MANY-BODY THEORY OF PHOTOEMISSION FROM METALS

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by

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ABSTRACT.

In the first part of this thesis the many-body theory of ultraviolet photoemission from metals is developed in terms of the correlation function where the photon-electron current and the surface tunnelling are both treated as first order perturbations. A critical survey of the related work is given and possible many-body effects are discussed. The solution to the problem of momentum nonconservation in the photoemission from noble and transition metals is suggested.

In the second part the spectra of X-ray induced fast photo electrons from a metal are investigated. It is pointed out that they should have a characteristic skew line-shape resulting from "Kondo-like" many electron interactions of the metallic conduction electrons with the accompanying deep hole in the final state. The same line-shape is also found for the discrete line-spectra of X-rays emitted from metals. This mechanism could account for the well known asymmetries observed for Kα lines.
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**REFERENCES.**

* Main results in these chapters have been reported in:


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CHAPTER 1. - INTRODUCTION.

Though photoemission was the first physical process which got a purely quantum mechanical explanation, due to its complexity it still poses many unsolved experimental and theoretical problems, so that there is still no satisfactory many-body description of the photoemission phenomena.

H. Hertz /1/ and W. Hallwachs /2/ first observed the process which was later called "external photoelectric effect", when they discovered the emission of negative electricity from electrodes exposed to ultraviolet light. P. Lenard /3/ and J.J. Thompson /4/ showed that the particles emitted in the process were electrons.

In 1905, A. Einstein /5/ suggested an explanation of the observed phenomenon on the basis of the Planck's quantum hypothesis. He postulated that the light must be absorbed or emitted in quanta of energy $h\nu$, so that

$$h\nu - W = \frac{1}{2} m v_{\text{max}}^2 = e V_{\text{max}}$$

where $v_{\text{max}}$ is the velocity of the fastest emitted particles, $V_{\text{max}}$ the retarding potential and $W$ the minimum energy required to remove an electron from its place inside the metal to the free field outside.

Einstein's explanation of the photoeffect was the first successful application of the quantum mechanical treatment of the microscopic
processes. It incited much experimental and theoretical work, which was often contradictory and unsuccessful because of the enormously complicated nature of the process. For the sake of convenience we may classify the various photoelectric phenomena which occur when an electron receives sufficient energy absorbing an incident quantum of radiation in four main groups:

1) The external photoelectric effect or simply (ultraviolet) photoemission: the ejection of electrons from (mostly metallic) solids in thin films or in bulk) by visible, ultraviolet or infrared radiation;

2) The X-ray photoelectric effect or X-ray photoemission: the ejection of electrons by X-rays;

3) Photoionization or atomic photoemission: ejection of electrons from gases or vapours;

4) Photoconductivity or internal photoeffect: freeing of electrons in some insulators by light so that they become conducting.

In this work we shall be interested only in the first and second of these, specifically in the ultraviolet photoemission, induced by ultraviolet radiation (5 eV ≤ ω ≤ 15 eV), and X-ray photoemission, induced by hard X-rays (ω ~ few keV).

In the first part of this thesis we consider the volume ultraviolet photoemission from metals which has become increasingly popular in the recent years as a useful tool to investigate experimentally the band structure of solids.
Theoretical work did not follow the progress in experimental research adequately and at present there is no consistent theory of photoemission based on microscopic considerations and using many-body techniques.

In Chapter 2, we develop the basic concepts of surface and volume photoemission and the simplest one-electron theory of volume photoemission. We review briefly the situation in alkali metals and semiconductors and Hopfield's theory as the only successful calculation of many-body effects in photoemission. Then we concentrate on noble and transition metals and describe in some detail the phenomenological approach of Berglund and Spicer, the only attempt to build a satisfactory explanation of the photoemission process in these materials. This approach is based on several assumptions which will later be compared with the many-body formulation of the theory. Among them the fundamental one is the treatment of the electron excitation as a non-direct process, i.e. non-momentum-conserving transition. The remarkable success of this theory in interpreting experimental results is a strong indication that non-one-electron processes have an important role in photoemission from noble and transition metals.

In Chapter 3, we attempt to build a many-body theory of photoemission which is treated as a second-order process where the optical excitation and the surface potential both act as first-order perturbations to the system. The transition probability is expressed in
terms of a rather complicated correlation function which includes all (Coulomb) scattering processes inside the solid. Assuming that the emitted electron is fast we treat its interaction with the rest of the solid by perturbation theory and in this approximation obtain first four contributions to the correlation function. Due to its second-order character and the introduction of the surface as a perturbation the theory in its present form is not suitable for actual computations and has to be simplified further. However, just this explicit treatment of the decoupling of the photoelectron from the solid enables us to visualize the possible higher order processes and in this framework in Chapter 4 we discuss various many-body contributions to the photoelectron spectra. In noble and transition metals at ultraviolet photon energies we exclude the possibility of surface resonances and vertex corrections. Coulomb scattering of a relatively fast outgoing electron is not likely to produce any self-energy effects leading to the lifetime broadening, but when treated as a first order perturbation can give recognizable structures in the measured photoelectron spectrum.

Most interesting many-body problem in ultraviolet photoemission is a question of momentum nonconservation, i.e. direct vs. nondirect excitation processes. We analyze the experimental evidence for nondirect processes which points to the deep hole relaxation as an explanation of a large non-direct contribution to the photoelectron spectra from the narrow bands in metals. We suggest a theoretical
solution of this problem and identify the hole relaxation process as a many-pair excitation similar to the one discussed later in the X-ray photoemission case.

In the second part of this thesis we consider the emission of electrons from deep core states excited by hard X-rays high above the Fermi energy. As we argue in Chapter 5, the scattering of these photoelectrons will decrease, but the relaxation of the suddenly created deep hole will become very strong and change the photoelectron spectrum. In Chapter 6, we describe the theory of such transient phenomena which was developed /52-54/ to explain soft X-ray emission and absorption threshold singularities, and in Chapter 7, we apply this theory to calculate the photoelectron spectra. We extend it to include the effect of the symmetric lifetime broadening of the deep level and the ingoing X-ray. The resulting skew lineshapes are indeed found after careful analysis in the experimental curves, but both for metals and (though systematically lower) for semiconductors, where they are not expected from the theory. We conclude that the origin of this skewness is the asymmetry of the primary X-ray spectrum, which leads to the additional skewness visible in the semiconductor photoelectron spectra.

Asymmetric X-ray lineshapes were measured as early as 1935 /83, 84/, but no theoretical explanation was attempted, and in the analysis of photoemission data they were usually assumed to have a Lorentzian
form. We suggest a mechanism which explains this asymmetry as a result of the singular readjustment of the Fermi sea to the change of the hole state after the X-ray emission. The calculated lineshapes agree with those observed, though further experiments with better resolution are needed to definitely verify our theory.

The same conclusion holds for X-ray photoelectron spectra which are in our analysis firmly linked with X-ray emission experiments. Systematic experimental investigation could provide some quantitative information about the scattering and asymmetry parameters of the solids which are now simply related in our theory.
CHAPTER 2. - ULTRAVIOLET PHOTOEMISSION.

Advantages and disadvantages of photoemission.

Ultraviolet photoemission can be a very useful complement to the optical studies of metals and give us much information about the electronic band structure. Not only the total quantum yield can be measured (as in X-ray emission and absorption), but also the energy spectrum of ejected electrons \( \frac{dN}{de} \); which might enable us to determine the exact position in the occupied band from which the electrons originate. On the contrary, in optical studies of solids, using absorption or emission experiments, from the ultraviolet to the infrared region the continuous distribution of states in conduction and valence bands makes possible very many various transitions for a given photon energy. Also the perturbation caused when creating or removing a core electron in X-ray spectroscopy gives rise to strong many-body effects which made the band structure analysis complicated.

Most other experimental techniques (e.g. transport properties) study effects connected with electrons near or on the Fermi surface of metals. Photoemission is particularly suitable if we want to investigate the band structure of deeper states, especially d and f electrons in noble, transition and rare earth metals.

On the other hand, photoemission is an extremely complicated process which could be in general split into three consecutive processes.
Only the first stage—electron excitation— involves the physical properties that we want to extract from the measured data, and these are (in this range of energies at least) the densities of states. Therefore all additional scattering of the outgoing electron and the hole that is left behind, and its tunnelling through the surface, must be either experimentally reduced or accounted for, because they distort the original spectra.

The scattering processes which most affect the excited electron are:

- Phonon emission (almost elastic)
- Inelastic electron-electron scattering
- Plasmon creation
- Auger processes

The first analysis of these processes was done on a phenomenological basis by Berglund and Spicer /6/, and most of the later work follows their approach. We shall explain their theory later in detail.

The surface effects can, for energies near the threshold, dominate the process and completely screen the band structure by mixing different momenta in the outgoing wave packet. Even if we knew the threshold function or escape probability, and we do not, we could not reconstruct the initial electron state from the final spectrum. To avoid this we must use higher photon energies and electrons excited well above the threshold, where the escape probability can be approximated by the step function, and the electrons cross the surface without
scattering. They only change the wave vector due to the difference in the potential \(W\), and this approximation brings us to the "critical angle" and "escape cone" treatments of the first theories.

Unfortunately the use of electrons excited to higher energies increases the scattering of these electrons in the solid, and one must look very carefully for the region of energies where these two effects cause the least trouble. It seems that the ultraviolet region (e.g. photons with energy 5 to 15 eV) satisfies that requirement.

Experimentally photoemission measurements are very sensitive to the condition of the surface which can deteriorate rapidly and can show many spurious effects coming usually from the spatial variation of the work function. Many very interesting "anomalies" and "resonances" in this field were rapidly oscillating functions of time and finally disappeared after careful measurements, to the great distress of the theoreticians who provided their many-body explanations. A useful experimental trick is the lowering of the work function by caesiating, so that it reduces to 1 - 2 eV, but again one must be careful, because this increases the proportion of low energy electrons in the photoelectron spectrum /7/.

Another difficulty comes also from the work function which creates the gap between the Fermi energy and the vacuum energy. States in this gap we cannot directly detect either in initial or final state, but
only indirectly, combining results of measurements of electron spectrum and quantum yield /6/.

From all these arguments it is obvious that, in order to get any information from the experiments or theory, one must find a simplified approach to the general problem: determine the suitable range of energies where two steps in the photoemission process could be reasonably approximated and then treat the third as exactly as possible. In order to connect the photoemission spectra with the band structure and the many-body effects in the electron excitation process we shall try to eliminate the effects of the scattering of the primary electron on the way to the surface and its escape into vacuum.

Surface photoemission.

Early experimental and theoretical work was mainly concerned with properties near the photoemission thresholds, i.e. frequencies of radiation at which the ejection of electrons (with zero kinetic energy) just started. Richardson and Compton /8/ and Millikan /9/ measured the thresholds for visible light on alkali metals, Hamer /10/ did the same for transition and noble metals. Fowler /11/, Frenkel /12/, Wilson /13/ and many others tried to find the correct temperature and energy dependence of the electron yield near the thresholds.

First theories of photoelectric emission were based on Sommerfeld's model of the metal, where electrons were treated as free particles inside a potential well. Since a free electron cannot absorb or emit a quantum of radiation because of the conservation of energy and momentum, the
The photoemission process in this model can take place only at the surface where the surface potential acts. In this "surface photoemission" the surface provides a source or sink of momentum.

For energies near the threshold (E ≤ 3 eV) this is the dominant photoemission process, and has been extensively investigated. In fact, all the early experimental and theoretical work has been concerned with surface photoemission, and a review of it can be found in Linford /14/. Various theories of surface photoemission were developed by Mitchell /15/ and Nakinson /16, 17/ for metals and Huntington and Apker /18/ for semi-conductors. They all use basically the same method of matching the electronic wave functions on the surface of the metal where the potential energy changes. The
boundary conditions then give the transition probability for excited electrons to cross the surface. Huntington /19/ extended this treatment to include the effect of a periodic potential inside the metal. With the improvement of experimental techniques the observation of new and very interesting phenomena in this region of energy could be expected /20/.

However, in this work we shall not be concerned with surface photoemission for two reasons. Firstly, in the ultraviolet region of photon energies it already ceases to be the only and even dominant effect, and secondly, as a purely surface-dependent phenomenon it gives us no information about the real electronic states inside the metal.

**Volume photoemission: one-electron theory.**

When the band structure of the metal was introduced (Bloch /21/) in 1928, it was realized that absorption of radiation can take place inside the volume of the metal due to the periodic crystal potential. Electrons can be excited from a band to a higher one and subsequently ejected through the surface if their energy is high enough to cross the potential barrier at the surface. Rough estimates by Tamm and Schubin /22/ predicted a very high threshold frequency for this "volume photoemission", and led to this effect being neglected for some time.

In 1945 H.Y. Fan /23/ developed the theory of the volume photoemission in alkali metals and showed that its threshold is higher but
of the same order as that of the surface photoemission, and that the
electron yield is of comparable magnitude. We shall review the basic
ideas of this theory.

Fan considers the electron in a periodic crystal potential which
are described by Bloch wave functions $\psi_k(r) = u_k(r)e^{i kr}$.
The damping of the electromagnetic wave, described by the vector
potential $A = \vec{n} e^{i \omega t}$, in the metal can be neglected, as well as its
wave vector. Interaction of the electron current and the electromag-
netic field is of the form

$$\frac{e}{mc} \vec{p} \cdot \vec{A}$$

(2.1)

where $\vec{p} = -i \nabla$ is the electron momentum operator.
This interaction together with the choice of Bloch wave functions to
describe electron states instead of plane waves makes volume photo-
emission possible. Actual transitions are determined by the matrix
element

$$\langle \psi_k | \vec{p} \cdot \vec{A} | \psi_{k'} \rangle$$

(2.2)

which is different from zero for $k' = k + g$, where $g$ is the reciprocal
lattice vector. In other words, this model considers all one-electron
transitions where electrons are excited by the absorption of a photon
from one zone into another. Fig. 2.2 shows this
process in the reduced zone scheme, where the transition is vertical.

The number of emitted electrons is made up of all the excited electrons having energy large enough to overcome the surface barrier, so that in the Born approximation expression

$$\sum_g \int \left| \langle \psi_k | \vec{p} \cdot \vec{A} | \psi_{k+g} \rangle \right|^2 \delta \left( e_k + \omega - e_{k+g} \right) \, dk (2.3)$$

we must integrate only over the part of the constant energy surface

$$e_{k+g} - e_k \geq \omega. \text{ This part is defined by the requirement}$$

$$e_{k+g} \geq \omega + \frac{1}{2m} (\vec{k} + \vec{g})_t^2 (2.4)$$
where \((\vec{k} + \vec{g})_t\) is the component of the vector tangential to the surface. The first term on the right-hand side of (2.4) is the change of the potential between the metal and vacuum and the second is the electron energy in the vacuum due to the tangential component of the electron momentum, which is conserved in the surface crossing. Thus (2.4) simply means that the electron appears in the vacuum with the positive normal component of the momentum.

Fan applied this theory to the alkali metals sodium and potassium where the conduction electrons are nearly free and have energies

\[
e_{k} = \frac{k^2}{2m}
\]  

(2.5)

In this case condition (2.4) simplifies further into

\[
\frac{1}{2m} (k + g)_n^2 \geq V
\]  

(2.6)

(2.6) determines the "emission cone" or "critical angle" \(\theta\):

\[
\theta \leq \frac{V}{e^{k+g}}
\]  

(2.6a)

Fig. 2.3.
which contains all excited electrons of energy $e_{K+g}$ able to cross the surface potential $W$.

We explain the basic ideas of Fan's theory in some detail because they are fundamental in volume photoemission and present in all later work. His treatment of surface crossing, however simple, is a good approximation in the ultraviolet region for electron energies far from the threshold.

The electron excitation in the solid is calculated as a one-electron process, and until the present day except for a few notable exceptions /24, 25/ no theoretical attempt has been made to include many-electron effects.

Hopfield's theory of ultraviolet anomalies in alkali metals.

Here we shall briefly describe the situation in alkali metals where experimental results of photoemission measurements have been adequately explained by the only successful attempt to include more than one-electron processes in the theory.

Photoemission for alkali metals was experimentally investigated by J. Dickey /26/. She could not detect any volume effect of the type Fan calculated, but she found unexplained ultraviolet anomalies in the photoelectron spectra from Na and K.

For the energies above the threshold in the nearly-free-electron model one would expect a simple interband spectrum, which would roughly mirror the density of the initial states $\frac{dN}{dE_i}$. Instead, a pronounced peak was found which would, in this model, correspond to a peak in $\frac{dN}{dE_i}$
just below the Fermi energy, where no such peak is known from band
calculations /27, 28/.

Fig. 2.4.

This peak persists for a wide range of photon energies \( w > w_p \) \((w_p\)-plasmon
energy\) in Na and K and also in Ag /6/, which has a well defined
plasmon \((w_p\ (k=0) \approx 3.8 \text{ eV})\).

The simple Sommerfeld model of one-electron transitions obviously
could not explain this anomaly, and several unsuccessful many-body
theories have been attempted /29 - 37/.

J.J. Hopfield /24/ gave a simple explanation of these ultra-
 violet anomalies. He considered the model of a simple metal in which
the conduction electrons are weakly perturbed by the unscreened
pseudopotential of the ions with the Fourier component \( V_q \).

He noticed that in optical absorption the important part of the
conduction charge density is the one that oscillates with the frequency
\( w \) of the absorbed photon. Static screening of the ion potential \( V_q \)
must be replaced by

\[
V(q,w) = \frac{V_q}{\varepsilon(q,w)} \tag{2.7}
\]

where \( \varepsilon(q,w) \) is the complex dynamical screening factor. In the infrared
region (2.7) is approximately equal to the static screening

$$V(q, o) = \frac{V_q}{\varepsilon_1(q, o)}$$ (2.8)

but for $w > w_p$ $\varepsilon_1(q, w)$ is much smaller than $\varepsilon_1(q, o)$.

This leads to a dynamical breakdown of the adiabatic screening of the bare ion potential and large lattice-induced absorption. Hopfield used the Hartree approximation for the dielectric function and obtained great enhancement of $1/\varepsilon_1(q, w)$, as is shown on Fig. 2.5.

This result also gives the enhanced primary photoelectron distributions (Fig. 2.6).
Hopfield's mechanism differs from the usual phonon-assisted indirect transitions, where the direct transition is followed by the electron-phonon scattering described by (2.8). The reduction of Coulomb screening at high frequencies also leads to inelastic scattering with large energy transfer (Auger transitions) and small energy transfer (electron-ion or electron-phonon interactions).

In his calculation Hopfield assumed a weak ion pseudopotential $V_q$ which makes it applicable only to Na and K. Also the treatment of photoemission process, though giving the desired enhancement for photoelectron spectra, is not visible from his paper. For all these
reasons his approach cannot be generalized to other metals where physical considerations imply that this particular model does not include all important aspects of the photoemission process.

**Semiconductors.**

Very much experimental work has been done on photoemission from semiconductors, especially when it was realized in the 1950's that ultraviolet photoemission is largely the volume process and can reveal much information about electronic band structure. Details about these experiments can be found in the review article by Eden and Spicer /32/. We shall not be interested in photoemission from semiconductors, but only mention the theory of E.O. Kane /33/. He developed a theory of photoelectric emission from semiconductors for a general band structure and for various photoelectron production and scattering processes but only near the threshold. He, like Fan, used the "golden rule" expression for the rate of photon absorption and quantum yield in the one-electron approximation:

$$Y = \sum_{\text{B.Z.}} \sum_{1,2} \left| \overrightarrow{A} \cdot \overrightarrow{p}_{12}(k) \right|^2 \delta \left( e_1(k) - e_2(k) - \omega \right) dk$$

where index 1 runs over all empty bands and 2 over full bands, and the integration is over all \( k \) states which satisfy the condition for escape:

$$\frac{\partial e_1}{\partial k_n} > 0 \quad \text{and} \quad e_1(k) = \frac{k_t^2 + k_n^2}{2m}$$

\( k_t \) is a component of momentum tangential to the surface and is conserved.
across the surface, $k_n$ and $k_n'$ are normal components in the solid and vacuum.

Expressions (2.9) and (2.10) are exactly equivalent to (2.3) and (2.4) of Fan's theory because they are obtained under the same assumptions.

Kane also considered second order processes, where the excited electron or the hole are scattered by a phonon or some imperfection to the final state and calculated the energy dependence of the electron yield near the threshold.

The experimental photoelectron curves for semiconductors have usually been analysed by means of a direct transition model, where electrons are excited vertically in the reduced zone scheme conserving the momentum in the process. Recently it has been noticed /32, 37 / that for higher photon energies better results can be achieved by simply ignoring k-conservation and treating matrix elements like (2.2) as constants.

This question of momentum nonconservation will be discussed later for the case of noble and transition metals, where it is much more pronounced.

**Noble and transition metals.**

We reviewed briefly the measurements and theoretical work in the photoemission from alkali metals and semiconductors. From now on we shall concentrate on noble and transition metals, where extensive
photoemission studies have been carried out in the region of photon energies $1.5 \, \text{eV} < \omega < 15 \, \text{eV}$, mostly by Spicer and co-workers /34 - 37/. The situation is here different from the one in alkali metals due to the existence of d- bands, (or f in rare earths), so that electronic transitions are true interband transitions from a relatively narrow d-band to the s- and p- like conduction band, while in alkali they are due to the Umklapp process from the conduction band.

To explain the measured electron spectra Berglund and Spicer /6/ (referred hereafter as BS) developed a phenomenological theory of photoemission which was very successful in correlating the experimental data and even connecting them with the densities of states of a solid. This theory has been the only attempt to extend the considerations beyond the simple one body approach, with the exception of Hopfield's work which is not applicable here, and few other unworkable ad hoc models.

Though a purely phenomenological theory based on rather strong assumptions about the character of the processes calculated, it was remarkably successful and used to interpret all subsequent experimental work in transition and noble metals, and metallic alloys /7,38-48/.

This is an indication that the analysis of its basic assumptions could reveal some interesting phenomena, and we shall attempt to justify some of them in the microscopic treatment. In order to connect the many-body formalism with the phenomenological theory of BS, we shall review its main ideas and results.
Phenomenological theory of ultraviolet photoemission.

