Time-resolved photoemission on the attosecond scale: opportunities and challenges

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The interaction of laser pulses of sub-femtosecond duration with matter opened up the opportunity to explore electronic processes on their natural time scale. One central conceptual question posed by the observation of photoemission in real time is whether the ejection of the photoelectron wave packet occurs instantaneously or whether the response time to photoabsorption is finite leading to a time delay in photoemission. Recent experimental progress exploring attosecond streaking and RABBIT techniques find relative time delays between photoemission from different atomic sublevels to be of the order of ~ 20 attoseconds. We present ab initio simulations for both one- and two-electron systems which allow to determine both absolute and relative time delays with ~ 1 attosecond precision. We show that the intrinsic time shift of the photoionization process encoded in the Eisenbud-Wigner-Smith delay time can be unambiguously disentangled from measurement-induced time delays in a pump-probe setting when the photoionized electronic wave packet is probed by a modestly strong infrared streaking field. We identify distinct contributions due to initial-state polarization, Coulomb-laser coupling in the final continuum state as well as final-state interaction with the entangled residual ionic state. Extension to multi-electron systems and to extraction of time information in the presence of decohering processes are discussed.

1 Introduction

Following electronic dynamics in real time, watching the formation or breaking of a chemical bond, the transfer of electrons from one constituent to another, or the ejection of electrons from an atom or molecule has been a dream and challenge of time-resolved quantum physics for a long time. The extent to which such ultrafast processes are accessible to measurements at all has remained a matter of debate. Observing the temporal electronic evolution requires interrogation of the system on ultrafast time scales. Yet, such probes are subject to both time-energy and position-momentum uncertainty. Moreover, they are prone to distortion of the evolution to be observed. To put it simply: the challenge is not just to take "snapshots" of ultrafast electronic motion but also to identify, to extract, and to resolve the information on the underlying processes such snapshots may contain.

Through recent advances in the creation of (sub) femtosecond laser pulses, the real-time observation of electronic dynamics in atoms, molecules, and solids

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has come into reach¹⁻⁴. Phase-controlled few-cycle infrared (IR) laser pulses (cycle period $T_{\rm IR} \simeq 2.6$ fs at $\lambda = 800$ nm) and ~ 100 attosecond XUV pulses, temporally well correlated with each other through to the underlying high-harmonic generation (HHG) process open the opportunity to confine the photoelectric effect to a ~ 100 attosecond time interval and to interrogate the excited or ionized electronic state by the few-cycle IR field. This so called "attosecond streaking"⁵⁻⁸ technique is now being utilized to explore a wide range of fundamental photophysical and photochemical processes in the time domain, including Auger⁹ and autoionization processes¹⁰, photoemission from surfaces¹¹, and photoemission of atoms¹². Closely related techniques include RABBIT ("reconstruction of attosecond harmonic beating by interference of two-photon transitions")^{13–17} and the attosecond clock for circularly polarized fields^{18,19}. Similarily, in attosecond transient absorption (ATA)^{20,21} the IR pulse creates the wavepackets while the modulation of the absorption of the attosecond XUV pulse probes the time evolution of the electronically excited system. These variants of attosecond chronoscopy have in common that they promise to deliver real time information on electronic processes on ultrafast time scales. The ultimate goal is not only to observe but to actively control electronic motion by light fields, i.e., "lightfield electronics"^{22–24}. An understanding of the wealth of information to be extracted is still in its infancy and is only now beginning to emerge.

In the present communication we address one prototypical example, the "time delay" in photoemission. Time and time delay as a quantum dynamical observable was originally introduced by Eisenbud, Wigner, and Smith (EWS)²⁵⁻²⁷ for resonant scattering. Photoemission representing a half-scattering process allows the application of this concept. The corresponding delay, $t_{\rm EWS}$, can be viewed as the finite response time in the formation of the outgoing electronic wavepacket during the photoabsorption event. In this sense, photoionization is not instantaneous, as conventionally being thought, but the departure of the outgoing wavepacket is temporally shifted relative to the arrival of the XUV pulse, typically by a few attoseconds. We present in the following an outline of a theoretical framework which unambiguously indentifies $t_{\rm EWS}$ as an observable accessible by attosecond streaking. The key is the determination of measurementinduced phase shifts due to the presence of the IR field which tends to taint the timing information. We discuss both one- and two-electron systems and address the influence of electronic correlation on the time-resolved photoemission processes. We point to future directions aiming at the observation and control of electronic motion in more complex nanoscale structures. Unless otherwise stated, atomic units (a.u.) are used.

2 Time Delay in Photoemission

Association of time *t* with a Hilbert space operator following standard correspondence identities,

$$t = -i\frac{\partial}{\partial E}\,,\tag{1}$$

faces fundamental conceptual difficulties^{28,29} as the spectrum of the canonically conjugate Hamilton operator H is bounded from below. Eisenbud²⁵, Wigner²⁶

and Smith²⁷ pointed out that, when restricted to the domain of scattering states, an expectation value of the time operator can be constructed,

$$t_{\rm EWS} = -iS^{\dagger}(E)\frac{\partial}{\partial E}S(E)\,,\tag{2}$$

where S(E) is the scattering operator (matrix). t_{EWS} corresponds to the observable time delay in scattering. A prototypical case is resonant scattering where t_{EWS} describes the "sticking time" of the incoming particle due to transient trapping in a quasi-bound state before leaving the interaction region as an outgoing wavepacket. This sticking time amounts to the time delay of the outgoing wavepacket relative to that of the incoming wavepacket passing by the scattering region in the absence of the interaction potential. In the special case of potential scattering with spherical symmetry, the *S* matrix is diagonal in the angular momentum representation S_{ℓ} ,

$$S_{\ell}(E) = e^{2i\delta_{\ell}(E)} \,. \tag{3}$$

The corresponding time delay for the partial wave ℓ follows from (Eq. 2) as

$$t_{\rm EWS}(E,\ell) = 2\frac{\rm d}{{\rm d}E}\delta_\ell(E) \tag{4}$$

and is given by the energy variation of the partial wave scattering phase shift $\delta_{\ell}(E)$. Photoemission, the focus of the following discussion, corresponds to a half-scattering process in which only in the exit channel a matter wavepacket resides in the continuum while in the entrance channel the wave function represents a bound rather than a continuum state. Accordingly, for photoemission by a dipole transition to a specific partial wave ℓ , the EWS time is only one-half of Eq. 4,

$$t_{\rm EWS}(E,\ell) = \frac{\rm d}{{\rm d}E} \delta_\ell(E). \tag{5}$$

More generally, when the final state does not consist of just a single partial wave, the time delay is given by the matrix element of the dipole transition operator \vec{d} between the initial bound state ψ_i and the final scattering state ψ_f describing emission into the solid angle (θ, φ) ,

$$t_{\rm EWS}(E,\theta,\phi) = \frac{\rm d}{{\rm d}E} \arg\left[\langle \Psi_f(E,\theta,\phi) | \vec{d} | \Psi_i \rangle\right]. \tag{6}$$

When only one partial wave in the continuum is accessed, Eq. 6 reduces to Eq. 5.

