BUNSEN-MAGAZIN · 25. JAHRGANG · 5/2023

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Attosecond Electron Dynamics in Solids as Testbed for Electronic Structure Theory

Even more than 100 years after Albert Einstein's seminal work on the photoelectric effect [1] the process and in particular its dynamics still pose fascinating challenges. Although the majority of photoemission signatures are quite successfully described based on Einstein's model of the process this does not work for all phenomena. For example, in non-negligible cases the absorption of a photon leads to the emission of more than one electron due to correlation effects in the electronic system demonstrating that more complex many-body effects must be considered [2]. As briefly outlined here, the dynamics of the photoelectron emission process also provide insight into the intricacies of the many-body physics and could challenge and test our present understanding of the electronic structure theory. Hence, the time-resolved investigation of photoelectron emission dynamics opens an interesting and valuable pathway to improve our understanding of complex electronic systems such as solids or molecules.

What are the typical timescales of the photoelectric effect? Valence, conduction and continuum electrons in solids move at typical velocities of few 10^6 m s^{-1}, i.e., about and above typical Fermi velocities of a material. After photoexcitation of an electron this electron interacts strongly with the surrounding other electrons and thus quickly looses energy in scattering events. Such inelastic events determine the mean free path of a photoexcited electron and give rise to the so-called universal curve of photoemission [3]. Notably electrons with roughly 10-100 eV kinetic energy have an inelastic mean free path of down to a few Ångstrom enabling the surface sensitivity of photoelectron spectroscopies. Based on the typical velocity and inelastic mean free path the timescale of the photoemission process can be estimated to lie in the range a 100 to a few 100·10^{-18} s (1 attosecond = 10^{-18} s), depending from how deep inside the material the emitted electron has to travel until it is emitted into the vacuum.

Advances in Laser Technology and Spectroscopy Methods

To directly time-resolve photoelectron dynamics sub-femtosecond (< 10^{-15} s) time-resolution is needed. High harmonic generation (HHG) [4] and carrier envelope phase (CEP) stabilization of few-cycle IR laser pulses [5] has paved the way to spectroscopies with attosecond time resolution and attosecond physics in general [6]. In HHG the non-perturbative interaction of intense short light pulses with atoms leads to the emission of attosecond pulse trains of radiation. The HHG spectrum is composed of equidistant spectral peaks at odd harmonics of the driving field up to a maximum energy, i.e., the high-energy cut-off of the HHG spectrum. When driving the atoms with few-cycle light pulses with an electric field that is always maximal at the pulse peak intensity, i.e., with a CEP stable laser pulse having a cosine-shaped electric field with respect to the center of the pulse envelope, the harmonic radiation with the highest photon energy is produced only once during the interaction of a single laser pulse with the atom and thus the modulation of the HHG spectrum in the cut-off range vanishes. Spectral filtering using a band-pass mirror yields then single light pulse with attosecond pulse duration [6]. These developments of laser technology enabled investigating photoelectron dynamics directly in the time domain.

An attosecond light pulse or an attosecond pulse train alone does not yet provide temporal resolution. This is typically achieved by using a temporal gate which also interacts with the system. Several techniques have been established to monitor electron dynamics with attosecond time resolution. For example, attosecond streaking spectroscopy relies on the generation of a photoelectron with a single attosecond light pulse and its subsequent interaction with a time-correlated intense few-cycle laser field and allowed to directly monitor the electric field evolution of an ultrashort laser pulse [7]. As soon as the photoelectron is excited it is exposed to the also present strong streaking field and depending on the time-delay of the attosecond pulse excitation with respect to this streaking field the emitted electrons are either accelerated or decelerated. From the energy shift as function of this delay the electric field of the streaking field can be reconstructed.

Attosecond time resolution is also achieved using attosecond pulse trains and longer gate pulses as they are for example employed for the reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) [8]. Streaking and RABBITT rely on the interaction of a photoelectron with the time-correlated gate field. In both cases the attosecond pulse sets the excitation time marker. However, the role of excitation and gate can also be reversed. In attosecond time-resolved absorption spectroscopy the transient system modification by the strong field of a few-cycle pulse is probed by the time-correlated absorption of a single attosecond pulse [9].

