Streaking and Wigner time delays in photoemission from atoms and surfaces

C.-H. Zhang and U. Thumm

Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA

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Streaked photoemission metrology allows the observation of an apparent relative time delay between the detection of photoelectrons from different initial electronic states. This relative delay is obtained by recording the photoelectron yield as a function of the delay between an ionizing ultrashort extended ultraviolet pulse and a streaking infrared (IR) pulse. Theoretically, photoemission delays can be defined based on (i) the phase shift of the photoelectron wave function accumulates during the release and propagation of the photoelectron ("Wigner delay") and, alternatively, (ii) the streaking trace in the calculated photoemission spectrum ("streaking delay"). We investigate the relation between Wigner and streaking delays in the photoemission from atomic and solid-surface targets. For solid targets and assuming a vanishing IR skin depth, both Wigner and streaking delays can be interpreted as an average propagation time needed by photoelectrons to reach the surface, while the two delays differ for nonvanishing skin depths. For atomic targets, the difference between Wigner and streaking delays depends on the range of the ionic potential.

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I. INTRODUCTION

Streaked photoemission spectroscopy is increasingly applied to resolve ultra-fast electronic processes at the natural time scale (≈1 atomic unit = 2.4 × 10⁻¹⁷ s = 24 as) of the motion of valence electrons in matter. Streaking metrology uses ultra-short pulses of extreme ultraviolet (XUV) radiation to emit electrons into the electric field of a delayed infrared (IR) laser pulse. The XUV and IR pulses in this pump-probe setup are phase coherent, and the yield of emitted photoelectrons is recorded as a function of the delay \( \Delta \tau \) between the two pulses [1]. The resulting energy-resolved photoemission spectra show stripes that oscillate in \( \Delta \tau \) with the period of the IR-laser electric field. These streaking traces occur in distinct photoelectron kinetic energy intervals that are determined by the spectral width of the XUV pulse, the IR-laser intensity, and the density of states of the target. For photoemission out of energetically resolved discrete atomic levels, streaking traces can be related to a given initial state, while for photoemission from electronic states in solids they are modulated by the density of states within a given band of occupied states. The analysis of streaked photoemission spectra proceeds by fitting the center of energy (COE) of a given streaking trace as a function of \( \Delta \tau \) to a sine function with an adjustable phase, thereby mapping energy shifts induced by the IR laser onto a time delay between the apparent release of the photoelectron and the arrival of the XUV pulse [2,3].

Streaked photoelectron spectra from localized states of atomic targets [4] and both delocalized conduction band (CB) and localized core-level bands of solids [2] have recently been recorded, leading to an ongoing debate about (i) the interpretation of the deduced photoemission time delays and (ii) the possibility of distinguishing delay contributions from the primary XUV-photorelease process and subsequent photoelectron propagation in the ionic potential of the target and the streaking IR-laser electric field [5–8]. Applying streaking metrology to neon atoms, Schultze et al. [4] measured a relative photoemission streaking delay of \( \Delta \tau_s = 21 \pm 5 \) as for the release of electrons from \( 2p \) orbitals relative to emission from \( 2s \) orbitals. The authors analyzed their measured relative delay in terms of the relative Wigner delay \( \Delta \tau_W(\epsilon) \), which is given by the energy derivative of the spectral phase of the calculated photoelectron wave function [9,10], and averaged \( \Delta \tau_W(\epsilon) \) over the spectral profile of the XUV pulse. The difference between their calculated averaged relative Wigner delays \( \Delta \tau_W \) for emission from the \( 2s \) and \( 2p \) orbitals did not exceed \( \Delta \tau(2p - 2s) = \tau_W(2p) - \tau_W(2s) = 6.4 \) as, even for calculations that included electronic correlation in neon at the multiconfiguration-Hartree-Fock level. The authors linked the mismatch between their measured relative streaking and calculated Wigner delays to the extreme sensitivity of the photoelectron wave function’s spectral phase to electronic correlation effects in multielectron atoms.

