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Electron energy band and magnetic field effects on non-local optical properties of simple metals

by

Mohammed Shahidul Haque

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PART I. ELECTRON ENERGY BAND EFFECTS ON OPTICAL EXCITATION OF PLASMONS IN SOLIDS
CHAPTER I. INTRODUCTION

The object of this work is to investigate the modification of the plasmon dispersion relation of the free-electron gas due to the presence of a lattice for two simple alkali metals, sodium and potassium. Sodium and potassium are probably the two most free-electron-like metals known with Fermi surfaces possessing only very slight deviations from sphericity. Since ordinary plasma oscillations are manifestations of essentially the free-particle aspects of conduction electrons these two elements were the most natural choice as a starting point for an investigation of this kind. Besides this, potassium has the added distinction of being, to date, the only substance for which a very complete plasmon dispersion curve has been experimentally determined.¹

In the free-electron gas model, the metal is considered as an aggregate of free electrons embedded in a uniform, rigid background of positive charge which has an average density equal to that of the electrons. Such a system, characterized in addition by very high densities and temperatures low enough such that the proper statistical behavior is governed by the laws of quantum statistics (Fermi-Dirac for electrons), constitutes a quantum plasma. This serves as an adequate model for discussing qualitatively the behavior of the conduction electrons in many metals. Pines and Bohm² were the first to investigate the properties of a quantum plasma in order to understand the effect of the long-range Coulomb interaction on the conduction
electrons in solids. They found that the electrons could display a very high degree of correlated behavior manifested through the phenomena of screening and collective oscillations. Plasmons can be defined as the normal modes of these collective oscillations inside the electron gas. It can be shown\(^3\) that these modes are well defined for wavelength \(\lambda > \lambda_c\), where \(\lambda_c\) is some cut-off value which has a value roughly equal to the mean interparticle spacing. For \(\lambda \leq \lambda_c\) it is, thus, no longer meaningful to talk about collective oscillations. For such short wavelengths energy is transferred from plasmons to single-particle excitations, and the collective modes are damped out. This is the phenomena of Landau damping. Physically, one can look upon Landau damping in the following way. When the velocity of the electron in the direction of plasmon propagation equals the phase velocity of the plasmons, the electrons will ride in phase with the plasmons and extract energy from them, consequently damping out the plasmons. \(\lambda_c\) is the value of the plasmon wavelength at which Landau damping begins.

Since the plasmons are essentially density fluctuations of the electrons, they are longitudinal excitations of the electron gas. The response of an infinite system to longitudinal excitations is fully described by the frequency- and wave-vector-dependent longitudinal dielectric function \(\varepsilon_L(\mathbf{q}, \omega)\). It can be shown\(^3\) that the condition for existence of undamped plasma oscillations is given by

\[
\varepsilon_L(\mathbf{q}, \omega) = 0 .
\] (1.1)
Eq. (1.1) provides a theoretical basis not only for defining the plasmon but also for evaluating its dispersion relation. The question then arises as to how one might experimentally observe plasmons for \( q \neq 0 \), and thus obtain the plasmon dispersion relation. The technique that has been most frequently used in the past is electron energy loss in thin foils. The passage of fast (keV) electrons through thin foils produces longitudinal fields inside the sample and consequently excites plasmons. The measured energy loss of scattered electrons then yields the plasmon energy, and their angular distribution can in principle give the momentum transfer from the incident electrons to the plasmons. Unfortunately, due to the rapid loss of intensity of scattered electrons at wide angles and multiple-scattering difficulties, this technique has not been very fruitful for obtaining the plasmon dispersion for large momentum transfer.

Although there is no direct way of obtaining the wave-vector-dependent dielectric function by optical experiments, it has been demonstrated by Melnyk and Harrison, and independently by Jones, Kliwer, and Fuchs that reflection and transmission data from optical experiments on thin films yield all the relevant information on plasmons for \( q \neq 0 \). Normally, in an optical experiment, the photon momentum is so small that no appreciable momentum transfer to the electrons can occur. In such instances it suffices to describe the response of the system in terms of a local (zero wave-vector), frequency-dependent dielectric function. However, there are two
frequency regions where non-local effects (described by a wave-vector-dependent dielectric function) are significant. One is the anomalous skin effect region\(^7\), which is purely a transverse effect and is of no interest in the present work. It occurs at a frequency \(\sim 10^{-3}\omega_p\), where \(\omega_p\) is the plasma frequency. The other region is at higher frequencies (\(\sim \omega_p\)) where longitudinal polarization waves are excited in the electron gas. This was first predicted by Silin and Fetisov\(^8\), and later by Kliewer and Fuchs\(^9\), who presented more detailed calculations and results. It was observed by these authors that for p-polarized light (electric field vector polarized in the plane of incidence) incident on the sample surface, there is a component of electric field vector normal to the surface which can excite charge density fluctuations inside the medium. Indeed, they\(^9\) observed an additional absorption peak for a semi-infinite slab in the frequency range \(0.1\omega_p \leq \omega \leq \omega_p\). Such a structure does not exist for normally incident light or for s-polarized light (electric field vector polarized perpendicular to the plane of incidence), where the electric field vector is always parallel to the surface of the slab. Similar results for p-polarized light were also obtained by Melnyk and Harrison\(^5\) who extended their calculation to thin films of Na and K for frequencies above the plasma frequency. They found that the absorption spectrum for such a geometry was dominated by a series of very sharp, well-defined peaks for \(\omega \geq \omega_p\), and concluded that this structure was due to resonances when standing waves of plasmons are set up inside a thin film. Similar observations were made by Jones, Kliewer, and Fuchs,\(^6\)
who pointed out that each of the resonant peaks corresponded to the excitation of a plasmon of a definite wave vector. This then provides a technique for obtaining the plasmon dispersion relation experimentally. Such experiments have been reported by Yamaguchi, Lindau and Nilsson, and more recently by Anderegg, Feuerbacher, and Fitton.

As mentioned earlier, Eq. (1.1) gives the dispersion relation for undamped plasmon propagation. Thus, for a theoretical calculation of the plasmon dispersion curve, all that is necessary is the longitudinal dielectric function. One way of obtaining this is to solve the Boltzmann equation for the single-particle distribution function in the presence of an applied field and thus evaluate the response to the given field. An alternative procedure, which yields a far better physical description of the system, is to use the quantum-mechanical longitudinal dielectric function obtained in the random-phase (RPA) or self-consistent-field (SCF) approximation first by Lindhard. The longitudinal dielectric function for the free-electron gas in these two approximations will be given in the following chapter where it will also be demonstrated that the semi-classical Boltzmann equation approach does not provide for the phenomenon of Landau damping at absolute zero temperature. Also, because of its semi-classical nature, the Boltzmann equation is not valid in the region where quantum effects become important. This occurs for values of $q \geq k_F$, where $k_F$ is the Fermi wave-vector. The free-electron plasmon dispersion curve as obtained by the Lindhard dielectric
function will therefore differ from the one obtained by the Boltzmann
dielectric function at large values of $q$. It seems clear that the
former provides a more accurate description of the electron gas.
Therefore, it is rather surprising that the experimental results of
Anderegg et al.\textsuperscript{1} appear to agree so well with calculations based
upon the Boltzmann dielectric function.

It is possible that the deviations of the experimentally deter-
mined plasma dispersion relation for potassium\textsuperscript{1} from the theoret-
ically predicted value as obtained from the finite electron lifetime
generalization of the Lindhard dielectric function\textsuperscript{14} might be due
to the effect of interband transitions. The plasma frequency $\omega_p$
which is the frequency of plasma oscillations for zero wave-vector, is
well above the threshold for interband transitions in both sodium
and potassium. It is therefore reasonable to include the effect of
interband transitions at frequencies where plasma oscillations might
be expected to occur. This is accomplished by including the effect of
interband transitions in the longitudinal response of the system. In
other words, a calculation of the frequency- and wave-vector-dependent
dielectric function including the actual electronic energy band struc-
ture has to be performed.

The traditional way of analyzing the results of optical exper-
iments is via a local dielectric function for which interband transi-
tions are momentum conserving, i.e., vertical transitions. Wave vectors
for the initial and final states are the same in the reduced zone scheme
and differ at most by integral multiples of reciprocal lattice vectors
in the extended zone scheme. When non-local effects are included, the final state momentum can differ from the initial state momentum by the addition of the momentum $\mathbf{q}$ of the excitation. This is schematically represented for a one-dimensional two-band model in Fig. 1.

The effect of interband transitions on the plasmon dispersion relation is very difficult to demonstrate analytically. However, under certain conditions, it can be shown that in general: (1.) The interband transitions will shift the plasma frequency $\omega_p$ at $\mathbf{q} = 0$. (2.) Interband transitions will cause plasmon damping even outside the single-particle excitation region.

Introduction of the multi-band model requires knowledge of the electron energy bands and the corresponding wavefunctions. The augmented plane wave (APW) method will be employed in this work for energy band calculations. The wavefunction of a conduction electron in a metal has plane-wave like characteristics in the region between the ion cores but behaves more like an atomic state in the region where the ion core potential is strong. Any wavefunction can be expanded in a complete set of states, and plane waves constitute a rapidly

---

$^a$For a free-electron gas in which there exists no mechanism for electron scattering, plasmons can be damped only when conditions are such that plasmons can excite an electron out of the Fermi sea creating an electron-hole pair, i.e., Landau damping can occur. The limited region of energy-momentum space where electron-hole pair excitations can occur with conservation of energy and momentum is referred to as the single-particle excitation region. When interband transitions are present, plasmons can lose energy by exciting electrons from occupied bands to empty bands, and such excitations can occur for all energy and momenta above the threshold for interband transitions.
Fig. 1. One-dimensional, two-band picture in reduced zone scheme showing vertical transition 1, non-vertical transition 2 of wave vector \( q \). \( k \) is the electron wave vector, \( E(k) \) the corresponding energy, and \( E_F \) the Fermi energy.
$E(k)$

$E_F$

0

$k$

1

$q$

2
convergent set which can represent the wavefunction of a conduction electron in the region between the ion cores. However, it requires an inordinately large number of plane waves to represent adequately the true character of the wavefunction near the ion cores. The APW method overcomes this difficulty by expanding the wavefunction in a set of states which are like atomic states near the core but are plane waves elsewhere.