The time delay t_{EWS} can be alternatively extracted from the motion of the outgoing wavepacket without invoking the *S* matrix³⁰. Such a wavepacket is formed by a coherent superposition of a band of continuum states around a central energy E_0 . The time evolution of the radial position of its crest, $r_c(t)$, or its first moment, $\langle r(t) \rangle$, eventually follows asymptotically $(t \to \infty)$ the motion of a free particle,

$$r_c(t) = v_g(t - t_{\rm EWS}), \qquad (7)$$

$$\langle r \rangle_t = v_g (t - t_{\rm EWS}),$$
 (8)

after the wavepacket has left the scattering region, however delayed ³¹ by the time t_{EWS} . In Eq. 7 and Eq. 8 the group velocity v_g is given by

$$v_g = \left(\frac{\partial E}{\partial k}\right)_{E=E_0}.$$
(9)

One key condition of the applicability of Eqs. 4 to 8 is that the interaction potential is short-ranged such that the wavepacket reaches, indeed, the free-particle motion at large distances.^{26,27}

Both the challenges and the opportunities of time-resolved photoemission are direct consequences of the implications and limitations of Eqs. 4 to 8. Typical intrinsic delay times $t_{\rm EWS}$ are only of the order of ~10 attoseconds. Such time scales have only now become accessible with the advances of attosecond chronoscopy. However, except for the case of photodetachment, the exit-channel interaction between the outgoing electron and the ion core is Coulombic (~ 1/*r*) and, thus, the intrinsic EWS atomic or molecular time delay is, strictly speaking, not well defined.^{26,27,32,33} We show in the following that, with suitable modifications, $t_{\rm EWS}$ can, indeed, be theoretically unambiguously determined and, furthermore, experimentally extracted from attosecond streaking or RABBIT measurements.

The extraction of t_{EWS} from the radial expectation value $\langle r(t) \rangle$ (Eq. 8) in the absence of Coulomb interactions in the exit channel is illustrated in Fig. 1 for the simulated photodetachment by an attosecond XUV pulse (pulse duration $\tau_{\rm p} = 200$ as, energy $\omega = 80$ eV, intensity $I = 10^{13}$ W/cm²) of an electron initially bound in an *s*-like state by an exponentially screened Coulomb (or Yukawa) potential,

$$V_{\rm Y}(r) = -\frac{Z}{r} \exp(-r/a), \qquad (10)$$

with the screening length *a*. For later comparison with photoionization of He⁺ we choose the charge parameter *Z* for a given screening length *a* such that the binding energy of the detached and the ionized He⁺(1s) electron coincide ($\varepsilon_i = -2 \text{ a.u.}$). The radial expectation value rapidly approaches the linear distance vs. time relation (Eq. 8) after the conclusion of the XUV pulse (FWHM) at $t \approx 4 \text{ a.u.}$ (~ 100 as). Here and in the following, the peak of the XUV-pulse envelope is chosen to be at t = 0. Tracing back the linear time dependence $\langle r \rangle_t$ to small times allows to determine t_{EWS} from the intercept with the *t* axis as $t_{\text{EWS}} = 6.6$ attoseconds. This value agrees with the one extracted from the *p*-wave ($\ell = 1$) phase shift $\delta_{\ell=1}$ at $E = \omega + \varepsilon_i$, (Eq. 5), to within 0.1 attoseconds, illustrating the equivalence of Eq. 5 and Eq. 8 for photodetachment with sub-attosecond level precision.

For photoionization of H(1s) under otherwise identical conditions a dramatically different picture emerges (Fig. 2). The delay times as extracted from the intercept of the linear extrapolation with the *t* axis,

$$t_{\rm EWS} = t - \frac{\langle r \rangle_t}{k} \tag{11}$$

strongly depend on the time t (or position $\langle r \rangle$) when the linear backward extrapolation is applied. Convergence to a finite value cannot be achieved no matter for how long and how far the wavepacket is propagated into the asymptotic



Fig. 1 (a) Extraction of t_{EWS} from the linear extrapolation of the time dependence of $\langle r \rangle_t$ (Eq. 11), for photoionization from an initial 1*s* state from a Yukawa potential (Eq. 10) with Z = 3.8166 and a = 0.5, which results in a binding energy of -2a.u.. The intercept with the *t* axis (inset) gives t_{EWS} in excellent agreement with the direct calculation for the *S* matrix (Eq. 5). (b) The temporal variation of the XUV pulse.

regime. This divergence reflects the fundamental difficulty in applying standard *S*-matrix scattering theory and the concept of time delay to photoionization where long-range Coulomb interactions are ubiquitously present.^{32,33} This difficulty is closely related to the well-known logarithmic phase distortion by the Coulomb field which precludes equispaced wave crests and nodes even as $r \rightarrow \infty$.

In order to extend the concept of the EWS time delay to photoionization, the logarithmic phase distortion should be included from the outset in the determination of the time delay for the Coulombic systems. We therefore start from the energy and position dependent phase of the Coulomb wave,

$$\phi^{\text{Coul}}(E,\ell,r) = \sigma_{\ell}^{C}(E) + \frac{Z}{k}\ln(2kr), \qquad (12)$$

where $k = \sqrt{2E}$ is the asymptotic momentum (or wavenumber) and

$$\sigma_{\ell}^{C}(E) = \arg \Gamma(1 + \ell - i\eta).$$
(13)

The *r*-independent term (Eq. 13) is the Coulomb analogue to the phase shift in standard scattering theory for short-ranged potentials and is often referred to as the "Coulomb phaseshift" with $\eta = Z/k$ the Coulomb-Sommerfeld parameter. Extending now the recipe for determining the time delay (Eq. 5) to the Coulomb phase (Eq. 12) we start from the spectral derivative

$$t_{\text{Coul}}(E,\ell,r) = \frac{\partial}{\partial E} \phi^{\text{Coul}}(E,\ell,r) = t_{\text{EWS}}^{C}(E,\ell) + \Delta t_{\text{Coul}}(E,r)$$
(14)



Fig. 2 Comparison between the time delay determined from the linear extrapolation with the slope taken at increasing propagation times (Eq. 11, points) with the Coulomb time $t_{\text{Coul}}(E, \ell = 1, r = kt)$ (Eq. 14, line) for ionization from the H(1*s*) state with an XUV pulse with $\omega = 80 \text{ eV}$.

where we have introduced the Coulomb analogue of the EWS time delay associated with the Coulomb phaseshift as

$$t_{\rm EWS}^{C}(E,\ell) = \frac{\partial}{\partial E} \sigma_{\ell}^{C}(E)$$
(15)

and an additional contribution due to the logarithmic distortion of the wavefront,

$$\Delta t_{\text{Coul}}(E,r) = \frac{Z}{(2E)^{\frac{3}{2}}} \left(1 - \ln(2\sqrt{2E}r) \right).$$
(16)