The same experiment [4] was subsequently analyzed by Kheifets and Ivanov [5] based on numerical solutions of the time-dependent Schrödinger equation (TDSE) for a single active electron moving in the Hartree-Fock potential of a Ne\(^+\) ion and, in a separate approach, by including electronic correlation effects to some extent by numerically solving a set of coupled equations in a random-phase-approximation-with-exchange model. These calculations reproduce only less than one half of the measured relative delay of 21 as, and the authors speculated that the much larger observed relative delay might not be due solely to the XUV-induced release process, even if electronic correlation effects were accurately accounted for. The measured relative streaking delay might thus include significant contributions from the photoelectron’s interaction with the streaking IR-laser electric field. Indeed, the single-electron TSDE calculations by Ivanov [7] showed that the IR electric field has a considerable influence on the Wigner delay for photoemission. The question then arises whether this IR-dressed Wigner delay can be used to interpret the measured relative streaking delay. As shown in our previous investigation of time-resolved photoemission from a one-dimensional (1D) model hydrogen atom [6], the streaking delay is independent of the IR-laser intensity. This was confirmed recently in a full-dimensionality calculation for atoms by Nagele et al. [8].

Investigating photoemission from a tungsten surface, Cavalieri et al. [2] have measured a relative streaking
delay of $\Delta T_{\psi}(CB - 4f) = \tau_{\psi}(CB) - \tau_{\psi}(4f) = 110 \pm 70$ as for electrons emitted from 4$f$ core levels relative to electrons released from the CB. This relative delay was interpreted as the delayed onset of IR streaking, i.e., as the difference in time needed by 4$f$ and CB electrons to reach the surface [2,11]. However, as we will argue in Sec. III B, this interpretation is only valid under the assumption that the streaking IR field is fully screened inside the solid. We will also show in this work that Wigner and streaking delays become identical only in this limit of a sudden onset of IR streaking at the surface.

We will show that the streaking delay sensitively depends on the IR skin depth $\delta L$. Therefore, the intuitive interpretation of relative streaking delays in terms of an effective photoelectron path length inside the solid becomes questionable for realistic values of $\delta L$, depending on how exactly the IR electric field becomes screened in the solid.

While only relative streaking delays can be deduced from measured photoemission spectra, Wigner time delays are conveniently derived from calculated photoelectron wave functions. Wigner and streaking delays in time-resolved atomic photoemission were examined recently [7,8], and the nature of delays within the general context of scattering, decay, and photo- and particle-induced emission processes in atomic, nuclear, and other branches of physics has been discussed by theorists for more than half a century [9,10] (for a recent review see [12].) In this work, we investigate the relation between Wigner and streaking delays for photoemission from atoms in the gas phase and solid surfaces. In Sec. II, we present the underlying theoretical models and our schemes for calculating time delays in photoemission. In Sec. III, we compare and discuss our numerical results of time-resolved photoemission spectra from atoms (Sec. III A) and core-level and conduction bands of solid targets (Sec. III B). In particular, we investigate the dependence of the corresponding time delays on the XUV photon energy, the effective range $z_c$ of the atomic model potential, the initial state, the IR skin depth, and the position of the Fermi level. Our conclusions follow in Sec. IV. Unless indicated otherwise, we use atomic units (a.u.) throughout this work.

II. DEFINITION AND COMPUTATION OF WIGNER AND STREAKING TIME DELAYS

The essence of the time delay introduced by Wigner and Smith [9,10] can be understood for the elementary example of potential scattering in one spatial dimension, by representing the projectile as an incident wave packet

$$\delta \psi_{in}(z,t) = \int dk a_k e^{ikz - i\epsilon_k t},$$  (1)

in terms of a superposition with amplitudes $a_k$ of plane waves with momenta $k$ centered about $k$, and energies $\epsilon_k$. Scattering subject to the projectile-target-interaction potential $V$ of finite range results in the outgoing wave

$$\delta \psi_{out}(z,t) = \int dk a_k e^{i\epsilon_k z - i\epsilon_k t},$$  (2)

for which each spectral component is phase shifted by $\phi_k$ relative to the corresponding component of the incident wave. Depending on the values of the scattering phase shifts $\phi_k$, wave fronts of the scattered wave are shifted relative to the incident wave. The phase shifts $\phi_k$ thus quantify the effect of $V$ on $\delta \psi_{in}$. Depending on the nature of $V$, wave fronts of all plane-wave components and the center and crest of the scattered wave packet may appear behind or ahead of the corresponding terms of the incident wave packet. The scattered wave packet can thus be characterized by a positive or negative delay time $\tau$, depending on whether its wave fronts or center are detected after or before they would be detected in the absence of $V$, respectively. More precisely, the phase shifts of individual traveling plane wave components lead to spectral delays

