CHAPTER I

INTRODUCTION

Photoemission spectroscopy is now widely used as an investigative method for the electronic states of the surface and the bulk of a solid. The high absorption coefficient of ultraviolet radiation and the small escape depth of the electrons photoemitted from solid gives the ultraviolet photoemission spectroscopy a big advantage over the other methods of investigating the electronic states on the surface of solids. Angle resolved ultraviolet photoemission spectroscopy (ARUPS) allows the determination of the energy and the momentum of the photoemitted electrons and can be used to reveal the electronic structure of the surface and the bulk of the crystal. In the ultraviolet (UV) photoemission experiments, ultraviolet radiation in the range of 10 to about 300 eV excites electrons of which those within the escape depth, which may be a few to about a hundred layers, can get out of the solid. The small value of the escape depth in the region of 10 - 100 eV makes photoemission an useful technique for surface studies. In addition, variation of the photon energy leads to a variation in escape depth whereby the relative importance of the surface and the bulk features can be varied.

To measure the energy distribution of the photoemitted electrons, two kinds of the energy analyzer are usually used. In one method, electrons emitted in all angles are collected in a hemispherical analyser. This is known as angle-integrated ultraviolet photoemission spectroscopy. The other one can analyse the energy of the electrons emitted at a prescribed angle giving the angle resolved energy distribution curves (AREDC). Knowing the kinetic energy and the direction of the photoemitted electrons, one can determine the momentum of the electrons creating the maximum on the ARDEC and establish the energy-momentum dependence corresponding to the band creating this maximum. Measuring the shift in energy positions of the maxima on the AREDC's with the change of momentum obtained by varying the angle of the analyser or the energy $\hbar\omega$ of the UV radiation, the energy-wave vector relationship can be determined. Knowing the kinetic energy of the electron one can determine the absolute value of the momentum K of the electron in vacuum from the relation $E=\hbar^2K/2m$. In Fig. (1.1), the method of ARUPS is illustrated. The incoming UV radiation is incident on the sample at an angle of 45^o with respect to the normal. The angle θ of the electron analyser can be varied between 0 and 90^o. The azimuthal angle can be set to any desired value. One can determine the energy and angular distributions of the photoemitted electrons as a function of

