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Angle resolved photoemission spectroscopy and surface states

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Abstract. Angle Resolved Photo Emission Spectroscopy (ARPES) has been a very effective tool to study the electronic states of solids, from simple metals to complex systems like cuprate superconductors. For photon energy in the range of 10 - 100 eV, it is a surface sensitive process as the free path of the photo emitted electrons is of the order of a few lattice parameters. However to interpret the experimental data one needs to have a theoretical foundation for the photoemission process. From the theory of photoemission it may be seen that one can get information about the state from which the electron has been excited. As the translational periodicity is broken normal to the surface, a new type of electron state in the forbidden energy gap can exist localized in the surface region. ARPES can reveal the existence and the property of such surface states. We shall also discuss briefly how the electromagnetic field of the photons are influenced by the presence of the surface and how one can try to take that into account in photoemission theory.

1. Introduction

Angle Resolved Photoemission Spectroscopy (ARPES) has been an important technique for studying the electronic states of metals, semiconductors (both clean and adsorbate covered) as well as more complex systems e.g. High Temperature cuprate superconductors. The development in making clean surfaces, working in ultra-high vacuum environment and the availability of photons with continuously varying wave lengths from synchrotron sources led to accurate measurements. The schematic experimental setup is shown in the figure below.



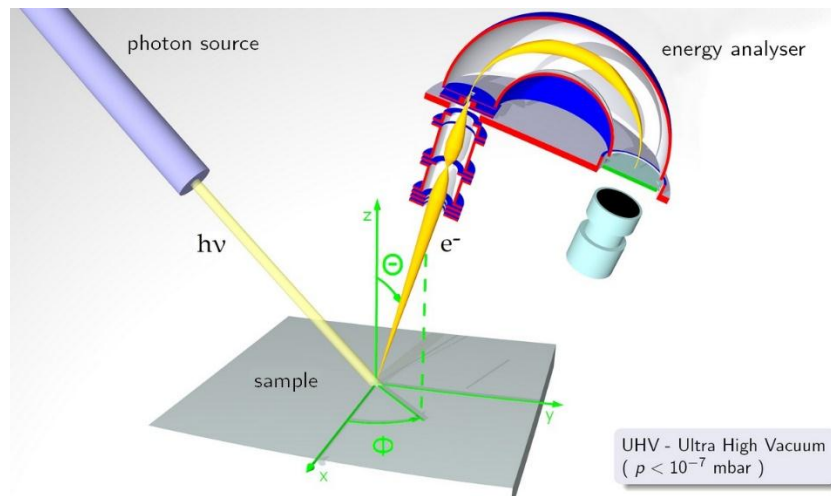


Figure 1: Schematic Experimental Setup

There are a large number of variables in the experiment e.g.

- (i) Electron energy
- (ii) Direction of emission (angle at which the electron is collected)
- (iii) angle of incidence of the photons.
- (iv) Photon energy
- (v) Polarization of the photon beam

1.1. Photoemission Theory

The photocurrent in the independent electron approximation by application of Fermi's Golden Rule

$$\frac{dj(E)}{d\Omega} = \frac{2\pi}{h} \sum |\langle \psi_f | H' | \psi_i \rangle|^2 \delta(E - E_f) \delta(E_f - E_i - h\omega) f_0(E_i) [1 - f_0(E_f)] \quad (1)$$

$|\psi_i\rangle$ and $|\psi_f\rangle$ are the initial and final states and $H' = \frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A})$

is the perturbing Hamiltonian up to first order in the photon field vector potential \mathbf{A} . The two Fermi distribution functions f_0 ensure that the initial state is occupied while the final state is unoccupied. The final state energy E_f is greater than the initial state energy E_i by $h\omega$ where ω is the photon frequency.

$|\psi_f\rangle$ and $|\psi_i\rangle$ in equation (1) are in principle many body states with N and $(N-1)$ electrons (N is the total number of electrons). Since it is virtually impossible to deal with a system of $\sim 10^{23}$ particles, $|\psi_f\rangle$ and $|\psi_i\rangle$ are almost always taken as single particle states in one electron approximation.

