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Orbital tomography: Molecular band maps, momentum maps and the imaging of real space orbitals of adsorbed molecules



Hannes Offenbacher, Daniel Lüftner, Thomas Ules, Eva Maria Reinisch, Georg Koller*, Peter Puschnig, Michael G. Ramsey*

Institute of Physics, University of Graz, Universitätsplatz 5, 8010 Graz, Austria

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ABSTRACT

The frontier orbitals of molecules are the prime determinants of their chemical, optical and electronic properties. Arguably, the most direct method of addressing the (filled) frontier orbitals is ultra-violet photoemission spectroscopy (UPS). Although UPS is a mature technique from the early 1970s on, the angular distribution of the photoemitted electrons was thought to be too complex to be analysed *quantitatively*. Recently angle resolved UPS (ARUPS) work on conjugated molecules both, in ordered thick films and chemisorbed monolayers, has shown that the angular (momentum) distribution of the photocurrent from orbital emissions can be simply understood. The approach, based on the assumption of a plane wave final state is becoming known as orbital tomography. Here we will demonstrate, with selected examples of pentacene (5A) and sexiphenyl (6P), the potential of orbital tomography. First it will be shown how the full angular distribution of the photocurrent (momentum map) from a specific orbital is related to the real space orbital by a Fourier transform. Examples of the reconstruction of 5A orbitals will be given and the procedure for recovering the lost phase information will be outlined. We then move to examples of sexiphenyl where we interrogate the original band maps of thick sexiphenyl in the light of our understanding of orbital tomography that has developed since then. With comparison to theoretical simulations of the molecular band maps, the molecular conformation and orientation will be concluded. New results for the sexiphenyl monolayer on Al(1 1 0) will then be presented. From the band maps it will be concluded that the molecule is planarised and adopts a tilted geometry. Finally the momentum maps down to HOMO-11 will be analysed and real space orbitals reconstructed.

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The frontier orbitals of molecules are the prime determinants of their chemical, optical and electronic properties. Arguably, the most direct method of addressing the (filled) frontier orbitals is ultra-violet photoemission spectroscopy (UPS). For instance, in the field of organic electronics, standard UPS is often used for studying energy level alignment and charge injection barriers of organic films. Organic molecules have a high propensity to form oriented and ordered structures. This leads to their photoemission having a very distinct angular distribution and the UPS spectra being extremely dependent on the experimental geometry and molecular orientation. If, as is often the case, this is ignored UPS can be misleading as, for instance, the frontier orbitals often have no emission intensity in standard experimental geometries. However, if it is understood angle resolved UPS (ARUPS or ARPES) can be an

extremely powerful tool for studying both the geometric and electronic structure of molecular films and their interfaces [1–24]. Prof. Ueno and his group at Chiba University were one of the first groups to highlight the importance of considering the full hemisphere of photoelectron emission to understand the electronic structure of device relevant conjugated molecules [12–16].

Although UPS is a mature technique, the angular distribution of the photoemitted electrons is generally thought to be too complex to be analysed *quantitatively*. The problem is how to treat the final state. In the early 1970s Gadzuk [25] proposed treating it as a single plane wave which leads to the simple result that the photoemission intensity distribution would be proportional to the Fourier transform (FT) of the initial state. A number of results in the mid 1970s, however, led to it being considered inadequate for the low emission energies of UPS [26]. With the plane wave approximation considered too simple the independent atomic center approximation (IAC) was then adopted. The IAC approximation calculates the emission as an independent, but coherent, sum of spherical waves from individual atomic centres. The IAC can be further developed by

* Corresponding authors. Tel.: +43 3163805219.

E-mail addresses: georg.koller@uni-graz.at (G. Koller), michael.ramsey@uni-graz.at (M.G. Ramsey).

considering scattering of the photoemitted electrons. Ueno and his group have been applying the IAC to interpret the angular dependence of their photoemission results from large molecules [12–16].

More recently it was found that the band maps of thick crystalline films of linear molecules could be well described by the FT of the initial state orbitals making up the molecular bands [1–5], suggesting that the plane wave approximation was a useful description. These, essentially 1 dimensional examples inspired work on 2 dimensional systems where it was found that the momentum distribution for a variety of adsorbate monolayers also agreed with expectations from the FT of the initial state wave functions [3–11]. In the last few years it has been demonstrated that by slicing up the photoemission data cube (photocurrent $I(E, k_x, k_y)$), the thus generated band maps ($I(E, k)$) and momentum maps ($I(k_x, k_y)$ at constant binding energy) can usefully be interpreted within the plane wave approximation. This is becoming known as orbital tomography which allows one to determine molecular geometries [3,11], gain insight into the nature of the surface chemical bond [7,17,18], unambiguously determine the orbital energy ordering in molecular homo- and heterostructures [8,9,18] and even reconstruct orbitals in real space [3,10]. All these results indicate that a simple Fourier transform of the initial state wave functions describes the photoelectron distribution and imply that a plane wave is a good approximation for the final state in photoemission [3]. It is worth noting here that the independent atomic centre approximation (IAC) can be shown to reduce to the plane wave final state result [3,27] if;

- all contributing atomic orbitals are of the same type (e.g. p_z-orbitals),
- the electron emission direction is close to the polarisation vector of the incoming photon,
- the molecule consists of only light atoms (C, N, O) with small scattering cross sections.

