

Distinguishing attosecond electron–electron scattering and screening in transition metals

Cong Chen^a, Zhensheng Tao^{a,1}, Adra Carr^a, Piotr Matyba^{a,2}, Tibor Szilvási^b, Sebastian Emmerich^c, Martin Piecuch^c, Mark Keller^d, Dmitriy Zusin^a, Steffen Eich^c, Markus Rollinger^c, Wenjing You^a, Stefan Mathias^{c,3}, Uwe Thumm^e, Manos Mavrikakis^b, Martin Aeschlimann^c, Peter M. Oppeneer^f, Henry Kapteyn^a, and Margaret Murnane^{a,1}

^aJILA, Department of Physics, University of Colorado and National Institute of Standards and Technology, Boulder, CO 80309; ^bDepartment of Chemical and Biological Engineering, University of Wisconsin–Madison, Madison, WI 53706; ^cResearch Center OPTIMAS, Department of Physics, University of Kaiserslautern, 67663 Kaiserslautern, Germany; ^dNational Institute of Standards and Technology, Boulder, CO 80305; ^eDepartment of Physics, Kansas State University, Manhattan, KS 66506; and ^fDepartment of Physics and Astronomy, Uppsala University, 75120 Uppsala, Sweden

Contributed by Margaret Murnane, May 18, 2017 (sent for review April 19, 2017; reviewed by Shaul Mukamel and Xiaoyang Zhu)

Electron–electron interactions are the fastest processes in materials, occurring on femtosecond to attosecond timescales, depending on the electronic band structure of the material and the excitation energy. Such interactions can play a dominant role in light-induced processes such as nano-enhanced plasmonics and catalysis, light harvesting, or phase transitions. However, to date it has not been possible to experimentally distinguish fundamental electron interactions such as scattering and screening. Here, we use sequences of attosecond pulses to directly measure electron–electron interactions in different bands of different materials with both simple and complex Fermi surfaces. By extracting the time delays associated with photoemission we show that the lifetime of photoelectrons from the *d* band of Cu are longer by ~ 100 as compared with those from the same band of Ni. We attribute this to the enhanced electron–electron scattering in the unfilled *d* band of Ni. Using theoretical modeling, we can extract the contributions of electron–electron scattering and screening in different bands of different materials with both simple and complex Fermi surfaces. Our results also show that screening influences high-energy photoelectrons (≈ 20 eV) significantly less than low-energy photoelectrons. As a result, high-energy photoelectrons can serve as a direct probe of spin-dependent electron–electron scattering by neglecting screening. This can then be applied to quantifying the contribution of electron interactions and screening to low-energy excitations near the Fermi level. The information derived here provides valuable and unique information for a host of quantum materials.

attosecond science | high harmonic generation | ARPES | electron–electron interactions

Excited-state electron dynamics in materials play a critical role in light-induced phase transitions in magnetic and charge density wave materials, in superdiffusive spin flow, in catalytic processes, and in many nano-enhanced processes. However, to date exploring such dynamics is challenging both experimentally and theoretically. Using femtosecond lasers in combination with advanced spectroscopies, it is possible to measure the lifetime of excited charges and spins directly in the time domain (1). To date, such studies have been applied to a wide variety of materials, including noble metals and semiconductors (1–4), ferromagnetic metals (5–8), strongly correlated materials (9) and high- T_c superconductors (10, 11). These studies have significantly improved our understanding of the fastest coupled interactions and relaxation mechanisms in matter. However, to date experimental investigations of electron dynamics have been limited to femtosecond time-scale processes in materials with low charge densities (9–12) or to Fermi-liquid metals with low excitation energies (< 3.0 eV above E_F , where E_F is the Fermi energy) (3–5), due to the visible-to-UV-wavelength photon energies used in these experiments. In this region, two fundamental electron interactions—electron–electron scattering and charge screening due to a rearrangement of adjacent charges—contribute to the signal, making it challenging to

independently probe these dynamics. On the theory side, initial studies in the late 1950s were enabled by the seminal Fermi-liquid theory of Landau (13–16). In exciting recent developments using the self-energy formalism of many-body theory and the random phase approximation, calculations of electron–electron interaction in materials—that include the material band structure—have now become possible (17–22). Thus, experimental approaches that can distinguish between different electron–electron interactions, particular with band specificity, are very important and timely.

High harmonic generation (HHG) provides attosecond pulses and pulse trains that are perfectly synchronized to the driving laser and that are ideal for probing the fastest coupled charge and spin dynamics in atoms, molecules, and materials (23–33). To date, two approaches have been used to probe attosecond electron dynamics in matter through photoemission, taking advantage of laser-assisted photoemission sidebands (24, 25). For atoms, because the energy separation between different states is large, attosecond streaking using isolated attosecond pulses (with an energy resolution of several electronvolts) has been applied very successfully (26, 27). The same approach has also been used to measure the transit time for a photoelectron to be emitted

Significance

Electron–electron interactions are among the fastest processes in materials that determine their fascinating properties, occurring on attosecond timescales on up ($1 \text{ as} = 10^{-18} \text{ s}$). The recent development of attosecond angle-resolved photoemission spectroscopy (atto-ARPES) using high harmonic generation has opened up the possibility of probing electron–electron interactions in real time. In this paper, we distinguish electron–electron screening and charge scattering in the time domain in individual energy bands within a solid. These results open up new possibilities for probing fundamental electron–electron interactions in a host of materials including magnetic, superconducting, and advanced quantum materials.

Author contributions: H.K. and M. Murnane designed research; C.C., Z.T., A.C., P.M., T.S., S. Emmerich, M.P., M.K., D.Z., S. Eich, M.R., W.Y., S.M., U.T., M. Mavrikakis, M.A., P.M.O., H.K., and M. Murnane performed research; C.C. and Z.T. analyzed data; C.C., Z.T., P.M.O., H.K., and M. Murnane wrote the paper; T.S. conducted the band structure calculation under the supervision of M. Mavrikakis; M.K. performed the sample growth; and U.T. and M. Mavrikakis wrote the theory portion of the manuscript.

Reviewers: S.M., University of California, Irvine; and X.Z., Columbia University.

The authors declare no conflict of interest.

Freely available online through the PNAS open access option.

¹To whom correspondence may be addressed. Email: Zhensheng.Tao@colorado.edu or Margaret.Murnane@colorado.edu.