Numerical computation of matrix elements using the correct form of the APW wavefunction is very lengthy and involved. However, sodium and potassium are known to be free-electron-like. In other words, they have a weak pseudo-potential, which has the effect of reducing the number of atomic-like nodes in the wavefunction near the core. For such metals a relatively small number (~ 20-50) of plane waves can be used as a complete set for expanding the conduction electron wavefunction throughout the crystal.

In this work, the APW wavefunction in the region between the ion cores, which is a linear combination of plane waves, will be used to approximate the wavefunction of the conduction electrons for the entire crystal. We emphasize here that the above arguments are by no means a justification for expanding the wavefunction in plane waves. However, on account of the enormous simplification that results from it, this approximation is a reasonable starting point for a computation as complex as the one in this work.

In Chapter 11 the theory of optical absorption of p-polarized light by a thin film is briefly reviewed. The derivation of the
longitudinal dielectric function for real solids as well as a brief
survey of the APW method is also provided in this chapter.

Chapter III gives the numerical techniques used in the computation,
Chapter IV contains the results and a discussion of them, and the
conclusions are presented in Chapter V.
CHAPTER II. THEORY

Optical Absorption by a Thin Film

Consider a metallic film of thickness $d$ whose two faces lie on the planes $z = 0$ and $z = -d$. Let a $p$-polarized electromagnetic wave be incident on the film from the $+z$ side with an angle of incidence $\theta$ measured from the surface normal. A coordinate system is now defined such that the wave vector of the incident radiation is in the $x$-$z$ plane. If the frequency of the incident light is $\omega$, then its wave vector is given by $k = (k_x, 0, k_z)$, with $k_x = (\omega/c)\sin\theta$ and $k_z = -(\omega/c)\cos\theta$. The geometry is described in Fig. 2.

For specular scattering of electrons at the boundaries, the slab can be extended infinitely throughout space, provided we impose the following boundary conditions on the fields:

\[
E_x(m_d - z) = E_x(m_d + z),
\]

\[
H_y(m_d - z) = -H_y(m_d + z),
\]

\[
E_z(m_d - z) = -E_z(m_d + z),
\]

where $m$ is an integer. If the fields are now divided into those having even or odd parity about the center of the slab ($z = -\frac{1}{2}d$), it can be shown that the surface impedances for these two cases for $p$-polarized light are given by
Fig. 2. Geometry for a slab of thickness \( d \) with \( p \)-polarized light incident on the \( z = 0 \) plane at an angle of incidence \( \theta \).
\[ z^{(1,2)} = \frac{E_z(0)}{H_y(0)} = -\frac{2i\Omega}{W} \sum_{m=-\infty}^{\infty} \left[ \frac{Q_x^2}{\Omega^2 \epsilon_x^t} + \frac{Q_z^2}{\Omega^2 \epsilon_z^t} \right], \]

where

\[ \Omega = \omega/\omega_p, \]

\[ W = \omega_p d/c, \]

\[ Q_x = q_x c/\omega_p, \]

\[ Q_z = q_z c/\omega_p, \]

\[ Q^2 = Q_x^2 + Q_z^2. \]

\( \epsilon_x^t \) and \( \epsilon_z^t \) are the frequency- and wave-vector-dependent longitudinal and transverse dielectric functions, respectively, \( \omega_p = (4\pi n e^2/m_e)^{\frac{1}{2}} \) is the plasma frequency, \( m_e \) is the electron mass, \( n \) is the electron density, and \( q_x \) and \( q_z = m_\nu/d \) are the \( x- \) and \( z- \) components of the wave vector of the fields inside the slab.

The superscript 1 refers to the case where \( E_x(z) \) has odd parity about \( z = -\frac{1}{2}d \), so that \( E_z(z) \) and \( H_y(z) \) have even parities. The superscript 2 refers to \( E_x(z) \) having even parity, with \( E_z(z) \) and \( H_y(z) \) having odd parities.

The expressions for the reflection, transmission, and absorption coefficients can now be derived in terms of the surface impedances \( Z^{(1)} \) and \( Z^{(2)} \). From Ref. 6 we have for the reflection...
coefficient \( R \) and the transmission coefficient \( T \),

\[
R = \frac{1}{\zeta} |p^{(1)} + p^{(2)}|^2 ,
\]

(11.2)

and

\[
T = \frac{1}{\zeta} |p^{(1)} - p^{(2)}|^2 ,
\]

(11.3)

where

\[
p^{(1,2)} = \frac{\cos \theta + Z^{(1,2)}}{\cos \theta - Z^{(1,2)}} .
\]

(11.4)

The absorption coefficient is therefore given by

\[
A = 1 - T - R .
\]

(11.5)

Substituting Eqs. (11.2) and (11.3) into Eq. (11.5) we obtain

\[
A = 1 - \frac{1}{\zeta} \left[ |p^{(1)}|^2 + |p^{(2)}|^2 \right] .
\]

(11.6)

If we now apply the definitions of \( p^{(1)} \) and \( p^{(2)} \) from Eq. (11.4) in Eq. (11.6) we can show that

\[
A = - \frac{2 \cos \theta \text{Re}(Z^{(1)})}{|\cos \theta - Z^{(1)}|^2} - \frac{2 \cos \theta \text{Re}(Z^{(2)})}{|\cos \theta - Z^{(2)}|^2} ,
\]

(11.7)

where \( \text{Re}(Z^{(1,2)}) \) denotes the real part of \( Z^{(1,2)} \). Insofar as
contributions from longitudinal effects are concerned, we can see from Eq. (11.1) that \( \text{Re}(Z^{(1,2)}) \cdot \text{Im}(-1/\epsilon^z) \). From Eq. (11.7) we can then conclude that longitudinal effects are manifested most strongly in the absorptance through \( \text{Im}(-1/\epsilon^z) \). It has been shown that in a free-electron film, the resonant peaks in the absorptance for \( \Omega > 1 \) are associated with the peaks in \( \text{Im}(-1/\epsilon^z) \). It has been also demonstrated that the contributions to the absorptance arising from a given longitudinal excitation (plasmon or single-particle) appear in a thin film at \( Q_z = m\pi c/\omega_p \), where \( m = 1, 3, 5, \ldots \). This has been explained from physical considerations by Fuchs and Kliewer. They noted that energy is transferred resonantly from the \( z \)-component of the electric field inside the thin film to the longitudinal excitation if the field goes through an odd number of half-periods of oscillation in the time taken by the excitation to traverse the thickness of the film. This leads precisely to the condition \( Q_z = m\pi c/\omega_p \), where \( m = 1, 3, 5, \ldots \) for resonant absorption.

Since \( Z^{(2)} \) in Eq. (11.1) consists of a sum over even values of \( m \), only the first term on the right-hand side of Eq. (11.7) will contribute to the resonant structure in the absorption associated with longitudinal excitations.

As noted above, in optical experiments on thin films with \( p \)-polarized light, resonant peaks associated with peaks of \( \text{Im}(-1/\epsilon^z) \) show up in the absorption spectra for \( \Omega > 1 \). Experimentally, the positions of the resonant structure yield the frequencies of the plasmons, while geometric requirements determine the wave vectors,
so the plasmon dispersion curve can be obtained. In the present work, where band effects are included, this criterion will be used as the definition of a plasmon, that is, the peaks of \( \text{Im}(-1/e_\parallel) \) will be interpreted as plasmons. We shall therefore evaluate \( e_\parallel \) explicitly and obtain the frequencies and the corresponding wave vectors of the plasmons, i.e., the plasmon dispersion curve, from the peak positions of \( \text{Im}(-1/e_\parallel) \). Since interband effects will be present in our calculations, the plasmon peaks will be considerably broader than the corresponding free-electron peaks with moderate damping. Thus the peak of \( \text{Im}(-1/e_\parallel) \) will not necessarily coincide with \( \text{Re}(e_\parallel) = 0 \). Also, on account of interband transitions being present, other peaks may show up in \( \text{Im}(-1/e_\parallel) \) besides the plasmon peak. In the event that such peaks do show up, the plasmon peak will in general be chosen as the one which is most prominent, primarily on the basis of height. Proximity to the condition \( \text{Re}(e_\parallel) = 0 \) will also be used as a qualitative guide in this determination. This method for determining the plasmon dispersion curve is completely analogous to performing an optical experiment on a thin film and interpreting the resonances as being associated with plasmons. Our technique is also compatible with the observations of electron energy-loss experiments, where \( \text{Im}(-1/e_\parallel) \) is the energy-loss function, and peaks in this function are associated with the elementary excitations of which the plasmon is an example.

Longitudinal Dielectric Function for a Real Solid

The longitudinal dielectric function will be calculated here by the self-consistent-field (SCF) method of Ehrenreich and Cohen, 18
in which the response of a many-electron system is obtained by investigating the dynamics of a single electron interacting with the self-consistent-field inside the metal. The self-consistent-field includes the external impulse plus the field produced by the response of the electrons in the system. To this end the one-electron Hamiltonian is given by

$$ H = H_0 + V(\vec{x}, t). $$

Here, $H_0$ is the unperturbed Hamiltonian of an electron in the periodic crystal field and $V(\vec{x}, t)$ is the self-consistent potential. We define the one-electron states of the system by

$$ H_0 |\vec{k}, \varepsilon\rangle = E_{k\varepsilon} |\vec{k}, \varepsilon\rangle, $$

where $\varepsilon$ is the band index.

$|\vec{k}, \varepsilon\rangle$ satisfies the Bloch condition and is of the form

$$ |\vec{k}, \varepsilon\rangle = \frac{1}{\sqrt{v}} e^{i\vec{k}\cdot\vec{x}} u_{k\varepsilon}(\vec{x}), $$

where $v$ is the volume of the system and $u_{k\varepsilon}(\vec{x})$ has the periodicity of the lattice.

