Control of photoemission delay in resonant two-photon transitions

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The photoelectron emission time delay τ associated with one-photon absorption, which coincides with half the Wigner delay τ_W experienced by an electron scattered off the ionic potential, is a fundamental descriptor of the photoelectric effect. Although it is hard to access directly from experiment, it is possible to infer it from the time delay of two-photon transitions, $\tau^{(2)}$, measured with attosecond pump-probe schemes, provided that the contribution of the probe stage can be factored out. In the absence of resonances, τ can be expressed as the energy derivative of the one-photon ionization amplitude phase, $\tau = \partial_E \arg D_{Eg}$, and, to a good approximation, $\tau = \tau^{(2)} - \tau_{cc}$, where τ_{cc} is associated with the dipole transition between Coulomb functions. Here we show that, in the presence of a resonance, the correspondence between τ and $\partial_E \arg D_{Eg}$ is lost. Furthermore, while $\tau^{(2)}$ can still be written as the energy derivative of the two-photon ionization amplitude phase, $\partial_E \arg D^{(2)}_{Eg}$, it does not have any scattering counterpart. Indeed, $\tau^{(2)}$ can be much larger than the lifetime of an intermediate resonance in the two-photon process or more negative than the lower bound imposed on scattering delays by causality. Finally, we show that $\tau^{(2)}$ is controlled by the frequency of the probe pulse, ω_{IR}, so that by varying ω_{IR}, it is possible to radically alter the photoelectron group delay.

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I. INTRODUCTION

When a wave packet scatters off a short-range potential, it acquires a delay, compared with a reference free wave. For example, a particle accelerates when it enters an attractive potential, and hence its time delay is negative (see Fig. 1). For spectrally narrow, unstructured wave packets, the scattering delay coincides with the wave-packet group delay and can be expressed as the energy derivative of the phase shift δ_E experienced by the scattered particle. This is known as the Wigner [1,2] time delay,

$$\tau_W = 2\hbar \frac{\partial \delta_E}{\partial E}. \tag{1}$$

Scattering delay is subject to constraints. For example, a particle cannot traverse the whole interaction region in a negative time. As a result, the time delay is bounded from below by $\tau_{min} = -2a/v$, where $v = \hbar k/m$ is the asymptotic speed of the particle and a is the effective range of the potential [1]. Conversely, an energy derivative of the phase shift more negative than $-a/v$ would violate causality, since it would then be possible to build a wave packet that bounces off the potential before colliding with it.

Until recently, the temporal aspects of electron scattering were confined to theoretical speculation, since typical scattering time delays are much smaller than the time it takes a wave packet, at macroscopic distances from the interaction center, to traverse any given point (e.g., the detector) and are therefore not realistically measurable. The advent of attosecond science [3], which does provide the necessary time resolution, has renewed the interest in scattering delays (see [4] and [5] for an in-depth treatment of this subject). It has also given rise to controversies, due to the role of the probe stage inherent to pump-probe interferometric schemes. On the one hand, for one-photon absorption, the photoelectron emission delay,

$$\tau = \hbar \partial_E \arg D_{Eg}, \tag{2}$$

where D_{Eg} is the one-photon ionization amplitude, and the Wigner time delay [Eq. (1)] coincide (within a factor of 2). On the other hand, the phase of one-photon transition amplitudes is not accessed directly. Instead, what is measured is the interference between two alternative paths that involve the exchange of multiple photons, as, e.g., in the reconstruction of attosecond beatings by interference of two-photon transitions (RABITT) spectroscopy [6]. When the time delay for the two-photon transition, $\tau^{(2)}$, can be formulated as the sum of the time delays for the individual steps, it is possible to recover the contribution of the one-photon transition and, hence, to reconstruct the scattering time delay as well. However, this is not always the case.

Here we show that, when the two-photon transition is resonant, the traditional relations between wave-packet group delay, Wigner delay, one-photon delay, and two-photon delay do not hold anymore. First, the one-photon transition amplitude between the ground state and the continuum, D_{Eg}, vanishes at an isolated energy. As a consequence, the photoelectron wave packet acquires a radial node and its dynamics is no longer properly described by a group delay defined as the derivative of a matrix element argument, which is now singular. Yet, it is still possible to identify a one-photon

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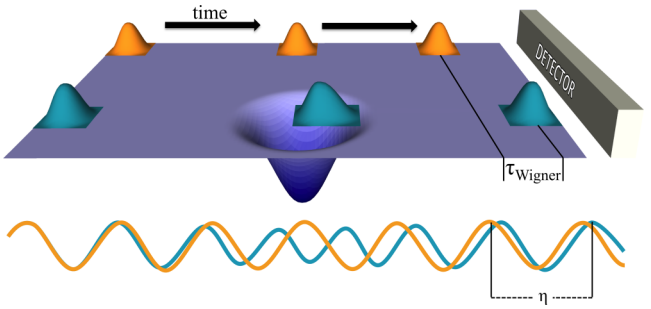

FIG. 1. Sketch of the Wigner time delay. As the electron wave packet (green symbols) scatters off the potential, it acquires a phase shift η compared to a reference free electron (orange symbols). This phase shift is related to the time lapsed between the detection of the scattered electronic wave packet and the detection of the unscattered free electron, called the Wigner time delay.

