolved photoelectron spectra for H(1s) and a 1.45 fs 4.0×10^{12} W cm⁻² pulse with a central photon energy of 27.2 eV. The panels are: (a) The left panel is for the Volkov-state projection (iSURFV); (b) The right panel is for the Coulomb scattering state projection (iSURFC); (c) Spectral content of the ionizing pulse; (d) Energy-resolved PES for the iSURFC projection. The background features are due to one-photon ionization by the pulse wings, arising from temporal truncation of the Gaussian.

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 (Sec. 3.1). The laser field is a linearly-polarized Gaussian pulse along the Cartesian Z direction, with a peak intensity of 1.0×10^{14} 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 5 cycles. The simulations used a time step of 0.0025 jiffies and $L_{\text{max}} = 60$.

We start by calculating the PES using a large, $R_{\text{max}} = 870$ Bohr simulation box. This box is sufficient to contain the entire wavefunction at the end of the laser pulse.

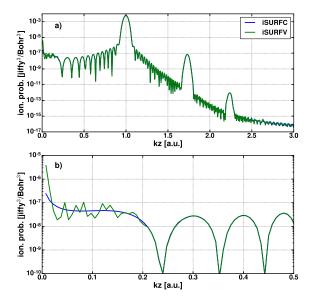
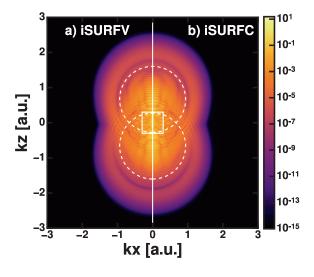


Figure 2. Cuts of the photoelectron spectra of Fig. 1 along the positive direction of the k_z axis. The Coulomb-wave (iSURFC) and Volkov-state (iSURFV) projections are given by blue and green lines, respectively. Panel (a) shows the full range of photoelectron momenta; panel (b) shoes the low-momentum part of the spectrum.

The resulting angle-resolved spectra are shown in Figure 3. All the expected features [45] 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 3c), the $2U_p$ and $10U_p$ cut-offs and the low-energy structure are clearly visible. At final photoelectron momenta ≥ 0.3 Bohr/jiffy, 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 jiffies (≈ 50 fs; magenta curve), the spectra are converged in the plateau region ($0.5 \le K_z \le 1.3$ Bohr/jiffy). Fully converging the spectrum within the second plateau region ($K_z \le 2.1$ Bohr/jiffy) requires the simulation to continue for 10^5 jiffies (2.5 picoseconds; brown curve). At lower simulation times, the spectrum may appear to converge in some regions, but remains unconverged for similar momenta in the opposite direction (10^4 Bohr/jiffy, gold curve). Remarkably, coherently adding the



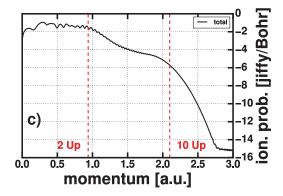


Figure 3. Angle-resolved photoelectron spectrum for H(1s) and a 4.84 fs 1.0×10^{14} W cm⁻², 800 nm pulse, with the dividing surface at 827.9 Bohr, 10 Bohr before the start of the absorber. The panels are: (a) The left panel is for the Volkov-state projection (iSURFV); (b) The right panel is for the Coulomb scattering state projection (iSURFC); (c) The energy-resolved iSURFC photoelectron spectrum. The $2U_p$ re-scattering rings are indicated with dotted rings. The iSURFV and iSURFC PES are visually indistinguishable on this scale. The part of the spectrum indicated by the white square in panel (a) is shown in Fig. 4.

iSURFV term 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 [35].

None of the tSURFF and/or 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.

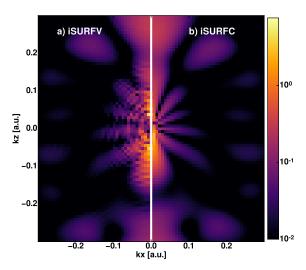


Figure 4. The low-energy structures in the photoelectron spectra for H(1s) strong-field ionization. The pulse parameters are the same as in Fig. 3. The panels are: (a) The left panel is for the Volkov-state projection (iSURFV); (b) The right panel is for the Coulomb scattering state projection (iSURFC).