Berglund and Spicer make these basic assumptions about the ultraviolet photoemission process:

1) The directional distribution of the excited electrons in the metal is isotropic. For unoriented polycrystals this is macroscopically satisfied, and should come out from the exact treatment after averaging over photon polarisations and directions.

2) Excited electrons can escape from the metal if the normal component of their momentum is greater than some critical value:

\[ |\mathbf{k}_e| \cos \theta > k_c \] (2.11)

This assumption is equivalent to the critical angle approach (Fig. 2.3) of Fan (2.6) or Kane (2.10) and is reasonable for electron energies well above the threshold. The critical momentum \( k_c \) may be connected with the work function \( W \):

\[ k_c = \sqrt{2mW} \]

Actual scattering on the surface is neglected and electrons crossing from one medium into another only change the normal component of the wave vector. \( k_c \) appears in the calculation only in terms of the form \( 1 - k_c/k \), so in the refined treatment of the experimental data Berglund and Spicer introduce a threshold function \( G(e) \)
which they later determine numerically by comparing various electron emission curves.

3) The spectrum of primary electrons will be affected only by inelastic scattering, which is isotropic and can be described in terms of the energy-dependent mean free path $l(e)$. Only non-scattered and once-scattered electrons have to be considered. The effect of the elastic collisions will be to scatter electrons in and out of the escape cone, and this small effect can be included in the threshold function $C(e)$.

![Figure 2.7](image)

**Fig. 2.7.**

BS first calculate the probability $R_1(e)$ that an electron with energy between energy $e$ and $e + de$ escapes without scattering. The excitation rate for such an electron at the distance $x$ from the surface is:

$$G(e, x) \, de \, dx = G_0(e) \, de \, e^{-\alpha x} \, dx \quad (2.13)$$
where \( \alpha \) is the optical absorption coefficient for ultraviolet light \((\approx 5 \times 10^5 \text{ cm}^{-1} \text{ in Cu and Ag})\), and \( G_0(e) \) will be defined later. The electron must travel the distance \( x/z \) (\( z = \cos \Theta \)) to reach the surface. If its mean free path for inelastic scattering is 1, it will be damped by the factor \( e^{-x/1z} \), and the probability \( R_1 \) becomes:

\[
R_1(e) \, de = G_0(e) \, de \int_0^\infty dx \int_0^1 \frac{dz}{k} e^{-x(\alpha + 1 / \lambda)} \quad \text{if } k > k_c
\]

or after the integration:

\[
R_1(e) \, de = \frac{G_0(e) \, de}{2\alpha} \left\{ 1 - \frac{k_c}{k} - \frac{1}{\alpha_1} \ln \frac{1 + \alpha_1}{1 + k_c \alpha_1} \right\} \quad \text{if } k > k_c
\]

\[
= 0 \quad \text{if } k < k_c
\]

If we expand the ln term of (2.14) in an infinite series in

\[
\left(1 - \frac{k_c}{k}\right) \alpha_1 / (1 + \alpha_1) \text{ and take out the factor } (1 - \frac{k_c}{k}),
\]

(2.14) can be written as

\[
R_1(e) \, de = \frac{KC(e) \, G_0(e) \, de}{\alpha + 1 / \lambda}
\]  

(2.15)

\( K \) is the correction factor and comes when the summation of the rest of the series in (2.14) is carried out. Its value is between 1 and 1 for various energies \( e \).

The probability of electron escape after one inelastic scattering is calculated in a similar manner and is a product of three probabilities:
(1) that the primary electron will scatter after moving a distance at an angle $\theta$;

(2) that it will be scattered to an energy between $e$ and $e + de$; and

(3) that it will escape without further scattering.

\[ R_2(e) \, de = \frac{K \, C(e) \, de}{\alpha + \frac{1}{l}} \, \int_{e}^{\infty} \left[ \frac{1}{\alpha l} \ln \left(1+\alpha l'\right) + \frac{1}{l'} \ln \left(1+\frac{l}{l'}\right) \right] \cdot p_2 \, G_0(e') \, de' \]

(2.16)

$1$ and $l'$ are the mean free paths for electrons at energy $e$ and $e'$. In this case $e < e'$ and therefore $1 > l'$. $p_2$ is the probability that an electron of energy $e'$ will be scattered to an energy $e$. $p_2$ will depend on the scattering mechanism and must be derived for particular
cases separately. BS consider electron-electron and electron-plasmon scattering, while electron-phonon scattering can be treated as elastic because in Cu and Ag it involves a very small energy loss compared to the resolution of the measurements. They also point out the possibility of Auger effect contribution to the photoelectron spectrum.

Optical transition probability.

Before we proceed with the analysis of various electron and hole scattering mechanisms, it is necessary to see how BS describe the electron excitation. The absorption coefficient of a solid $\alpha$ for photons of frequency $\omega$ may be defined as

$$\alpha (\omega) = \int_0^\infty \alpha (\omega, e) \, de$$

(2.17)

if all photons of frequency $\omega$ are absorbed in exciting electrons in the solid to higher energy states. $\alpha(\omega, e)$ is that part of $\alpha$ corresponding to electronic transitions to energy states between $e$ and $e + de$. If $n_p$ is the flux of photons per unit area absorbed in the solid, then

$$G(e, x) \, de \, dx = n_p \alpha (\omega, e) \, de \, e^{-\alpha(\omega)x} \, dx$$

(2.18)

(2.18) defines $G_0(e)$ of equation (2.13) as

$$G_0(e) = n_p \alpha (\omega, e)$$

(2.19)

As we shall show later, this approach is equivalent to the assumption that the hole left in the $d$-band is completely immobile, i.e. has no momentum-dependence, so that only variable entering the
expressions for the transition probability is energy. As a result of this assumption the photoelectron distribution curve will generally be a convolution of the initial and final densities of states, disregarding the momentum conservation law. This is really the basic assumption of BS theory, and the intriguing fact that the experiments can be reasonably well explained in this "non-direct transition model" is the indication of the strong many-body effects in these solids.

Effect of elastic scattering.

Electron-phonon scattering is a moderately strong scattering mechanism in copper and silver, and compared to the resolution of photoemission measurements the energy loss in it is so small that the process can be considered as elastic. To get an estimate of the average energy loss per collision, let us assume that the phonon energy corresponds to the Debye temperature ($\approx 0.03$ eV in Cu, $\approx 0.02$ eV in Ag). The probability of phonon emission or absorption is proportional to $n+1$ or $n$ respectively, where $n$ is the equilibrium density of phonons in the metal. At $300^\circ$K, averaging over the probabilities, the average energy loss in Cu and Ag is $\approx 0.016$ eV and 0.0075 eV respectively. This confirms the approximation that electron-phonon scattering is elastic.

The effect of elastic scattering, as we already stated, can be visualized from geometrical considerations to increase the number of electrons inside the escape cone. Stuart, Wooten and Spicer/49/ found that this effect is small over the range of energies studied,
and it can be included in some empirically determined threshold function $C(e)$.

Effect of electron-electron scattering.

This is an important scattering mechanism which is expected to increase the number of low-energy photoelectrons, which has indeed been observed over the whole range of ultraviolet frequencies. To find $p_2$ in (2.14) and (2.16) BS take the usual expression for the probability of an electron $e'$ being scattered to state $e$:

$$p_s(e', e) d e = \int_0^\infty 2\pi |M_s|^2 \rho(e) \rho(e_o) \rho(e_o + e' - e) F(e_o) \left[ 1 - F(e_o + e' - e) \right] \left[ 1 - F(e) \right] d e \ d e_o \quad (2.20)$$

$\rho$ is the density of states, $F$ is the Fermi function, and matrix elements for the interaction have been assumed to be momentum-independent. The same expression (2.20) gives the probability of an electron being scattered into a state $e$ from below the Fermi energy. This gives:

$$p_2 = 2 \frac{p_s(e', e) \ d e}{p_s(e')} \quad (2.21)$$

where $p_s(e')$ is the total probability of an electron of energy $e'$ being scattered. Using (2.21) and (2.19) the results (2.15) and (2.16) can be written together as:

$$N(e) \ d e = \frac{K C(e)}{\alpha + 1/1} \left\{ \alpha(v,e) + 2 \int_0^\infty \frac{1}{2} \left[ \frac{1}{\alpha} \ln(1+\alpha) + \frac{1}{1} \ln(1+1') \right] \right\}$$
This formula can be simplified in various cases, but let us now use it in the simplest model to see quantitatively the effect of the scattering:

1) Constant electron density of states $\rho(e) = \rho_0$;
2) Absorption independent of electron energy $\alpha(w,e) = \alpha(w)$;
3) Energy (and momentum) independent matrix elements.

Let us also assume that $\alpha \ll 1$ and $l'/l \ll 1$. In this model:

$$P_s(e',e) = 2\pi |M_s|^2 \rho_0^3 (e'-e)$$

$$P_s(e') = 2\pi |M_s|^2 \rho_0^3 (e'-\mu)^2 de$$

Equation (2.22) now becomes:

$$N(e) de = \frac{K C(e) \alpha(w) de}{\alpha + \frac{1}{1}} \left[ 1 + 2 \int_{\frac{\mu+w}{\mu-w}} \frac{2(e'-e)}{(e'-\mu)^2} de' \right]$$

(2.24)

If we neglect $\frac{1}{1}$ compared to $\alpha$ and integrate:

$$N(e) de = K C(e) de \left[ 1 + 4 \left( \frac{e-\mu}{w} - 1 + \ln \frac{w}{e-\mu} \right) \right]$$

(2.25)

Assuming in the first approximation $C(e)$ to be the step function (2.25) is given in Fig. 2.9.
The constant unhatched area of the curves on Fig. 2.9 corresponds to the first term in the square bracket of (2.25) and comes from nonscattered electrons. The second term comes from the scattered electrons and is given by the hatched part of the curves. Its peak is just above the Fermi level and its size increases with the photon energy, but its position remains fairly constant. This very crude theoretical prediction can be compared with the measured energy distributions from Cu (Fig. 2.10) which contain the same qualitative features of Fig. 2.9. Thus it will be possible to identify the structure in the measured spectra coming from the inelastically scattered electrons by varying the photon energy and following the behaviour of the peak.
Effect of plasmon creation.

In the previous section we have analyzed the photoemission probability in the system where only inelastic electron-electron scattering is important, and by that we mean short-range (screened) Coulomb interaction. In some metals (e.g., Ag), however, the long-range part of the Coulomb interaction may be important and result in a strong plasmon emission and absorption contribution.
To illustrate the effect of plasmon scattering let us assume that this is the only dominant scattering mechanism. The energy loss of an electron in the plasmon creation must be equal to the plasmon energy $w_p$, so that $p_2$ in (2.16) becomes

$$p_2 = \delta (e'_e - e - w_p) \quad (2.26)$$

and the transition probability (2.15) plus (2.16):

$$N(e) \, de = \frac{K C(e)}{\alpha + \frac{1}{1}} \left\{ \alpha(w_e, e) + \frac{1}{2} \left[ \frac{1}{\alpha l} \ln(1+\alpha l) + \frac{1}{1} \ln(1+\frac{l}{1}) \right] \right\} \alpha(w_e + w_p) \quad (2.27)$$

The meaning of (2.27) is obvious. In addition to the unscattered electrons there is the scattered part shifted by $w_p$ in energy and multiplied by the usual factor (square bracket) coming from the geometrical considerations. In practice the photoelectron distribution will depend on both the plasmon effect and electron-electron scattering, but the plasmon peak will still be easy to recognize (Fig. 2.11).
Effect of the Auger process.

Another emission mechanism may contribute to the measured photoelectron spectra - radiative Auger process. After the hole is left at the energy $e_0$ in the metal, an electron with energy $e_1$ may recombinewith it thus releasing energy $(e_1-e_0)$ which might excite an electron near the Fermi surface into a state with energy $e = e_2 + (e_1-e_0)$, high enough to leave the metal and escape into the vacuum.

This process may also be considered as the scattering of an energetic hole and treated in the same way as the electron-electron scattering. The probability that a hole with energy $e_0$ produces an electron with energy $e$ through the Auger process may be written as:

$$P_a(e_0,e) = \int_0^\infty 2\pi |H_a|^2 \rho(e) \rho(e_1) \rho(e+e_1-e_0) \cdot F(e_1) F(e+e_0-e_1) [1-F(e)] de_1$$

$|H_a|^2$ is the squared matrix element applicable to the Auger process; otherwise (2.28) corresponds to (2.20). The total probability of a hole with energy $e_0$ being involved in the Auger process is:

$$P_a(e_0) = \int_0^\infty p_a(e_0,e) de$$

(2.29)

The contribution $N_a(e)$ of the Auger process to the number of electrons emitted with energy $e$ can be derived in the same way as for electron-electron scattering. For $\alpha \lambda_o \ll 1$ and $\lambda/\lambda_o \ll 1$, where $\lambda_o$ is the mean free path for the Auger process for holes of
energy $e_0$, and at zero temperature:

$$N_a(e) \, d\, e = \frac{K \, C(e) \, d\, e}{\alpha + \frac{1}{\Gamma}} \int_{0}^{\mu-\mu(e)} \frac{P_a(e_0, e)}{P_a(e_0)} \, d\, e_0 \quad (2.30)$$

**Anomalous peaks in noble and transition metals.**

The experimental densities of states derived some years ago from photoemission energy spectra in nickel, cobalt and iron /6, 34-36/ showed some unexpectedly strong peaks at 5 eV below the Fermi energy. These results were observed in all three transition metals and were contrary to all band calculations. They caused much interest, several theoretical explanations were offered such as many body resonances in the d-band /50/.

Later measurements /43, 44, 7, 41/ gave results which agreed much better with the expected band structure and revealed that these peaks were extremely sensitive to surface conditions. They increased with air exposure and also when covered with monolayers of caesium or yttrium which lowered the work function. We shall not analyze the gradual disappearance of these anomalous features in each of the transition and noble metals, but instead quote the evidence of Vehse and Arakawa /7/. They measured the photoelectron distribution from Ni as a function of sample deterioration with time. The curves (Fig. 2.12) showed marked increase of low energy electrons and appearance the "anomalous" peak.
Fig. 2.12.
CHAPTER 3. - MANY-BODY THEORY OF PHOTOEMISSION.

Hamiltonian of the system.

Volume photoemission from metals can be treated as a one-, two- or three-stage process, depending on the energies of electrons and electromagnetic waves involved and the appropriate approximations. But in general we must consider all three phases of the process and therefore define the Hamiltonian of the whole system as

$$H = H_0 + H_c + H_x + T$$  \hspace{1cm} (3.1)

$H_0$ is the energy of the non-interacting particles in the solid

$$H_0 = \sum_{m,k,s} e_{k,s}^m n_{k,s}^m$$  \hspace{1cm} (3.2)

where $m$ is the band index, $k$ is momentum and $s$ spin of the electrons, $e$ their energy and $n$ is the number operator. In transition, noble and rare earth metals we shall usually be interested in the transitions between one of the valence bands and the conduction band. In this case, if the interactions in the system are spin independent, we may specify (3.2) and write it as:

$$H_0 = \sum_k e_k c_k^c c_k^v + \sum_k E_k d_k^c d_k^v$$  \hspace{1cm} (3.3)

where $c_k^c$ and $d_k^v$ create conduction and valence electrons with energies $e_k$ and $E_k$ respectively.

$H_c$ is the Coulomb interaction between electrons inside the metal.

It is turned on suddenly when the electromagnetic wave excites the
electron, in contrast to the usual scattering problems where it is turned on adiabatically.

In our two-band situation $H_e$ can be split into several parts:

a) Scattering of the outgoing electron in the conduction band from the moment of excitation till it reaches the surface. Since we shall consider the ejection of electrons with energies well above the threshold, it is a reasonable assumption that this electron will have no time to build a self-energy renormalizing cloud, i.e. instead of using a self-energy approach we can calculate the first few orders in the perturbation expansion. When the excited electrons are near the Fermi energy they could be treated as quasi particles with spectral distribution broadened by the repeated scattering. This broadening or lifetime can also be interpreted in real space in terms of the mean free path.

It is much more probable that the electron will excite a conduction electron-hole pair than a pair in the deeper and less mobile valence band, so that we can define this part of the Coulomb interaction

$$H^I_c = \sum_{kk'} V^I_{kk'} c^+_k c^+_k c^+_{k-q} c^+_{k'+q}$$  \hspace{1cm} (3.4)

where the matrix elements $V^I_{kk'}$ have to be determined.

b) Vertex corrections, i.e. the scattering between the created electron-hole pair, will be dominant for energies near the threshold where one might even expect some exciton-like diagrams to contribute strongly to the inelastic scattering. In volume photoemission these
effects will be negligible, but for the sake of completeness we include the term:

\[ H^2_c = \sum_{kk'} \sum_{q} V_{kk'} c^+_k c^+_k d^+_k d^+_k q q \]  \tag{3.5} 

to represent these effects.

c) Scattering of the hole left in the metal. This will be a very important effect if the hole is in a localized state. Then, according to Anderson /51/, it will take the Fermi sea a very long time to adjust to the new situation created by the sudden excitation after the absorption of the quantum of radiation. During that time the hole acts as a localized potential and strongly scatters the electrons about the Fermi energy, creating a large number of pairs with energy going to zero. This process is equivalent to the infrared catastrophe in quantum electrodynamics, only instead of soft photons the hole \(-\hbar\omega\) excites the electron pairs which behave like bosons. Similar effects have been investigated in X-ray absorption and emission by Nozières et al. /52 - 54/.

If the hole is not localized but in a band, this effect is weakened due to the recoil of the hole after scattering. Still it can be expected to increase and become important with increasing hole mass, i.e. diminishing bandwidth. Again the hamiltonian can be written as

\[ H^3_c = \sum_{kk'} \sum_{q} V_{kk'} c^+_k c^+_k d^+_k d^+_k q q \]  \tag{3.6} 

where \( V_{kk'} \) has to be defined to describe the dominant physical
processes just mentioned. This means that it has to reduce $H^3_c$ to include only the scattering of conduction electrons with energies near the Fermi level. From (3.6) it is also obvious that $H^3_c$ acts only when there is a d-hole in the system, i.e. after the absorption of the radiation quantum.

d) In some cases it might be necessary to consider the radiative or external Auger processes, when a very energetic hole scatters an electron and transfers enough energy so that the electron can leave the solid. These transitions would involve operators of the type $c^+ d d^+ d$, i.e. creation of two d-holes and large energy transfers and in some physical situations they could be important.

We have mentioned a few possible Coulomb scattering processes which we shall take into account in our discussion of photoemission, but there are many others which we do not expect to be important here. Actual choices of the processes and diagrams will have to be adapted to the specific problem and the form of the hamiltonian simplified further.

$H_x$ denotes the interaction between electrons and photons and in the first order is given by:

$$H_x = \frac{e}{mc} \vec{p} \cdot \vec{A}(\vec{r})$$  \hspace{1cm} (3.7a)

$\vec{A}(\vec{r})$ is the vector potential of the electromagnetic field and varies with distance and time as:

$$\vec{A}(\vec{r}) \sim \vec{n} \exp (i \vec{q} \cdot \vec{r} - i t) + c.c.$$  \hspace{1cm} (3.8)

$\vec{n}$ is the polarization vector of the electromagnetic field, $\vec{q}$ is the
photon wave vector and \( w \) is the photon frequency. \( \mathbf{A} \) is the transverse potential, i.e.

\[
\mathbf{q} \cdot \mathbf{n} = 0
\]  

(3.9)

\( \mathbf{p} \) is the electron momentum operator.

In the second-quantized form \( H_x \) can be written as:

\[
H_x = \frac{e}{mc} \sum_{q,k,\alpha} \mathbf{k} \cdot \mathbf{n} \left( c_{k+q}^{\dagger} d_k^\alpha \right) \exp(iw t - i \mathbf{q} \cdot \mathbf{r}) + c.c
\]  

(3.7b)

The perturbation (3.7) causes creation or annihilation of an electron hole pair, i.e. transition from an occupied state \((k', n')\) with momentum \( k \) in the band \( n \) to an unoccupied state \((k', n')\) or vice versa, accompanied by absorption or emission of a photon \((q, w)\) with energy \( w \) and momentum \( \mathbf{q} \).

Periodicity of the crystal imposes the conservation law for wave vectors or momenta:

\[
\mathbf{k}' = \mathbf{k} + \mathbf{q}
\]  

(3.11)

Photons with energies that are of interest to us have \( q \sim 2 \times 10^6 \), which is negligibly small compared to the dimension of the Brillouin zone, which is typically \( 2 \times 10^8 \). Thus we may assume

\[
k' = k.
\]  

(3.10a)

Therefore electronic transitions in photoemission in this region of photon frequencies are vertical on the energy vs. momentum plot shown on Fig. 3.1.
Transitions b and c are vertical and are called direct. Transitions between different bands \((n \neq n')\) are called interband, those within a single band intraband transitions. Energy cannot be conserved in intraband processes because

\[ E_{k+q,n} - E_{k,n} \approx \frac{\partial E_{k,n}}{\partial k} \cdot q = v_n \cdot q \ll c.q = w \quad (3.11) \]

where \(v_n(k) = \frac{\partial E_{k,n}}{\partial k}\) is the velocity of the electron in the state. Therefore intraband transitions are virtual and contribute only to the real part of the dielectric function.

Real transitions occur when energy is conserved,

\[ w = E_{k,n'} - E_{k,n} \quad (3.12) \]

Energy absorbed from the electromagnetic wave excites the electron to a higher band. The imaginary part of dielectric function is nonzero and gives the transition probability for this process.
We assume that the interaction of electrons with the electromagnetic field can be treated in the first order, which is a good approximation if we are not in the region of a photon resonance in the medium, where a dielectric function approach ought to be used.

Another term in the Hamiltonian that will be treated as a perturbation is the effect of the surface. This is the interaction which transfers excited electrons with energy greater than the vacuum energy $E_{F+\hbar\omega}$ into the continuum of the states in the vacuum outside the metal, and vice versa.

$$T = \sum_{k,e} T(k,e) c_k s_e^+ c.c. \quad (3.13)$$

$s_e^+$ is the creation operator for free electrons of energy $e$ measured from the vacuum energy.

