CHAPTER-I

Introduction

In photoemission, electrons are emitted when electromagnetic radiation, typically in the visible or ultraviolet region is incident on the surface. Photoemission phenomenon was first observed by Hertz[1] (1887) and later on, Einstein[2] described it as a quantum phenomenon. Nowadays, photoemission spectroscopy has become a very popular probe to know both the surface and the bulk electronic properties of a solid.

In Ultraviolet Photoemission Spectroscopy (UPS) and X-ray Photoemission Spectroscopy (XPS) the source of radiations are respectively an ultraviolet lamp and an X-ray tube. The availability of synchrotron radiation has been very important to the development of photoemission experiment. Synchrotron radiation provides a continuous spectrum extending from the infra-red to the X-ray region. UPS is conceptually identical to XPS except that the incident photons are in the energy range of 20-150 eV. It is ideally suited for the study of the valence band electrons in the surface region. The Universal Curve of mean free path shows that UPS photoelectrons originate from the surface region and valence band photo cross-section is large at UPS excitation energies.

The variables involved in the photoemission spectroscopy process are the energy, polarization, and the angle of incidence of the incident photon and also the energy, polarization and the emission angle of the emitted electrons (fig 1.1). In various photoelectron spectroscopy techniques, only a few of such variables are varied keeping others to be constant. In the constant final state spectroscopy (CFS), the energy analyzer is set to a specific energy, and the incident photon energy is swept. CFS provides a direct measure of both the initial density of states and the surface sensitivity. In constant initial state spectroscopy (CIS), the photon energy ($\hbar\omega$) and the electron kinetic