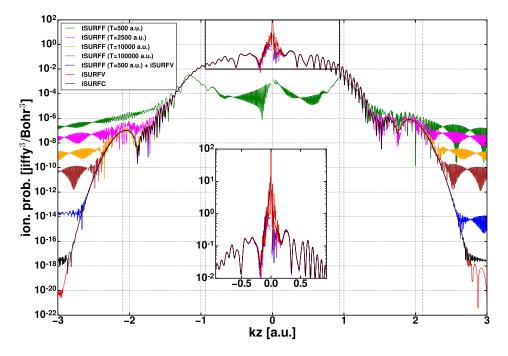


Figure 5. Photoionization probabilities for $K_x = K_y = 0$, calculated with the tSURFF method for different time delays. Pulse parameters are the same as in Figure 3. The dividing surface is taken at 266 Bohr, with the interaction potential truncated smoothly to zero between 240 and 260 Bohr. Photoelectron spectra sections calculated with the iSURFV and iSURFC (using dividing surface at 828 Bohr), and the coherent sum of the tSURFF and iSURFV spectra at the end of the pulse are shown for comparison. The insert shows the PES convergence in the low-energy region for the iSURFC, iSURFV, and tSURFF calculations.

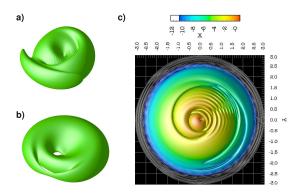


Figure 6. Magnitudes of the ionization amplitudes for the "Argon 2P" $3p_{-1}$ in a 0.73 fs, circularly polarized (XY plane) field with a peak intensity of 2×10^{14} W cm⁻² and a central photon energy of 4.08 eV. a) Amplitude isosurface for the counterrotating field; b) Amplitude isosurface for the co-rotating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

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-particle states of the Argon atom:

$$v_{Ar2P}(r) = -\frac{1}{r} \left(1 + 7.625195 \mathbf{e}^{-1.02557r} - \frac{124.55}{1 + \mathbf{e}^{10(r - 0.37110)}} \right). \tag{17}$$

The laser field is a Gaussian pulse, circularly-polarized within the Cartesian XY plane. The pulse has a peak intensity of 2.0×10^{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 eqs. 71-72 of Ref. [4]). We use a non-uniform grid, consisting of 50 points with a grid spacing of 0.0392 Bohr at the the origin, followed by a 104-point logarithmic grid with the scaling parameter of 1.02, starting at 2.0 Bohr, and a uniform grid with a spacing of 0.3 Bohr starting at 15.4 Bohr. A transmission-free complex absorbing potential [40] ($k_{min} = 0.2$, $\delta = 0.2$) with a width of 32.8 Bohr is used. The energy of the initial ground state calculated on this grid is -0.569 Hartree. We use a time step of 0.005 jiffy. 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 photoelectron spectra in the large, 455 Bohr 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

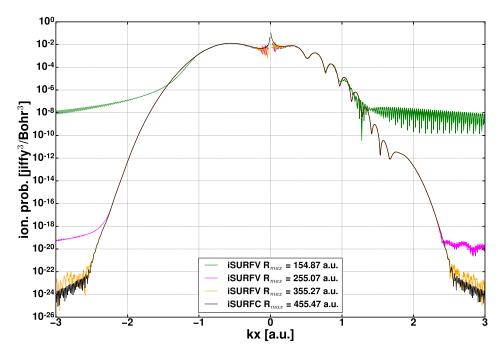


Figure 7. Cut through $K_y = K_z = 0$ for the co-rotating angular distribution in Figure 6b. The projection of the Coulomb states (iSURFC, black) is for the 455 Bohr box. The Volkov-state projections are calculated as a coherent sum of the "tSURFF" projection up to the end of the pulse and the iSURFV infinite-time correction. The Volkov-state projections are for the boxes of 155 (green), 255 (magenta), and 355 Bohr (orange). In all cases, the matching surface is placed 42 Bohr before the end of the box.