This is certainly the most awkward term because we do not know its exact form, and we shall have to make drastic approximations to $T(k,e)$. In surface photoemission this interaction is dominant and it actually enables electrons, acting as a source or sink of momentum, to absorb the radiation quantum in an intraband transition, and leave the metal after the excitation. Matrix elements $T(k,e)$ should be determined by the matching of the wave functions on the surface /15 - 19/. When we want to use this boundary condition method we require that the surface be well defined compared to the electronic wavelength. "Sharpness" of the surface
can be intuitively connected with the strength of the surface potential $W$:

$$\Delta x = \frac{1}{\Delta k_{\text{max}}} \quad \text{and} \quad \Delta k_{\text{max}} \approx \sqrt{2mW}$$

If the surface is "sharp" compared to the wavelength of the excited electrons,

$$\Delta x \ll \frac{1}{k}$$

the maximum momentum that it can give to the scattered electron is determined by

$$\Delta k_{\text{max}} = \frac{1}{\Delta x}$$

This is a simple consequence of the Fourier transformation procedure. Matrix elements defined in the $x$-space with the precision $\Delta x$ are diffuse and spread in the inverse $k$-space in the region $\Delta k_{\text{max}}$. This means that the initial momentum of the electron is changed by an amount which is of the same order of magnitude. There is an infinite number of non-zero matrix elements $T(k,e)$, and in general the initial momentum states are completely mixed so that we cannot see the band structure inside the metal.

However, characteristic surface effects near the threshold become less important as the electron energy is increased, and for energies well above the threshold we may assume that the electrons cross the surface without scattering. They only feel the change in energy between two media, which changes the normal component of
the wavevector

\[ k_n \rightarrow k_n' = \sqrt{k^2 - 2mW} \] (3.14)

Thus we can write for high electron energies:

\[ T(k,e) = \delta (e-e_{k} + W) \] (3.15)

where \( e_{k} \) is the energy of the excited band electron in the metal.

Further refinement would be to multiply this expression by a correction factor \( \sqrt{1 - \left( \frac{e}{W} \right)^2} \) which can be calculated as a transmission probability in the usual quantum mechanical manner.

The correlation function.

We shall treat \( H_x \) and \( T \) as perturbations to the unperturbed hamiltonian \( H_o + H_c \) to get the probability that an electron absorbs the quantum of radiation and subsequently crosses the surface.

This problem is similar to the scattering on two scattering centres / 55 / . The transition matrix \( T \) can in general be written as:

\[ T = H' + \frac{1}{E - \tilde{H} + i\epsilon} \] (3.16)

where \( \tilde{H} \) is the "unperturbed" hamiltonian \( H_o + H_c \) and \( H' = H_x + T \).

\[ G = \frac{1}{E - \tilde{H} + i\epsilon} \] is the propagator of the particles between the various scattering events. \( E \) is the eigenvalue of \( \tilde{H} \). The transition matrix can be expanded by iterating (3.16):

\[ T = H_x + T + H_x GH_x + TGT + TGH_x + H_x GT + \ldots \ldots \] (3.17)
To determine which terms of expansion (3.17) should be inserted in the expression $|I | S | F \rangle^2$ that gives the scattering cross section, we must make a particular choice of initial $|I\rangle$ and final $|F\rangle$ states of the whole system. They will be direct products of the states of a solid, vacuum and electromagnetic field.

$$|I\rangle = |i\rangle |\text{o vac}\rangle \eta^+ w |\text{photon}\rangle; |F\rangle = \gamma |e_+ \text{o vac}\rangle |\text{photon}\rangle$$

(3.18)

$|i\rangle$ and $|f\rangle$ are complete sets of eigenstates with eigenvalues $e_i$ and $e_f$ of the solid hamiltonian for $N$ and $N-1$ electrons respectively:

$$H_N^0 |i\rangle = e_i |i\rangle \quad H_{N-1}^0 |f\rangle = e_f |f\rangle$$

In making this choice we have assumed that only one electron crosses the surface. This is a good approximation if we are interested only in the spectrum of primary electrons, because the secondaries will be lower in the emitted spectrum by at least energy $W$. To take into account the emission of secondary electrons one would have to include final states of the form $s_e^+ s_e^+ |\text{o vac}\rangle$ and similarly for higher numbers, and therefore include higher terms in the interaction $T$ in the expansion (3.17).

The choice (3.18) gives for the probability of measuring an electron of energy $e$ in the vacuum after absorption of a photon of energy $w$:

$$\frac{d\sigma(w)}{de} = 2\pi \sum_\alpha \sum_{i f} |\langle I | H G T | F \rangle|^2 \delta(e_i - e_f - e + W)$$

(3.19)
As we are going to use nonpolarized photons and crystals, the sum is made over all final states of the solid and averaged over its initial states and states of polarization of the photon.

If we insert (3.8), (3.7b) and (3.15) into (3.19), the matrix element becomes:

\[
\langle i | \sum_{k,\alpha} \vec{k} \cdot \vec{n}_\alpha \ c_k \ d_k^+ \ G \ \sum_{q,\varepsilon} \delta (\varepsilon_q - e' - \omega) \ c_q^+ | f \rangle
\]

\[
\langle \text{vac} \ 0 | s_{\varepsilon'} s_{\varepsilon}^+ | 0 \ \text{vac photon} \ 0 \ | \eta_i^{\alpha+} \ \eta_i^{d^+} | 0 \ \text{photon} \rangle
\]

\[
= \sum_{k, q} \delta (e_q - e - \omega) \langle i | \vec{k} \cdot \vec{n}_\alpha \ c_k \ d_k^+ \ G \ c_q^+ | f \rangle
\]

where \(e_q\) is the electron energy renormalized by the interaction with the solid.

If we put \(\varepsilon_q\) to be the renormalized electron energy instead of the band energy \(e_q\) we take into account all self-energy effects in the electron propagator and the T operator describes the tunnelling of quasi particles. In that case we must be careful to avoid double counting of diagrams. Usually, however, this energy shift will be small for highly excited electrons and we shall neglect it.

Vacuum and photon operators have dropped out from (3.20) and we are left with an expression that contains only the states of the solid.
The matrix elements:

\[
\langle k, l \mid p \cdot n^\alpha \mid k', l' \rangle = \frac{1}{v} \int_{\text{unit cell}} u_{kl}^+ p \cdot n^\alpha u_{k'l'}, \, dp (3.21)
\]

where \( v \) is the volume of the unit cell, give the momentum selection rule (if we ignore Umklapp-processes):

\[ k' = k \]

In general these matrix elements will give oscillator strengths of transitions between different bands and depend on the energy. They are not independent but have to satisfy the \( f \)-sum rule. In our case \( l \) and \( l' \) are conduction and one of the valence bands, we consider only one fraction of all possible optical transitions, and the sum rule will not be much violated if we approximate

\[
\sum_\alpha \left| \langle k \mid p \cdot n^\alpha \mid k \rangle \right|^2 = |N|^2 \quad (3.22)
\]

When the matrix element (3.20) is squared and we use (3.22), we obtain

\[
\frac{d\sigma(v)}{de} = 2\pi |N|^2 \sum \delta(e_q - e_v) \delta(e_{q'} - e_{v'}) \delta(e_{q''} - e_{v''}) |i\rangle, \langle f|
\]

\[ q, q', k, k' \]

\[
\langle i \mid c_k^+ d_{k'}^+ G c_{q'}^+ \mid f \rangle \langle f \mid c_{q}^+ G^+ d_{k'} c_{k'}^+ \mid i \rangle \quad (3.23)
\]
The first two δ-functions are equal to \( \delta(e_q - e_{q'}) \cdot \delta(e_q - e_w) \) and one of them cancels the sum over \( q' \). The next step is made by writing:

\[
\delta(e_i - e_f - e + w) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left[i(e_i - e_f - e + w)t \right] dt \quad (3.24)
\]

\[
\delta(e_q - e_w) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left[i(e_q - e + w)\tau \right] d\tau
\]

and using the fact that \( H^N_0 |i\rangle = e_i |i\rangle, \quad H^{N-1}_i |i\rangle = e_f |f\rangle, \quad -ie_q \tau = c^+_q(\tau) = e^{iN_0 \tau} c^+_q e^{iN_0 \tau} \)

Then the sum over final states of the \( N-1 \) particle solid can be taken out because of the completeness of the \( f \) states, and the transition probability becomes:

\[
\frac{d\sigma(\nu)}{d\epsilon} = 2\pi |\mathcal{M}|^2 \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt \, d\tau \, e^{i(\nu - \epsilon)t - i(\nu + e)\tau} \quad (3.25)
\]

where the correlation function \( R(t, \tau) \) is defined as:

\[
\sum_{k, k', q} \langle i | e^{iH^N_0 t} c_k d_{k'} G e^{-iH^N_0 \tau} c^+_q e^{-iH_{N-1}^N \tau} e^{-iH_{N-1}^L t} c^+_q G^+ d_{k'} c_{k'} | i \rangle \quad (3.26)
\]

The correlation function \( R(t, \tau) \) is very complicated in comparison with the usual correlation function one finds in optical emission and absorption, which is of the type
The difference comes from the fact that in the photoemission case we have to take account of the boundary conditions on the surface which determine the decoupling of the emitted electron from the solid. In the one-electron theory this is not necessary because the electron after excitation does not interact with the solid and is de facto decoupled from it. When higher order processes are included we must specify that the emitted electron interacts with the solid until the moment when it comes to the surface. All the other particles in the final state form a part of an N-particle excited state but again have to cease interacting with the outgoing electron and continue to develop as an N-1 particle system.

Thus the whole process can be split into three phases:

1) Before the excitation the system is in the ground state \( |i\rangle \) and consists of free electrons (or quasiparticles) with energy \( H_o \):
\[
H_o^N = \sum_k e_k c_k^+ c_k + \sum_k E_k d_k^+ d_k = H_o^{N-1} + H_1
\] (3.27)

2) When the electromagnetic field excites a valence electron into the conduction band, the whole system suddenly starts interacting with the N-particle hamiltonian \( H_N = H_o^N + H_c \), where the main contribution to \( H_c \) will probably come from the Coulomb scattering of the created electron-hole pair. Coulomb interaction term \( H_c \) couples single particle and (N-1) particle parts in the hamiltonian.
and it is not possible to write it as a simple sum like in (3.27).

3) One of the highly excited conduction electrons, not necessarily the one originally excited, will reach the surface and be transferred into the vacuum by the tunnelling term in the hamiltonian. The solid is now in the final many-body excited state which contains the result of all the interactions of the N-1 particles.

Expression (3.25) comes from the first term in the double perturbation expansion (3.17) which gives the required condition probability. It is also the generating expression for an infinite perturbation expansion in the Coulomb interaction $H_c$ contained in operators $G$, $H_N$, and $H_{N-1}$.

The main difficulty arises from the unknown propagator $G$ of the created electron and the rest of the system. Because of the Coulomb interaction it will include all possible scattering with the rest of the solid and we cannot write it explicitly in a general case.

The one-body theory of potential scattering has to be generalized and $G$ propagates all particles created in the system by the Coulomb scattering of the original electron. The difference from the one-body scattering comes from the possibility that two different electrons undergo the scattering, while previously that was the same electron. Fig. 3.1 shows simple Feynman diagrams of the processes where (a) $G$ could be interpreted as a one-body propagator and (b) where it is impossible.
As the $N$-body scattering problem suitable to this particular case seems not to have been solved, we shall have to rely on our physical insight and try to represent the structure of the correlation function (3.26) schematically by the following diagram (Fig. 3.2):
The wavy line represents a photon which creates an electron-hole pair in a solid in the ground state $|i\rangle$.

The $N$-block is the excited $N$-body state with all effects of the Coulomb scattering in which electrons are propagated until a moment when one of them is to decouple from the solid and reach the surface in the state $q_i$. Then the $N$-body state must be split into the aforementioned product of $(N-1)$ and 1-body states. The electron reaching the surface is finally transferred into the vacuum by the interaction $T$ denoted by a dotted line, while the $(N-1)$-body solid undergoes further processes (propagated by $e^{-iH_{N-1}t}$) and approaches some unknown final state over which we have sealed our diagram.

The representation of $R(t, \mathcal{C})$ by the diagram of Fig. 3.2 will be confirmed by the exact diagrams that we can construct for an approximate case.

**Fast electron approximation.**

This complicated problem can be simplified if we assume that the excited electron has relatively high energy and is only weakly coupled to the rest of the solid /56/. Then its interaction with other $N-1$ electrons can be treated by perturbation theory. Thus the Hamiltonian can be split into:

$$H_N = H_{N-1} + H_1 + h$$

where $h$ is the interaction of the emitted electron with the remaining
electrons in the system. We have preserved all interactions of these N-1 electrons and they are treated exactly, to all orders of perturbation.

Let us consider the matrix element \( \langle i | c_k d_k^+ G c_q^+ | f \rangle \).

The propagator \( G \) can be written as
\[
\frac{1}{E_1 - H + i\epsilon} = -i \int_0^\infty e^{i(E_1 - H)t'} dt'
\]
where \( E_1 = w + e_i \).

The exponential contains the perturbation term \( h \) and to separate it from \( H_{N-1} \) and \( H_1 \) we may use the well-known relation:
\[
e^{-iH_{N-1}t'} e^{-i(H_{N-1} + H_1)t'} - e^{-iH_1t'}
\]
where \( h(t'') = e^{i(H_{N-1} + H_1)t''} - e^{-i(H_{N-1} + H_1)t''} \).

The matrix element now becomes:
\[
-\int_0^\infty dt' \langle i | e^{i(H_{N-1}+H_1)t'} c_k d_k^+ e^{-i(H_{N-1}+H_1)t'} \sum t' \int_0^{t} \tilde{h}(t'') dt'' c_q^+ | f \rangle
\]

The interaction term can be expanded to give:
\[
1 - i \int_0^t \tilde{h}(t'') dt'' + ...
\]

We shall retain only the zero and first order in this expansion, which gives four terms for the correlation function \( R \) and the transition probability.
The term without scattering of the initial electron is

\[ R_0(t, \tau) = \sum_{k'kq} \int_0^\infty dt' \int_0^\infty dt'' \ e^{i(w(t'+t''-t))} \]

\[ \sum \langle i | c_k(t') d_k^+(t') d_k^+(t') c_q^+(\tau) c_q(o) d_{k'}(t'') c_{k'}^+(t'') | i \rangle \]

\[ \langle i | c_k(t') d_k^+(t') h(t_1) c_q^+(\tau) c_q(o) d_{k'}(t'') c_{k'}^+(t'') | i \rangle \]

(3.34)

The next two terms involve single scattering of the outgoing electron with the solid:

\[ R_1^{(a)}(t, \tau) = -i \sum_{k'kq} \int_0^\infty dt' \int_0^\infty dt'' \ e^{i(w(t'+t''-t))} \int_0^t \ e^{i \omega(t_2-t')} \int dt_1 \]

\[ \sum \langle i | c_k(t') d_k^+(t') h(t_1) c_q^+(\tau) c_q(o) d_{k'}(t'') c_{k'}^+(t'') | i \rangle \]

(3.35)

and the similar expression for \( R_1^{(b)} \) with \( h(t_1) \) on the right side of \( c_q^+(\tau) c_q(o) \) operators.

The second order term is

\[ R_2(t, \tau) = \sum_{k'k'lq} \int_0^\infty dt' \int_0^\infty dt'' \ e^{i(w(t'+t''-t))} \int_0^t \ e^{i \omega(t_2-t')} \int dt_2 \]

\[ \sum \langle i | c_k(t') d_k^+(t') h(t_1) c_q^+(\tau) c_q(o) d_{k'}(t'') c_{k'}^+(t'') | i \rangle \]

and the similar expression for \( R_1^{(b)} \) with \( h(t_1) \) on the right side of \( c_q^+(\tau) c_q(o) \) operators.
\[ \sum \langle i \mid c_k(t') a_k(t') \hat{h}(t_1) c_q(t) c_q(o) \hat{h}(t_1) a_k(t'') c_k(t'') \mid i \rangle \]

(3.36)

These four terms can be represented by four diagrams similar to the one on Fig. 3.2.

![Diagrams](image)

Fig. 3.3.

There are two more second order contributions which would come from the second order terms in the expansion (3.33) and are represented by the diagrams on Fig. 3.4:
However, they correspond to the double scattering of the same conduction electron and consequently we shall neglect them.

The dotted line represents the interaction $h$ which has to be specified in the particular case, and the $(N-1)$-particle system contains all possible processes initiated by the Coulomb interaction $H_c$.

Approximation (3.28) and perturbation expansion (3.33) should be valid in the photoelectron energy region we are considering, i.e. far from the Fermi surface, where the electron rapidly escapes from the solid and does not build the self-energy. One consequence of this approximation is that we have neglected the exchange diagrams like the one on Fig. 3.1b, which could be important. But now we already know the general structure of $R(t,T)$ and can easily construct the diagram for the exchange process.

Conclusions.

In this chapter we tried to develop a many-body formulation of the photoemission process in the ultraviolet region of photon energies. The transition probability (3.25), i.e. the number of
emitted electrons of some energy \( e \) per absorbed photon of energy \( w \), was expressed in terms of correlation function (3.26). This is a very interesting example of the scattering theory because two different scattering potentials (\( H_x \) and \( T \)) have to act consecutively to bring the system from the initial one-photon state to the final state where the photoelectron is measured in the vacuum. In addition there is the third mechanism (\( H_c \)) scattering the particles inside the solid which has to be treated, in general, to any order in perturbation theory.

The fact that we treated the surface as another perturbation, which resulted in correlation function (3.36) being a second-order expression, enables us to distinguish clearly between the two phases of the process—before and after the electron leaves the solid, and thus explicitly restrict the action of the Coulomb scattering on the emitted electron to the first phase only. But this formal advantage of our treatment leads to the very complicated structure of the expression for the transition probability. We have introduced the tunnelling term \( T \) as a perturbation somewhat artificially, because electrons at the surface are not really scattered: they conserve energy in this process. This means that the intermediate state between the last Coulomb scattering and the surface is on the energy shell, so that the general second order transition matrix element degenerates and leaves two spurious \( \delta \)-functions conserving energy. This can be illustrated in the case of non-interacting electrons:
Thus it seems that it is not simple to perform actual calculations in this formulation of the second-order perturbation theory and that it should be further improved and simplified.

One such possibility might be to formulate the problem as a first-order process and ignore the surface term except in the final integration over the directions of the emitted electron which has to consider only electrons inside the critical angle. Then the correlation function and the corresponding diagrams become equivalent to the ones for the photon absorption, the only difference being that we must open one electron line and put the particle on the energy shell. This means that instead of the electron Green's function we insert a δ-function in energy. Though simpler, this procedure does not distinguish between band electrons in the solid where they can interact with the rest of the system, and free electrons in the continuum, and we shall not pursue it further.

Another interesting comment that should be made about photo-emission concerns the transient character of the interaction. Only recently the importance of transients in physical processes was realised (e.g. in soft X-ray emission and absorption) and methods were developed to calculate these effects. All conventional scattering theories introduce the perturbing potential adiabatically to avoid these transients and have to be modified in the cases where we expect sudden changes of the potential in the system.
In the photoemission strictly speaking two such transients are present - one from the sudden electron-hole creation and another from the electron leaving the solid. We do not expect this second transient to give a very important contribution, because it is a one-electron effect compared to the first one where the whole Fermi sea participates, but from the formal point of view one has to reconsider the use of the normal scattering theory.
CHAPTER 4 - MANY-BODY EFFECTS.

In this chapter we shall discuss possible many-body effects in the photoemission from transition and noble metals in the framework of the many-body approach developed in Chapter 3. We also compare our approach with the assumptions of BS theory described in Chapter 2 to find out the reason why this theory was able to give satisfactory explanation of experimental results, and we try to outline the corresponding microscopic formulation.

Photon absorption.

We assume that the photon absorption can be treated in the Born approximation, and the rate of absorption is equal to the pair excitation scattering cross section and proportional to the imaginary part of the bubble diagram (Fig. 4.1)

![Fig. 4.1.]

This is equivalent to the assumption that the photons are not damped in the solid and excite electron-hole pairs at the same rate everywhere in the volume. The approximation is reasonable in a thin film experiment but also in the semi-infinite solid because most electrons
originate from a thin layer near the surface where the escape probability is largest. For small damping in a semi-infinite volume the number of absorbed photons becomes infinitely large, and we must calculate the number of emitted electrons in the photoemission process per absorbed photon and not per incoming photon.

To be able to use the geometry of a semi-infinite solid with one surface only and still obtain some absolute results BS assume a finite damping constant $\alpha$ which is equivalent to the renormalization of the photon propagator by the infinite sum of the diagrams:

![Diagram](image.png)

However, we do not believe that this could be an important effect.
in this range of photon frequencies.

Absorbed photons have a negligible wavevector \( q \approx 0 \) so that it does not introduce any preferential direction in space. We also average over the photon polarization and get some approximate matrix element (3.22). This statement is equivalent to BS assumption that the distribution of excited electrons in a nonpolarized crystal is isotropic.

**Surface effects.**

The difference in shape between the broad photoelectron spectra in non-direct transitions and sharp peaks in the direct transitions has a striking similarity with the situation in nuclear reactions where the optical model provides an explanation for the giant resonance in the spectra of scattered nucleons. It was a tempting idea to attribute the large contribution of non-direct processes to some kind of surface resonance, but the analogy with the optical model is not really justified in this case. The main reason, among others, is that the basic assumption of the optical model is not here fulfilled, i.e. the ratio of the kinetic energy of emitted particles versus the depth of the potential well \( e/W \) is not small so that the potential does not bind excited electrons inside the metal for any appreciable time. Thus our previous conclusion that the surface does not scatter electrons is still valid and excludes the possibility of any additional contribution to the observed
photoemission spectra. On the other hand, in surface photoemission for electron energies near the threshold \( \frac{e}{W} \ll 1 \) might expect such resonances, but this is already outside the scope of this work.

BS theory makes the same assumption about the surface potential, though in the analysis of the experiments they modify the step-function which represents the emission probability into some numerically fitted empirical curve.

