Hole Dynamics in Noble Metals

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Hole dynamics in noble metals (Cu and Au) is investigated by means of first-principles many-body calculations. While holes in a free-electron gas are known to live shorter than electrons with the same excitation energy, our results indicate that d holes in noble metals exhibit longer inelastic lifetimes than excited sp electrons, in agreement with experiment. The density of states available for d-hole decay is larger than that for the decay of excited electrons; however, the small overlap between d and sp states below the Fermi level increases the d-hole lifetime. The impact of d-hole dynamics on electron-hole correlation effects is also addressed.

Detailed and quantitative understanding of hot-electron and photohole dynamics is the prerequisite for any tailoring of technological processes in solid-state physics and surface chemistry, which are governed by charge transfer and electronic excitations [1–4]. In particular, the quasiparticle lifetime, i.e., the time a quasiparticle propagates without losing its phase memory, represents a basic quantity in the analysis of these processes. Experimentally, angle-resolved photoemission (PE) spectroscopy provides direct information on hole lifetimes [5–8]. A new path for the study of both electron and hole (and spin) dynamics in the time domain was opened by the advent of the time-resolved two-photon photoemission (TR-TPPE) technique [9,10]. In these "pump-probe" experiments, the emitted photoelectron is measured both with energy and momentum resolution; electron and hole lifetimes are then measured at well-defined **k**-space points, by combining the band mapping capabilities of photoemission with the time resolution of nonlinear optical spectroscopy [11].

The theoretical framework to investigate the quasiparticle lifetime has been based for many years on the free-electron gas (FEG) model of Fermi liquids [12], characterized by the electron-density parameter r_s [13]. In this simple model and for either electrons or holes with energy E very near the Fermi level ($E \sim E_F$), the inelastic lifetime is found to be, in the high-density limit ($r_s \ll 1$), $\tau(E) = 263 r_s^{-5/2}(E - E_F)^{-2}$ fs, where E and E_F are expressed in eV [14]. Several other free-electron calculations of electron-electron scattering rates have also been carried out, for electron/hole energies that deviate from the Fermi level, within the random-phase approximation (RPA) [15,16] and with inclusion of exchange and correlation effects [17,18]. Nevertheless, detailed TR-TPPE experiments have reported large deviations

of measured hot-electron lifetimes from those predicted within the FEG model [19–25]. Moreover, while holes ($E < E_F$) in a FEG are known to live shorter than their electron counterparts ($E > E_F$) (for the same excitation energy, the momentum of the hole is smaller than the electron momentum, thus yielding a larger number of available transitions), recent TR-TPPE measurements [26] have demonstrated clearly that the d-hole lifetime at the top of the Cu d bands is considerably slower than that of excited electrons with the same excitation energy. Subsequently, recent PE measurements [27] have arrived at the same conclusion for all three noble metals Cu, Ag, and Au. First-principles calculations of electron lifetimes in a variety of metals have been carried out only very recently [28,29], by using the GW approximation of many-body theory [30]. These calculations [31] show that band-structure effects play a key role in the quasiparticle-decay mechanism. Furthermore, hot-electron lifetimes are found to strongly depend on the momentum of the quasiparticle, especially in the case of metals with a band structure having Van Hove-like singularities in the vicinity of the Fermi level [28].

During the electron-pump process induced by the first ultrashort laser in TR-TPPE experiments, a hole is created in the Fermi sea. This hole can be filled with an electron from below the Fermi level, via Auger decay, higher-order excitations, or electron-phonon interactions. The understanding of the hole decay is fundamental for the description of the ulterior dynamics of the excited electron (probed by the second laser). Furthermore, the dynamics of the hole is interesting by itself, as it is a fingerprint of differences between electron and hole wave functions. These differences yield distinct behaviors of electron and hole lifetimes, which depend on both the energy and the momentum of the quasiparticle.

