Photo-electron momentum spectra from minimal volumes: the time-dependent surface flux method

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\textbf{Abstract.} The time-dependent surface flux (t-SURFF) method is introduced for computing strong-field infrared (IR) photo-ionization spectra of atoms by numerically solving the time-dependent Schrödinger equation on minimal simulation volumes. The volumes only need to accommodate the electron quiver motion and the relevant range of the atomic binding potential. Spectra are computed from the electron flux through a surface, beyond which the outgoing flux is absorbed by infinite range exterior complex scaling (irECS). Highly accurate IR photo-electron spectra are calculated in single active electron approximation and compared to the literature results. Detailed numerical evidence for performance and accuracy is given. Extensions to multi-electron systems and double ionization are discussed.

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1. Introduction

In a broad range of recent experiments, strong infrared (IR) laser pulses, often combined with high harmonic pulses, are used to study the electronic dynamics of atoms and molecules on the natural time scale of valence electron motion $\lesssim 1 \text{ fs}$. Basic mechanisms of the IR–electron interaction are well understood within the simple semi-classical recollision model [1], but for a more detailed understanding numerical simulations must be employed. This is due to the fundamentally non-perturbative interaction of near-IR fields with the valence electrons at intensities of $\gtrsim 10^{14} \text{ W cm}^{-2}$. Even for the simplest single-electron models the simulation remains challenging, especially when accurate photo-electron momentum spectra are required, such as, e.g., for recollision imaging [2–4]. When two-electron processes are involved, one quickly reaches the limits of present-day computer resources [5, 6].

The surprising difficulty in simulating a seemingly simple process like ionization by a dipole field is due to the presence of vastly different length and time scales: first, even though the laser pulses can be as short as a single optical cycle, at the Ti:sapphire wave length of $\lambda = 800 \text{ nm}$, this still corresponds to a full-width at half-maximum (FWHM) duration of $\gtrsim 2.5 \text{ fs}$ or about 110 atomic units (au, $\hbar = e^2 = m_e = 1$). During that time, a photo-electron with an energy of $13 \text{ eV} \approx 1/2 \text{ au}$ moves a distance of $\approx 110 \text{ Bohr}$, which sets a lower limit for the required box size, if reflections from box boundaries are to be avoided. In practice, higher energies and longer pulse durations including the rise and fall of the pulses are of interest, leading to simulation volumes with diameters of thousands of atomic units. At the same time, photo-electron spectra are broad, extending to at least $2 U_p$ for the ‘direct’ photo-electrons and further up to about $10 U_p$ for the ‘rescattered’ electrons. Rescattered electrons are those which after ionization are redirected to the nucleus by the laser field, where they absorb more photons in an inelastic scattering process. The ponderomotive potential at laser frequency $\omega U_p = I/(4\omega^2)$ grows linearly with laser intensity $I$ and quadratically with wavelength. At the moderate intensity $I = 10^{14} \text{ W cm}^{-2}$ and $\lambda = 800 \text{ nm}$ it is $U_p = 0.22 \text{ au} \approx 6 \text{ eV}$. The rescattering momentum energy cutoff of $10 U_p$ corresponds to a photo-electron momentum of $2.2 \text{ au}$. To represent such momenta on a spatial grid, we need grid spacings of at least $\Delta x \lesssim 2\pi/2 \text{ au}$,
and for accurate results, usually significantly more than this. This leaves us with thousands of grid points in each spatial direction even for moderate laser parameters. The situation quickly worsens at higher intensities and longer wavelengths.

This general requirement on discretization cannot be overcome by any specific representation of the wave function: speaking in terms of classical mechanics, we must represent the phase space that is covered by the electrons, which involves a certain range of momenta and positions. If we have no additional knowledge of the structure of the solution, the number of discretization points we need is the phase space volume divided by the Planck constant $\hbar$. In some cases such as, for example, single-photon ionization, we can exploit the fact that at long distances the solution covers only a very narrow range of momenta and only the spatially well-localized initial bound state requires a broader range of momenta: the phase-space volume remains small, and simple models such as perturbation theory allow the physics to be reproduced. We have no such simplifying physical insight for strong-field IR photo-ionization.

The lower limit for the number of discretization points for the complete wave function can be approached by different strategies: the choice of velocity gauge \(^7\), working in the Kramers–Henneberger frame \(^8\) or in momentum space \(^9\), by variable grid spacings or by expanding into time-dependent basis functions \(^10\). A promising strategy is to follow the solution in time \(^11\).

