The role of occupied $d$ states in the relaxation of hot electrons in Au

I. Campillo$^{1,3}$, J. M. Pitarke$^{1,4}$, A. Rubio$^2$, and P. M. Echenique$^{3,4}$

$^1$ Materia Condensatuaaren Fisika Saila, Zientzi Fakultatea, Euskal Herriko Unibertsitatea, 644 Posta Kutxatila, 48080 Bilbo, Basque Country, Spain
$^2$Departamento de Física Teórica, Universidad de Valladolid, 47011 Valladolid, Spain
$^3$ Materialen Fisika Saila, Kimika Fakultatea, Euskal Herriko Unibertsitatea, 1072 Posta Kutxatila, 20080 Donostia, Basque Country, Spain
$^4$Donostia International Physics Center (DIPC) and Centro Mixto CSIC-UPV/EHU, Donostia, Basque Country, Spain
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We present first-principles calculations of electron-electron scattering rates of low-energy electrons in Au. Our full band-structure calculations indicate that a major contribution from occupied $d$ states participating in the screening of electron-electron interactions yields lifetimes of electrons in Au with energies of $1.0 - 3.0$ eV above the Fermi level that are larger than those of electrons in a free-electron gas by a factor of $\sim 4.5$. This prediction is in agreement with a recent experimental study of ultrafast electron dynamics in Au(111) films (J. Cao et al., Phys. Rev. B 58, 10948 (1998)), where electron transport has been shown to play a minor role in the measured lifetimes of hot electrons in this material.

Relaxation lifetimes of excited electrons in solids with energies below the vacuum level can be attributed to a variety of inelastic and elastic scattering mechanisms, such as electron-electron (e-e), electron-phonon (e-p), and electron-imperfection interactions. Besides, when these so-called hot electrons are generated by absorption of an optical pulse, as occurs in the case of time-resolved two-photon photoemission (TR-2PPE) techniques, electron transport provides an additional decay component to the photoexcited electron population. Since inelastic lifetimes of hot electrons become infinitely long as they approach the Fermi level, e-p scattering and the scattering by defects both play a key role in the relaxation process of electrons very near the Fermi level. However, in the case of hot electrons with energies larger than $\sim 0.5 - 1.0$ eV above the Fermi level, e-e interactions yield inelastic lifetimes that are in the femtosecond time scale and they provide the main scattering mechanism.

Experimental femtosecond time-resolved photoemission studies of electron dynamics have been performed in a variety of solid surfaces, the role of e-e inelastic scattering and that of electron transport being difficult to identify. However, recent TR-TPPE experiments in Au(111) films with thicknesses ranging from 150 to 3000 Å have shown the relaxation from electron transport to be negligible and the hot-electron lifetime to be solely determined, at energies larger than $\sim 0.5 - 1.0$ eV above the Fermi level, by e-e inelastic scattering processes. Hence, these measurements provide an excellent benchmark against which to investigate the importance of band-structure and many-body effects on electron dynamics in solids. Also, ballistic electron emission spectroscopy (BEES) has shown to be capable of determining hot-electron relaxation times in solid materials.

In this paper, we report first-principles calculations of the energy-dependent inelastic lifetime of hot electrons in Au. We follow the many-body scheme first developed by Quinn and Ferrell but we now include the full band structure of the solid. This approach has already been successfully incorporated in the description of inelastic lifetimes of excited electrons in a variety of simple (Al, Mg, and Be) and noble (Cu) metals. A similar methodology, which is also based on the GW approximation of many-body theory, has been used by other authors to evaluate hot-electron lifetimes in Al and Cu.

Our many-body scheme for the calculation of inelastic lifetimes in real solids has been described elsewhere. For periodic crystals, the basic equation for the decay rate $\tau_i^{-1}$ of an electron in the state $\phi_{k_n}$ of energy $E_{k_n}$ is (we use atomic units throughout, i.e., $\hbar = m_e = 1$)

$$
\tau_i^{-1} = \frac{1}{\pi^2} \sum_{n_f} \int_{\text{BZ}} dq \sum_{G,G'} B_{if}(q+G) B_{if}^*(q+G') \frac{|<G,G'|q>|^2}{|q+G|^2} \text{Im} \left[ -\epsilon_{G,G'}^{-1}(q,\omega) \right],
$$

where $B_{if}(q + G)$ represent the coupling between the hot-electron initial and final states [see Eq. (5) of Ref. 4], and $\epsilon_{G,G'}^{-1}(q,\omega)$ are the Fourier coefficients of the inverse dielectric function of the solid, which we compute in the random-phase approximation (RPA). $G$ and $G'$ represent reciprocal lattice vectors, the integration over $q$ is extended over the first Brillouin zone (BZ), the sum over $n_f$ is extended over the band structure for each wave vector in the first BZ, $\omega = E_{k_n} - E_{k-q_n} - E_F$ is the energy transfer (0 $< \omega < E_{k_n} - E_F$), and $E_F$ is the Fermi energy.