**Vertex corrections.**

We do not expect vertex corrections to be important in volume photoemission because of the relatively large energy difference between the particles of a created pair and because the electron is excited far above the Fermi level. To show this let us consider a particular (and usually most important) class of vertex corrections: repeated electron-hole scattering, represented by the correlation function diagrams of the following type (Fig. 4.3):

![Fig. 4.3.](image-url)
If we assume that the electron-hole pair interact by a perfectly screened Coulomb potential $V$, these ladder diagrams can be summed as in the ordinary RPA, and they give an expression with a denominator $(1 - V X_0(w))$, where

$$X_0(w) = \frac{i}{(2\pi)^4} \int \frac{D(q, w') C(q, w+w')} dq \, dw', \quad (4.1)$$

corresponding to the diagram

\[ Fig. 4.4. \]

C and D are electron and hole Green's functions respectively. Ladder diagrams can be important when the denominator becomes small. Such resonance will occur at the energy $w_r$ defined by

$$1 - V \text{ Re } X_0(w_r) = 0 \quad (4.2)$$

which has the width $V \text{ Im } X_0(w_r)$.

To calculate $X_0$ we can use for C and D:
\[ C(q,w) = \left[ w - E_e - \frac{q^2}{2m} + i\delta \right]^{-1} \]

\[ D(q,w) = \left[ w - E_h - \frac{q^2}{2M} + i\delta \right]^{-1} \]  

(4.3)

If we define the reduced mass \( \nu \) as \( \frac{1}{\nu} = \frac{1}{m} + \frac{1}{M} \) and the "energy gap" \( \Delta = E_e - E_h \) and introduce a cutoff \( d \) in the Coulomb potential, the calculation gives:

\[ \text{Im} \chi_0(w) = \frac{\nu}{m} \nu_0 \pi \Theta (w - \Delta - \frac{m}{\nu} \mu) \]

and \[ \text{Re} \chi_0(w) = \frac{\nu_0 \nu}{m} \ln \left( \frac{\frac{w-m}{\nu} (\mu+d)-\Delta}{\frac{w-m}{\nu} \mu - \Delta} \right) \]  

(4.4)

\( \nu_0 \) is the density of states at the Fermi energy \( \mu \). The position of the resonance level is given by (4.2) and (4.7) as:

\[ w_r = \Delta + \frac{m}{\nu} \mu - \frac{m}{\nu} d (e^\alpha - 1) \]  

(4.5)

where \( \alpha = \frac{\nu_0}{m} \nu \)  

In X-ray absorption near the threshold these resonances could be important, but in ultraviolet photoemission we are far from them \( (w \gg w_r) \) and the formation of these bound electron-hole excitonic states is out of question.
Electron scattering.

In the previous chapter we assumed that the emitted electron leaves the metal unscattered or after interacting inelastically once with the rest of the solid, which gave diagrams (Fig. 3.3 a, b, c, d) for the correlation function. If we specify this interaction to be electron-electron scattering and plasmon emission we find the following correlation function diagrams.

![Diagram](a)

![Diagram](b)

![Diagram](c)

Fig. 4.5.

In this approximation we have excluded the exchange process when the created electron gives enough energy to another electron which leaves the metal.
though we expect them to be equally possible as the direct ones. Electron scattering will also lead to the emission of secondary electrons, which would correspond to the higher order terms of the transition matrix $T$ given by (3.17). The diagrams can be easily generalized to describe this process:

but the calculation of the corresponding general correlation function would probably be very tedious.

Processes described by diagrams on Fig. 4.6 and Fig. 4.7 are equivalent to the ones that BS take into account in their work and calculate in (2.22).
However there are two basic differences. Firstly, and that we shall discuss later in detail, the nondirect excitation model of BS assumes that the d-hole Green's function $D$ has no momentum dependence:

$$D(q,w) = \left[ w - E_o + i \delta \right]^{-1} \quad (4.6)$$

Secondly, conduction electrons in BS theory between the scattering events are not described by free propagators as in our approach but are damped by the mean free path factor $e^{-\frac{q}{\xi}}$. This assumption contradicts the first one - that only non-scattered and once-scattered electrons contribute in the photoemission, if the same mechanism is attributed to both types of scattering (as BS indeed suggest).

Mean free path description of a decay of the excited electron is equivalent to the self-energy approach and is valid for low lying excitations with energy near the Fermi-level. It is physically inconsistent to use this renormalized electron propagator when calculating the scattering diagram (e.g. Fig. 4.5b) for electrons with relatively high energy and formally it leads to the over-counting of diagrams.

However, we can agree with the final conclusion of BS that electron-electron scattering enhances the low energy part of the photoelectron spectrum because the result (2.25) was calculated in
a limit $\alpha \to 0$ and $l \to \infty$, i.e. for free outgoing electrons.

If there is a well defined plasmon mode of energy $\omega_p$ in the metal the diagram of Fig. 4.5c can give a structure in the measured electron distribution at a distance $\omega_p$ from the main unscattered part.

Problem of momentum conservation.

In Chapter 3 we defined direct and indirect processes in electronic transitions and pointed out that the matrix element of the photon-electron current interaction (3.76) gave a selection rule (3.104) which required momentum to be conserved in the process. However, it is a striking fact that many experimental results seem to be fairly well explained by the "non-direct transition model" which ignores momentum conservation and which is the basis of BS theory. We call it "non-direct" to distinguish from "indirect" two-step processes where momentum is changed through the emission or absorption of a phonon or some other scattering.

In BS theory this assumption is stated e.g. in the expression for the optical excitation probability (2.19) or final photoelectron distribution (A.1) or in words /37/:

a) That the photon produces a many-body excitation with energy $E$ and an electron in an excited band state with energy $e_k$; and

b) that $E$ is independent of $e_k$ except for condition $E = e_k - \omega = (e + \omega) - \omega$.

Let us see what are the consequences of these assumptions on
the experimental results. Experimentally we could not distinguish between direct and non-direct transitions from the narrow and flat bands, but the resolution of photoemission measurements is 0.1 eV and the measured bands are never so flat (e.g. in Cu d-bands extend over 3.5 eV). We shall assume that a structure in density of initial or final states will produce a corresponding structure in the energy distribution of the emitted electrons, and the easiest such structure to observe is a peak. The detailed analysis of the different behaviour of these peaks for various photon energies in direct and non-direct processes is given in Appendix C., and here we shall only summarize them analyzing Fig. 4.8. (from /37/).

Here the distribution of photoelectrons from Cu is given as a function of the initial energy \( E = e + W - w \) for various photon energies. Apart from the low energy region which is not reliable because of the scattered-electron contributions and some spurious surface effects mentioned in Chapter 2., we observe two main structures in these curves: the peak at \( \approx 2 \) eV below the Fermi level attributed to the transitions from the d-band and the peak near the Fermi energy associated with transitions from s- and p- bands. When photon energy is increased the low energy peak does not change its position which indicates the non-direct process, while the conduction band peak follows the photon energy and slowly disappears. Thus at a short range of energies we can detect both direct and non-direct processes.
Fig. 4.8
Spicer collected impressive evidence that there is a definite connection between the localization of the electrons in the initial state and the occurrence of non-direct processes in metals and other materials like alkali and cuprous halides. In all cases where initial states were well localized, for instance d-bands in noble and transition metals, the experimental results could be explained without momentum conservation, while the photo-emission from more mobile electronic bands (s,p) obeyed the momentum selection rule.

Spicer's physical argument to explain this curious behaviour is, in short, that the created hole in the d-band undergoes a many-body relaxation process and shares its momentum with other electrons, so that momentum is not conserved in the transition. More specifically, the localized hole will act as a transient potential for the electrons within the screening length and create a many-body excited state.

In the second part of this thesis we examine a similar problem when the electrons are excited from deep core levels which are perfectly localized and calculate the effect of the relaxation of the conduction electron sea to this sudden change of the hamiltonian. We suggest that exactly the same mechanism can explain the momentum nonconservation and nondirect processes if we extend it to include the recoil, i.e., the momentum dependence of the hole energy. The recoil, which is inversely proportional to the effective band mass $M$, weakens this effect so that it is appreciable only in the
localized narrow bands.

The scattering of conduction electrons near the Fermi surface during the relaxation of the hole which is singular for a sharp hole level now is smeared over the band and the singularity becomes broader proportionately to the band width. The generalization of the theory to include the recoil effects is not trivial but the main features of the results can be seen from the physical model sketched here.
CHAPTER 5.

X-RAY PHOTOEMISSION.

When a metal is bombarded by hard X-rays they can eject electrons originating either from the broad higher lying bands or from the deeper tightly-bound levels.

In the first case one tries to obtain some information about the band structure of metals. Experimental results of Fadley and Shirley \(^57/\) for iron, cobalt, nickel, copper and platinum are in rough agreement with the band calculations \(^58,59/\) as regards the position and width of d-bands in these metals. However, the measured photoelectron spectra are broad and rather insensitive to the details of the band structure, though this fine structure should be seen according to the high resolution (1 eV) claimed for these experiments.

The characteristic shape can be connected with the work of Baer \(^60/\) who showed that for X-rays of energies high compared with electronic energies in metals conservation of momentum ceases to be an important selection rule. He analyzed the matrix element \(\langle k | \hat{A} \nu | k' \rangle\) in the free-electron model and used the approximations based on the relatively high photon energy to prove that transition matrix element becomes a constant in this limit, which gives the energy distribution of excited electrons proportional to the density of initial states.

We shall here consider the other case: photoemission from the
deep core states, say 40 to 100 eV below the Fermi level, which are very narrow and where the electrons are well localized on the lattice sites. An X-ray, with the energy of 100 to 1000 eV or even a few kV, excites an electron from the deep level into a continuum of free states outside the metal, with an energy far above the Fermi level, leaving the deep hole behind.

Fig. 5.1 shows the energy scheme of the described process.

Because the excited electrons have an energy extremely high compared to the Fermi energy they are not inelastically scattered on their passage through the solid, and many problems (e.g. in ultraviolet photoemission) connected with this stage of the process are simplified. The only significant scattering process is a plasmon emission, which can be easily identified, because it gives an additional peak in the
photo electron spectrum located at an energy \( w_p \) lower than the peak of non-scattered electrons. Very high energy also makes the approximation (3.15), that the electrons cross the surface with a charge of wavevector only, even better than in the ultraviolet emission.

Discussing a closely related problem, Mahan /61,62/ suggested that an electron excited up to the Fermi surface of a metal from a core state by the absorption of an X-ray (or the converse emission process) would scatter in a singular way, analogous to that occurring in the Kondo effect, from the transient, screened Coulomb potential of the accompanying deep (and immobile) hole and thus lead to a singular peak in the soft X-ray absorption (emission) cross section at threshold. More recently Nozières and de Dominicis /52-54/ (referred to hereafter as ND) have shown that what actually happens is a combination of the above singular electron-hole scattering together with a transient and singular re-adjustment of the ground state of the entire Fermi gas to the presence of the hole effective potential. Depending on the sign and strength of this potential, these two effects may reinforce or cancel, leading to the possibility of either threshold peaks or zeroes in the X-ray absorption cross-section.

In this section we shall consider two related processes which also depend on the transient re-adjustment of the ground state of the Fermi gas to the sudden appearance of the hole potential. These are emission of fast photo-electrons after the absorption of mono-chromatic X-rays in the metal and the emission of discrete X-ray lines as a result of
electron transitions between inner shell states of an excited atom in a metal.

Besides the fact that in both processes the same type of many-body effects can be expected, another reason for discussing X-ray lineshapes is that they can strongly modify the shape of the ejected photoelectron spectra. Any deviation from the symmetric resonance shape in X-rays is reflected in the asymmetry of the photoelectron distribution, which is calculated as a convolution of spectral functions of all particles involved in the transition. This will produce some difficulties and ambiguities in the analysis of experimental data for X-ray photoemission where no account was previously taken of these anomalies in the X-ray lineshapes.

The physical reasoning which leads to the prediction of singular many-body effects in these two processes can be summarized in the following way. In the photoemission case the energy of the emitted photoelectron \( e_k \) is a direct measure of the energy of the hole-state \( e_h \) (measured relative to the Fermi level) left behind in the metal:

\[
e_k = w + E_g - e_h - W
\]

where \( w \) is the X-ray energy (\( \hbar = 1 \)), \( E_g \) the initial ground state energy of the metal, and \( W \) is the work function. Thus the maximum photoelectron energy \( e_{\text{max}}^{e} \) corresponds to the ground state of the hole plus metal, while photo-electrons emitted below the maximum correspond to events in which the hole plus Fermi sea is left in an excited state. Excited states
with energies very close (a fraction of an eV) to the ground state are those in which the Fermi sea is excited by the creation of low energy conduction electron-hole pairs (i.e. charge density fluctuations). It turns out that since the energy of creating pairs goes continuously to zero as the momentum transfer to the pair, an infra-red catastrophe occurs in which it is very favourable to produce a large number of very low energy pairs. Thus the photo-emission cross-section \( \frac{d\sigma}{de} \) is changed from a \( \delta \)-function (if we assume that the ingoing X-ray spectrum has the same shape) in the absence of pair formation to a singular (though integrable) curve tailing off on the low energy side of \( e_{\text{max}} \) (Fig. 7.2b).

In the hard X-ray emission, a deep hole which has previously been formed by the absorption of an X-ray (or by knocking out an inner shell electron with a fast primary electron) captures an electron from an adjacent inner shell of the atom with emission of an X-ray, i.e. the hole moves "up" to a higher atomic level. When this happens the effective screened potential acting on the conduction electrons changes somewhat, so that again the Fermi sea has to undergo a drastic re-adjustment to the new potential. The emitted X-ray can thus leave the Fermi sea in a many pair excited state, with accompanying distortion of the X-ray lineshape.
CHAPTER 6.

SINGULARITIES IN TRANSIENT PHENOMENA

As was already indicated, sudden creation of a localized scattering potential in a metal will result in singular effects which are basically a consequence of the electron distribution discontinuity at the Fermi level. In this chapter we shall develop a method which will enable us to treat these divergent phenomena, i.e. collect all the most divergent diagrams in the perturbation calculation of such a process. This method will be used later in a modified form to find the spectral distribution of photoelectrons ejected by hard X-rays from the metallic core states. The method described was first used in high energy meson-meson scattering /63,64/ , later applied by Abrikosov to the Kondo problem /65/. Hopfield /66/ and Anderson /51/ noticed that this divergent behaviour is typical for any problem which involves the transient response to the sudden creation of a scattering centre. X-ray absorption and emission of metals was an obvious candidate for this approach, as was shown by Roulet et al. /52/ and Nozières et al. /53, 54/, who confirmed the results that Mahan /61, 62/ guessed in the perturbation calculation.

Description of the model.

In the model we shall use /54/ , due to its simplifications the many-body technique of /52/ and /53/ will not be necessary.
The metal can be assumed to consist of free conduction electrons and deep well localized states. Coulomb interaction inside the conduction band can be taken into account if we define the electron energies as already being renormalized, because near the Fermi surface its only effect could be to renormalize them. We shall neglect the lattice potential, and in this approximation the Fermi surface of conduction electrons is spherical.

The hole is left after excitation in a single deep core state with unrenormalized energy $E_0$. We assume that it is localized or immobile and that its recoil may be neglected. Also in the first approximation the lifetime of the deep level is not taken into account. In this model only interband scattering between the deep hole and conduction electrons remains, in which conduction electrons stay in the same band, and the deep hole does not change its state.

Hamiltonian.

The assumptions of the described model are summarized in the hamiltonian:

\[
H = H_o + H_c + H_x \tag{6.1}
\]

\[
H_o = \sum_{k<k_f} \varepsilon_k c_k^+ c_k + E d^+ d \tag{6.2}
\]

\[
H_c = \sum_{k<k'} V_{kk'} c_k^+ c_{k'} d^+ d' \tag{6.3}
\]

\[
H_x = \sum_k W_k c_k^+ d e^{-i\omega t} + c. c. \tag{6.3}
\]
$H_0$ is the kinetic energy of conduction electrons with renormalized energies $e_k$ and creation operators $e_k^+$, and core electrons with energy $E_0$ and creation operators $a^+$. $H_0$ is equal to (3.3) in the limiting case when the effective mass and binding energy of the valence band increase.

$H_x$ is the perturbation term and will be treated in the Born approximation. It represents the coupling between the X-ray field and the electrons. $w$ is the X-ray frequency. The general form of the matrix element $W_k$ is

$$W_k \sim \langle \psi_d | -i \nabla \cdot \vec{n} | \psi_k \rangle$$

where $n$ is the X-ray polarization vector, $\psi_d$ the core electron wave function, and $\psi_k$ the Bloch wave function of the conduction electron:

$$\psi_k = e^{ikr} u_k (r)$$

For the soft X-ray absorption, where the core electrons are excited to the vicinity of the Fermi level it is appropriate to approximate

$$W_k = W u_k$$

(6.4)

where $u_k = 1$ for $| e_k - \mu | < d$

(6.5)

0 for $| e_k - \mu | > d$

and $W$ is a constant.
For photoelectrons ejected by hard X-rays far above the Fermi level we may approximate \( W_k \) by a constant.

\( H_c \) represents the scattering of the conduction electrons by the deep hole. It is applied suddenly when the X-ray is absorbed and due to its transient nature leads to the singular effects already described. In the case of a deep immobile hole instead of the many-body treatment the problem can be significantly simplified and treated as a one-body problem.

This simplification comes from the momentum independence of the hole, which does not change its state in the scattering and cannot therefore have any memory of its history. All the scattering processes are independent and the only dynamical aspect of the problem is the fact that the hole exists in a fixed time interval. It is created or destroyed by absorption or emission of the X-ray, and with this time restriction it can scatter the conduction electrons. Thus we may treat

\[
\sum_{kk'} V_{kk'} c_k^+ c_{k'} d d^+ \text{ as a one body potential } \sum_{kk'} V_{kk'} c_k^+ c_{k'}
\]

which scatters conduction electrons while the hole is present in the system.

In general, the potential matrix element \( V_{kk'} \) can be expanded into spherical harmonics:

\[
V_{kk'} = \sum_{l,m} V_l (k,k') Y_{lm} (k) Y_{lm} (k^*) \quad (6.6)
\]

Our assumption is that we can treat the components \( V_l (k,k') \) as
separable: \[ V_{1}(k,k') = - V_{1} u_{1}(e_{k}) u_{1}(e_{k'}) \] (6.6a)

with some cut off functions \( u_{1} \) centered on the Fermi surface. This is justified for the small energy transfer interactions near the Fermi level, where (6.6a) is a reasonable approximation to the average \( V_{1}(k,k') \).

The minus sign of the potential \( V_{1} \) ensures that it represents the Coulomb' attraction between the hole and the electron.

Though in a more refined treatment it would be possible to calculate the general \( l \)-wave scattering, it is much simpler and for our purpose quite satisfactory to consider only \( s \)-wave scattering. Then we can approximate \( V_{1}(k,k') \) by:

\[ V_{1}(k,k') = -V u_{k} u_{k'} \] (6.7)

and for cut off functions we may again choose:

\[ u_{k} = \begin{cases} 1 & \text{for } |e_{k} - \mu| < d \\ 0 & \text{for } |e_{k} - \mu| > d \end{cases} \] (6.5)

d is a cut off of the order of the conduction electron bandwidth and is necessary to eliminate physically spurious ultraviolet anomalies. (6.7) describes well \( s \)-wave scattering of electrons around the Fermi surface where the conduction band is approximately flat.

Making all these approximations we have neglected some information about the nature of the transitions (\( K, L, M \), etc) and the symmetry properties of the electron states (\( s, p \) or \( d \) orbitals). Lifetime of
the deep hole (e.g. due to internal Auger processes) was also neglected, though for heavier elements it could blurr the singularities. In the later calculation of the photoelectron spectra we shall show that, when included, it drastically changes their shapes and removes the divergency.

Equations for Green's functions.

To proceed with the calculation of required physical quantities we introduce the conduction electron Green's function, defined in a usual way:

\[
C_{kk'}(t - t') = \langle 0 | \mathcal{T} \{ C_k(t) C_{k'}^+(t') \} | 0 \rangle
\]  

(6.8)

where \( \mathcal{T} \) is the time ordering operator and the average is made over the initial ground states \( |0\rangle \) of the solid.

In absorption it describes a free electron:

\[
C_{kk'}(t) = \delta_{kk'} C_k(t) = \begin{cases} 
\delta_{kk'} e^{-i e_k t} \theta(t) & \text{if } e_k > \mu \\
-\delta_{kk'} e^{-i e_k t} \theta(-t) & \text{if } e_k < \mu 
\end{cases}
\]  

(6.9)

In emission the initial state contains the scattering potential of the deep hole and all its effects. \( C_{kk'}(t) \) is then given by the Dyson equation:

\[
C_{kk'}(t) = C_{ko}(t) d_{kk'} - i \sum_{k''} \int_{-\infty}^{\infty} dt' C_{ko}(t') V_{kk''} C_{kk''}(t-t')
\]  

(6.10)
or diagrammatically:

\[
\begin{array}{c}
\text{k',0} \\
\downarrow \\
\text{k,t} = \quad \text{0} \rightarrow \text{t} \quad \text{o} \rightarrow \text{t''} \\
\downarrow \\
\text{t} \\
\end{array}
\]

Fig. 6.1

The deep electron Green's function is:

\[
D(t-t') = \langle 0 | T \left\{ d(t) d^+(t') \right\} | 0 \rangle \quad (6.11)
\]

and will be denoted by a dotted line.

Because of the extremely large energy required for the creation of another d-hole in the metal, there is always only one deep level and \( D \) always propagates in the same direction of time, e.g. the free propagator is given by:

\[
D_o(t) = e^{-i E_o t} \theta(t) \quad \text{for emission}
\]

\[
- e^{-i E_o t} \theta(-t) \quad \text{for absorption} \quad (6.12)
\]

To obtain X-ray absorption spectrum or photoelectron distribution we shall have to calculate quantities of the type

\[
F_{kk'}(t-t') = \langle 0 | T \left\{ c_k^+(t) d(t) d^+(t') c_{k'}(t') \right\} | 0 \rangle \quad (6.13)
\]

which can be represented by a diagram:
Propagation of the deep hole from \( t \) to \( t' \) introduces only the phase factor
\[ e^{-i E_0 (t-t')} \]
in \( F \) and \( D \), because its only time dependence as a scattering potential is its limitation to the interval \((t,t')\). It is convenient to factorize out this dependence by introducing the reduced quantities:

\[
\overline{F}_{kk'}(t) = \pm e^{i E_0 t} F_{kk'}(t) \\
D(t) = \pm e^{i E_0 t} D(t)
\]  
(6.14)

where \( \pm \) correspond to emission and absorption, to account for the different signs in (6.12).