Alternatively, we can abandon the attempt at representing the complete wave-function and instead use absorbing boundaries and extract momenta at finite distances. The time-dependent surface flux method (t-SURFF) introduced here is such an approach. After its mathematical derivation, numerical implementation is briefly discussed. Angle-resolved photo-electron spectra are presented using between 75 and 200 radial discretization points for truncated and full Coulomb potentials. We discuss accuracies and demonstrate the efficiency of t-SURFF in comparison with the recent literature. Finally, possible extensions to few-electron systems and double photo-electron spectra are outlined.

2. The time-dependent surface flux method

Scattering measurements and theory are both based on the plausible idea that interactions are limited to finite ranges in space and time and that at large times $T$ and large distances $R$ the time evolution of the scattering particle is that of free motion:

$$\Psi(\vec{r}, t) \sim \int d\vec{k} \exp(-i\vec{k}^2/2)b(\vec{k})\chi_{\vec{k}}(\vec{r}) \quad \text{for } t > T, \ |\vec{r}| > R,$$

where $\chi_{\vec{k}}(\vec{r}) = (2\pi)^{-3/2} \exp(i\vec{k} \cdot \vec{r})$ are $\delta$-normalized plane waves. The measured momentum spectrum is proportional to the square of the spectral amplitudes $b(\vec{k})$

$$\sigma(\vec{k}) \propto |b^2(\vec{k})|.$$

For Hamiltonians that are time independent beyond a certain time $T$, we can readily obtain the spectral amplitudes $b(\vec{k})$ by decomposing the wave function $\Psi(\vec{r}, T)$ into its spectral components

$$b(\vec{k}) = \langle \psi_{\vec{k}} | \Psi(T) \rangle \exp(-iT\vec{k}^2/2),$$

where the scattering solutions

$$H(T) |\psi_{\vec{k}}\rangle = \frac{T}{2} |\psi_{\vec{k}}\rangle.$$
have the asymptotic behavior
\[ \psi_k(\vec{r}) \sim \chi_k(\vec{r}) \quad \text{for} \quad |\vec{r}| \to \infty. \] (5)

For computing \( b(\vec{k}) \), one needs to (i) propagate a solution \( \Psi(\vec{r}, t) \) until time \( T \) and (ii) obtain the scattering solutions \( \psi_k \). Unfortunately, both of these tasks are non-trivial in all except the simplest cases. As discussed above, solving the time-dependent Schrödinger equation (TDSE) with IR fields is numerically challenging because of the large box sizes needed. ‘Obtaining the scattering solution’ amounts to outright solving a time-independent scattering problem for \( H(T) \), but analytic scattering wave functions are only known for simple model potentials and for the Coulomb potential.

Rather than letting the system evolve and analyzing it at the end of the evolution, we can record the particle flux leaving a finite volume as the systems evolves. Such a procedure requires neither stationary scattering solutions nor the complete wave function in an asymptotically large volume. It is practical either if we know the further time evolution of the system outside the finite volume in analytic form or if it can be obtained with little numerical effort. This type of method has been applied to reactive scattering with time-independent Hamiltonians [12, 13], where obtaining scattering solutions would be tantamount to solving the complete stationary scattering problem, a daunting task for few-body systems.

Photo-ionization cannot be computed by existing surface flux methods, as the dipole interaction is non-local and the external field modifies the particle energies everywhere, in particular also after the particle has left the finite simulation volume. To handle this, we have developed the time-dependent surface flux (t-SURFF) method, which will be derived in the following. A preliminary version of the method has been published in [14].

Let us choose a surface radius \( R_c \) large enough such that the particle motion can be considered as a free motion and that all occupied bound states of the system have negligible probability density at \( |\vec{r}| > R_c \). Let us further pick a sufficiently large time \( T \) such that all particles that will ever reach our detector with energy \( \vec{k}^2/2 > 0 \) are outside the finite volume \( |\vec{r}| < R_c \). At that time, the wave function has split into bound and asymptotic parts

\[ \Psi(\vec{r}, T) = \Psi_b(\vec{r}, T) + \Psi_s(\vec{r}, T) \] (6)

with

\[ \Psi_b(\vec{r}, T) \approx 0 \quad \text{for} \quad |\vec{r}| \geq R_c, \] (7)

\[ \Psi_s(\vec{r}, T) := \int d\vec{k} \exp(-iT\vec{k}^2/2)b(\vec{k})\psi_k(\vec{r}) \approx 0 \quad \text{for} \quad |\vec{r}| \leq R_c. \] (8)

The approximate sign in (8) refers to the fact that very-low-energy particles \( \vec{k}^2/2 \sim 0 \) may not have left the finite volume at time \( T \). It follows that the lower the energy, the larger the \( T \) that will be required for the splitting to hold. Although each individual \( \chi_k \) extends over the complete space, the scattering wave packet is localized outside \( R_c \) up to a small error that quickly decays with growing \( T \). The scattering amplitudes \( b_k \) can be obtained as

\[ e^{iT\vec{k}^2/2}b(\vec{k}) = \langle \psi_k|\Psi_s(T) \rangle \approx \langle \psi_k|\theta(R_c)|\Psi_s(T) \rangle = \langle \chi_k|\theta(R_c)|\Psi_s(T) \rangle. \] (9)

