Angle-resolved photoemission from organic semiconductors: beyond the plane-wave final state

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Angle-resolved photoemission spectroscopy (ARPES) is traditionally described with the help of Fermi's Golden rule. This typically requires an approximation for the state of the emitted photoelectron. For an instructive interpretation of ARPES data it was a huge step forward to realize that a plane-wave final state can be sufficient in certain situations. However, we here demonstrate that the plane-wave approximation has its limits and can even engender severe deviations from measured ARPES. Examples for such situations are cases in which wave-vector of the outgoing electron and the light polarization are perpendicular to each other and situations where the photoemission signal depends on the photon energy.

To comprehensively predict ARPES, our aim is to go beyond restrictions imposed by common final-state approximations. Therefore, we apply a first principles time-dependent density-functional theory (TDDFT) approach that simulates the entire photoemission process in real-time. In this way we sidestep Fermi's Golden rule. Since the dynamics of the photoelectrons is intrinsically embodied in the time evolution of the entire system, the major strength of the real-time approach is that it completely obviates stationary final-state approximations. Furthermore, the interaction of the photoelectron with the remaining system is fully treated on the DFT level.

For the organic semiconductor benchmark molecule PTCDA we demonstrate that the TDDFT approach is able to predict ARPES for situations beyond the plane-wave approximation. A prominent example is the circular dichroism in the angular distribution (CDAD) which quantifies the difference in the photoemission signal depending upon the photon helicity. It is strongly pronounced for ordered monolayers of PTCDA. Similarly challenging to predict is the significant energy dependence of CDAD intensities which can even result in a complete inversion of the CDAD pattern in the case of the PTCDA HOMO.

One-step theory of pump-probe photoemission with applications to two-photon photoemission

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A general theoretical framework for the description of pump-probe photoemission will be presented. The approach is based on a general treatment of the photo emission process using the Keldysh formalism for the lesser Green function to describe the real-time evolution of the electronic degrees of freedom in the initial state after a strong pump pulse that drives the system out of equilibrium. The final state is represented by a time-reversed low energy electron diffraction (LEED) state. The formalism allows for a quantitative calculation of the time-dependent photocurrent that results from core or valence-band excitations, and is applicable to simple metals or more complex materials like topological insulators. Our approach covers as a special case the two-photon photoemission (2PPE) scenario where both the pump-pulse and the probe pulse are weak in intensity. We present as a first application of our fully relativistic implementation within the Munich SPR-KKR package [2] calculated 2PPE spectra from Ag(100), where the first image state serves as intermediate state to probe the occupied bandstructure below the Fermi level [3]. Extensions of the approach to more complex situations as well as its application to other types of spectroscopy will be discussed.

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Moire superlattice effects in ARPES of graphene/hBN heterostructures

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We model the angle-resolved photoemission spectra (ARPES) of graphene on hexagonal boron nitride (hBN) and show their characteristic features arising due to the formation of miniband structure for graphene electrons in the periodic moir´e pattern. We show that detailed analysis of these features can be used to pin down the microscopic mechanism of the interaction between graphene and hBN. We also show how the presence of a moir´e-periodic strain in graphene or scattering of photoemitted electrons off hBN can be distinguished from the miniband formation.

Bridging density-functional and many-body perturbation theory: orbital-density dependence in electronic-structure functionals

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Energy functionals which depend explicitly on the orbital densities (ODD), instead of the total charge density, appear when applying self-interaction corrections to density-functional theory. In these cases (e.g. the Perdew-Zunger [1] and Koopmans-compliant [2,3] approaches) the total energy loses invariance under unitary rotations of the orbitals, and the minimization of the functionals leads to orbital-dependent Hamiltonians.

We show that it is possible to identify the orbital-dependency of densities and potentials with an effective and discretized frequency-dependency, in close analogy to the quasi-particle approximation of frequency-dependent self-energies and naturally oriented to interpret electronic spectroscopies [4]. Some of the existing ODD functionals are analyzed from this new perspective. Numerical results for the electronic structure of gas-phase molecules (within the Koopmans-corrected class of functionals) are computed and found in excellent agreement with photoemission (UPS) data [5,6]. \\

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Time-resolved spectroscopy of surface and interface electronic states with two-photon photoemission

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Photoemission spectroscopy from optimally-tuned range-separated hybrid functionals

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Characterization of Valence Band Atomic Orbitals by Detection of Angular-Momentum-Polarized Auger Electrons