Let $\rho_0$ be the one-electron density operator for the system in equilibrium. Then
\[ \rho_o |\vec{k}\rangle = f_o (\vec{k}) |\vec{k}\rangle, \]  

where \[ f_o (\vec{k}) = [\exp(\beta (E_k - E_F)] + 1]^{-1}, \] \[ \beta = (k_B T)^{-1}, \] and \( E_F \) is the Fermi energy. Let \( \rho \) be the one-electron density operator for the system in the presence of the self-consistent field \( V(\vec{x}, t) \). The equation of motion satisfied by \( \rho \) is

\[ \frac{\partial \rho}{\partial t} + \frac{i}{\hbar} [H, \rho] = \frac{\partial \rho}{\partial t}_{\text{coll}}, \]  

\( \frac{\partial \rho}{\partial t}_{\text{coll}} \) represents the change in \( \rho \) due to electron collisions with lattice imperfections. We shall introduce here the simple relaxation time approximation in which the collision term may be written as

\[ \frac{\partial \rho}{\partial t}_{\text{coll}} = - \frac{\rho - \rho_0}{\tau}. \]

Here \( \tau \) is a phenomenological electron lifetime. Actually, the relaxation time approximation is not appropriate when charge density fluctuations are induced in the system, as indeed they are when the longitudinal response of the system is being considered. However, Kliewer and Fuchs\(^1\) have shown that for frequencies which are high enough such that \( \omega \tau \gg 1 \), these effects make a negligible contribution to the dielectric function.

If we now consider a linear response of the system to the
self-consistent field and expand \( \rho = \rho_0 + \rho_1 \), Eq. (11.12) may be written as

\[
\frac{\partial \rho_1}{\partial t} + \frac{i}{\hbar} \left[ H_0, \rho_1 \right] + \frac{i}{\hbar} \left[ V(\mathbf{x}, t), \rho_0 \right] = -\rho_1 / \tau.
\]

It then follows that

\[
\langle \mathbf{k}_\ell | \rho_1 | \mathbf{k} + \mathbf{q} \mathbf{r} \rangle = \frac{f_0 (\mathbf{k} + \mathbf{q} \mathbf{r}) - f_0 (\mathbf{k}_\ell)}{E_{\mathbf{k} + \mathbf{q} \mathbf{r}} - E_{\mathbf{k}_\ell} + \hbar (\omega + i / \tau)} \langle \mathbf{k}_\ell | V(\mathbf{x}, t) | \mathbf{k} + \mathbf{q} \mathbf{r} \rangle.
\]

The electronic density can be written as

\[
n(\mathbf{x}, t) = n + \delta n(\mathbf{x}, t),
\]

where \( n \) is the equilibrium density, and \( \delta n(\mathbf{x}, t) \) is the change in density induced by \( V(\mathbf{x}, t) \).

We have

\[
\delta n(\mathbf{x}, t) = \sum_\alpha \langle \alpha | \delta (\mathbf{x} - \mathbf{x}_0) | \rho_1 | \alpha \rangle,
\]

where \( | \alpha \rangle \) refers to the complete set of eigenstates for the system including the spin states.

We can Fourier analyze the self-consistent potential \( V(\mathbf{x}, t) \) by

\[
V(\mathbf{x}, t) = \sum_{\mathbf{q}, \mathbf{r}} e^{-i (\mathbf{q} + \mathbf{r}) \cdot \mathbf{x}} V(\mathbf{q}, \mathbf{r}, t).
\]
where $\mathbf{q}$ is restricted to the first Brillouin zone, and $\mathbf{H}$ is a reciprocal lattice vector. For sodium and potassium it is reasonable to make the simplifying assumption that the core states are sufficiently tightly bound, and the conduction band states are sufficiently broad, so that local-field corrections, and consequently umklapp processes associated with the reciprocal lattice vector $\mathbf{H}$, are not important. Hence, we shall approximate Eq. (11.15') by

$$V(\mathbf{x}, t) = \sum_{\mathbf{q}} e^{-i\mathbf{q} \cdot \mathbf{x}} V(q, t). \quad (11.16)$$

Therefore the inverse Fourier transform gives

$$V(q, t) = \frac{1}{\nu} \int_{\nu} d\mathbf{x} e^{i\mathbf{q} \cdot \mathbf{x}} V(\mathbf{x}, t). \quad (11.17)$$

Then using Eqs. (11.13), (11.15), and (11.17), we can write

$$\delta n(\mathbf{x}, t) = \sum_{\mathbf{k}, \mathbf{q}} \frac{f_0(\mathbf{k}+\mathbf{q} \mathbf{\ell}')}{E_{\mathbf{k}+\mathbf{q} \mathbf{\ell}'} - E_{\mathbf{k} \mathbf{\ell}} + \hbar (\omega t / \tau)} V(q, t) e^{-i\mathbf{q} \cdot \mathbf{x}_0} \langle \mathbf{k}+\mathbf{q} \mathbf{\ell}' | \delta(\mathbf{x} - \mathbf{x}_0) | \mathbf{k} \mathbf{\ell} \rangle, \quad (11.18)$$

where the sum includes a sum over spin states as well.

The integration involved in evaluating $\langle \mathbf{k} \mathbf{\ell} | e^{-i\mathbf{q} \cdot \mathbf{x}_0} | \mathbf{k}+\mathbf{q} \mathbf{\ell}' \rangle$ can be carried out by integrating over the volume of a unit cell at the origin, and then summing over all the unit cells in the volume $\nu$ of
the crystal. Upon doing that we obtain

$$\delta n(\mathbf{x}, t) = \sum_{\mathbf{k}, \mathbf{q}} \frac{f_0(K+q,l') - f_0(Kl)}{E_{K+q,l'} - E_{Kl} + \hbar(\omega + i/\tau)} V(q, t) M_{Kl, K+q,l'}$$

$$\times \langle K+q,l' | \delta(x-x_0) | Kl \rangle ,$$  \hspace{1cm} (11.19)

where

$$M_{Kl, K+q,l'} = \frac{i}{V_c} \int \frac{d^3x}{V_c} u_{Kl}^* \cdot u_{K+q,l'}^* ,$$  \hspace{1cm} (11.20)

and $V_c$ is the volume of a unit cell.

Taking the Fourier transform of both sides of Eq. (11.19) over space and time we obtain

$$\delta n(q, \omega) = \frac{1}{V} V(q) \sum_{K, l, l'} \frac{f_0(K+q,l') - f_0(Kl)}{E_{K+q,l'} - E_{Kl} + \hbar(\omega + i/\tau)} |M_{Kl, K+q,l'}|^2 .$$  \hspace{1cm} (11.21)

The self-consistent potential $V(\mathbf{x}, t)$ can be written as

$$V(\mathbf{x}, t) = V_e(\mathbf{x}, t) + V_s(\mathbf{x}, t) ,$$  \hspace{1cm} (11.22)

where $V_e(\mathbf{x}, t)$ is the external perturbing potential, and $V_s(\mathbf{x}, t)$, which we shall call the screening potential, is induced by charge density fluctuations. The screening potential is related to the charge density fluctuation by Poisson's equation,
\[ \nabla^2 V_s(\mathbf{x}, t) = -4\pi e^2 \delta n(\mathbf{x}, t), \]

which, upon Fourier transformation, yields

\[ V_s(q, \omega) = \frac{4\pi e^2}{q^2} \delta n(q, \omega). \tag{11.23} \]

Then using Eqs. (11.21) and (11.23) in Eq. (11.22) we get

\[ V_e(q, \omega) = V(q, \omega) \left[ 1 - \frac{4\pi e^2}{q^2} \sum_{K, \ell, \ell'} \frac{f_0(K+q, \ell') - f_0(K\ell)}{E_{K+q, \ell'} - E_{K\ell} + \hbar(\omega + i/\tau)} \right] \left[ M_{K\ell, K+q, \ell'} \right]^2. \]

Writing \( V(q, \omega) = V_e(q, \omega)/\epsilon_L(q, \omega) \) as the definition for the longitudinal dielectric function \( \epsilon_L(q, \omega) \), we have

\[ \epsilon_L(q, \omega) = 1 - \frac{4\pi e^2}{q^2} \sum_{K, \ell, \ell'} \frac{f_0(K+q, \ell') - f_0(K\ell)}{E_{K+q, \ell'} - E_{K\ell} + \hbar(\omega + i/\tau)} \left[ M_{K\ell, K+q, \ell'} \right]^2. \tag{11.24} \]

This can also be written as

\[ \epsilon_L(q, \omega) = 1 + \frac{4\pi e^2}{q^2} \sum_{K, \ell, \ell'} f_0(K\ell)[1 - f_0(K+q, \ell')] \left| M_{K\ell, K+q, \ell'} \right|^2 \times \left[ \frac{1}{E_{K+q, \ell'} - E_{K\ell} + \hbar(\omega + i/\tau)} + \frac{1}{E_{K+q, \ell'} - E_{K\ell} - \hbar(\omega + i/\tau)} \right]. \tag{11.25} \]
In the free-electron limit Eqs. (11.24) and (11.25) reduce to

\[ \epsilon_{\mathbf{r}}(Q,\omega) = 1 - \frac{4\pi e^2}{q^2} \sum_{\mathbf{k}} \frac{f_0(\mathbf{k}+\mathbf{q}) - f_0(\mathbf{k})}{E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}} + \hbar(\omega+i/\tau)}, \] (11.26)

where \( E_{\mathbf{k}} = \hbar^2 k^2/2m \), and the sum is over all of \( \mathbf{k} \)-space with summation over spin indices implied.