Here we introduced the notation

\[ \langle \psi_k|\theta(R_c)|\Psi_s(T) \rangle := \int_{|\vec{r}|>R_c} d^3r \psi_k^*(\vec{r})\Psi_s(\vec{r}, T). \] (10)
The substitution of the scattering solution with a plane wave \( \psi_k \rightarrow \chi_k \) in the last step uses the asymptotic behavior (5). It is exact when all interactions vanish beyond \( R_c \).

To convert the above matrix element into a time integral over surface values, we must assume that we know the time evolution of the particle after it has passed through the surface.

For that we assume that there is a ‘channel Hamiltonian’ \( H_c(t) \) such that

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

In the case of a short-range potential \( V(\vec{r}) = 0 \) for \( |\vec{r}| > R_c \), this is exactly fulfilled by the Hamiltonian for the free motion in the laser field

\[
H_c(t) = \frac{i}{2} [-i \vec{V} - \vec{A}(t)]^2,
\]

where \( \vec{A}(t) = -\int_{-\infty}^{t} \vec{E}(t') \, dt' \) for the dipole field \( \vec{E}(t) \). If not specified otherwise, atomic units (au) are used throughout this paper. The Volkov solutions

\[
\chi_k(\vec{r}) = (2\pi)^{-3/2} e^{-i\Phi(\vec{k}, t)} e^{i\vec{k} \cdot \vec{r}}, \quad \Phi(\vec{k}, t) = \frac{1}{2} \int_0^t d\tau |\vec{k} - \vec{A}(t)|^2
\]

solves the TDSE

\[
i \frac{d}{dt} |\chi_k(t)\rangle = H_c(t) |\chi_k(t)\rangle.
\]

We can now write

\[
\langle \chi_k(T) | \theta(R_c) | \Psi_s(T) \rangle = \int_0^T dt \frac{d}{dt} \langle \chi_k(t) | \theta(R_c) | \Psi_s(t) \rangle
\]

\[
= i \int_0^T dt \langle \chi_k(t) | H_c(t) \theta(R_c) - \theta(R_c) H(t) | \Psi_s(t) \rangle
\]

\[
= i \int_0^T dt \langle \chi_k(t) | \left[ -\frac{1}{2} \Delta + iA(t) \cdot \vec{V}, \theta(R_c) \right] | \Psi_s(t) \rangle.
\]

The commutator vanishes everywhere except on the surface \( |\vec{r}| = R_c \). Assuming linear polarization in the \( z \)-direction \( \vec{A}(t) = (0, 0, A(t)) \), it can be written in polar coordinates \((r, \theta, \phi)\) as

\[
\left[ -\frac{1}{2} \Delta + iA(t) \partial_r, \theta(R_c) \right] = -\frac{1}{2} r^{-2} \partial_r r^2 \delta(r - R_c) - \frac{1}{2} \delta(r - R_c) \partial_r - iA(t) \cos \theta \delta(r - R_c).
\]

With this, the volume integral over the solution at time \( T \) has been converted into a time integral up to \( T \) and a surface integral over \( |\vec{r}| = R_c \).

We would like to remark that without time dependence we can make one more step, as then the Volkov phase reduces to \( \Phi(\vec{k}, t) = t\vec{k}^2/2 \) and time integration turns into the time energy Fourier transform of the surface integral, which connects to the well-known results of, e.g., [13].

3. Finite-element discretization and infinite-range exterior complex scaling

For efficient use of t-SURFF, a reliable mechanism for truncating the solution outside the finite volume without generating reflections or other artefacts is needed. Complex absorbing potentials are commonly employed for that purpose (for a recent review, see [15]). We use the infinite-range exterior scaling (irECS) introduced and discussed in detail in [16]. Here we only briefly summarize the procedure.

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Exterior complex scaling (ECS) consists in making an analytic continuation of the Hamiltonian by rotating the coordinates into the upper complex plane beyond the ‘scaling radius’ \( R_0 \):

\[
\vec{r} \rightarrow \vec{r}_{\theta R_0} = \begin{cases} 
\vec{r} & \text{for } |\vec{r}| \leq R_0, \\
\frac{1}{|\vec{r}|} \left[ R_0 + e^{i\theta} (|\vec{r}| - R_0) \right] & \text{for } |\vec{r}| > R_0.
\end{cases}
\] (17)

The resulting complex scaled Hamiltonian \( H_{\theta R_0} \) can be used in a complex scaled TDSE

\[
i \frac{d}{dt} \Psi_{\theta R_0}(t) = H_{\theta R_0}(t) \Psi_{\theta R_0}(t).
\] (18)

It was observed in [16] that for the velocity form of the TDSE, in the unscaled region \(|\vec{r}| < R_0\), exact and complex scaled solutions agree: \( \Psi_{\theta R_0}(\vec{r}, t) \equiv \Psi_v(\vec{r}, t) \). Mathematical proof is absent, but numerical agreement can be pushed to machine precision with relative errors \( \sim 10^{-14} \).

