

Spectral Line Shape Variations in Time-Resolved Photoemission from a Solid

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Laser assisted photoemission by a subfemtosecond ultraviolet pulse is studied by solving the time-dependent Schrödinger equation for a one-dimensional model crystal. Without the laser field, the shape and the energy location of the spectrum are determined by the energy dependence of the photoemission cross section. In the presence of the laser field, the time growth of the population of the final state is predicted to cause extremely sharp variations of spectral width as a function of release time. This can help enhance time resolution of the measurements. A simple phenomenological model to describe the line shape is proposed.

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With the rapid development of attosecond metrology [1], the time-resolved photoelectron spectroscopy has been becoming a powerful tool to study the dynamics of electronic excitations. A subfemtosecond pulse of extreme ultraviolet radiation (XUV) creates a photoelectron wave packet with a temporal spread within a fraction of the oscillation period T_L of the laser light. The wave packet is accelerated or decelerated by the laser field, and its energy spectrum is up- or down-shifted [2]. The dependence of the kinetic energy of the detected photoelectrons on the release time allows us to record the time-dependent spectra with a resolution around 100 as [3].

In studying ultrafast processes in an electronic system it is important to know as exactly as possible the timing of the XUV pulse relative to the laser pulse. Thus, a detailed understanding of how the spectrum of the photoelectron wave packet depends upon its moment of release is required. Or inversely, how the properties of the system affect the parameters relevant for the cross correlation between the two pulses. For pulses much shorter than T_L the spectrum formation is well understood [3–5]. In this work we concentrate on XUV pulses of duration D_X comparable to the laser light period T_L , in which case the photoionization cannot be divided into two sequential steps: creation of the photoelectron wave packet followed by acceleration by the laser field—the two processes overlap in time. At the same time the duration of the laser pulse D_L is too short to cause quantum transitions with the laser photon energy $\hbar\omega_L$ (sidebands). The problem of electric field changing during the excitation is especially important in application to solid state spectroscopy where, owing to the field inhomogeneity at the surface, the field felt by the electron depends also on its equation of motion, i.e., on the location of the atom it is emitted from and on the group velocity.

We consider a photoemission setup typical of angle-resolved measurements of crystal surfaces. The light is assumed linearly polarized with electric field parallel to the surface normal, $\mathbf{E} \parallel \mathbf{z}$, so the system is translationally

invariant along the surface. Then the electrons observed at a given angle correspond to a certain Bloch vector $\mathbf{k}_{\parallel}$ parallel to the surface. We consider electrons emitted normal to the surface, which are accelerated or decelerated depending on the sign of momentum transfer $\Delta p(t) = (e/c)A(t)$. As a result, the spectrum shifts as a whole on the kinetic energy scale and distorts. One reason for the distortion is a finite spectral width Γ_{PES} (PES, photoelectron spectrum): electrons with different initial momenta p acquire different energies, so the spectrum broadens when accelerated and narrows when decelerated. Another source of distortion is the finite duration D_X of the XUV pulse: electrons created at different moments t are differently accelerated according to the current value of the momentum transfer $\Delta p(t)$ [4]. The latter effect becomes large already at durations D_X around the laser light quarter

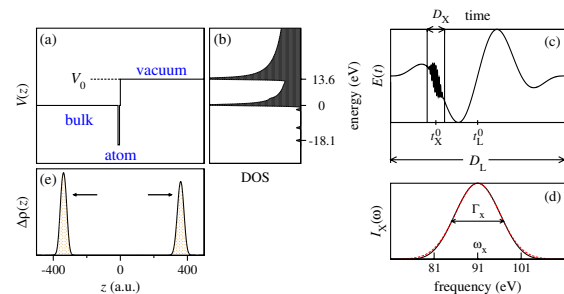


FIG. 1 (color online). (a) Potential profile $V(z)$ of the model 1D system. The atom studied is given by a 6 a.u. wide potential well centered at $z = -8$ a.u. relative to the surface barrier. (b) Density of states of the system convoluted with a Lorentzian of 0.5 eV FWHM. (c) Superposition of the electric field of the XUV pulse of duration D_X and the laser pulse of duration D_L . (d) Light intensity distribution in the XUV pulse (solid line) compared to a Gaussian distribution with the same FWHM (dashed line). (e) Perturbed electron density $\Delta\rho$ at $t = 4.7$ fs after the excitation by a 400 as XUV pulse of $\omega = 81$ eV comprises two wave packets traveling in opposite directions and differently accelerated by the laser field.

period, and its value cannot be estimated from qualitative considerations because the laser electric field cannot be assumed constant.