²Present address: Department of Physics, Umeå University, SE-901 87 Umeå, Sweden.

³Present address: Physikalisches Institut, Georg-August-Universität Göttingen, 37077 Göttingen, Germany.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1706466114/-DCSupplemental.

thus makes it possible to independently distinguish the fastest electron–electron scattering and screening dynamics in metals on attosecond time scales, providing valuable information for a host of magnetic materials.

Experiment

The concept behind our study is shown in Fig. 1A. Most of the output of a near-IR femtosecond laser is used to generate high harmonics in various noble gases (Xe, Kr, and Ar), which are then focused onto single crystal Cu(111) and Ni(111) surfaces. In the spectral domain, these harmonics span ~ 15 – 45 eV (corresponding to 11ω – 27ω), each with a linewidth of ~ 0.3 eV, and separated by $2\omega_L \approx 3.2$ eV, where ω_L is the frequency of the driving IR laser. The residual phase-locked laser field is used to simultaneously irradiate the material together with a high harmonic field, which induces sidebands of the photoelectron peaks corresponding to the absorption or emission of an IR laser photon. The photoelectron spectrum is then collected using a hemispherical photoelectron analyzer (Specs Phoibos 100). Note that it has already been shown that RABBITT and attosecond-streaking yield the same temporal information about the photoemission process (31), whereas ARPES adds significant advantages of band specificity (33). Moreover, by simultaneously measuring two photoelectron wavepackets from different initial states excited by the same harmonic orders we can eliminate the influence of the HHG phase (28).

The band structure of Cu(111) is plotted in Fig. 1B. Similar to Ni(111) (33), there are three valence bands along the Γ –L direction of Cu(111): the Λ_3^α band with a binding energy of ~ 2.8 eV, Λ_3^β with ~ 3.5 eV, and Λ_1 with ~ 3.8 eV. By using an s-polarized HHG field we can exclusively excite photoelectrons from the Λ_3^α and Λ_3^β bands (34, 35). The band-mapping results are also plotted in Fig. 1B, which shows a strong dispersion of the photoemission peaks as a function of photon energy, indicating that photoemission from bulk states contributes to the signal [S3. *Static HHG Photoelectron Spectra Analysis of Cu(111)*]. In our experiments, photoemission from the Cu(100) surface is also measured, which corresponds to a band structure along Γ –X direction (Fig. 1C). As shown in Fig. 1D, photoemission dipole transitions couple different initial and final states (bands) of Cu(111) that can be selected using different harmonic orders and polarizations, by harnessing photoemission selection rules (34, 35). To distinguish the influence of wavefunction localization (excited bulk states vs. free-electron final states) as well as the influence of the fundamental electron interactions on the photoelectron lifetimes, we first identify where the final-state resonances occur in Cu(111). The spectral intensity of Λ_3^β band photoelectrons excited by the s-polarized HHG field is plotted in Fig. 2A. A strong enhancement of the spectral intensity peaked at the resonant photon energy of ~ 26 eV can be observed, which can be attributed to the interband transition from the Λ_3^β initial band to the excited Λ_1^B final band (Fig. 1B). The Lorentzian linewidth is $\gamma_{\text{spec}} = 2.13 \pm 0.65$ eV (Fig. 2A), which is consistent with the linewidth recently obtained using high-resolution photoemission at a synchrotron radiation source (36). The predicted final-state lifetime is therefore given by $\tau_{\text{spec}} = \hbar/\gamma_{\text{spec}} = 309 \pm 94$ as.

The photoemission time delay $\tau_{PE}(\Lambda_3^\beta) - \tau_{PE}(\Lambda_3^\alpha)$ at the Γ point can be extracted from the RABBITT interferogram (Fig. 2D) and is summarized in Fig. 2B. The quantum paths involved in RABBITT interference are illustrated in Fig. 2C. These interferograms (Fig. 2D) were obtained by integrating the photoelectron spectra over $\pm 2.5^\circ$ around the Γ point (normal-emission direction). Comparing Fig. 2A and B, we find that $\tau_{PE}(\Lambda_3^\beta) - \tau_{PE}(\Lambda_3^\alpha)$ at the Γ point reaches its maximum value $\tau_{\text{chron}} = 291 \pm 48$ as at the resonant photon energy for the interband transition $\Lambda_3^\beta \rightarrow \Lambda_1^B$ (Fig. 1B), which is in good agreement with $\tau_{\text{spec}} \approx 309 \pm 94$ as. This agreement indicates that the lifetime of photoelectrons emitted from the initial Λ_3^α band [$\tau_{PE}(\Lambda_3^\alpha)$] is short at the Γ point. Considering the fact that the

spectral intensity of Λ_3^α is a smooth function of photon energy (*Supporting Information, Fig. S4*), it allows us to directly assign the measured time delay to the lifetime of photoelectrons from the Λ_3^β band. Compared with Ni(111) (33), the resonant linewidth from the initial Λ_3^β band in Cu is narrower, which is consistent with the longer lifetime measured in the time domain (291 ± 48 as for Cu vs. 212 ± 30 as for Ni).

For photoemission through free-electron final states (away from any final-state resonances, >25 eV in Fig. 3A), we find that the photoelectron lifetime from the Λ_3^β band of Cu(111) is ~ 100 as in the normal-emission geometry. Moreover, this lifetime is a smooth function of the final-state energy (Fig. 3A). The associated time delay can be clearly seen in the experimentally measured interferograms of Cu(111) as an obvious phase shift in the oscillations of the RABBITT quantum interferences (Fig. 3B), which interestingly is absent in Ni(111) for free-electron final states (33). We note that we can exclude the possibility that the finite photoelectron lifetime in this energy range in Cu(111) is caused by another final-state resonance because we did not observe any photoelectron yield enhancement in this energy range (Fig. 2A), and because it exhibits little momentum (angle) dispersion—unlike the lifetime on resonance (Fig. 3C). To further reinforce this conclusion, we also measured the photoemission time delay between the Δ_5 and Δ_1 bands along the Γ –X direction for Cu(100) as the two Λ_3 bands cross the Γ point of the Brillouin zone (BZ) [Fig. 1C; see S2. *Static ARPES Spectra of Cu(111) and Cu(001)* for more details]. As shown in Fig. 2B, a similar lifetime difference between Δ_5 and Δ_1 band photoelectrons was observed on the Cu(100) surface when there is no spectral resonance. Excluding final-state effects, the ~ 100 as lifetime difference of photoelectrons from the Λ_3^β band for Cu(111) and Ni(111) must be attributed to differences in the fundamental electron–electron interactions experienced by the high-energy photoexcited electrons during photoemission from these two materials.