At absolute zero temperature, the Fermi distribution function \( f_0(\mathbf{k}) \) is a step function, and Eq. (11.26) can be integrated to yield

\[ e^{\frac{\omega}{(\omega^2 + \omega^2 v_f^2)}} = 1 + \left( \frac{3\omega_p^2}{q^2} \frac{v_F^2}{2} \right) f_{\mathbf{r}}, \] (11.27)

with

\[ f_{\mathbf{r}} = \frac{1}{2} + \frac{1}{8z} \left[ [1 - (z-u')^2] \ln \left( \frac{z-u' + 1}{z-u' - 1} \right) + [1 - (z+u')^2] \ln \left( \frac{z+u' + 1}{z+u' - 1} \right) \right], \] (11.28)

where

\[ z = q/2k_F, \] (11.29a)

\[ \omega' = \omega + i/\tau \] (11.29b)

\[ u' = \omega'/qv_F. \] (11.29c)

\( k_F \) is the Fermi wave-vector, and \( v_F \) is the Fermi velocity.
In this work, calculation of the free-electron plasmon dispersion relation using the Boltzmann dielectric function will also be performed. The longitudinal dielectric function calculated from the solution of the Boltzmann equation is given by

\[ \epsilon_{\ell, B}(q, \omega) = 1 - \frac{1}{\Omega(\Omega + i\gamma)} \left( -\frac{3i\Omega}{\gamma} \frac{1}{(b'q)^2} \right) \times \left[ \left( b'q - \frac{1}{2i} \ln \left( \frac{1 + ib'q}{1 - ib'q} \right) \right) / \left( bq - \frac{1}{2i} \ln \left( \frac{1 + ibq}{1 - ibq} \right) \right) \right] . \]  

(11.30)

where

\[ \gamma = \frac{1}{\omega_p \tau} ; \]  

(11.31a)

\[ b = \frac{\nu}{c\gamma} ; \]  

(11.31b)

and

\[ b' = \frac{1}{(1 - i\Omega/\gamma)} . \]  

(11.31c)

In deriving this expression for \( \epsilon_{\ell, B}(q, \omega) \), relaxation of the charge distribution was assumed to take place towards states of local equilibrium, as opposed to a single state of uniform equilibrium throughout the electron gas.

If we assume for the moment that there is no mechanism for electron scattering in the crystal, or \( \tau \to \infty \), \( \epsilon_{\ell}(q, \omega) \) from Eq. (11.26) can be written as
\[ \varepsilon_2(q, \omega) = \varepsilon_1(q, \omega) + i \varepsilon_2(q, \omega), \quad (11.32) \]

where

\[ \varepsilon_1(q, \omega) = \epsilon_1 \left( \frac{4 \pi e^2}{q^2} \right) \sum_{k} f_0(k+q) - f_0(k), \quad (11.33) \]

and

\[ \varepsilon_2(q, \omega) = \frac{4 \pi e^2}{q^2} \sum_{k} \delta(E_{k+q} - E_k - \omega)(f_0(k+q) - f_0(k)). \quad (11.34) \]

P denotes that the principal part of the sum is to be taken.

Eq. (11.34) indicates that \( \varepsilon_2 \) is non-zero only when an electron is excited out of the Fermi sea, creating an electron-hole pair.

Plasmon damping occurs in the region where \( \varepsilon_2 \) is non-zero. When no scattering mechanism is present in the system, these single-particle excitations are the only source of plasmon damping. It is to be emphasized that these conclusions hold strictly for the free-electron gas in the random phase approximation (RPA).

At absolute zero temperature, the right-hand side of Eq. (11.34) can be evaluated by the replacement

\[ \sum_{k} \rightarrow \frac{2 \nu}{(2 \pi)^3} \int d^3k, \]

and we have
\[ \epsilon_2(q, \omega) = e^2m/\hbar^2 \left[ (k_F^2 - (q/2 + \frac{m_\omega}{\hbar q})^2) U(k_F^2 - (q/2 + \frac{m_\omega}{\hbar q})^2) ight. \\
- \left. (k_F^2 - (q/2 - \frac{m_\omega}{\hbar q})^2) U(k_F^2 - (q/2 - \frac{m_\omega}{\hbar q})^2) \right], \quad (11.35) \]

where

\[ U(x) = 0 \quad \text{for } x < 0 \]
\[ = 1 \quad \text{for } x \geq 0. \]

In terms of the dimensionless quantities introduced in Eq. (11.1'), the single-particle excitation region is given by Eq. (11.35) to be

\[ \frac{\hbar \omega_p}{2mc^2} (Q^2 - 2QK_F) \leq \Omega \leq \frac{\hbar \omega_p}{2mc^2} (Q^2 + 2QK_F), \quad (11.36) \]

where

\[ K_F = k_F c/\omega_p. \]

Eq. (11.36) defines a region in \((Q, \Omega)\) space confined by the two parabolas

\[ \Omega = \frac{\hbar \omega_p}{2mc^2} (Q^2 + 2QK_F). \quad (11.37) \]

The + sign in Eq. (11.37) refers to the front (or low \(Q\) if \(Q > 0\)) edge of the single-particle excitation region, and the - sign refers to
the back (or high Q if Q > 0) edge. Consider what happens to the single-particle excitation region on the semi-classical limit (ℏ → 0).

Suppose an electron is excited from a state \( \vec{k} \) to a state \( \vec{k} + \vec{q} \). Then from energy conservation principles

\[
\hbar \omega = \frac{\hbar^2}{2m_e} [ (\vec{k} + \vec{q})^2 - \vec{k}^2 ].
\]

If we now take the limit \( \hbar \to 0 \) in the above equation, we have

\[
\lim_{\hbar \to 0} \omega = v_q q ,
\]

where \( v_q = \frac{\hbar \vec{k} \cdot \vec{q}}{m_e} \) is the velocity of the electron in the \( \vec{q} \) direction. For a Fermi gas at absolute zero temperature the maximum value \( v_q \) can have is the Fermi velocity \( v_F \). Hence, in the semi-classical limit the single-particle excitation region corresponds to

\[
\Omega \leq \frac{v_F}{c} Q .
\] (11.38)

Therefore, in the semi-classical description, plasmons cannot exist in the region defined by Eq. (11.38) since this is the region where Landau damping would occur. It will be demonstrated in Chapter IV that the plasmon dispersion curve as obtained from the Boltzmann dielectric function \( \varepsilon_{\text{B}} (Q, \Omega) \) [see Eq. (11.30)] asymptotically approaches the line \( \Omega = (v_F / c) Q \) on the high frequency side. Therefore, no Landau damping occurs in an electron gas at absolute zero temperature.
if the gas is described by the Boltzmann dielectric function. This fact can also be seen by noting [(see Eqs. (11.30) and (11.31)]

\[ \lim_{T \to \infty} \text{Im}(\epsilon_{\omega B}) = 0. \]

In other words, in the absence of electron scattering mechanism, no means exist for damping plasmons in the semi-classical description.

**Augmented Plane Wave (APW) Method**

In the augmented plane wave (APW) method the crystal is divided into a series of muffin-tin spheres centered around each atomic site. The radius \( R_s \), of the muffin-tin sphere, is chosen large enough so as to include most of the atomic-like states without allowing neighboring spheres to overlap. The principal approximation in the APW method is the replacement of the actual crystal potential \( V(r) \) by a spherically symmetric potential inside each muffin-tin sphere, and by a constant potential in the interstitial region between the spheres. A schematic representation of the potential is given in Fig. 3. Rigorous solutions to the Schrödinger equation can now be found in each of the regions mentioned above. Inside the muffin-tin sphere the solutions are those corresponding to a spherically symmetric potential well. In the interstitial region the solutions are given by plane waves. By piecing together these solutions, the wavefunctions for the entire crystal may be obtained.

Consider a crystal with \( N \) atoms per unit cell. Let the spherically symmetric muffin-tin potential for the \( v \)-th atom be
Fig. 3. Schematic representation of the muffin-tin potential for a crystal with two atomic species, A and B, per unit cell.

Fig. 4. General geometry with region I denoting inside of muffin-tin and region II denoting outside. $ds$ is the surface area of a pill-box constructed at the surface. $\hat{n}_1$, $\hat{n}_2$ are outward drawn normals to the pill-box. $\hat{n}$ is the outward drawn normal to the generalized muffin-tin.
denoted by $V_{\nu}(\rho)$, where $\rho$ is measured from the center of the muffin-tin sphere. The Schrödinger equation for the $\nu$th sphere is then given by

$$[-\frac{\hbar^2}{2m} \nabla^2 + V_{\nu}(\rho)]u = E'u.$$ 

The solution to this equation can be immediately written as

$$u_{\ell m}(\rho) = R_{\ell}(\rho)Y_{\ell m}(\hat{\rho}),$$  \hspace{1cm} (11.39)

where $R_{\ell}(\rho)$ satisfies the radial equation,

$$-\frac{1}{\rho} \frac{d}{d\rho} \left( \rho^2 \frac{d}{d\rho} R_{\ell}(\rho) \right) + \frac{(\ell(\ell+1)}{\rho} + \frac{2mV_{\nu}(\rho)}{\hbar^2} R_{\ell}(\rho)$$

$$= \frac{2mE'}{\hbar^2}R_{\ell}(\rho).$$  \hspace{1cm} (11.40)

$Y_{\ell m}(\hat{\rho})$ are the spherical harmonics, with $\ell = 0, 1, 2, \ldots$

$m = -\ell, -\ell+1, \ldots, \ell-1, \ell$, and $\hat{\rho}$ is a unit vector in the direction of $\hat{\mathbf{p}}$.

