A THEORETICAL FORMULATION OF INITIAL STATE WAVEFUNCTIONS FOR PHOTOEMISSION CALCULATIONS

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Introduction :

Over the last few years interests in a detailed understanding of physical properties of condensed materials and their surfaces has grown enormously for many reasons. Catalytic reactions, for example, which are of great technical importance, strongly depend on the electronic and geometric structure of a solid surface. Furthermore, the miniaturization in microelectronics has reached a point where surface properties become dominant. Also great progress has been made in the production of nearly two-dimensional structures like multilayers or thin films, which have new and fascinating features. For investigating the electronic properties of clean and adsorbate-covered surfaces and thin films, angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) has become important tools, because these experimental techniques allows measuring the dispersion of occupied bands as well the unoccupied bands in and around Fermi level. More detailed informations about the ARUPS has been provided by Feuerbacher *et. al.*[1], Inglesfield[2], Willis *et. al.*[3], Dose[4], Glasser *et. al.*[5] , Plummer and Eberhardt[6], Kar[7], Schattke[8], Braun[9] etc.

Photoemission is concerned with the emission of electrons from the surface/bulk of metals by the reaction of incident photon radiation with the electrons. *The high absorption coefficient of the ultra-violet (U.V.) radiation and the small* escape depth of the electrons emitted from the solid gives U.V. spectroscopy a big advantage over the other methods of investigating the electronic states on the surface of solids. Basically, the understanding of the electronic structure of solids and solid surfaces depends on the quality of the photoemission results. Therefore, a steady improvement and growing amount of data will be necessary to put the actual *ab-initio* results of electronic structure calculations into a physically realistic context. The knowledge of the electronic energy spectrum is fundamental to many equilibrium and transport properties and thereby photoemission deserves high interest from basic research as well as from technical application. The interplay between band structure calculation and photoemission measurement is controlled by the interpretation schemes to extract the information about the electronic states and their energies from the spectra. There are a lot of more or less heuristic methods which allow a quick access to a part of the physical content in the experimental data. However, all of them lack the accuracy required if the actual high quality of measurement and the actual state of the art of *ab-initio* calculations should make sense. As in many other techniques the spectra cannot be formally inverted to yield the electronic structure but have to be brought to convergence with theory by trial and error procedures.

In its simplest version the golden rule formula contains the matrix elements between the initial bound states and the final states which are scattering solutions of the same hamiltonian for the dipole operator of the electromagnetic field, and the delta function for energy conservation. The numerical evaluation of golden rule formula yields the photocurrent at the detector which has to be compared with the experimental value. As even *ab-initio* electronic structure calculations are not free of parameters, one can only minimize the disagreement between experiment and theory in choosing the available quantities appropriately. There may be various approximations in the evaluation of the wavefunctions according to the specific intentions. In the best case one can selfconsistently construct one particle potential adapted to the real surface. Bloch states or equivalently the Green functions for the valence band part as well as the scattering states for conduction bands are calculated. The latter are equivalent to the time inverse states of a low energy electron diffraction (LEED) system representing the final states accepted by the photoemission detector. The transfer of these ideas into a working numerical programme is far from being trivial and has been first accomplished in a closed form by neglecting the relativistic effects and choosing muffin-tin potential[10] obtained from atomic calculations. However, this does not guarantee that the agreement with the experiment is splendid. Especially, semiconductors with their reconstructed surfaces[1, 11] still represent a challenge to the theoretical photoemission.

2. **Research design and Methodology** :

The golden rule formula for calculating the photocurrent density is given by,

$$\frac{dj(E)}{d\Omega}=\frac{2\pi}{\hbar}\sum|<\psi_f|\Delta|\psi_i>|^2\,\delta(E-E_f)\delta(E_f-E_i-\hbar\omega)f_o(E-\hbar\omega)[1-f_o(E)]\ldots\ (1)$$

where Δ is the perturbation responsible for photoemission by radiation of frequency ω and $\psi_i(\psi_f)$ refers to the initial (final) state wavefunction, $E_i(E_f)$ the initial (final) state energy, $f_o(E)$ denotes the Fermi occupation function. We are considering the photoemission to take place along z - axis which is normal to the surface. We may therefore write Δ as

$$\Delta \approx \frac{e}{mc}\left[\widetilde{A}_\omega(z)\frac{d}{dz}+\frac{1}{2}\frac{d}{dz}\widetilde{A}_\omega(z)\right] \qquad \ldots \qquad (2)$$

where $\widetilde{A}_\omega(z)=\frac{A^z_\omega(z)}{A_o}$ is the component of vector potential along z -axis, A_o is the amplitude of the incident beam. The model of Bagchi and Kar[12] is employed for the computation $\widetilde{A}_\omega(z)$. We assume the z-direction to be perpendicular to the surface which is chosen as z = 0 plane. The response of the electromagnetic field is bulk-like every where except in the surface region defined by $-a \le z \le 0$ In this region, the model dielectric function is chosen to be local one which interpolates linearly between the bulk value inside the metal and the vacuum value (unity) outside. The model frequency-dependent dielectric function is therefore given by,

$$\varepsilon(\omega,z) = \begin{cases} \varepsilon(\omega) \equiv \varepsilon_1(\omega)+i\varepsilon_2(\omega), & z \le -a \\ 1+[1-\varepsilon(\omega)]\dfrac{z}{a}, & -a \le z \le 0 \\ 1, & z \ge 0 \end{cases} \qquad \ldots \qquad (3)$$