ionization time delay τ that is a smooth function of the energy and coincides with an electron-ion scattering time delay. Hence, it is the correspondence between time delay and $\partial_E \arg D_{Eg}$, rather than a time-delay interpretation, that is lost. Second, in the two-photon transition matrix element, $D^{(2)}_{Eg}$, the path through a continuum-continuum transition in the last stage also vanishes, and two alternative paths, a nonresonant and a resonant one, become dominant. In the nonresonant path, the probe photon is exchanged first, whereas the resonant path involves the radiative transition between the intermediate metastable state and the final continuum. In this case, $\hbar\partial_E \arg D^{(2)}_{Eg}$ differs from $\tau_{\rm w}$ by a new sharply peaked resonant term with no scattering counterpart. Thus $\hbar\partial_E \arg D^{(2)}_{Eg}$ can exhibit extreme values that are incompatible with a scattering delay, namely, larger than the lifetime of the metastable state or more negative than the lower bound imposed on $\tau_{\rm w}$ by causality. Furthermore, $\hbar\partial_E \arg D^{(2)}_{Eg}$ can strongly vary within a narrow interval of photoelectron energies, comparable to the resonance autoionization width. The relative strength of the resonant and nonresonant paths is controlled by the probe frequency $\omega_{\rm IR}$. Therefore, by varying this frequency and keeping the pump frequency (and all other parameters) constant, it is possible to radically alter the group delay $\tau^{(2)}$ of the two-photon photoelectron wave packet.

The paper is organized as follows. In Sec. II we revisit the relevant assumptions behind the correspondence between scattering time delay and photoionization time delay and offer a definition for the latter that allows us to interpret consistently the case in which such correspondence no longer holds. In Sec. III, we examine the case of the resonant ionization of an atom in the context of RABITT spectroscopy and show how the measured delay does describe the photoemission delay of a two-photon photoelectron wave packet, but that this delay does not correspond to the one-photon ionization time delay and cannot be formulated as a field-free scattering delay either. In Sec. IV, we apply our formalism to investigate a realistic case: two-photon ionization of the helium atom induced by an XUV resonant transition to an sp^+ doubly excited state followed by absorption or emission of an IR photon (as in recent RABITT-like experiments [7]). Finally, we summarize the main conclusions of our work in Sec. V.

To simplify notation, we use atomic units throughout ($\hbar = 1, e = 1, m_e = 1$), unless otherwise stated.

II. PHOTOIONIZATION TIME DELAY

Let us assume that an atom is ionized from the ground state $|g\rangle$ by the absorption of one photon from a single, long, and weak Fourier-limited XUV pulse $\mathcal{E}(t)$, with the spectrum sharply peaked around $\omega_0 = E_0 - E_g$, where E_g and E_0 are the ground- and final-state eigenenergies, respectively. After ionization, the photoelectron wave packet $\Psi(t)$ can be written, in the interaction representation and to first order in the radiation-atom interaction, as

$$|\Psi(t)\rangle = \frac{\sqrt{2\pi}}{i}\int dE|\psi_E^-\rangle\, e^{-iEt}\,\langle\psi_E^-|\mathcal{O}|g\rangle\tilde{\mathcal{E}}(E-E_g), \quad (3)$$

where $\mathcal{O} = -\hat{\epsilon}\cdot\vec{\mu}$ is the dipole operator and $\tilde{\mathcal{E}}(\omega)$ is the Fourier transform of the ionizing pulse, $\tilde{\mathcal{E}}(\omega) \equiv (2\pi)^{-1/2}\int dt\mathcal{E}(t)\exp(i\omega t)$. The states $|\psi_E^-\rangle$ are the generalized eigenstates of the field-free Hamiltonian H of the atom above the ionization threshold, $H|\psi_E^-\rangle = E|\psi_E^-\rangle$, $\langle\psi_E^-|\psi_{E'}^-\rangle = \delta(E-E')$. Furthermore, they are assumed to fulfill incoming-boundary conditions with respect to the continuum eigenstates of a Hamiltonian H_0 chosen as a reference [8],

$$|\psi_E^-\rangle = |\phi_E\rangle + G_0^-(E)(H-H_0)|\psi_E^-\rangle, \quad (4)$$

with $H_0|\phi_E\rangle = |\phi_E\rangle E$, $\langle\phi_E|\phi_{E'}\rangle = \delta(E-E')$, $G_0^{\pm}(E) \equiv (E - H_0 \pm i0^+)^{-1}$, and $H - H_0$ is assumed to be short-range. The phase of $\tilde{\mathcal{E}}(\omega)$ depends on the choice of the time origin. For a Gaussian pulse, for example, the phase is constant if the time origin, t_0, coincides with the center of the pulse envelope, $t_{\rm XUV}$. In analogy with this circumstance, therefore, we choose the time origin in such a way that the phase of $\tilde{\mathcal{E}}(\omega)$ is flat at the peak of $\tilde{\mathcal{E}}(\omega)$,

$$\partial_\omega \arg[\tilde{\mathcal{E}}(\omega)]|_{\omega_0} = 0 \iff t_{\rm XUV} = 0. \quad (5)$$

Furthermore, we assume that the pulse is such that the phase of $\tilde{\mathcal{E}}(\omega)$ is flat across its whole peak (i.e., the pulse is Fourier limited, or unchirped).

