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Molecular orbital tomography for adsorbed molecules: is a correct description of the final state really unimportant?

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Abstract

The application of the ‘orbital tomography’ technique to obtain direct images of molecular orbitals of adsorbed molecules from angle-resolved photoemission data, first proposed by Puschnig *et al* (2009 *Science* **326** 702), is an extremely attractive idea, but is based on the assumption that the photoemission can be described by a plane wave final state. It is well known that this neglect of the spherical-wave nature of the initial emission and of the role of final state scattering both within the molecule and from the substrate can lead to serious errors. Despite this, in the albeit simple systems studied so far the method appears to work reasonably well. Here we provide a detailed critique of this problem, high-light situations in which the orbital tomography approach is likely to lead to major errors, and propose test experiments that could provide clear information on the extent of these problems.

Introduction

Ultra-violet photoemission (UPS) has proved to be a valuable probe of the molecular orbitals of adsorbed molecules as first demonstrated in studies of the simple diatomic molecule, CO, on Ni surfaces by Eastman and Cashion [1]. Nevertheless, it is not always straightforward to assign specific peaks in the UP spectra to specific molecular orbitals due, in particular, to energy shifts associated with their hybridization with the substrate. Indeed, this problem even arose initially in the case of adsorbed CO [2], and the problem is clearly more severe in much larger molecules with many more energetically closely spaced orbitals. In this regard, the recent suggestion by Puschnig *et al* that one can use measurements of the angular dependence of individual peaks in the UP spectra to *image* the emitting orbital [3–6] (‘orbital tomography’) is extremely attractive, not only aiding identification but potentially showing the influence of chemisorption. The concept has been further developed [7–9] while this general approach has been applied to a range of other multilayer [10, 11] and monolayer molecular adsorption systems [12–16]. An important limitation of this method, however, is that the calculation of the angular distribution of the photoelectron current is based on the assumption that the final state can be approximated by a single plane wave. This means that both the spherical-wave character of the outgoing photoelectron wavefield and the role of final-state elastic scattering by atoms surrounding the emitter(s) are ignored.

Plane wave approximation

In the early development of the theory of angle-resolved UPS (ARUPS) Gadzuk [17–19] proposed that the dominant effect was likely to be the initial-state distribution of the electrons (for example in the bonding orbitals of a chemisorbed atom) and he investigated the photoelectron angular distribution assuming that the final state can be treated as a plane wave. The general form of the photoemission matrix element is $\langle f | \mathbf{A} \cdot \mathbf{p} | i \rangle$, where \mathbf{A} is the vector potential of the field and \mathbf{p} is the momentum operator. Exploiting the Hermitian character of the operator allows it to be applied to the final state, so if the final state is represented by a plane wave, one obtains the simple result that the angle-resolved photoemission current is proportional to the square of the product of the Fourier transform of the initial state wave function and the factor $\mathbf{A} \cdot \mathbf{k}$, where \mathbf{k} is the photoelectron wavevector. This in

turn provides the opportunity to measure the spatial distribution of the initial state wave function. However, as many authors [20–33] subsequently pointed out, the interaction of the out-going spherical wave with the atomic potential and, in particular, the interference between the resulting partial wave components (e.g. between s and d waves for emission from a p orbital) must be properly taken into account, not only for an isolated atom, but also for the molecular orbitals in an adsorbed molecule. In this more exact description the final state interaction redistributes the plane wave intensity into different directions. In particular, the restriction imposed by the $\mathbf{A} \cdot \mathbf{k}$ factor in the plane wave approximation is relaxed. As Richardson pointed out [33], this can be seen by application of the photoemission selection rules [34, 35]. The latter are entirely based on symmetry considerations, and are necessarily compatible with the more correct spherical wave final state (and indeed with the effects of substrate scattering discussed below). For emission in a mirror plane they tell us that states anti-symmetric with respect to reflection in that plane will be observed when the \mathbf{A} vector is oriented perpendicular to the plane. (This geometry is often referred to simply as $\mathbf{A} \perp \mathbf{k}$.) States that are symmetric with respect to the mirror plane will not be observed. In the plane wave final state approximation no emission is expected from *any* initial state because of the $\mathbf{A} \cdot \mathbf{k}$ term. Thus for the case of CO adsorbed with its axis perpendicular to the surface, emission in a mirror plane, with \mathbf{A} perpendicular to that mirror plane, is expected to be observed from the 1π orbital according to these selection rules. This result was first confirmed experimentally—actually for the special case of normal emission—in the classic paper of Smith *et al* for CO on Ni(100) [36], and is clearly inconsistent with the predictions of the plane wave approximation. We note further that emission from the 4σ and 5σ orbitals is not allowed, and not observed, in this geometry.