For the complex dielectric function $\varepsilon(\omega,z)$, we use the experimentally determined values. We consider a *p*-polarized light to be incident on the surface plane making an angle θ_i with the z-axis. The vector potential of interest in the long wavelength $(\omega a/c) \rightarrow 0$ is given by

$$\widetilde{A}_\omega(z)=\begin{cases} -\dfrac{\sin 2\theta_i}{[\varepsilon(\omega-\sin^2\theta_i]^{\frac{1}{2}}+\varepsilon(\omega)\cos\theta_i}, & z \le -a \\ -\dfrac{\sin 2\theta_i}{[\varepsilon(\omega-\sin^2\theta_i]^{\frac{1}{2}}+\varepsilon(\omega)\cos\theta_i}\cdot\dfrac{a\,\varepsilon(\omega)}{[1-\varepsilon(\omega)]z+a}, & -a \le z \le 0 \\ -\dfrac{\varepsilon(\omega)\,\sin 2\theta_i}{[\varepsilon(\omega-\sin^2\theta_i]^{\frac{1}{2}}+\varepsilon(\omega)\cos\theta_i}, & z \ge 0. \end{cases} \qquad \ldots\ldots \qquad (4)$$

We plan in this thesis to develop formalism for calculating ψ_i which will describe the electron states in the surface and the bulk regions.

3. **Review of works done**:

The formulation of the initial state wavefunction by choosing the exact potential model for the surface and the bulk regions of the solid is very important and complex too. There are various approaches to surface and bulk photoemission calculations which had been applied to real cases. Feibelman[13] was perhaps the first one to report the surface photocurrents in which the surface potential barrier was used to solve Schrödinger's equation for deriving ψ_i and ψ_f. However, his calculations were restricted to jellium models only and were complex too. Weng *et. al.*[14] have done the surface studies of (100) faces of *W* and *Mo*. To explain the photoemission spectra, they have used the Wannier type localized wavefunction to define the orbital basis. Smith[15] has also presented surface state calculations from various faces of *Cu* but by using a simple type of wavefunctions. Pendry[10] has given a detailed method of photoemission calculations by employing multiple-scattering formalism and this has been the most widely accepted technique. The method of Levinson *et. al.*[16] was restricted to only free electron type of metals but however could explain the effect of spatial variation of vector potential on photoemission. With their very simple approach, Thapa *et. al.* have used the free electron[17] and Kronig-Penney[18] model potentials to calculate photocurrent from metals and semiconductors. Behaviour of photocurrent in the U.V. range for the values of photon energy below and above the plasmon energy showed interesting features. Pachuau *et. al.*[19] have recently used the sinusoidal Mathieu potential to derive the ψ_i, and used it to the case of photoemission from metals.

4. Proposed work of investigation:

The purpose of the proposed Ph.D. programme is to develop a formalism for calculating $|\psi_i>$ which will be calculated in such a manner that it should be able to describe both the electronic states at the surface and the bulk regions of the metal. For this purpose, one has to first define the crystal potential. To begin with, we will consider at first the free electron type of potential, then a potential which will be periodic with the periodicity of the lattice namely, the muffin-tin type of potential and sinusoidal Mathieu potential. We propose to explore the symmetry properties of the surface states. The LCAO procedure will be used to obtain the symmetry-adapted surface state wavefunctions which are very convenient for visualizing the surface state wavefunctions[20], analyzing their symmetry and in interpreting the experimental results. Our primary objective then would be to derive the atomic orbitals in terms of appropriate basis functions. These basis functions will be deduced by using the projection operator techniques of group theory[20, 21]. By identifying the point groups to which the metal under investigation belongs, we can then construct the atomic orbitals which will enable one to develop appropriately the initial state wavefunction ψ_i.

The final state wavefunction ψ_f will be the scattering state[12] of the step potential existing at the surface. We can now expand the matrix element in Eq. (1) to calculate photocurrent into a number of integrals. As these integrals cannot be solved analytically, hence FORTRAN programs will be developed to evaluate them for computing the photocurrent. Photocurrent will be calculated as a function of a number of parameters like photon energy, surface width, width of the potential, scattering factor, potential strength etc. The behaviour of photocurrent especially near the plasmon energy of crystals would be of our interest. The photoemission data thus obtained will be compared with other models.

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