To calculate \( \overline{F} \) and \( D \) we must sum all possible diagrams arising from interaction (6.7) acting between \( t \) and \( t' \). For \( F \) a typical diagram is shown on Fig. 6.3a:
contains diagrams of the following type (Fig. 6.3a):

Fig. 6.3a

contains diagrams of the following type (Fig. 6.4a):

Fig. 6.4a
If we treat the hole as a transient one-body potential, it can be eliminated from the problem, and these diagrams become much simpler (Figs. 6.3b and 6.4b).

The deep hole lines have been erased and the interaction vertices replaced by static potential vertices represented by dots with matrix elements \( V_{kk'} \) for absorption/emission.

Conduction electron lines are renormalised propagators \( C_{kk'} \).

Diagrams for \( \overline{F} \) include one open electron line between \( t \) and \( t' \) and any possible combination of closed loops in various time orderings. These loops describe the readjustment of the Fermi sea to the new hamiltonian of the system which contains the scattering potential.

Diagrams for \( \overline{D} \) on the other hand contain no open electron line but only closed loops, which play the role of vacuum fluctuations in
ordinary perturbation theory. They can be summed using the linked
cluster theorem and give

\[ \bar{D}(t) = e^{K(t)} \]

\[ \bar{F}_{kk'}(t) = L_{kk'} e^{K(t)} \]  \hspace{1cm} (6.15)

where \( K(t) \) is the sum of all single closed loops and \( L_{kk'}(t) \) is the
open electron line.

It may be easier to understand the physical meaning of \( \bar{F}_{kk'}(t) \) if
we Fourier transform it back to energy space. In the energy-representa-
tion \( \bar{F}(e) \) becomes the convolution of the conduction electron term \( L_{kk'}(e) \),
which gives the iterated scattering of the excited electron, and the deep
hole propagator \( \bar{D}(e) \). When the electron is excited to or from the
Fermi level, as in X-ray absorption or emission, the main singularity
occurs in the \( L_{kk'} \) term, while renormalization of \( \bar{D} \), as will be shown
later, weakens and blurs this divergence. On the contrary, in X-ray
photoemission the electrons will be excited far from the Fermi level
and \( L_{kk'} \) will reduce to the unscattered free electron propagator. Thus
we shall need only the hole propagator \( \bar{D} \).

In order to calculate \( L_{kk'} \) and \( K \) it is convenient to introduce the
conduction electron Green's function evaluated in the presence of the
transient potential.

\[ \phi_{kk'}(\tau, \tau'; t, t') = \langle \psi(t) | T \left\{ c_k(\tau) c^{+}_{k'}(\tau') \right\} | \psi(t') \rangle \]  \hspace{1cm} (6.16)
where $\psi(t)$ is different for absorption and emission and represents the scattered state of the Fermi sea with no or one hole respectively.

For the absorption case $t < t'$, and the Dyson equation reads:

$$
\Phi_{kk'}^a (\tau, \tau'; t, t') = C_{kk'}^a (\tau - \tau') - i \int_{t}^{t'} dt'' \sum_{qq'} C_{kq}^a (\tau - t'').
$$

For the emission case $t > t'$, and we must substitute in (6.17) $C^a \rightarrow C^e$ and $V_{qq'} \rightarrow -V_{qq'}$:

$$
\Phi_{kk'}^e (\tau, \tau'; t, t') = C_{kk'}^e (\tau - \tau) + i \int_{t}^{t'} dt'' \sum_{qq'} C_{kq}^e (\tau - t'').
$$

These equations take into account all diagrams of the type:

![Fig. 6.5](image.png)

It is obvious from Fig. 6.5 that

$$
\lim_{\tau \rightarrow t'} \Phi_{kk'}^e (\tau, \tau'; t, t') = - I_{kk'} (t - t')
$$

(6.19)
Also, if we let \( t \) and \( t' \) go to infinity, \( \phi_{kk'} \) reduces to the Green's function averaged in the final state, which is the same as the initial state for the inverse case:

\[
\lim_{t \to \infty} \phi_{kk'}^a (\tau, \tau'; t, t') = c_{kk'}^e (\tau-\tau')
\]

\[ t' \to \infty \]

\[
\lim_{t \to \infty} \phi_{kk'}^e (\tau, \tau'; t, t') = c_{kk'}^a (\tau-\tau')
\]

\[ t' \to -\infty \]

(6.20)

Thus when \( \phi_{kk'} \) is known \( L_{kk'} \) and \( C_{kk'} \) follow from it as the limiting cases. There is still \( K(t) \) to be connected with \( \phi_{kk'} \). To do this we multiply each vertex appearing in the expansion for \( K \) by a constant \( \lambda \), apply \( \frac{\partial}{\partial \lambda} \) and put \( \lambda = 1 \). This has the effect of multiplying each diagram of \( K \) by the number of its vertices \( n \). But, when done in an infinite series of diagrams for \( K \), this is equivalent to picking out successively each vertex of the particular graph whose time \( \tau \) is between \( t' \) and \( t \) and gives:

\[
(\lambda \frac{\partial K(t-t')}{\partial \lambda})_{\lambda=1} = -i \sum_{qq'} \int_{t'}^{t} V_{qq'} \phi_{q'q} (\tau, \tau) d\tau \quad (6.21)
\]

Equations (6.17), (6.18) and (6.21) can also be derived using an equation of motion procedure (Langreth /67/ ). That approach is formally much simpler, (see Appendix D) because it exploits the fact that there could be only one deep hole in a system explicitly to
eliminate the hole propagator. However, the equation of motion derivation is more formal and the transient character of the problem is not so visible as in the original approach of /52 - 54/.

**Asymptotic solution.**

Because of the assumed separability of the potential (6.7), instead of the functions $\varphi_{kk}', C_{kk}', \text{ and } F_{kk}'$, we may consider only the combinations:

$$\varphi = \sum_{kk'} \varphi_{kk'} u_k u_{k'},$$

$$C = \sum_{kk'} C_{kk'} u_k u_{k'},$$

$$F = \sum_{kk'} F_{kk'} u_k u_{k'}.$$

For the absorption, according to (6.22) and (6.7), $C^a(t)$ is given by

$$C^a(t) = \int_0^\infty \nu(e) u^2(e) e^{-iet} \, de \quad \text{for } t > 0$$

$$= -\int_{-\infty}^0 \nu(e) u^2(e) e^{iet} \, de \quad \text{for } t < 0$$

where $\nu(e)$ is the electron density of states for one spin direction, and we have chosen the energy variable $e$ relative to the Fermi level (i.e. $\mu = 0$).

We shall now make the fundamental step in our theory and approximate Green's function $C^a$ and $C^g$ by their asymptotic form for large times:

$$C^a(t) = -i\nu_o \left( \frac{p}{t} + \tan \theta \pi \delta(t) \right)$$

(6.24)
\[ \nu \tan \theta = \frac{1}{\pi} \int_{-\infty}^{\infty} \nu(e) u(e) P \frac{1}{e} \, de \quad (6.25) \]

The first term on the right side of (6.24) comes from the discontinuity at the Fermi surface and is the main contribution from the integral (6.23) in the limit \( t \to \pm \infty \). It will not contribute to (6.23) for small times \( t \). We can show that

\[ C^a(t) = -i \nu \frac{1}{t} \quad \text{for } t \to \pm \infty \]

in a specific choice of \( \nu(e) \) and cut off function \( u(e) \):

\[ \nu(e) = \nu_0 \quad (6.26) \]
\[ u(e) = e^{-|e|} \]

From (6.23) integration gives for \( C^a \);

\[ C^a(t) = \frac{\nu_0}{it + 1 \, \text{sgn } t} \quad (6.27) \]

For times \( t \) larger that the inverse cutoff \( \frac{1}{d} \) (6.27) reduces to the first term of (6.24).

The approximate expression (6.24) will be used in the integral equation.

\[ \phi^a(\tau, \tau'; t, t') = C^a(\tau - \tau) + iV \int_{t}^{t'} C^a(-t'') \phi^a(\tau'-t''; t, t') \, dt'' \quad (6.28) \]

which is obtained from (6.17) when momentum summation (6.22) is carried out.
For the emission case (6.10) after Fourier transformation can be written as

$$C^e(e) = \frac{C^a(e)}{1 - iVC^a(e)}$$  \hspace{1cm} (6.29)

After similar analysis we find an asymptotic expression for $C^e$ which is valid for large times:

$$C^e(t) = -\frac{i\gamma}{\beta} \left( \frac{1}{t} + \tan \theta' \pi \delta(t) \right)$$

where $\tan \theta' = \tan \theta - \frac{\pi g}{\cos^2 \theta}$ and $\beta = 1 - 2 \pi g \tan \theta + \frac{\pi^2 g^2}{\cos^2 \theta}$  \hspace{1cm} (6.30)

$g = \gamma V$ is the coupling constant.

The asymptotic forms of $C^a$ and $C^e$ for large times are fundamental approximations in the following calculation. They will give the correct behaviour of the solutions for large times. In energy representation this means small energies compared to $d$, and the results we obtain will be valid only in this energy interval about the threshold or, in the photoemission case, the main emission line.

It is convenient to express all results in terms of the phase shift of conduction electron wave functions at the Fermi level $\delta(\mu)$. In Appendix E, we have found this relationship following the approach of W. Kohn. When the expression (E.16) is adapted to the attractive separable contact potential (6.7) we obtain:

$$\tan \delta(e) = \frac{\pi V u^2(e) v(e)}{1 - V y(e)}$$  \hspace{1cm} (6.31)
where \( y(e) = \int_{-\infty}^{\infty} u^2(e') P \frac{1}{e' - e} \) \( \) \( (6.32) \)

On the Fermi surface \( e = \mu \): \( u(\mu) = 1 \). From \( (6.31) \) follows:

\[
y(\mu) = \pi \nu_0 \tan \theta
\]

and \( \tan \delta = \frac{\pi g}{1 - \pi g \tan \theta} \) \( (6.33) \)

\( (6.30) \) and \( (6.33) \) give:

\[
\theta' = \theta - \delta
\]

\[
\frac{1}{\beta} = \frac{1}{\pi} \frac{d\delta}{dg}
\] \( (6.34) \)

Thus we have reduced all quantities determining the scattering effects to only one: phase shift \( \delta \).

Integral equation \( (6.23) \) can be solved exactly, if for the Green's functions \( C^a \) and \( C^e \) we take asymptotic expressions \( (6.27) \) and \( (6.30) \), using the method of Muskhelishvili. Of all possible solutions of the integral equation we shall look for a perturbative one, which reduces to \( C^a \) when the interaction is turned off \( (g \to 0) \).

After a rather long calculation which is done in the Appendix F, this solution of the integral equation \( (6.28) \) is found to have the form:

\[
\phi^a(\tau, \tau'; t, t') = C^e(\tau - \tau') \left( \frac{(t' - \tau)(\tau - t)}{(t' - \tau)(t' - t)} \right) \delta \frac{1}{2\pi}
\]

\( (6.34) \)

In the emission case to calculate \( \phi^e \) we have to replace in \( (6.28) \):

\[
C^a \to C^e, \quad V \to -V \quad t' \leftrightarrow t.
\]
and after some algebra (see Appendix F.)

\[ \varphi^\phi(t, t'; \tau, \tau') = C^a (\tau - \tau') \left( \frac{(t' - t')(t - \tau)}{(\tau - \tau')(t - t')} \right)^{\delta \pi} \]  (6.35)

for \( t' < \tau, \tau' < t \). (6.34) and (6.35) have the same "transient factor".

\[ \left( \frac{(t' - t')(t - \tau)}{(\tau - \tau')(t - t')} \right)^{\delta \pi} \]

It is obvious at once that \( \varphi^a \) and \( \varphi^\phi \) satisfy (6.20) because for \( t \) and \( t' \) going to infinity they reduce to \( C^\phi \) and \( C^a \) as expected.

We proceed by calculating \( L_{kk}^a \) and \( K \) from \( \varphi \) as indicated in (6.19) and (6.21). The quantity \( L_{kk}^a \) is obtained from (6.34) and (6.35) by letting \( t \to \tau \) and \( t' \to \tau \), but as given here these expressions diverge.

This is the consequence of the approximations made for \( C^\phi \) and \( C^a \) which are not valid for short times \( |t - \tau|, |t' - \tau| \), and so on.

To avoid these spurious divergences we have to introduce a cut off \( d \) in the energy. As we are not going to need \( L^a \) and \( L^\phi \) we shall only quote the results:

\[
\begin{align*}
L^a(t) &= \frac{iV_0}{t} (i \, dt)^2 \frac{\delta}{\pi} \theta(-t) \\
L^\phi(t) &= \frac{iV_0}{\beta t} (i \, dt)^2 \frac{\delta}{\pi} \theta(t) \text{ for } |dt| < 1
\end{align*}
\]  (6.36)

For photoelectron distribution we shall need the deep hole Green's function \( D = e^K \). \( K \) can be found from equation (6.21):

\[
\left( \frac{\partial K(t, t')}{\partial \lambda} \right) = -i \sum_{qq} \int_t^{t'} V_{qq'} \varphi_q^{q'}(\tau, \tau') d\tau
\]
Our calculation (6.34) and (6.35) for $\phi(\tau, \tau')$ is not valid for short times, so that $\phi(\tau, \tau')$ diverges. This is an artefact of our approximation, and to avoid this difficulty we expand $\phi$ in powers of $(\tau-\tau')$:

$$
\phi^a(\tau, \tau') = C^a(\tau-\tau') - \frac{i\gamma_0}{\beta} \frac{\delta}{\pi} \left( \frac{1}{\tau'-\tau} + \frac{1}{\tau-\tau'} \right) + \ldots
$$

$$
\phi^e(\tau, \tau') = C^a(\tau-\tau') + \frac{i\gamma_0}{\beta} \frac{\delta}{\pi} \left( \frac{1}{\tau'-\tau} + \frac{1}{\tau-\tau'} \right) + \ldots \quad (6.37)
$$

In the limit $\tau-\tau' \to 0$ the only singular terms appear in the electron Green's functions $C^a$ and $C^e$ and are obviously a result of the approximation procedure which would disappear in a better approximation for short time behaviour of $\phi$. Also it is very important to notice that these terms are independent of $\tau$ and $\tau'$, and will give a contribution proportional to $\tau-\tau'$ in the calculation of $K$. This part will only shift the energy of the deep hole level from $E_0$ to $E_0 + \Delta$, while the other terms depend on $\tau$ and $\tau'$ and thus give the decay rate of the hole level which we are looking for.

The energy shift can be simply absorbed into some phenomenological threshold $\nu_0 = E_0 + w + \Delta$, so we keep only the last two terms in (6.37):

$$
\lambda \frac{\partial K^a(t-t')}{\partial \lambda} = -i \sum_{qq'} u_q u_{q'} V_{qq'} \int_t^{t'} \left( \frac{-i\gamma_0}{\beta} \frac{\delta}{\pi} \left( \frac{1}{\tau'-\tau} + \frac{1}{\tau-\tau'} \right) \right) d\tau
$$

$$
\lambda \frac{\partial K^e(t-t')}{\partial \lambda} = -i \sum_{qq'} u_q u_{q'} V_{qq'} \int_t^{-t} \left( \frac{i\gamma_0}{\beta} \frac{\delta}{\pi} \left( \ldots \right) \right) d\tau
$$

(6.38)
To avoid logarithmic divergencies at the ends of the r-integral one
must again introduce the cutoff $a^{-1}$, which gives:

$$\lambda \frac{\partial K^a(t)}{\partial \lambda} = -\frac{2g}{\beta} \frac{\partial}{\pi} \ln |d\ t|$$
$$\lambda \frac{\partial K^a(t)}{\partial \lambda} = -\frac{2g}{\beta} \frac{\partial}{\pi} \ln |d\ t|$$

(6.39)

In the absorption case $K^a$ is independent of $g$, so

$$\lambda \frac{\partial K^a}{\partial \lambda} = g \frac{\partial K^a}{\partial g}$$

(6.40)

When we insert $\frac{1}{\beta} = \frac{1}{\pi} \frac{d\delta}{dg}$ into (6.40), after integration we find

$$K^a(t) = -\left(\frac{\delta}{\pi}\right)^2 \ln |d\ t|$$

(6.41)

In the emission case $K^e$ depends on $g$ through $C^e$ via parameters $\theta'$ and

$\beta$ and they must be kept constant in derivation:

$$\lambda \frac{\partial K^e}{\partial \lambda} = g \frac{\partial K^e}{\partial g} \left(\frac{\partial \delta}{\partial g}\right)_{\beta, \theta'} = g \frac{\partial K^e}{\partial \delta} \left(\frac{\partial \delta}{\partial g}\right)_{\beta, \theta'}$$

(6.42)

From (6.30) and (6.34) one finds

$$\tan \delta = \frac{\pi g}{\beta + \pi g \tan \theta'}$$

(6.43)

and

$$\left(\frac{\partial \delta}{\partial g}\right)_{\beta, \theta'} = 1.$$

Thus from (6.42) and (6.39) we get the same expression for $K^e$ as for $K^a$:

$$K^e(t) = -\left(\frac{\delta}{\pi}\right)^2 \ln |d\ t|$$

(6.44)
The cut off \( d \) we have introduced must be pure imaginary to give a real spectral density of the deep level Green's function \( D \), as can be seen from (6.14) and (6.15). The final expression for \( D \) reads:

\[
D(t) = e^{\frac{-i(E_0 + \Delta) t}{(\alpha t)^2}} \begin{cases} 
\Theta(-t) & \text{for absorption} \\
\Theta(t) & \text{for emission}
\end{cases}
\]  

(6.45)

The X-ray response function \( F \) can be calculated from (6.14) and (6.15)

\[
F(t) = i\omega_0 (\alpha t)^2 e^{-\frac{\omega_0 t}{\alpha t}} \Theta(-t) \quad \text{for absorption}
\]

\[
F(t) = \frac{1}{\alpha} \Theta(t) \quad \text{for emission}
\]  

(6.46)

where \( \omega_0 = \mu - E_0 + \Delta \) is the threshold of emission. Expressions (6.45) and (6.46) for the deep level Green's function and the X-ray response function have the same general form

\[
y(t) = \frac{\alpha}{\alpha t} (\alpha t)^2 e^{-i\alpha t} \Theta(\pm t)
\]  

(6.47)

as functions of time. To see their spectral shapes it is necessary to Fourier transform them and find their energy dependence. The Fourier transform is defined by

\[
y(e) = \int_{-\infty}^{\infty} y(t) e^{i\alpha t} dt
\]  

(6.48)

Because of the \( \Theta \) -functions in \( y(t) \) this will actually be a one-sided Fourier transform and lead to a characteristic \( \Gamma \) - function of exponent \( \alpha \). For the emission case, for instance:

\[
y(e) = -i \Lambda e^{\frac{i\alpha}{\alpha}} \Gamma(\alpha)(\frac{\alpha}{\alpha})
\]  

(6.49)
The spectral densities will have a peculiar shape due to the transient potential induced scattering:

\[ D(e) \sim \frac{1}{e-s} \left( \frac{e-s}{\delta} \right)^2 \]  \hspace{1cm} (6.50)

\[ F(e) \sim \left( \frac{d}{e-s} \right)^2 \left( \frac{\delta}{\pi} \right)^2 \]  \hspace{1cm} (6.51)

where we see that the relevant energy variable is measured from the branch points.

\( F(e) \) in (6.51) is a convolution of two factors, which contribute to the divergency. It is easier to see that in the time representation, where they are a simple product

\[ F(t) = L(t) D(t) \]

where \( L(t) \sim t^2 \left( \frac{\delta}{\pi} \right)^2 \) (see (6.36)) and \( D(t) \sim -\left( \frac{\delta}{\pi} \right)^2 \) (see 6.45).

\( L(t) \) comes from the repeated electron-deep hole scattering near the Fermi surface and is the main origin of the singular behaviour. Creation of the electron hole pairs in conduction band on the other hand broadens the spectrum of the deep hole and quenches the singularity. The divergency of the total response function \( F \)

\[ F(e) \sim (e-s) \left( \frac{\delta}{\pi} \right)^2 - 2 \frac{\delta}{\pi} \]

can be in some cases \( \left( \left( \frac{\delta}{\pi} \right)^2 \right) \) depressed and result in the destruction of the threshold instead of its enhancement.

In the photoemission case the ejected particle will be far from the Fermi level and \( L(t) \) will not be singular, so that all divergency
in the spectral function will come from the singular shape of the deep hole propagator $D(t)$. 
CHAPTER 7.

PHOTO ELECTRON SPECTRA

In this chapter we are going to use the results of the previous chapter to find the distortion of the photoelectron spectra due to the many-body effects. The singularity which comes from the discontinuity in the distribution of conduction electrons is involved in the process only indirectly via the interaction of the Fermi sea with the deep hole, contrary to the X-ray emission or absorption, where the electrons are excited into the conduction band near the Fermi level. This will simplify the calculation, as only one type of singularity will be important, the one that changes the hole spectral function into (6.50), while vertex corrections coming from the repeated scattering between the hole and created electron (6.36) can be neglected.

The emitted electron in this case is very fast (several hundred eV) and we may assume that its scattering on the way to the surface can be approximated by the excitation of the plasmon only. This will give an additional peak in the emission spectrum at \( \omega_p \sim 20 \text{ eV} \) lower energy than the energy of the unscattered electrons. The intensity of the plasmon peak will be proportional to the thickness of the metallic target, its position and width usually rather inconvenient, so that both peaks get mixed and distorted. Experiments on thin films of various thicknesses and the extrapolation of the results as the thickness goes to zero could eventually remove this difficulty.
This analysis could not be applied to the energy loss on the surface but presumably the probability of this process will decrease with increasing energy of the photo-electron, so that the surface effects can be distinguished by varying the incident photon energy. In contrast, the excitations of the Fermi sea accompanying the final hole state are an intrinsic property of the metal, so should not depend either on film thickness (above a few atomic layers) or on incident photon energy.