The simplest approximation is to consider that as the electron coming to the detector may be taken to be a free electron, there is no structure from the final state; the vector potential is also taken to be constant and so all the features seen in the photocurrent are from the initial state density of states. However such an approach is too simplistic and one needs to have a better interpretation. One way of doing that is the so called three step process.

In the first step one calculates the matrix element $\langle \psi_f | H | \psi_i \rangle$ between the initial band state $\langle \psi_i |$ and the final band state $\langle \psi_f |$ - both calculated by some band structure method, e.g. self-consistent LAPW or LKKR method in density functional formalism. The second step is to consider the travel of the electron to the surface and the third step is the transmission through the surface. This is discussed in more detail in references [1] and [2].

In this review, we shall be focusing our attention to the so called one-step calculation, which starts by recognising that the presence of the surface destroys the three dimensional periodicity intrinsic to band structure calculations. The wave-vector \mathbf{k} in Bloch's theorem $\psi(\mathbf{r}+\mathbf{R}) = \exp(i\mathbf{k}\cdot\mathbf{R})\psi(\mathbf{r})$ is a vector with three real components only because of three-dimensional periodicity. In the presence of the surface we may have two-dimensional periodicity and while the components of \mathbf{k} parallel to the surface, \mathbf{k}_{\parallel} would be real - the component \mathbf{k}_{\perp} , perpendicular to the surface need not be real, but would in general be complex. In the following we discuss the photocurrent calculation in such a context.

1.2. Final State

For the final state, we have an electron (free electron) going to the detector. Constructing the free electron wave function by starting with a band wave-function and then matching at the surface is a difficult problem. So the usual technique is to take a different approach.

Let us consider an electron coming from the detector ($\psi \sim e^{(ik_f \cdot r)}$). After it is incident at the surface there will be reflected and transmitted waves with proper wave function matching. This is the Low Energy Electron Diffraction (LEED) problem and for that problem the theory and computational techniques are easily available (see for example [5]). Now, if we consider that state to be time-reversed, we get a free electron going to the detector! The 'Time Reversed LEED state' discussed by Liebsch [6], Pendry [7] and others (see [3]) has been the standard technique for final state calculations. Pendry has shown that one can write down the photocurrent in terms of an appropriate Green's function - the multiple scattering and lifetime effects can then be included in the calculation. Using atomic units Pendry derived an expression for the current as

$$I(k_{\parallel}, E_f) = K_{2\perp} \rho(k_{\parallel}, E_i) |\langle k_{\parallel} | G_2^+ H | \psi_f \rangle|^2 \quad (2)$$

$$\langle r | k_{\parallel} \rangle = \frac{1}{L} \delta(z - Z) \exp(ik_{\parallel} \cdot r_{\parallel}) \quad (3)$$

Where Z is the plane of observation and L is the dimension of the box containing the system. Pendry [3] showed that this is equivalent to the "Time Reversed LEED State" formalism and can be incorporated in the photoemission calculation.

1.3. Initial State

The initial state is usually that of an electron in a band. However, as mentioned before, because of the surface, the three dimensional periodicity is not valid. Assuming a semi-infinite surface would allow us to have two dimensional periodicity. This implies that the wave-vector \mathbf{k} will have its component k_{\parallel} as real but the normal component k_{\perp} may now be complex! Normally one may think of computing the initial state wave function in a density functional framework but the standard methods based on three dimensional periodicity will not be

appropriate. One has to do a layer by layer calculation (with the layers parallel to the surface plane) to be consistent with the final state calculation.

The wavefunction for a complex band with band index α may be written as, (z taken as the direction perpendicular to the surface)

$$\phi_{\alpha} = \sum_g \phi_{ga}(z) \exp i(k_{\parallel} \cdot r_{\parallel}) \quad (4)$$

where, g is a set of 2 dimensional reciprocal lattice vectors. In the region outside the surface

$u_g(z)$ is a function decaying exponentially away from the surface plane ($z=0$).