The APW function inside the $\nu$th sphere is taken as the general solution

$$\psi(\mathbf{r}) = \sum_{\ell=-\ell}^{\ell} \sum_{m=-\ell}^{\ell} \mathcal{C}_{\ell m} R_{\ell}(\rho) Y_{\ell m}(\hat{\rho}),$$  \hspace{1cm} (11.41)

where the $\mathcal{C}_{\ell m}$ are a set of as yet undetermined coefficients.
Let the constant potential in the interstitial region be $V_0$. For convenience shift the energy scale such that $V_0 = 0$. Then the solution to the Schrödinger equation outside the muffin-tin sphere is given by

$$\phi(r) = e^{iK \cdot r}.$$  \hspace{1cm} (11.42)

Writing $r = r_v + r_\rho$, where $r_v$ is the radius vector to the center of the $v$th muffin-tin sphere, $e^{iK \cdot r}$ may be expanded in spherical harmonics about the center of the $v$th muffin-tin sphere,

$$e^{iK \cdot r} = 4\pi e^{iK \cdot r_v} \sum_{l=0}^\infty i^l j_{l+\frac{1}{2}}(k_\rho) Y_{l,m}^*(k) Y_{l,m}(\hat{r}_\rho),$$  \hspace{1cm} (11.43)

where $j_{\ell}(x)$ are spherical Bessel functions.\textsuperscript{21} We now choose $C_{l,m}$ in Eq. (11.41) to make the APW function inside the muffin-tin sphere match with the one outside [Eq. (11.43)] at the surface of the sphere ($\rho = R_s$). We find

$$C_{l,m} = 4\pi e^{iK \cdot r_v} i^l \frac{j_{\ell}(kR_s)}{R_\ell(kR_s)} Y_{l,m}^*(k).$$  \hspace{1cm} (11.44)

Hence the APW function is given by

$$\phi(K, r) = e^{iK \cdot r} \text{ (in the interstitial region).} \hspace{1cm} (11.45a)$$
\[ \phi(\overline{K}, \overline{r}) = 4\pi e^{\frac{i}{2}} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^\ell j_{\ell}(kR_s) Y_{\ell m}(k) Y_{\ell m}(\overline{r}) \]

\[ R_{\ell}(\overline{r})/R_{\ell}(R_s) \text{ (inside the } \nu \text{th sphere).} \quad (11.45b) \]

These two forms of the APW function match up at the sphere boundary, but have a discontinuity in their slopes.

The stationary states of the crystal will now be determined variationally starting with a trial wavefunction \( \psi(\overline{K}, \overline{r}) \) given by a linear combination of the APW's,

\[ \psi(\overline{K}, \overline{r}) = \sum_i \sum_{\overrightarrow{g}_i} \alpha^i_\overrightarrow{g}_i \phi(\overline{K} + \overrightarrow{g}_i, \overline{r}) \],

(11.46)

where the sum is extended over a complete set of reciprocal lattice vectors \( \overrightarrow{g}_i \). It can be seen from Eq. (11.46) that \( \psi(\overline{K}, \overline{r}) \) is a valid Bloch state. The as yet unknown expansion coefficients \( \alpha^i_\overrightarrow{g}_i \) are the variational parameters.

The finite discontinuity in the first derivative of the variational function \( \psi(\overline{K}, \overline{r}) \) implies a delta-function potential on the surface of the APW sphere. This can be taken into account by introducing an effective Hamiltonian \( H' \) given by

\[ H' = H + A(\overline{r}) \delta[f(\overline{r}) - c] \],

(11.47)

where \( H \) is the actual Hamiltonian of the system, \( f(\overline{r}) = c \) determines the APW spheres, and \( A(\overline{r}) \) is to be determined. The quantity to be
varied is then

\[ \langle \psi | H' | \psi \rangle - E \langle \psi | \psi \rangle . \]

Consider a very general geometry as shown in Fig. 4 with

\[ \psi_I \text{ in region I .} \]
\[ \psi = \psi_{\text{II}} \text{ in region II .} \]

On the surface, \( \psi_I = \psi_{\text{II}} \) and \( \nabla \cdot \mathbf{A} \psi_I \neq \nabla \cdot \mathbf{A} \psi_{\text{II}} \). Integrate the Schrödinger equation \( H' \psi = E \psi \) over the volume \( V_p \) of the pill-box (Fig. 4) to obtain

\[
\int_{V_p} \left( \frac{p^2}{2m_e} + V(\mathbf{r}) + A(\mathbf{r}) \delta(f(\mathbf{r}) - c) \right) \psi(\mathbf{r})d^3r = E \int_{V_p} \psi(\mathbf{r})d^3r. \tag{11.48}
\]

As we let the thickness of the pill-box go to zero the terms \( E \int_{V_p} \psi(\mathbf{r})d^3r \) and \( \int_{V_p} (\mathbf{r}) \psi(\mathbf{r})d^3r \) drop out as \( E, V, \) and \( \psi \) are finite.

Also, we can write

\[
\int_{V} A(\mathbf{r}) \delta[f(\mathbf{r}) - c] \psi(\mathbf{r})d^3r = \int_{V} A(\mathbf{r})[f(\mathbf{r}) - c] \psi(\mathbf{r})dn ds .
\]

\[= A(\mathbf{r}) \psi(\mathbf{r})ds \]

where \( \mathbf{r} \) is on the surface. In addition
\[ \int_{Vp} \frac{p^2}{2m_e} \psi(\vec{r})d^3r = -\frac{\hbar^2}{2m_e} \int_{Vp} \nabla^2 \psi(\vec{r})d^3r \]

\[ = -\frac{\hbar^2}{2m_e} \hat{n} \cdot (\nabla \psi_{II} - \nabla \psi_I)ds . \]

Using these results in Eq. (11.43) we obtain

\[ A(\vec{r})\psi(\vec{r}) = \frac{\hbar^2}{2m_e} \hat{n} \cdot (\nabla \psi_{II} - \nabla \psi_I) . \quad (11.49) \]

Hence the quantity to be varied can be set up as

\[ \langle \psi | H' | \psi \rangle - E \langle \psi | \psi \rangle \]

\[ = \int_{\text{surface}} \psi^* \hat{H} \psi d^3r - E \int_{\text{surface}} \psi^* \psi d^3r + \int_{\text{I+II}} \psi^* A(\vec{r}) \delta[f(\vec{r}) - c] \psi d^3r \]

\[ = \int_{\text{I+II}} \psi^* \hat{H} \psi d^3r + \frac{\hbar^2}{2m_e} \int_{\text{surface}} \psi^* \hat{n} \cdot (\nabla \psi_{II} - \psi_I)ds - E \int_{\text{I+II}} \psi^* \psi d^3r . \]

A variational calculation can now be performed by minimizing the above expression with respect to the variational parameters \( \alpha_{-q_i} \).

If it is assumed that the energy eigenvalues \( E' \) correspond to the energy eigenvalues \( E \) of the stationary states of the system, it can be shown that we have the matrix equation

\[ [\delta_{ij} \frac{2}{2m_e} (k^2 + g_j) - E] \frac{h^2}{\nu_c} \sum_{R_s, \nu} \frac{N}{2} e^{2i \vec{k}_j \cdot \vec{r}_v} g_{ij} \alpha_{-q_j} = 0 , \quad (11.50) \]
where \( \vec{R}_{ij} = \vec{g}_j - \vec{g}_i \),

\( R_{s,\nu} \) is the muffin-tin radius for the \( \nu \)th atom,

\( V_c \) is the volume of a unit cell, and

\[
G_{\nu}^{ij} = \frac{2}{2m_e} (\vec{R}_{ij} + \vec{g}_i) \cdot (\vec{R}_{ij} + \vec{g}_j) - E^2 j_{ij}(\vec{k}_s R_{s,\nu}) / k_{ij} \\
- \sum_{\ell=0}^{\infty} (2\ell+1)p_{\ell} (\cos \theta \to g_{ij}) j_{\ell}(\|\vec{R}_{ij} + \vec{g}_i R_{s,\nu}) j_{\ell}(\|\vec{R}_{ij} + \vec{g}_j R_{s,\nu}) \\
\times R_{\ell}^{\prime}(R_{s,\nu})/R_{\ell}(R_{s,\nu}) \quad (11.51)
\]

where the prime on \( R_{\ell} \) denotes the derivative with respect to the distance from the center of the muffin-tin sphere. The energy bands can now be obtained by solving the linear Eq. (11.50). A solution exists only if the secular determinant vanishes. All the coefficients depend on the energy eigenvalue \( E \) to be solved for, either explicitly through Eq. (11.50) or implicitly through the term \( G_{\nu}^{ij} \). For a given \( \vec{k} \), \( E \) is obtained by feeding in different values of \( E \) until a root is found. Once the energy eigenvalues are known, the plane-wave coefficients \( \xi_{\vec{k}} \) can be obtained from Eq. (11.50).
CHAPTER III. NUMERICAL METHODS

Energy Band Calculation

Both sodium and potassium have been assumed to possess a BCC lattice. This is strictly true for temperatures above liquid nitrogen temperature. For temperatures somewhat below this temperature, sodium is known to undergo a martensitic transformation, and partially change its crystal structure from BCC to HCP. The behavior of potassium at low temperatures is not completely understood. For most optical experiments, it is reasonable to assume the crystal structure for these metals to be BCC.

