CHAPTER - 1

INTRODUCTION
Photoemission is basically a process in which electrons are emitted when electromagnetic radiation, typically in the visible or ultraviolet region is incident on the surface. Photoemission spectroscopy has become a very useful probe in understanding both the surface and the bulk electronic properties of metals and semiconductors. In Ultraviolet Photoemission Spectroscopy (UPS), the source of radiation is ultraviolet lamp. The ultraviolet radiation in the range of 10 - 300 eV brings the excitation of electrons within a small value of escape depth which can come out of a solid and make photoemission a useful technique for the study of properties of surface of solids. Also, the variation of photon energy leads to a variation in escape depth of the electrons by means of which its relative importance to the surface and the bulk effects can be varied. In X-ray Photoelectron Spectroscopy (XPS), the source of radiation is an X-ray tube. An X-ray in the range of 1000 eV or more is also used to study the inner core level of the solid due to its highly penetrating characteristic. The high absorption coefficient of ultra-violet radiation and small escape depth of the electron emitted from solids gives the UPS a greater advantage over other methods of investigating the electronic states of solids.

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. In Angle-integrated Ultraviolet Photoemission, all emitted electrons are collected by a hemispherical detector while in angle-resolved photoemission the emitted electrons are collected for a specified angle. Angle integrated photoemission gives a joint density of states while, the angle-resolved photoemission gives a detailed information of band structure, surface sensitiveness etc. In Angle-Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS), the energy of the electrons emitted
at a fixed angle is analysed and this gives rise to energy distribution curve. By
determining the momentum of electrons which shows a maximum on the curve and
by measuring the change in energy position of the maximum on the energy
distribution curve with the change of momentum, one can determine the energy-wave
vector relationship. The method of ARUPS is shown in Fig. (1.1) where $\theta$ is the angle
of incidence of the incoming UV radiation, $\theta$ is the angle of the energy analyser with
respect to the normal which can be varied from 0° to 90°. As these experimental
techniques allows measuring the dispersion of occupied bands as well the unoccupied
bands in and around Fermi level, they have become an important tool for investigating
the electronic properties of clean and adsorbate-covered surfaces and thin films. The
detailed interpretation of photoemission data obtained from experiments requires the
use of theory which should be able to incorporate appropriately the initial and final
state wavefunctions of the electrons as well as the spatial form of the electromagnetic
field which is responsible for photoexcitation in the first place. More detailed
information about the ARUPS has been provided by Feuerbacher et al.\textsuperscript{1}, Inglesfield\textsuperscript{2},
Willis et al.\textsuperscript{3}, Dose\textsuperscript{4}, Glasser et al.\textsuperscript{5}, Plummer and Eberhardt\textsuperscript{6}, Kar\textsuperscript{7}, Schattke\textsuperscript{8},
Braun\textsuperscript{9}, Rotenberg \textsuperscript{10} etc.

The photocurrent density formula may be written with the help of Golden Rule
formula\textsuperscript{11} as

$$\frac{dI(E)}{d\Omega} = \frac{2\pi}{\hbar} \sum \left| \langle \psi_f | H' | \psi_i \rangle \right|^2 \delta(E - E_f)\delta(E_i - E_f - \hbar\omega)f_o(E - \hbar\omega)[1 - f_o(E)]$$

(1.1)

where $E_i$ and $E_f$ are the initial and final state of energy, $\psi_i$ and $\psi_f$ are the initial and
final state wavefunction, $f_o$ denotes the fermi occupation function and $\delta$ - function
Figure (1.1): Schematic diagram of Angle-Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS).
establish the energy selection rule. The perturbation in the Hamiltonian responsible for the photoexcitation of the electron is given by

\[
H' = \frac{e}{2mc} (p \cdot A + A \cdot p)
\] (1.2)

where \( p \) is the one electron momentum vector and \( A \) is the vector potential.

Now, formula for photoemission cross-section can be written as

\[
\frac{d\sigma}{d\Omega} = \frac{k^2}{\omega} \left| \langle \psi_f | H' | \psi_i \rangle \right|^2
\] (1.3)

Hence, the calculation of the photoemission cross-section is essentially the calculation of the matrix element \( \langle \psi_f | H' | \psi_i \rangle \) and one has to know the initial and final state wavefunction and the photon field at the surface. The initial state wavefunction describes the bound electron before excitation while the final state wavefunction represents the electron arriving at the detector.

