Time delays in correlated photoemission processes

R. Pazourek¹, S. Nagele², and J. Burgdörfer²

¹ Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803, USA
² Institute for Theoretical Physics, Vienna University of Technology, 1040 Vienna, Austria, EU
E-mail: rpazourek@lsu.edu

Abstract. We theoretically study time-resolved two-photon double ionization (TPDI) of helium as probed by attosecond streaking. We review recent advances in the understanding of the photoelectric effect in the time domain and discuss the differences between one- and two-photon ionization, as well as one- and two-electron emission. We perform exact ab-initio simulations for attosecond streaking experiments in the sequential TPDI regime and compare the results to the two-electron Eisenbud-Wigner-Smith delay for the process. Our calculations directly show that the timing of the emission process sensitively depends on the energy sharing between the two outgoing electrons. In particular, we identify Fano-like interferences in the relative time delay of the two emitted electrons when the sequential ionization channel occurs via intermediate excited ionic (shake-up) states. Furthermore, we find that the photoemission time delays are only weakly dependent on the relative emission angle of the ejected electrons.

1. Introduction

Time-resolved photoemission and real time information on electronic dynamics has become accessible with the advances of new light sources. First measurements and theoretical investigations on the photoelectric effect in atoms, molecules, and solids have become available [1–3]. A commonly employed pump-probe setup used to extract photoemission time delays is attosecond streaking [4–6] which employs a phase-controlled (few-cycle) infrared (IR) field and an extreme ultraviolet (XUV) attosecond pulse to determine the arrival time of the photoelectrons in the continuum. The streaking time shifts contain information on the Eisenbud-Wigner-Smith (EWS) time delay [7–9] which has evolved as the key physical observable describing time-resolved photoemission. In addition to the EWS time delay which describes the short-ranged properties of the atomic potential, the long-range Coulomb potential gives rise to a so-called Coulomb-laser-coupling (CLC) time shift in the IR field [10–12]. Polarization of the initial and final states by the probing IR-field can lead to additional modifications of the streaking time shift [13–16]. Probe-field induced modifications are strictly additive to the EWS delay. This holds true also for atoms with more than one active electron [16, 17] as well as for small molecules [18]. In larger molecular systems or for the escape of electrons from a solid surface, transport effects and modifications of the IR streaking field by screening and field enhancement become important [1, 19, 20].

In this contribution, we review the ionization dynamics of two-photon double ionization (TPDI) in helium which is a fundamental three-body process and therefore has been the focus of a large number of studies in the spectral domain (see [21–28] and references therein). In the limit of long XUV pulses it is possible to distinguish two different ionization regimes for TPDI
depending on the photon energy: for \( \hbar \omega_{\text{XUV}} > I_2 = 54.4 \text{ eV} \), where \( I_2 \) is the second ionization potential, the second, deeper bound electron can be ejected independently irrespective of the time that has elapsed since the first emission event. This is the so-called sequential regime. For \( (I_1 + I_2)/2 = 39.5 \text{ eV} \leq \hbar \omega_{\text{XUV}} \leq 54.4 \text{ eV} \) only the combined photon energy of both photons exceeds the second ionization potential. Therefore, only nonsequential ionization is possible since the electrons need to share the available energy. In [29] we have presented first studies of this process in the temporal domain and could show that for sequential TPDI the relative emission delays also depend on the absorption times of the two photons and hence on the pulse duration of the ionizing XUV pulse. Moreover, time-ordering of the photoionization process becomes accessible directly in the time domain by attosecond streaking, see Fig. 1.

Here we extend this study to the angular dependence of the process. Furthermore, we investigate in detail the photoemission dynamics when the first ionization step is accompanied by shake-up of the second electron which gives rise to Fano-‘resonance-like’ lineshapes [30] in the energy-resolved EWS time delays. Similar to the one-photon case, the relative streaking time shift of TPDI can be quantitatively described by an EWS time. The generalization of the EWS time delay to two-photon ionization contains, besides the usual one-photon contributions determined by the scattering phase of the outgoing electron, also an XUV-pulse dependent part. The latter has also been recently investigated for two-photon resonant single ionization where it has been referred to as absorption delay [31]. The pulse-dependent part can be separately described within lowest-order time dependent perturbation theory (TDPT) and exhibits a strong variation as a function of electron energy or, in the case of TPDI, on the energy sharing between the two emitted electrons. True sequential ionization characterized by a linear scaling of the delay with the pulse duration can only be found for on-shell energies.