Discussion

The photoexcited electron lifetime for free-electron final states is mainly determined by the competition between dynamic screening and inelastic electron–electron scattering during the photoemission process (18). This is because for highly excited electronic states (>20 eV) other decay channels, including scattering with photoholes, phonons, and impurities, are expected to have negligible contributions. In Fig. 3A we compare our measured photoelectron lifetime from the Λ_3^β band of Cu to two empirical models [Goldmann et al. (37) and Eberhardt and co-workers (36)] that are based on bulk excited-state linewidths, as well as a free-electron gas (FEG) model with $r_s = 2.67$ for Cu (18), where r_s is the electron-density parameter defined for an electron density n by $n = 3/(4\pi r_s^3)$. As shown in Fig. 3A, both empirical models agree well with the photoelectron lifetime on resonance (SB16) as expected; however, they overestimate the photoelectron lifetime off-resonance. This is not surprising—the Goldmann and Eberhardt models are derived from a linewidth analysis of photoemission and inverse photoemission experiments (36, 37) that are mainly based on contributions from resonant (bulk final state) excitations. Compared with steady-state photoemission and inverse photoemission studies, our time-domain approach has unique advantages that allow us to measure the intrinsic high-energy photoelectron lifetime at arbitrary energies (including transitions both on and off final-state resonance). Note that the FEG model cannot reproduce the photoelectron lifetime on resonance, which is also not surprising because it does not account for the real band structure of the material. Most interestingly, the FEG model matches the off-resonance (i.e., free-electron final-state) lifetime measured on Cu(111) very well, but not for Ni(111), which is ~ 100 as shorter. Note that this trend is very different from the hot-electron lifetimes measured at low energy (<3 eV above E_F), which exhibit a strong