A photoemission calculation has been done by using a number of approaches. Mahan\textsuperscript{12} performed extensive calculations on the angular dependence of photoemission. He extended the wave mechanical scattering theory originally proposed by Adawi\textsuperscript{13} which regards the emitted electron wavefunction as equivalent to the time reversed form of an incident electron along with the scattered part. In his calculations, Mahan started with the free electron model and calculated the effects of the surface and volume on photoemission. Then he extended his calculation to band structure effect on photoemission in the alkali metals. Schaich and Ashcroft\textsuperscript{14} had developed a model theory of photoemission on the basis of quadratic response formalism and independent particle approximation. To incorporate the band structure effect, they used Kronig-Penny Potential model. Their calculated results are similar to
that of Mahan. Endriz\textsuperscript{15} developed a modified form of the Mitchell-Makinson\textsuperscript{16,17} time dependent perturbation for the calculation of the surface photoeffect in which both the electron excited back into the metal as well as electron emitted into the vacuum are considered. His calculation was based on hydrodynamic approximation and applied it to the case of aluminium and other nearly free electron type of metals. The result agrees well with the experimental data but fails to reproduce the direct optical excitation of the surface photoelectric effect in the alkali metals.

Liebsch\textsuperscript{18} and Pendry\textsuperscript{19,20} have recognised that in principle, the calculation of initial state wavefunction $\psi_i$, and final state wavefunction $\psi_f$, was similar to Low Energy Electron Diffraction (LEED) calculation. In their model, they described the semi-infinite solid to be a 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 which had an electron going into the detector was shown to be a time-reversed LEED state. The photoemission calculation of Pendry\textsuperscript{19} gave accurate computational results for the initial and final electronic states. Even though Pendry recognised that the vector potential would vary in the surface region, the vector potential was taken to be a constant as this simplifies the calculation of the matrix element involved in the photoemission calculation.

Ishii and Aisaka\textsuperscript{21} by using a dynamical multiple scattering formalism have presented a theoretical analysis of the angle-resolved photoemission spectrum for simple metals. Due to the multiple scattering effect of photoelectrons and the mean free path effect for both the initial and final states of photoexcited electrons, their calculated spectrum shows a different peak position compared with that of band
calculation with the same muffin-tin potential. They have also discussed the surface effects.

In photoemission theory of solids, the essential ingredient is the proper treatment of the electromagnetic fields within the solid. Kliewer\textsuperscript{22} presented both local and non local theory of photoemission in detail. He explained that the excitation of photoelectrons by the longitudinal electric field represents an excitation mechanism which is unique to $p$-polarization and which requires the presence of a surface. He identified this as the surface photoeffect. For the calculation of electromagnetic field, Feibelman\textsuperscript{23} proposed a realistic model called Random Phase Approximation (RPA). The required one electron wave functions were evaluated from the self-consistent surface barrier potential of Lang and Kohn. Vector potential as a function of the parameters of the surface and the photon energy was studied in detail. The prediction of RPA agrees well with the photoemission experiments that describe the nature of electromagnetic field in the case of free electron metal surfaces. Feibelman assumed that spatial variation parallel to the surface is negligible compared to those perpendicular to the surface. He found that the shape 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. His calculation was in good agreement with the measured data of Levinson \textit{et al.}\textsuperscript{24}. Mativ and Metiu\textsuperscript{25} were concerned with the fields in the immediate vicinity of the interface and developed a scheme for a general solution of Feibelman’s model\textsuperscript{23}. They determined a dielectric function which is continuous across the interface. Their result did not show a similar behaviour as that of Feibelman\textsuperscript{13} and Levinson \textit{et al.}\textsuperscript{24} for aluminium. They found their model to be valid for photon energy greater than the plasmon energy and
are applicable only to free electron type of solids. Mukhopadhyay and Lundqvist\(^{26}\) also calculated electromagnetic field near a semi infinite jellium surface. The vector potential in the bulk and vacuum region are of asymptotic form and in the surface region, it is modified due to the potential. The model was used to study the semi classical infinite barrier (SCIB) model of the metal surface and the long wavelength limit for the electromagnetic wave incident on a diffuse metal surface. Bagchi and Kar\(^{27}\) developed a frequency-dependent dielectric model which is chosen to be a local one, which interpolates linearly between the bulk value inside the metal and the vacuum value (unity) outside. They showed that even with 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.