To a certain extent most of the orbital tomography experiments on the orbitals of conjugated molecules till now do indeed come close to satisfying these conditions.

In the following we will demonstrate, with selected examples of pentacene (5A) and sexiphenyl (6P), the potential of orbital tomography. First it will be shown how the full angular distribution of the photocurrent (momentum map) from a specific orbital is related to the real space orbital by a Fourier transform. Examples of the reconstruction of 5A orbitals will be given and the procedure for recovering the lost phase information will be outlined. We then move to examples of sexiphenyl. Here we will interrogate the original band maps of thick sexiphenyl [1] in the light of our understanding of orbital tomography that has developed since then. With comparison to theoretical simulations of the molecular band maps, the molecular conformation and orientation will be concluded. New results for the sexiphenyl monolayer on Al(110) will then be presented. From the band maps it will be concluded that the molecule is planarised and adopts a tilted geometry. Finally the momentum maps down to HOMO-11 will be analysed and real space orbitals reconstructed.

The experiments (base pressure $< 5 \times 10^{-10}$ mbar) have been performed on the toroidal energy analyser at the synchrotron radiation facility BESSY II of the Helmholtz-Center Berlin (HZB) (see Refs. [3,7]). This spectrometer is unique in that it can collect the full hemisphere of emitted electrons without changing the photon incident angle (polarisation). Moreover, there is no restriction on the photon incident angle. The Al(110) substrate was judged clean after sputter and annealing cycles if ARUPS of the valence band region only showed the weak Al sp-band (i.e. no contaminant emissions) and a work function of 4.3 eV. The simulated band maps were obtained via Fourier transformed orbitals resulting from ab-initio density functional theory (DFT). Details of the calculations can

be found in the comprehensive theoretical investigation of phenyl and acene oligomers of Ref. [28].

The relationship between the measured photoemission intensity and the FT of the emitting orbital can be illustrated with an Ewald sphere like construction. Fig. 1 shows the HOMO of pentacene (5A) in real space and its corresponding three-dimensional FT, the orbital in reciprocal space. The colour represents the sign or phase of the wave function. The photoemission from the orbital will lead to a particular kinetic energy and k value, represented by the red hemisphere. The intersection of this hemisphere with the orbital in reciprocal space gives the coordinates for the emission from this orbital. The value of the FT on the hemisphere for a kinetic energy of 29.8 eV is shown in Fig. 1. The square of this hemispherical cut yields the prediction for the experimental momentum map for a flat lying 5A molecule.

The first back FT from measured momentum maps to real space orbitals were performed for the HOMO and LUMO orbitals (the latter occupied on bonding) of sexiphenyl adsorbed on Cu(110) [3]. For this the phase, which is naturally lost in experiment, was imposed onto the momentum map data. This procedure is illustrated in Fig. 2 for data from the HOMO of pentacene adsorbed on both Ag(110) and Cu(110) surfaces. From the momentum maps one sees immediately that the molecule adopts different azimuthal orientations on the two surfaces; on Ag it aligns along the [001] while on Cu it is aligned parallel to the close packed row in the [1–10] direction. Comparison to the theoretical real space orbital and predicted momentum map of Fig. 1 also indicates that the molecules have their aromatic plane parallel to the surface. Moreover, the results suggest that the HOMO orbitals of the adsorbed molecules on both surfaces are essentially unaltered from that of the free molecule. This is somewhat surprising as in the case for 5A on Cu(110) the molecule shows strong hybridisation with the surface with the LUMO expressing a large substrate induced intermolecular dispersion and a momentum map that indicates a lateral expansion of 20%. A detailed comparison of 5A on Ag and Cu may be found in Ref. [29]. It is also worth noting that if scattering was to be a major problem to the plane wave approximation it should have manifested itself in the maps of Fig. 2 due to the differences of orientation on Ag and Cu.

Unlike the case for the 5A HOMO of Fig. 2 or the LUMO and HOMO of 6P [3], for many orbitals assuming the phase in the momentum maps is a priori not possible. An example of this would be the LUMO of 5A whose calculated real space orbital and simulated momentum map is shown in Fig. 3. This figure illustrates the phase problem where it is seen that without phase information the FT of the momentum map will lead to a real space orbital of twice the size with an incorrect phase. Recently we have shown how the phase information lost in photoemission can be objectively retrieved by applying an iterative oversampling procedure to the ARUPS momentum maps with the only assumption being the spatial confinement of the orbitals [10]. The procedure is illustrated for the case of the LUMO of 5A which is half filled and appears at the Fermi level when adsorbed on Ag(110). One starts with the experimental momentum map, expressed in Fig. 4 by the black isolines of the square root of the ARUPS intensity, with an arbitrary phase imposed, in this case a random phase. The FT of step 1 leads to a wave function randomly distributed over real space. The not unreasonable assumption that the wave function should be confined to the molecule is then made. This is done by creating a simple rectangular confinement box with roughly the Van der Waals dimensions of 5A and reducing the intensity outside the box by 90% in step 2. The inverse FT (step 3) then leads to a new phase (colour map) and intensity distribution (isolines) in momentum space. The new phase is then applied to the original ARUPS intensity in step 4 to close the iterative loop. As the procedure is repeated the probability distribution inside the confinement box increases at each

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