It is precisely this additional time shift, Δt_{Coul} that accounts for the *r* or (since $r \approx kt$) *t* dependence of the time delay when extracted from the linear extrapolation. $t_{\text{Coul}}(E, \ell, r)$ (Eq. 14) agrees to within the graphical resolution with $t - \langle r \rangle_t / k$ for the wavepacket in the Coulomb field (Fig. 2). We therefore arrive at the relation between the effective time shift ("time delay") and the distance-time relation for a Coulomb wavepacket as

$$t_{\text{Coul}}(E,\ell,r=kt) = t - \frac{\langle r \rangle_t}{k}, \qquad (17)$$

generalizing the relation Eq. 11 for short-ranged potentials to the case of Coulomb exit-channel interactions. From the Coulomb time shift t_{Coul} (Eq. 14) the Coulomb EWS time delay (Eq. 15) can be determined by subtracting from t_{Coul} the correction

$$\Delta t_{\text{Coul}}(E, r = kt) = \frac{Z}{(2E)^{\frac{3}{2}}} \left(1 - \ln(4Et)\right)$$
(18)

evaluated at r = kt. The correction given by Eq. 18 is universal as it depends only on the energy $E = k^2/2$ of the electron and the strength of the Coulomb field, Z, but is independent of the partial wave ℓ or the initial state to be photoionized. It accounts for the "slowing down" of the outgoing electron by the retarding Coulomb field resulting in an apparent negative timeshift (see Fig. 2).

The Coulomb time shift (Eq. 14) possesses a remarkably close classical counterpart first explored in a little known paper by Clark³⁴. Solving the equation of motion for a hyperbolic Kepler trajectory of fixed classical angular momentum L, we find a classical time shift t_{Coul}^{cl} relative to that of a free electron at large distance as

$$t_{\text{Coul}}^{\text{cl.}}(E,L,r=kt) = t(r) - \frac{r}{k} \approx \frac{Z}{(2E)^{\frac{3}{2}}} \left(1 - \ln\left(\frac{4Et}{\sqrt{\eta^2 + L^2}}\right) \right).$$
 (19)

Eq. 19 can be rewritten in terms of the logarithmic distortion term of quantum scattering (Eq. 16),

$$t_{\text{Coul}}^{\text{cl.}}(E,L,r=kt) = \frac{Z}{(2E)^{\frac{3}{2}}} \ln(\sqrt{\eta^2 + L^2}) + \Delta t_{\text{Coul}}(E,r=kt).$$
 (20)

Comparing now Eq. 14 with Eq. 20 suggests to identify the first term in Eq. 20 as the classical analogue to the intrinsic Eisenbud-Wigner-Smith delay,

$$t_{\rm EWS}^{\rm C,\,cl.}(E,L) = \frac{Z}{(2E)^{\frac{3}{2}}} \ln(\sqrt{\eta^2 + L^2}).$$
 (21)

This identification can be readily justified by an asymptotic expansion of the quantum EWS delay (Eq. 15), expressed in terms of the digamma function $\Psi(x)$,

$$t_{\rm EWS}^{\rm C}(E,\ell) = \frac{Z}{(2E)^{\frac{3}{2}}} \operatorname{Re}\left[\Psi(1+\ell-i\eta)\right].$$
 (22)

In the (semi) classical limit of large arguments |x|,

$$\Psi(1+\ell-i\eta) \sim \ln(1+\ell-i\eta), \tag{23}$$

reached for either large ℓ or large Sommerfeld parameter η we find

$$t_{\rm EWS}^{\rm C}(E,\ell) \stackrel{|x|\gg1}{=} \frac{Z}{(2E)^{\frac{3}{2}}} \ln\left(\sqrt{(1+\ell)^2 + \eta^2}\right) \\ \simeq \frac{Z}{(2E)^{\frac{3}{2}}} \ln\left(\sqrt{L^2 + \eta^2}\right) = t_{\rm EWS}^{\rm C,\,cl.}(E,L)\,, \quad (24)$$

in complete agreement with the intrinsic delay of the classical trajectory (Eq. 21), see Fig. 7 below. Note that in the (semi) classical limit, the proper mapping of the classical angular momentum *L* onto the ℓ quantum number is given by ^{35,36} $L = \ell + 1/2$. This result has far-reaching implications for time-resolved photoionization studies: distortion of the timing information due to long-range Coulomb interactions in the exit channel can be accounted for both classically and quantum mechanically to a high degree of accuracy, thereby allowing to clearly disentangle intrinsic delay times in complex atoms or molecules from Coulomb induced time shifts.

3 Attosecond streaking of photoemission

Attosecond streaking has developed into one of the most important and versatile tools of attosecond science. It is a variant of a pump-probe technique in which the attosecond XUV pulse (with, typically, $\tau_p = 100$ to 300 as) serves as pump creating the photoelectron wavepacket while the carrier-envelope phase (CEP) controlled few-cycle IR pulse streakes, i.e., probes the wavepacket. In direct analogy to classical streaking, attosecond streaking maps time information onto energy thereby allowing to extract time information from the photoelectron spectrum with attosecond precision.

Point of departure for attosecond streaking is that the momentum of the emitted electron receives in the presence of the IR field a ponderomotive shift^{5,7,8,37},

$$\vec{p}_f(\tau) = \vec{p}_0 - \vec{A}_{\rm IR}(\tau), \qquad (25)$$

given by the value of the (rescaled) vector potential $A_{IR} = \tilde{A}_{IR}(\tau)/c$ at the instant of the arrival in the continuum, τ . In Eq. 25, \vec{p}_0 is the asymptotic momentum associated with the energy of the photoelectron, $E_0 = p_0^2/2$, $(E_0 = \omega_{XUV} + \varepsilon_i)$, in the absence of the streaking field. Consequently, the momentum $\vec{p}_f(\tau)$ and the energy $E_f(\tau) = p_f^2(\tau)/2$ in the presence of the IR field become functions of τ via \vec{A}_{IR} . Since the temporal distribution of the IR laser field $\vec{F}_{IR}(\tau)$ and of the vector potential $\vec{A}_{IR}(\tau)$,

$$\vec{A}_{\rm IR}(\tau) = \int_{\tau}^{\infty} \vec{F}_{\rm IR}(t) dt \,, \tag{26}$$

can be well controlled with subcycle precision, Eq. 25 amounts to a mapping of the arrival time in the continuum, τ , onto a modulation of the linear momentum and of the energy, $E_f(\tau)$, of the photoelectron.

The implicit assumption underlying Eq. 25 is that the emitted electron attains instantaneously the asymptotic momentum \vec{p}_0 on a time scale that is resolved by attosecond streaking. This approximation of a sudden transition holds for the streaking of Auger decay with typical lifetimes of femtoseconds, for which this technique was first pioneered⁹. For dynamical processes on the few attosecond scale and, in particular, for photoemission where the long-range Coulomb interaction implies that the local momentum of the outgoing electron $\vec{p}(r)$ approaches the asymptotic momentum only after ~ 100 attoseconds, application of the mapping Eq. 25 requires modification. Furthermore, the presence of the IR field may distort the timing information to be extracted. Since for easily resolvable energy shifts IR fields with intensities of the order $I_{\rm IR} \approx 10^{11} - 10^{12} \,\text{W/cm}^2$ are needed, distortion effects generally cannot be neglected. As we will discuss in the following, the influence of the IR field on the time shift in photoemission extracted from streaking is significant, yet remarkably insensitive to the strength of the streaking field.

