Angle-resolved photoemission: From reciprocal space to real space

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ABSTRACT

The prospects for converting angle-resolved photoemission data from reciprocal space to real space are evaluated. Examples are given for one- and two-dimensional systems, where wave functions have been obtained for quantum well states confined between steps and for planar molecules adsorbed at a surface. The extension to three-dimensional systems via variable photon energies is discussed. The uncertainty relation between position and momentum makes such a capability complementary to imaging in real space by scanning tunneling microscopy. Angle-resolved photoemission provides access to the internal structure of an electronic orbital and penetrates below the surface.

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It was recognized as early as 1970 by Siegbahn and coworkers [1,2] that photoelectrons have a distinct momentum distribution. Early results are shown in Fig. 1 (from [1]), where the angular dependence of the photoemission intensity from a NaCl single crystal is plotted versus the polar angle θ. The Na 1s and Na 2s core levels, as well as the Cl 3p valence band, exhibit distinct modulations of up to 30% which seem to be tied to the crystal lattice in real space. It was quickly found [3] that this phenomenon was not restricted to ionic insulators but rather wide spread. Such observations eventually led to the concepts of photoelectron diffraction [4–6] and photoelectron holography [7]. The angular distribution of elastic photoelectrons from a core level is explained by scattering of the outgoing photoelectrons at neighbor atoms. In the forward direction this leads to a focusing effect along rows of atoms which explains the connection with the crystal lattice in real space rather than the Brillouin zone in reciprocal space. By appropriate modeling [4–6] or by direct holographic inversion [7] it is now possible to determine the positions of atoms at surfaces. This is particularly useful for finding the location of adsorbed molecules relative to the substrate lattice.

When going from X-rays to the vacuum ultraviolet and from core levels to valence electrons one finds again a strong angular dependence of the photoemission intensity, as shown in Fig. 2 for NaCl(1 0 0) (from [8–10]). The angular dependence is shaped by the outgoing photoelectrons for the data in Figs. 1 and 2, i.e., one observes predominantly a final state effect. This can be verified by varying the photon energy with synchrotron radiation and exciting the same final state from different initial states. With valence electrons, however, there is also a strong initial

state effect when the electron escape depth becomes small compared to the electron–phonon scattering length. That eliminates electron–phonon scattering, which scrambles the momentum information without changing the energy significantly.

For truly elastic photoelectrons it becomes possible to determine the momentum distribution of the valence electrons in the initial state and measure their $E(k)$ band dispersion and Fermi surface (for early work see [11] and references therein, for reviews see [12–14]). Initial and final state effects can be separated using tunable synchrotron radiation, which allows constant initial state spectra (CIS) and constant final state spectra (CFS) to be taken [15]. Synchrotron radiation also makes it possible to tune the momentum perpendicular to the surface, $k_\perp$, which can be varied with the photon energy. An example is shown in Fig. 3 for LiF(1 0 0), now at energies high enough to avoid electron–phonon scattering (from [16]). The angular distribution is shown for several initial state energies E across the F 2p valence band. E is measured relative to the valence band maximum which lies at $k = 0$ (Γ-point). The valence band minimum lies at the X-point of the Brillouin zone boundary at -3.5 eV. The upper row of images is taken at a photon energy where $k_\perp$ corresponds to the $(3\,0\,0)$ X-point in normal emission (with k in units of $2\pi/a$). Consequently, one sees a bright dot at the center when E is set to -3.4 eV, close to the X-point (left end of the upper row). In the lower row of images the photon energy is set for the $(4\,0\,0)$ Γ-point in normal emission. Consequently, one sees a bright dot at the center when E is set to $+0.2$ eV, near the Γ-point (right end of the lower row).

While the photoelectrons in the final state behave like a nearly free electron with an inner potential at higher energies, the electrons in the initial state are strongly affected by the crystal potential and exhibit correlations with the other electrons in the solid. Therefore, a more sophisticated theory is required to describe initial state effects. In Fig. 3 a many-body, quasiparticle approach was used