These high accuracies can be reached with little effort by infinite-range ECS (irECS), where very few (about 20) discretization coefficients are needed at radii \( > R_0 \). It consists in using an expansion into spherical harmonics and discretizing the radial parts by high-order finite elements. As the last element, irECS uses the infinite interval \([R_0, \infty)\) and functions of the form \( L_n(2\alpha r) \exp(-\alpha r) \) for its discretization, where \( L_n \) are the Laguerre polynomials. The idea is that low-momentum/long-de-Broglie wave length electrons need rather large absorption ranges to become absorbed, but that the solution at large distances is rather smooth, i.e. that the more oscillatory short-wave-length content of the wave function becomes absorbed within a few oscillations. The exponentially damped functions turned out be very efficient in emulating that behavior: in most cases, about 20 functions at \(|\vec{r}| > R_0\) are sufficient for complete absorption.

In [16], it was observed that the quality of absorption by irECS improves with finite-element order in both the scaled and the unscaled region. This numerical observation is most likely due to the inherently analytical character of irECS, as higher orders allow better approximation of analytical behavior. While good results can be obtained starting from order \( \sim 8 \), for the present calculations finite-element orders between 15 and 25 were used in the unscaled region. A maximally sparse, near orthogonal representation of the finite-element functions allows efficient inversion of the overlap matrix and ensures numerical stability to orders as high as 40. A detailed description of the construction of the finite elements is given in [16].

Although in irECS there is no strict box boundary, the number of discretization points and the phase-space volume that can be represented remain finite. There is a correlation between position discretization and momentum discretization in irECS: large electron momenta can only be represented in the unscaled region and at the beginning of the scaled region. At long distances into the scaled region, only gentle oscillations and therefore low momenta can be represented until the wave function dies out exponentially.

As the finite-element basis is local, the discretization coefficients are approximately associated with positions in space. In fact, we can establish a one-to-one relation between the \( M \) functions belonging to an element and the function values at \( M \) different points within that element. In that sense, we will refer to the discretization coefficients as ‘discretization points’, emphasizing the locality of the finite-element functions.

The exact choice of the scaling parameters \( \theta, R_0 \) and \( \alpha \) is not critical. In [16], we found little variation of accuracy for values in the intervals \( \theta \sim [0.5, 0.9] \) and \( \alpha \sim [0.2, 0.6] \). Variations of the results with \( R_0 \), as a rule, reflect the spatial discretization error of the calculation. We found
this behavior confirmed also for the calculation of the photo-electron spectra presented here.

The plots shown below were all calculated with $\theta = \alpha = 0.5$.

The discretized complex scaled TDSE (18) was integrated using an explicit Runge–Kutta scheme with automatic step control and self-adaptive order up to 6. Stiffness problems could be strongly reduced by removing from the basis by explicit projection the eigenvectors of the field-free problem with eigenvalues $\gtrsim 40$ au. The extra cost of the projection is far outweighed by the increased time step. Implementation of an implicit scheme clearly would further improve the efficiency of propagation.

4. Photo-electron momentum spectra for a short-range potential

We solve the TDSE in velocity gauge

$$i \frac{d}{dr} \Psi_v(\vec{r}, t) = \left\{ \frac{1}{2} [-i\vec{\nabla} - \vec{A}(t)]^2 + V(\vec{r}) \right\} \Psi_v(\vec{r}, t),$$

(19)

where we first use the short-range ‘Coulomb’ potential

$$V(r) = \begin{cases} \frac{c}{r} - \frac{1}{2} \frac{r^2}{(2R^3)} + \frac{3}{(2R)} & \text{for } r \leq R, \\ 0 & \text{for } r > R. \end{cases}$$

(20)

With $R = 20$ and an effective charge $c = 1.1664$ the ground state energy is $-0.5$. The laser pulse is linearly polarized in the $z$-direction with the vector potential

$$A_z(t) = \frac{E_0}{\omega} \cos \left( \frac{\pi t}{2T} \right) \sin(\omega t).$$

(21)