On the basis of the discussion so far we are entitled to ask the question: Is the plane wave final state approximation really adequate for the reliable application of an orbital tomography method? We have just seen how—because of the $|\mathbf{A} \cdot \mathbf{k}|^2$ factor—it fails completely in a particular range of parameter space. On the other hand, as Goldberg *et al* [27, 28] and Kambe and Scheffler [32] have noted, there is one specific geometry, namely, when the \mathbf{A} vector is parallel to the direction of the photoelectron, i.e. $\mathbf{A} \parallel \mathbf{k}$, for which the plane wave final state and the more correct spherical wave approximation give exactly the same result. Puschnig *et al* [3] note that this is indeed the case, but also claim that there are other geometries where the two approximations give essentially the same result, because the atomic matrix element in the spherical wave approximation is thought to act only as a ‘weakly varying envelope function’ as a function of emission angle. They therefore argue that the angle-resolved cross-section is expected to remain essentially the same as in the plane wave final state approximation, even when the condition $\mathbf{A} \parallel \mathbf{k}$ no longer pertains. The relatively small differences between the plane wave final state and spherical wave approximations (except for geometries close to $\mathbf{A} \perp \mathbf{k}$) seen in the calculations of the angle-resolved cross-sections by Goldberg *et al* [28] for oriented O 2p orbitals, at least at $h\nu = 40$ eV, also seem to support the assumptions of Puschnig *et al*, and thus the viability of orbital tomography. The same is also true when Goldberg’s plane wave final state results are compared with the SW X α calculations of Davenport for oriented CO [24]. However, experimental data seem to tell a different story. In the specific example of adsorbed CO mentioned above [36], where according to the plane wave final state approximation the 1π orbital is not expected in normal emission with s-polarized light ($\mathbf{A} \perp \mathbf{k}$), the actually observed 1π feature in the spectrum has approximately the same intensity as the other two features (4σ and 5σ) in the spectrum with p-polarized light. Similar effects have been seen in numerous photoemission studies of adsorbed molecules with polarized radiation in the last three decades. Benzene is a good example [37, 38].

Subsequent to the early work quoted here, most angle-resolved photoemission of adsorbates has concentrated on the application of selection rules for orbital assignment or for orientation determination as well as on mapping adsorbate band structures. Quantitative analysis of spectra has rarely been performed, one of the main exceptions being the work of Ueno and colleagues [39–41]. They have used the so-called independent-atomic-centre (IAC) model of Grobman [30], which also uses the spherical wave approximation in the final state. In some cases they have also included single intramolecular scattering (the SS/IAC model), and most recently the potentially important multiple intramolecular scattering [42].

Despite the problems potentially associated with the assumption of the plane wave final state, the results obtained with ‘orbital tomography’ so far do appear to yield spatial variations of the π molecular orbitals in surprisingly good agreement with those predicted by (density functional) theory [3–6]. As explained by Puschnig *et al* in the supporting material for [3], there are two conditions that may be especially favourable to the application of ‘orbital tomography’ in the systems they have investigated [3–6]. In particular, they have investigated π -orbital emission from large planar molecules which contain only low-atomic number elements and lie flat on the surface. Low atomic number constituent elements means that intramolecular scattering in the final state should be weak, while the fact that the π -orbitals in these lying-down molecules can be represented by a summation over atomic p_z orbitals of the same chemical character leads to a particularly simple result. Single heavier atoms within these large molecules, such as in the phthalocyanines (e.g. [14]), are unlikely to make a qualitative change to this conclusion. Notice, too, that in the case of photoemission from adsorbed CO described above, the large discrepancy between the symmetry selection rules and the $\mathbf{A} \cdot \mathbf{k}$ factor of the plane wave