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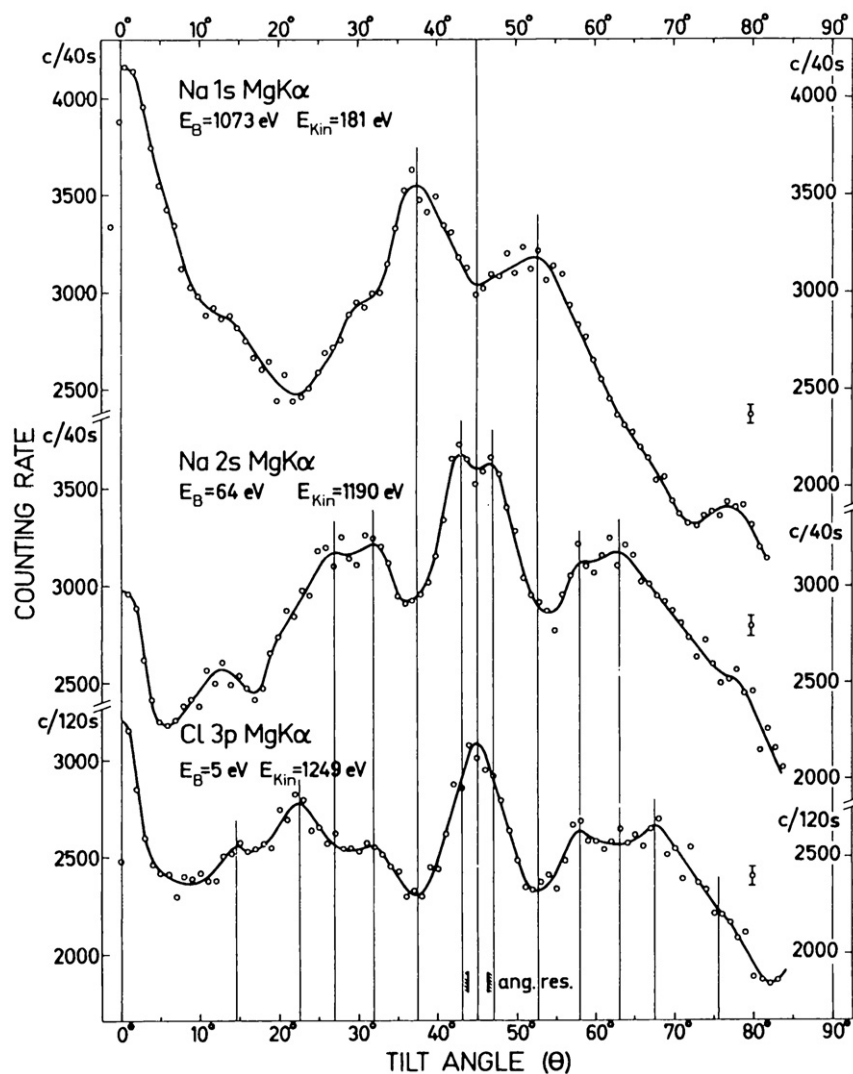 E-mail address: fhimpsel@wisc.edu.

Fig. 1. Observation of angular (momentum) dependence of the photoemission signal from a NaCl single crystal using MgK$_\alpha$ radiation with a photon energy $\hbar\omega = 1.25$ keV. From Siegbahn et al. [1].

to describe the initial states and a nearly-free-electron model for the final states [16]. Sophisticated many body theory is required to get the correct band width for correlated electrons, such as the localized F 2p electrons in the valence band of LiF. In Fig. 3 the calculated angular pattern is shown in the bottom half of each image and compared to the experiment in the top half. All the experimental features are reproduced by this *first-principles* theory, and even the intensities can be compared in semi-quantitative fashion.

With both initial and final states under control, one can ask whether it is possible to extend the concept of photoelectron diffraction from core levels (where the initial state is a simple δ-function) to valence states (where one has to deal with extended orbitals). Experimentally, the analogy is rather straightforward: just measure the angular photoemission pattern of valence electrons instead of core levels. Due to the finite energy width of the valence band one obtains a set of data at several initial state energies across the band width, as shown in Fig. 3. These correspond to different initial state wave functions. Can a straightforward inversion procedure, such as the reconstruction of a hologram [7], produce a reasonable initial state wave function? In contrast to photoelectron holography, one cannot use the spherical wave emitted from a core level as reference wave.

The same problem is currently receiving a lot of attention for the reconstruction of a coherent X-ray diffraction pattern from an isolated nano-object. One faces the usual problem of X-ray crystallography: only the intensity distribution in reciprocal space is known, not the phases. For periodic crystals there are several standard ways to overcome the phase problem, such as substitution by heavy atoms and anomalous scattering at an absorption edge. For an aperiodic object, such as a single protein molecule or a single nanocrystal, the phase problem can be overcome as long as the object is located in a well-defined spatial region (for example inside a small aperture) and isolated from neighboring objects [17–20]. In such a situation one can employ an iterative method to retrieve the phases. To begin, the measured intensities in reciprocal space are combined with arbitrary phases to enable an inverse Fourier transform into real space. The spurious intensity outside the aperture is then set to zero and the rest of the data is Fourier transformed into reciprocal space. The resulting diffraction intensities are corrected to the experimental values while keeping the phases. A second inverse Fourier transform leads back into real space. This procedure can be iterated many times, and it eventually converges to the correct result. Quite a few refinements have been devised, but there is a common condition for this method to work: The diffraction pattern needs to be "oversampled" in reciprocal space, i.e., the k-points