$$\tau_{\psi}(\epsilon_k) = \frac{\partial \phi_k}{\partial \epsilon_k},$$  (3)

which, evaluated at the spectral center $\epsilon_c = k^2/2$ of the incident wave packet, define the Wigner delay [9,10]

$$\tau_{\psi}^{I} = \tau_{\psi}(\epsilon_c).$$  (4)

An alternative method for assessing the delay of the scattered relative to the incident wave packet is given in terms of the expectation values for the position,

$$\langle z \rangle(t) = \int_0^\infty dzz|\delta \psi_{out}(z,t)|^2,$$  (5)

and velocity,

$$\langle v \rangle(t) = \int_0^\infty dk|k|\delta \psi_{out}(k,t)|^2,$$  (6)

of the scattered wave packet at a sufficiently large time $t > T$ after the interaction according to [12,13]

$$\langle z \rangle = \langle v \rangle(t - \tau_{\psi}^{II}),$$  (7)

where $\delta \psi_{out}(k,t)$ is the Fourier transformation of $\delta \psi_{out}(z,t)$. The time $T$ is chosen so that $V(\langle z \rangle(t)) \sim 0$ and all spectral phases $\phi_k$ and $\langle v \rangle(t)$ of the outgoing wave packet remain time independent to a very good approximation for $t > T$. This fitting procedure can be understood classically by identifying the expectation values for position and velocity in Eq. (7) with the motion of a point particle (Fig. 1). We refer to both $\tau_{\psi}^{I}$ and $\tau_{\psi}^{II}$ as “Wigner delay” since it can be shown [12] that they are closely related by the expression

$$\tau_{\psi}^{II} = \int dk|\delta \psi_{out}(k,t)|^2 \tau_{\psi}^{I}(\epsilon_k).$$  (8)

Indeed, our numerical results in Sec. III will confirm that $\tau_{\psi}^{I}$ and $\tau_{\psi}^{II}$ are almost identical.

Both definitions of the Wigner time delay, $\tau_{\psi}^{I}$ and $\tau_{\psi}^{II}$, have been used to characterize scattering processes [12] and can also be applied to determine delays in photoemission. They were recently used to interpret the relative delay in the IR-streaked XUV spectra from the $1s$ and $2p$ shells in neon [4,5,7]. We thus believe that it is important to carefully investigate the relation between the Wigner and streaking delays.

We calculate the two Wigner delays for photoionization by solving the TDSE for photoelectron wave packets $\delta \psi(z,t)$ emitted from an initial state $\psi_i(z,t)$ [6],

$$i \frac{\partial}{\partial t} \delta \psi(z,t) = \left[ -\frac{p^2}{2} + V(z) \right] \delta \psi(z,t) + z E_X(t) \psi_i(z,t),$$  (9)
The XUV pulse is centered at potential of a solid. For the atomic case, we choose and $\tilde{\varepsilon}_k$ expectation values for the position $\langle \tilde{Z} \rangle$ of the photoionization of atoms. The solid line shows schematically the outgoing photoelectron wave simply as $\delta \psi(z, t)$. We consider photoionization by an attosecond XUV pulse from either the ground state of a 1D model atom or from the energetically lowest bands of occupied initial states in the periodic 1D model potential of a solid. For the atomic case, we choose $\psi_i(z, t)$ to be the ground state of the model atom with a potential $V(z)$. For photoemission from a surface, $\psi_i(z, t)$ designates Bloch waves from within a given band with Bloch momenta $k_f$.

We represent the coupling of the XUV pulse electric field $E_X$ to the electron in the dipole-length form and assume a Gaussian pulse profile,

$$E_X(t) \sim e^{-2\ln 2(t/\tau_X)^2} \sin(\omega_X t).$$

We assume a pulse duration $\tau_X = 300 \text{ as}$ and a variable central frequency $\omega_X$.