In the present Letter, we address the first stage of a TR-TPPE experiment by investigating the hole-quasiparticle dynamics and report first-principles many-body calculations of the decay rate of d-like holes in Cu and Au. Details of the formalism we use for the evaluation of decay rates are described in Ref. [28]. The basic equation for the damping rate of a hole in the state $\phi_{n,\mathbf{k}}(\mathbf{r})$ with energy $\varepsilon_{n,\mathbf{k}} < E_F$ is (we use atomic units throughout, i.e., $e^2 = \hbar = m_e = 1$)

$$\tau_{n,\mathbf{k}}^{-1} = -2 \int d\mathbf{r} \int d\mathbf{r}' \, \phi_{n,\mathbf{k}}^{*}(\mathbf{r}) \, \mathrm{Im}\Sigma(\mathbf{r},\mathbf{r}'; \varepsilon_{n,\mathbf{k}}) \phi_{n,\mathbf{k}}(\mathbf{r}'),$$
(1)

where $\Sigma(\mathbf{r},\mathbf{r}'; \varepsilon_{n,\mathbf{k}})$ represents the quasiparticle self-energy, which we compute within the GW approximation of many-body theory [30]. For the evaluation of both the initial state of Eq. (1) and all wave functions entering the quasiparticle self-energy, we first expand the one-electron Bloch states in a plane-wave (PW) basis and then solve self-consistently the Kohn-Sham equation [32] of density-functional theory (DFT). Though all-electron schemes, such as the full-potential linearized augmented plane-wave (LAPW) method [33], are expected to be better suited for the description of d bands, the PW pseudopotential approach has already been successfully incorporated in the description of the dynamical response of copper [34]. Both PW and LAPW calculations produce almost identical results, showing the correct overall band structure. Nevertheless, they both predict the entire d-band manifold to be ~ 0.5 eV higher than shown by photoemission experiments [35,36].

The quasiparticle decay rate in periodic crystals depends on both the wave vector $\mathbf{k}$ and the band index n of the initial Bloch state. Nevertheless, we also define $\tau^{-1}(E)$ as the average of $\tau^{-1}(\mathbf{k}, n)$ over all wave vectors and bands lying with the same energy E in the irreducible wedge of the Brillouin zone (BZ). Our full band-structure calculations of the average lifetime $\tau(E)$ of holes $(E < E_F)$ in Cu and Au are presented by open circles in Figs. 1a and 1b, respectively [37,38]. For comparison, full band-structure calculations of the average lifetime of electrons $(E > E_F)$ are exhibited by solid circles, and FEG calculations (with $r_s = 2.67$ for Cu and $r_s = 3.01$ for Au) are represented by solid $(E > E_F)$ and dotted $(E < E_F)$ lines. These results indicate that holes in noble metals exhibit considerably longer lifetimes than electrons with the same excitation energy, which is in agreement with accurate TR-TPPE and PE measurements of d-hole lifetimes reported in Refs. [26] and [27], respectively. Moreover, at energies near the top of the d bands the hole lifetime strongly deviates from the $\tau(E) \propto (E - E_F)^{-2}$ quadratic dependence predicted within the FEG model, as first pointed out by Petek *et al.* [26].

Both electrons and holes exhibit lifetimes that are well over those predicted within the FEG model of the solid, due to a major contribution from occupied d states participat-
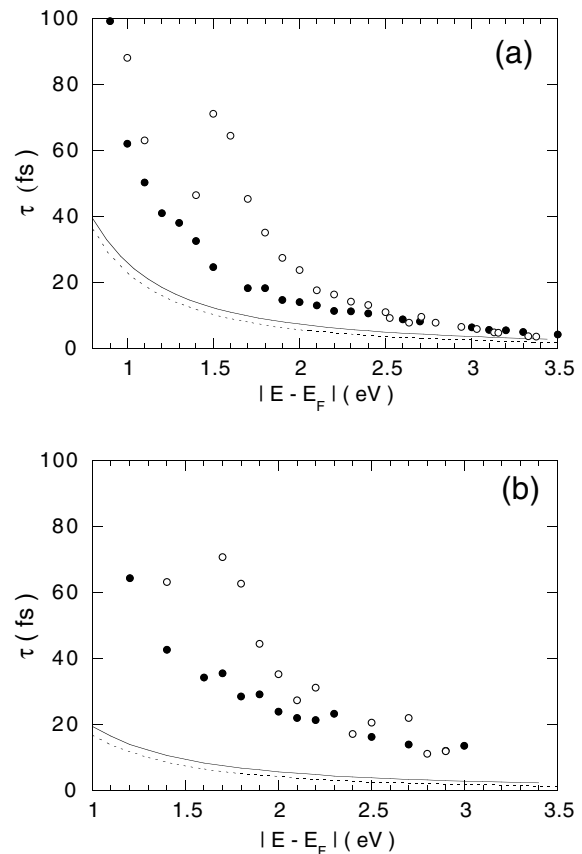