We study angle-resolved photoelectron (PE) spectra of a crystal within a numerical quantum mechanical approach, which takes into account both distorting effects on the same footing. If the electron scattering along the surface can be neglected the problem for a given value of the photoelectron momentum $\mathbf{k}_{\parallel}$ reduces to a one-dimensional problem. The quasi-1D approach is widely used in surface science and is known to catch all essential features of the photoemission process [6]. The unperturbed Hamiltonian is then $\hat{H} = -\Delta + V(z)$. (We use the units $\hbar = 1$, $m = 1/2$.) The model crystal potential $V(z)$ is chosen for simplicity to be piecewise constant as shown in Fig. 1(a). For this system the time-dependent Schrödinger equation can be solved numerically with any desired accuracy. The system in Fig. 1(a) is enclosed in a box, and all calculations are performed in matrix form in terms of exact eigenfunctions (discrete spectrum) of $\hat{H}$.

In dipole approximation the perturbed Hamiltonian is $\hat{H} + zeE(t)$ (the field inhomogeneity at the surface is neglected). The time-dependent electric field $E(t)$ is a superposition of an XUV and a laser pulse with frequencies ω_X and ω_L , respectively, see Fig. 1(c):

$$E(t) = E_X(t - t_X^0) \cos[\omega_X(t - t_X^0)] \\ + E_L(t - t_L^0) \sin[\omega_L(t - t_L^0)].$$

Both envelopes have the shape $E_P(t) = E_P^M \cos^2(\pi t/D_P)$ in the intervals $t - t_P^0 \in [-D_P/2, D_P/2]$ ($P = X, L$) and vanish outside, see Fig. 1(c). (Note that D_P are twice the

FWHM duration often used in the literature.) The intensity spectrum $I_X(\omega)$ of such XUV pulse is close to Gaussian [Fig. 1(d)]. We consider a laser pulse of $\omega = 1.65$ eV ($T_L = 2.5$ fs) and duration $D_L = 5$ fs with the amplitude $E_L^0 = 6 \times 10^7$ V/cm typical of attosecond spectroscopy [7].

We shall consider photoemission from a spatially localized atomiclike state. In a crystal such (semi-)core states form energy bands much narrower than the spectral FWHM Γ_X of the XUV pulse and can be modeled by a single atom. (Also the intrinsic linewidth of the hole is much smaller than Γ_X .) After the XUV excitation the perturbed wave function splits into two wave packets traveling in opposite directions, Fig. 1(e). The packet traveling to the right is cut out and reexpanded in terms of the eigenfunctions of the system. This gives the spectrum recorded by the detector. Let us first consider the case without the laser field. Figure 2(a) shows PES of the lowest state of the model atom [$\epsilon_i = -18.1$ eV, see Fig. 1(b)] for photon energies 70 and 91 eV for three pulse durations. With decreasing duration, the maximum $\epsilon_{\text{PES}}^{\text{max}}$ and the spectral center of gravity gradually move away from $\omega_X + \epsilon_i$, see Fig. 2(c) for $\omega_X = 91$ eV, and the photoelectron spectrum J_{PES} narrows compared to the XUV radiation spectrum I_X , see Fig. 2(d) and the inset.

This is caused by a strong dependence of the PE cross section $S(\omega)$ on the photon energy [Fig. 2(b)]: when $S(\omega)$ grows with ω (as at $\omega = 70$ eV) the spectrum shifts to higher energies and vice versa (91 eV). For atomiclike states such strong variations of cross section are encountered in the vicinity of Cooper minima [5,8]. Rapid changes of $S(\omega)$ for surface states are also well documented experimentally [9,10] and theoretically explained [11]. Figure 2(b) compares the $S(\omega)$ curve in our calculation with the measurement for the surface state on the (100) surface of aluminum [9]. The variations of $S(\omega)$ in our model are seen to be of a realistic order of magnitude, and for short pulses they lead to a shift of the spectral weight by several electron volts [Fig. 2(c)]. Thus, in analyzing a photoelectron spectrum produced by an ultrashort XUV pulse the energy variation of the photoemission cross section must be taken into account.