We propagate the photoelectron wave packet from $-4 \text{ to } 8 \text{ fs}$ on a spatial grid that extends over 32,000 a.u. and calculate the Wigner delays $\tau_{W}^{13}$ according to (4) and (7). Rewriting the photoelectron wave packet at the large time $T \gg \tau_X$ as [6,7]

$$\delta \psi(z, t = T) \sim \int dk \psi_k(z) d_k \tilde{E}_X(z, k) e^{-i\varepsilon_c T},$$

where $\psi_k(z)$ is a continuum eigenstate in the potential $V(z)$ with energy $\varepsilon_k$, $d_k = \langle \psi_k(z) | \psi_i(z) \rangle$ is the dipole matrix element, and $\tilde{E}_X(\omega) = \int dt E_X(t) e^{i\omega t}$ is the spectrum of $E_X(t)$, demonstrates that the Wigner delays depend on both the electron release during the dipole coupling of the XUV electric field and the propagation of the photoelectron in the continuum.

In order to calculate streaking delays from the streaked photoemission spectra, the influence of the streaking IR-laser field on the active electron needs to be investigated. The IR streaking effect on the release and propagation of the photoelectron is included by replacing $p$ with $p + A_L(z, t - \Delta t)$ in Eq. (9). The influence of the IR laser on the initial state can be included by numerically propagating the initial state in the IR-laser electric field according to [6]

$$i \frac{\partial}{\partial t} \psi_i(z, t) = \left\{ \frac{1}{2} [p + A_L(z, t - \Delta t)]^2 + V(z) \right\} \psi_i(z, t),$$

where $\Delta t$ is the delay between the centers of the XUV and IR pulses, and the convention is used that $\Delta t > 0$ corresponds to the XUV pulse preceding the IR pulse. We model the vector potential of the IR-laser pulse as

$$A_L(t) = A_0 \sin^2(\pi t / \tau_L) \cos(\omega_L (t - \tau_L/2))$$

for $0 \leq t \leq \tau_L$ and set $A_L$ to 0 otherwise. As pulse parameters, we choose the central photon energy $\hbar \omega_L = 1.57 \text{ eV}$ (corresponding to a wavelength of $\lambda_L = 800 \text{ nm}$), peak intensity $I_L = A_0^2 \omega_L^2/2 = 5 \times 10^{11} \text{ W/cm}^2$, and pulse length $\tau_L = 8 \text{ fs}$.

In free-electron dispersion is assumed ($\varepsilon = k^2/2$), the energy-differential photoemission probability is given by

$$P(\varepsilon, \Delta \varepsilon) = \frac{1}{2P_{\text{tot}}(\Delta \varepsilon)} \int dk |\delta \phi(k, \omega_L; \Delta \varepsilon)|^2,$$

with the total emission probability

$$P_{\text{tot}}(\Delta \varepsilon) = \int dk |\delta \phi(k, \omega_L; \Delta \varepsilon)|^2.$$

After calculating $E_{\text{COE}}(\Delta \varepsilon)$ for a range of XUV-IR delays $-\tau_L/2 \leq \Delta \varepsilon \leq \tau_L/2$, we obtain the streaking delay $\tau_S$ relative to $A_L$ by fitting the parameters $a, b$, and $\tau_S$ to the expression [3,6]

$$E_{\text{COE}}(\Delta \varepsilon) = a + b A_L(\Delta \varepsilon - \tau_S).$$

For XUV photoemission from solids, Eqs. (14)–(17) remain valid. In this case, the initial states in Eq. (9) are individual Bloch waves with momenta in the first Brillouin zone of either core-level or conduction band. We will show in Sec. III B how to calculate band-averaged results.

