Extreme Ultrafast Dynamics of Quasiparticles Excited in Surface Electronic Bands

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We develop a many-body description of the nonadiabatic dynamics of quasiparticles in surface bands valid on an extremely ultrashort time scale by combining the formalism for the calculation of quasiparticle survival probabilities with the self-consistent treatment of the electronic response of the system. Applying this approach to the benchmark Cu(111) surface, we assess the behavior and intervals of preasymptotic electron and hole dynamics in surface bands and locate the transition to the asymptotic regime of the exponential quasiparticle decay characterized by the corrected Fermi golden rule-type of transition rate. The general validity of these findings enables distinguishing the various regimes of ultrafast electron dynamics that may be revealed in time resolved experiments.

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The development of time resolved electron spectroscopies has enabled measurements of the surface electronic processes in the real time domain [1–5]. Such experiments provide direct insight into the temporal evolution of the studied systems from which information on the various relaxation processes that govern the dynamics of excited quasiparticles can be deduced. Experiments in which the time scales of relaxation are much shorter than the duration of measurement provide information on the asymptotic steady state dynamics of the excited system in its passage towards thermodynamic equilibrium. Descriptions of these processes are commonly given in terms of the rate constants that characterize asymptotic relaxation of quasiparticle states.

Methods for probing the dynamics of electronic states in confined systems are usually based on electron excitation from or injection into the system, either in the one-step processes, as in direct photoemission (PE) or inverse photoemission (IPE) spectroscopy, or in the two-step laser pump-probe induced transitions, as in two-photon photoemission (2PPE) experiments. Common to all these experiments is a sudden promotion of electrons (holes) in the initially unoccupied (occupied) states after which their promotion into states within unoccupied (occupied) bands is recovered in the same state at.

\[
L_{K,n}(t) = |G(K, n, t)|^2, \tag{1}
\]
where \(G(K, n, t)\) is the diagonal single electron (hole) propagator or Green’s function giving the probability amplitude that a quasiparticle prepared at \(t = 0\) in the state \([K, n]\) and subjected to a perturbation arising from the coupling to charge density excitations in the system be recovered in the same state at \(t > 0\). The thus obtained quasiparticle Green’s functions are prerequisites for the calculations of PE, IPE, and 2PPE spectra and rates [9–13]. In the case of electron injection into an empty (occupied) band, the survival probability is obtained as:

\[
G(K, n, t) = G_0(K, n, t) \exp[C(K, n, t)], \tag{2}
\]
where \(G_0(\mathbf{K}, n, t) = -i\exp(-i\epsilon_{\mathbf{K}, n} t)\theta(t)\) is the unperturbed propagator of a particle of effective mass \(m^*_n\), charge \(e\), and band energy \(\epsilon_{\mathbf{K}, n} = E_n + \mathbf{K}^2/2m^*_n\), where \(E_n\) denotes the energy of the bottom of the \(n\)th surface band. \(C(\mathbf{K}, n, t)\) is the sum of all even order cumulants generated by the particle coupling to linear electronic response of the system [16]. For the coupling strengths typical of quasiparticles in Q2D electronic bands on metal surfaces, \(C(\mathbf{K}, n, t)\) is represented with high accuracy by the second order cumulant [16] whose real and imaginary parts at zero substrate temperature assume the form:

\[
\text{Re} \, C_2(\mathbf{K}, n, t) = -\sum_{\mathbf{Q}, n'} |V_\mathbf{Q}|^2 \int_0^\infty d\omega S_{\mathbf{n}', n}(\mathbf{Q}, \omega) \times \left(1 - \cos\left[\frac{\epsilon_{\mathbf{K}, n} - \epsilon_{\mathbf{K}+\mathbf{Q}, n'} - \omega}{\epsilon_{\mathbf{K}, n} - \epsilon_{\mathbf{K}+\mathbf{Q}, n'} - \omega} \right]\right),
\]

\[\text{Im} \, C_2(\mathbf{K}, n, t) = -\sum_{\mathbf{Q}, n'} |V_\mathbf{Q}|^2 \int_0^\infty d\omega S_{\mathbf{n}', n}(\mathbf{Q}, \omega) \times \left(1 - \sin\left[\frac{\epsilon_{\mathbf{K}, n} - \epsilon_{\mathbf{K}+\mathbf{Q}, n'} - \omega}{\epsilon_{\mathbf{K}, n} - \epsilon_{\mathbf{K}+\mathbf{Q}, n'} - \omega} \right]\right).
\]

The index \(n'\) denotes unoccupied parts of the bands allowed in intra- and interband electron transitions so that \(\epsilon_{\mathbf{K}+\mathbf{Q}, n'} \geq E_F\). \(V_\mathbf{Q} = 2\pi e/\mathbf{Q}\), and the spectrum of band-projected substrate electronic excitations is given by

\[
S_{\mathbf{n}', n}(\mathbf{Q}, \omega) = \int dz_1 \int dz_2 f_{\mathbf{n}', n}(z_1, \mathbf{Q}) \times \left[-\frac{1}{\pi} \text{Im} \chi(z_1, z_2, \mathbf{Q}, \omega)\right] f_{\mathbf{n}', n}(z_2, \mathbf{Q}).
\]