An important observation is that the spectra $J_{\text{PES}}(\omega)$ calculated from the time-dependent Schrödinger equation practically exactly coincide with the product $I_X(\omega)S(\omega)$. In agreement with previous experience [5], this simple relation is found to hold down to very small durations D_X and up to XUV pulse intensities exceeding typical laser intensities. This means that the limit $t \rightarrow \infty$ (Fermi golden rule for a monochromatic radiation) is achieved already in a subfemtosecond range. The function $S(\omega)$ is a linear response to a single-frequency perturbation and is fully determined by the stationary states of the system. For real solids it can be calculated *ab initio* with a very high accuracy [12] within the one-step theory of photoemission [6,13].

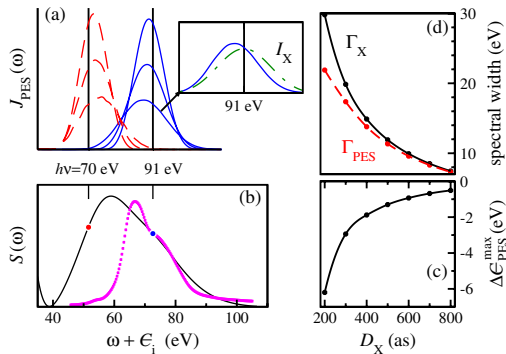


FIG. 2 (color online). (a) Excitation spectra of the lowest state of the model atom for $\omega_X = 70$ (dashed lines) and 91 eV (solid lines) for $D_X = 300, 400$, and 500 as. The inset compares the PE spectrum J_{PES} with the XUV radiation spectrum I_X (dot-dashed line) for $D_X = 300$ as. (b) Photoemission cross section of this state versus final state energy (solid line) compared to the cross section of the Al(100) surface state from Ref. [9] (dots). (c) Dependence of the spectral maximum energy location $\Delta \epsilon_{\text{PES}}^{\text{max}} = \epsilon_{\text{PES}}^{\text{max}} - \epsilon_i - \omega_X$ on the duration D_X for $\omega_X = 91$ eV. (d) Spectral FWHM of the XUV pulse Γ_X (solid line) and of the PE spectrum Γ_{PES} (dashed line) versus D_X .

In the following we generalize the relation $J_{\text{PES}}(\omega) \sim I_X(\omega)S(\omega)$ to the case of a laser assisted photoemission. Photoelectron spectra in the presence of the laser field [Fig. 1(c)] are shown in Fig. 3 for two pulse durations and for different values of the release time $t_X^0 - t_L^0$. Apart from being shifted as a whole, the spectrum broadens, and for $D_X = 2$ fs it strongly distorts already at small values of momentum transfer at the pulse maximum (curves 4 and 9). For $D_X = 1$ fs the broadening due to the temporal spread of the XUV pulse (curve 4) exceeds that due to its energy spread (curve 7). Depending on the release time the longer pulse may produce a narrower spectrum (curves 1–4, 9, 10) or a broader one (5, 8). At the same time, the energy shift of the spectrum is found rather stable to the pulse duration in a wide range of D_X . The data on the dependence of the PES linewidth on the release time for several pulse durations are summarized in Fig. 4. Already at $D_X = 800$ as the increase of line width at the point of strong electric field is much sharper than one would expect by extrapolating the limit $D_X \ll T_L$, in which the time