III. NUMERICAL RESULTS

A. One-dimensional model hydrogen atom

In this section, we discuss our numerical results for Wigner and streaking delays for XUV photoemission from the ground state with binding energy $\varepsilon_B = 13.6 \text{ eV}$ of the soft-core Coulomb potential

$$V(z) = V_c(z) = -1/\sqrt{z^2 + 2}.$$ (18)

In the calculation of the Wigner delay $\tau_W$, the direct numerical determination of the phase of the photoelectron wave packet according to $\varphi_k = \ln |\delta \phi(k, T)|/|\delta \phi(k, T)|$ is inaccurate or impossible for values of $k$ where $|\delta \phi(k, T)|$ is extremely small. Furthermore, $\varepsilon_c$ is difficult to determine from $\delta \phi(k, T)$ [see Fig. 2(a)]. In order to overcome these two difficulties, we fit the real part $\text{Re}[\delta \phi(k, T)]$ of the calculated photoelectron wave packet to the function

$$f(\varepsilon) = A e^{-2\ln 2[(\varepsilon - \varepsilon_c)/\Delta \varepsilon]^2} \cos(\varphi_k),$$

with

$$\varphi_k = \alpha(\varepsilon - \varepsilon_c) + \beta(\varepsilon - \varepsilon_c)^2 + \gamma.$$ (20)
and determine (by least-squares fit over a large range of $\varepsilon = k^2/2$ values) the parameters $\varepsilon_c$, $\Delta \varepsilon$, $\alpha = \tau^I_{W}$, $\beta$, and $\gamma$. As shown in Fig. 3 for photoionization with $\hbar \omega_X = 25$ and 50 eV, the spectra of the calculated (by numerically solving the TDSE) and fitted photoelectron wave packets are in excellent agreement. Since according to Eq. (11) the XUV pulse spectral profile is imprinted on the photoelectron wave packet, we find that the fitted values $\Delta \varepsilon(\hbar \omega_X = 25$ eV) = 5.96 eV and $\Delta \varepsilon(\hbar \omega_X = 50$ eV) = 6.11 eV are close to the spectral width $\hbar \Delta \omega_X = 6.08$ eV of the XUV pulse.

Figure 3 shows the Wigner delays $\tau^I_{W}$ and the streaking delay $\tau_S$ for the 1D model hydrogen atom, calculated according to Eqs. (7) and (19) and (20), in comparison with the streaking delay $\tau_S$, calculated as described in Sec. II [6]. All delays are negative. The two Wigner delays are almost identical and their absolute values are much larger than the streaking delay. Having established that the two Wigner delays almost coincide for all parameters considered in this work, we only show results for $\tau^I_{W}$ from now on and drop the superscript “I” for convenience, unless noted otherwise. In order to investigate the difference between the Wigner and streaking delays, we modify the infinite range of the potential Eq. (18) with a Wood-Saxon factor,

$$V_s(z) = V_c(z) \left[ 1 - \frac{1}{1 + e^{-|z|-z_c}/a} \right].$$

The range of $V_s(z)$ is controlled by $z_c$. The parameter $a$ defines the lengths over which $V_s(z)$ is screened to approach zero. In our calculation, we use $a = 1$. For $z_c \to \infty$, $V_s$ converges to $V_c$ [Fig. 4(a)]. We numerically verified that for values of $z_c$ larger than a few atomic units, the ground-state wave function and energy in $V_s(z)$ are practically independent of $z_c$ [Fig. 4(b)].

In Fig. 5 and Table I we compare the Wigner and streaking delays at three different ranges $z_c$. The comparison shows that for an interaction range slightly larger than the extent of the ground-state probability distribution, say, $z_d \sim 2$, the Wigner and streaking delays coincide [see Fig. 5(a)]. In contrast, for $z_c > z_d$, $|\tau^I_{W}| > |\tau_S|$, and both delays approach their values for the 1D model potential, Eq. (18). In this case the difference of the two delays is largest at lower photoelectron kinetic energies [Figs. 5(b) and 5(c)]. The comparison of the three graphs also

FIG. 2. (Color online) Real part of the calculated and the fitted momentum-space photoelectron wave packets for ionization from 1D model hydrogen atoms by XUV pulses with energies of (a) 25 eV and (b) 50 eV.

FIG. 3. (Color online) Comparison of the Wigner delays $\tau^I_{W}$ and the streaking delay $\tau_S$ for photoionization of 1D model hydrogen atoms as a function of the XUV photon energy $\hbar \omega_X$.

FIG. 4. (Color online) The modified Coulomb potential (21) (a) and its ground-state wave function (b) for three different interaction ranges $z_c$.

FIG. 5. (Color online) Comparison of the Wigner delay $\tau^I_{W}$ and the streaking delay $\tau_S$ for three interaction ranges $z_c$ in Eq. (21) as a function of the XUV photon energy $\hbar \omega_X$. 