We first probe extraction of timing information of photoemission for the detachment of a 1*s* electron bound by the Yukawa potential (Eq. 10). The photodetachment is initiated by an attosecond pump pulse with its peak amplitude centered at t = 0, an intensity of 10^{13} W/cm², and a pulse duration $\tau_p^{XUV} = 200$ as (FWHM). We expect for such short-ranged potentials the emission time (arrival in the continuum) to be delayed by the EWS time, i.e., the ponderomotive momentum $\vec{A}_{IR}(\tau)$ (Eq. 25) to be shifted by t_{EWS} , $\vec{A}_{IR}(\tau + t_{EWS})$. In turn, the time shift determined by streaking should agree with this intrinsic atomic time delay (Fig. 1),

$$t_{\rm S} = t_{\rm EWS} \,, \tag{27}$$

and, hence

$$\vec{p}_f(\tau) = \vec{p}_0 - \vec{A}_{\rm IR}(\tau + t_{\rm S}) = \vec{p}_0 - \vec{A}_{\rm IR}(\tau + t_{\rm EWS}).$$
(28)

In the simulation ³⁸ as well as in the experiment ¹², t_S can be determined by a fit of the first moment of the emission line in the time modulated spectrum (usually for emission parallel to the electric field polarization direction). An example of such a so called spectrogram will be shown below in section 5 (Fig. 10). Indeed, we find Eq. 27 to be fulfilled for a wide range of final kinetic energies *E* corresponding to different pump frequencies ω_{XUV} and for different screening lengths (Fig. 3) to within sub-attosecond precision. As discussed in section 2, the pair of



Fig. 3 Streaking time shifts t_S (dots) extracted from quantum mechanical streaking simulations for the short-ranged Yukawa potential V_Y (Eq. 10) with screening lengths a = 0.5, a = 1, and a = 2 a.u.. The streaking IR laser field has a wavelength of 800 nm, a duration of 3 fs, and an intensity of 10^{12} W/cm². The Eisenbud-Wigner-Smith delay times t_{EWS} (lines) are determined from the spectral variation of the scattering phase (Eq. 5).

parameters of charge and screening length is adjusted such that the initial-state binding energy remains constant at the value $\varepsilon_{1s} = -54.4 \text{ eV}$ corresponding to He⁺(1s). For later reference we note that polarization of the initial state by the IR field is negligible. The excellent agreement of t_S with t_{EWS} validates streaking as a measurement protocol of fundamental intrinsic timing information (Eq. 28). It is worth stressing the remarkable level of time resolution in reach. The arrival of the photoelectron in the continuum is delayed by $t_{EWS} \approx 6 \text{ as}$ (Fig. 1) relative to the peak of the XUV pulse at t = 0 when photoemission, if instantaneous, would, on average, occur. Yet, this minute delay, almost two orders of magnitude shorter than τ_p^{XUV} of the pump pulse is unambiguously and accurately accessible.



Fig. 4 Comparison between the streaking time shift t_S and the Coulomb EWS time delay t_{EWS}^C for photoionization of hydrogen as a function of the kinetic energy *E* of the outgoing electron ($E = \omega + \varepsilon_i$). t_S (red dots) agrees well with the classical streaking time shift $t_S^{cl.}$ (black boxes) calculated with the CTMC method.

A drastically different picture emerges for photoionization with Coulombic long-range interaction present, Fig. 4. In that case the streaking time t_S is not directly associated with t_{EWS}^C but is strongly influenced by the Coulomb-field induced time shift (Eq. 18).^{38–40} Remarkably, the time shift t_S calculated by the solution of the TDSE in its full dimensionality⁴¹ agrees quite well with a fully classical calculation of the time shift, t_S^{cl} , using the classical trajectory Monte-Carlo (CTMC) method^{42,43}. This agreement indicates that the lion's share of the difference between t_S and t_{EWS}^C is due to the logarithmic distortion term in Eq. 16 which has a direct classical counterpart (see Eq. 20).

For a deeper insight into the interplay between the Coulomb and laser fields and the resulting time shifts in a streaking setting, we consider a typical trajectory of outgoing electrons³⁸. The final momentum after taking off at $\vec{r}(\tau) \approx 0$ near the ionic core is given by

$$\vec{p}_f(\tau) = \vec{p}_0 + \int_{\tau}^{0} dt \, \vec{a} \left[\vec{F}_C(\vec{r}(t)), \vec{F}_{\rm IR}(t) \right],$$
(29)

where $\vec{a} \begin{bmatrix} \vec{F}_C, \vec{F}_{IR} \end{bmatrix}$ is the acceleration in the combined laser and Coulomb fields. In the limit of vanishing Coulomb field, $\vec{F}_C(t) = 0$, the acceleration \vec{a} reduces to $\vec{a}[\vec{F}_{IR}(t)] = -\vec{F}_{IR}(t)$ and Eq. 29 becomes equal to Eq. 25. Accordingly, the Coulomb corrected mapping from emission time to momentum shift becomes

$$\vec{p}_{f}(\tau) = \vec{p}_{0} - \vec{A}_{\rm IR}(\tau) + \int_{\tau}^{\infty} dt \, \left(\vec{a} \left[\vec{F}_{C}(\vec{r}(t)), \vec{F}_{\rm IR}(t) \right] - \vec{a} \left[0, \vec{F}_{\rm IR}(t) \right] \right), \tag{30}$$

replacing Eq. 25 as the working equation for streaking in the presence of a Coulomb field.

Eq. 30 can be viewed as the classical realization of Coulomb-laser coupling (cf. ^{44,45}) in the exit channel through the modification of the trajectory probing the Coulomb field by the simultaneous presence of the IR field. It treats the IR field and the Coulomb field non-perturbatively and on equal footing. Note that within a CTMC treatment an average over the microcanonical ensemble of starting positions $\vec{r}(\tau)$ representing the initial state is taken and, therefore, the results are independent of a particular choice of initial conditions. This differs from a recent semi-classical model⁴⁶ where $\vec{r}(\tau)$ is introduced as a matching parameter influencing the resulting time shift. One remarkable and, at first glance, counterinuitive consequence of Eq. 30 is that the time shift due to the interplay between Coulomb and laser fields, or Coulomb-laser coupling, t_{CLC} , is, to leading order, independent of the IR laser intensity. Taylor expansion of the CLC correction term in Eq. 30 using that both F_C and F_{IR} vanish for $t \to \infty$, leads to