At sufficiently long times, the wave packet has a purely outgoing character and the expansion in terms of $|\psi_E^-\rangle$ can be replaced with an expression over the outgoing asymptotes $|\phi_E\rangle$ [9],

$$|\Psi(t)\rangle \underset{t\to\infty}{=} \frac{\sqrt{2\pi}}{i}\int dE|\phi_E\rangle e^{-iEt}\langle\psi_E^-|\mathcal{O}|g\rangle\tilde{\mathcal{E}}(E-E_g). \quad (6)$$

What is the time delay of such a wave packet? To qualify this question, it is necessary to define a reference free-evolving wave packet, as well as the condition for the reference wave packet to be located at the origin. Here, we assume that the free evolution is defined by H_0. If one propagates back the wave packet with the $U_0(t,t') = e^{-iH_0(t-t')}$ free time-evolution operator, the result at a time t_0 is

$$U_0(t_0,t)|\Psi(t)\rangle = \frac{\sqrt{2\pi}}{i}\int dE|\phi_E\rangle e^{-iEt_0}\langle\psi_E^-|\mathcal{O}|g\rangle\tilde{\mathcal{E}}(E-E_g). \quad (7)$$

In single-channel scattering, $|\phi_E\rangle$ can be chosen up to an arbitrary and immaterial phase factor. In particular, the radial part of $\phi_E(\vec{r})$ can be chosen to be real in all space. By hypothesis, $\tilde{\mathcal{E}}(E-E_g)$ is narrowly peaked at $E=E_0$. If the transition amplitude does not vanish at E_0, i.e., $\langle\psi_{E_0}^-|\mathcal{O}|g\rangle \neq 0$, its phase

$$\varphi_E \equiv \arg\langle\psi_E^-|\mathcal{O}|g\rangle \tag{8}$$

is a smooth function of the energy. Therefore, we can approximate $\varphi_E \approx \varphi_{E_0} + (E-E_0)\varphi'_{E_0}$ and isolate the complex components of the wave packet back-propagated at t_0 as

$$\begin{aligned} U_0(t_0,t)|\psi(t)\rangle \simeq{}& \frac{\sqrt{2\pi}}{i} e^{-iE_0t_0} e^{i\varphi_{E_0}} \\ &\times \int dE|\phi_E\rangle e^{-i(E-E_0)(t_0-\varphi'_{E_0})} \\ &\times |\langle\psi_E^-|\mathcal{O}|g\rangle|\tilde{\mathcal{E}}(E-E_g). \end{aligned} \tag{9}$$

Note that this approximation is not valid if the transition amplitude does vanish within the support of $\tilde{\mathcal{E}}(\omega_{Eg})$, because φ_E is then discontinuous. We examine this more subtle case in more detail in Sec. III. The global phase factors outside the integral in (9) do not affect the spatial distribution of the wave packet and can thus be safely ignored. Except for the phase factor $\exp[-i(E-E_0)(t_0-\varphi'_{E_0})]$, all the other factors in the argument of the integral are real by construction. As a consequence, for

$$t_0 = \partial_E\varphi_E|_{E_0} \equiv \partial_E \arg\langle\psi_E^-|\mathcal{O}|g\rangle|_{E_0} \tag{10}$$

the wave packet described by the integral in (9) is purely real. This means that the wave packet has everywhere outgoing and incoming components in equal proportions and it is hence arguably at the stage of closest approach to the scattering center. If the system under study was really an unperturbed system described by H_0, t_0 would also be the time at which the XUV pulse impinges on the target ($t_{\mathrm{XUV}}=0$). In general, however, $t_0 \neq 0$. If $t_0>0$, the wave packet *seems* to have waited a time t_0 after the XUV before being released, and then we talk of a positive time delay, $\tau = t_0 - t_{\mathrm{XUV}} = t_0$. Conversely, knowing the time at which the XUV has reached the target and estimating the travel time on the basis of the free propagation, one can infer that the actual wave packet travels with a delay $\tau = t_0$.

How does this apparent delay compare with the scattering (Wigner) time delay? Remaining in the case of a single channel perturbed by a short-range potential, a generalized eigenstate ψ_E of the full Hamiltonian can also be normalized so as to be real across the whole space [10], in which case it differs from the reference state in the asymptotic region by a radial phase shift, δ_E: $\psi_E(\vec{r}) \simeq \phi_E[\hat{r}(r+\delta_E/k)]$, where k is the asymptotic de Broglie electron wave number. This means that the outgoing components of the real ψ_E and ϕ_E generalized functions differ asymptotically by a phase factor, $[\psi_E]_{\mathrm{out}} = e^{i\delta_E}[\phi_E]_{\mathrm{out}}$. The scattering states $\psi_E^-(\vec{r})$, on the other hand, are defined in such a way that their outgoing component coincides asymptotically with that of the reference states $\phi_E(\vec{r})$. As a consequence,

$$\psi_E^- = e^{i\delta_E}\psi_E, \tag{11}$$

which means that the argument of the transition amplitude $\langle\psi_E^-|\mathcal{O}|g\rangle$ is

$$\varphi_E \equiv \arg\langle\psi_E^-|\mathcal{O}|g\rangle = \delta_E, \tag{12}$$

where we have used the fact that the spatial representations of $|\psi_E\rangle$, $|g\rangle$, and $\mathcal{O}$ are real functions. From Eq. (10), the photoionization time delay becomes

$$\tau = \partial_E\varphi_E|_{E_0} = \partial_E\delta_E|_{E_0}. \tag{13}$$

Apart from a factor of 2, therefore, the time delay in a photoionization process coincides with the Wigner time delay [see Eq. (1)]. This agrees with the idea that photoionization is in fact a half-collision process. Indeed, in photoionization, we are neglecting the retardation or anticipation associated with the first half of the collision, i.e., the one experienced by the electromagnetic field as it approaches the atom, compared to the case in which the electromagnetic field can propagate freely. This effect could in principle be taken into account, by means of Kramers-Kronig relations, through the derivative of the dispersive component of the optical susceptibility of the atom. Due to the high speed of light, however, such temporal effects are much smaller than those observed for the electrons, and hence it is safe to neglect them.