**Scattering cross section**

In the photo-emission case the final state of the system may be written

\[ | \psi_f \rangle = c_k^+ | \psi_{\text{hole}} \rangle \]  

(7.1)

where \( c_k^+ \) is a creation operator for the fast photo-electron and \( | \psi_{\text{hole}} \rangle \) is a wave function of the hole plus Fermi sea. The photo-emission scattering cross-section may then be written, to the lowest order in the X-ray field,

\[ \frac{d\sigma}{de_k} \sim \sum_{\text{hole states}} | \langle 0 | H_x c_k^+ | \psi_{\text{hole}} \rangle |^2 \delta (\omega - e_k - e_h) \]  

(7.2)

where \( | 0 \rangle \) is the initial ground state of the metal, \( H_x \) is the electron-hole current coupling to the X-ray field and is given by (6.3):

\[ H_x = \sum_{k'} W_{k'} (c_{k'}^+ d + c_{k'} d^+) \]

\[ e_h = \omega - E_g + W \]
We will treat the matrix elements $W_{kl}$ as constants.

The scattering cross section (7.2) corresponds to the diagram (Fig. 3.3a):

![Diagram](image)

Fig. 7.1

after we make the important approximation, discussed in the previous section, of neglecting all interactions of the escaping electron with the other electrons in the metal. We may thus rewrite (7.2) as:

$$\frac{d\sigma}{de} \sim \Re \int_{0}^{\infty} dt \, \langle 0 \mid d^+(t) \, d(0) \mid 0 \rangle \, e^{i(w-e_k)t}$$  \hspace{1cm} (7.3)

where $d(t) = e^{i(H_0 + H_c)t} \, d e^{-i(H_0 + H_c)t}$, $H_0$ and $H_c$ being defined by (6.2) and (6.3).

The hole-hole correlation function in (7.3) is the hole propagator $D(t)$ introduced in Chapter 6. To obtain a rough estimate of the photoemission cross-section (7.3) we may use the asymptotic expression (6.45) for the hole propagator, valid for long times, i.e. for small energy transfers

$$e = e_{\text{max}} - e_k \ll d,$$

where $d$ is the cut off of the order of the conduction band width. If we assume that in-going X-rays have very well defined energies (i.e. $\delta$-like spectrum) and ignore the lifetime of the deep level, so that

$$D(t) = e^{-i(E_0 + \Delta)t} \, \frac{1}{(idt)^{\alpha}}$$  \hspace{1cm} (7.4)
where \( \alpha = \left( \frac{5}{\pi} \right)^2 \) and \( \alpha < 1 \), (7.3) can be integrated and gives:

\[
\frac{d\sigma}{de} \sim \frac{1}{\Gamma(\alpha) e^{1-\alpha}}
\]  

(7.5)

\( \Gamma \) is the gamma-function, and \( e \) is the electron energy measured from the maximum energy \( e_{\text{max}} \):

\[
e = e_{\text{max}} - e_k
\]

Curve (7.5) is singular at \( e_k = e_{\text{max}} \), as can be seen from Fig. 7.2, curve a.

The above singular line shapes will in practice be modified by the finite lifetime of destruction of the hole states by electron capture. The detailed theory of the resulting time dependence would require a higher order treatment of the interaction with the X-ray field. The simplest way to take into account the broadening of the deep level is to assume that it will not be modified by the singular relaxation of the Fermi sea, and therefore these two processes can be treated separately. This means that the resulting deep level propagator can be written as a convolution of the original Lorentzian

\[
D_h(e) = \frac{2}{(e-E_0)^2 + \gamma_h^2}
\]

(7.6a)

where \( \gamma_h = \frac{1}{\tau_h} \) is the width of the deep level due to any possible decay process, and the term

\[
D(e) = \frac{1}{e - (E + \Delta)} \left( \frac{e - (E + \Delta)}{d} \right) \left( \frac{5}{\pi} \right)^2
\]

(7.6b)
describing the effect of singular interaction with the Fermi sea. We may also take into account the symmetric broadening of the ingoing X-rays and fold previous distributions with the X-ray spectrum of the width $\gamma_x$:

$$X(e) = \frac{2 \gamma_x}{(e-\omega)^2 + \gamma_x^2}$$  

(7.6c)

The easiest way to perform this multiple convolution is to transform all these functions into $t$-space, where they are simply multiplied, as they have a similar form $t^\alpha e^{(x+iy)t}$. To find the photo-electron spectral function $Y(e)$ we perform the Fourier transform and get:

$$Y(e) = \frac{\Gamma(1-\alpha)}{(e^2+\gamma^2)^{1-\alpha/2}} \cos \left( \frac{\pi \alpha}{2} + \Theta(e) \right)$$  

(7.7)

with $\Theta(e) = (1-\alpha) \tan^{-1} \left( \frac{e}{\gamma} \right)$

$$\gamma = \gamma_h + \gamma_x$$

where $e$ is measured relative to the maximum energy in the absence of lifetime broadening. This function is plotted in Fig. 7.2, curve b, for the value $\alpha = 0.3$. Due to the broadening it is not singular any more but leads to an asymmetric spectral line for $\alpha < 0$.

It is easy to show that (7.7) gives the expected results in various limiting cases. In the absence of scattering ($\alpha = 0$) it reduces to the Lorentzian,

$$Y(e) \sim \frac{2\gamma}{\gamma^2 + e^2}$$
Fig. 7.2.
Singular line shapes for singularity index $\alpha = 0.3$:

(a) in the absence of lifetime broadening - dashed curve, arbitrary units;
(b) with finite hole lifetime - full curve, energy measured in units of $\gamma$.

$\alpha = 0.3$
for \( \gamma \to 0 \) we recover expression (7.5). The shift of the peak for the curve \( Y(e) \) can be calculated from (7.7) and due to the broadening, is given by

\[
\Delta e_{\text{max}} = \gamma \cot \frac{\pi}{2-a}
\]  

(7.8)

This shift and the position of the peak in general cannot be connected with experimental results, as our theory includes an unknown energy shift \( \Delta \) of the deep hole level. Thus the only observable features which can be compared with theory are the actual shapes of the emission lines, which are predicted by (7.7) to be asymmetric and enhanced towards lower energies. A simple measure of this skewness is the asymmetry index used by X-ray spectroscopists: the ratio of the "half-width" on the low frequency to that on the high frequency side of the line. This asymmetry index was calculated numerically for \( Y(e) \) as a function of \( \alpha \) and tabulated in Table 1.

**TABLE 1.**

Asymmetry Index as a function of singularity index \( \alpha \) for line shape given by equation (7.7)

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>Asymmetry index</th>
<th>( \alpha )</th>
<th>Asymmetry index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.000</td>
<td>0.16</td>
<td>1.348</td>
</tr>
<tr>
<td>0.02</td>
<td>1.033</td>
<td>0.18</td>
<td>1.411</td>
</tr>
<tr>
<td>0.04</td>
<td>1.067</td>
<td>0.20</td>
<td>1.478</td>
</tr>
<tr>
<td>0.06</td>
<td>1.106</td>
<td>0.22</td>
<td>1.553</td>
</tr>
<tr>
<td>0.08</td>
<td>1.147</td>
<td>0.24</td>
<td>1.635</td>
</tr>
<tr>
<td>0.10</td>
<td>1.191</td>
<td>0.26</td>
<td>1.725</td>
</tr>
<tr>
<td>0.12</td>
<td>1.238</td>
<td>0.28</td>
<td>1.825</td>
</tr>
<tr>
<td>0.14</td>
<td>1.291</td>
<td>0.30</td>
<td>1.935</td>
</tr>
</tbody>
</table>
Discussion of photoelectron spectra.

Experimentally the line shapes of emitted photoelectrons have been measured by Siegbahn and collaborators /71 - 81/, who wanted to determine the binding energies of core electrons in various elements. They bombarded the metallic samples, either in bulk (reflection) or thin films (transmission), with X-rays of very high energies:

\[ \text{Mo K}_\alpha_1 \quad 17,4795 \text{ keV} \]
\[ \text{Cr K}_\alpha_1 \quad 5,4147 \text{ keV} \]
\[ \text{Cu K}_\alpha_1 \quad 8,0477 \text{ keV} \]

The observed peak in the distribution of ejected electrons at energy \( E_e \) reduced by the work function of the metal and X-ray energy \( w_x \) gave directly the binding energies \( E_b \):

\[ E_b = -E_e - W + w_x \]

The measured photoelectron curves have a very complicated structure for the following reasons:

a) X-rays are not monochromatised and the main emission line (e.g. \( K_{\alpha_1} \)) is accompanied by the admixture of L and M lines and various satellites;

b) In addition to photoelectron lines, where the electrons are expelled from the core states by the incoming X-radiation, some electrons are the result of the Auger-effect, where an already ionized atom makes a transition to a lower excited state by expelling an electron.
c) As already mentioned, the ejected electrons lose a discrete amount of energy on their passage through the metal due to inelastic scattering, and this gives a rather broad additional peak in the spectrum.

To illustrate this we show in Fig. 7.3 the low-energy part of the spectrum of electrons ejected from the copper K shell by Mo Kα radiation (from ref. /78/).
The peaks on Fig. 7.3 are sharp and very well defined, which makes this method of absolute determination of binding energies very successful, but it is not easy to see the structure of photoelectron lines. Cu K (MoK$_{\alpha_1}$) peak for instance consists of the main unscattered part and the shoulder from the inelastically scattered electrons. Sokolowski /71/ attempted a rough analysis of this experimental curve adding this plasmon satellite to the unscattered line, as is illustrated in Fig. 7.4:

![Diagram](image)

Fig. 7.4.
Sokolowski was satisfied that this interpretation of the observed curve was correct, especially as he was concerned only with the position of the unscattered peak and this was not shifted due to the plasmon tail. Still there is a noticeable difference between the experimental and theoretical curves, an increase in the number of low energy electrons and a sudden drop on the high energy side of the measured distribution compared to the calculated one. This asymmetry is in accord with our prediction of the photoelectron line shape (7.7).

To find some more conclusive evidence about the deviations of photoemission curves from the Lorentzian shape we analyzed the spectra of several metals (Sn, Cu, and Cd) and their oxides (Sn O, Sn O₂, Cu O, Cd O) measured by Nordling /74/. If our theory is right, there should be a systematic difference between these two groups. Metals, according to (7.7) should have asymmetric distributions, while oxides which are semi-conductors have Fermi surfaces in a region of forbidden states so that transitions close to the Fermi surface do not exist.

Though the problem of a plasmon tail is still present in these measurements, in the case of Sn and SnO it does not spoil the analysis, because the peaks are well separated and almost resolved, as can be seen in Fig. 7.5 /71/.
To detect any deviation from the Lorentzian shape it was necessary to find a very sensitive method, as the expected asymmetries are very small and the curves also look rather symmetric. If we write a Lorentzian distribution as:

$$Y(e) = A + \frac{2B}{B^2 + (e - e_{\text{max}})^2}$$  \hspace{1cm} (7.9)

where $A$ is the background and $B$ the width, its inverse curve

$$X(e) = \frac{1}{Y(e) - A} = \frac{B}{2} + \frac{1}{2B} (e - e_{\text{max}})^2$$  \hspace{1cm} (7.10)

is a linear function of $(e - e_{\text{max}})^2$ shown on Fig. 7.6 with the minimum value
at the peak $e = e_{\text{max}}$ of the original Lorentzian. Both sides of the symmetric curve (7.9) fall on the same straight line with the slope $\frac{1}{2B}$. For a very small asymmetry, which cannot be noticed on the original plot, these two branches split and have different slopes though still look remarkably straight for $(e - e_{\text{max}})$. Fig. 7.7 shows a plot of the function (7.7) for the values 0.07 and 0.24 of the scattering parameter $\alpha = (\frac{\delta}{\mu})^2$. 

Fig. 7.6

$X(e)$

$(e - e_{\text{max}})^2$
Fig. 7.7a

\[ \alpha = 0.07 \]

\[ X(e) \]

\[ \frac{(e - e_{\text{max}})^2}{\gamma^2} \]
Fig. 7.7b.

\[ x(e) \]

\[ d = 0.24 \]

\[ (e - e_{\text{max}})^2 / \gamma^2 \]
The analysis was complicated by the fact that parameter $A$ representing the background was unknown and was determined only approximately. This introduced the same additional quadratic curvature in both branches of the $X(e)$ plot, so that the qualitative test of asymmetry could be still carried out, though without hope to determine quantitatively any parameters. In this way we have analysed among others photoemission curves /74/ shown on Fig. 7.8, plots a, b, c and d, for electrons ejected by Cu $K_{\alpha_1}$ radiation from three L shells of Sn and SnO.

As a typical example on Figs. 7.9 and 7.10 are plotted experimental points from Fig. 7.8 a on the inverse plot $X(e)$. The result is striking: asymmetry can be seen not only for the metal but also for the semiconductor SnO, though systematically lower than in the metal. Thus, instead of performing a crucial test of the suggested mechanism for the photoelectron emission we come to the new phenomenon which requires explanation. It is obvious that one of the assumptions in the derivation of (7.7) was wrong, and our conclusion is that the assumed symmetric shape of ingoing X-rays was not correct. We argue that the X-ray lineshape is asymmetric due to the very same many-body effects that happen in the photoemission, and this asymmetry can be seen in the photoelectron spectrum from semiconductors. In the metal the asymmetry is increased by the described mechanism, as the analysis of Fig. 7.8a indicates.
Fig. 7.8
Fig. 7.9

\[ X(e) \]

\[ (e - e_{\text{max}})^2 \]

Sn
X-ray line spectrum.

In this section we shall consider a transition between two deep hole states, which gives a hard X-ray. The Hamiltonian is now

$$H = H_{\text{cond}} + e_1 d_1^+ d_1 + e_2 d_2^+ d_2 + H_{1} d_1^+ d_1 + H_{2} d_2^+ d_2$$  \hspace{1cm} (7.11)

where

$$H_{\text{cond}} = \sum_k e_k c_k^+ c_k$$  \hspace{1cm} (7.12)

$$H_{1,2} = V_{1,2} \sum_{k,k'} u_k u_{k'} c_k^+ c_{k'}$$  \hspace{1cm} (7.13)

$e_1,2$ and $d_1,2^+$ are energies and creation operators of the unperturbed hole states. The Hamiltonian $H$ scatters conduction electrons in the presence of either hole with the potential $V_1$ or $V_2$.

The transition probability per unit time for emission of an X-ray of frequency $\omega$ is given by

$$\frac{d\sigma(\omega)}{d\Omega} \sim \sum_2 \left| \langle \Psi_1 | H_x | \Psi_2 \rangle \right|^2 \delta(\omega + E_2 - E_1)$$  \hspace{1cm} (7.14)

where $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are assumed to be the ground state of the Fermi sea in the presence of the hole of and the set of excited 2-states respectively. $H_x$ is now:

$$H_x = \sum_{1,2} W_{12} (d_1^+ d_2 + d_2^+ d_1)$$

and matrix element $W_{12}$ is again assumed to be constant.

Energies $E_1$ and $E_2$ are eigen values of operators $h_1$ and $h_2$:
\[ h_1 = H_{\text{cond}} + e_1 d_1^+ d_1 + V_1 \sum_{kk'} c_{k}^+ c_{k'}, d_1 d_1^+ \]  
(7.15) 

\[ h_2 = H_{\text{cond}} + e_2 d_2^+ d_2 + V_2 \sum_{kk'} c_{k}^+ c_{k'}, d_2 d_2^+ \] 

\[ h_1 |\psi_1\rangle = E_1 |\psi_1\rangle \quad h_2 |\psi_2\rangle = E_2 |\psi_2\rangle \]  
(7.16)

If we write the \( \delta \)-function as an integral and use (7.15), after summation over final states \(|\psi_2\rangle\) (7.14) becomes:

\[ \frac{d\sigma(w)}{d\Omega} \sim \text{Re} \frac{1}{\pi} \int_0^\infty e^{iwt} \langle \psi_1 | e^{-iH_1 t} d_1 d_2^+ e^{+iH_2 t} d_2 d_1^+ |\psi\rangle dt \]  
(7.16)

From (7.15) it can be verified that

\[ [h_1, d_2^+] = [h_1, d_2] = 0 \]  
(7.17) 

\[ [h_2, d_1^+] = [h_2, d_1] = 0 \]

Thus applying (7.17) and taking account of the cyclical invariance of the trace we can eliminate hole operators from (7.16) and obtain the X-ray spectral function \( Y_0(w) \):

\[ Y_0(w) = \frac{d\sigma(w)}{d\Omega} \sim \text{Re} \frac{1}{\pi} \int_0^\infty e^{iwt} \langle \psi_1 | e^{-iH_1 t} e^{iH_2 t} |\psi\rangle dt \]  
(7.18)

or, if we notice that \( H_{\text{cond}} + H_1, d_1^+ d_1 = 0 \), and similarly for hole 2, and use relation (G.27)

\[ Y_0(w) \sim \text{Re} \frac{1}{\pi} \int_0^\infty e^{i(w+e_2-e_1)t} \langle \psi_1 | e^{-iH_{\text{cond}} + H_1} e^{iH_{\text{cond}} + H_2} |\psi\rangle dt \]  
(7.19)

(7.19) could be evaluated by the method of Nozieres and de Dominicis.
developed in Chapter 6. However, a much simpler way of evaluating similar quantities in the weak coupling limit $V N(0) \ll 1$ (where $N(0)$ is the density of conduction electron states at the Fermi level) has recently been given by Schotte and Schotte /82/. They observe that the effect of the hole potential is to displace the electron density "oscillators" of the Fermi sea. We shall use their method as developed in Appendix G. to show that (7.19) has the same form as (7.5), except that, in the weak coupling limit, the phase shift that comes in is the difference of the scattering phase shifts in the two hole states:

$$Y_0(w) \sim \frac{1}{(w + e_2 - e_1)^{1-\beta}}$$

(7.20)

where $\beta = \left(\frac{\delta_2}{\pi} - \frac{\delta_1}{\pi}\right)^2$

We have used here the Born approximation result

$$\tan \delta \approx \delta = -\pi V N(0)$$

(7.21)

To calculate (7.19) we introduce boson operators $b_k$ and $b_k^+$ defined by (G.6) and (G.7) and write initial and final state Hamiltonians in the approximate form:

$$H_i = \frac{1}{\sqrt{V}} \sum_{k \geq 0} k (b_k^+ + \frac{V_1}{k N})(b_k + \frac{V_1}{k N})$$

$$H_f = \frac{1}{\sqrt{V}} \sum_{k \geq 0} k (b_k^+ + \frac{V_2}{k N})(b_k + \frac{V_2}{k N})$$

(7.22)
This is analogous to (G.11) and (G.12) and is obtained by the same procedure. To calculate \( \langle \psi_1 | e^{-iH_1 t} e^{iH_f t} | \psi_1 \rangle \) we must find the canonical transformation \( u_v \) connecting \( H_1 \) and \( H_f \):

\[
H_f = u_v^+ H_1 u_v \tag{7.23}
\]

this is given by:

\[
u_v = \exp \left\{ \nu (V_2 - V_1) \sum_k \frac{1}{\sqrt{kN}} \left( b_k^+ - b_k \right) \right\} \tag{7.24}
\]

which is the same as (G.20) and represents the energy shift of "harmonic oscillators", representing the Fermi sea, due to the change of hole potential from \( V_1 \) to \( V_2 \).

From (7.23) follows

\[
F(t) = \langle \psi_1 | e^{-iH_1 t} u_v^+ e^{iH_f t} u_v | \psi_1 \rangle
= \langle \psi_1 | B(t) B(0) | \psi_1 \rangle \tag{7.25}
\]

where \( B(t) = \exp \left\{ \nu (V_2 - V_1) \sum_k \frac{1}{\sqrt{kN}} \left( b_k^+ e^{ik \nu t} - b_k e^{ik \nu t} \right) \right\} \) (7.26)

After the algebra described in Appendix G, leading from (G.26 to (G.35) we get the result:

\[
F(t) = \frac{1}{( \pi d t )^\beta} \tag{7.27}
\]

where we have written \( d \) instead of the equivalent cutoff \( \frac{k_\nu}{\nu} \), \( \nu \equiv N(\phi) \), and

\[
\beta = (\nu V_2 - \nu V_1)^2 = \left( \frac{\delta_2}{\pi} - \frac{\delta_1}{\pi} \right)^2 \tag{7.28}
\]

Fourier transformation of (7.19) finally gives the transition rate
The lineshape (7.29) has again the singular shape at the energy $w = e_1 - e_2$ characteristic of all transient phenomena. It has been calculated under the assumption that the deep levels $e_1$ and $e_2$ are sharp and have infinite lifetime. In reality this is not true and lifetime effects will remove the divergency in (7.29). The detailed theory of this effect would eventually require a higher order treatment of the interaction of the X-ray field and the deep hole states.

We shall use the simplest approach, which is satisfactory for the present purpose, and this is to treat the processes contributing to the natural widths $\gamma_1$ and $\gamma_2$ of hole states separately from the readjustment of the Fermi sea after the change of the potential. Then we can claim that the X-ray spectrum $Y(w)$ is the convolution of the spectral functions of hole states and the function $Y_0(w)$ given by (7.29):

$$Y(w) = \int_{-\infty}^{\infty} Y_0(w-x) X_1(x) X_2(y) \, dx \, dy \quad (7.30)$$

where $X_1$ and $X_2$ have a Lorentzian shape:

$$X_1(x) = \frac{2\gamma_1}{\pi} \frac{1}{(x-e_1)^2 + \gamma_1^2} \quad (7.31)$$

(7.30) can be calculated by first Fourier transforming into $t$-space, where the integration is easier, and then back to energy space. The
The final result has exactly the same form as \( Y(e) \) in the photoemission case (7.7):

\[
Y(w) \sim \Gamma(1-\beta) \left( \frac{w^2 + y^2}{w^2 + y^2} \right)^{1-\beta/2} \cos \left( \frac{\pi \beta}{2} + \Theta(e) \right)
\]

with \( \Theta(e) = (1-\beta) \tan^{-1} \frac{w}{y} \), where \( w = w + e_2 - e_1 \) and \( y = y_1 + y_2 \).