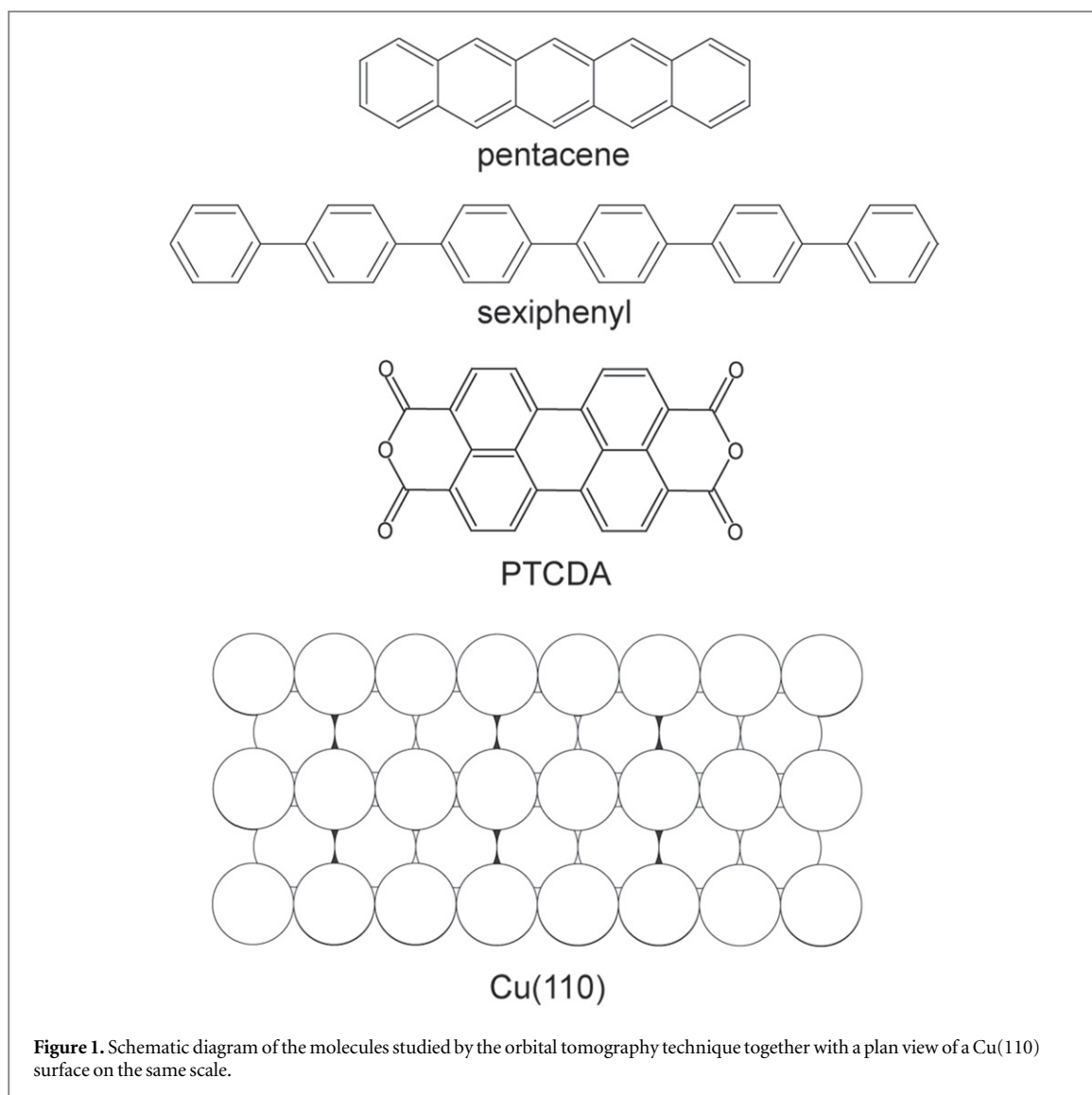
approximation arose for the π -orbitals of this standing-up molecule, thus composed of p_x and p_y orbitals, whereas no such strong conflict is found for the σ -symmetry states comprising p_z orbitals in this system. Evidently the situation for orbital tomography would be quite different for emission from π -orbitals of a planar standing-up molecule, such as a simple carboxylate. These are, of course, significant constraints to bear in mind in the application of the orbital tomography technique.