The paper is organized as follows: We first review the theoretical and numerical models used to describe time-resolved photoemission and describe the difference between one- and two-photon ionization time delays. We then present new results on energy- and angular resolved EWS time delays and compare them to ab-initio results for angular-resolved streaking time shifts. Finally, we show how the ionization dynamics changes as a function of energy sharing between the two emitted electrons, in particular when the first ionization step is accompanied by shake-up of the
second electron, giving rise to Fano-‘resonance-like’ lineshapes not only in the spectral but also in the temporal domain.

Atomic units are used throughout the manuscript unless indicated otherwise.

2. Methods

Attosecond streaking exploits the fact that once a photoelectron is liberated by the XUV pulse into the continuum in the presence of a probing IR field it obtains a final momentum

$$\vec{p}_f(\tau) = \vec{p}_0 - \vec{A}_{\text{IR}}(\tau + t_S)$$

(1)

where $\tau$ is the delay between XUV and IR pulse and $\vec{p}_0$ is the asymptotic momentum in the absence of the streaking field. The streaking time shift $t_S$ can then be obtained by fitting the first moments (or peak positions) of the final momentum distribution $p_f(\tau)$ along the laser polarization to the IR vector potential according to Eq. 1. It describes the time shift relative to the peak of the XUV pulse that triggers the photoionization event. For one-photon ionization by a chirp-free and symmetric XUV pulse, the peak, or time zero of the pulse, coincides with the (average) photoabsorption time while for two-photon ionization, in general, the two photons are absorbed at different times and the streaking time shift becomes dependent on the XUV pulse duration [29, 31].

For the numerical simulation of a streaking experiment we solve the time-dependent Schrödinger equation (TDSE) for helium in its full dimension (for details about the method see [23, 32]) in the presence of the linearly-polarized ionizing XUV field $F_{\text{XUV}}(t)$ and the streaking IR field $F_{\text{IR}}(t)$. We employ a time-dependent close coupling scheme, where the angular part of the wave function is expanded in coupled spherical harmonics. Convergence was reached for single-electron angular momenta up to values of $l_{1,\text{max}} = l_{2,\text{max}} = 15$ and total angular momenta up to $L_{\text{max}} = 6$ in the presence of a streaking field with an intensity $I_{\text{IR}} = 10^{10}$ W/cm$^2$ (for calculations in the absence of a streaking field $L_{\text{max}} = 2$ is sufficient to describe the absorption of two XUV photons). For the discretization of the two radial variables, we employ a discrete variable representation (FEDVR) [33, 34] with a maximal extension of the radial box of 576 a.u., while the temporal propagation is performed using a short iterative Lanczos method [35–37] with adaptive time-step control.

The intrinsic time delays in the absence of a probing IR field can be described to a good degree of approximation within the framework of lowest-order time-dependent perturbation theory (TDPT) which we use as guide for interpreting the simulated results.

For one-photon single ionization the transition amplitude in first-order TDPT reads

$$t^{(1)}_{i\rightarrow f} = -i \int_{t_0}^\infty dt_1 \langle f|\hat{V}_I(t_1)|i\rangle = -i \langle f|\hat{\mu}|i\rangle \int_{t_0}^\infty dt_1 e^{i(E_f-E_i)t_1} F_{\text{XUV}}(t_1) = -i \langle f|\hat{\mu}|i\rangle \tilde{F}_{\text{XUV}}(\omega)$$

(2)

with $\hat{\mu} = \sum_{i=1}^{n_e} \hat{z}_i$ and the perturbation operator in the interaction representation given in length gauge by

$$V_I(t) = e^{iH_0t}\hat{\mu}\tilde{F}_{\text{XUV}}(t)e^{-iH_0t}$$

(3)

for $n_e$ active electrons in the system. $\tilde{F}_{\text{XUV}}(t) = F_0 \exp(-\ln 4\tau^2_{\text{XUV}}) \cos(\omega_{\text{XUV}}t)\tilde{z}$ is the linearly polarized attosecond XUV pulse, $H_0$ is the atomic Hamiltonian, and $E_i = E_0$ is the initial state energy. The group delay for one-photon single ionization with a final continuum state $|f\rangle = |\vec{k}\rangle$ ($E_f = k^2/2$) follows as

$$\frac{\partial}{\partial E} \arg t^{(1)}_{i\rightarrow f} = \frac{\partial}{\partial E} \arg \langle \vec{k}|\hat{\mu}|i\rangle + \frac{\partial}{\partial E} \arg \tilde{F}_{\text{XUV}}(\omega).$$