If one neglects crystalline local-field effects, Eq. (1) can be expressed as follows:

$$
\tau_i^{-1} \approx \frac{1}{\pi^2} \sum_{n_f} \int_{\text{BZ}} dq \sum_{G,G'} B_{if}(q+G) B_{if}^*(q+G') \frac{|<G,G'|q>|^2}{|q+G|^2} \text{Im} \left[ -\epsilon_{G,G'}^{-1}(q,\omega) \right],
$$

where...
\[ \tau_i^{-1} = \frac{1}{n^2} \sum_{n_f} \int_{BZ} \text{d}q \sum_{G} \frac{|B_{if}(q + G)|^2}{|q + G|^2} \frac{\text{Im} \left[ \epsilon_{G,G}(q,\omega) \right]}{|\epsilon_{G,G}(q,\omega)|^2}. \]

Here, initial and final states of the hot electron enter through the coefficients \( B_{if}(q + G) \). The imaginary part of \( \epsilon_{G,G}(q,\omega) \) represents a measure of the number of states available for the creation of an electron-hole pair involving a given momentum and energy transfer \( q + G \) and \( \omega \), respectively, renormalized by the coupling between electron and hole states. The factor \( |\epsilon_{G,G}(q,\omega)|^{-2} \) accounts for the dynamically screened e-e interaction.

The decay rate of Eqs. (1) and (2) depends on both the wave vector \( k \) and the band index \( n_i \) of the initial Bloch state. Since measurements of hot-electron lifetimes are reported as a function of energy and the proper choice of the wave vector \( k \) and the band index \( n_i \) is usually not easy to be determined, we define \( \tau^{-1}(E) \) as the average of \( \tau^{-1}(k, n) \) over all wave vectors and bands lying with the same energy in the irreducible wedge of the Brillouin zone (IBZ).

If all one-electron Bloch states entering both the coefficients \( B_{if}(q + G) \) and the dielectric function \( \epsilon_{G,G}(q,\omega) \) were represented by plane waves and, at the same time, all energy bands were replaced by those of free electrons, then decay rates would not be direction-dependent and both Eqs. (1) and (2) would exactly coincide with the GW scattering rate of hot electrons in a FEG. The sampling over the BZ required for the evaluation of the dielectric response of Cu is exhibited in the same figure. We thus observe great qualitative differences between our full band-structure calculation and the experimental results. Nevertheless, one must be cautious with the comparison between our full band-structure calculations and the experiment. Since Au has a wide energy gap along the \( \Gamma L \) direction just over the Fermi level, the \( k_{||} = 0 \) pho-
toemission in Au(111) cannot be associated, in the energy range under study ($E - E_F \sim 1.0 - 3.0\,\text{eV}$), with hot-electron Bloch states in the same direction, and therefore the proper choice of the wave vector $k$ appears to be unclear. We have evaluated hot-electron lifetimes along various directions of the wave vector, and have found that differences between these results and the average lifetimes presented in Fig. 2 are within $\sim 20\%$, which gives support to our comparison with the experiment. 

In order to investigate the role that occupied $d$ states play in the relaxation of hot electrons in Au, now we neglect crystalline local-field effects and compute hot-electron lifetimes from Eq. (3). Scaled lifetimes $\tau(E)\times(E-E_F)^2$ of hot electrons in Au, as obtained from Eq. (3) by replacing the hot-electron Bloch states and bands entering $|B_{ij}(q+G)|^2$ by those of free electrons and the dielectric function in $|\epsilon_{G,G}(q,\omega)|^{-2}$ by that of a FEG with $r_s = 3.01$, are represented in the inset of Fig. 2 by open triangles. These calculated lifetimes, which have been obtained with full inclusion of the band structure of the crystal in the evaluation of $\text{Im}[\epsilon_{G,G}(q,\omega)]$, are close to those obtained within the FEG model of the solid (solid line), showing that the combined effect of the density of states (DOS) available for $e-h$ pair creation and the small overlap between $d$ states below and $sp$ states above the Fermi level nearly compensate. Hence, deviations of actual hot-electron lifetimes from FEG predictions are mainly originated in the deviation of the hot-electron momentum from the FEG prediction [the momentum of hot electrons depends on the actual DOS at the Fermi level] and the participation of $d$ electrons in the screening of $e-e$ interactions.

