Exploring the foundations of photoemission tomography

Project number: I 3731

As is generally known, in quantum mechanics a well-defined position and momentum of a particle has to be replaced by a complex-valued wave function, an orbital, whose absolute value squared describes the probability density of finding a particle. Of particular interest are the orbitals of the valence band which exhibit the lowest binding energies and are involved in chemical interactions. These valence band orbitals constitute the specific chemical, electrical and optical properties of atoms, molecules or novel nano-structures. Experimental methods to determine the characteristics of orbitals are ranging from femto-second laser spectroscopy to scanning probe techniques at ultra-cold temperatures. Although these approaches have attracted broad interest, there are several limitations, for instance, only rather simple molecules under restricted conditions, such as ultra-cold temperatures to prevent molecular diffusion, can be investigated. In contrast, the experimental approach used within this proposal, angle-resolved photoemission spectroscopy, can also be applied at technological relevant temperatures and for a large range of molecule / substrate combinations. Moreover, our method, that we termed photoemission tomography, offers the possibility to obtain images of molecular orbitals in three dimensions. To this end, a single crystalline sample, onto which the organic molecules have been deposited under ultra high vacuum conditions, is illuminated with ultra-violet (UV) light. The photoemitted electrons (photoelectric effect) are then analyzed in terms of their energy and their angular distribution. However, the interpretation of the experimental data is not straight forward. Specifically, certain assumptions have to be made about the quantum mechanical final state into which the electron is transferred from its initial bound state. The most simple ansatz is to use a free electron state, a plane wave, for this final state. This approximation offers the advantage that the experimental data can be interpreted in a particularly simple manner, which allows one, among other possibilities, to determine molecular geometries, measure momentum distributions of electrons in orbitals and to reconstruct orbital images. The aim of this project is to explore under which experimental conditions - including the geometry of the experimental setup, the energy of the exciting UV light, or the type and size of the investigated molecules - these simplifying assumptions about the final state lead to reliable results. Our team, consisting of surface scientists from the University of Graz and the Forschungszentrum Jülich and experts in metrology and the generation of UV light from synchrotron radiation from the Physikalisch-Technischen Bundesanstalt Berlin, will conduct a series of well-designed experiments to trace out the range of validity of the plane wave approximation. In order to interpret the experimental results and to theoretically predict to which extent the final state differs from such a free-electron state, the project team also comprises experts from the University of Graz in the field of quantum mechanical ab-initio calculations for the electronic structure of molecules and molecular interfaces. The possibility to image molecular orbitals of technological relevant molecules will, on the one hand, certainly widen our fundamental understanding of the concept of quantum mechanical electron orbitals. On the other hand, our results will also allow for the detailed investigation of physical and chemical processes and the interface between organic molecules and inorganic surfaces. Possible technological applications include the tailoring of catalytic surfaces, sensors, novel molecules and nano-structures to be used for energy harvesting (e.g. photovoltaics) or energy storage, or the identification and characterization of yet unknown molecular species.