In the energy band calculations, we have used atomic units. The construction of the muffin-tin potential, $V(r)$, is the first step in the APW band calculation. The method for constructing $V(r)$ used in this work is essentially that of Mattheiss. The crystal potential is approximated by a superposition of spherically symmetric atomic potentials, calculated relativistically by Libermann, Waber, and Cromer, from the self-consistent-field solutions of the Dirac equation. Exchange is treated by Slater's free-electron exchange approximation. The total Coulomb potential at any given lattice site is constructed from the Coulomb potential of the neutral atom at that lattice site plus the contributions from atoms in the neighboring lattice sites. In this work, these contributions were taken from atoms up to the 14th nearest neighbor shell. A list of these nearest neighbor atoms is given in Table 1. The contributions of the
<table>
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</table>
neighboring potentials is taken into account by expanding them about the origin by Löwdin's alpha-expansion formula. If 1 and 2 are two neighboring lattice sites separated by a distance $a$, then the contribution at $r_2$, measured from the origin at 2, due to a function $f(r_1)$ centered at the origin at 1 is given by

$$f(a|r_2) = \frac{1}{2a^2} \int_{|a-r_2|}^{a+r_2} r_1 f(r_1) dr_1 . \quad (\text{III.1})$$

Following the method outlined by Mattheiss, the Coulomb and exchange contributions to the potential are treated separately. The first step in obtaining the coulombic contribution is to calculate the electronic density

$$\rho_0(r) = \sum_{\text{occupied}} |\psi_{\ell m}|^2 , \quad (\text{III.2})$$

where the $\psi_{\ell m}$ are taken from the self-consistent-field calculations of Liberman et al. Having obtained $\rho_0(r)$, the electronic contribution to the Coulomb potential is given by $U_0(r)$ which is obtained from the solution to Poisson's equation,

$$\nabla^2 U_0(r) = -4\pi \rho_0(r) . \quad (\text{III.3})$$

The numerical method for solving (III.3) along with a Fortran subroutine is given in Ref. 22.
The Coulomb part of the potential then consists of contributions of the form

\[ V_0(r) = -\frac{2Z}{r} + U_0(r), \]  

(111.4)

where \( Z \) is the nuclear charge. The contributions from the neighboring lattice sites is obtained from Eq. (111.1). Finally, the total Coulomb potential at a given lattice site is given by

\[ V_c(r) = V_0(r) + \sum_{i=1}^{k} V_0(a_i | r), \]  

(111.5)

where \( k \) is the total number of neighboring atoms contributing to the muffin-tin potential at the given lattice site. The exchange part of the potential is calculated using a modified form of Slater's free-electron exchange formula in which the exchange potential \( V_{ex}(r) \) is given by

\[ V_{ex}(r) = -6 \frac{3}{8\pi} \rho(r) \epsilon, \]  

(111.6)

where \( \epsilon \) is some number \( \sim 2/3 \), and \( \rho(r) \) is the total charge density given by

\[ \rho(r) = \rho_0(r) + \sum_{i=1}^{k} \rho_0(a_i | r), \]  

(111.7)

where \( \rho_0(a_i | r) \) is obtained from Eq. (111.1).
The resultant muffin-tin potential, which is a combined contribution of the coulombic part (111.5) and exchange part (111.6), is given by

\[ V_T(r) = V_C(r) + V_{ex}(r) \]  

(111.8)

The constant potential in the interstitial region is obtained by averaging \( V_T(r) \) in the region between the muffin-tin spheres. In this work the averaging is accomplished by performing a spherical average of \( V_T(r) \) between the muffin-tin sphere and the Wigner-Seitz sphere. The Wigner-Seitz sphere is a sphere described about the lattice point whose volume is equal to the atomic volume. Thus the average potential in the interstitial region \( V_{int} \) is given by

\[ V_{int} = \frac{3}{r_0^3 - r_s^3} \int_{r_s}^{r_0} V_T(r) r^2 dr \]  

(111.9)

where \( r_s \) is the radius of the muffin-tin sphere, and \( r_0 \) the radius of the Wigner-Seitz sphere. The actual muffin-tin potential used in the computation is one in which the energy scale has been shifted so that the constant potential in the interstitial region is zero. Thus

\[ V(r) = V_T(r) - V_{int} \]  

(111.10)

Having obtained the muffin-tin potential (111.10), the next step is to solve the radial wave equation (11.40). Actually, the quantity
of interest which occurs in the APW matrix, Eq. (11.50), is the logarithmic derivative of the radial wavefunction evaluated on the muffin-tin sphere,

$$L_{\ell}(R_s, E) = R'_{\ell}(R_s)/R_{\ell}(R_s).$$  \hspace{1cm} (11.11)

The dependence of the logarithmic derivative on the energy eigenvalue $E$ is explicitly stated in Eq. (11.11). In principle, $L_{\ell}$ is required for all values of $\ell$ from zero to infinity. In this work $\ell$ values were taken from 0 up to 10. The numerical method along with a Fortran subroutine is given in Ref. 22. According to this scheme, the radial wave equation is solved by two methods. One is the Noumerov method, and the other is a composite of the Milne method and the Runge-Kutta method. The energy dependence of the logarithmic derivative by the Noumerov method is fitted to a 7th degree polynomial and the result is compared to the original Noumerov result and the Milne-Runge-Kutta result.

After the logarithmic derivatives are calculated, the APW matrix, Eq. (11.50), is set up. According to Eq. (11.46) the crystal wavefunction is to be expanded over a complete set of reciprocal lattice vectors. In practice, reasonable convergence of the energy eigenvalues is obtained for a BCC structure with the number of recips (reciprocal lattice vectors) $\sim$20-40. Ideally, the best set of recips $\{g_i\}$ for a point $\vec{R}$ in reciprocal space are those which minimize $|\vec{R} + g_i|$. It is rather cumbersome to choose a special set of recips for each point,
so in this computation a set of 43 recips were chosen which satisfied
the above criterion for the \( 1/48 \text{th} \) irreducible part of the Brillouin
zone as a whole. The Brillouin zone for a BCC lattice is shown in
Fig. 5. Also indicated in this figure is an irreducible zone. The
43 recips for the irreducible zone shown in Fig. 5 are listed in
Table 2. The choice of 43 recips was dictated by the following reasons.
The accuracy of the calculated energy eigenvalues increase as more
recips are used, especially for higher bands. In our calculations,
it was found that the first 26 recips of Table 2 were sufficient for
this purpose. We, however, chose 43 recips in order to expand the
crystal wavefunction in as complete a set of plane waves as possible.
This requirement is important for calculating the matrix elements
(Eq. (11.20)) for large values of \( \vec{q} \).

Energy eigenvalues were determined for a uniform mesh of 1024
points in the Brillouin zone by solving the APW matrix for roots.
Energies were actually obtained for 55 points in the irreducible zone.
The energies at all other points can be determined from these since

\[
E(\hat{R}\vec{k}) = E(R),
\]

where \( \hat{R} \) is a symmetry operation of the crystal. The point group con­
taining all 48 symmetry operations for a cubic structure is the group
\( O_h^{28} \). The symmetry for this group are listed in Table 3.

Once the energy eigenvalues have been determined, the APW expansion
coefficients \( \alpha_{\vec{k}} \) can be obtained for each root by solving the set
Fig. 5. Brillouin zone of a body-centered cubic (BCC) lattice. Shaded region represents a $1/48$th irreducible zone. Filled circles denote high-symmetry points and open circles denote high-symmetry directions.
Table 2. Set of 43 reciprocal lattice vectors for the 1/48th irreducible zone as a whole (Fig. 5). They are listed in order of importance (based on \(k+g\)), in units of \(2\pi/a\), where \(a\) is the lattice constant.

<table>
<thead>
<tr>
<th>Vector</th>
<th>Vector</th>
<th>Vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>((0 \ 0 \ 0))</td>
<td>((-1 \ -1 \ 0))</td>
<td>((0 \ -1 \ -1))</td>
</tr>
<tr>
<td>((-1 \ 0 \ -1))</td>
<td>((-2 \ 0 \ 0))</td>
<td>((-1 \ 1 \ 0))</td>
</tr>
<tr>
<td>((-1 \ 0 \ 1))</td>
<td>((0 \ -1 \ 1))</td>
<td>((1 \ 0 \ -1))</td>
</tr>
<tr>
<td>((1 \ -1 \ 0))</td>
<td>((0 \ 1 \ -1))</td>
<td>((1 \ 1 \ 0))</td>
</tr>
<tr>
<td>((1 \ 0 \ 1))</td>
<td>((0 \ 1 \ 1))</td>
<td>((0 \ -2 \ 0))</td>
</tr>
<tr>
<td>((-1 \ -1 \ -2))</td>
<td>((-1 \ -2 \ -1))</td>
<td>((-2 \ -1 \ -1))</td>
</tr>
<tr>
<td>((0 \ 0 \ -2))</td>
<td>((-2 \ 1 \ 1))</td>
<td>((-2 \ -1 \ 1))</td>
</tr>
<tr>
<td>((-2 \ 1 \ 1))</td>
<td>((-2 \ -1 \ 1))</td>
<td>((2 \ 0 \ 0))</td>
</tr>
<tr>
<td>((0 \ 2 \ 0))</td>
<td>((0 \ 0 \ 2))</td>
<td>((-2 \ -2 \ 0))</td>
</tr>
<tr>
<td>((-1 \ -1 \ 2))</td>
<td>((1 \ -1 \ -2))</td>
<td>((1 \ -2 \ -1))</td>
</tr>
<tr>
<td>((-1 \ 1 \ -2))</td>
<td>((0 \ -2 \ -2))</td>
<td>((-2 \ 0 \ -2))</td>
</tr>
<tr>
<td>((-3 \ 0 \ -1))</td>
<td>((-1 \ 2 \ -1))</td>
<td>((-3 \ -1 \ 0))</td>
</tr>
<tr>
<td>((-3 \ 1 \ 0))</td>
<td>((-2 \ 2 \ 0))</td>
<td>((-3 \ 0 \ 1))</td>
</tr>
<tr>
<td>((-1 \ 2 \ 1))</td>
<td>((-2 \ 0 \ 2))</td>
<td>((-1 \ 1 \ 2))</td>
</tr>
<tr>
<td>((1 \ -2 \ 1))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Operations of the group $0_h$. Additional 24 operators of this group are indicated by primed symbols, $\hat{R}_1', \ldots, \hat{R}_{24}'$, where each primed operation is identical with the corresponding unprimed operation except for an additional inversion. Thus $\hat{R}_1'f(x,y,z) = f(-x,-y,-z)$, etc.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Description</th>
<th>Operation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hat{R}_1 f(x,y,z)$</td>
<td>$f(x,y,z)$</td>
<td>$\hat{R}_{13} f(x,y,z)$</td>
<td>$f(-x,z,-y)$</td>
</tr>
<tr>
<td>$\hat{R}_2 f(x,y,z)$</td>
<td>$f(x,-y,-z)$</td>
<td>$\hat{R}_{14} f(x,y,z)$</td>
<td>$f(-x,-z,y)$</td>
</tr>
<tr>
<td>$\hat{R}_3 f(x,y,z)$</td>
<td>$f(-x,y,-z)$</td>
<td>$\hat{R}_{15} f(x,y,z)$</td>
<td>$f(-z,-y,x)$</td>
</tr>
<tr>
<td>$\hat{R}_4 f(x,y,z)$</td>
<td>$f(-x,-y,z)$</td>
<td>$\hat{R}_{16} f(x,y,z)$</td>
<td>$f(z,-y,-x)$</td>
</tr>
<tr>
<td>$\hat{R}_5 f(x,y,z)$</td>
<td>$f(y,z,x)$</td>
<td>$\hat{R}_{17} f(x,y,z)$</td>
<td>$f(y,-x,-z)$</td>
</tr>
<tr>
<td>$\hat{R}_6 f(x,y,z)$</td>
<td>$f(-y,z,-x)$</td>
<td>$\hat{R}_{18} f(x,y,z)$</td>
<td>$f(-y,x,-z)$</td>
</tr>
<tr>
<td>$\hat{R}_7 f(x,y,z)$</td>
<td>$f(-y,-z,x)$</td>
<td>$\hat{R}_{19} f(x,y,z)$</td>
<td>$f(x,z,y)$</td>
</tr>
<tr>
<td>$\hat{R}_8 f(x,y,z)$</td>
<td>$f(y,-z,-x)$</td>
<td>$\hat{R}_{20} f(x,y,z)$</td>
<td>$f(x,-z,-y)$</td>
</tr>
<tr>
<td>$\hat{R}_9 f(x,y,z)$</td>
<td>$f(z,x,y)$</td>
<td>$\hat{R}_{21} f(x,y,z)$</td>
<td>$f(z,y,x)$</td>
</tr>
<tr>
<td>$\hat{R}_{10} f(x,y,z)$</td>
<td>$f(-z,-x,y)$</td>
<td>$\hat{R}_{22} f(x,y,z)$</td>
<td>$f(-z,y,-x)$</td>
</tr>
<tr>
<td>$\hat{R}_{11} f(x,y,z)$</td>
<td>$f(z,-x,-y)$</td>
<td>$\hat{R}_{23} f(x,y,z)$</td>
<td>$f(y,x,z)$</td>
</tr>
<tr>
<td>$\hat{R}_{12} f(x,y,z)$</td>
<td>$f(-z,x,-y)$</td>
<td>$\hat{R}_{24} f(x,y,z)$</td>
<td>$f(-y,-x,z)$</td>
</tr>
</tbody>
</table>
of linear equations given by Eq. (11.50). Since the secular determinant of the APW matrix is known to be zero at these points, non-trivial solutions must exist.