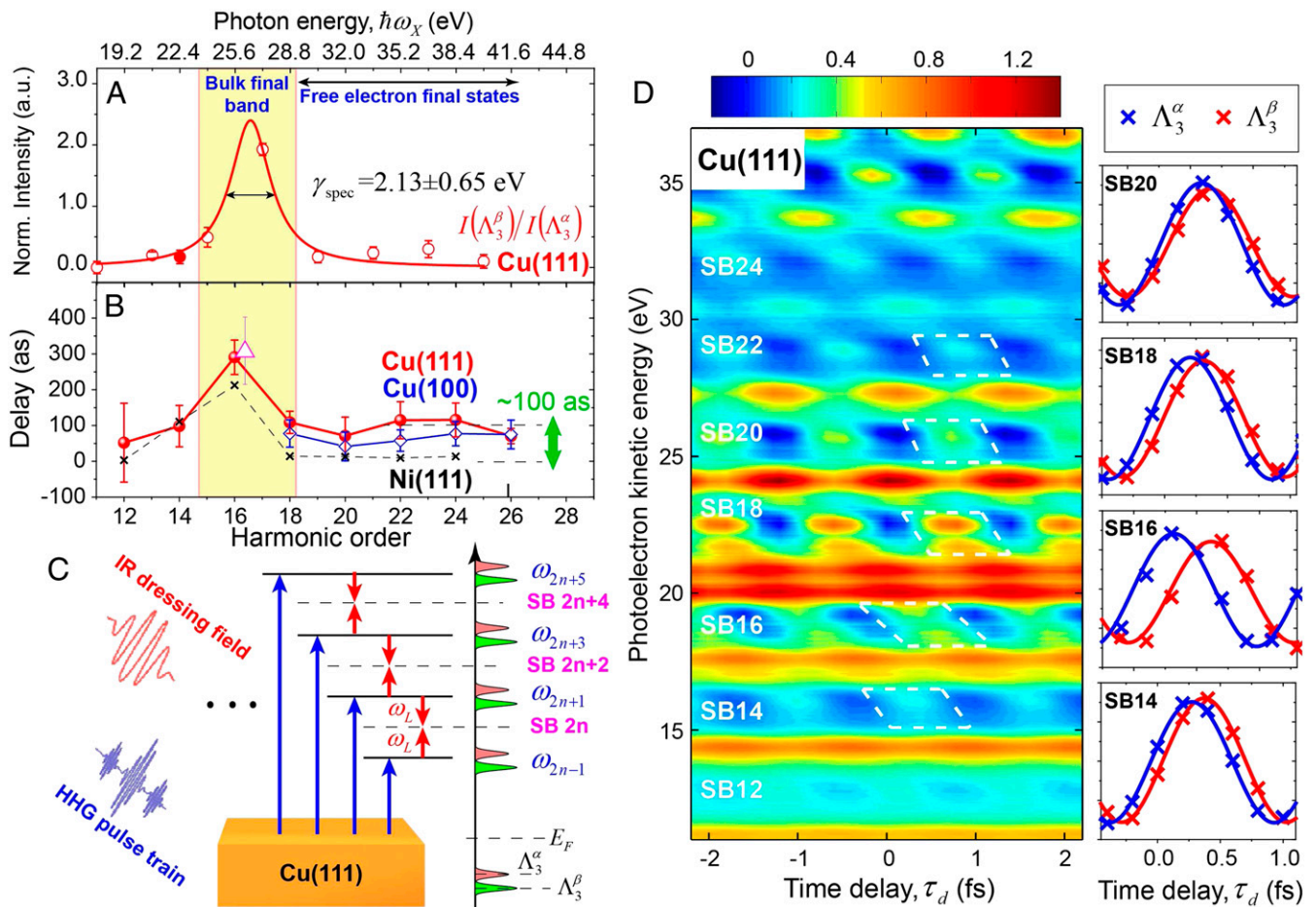


Fig. 2. Comparison of photoelectron lifetimes in Cu(111) and Ni(111) for photoemission either into excited states (on resonance, ≈ 25 eV) or into free-electron states (off resonance). (A) Normalized spectral intensity of the Cu(111) Λ_3^β band as a function of photon energy. The filled symbol (14th order) is obtained from HHG driven by 390-nm laser field. The red solid line represents the Lorentzian fitting to the spectral intensity, which yields a linewidth of 2.13 ± 0.65 eV. The center of Lorentzian fitting is given by the final-band energy obtained from DFT calculation (Fig. 1B). (B) Photoemission time delay $\tau_{PE}(\Lambda_3^\beta) - \tau_{PE}(\Lambda_3^\alpha)$ as a function of photon energy for both Cu(111) and Ni(111) surfaces. The time delay $\tau_{PE}(\Delta_5) - \tau_{PE}(\Delta_1)$ measured for a Cu(100) surface is also plotted for comparison. The open triangle represents the lifetime derived from the linewidth in A. (C) Illustration of the quantum-path interference in RABBITT measurements. Electrons from two initial states (Λ_3^α and Λ_3^β) are excited by multiple harmonic orders into different final states. By absorbing and emitting one additional IR photon (ω_L), quantum-path interference causes spectral modulation at the sidebands (SB) in between neighboring harmonic orders. (D) Two-dimensional map of photoelectron spectral intensity as a function of photoelectron energy and HHG-laser field time delay τ_d . The relative time delay between photoelectrons from Λ_3^β and Λ_3^α initial bands is highlighted as large offsets in oscillations in the sideband region by white dashed boxes. (Right) One-dimensional lineouts for the spectral modulations with angular integration of $\pm 2.5^\circ$ around the Γ point of photoelectrons from Λ_3^β and Λ_3^α initial bands in the selected sideband regions.

deviation from the FEG model due to the added presence of screening of d -band electrons (17, 19).

The absence of electron screening effects in high-energy photoemission can be understood by considering two different aspects. First, screening of d band electrons can be estimated by considering an effective dielectric constant $\epsilon_d = 1 + \delta\epsilon_d$, which is induced by the polarizable background of d electrons. At low energies, the corrected lifetime is larger than the value predicted by the FEG model by $\sqrt{\epsilon_d}$ (38–40). As pointed out by Quinn (41, 42), $\delta\epsilon_d$ reduces as a function of excitation photon energy. As a result, the variation of the photoelectron lifetime due to d -electron screening is estimated to be only a few percent of the FEG lifetime at energies >20 eV (S8. Approximate Estimate of d -Electron Screening). Second, on ~ 100 -as time scales, we also need to consider the dynamics of electron screening in metals. As shown in previous theoretical studies, the buildup of charge screening in metals is not instantaneous but takes approximately half of a plasma period to fully develop (43), which corresponds to ~ 200 as in both Cu and Ni. Because the off-resonance photo-

electron lifetimes are much less than this, it seems that photoelectrons from Cu (and Ni) escape before dynamic screening can influence the photoelectron lifetime in this energy range. As a result, dynamic electron screening has negligible influence on the photoelectron lifetimes at energies >20 eV.

However, the ~ 100 -as lifetime difference between photoelectrons from the d bands of Cu and Ni can be attributed to the differences in the band structure of these materials, which results in different electron–electron scattering rates between photoelectrons and other electrons in the conduction bands during photoemission. Here, we consider a high-energy photoexcited electron with energy E above E_F . This electron decays into a lower energy state E' by exciting one of the other electrons in the band (a scattering partner) from its original state ϵ into an unoccupied state above E_F , $\epsilon + \Delta$, where $\Delta = E - E'$ is the energy transfer (Fig. 4A). We note that the scattering process illustrated in Fig. 4A is responsible for removing photoelectron signal from our measurement. Thus, the experimentally measured photoelectrons are those that escape without scattering; nevertheless,