It seems to the present authors, however, that there is a simple control experiment, possible with many angle-resolving photoemission spectrometers, that would provide a clear experimental test of the importance of the neglect of the spherical wave character of the initial outgoing photoelectron wavefield. Specifically, it should be possible to measure the angular distributions in the geometry proposed by Goldberg *et al* [27], where \mathbf{k} is held parallel to \mathbf{A} , i.e. the angle-resolved photoemission current is always measured in the direction of the polarization vector of the incident light. Under these conditions, as we have noted above, the plane wave and spherical wave approximations lead to the same result for the polar angular distribution of emission in the incident plane. If the measured angular distribution is not the same (or very closely similar) for the two modes of measurement, it is clear that only the $\mathbf{A}||\mathbf{k}$ geometry should be used in future. We also note that the angular distribution in this geometry has a very simple analytical form [27, 32], which would serve as an extra check. It is important to remember, however, that in the $\mathbf{A}||\mathbf{k}$ geometry the polar angle of incidence is varied, which means that the change in the reflection of the light must be specifically taken into account by calculation, using the Fresnel formulae and the optical constants of the substrate, as described by Scheffler *et al* [31]. The dependence of the current in normal emission on the polar angle of incidence was used in the early days of adsorbate photoemission—before polarized radiation was available—to determine orbital symmetry [31, 43, 44]. Incidentally, these early papers also showed that the dependence of the intensity of adsorbate features on polar angle of emission could only be correctly described when proper account was taken of the refraction of the photoelectron at the surface barrier. This effect changes the polar angle of emission from θ with which the photoelectrons leave the adlayer to a larger angle θ' at which it is energy-analysed and detected. For this purpose it is necessary—as in LEED—to assume a value for the inner potential. We do not know how Puschnig *et al* [3–6] have treated this problem in their ‘orbital tomography’ studies. Of course, measurements only in the $\mathbf{A}||\mathbf{k}$ geometry cannot exploit the parallel detection of multiple emission directions that characterizes many modern experimental arrangements, but even measurements of such parallel detection angular distributions, recorded at a few very different incident angles, would cast some light on this issue.

Final state scattering

So far we have considered only the problems associated with treating the initial outgoing photoelectron wavefield from an isolated molecule by a plane wave, together with the influence of intramolecular final-state scattering. For a molecule adsorbed on a surface, however, we must also consider (as first stressed by Liebsch [20–23], and later Scheffler *et al* [31, 32]), the influence of an additional final state effect, namely, the scattering of the emitted electrons by the substrate. Liebsch showed clearly that this final-state scattering was an extremely important effect, even for delocalized initial states. Kambe and Scheffler [32] showed how the inclusion of multiple scattering via LEED-type final states produces substantial changes in calculated angle-resolved photoemission distributions from the Ni(100)-O system. The importance of final state scattering in emission from localized *core* levels of atoms in adsorbates has also been clearly demonstrated experimentally, and indeed it forms the basis of the technique of photoelectron diffraction that has proved to be an extremely effective method to achieve quantitative structural information for adsorbates on surfaces [45, 46].

A further implication of the apparently reasonable description provided by the plane wave final state approximation in the work of Puschnig *et al* is that, for the specific systems studied, the final state (multiple) scattering by atoms outside the adsorbed molecules apparently leads to very little modification of the observed angular distribution of the photoemission. One way to understand this is to consider experience gained in the technique of photoelectron diffraction mentioned above, corresponding to a situation in which the angular (and energy) distribution is *entirely* determined by this final state scattering. In these experiments it has been found that if the emitter atom is in a high-symmetry site relative to the underlying substrate the final state scattering leads to very strong variations in the angle-resolved photoemission intensity. This effect is significantly weaker if the emitter site is of low symmetry because of the effect of averaging over directions that are symmetrically equivalent relative to the underlying substrate point group symmetry. A further effect that causes weakening of the photoelectron diffraction modulations is if there are several different emitter sites as, for example in an adsorbed molecule containing several chemically-equivalent emitter atoms. A particular example of this type is adsorption of benzene in a flat-lying configuration on Ni(111) [47] or Ni(110) [48]. The mismatch of the C–C distance in the benzene and the Ni–Ni distance in the substrate inevitably leads to local C atom sites of low symmetry relative to the underlying substrate, while on Ni(110) the lower symmetry (2-fold) of the substrate



means that at least two inequivalent local C sites are co-occupied. Both effects lead to some reduction in the observed variations in the angular distribution of the emitted C 1s photoelectrons, although in both of these systems the observed variations are sufficient to achieve a full local structure determination. The molecule-substrate spacings in these systems (1.81–1.92 Å) are a little smaller than those found for the larger molecules studied by the tomography method, but the difference in most cases is too small to account for a qualitative difference in the role of backscattering. Of course, in this core level photoemission the final-state scattering effects from each of the C emitter atoms are summed incoherently. By contrast, in emission from a molecular orbital, a summation over the contributing local atomic orbitals (explicitly considered in the IAC model) is coherent. The qualitative influence of the multiple emitter sites on modification of the angular distribution due to final state scattering is, however, likely to be similar.