(4)
For a chirp-free and symmetric XUV pulse the Fourier transform \( \tilde{F}_{\text{XUV}}(\omega) \) is real and the group delay reduces to

\[
t_{\text{EWS}} = \frac{\partial}{\partial E} \arg(\tilde{K}|\hat{\mu}|i) .
\] (5)

This coincides with the usual expression for the EWS delay \([12, 38]\) and reduces for a single partial wave in the final state to the spectral derivative of the scattering phase. In the presence of a Coulomb potential the evaluation of the EWS delay from the transition matrix elements becomes ill-defined since the outgoing Coulomb wave contains besides the Coulomb scattering phase \( \sigma_{\ell}(E) \), which is the analogue to the short-ranged scattering phase, also a diverging part \( \propto \ln(Zk\tau)/k \). The streaking field only probes the system over a finite time (and space) and thus also only probes a finite part of the diverging Coulomb time shift. This gives rise to the CLC time delay \([10–12]\) which depends on the asymptotic ionic charge \( Z \), the kinetic electron energy \( E \), and the wavelength of the probing IR field \( \lambda_{\text{IR}} \). Since it is independent of the atomic species an analytical approximation can be given or, alternatively, it can be numerically determined by an independent reference streaking simulation for a pure Coulomb potential \([12, 38]\).

For two-photon ionization we consider the second-order TDPT amplitude

\[
a^{(2)}_{i \rightarrow f} = -\int_{-\infty}^{\infty} dt_{1} \int_{-\infty}^{t_{1}} dt_{2} \langle \psi_{f}|V_{f}(t_{1})V_{f}(t_{2})|\psi_{i}\rangle
\] (6)

which can be factorized as

\[
a^{(2)}_{i \rightarrow f} = -\sum_{n} \langle f|\hat{\mu}|n\rangle \langle n|\hat{\mu}|i\rangle G[E_{f}, E_{n}, E_{i}, F_{\text{XUV}}(t)]
\] (7)

with

\[
G[E_{f}, E_{n}, E_{i}, F_{\text{XUV}}(t)] = \int_{t_{0}}^{\infty} dt_{1} \int_{t_{0}}^{t_{1}} dt_{2} e^{iE_{n}t_{1}} e^{iE_{n}t_{2}} \tilde{F}_{\text{XUV}}(t_{1})F_{\text{XUV}}(t_{2}) .
\] (8)

For TPDI, Eq. 7 describes the transition between the initial state \( |\psi_{i}\rangle \) taken in the following to be the fully correlated He ground state and the final state \( |\psi_{f}\rangle = |\psi(\vec{p}_{1}, \vec{p}_{2})\rangle \) of two continuum electrons with asymptotic momenta \( \vec{p}_{1} \) and \( \vec{p}_{2} \) and energy \( E_{\text{tot}} = \sum \vec{p}_{\ell}^{2}/2 \). The energies are given by \( E_{i} = E_{0}, E_{n} = E[\text{He}^{+}(n)] + E_{1} \) and \( E_{f} = E_{1} + E_{2} \) \((E_{1} = k_{f}^{2}/2, E_{2} = E_{n}^{2}/2)\). The sum over intermediate states \( \sum_{n} |n\rangle \langle n| \) contains virtual and (near) on-shell singly ionized states \( \text{He}^{+}(n\ell) \). The so-called shape function \( G \) \([21, 24]\) (which reduces to the simple Fourier transform of the field in the one-photon case) is a functional of \( F_{\text{XUV}}(t) \) and a function of the energy differences \( E_{f} - E_{n} \) and \( E_{n} = E_{n} - E_{i} \). As such it contains information on the probing XUV field but also on the atomic system through the spectral information of the initial, intermediate, and final states. For a Gaussian pulse envelope function an analytical expression can be found for the integral in Eq. 8 the argument of which only depends on the relative energy between the two electrons but is independent of the photon energy.