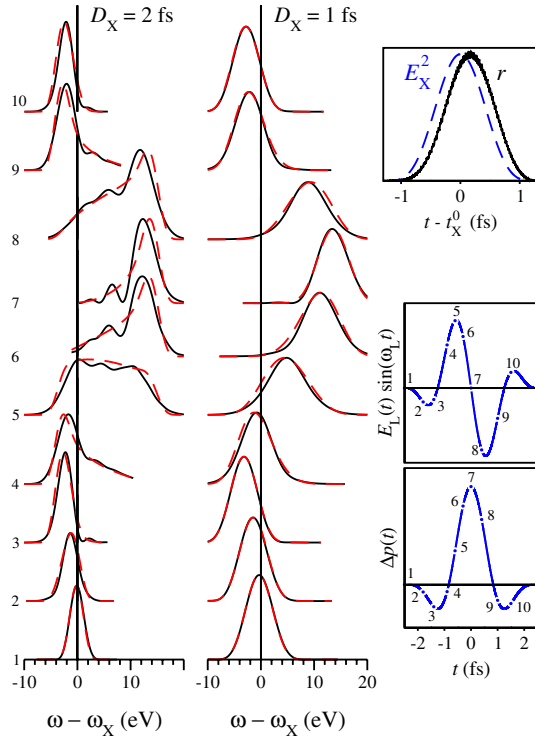


FIG. 3 (color online). Comparison of PE spectra calculated by solving the time-dependent Schrödinger equation (solid lines) with the spectra derived from the phenomenological model (dashed lines). The lower insets show the time dependence of momentum transfer $\Delta p(t)$ and of the laser electric field $E_L(t) \times \sin(\omega_L t)$. Numbers mark the release points t_X^0 of the corresponding spectra. The upper inset compares the intensity envelope of the XUV field $E_X^2(t - t_X^0)$ (dashed line) with the transition rate $r(t - t_X^0)$ (solid line) that enters Eq. (1) averaged over time intervals of 100 as and over an energy range of several electron volts around the energy $\epsilon_i + \omega$.

spread contribution to Γ_{PES} is proportional to the strength of the laser field [4].

We now develop a phenomenological model to describe the dependence of the line shape on the XUV pulse duration and the release time. Let $r(p, t)$ be the transition rate from the initial state to the final state of momentum p in the absence of the laser field. Following the classical approach of Ref. [3], let us write the PE spectrum (in terms of final momentum p) after both pulses are off as

$$J_{\text{PES}}(p) = \int_{t_X^0 - (1/2)D_X}^{t_X^0 + (1/2)D_X} r[p - \Delta p(t), t] dt. \quad (1)$$

This means that the electron can get into the state p by being created at a moment t in the state $p - \Delta p(t)$ or by being created with, say, a lower energy but at a time when the momentum transfer is larger. These processes are summed up incoherently. Note that for a sufficiently long pulse the time integration is nontrivial not only in the case of a frequency sweep (considered in Ref. [3]) but simply because the pulse is still broad enough, and electrons are being created in *all* states during the pulse, but with different rate. For the resonant single-frequency transition ($p^2 + V_0 = \epsilon_i + \omega$) of a constant intensity $I_X(\omega)$ for $t \rightarrow \infty$ the

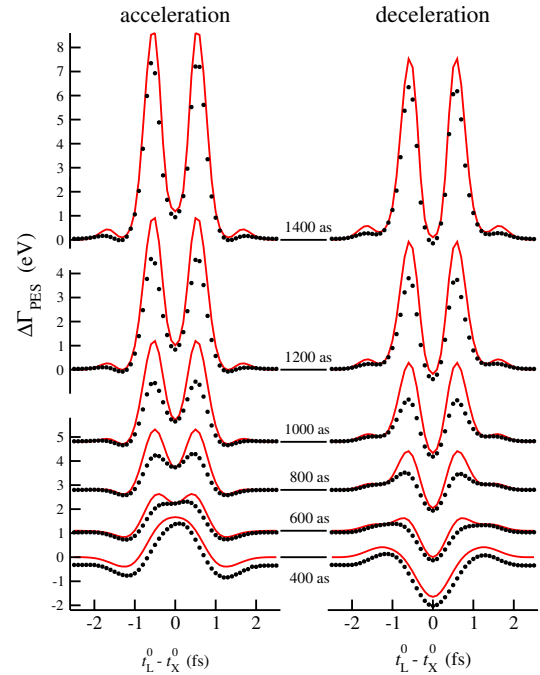


FIG. 4 (color online). Release time dependence of the spectral width Γ_{PES} relative to the spectral width Γ_{PES}^0 of the $I_X(\omega)S(\omega)$ curve ($\Delta\Gamma_{\text{PES}} = \Gamma_{\text{PES}} - \Gamma_{\text{PES}}^0$) for XUV pulse durations from 400 to 1400 as. Circles show the exact quantum mechanical result. Lines are the prediction by the phenomenological formula (2). Left column corresponds to the envelope $E_L(t)$ in Fig. 3, and right column to the opposite phase, $-E_L(t)$. Curves for different D_X are shifted but not stretched; zeroes for the curves are shown by the horizontal bars between the panels. The left-hand $\Delta\Gamma$ scales are shown for $D_X = 400, 1200$, and 1400 as.