The wavefunction when properly matched across the surface plane will give the initial state wave function.

1.4. Perturbing Hamiltonian

The perturbing Hamiltonian $H' = \frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A})$ can be simplified by using the commutator relation $[\mathbf{p}, \mathbf{A}] = -i\hbar \nabla \cdot \mathbf{A}$ and choosing the gauge $\nabla \cdot \mathbf{A} = 0$, one may write

$$H' = -(e/mc) \mathbf{A} \cdot \mathbf{p} \quad (6)$$

Usually the spatial variation of \mathbf{A} is neglected and the vector potential \mathbf{A} is taken as a constant. We shall discuss this point in more detail later.

1.5. Example of Photocurrent Calculation

Photoemission computer programs were developed to include the matrix element calculation taking care of the various terms as discussed above. The details of computational technique of the photocurrent calculation have been given by Hopkinson, Pendry and Titterington [8]. Kar [9] used the program to calculate the photoemission spectra for bromine adsorbed on copper. The experimental data for the spectra were from Richardson and Sass [10]. We show below the experimental data for normal photoemission from clean Cu (100) surface and with a c(2×2) Bromine over layer. B, C and D identify the new features due to the adsorption of bromine. The theoretically calculated spectra for normal emission is given in the next figure (from [9]). The next two figures show the experimental and calculated data for angles of emission from 0 to 50 degrees at 10 degree interval. It may be seen that the theoretically calculated spectra qualitatively reproduce the new features for normal photoemission and also the trends when the angles of detection are changed,