We choose parameters $\omega = 0.057$ and $E_0 = 0.0755$ corresponding to a laser wave length of 800 nm and a peak intensity of $2 \times 10^{14}$ W cm$^{-2}$. $T$ is the FWHM of the vector potential and the total pulse duration is $2T$. Figure 1 shows the total and partial wave photo-electron spectra for potential range $R = 20$ and $T = 5$ optical cycles. At these parameters, more than 90% of the electrons get detached. For accuracy $\lesssim 1\%$ up to energies of $10U_p \approx 120$ eV, we need $L_{\text{max}} = 30$ partial waves with only 90 radial discretization points. We define the error relative to an accurate reference spectrum $\sigma_{\text{ref}}$ as

$$\mathcal{D}(E) = \frac{|\sigma(E) - \sigma_{\text{ref}}(E)|}{\max(\sigma(E), \langle \sigma(E) \rangle_{\delta E})}, \quad \langle \sigma(E) \rangle_{\delta E} := \frac{1}{2\delta E} \int_{E-\delta E}^{E+\delta E} dE' \sigma(E').$$

(22)

By including in the denominator the average over the interval $[E - \delta E, E + \delta E]$ we suppress spurious spikes in the error due to near-zeros of the spectrum. We choose $\delta E = 0.05$ au $\approx 1.5$ eV, which at 800 nm corresponds to averaging over about two photo-electron peaks.

In the unscaled region we use 60 points; 30 points are located in $|\vec{r}| > R_0$. The accuracy estimate shown in figure 1 is obtained by comparing to a fully converged calculation. When we increase the number of points to 180, the error drops to $\lesssim 10^{-3}$. The increase of relative errors with energy can be attributed to the decrease of the signal: note that from 0 to 10$U_p$, the spectrum drops by more than 5 orders of magnitude.

As a consistency check, we find that spectra up to 10$U_p$ computed with largely different surface radii $R_c = 21$ and 29 coincide within relative accuracies of better than $\lesssim 10^{-3}$. As beyond $R_c$ we assume the exact Volkov propagation, this demonstrates that the solution of the TDSE
Figure 1. Upper panels: total and partial wave photo-electron spectra obtained for the smoothly truncated Coulomb potential equation (20). The lower panels show the relative errors for each spectrum according to equation (22) of a calculation with only 90 discretization points per angular momentum compared to a fully converged calculation. Pulse parameters: $\lambda = 800\,\text{nm}$, $T = 5$ optical cycles and intensity $= 2 \times 10^{14}\,\text{W cm}^{-2}$.

and the integrals (15) are correct and that also reflections are suppressed on at least that level of accuracy.

The calculated spectra are independent of the complex scaling parameters: over the ranges $R_0 \in [20, 30]$ and $\theta = [0.4, 0.7]$ results vary by less than $10^{-3}$. The lower limit for $R_0$ is not dictated by complex scaling: rather, as we want to obtain exact results, we must pick up the wave-function outside the range of the potential $R_c \geq R = 20$, and therefore also $R_0 \geq R_c > R$. Already with these parameters the quiver amplitude, i.e. the excursion of free electrons in the laser field, $E_0/\omega^2 \approx 23$ reaches beyond $R_0$ and into the complex scaled region. This confirms an earlier observation that the dynamics is correctly reproduced also in the complex scaled region [16].

For correct electron spectra, the effective box size of the combined unscaled and scaled regions must be large enough to accommodate the quiver motion. To study this further, we use a somewhat shorter effective range of $R = 15$ and choose $R_0 = R_c = R$. From figure 2, we see that with only 45 discretization points in the unscaled region $r < R_0$, 1% accuracy is reached at the same laser parameters as before. With 30 points for absorptions we have a total of 75 points. Note that the quiver radius of $\approx 23\,\text{au}$ now reaches rather deep into scaled region, but still fits into the total box.

Keeping the intensity constant, a longer wave length of 1000 nm leads to a larger quiver radius of $\approx 36\,\text{au}$. We expect to need a factor of $(1000/800)^2 \approx 1.6$ more discretization points. Indeed, we can reach $\lesssim 1\%$ accuracy with a total of 120 points in this case (figure 2). All additional coefficients and at least half of the quiver motion now are located in the scaled region. Note that also $U_p$ and with it the peak momentum grows with wave length: for describing energies $> 120\,\text{eV}$, we would also need to increase the density of points by 25%. However, just
Figure 2. Required box sizes depend on the quiver amplitude. Left panels: spectrum (top) for a 5-cycle FWHM pulse at 800 nm and $E_0 = 0.0755$ (intensity $2 \times 10^{14}$ W cm$^{-2}$). Accuracies (bottom) are calculated with 75 (black line) and 100 (red line) discretization points. Errors $\lesssim 1\%$ relative to an accurate reference calculation are reached with 75 points. At 100 points the error is $\lesssim 10^{-3}$. Right panels: spectrum (top) and accuracies (bottom) for a 5-cycle FWHM pulse at 1000 nm and the same intensity. Because of the larger quiver amplitude, a $\sim 60\%$ larger box with 120 points is needed for $< 1\%$ accurate results. When using a smaller box with 120 points at 30\% higher density, errors increase to nearly 10\% (red line).

increasing the number of points without increasing the box size gives incorrect results: it appears that we need to accommodate the full quiver motion up to $\sim 36$ au in the simulation box.