To measure the transition phases φ_E, the photoelectron wave packet needs to be probed. Doing so in traditional one-photon absorption experiments, however, is virtually impossible, since no electron detector has the sufficient time resolution. Two-photon attosecond interferometric techniques such as RABITT, on the other hand, do provide access to the relative delay between two two-photon photoelectron wave packets. In contrast to single-photon processes, multiphoton transition matrix elements can be complex even if all the states involved are real. In particular, even in the case of the ionization of a reference system H_0, the expansion coefficients of a multiphoton wave packet have a phase modulation even if $\langle\phi_E|\mathcal{O}|g\rangle$ is real,

$$\partial_E \arg\mathcal{M}_{Eg}(\omega) \neq 0, \tag{14}$$

where $\mathcal{M}_{Eg}(\omega) = \langle\phi_E|\mathcal{O}G^+(E_g+\omega)\mathcal{O}|g\rangle$, and $G^+(E) = (E-H+i0^+)^{-1}$ is the retarded resolvent of the field-free Hamiltonian. This means that multiphoton wave packets are inherently delayed with respect to one-photon wave packets, even in the absence of intermediate resonances. If, furthermore, the system is not the reference one, both the multiphoton delay and the short-range effects of the perturbative potential affect the total delay.

In the special case in which the second photon interacts with a wave packet asymptotic in character, the relation between one- and multiphoton time delays has been explored in detail by several authors [11–13]. In particular, Dahlström *et al.* [14] have shown that, when a single ionization continuum $|\psi_{\alpha E}\rangle$ is accessible by one-photon absorption, the atomic time delay of the two-photon ionization from the ground state $|g\rangle$ to a final continuum channel $|\psi_{\beta E}\rangle$, such as the one recorded with the RABITT technique, can be written as the sum of two contributions,

$$\tau^{(2),\mathrm{nr}} = \tau_{\mathrm{w}}^{\mathrm{nr}} + \tau_{\mathrm{cc}}, \tag{15}$$

where $\tau_{\mathrm{w}}^{\mathrm{nr}}$ is a Wigner-like sequential two-photon ionization time delay that includes the on-shell IR-induced continuum-continuum transition between Coulomb scattering states (direct and inverse stimulated Bremsstrahlung), and τ_{cc}, the so-called continuum-continuum time delay, represents the measurement-induced delay associated with the off-shell

contributions to the two-photon transition (see Eqs. (25), (44) and (45) in [14]). When multiple final continua are available, the measurement-induced delays, i.e., the on-shell continuum-continuum contribution in $\tau_{\rm w}^{\rm nr}$ and the whole τ_{cc} delay, can be different for each of them. In particular, if the final channels do not have the same angular distribution, the time delay is expected to exhibit an angular dependence induced by the probe stage. In a recent joint theoretical and experimental work, Heuser *et al.* [15] investigated the angular dependence of the atomic photoemission time delay for the ionization from an isotropic atomic state and demonstrated that the IR-induced delay is not isotropic.

There are cases, however, in which the intermediate wave packet prior to the absorption of a second photon is not asymptotic in character yet. The most evident counterexample is when an intermediate resonant state, not contemplated by the H_0 Hamiltonian, is populated and subsequently undergoes a radiative transition to the final continuum.

III. RESONANT PHOTOEMISSION TIME DELAY

To treat the resonant case, it is convenient to distinguish three different Hamiltonians: (i) The reference Hamiltonian H_0 serves the purpose of defining the asymptotic evolution of a wave packet in the presence of the long-range components of the potential (e.g., the pure Coulomb potential) and, hence, the reference wave packet with respect to which we measure the time delay, $H_0|\phi_{\alpha E}\rangle = |\phi_{\alpha E}\rangle E$. (ii) The unperturbed Hamiltonian $H_0' = H_0 + H_{\rm sr}$ differs from the reference by a short-range component $H_{\rm sr}$, whose associated eigenstates comprise a featureless continuum $|\varphi_{\alpha E}^-\rangle$ and a bound state $|a\rangle$ immersed in that continuum, so that $H_0'|a\rangle = E_a|a\rangle, H_0'|\varphi_{\alpha E}^-\rangle = |\varphi_{\alpha E}^-\rangle E, |\varphi_{\alpha E}^-\rangle = |\phi_{\alpha E}\rangle + G_0^-(E)H_{\rm sr}|\varphi_{\alpha E}^-\rangle$. (iii) The full field-free Hamiltonian $H = H_0' + V$ includes a short-range "configuration interaction" component V that couples the bound state $|a\rangle$ to the continuum $|\varphi_{\alpha E}^-\rangle$ (i.e., $V_{a,\alpha E} \equiv \langle a|V|\varphi_{\alpha E}^-\rangle \neq 0$) and, therefore, accounts for autoionization, $|\psi_{\alpha E}^-\rangle = |\varphi_{\alpha E}^-\rangle + G_0'^-(E)V|\psi_{\alpha E}^-\rangle$. Here we focus on the simpler case in which a single $|a\rangle$ bound state interacts with a set of nondegenerate $|\varphi_{\alpha E}^-\rangle$ continuum eigenstates. Therefore, our definitions in (ii) and (iii) closely follow Fano's formalism of autoionization of isolated resonances in the continuum [16].