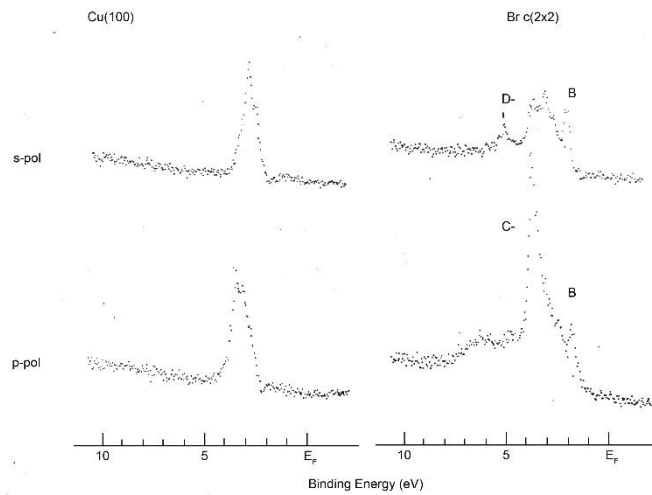


Figure 2: Experimental data for normal photoemission: s and p polarisation

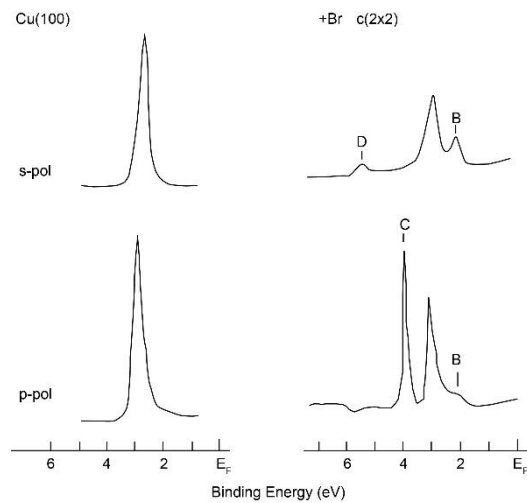


Figure 3: Calculated spectra for normal photoemission: s and p polarization

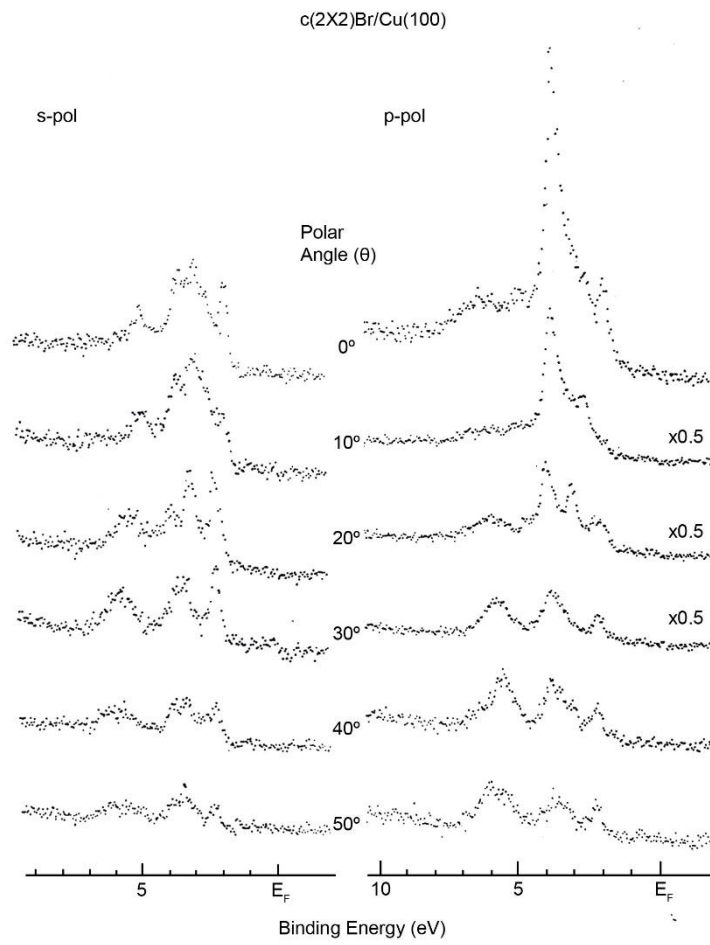


Figure 4: Experimental data 0 to 50 degrees: s and p polarization

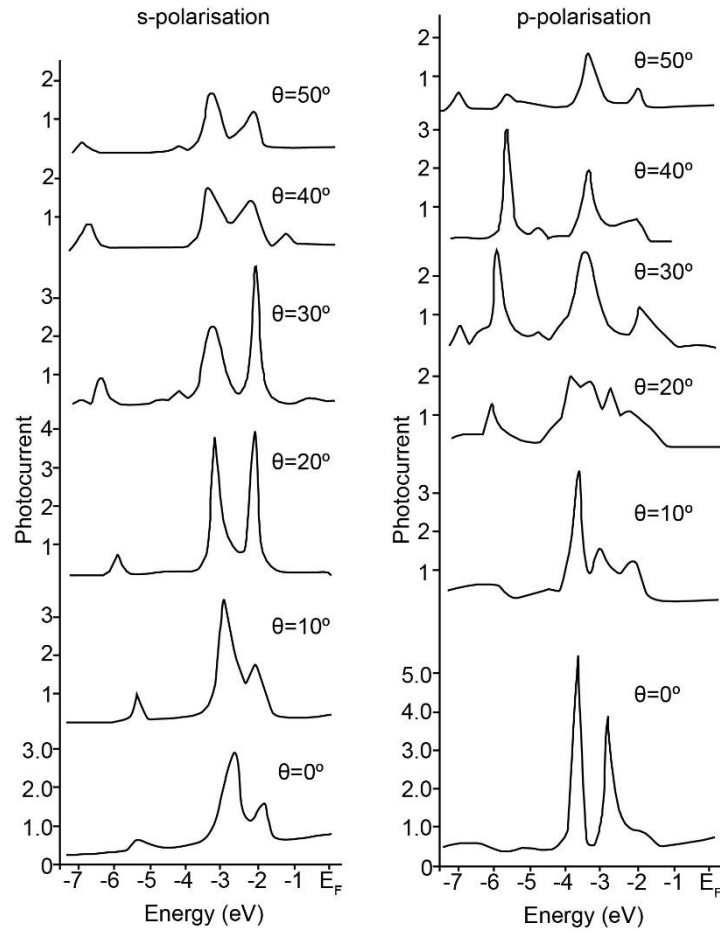


Figure 5: Calculated spectra 0 to 50 degrees: s and p polarization

1.6 Surface State

As we have discussed in the discussion for initial state calculation, the presence of the surface destroys the three dimensional periodicity. Since k_{\perp} can be complex, it may be possible for some energy E that the matching

$$\phi_{\alpha} = \sum_g \phi_{g\alpha}(z) \exp i(k_{\parallel} \cdot r_{\parallel}) \quad (7)$$

$$\psi k_{\parallel} = \sum_g T_g \frac{u_g(z)}{u_g(0)} \exp i(k_{\parallel} \cdot r_{\parallel}) \quad (8)$$

will be satisfied for some complex k_{\perp} with the wavefunction localised in the surface region. A schematic picture of such a wavefunction in one dimension is given below.

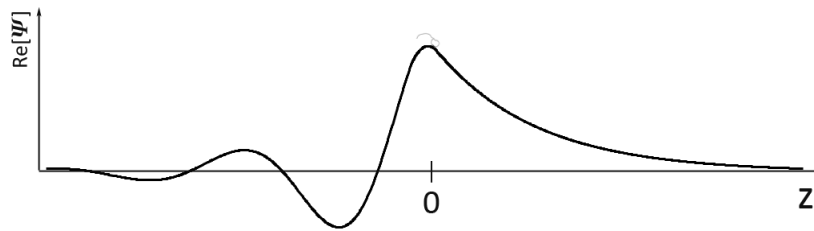


Figure 6: Schematic surface state wavefunction in 1 dimension

Such states are called surface states -they would exist in a band gap. If there are band states at the same energy then they would mix with the surface state, unless there are symmetry restrictions and these states are then known as surface resonances. However, the density