FIG. 1. Electron and hole lifetimes in (a) Cu and (b) Au. Solid and open circles represent our full *ab initio* calculation of $\tau(E)$ for electrons $(E > E_F)$ and holes $(E < E_F)$, respectively, as obtained after averaging $\tau(\mathbf{k}, n)^{-1}$ of Eq. (1) over wave vectors and the band structure for each $\mathbf{k}$. The solid and dotted lines represent the corresponding lifetime of electrons (solid line) and holes (dotted line) in a FEG with $r_s = 2.67$ for Cu and $r_s = 3.01$ for Au.

ing in the screening of electron-electron interactions, and differences between electron and hole lifetimes stem from the intrinsic properties of Bloch states above and below the Fermi level. Whereas Bloch states above the Fermi level have mainly sp-like character, states just below the Fermi level have a small but significant d component, which increases when the d-band threshold is reached. This difference accounts for the larger hole lifetime for energies very near the Fermi level, as shown in Fig. 1. At the top of the d bands (1.5 and 1.7 eV below the Fermi level in Cu and Au, respectively), the low overlap between d and sp states below the Fermi level yields a dramatic increase in the hole lifetime, especially in the case of Cu, which cannot be explained with the use of the FEG model. As the hole energy decreases ($|E - E_F|$ increases), both the increased phase space for the hole to decay and the larger overlap for hole-hole scattering within the d bands lead to a rapid decrease of the hole lifetime [26].

This physical scenario for the hole dynamics in noble metals is drawn in Fig. 2, where the ratio between hole

and electron lifetimes in Cu (solid circles) and Au (open circles) is plotted as a function of the hole/electron energy with respect to the Fermi level. Though calculated lifetimes of both electrons and holes in Au are much longer than in Cu, due to a larger participation of occupied d states in the dynamical screening of the former [39], different ratios between hole and electron lifetimes are observed only at energies near the top of the d bands. As $5d$ bands in Au are more free-electron-like than $3d$ bands in Cu, the larger overlap between d and sp states below the Fermi level in Au yields an increase in the hole lifetime at $|E - E_F| \sim 1.7$ eV in this material that is not as dramatic as in the case of Cu. This different behavior of hole lifetimes in Cu and Au emphasizes the crucial role that the overlap of the d hole with unoccupied sp- and d-hole states play in the hole decay mechanism. As $|E - E_F|$ increases, the ratio between hole and electron lifetimes resembles that predicted by the FEG model of the solid, which is plotted in the inset in Fig. 2 for $r_s = 2.67$.

d bands in the noble metals open in the vicinity of the high-symmetry X point. Hence, we have calculated lifetimes of holes with the wave vector along the ΓX direction in Cu. At the top of the d bands, at the X_5 point with $E - E_F = -1.5$ eV and the X_2 point with $E - E_F = -1.7$, we obtain d-hole lifetimes of 99 and 90 fs, respectively, much larger than lifetimes of electrons with the same energy, showing the role that the low overlap of d holes with unoccupied sp-hole states play in the determination of the hole lifetime. Though these calculated values of d-hole lifetimes cannot be directly compared with experiment, since the measured d-band threshold in Cu is located at ~ 2 eV below the Fermi level, our calculations are in agreement with the experimental observation that the narrowest linewidths correspond to the top of the d bands [26,27]. In the case of holes with the

wave vector along the ΓL direction in Cu, the hump of Fig. 1a at $E - E_F \sim -1.5$ eV is absent and the calculated lifetimes decrease with a quadratic $[\tau \propto (E - E_F)^{-2}]$ energy scaling. Instead, the hump of Fig. 1a is mainly originated in the contribution to the average lifetime from **k** vectors along the ΓX direction, where the opening of the d bands occurs, thereby showing a distinct behavior of hole lifetimes along various symmetry directions [40].