states with L=0, filling out the spectrum at low final momenta. In both cases, the peak of the ionization probability is found at ≈ 0.54 Bohr/jiffy, close to where the first ATI peak would be expected in a CW field of the same intensity and frequency (≈ 0.4 Bohr/jiffy). 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 [3], we truncate the long-range part of the potential by applying the transformation:

$$v_{\text{cut}}(r) = (v(r) + v_{\text{shift}}) f_{\text{mask}}(r)$$

$$f_{\text{mask}} = \begin{cases} 1, & r \leq R_0 \\ \frac{1}{2} - \frac{1}{2} f_{\text{B}} \left(f_{\text{B}} \left(f_{\text{B}} \left(2 \frac{r - R_0}{r - R_{\text{X}}} - 1 \right) \right) \right), & R_0 \leq r \leq R_{\text{X}} \\ 0, & r \geq R_{\text{X}} \end{cases}$$
(18)

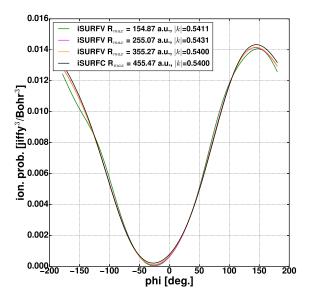


Figure 8. Cut through $K_z = 0$, |K| = 0.54 for the co-rotating angular distribution in Figure 6b. The K magnitude was adjusted for the overall shift in the potential due to the long-range part truncation (see text). The simulation parameters and line colors are the same as in Figure 7.

$$f_{\rm B} = \frac{3}{2}x - \frac{1}{2}x^3.$$

In eq. 18, $f_{\rm B}$ is the Becke's switching function [46]. The resulting shifted and masked potential $v_{\rm cut}$ is smooth to $O(r^7)$. The masking radii R_0 and $R_{\rm X}$ are chosen 22 and 2 Bohr 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 Bohr.

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 Bohr, green line) agrees well with the "exact" iSURFC spectrum for final momenta between 0.3 and 1.0 Bohr/jiffy. Matching further away from the origin (255 Bohr, magenta line) leads to a virtually converged spectrum for $0.2 \le |K| \le 2.4$ Bohr/jiffy. Finally, Volkov projection at 355 Bohr (gold line) is identical to the exact result for $|k| \ge 0.2$, 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/iSURFV 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 degrees with respect to the laboratory X axis direction. For the smallest (155 Bohr) matching sphere, the Volkov projection leads to

the maximum appearing at 148.0 degrees, with the minimum at -26.0 degrees. 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 Bohr spheres. The minimum is found at -26.0 degree for both spheres. While a 1.0 degree deviation in the position of the maximum does not appear to be critical, for 1.6μ m driving field, for example, this would correspond to a 15-attosecond error in an attoclock measurement [14] – comparable to the measured time delays [47]. Furthermore, the convergence of the tSURFF and iSURFV angular distributions with the matching-sphere radius appears to be extremely slow.

4. Conclusions

We show that the surface-flux approach for calculation of photoelectron spectra [1, 2, 34, 3] 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 in 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 iSURFV 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.

5. 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. We would like to acknowledge support from the Deutsche Forschungsgemeinschaft project SM 292/2-3.

6. Appendix

6.1. Implementation of tSURFF and iSURFV

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

$$\Psi(\vec{r},t) = \frac{1}{r} \sum_{LM} \Psi_{LM}^R(r,t) Y_{LM}(\Omega_r). \tag{19}$$

The Volkov functions are given by:

$$X = \frac{1}{(2\pi)^{2/3}} exp\left(i\vec{k}\vec{r}\right) exp\left(-\frac{i}{2\hbar m} \int_{t_i}^t (\hbar \vec{k} - e\vec{A})^2 dt\right),\tag{20}$$

where the plane wave term can be expressed in a spherical harmonics expansion (see [48], section 5.17, formula 14, page 165)

$$exp\left(i\vec{k}\cdot\vec{r}\right) = 4\pi \sum_{LM} i^L j_L(kr) Y_{LM}(\Omega_k) Y_{LM}^*(\Omega_r), \tag{21}$$