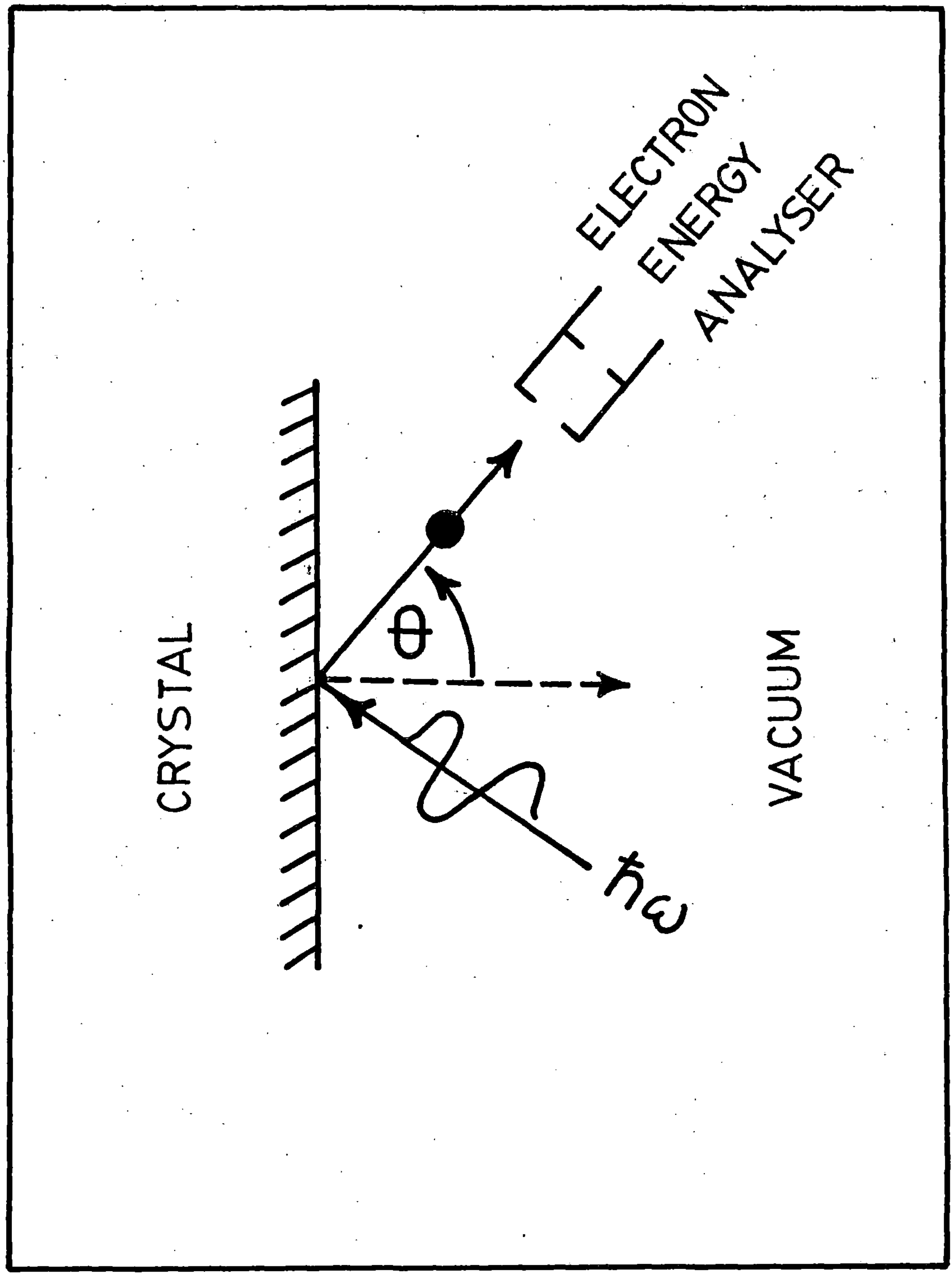

Figure 1.1

the energy, polarization and angle of incidence of the applied radiation. The theoretical explanation of such data clearly requires a detailed knowledge of both the electronic structure of the photoemitting substance and its interaction with the radiation.

There had been a great deal of interest in photoemission as a probe of bonding of atoms which lie in the outermost layers of a solid. But the detailed interpretation of the photoemission (PE) data requires the use of a theory of PE which should in its simplest form be able to calculate the initial and final state electron wavefunctions as well as the spatial form of the vector potential which is involved in the photoemission matrix element. Considerable progress have been made in the past for calculating the self-consistent wavefunctions corresponding to electron states below the vacuum level for semi-infinite solids[1,2]. Reliable techniques have been developed for the calculation of electron wavefunctions at energies 30 - 300 eV above the vacuum level. But the same cannot be said for calculation of the electromagnetic fields which excites photoelectrons especially from the surface of the solid where the electrons have a very short mean free path. For consistency one should include the variation of the electromagnetic field in the presence of the surface. The calculation of the vector potential is an extremely difficult problem in the general case. In most of the calculations therefore, one proceeds with the assumptions of spatially constant vector potential for computational simplicity. However in certain situations one has to include the photon field variation to get even qualitative agreement with the experimental value.

A simple calculation of photocurrent involves the evaluation of the *matrix element* $\langle\psi_f|H'|\psi_i\rangle$ *where* ψ_i and ψ_f are the initial and final one electron states whose energies are connected by $E_f=E_i-\hbar\omega$. The perturbation in the hamiltonian responsible for the photo excitation of the electron is given by

$$H'= \frac{e}{2mc}\,(\vec{p}.\vec{A}+\vec{A}.\vec{p}) \qquad (1.1)$$

where $\vec{p}$ is the one electron momentum operator and $\vec{A}$ is the vector potential. In the standard photoemission calculation, the one electron states are calculated with a high degree of accuracy but the variation of the photon field is generally neglected. In the case where one looks at the photoemission current as a function of the photon energy with the constant initial state, the photon field variation in the surface region needs to be considered more carefully. A first principle calculation of the electromagnetic field in the presence of the surface is an extremely complex problem. The calculation of the vector potential in the surface region therefore needs a detailed microscopic analysis of the surface in terms of the dielectric response function. This is because the usual theory of refraction breaks down at a microscopic level which therefore calls for the consideration of the factors like surface discontinuity, non-locality etc.

The photocurrent arising from the interaction of the electromagnetic field with the solid has been derived by a number of authors[3-6]. The current density may be written with the help of golden rule expression[7] as

$$\frac{dj(E)}{d\Omega} = \frac{2\pi}{\hbar} \sum_f |\langle\psi_f|H'|\psi_i\rangle|^2 \delta(E-E_f)\delta(E_f-E_i-\hbar\omega) f_0(E-\hbar\omega)[1-f_0(E)] \tag{1.2}$$

In Eq. (1.2), E_i (E_f) is the initial (final) state energy and f_0 is the Fermi occupation function. δ – function describes the energy conservation. Thus we see that the calculation of the photocurrent density is based on the evaluation of the matrix element $\langle\psi_f|H'|\psi_i\rangle$.