As d holes in noble metals are found to live longer than sp electrons with the same excitation energy, the majority of electrons excited by the first probe pulse in a TR-TPPE experiment feels the field created by the existing hole, thereby altering the electron dynamics. Hence, the TR-TPPE hot-electron lifetime measurements include, in a complex way, contributions from the joint electron-hole (exciton) dynamics [41]. In the case of semiconductors, this excitonic renormalization is known to strongly modify the single-particle optical absorption profile, so it certainly needs to be included in electronic-screening calculations [42]. In principle, excitonic normalization does not play such an important role in the case of metals, because of the large dynamical screening in these materials. However, there is a femtosecond time scale for the building up of the screening. During this ultrashort time, the electron-hole interaction is not fully screened and might modify the lifetime of the excited electron, as measured by the second probe pulse. Hence, there is still much to be done to understand the time-dependent building up of the screening in real metals, as well as the many-body electron and hole correlation effects in the quasiparticle dynamics.

In summary, we have presented a detailed theoretical investigation of inelastic lifetimes of holes in Cu and Au. We have reached the important conclusion that d holes in these materials exhibit longer lifetimes than sp electrons with the same excitation energy, in agreement with experiment. While a major contribution from occupied d states participating in the screening of electron-electron interactions yields both electron and hole lifetimes that are much longer than those of electrons and holes in a FEG, the small overlap between d and sp states below the Fermi level is responsible for the lifetime of d holes being longer than that of sp electrons, especially at the top of the d band. As the d-hole energy decreases ($|E - E_F|$ increases), both the increased density of states available for the hole-decay mechanism and the larger overlap for hole-hole scattering within the d bands yield a rapid decrease of the hole lifetime. Although our full band-structure calculations predict longer lifetimes than measured in the experiment [43], they are in agreement with the experimental observation that the narrowest linewidths correspond to the top of the d bands. Also, our results highlight new effects related to the electron-hole interaction occurring during the time delay between the two laser pulses in TR-TPPE spectroscopy, which may be of great importance in the interpretation of these experiments. The present results are general, they can be applied to the study of other d metals,
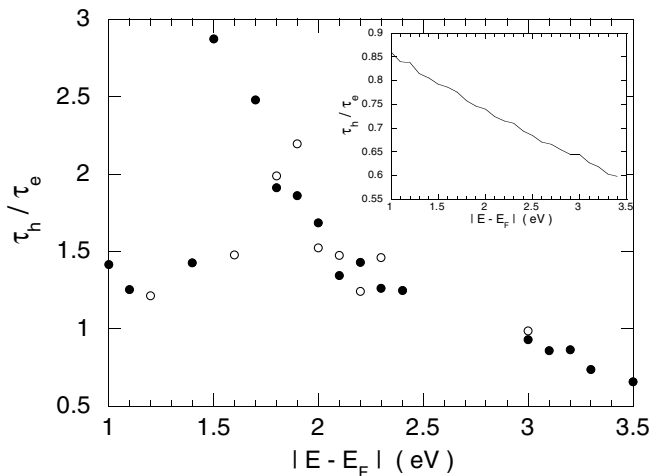

FIG. 2. Ratio between hole and electron lifetimes in Cu (solid circles) and Au (open circles). The inset exhibits the corresponding ratio between hole and electron lifetimes in a FEG with $r_s = 2.67$.

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[37] Well-converged results have been found with the introduction of a kinetic-energy cutoff of 75 Ry, thereby accounting for all $3d^{10}$ and $5d^{10}$ electrons of Cu and Au, respectively. The electron-ion interaction has been described by means of a nonlocal, norm conserving Troullier-Martins pseudopotential. The dielectric matrix has been evaluated in the RPA, by including bands up to a maximum energy of 25 eV above the Fermi level. The sampling over the BZ has been performed on a $16 \times 6 \times 16$ Monkhorst-Pack mesh. The exchange-correlation potential has been evaluated within the LDA, by using the Perdew-Zunger parametrization of the Ceperley-Alder correlation energy. Crystalline local-field effects are fully included in our calculations.

[38] These calculations have been carried out by computing the self-energy on the energy shell, with no explicit inclusion of the excitation-spectral-weight renormalization that is due to changes of the self-energy near the Fermi level. Within a FEG model of the solid this renormalization is known to yield lifetimes that are *longer* than those obtained on the energy shell by $\sim 20\%$ (see Ref. [12]).

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