5. Photo-electron momentum spectra for the hydrogen atom

As always in scattering problems, the long-range nature of the Coulomb potential introduces extra mathematical and practical complications. Considering t-SURFF, there is no surface radius $R_c$ such that the Volkov solutions become exact. In addition, the Rydberg bound states extend to arbitrarily large distances. We will discuss below how these problems can be eliminated with moderate extra computational effort. Here we present the pragmatic solution of using larger $R_c$ such that the remaining error due to the presence of the Coulomb potential becomes acceptable.

Figure 3 shows a spectrum calculated for the hydrogen atom with an FWHM $T = 20$ optical cycle pulses at 800 nm wave length and peak intensity $10^{14}$ W cm$^{-2}$. All discretization errors can be controlled in the same way as discussed for the short-range potential. The error is dominated by the dependence on the surface radius $R_c$: on an absolute (logarithmic) scale, two calculations with $R_c = 110$ and $R_c = 140$ are hardly discernable. The error level of the calculation with $R_c = 110$ and 180 discretization points is $\lesssim 10\%$ and decreases slowly as $R_c$ increases. In the linear plot of the spectra (lowest panels of figure 3), we see that the largest errors occur at lower energies due to the larger influence of the weak Coulomb tail on
low-energy scattering states. Agreement at intermediate energies is near perfect. The increase of relative errors at the highest energies is due to a displacement of peaks caused by slightly incorrect dispersion due to spatial discretization.

Figure 4 shows angle-resolved photo-electron spectra for FWHM durations of $T = 10, 20$ and 30 optical cycles. In the region up to $10U_p \approx 60$ eV, circular structures with their centers offset along the polarization axis are clearly distinguishable, best visible at the shortest pulse $T = 10$. These structures were first explained in [17] and are due to rescattering. The intensity around each circle is related to the electron–ion scattering differential cross-section [18]. In the enlarged plots of the energy region up to energies of $2U_p \approx 12$ eV, we reproduce rings and fan-like structures that are related to particular partial waves, as has been extensively discussed in [19]. Sub-structures between the photo-electron energy peaks are clearly resolved. These are related to the pulse envelope: the spacing decreases and the number of peaks increases as the
Figure 4. Angle-resolved photo-electron energy spectra for the hydrogen atom at $\lambda = 800$ nm, intensity $10^{14}$ W cm$^{-2}$ and FWHM pulse durations $T = 10$, 20 and 30 (upper panels). In the lower panels, the region up to $2U_p \approx 12$ eV is enlarged.

pulse duration increases. In different wording, one can say that they are caused by interference between the rising and trailing edges of the pulse [20].

For comparison with the results reported in [9], we also computed the spectrum at the lower intensity of $5 \times 10^{13}$ W cm$^{-2}$ and $T = 10$ cycles FWHM (corresponding to 20 cycles total pulse duration). Figure 5 shows our result for the total photo-ionization spectrum obtained with only 192 discretization points and 25 angular momenta. We have estimated the accuracy of our results to be $\lesssim 10\%$ throughout the spectrum using the same procedures as for figure 3. Our result qualitatively differs from figure 2 in [9], where a surprising irregularity appears near $10U_p$, while no such structure exists in our spectrum. Unfortunately no detailed discussion of accuracy or convergence is given in [9]. One possible source of the discrepancy is insufficient discretization. With a peak energy of $40U_p \sim 4$ au included in the calculation the maximal
momenta are $p_{\text{max}} \sim 2.8$ au. During 20 optical cycles (2200 au of time), these electrons move to distances $\sim 6000$ au. With the 2000 discretization points used in [9], one obtains average momentum grid spacing of $\Delta p = p_{\text{max}}/2000$ and an effective spatial box size $\sim 2\pi/\Delta p \approx 4500$, which appears somewhat below the necessary limit. However, the uneven distribution of grid points and additional spectral cuts in the energy domain used in [9] make it difficult to carry out this analysis further. Rather, a systematic convergence study would be required. The present number of discretization points also compares well to the 1000–2000 discretization coefficients used in [11] at photon energies of 0.3–0.7 au. The results of the benchmark calculations [21] obtained with a box size of 3000 atomic units and about 4000 discretization points at a somewhat shorter wave length of 620 nm could be reproduced using only 200 radial discretization points up to energies of $10U_p$, except at the lowest energies, where our method is limited by the use of Volkov solutions beyond the surface radius $R_c \lesssim 150$ au.