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shows that the Wigner delay is more sensitive to changes in $z_e$ than the streaking delay.

We emphasize that Wigner delays are calculated without including the action of an IR-laser pulse, which might give rise to the question of whether we should instead compare the streaking delay with the Wigner delay obtained in the same IR field, as mentioned in the introduction. Obviously, inclusion of the IR-laser electric field would change the Wigner delay [7]. In this case the photoelectron velocity in Eq. (7) would depend on the XUV-IR delay $\Delta t$, and the use of this equation would determine a Wigner delay $\tau_W$ that varies with $\Delta t$ and the IR-pulse intensity. The streaking delay, in contrast, does not depend on $\Delta t$. It also does not depend on the intensity of the streaking laser, if its intensity is sufficiently low [3,6,8]. Therefore, it is only meaningful to compare streaking delays with IR-field-free Wigner delays. We note that, even though our results do not explain the measured relative streaking delay between photoemission from the 2s and 2p core levels of neon [4], we therefore expect initial-state polarization effects to be irrelevant, due to the large energy gap between the ground state and the excited states [6]. With regard to the experiment by Schultze et al. [4], we therefore expect initial-state polarization effects to be negligible, due to the large energy gap of $\approx 27$ eV [14]. In contrast, the initial-state polarization is relevant for the case of photoemission from solid surfaces discussed in the following section.

### B. One-dimensional solid

We model the 1D solid surface as a row of $N$ equidistant atomic layers and represent each atom by a Gaussian potential well to form the lattice potential

$$V_{\text{lat}}(z) = V_0 - \frac{A_0}{\sqrt{2\pi}\sigma} \sum_{i=1}^{N} e^{-|z+i(0.5)a_{\text{lat}}|^2/(2\sigma^2)},$$

where $a_{\text{lat}}$ is the lattice constant, $\sigma$ controls the overlap of the two adjacent atomic potentials, and $V_0$ and $A_0$ are chosen to match the known Fermi energy [Fig. 6(a)]. We have oriented the $z$ axis with increasing values toward the vacuum side and put the origin ($z = 0$) at the distance $0.5a_{\text{lat}}$ in front of the top nucleus. Diagonalizing the time-independent Schrödinger equation

$$\varepsilon_n \psi_n(z) = \left[-\frac{1}{2} \frac{d^2}{dz^2} + V_{\text{lat}}(z)\right] \psi_n(z)$$

for $N = 47$, $V_0 = -0.5$, $A_0 = 2$, $a_{\text{lat}} = 6$, and $\sigma = 0.1a_{\text{lat}}$, we obtain the core-level and conduction-level bands shown in Fig. 6(b). The Fermi energy is $\varepsilon_F = -10.9$ eV.

For the calculation of the XUV photoemission spectrum, we replace $V(z)$ in Eq. (9) by $V_{\text{lat}}(z)$ and add the damping term $-i\varepsilon_0/2\lambda$, with the velocity $v_0 = \sqrt{2\varepsilon_0/(\varepsilon_n)}$, to $V_{\text{lat}}(z)$, in order to model scattering of the photoelectrons inside the solid. In a previous study [3], we adjusted the electron mean-free path inside the solid to $\lambda = 5$ Å. This value corresponds to the minimum of the universal curve for $\lambda$ as a function of the electron’s kinetic energy [15]. We continue to use this value for the present investigation. In the calculation of the streaked spectra, we further assume an exponential damping of the IR-laser field inside the solid,

$$A_L(z,t) = A_L(t)e^{i\varepsilon_0 t/\Delta t} \Theta(-z) + \Theta(z),$$

characterized by the IR skin depth $\delta_L$.