$$\int_{\tau} \mathrm{d}t \, \left(\vec{a} \left[\vec{F}_C(\vec{r}(t)), \vec{F}_{\mathrm{IR}}(t) \right] - \vec{a} \left[0, \vec{F}_{\mathrm{IR}}(t) \right] \right) \approx c(E, Z, \omega_{\mathrm{IR}}) \vec{F}_{\mathrm{IR}}(\tau) \,, \tag{31}$$

with $c(E, Z, \omega_{IR})$ a constant depending on the kinetic energy of the emitted electron, the strength of the Coulomb field in the exit channel, and the frequency, but not on the field strength F_{IR} of the IR field. Inserting Eq. 31 into Eq. 30 yields, in the absence of any intrinsic delay, the Coulomb modified streaking equation (see Eqs. 25, 35),

$$\vec{p}_f(\tau) = \vec{p}_0 - \alpha \vec{A}_{\rm IR}(\tau + t_{\rm CLC}), \qquad (32)$$

with

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$$_{\rm CLC} = \frac{1}{\omega_{\rm IR}} \tan^{-1} c(E, Z, \omega_{\rm IR})$$
(33)

independent of F_{IR} , and

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$$\alpha = \frac{F_{\mathrm{IR}}}{\omega_{\mathrm{IR}}} \left(1 + c(E, Z, \omega_{\mathrm{IR}})^2 \right)^{1/2} \,. \tag{34}$$

Consequently, the total time shift t_S mapped out by streaking and given by the time (or phase) shift of the vector potential $\vec{A}_{IR}(\tau + t_S)$ contains now two contributions, the intrinsic atomic EWS delay t_{EWS} (Eq. 27) and the contributions from Coulomb-laser coupling (Eq. 33), with

$$t_{\rm S} = t_{\rm EWS}^C + t_{\rm CLC} \,. \tag{35}$$

The important consequence of the additivity (Eq. 35) is that EWS delays for photoionization in the presence of long-range Coulomb interactions become accessible by attosecond streaking provided that the time shift t_{CLC} can be independently



Fig. 5 Photoionization of H(1s) by an XUV pulse $(I_{XUV} = 10^{13} \text{ W/cm}^2, \tau_p = 200 \text{ as})$ as a function of E ($E = \omega_{XUV} + \varepsilon_{1s}$) streaked by an IR field with $I_{IR} = 10^{12} \text{ W/cm}^2$, $\omega_{IR} = 0.057 \text{ a.u.}$ (800 nm). Shown are both the quantum and classical EWS delay time and the streaking time t_S . Classical and quantum t_{CLC} determined by subtraction (Eq. 35) agree with each other to within the graphical resolution when taking into account that the classical angular momentum corresponding to a quantum wave with well defined ℓ is $L = \ell + \frac{1}{2}$. The analytic estimation Eq. 37 coincides as well.

determined. Key for the latter is that t_{CLC} is universal for Coulomb exit channel interactions, i.e., is independent of the atomic species and initial state. Since the Coulomb-laser coupling is of classical origin, we can determine t_{CLC} classically by subtracting from the classical streaking time $t_{S}^{cl.}$ determined by the CTMC the classical limit of the EWS time delay $t_{EWS}^{cl.}$ (Eq. 21),

$$t_{\text{CLC}}(E,\ell) = t_{\text{S}}^{\text{cl.}}(E,L) - t_{\text{EWS}}^{\text{C, cl.}}(E,L).$$
(36)

Fig. 5 illustrates the determination of t_{CLC} for the prototypical case of hydrogen 1s photoionization by an XUV pulse ($I_{\text{XUV}} = 10^{13} \text{ W/cm}^2$, $\tau_p^{\text{XUV}} = 200 \text{ as}$) where the angular momentum of the ionized electron is $\ell = 1$ and the classical L = 1 + 1/2 (see Eq. 21). The accuracy of t_{CLC} as determined classically can be checked independently by applying Eq. 36 to the full TDSE simulation for t_s and the quantum EWS delay t_{EWS} (Eqs. 6, 35). These two completely independent methods for determining t_{CLC} agree with each other on a sub-attosecond precision level allowing for unambiguous identification of the Coulomb distortion on the timing information extracted by streaking.

The analysis of Coulomb-specific contributions to emission time delays discussed in section 2 provides further insights into the origin of the time shift t_{CLC} present in Coulomb interacting systems. Starting point is the remarkable similarity between the expression for the Coulomb time shift $t_{Coul}(E, \ell, r = kt)$ (Eq. 14)

in the absence of an IR field and t_S (Eq. 35) in the presence of a streaking field. This comparison suggests to associate the additional time shift due to the logarithmic distortion $\Delta t_{Coul}(E, r = kt)$ (Eq. 18) with t_{CLC} . We recall that Δt_{Coul} is, just as t_{CLC} is, independent of the state-specific properties such as the partial wave ℓ of the continuum electron involved. It was therefore neglected in early discussions of time delay³⁴. In the present case of an explicitly time-dependent streaking field, $\Delta t_{Coul}(E, t)$ becomes dynamically relevant and observable through its explicit dependence on time. We therefore surmise that the time t_0 over which the shift Δt_{Coul} is accumulated is given by the time over which the streaking field significantly varies. We therefore identify

$$t_{\rm CLC}(E) = \frac{Z}{(2E)^{3/2}} \left(1 - \ln(2k^2 t_0) \right) \simeq \frac{Z}{(2E)^{3/2}} \left(1 - \ln(0.37ET_{\rm IR}) \right).$$
(37)

In the last step of Eq. 37 we have chosen t_0 to achieve a near perfect fit to the numerically determined t_{CLC} ($\omega_{IR}t_0 \leq 1$). Because of the logarithmic dependence on t_0 , t_{CLC} depends only relatively weakly on the precise value chosen for t_0 . Eq. 37 provides a simple and remarkably accurate analytic estimate for t_{CLC} . We have numerically checked that Eq. 37 accounts correctly for the dependence on the strength of the Coulomb field (*Z*), the period T_{IR} of the streaking field and the kinetic energy *E* of the ionized electron. Eqs. 35 to 37 provide a self-contained protocol to extract timing information on photoemission for both short-ranged (Eq. 28) and Coulomb final state interactions on the attosecond scale provided no other long-range interactions are present.

We conclude this section with a comparison between streaking and an alternative interferometric method for extracting time information, "reconstruction of attosecond harmonic beating by interference of two-photon transitions" (RAB-BIT)^{13–17,40,47,48}. The time shift observed by RABBIT, t_R , can also be written as a sum of an intrinsic atomic delay and an IR field induced shift^{16,40,48}, referred to in this context as continuum-continuum coupling, t_{cc} . It is now instructive to directly and quantitatively compare t_R with t_S . In Fig. 6 we compare t_R and t_S for photoemission of He⁺(1s) and H(1s) over a wide range of energies⁴⁹. Since RABBIT employs attosecond pulse trains (APTs) rather than single attosecond pulses, the frequency range in Fig. 6 is covered by APTs encompassing harmonics ranging from q = 9 to q = 81 of the fundamental ω_{IR} with $\lambda = 800$ nm. The excellent agreement underlines that t_{EWS} can be unambiguously extracted by conceptually entirely different methods provided that the additional contributions t_{CLC} or the equivalent t_{cc} are accounted for.