Several authors have done the photocurrent calculations by using various approaches. For example, Endriz[8] has used the modified form of the Mitchell-Makinson time dependent perturbation calculation of the surface photoeffect. He calculated the photocurrent by using the hydrodynamic approximation and applied it to the case of aluminium and other alkali metals where the results for photon energy at plasmon energy($\hbar\omega_p$) agreed with the experimental data. However the model of Endriz did not reproduce the experimental data of Petersen and Hagstrom[9] which showed a maximum at 12 eV in photoemission cross-section. Schaich and Ashcroft[4] had also developed a model theory of photoemission on the basis of quadratic response and independent particle formalism but had not assumed any detailed model of the dielectric response function for the surface. They used a computationally simple model to study the electronic structure in solids and surfaces to understand photoemission.. To incorporate band structure effects, the model of Kronig-Penney was used. In this model spatial dependence of the vector potential was neglected and throughout the calculation it was assumed to be a constant. The approach of Mahan[3] was to extend the wave mechanical scattering theory originally proposed by Adawi[10] which regards the emitted electron wavefunction as equivalent to the time reversed form of an incident electron along with the scattered part.

The evaluation of the matrix element $\langle\psi_f|\vec{A}.\vec{p}+\vec{p}.\vec{A}|\psi_i\rangle$ involves the knowledge of ψ_i and ψ_f. Leibsch[11], Pendry[12] and others have recognised that the calculation of ψ_i and ψ_f was similar in principle to Low Energy Electron Diffraction calculation. Their approach was to consider the solid to be a stack of identical layers terminated at the surface. The final state, which had an electron going into the detector, was shown to be a time-reversed LEED state. The initial state can also be constructed similarly. Pendry[12], for example, has given a detailed method of calculation using these ideas and has also developed a detailed program for application to real system with notable success. In his calculations, the initial and final states are computed quite accurately but the vector potential is taken to be a constant. Although Pendry recognised the fact that the vector potential would vary in the surface region, to take exact account of that was too complex a problem. Also taking $\vec{A}$ to be constant simplified the calculation of the matrix element by using certain commutation relations and choosing a convenient gauge for $\vec{A}$. This method of calculation has been quite successful in different cases. However for the case of photocurrent against photon energy from a constant initial state, this method does not give the right behaviour, especially near the plasmon energy.

Feibelman[13] thought that if the theory of surface electromagnetic field is to be used to interpret the results of the photoemission experiments that probe the outer few layers of a solid, one should use a scheme of calculations to get the correct responses of the external field even in the presence of the surface. This was the motivation which led

Feibelman to envisage the concept of Random Phase Approximation (RPA) dielectric tensor to study the plasmon dispersion and the microscopic refraction problem. In RPA calculation, the surface is smooth and the dielectric response naturally includes the effect of the electron spill-out in the region of the dipolar layer. The only inputs are the electron radius (r_s) and the single-electron surface potential barrier. The potential barrier completely determines the electronic structure of the surface. This can be taken to be output of a self-consistent jellium ground state calculation. But it can also be varied at will to test the similarity of the aspects of the surface responses to various features of the ground state. The RPA is exact for the bulk high density electron gas ($r_s \rightarrow 0$) where it is assumed that the single-electron wavefunction and the energies are based on a Hartee-Fock type calculation. None of these conditions apply to the RPA description of the surface dielectric response. Here the electron gas is not infinite, therefore RPA is not only not exact but it is also not clear how one might write down the first correction to it. The importance of RPA model lies in the fact that it incorporates many electron features that are expected to be important. The RPA dielectric function ε is non-local and interpolates smoothly from 1 in the vacuum to ε_B in the bulk. It includes the single-electron excitation spectrum and it gives rise to bulk and surface plasma oscillations and satisfies the requirement of charge conservation. Also the prediction of RPA agree remarkably well with photoemission experiments that tests the nature of the 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 evaluated A_z within the RPA using $r_s=2$ and incorporated this to the calculation of photoexcitation matrix element using the Lang-Kohn potential for the initial and final state. It was found that his calculated data of jellium was in good agreement with the measured data of Levinson et al[14]. However the calculations of Feibelman which has the most accurate description of the field variation could be applied only to metals which may be represented by jellium model. Mukhopadhayay and Lundqvist[15] and Bagchi[16] have also developed similar methods for calculating the electromagnetic fields near the surfaces.