The exact determination of an EWS time delay in terms of the spectral derivative of the scattering phase or the argument of a complex transition matrix element \([7–9, 38, 39]\) as in the one-electron case (cf. Eq. 5) is not straightforward since an analytic form of the asymptotic scattering states is not known. We therefore extract the EWS delay by separately solving the TDSE for photoionization by the XUV pulse in the absence of the probing IR field, taking the energy derivative of the phase of the final two-electron wavepacket propagated to a large time \( t_{f} \), and subtracting the free propagation phase, \( -Et_{f} \). Thus, the EWS time delay for an electron...
emitted in TPDI with energy $E_1$, fixed energy $E_2$ of the other electron, and fixed emission angles $\theta_1$ and $\theta_2$, follows from \cite{29}

\begin{equation}
t_{\text{EWS,1}}^{\text{DI}}(E_1, E_2, \theta_1, \theta_2) = \frac{\partial}{\partial E_1} \left[ \text{arg} e^{\text{DI}}(E_1', E_2, \theta_1, \theta_2, t_f) + E_1' t_f \right] \bigg|_{E_1'=E_1},
\end{equation}

where $e^{\text{DI}}(E_1, E_2, \theta_1, \theta_2, t_f)$ is the double ionization amplitude in coplanar geometry ($\phi_1 = \phi_2 = 0$). In the following, we will discuss the relative emission delay, i.e., the time interval between the two emission events,

\begin{equation}
\Delta t_{\text{EWS}}^{\text{DI}}(\Delta E) = t_{\text{EWS,1}}^{\text{DI}}(E_1, E_2, \theta_1, \theta_2) - t_{\text{EWS,2}}^{\text{DI}}(E_1, E_2, \theta_1, \theta_2)
\end{equation}

which can be conveniently determined by taking the spectral derivative in Eq. 9 with respect to $\Delta E = E_1 - E_2$ at a constant total energy.

### 3. Angle- and energy-resolved relative emission delay

Sequential TPDI is characterized by two prominent peaks in the differential energy distribution (see Fig. 1a,b). Since the spectrum and relative emission delays are nearly universal functions of the energy difference $\Delta E$ (along the diagonal indicated in Fig. 1a) and only weakly dependent on the total energy (i.e., the photon energy) \cite{24,29}, we focus in the following on relative EWS delays $\Delta t_{\text{EWS}}^{\text{DI}}(\Delta E)$ (Eq. 10). The relative energy $\Delta E = \pm 30 \text{eV}$ corresponds to the \textit{sequential} energy sharing where we observe a peak in the spectral distribution and an enhanced relative emission delay. This is illustrated in Fig. 2a for the relative emission time shifts $\Delta t_{\text{EWS}}^{\text{DI}}(\Delta E)$ (given by the color code) in addition to the ionization yield (encoded in the amplitude) as a function of $\Delta E$ and $\theta_2$, for $\theta_1 = 0^\circ$ and $E_{\text{tot}} = 2\hbar \omega + I_0$. For $\Delta E = E_1 - E_2 > 0$ the electron with $E_1$ is the faster one that was ejected first from He, leaving behind a (near) on-shell intermediate state $\text{He}^+(1s)$ from which the second (slow) electron with energy $E_2$ is emitted. We therefore expect $t_{\text{EWS,1}}^{\text{DI}} < t_{\text{EWS,2}}^{\text{DI}}$ and correspondingly a negative (blue) relative time shift (Eq. 10) at $\Delta E = 30 \text{eV}$ in Fig. 3a. The relative time delay $\Delta t_{\text{EWS}}^{\text{DI}}(\Delta E)$ is antisymmetric in $\Delta E$ since the indistinguishability of the two electrons requires opposite time-ordering for $E_1 < E_2$. In between the sequential peaks, the ionization yield as well as the relative delay drop to very small values.

Those energy configurations far from \textit{on-shell} intermediate states require large energy sharing between the electrons which can only be achieved if the first electron is still close to the nucleus when the second photon is absorbed. The ionization process is, in fact, \textit{nonsequential} in this energy region despite the high photon energy in the nominally ‘sequential’ regime.

The overall structure of the TPDI process remains valid for all angular configurations (Fig. 2a). Interesting structures appear at $|\Delta E| > 50 \text{eV}$ where shake-up ionization channels in the intermediate state open, discussed in more detail in the next section. At those energies we also observe larger angular variation in the delay around $\theta_2 = 90^\circ$ where the main sequential process (without shake-up) has a nodal plane. Note that nodal lines imply a phase jump by $\pi$ in the wavefunction and hence a discontinuity in the EWS delay.