Let us now consider a two-photon transition triggered by two monochromatic pulses of arbitrary frequencies ω_1 and ω_2 in which the intermediate step is resonant through absorption of photons with frequency ω_1. In the context of RABITT spectroscopy, ω_1 and ω_2 stand for $\omega_{\rm XUV}$ and $\omega_{\rm IR}$, respectively, but our treatment is not limited to this particular case. If we neglect the contribution to the transition amplitude from the path in which ω_2 is absorbed first, the photoemission time delay to a final channel $|\psi_{\beta E_f}^-\rangle$ becomes

$$\tau^{(2)} \simeq \partial_E \arg \mathcal{M}_{\beta E_f,g}(\omega_1), \tag{16}$$

where

$$\mathcal{M}_{\beta E_f,g}(\omega_1) = \langle \psi_{\beta E_f}^-|\mathcal{O}G^+(E_g+\omega_1)\mathcal{O}|g\rangle \tag{17}$$

is the usual two-photon matrix element describing the transition from the ground state $|g\rangle$, with energy E_g, to the final state $|\psi_{\beta E_f}^-\rangle$, with energy $E_f = E_g + \omega_1 \pm \omega_2$. In the context of the two-photon resonant model developed in [17] and [18], which is an extension of the Fano model [16] to the case of two-photon transitions, this matrix element can be simply written as

$$\mathcal{M}_{\beta E_f,g}(\omega_1) \simeq -\frac{\bar{\mathcal{O}}_{\beta\alpha}\mathcal{O}_{\alpha,g}}{\omega_2}\,\mathcal{M}_R(\omega_1), \tag{18}$$

where

$$\bar{\mathcal{O}}_{\beta\alpha} = \int dE_f\ \langle \varphi_{\beta E_f}^-|\mathcal{O}|\varphi_{\alpha E}^-\rangle, \quad \mathcal{O}_{\alpha,g} = \langle \varphi_{\alpha E}^-|\mathcal{O}|g\rangle, \tag{19}$$

with $E = E_g + \omega_1$, and

$$\mathcal{M}_R(\omega_1) = \frac{\epsilon + \bar{q} + i\gamma}{\epsilon + i}. \tag{20}$$

In Eq. (20), ϵ is the Fano reduced energy given by

$$\epsilon = 2(E_g + \omega_1 - \bar{E}_a)/\Gamma, \quad \bar{E}_a = E_a + \Delta, \tag{21}$$

$\bar{q}$ is related to the usual Fano profile parameter of one-photon ionization, $q = \mathcal{O}_{ag}/\pi V_{\alpha E,a}\mathcal{O}_{\alpha g}$, as

$$\bar{q} = q(1-\gamma), \quad \gamma = \frac{\omega_2 \mathcal{O}_{\beta a}}{\bar{\mathcal{O}}_{\beta\alpha}V_{\alpha E,a}}, \tag{22}$$

$\Gamma = 2\pi|V_{\alpha E,a}|^2$ and Δ are the autoionization width and energy shift of the resonant state $|a\rangle$, respectively, $\mathcal{O}_{ag} = \langle a|\mathcal{O}|g\rangle$, and $\mathcal{O}_{\beta a} = \langle \varphi_{\beta E_f}^-|\mathcal{O}|a\rangle$. We note that γ measures the relative strength of the IR-induced radiative transitions from the resonant state $|a\rangle$ and the nonresonant state $|\psi_{\alpha E}^-\rangle$ to the continuum and that this relative strength depends on the IR frequency ω_2.

The energy derivative of the argument of Eq. (18) leads to the following expression for the two-photon time delay

$$\tau^{(2)} = \tau^{(2),\rm nr} + \partial_E \arg \mathcal{M}_{\rm R}(\omega_1), \tag{23}$$

where the first term is similar to the two-photon time delay in the nonresonant case [see Eq. (15)], and the last term is the time delay resulting from the resonance,

$$\tau^{(2),R} = \partial_E \arg \mathcal{M}_{\rm R}(\omega_1). \tag{24}$$

Note that with approximation (18), which is based on the *on-shell* approximation for the cc transition amplitude, we have lost reference to off-shell contributions to the time delay, which is not a severe limitation, since those contributions become negligible already a few electron volts above threshold. Also, near threshold, the Fano resonant model is not applicable any more, since in this region nonresonant continuum states vary rapidly with the electron energy. In the special case of near-threshold resonances (e.g., shape resonances in molecular ionization) the time delay arguably cannot be partitioned in the sum of contributions associated with separate mechanisms.

We focus now on this resonant factor, $\tau^{(2),R}$, which leads to the dominant contribution to the time delay in the vicinity of the resonance due to the strong variation of $\arg \mathcal{M}_{\rm R}(\omega_1)$ with E. We distinguish three possible scenarios corresponding to resonance characteristics. When the resonance dominates the radiative coupling from the ground state, i.e., $q \to \infty$, we can write

$$\tau^{(2),R} = \partial_E \arg \mathcal{M}_R(\omega_1) = \frac{\Gamma/2}{(E-\bar{E}_a)^2 + (\Gamma/2)^2} = \tau_{\rm w}^R. \tag{25}$$

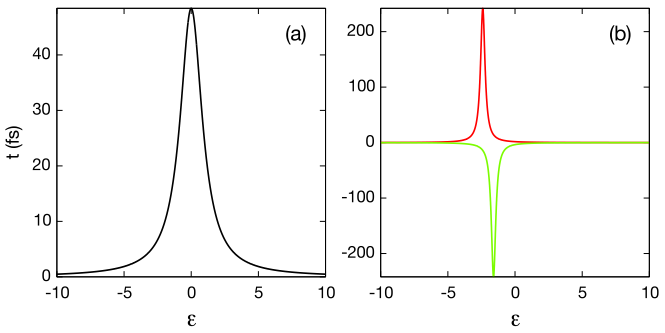

FIG. 2. Resonant photoemission time delay $\tau^{(2),R}$ as a function of the reduced energy ϵ [see Eq. (21)] (a) for $q \to \infty$ and $\Gamma = 0.001$ and (b) for $\Gamma = 0.001, q = 2$, and $\gamma = 0.2$ (red line) and $\gamma = -0.2$ (green line). The chosen values of the resonance parameters are typical of most atomic systems.