The semi-classical infinite barrier (SCIB) model of Kliewer[17] considers a sharp surface but it does take into consideration the particle-hole and plasmon excitation. The SCIB model apparently violates the nature of the surface from its very assumption as the infinite barrier is not an accurate approximation to the potential existing at the surface. In this model the electron cannot tunnel out of the solid; therefore, SCIB power absorptance is assumed to represent the photocurrent emitted. For example, the photocurrent is larger above the plasmon energy $\hbar\omega_p$ and below it is completely in disagreement with the experimental data of Levinson et al[14].

The hydrodynamical model of Forstman and Stenschke[18] takes into account the electron-hole spectrum and the dielectric function used is a very simple one from which one can very easily evaluate the photon field $\vec{A}$. Kempa and Forstman[19] have performed the detailed calculations of the electromagnetic field using the hydrodynamical model and had incorporated the field to calculations of the photoyield. This was applied to the case of aluminium and was found that the frequency dependence of the surface photoemission yield is due to the behaviour of the electric field and does not depend very much on the initial and final state wavefunction. Photoyield results obtained by them showed similar experimental behavior as found by Levinson et al[14]. Barberan and Inglesfield[20] have also done a detailed calculations on photoemission using the hydrodynamical screening of the photon field. They had shown that both the uniform vector potential and the Fresnel field are inadequate description of the screened electromagnetic field inside the metal to explain the photoemission results. They found that below ω_z, A_z rises rapidly near the surface due to polarization charge but at ω_p, the rise becomes less rapid and above ω_p there are plasma oscillations. But A_z is almost zero inside the metal at ω_p. This follows as a result of matching the normal component of P which is zero at $\hbar\omega=\hbar\omega_p$ and hence $P_z=0$. It means that E_z is zero inside the metal. This results of Barberan and Inglesfield[20] for the case of aluminium is in good agreement with the microscopic calculation of Feibelman[13] apart from the oscillations in A_z below ω_p. This had been attributed to the excitations in A_z below ω_p which has arisen due to Friedel type of oscillations from the electron-hole excitations which were not included in the hydrodynamic calculation. Maniv and Metiv[6] have achieved also a considerable progress in the calculation of the electromagnetic field in the metal-vacuum interfacial region. They primarily considered the near fields in the immediate vicinity of the interface. They developed a scheme for a more general solution of the Feibelman's model[13] and were thus able to determine a dielectric response function which in contrast to more conventional models is continuous across the interfacial region. The plot of the photoyield versus the photon energy did not show the behavior as obtained by Feibelman[13] and Levinson et al[14] in the case of aluminium. They found that the model was true for photon energy larger than plasmon energy and was applicable to only free electron type of solids.

We find therefore that no such calculations have been done in photoemisssion which considered simultaneously the photon field variation as well as the LEED type states in the matrix. Also not much attention have been paid to the calculation of the fields in the surface region for transition metals and semiconductor. In this thesis we shall at first calculate the spatial variation of the photon field and apply it to the case of a number of elements. The dielectric model of Bagchi and Kar[21] will be used to calculate the photon field. The field calculation will also include the solids like aluminium, silver, rhodium, molybdenum, palladium and semiconductor silicon. The field variations so calculated will be incorporated to the matrix element $<\psi_f|\vec{A}.\vec{p}+\vec{p}.\vec{A}|\psi_i>$ in Eq. (1.1) for calculating photoemission cross-sections. We first used free electron type wavefunctions for the initial and final states and applied this model to aluminium with the appropriate parameters. The calculated photocurrent in aluminium showed a qualitative features in agreement with the experimental data of Levinson et al[14]. To incorporate band structure effects, we used a simple model given first by Kronig and Penney. With the initial state calculated with this model we used the field derived from the experimentally determined dielectric functions of a number of materials and analysed our results.

The material in this thesis is arranged as follows. In chapter II, we shall discuss the model theory of dielectric response function used for the calculations of the electromagnetic field (vector potential) for the vacuum, surface and bulk region of the solids. In chapter III, photoemission calculations using the free electron model of the solid will be discussed. This will be applied to the case of aluminium as it is a weakly s-p bonded metal where free electron theory is applicable. In chapter IV, we shall discuss the general formulation of the initial state wavefunction ψ_i by using the Kronig-Penney model and discuss a number of applications.