Using the dielectric model developed by Bagchi and Kar\(^{27}\), Thapa\(^{28}\) studied the variation of electromagnetic field from various metals and showed that the results were in good agreement with experimental results. Using the same dielectric model and by considering the crystal potential to be Kronig-Penny potential\(^{29}\), Thapa et al\(^{30,31}\) also calculated the photocurrent in the case of a number of metals and semiconductors. Pachuau et al\(^{32,33}\) have calculated photoemission using Mathieu potential model as described by Davison and Steslicka\(^{34}\) to various metals which reproduces qualitatively the behaviour of the experimental results as reported by Bartynski et al\(^{35}\). Zoliana et al\(^{36}\) have used projection operator method of group theory to develop the initial state wavefunction which is used for the evaluation of photocurrent. In their calculations, they deduced the basis function for Cu which they
had incorporated in the formulation of the initial state wavefunction. This had been
applied to the case of metals and semiconductors,

Much of scattering theory can be conveniently expressed in terms of Green functions. The Green function concept is useful, general and pleasing that its use has become practically a standard method in many fields of solid state physics. In solid state physics, Green function’s method was originally used for the solution of the one-particle Schrödinger’s equation in periodic lattice. W. Kohn and N. Rostoker\textsuperscript{37} solved the Schrödinger’s equation by employing variational-iteration method and using Green function. They obtained the geometrical structure constants and apply it to obtain the conduction band of metallic lithium. At the same time an essentially equivalent scheme was developed from different point of view by Korringa\textsuperscript{38}. Hence, together they named their method as Korringa-Kohn-Rostoker (KKR) method and developed a standard computer code known as KKR code. Their method was standard and used by many research workers, but the mathematical calculations involved were complex and involved heavy computations. Kohn\textsuperscript{39} also used Green’s function method similar to that of Kohn and Rostoker\textsuperscript{37} for studying electronic structure of films and surfaces. Even though he simplified it, the method still involved rigorous calculations.

Band structure calculations have been done by using various methods. Using empirical pseudopotential method, Kohn \textit{et al.}\textsuperscript{50} had calculated the band structures of Lead salts namely PbS, PbSe and PbTe. Slater and Kosker\textsuperscript{41} have introduced the Tight-Binding method for the calculation of band structures of a chosen structure based on the parametrization of Hamiltonian matrix elements. Since then, tight-binding method has been used successfully for the calculation of band structures and
total energies of various systems. Yang et al. had calculated band structures by using tight binding approximation and applied it to s-p metals Al, Ga and In. Their results showed that the method they employed successfully predicts the correct ground states without the inclusion of the corresponding first principles data in the fit. Kar and Soven have also calculated band structure of thin films by using multiple-scattering technique. By using orthogonalized plane wave method, Herman et al. have calculated band structure of Lead salts. Hohenberg and Kohn have used Density functional theory (DFT) for the calculation of electronic properties of solids. They have shown that the electron density uniquely defines the total energy of a system and is a functional of the density. For solving the DFT equation, the full potential linearized augmented plane wave (FP-LAPW) method was developed by Madsen et al. They solved the Kohn-Sham equations for studying the band structure, density of states, optical properties etc. by writing several FORTRAN programs. This in the form of a standard program is known as WIEN2k code.

In this thesis we will present a simple method of calculating the initial state wavefunction by Green function’s method which will be used in photoemission calculations. The crystal potential will be considered to be Kronig-Penny potential. For the surface photoemission, the initial state wavefunction will be taken to be a Gaussian type of wavefunction. Photoemission from metals and semiconductors will be calculated. Further, to include the band structure effects of solids, basis functions will be deduced by using projection operator method of group theory. These basis functions will be incorporated in the initial state wavefunction deduced by Green function’s method which will then be used to calculate photocurrents from metals and
semiconductors by evaluating the matrix element. Lastly, band structures will be calculated by using the full-potential linearized (FP-LAPW) method.

The materials in this thesis are organized as follows:

1. In chapter 2, the basic theory involved in the calculation of the vector potential \( \vec{A}_w(\omega, z) \) will be briefly discussed. This vector potential is spatially dependent and is defined separately for the bulk, surface and vacuum regions. For different metals and semiconductors, the variation of the vector potential \( \vec{A}_w(\omega, z) \) against the incident photon energy \( h\omega \) and the location of the surface plane \( z \) will be calculated.

2. In chapter 3, we will first present the formulation of the initial state wavefunction by using Green function’s method followed by its application for photocurrent calculations. Results of photocurrent calculations from different metals and semiconductors will be presented and discussed. Then by using projection operator method of Group theory, the basis functions for \( Cu \) and \( W \) will be deduced which will be used to developed the initial state wavefunctions. This will in turn be used in the photoemission calculations from solids having fcc and bcc crystal structures respectively.

3. In chapter 4, we will present the calculation of band structure of metals and semiconductors by using FP-LAPW method.

This will be followed by the conclusion and references.