Attosecond Time-Resolved Photoemission from Solids

In a first demonstration that the dynamics of the photoemission process from solids can indeed be resolved Cavalieri et al. em-

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DOI-Nr.: 10.26125/21p3-7z29

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ployed attosecond streaking spectroscopy for investigating the photoelectron emission dynamics for a W(110) surface [10]. The streaking effect for photoelectrons emitted from the W 4f core level and the conduction band showed a relative temporal shift of 110±70 as, with the emission from the conduction band happening first. This observation demonstrated for the first time that the photoemission process is not instantaneous and that intrinsic relative delays between different emission channels are in the order of several tens to hundreds of attoseconds. In addition, the occurrence of streaking sets also an upper limit for duration of the photoemission process itself. The emission process may not take longer than about half of the oscillation period of the streaking field since otherwise the streaking signature would be smeared out. At the time being the observed relative delay was attributed to the dispersion of the continuum band structure of tungsten and a theoretically determined inelastic mean free path [10].

Since this first demonstration several other attosecond time-resolved photoemission experiments have been performed. Using again W 4f emission from a W substrate through Mg overlayers with variable thickness demonstrated the impact of propagation effects on the photoemission delay seen in streaking spectroscopy [11]. Each atomic Mg layer adds about 45 as to the relative delay which is in good agreement with a free electron-like propagation of the 4f-photoelectrons in the Mg layers. For other more complex materials the continuum band structure can no longer be approximated by almost free electron-like bands and additional delays occur. This has been reported for Ag(111) and Au(111) [12], Ni(111) [13], Mg(0001) [14], and Cu(111) [15] surfaces. In these cases, significant changes of the photoemission delay as function of the final state energy are reported and attributed to the continuum band structure of the materials.

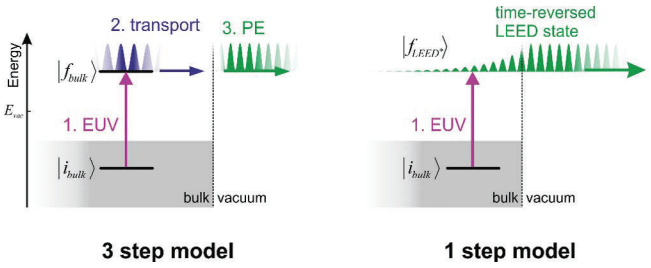

Fig. 1: Comparison of three-step and one step model for photoemission.
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Solid state photoemission is conceived predominantly within either the three-step or the one-step model (Fig. 1). In the three-step model unoccupied bulk states, transport in these states and finally refraction into vacuum states at the bulk-vacuum interface determine the photoemission process. In the three-step model the close vicinity of the bulk-vacuum interface on the photoexcitation step is neglected and it is questionable whether a Bloch state properly describes an excited electron that has an inelastic mean free path of only a few Ångstrom. In contrast, the one-step model relies on time-reversed low energy electron diffraction (LEED) states as final states for the photoemission process [16], which are directly populated by the extreme ultraviolet (EUV) pulse. The one-step model thus captures the bulk-vacuum interface by including also evanescent waves penetrating from the vacuum into the bulk as possible photoemission final states. However, note that both models have their limitations and it is a worthwhile question whether attosecond time-resolved spectroscopy could provide new insights into the photoemission process and thus could serve to improve these fundamental models.

Intra-Atomic Delays in Photoemission

Attosecond time-resolved photoemission from WSe_2 shows that intra-atomic delays must be considered in the photoemission process [17]. The relative delays between four different photoemission channels revealed that the angular momentum of the initial state significantly affects the emission dynamics. Emission from initial states with larger angular momentum are delayed with respect to photoelectrons, which are emitted from initial states with lower angular momentum. This effect can be understood in a rather intuitive picture: The dipole selection rule for dipole transitions dictates an angular momentum change by ±ħ and thus an initial state with high angular momentum couples to final states with high angular momentum. An angular momentum in the final state however means that the excited photoelectron travels on a curved trajectory and thus has a smaller radial velocity. Only in a s-like final state the photoelectron will be emitted from its origin on a straight outward trajectory. WSe_2 is a well suited system for investigating the impact of such angular momentum effects since the four investigated emission channels correspond to sp valence band, Se 4s, Se 3d, and W 4f initial states, i.e., largely different angular momenta are involved in the different emission processes. Explaining the observed relative delays between these emission channels required to take into account both excited electron wave packet propagation and the inelastic mean free path as well as inter-atomic delays. Both effects contribute with the same magnitude to the relative emission delays.