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

Then, the integral in eq.10 becomes:

$$\int dr X^* \frac{i}{\hbar} [\hat{H}_S, \Theta] \Psi = \sum_{LM} \{ F_{LM} \Psi_{LM}^R + G_{LM} \frac{\partial}{\partial r} \Psi_{LM}^R \}, \tag{22}$$

where

$$F_{LM} = \frac{c^* r}{m} (-i)^{L+1} \left[\frac{\hbar k}{2} Y_{LM} (\Omega_k) \frac{1}{2L+1} (L j_{L+1} (kr) - (L+1) j_{L-1} (kr)) \right]$$

$$+eA_{z}\left(C_{L,M}Y_{L-1,M}\left(\Omega_{k}\right)j_{L-1}\left(kr\right)-C_{L+1,M}Y_{L+1,M}\left(\Omega_{k}\right)j_{L+1}\left(kr\right)\right)\right],\quad(23)$$

$$G_{LM} = \frac{c^* r}{m} (-i)^{L+1} \frac{\hbar}{2} Y_{LM} (\Omega_k) j_L(kr),$$
(24)

$$C_{LM} = \left(\frac{L^2 - M^2}{4L^2 - 1}\right)^{1/2},\tag{25}$$

and

$$c^* = \frac{4\pi}{(2\pi)^{3/2}} exp\left(\frac{i}{2\hbar m} \int_{t_i}^t \left(h\vec{k} - e\vec{A}\right)^2 dt\right). \tag{26}$$

6.2. Implementation of iSURFC

For the Coulomb-state projection in eqs. 15,16, 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 eq. 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 [49]. The Coulomb wavepacket with the radial wavevector k is given by:

$$\Psi_k(\vec{r}) = \frac{1}{r} \sum_{LM} a_{kLM} Y_{LM}(\Omega_r) F_{kLM}(r), \tag{27}$$

where $F_{kLM}(r)$ are Coulomb spherical waves. F_{kLM} are normalized to $\delta\left(\frac{k-k'}{2\pi}\right)$. At large r, it is given by [49]:

$$F_{kLM} \to 2sin\left(kr + \frac{z}{k}log\left(2kr\right) - \frac{\pi L}{2} + \varphi_L\right),$$
 (28)

where

$$\varphi_L = Arg\left(\Gamma\left(L + 1 - \frac{iz}{k}\right)\right). \tag{29}$$

The Rutherford scattering solution (the "Coulomb plane wave") normalized $\delta(\vec{k} - \vec{k'})$, is asymptotically given by [49]:

$$w\left(\vec{k}\right) = \sqrt{\frac{2}{\pi}} \frac{1}{k'r} \sum_{L'M'} i^{L'} exp\left(i\varphi_{L'}\right) sin\left(k'r + \frac{z}{k'}log\left(2k'r\right) - \frac{\pi L}{2} + \varphi_{L'}\right)$$

$$Y_{LM}^{*}\left(\Omega_{k}\right) Y_{LM}\left(\Omega_{r}\right)$$
(30)

Calculating an overlap between Ψ_k and $w(\vec{k})$, we immediately obtain amplitudes $b_{\vec{k}}$ of the Rutherford states:

$$b_{\vec{k}} = \sum_{LM} \sqrt{\frac{1}{2\pi}} \frac{1}{k} (-i)^L exp(-i\varphi_L) Y_{LM}(\Omega_k) a_{LM}.$$
(31)

6.3. Evaluation of spherical harmonics

The calculation of photoelectron spectrum requires the repeated evaluation of spherical harmonics Y_{LM} , potentially for high values of angular momenta L and M. We find that the following recurrence formulas are fast and numerically stable for large L and M:

$$Y_{00} = \frac{1}{\sqrt{4\pi}},\tag{32}$$

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

$$\frac{Y_{L,-L}}{Y_{L-1,-(L-1)}} = -i\sqrt{\frac{2L+1}{2L}} exp(-i\varphi) sin(\theta),$$
(33)

and finally:

$$Y_{LM} = iz\sqrt{\frac{4L^2 - 1}{L^2 - M^2}}Y_{L-1,M} + \sqrt{\frac{2L + 1}{2L - 3}\frac{(L - 1)^2 - M^2}{L^2 - M^2}}Y_{L-2,M}.$$
 (34)