Streaking time shifts for TPDI ionization can be extracted from streaking spectrograms (Fig. 1c) from the fit of the modulation $\Delta p(\tau) = -\alpha A(\tau + t_S)$ for the two main sequential peaks. The error in the extraction of the streaking delay due to the integration over the energy of one electron, can be corrected for by performing a reference calculation for a non-interacting reference system described by second-order TDPTP (for more details see the appendix of \cite{29}). The generalization of the relationship between streaking time shifts $t_S$ and EWS delays for TPDI of the fully Coulomb-interacting system reads for the relative time shifts

\begin{equation}
\Delta t_{\text{S}}^{\text{DI}} = \Delta t_{\text{EWS}}^{\text{DI}} + \Delta t_{\text{CLC}} + \Delta t_{(2\gamma,2e)}
\end{equation}
with the contribution of the relative CLC time shift $\Delta t_{\text{CLC}}$ and the correction for TPDI $\Delta \delta^{(2\gamma,2\epsilon)}$.

We find overall very good agreement between the ab initio simulation for $\Delta t_{\text{S}}^{\text{DI}}$ and the right hand side of Eq. 11 for which all terms can be independently and accurately determined (Fig. 2b). Near collinear emission ($\theta_1 = \theta_2 = 0^\circ$) electron-electron correlations become important since the outgoing electrons strongly repel each other. This results in a slightly enhanced relative time shift, since emission into the same direction becomes more probable when the time interval between two emission events is larger, but also in stronger variations as a function of $\Delta E$ in the otherwise mostly angular-independent relative time delay (Fig. 2a). We note that collinear emission is also the region most sensitive to the convergence as a function of the number of included partial waves and, hence, total angular momentum, which might be the reason for the slightly worse agreement between the simulation and the prediction (Eq. 11) for $\theta_2 < 20^\circ$ (Fig. 2b). The discontinuity of the spectral phase at the nodal line at $\theta_2 = 90^\circ$ is reflected in both the streaking and EWS time delays.

4. Dynamical Fano interferences

We investigate now the emission time delays when the ejection of the first electron is accompanied by the formation of an intermediate shake-up state $\text{He}^+ (n = 2)$ in more detail. When the spectral width of the XUV pulse $\sim 1/\tau_{\text{XUV}}$ becomes comparable to the spacing between different (shake-up) intermediate states $\text{He}^+ (n)$, $(n = 1, 2, 3, \ldots)$ the coherent superposition of the double ionization amplitudes through different intermediate states must be considered in Eq. 7. The existence of the different sequential pathways to the same two-electron final state in the double continuum gives rise to a Fano-like lineshape in the time delay $\Delta t^{\text{DI}}_{\text{EWS}}(\Delta E)$ as a function of $\Delta E$ (Fig. 3a,b). Note that this differs from the well-know Fano-resonances in the single ionization channel which result from the interference between directly ionized electrons and a decaying doubly excited state. Unlike the single-ionization resonances, the interferences in TPDI can be understood by the XUV-pulse dependent part of the EWS delay, $t_{EWS}^G$, encoded in the shape-function within second-order TDPT. For different intermediate states, $t_{EWS}^G$ follows from Eq. 7.
Delay/τ4
12 (fs)
-0.4
-0.2
0
0.2
0.4
0.6

(b) TDSE
TDPT
Fano fit

Figure 3: (a) Relative EWS time delay ΔtEWS(ΔE)/τXUV (Eq. 12) as a function of ΔE and pulse duration τXUV. For longer pulse durations the line shapes convergence to Lorentzians at the sequential peaks with a maximum value of a delay of ∼ ±0.4τXUV (color scale of relative delay, see bar on the right). (b) Comparison of the relative EWS time delay for τXUV = 500 as from the solution of the TDSE (ΔtEWS(ΔE)/τXUV), with the shape-function model (ΔtEWS(ΔE)/τXUV) and a fit to a Fano lineshape for the n = 2 shake-up region, see text for details. (c)-(e) Parameters of the shake-up peak interference behaviour based on the shape-function model with negative as a function of ∆E with a background dependence of the obtained fit parameters on the pulse duration, confirming the expected behaviour: with decreasing spectral width of the XUV pulse, i.e., longer duration τXUV, the peaks converge to the satellite lines, i.e., Lorentzians of vanishing width, near |ΔE| → I1−I2+2E2/uniEBC91−/uniEBC92 /uniEBC92−/uniEBC91 /uniEBC91−/uniEBC92+2E2/uniEBC92−/uniEBC91−2E2 of the intermediate state (and for photon energies E ∼ 100 eV small compared to the XUV-pulse dependent part, Eq. 12).