Within each band, we use the index $n$ to label Bloch wave functions $\psi_n$ with energies $\varepsilon_n$, starting with $\varepsilon_1$ for the lowest energy Bloch wave at the band bottom. Each initial Bloch wave below the Fermi level contributes to the photoemission spectrum with the energy-differential emission probability

$$P_n = P(\varepsilon_n, \Delta t) = \frac{1}{k} |\delta \phi_n(k, \infty; \Delta t)|^2.$$
Similarly, each Bloch wave yields to the COE \( E_{\text{COE}a}(\Delta t) \), Wigner delays \( \tau_{W,n}^{\text{II}} \), and streaking delays \( \tau_{S,n} \). We first calculate the band-averaged COE,

\[
E_{\text{COE}}(\Delta t) = \frac{1}{\sum_n P_n} \sum_n P_n E_{\text{COE}a}(\Delta t),
\]

separately for each band. Next we use Eq. \( (17) \) to obtain the band-averaged streaking delay \( \tau_S \). Similarly, we find the band-averaged Wigner delays according to

\[
\tau_{W}^{\text{II}} = \frac{1}{\sum_n P_n} \sum_n P_n \tau_{W,n}^{\text{II}}.
\]

A comparison of streaking and the two Wigner delays for an XUV photon energy \( \hbar \omega_X = 100 \text{ eV} \) and emission from the core-level band is shown in Fig. 7 as a function of the core-level index \( n \). The monotonic increase in level index \( n \) in Fig. 7 is just a coincidence. For other energies, these delays do not necessarily increase with \( n \). As for the case of atomic targets (cf., Sec. III A), we find that the difference between the two Wigner delays is negligible. We therefore only present results for \( \tau_{W}^{\text{II}} \), which we denote simply as \( \tau_W \) below. All numerical results shown below are converged in the number of included atomic layers, \( N \).

Wigner and streaking delays as a function of the XUV photon energy \( \hbar \omega_X \) for photoemission from three individual core- and three conduction-band Bloch levels are shown in Figs. 8 and 9, respectively. According to its definition in Eq. \( (7) \), the Wigner delay can be regarded as an “effective” propagation time for the photoelectron to emerge from the solid. For the special case \( \delta_L = 0 \), the streaking delay is the travel time photoelectrons need before getting exposed to the streaking IR field outside the solid. Therefore, intuitively, for \( \delta_L = 0 \) only, one would expect the streaking delay to be almost identical to the Wigner delay. As Figs. 7–10 show, this is confirmed by our numerical results.

It is interesting to observe that, for emission from the core-level band, the band-averaged Wigner and streaking delays decrease monotonically with increasing \( \hbar \omega_X \) [Fig. 10(a)]. This decrease closely follows the effective propagation time \( \lambda/\sqrt{2\sigma} \) of photoelectrons inside the solid prior to reaching the solid-vacuum interface at \( z = 0 \), even though delay contributions from individual Bloch levels, \( \tau_n \) (see Fig. 8), do not show this behavior. This confirms the interpretation that band-averaged Wigner and streaking delays for emission from the core-level band can be regarded as an average time needed for a released photoelectron to travel a distance \( \lambda \) inside the solid [2,11].

However, this interpretation is not valid for photoemission from the CB, where the band-averaged delays behave non-monotonically as a function of \( \hbar \omega_X \) as shown in Fig. 10(b). A possible explanation for this difference is the delocalized nature of the CB Bloch wave. This can be checked by examining the core-level-band-averaged delay as a function of the overlap parameter \( \sigma \) in \( V_{\text{lat}}(z) \) and will be discussed.
in a forthcoming publication [16]. This means that, even for 
\( \delta L = 0 \), the relative delays between photoemission from the 
core-level and CB cannot be due solely to the photoelectron’s 
average travel time in the solid [2,11].