Here \(\chi(z_1, z_2, \mathbf{Q}, \omega)\) is the standard electron density response function for a system translationally invariant along the surface [5], and the oscillator strengths

\[
f_{\mathbf{n}', n}(\mathbf{Q}, z_i) = \int dz \phi_{\mathbf{n}', n}(z)e^{-Q|z-z_i|}\phi_{\mathbf{n}, n}(z)
\]

are calculated with the normal-to-the-surface component \(\phi_{\mathbf{n}, n}(z)\) of the \(n\)th band electron wave functions. Reformulation of Eqs. (3) and (4) to describe hole dynamics in occupied Q2D surface bands is straightforward [16].

Quite generally, \(\text{Re} \, C_2(\mathbf{K}, n, t)\) describes the decay and \(\text{Im} \, C_2(\mathbf{K}, n, t)\) the energy relaxation and dephasing of the initial quasiparticle state \((\mathbf{K}, n)\). The evolution of \(\text{Re} \, C_2(\mathbf{K}, n, t)\) in the ultrashort early interval set by the Heisenberg uncertainty follows the universal “Zeno behavior” \(-t^2/\tau^2 + O(t^4)\) [17], which gives rise to Gaussian initial decoherence of \(L_{\mathbf{K}, n}(t)\). In the same temporal interval, the energy relaxation and dephasing processes described by Eq. (4) cancel each other, so as that \(\text{Im} \, C_2(\mathbf{K}, n, t \to 0) = O(t^3)\). By contrast, in the opposite limit of long times, several scenarios concerning the temporal dependence of \(C_2(\mathbf{K}, n, t)\) are possible, depending on the variation of the excitation spectrum \(S_{\mathbf{n}', n}(\mathbf{Q}, \omega)\) across the resonant limit \(\epsilon_{\mathbf{K}, n} = \epsilon_{\mathbf{K}+\mathbf{Q}, n'} + \omega\) of the time-dependent factor in the integrands in Eqs. (3) and (4). A nonvanishing and smoothly varying \(S_{\mathbf{n}', n}(\mathbf{Q}, \omega)\) across the resonant limit gives rise to asymptotic behavior

\[
C_2(\mathbf{K}, n, t \to \infty) \to -(\Gamma_{\mathbf{K}, n}/2 + i\Lambda_{\mathbf{K}, n})t - w_{\mathbf{K}, n}.
\]

Here the asymptotic decay rate or inverse lifetime

\[
\Gamma_{\mathbf{K}, n} = 2\pi \sum_{\mathbf{Q}, n'} |V_\mathbf{Q}|^2 \int_0^\infty d\omega S_{\mathbf{n}', n}(\mathbf{Q}, \omega) \delta(\epsilon_{\mathbf{K}, n} - \epsilon_{\mathbf{K}+\mathbf{Q}, n'} - \omega) > 0,
\]

(asympotic) time scales requires specification of the excitation spectrum (5).

In this Letter, we illustrate different stages of ultrafast quasiparticle dynamics in surface bands for the benchmark surface Cu(111) with one electron introduced in the first image state (IS) band or one hole created in the surface state (SS) band, for which the asymptotic excited state energies and lifetimes are available from experimental and theoretical studies [1–5]. We start from the self-consistent RPA response function \(\chi(z_1, z_2, \mathbf{Q}, \omega)\) calculated for a \(N\)-layer slab \((N = 31)\) that models the Cu(111) surface by using the effective potential [20] and the method described in Ref. [21]. This model enables a systematic treatment of intra- and interband transitions on equivalent footing. The oscillator strengths (6) were calculated using linear combinations of pairs of symmetric and antisymmetric electron wave functions from the same slab calculation. From this, we computed the excitation spectrum (5) on a \((\mathbf{Q}, \omega)\) grid for combinations of indices.
\(0 \leq n, n' \leq n_{\text{max}}\) that cover the relevant intra- and interband transitions. Details of this calculation and the results for electron dynamics on other surfaces will be presented elsewhere.