The same Fig. 7.2 represents now \( Y(w) \) and the same method of analysis could be used as before in the case of photoelectron emission spectra. We shall again predict possible asymmetric lineshapes in the experimental data to find the connection between our theory and measurements.

**Observed X-ray line shapes.**

Asymmetric emission spectra of Ka lines from the metals have been known since 1935. (Bearden and Shaw / 83 /, Parratt / 84 /), but no theoretical explanation has been attempted or given. Observed asymmetries were quantitatively described by the asymmetry index, and its measured values for the Ka line are given in the following table (from Sandstrom / 85 /):

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_4 )</th>
<th>( a_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 S</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.44</td>
<td>1.36</td>
</tr>
<tr>
<td>17 Cl</td>
<td>0.92</td>
<td>0.94</td>
<td>1.05</td>
<td>2.22</td>
<td>1.23</td>
</tr>
<tr>
<td>19 K</td>
<td>0.96</td>
<td>0.92</td>
<td>1.12</td>
<td>2.28</td>
<td>1.27</td>
</tr>
<tr>
<td>20 Ca</td>
<td>0.81</td>
<td>1.01</td>
<td>1.33</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>21 Sc</td>
<td>0.97</td>
<td>1.04</td>
<td>1.04</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>22 Ti</td>
<td>1.17</td>
<td>1.24</td>
<td>1.04</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>23 V</td>
<td>1.23</td>
<td>1.23</td>
<td>1.09</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>24 Cr</td>
<td>1.33</td>
<td>1.39</td>
<td>1.14</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>25 Mn</td>
<td>1.43</td>
<td>1.51</td>
<td>1.27</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>26 Fe</td>
<td>1.60</td>
<td>1.61</td>
<td>1.35</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

Indices of asymmetry for the L-lines of Ag according to L. G. Parratt [Phys. Rev. 54, 99 (1938)].

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_4 )</th>
<th>( a_5 )</th>
<th>( a_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.9</td>
<td>1.05</td>
<td>1.0</td>
<td>0.9</td>
<td>1.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>
X-ray linewidths and deviations from the expected Lorentzian distributions can be attributed to the following factors:

1) radiation damping;
2) radiationless transitions or Auger effects;
3) linkage with neighbouring atoms, i.e. chemical and alloying effects;
4) the presence of the unresolved component lines;
5) the external screening effects due to the various degrees of ionization of the radiating atoms.

To avoid complications due to satellite lines we are compelled to analyze only K lines, which have no additional structure or splitting. The third factor comes from experimental conditions, as it is sometimes necessary to work with alloys or compounds, and it can in principle produce any change of the shape. The results still show that the data are not greatly distorted.

The Auger effect and the radiation damping will dominate for the elements of atomic number less than 36, but these processes contribute symmetrically to the lineshape broadening. We have already included them in the calculation of (7.32) and denoted the resulting width by $\gamma_x = \frac{1}{c_x}$.

The last effect is exactly the one we are investigating: the change in the potential which is felt by the screening cloud of conduction electrons before and after the transition between inner levels, i.e.
different degrees of ionization. Parratt in 1935 intuitively guessed the explanation of this anomalous X-ray lineshape and indicated the many body contribution to it.

The number of effects that have to be taken into account simultaneously could eventually make the comparison with our theory impossible. Still, if we assume this last effect to be dominant, as is reasonable from the analogy with X-ray emission and absorption, and restrict our analysis to the X-ray lineshapes, we may expect to get some fairly conclusive evidence. Again this can be done by comparing the data for metals and insulators as we have done in the analysis of photoemission data.

The change of X-ray line spectrum on going from metals to their oxides was looked for by Sanner. Unfortunately the resolution of his data does not appear to allow for a detailed study of the line shape. Sanner reported no detectable shift of the $K_\alpha_1$ line for Fe to FeO (such as would be expected from equation (7.8)). However, a similar observation for Cu $\rightarrow$ CuO was later contradicted by Nordling et al. who found a small shift on oxidation in disagreement with Sanner. Thus detailed measurement of $K_\alpha$ line shapes in metal oxides appears not to have been carried out, and this is an experiment which should be done to provide a conclusive test of the mechanism of the present work.

However, until such systematic experimental results become available for analysis, recent high resolution measurements of fine structure of
chromium $K_{\alpha 1,2}$ lines made by Shah and Das Gupta could be interpreted as corroborating our theory. They obtained X-ray lineshapes (Fig. 7.11) which are remarkably similar to our calculated curve $Y(\nu)$ as shown on Fig. 7.2.

![Graphs showing chromium lines](image)

(a). Cr K$\alpha_1$ and K$\alpha_2$ with two crystals.
(b). Cr K$\alpha_1$ with three crystals in (1, 1, 1) position.
(c). Cr K$\alpha_1$ with three crystals in (1, 1, 2) position. The energy separation between structures (1) and (2) = 0.2 eV, (1) and (3) = 0.5 eV and (1) and (4) = 1.8 eV.

and also some unexplained fine structure. Though the authors do not give enough numerical data in their paper, the precision of these experiments seems to be so great, that even quantitative analysis could be attempted.
Appendix A: Notation.

Here we shall review some of the symbols frequently used in the text. We always assume $\hbar = 1$.

$\alpha, \alpha(w)$ - photon attenuation constant
$b, b^+$ - Boson operators
$c_k, c_k^+$ - conduction electron operators
$d_k, d_k^+$ - valence electron operators
$\delta$ - scattering phase shift
$e, e_k$ - free and conduction electron energies respectively
$E_0, E_k$ - deep level and deep band energies respectively
$\varepsilon(q, w)$ - dielectric function
$g = \nu_0 V$ - coupling constant
$h$ - Plank's constant
$k$ - electron momentum
$l$ - mean free path
$m, M$ - band mass of the conduction and valence electron respectively.
$\mu$ - Fermi energy
$\nu_0$ - density of states at the Fermi surface
$\rho(e)$ - electron density of states
$\rho_k$ - electron density operator
$\hat{s}_e, \hat{s}_e^+$ - free electron operators
$t, \tau$ - time variables
$w$ - photon or X-ray energy
$W$ - work function of a solid
In the Feynman and correlation function diagrams we use the following graphical symbols:

- --- conduction electron bare propagator
- --- " " full "
- --- deep hole bare propagator
- --- " " full "
- ~~~~ photon or X-ray propagator
- ~~~~ plasmon propagator
- \( V \) Coulomb interaction
- \( x \) The surface tunnelling term
Appendix B: Densities of states from photoemission measurements.

It might seem, after analyzing all possible scatterings of the excited photoelectron, that it is practically impossible to connect the measured electron distribution curves with the initial (and final) densities of states from which they originate. Still, even when this scattering is strong, careful analysis of data from photoemission measurements can reveal most of the features of the density of states.

In those metals where nondirect transitions are shown to be dominant, if we neglect the scattering and the factor \((\alpha + 1/1)^{-1}\) due in BS theory to lifetime broadening, the transition probability can be written as:

\[
N(e) \frac{d\varepsilon}{d\varepsilon} = \int_0^{w} \frac{f C(e)}{\int_0^{w} f \rho(e) \rho(e-w) \frac{d\varepsilon}{d\varepsilon}}
\]

\[B.1\]

\(f\) is some oscillator strength and can be assumed to be constant. In (B.1) we have neglected the momentum conservation in the process so that the energy distribution of photoelectrons becomes simply the product of the initial and final densities of states. Measuring and comparing \(N(e)\) at several photon energies it is possible to determine the density of initial states below the Fermi level and final states above the vacuum level. Between the Fermi level and the vacuum level one must assume a trial density of states to integrate.
the quantum yield \( Y(\omega) \) knowing all \( C(\epsilon) \) and \( \rho^i \)'s from experiment:

\[
Y(\omega) = \frac{\int_{\mu}^{\mu+\omega} \epsilon \, \rho(\epsilon) \rho(\epsilon-\omega) \, d\epsilon}{\int_{\mu}^{\mu+\omega} \rho(\epsilon) \rho(\epsilon-\omega) \, d\epsilon} \quad (B.2)
\]

The denominator in (2.32) depends on the unknown density of states in the gap, so the comparison with the observed yield can be used to determine indirectly the density of states.

If the scattering is strong (B.1) is not valid any more. The contribution of once-scattered and Auger electrons must be estimated and separated from the unscattered part. To do this in BS theory we must know mean free paths for various processes in (2.22), (2.27) and (2.30).
Appendix C: Direct observation of momentum conservation.

There are two methods to check the momentum conservation in the photoemission from metals. The first one works a posteriori: the results of photoemission measurements can be fairly well interpreted by the direct or non-direct model in each particular case, and this method is not very enlightening. The direct observation of the momentum conservation is based on the assumption that an easily recognizable structure in the initial (or final) density of states produces a similar structure in the photoelectron spectrum. Such peaks (which are easiest to follow) in the density of states are usually associated with critical points \((\nabla_k E_k = 0)\). We shall choose for our purposes the saddle point \(L_2'\) in the \(s-p\) band of Cu (Fig. C.1).

![Diagram of energy bands](image)

Fig. C.1.

When the photon energy \(h\nu_1\) is less than the distance between bands \(h\nu_2\) only non-direct transitions from the lower band to \(L_1\) can occur and they give the peak A on Fig. C.2 connected with the maximum
in the final density of states. When the photon energy is increased another peak B will appear due to the peak in the initial density of states and closely follow the change in photon energy. The different behaviour of these two peaks is possible only for non-direct transitions and may be taken as their indication. In direct transitions, as is visible from Fig. C.1, peak B moves at a slower rate and becomes less pronounced when photon energy is changed. To summarize: Non-direct processes seem to follow the density of states peaks more closely than the direct ones.
Appendix D: Equation of motion method.

Here we shall derive equations (6.17), (6.18) and (6.21) by the equation of motion method (Langreth / 67 /). Again the hamiltonian is

\[ H = \sum_k e_k c_k^+ c_k + E_0 d^+ d + \sum_{kk'} V_{kk'} c_k^+ c_{k'}^+ d d^+ \quad (D.1) \]

and Green's functions for conduction and core electrons are defined by

\[ C_{kk'}^T(t-t') = \langle 0 | T \{ c_k(t) c_{k'}^+(t') \} | 0 \rangle \quad (6.8) \]

\[ D(t-t') = \langle 0 | T \{ d(t) d^+(t') \} | 0 \rangle \quad (6.11) \]

The expectation value is taken in the initial ground state \( |0\rangle \) which for absorption contains no deep holes ( \( d^+ |0\rangle = 0 \) ) and for emission contains no deep electrons ( \( d |0\rangle = 0 \) ). This fact enables us to close the equations of motion. The X-ray transition probability will be determined from the function

\[ F_{kk'}(t-t') = -F_{kk'}(t',t; t, t') \quad (D.3) \]

To obtain the equation of motion for \( F_{kk'} \), we calculate the commutator

\[ i \partial_t c_k(t) = [c_k(t), H] = e_k c_k(t) + \sum_{k'} V_{kk'} d^+(t) \quad (D.4) \]

Multiplying both sides by \( c_{k'}(t') d(t) d^+(t') \) and taking the average we find:

\[ (\partial_t + i e_k) F_{kk'}(t,t',t; t', t') = \delta_{kk'} \delta(t-t') D(t-t') - i \sum_{q} V_{kq} \]

\[ \cdot \langle 0 | T \{ c_q(t) d(t) d^+(t) c_{k'}^+(t') d(t) d^+(t') \} | 0 \rangle \quad (D.5) \]

The first term on the right comes from commuting time derivation through time ordering operator.
The higher order Green's function on the right can be reduced if we notice that the hole number operator $d(\tau) d^+(\tau)$ in the $T$-product can give only 0 or 1 when applied to the ground state $|0\rangle$, depending on the particular time ordering. In the absorption case $|0\rangle$ contains no $d$-holes, and $d(\tau) d^+(\tau)$ gives zero unless time-ordered between $d^+(t')$ on the left and $d(t)$ on the right, in which case it is equal to unity, and (D.5) can be written as

\[
(\partial_t + i e_k) F^a_{kk'} (\tau, \tau'; t, t') = \delta_{kk'} \delta(\tau - \tau') D(t-t') - i \sum_q V_{kq} \cdot F^a_{qk'} (\tau, \tau'; t, t') X(\tau; t, t')
\]

(D.6a)

where $X(\tau; t, t')$ is a two sided step function which vanishes unless $t' > \tau > t$.

In the emission case we may commute $d(\tau)$ and $d^+(\tau)$ and consider the electron number operator $d^+(\tau) d(\tau)$. Commutation gives an extra term $\sum_q V_{kq} F_{kq} (\tau, \tau'; t, t')$ and the minus sign.

By the same reasoning as before we find the requirement:

$t > \tau > t'$

and (D.5) becomes for the emission

\[
\sum_q \left[ (\partial_t + i e_k) \delta_{kq} + V_{kq} \right] F^e_{kk'} (\tau, \tau'; t, t') = \delta_{kk'} \delta(\tau - \tau') D(t-t') + i \sum_q V_{kq} F^e_{qk'} (\tau, \tau'; t, t') X(\tau; t, t')
\]

(D.6b)

To get (6.17) and (6.18) we must transform (D.6a) and (D.6b) into integral equations. The first step is to determine equations for
conduction electron Green's function $C(\tau-\tau')$. In the absorption case we multiply the same commutator $(D.4)$ by $c^+_k(\tau')$, take the average and find:

$$\left( \partial_\tau + i e_k \right) C_{kk'}(\tau-\tau') = \delta_{kk'} \delta(\tau-\tau') - i \sum_q v_{kq} \langle 0 \left| T \left\{ c_q(\tau)d(\tau)d^+(\tau)c_{k'}(\tau') \right\} \right| 0 \rangle \quad (D.7)$$

In the absorption case $d(\tau)d^+(\tau)$ always gives zero and $(D.7)$ becomes:

$$\left( \partial_\tau + i e_k \right) C^a_{kk'}(\tau-\tau') = \delta_{kk'} \delta(\tau-\tau') \quad (D.8)$$

which is equivalent to the equation $(6.9)$. This also shows that the factor multiplying $F_{kk'}$ on the left side of $(D.6a)$ is the inverse operator of $C^a$, so that we can finally write

$$F_{kk'}(\tau,\tau'; t,t') = C_{kk'}(\tau-\tau') D(t-t') + i \int d\tau'' \sum_{qq'} v_{qq'} F_{qq'}(\tau''; t,t') \quad (D.9)$$

In the emission case we repeat the procedure we used to get $F_{kk'}$ and find:

$$\sum_q \left[ ( \partial_\tau + i e_k ) \delta_{kq} + v_{kq} \right] C^e_{kk'}(\tau-\tau') = \delta_{kk'} \delta(\tau-\tau') \quad (D.10)$$

This is equivalent to equation $(6.10)$ for $C^e$ and shows us that $(D.9)$ is valid in both emission and absorption, though the functions $C$ differ for these two cases. Thus we have recovered equations $(6.17)$ and $(6.18)$, if we note that
To derive the formula (6.21) which gives $K$ in terms of $F$ or $\emptyset$ we define a slightly modified Hamiltonian.

For absorption we write

$$H_\lambda = \sum_k e_k c_k^+ c_k^+ + E_0 d^+ d + \lambda \sum_{k,k'} V_{k,k'} c_k^+ c_{k'}^+ d d^+ \quad (D.12a)$$

and for emission:

$$H_\lambda = \sum_{k,k'} (e_k \delta_{k,k'} + V_{k,k'}) c_k^+ c_{k'}^+ + E_0 d^+ d + \lambda \sum_{k,k'} V_{k,k'} c_k^+ c_{k'}^+ d d^+ \quad (D.12b)$$

For $\lambda=1$ (D.12a) and (D.12b) are equal to (D.1).

In the absorption case from the definition (6.11) of $D(t-t')$ there follows:

$$D_\lambda(t-t') = \langle 0 | d^+(t')d(t) | 0 \rangle \theta(t'-t)$$

$$= \langle 0 | e^{iH_\lambda t'} d^+ e^{iH_\lambda t} \frac{iH_\lambda t'}{iH_\lambda} \frac{iH_\lambda t}{iH_\lambda} d e | 0 \rangle \theta(t'-t)$$

$$= -e^{iE_0(t'-t)} \langle 0 | d^+ e^{-iH_\lambda(t'-t)} d | 0 \rangle \theta(t'-t) \quad (D.13)$$

as can be verified using (D.12a).

If we use the mathematical identity

$$\frac{\partial}{\partial \lambda} e^{-iH_\lambda(t'-t)} = -ie^{-iH_\lambda(t'-t)} \int_0^{t'-t} d\tau e^{iH_\lambda \tau} \frac{\partial}{\partial \lambda} e^{-iH_\lambda \tau} \quad (D.14)$$

we can find the derivative:
\[
\frac{\partial}{\partial \lambda} D(t-t') = e^{-iE_0(t-t')} \sum_{kk'} V_{kk'} \int_0^{t'-t} e^{i\lambda(t'-t)} e^{i\lambda\tau} c_k^+ c_{k'} d\tau. 
\]

or

\[
\frac{\partial}{\partial \lambda} \tilde{D}(t-t') = i \sum_{kk'} V_{kk'} \int_0^{t'} F_{k',k} (\tau, \tau'; t, t') d\tau. 
\]  

where by \(\tilde{D}\) we denote the reduced Green's function (6.12).

Taking into account (D.11)

\[
\frac{1}{\tilde{D}} \frac{\partial}{\partial \lambda} \tilde{D} = \frac{\partial}{\partial \lambda} K 
\]

and from (D.16) we obtain exactly equation (6.21).
Appendix E: Connection between phase shifts and scattering potential.

In order to find the connection between the scattering potential \( V_{\text{scat}} \) and the phase shifts \( \delta \) we shall use the method of W. Kohn. We examine single particle scattering on the spherically symmetrical potential \( V(x) \). The Schrödinger equation can be separated and leads to a radial equation for each angular momentum \( l \). For s-wave scattering

\[
\left( -\frac{\alpha^2}{dx^2} + V(x) - k^2 \right) \psi(x) = 0 \tag{E.1}
\]

If the potential falls off faster than \( \frac{1}{x} \), the wave function satisfies the boundary conditions:

\[
\psi(0) = 0, \quad \lim_{x \to \infty} \psi(x) = \sin kx + \cos kx \cdot \tan \delta \tag{E.2}
\]

where \( \delta \) is the phase shift.

We notice that \( \sin px \) are eigen functions of \( k^2 \) satisfying the boundary condition \( \psi(0) = 0 \), and therefore we expand \( \psi(x) \) as

\[
\psi(x) = \int_0^\infty \varphi(p) \sin px \, dp \tag{E.3}
\]

If \( \varphi(p) \) is singular the principal value of the integral must be taken.

Let us define the Fourier transform of the potential \( V(x) \):

\[
V(p,p') = V(p',p) = \frac{2}{\pi} \int_0^\infty \sin p' x V(x) \sin px \, dx \tag{E.4}
\]

Substituting (E.3) into (E.1) we get the Schrödinger equation in momentum space:

\[
(p^2 - k^2) \varphi(p) + \int V(p') \, dp' = 0 \tag{E.5}
\]
We want to investigate the behaviour of $\psi(x)$ for large $x$:

$$\lim_{x \to \infty} \psi(x) = \lim_{x \to \infty} \int_0^\infty \phi(p) \sin px \, dp$$

(E.6)

If $\phi(p)$ is free from singularities, (E.6) is zero, because the highly oscillatory character of $\sin px$ causes the positive and negative contributions to the integral to cancel. This means that only the singularities of $\phi(p)$ determine the asymptotic behaviour of $\psi(x)$.

To examine the singular behaviour of $\phi(p)$ we write (E.6) as the integral equation

$$\phi(p) = \delta(p-k) - \frac{1}{p^2-k^2} \int_0^\infty V(p,p') \phi(p') \, dp'$$

(E.7)

where the coefficient of the inhomogeneous term $\delta(p-k)$ has been chosen to be 1, corresponding to normalization of the wave function.

The integral in (E.7)

$$B(p) = \int_0^\infty V(p,p') \phi(p') \, dp'$$

(E.8)

is free from singularities since $V(p,p')$ is regular in both $p$ and $p'$; thus the singular behaviour of $\phi(p)$ is completely described by the expression

$$\phi(p) = \delta(p-k) - \frac{B(p)}{p^2-k^2}$$

(E.9)

Transforming (E.9) back into coordinate space we get

$$\psi(x) = \sin kx - \int_0^\infty \frac{B(p)}{p^2-k^2} \sin px \, dp$$

(E.10)
The phase shift $\delta$ is determined by the value of $B$ at the singularity $p = k$. To show this we may use the identity

$$\frac{B(p)}{p^2 - k^2} = \frac{B(k)}{2k} \frac{1}{p-k} + \left( \frac{B(p)}{p^2 - k^2} - \frac{B(k)}{2k(p-k)} \right)$$  \hspace{1cm} (E.11)

to separate the first term on the r.h.s. which is singular for large $x$ from the second term which is regular and does not contribute to the integral in (A.10). We only need

$$\lim_{x \to \infty} \int_0^\infty \frac{\sin px \, dp}{p-k} = \pi \cos kx$$  \hspace{1cm} (E.12)

(E.10) becomes

$$\lim_{x \to \infty} \psi(x) = \sin kx - \frac{2k}{2k} \frac{B(k)}{\cos kx}$$  \hspace{1cm} (E.13)

From the definition (E.2) of $\delta$:

$$\tan \delta = -\pi \frac{B(k)}{2k}$$  \hspace{1cm} (E.13)

$B(k)$ is defined by the trial function $\phi(p)$. In the first approximation we may use (E.13) to define the function

$$\phi_o(p) = \delta(p-k) + \frac{1}{\pi} \frac{2k \tan \delta p}{p^2 - k^2} + (\text{regular terms})$$  \hspace{1cm} (E.14)

Inserting this trial function into (E.8) gives

$$B(p) = \int_0^\infty V(p,p') \left( \delta(p'-k) + \frac{1}{\pi} \frac{2k \tan \delta p}{p'^2 - k^2} + (\text{regular terms}) \right) dp'$$

$$= V(p,k) + \tan \delta \int_0^\infty V(pp') \frac{1}{p'^2 - k^2} 2k \, dp'$$  \hspace{1cm} (E.15)

Regular terms again do not contribute. Equations (E.13) and (E.15)
together determine the phase shift $\delta$ in terms of the scattering potential $V(p p')$:

$$\tan \delta = \frac{-\frac{\pi}{2k} V(k, k)}{1 - \frac{1}{\pi} \int_0^\infty V(k, p') p \frac{1}{p'^2 - k^2} dp'}$$

(Eq. 16)
Appendix F: Asymptotic solution of the integral equation.