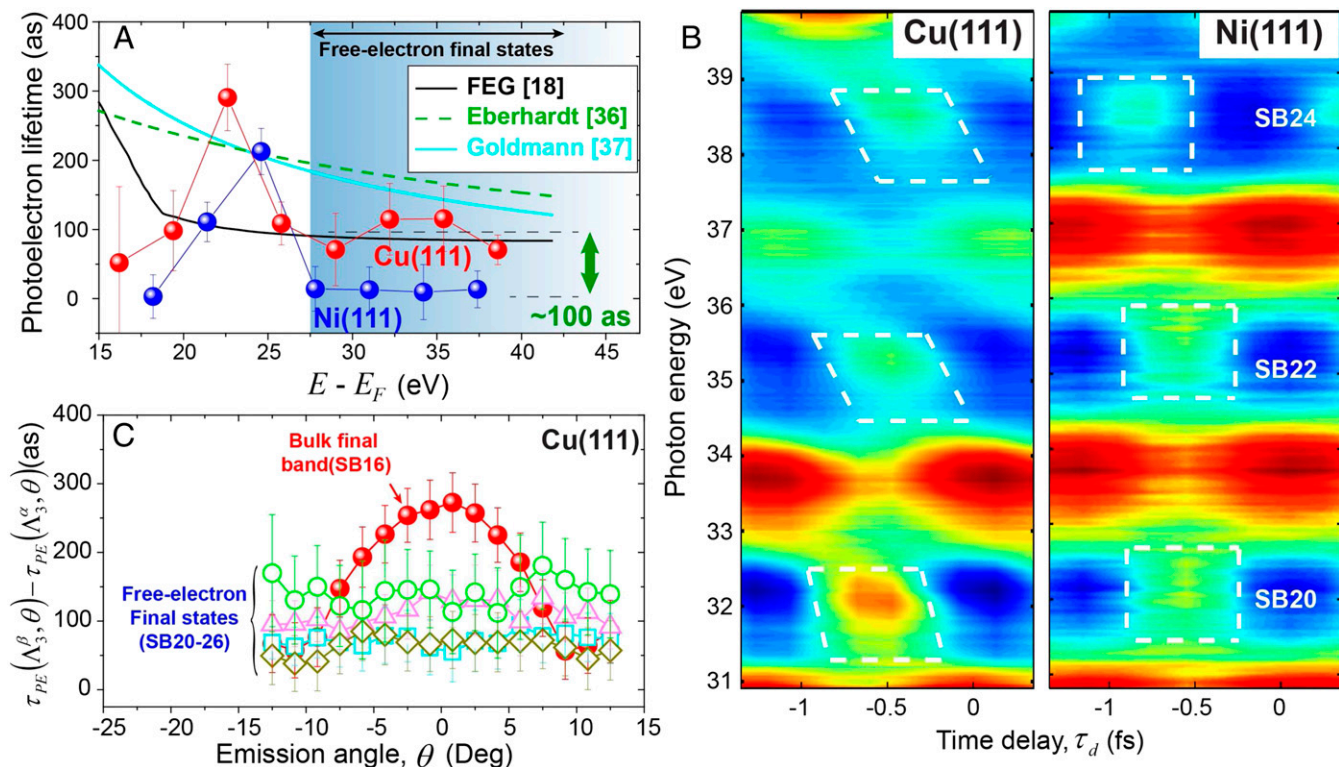


Fig. 3. Origin of different photoelectron lifetimes for photoemission into free-electron final states for Cu and Ni. (A) Photoelectron lifetime emitted from Λ_3^β band measured using atto-ARPES as a function of the final-state energy ($E - E_F$) for both Cu(111) and Ni(111), in comparison with the FEG model (black) (18), Goldmann et al. (cyan) (37) and Eberhardt and coworkers (green dashed) (36) models. The lifetime corresponding to free-electron final states are highlighted in the colored region. (B) Interferograms for sidebands 20–24 (off-resonance, away from final-band resonance) measured from Cu(111) and Ni(111) (33) surfaces. Large offsets in the sideband regions can be observed in the Cu(111) data, as highlighted by the white dashed boxes. Such offsets are absent for Ni(111). (C) Angle-dependent photoemission time delay of $\tau_{PE}(\Lambda_3^\beta, \theta) - \tau_{PE}(\Lambda_3^\alpha, \theta)$ measured on Cu(111), which clearly shows the difference between a resonant transition to a bulk final band (sideband 16) and those to free-electron final states (sideband 20, square; sideband 22, triangle; sideband 24, circle; and sideband 26, diamond).

the lifetimes of these electrons are influenced by scattering within the occupied bands and experience different phase shifts in our RABBITT measurement. The scattering rate (which will correspond to the inverse of the lifetime τ_σ) can be calculated using Fermi's golden rule in the random- k approximation (6, 44–46) (*S7. Spin-Dependent Scattering Model*),

$$\frac{1}{\tau_\sigma(E)} = \frac{\pi}{\hbar} \int_{E_F}^E dE' \left\{ \sum_{\beta=s,p,d} \rho_\sigma^{\beta,>}(E') \sum_{\alpha=s,p,d} \int_{E_F-\Delta}^{E_F} d\varepsilon \left[\rho_\sigma^{\alpha,<}(\varepsilon) \rho_\sigma^{\alpha,>}(\varepsilon + \Delta) 2|M^{\sigma\sigma}|^2 + \rho_\sigma^{\alpha,<}(\varepsilon) \rho_\sigma^{\alpha,>}(\varepsilon + \Delta) |M^{\sigma\bar{\sigma}}|^2 \right] + \sum_{\beta=s,p,d} \rho_\sigma^{\beta,>}(E') \sum_{\alpha=s,p,d} \int_{E_F-\Delta}^{E_F} d\varepsilon \rho_\sigma^{\alpha,<}(\varepsilon) \rho_\sigma^{\alpha,>}(\varepsilon + \Delta) |M^{\sigma\bar{\sigma}}|^2 \right\}, \quad [1]$$

where $\sigma = \uparrow, \downarrow$ is the electron spin ($\bar{\sigma}$ is the opposite spin to σ), α and β designate the s -, p -, or d -like wavefunction of the scattering partners and the photoexcited electrons, respectively, and

$$\begin{aligned} \rho_\sigma^{\alpha,>}(E) &= [1 - f(E)] \rho_\sigma^\alpha(E) \\ \rho_\sigma^{\alpha,<}(E) &= f(E) \rho_\sigma^\alpha(E), \end{aligned} \quad [2]$$

where $f(E)$ is the Fermi–Dirac distribution function and $\rho_\sigma^\alpha(E)$ is the spin-dependent density of states (DOS) of the α orbital that is obtained from a density-functional theory (DFT) calculation

(Fig. 4C, *Inset*). We note that because the unoccupied states above the Fermi energy in Ni are dominated by electronic states with minority-spin polarization (\downarrow), spin-dependent scattering needs to be taken into account, which results in spin-dependent excited-electron lifetime in the ferromagnetic materials such as Ni (5, 6, 46). Here $M^{\sigma\sigma}$ is the spin-dependent, crystal momentum- and orbital-averaged Coulomb matrix element, assuming $M^{\uparrow\uparrow} = M^{\downarrow\downarrow}$ and $M^{\uparrow\downarrow} = M^{\downarrow\uparrow}$ (see *S7. Spin-Dependent Scattering Model* for more details). Indeed, as shown in Fig. 3C, we verified experimentally that the assumption of a momentum-averaged Coulomb matrix element M is valid, as originally suggested by Berglund and Spicer (44). Similar models have also been successfully used to explain the hot-electron lifetimes of intermediate states measured using time-resolved two-photon photoemission (Tr-2PPE) (6, 46). Assuming $\rho_\uparrow = \rho_\downarrow = \rho$ and $M^{\uparrow\uparrow} = M^{\downarrow\downarrow} = M$, Eq. 1 is simply reduced to $\frac{1}{\tau(E)} = \frac{2\pi}{\hbar} \rho^3 |M|^2 (E - E_F)^2$, which is the well-known $(E - E_F)^{-2}$ scaling of hot-electron lifetimes excited close to the E_F (44).