Whereas this effect was known for free atoms [18] it was until then neglected for solid state photoemission since angular momentum is no longer a conserved quantity in a system with discrete translational symmetries. Although the Bloch states are derived from atomic states their spherical symmetry is broken in the crystal. Based on the reported intra-atomic delays due to various involved angular momentum states [17] we propose to expand the photoemission model accordingly. In an individual photoexcitation process initially a spatially correlated electron-hole pair is generated within the atom from which the photoelectron is emitted. Similar to an exciton this breaks the discrete translational symmetry of the lattice and the involved electronic states still have the signature of a Coulomb bound system and angular momentum is conserved in the initial emission step. An adapted photoemission model (Fig. 2) must therefore capture the exciton-like behavior in the initial step and has to account for the complete many-body correlation effects within the atom. The resulting atom-like excited wave packet couples to the spatially extended photoemission final state, which might be modelled based either within the one-step or three-step model. Up to now such a unified model of the photoemission process is missing and the theoretical treatment of photoemission delays still relies on separating the intra-atomic and propagation effects [17]. This is clear evidence that attosecond time-resolved photoemission spectroscopy challenges our present understanding of the photoemission process and could serve as a testbed for further developing the non-equilibrium electronic structure theory.

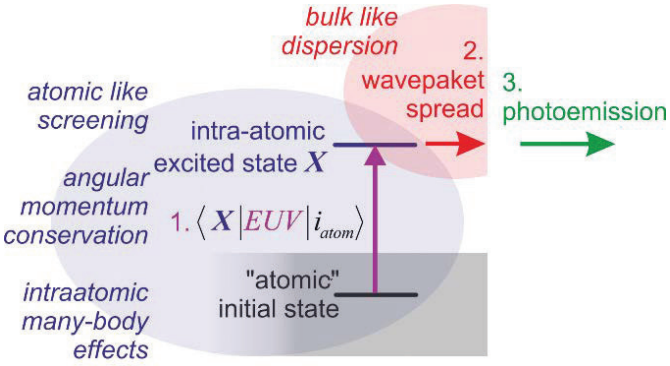

Fig. 2: Adapted photoemission model taking intra-atomic delays into account. © Walter Pfeiffer.

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Since 2006 Walter Pfeiffer leads a research group at Bielefeld University focusing on attosecond time resolved spectroscopy of electron dynamics in solids and ultrafast nanooptics. Having studied Physics at the University of Konstanz finalizing with a PhD in the field of nuclear solid state physics he decided to switch fields completely and started working in the field of ultrafast science. Under the guidance of Prof. Dr. Gustav Gerber Walter Pfeiffer pioneered the combination of femtosecond laser spectroscopy and scanning tunneling microscopy as well as studies of ultrafast dynamics in nanoscale systems. The demonstration of plasmon enhanced multiphoton photoemission from supported metal nanoparticles laid the ground for subsequent research on spatio-temporal coherent control of nanoscale excitations and multidimensional coherent spectroscopy. Much of the related research is performed in close collaboration with Prof. Tobias Brixner (University of Würzburg) and Prof. Martin Aeschlimann (TU Kaiserslautern), with whom Walter Pfeiffer chaired the DFG Priority Program "Ultrafast Nanooptics" from 2009 to 2015. Ultrafast photoemission electron microscopy is now an established tool for investigating ultrafast nanoscale phenomena. Since his move to Bielefeld Walter Pfeiffer together with Prof. Dr. Dr. Sc. h.c. Ulrich Heinzmann has built up a laboratory for attosecond time-resolved photoelectron spectroscopy from solids. Besides fundamental research Walter Pfeiffer is involved as Scientist for Future and organizes outreach events to the public such as for example the Klimabahn in Bielefeld or public lectures.