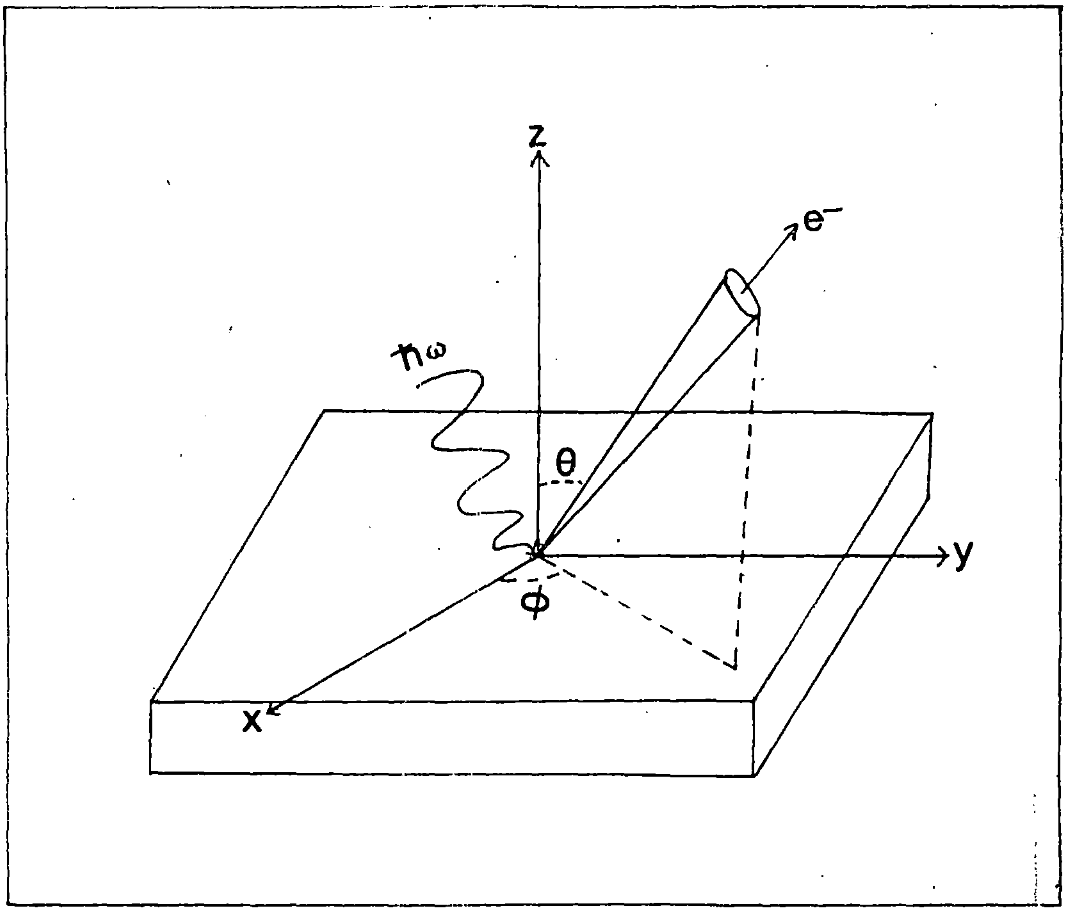

Fig 1.1 Schematic representation of photoemission

energy (E) are varied simultaneously so that $E-\hbar\omega$ is kept constant. In this mode of operation a direct measure of the final state density is obtained. In the vectorial photoeffect polarization of the incoming photon is varied while by analyzing the electron spin one obtains spin polarized photoemission.

Photoemission techniques can be classified according to the manner in which the energy and momentum of the incident photon and the ejected photoelectron are controlled. When the emitted electrons are collected for a specified angle (θ,ϕ) we get angle-resolved photoemission and when all emitted electros are collected by a hemispherical detector we get the angle integrated photoemission. Escape length for electrons in the 10 eV -100 eV range is of the order of 10 A^0, so the process is surface sensitive. Angle integrated photoemission gives joint density of states while, the angle-resolved photoemission gives a detailed information of band structure, surface sensitiveness etc. In angle resolved photoemission spectroscopy the direction and energy of an ejected photoelectron is measured to determine the photoelectron wavevector $\vec{K}$. At the surface the wavevector conservation breaks down in the direction perpendicular to the surface due to the lack of periodicity in this direction. But, in the direction parallel to the surface periodicity remains and the wavevector conservation still holds as

$$\vec{K}_{\parallel}=\vec{k}_{\parallel}+\vec{g}$$

where, $\vec{k}_{\parallel}$ and $\vec{g}$ are the parallel component of the bulk electron wavevector and reciprocal lattice vector respectively. From the energy conservation at the surface we may write

$$\frac{\hbar^2 \vec{K}_\perp^2}{2m} = [E_f(\vec{k}) - E_v] - \frac{\hbar^2}{2m}(\vec{k}_\parallel^2 + \vec{g}^2)$$

Therefore, we see that if we know the energy at the final state $E_f(\vec{k})$ and the vacuum level E_v we can calculate the directions of photoelectrons generated by a bulk transitions.

In normal photoemission, photoelectrons are emitted in the direction normal to the crystalline surface and we have $\vec{k}_\parallel = 0$. This considerably simplifies the problem as we are confined to sampling bulk states as a function of $\vec{k}_\perp$ along a specific line in $\vec{k}$ space.

In the independent-particle approximation the expression for current density in three-step model of photoemission process may be written from Fermi Golden rule[3] as

$$\frac{di(E)}{d\Omega} = \frac{2\pi}{\hbar} \sum_i |\langle\psi_f|H'|\psi_i\rangle|^2 \delta(E-E_f)\, \delta(E_f-E_i-\hbar\omega)\, f_0(E-\hbar\omega)\, [1-f_0(E)]$$

(1.1)

where H′ is the perturbation responsible for photoemission by radiation of frequency ω, given by $H' = (e/2mc)(\vec{A}\cdot\vec{p}+\vec{p}\cdot\vec{A})$, $\vec{p}$ being the one electron momentum operator and $\vec{A}$ is vector potential of the photon field. $|\psi_i\rangle$ and E_i refer to initial state wavefunction and energy and $|\psi_f\rangle$ and E_f to the final state wavefunctions and energy, and $f_0(E)$ denotes the Fermi occupation function. The sum is taken over all occupied states and the δ-functions establish the energy selection rule. Therefore, the photoemission cross-section calculation is essentially the evaluation of the matrix element $\langle\psi_f|H'|\psi_i\rangle$ and one has to know the initial and final state wavefunctions and the photon field at the surface.

The final state wavefunction is nonvanishing outside the solid and represents the electron arriving at the detector while the initial state wavefunction describes the bound electron before excitation, both the wavefunctions being the solution of Schrödinger equation of the unperturbed system. The initial and the final states are modified from the bulk states by the presence of the surface. The electronic states in the presence of surface have been calculated self-consistently by a number of authors. These methods are generally based on Linear Augmented Plane Wave (LAPW)[4-7] and Linear Muffin Tin Orbitals (LMTO)[8-10] methods - and these involve a substantial computational effort. However, so far, photoemission calculations have not incorporated the wavefunctions resulting from such self-consistent procedure.