The first systems that were studied by the orbital tomography method were (i) pentacene in a multilayer film [3], (ii) single layer sexiphenyl adsorbed on Cu(110) [3, 5], (iii) PTCDA (3,4,9,10-perylene-tetracarboxylic-dianhydride) on Ag(110) [4], and (iv) PTCDA on Ag(111) [6]. A range of other systems have been studied subsequently, but these four are largely representative. These molecules are shown in figure 1, together with a plan view of the Cu(110) surface on the same scale. The absence of strong extramolecular final state scattering in the case of the multilayer pentacene film is easy to understand, as all the molecules surrounding the emitter comprise weakly-scattering C (and H) atoms. By contrast, both Cu and Ag atoms are strong electron scatterers. Moreover, the overlayer structures are commensurate. Specifically, on Cu(110) sexiphenyl forms a $c(22 \times 2)$ phase [49], while for PTCDA on Ag(110) the investigation appears to have been based on a $c(6 \times 4)$ phase [4, 50, 51], and on Ag(111) the unit mesh has been described as $\begin{bmatrix} 6 & 1 \\ -3 & 5 \end{bmatrix}$ in the matrix notation (based on primitive translations vectors of the substrate separated by an acute angle) [50, 52] (equivalent to $\begin{bmatrix} 7 & 1 \\ 2 & 5 \end{bmatrix}$ using

the more conventional crystallographic notation with the primitive translation vectors separated by the obtuse angle). In the first two cases these structures contain only one molecule per primitive unit mesh although on Ag (111) the unit mesh contains two locally-inequivalent molecules.

For a single atomic adsorbate or a small molecule, these are the conditions that would be expected to give strong final-state scattering effects (photoelectron diffraction) rendering the orbital tomography technique untenable. This is also shown clearly by the calculations of Kambe und Scheffler for Ni(100)-p(2 × 2)-O [32]. However, as is clear from figure 1, the adsorbed molecules are very much larger than the Cu–Cu interatomic spacing; this is also true for the Ag surfaces, for which the interatomic spacing is only 13% larger. The many C atoms in these molecules and the mismatch of the interatomic spacings between the molecules and the substrate means that they occupy a large number of different (and in many cases low-symmetry) registry sites relative to the underlying substrate. In this situation a photoelectron diffraction study of the C 1s core level emission would be expected to show only very weak angle- or energy-dependent modulations due to the different contributions from the different emitter atoms. A similar effect may therefore be anticipated in the photoemission from one of the molecular orbital π -states. Interestingly, a recent study of pentacene on Cu(110) and Ag(110) [13] does reveal significant differences in the molecular tomographs, but this appears to be due to a different molecular orientation combined with a much stronger molecule–metal bonding interaction on the Cu surface rather than any difference in substrate scattering

Conclusions

We draw two conclusions from the present discussion. Firstly, it is not proven that the plane wave final state approximation is (nearly) equivalent to the more correct spherical wave approximation in the experimental geometry used by Puschnig *et al* [3], except for the special case Alk. We have therefore proposed a simple control experiment in which the polar angle dependence of the photoelectron current is measured in the incident plane such that **A** is held parallel to **k**. This requires rotating the crystal about an axis in the surface plane perpendicular to the incident plane, which in many angle-resolved photoemission experiments corresponds to the axis of the sample manipulator. Under these conditions the plane wave final state gives the ‘correct’ angular distribution for all polar angles of emission (‘correct’ in the sense of the spherical wave approximation!). Back-transforming the angular distribution should deliver orbital densities in real space. The reflection of the photon beam must, however, be explicitly taken into account and—as in all angle-resolved experiments of this kind—must the refraction of the photoelectron. Secondly, as a result of photoelectron diffraction effects, ‘ π -orbital emission from large planar (lying-down) molecules which contain only low-atomic number elements’ is likely to be a requirement for the ‘orbital tomography’ method to produce reasonably reliable results. Exactly how large is large enough is unclear. The results of photoelectron diffraction studies on adsorbed benzene indicate that a single phenyl ring is not enough. Apparently five or more such rings do appear to be sufficient.

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