We first evaluate the influence of the DOS on the available phase space for scattering by assuming $M^{\uparrow\uparrow} = M^{\downarrow\downarrow} = 1.0$ in Eq. 1. As shown in Fig. 4B, *Inset*, the phase space increases monotonically as a function of the photoexcited electron energy above E_F for both Ni and Cu, and indeed the phase space of Ni is larger than that of Cu in the energy range of our experiments, indicating that a higher scattering rate and a shorter photoelectron lifetime would indeed be expected. The additional phase space of Ni is dominated by the unoccupied DOS above E_F , as evidenced by the fact that the available phase space of Ni moves closer to Cu as its DOS is down-shifted by 1.8 eV to artificially remove the peaked unoccupied DOS (dashed line in Fig. 4B,

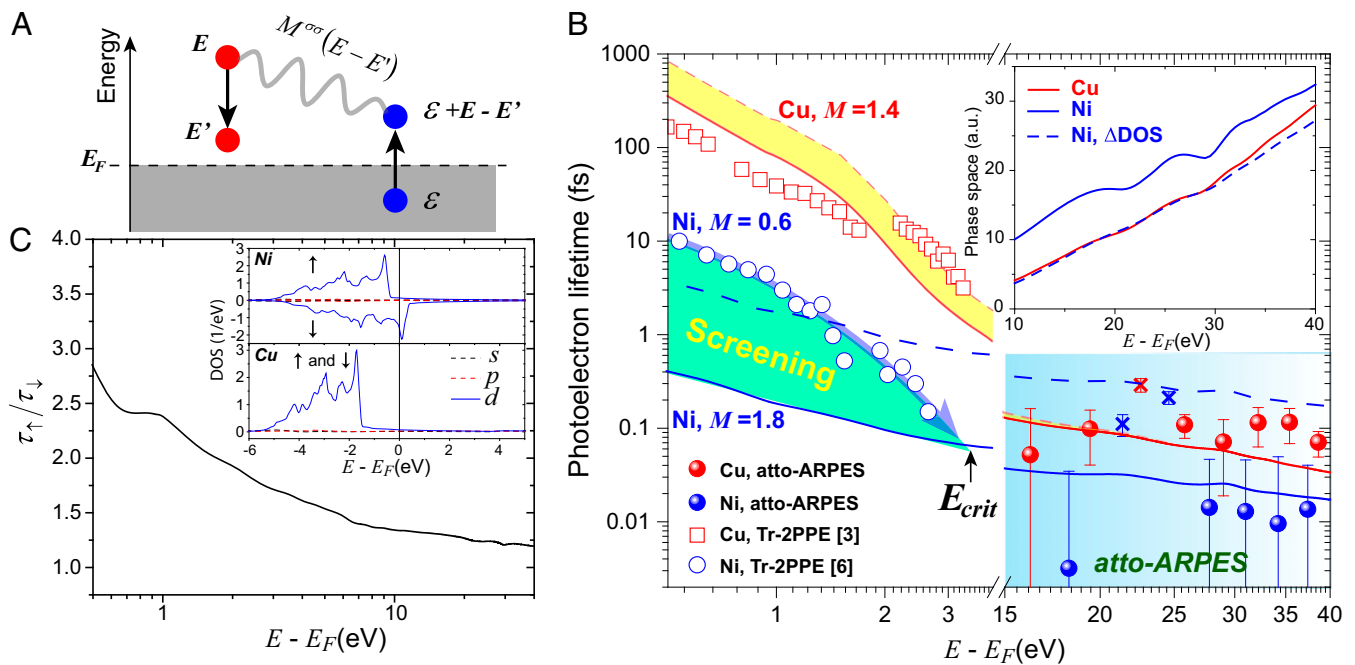


Fig. 4. Spin-dependent model of electron–electron scattering. (A) Illustration of the electron–electron scattering process described by Eq. 1. The photoexcited electron (red circle) can decay by exciting another unexcited electron (blue circle) to a state above E_F . $M^{σσ}(E - E')$ is the Coulomb matrix element, which we find is mostly constant for Cu (at 1.4) across a broad energy range but varies for Ni due to stronger screening at low energies. (B) Comparison between the spin-dependent scattering model [red (Cu) and blue (Ni)] and the experimentally measured lifetime of photoexcited electrons in Cu and Ni. The low-energy data (0.5–3 eV) are measured using Tr-2PPE method, extracted from ref. 3 for Cu and from ref. 6 for Ni. The high-energy data (15–40 eV) are directly measured in our experiment using atto-ARPES. The data that overlap final-state resonances in both materials are represented by crosses to distinguish them from the off-resonant results of interest here. The yellow area estimates d -electron screening effects by considering the optical constants of Cu (47). The experimentally measured low-energy electron lifetime approaches the bare electron–electron scattering limit (solid blue line, $M = 1.8$ for Ni) at an energy $E_{crit} \sim 3$ eV. (Inset) The phase space of the two materials calculated from Eq. 1, assuming $M^{\uparrow\uparrow} = M^{\downarrow\downarrow} = 1.0$. The blue dashed line (Ni, Δ DOS) is the results with the DOS of Ni downshifted by 1.8 eV. (C) Lifetime ratio τ_1/τ_2 as a function of excited electron energy ($E - E_F$) for Ni obtained using Eq. 1. (Inset) Spin and orbital-dependent DOS of Ni and Cu obtained from DFT calculations.

Inset). Fig. 4B plots the experimentally measured and theoretically calculated lifetimes of photoexcited electrons from 0.5 to 40 eV. Although the focus of this work is on photoelectron lifetimes in the high-energy >20 -eV region, a comparison with Tr-2PPE data allows us to gain valuable physical insights. In general, electron–electron Coulomb interactions are energy-dependent due to different screening properties at different energies in a material (44). Here, for convenience, we assume the Coulomb matrix element M is a constant and select values by fitting to the experimental data. To further determine the Coulomb matrix element, we compare the photoexcited electron lifetimes measured using spin-integrated Tr-2PPE on Cu (3) and Ni (6) with our atto-ARPES results and models. For Cu, we have $M^{\uparrow\uparrow} = M^{\downarrow\downarrow} = M$, because the DOS for electrons with majority (\uparrow) and minority (\downarrow) spins are the same. For Ni, as shown in Fig. 4C, *Inset*, there are spin-dependent DOS differences, so we assume $|M^{\uparrow\uparrow}/M^{\downarrow\downarrow}| = 0.5$ and $M = \sqrt{\frac{|M^{\uparrow\uparrow}|^2 + |M^{\downarrow\downarrow}|^2}{2}}$ to get agreement with the spin-dependent electron lifetime measured at low energies (6). The spin-averaged excited electron lifetime $\tau = \frac{2\tau_1\tau_2}{\tau_1 + \tau_2}$ is plotted in Fig. 4B as solid lines for Cu and Ni, and Fig. 4C plots the ratio between spin-up and spin-down electron lifetimes (τ_1/τ_2). Most interestingly, we find that the photoexcited-electron lifetime in Cu can be explained by a mostly energy-independent Coulomb matrix element ($M = 1.4$) throughout the entire energy range from 0.5 to 40 eV. The presence of the d -band screening in the low energy range (<3 eV) is well known for Cu, which increases the lifetime by approximately a factor of 2.5 (17, 47). In stark contrast, our atto-ARPES measurements suggest a stronger energy dependence of the Coulomb matrix element in Ni: $M = 1.8$ is best for high-energy photoelectrons and is close to that observed in Cu, whereas $M =$

0.6 is best for low-energy photoelectrons, which are influenced by both screening and scattering.