There has been a number of approaches for photocurrent calculation. Mahan[11](1970) gave a scattering approach (first proposed by Adawi[12] (1964)) of photoemission in the free electron model and considered the angular distributions of photoelectrons. Ashcroft and Schaich[13] (1970) developed a model of photoemission theory on the basis of quadratic response theory and independent particle approximation. The calculated results are similar to that of Mahan. Also, they have studied photoemission from nearly free electron and tight binding model of a solid and the photoyield from the surface states. Endriz[14] (1973) developed a modified form of the Mitchell-Makinson[15,16] time dependent perturbative calculation of the surface photoeffect considering both the electron excitation back into the metal as well as electron emission into the vacuum. The calculation was based on Bloch hydro-dynamic equations where an improved treatment of surface polarization charge density variations had been considered. The results for the case of aluminium and other nearly free electron metals agree with the experimental data but fails to reproduce the direct optical excitation of the surface photoelectric effect in the alkali metals.

Kliwer (1976)[17] presented both local and non local theory of photoemission in detail in which the surface photoeffect was identified as being exclusively due to the presence of a longitudinal component of the vector potential inside the solid.

Mativ & Metiu[18] (1980) were primarily concerned with the fields in the immediate vicinity of the interface and developed a scheme for a general solution of Feibelman's model. They determined a dielectric function which in contrast to conventional models is continuous across the interface. The plot of the photoyield versus photon energy did not show the behaviour as obtained by Feibelman[19] and Levinson *et al*[20] for aluminium. They found their model to be valid for photon energy greater than the plasmon energy and the model was applicable only to free electron type of solids.

The photon field can also be calculated from hydrodynamical model which considers the electron hole-spectrum and uses the dielectric function. Using this model Kempa and others[21] (1983, 1985) calculated the vector potential for aluminium and also had incorporated the photon field in the photoyield calculation. It is shown that the frequency dependence of the photoyield is essentially due to the behaviour of the electric field but does not depend very much on the initial and final state wavefunction. Their results for photoyield agree with the experimental data. Barberan and Inglesfield[22] (1981) calculated photoemission from aluminium considering the band structure effects but they have neglected the screening of the photon field. Although their results fail to produce the observed variation of photoemission intensity from a constant initial state as a function of photon energy - it gives good agreement with the experimental data at fixed photon energy. Further, using the simple hydro dynamical method for non-local screening at a metal surface they have calculated photocurrent from both the surface state and the Fermi level of aluminium which gives good agreement with the experimental results.

Meyers & Feuchtwang[23] (1983) developed a detailed theory of photoemission from a free electron metal with a vanishingly small optical absorption above the plasmon energy. Calculated photoelectron energy distribution curves (EDC) differ significantly both in magnitude and dependence on photon energy from the conventional free electron results. Lee & Schaich[24] (1988) presented a series of model calculations on a simple theory of photoemission yield for jellium metals considering the spatial variation for both the potential energy barrier and the photon field. They have shown that a suitable choice of the parameters can made the predictions to agree with experimental data retaining the surface effect mechanism.

Feibelman[19] (1975) calculated the vector potential in the neighbourhood of a flat jellium-vacuum interface, for the case of long wavelength transverse electromagnetic wave incident form the vacuum. The Random Phase Approximation (RPA) to the conductivity tensor was used and the required one electron wave functions were evaluated from the self-consistent surface barrier potential of Lang and Khon[25]. Vector potential was studied in detail, as a function of the parameters of the surface and the photon energy which may be used for the calculation of refraction effects in surface photoemission and in reflection spectroscopy. Again for the jellium model, he calculated the surface photocurrent using the same surface potential barrier model to evaluate the initial and final state wavefunctions and the spatial behaviour of the photon field. The shapes of the surface photoelectron energy and the angular distribution are independent of the surface structure, while, the total surface photoyield versus frequency is strongly dependent on it.

Mukhohopadhay & Lundqvist[26] (1978) calculated the electromagnetic field near a semi infinite jellium surface. The solutions for the vector potential in the vacuum and bulk regions are of asymptotic form and in the surface region this form becomes modified due to the potential. They concluded that the solution in the surface region depend essentially on the particle-hole excitation. They used their formulation to study the semi classical infinite barrier (SCIB) model of the sharp metal surface and the long wavelength limit for the electromagnetic wave incident on a diffuse metal surface which have been considered by Kliewer and Feibelman.