4 Dipole-laser interactions

Interactions decaying asymptotically as $V \sim r^{-2}$ provide an interesting case at the borderline between short- and long-ranged interactions. A prominent example is the centrifugal potential

$$V(\ell, r) = \frac{\ell(\ell+1)}{2r^2}.$$
(38)

Standard scattering theory applies to $V(\ell, r)$ and gives for a free particle and for all short-ranged potentials decaying faster than r^{-2} , a constant phase shift



Fig. 6 Comparison between the streaking times $t_{\rm S}$ and RABBIT time shifts $t_{\rm R}$. For streaking single attosecond pulses with $\tau_{\rm p} = 200$ as and variable $\omega_{\rm XUV}$ are used, for RABBIT APTs built of harmonics from q = 9 to q = 81 of the fundamental $\omega_{\rm IR}$ ($\lambda = 800$ nm) are employed.

 $-\ell \pi/2$ and hence a vanishing contribution to the time delay. In the simultaneous presence of the Coulomb potential, however, the centrifugal potential gives rise to an additional non-trivial ℓ -dependent contribution ⁵⁰ to $t_{\rm EWS}^C$ through the non-separable dependence of the argument of the digamma function on ℓ (Eq. 22), see Fig. 7. Analogously, the classical $t_{\rm EWS}^{\rm cl}$ depends on the *L* dependence of the Kepler hyperbola (Eq. 21). For the Coulomb exit channel interaction, the non-trivial contribution of the centrifugal potential to the Coulomb-EWS time delay can be determined by the difference to the $\ell = 0$ partial wave where the centrifugal potential vanishes,

$$t_{\text{EWS}}^{\Delta \ell}(E,\ell) = t_{\text{EWS}}(E,\ell) - t_{\text{EWS}}(E,0).$$
(39)

Despite being the result of the interplay with the long-range Coulomb interaction these contributions are fully accounted for by the Coulomb EWS time delay.

Another important case are (permanent) dipole interactions also decaying as $V_d \sim r^{-2}$. Their influence on streaking were first discussed by Baggesen *et al.*^{51,52}. A prototypical case is photoionization of degenerate hydrogenic manifolds where dipolar interactions are present in the entrance channel and Coulomb interactions in the exit channel. We consider in the following ionization of He⁺(n=2). While for the states He⁺(2s) and He⁺(2 p_1) only one partial wave in the continuum is accessed (ℓ = 1 and ℓ = 2, respectively), for He⁺(2 p_0) and the parabolic states⁵³ He⁺(n=2,k=±1) the dipole selection rule for photoionization leads to the coherent superposition of partial waves with ℓ = 0,1,2 and, according to Eq. 6, to variations of the Coulomb-EWS times with the angle of photoemission.

The two parabolic states feature a permanent electric dipole moment⁵³ of



Fig. 7 Coulomb EWS times for photoionization of $\text{He}^+(n=2)$ substates as a function of the kinetic energy $E = \omega_{\text{XUV}} + \varepsilon_{1s}$. Also shown is $t_{\text{EWS}}^{\text{C, cl.}}$ for different $L = \ell + 1/2$ (Eq. 21).

 $d_{k=\pm 1} = \pm 3n/2Z$. The effect of the initial state polarization on the photoionization transition matrix element is fully contained in the Coulomb-EWS time (see Eq. 39). However, in the presence of the IR streaking field, its interaction with the initial-state dipole leads to a time-dependent initial-state energy shift

$$\Delta E(\tau) = -\vec{d}\vec{F}_{\rm IR}(\tau) \tag{40}$$

and, in turn, to a phase shift

$$\Phi(t) = -\vec{d} \int_{-\infty}^{t} \vec{F}_{\rm IR}(t') dt' = \vec{d} \vec{A}_{\rm IR}(t).$$
(41)

This dipole-laser coupling (dLC) induced energy and phase shift gives rise to additional streaking-measurement related time shifts which distort the intrinsic time information to be extracted. Indeed, the streaking time t_S for the He⁺(n=2) initial states significantly differ from those predicted by Eq. 35 (Fig. 8). This dLC contribution can be easily accounted for by including the IR field induced energy shift of the initial state. The additional modulation of the final-state energy (see Eq. 40), neglecting terms to second order in the streaking field, is given by

$$E_f(\tau) = \frac{p_f^2(\tau)}{2} = E_0 - \vec{p}_0 \vec{A}(\tau) - \vec{d} \vec{F}_{\rm IR}(\tau).$$
(42)

In direct analogy to Eq. 32 and Eq. 33, the dipole contribution $\sim F_{IR}(\tau)$, being $\pi/2$ out of phase with the streaking momentum $A_{IR}(\tau)$, gives rise to an additional time shift⁵¹ of the streaking momentum

$$\alpha_{\rm dl} A_{\rm IR}(\tau + t_{\rm dLC}^{(i)}) = A_{\rm IR}(\tau) + d_k F_{\rm IR}(\tau) / p_0, \qquad (43)$$



Fig. 8 Streaking time shifts t_s for He⁺(n=2) substates, 2s, $2p_0$, $2p_1$ and the parabolic states ($n=2, k=\pm 1$) (points) compared to (a) the analytic prediction without initial-state polarization (Eq. 35, lines), (b) including the dipole-laser coupling contribution (Eq. 46, lines).

evaluated for emission along the laser polarization axis, with

$$t_{\rm dLC}^{(i)} = \frac{1}{\omega_{\rm IR}} \tan^{-1} \left(\frac{d_k \omega_{\rm IR}}{p_0} \right) \tag{44}$$

and

$$\alpha_{\rm dLC} = \left(1 + \left(\frac{d_k \omega_{\rm IR}}{p_0}\right)^2\right)^{1/2}.$$
(45)

Thus, for photoionization of atomic or molecular initial states (*i*) with a permanent electric dipole the relation Eq. 35 between the observable streaking time shift t_S and the intrinsic EWS time delay t_{EWS} has to be modified to

$$t_{\rm S} = t_{\rm EWS} + t_{\rm CLC} + t_{\rm dLC}^{(i)}.$$
(46)

Eq. 46 can account for all time shifts observed for the degenerate hydrogenic manifolds with (sub-)attosecond precision (Fig. 8b). Most remarkably, Eq. 46 allows to accurately account for the corrections to initial states that have no permanent dipole $(2s, 2p_0)$ but are highly polarizable due to the degeneracy of the manifold. Expanding $|2s\rangle$ and $|2p_0\rangle$ in terms of the two parabolic states

$$|n=2, \ell=0 (\ell=1)\rangle = \frac{1}{\sqrt{2}} (|k=1\rangle + (-)|k=-1\rangle), \qquad (47)$$

the effective induced dipole moment follows as

$$\langle d_{\text{eff}}^{\ell} \rangle = \frac{1}{2 \left| c_{\ell} \right|^2} \sum_{k} d_k \left| c_k \right|^2 \tag{48}$$

where $|c_k|^2$ and $|c_\ell|^2$ are the square moduli of the dipole transition matrix elements (Eq. 6) from the initial state *k* or ℓ to the continuum with final momentum along the polarization axis. We note that the present findings of a dLC shift of polarizable states without a permanent dipole moment is at variance with recent claims⁵².