The above is the celebrated expression of the resonant Wigner time delay [19], corresponding to a Lorentzian function centered at $E = \bar{E}_a$, of width $\Gamma/2$ and maximum value $2/\Gamma$ [see Fig. 2(a)].

When the continuum in which the resonant is embedded is radiatively coupled to the ground state (q is finite), but the localized component $|a\rangle$ is not radiatively coupled to the final continuum ($\gamma = 0$), then the two-photon transition amplitude vanishes at $\epsilon = -q$ and the energy derivative of the two-photon transition amplitude gives rise to a singular term,

$$\begin{aligned}\tau^{(2),R} &= \partial_E\left[\arg(\epsilon+q) + \arg\left(\frac{1}{\epsilon+i}\right)\right] \\ &= \partial_E[\pi\{1-\theta(\epsilon+q)\}] + \tau_{\rm w}^R \\ &= -\frac{2\pi}{\Gamma}\delta(\epsilon+q) + \tau_{\rm w}^R. \end{aligned} \tag{26}$$

Can such a singular term be construed as a meaningful delay? As already mentioned, in this special case the derivation followed in Sec. II does not apply and must be modified. Let us go back to first principles and examine what the photoelectron wave packet looks like when generated by a one-photon transition from the ground state to the continuum in the vicinity of a resonance. This wave packet is given by

$$|\Psi(t)\rangle = \frac{\sqrt{2\pi}}{i}\int dE\, |\psi^-_{\alpha E}\rangle e^{-iEt}\langle\psi^-_{\alpha E}|\mathcal{O}|g\rangle\frac{\epsilon+q}{q+i}\tilde{\mathcal{E}}(E-E_g). \tag{27}$$

Let us consider a long Gaussian light pulse with spectrum centered on the anomalous delta. The Taylor expansion of the resonant one-photon transition amplitude about $\epsilon = -q$ is given by $(\epsilon+q)(\epsilon-i)^{-1} \sim -(\epsilon+q)(q+i)^{-1} \propto E - E_0$, where $E_0 = E_a - q\Gamma/2$. The wave packet generated by a Gaussian pulse of center $k_0 = \sqrt{2E_0}$, therefore, is proportional to

$$\Psi(r,t) \propto \int_{-\infty}^{\infty} e^{ikr} e^{-\alpha(k-k_0)^2}(k-k_0)e^{-ik^2t/2}dk, \tag{28}$$

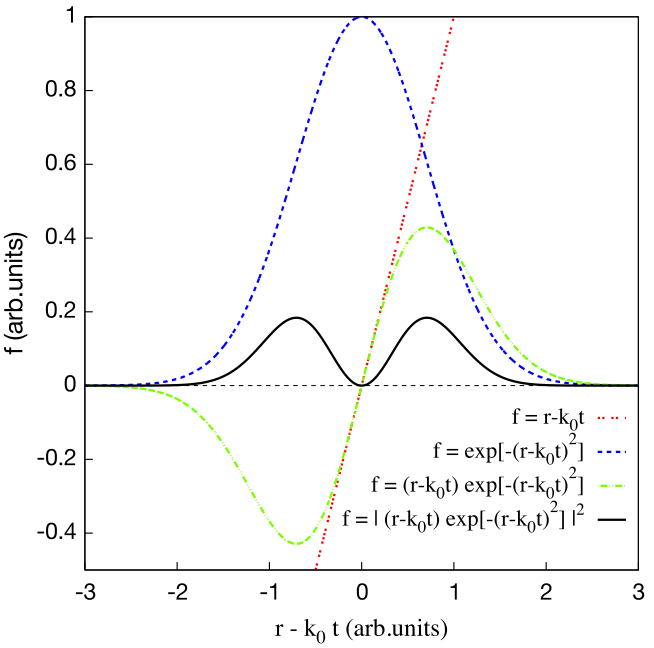

FIG. 3. Graph of the wave packet in Eq. (29) and of its different components. The product of the linear function $r - k_0 t$ (dotted red line) and the Gaussian function $e^{-\alpha(r-k_0t)^2}$ (dashed blue line) results in a wave packet (amplitude, long-dashed green line; intensity, solid black line) that is separated into two peaks.

where we have used $E - E_0 \simeq (k-k_0)k_0$. Integrating by parts, we obtain

$$\Psi(r,t) \propto (r-k_0t)\int_{-\infty}^{\infty} dk e^{-\alpha(k-k_0)^2}e^{ikr}e^{-ik^2t/2}. \tag{29}$$

The integral on the right-hand side of the latter expression is a wave packet with the Gaussian envelope centered at $r = k_0 t$. As a result, the wave packet $\Psi(r,t)$ vanishes right at its center and features two separated peaks (see Fig. 3), which remain separated at any time and whose both separation and widths increase linearly with time. In this case, therefore, the profile of the photoelectron wave packet does not reproduce that of the impinging light. Nevertheless, the definition we employed for time delay as the difference between the time of birth of a freely back propagated wave packet and the time of encounter with an external excitation pulse still applies. Indeed, even if it does not have a Gaussian spectrum, the split wave packet preserves its shape under the propagation of both the full and the reference Hamiltonian, and hence it is a perfectly valid asymptotic reference. When propagated back in time, the phase modulation of the wave-packet spectrum can still be compensated by an apparent time shift. Time delay, therefore, is well defined and it happens to be continuous across the $\epsilon = -q$ energy. Furthermore, as before, it coincides with the Wigner time delay, which is given by the argument of the resonant scattering matrix $S(E) = e^{2i\phi(E)}$, for $E = \bar{E}_a - q\Gamma/2$. This line of reasoning applies also in the presence of either a positive or a negative detuning from $\epsilon = -q$.