Photoemission calculations based on LEED formalism have been done by several authors e.g., Liebsch[27], Pendry[28], Pendry & Hopkinson[29]. Liebsch (1974) presented a detailed theory of angle-resolved photoemission from the localized adsorbate orbital considering the effects of final states. In some theoretical approaches, photoemission process is considered as a one-step quantum mechanical event in which an electron, under the influence of the electromagnetic field, is removed from an occupied state and deposited at the detector. Liebsch (1976) expresses the initial state wavefunction as the sum of the spherical waves emanating directly from the atom at the origin and also the scattered waves from the surrounding atoms, to the detector. Both multiple and single scattering processes are included. The approach is similar to LEED but here, electron source is the spherical wave rather than the external beam of plane wave electrons.

A sophisticated theory of photoemission has been developed by

Pendry[28] (1976) where, the wavefunctions for both the initial and final states for the semi-infinite solid are constructed accurately. The semi-infinite solid is supposed to be composed of stack of parallel layers of atoms with a potential of muffin-tin form. The initial state wavefunction has different forms in the interstitial and muffin-tin regions. The final state wavefunction is represented by an electron going to the detector as in Low Energy Electron Diffraction. The vector potential was taken to be a constant and a convenient choice of a gauge for the vector potential simplifies the mathematical calculations. For the scattering from each layer, the reflection and transmission matrices have been calculated and this procedure is continued first for a pair of layers and then pair of pairs and so on. This is called the layer doubling method to consider the finite thickness of the crystal. The conditions for the convergence of the method is to introduce an imaginary part of the potential ($V_{0i} < 0$) to consider some finite absorption. This is computationaly a fast method and can also be extended to photoemission from surfaces covered with overlayers. The formalism has been applied to both clear and adsorbate covered surfaces[30].

Ishii & Aisaka[31] (1991) presented a theoretical analysis of the angle-resolved photoemission spectrum by using a dynamical multiple scattering formalism for photoelectrons. Their calculated spectrum shows a different peak position compared with that of band calculation with the same muffin-tin potential which may be due to the multiple scattering effect of the photoelectrons and the mean free path effect for both the initial and final states of photoexcited electrons. However, the discrepancy between the calculated and the experimental results[32] is very small in case of Al(100) but large for Na(110).

The wavelengths of radiation typically used for exciting the photoelectrons are long compared to atomic dimensions. This is the argument for ignoring the spatial variation of the incident electromagnetic field and take it to be constant. This assumption of constant field can be utilised to make the computation simpler by using the commutation relation between $\vec{p}$ and $\vec{A}$ and choosing a convenient gauge - as has been done, for example, by Pendry.

In many cases the results of such calculations gave reasonable agreement with experiment. However, in certain situations, e.g. variation of photocurrent with photon energy, the consideration of spatial variation of photon field is important. Bagchi & Kar[33] showed that, even with a simple model, consideration of variation of field near the surface gave a reasonable qualitative agreement with experimental results for the photocurrent from the tungsten surface as a function of photon energy. Feibelman has also considered this problem in some detail with his much more sophisticated self-consistent field calculation with the jellium model, and applying this to the case of aluminium showed that the spatial variation of the photon field should not be ignored. Feibelman's calculation is, however, applicable only to free electron metals, and further, the self-consistent field calculation is an extremely involved process and no attempt has been made so far to incorporate this field variation into a LEED type calculation.

The model of Bagchi & Kar, on the other hand, uses experimentally measured optical data as input and is therefore, much more empirical in character. However, the expression for field can be analytically derived in the long wavelength limit for this model and so it is easier to incorporate into a photoemission calculation. In addition, this model may be applied to metals other than free electron types. We note that being a 'local' model - it is inadequate for the exact description of fields -- but it is definitely an improvement on constant field. The fields for a number of elements have been calculated with this model[34]. We have used this model in our photoemission calculations and so, at this point we give a brief description of the fields resulting as solutions of this model.