Since (i) the very close correspondence of \( \tau_S \) and \( \tau_W \) 
and (ii) the interpretation of streaking delays in terms of an 
effective propagation time in the solid are only valid for the 
special case of \( \delta L = 0 \), we next investigate the dependence of 
photoemission delays on the IR skin depth \( \delta L \). Figure 11 
shows the band-averaged streaking delay for emission from the 
core-level band for two XUV photon energies. These 
results show a very sensitive dependence of 
\( \tau_S \) on the IR skin depth, with \( \tau_S \) changing from positive to negative delays. 
In contrast to photoemission from the energetically isolated 
ground states of atoms (Sec. III A), the \( N \) Bloch waves 
form a quasicontinuum and can be easily hybridized in the 
IR-laser electric field. This initial-state hybridization effect 
gets stronger the deeper the IR electric field penetrates the solid 
and accounts for the \( \delta L \) dependence of \( \tau_S \). We note that the 
actual IR skin depth is much larger than the electron mean-free 
path, such that the effective depth over which photoelectrons 
are assembled is limited by \( \lambda \), and the IR skin depth tends 
to become irrelevant for the photocurrent [3]. Accordingly, 
the photoemission delays in Fig. 11 converge in the limit of 
large \( \delta L/\lambda \). We also note that the effective IR-skin depth for 
photoelectron streaking depends on the direction under which 
photoelectrons are observed and on the angle of incidence 
of the IR pulse. In the experiment of Cavalieri et al. [2], 
the angle of incidence of the IR pulse was selected as the 
Brewster angle, and photoelectrons that are emitted along the 
surface normal were recorded. For this particular geometry, 
the normal component of the refracted IR electric field is very 
small and photoelectron streaking inside the solid becomes 
negligible [17].

Another interesting observation, as shown in Fig. 12, is that 
the band-averaged \( \tau_W \) and \( \tau_S \) from the conduction band depend 
on the position of the Fermi level. Therefore, changing the 
occupation probability of Bloch waves in the CB, for example, 
by increasing the temperature or by doping, will change the 
band-averaged delay. This dependence is absent in the core-
level band because all the core levels are below the Fermi level 
and fully occupied.

IV. CONCLUSIONS

We have examined the relation between Wigner and 
streaking delays in the XUV photoelectron emission from 
model atoms and solid surfaces. We showed that both the 
creation of the photoelectron and its propagation contribute 
to the Wigner delay. For photoemission from atoms, the two 
delays are only identical for short-range ionic potentials. For 
photoemission from surfaces, Wigner and streaking delays 
become identical only in the limit of no IR-field penetration 
into the solid, and both delays can be interpreted as the travel 
time of the photoelectron to the surface. For this case only and 
for electron emission from the core-level band, both delays 
can be understood as the average time photoelectrons need to 
travel a distance equal to the mean-free path in the solid. This 
interpretation does not hold for photoelectron emission from 
the conduction band. This dissimilarity is expected to be due 
to the different (localized versus delocalized) nature of core 
and conduction-band levels.
We find that streaking delays are very sensitive to changes in the IR skin depth and Fermi energy and deviate from Wigner delays for nonzero IR skin depths. Their dependence on the substrate temperature, impurities, and adsorbate coverage may leave a measurable signature in relative photoemission delays.

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[1] F. Krausz and M. Ivanov, Rev. Mod. Phys. 81, 163 (2009).
[2] A. L. Cavalieri et al., Nature (London) 449, 1029 (2007).
[3] C.-H. Zhang and U. Thumm, Phys. Rev. Lett. 102, 123601 (2009); 103, 239902(E) (2009).
[4] M. Schultze et al., Science 328, 1658 (2010).
[5] A. S. Kheifets and I. A. Ivanov, Phys. Rev. Lett. 105, 233002 (2010).
[6] C.-H. Zhang and U. Thumm, Phys. Rev. A 82, 043405 (2010).
[7] I. A. Ivanov, Phys. Rev. A 83, 023421 (2011).
[8] S. Nagele, R. Pazourek, J. Feist, K. Doblhoff-Dier, C. Lemell, K. Tókési, and J. Burgdörfer, J. Phys. B 44, 081001 (2011).
[9] E. P. Wigner, Phys. Rev. 98, 145 (1955).
[10] F. T. Smith, Phys. Rev. 118, 349 (1960).
[11] A. K. Kazansky and P. M. Echenique, Phys. Rev. Lett. 102, 177401 (2009).
[12] C. A. de Carvalho and H. M. Nussenzweig, Phys. Rep. 364, 83 (2002).
[13] W. Brenig and R. Haag, Fortschr. Phys. 7, 183 (1959).
[14] S. Hüfner, Photoelectron Spectroscopy, 3rd ed. (Springer, Berlin, 2003).
[15] A. Zangwill, Physics at Surfaces (Cambridge University Press, New York, 1988).
[16] C.-H. Zhang and U. Thumm (submitted for publication).
[17] P. Gibbon, Short Pulse Laser Interactions with Matter (Imperial College Press, London, 2005).