### 6. Extensions of the method

#### 6.1. Handling long-range potentials

In the section above, we were able to obtain good results for quite demanding laser parameters using only $R_c \approx 140$. Still, the problem remains big, and in particular when considering extension of the approach to multi-electron systems, multi-dimensional simulation volumes would quickly exhaust computational resources. In turn, a reduction of $R_c$ to the necessary minimum of 20–50 set by the quiver radius would constitute an essential gain, possibly deciding about the feasibility of the multi-electron calculation. Here we show how to correctly handle long-range potentials in t-SURFF.
For computing exact spectra, we must know the exact solution of the TDSE beyond $R_c$. In the derivation of equation (15), we have only used $H(t) \equiv H_c(t)$ for $|\vec{r}| > R_c$ and that we can by some means obtain accurate solutions $\chi_k(r, t)$ for the TDSE with $H_c(t)$. A suitable $H_c$ is obtained by using in equation (19) the potential

$$V_c(r) = \begin{cases} -1/R_c & \text{for } r \leq R_c, \\ -1/r & \text{for } r > R_c. \end{cases}$$

Partial wave solutions $\phi_{k,l}(r)$ for the field-free case $\vec{A} = 0$ with $V_c$ are the spherical Bessel functions up to $R_c$, which are connected smoothly to values and derivatives of regular and irregular Coulomb functions in the region $r > R_c$, where one must pay attention to proper $\delta$-normalization. With nonzero field $\vec{E}(t)$, no exact solution is known. We found that a simple Coulomb–Volkov approximation [22] for the time dependence is insufficient: we could not observe any acceleration of convergence by replacing the plane waves of the Volkov solution with the field-free scattering solutions. Lacking a reliable approximation for the scattering solution, we must solve the TDSE for the $\chi_k(r, t)$ with the final condition

$$\chi_k(r, T) = \phi_{k,l}(r).$$

As the potential is weak, little actual scattering occurs and accurate solutions can be obtained by expanding into $\phi_{k,l}(r)$ for small intervals around the asymptotic radial and angular momenta, $k' \in [k - \Delta k, k + \Delta k]$ and $l' \in [l - \Delta l, l + \Delta l]$. Numerical results using this procedure will be presented elsewhere.

Finally, there remains the problem that Rydberg states may become occupied, which have non-negligible amplitude at $r = R_c$. Such a non-decaying amplitude at the surface leads to slow, oscillatory convergence of the integrals (15) as $T \to \infty$. Again, there is an efficient and rather pragmatic solution to this problem: by averaging the value over several optical cycles, we find that convergence is speeded up and the reported accuracies are reached quickly.

If the Rydberg states are known exactly, we can remove them after the pulse is over. This removes all oscillations and the asymptotic value is reached rapidly. For the procedure we define the projector onto the (field-free) Rydberg states $|n\rangle$ and its complement as

$$P := \sum_n |n\rangle\langle n| \quad \text{and} \quad Q := 1 - P.$$  

A simple calculation shows that the spectral amplitude with the Rydberg states removed is

$$\langle \chi_k(T)|\theta(R_c)Q|\Psi(T)\rangle = i \int_{-\infty}^{T_0} dt \langle \chi_k(t)|[H_c(t), \theta(R_c)]|\Psi(t)\rangle + i \int_{T_0}^{T} dt \langle \chi_k|[H_c(t), \theta(R_c)]Q|\Psi(t)\rangle - \langle \chi_k(T_0)|\theta(R_c)P|\Psi(T_0)\rangle,$$

where $T_0$ is any time after the end of the pulse. If high precision is wanted and if long time propagation is costly, the extra effort of implementing the explicit projection (26) may be justified.

6.2. Single ionization of multi-electron systems

The procedure can be extended to describe single ionization of multi-electron systems. The main new feature here is that we have several ionization channels, depending on the state in which
the ion is left behind. The spectral density in a specific channel \( c \) can be written, as before, as
\[
\sigma_c(\vec{k}) = |\langle \chi_{c,\vec{k}}(T) | \theta(R_c) | \Psi_s(T) \rangle |^2.
\] (27)