The situation changes if the resonance *is* radiatively coupled to the final continuum (γ finite), since the transition amplitude never vanishes completely. Yet, it can still attain

very small absolute values, resulting in a pronounced peak in the derivative of its argument (which becomes a delta in the limit of $\gamma \to 0$),

$$\tau^{(2),R} = \partial_E \left[\arg(\epsilon + \bar{q} + i\gamma) + \arg\left(\frac{1}{\epsilon_{E_1 a} + i}\right)\right] = -\frac{\Gamma}{2}\frac{\gamma}{(\gamma\,\Gamma/2)^2 + (E - \bar{E}_a + \bar{q}\Gamma/2)^2} + \tau^R_{\rm w}. \quad (30)$$

The radiative coupling of the localized component of the resonance with the final continuum "smoothens" the Dirac delta function in Eq. (26) into a Lorentzian profile of center $E = \bar{E}_a - \bar{q}\Gamma/2$, width $\gamma\Gamma/2$, and maximum value $2/(\gamma\Gamma)$ [see Fig. 2(b)]. Here, the derivation followed in Sec. II, and the interpretation of the energy derivative of the transition amplitude argument as a time delay, does apply. In particular, in contrast to the previous case, the new peak associated with the cross-section minimum corresponds to an observable time delay,

$$\tau^R_{\rm bc} = \frac{\gamma\Gamma/2}{(\gamma\,\Gamma/2)^2 + (E - \bar{E}_a + \bar{q}\Gamma/2)^2}. \quad (31)$$

We can understand why this is the case by regarding the photoionization as proceeding through two independent channels, with the last step involving a bound-continuum radiative transition. Near the minimum of the cross section, the first term gives rise to a strongly distorted wave packet, with a front and a back peak component in antiphase and with a vanishingly low amplitude, while the second term gives rise to a normal Gaussian wave packet that overlaps with the first. Considered separately, neither of these two components exhibit any anomalous delay. As can be explicitly shown analytically, it is their interplay that results in a measurably displaced wave packet.

The sign of γ depends on whether the second photon is absorbed or emitted. This means that the photoemission delay of the wave packet in the upper sideband will be either retarded or anticipated by $2\tau^R_{\rm bc}$ with respect to that in the lower sideband. Figure 4 shows how the resonant photoemission time delay varies depending on the values of q and γ. For $q = 0$, both the $\tau^R_{\rm w}$ and the $\tau^R_{\rm bc}$ contributions are centered at the same energy, so that the value of the total resonant time delay is either enhanced or canceled, depending on their relative phase. Indeed, for the case of $\gamma = 1$, the $\tau^R_{\rm bc}$ contribution coincides, with an opposite sign, with that of $\tau^R_{\rm w}$, so that there is no net resonant photoemission delay. When $q \neq 0$, the two contributions are centered at different values, giving rise to two separate Lorentzian peaks. We also note that the relative contribution of $\tau^R_{\rm w}$ and the $\tau^R_{\rm bc}$, hence the absolute value of $\tau^{(2)}$, strongly depends on γ. Since the latter depends on the probe-pulse frequency ω_2 [see Eq. (22)], one can exert some control on the resonant time delays by varying that frequency.

In the limit of $\gamma \to 0$, $\tau^R_{\rm bc}$ [Eq. (31)] tends to the same Dirac delta function as that appearing in Eq. (26),

$$\lim_{\gamma\to 0} \tau^R_{\rm bc} = \pi\,\delta(E - \bar{E}_a + q\Gamma/2). \quad (32)$$

In principle, therefore, it is possible to reach arbitrarily long time delays. However, diverging time delays are not observable in practice. On the one hand, as γ approaches 0, such long time delays concern, in the long-pulse limit, a progressively smaller number of photoelectrons until, for $\gamma = 0$, no photoelectrons are generated. On the other hand, for any finite bandwidth of the impinging pulse, as the limit $\gamma \to 0$ is approached, the photoelectron wave packet eventually loses its single-peaked shape to give rise to the double-peaked structure we have discussed above and which does not exhibit any diverging time delay. A similar behavior has been observed in molecular RABITT [20], where diverging delay at vanishing photoemission appears in the region between two vibrational states of an electronic resonance.

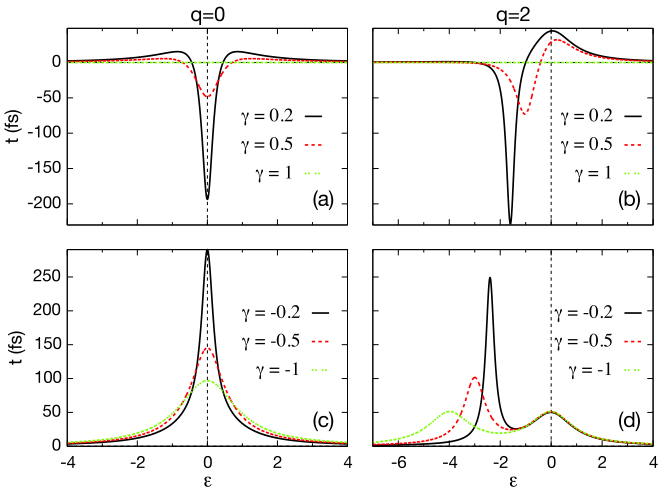

FIG. 4. Resonant photoemission time delay, $\tau^{(2),R}$, as a function of the reduced energy ϵ [see Eq. (21)] for various representative cases: (a) $q = 0$ and $\gamma > 0$, (b) $q = 2$ and $\gamma > 0$, (c) $q = 0$ and $\gamma < 0$, and (d) $q = 2$ and $\gamma < 0$. The chosen values of the resonance parameters are typical of most atomic systems.