of states would have a peak in the surface region. Photoemission is an excellent probe for detecting such surface states/resonances. The mean free path of electrons due to inelastic scattering in metals is of the order of 10 - 20 angstroms for the electron energy in the range of 10 - 100 eV (see e.g. [2] and [4]). So for photon frequency in the ultraviolet range, the electrons that are photoemitted come from a few layers in the surface region - the surface state/resonance effects do not get swamped by the bulk data.

Historically, the first surface state was observed by Field Emission on (100) face of tungsten about 0.4 eV below the Fermi energy (see [11] for details). Weng, Plummer and Gustafsson [12] showed that such states could also be observed by angle resolved photoemission experiments on tungsten and molybdenum. The peaks due to such states go away if the clean surface has any contaminant and their position with respect to the Fermi energy is independent of the photon energy. We show their data below.

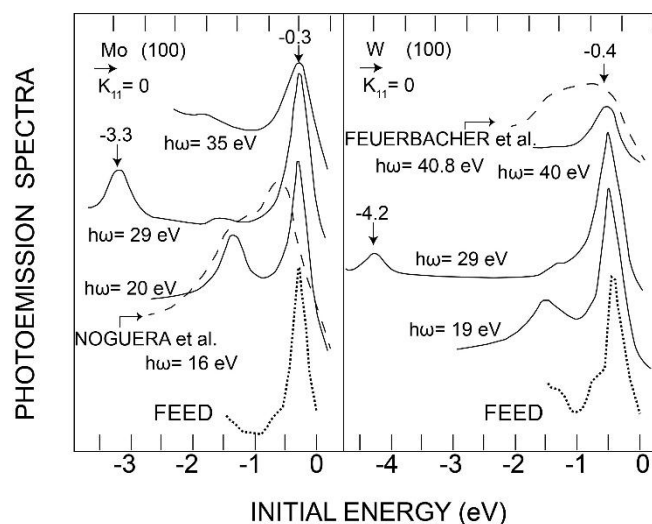


Figure 7: Surface states on W(100) and Mo(100) faces

The theoretical calculation of such surface states is a problem which needs accurate electronic state calculations in the presence of surfaces. Inglesfield [13] has given a very good review of surface

electronic structure calculation. Such calculations can also be done in the framework of density functional theory by taking a layer by layer approach.