5 Many-electron systems

The analysis of the preceding section focussed on one (active) electron systems for which both classical and quantum dynamics in a streaking setting can be solved (to within numerical precision) exactly, and, moreover, accurate analytical estimates for the time-shifts involved can be given. Since in the pioneering experiment the relative time delay between photoionization of the 2*s* an 2*p* electrons was measured for neon¹², the influence of many-electron and correlation effects on the intrinsic time delay and on streaking-measurement related time shifts became important issues. We briefly address this topic with the help of two prototypical two (active) electron systems for which numerically exact solutions of the TDSE are still feasible ^{54–56}.

We first discuss a fully correlated two-active electron (TAE) model⁵⁷ for two non-equivalent electrons denoted in the following as (1s, 2p). These two active electrons move in a mean field of N-2 passive electrons. We choose a background potential, V_{N-2} , such that the work function of the 2p electron matches that of the Ne 2p electron while the work function of the 1s electron corresponds to that of the Ne 2s subshell. This model thus shares several features of the neon atom including identical kinetic energies, identical t_{CLC} (Eq. 33), and identical angular momenta of the two electrons the difference in emission time of which has been experimentally explored ¹². While the model is not intended to provide a realistic approximation to the 10-electron system it allows to fully account for the effect of e-e interactions of the two non-equivalent electrons on streaking. Moreover, by comparison with a corresponding single-active electron (SAE) model for electrons moving in a corresponding N-1 electron mean field potential $V_{N-1}(r)$, e-e effects on both the EWS time delay and on the measurement induced time shifts can be probed. Fig. 9 illustrates similarities and differences of the observable streaking shifts $t_{\rm S}$ within TAE and SAE approaches for two different XUV energies. Significant differences between the TAE and SAE models of about



Fig. 9 Streaking times $t_{\rm S}$ for a fully correlated two-electron "neon model" atom (see text) employing a two-active electron (TAE) description and comparison with a mean-field single-active (SAE) model. Also shown is $t_{\rm CLC}$ (Eq. 33).

2.5 as can be observed for emission of the 2p electron at $\omega_{XUV} = 122 \text{ eV}$. This difference can be traced to differences in the (negative) EWS delay times while the CLC contribution (also shown in Fig. 9) is identical within the TAE and SAE models. We have numerically verified the additivity relation Eq. 35 with subattosecond precision. Note that the initial-state polarizability for this model system with well separated energy levels is negligible and, hence, $t_{dLC}^{(i)} = 0$. We also stress that additional contributions to the streaking-related time shifts analogous to t_{CLC} due to short-ranged portions of many-electron potentials V_N , as recently proposed⁴⁶, can be ruled out based on the present numerical evidence. Moreover, simple semi-classical considerations argue strongly against additional CLC-like contributions from short-ranged potentials: for typical XUV frequencies currently accessible by HHG, kinetic energies of the released electrons are $E \lesssim 100 \,\mathrm{eV}$. Their large de-Broglie wavelength $\lambda_{\mathrm{dB}} = 2\pi/\sqrt{2E} \gtrsim 3 \,\mathrm{a.u.}$ precludes the spatial resolution of the short-ranged component of atomic potentials. Consequently, quasi-classical trajectory modifications induced by the interplay of short-ranged atomic potentials and the laser field in analogy to Eq. 30 are unlikely to occur.

The experimentally observed relative delay of $\Delta t_{\rm S} \approx 21$ as between the 2*p* and 2*s* electron of neon is, so far, theoretically unaccounted for. Several theoretical approaches contained in the original paper¹² as well as more recent works employing the random phase approximation with exchange for the photoionization matrix element⁵⁸, time-dependent R-matrix theory⁵⁹, and many-body perturbation theory⁶⁰ fall short by about a factor two to three. For the present Ne model system (Fig. 9) we find $\Delta t_{\rm S} \approx 4$ as.

Ionization of helium accompanied by shake-up forming so called spectroscopic "correlation satellite" lines represents the prototypical case of photoionization strongly driven by electron-electron interactions of two equivalent electrons^{61,62}. For these processes fully ab initio simulations for an attosecond streaking setting are feasible⁶³. We focus in the following on the shake-up to n = 2which becomes accessible for XUV energies exceeding the sum of the ionization potential (I_p) of He and the excitation energy $\Delta E(n = 1 \rightarrow 2)$ in He⁺. The streaking spectrogram of the main line (He⁺(1s)) and satellite (He⁺(n=2)) (Fig. 10) reflects the weakness of the shake-up channel (< 5% of the main line) and indicates the experimental challenge to perform a chronoscopic measurement with attosecond precision.



Fig. 10 Numerically simulated streaking spectrogram for helium and emission into a forward cone (opening angle 10°) around the polarization axis. XUV pulse with $\omega_{XUV} = 100 \text{eV}, \tau_p = 200 \text{ as}, I_{XUV} = 10^{12} \text{ W/cm}^2$, streaking field with $I_{IR} = 4 \cdot 10^{11} \text{ W/cm}^2, \lambda = 800 \text{ nm}$. Top: main line He⁺(1s), bottom: shake-up satellite (predominantly) to He⁺(n=2).

While for the main line, the sum of t_{CLC} and t_{EWS} (Eq. 35) accurately accounts for the numerically determined t_{S} , for the shake-up states to n = 2 Eq. 35 fails (Fig. 11). Note that the initial-state polarization of the helium ground state can be safely neglected as confirmed by the agreement for the main line and, thus, $t_{\text{dLC}}^{(i)} = 0$. In this case, it is the high polarizability of the degenerate hydrogenic He⁺(n=2) manifold of the residual ion that causes the discrepancy between the extracted streaking time and contributions from Coulomb-laser coupling and the EWS time.