IV. APPLICATION TO HELIUM RESONANCES

We have used the formalism described in the previous section to evaluate resonant two-photon ionization time delays in a helium atom excited from the ground state to the region below the $N = 2$ ionization threshold by means of the absorption of an XUV photon followed by the exchange of an IR photon. All the necessary coupling matrix elements and resonant parameters have been evaluated by using nearly exact solutions of the unperturbed time-independent Schrödinger equations $H_0'|a\rangle = E_a|a\rangle$ and $H_0'|\varphi^-_{\alpha E}\rangle = E|\varphi^-_{\alpha E}\rangle$ in the basis of B-spline basis functions (see the beginning of the previous section). The details of the method can be found elsewhere [21,22]. Figure 5 shows the results for the sp^+_2 and sp^+_3 resonances, for which $q = -2.77$ and -2.58 and $\gamma = -0.025$ and -0.114, respectively, for a probe frequency $\omega_2 = 0.057$ a.u. As expected, the variation of the time delays with the reduced energy follows patterns qualitatively similar to those described in the preceding section. Not surprisingly, for such small values of γ, peaks in the resonant delay arising from the $\tau^R_{\rm bc}$ contribution, which are centered at $\epsilon \sim -q$, are much narrower and higher than those arising from the $\tau^R_{\rm w}$ contribution, which appear at resonance, $\epsilon \sim 0$. While the latter do not exceed 100 fs, the former may reach values as large as 1 ps.

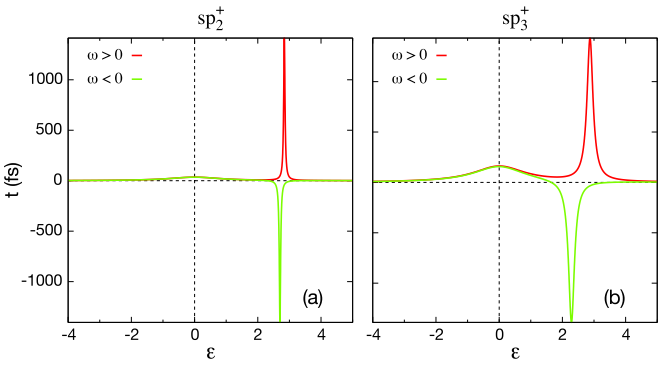

FIG. 5. Resonant time delay, $\tau^{(2),R}$, as a function of the reduced energy ϵ [see Eq. (21)], in the vicinity of the lowest two sp_n^+ resonances of He below the $N = 2$ threshold, for a probe frequency $\omega_2 = 0.057$ a.u. All resonant parameters have been obtained from *ab initio* calculations (see text for details).

The dynamics of the sp_2^+ resonance has been recently investigated [7] using the so-called rainbow-RABITT method. At variance with the standard RABITT, in this method the photoelectron spectrum is spectrally resolved *within* the harmonic and sideband widths, so that both the resonant harmonic and the associated sidebands exhibit Fano-type structures as a function of the photoelectron energy. As a result of this, a scan of the ω_{XUV} photon energy is not necessary, which greatly simplifies the analysis of the dynamics. The method was successfully used to reconstruct the electron wave packet created upon autoionization of the sp_2^+ resonance and, therefore, could be equally applied to extract the resonant time delays presented in Figure 5 without any major difficulty. Incidentally, the electron wave packet resulting from the present calculations is identical to that obtained in Ref. [7].

V. CONCLUSIONS

We have shown that, when intermediate resonances are populated in two-photon ionization processes, the usual relationships between one-photon induced ionization time delay, electron wave-packet group delay, Wigner time delay, and multiphoton time delay no longer hold. This is because the one-photon dipole coupling between the ground state and the continuum, D_{Eg}, vanishes at a specific energy, so that one-photon time delays cannot be defined as the energy derivative of the corresponding matrix element. Still one can define a resonant two-photon ionization delay $\tau^{(2)}$, which can be readily obtained from standard RABITT measurements, as the energy derivative of the corresponding two-photon matrix element $\partial_E \arg D_{Eg}^{(2)}$, which is a smooth function of the energy. This time delay does not, however, have any scattering counterpart, since $\tau^{(2)}$ can exhibit sharp peaks that can be much larger than the resonance lifetime or more negative than the lower bound imposed on scattering delays by causality.

The counterpart of this awkward behavior is that, as the relative strength of the nonresonant and the resonant two-photon absorption paths depends on the probe-pulse frequency ω_{IR} through the so-called γ parameter, one can easily control the two-photon ionization delay $\tau^{(2)}$ by just varying this frequency, thus allowing for an accurate determination of the amplitude and phase of the electron wave packet generated in single-photon ionization, e.g., as in Ref. [23].

Finally, it is interesting to point out that a similar causality problem in the measured delays has also been reported in strong-field ionization: experiments performed by using the attoclock technique have shown that tunnel ionization can be much faster than the measured delay. This is again the consequence of a propagation-induced chirp of the electron wave packet in combination with an energy-dependent transmission probability, which shifts the center of the wave packet in time without any direct physically meaningful connection to the semiclassical motion of the electron [24].

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