2. Spatial Variation of Photon Field

So far the spatial variation of the photon field has been completely neglected. However, photoemission experiments by Weng, Gustafsson and Plummer [14] on the surface state of tungsten(100) face, plotted against photon energy showed that the peak strength goes through a minimum near the bulk plasmon energy. This observed suppression in normal photoemission seems to be due to field variation in the surface region. In the context of jellium model Feibelman [15] calculated non-local response function and the electromagnetic field in the surface region and applied his results to free electron metals. Apart from some problems with photoemission results from aluminium his calculations were (i) too complex to be incorporated into photoemission programs and (ii) the jellium model could not be applied to transition metals or semiconductors. Bagchi and Kar [16] used a simple model - linearly interpolating the (local) dielectric function in the surface region from the bulk value (experimentally determined) and the vacuum value (unity). Taking the nominal surface plane to be at $z = 0$, the dielectric function in the surface region ($-a/2 \leq z \leq a/2$) can be written as

$$\varepsilon(\omega, z) = [1 + \varepsilon(\omega)]/2 + [1 + \varepsilon(\omega)](z/a)$$

This is a very simplistic model but the nice feature of this model is that the vector potential $\mathbf{A}_\omega(z)$ can be calculated analytically. For the wavefunctions a gaussian function was used for the surface state and free electron functions for the final state by Bagchi and Kar. The results showed that there was a valley in the plasma frequency region, in accordance with observed results. Thapa, Das and Kar used the model with Kronig-Penney and free electron wavefunctions and applied it to different materials to see the effect of spatially varying photon field (see [17] and [18]). Thapa and his co-workers are still using this model. Currently, Thapa and his student Rebecca are doing calculations with this model and combining it with density functional method for calculating and also wavefunctions with muffin tin potentials with 2 dimensional periodicity. Let me conclude by showing a photoemission calculation from Boron Arsenide done by Rebecca and Thapa[19].

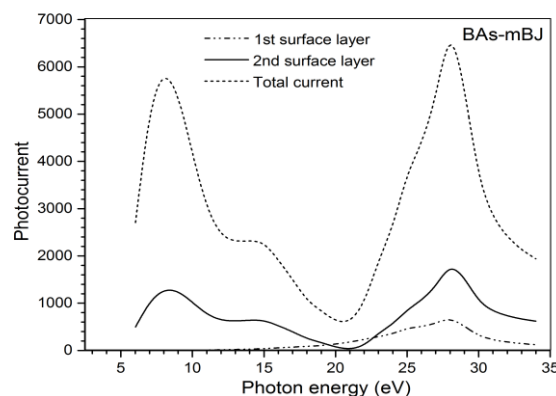


Figure 8: Calculated spectra from BAs

3. Conclusion

Angle Resolved Photoemission can give a wealth of data for material starting from clean and adsorbate covered metals to semi-conductors to cuprate superconductors. With the availability

of synchrotron radiation, one can use a large range of photon frequencies. Both bulk electronic states as well as surface states and resonances can be probed. However, a complete theory of photoemission with all the quantities treated from first principles is not available. But focussing on appropriate choice of data one can make judicious approximations to theoretically interpret the experimental results.

Acknowledgment

Figures 1 and 6 are downloaded from Wikipedia and used here. Some old figures have been cleaned up with the help of Nandini Kar. The author is grateful to Prof. R. K. Thapa and the Organising Committee of the Condensed Matter Days 2016 (CMDAYS-2016) for the invitation to attend the conference and present the talk on which this article is based.

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