For spectrally well separated intermediate states (e.g. near n = 1) ΔtEWS(ΔE) exhibits a single peak (or dip) with a Lorentzian line shape. For shake-up channels (n ≥ 2), the time delay displays Fano profiles for short pulses which converge to Lorentzian line shapes for long pulse durations. This can be quantified by fitting our numerical data to a Fano profile [30]

\[ ΔtEWS(ΔE) \propto cbg + cF \frac{(qΓ/2 + E - E_F)^2}{(E - E_F)^2 + (Γ/2)^2} \]  

with a background cbg to account for the fact that the time delays are not strictly positive or negative as a function of ΔE (see black solid line in Fig. 3b). For simplicity, we analyze the interference behaviour based on the shape-function model with n = 1 and n = 2 intermediate states which agrees well with the full TDSE results (Fig. 3b). Fig. 3(c)-(e) illustrates the dependence of the obtained fit parameters on the pulse duration, confirming the expected behaviour: with decreasing spectral width of the XUV pulse, i.e., longer duration τXUV, the peaks converge to the satellite lines, i.e., Lorentzians of vanishing width, near |ΔE| → I1−I2+2E2 with Γ → 0 and |q| ≫ 1.

\[ ΔtEWS(ΔE) = \frac{∂}{∂ΔE} \arg \left[ \sum_n \alpha_n G(E_f, E_n, E_i, F_{XUV}(t)) \right] \]  

where \( α_n \) is the relative weight of the intermediate channel \( n \). Since \( G \) is a complex quantity the coherent sum of the contributions from pathways with different intermediate states leads to interferences in the spectra with a Fano lineshape, but also to a complex behaviour of the spectral phase. The delay due to the atomic transition matrix element given by the scattering phase \( \langle f|\hat{u}|n\rangle\langle n|\hat{u}|i\rangle \) only depends on the final energy of the electrons and is thus independent of the intermediate state (and for photon energies ∼ 100 eV small compared to the XUV-pulse dependent part, Eq. 12).
Exactly at the sequential peaks the relative EWS time shift scales linearly with the pulse duration (constant in the scaled relative time delay \( \Delta t_{\text{EWS}}^t (\Delta E) / \tau_{\text{XUV}} \) in Fig. 3a), characteristic for a sequential process. For larger pulse durations of a few femtoseconds, the linear scaling \( \sim \pm 0.4 \tau_{\text{XUV}} \) (corresponding to a constant value \( \sim \pm 0.4 \), orange and turquoise in the color scale of Fig. 3a) is independent of the intermediate state, i.e., we observe the same time interval between the emission of the two electrons regardless whether the first ionization step was accompanied by shake-up or not. Once the lineshape for intermediate shake-up states converges to a Lorentzian also the expected time-ordering of the photoemission event emerges: in contrary to the process without shake-up, now the second electron carries more energy and thus the shake-up peaks show reversed time-ordering compared to the direct peaks.

5. Conclusions
We have reviewed the dynamics of sequential two-photon double ionization (TPDI) in helium. We have shown that the relative emission delays as well as the time-ordering become accessible by attosecond streaking and are in good agreement with the two-electron Eisenbud-Wigner-Smith (EWS) time delay taking into account IR-field modifications. The two-electron EWS time delay reveals a strong dependence of the time shift on the energy sharing between the outgoing electrons while only a weak dependence on the relative emission angle could be found. For ionization via an intermediate shake-up state we observe dynamical Fano-like interferences in the energy-resolved relative EWS time delay. For longer pulses they converge to a Lorentzian with a linear scaling of the relative delay with the pulse duration, characteristic for the sequential ionization process.

We thank Johannes Feist for his work on the helium code and for fruitful discussions in the early stage of this work. This work was supported by the Austrian Science Fund (FWF): Grant No. P21141-N16, P23359-N16, SFB 041 (VicCoM) and SFB 049 (Next-Lite), the COST Action CM1204 (XLIC), and in part by the National Science Foundation through XSEDE resources provided by NICS and TACC under Grant TG-PHY090031. The computational results presented have also been achieved in part using the Vienna Scientific Cluster (VSC).