The effect of virtual interband transitions giving rise to additional screening is to largely increase the hot-electron lifetime in Au, as occurs in the case of Cu, a noble metal with analogous electronic structure. Since the change $\delta\epsilon_1^b$ in $\epsilon_1(\omega)$ due to the presence of $d$ electrons in the noble metal is found to be practically constant at low frequencies, Quinn treated the FEG as if it were embedded in a medium of dielectric constant $\epsilon_0 = 1 + \delta\epsilon_1^b$ instead of unity. The corrected lifetime is then found to be larger by roughly a factor of $\epsilon_0^{-1/2}$, i.e., $\sim 2.5$ for both Cu and Au. Nevertheless, our first-principles evaluation of the wave-vector and frequency dependent dielectric matrix leads us to the conclusion that the role that occupied $d$ states play in the screening of $e-e$ interactions is much more important in Au than in Cu. This is an expected result, since Au $5d$ electrons lie further away from the nucleus than Cu $3d$ electrons, and $5d$ bands in Au are, therefore, more free-electron-like than $3d$ bands in Cu ($d$ bands in Cu are concentrated within a width of $\sim 3\,\text{eV}$ smaller than in the case of Au).

The result we obtain with full inclusion of the band structure of the crystal in the evaluation of Eq. (3), but still neglecting crystalline local-field effects, is represented in the inset of Fig. 2 by open circles. Our full band-structure calculation of Eq. (1) for Au is represented in the same figure by solid circles, showing that neglecting crystalline local-field corrections results in an overestimation of hot-electron lifetimes of 40% – 50%. These crystalline local-field effects, which partially compensate the pronounced participation of $d$ electrons in the screened $e-e$ interaction, are due to large electron-density variations in this material.

In conclusion, we have presented full band-structure calculations of the inelastic lifetime of hot electrons in Au. We have found that a major contribution from occupied $d$ states participating in the screening of $e-e$ interactions yields lifetimes of electrons with energies of $1.0 - 3.0\,\text{eV}$ above the Fermi level that are larger than those of electrons in a FEG by a factor of $\sim 4.5$, in agreement with the experiment. The effect of virtual interband transitions giving rise to additional screening does not depend on whether the hot electron can excite $d$ electrons [the $d$-band scattering channel opens at $\sim 2\,\text{eV}$ below the Fermi level] or not. On the other hand, the actual density of occupied states available for real transitions is found not to play an important role in the relaxation mechanism. Consequently, actual lifetimes approximately scale as $(E - E_F)^{-2}$, as in the case of a FEG. That lifetimes of hot electrons in Au can be fitted within this scaling behaviour has also been demonstrated by a theoretical analysis of electron-electron mean free paths in BEES experiments.

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The exchange-correlation (XC) potential has been evaluated within the local-density approximation (LDA), by using the XC energy of Ceperley and Alder [D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 1196 (1980)] as parametrized by Perdew and Zunger [J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981)]. We performed a scalar relativistic calculation of the all-electron atom. Spin-orbit effects were then averaged in the generation of a non-local, norm-conserving Troullier-Martins [N. Troullier and J. L. Martins, Phys. Rev. B 43, 1357 (1991)] pseudopotential, since these effects are not expected to be important in the evaluation of the average lifetime, $\tau(E)$. We checked the transferability of the pseudopotential by comparing different electronic configurations for the pseudo-atom with the corresponding all-electron calculations. This ensured a transferability for the bulk calculations up to energies of $\sim 20$ eV above the Fermi level.

The so-called electron-density parameter $r_s$ is defined by the relation $1/n_0 = (4/3)\pi r_s^3$, $n_0$ being the average electron density.

The anisotropy of hot-electron lifetimes in Au is only found to play an important role at higher energies, where Bloch states with the wave vector along the necks of the Fermi surface, in the $\Gamma L$ direction, are available.

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Figure 2

\[ \tau (\text{fs}) \]

\[ \tau x (E - E_F)^2 \text{ (fs x eV)} \]

\[ (E - E_F) \text{ (eV)} \]