Starting point is the observation that the two parabolic states He⁺($n=2, k=\pm 1$) possess a large permanent dipole moment (see section 4). The long-range interaction between the ionized electron and the residual ion in the exit channel contains now both a Coulombic and a dipolar interaction, $V_d = -\vec{d}\vec{r}/r^3$. Their direct contributions to $t_{\rm EWS}$ in the absence of a streaking field is included in the exact calculation of the dipole transition matrix for single ionization of He employing the extraction method based on exterior complex scaling^{64,65}. In the presence of a streaking field, however, both long-range portions give additional contributions. The Coulomb tail results in the time shift $t_{\rm CLC}$ (Eq. 33) while the dipolar interaction between the bound and ionized electron gives rise to a novel contribution which is a true field-induced electron-electron effect. The asymp-



Fig. 11 Streaking of shake-up ionization of helium (laser parameter as in Fig. 10). (a) Comparison between the prediciton Eq. 35 (lines) and the *ab initio* two-electron streaking data (points). (b) Comparison between Eq. 51 (lines) and streaking data for all n=2 substates and the n=2 shell average.

totic two-electron state representing one continuum and one bound electron in the presence of the streaking field has the time-dependent energy (or time derivative of its phase),

$$E_{e-e}(\tau) = \varepsilon_{nk} + E - \vec{p}_0 \vec{A}_{\mathrm{IR}}(\tau) - \vec{d}_k \vec{F}_{\mathrm{IR}}(\tau), \qquad (49)$$

where ε_{nk} is the binding energy of the residual parabolic state and *E* the kinetic energy of the ionized electron at zero field. The remaining two terms account for the interaction of the IR field with the continuum electron and with the dipole moment of the residual electronic bound state. The physical picture underlying the IR field induced dipole shift to streaking is illustrated in Fig. 12. The energy modulation of the parabolic states k = 1 and k = -1 are out of phase by π relative to each other (Fig. 12b). Following the derivation Eqs. 43 to 45 we find for the two-electron dipole laser coupling induced time shift (evaluated for emission



Fig. 12 (a) Two-electron dipole-laser interaction in the exit channel. (b) Resulting modulation of the kinetic energy of the ionized electron emitted at time τ .

along the laser polarization axis)

$$t_{\rm dLC}^{\rm (e-e)} = \frac{1}{\omega_{\rm IR}} \tan^{-1} \left(-\frac{d_k \omega_{\rm IR}}{p_0} \right).$$
 (50)

Note the opposite sign of the dipole term relative to the corresponding expression Eq. 44 for the entrance channel perturbation of the one-electron problem. Adding this term to Eq. 46,

$$t_{\rm S} = t_{\rm EWS} + t_{\rm CLC} + t_{\rm dLC}^{(i)} + t_{\rm dLC}^{(e-e)}, \qquad (51)$$

with $t_{dLC}^{(i)} = 0$ in the present case, leads to near-perfect agreement for all n = 2 shake-up substates (Fig. 11b) confirming, once more, the additivity rule for laser-modified long-range interactions. As in the one-electron case, not only ionic final states with a permanent dipole moment $|n,k,m\rangle$ but also highly polarizable states in degenerate manifolds with zero static dipole moment $|n, \ell, m\rangle$ suffer a dipole-laser induced time shift (see Eq. 48). A non-zero contribution survives even when an average over all n = 2 substates is taken (Fig. 11b). Conceptually, Eq. 50 and Eq. 51 reflect the entanglement in the exit channel. As a result, the streaking time shift of the observed ionized electron depends on the dipole moment of the substate of the residual ion. In turn, in such a setup the final quantum state $|n, \ell, m\rangle$ or $|n, k, m\rangle$ becomes accessible in a non-destructive measurement, i.e., without directly observing it.

6 Outlook: complex systems

We conclude the discussion of time-resolved photoemission by streaking with an outlook toward the extraction of dynamic information of more complex manyelectron systems. As the number of degrees of freedom increases, following the dynamic evolution on a state-resolved level becomes impossible. Instead of the fully coherent N-electron evolution, the partially coherent dynamics on the level of one- (or few-) particle reduced density matrices takes center stage. The streaked electron thus carries information on the interactions with the "bath" of the electrons and ionic cores it is immersed in prior to and during the emission process. Instead of an EWS time delay associated with an individual scattering state, dephasing, decoherence, and relaxation times become accessible. Concomitantly, the strict Fourier reciprocity between time domain and energy domain is broken. While for a fully coherent photoionization process the spectral variation of the scattering phase (see Eq. 6) determining the intrinsic atomic time delay, is, in principle, indirectly accessible in the energy domain by high-resolution angular spectroscopy, time-resolved photoemission in complex open systems can provide novel information on decohering processes such as collisions, energy exchange, and relaxation not easily accessible in the spectral domain. We therefore conjecture that the full potential of time-resolved photoelectron spectroscopy, i.e., chronoscopy, will emerge when applied to complex systems. Exploiting these opportunities, both experimentally and theoretically, remains a challenge.

One case in point is time-resolved photoemission from a tungsten surface¹¹. The time delay between conduction band electrons and core levels were associated with transport effects and steep variation of the group velocity near the points in *k*-space where Bragg reflections occur^{11,66}. Within a classical transport theory, multiple scattering processes and energy loss due to plasmon excitation have been shown to effectively contribute to the observed time delay⁶⁷. However, accounting quantitatively for the experimentally observed time delay has remained a widely open question^{68,69}.

An intriguing scenario at the borderline between an atomic and condensedmatter system is photoemission from an endohedral C_{60} complex, $A@C_{60}$, where a heavy atom A, for example xenon, with a well-defined core-level emission line is located at the center of the C_{60} cage ^{70,71} (Fig. 13a). The cage will act as a



Fig. 13 (a) Endohedral complex, He⁺@*C*₆₀, schematically. (b) Variation of *t*_S (dots) due to the modulation of *t*_{EWS} (lines, averaged over the XUV spectrum) as a function of the kinetic energy *E* of the outgoing electron, see Eq. 53. For *V*_{shell} we have chosen two sets of values previously used in the literature⁷². 1: *V*₀ = -0.302 a.u., $\Delta = 1.9 \text{ a.u.}$, $r_0 = 5.89 \text{ a.u.}$, 2: *V*₀ = -0.422 a.u., $\Delta = 1.25 \text{ a.u.}$, $r_0 = 6.01 \text{ a.u.}$.

finite-size bath with which the photoelectron interacts. Point of departure of a simplified SAE model is an effective potential for the core electron bound to the center atom $V_A(r)$ with a long-range Coulomb tail. As the outgoing electron traverses the cage, it experiences a short-ranged potential created by the shell of C_{60} atoms. A simple model potential for the shell is ⁷²

$$V_{\text{shell}}(r) = \begin{cases} -V_0 & \text{for } r_0 \le r \le r_0 + \Delta \\ 0 & \text{otherwise} \end{cases}$$
(52)

with r_0 the inner-radius of the C_{60} shell, Δ its width and V_0 the mean potential on a one-electron level. The short-ranged admixture would lead to an energy dependent modulation δt_{EWS} of the intrinsic atomic time delay, t_{EWS}^A ,

$$t_{\rm EWS}(E) = t^A_{\rm EWS}(E) + \delta t_{\rm EWS}(E)$$
(53)

on the fully coherent one-electron level. We find, for He⁺ enclosed in a C_{60} cage, good agreement for the prediction for the streaking time (Eq. 35) when the modified EWS time Eq. 53 is used (Fig. 13b). Future studies will go beyond such an SAE model and novel features are expected to emerge. The outgoing electron will interact with the 240 valence electrons of the C_{60} shell which represent environmental degrees of freedom. Among the channels to be considered are collective excitations, i.e., surface and bulk plasmons, and collisional excitation and ionization of the shell. Moreover, the highly polarizable C_{60} shell is expected to modify the streaking process itself. It is hoped that experimental data for streaking of such nanoplasmonic systems become accessible in the near future⁷³.

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