The asymptotic channel wave function \( \chi_{c,\vec{k}}(t) \) fulfills the channel TDSE
\[
\frac{i}{\hbar} \frac{d}{dt} \chi_{c,\vec{k}}(t) = H_c(t) \chi_{c,\vec{k}}(t),
\] (28)
with the channel Hamiltonian
\[
H_c(t) = \frac{1}{2} [-i\vec{\nabla} - \vec{A}(t)]^2 \otimes H_{ion}(t)
\] (29)
where for simplicity we neglect the ionic Coulomb potential. Note that we do not need to explicitly anti-symmetrize \( \chi_c \), if \( \Psi_s \) is anti-symmetric. A general solution of (28) has the form
\[
\chi_{c,\vec{k}}(t) = (2\pi)^{-3/2} e^{-i\vec{k}\vec{r}} \otimes \phi_c(t),
\] (30)
where \( \phi_c(t) \) solves the ionic TDSE with the Hamiltonian \( H_{ion}(t) \) and a final state condition that specifies the ionic state \( c \) of the channel:
\[
H_{ion}(T) \phi_c(T) = E_c \phi_c(T).
\] (31)

Assuming that double ionization is negligible, the further steps for computing the spectral amplitude as a time integral are the same as in the single-electron case. In addition to \( \Psi_s(t) \), we must also compute \( \phi_c(t) \). Values and derivatives of the \( c \)-channel scattering wave function \( \psi_c(\vec{r},t) := \langle \phi_c(t) | \Psi_s(t) \rangle \) at \( |\vec{r}| = R_c \) can be stored for a sufficiently dense time grid. Because of the stronger binding of electrons in the ion, computing the ionic wave function \( \phi_c(t) \) usually requires much less effort than obtaining \( \Psi_s(t) \).

6.3. Double ionization

For double-ionization spectra, we must know the two-electron solution in the asymptotic region. This may be less difficult than it appears to be at first glance. Neglecting the ionic potentials, we have a Volkov solution for the center-of-mass coordinate and Coulomb waves for the relative coordinate. What is left to do is to match that solution with an accurate solution on a five-dimensional (5D) surface, where all reflections from the simulation box boundaries are carefully suppressed. While this procedure has not been worked out in detail, it may be very feasible and bring IR two-electron spectra from the realm of herioc super-large-scale calculations [5] to manageable size, allowing systematic studies.

7. Conclusions and outlook

We have shown that the unfavorable scaling for the computation of photo-electron spectra with laser wave length can be largely overcome with t-SURFF, which picks up the exact solution at some finite surface and beyond that surface exploits knowledge about the long-range behavior of the solutions of the TDSE. The reduction of problem size is particularly striking for atomic binding potentials with a finite range, when the Volkov solutions become exact at distances where the potential is zero. In that case, the box sizes can be reduced to approximately the range of the potential plus the electron quiver amplitude. Electrons that move beyond that range will never scatter and will exactly follow the Volkov solution. For our parameters, the wave function
expands to several thousands of atomic units during the pulse and correspondingly large boxes would be needed if a spectral analysis of the wave function were performed after the end of the pulse. In contrast, we could present $\lesssim 1\%$ accurate spectra up to energies of 120 eV using a box size of only about 30 atomic units and as few as 75 discretization points per partial wave. With only a few more points, much higher accuracy can be reached.

The traceless absorption of the wave function beyond the surface by irECSs [16] is essential for the method. The good performance of irECS for 1D wave functions and for high-harmonic signals from 3D calculations presented in [16] could be confirmed also for the much more delicate observable of angle-resolved photo-electron spectra.

For the long-range Coulomb potential, the Volkov solutions are not exact asymptotically, let alone at any finite distance. In physical language, the electron will scatter in the long-range tail of the Coulomb potential and pick up more energy from the laser field, and therefore we cannot predict its final energy before the pulse is over. An attempt to approximate the asymptotic behavior by the Coulomb–Volkov instead of the pure Volkov solutions was futile. In a pragmatic approach, we could show that with a surface at distances of $R_c = 100–140$ atomic units, still impressively accurate spectra can be obtained using Volkov solutions as approximation to the exact asymptotic solutions.

For single-electron systems and with moderate accuracy requirements, simulation volumes on the scale of $\sim 100$ atomic units are quite acceptable. For experimentally interesting multi-electron systems, we have proposed to further reduce box sizes by solving the asymptotic laser-assisted scattering problem numerically. This may be done efficiently for an asymptotic Hamiltonian that only includes scattering at distances $> R_c$ and dismisses the main part of scattering from near the Coulomb singularity. The need to solve this weak scattering problem enhances the complexity of coding and significantly increases computation times. However, for few-electron systems, this extra effort is far compensated by an expected reduction to box sizes as little as 20–50 atomic units. We have also formulated the extension of t-SURFF to single and double ionization of multi-electron systems. A numerical demonstration of these methods will be the subject of future work.

In summary, t-SURFF, while producing highly accurate results, can reduce the box size for computing IR photo-electron spectra for single-electron systems by one order of magnitude or more. This drastic reduction of box sizes is particularly important for very high laser wavelengths and for multi-electron systems. For systems with two and more electrons, we believe, it opens the route to computing accurate IR photo-electron momentum spectra.

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