References
[1] Cavalieri A L, Müller N, Uphues T et al. 2007 Nature 449 1029
[2] Schultze M, Fiess M, Karpowicz N et al. 2010 Science 328 1658
[3] Klünder K, Dahlström J M, Gisselbrecht M et al. 2011 Phys. Rev. Lett. 106 143002
[4] Itatani J, Quéré F, Yudin G L et al. 2002 Phys. Rev. Lett. 88 173903
[5] Kienberger R, Goulielmakis E, Uiberacker M et al. 2004 Nature 427 817
[6] Yakovlev V S, Banmer F and Scrinzi A 2005 J. Mod. Opt. 52 395
[7] Eisenbud L 1948 Formal properties of nuclear collisions Ph.D. thesis Princeton University
[8] Wigner E P 1955 Phys. Rev. 98 145
[9] Smith F T 1960 Phys. Rev. 118 349
[10] Zhang C H and Thumm U 2010 Phys. Rev. A 82 043405
[11] Nagele S, Pazourek R, Feist J et al. 2011 J. Phys. B 44 081001
[12] Pazourek R, Nagele S and Burgdörfer J 2015 Rev. Mod. Phys. 87 765
[13] Baggesen J C and Madsen L B 2010 Phys. Rev. Lett. 104 043602
[14] Baggesen J C and Madsen L B 2010 Phys. Rev. Lett. 104 209903
[15] Pazourek R, Nagele S, Doblhoff-Dier K et al. 2012 J. Phys. Conf. Ser. 388 012029
[16] Pazourek R, Feist J, Nagele S et al. 2012 Phys. Rev. Lett. 108 163001
[17] Nagele S, Pazourek R, Feist J et al. 2012 *Phys. Rev. A* **85** 033401
[18] Ning Q C, Peng L Y, Song S N et al. 2014 *Phys. Rev. A* **90** 013423
[19] Neppi S, Ernstorfer R, Cavalieri A L et al. 2015 *Nature* **517** 342
[20] Nagele S, Pazourek R, Wais M et al. 2014 *J. Phys. Conf. Ser.* **488** 012004
[21] Palacios A, Rescigno T N and McCurdy C W 2009 *Phys. Rev. A* **79** 033402
[22] Ishikawa K L and Midorikawa K 2005 *Phys. Rev. A* **72** 013407
[23] Feist J, Nagele S, Pazourek R et al. 2008 *Phys. Rev. A* **77** 043420
[24] Pazourek R, Feist J, Nagele S et al. 2011 *Phys. Rev. A* **83** 053418
[25] Laulan S and Bachau H 2003 *Phys. Rev. A* **68** 013409
[26] Horner D A, Morales F, Rescigno T N et al. 2007 *Phys. Rev. A* **76** 030701(R)
[27] Nikolopoulos L A A and Lambropoulos P 2007 *J. Phys. B* **40** 1347
[28] Foumouo E, Hamido A, Antoine P et al. 2010 *J. Phys. B* **43** 091001
[29] Pazourek R, Nagele S and Burgdörfer J 2015 *J. Phys. B* **48** 061002
[30] Fano U 1961 *Phys. Rev.* **124** 1866
[31] Su J, Ni H, Jaroni-Becker A et al. 2014 *Phys. Rev. Lett.* **113** 263002
[32] Schneider B I, Feist J, Nagele S et al. 2011 in Bandrauk A D and Ivanov M (eds.), *Quantum Dynamic Imaging* (Springer) CRM Series in Mathematical Physics chap. 10
[33] Rescigno T N and McCurdy C W 2000 *Phys. Rev. A* **62** 032706
[34] Schneider B I and Collins L A 2005 *J. Non-Cryst. Solids* **351** 1551
[35] Park T J and Light J C 1986 *J. Chem. Phys.* **85** 5870
[36] Smyth E S, Parker J S and Taylor K T 1998 *Comput. Phys. Commun.* **114** 1
[37] Leforestier C, Bisseling R H, Cerjan C et al. 1991 *J. Comp. Phys.* **94** 59
[38] Pazourek R, Nagele S and Burgdörfer J 2013 *Faraday Discuss.* **163** 353
[39] de Carvalho C A A and Nussenzveig H M 2002 *Physics Reports* **364** 83