rate is constant in time: $r(p, t) = S(\omega)I_X(\omega)$. [V_0 is the surface barrier, see Fig. 1(a).] It turns out that also during the pulse the transition rate $r(p, t)$ (averaged over time intervals of about 100 as) follows rather closely the temporal intensity envelope $E_X^2(t)$; we compare the two curves in the upper inset of Fig. 3. We now make a heuristic assumption that the dependence of the transition rate on the XUV intensity can be used locally both in the time and in the frequency domain. This leads to the phenomenological expression for the photoelectron spectrum:

$$J_{\text{PES}}(p) = \int_{t_X^0 - (1/2)D_X}^{t_X^0 + (1/2)D_X} \left[\frac{E_X(t)}{E_X^M} \right]^2 I_X[\Omega(p, t)] S[\Omega(p, t)] dt, \quad (2)$$

with $\Omega(t)$ being determined by the momentum transfer at the moment t : $\Omega(p, t) = [p - \Delta p(t)]^2 + V_0 - \epsilon_i$. For an extremely short pulse, $\Delta p(t)$ can be considered constant, and Eq. (2) describes a shift of the spectrum as a whole. In the absence of the laser field it is $\Omega(p, t) = \omega$, and we recover the earlier verified result $J_{\text{PES}}(\omega) \sim I_X(\omega)S(\omega)$.

In Fig. 3 we compare the photoelectron spectra calculated by Eq. (2) (dashed lines) with the exact result. The phenomenological formula is seen to describe the spectral shape with high quality even when it is strongly non-Gaussian (curves 4–9 for $D_X = 2$ fs). Thus, not only a wave packet produced by a short pulse is accelerated as a classical particle, but also temporally distributed portions of an extended packet can, to a good approximation, be considered in the same way. Of course, quantum effects are not entirely negligible, and they cause noticeable wiggles in the spectrum (e.g., curves 6 and 7).

The observed strong sensitivity of photoelectron spectra produced by long XUV pulses to the release time suggests that the pulse can be rather accurately located in time even if its duration is comparable with the laser light period (provided that the laser pulse is short enough not to cause multiphoton emission). The line shape parameters provide additional information on the release time when it cannot be unambiguously judged by the energy location of the spectral maximum, compare curves 3 and 4 or 6 and 7 in Fig. 3.

Dramatic changes of line shape are observed in the present calculation for pulses of FWHM duration above 500 as. Today, much shorter pulses of about 100 as can be achieved. However, for a realistic solid, where the electric field rapidly grows at the surface, similar effects cannot be completely avoided for arbitrarily short pulses. First, the XUV pulse samples a surface region of 10–20 a.u., and electrons excited at different atoms reach vacuum (where

the electric field is strong) with a time spread of some 200 as. Second, a short pulse creates photoelectrons with a large spread of group velocities, which with $\Gamma_X = 20$ eV contributes more than 100 as to the effective time spread of the wave packet. These effects can be described within the present phenomenological model by incorporating into Eq. (2) the equation of motion of the electron as a classical particle.

To summarize, we have studied the dependence of photoelectron spectra on the release time. For short pulses the main factor that affects the line shape is the energy dependence of photoemission cross section, whereas the effect of the laser field reduces to a trivial rescaling of the energy axis. For longer pulses the line shape depends on the time growth of the population of the final states. When the momentum transfer rapidly changes during the excitation the line shape strongly deviates from the Gaussian. A phenomenological model to describe the behavior has been developed and verified. The properties of the system enter via the energy dependent cross section, and the XUV pulse enters twice: as a time intensity envelope and as a Fourier transform, which allows us to reproduce the spectral shape variations with a highly satisfactory quality over a wide range of pulse durations.

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