Considering that electron screening does not have a strong influence on the photoelectron lifetime in the high energy range (20, 22), we can extract the influence of the bare electron–electron Coulomb interactions (no screening) at high energies and extend the corresponding matrix element to the low energy range (the solid blue line in Fig. 4B). The measured lifetime at low energy in Ni is more than one order of magnitude longer than the bare electron–electron scattering limit, as shown in Fig. 4B. Most interestingly, we find that the experimentally measured low-energy excited electron lifetime in Ni gradually approaches the bare electron–electron scattering limit (solid blue line in Fig. 4B) defined by our atto-ARPES measurement at an energy $E_{crit} \sim 3$ eV above E_F . This further corroborates our findings, because screening is expected to diminish at these higher energies (22). Comparing Cu and Ni, our results strongly suggest the presence of enhanced electron screening in Ni at low energies, which can be attributed to the high DOS at the Fermi energy based on our DFT calculations (Fig. 4C, *Inset*) (6). From the above, we conclude that atto-ARPES can extend measurements of photoexcited-electron lifetimes to higher energies (>20 eV) to distinguish and quantify fundamental electron interactions such as electron scattering and screening, as well as the influence of resonant interband transitions. Compared with other approaches, atto-ARPES also has the unique ability to distinguish band-specific electron–electron scattering for direct comparison with theory and can exclude other contributions such as hot electrons and intermediate-state refilling (6, 8, 48).

Finally, we note that spin-dependent electron–electron scattering in ferromagnetic materials is responsible for many interesting

phenomena, including laser-induced demagnetization (8), superdiffusive spin transport, and giant magnetoresistance (49). Low-energy spin-dependent electron lifetimes have been studied, providing much valuable information (5, 6). However, to date it has not been possible to experimentally isolate electron–electron scattering, due to strong contributions to the measured lifetimes from electron screening from localized *d*- and *f*-band electrons, as well as contributions from other interactions (e.g., phonons and impurities). By probing high-energy photoelectron lifetimes, where electron screening becomes negligible, spin-resolved atto-ARPES could probe spin-dependent electron–electron scattering, which could help uncover fundamental magnetic properties.

Conclusion

In conclusion, we show that attosecond electron interactions in metals can be studied using energy-, polarization-, and angle-resolved atto-ARPES, allowing us to distinguish the contributions of occupied and unoccupied bands to the photoelectron lifetimes. Strong electron–electron scattering in the unfilled *d* band of Ni decreases the lifetime of photoelectrons by ~ 100 as relative to the photoelectrons emitted from the same band of Cu. Most interestingly, we find that dynamical screening influences high-energy photoelectrons much less than low-energy photoelectrons and is different for Cu and Ni due to the difference in material band structure. As a result, spin-dependent atto-ARPES with high-energy excitation is a unique tool to exclusively study the fundamental processes of spin-dependent electron–electron scattering in magnetic materials and also to quantify the contributions of scattering and screening for low-energy excitations. In the future, atto-ARPES can also be used to extract valuable information about fundamental electron–electron interactions in a host of

materials including strongly correlated materials and modern quantum materials.

Methods

We use laser-assisted photoemission and RABBITT to measure the photoelectron lifetimes for different initial and final states. Photoemission from the solid surface is induced by attosecond pulse trains from HHG. The HHG pulse trains are generated in a 150- μm -diameter, 1-cm-long, gas-filled capillary waveguide, driven by ~ 2 mJ, 26-fs laser pulses at 780 nm wavelength from a Ti:sapphire amplifier system. We use different noble gases (Xe, Kr, and Ar) to cover a broad extreme ultraviolet (EUV) photon energy range from 16 to 42 eV (corresponding to HHG orders 11–27). A phase-locked linearly polarized IR probe is recombined collinearly with the HHG pulse trains and focused onto the surface with a FWHM spot size of 250 μm and peak intensity of 2.8×10^{11} W/cm². The polarization of the IR probe is p-polarized for all our measurements. In the presence of both the attosecond pulse trains and the IR probing field, the angle-resolved photoelectron spectra are modulated as a function of the pump-probe time delays due to quantum-path interference (RABBITT, see Fig. 2C), which is recorded by a hemispherical photoelectron analyzer.

ACKNOWLEDGMENTS. We thank J. Ruz, A. Becker, C. Smallwood, G. Mancini, and C. Powell for helpful discussions. This work was done at JILA. This work was supported by the NSF through JILA Physics Frontiers Center Grant PHY-1125844 and Gordon and Betty Moore Foundation EPIQS Award GBMF4538 and Department of Energy (DOE) Office of Basic Energy Sciences X-Ray Scattering Program Award DE-SC0002002 for the spin-dependent scattering aspect of this work (all to M. Murnane and H.K.). Work at University of Wisconsin–Madison was supported by the Air Force Office of Scientific Research Grant FA9550-16-1-0141 (to T.S. and M. Mavrikakis). This work was also supported by the Swedish Research Council and Wallenberg Foundation Grant 2015.0060 (to P.M.O.); NSF Grant PHY 1464417, the DOE Chemical, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, and the Humboldt Foundation (U.T.); and Deutsche Forschungsgemeinschaft Grant SFB/TRR 173 “Spin+X” (to M.A., S. Eich, S. Emmerich, and M.P.).