**Dielectric Function**

In order to calculate the dielectric function $\varepsilon^*(q,\omega)$ it is necessary to perform a three-dimensional integration over $\mathbf{k}$-space as can be seen from Eq. (11.25), where $\varepsilon^*(q,\omega)$ is expressed as a sum over $\mathbf{k}$-space. None of the quantities appearing in the sum can be expressed analytically; hence, the integration has to be performed numerically. The technique chosen in this work is to divide $\mathbf{k}$-space into a uniform mesh of points, evaluate the summand in Eq. (11.25) at each mesh point and sum over all of $\mathbf{k}$-space. In the reduced-zone scheme the energy eigenvalues and the wavefunctions are folded back into the first Brillouin zone to form the various bands. It is necessary then to perform the sum over the volume of the Brillouin zone and over all bands in practice reasonable convergence is obtained by summing over a limited number of low-lying bands. The accuracy of the sum depends on how fine a mesh is chosen. The energy bands and wavefunctions were calculated from the APW matrix only for a coarse mesh of 1024 points in the Brillouin zone. This corresponds to 8 points along each axis in $\mathbf{k}$-space and is clearly inadequate for a numerical integration. Increasing the mesh size by even a factor of 8 made the calculation of energy bands by the APW matrix too expensive and time consuming. It therefore became necessary to generate energy eigenvalues and matrix
elements on a finer mesh by some interpolation scheme. The method chosen for this purpose was the "spline interpolation" technique. Spline interpolation is a third-degree polynomial interpolation in which the curve connecting the points, its slope and its curvature are all kept continuous everywhere.

Consider a set of points \((x_1, y_1), (x_2, y_2), \ldots, (x_m, y_m)\), arranged in order of increasing values of \(x\). Let segments of a third-degree polynomial connect these points in a manner such that the first and second derivatives are continuous at each point. Let \(g_1, g_2, \ldots, g_m\) be the values of the second derivative at the points. Then by linear interpolation, the value of the second derivative at \((x, y)\) between the points \((x_k, y_k)\) and \((x_{k+1}, y_{k+1})\) is given by

\[
y'' = g_k \frac{x_{k+1} - x}{\Delta_k} + g_{k+1} \frac{x - x_k}{\Delta_k},
\]

where \(\Delta_k = x_{k+1} - x_k\).

Upon integrating Eq. (111.12) we obtain

\[
y' = -g_k \left[ (x_{k+1} - x)^2/2\Delta_k \right] + g_{k+1} \left[ (x - x_k)^2/2\Delta_k \right] + c_1,
\]

where \(c_1\) is a constant of integration. Integrating again yields the equation of the curve,

\[
y = g_k \left[ (x_{k+1} - x)^3/6\Delta_k \right] + g_{k+1} \left[ (x - x_k)^3/6\Delta_k \right] + c_1 x + c_2,
\]
where \( c_2 \) is a constant of integration. Upon using the boundary conditions on the curve at \( (x_k, y_k) \) and \( (x_{k+1}, y_{k+1}) \) we find

\[
c_1 = \left[ \frac{(y_{k+1} - y_k)}{\Delta_k} \right] - \left[ \frac{(g_{k+1} - g_k)}{\Delta_k} \right], \quad (\text{111.15})
\]

and

\[
c_2 = \left[ \frac{(y_k x_{k+1} - y_{k+1} x_k)}{\Delta_k} \right] - \left[ \frac{(g_k x_{k+1} - g_{k+1} x_k)}{\Delta_k} \right]. \quad (\text{111.16})
\]

After substituting these into Eq. (111.14) we obtain the equation of the curve,

\[
y = \left[ g_k (x_{k+1} - x)^3 / 6\Delta_k \right] + \left[ g_{k+1} (x - x_k)^3 / 6\Delta_k \right] + \left[ (x_{k+1} - x) (y_k / \Delta_k - g_k \Delta_k / 6) \right],
\]

\[
+ \left[ (x - x_k) (y_{k+1} / \Delta_k - g_{k+1} \Delta_k / 6) \right]. \quad (\text{111.17})
\]

All quantities in this equation are known except \( g_k \) and \( g_{k+1} \). These can be determined by imposing the continuity conditions on the slope. In other words, the slope at \( (x_k, y_k) \) as determined by the curve between the points \( (x_{k+1}, y_{k+1}) \) and \( (x_k, y_k) \) must be the same as the one determined by the curve between the points \( (x_k, y_k) \) and \( (x_{k-1}, y_{k-1}) \). Imposing this condition on Eq. (111.13) with \( c_1 \) given by Eq. (111.15) we have

\[
g_{k-1} (\Delta_{k-1} / 6) + g_k \left[ (\Delta_{k-1} + \Delta_k) / 3 \right] + g_{k+1} (\Delta_k / 6)
\]

\[
= \left[ \frac{(y_{k+1} - y_k)}{\Delta_k} \right] - \left[ \frac{(y_k - y_{k-1})}{\Delta_{k-1}} \right]. \quad (\text{111.18})
\]
There are \( m-2 \) such equations for \( k = 2, \ldots, m-1 \). We are thus confronted with a set of \( m-2 \) simultaneous linear equations and \( m \) unknowns. Additional boundary conditions are then required to obtain the values of \( g_1 \) and \( g_m \), the slopes at the end points. The choice of these additional conditions will be dictated by the nature of the particular application. In the present problem spline interpolation will be applied to determine energy eigenvalues on a given band inside the Brillouin zone. Since it is imperative that energy bands have zero slope at the zone boundaries, we choose \( g_1 \) and \( g_m \) to be zero. Hence the set of \( m-2 \) equations, (111.18) along with the boundary conditions

\[
g_1 = 0, \quad g_m = 0, \quad (111.19)
\]

provide all values for \( g_k, k = 1, \ldots, m \). Eq. (111.17) along with Eqs. (111.18) and (111.19) provide the formalism of spline interpolation.

The mesh of 1024 points in the Brillouin zone is produced by dividing each of the axes, \( k_x, k_y, \) and \( k_z \) (see Fig. 5) of length \( 2\pi/a \) into 8 equal parts. Here \( a \) is the lattice constant. This can be further expanded into a mesh of 1024,000 points in the Brillouin zone by dividing each segment of length \( \pi/4a \) into 10 equal divisions. The energy eigenvalues for points on the finer mesh were found from the ones in the coarser mesh by spline interpolation.

In the performance of the actual computation it was not found feasible to store energy eigenvalues for 1024,000 points in the
memory core of the computer. Hence the following technique was devised.

The energy eigenvalues were generated on a mesh of 512,000 points in a cubic region of \( \mathbf{k} \)-space defined by \( 0 \leq k_x \leq 2\pi/a, \)
\( 0 \leq k_y \leq 2\pi/a, \)
\( 0 \leq k_z \leq 2\pi/a. \) This is shown in Fig. 6. The \( 1/48 \)th irreducible zone shown in Fig. 6 and used in the computation is defined by

\[
\begin{align*}
  k_x < \frac{2\pi}{a}, & \quad k_y < \frac{2\pi}{a}, \quad k_z < \frac{\pi}{a}, \quad k_x + k_y < \frac{2\pi}{a}, \\
  k_y + k_z < \frac{2\pi}{a}, & \quad k_z + k_x < \frac{2\pi}{a}, \quad k_x + k_y + k_z < \frac{3\pi}{a}.
\end{align*}
\]

It is easy to show that every point in the cubic zone is connected to some point in the irreducible zone by a symmetry operation of the crystal.