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

- [1] Ermolaev A M, Puzynin I V, Selin A V and Vinitsky S I 1999 Phys. Rev. A 60(6) 4831-4845 URL http://link.aps.org/doi/10.1103/PhysRevA.60.4831
- [2] Ermolaev A M and Selin A V 2000 Phys. Rev. A 62(1) 015401 URL http://link.aps.org/doi/10.1103/PhysRevA.62.015401
- [3] Tao L and Scrinzi A 2012 New Journal of Physics 14 013021 URL http://stacks.iop.org/1367-2630/14/i=1/a=013021
- [4] Patchkovskii S and Muller H 2016 Computer Physics Communications 199 153 169 ISSN 0010-4655 URL http://www.sciencedirect.com/science/article/pii/S001046551500394X
- [5] Wu G, Hockett P and Stolow A 2011 Physical Chemistry Chemical Physics 13 18447–18467
- [6] Chandler D W and Houston P L 1987 The Journal of Chemical Physics 87 1445-1447 URL http://scitation.aip.org/content/aip/journal/jcp/87/2/10.1063/1.453276
- [7] Bordas C, Paulig F, Helm H and Huestis D L 1996 Review of Scientific Instruments 67 2257–2268 URL http://scitation.aip.org/content/aip/journal/rsi/67/6/10.1063/1.1147044
- [8] Drner R, Mergel V, Jagutzki O, Spielberger L, Ullrich J, Moshammer R and Schmidt-Beking H 2000 Physics Reports 330 95 192 ISSN 0370-1573 URL http://www.sciencedirect.com/science/article/pii/S037015739900109X
- [9] Agostini P, Fabre F, Mainfray G, Petite G and Rahman N K 1979 Phys. Rev. Lett. 42(17) 1127-1130 URL http://link.aps.org/doi/10.1103/PhysRevLett.42.1127
- [10] Weber T, Giessen H, Weckenbrock M, Urbasch G, Staudte A, Spielberger L, Jagutzki O, Mergel V, Vollmer M and Dörner R 2000 Nature 405 658–661
- [11] Moshammer R, Feuerstein B, Schmitt W, Dorn A, Schröter C D, Ullrich J, Rottke H, Trump C, Wittmann M, Korn G, Hoffmann K and Sandner W 2000 Phys. Rev. Lett. 84(3) 447–450 URL http://link.aps.org/doi/10.1103/PhysRevLett.84.447
- [12] Feuerstein B, Moshammer R, Fischer D, Dorn A, Schröter C D, Deipenwisch J, Crespo Lopez-Urrutia J R, Höhr C, Neumayer P, Ullrich J, Rottke H, Trump C, Wittmann M, Korn G and Sandner W 2001 Phys. Rev. Lett. 87(4) 043003 URL http://link.aps.org/doi/10.1103/PhysRevLett.87.043003
- [13] Huismans Y, Rouzée A, Gijsbertsen A, Jungmann J H, Smolkowska A S, Logman P S W M, Lépine F, Cauchy C, Zamith S, Marchenko T, Bakker J M, Berden G, Redlich B, van der Meer A F G, Muller H G, Vermin W, Schafer K J, Spanner M, Ivanov M Y, Smirnova O, Bauer D, Popruzhenko S V and Vrakking M J J 2011 Science 331 61-64 ISSN 0036-8075 (Preprint http://science.sciencemag.org/content/331/6013/61.full.pdf) URL http://science.sciencemag.org/content/331/6013/61
- [14] Eckle P, Smolarski M, Schlup P, Biegert J, Staudte A, Schöffler M, Muller H G, Dörner R and Keller U 2008 Nature Physics 4 565–570
- [15] Torlina L, Morales F, Kaushal J, Ivanov I, Kheifets A, Zielinski A, Scrinzi A, Muller H G, Sukiasyan S, Ivanov M et al. 2015 Nature Physics 11 503–508
- [16] Paul P M, Toma E, Breger P, Mullot G, Augé F, Balcou P, Muller H and Agostini P 2001 Science 292 1689–1692
- [17] Itatani J, Quéré F, Yudin G L, Ivanov M Y, Krausz F and Corkum P B 2002 Phys. Rev. Lett. 88(17) 173903 URL http://link.aps.org/doi/10.1103/PhysRevLett.88.173903
- [18] Tong X M and Chu S I 1997 **217** 119 130
- [19] Nurhuda M and Faisal F H M 1999 **60** 3125–3133
- [20] Muller H G 1999 **9** 138–148
- [21] Borisov A G 2001 **114** 7770–7777
- [22] Bauer D and Koval P 2006 **174** 396 421
- [23] Guan X, Noble C J, Zatsarinny O, Bartschat K and Schneider B I 2009 180 2401 2409
- [24] Sørevik T, Birkeland T and Okša G 2009 **225** 56 67
- [25] Tong X M and Toshima N 2011 **182** 21 23
- [26]Dziubak T and Matulewski J $2012~\mathbf{183}~800-812$
- [27] Shen J, Sha W E, Huang Z, Chen M and Wu X 2013 184 480 492