- Haight R (1995) Electron dynamics at surfaces. *Surf Sci Rep* 21:275–325.
- Hertel T, Knoesel E, Wolf M, Ertl G (1996) Ultrafast electron dynamics at Cu(111): Response of an electron gas to optical excitation. *Phys Rev Lett* 76:535–538.
- Bauer M, Marienfeld A, Aeschlimann M (2015) Hot electron lifetimes in metals probed by time-resolved two-photon photoemission. *Prog Surf Sci* 90:319–376.
- Schmuttenmaer CA, et al. (1994) Time-resolved two-photon photoemission from Cu(100): Energy dependence of electron relaxation. *Phys Rev B Condens Matter* 50:8957–8960.
- Aeschlimann M, et al. (1997) Ultrafast spin-dependent electron dynamics in fcc Co. *Phys Rev Lett* 79:5158–5161.
- Knorren R, Bennemann KH, Burgermeister R, Aeschlimann M (2000) Dynamics of excited electrons in copper and ferromagnetic transition metals: Theory and experiment. *Phys Rev B* 61:9427–9440.
- Rudolf D, et al. (2012) Ultrafast magnetization enhancement in metallic multilayers driven by superdiffusive spin current. *Nat Commun* 3:1037.
- Mathias S, et al. (2012) Probing the timescale of the exchange interaction in a ferromagnetic alloy. *Proc Natl Acad Sci USA* 109:4792–4797.
- Hellmann S, et al. (2012) Time-domain classification of charge-density-wave insulators. *Nat Commun* 3:1069.
- Nessler W, et al. (1998) Femtosecond time-resolved study of the energy and temperature dependence of hot-electron lifetimes in Bi₂Sr₂CaCu₂O_{8+ δ} . *Phys Rev Lett* 81:4480–4483.
- Perfetti L, et al. (2007) Ultrafast electron relaxation in superconducting Bi(2)Sr(2)CaCu(2)O(8+ δ) by time-resolved photoelectron spectroscopy. *Phys Rev Lett* 99:197001.
- Huber R, et al. (2001) How many-particle interactions develop after ultrafast excitation of an electron-hole plasma. *Nature* 414:286–289.
- Lindhard J (1954) On the properties of a gas of charged particles. *Mat Fys Medd K Dan Vidensk Selsk* 28:37.
- Quinn JJ, Ferrell RA (1958) Electron self-energy approach to correlation in a degenerate electron gas. *Phys Rev* 112:812–827.
- Landau LD (1957) The theory of a Fermi liquid. *Sov Phys JETP* 3:920–925.
- Landau LD (1957) Oscillations in a Fermi liquid. *Sov Phys JETP* 5:101–108.
- Campillo I, Pitarke JM, Rubio A, Zarate E, Echenique PM (1999) Inelastic lifetimes of hot electrons in real metals. *Phys Rev Lett* 83:2230–2233.
- Echenique PM, Pitarke JM, Chulkov EV, Rubio A (2000) Theory of inelastic lifetimes of low-energy electrons in metals. *Chem Phys* 251:1–35.
- Ladstädter F, Hohenester U, Puschnig P, Ambrosch-Draxl C (2004) First-principles calculation of hot-electron scattering in metals. *Phys Rev B* 70:235125.
- Aryasetiawan F, et al. (2004) Frequency-dependent local interactions and low-energy effective models from electronic structure calculations. *Phys Rev B* 70:195104.
- Aryasetiawan F, Karlsson K, Jepsen O, Schönberger U (2006) Calculations of Hubbard U from first-principles. *Phys Rev B* 74:125106.
- Springer M, Aryasetiawan F (1998) Frequency-dependent screened interaction in Ni within the random-phase approximation. *Phys Rev B* 57:4364–4368.
- Rundquist A, et al. (1998) Phase-matched generation of coherent soft X-rays. *Science* 280:1412–1415.
- Zhang CH, Thumm U (2009) Laser-assisted photoemission from adsorbate-covered metal surfaces: Time-resolved core-hole relaxation dynamics from sideband profiles. *Phys Rev A* 80:32902.
- Miaja-Avila L, et al. (2006) Laser-assisted photoelectric effect from surfaces. *Phys Rev Lett* 97:113604.
- Pazourek R, Nagele S, Burgdörfer J (2015) Attosecond chronoscopy of photoemission. *Rev Mod Phys* 87:765–802.
- Schultze M, et al. (2010) Delay in photoemission. *Science* 328:1658–1662.
- Klüber K, et al. (2011) Probing single-photon ionization on the attosecond time scale. *Phys Rev Lett* 106:143002.
- Locher R, et al. (2015) Energy-dependent photoemission delays from noble metal surfaces by attosecond interferometry. *Optica* 2:405–410.
- Paul PM, et al. (2001) Observation of a train of attosecond pulses from high harmonic generation. *Science* 292:1689–1692.
- Zhang C-H, Thumm U (2010) Electron-ion interaction effects in attosecond time-resolved photoelectron spectra. *Phys Rev A* 82:43405.
- Bovensiepen U, Ligges M (2016) PHYSICS. Timing photoemission—Final state matters. *Science* 353:28–29.
- Tao Z, et al. (2016) Direct time-domain observation of attosecond final-state lifetimes in photoemission from solids. *Science* 353:62–67.
- Hermanson J (1977) Final-state symmetry and polarization effects in angle-resolved photoemission spectroscopy. *Solid State Commun* 22:9–11.
- Hüfner S (2003) *Photoelectron Spectroscopy: Principles and Applications* (Springer, Berlin), 3rd Ed.
- Roth F, Lupulescu C, Darlatt E, Gottwald A, Eberhardt W (2016) Angle resolved photoemission from Cu single crystals: Known facts and a few surprises about the photoemission process. *J Electron Spectrosc Relat Phenom* 208:2–10.
- Goldmann A, Altmann W, Dose V (1991) Experimental widths of excited electron states in metals. *Solid State Commun* 79:511–514.
- Gurtubay IG, Pitarke JM, Echenique PM (2004) Exchange and correlation effects in the relaxation of hot electrons in noble metals. *Phys Rev B* 69:245106.
- Kliwer J, et al. (2000) Dimensionality effects in the lifetime of surface states. *Science* 288:1399–1402.
- García-Lekue A, Pitarke JM, Chulkov EV, Liebsch A, Echenique PM (2003) Role of occupied *d* bands in the dynamics of excited electrons and holes in Ag. *Phys Rev B* 68:45103.
- Quinn JJ (1963) The range of hot electrons and holes in metals. *Appl Phys Lett* 2:167–169.
- Quinn JJ (1962) Range of excited electrons in metals. *Phys Rev* 126:1453–1457.
- Borisov A, Sánchez-Portal D, Muiño RD, Echenique PM (2004) Building up the screening below the femtosecond scale. *Chem Phys Lett* 387:95–100.