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Upon a core level excitation by circularly polarized light (CPL), the angular momentum of light, i.e. helicity, is transferred to the emitted photoelectron. This phenomenon can be confirmed by the parallax shift measurement of the forward focusing peak (FFP) direction in a stereograph of the atomic arrangement. The core hole may decay via Auger electron emission, where in this two electron process the angular momentum has to be conserved as well. We succeeded in detecting angular-momentum-polarized Cu LMM Auger electrons at the L absorption threshold, where the excited core electron is trapped at the conduction band. By combining Auger electron spectroscopy with the FFP shift measurements at absorption threshold, element- and magnetic-quantum-number-specific hole states can be generated in the valence band. This phenomenon can be used for the atomic orbital characterization of valence density of states at the specific atomic sites.

The free electron final state approximation in ARPES – how far can we get?

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Angle resolved photoemission spectroscopy (ARPES) is commonly known as a powerful probe of the one-electron removal spectral function in ordered solid state. With increasing efficiency of light sources and spectrometers, experiments over a wide range of emission angles become more common. Consequently, the angular variation of ARPES spectral weight – often times termed “matrix element effect” – enters as an additional source of information.

In this presentation, we will develop a simple free electron final state model to describe the ARPES intensity distribution. We will find that the spectral weight of a Bloch band is essentially determined by the Fourier transform of its associated Wannier orbital, modulo a polarization term. While the former is giving direct information on the shape of the electronic wave function, the latter can give rise to surprising geometric effects. We will discuss a variety of instructive experimental showcases for which this simple formalism works well and discuss the limits of this approach.

Final-state scattering in electronic structure imaging by ARPES

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Photoemission tomography: fundamentals and applications to the geometric and electronic structure of ordered organic layers

Puschnig, Peter

(Karl-Franzens-University Graz, Institut für Physik, Fachbereich Theoretische Physik, Graz, Austria)

Photoemission Tomography: Why didn´t we do this 30 years ago?

Ramsey, Michael

(Karl-Franzens-University Graz, Institute of Physics, Graz, Austria)

Exploring the Photoemission Intensity in ARPES: Information Beyond Band Structure

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Time-resolved angle resolved photoelectron spectroscopy within TDDFT: What can we learn and what are the limitations?

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Angle-resolved UPS of large and complex molecules: History, problems and future possibility

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We will briefly summarize history of angle-resolved UPS (ARUPS) studies of large and complex molecular systems to see experimental and theoretical problems in ARUPS studies of sufficient accuracy and precision. Then we will discuss (i) theoretical issues that must be grasped for better description of the ARUPS data from an experimentalist’s viewpoint, (ii) light and shadow of the ARUPS imaging, namely the orbital tomography, in obtaining information on the wave functions of molecular systems, and (iii) what is necessary for its glorious possibility.

Challenges and Prospects of Femtosecond Time-Resolved ARPES

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will be provided later

Strong-field control of photoelectron angular distributions

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The use of shaped ultrashort laser pulses with controllable envelope, instantaneous frequency and polarization allows manipulating the electron dynamics of quantum systems with unprecedented accuracy. We discuss control of photoelectron angular distributions (PAD) by multiphoton excitation and ionization with intense shaped laser pulses. For the measurement of the resulting three-dimensional PAD we combine velocity map imaging (VMI) with a novel tomographic reconstruction method [1].
The examples presented in the talk include strong-field control of multiple electronic states [2], generation and tomographic reconstruction of tailored free electron wave packets [3,4] along with a technique to derive transition matrix elements from tomographic data [4]. In addition, recent results on multiphoton photoelectron circular dichroism (PECD) of small organic chiral molecules with a femtosecond laser source [5,6] will be shown.

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Phase-dependent electronic structure in superstructure monolayers of polycyclic aromatic hydrocarbons

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The electronic structure of superstructure monolayers of polycyclic aromatic hydrocarbons physisorbed on Au(111) will be discussed. In the case of hexa-peri-hexabenzocoronene, we found two different ordering phases of (5 x 5) and (3\sqrt{3} x 3\sqrt{3})R30 by controlling the growth condition. High-resolution angle-resolved photoemission spectra of these superstructure monolayers show the phase-dependent angular distribution in the vibrationally-resolved photoemission intensity and its energy position. Based on these findings, we discuss (i) the anisotropic distribution in the photoemission intensity including the hole-vibration coupling and (ii) the unexpected lateral pi-band dispersion