

Quantifying photoemission of organic molecular films

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In recent years, a renaissance of angle-dependent photoemission spectroscopy in the field of organic electronics could be observed. This development was mainly driven by two circumstances. First, it could be shown that - opposite to the general belief - the angular dependence of the photoemission current from oriented molecular films can be understood by assuming a plane wave as the final state of the photoemission process. This approximation enables a simple and intuitive interpretation of the transition matrix element in terms of the Fourier transform of the initial state orbital. The second reason for the renewed interest in ARPES for organic molecular films has to do with developments in experimental instrumentation. To date a number of experimental facilities have been (or are being) developed which allow for an efficient collection and angle-resolved detection of photoelectrons over a wide angular range. Moreover, systematic studies of the photon energy or polarization dependence of ARPES intensity are in the focus of current and future experimental research. The current proposal builds on the expertise gathered during its predecessor FWF-P23190-N16 "Understanding photoemission of organic molecular films". In this project, the evaluation of the transition matrix element for the photoemission cross section had been simplified at several points. First, the initial state was taken to be a single-electron orbital. Second, the initial state energies and orbitals were taken from density functional theory. Third, the photon energy and polarization dependence has largely been restricted to linearly polarized light with a fixed photon energy. And last, the final state had been approximated by a plane wave. The current project aims at crossing the above-mentioned frontiers by improving (A) initial state energies and wave functions, (B) incorporate scattering effects in the final state, and (C) shed light on the polarization dependence of the photoemission cross section. Regarding (A), hybrid functionals, on the one hand, and quasi-particle corrections, on the other, will be employed to investigate initial state energies as well as wave functions. Both ingredients are essential for an accurate description of the photoemission cross section of organic molecular layers. Concerning the description of the final state (B), the project will go beyond the plane wave final state approximation by employing the Lippmann-Schwinger equation from quantum-mechanical scattering theory. By taking into account the scattering potential, resonances in the continuum final states, and thus dynamic effects in the photoemission cross section, will be taken into account. Thereby, the project will improve the description of photon energy dependence of the cross section aiming at a fully quantitative representation of its angular dependence. Regarding point (C), the project will extend the theoretical description of the photoemission cross section to circularly polarized light. This will allow for the simulation of ARPES experiments utilizing the circular dichroism in the angular distribution (CDAD). These CDAD simulations will be ideally suited to investigate final state effects beyond the plane wave approximation. Moreover, studying the CDAD effect offers the possibility recover additional information on the initial state (its phase symmetry).