- [28] Ó Broin C and Nikolopoulos L A A 2014 **185** 1791 1807
- [29] Barnett A 1982 Computer Physics Communications 27 147–166
- [30] Schafer K J and Kulander K C 1990 Phys. Rev. A 42(9) 5794-5797 URL http://link.aps.org/doi/10.1103/PhysRevA.42.5794
- [31] Palacios A, McCurdy C W and Rescigno T N 2007 Phys. Rev. A 76(4) 043420 URL http://link.aps.org/doi/10.1103/PhysRevA.76.043420
- [32] Feshchenko R M and Popov A V 2013 *Phys. Rev. E* **88**(5) 053308 URL http://link.aps.org/doi/10.1103/PhysRevE.88.053308
- [33] Ohmi M, Tolstikhin O I and Morishita T 2015 Phys. Rev. A 92(4) 043402 URL http://link.aps.org/doi/10.1103/PhysRevA.92.043402
- [34] Serov V V, Derbov V L, Joulakian B B and Vinitsky S I 2001 Phys. Rev. A 63(6) 062711 URL http://link.aps.org/doi/10.1103/PhysRevA.63.062711
- [35] Zielinski A, Majety V P and Scrinzi A 2016 Phys. Rev. A 93(2) 023406 URL http://link.aps.org/doi/10.1103/PhysRevA.93.023406
- [36] Riss U V and Meyer H D 1993 Journal of Physics B: Atomic, Molecular and Optical Physics 26 4503 URL http://stacks.iop.org/0953-4075/26/i=23/a=021
- [37] Riss U V and Meyer H 1996 The Journal of Chemical Physics 105 1409-1419 URL http://scitation.aip.org/content/aip/journal/jcp/105/4/10.1063/1.472003
- [38] Rescigno T N, Baertschy M, Byrum D and McCurdy C W 1997 Phys. Rev. A 55(6) 4253-4262 URL http://link.aps.org/doi/10.1103/PhysRevA.55.4253
- [39] Moiseyev N 1998 Journal of Physics B: Atomic, Molecular and Optical Physics 31 1431 URL http://stacks.iop.org/0953-4075/31/i=7/a=009
- [40] Manolopoulos D E 2002 The Journal of Chemical Physics 117 9552-9559 URL http://scitation.aip.org/content/aip/journal/jcp/117/21/10.1063/1.1517042
- [41] Poirier B and Carrington T 2003 The Journal of Chemical Physics 118 17-28 URL http://scitation.aip.org/content/aip/journal/jcp/118/1/10.1063/1.1524624
- [42] Sajeev Y, Santra R and Pal S 2005 The Journal of Chemical Physics 123 204110 URL http://scitation.aip.org/content/aip/journal/jcp/123/20/10.1063/1.2130338
- [43] Scrinzi A 2010 Phys. Rev. A 81(5) 053845 URL http://link.aps.org/doi/10.1103/PhysRevA.81.053845
- [44] Smirnova O, Spanner M and Ivanov M 2008 Phys. Rev. A 77(3) 033407 URL http://link.aps.org/doi/10.1103/PhysRevA.77.033407
- [45] Becker W and Miloevi D B 2016 Journal of Physics: Conference Series 691 012002 URL http://stacks.iop.org/1742-6596/691/i=1/a=012002
- [46] Becke A 1988 J Chem Phys 88 2547
- [47] Pfeiffer A N, Cirelli C, Smolarski M, Dimitrovski D, Abu-Samha M, Madsen L B and Keller U 2012 Nature Physics 8 76–80
- [48] Varshalovich D, Moskalev A and Khersonskii V 1988 Quantum Theory of Angular Momentum: Irreducible Tensors, Spherical Harmonics, Vector Coupling Coefficients, 3nj Symbols (World Scientific) ISBN 9789971509965 URL https://books.google.de/books?id=hQx_QgAACAAJ
- [49] Flügge S 1994 Practical Quantum Mechanics Classics in Mathematics (Springer Berlin Heidelberg) ISBN 9783540650355 URL https://books.google.de/books?id=VpggN9qIFUcC