In this model, the z-direction is taken to be perpendicular to the nominal surface chosen as z=0 plane and the metal is assumed to occupy all the space to the left of this plane. The response of the electromagnetic field is bulk like everywhere except in the surface region defined as $-a/2 \le z \le a/2$. In this region the model dielectric function is chosen to be a 'local' one which interpolates between the bulk value and the vacuum value (unity) out side as

$$\epsilon(\omega) = \begin{cases} \epsilon_1(\omega) + i\epsilon_2(\omega) & z \le -\dfrac{a}{2} \\ \dfrac{1}{2}[1+\epsilon(\omega)] + [1-\epsilon(\omega)]\dfrac{z}{a} & |z| \le \dfrac{a}{2} \\ 1 & z \ge \dfrac{a}{2} \end{cases}$$

(1.2)

For a p-polarised light, incident on the surface plane at an angle θ_i with z-axis, the magnetic field $B(z) = B(Q,\omega,z)$ (where $Q=(\omega/c)\sin\theta_i$ is small) is in the y-direction and it obeys the following equation with $\epsilon=\epsilon(\omega)$

$$\frac{d}{dz}\left(\frac{1}{\epsilon}\frac{dB}{dz}\right) + \left(\frac{\omega^2}{c^2} - \frac{Q^2}{\epsilon}\right)B = 0$$

This equation may be obtained from Maxwell's equations. The components of the electric field can be obtained from the magnetic field by using the relations

$$E^{x}(\vec{Q},\omega,z) = \frac{c}{i\omega\epsilon}\frac{dB}{dz}$$

$$E^{z}(\vec{Q},\omega,z) = -\frac{\sin\theta_i}{\epsilon}B$$

The solution of the above equation leads to the normal component of the electric field in the limit $\omega a/c \to 0$

$$\frac{E_z(\vec{Q}\to 0,\omega;z)}{E_0} = \begin{cases} -\dfrac{\sin 2\theta_i}{\sqrt{[\epsilon(\omega)-\sin^2\theta_i]}+\epsilon(\omega)\cos\theta_i} & z<-\dfrac{a}{2} \\[2ex] -\dfrac{\sin 2\theta_i}{\sqrt{[\epsilon(\omega)-\sin^2\theta_i]}+\epsilon(\omega)\cos\theta_i}\,\dfrac{\dfrac{a\epsilon(\omega)}{1-\epsilon(\omega)}}{\dfrac{z}{a}+\dfrac{1}{2}\dfrac{1+\epsilon(\omega)}{1-\epsilon(\omega)}} & -\dfrac{a}{2}\le z\le\dfrac{a}{2} \\[2ex] -\dfrac{\epsilon(\omega)\sin 2\theta_i}{\sqrt{[\epsilon(\omega)-\sin^2\theta_i]}+\epsilon(\omega)\cos\theta_i} & z>\dfrac{a}{2} \end{cases}$$

(1.3)

In our calculation, we have made a slight change by taking the surface region from -a to zero. This transformation does not change the qualitative behaviour of the field in the different regions.

In this thesis, we have first used the free electron model for initial and final state wavefunctions and the case of normal photoemission from the Fermi level of aluminium for the (100) face was considered as an application. For improving the free electron wavefunctions, the initial (free-electron like) state was replaced by that calculated with a periodic potential in muffin-tin form. The case of aluminium was considered again and the calculated results were compared with the free electron results. Finally, the formalism for photocurrent calculation with a LEED type final state and band initial state with the field given by this model has been developed. However, numerical results for this case have not yet been computed.

In addition, we have calculated the local field near the surface of some dipolar lattices with hexagonal, hexagonal close-packed and diamond structure. The major part of the works included in this thesis have been published[38,41,52].

We may mention that the fields calculated from Bagchi & Kar model, along with free electron wavefunctions have also been used subsequently by Thapa & Kar for normal photoemission from beryllium and the results are to be published soon[39]. Also calculations with Kronig-Penney wavefunctions and fields from this model and the dielectric functions for a number of elements have been performed and published[40].

The contents of the thesis are organized as follows. In chapter-II the photoemission calculation using free electron wavefunction with a simple model for the spatially varying photon field and its application to aluminium has been presented. The photocurrent using the same simple form for the photon field, band wavefunctions and also a muffin-tin potential for aluminium and tungsten surface are presented in chapter-III. Chapter-IV has formalism for photocurrent calculation with time reversed LEED type final states, band initial states and the photon field variation in the surface region. Chapter-V contains the calculation of the dipolar fields near the surface of crystals with simple hexagonal, hexagonal close-packed and diamond structure. Precise summary of the total work done in this thesis and conclusion are given in chapter VI. The details of some involved mathematical calculations and the FORTRAN programs used are given in the APPENDIX. Reprints of publications are also included.