In the absorption case the integral equation (6.28) has the form

\[ \phi^a(t, t'; \tau, \tau') = C^a(t-t') + i\nu \int_{\tau}^{t'} C^a(t-t'') \phi^a(t'', t'; \tau, \tau') \, dt'' \]  
\[ (F.1) \]

The variables \( \tau \) and \( \tau' \) act only as integration limits and we shall omit them in \( \phi^a \). (F.1) is basically a Dyson equation. For the asymptotic form (6.24) of \( C^a \)

\[ C^a(t) = -i \nu \left\{ \frac{P}{t} + \tan \theta \cdot \delta(t) \right\} \]  
\[ (F.2) \]

it becomes:

\[ \phi^a(t, t') \left[ 1 - \pi g \tan \theta \right] = C^a(t-t') + g \int_{\tau}^{t'} \phi^a(t'', t') \frac{1}{t-t''} \, dt'' \]  
\[ (F.3) \]

where \( g = \nu V \) is the coupling constant. (F.3) is an integral equation with respect to the variable \( t \), and it can be rewritten as

\[ \phi^a(t) = f^a(t) + \frac{1}{\pi} \tan \delta \int_{\tau}^{t'} \phi^a(t'') \frac{1}{t-t''} \, dt'' \]  
\[ (F.4) \]

where we have inserted (F.2) for \( C^a \) and used (6.23)

\[ \tan \delta = \frac{\pi g}{1 - \pi g \tan \theta} \]

The inhomogeneous part is:

\[ f^a(t) = -i \nu \frac{1}{1 - \pi g \tan \theta} \left( \frac{P}{t-t'} + \pi \tan \theta \delta(t-t') \right) \]  
\[ (F.5) \]

(F.4) is a singular integral equation and can be solved by standard methods (Muskhelishvili / 69 /). Among all possible solutions
we shall retain, as the physical solution, the perturbative one, which reduces to \( C^a \) when \( g \to 0 \), i.e. the perturbation is switched off.

In order to solve this equation we introduce the functions of the complex variable \( z \):

\[
y(z, t') = \frac{1}{2\pi i} \int_\Gamma \frac{\mathcal{G}^{a}(t'')}{t'' - z} \, dt'' \sim O\left( \frac{1}{|z|} \right) \text{ as } z \to \infty \quad (F.6)
\]

where \( \Gamma \) is some integration contour. \( t' \) is a dummy variable as in (F.3) and (F.4), and will be omitted.

From the definition (F.6) using Plemelj formulae we find:

\[
\mathcal{G}^{a}(t) = y^+(t) - y^-(t) \quad (F.7)
\]

\[
\frac{1}{\pi i} \int \frac{\mathcal{G}^{a}(t'')}{t'' - t} \, dt'' = y^+(t) + y^-(t) \quad (F.8)
\]

where \( y^\pm(t) = y(t \pm i\varepsilon) \) are the values of \( y(z) \) on the real axis when the limit is taken from the upper and lower complex half-plane respectively.

If we write

\[
1 = A \quad -i \tan \delta = B \quad (F.9)
\]

and substitute (F.7) and (F.8) into the integral equation (F.4) we get an algebraic equation:

\[
A \left( y^+ - y^- \right) = f - B \left( y^+ + y^- \right) \quad (F.10)
\]

which can be solved and shows that \( y \) must be a solution of an inhomogeneous Hilbert problem which vanishes at infinity:
\[ y^+ (t) = a y^- (t) + b f(t) \]  
(F.11)

where \( a = \frac{1 + i \tan \delta}{1 - i \tan \delta} \) and \( b = \frac{1}{1 - i \tan \delta} \)  
(F.12)

We shall first solve the homogeneous problem:

\[ K^+(t) = a K^-(t) \]  
(F.13)

or \( \ln K^+(t) = \ln a + \ln K^-(t) \)  
(F.13a)

The solution is

\[ \ln K(z) = \frac{1}{2\pi i} \int_{\gamma} \frac{\ln a}{t' - z} \, dt' \]  
(F.14)

as can be directly verified. \( \ln a \) is by definition

\[ \ln a = \ln \frac{1 + i \tan \delta}{1 - i \tan \delta} = 2i \delta \]  
(F.15)

which gives

\[ \ln K(z) = \frac{1}{\pi} \int_{\gamma} \frac{\delta}{t' - z} \, dt' = \frac{\delta}{\pi} \ln \frac{t' - z}{t - z} \]  
(F.16)

or \( K(z) = \left( \frac{t' - z}{t - z} \right)^{\delta/\pi} \)  
(F.17)

From (F.17) follows

\[ K^\pm(t) = \left( \frac{t' - t}{t - t} \right)^{\delta/\pi} e^{\pm i \delta} \]  
(F.18)

which is the solution of the homogeneous integral equation (F.13).

This can be substituted into the inhomogeneous equation (F.11):

\[ y^+ = \frac{K^+}{K^-} y^- + b f \]  
(F.19)
Dividing by \( K^{+} \) we get the equation for the function \( \frac{y}{K} \):

\[
\frac{y}{K^{+}} = \frac{y}{K^{-}} + \frac{b}{K^{+}} f
\]  

which has the solution:

\[
\frac{y(z)}{K(z)} = \frac{1}{2\pi i} \int \frac{b}{K^{+}} \frac{f(t'')}{t''-z} \, dt''
\]  

as can be checked easily.

When (F.18) is inserted for \( K^{+} \), we find (using \( e^{-i\delta} = \cos \delta \)) that:

\[
y(z) = K(z) \frac{1}{2\pi i} \int \frac{b}{K^{+}} \frac{f(t'')}{t''-z} \, dt''
\]  

The required solution of the equation (F.4) is given by (F.7) as:

\[
\phi(t) = y^{+}(t) - y^{-}(t)
\]

\[
= (K^{+} - K^{-}) \cos \delta \pi \int \frac{f(t'')}{t''-t} \, dt''
\]

After substituting expressions for \( K^{+} \) and \( f \) and rearranging the terms we obtain:

\[
\phi(t) = -\gamma_0 \cos^2 \delta \frac{1}{1 - \gamma_0 \tan \theta} \left\{ \tan \delta \pi \int \frac{1}{t-t'} + \pi \tan \delta \tan \theta \delta(t-t') + \right. \\
\left. + \pi \tan \theta \int \frac{1}{t''-t} \left| \frac{(t'\!-\!t)(t'\!-\!t)}{(t\!-\!t)(t'\!-\!t')} \right|^{\delta/\pi} \ldots \left|^{\delta/\pi} \right.ight. \\
\left. \ldots \int \frac{1}{t''-t} \right\}
\]  

(F.23)
The last term on the right of (F.23) may be transformed using the relation

\[ P \frac{1}{t''-t'} P \frac{1}{t'-t} = P \frac{1}{t-t'} P \frac{1}{t''-t} P \frac{1}{t''-t'} + \]

\[ + \pi^2 \delta(t''-t) \delta(t''-t') \]

We also integrate

\[ \int \frac{(t''_t'}{t''_t} \delta\frac{d}{dt'} \frac{d}{dt} = \left( \frac{t'-t}{t-t'} \right) \frac{\pi}{\tan \delta} \]

and the similar integral with \( t' \) in place of \( t \). This integration can be performed in the complex plane using the contour on Fig. F.1.

![Fig. F.1.](image)

After some calculation one finds the final result:

\[ \varphi^a(t,t';t',t') = G^e(t-t',t-t') \left( \frac{(t'-t')}{(t'-t)(t'-t')} \right)^{\frac{\delta}{\pi}} \]

(F.26)

where \( G^e \) is the emission Green's function and \( t < t', t' < t \). The last factor contains all the transient character of the solution \( \varphi^a \).
For the emission case a similar calculation can be performed. The integral equation is

\[ \phi^e(t) = f^e(t) - \frac{1}{\pi} \tan \delta \int_\tau^t \phi^e(t') \frac{1}{t-t'} \, dt' \quad (\text{F.27}) \]

where

\[ f^e(t) = \frac{C^e(t-t')}{1+\kappa g \tan \theta / \beta} \quad (\text{F.28}) \]

and \( \theta' \) and \( \beta \) are defined by (6.30).

The result is analogous to that for absorption.

\[ \phi^e(t, t'; \tau, \tau') = \frac{C^a}{(\tau-t') (\tau-t)} \left( \frac{(t-t')(\tau-t)}{(t-t')(\tau-t')} \right)^{\delta/\kappa} \quad (\text{F.29}) \]

for \( \tau' < t, t' < \tau \).
Appendix G: Tomonaga model

K.D. Schotte and U. Schotte / 82 / solve the problem of singularities near the threshold of X-ray spectra in metals by treating the conduction electrons in terms of density waves in the Tomonaga model / 86 /. They notice that for s-wave scattering the problem can be reduced to a one-dimensional problem and easily solved in the weak coupling limit.

We shall briefly review their method in order to apply it to the calculation of X-ray lineshapes. The Hamiltonian of the system is again

\[ H = \sum_k \varepsilon_k a_k^+ a_k + E_0 b^+ b + \frac{1}{N} \sum_{kk'} \delta_{kk'} a_k^+ a_k' b b^+ \] (G.1)

The hole (described by \( b^+ \) and \( b \)) has the non-degenerate state with energy \( E_0 \) and infinite lifetime. It interacts with conduction electrons (\( a_k^+ \) and \( a_k \)) via a contact potential \( \delta_{kk'} = V \).

The transition probability for the absorption is given by

\[ W(w) = 2\pi \sum_f \left| \sum_k W_k(w) \left< f | a_k^+ b | i \right> \right|^2 \delta(E_f + w - E_i) \] (G.2)

The matrix elements \( W_k(w) \) of the dipole operator are assumed to be constant. In the one body formulation we can eliminate the hole operators and write:

\[ W(w) = 2\pi \left| \sum_f \left< f_{n+1} | \frac{1}{\sqrt{N}} \sum_k a_k^+ | i_n \right> \right|^2 \delta(E_f + w + E_o) \] (G.3)

\[ |i_n) = \prod_{k < k_f} a_k^+ |0) \] is the n-particle ground state of the hamiltonian.
The excitations of the Fermi sea arising from the sudden change from $H_i$ to $H_f$ can be described in terms of density waves. The density operators are

$$\rho_k = \frac{1}{\sqrt{N}} \sum_{q=0}^{k_d} a_{q-k}^+ a_{q+k}^+, \quad \rho_{-k} = \frac{1}{\sqrt{N}} \sum_{q=0}^{k_d} a_{q-k}^+ a_{q-k}^+, \quad k > 0 \quad (G.6)$$

or normalized operators

$$b_k = \frac{1}{\sqrt{k}} \rho_k \quad \text{and} \quad b_k^+ = \frac{1}{\sqrt{k}} \rho_{-k} \quad (G.7)$$

We shall consider the processes which occur in the immediate vicinity of the Fermi surface in a band of the constant density of states $\nu$ and the width $d$, so that in the one-dimensional case the dispersion relation between electron energy and momentum is linear:

$$e_k = (k - k_F) / \nu \quad (G.8)$$

$k = 0$ and $k = k_d$ are the momenta at the bottom and at the top of the band respectively.

From (G.6) and $[a_k, a_k^+] = \delta_{kk'}$, follow rather complicated commutation relations for $\rho_k$ and $\rho_{-k}$, but if we neglect the processes
far from the Fermi level it is possible to approximate them by simpler ones.

\[ [\rho_k, \rho_{-k}] = k \delta_{kk'} \]  \hspace{1cm} (G.9)

(G.9) are valid in the subspace of states that we are going to investigate, namely those which do not have empty levels near the bottom of the band or occupied levels near the top, so that the omitted terms do not contribute much.

This reduces the validity of our approach to where the contact potential V is small.

The operators b, subject to the same approximations, satisfy simpler commutation relations

\[ [b_k, b_{k'}^+] = \delta_{kk'} \]  \hspace{1cm} (G.10)

and therefore represent boson "particles".

In terms of b's the hamiltonians can be written as:

\[ \widehat{H}_i = \frac{1}{\nu} \sum_{k>0} k b_k^+ b_k \]  \hspace{1cm} (G.11)

\[ \widehat{H}_f = \frac{1}{\nu} \sum_{k>0} k (b_k^+ + \frac{V}{\sqrt{kn}}) (b_k + \frac{V}{\sqrt{kn}}) - \frac{V^2}{N} \sum_k 1 \]  \hspace{1cm} (G.12)

\[ \widehat{H}_i \] and \[ \widehat{H}_f \] can be interpreted as the energy operators of two harmonic oscillators, and the effect of the potential V is simply to shift the zero energy of the oscillators. We shall neglect the constant term in (G.12) because the approximation method itself is only correct up to a constant.
To calculate the transition probability (G.3) we need to express \( a^+ = \frac{1}{N} \sum_k a_k^+ \) in terms of boson operators \( b \) and \( b^+ \).

From (G.6) and (G.10) one immediately finds:

\[
\begin{align*}
\left[ b_k^+, a^+ \right] &= \frac{1}{\sqrt{kN}} a^+ - \frac{1}{\sqrt{kN}} \sum_{q=k}^{k_d} a_q^+ \quad \text{for } k > 0 \\
\left[ b_k, a^+ \right] &= \frac{1}{\sqrt{kN}} a^+ - \frac{1}{\sqrt{kN}} \sum_{q=0}^{k_d} a_q^+ \quad \text{for } k > 0
\end{align*}
\]

In the spirit of the approximation (e.g. in (G.9)) we assume that the matrix element of the second operator on the right will be small and neglect it:

\[
\left[ b_k, a^+ \right] = \frac{1}{\sqrt{kN}} a^+ \quad \text{for all } k \quad \text{(G.14)}
\]

Let us define a canonical transformation

\[
U = e^{-\sum \alpha_k (b_k^+ - b_k)} \quad \alpha_k \text{ real} \quad \text{(G.15)}
\]

which acts as a translation operator for any function of \( b_k \) and \( b_k^+ \):

\[
U^+ b_k U = b_k + \alpha_k \quad \text{(G.16)}
\]

or, multiplying by \( U \) and using \(UU^+ = 1 \):

\[
\left[ b_k, U \right] = \alpha_k U \quad \text{(G.17)}
\]

(G.14) and (G.17) have identical forms if we put \( \alpha_k = \frac{1}{\sqrt{kN}} \) so,

\[
a^+ \sim e^\sum_k \frac{1}{\sqrt{kN}} (b_k^+ - b_k) \quad \text{(G.18)}
\]
According to our interpretation of (G.11) and (G.12), the transition from $\widetilde{H}_i$ to $\widetilde{H}_f$ expressed in terms of boson operators $b_k$ corresponds to a shift in energy of harmonic oscillators, and can be viewed as a canonical transformation:

$$\widetilde{H}_f = \mathbf{u}_v^+ \mathbf{H}_i \mathbf{u}_v$$

where $\mathbf{u}_v = \exp\left\{ \int \frac{1}{\sqrt{\nu_N}} (b_k^+ - b_k) \right\}$

The transition probability (G.3) may be written:

$$W(v) \sim \text{Re} \left( \int_0^\infty e^{i(\omega + E_0)t} F(t) \, dt \right)$$

where the correlation function $F$ is given by

$$F(t) = \langle i | e^{\frac{i\tilde{H}_t}{2}} a e^{-\frac{i\tilde{H}_t}{2}} a^+ | i \rangle$$

or

$$F(t) = \langle i | e^{\frac{i\tilde{H}_t}{2}} u_v^+ e^{-\frac{i\tilde{H}_t}{2}} u_v a^+ | i \rangle$$

From (G.18) and (G.20) it follows that if we define

$$B = u_a^+ = \exp\left\{ (1 + \nu) \sum_{k} \frac{1}{\sqrt{\nu_N}} (b_k^+ - b_k) \right\}$$

and

$$B(t) = e^{\frac{i\tilde{H}_t}{2}} B e^{-\frac{i\tilde{H}_t}{2}} = \exp\left\{ (1 + \nu) \sum_{k} \frac{1}{\sqrt{\nu_N}} \left[ b_k^+ e^{\frac{ikt}{\nu}} - b_k e^{-\frac{ikt}{\nu}} \right] \right\}$$

(G.25)

(G.23) now becomes

$$F(t) = \langle i | B(t) B(0) | i \rangle$$

To calculate (G.26) one must rewrite the exponential operators $B$
using the relation

$$e^A e^B = e^{A+ B + \frac{i}{2}[A,B]} \quad (G.27)$$

which holds if $[A,B]$ is a c-number. Then we get:

$$B(t) B(0) = e^{z^+(t) - z(t)} e^{z^+(0) - z(0)} = e^{z^+(t) - z(t) + z^+(0) - z(0)} \quad (G.28)$$

where $z(t) = (1 + \sqrt{V}) \sum_k \frac{1}{kN} e^{-ikt} b^k$ (G.28a)

and $y = \frac{1}{2} [(z^+(t) - z(t), z^+(0) - z(0)) = -\frac{1}{2} (1 + \sqrt{V}) \sum_k \frac{1}{kN} (e^{ikt} - e^{-ikt})$ (G.29)

Using the relation

$$\langle e^{L(b,b^+)} \rangle = e^{\frac{1}{2} \langle L^2(b,b^+) \rangle } \quad (G.30)$$

where $L$ is any linear combination of boson operators, (G.26)

can be further transformed into:

$$F(t) = e^y e^{-\frac{1}{2} \langle L^2 \rangle } \quad (G.31)$$

The only nonvanishing terms in $\langle L^2 \rangle$ are

$$-(1 + \sqrt{V})^2 \frac{1}{N} \sum_{k k'} (e^{ikt} + 1)(e^{-ikt} + 1)(b^+_k b^+_k + b^+_k b_k) \quad (G.32)$$

Thus from (G.31) and (G.32) we get for $F(t)$:

$$F(t) = \exp \left( (1 + \sqrt{V}) \frac{1}{N} \sum_{k > 0} \frac{1}{k} (e^{-ikt} - 1) \right) \quad (G.33)$$

Converting the sum into an integral and introducing a cut off
momentum $k_0$:

$$
\frac{1}{N} \sum_{k=0}^{k_{\text{max}}} \frac{1}{k} \left( e^{-\frac{i k t}{V}} - 1 \right) = \int_0 \frac{e^{-x} - 1}{x} \, dx \quad (G.34)
$$

The lower limit contribution gives a numerical factor which is unimportant because our calculation is correct up to a constant anyway. For large times we may neglect $e^{-x}$ and integrate to obtain:

$$
F(t) = \exp\left[-(1 + \nu V)^2 \ln \left( \frac{it k_0}{\nu} \right) \right]
$$

or

$$
F(t) = \frac{1}{(it k_0)^{1+2\nu V}} \quad (G.35)
$$

In the weak coupling approximation we may put

$$\tan \delta \approx \delta_B = -\pi \nu V,$$

where $\delta_B$ is the phase shift in the Born approximation. From (G.21) we get for the transition probability:

$$
W(w) \sim \frac{1}{\left( \frac{i k_0}{\nu} \right)^{\frac{1}{1+\frac{\delta_B}{\pi}}} \left( \frac{1}{w + \frac{E_0}{\nu}} \right)^2} \left( \frac{\delta_B}{\pi} \right)^2 \quad (G.36)
$$

This is the same energy dependence as in the result (6.51) from the rigorous calculation in Green's function technique, when we replace $\delta_B$ by exact phase shift $\delta$. 

REFERENCES.

2. W. Hallwachs; " 32, 301, (1888).
3. P. Lenard; " 2, 359, (1900).
8. Richardson, Compton; Science 35, 783 (1912).
11. R.H. Fowler; The analysis of photoelectric sensitivity curves for clean metals at various temperatures; Phys. Rev. 38, 45 (1931).
15. K. Mitchell: The theory of the surface photoelectric effect in metals: I. and II; Proc. Roy. Soc. A146, 442 (1934) and


27. F.S. Ham: Energy bands in alkali metals, I, Calculated bands;


37. W.A. Spicer: Possible non-one-electron effects in the fundamental optical excitation spectra of certain crystalline solids and their effect on photoemission; Phys. Rev. 154, 385 (1967).


53. P. Nozieres, J. Gavoret, B. Roulet: ... II Self-consistent treatment of divergencies; ibid. 1084.
A. Messiah: Quantum Mechanics, Chap. XIX.
56. S. Doniach, Private communication.
57. C.S. Fadley, D.A. Shirley: X-ray photoelectron spectroscopic study of Fe, Co, Ni, Cu and Pt; PR. Lett. 21, (68) 980.
63. V.V. Sudakov: Meson-meson scattering in meson field theory; Doklady 1, 662, (1956).


65. A.A. Abrikosov: Electron scattering on magnetic impurities in metals and anomalous resistivity effects; Physics 2, 5 (1965).

66. J.J. Hopfield, Private communication.


68. W. Kohn: Variation scattering theory in momentum space I. Central field problems; Phys. Rev. 84, 495 (1951).

69. N.I. Muskhelishvili: Singular Integral Equations; Noordhoff N.V. (Groningen 1953), Chapter XIV.


74. C. Nordling: Energy shifts of L-levels in some 5-th period


84. L.G. Parratt: Ka satellite lines; Phys. Rev. 50, 1 (1936).


87. M. Shah, K. das Gupta: Observation of fine structures of Cr Ka1,2 lines with a high resolution 3-crystal spectrometer; Physics Letters 29A, 570, (1969).