Figure 1 shows the computed intensity of the IS-projected intraband component \((n' = n = IS)\) of the excitation spectrum \(S_{n',n}(Q, \omega)\) over the phase space of excitation energies \(\omega\) and wave vectors \(Q\) relevant in the calculations of \(L_{K,n}(t)\). Dominant contributions to the intensity come from the surface plasmon which disperses along a parabolic curve starting at the point \(Q = 0\) and \(\omega = 7.6\ \text{eV}\), the bulk plasmon whose dispersion curve starts at \(\omega = 12.6\ \text{eV}\), and the electron-hole (-h) quasiparticle. However, it does not contribute to its exponential decay, because for \(K = 0\) only the interband transitions \(n' < IS\) can give a contribution to \(\Gamma_{K,IS}\) as is evident from the argument of the \(\delta\) function on the RHS of Eq. (8). For \(K > 0\), the singularity moves away and its weight is redistributed over a larger segment of the \((Q, \omega)\)-phase space [22]. This effective increase of the phase space for quasiparticle scattering by substrate excitations gives rise to the onset of intraband contributions and, thereby, to enhancement of the total decay rate \(\Gamma_{K,IS}\). On the other hand, the largest phase space for intraband hole decay is for initial states at the band bottom \((K = 0)\) because, in inelastic transitions, the holes decay only towards the Fermi level.

Temporal behavior of the survival probability \((\Gamma)\) can now be calculated for initial values of \(n\) and \(K\) using the above obtained results. Figure 3 shows \(L_{K,IS}(t)\) for an electron created in the IS band on Cu(111) surface with initial wave vectors \(K = 0.01\) and \(K = 0.05\ \text{a.u.}\) The very early Gaussian decay is superseded by a superposition of oscillations arising from nonadiabatic (off-resonant) excitations of surface plasmons in the slab and a gradual buildup of the \(w_{K,n}\)-corrected FGR decay (7) arising from resonant excitation of \(-h\) pairs. Because of the off-the-energy-shell character of plasmon excitations, their amplitude diminishes as \(t \rightarrow \infty\). We find that for \(K = 0.01\) interband IS \(\rightarrow\) SS transitions contribute about 39% to the total decay rate \(\Gamma_{K,IS}\), and the remaining 61% arise from interband transitions into bulk bands, in agreement with earlier calculations [5]. The contribution from interband IS \(\rightarrow\) IS electron transitions to the resonant decay rate \(\Gamma_{K,IS}\) is insignificant at this value of \(K\), as only very small initial kinetic energy is available for excitation of other electrons in the system. On the other hand, their role is dominant in the off-resonant excitation of surface plasmons.

**FIG. 1** (color). Intraband image potential state-projected component \((n' = n = IS)\) of the slab electronic density excitation spectrum \(S_{n',n}(Q, \omega)\) [Eq. (5)] shown as a function of energy \(\omega\) and momentum \(Q\) of the excitations.

**FIG. 2** (color). Intensity plot of the unbounded component \(\tilde{W}_{n',n}(K, Q, \omega)\) of the integrand in (3) showing the regions in \((Q, \omega)\)-phase space of substrate excitations that give major contributions to intraband-induced decoherence of an image potential state electron \((n = n' = IS)\) with initial \(K = 0\).
mons and the buildup of nonadiabatic correction $w_{K,SS} = 0.15$. Qualitatively similar trends are retained for initial electron wave vector $K = 0.05$ a.u.

Figure 4 shows various contributions to the survival probability (1) for a hole created in the SS band on Cu(111) with initial state wave vector $K = 0.01$ and $K = 0.05$ a.u. Here, in contrast to the case of IS-electron decay, the intraband SS $\rightarrow$ SS transitions for $K = 0.01$ a.u. contribute the major part ($\sim 70\%$) to the total decay rate $\Gamma_{K,SS}$, again in accord with earlier calculations [5]. They also give a dominant contribution ($\sim 60\%$) to the short time behavior of $L_{K,SS}(t)$ reflected in the magnitude of the total non-adiabatic correction $w_{K,SS} = 0.21$. A similar situation holds for $K = 0.05$ a.u.

In conclusion, the results of calculations of quasiparticle survival probabilities shown in Figs. 3 and 4 enable the identification of three distinct regimes of ultrafast quasiparticle dynamics in IS and SS bands on Cu(111). The early Zeno regime ($0 < t < 1$ fs) is followed by preasymptotic non-Markovian evolution with superimposed off-resonant excitation of surface plasmons and resonant excitation of $e$-$h$ pairs. This structure persists up to $t \sim 10$ fs, and only past that time do the off-resonant plasmon excitations die out, and the steady state asymptotic evolution governed by the corrected FGR decay (7) takes over. However, even long past that time, the bare FGR decay $\exp(-\Gamma_{K,SS}t)$ is not yet approached, signifying that extreme ultrafast dynamics of quasiparticles promoted in surface bands requires preasymptotic description of relaxation and decay processes. Hence, further progress in theoretical interpretations of the corresponding PE, IPE, and 2PPE spectra should be sought in terms of the above elucidated quasiparticle evolution rather than its approximations based on asymptotic rate constants.

[17] See EPAPS Document No. E-PRLTAO-97-049635 for an animated illustration of the redistribution of the quantity shown in Fig. 2 with the variation of the IS-electron incident wave vector $K$ in the interval $0 < K < 1.9$ a.u. For more information on EPAPS, see http://www.aip.org/pubservers/epaps.html.