Initially a mesh of 512 points is generated in the cubic zone by dividing each of the axes into 8 equal segments. The energy eigenvalues are known for all points in this mesh since they are known in the irreducible zone. Each segment of length \( \pi/4a \) along the \( k_z \)-axis is now divided further into 10 equal segments. The energy eigenvalues on the 81 new points are then determined from the 9 old points by spline interpolation. Planes perpendicular to the \( k_z \)-axis are now drawn through each of these points so that the cubic zone is chopped up into a series of 81 parallel planes each defined by the particular value of \( k_z \), and by
Fig. 6. Cubic region of $\mathbf{R}$-space used in the performance of $\mathbf{R}$-space summation. Shaded area representing the $\frac{1}{48}$th irreducible zone.
\[ 0 \leq k_x \leq 2\pi/a, \quad 0 \leq k_y \leq 2\pi/a. \]

Each of these squares are now segmented into a mesh of 81 x 81 points. The energy eigenvalues at each of these points is determined by spline interpolation. If the wave vector \( \vec{q} \) in \( E(q,\omega) \) is taken to be in the \((k_x,k_y)\) plane, then for any value of \( \vec{k} \) lying in a given plane, \( \vec{k} + \vec{q} \) lies in the same plane. In performing the computation, it is then necessary to store the energy eigenvalues for only one plane at a time in the core, thereby reducing the core usage drastically and making the computation feasible. The spline-interpolated energy eigenvalues are stored on magnetic tape, one plane per record for each band. Actually, the information is stored only for the first 41 planes. The others are identical to these through symmetry considerations.

Once the energy bands are obtained, the Fermi energy can be calculated. Two different methods can be used for computing the Fermi Energy, \( E_F \). One method consists in counting the filled states in the Brillouin zone. Both Na and K have one atom per unit cell which contributes one conduction electron. Hence in these crystals the first energy band is exactly half-filled, i.e., the first Brillouin zone is half-filled. The technique for determining the Fermi energy consists in counting states until half the Brillouin zone is filled. The energy in the first band corresponding to this state is the Fermi energy. This was done by first evaluating the density of states for the first band. The density of states

\[ D(E) = \frac{dN(E)}{dE} \]
gives the number of states per unit energy per atom. The Fermi energy was then obtained from

\[ \int_0^{E_F} D(E) dE = 1. \]

The second method is based on the assumption that the Fermi surfaces for Na and K are essentially spherical. Now, the volume of the Fermi sphere must be half the volume of the Brillouin zone, which is given by

\[ V_{BZ} = \frac{(2\pi)^3}{\nu_c}, \]

where \( \nu_c = a^3/2 \) for a BCC lattice. Then, assuming the Fermi surface to be perfectly spherical, one has

\[ \frac{4}{3} \pi k_F^3 = \frac{2}{3} V_{BZ}. \]

Therefore,

\[ k_F = \left( \frac{6\pi^2}{a} \right)^{1/3}. \quad (111.20) \]

In this work, the Fermi energy obtained by the first method was fed into the APW matrix to test if it yielded the free-electron Fermi wave-vector for all directions in \( \overrightarrow{k} \)-space. Results are given and discussed in Chapter IV.
In calculating the density of states, the states were counted in the cubic zone shown in Fig. 6. Points inside the zone were assigned the weight 1, on zone faces the weight was $\frac{1}{2}$, on zone edges $\frac{1}{4}$, and on zone corners $\frac{1}{8}$.

The wave vector $\vec{q}$ in $\epsilon_{(q, \omega)}$ was chosen to lie in the $(k_x, k_y)$ plane. To illustrate the technique consider $\vec{q}$ to lie along $k_y$. For this particular geometry the region in $k$-space that must be summed over is shown in Fig. 7. Energy eigenvalues in the region ABGDE were obtained by symmetry considerations from those in the corresponding region ACGDF. However, the matrix elements $M_{k,q}^{k+q}$ (Eq. (11.20)) were calculated explicitly in both regions. The matrix elements were calculated only over the coarse mesh of 1024 points in the Brillouin zone. These matrix elements were used in performing the sum over the fine mesh. This is a reasonable approximation since the matrix elements are, in general, slowly varying functions of $\vec{q}$.

In calculating the matrix elements, the wavefunctions were taken to be linear combinations of plane waves,

$$
\psi_K(\vec{r}) = \sum_{i=1}^{M} \alpha_k^{\vec{g}_i} e^{i(\vec{k}+\vec{g}_i) \cdot \vec{r}},
$$

(111.21)

where $M$ is the number of reciprocals being used in the calculation, and the plane-wave coefficients $\alpha_k^{\vec{g}_i}$ are known for 55 points in the irreducible zone from the solutions of the APW matrix equation (Eq. (11.50)).

From Eq. (11.20) the matrix element is defined as
Fig. 7. The prism defined by ABCDEF is the region in \( \mathbf{k} \)-space used in the summation when \( \mathbf{q} \) lies along \( k_y \). The cubes are of dimension \( 2\pi/a \) and the prism height is \( \pi/a \).
\[ M_{\ell, \ell', \mathbf{k} + \mathbf{q}} = \frac{1}{\nu_c} \int_{\nu_c} d^3 r \ u_{\ell, \mathbf{k}}^*(r) u_{\ell', \mathbf{k} + \mathbf{q}, l}(r), \quad (111.22) \]

where

\[ u_{\ell, \mathbf{k}}(r) = \sum_{i=1}^{M} \alpha_{\ell, k} \mathbf{g}_i e^{i\mathbf{g}_i \cdot r}. \quad (111.23) \]

Then from Eqs. \((111.22)\) and \((111.23)\)

\[ M_{\ell, \ell', \mathbf{k} + \mathbf{q}} = \frac{1}{\nu_c} \sum_i \sum_j \alpha_{\ell, k} \alpha_{\ell', \mathbf{k} + \mathbf{q}, l'} \int_{\nu_c} d^3 r e^{-i\mathbf{g}_i \cdot r} e^{i\mathbf{g}_j \cdot r}, \]

or

\[ M_{\ell, \ell', \mathbf{k} + \mathbf{q}} = \sum_i \alpha_{\ell, k} \alpha_{\ell', \mathbf{k} + \mathbf{q}, l'} \mathbf{g}_i. \quad (111.24) \]

While computing \( M_{\ell, \ell', \mathbf{k} + \mathbf{q}} \) from Eq. \((111.24)\), it may happen that the point \( \mathbf{k} + \mathbf{q} \) lies outside the irreducible zone where the plane-wave coefficients are unknown. These may then be calculated by the following procedure.

Consider the wavefunction \((111.21)\), where the point \( \mathbf{k} \) lies within the irreducible zone. If we now apply a symmetry operation \( \hat{R} \) of the appropriate point group of the crystal, then

\[ \psi_{\ell, \mathbf{k}}(\mathbf{r}) = \sum_i e^{i(\mathbf{R} \mathbf{k} + \mathbf{g}_i) \cdot \mathbf{r}} \alpha_{\ell, \mathbf{k}} \mathbf{g}_i. \quad (111.25) \]
There is a theorem\textsuperscript{7} for Bloch functions which states: "If $\psi_{rK}(r)$ is a solution of the wave equation, then $\psi_{rK}(R^{-1}r)$ is also a solution with the same eigenvalue." Hence, $\psi_{rK}(r)$ and $\psi_{rK}(R^{-1}r)$ will differ at the most by a phase factor, which is of no consequence for the evaluation of matrix elements for this particular application (see Eqs. (11.10) and (11.20)). Now

$$\psi_{rK}(R^{-1}r) = \sum_i \alpha_{rK} e^{i(R + \theta \vec{g}_i) \cdot \vec{r}} \vec{g}_i$$

Let $\hat{\theta} \vec{g}_i = \vec{g}_j$, where $\vec{g}_j$ is some reciprocal lattice vector belonging to the complete set. Hence $\vec{g}_i = R^{-1} \vec{g}_j$, and hence,

$$\psi_{rK}(R^{-1}r) = \sum_i \alpha_{rK} e^{i(R + \hat{\theta} \vec{g}_i) \cdot \vec{r}} R^{-1} \vec{g}_i$$

According to the theorem stated above

$$\psi_{rK}(r) = \psi_{rK}(R^{-1}r).$$

Hence from Eqs. (11.25) and (11.26) we have

$$\alpha_{rK} \vec{g}_i = \alpha_{rK} R^{-1} \vec{g}_i$$

(11.27)
Consider now the effect of adding a reciprocal lattice vector \( \mathbf{G} \) to a point \( \mathbf{k} \) inside the Brillouin zone. Starting again with the wavefunction given by Eq. (111.21), we have

\[
\psi_{\mathbf{k}+\mathbf{g}+\mathbf{G}}(\mathbf{r}) = \sum_i e^{i(\mathbf{k}+\mathbf{g}+\mathbf{G}) \cdot \mathbf{r}} \hat{\alpha}_{\mathbf{k}+\mathbf{g}+\mathbf{G}}^{(i)} \cdot \mathbf{g}_j.
\]

In Eq. (111.21) the recip \( \mathbf{g}_j \) can be written as

\[
\mathbf{g}_j = \mathbf{g}_j + \mathbf{G},
\]

since \( \{\mathbf{g}_j\} \) forms a complete set, and any reciprocal lattice vector such as \( \mathbf{G} \) must belong to this set. Hence,

\[
\psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \sum_i e^{i(\mathbf{k}+\mathbf{g}_j+\mathbf{G}) \cdot \mathbf{r}} \hat{\alpha}_{\mathbf{k}+\mathbf{G}}^{(i)} \cdot \mathbf{g}_j + \mathbf{G}.
\]

We know from the properties of Bloch functions that \( \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \) and \( \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) \) are both solutions of the wave equation with the same eigenvalues. Hence, as in the previous case, we have

\[
\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}).
\]

Then from Eqs. (111.23) and (111.29),

\[
\hat{\alpha}_{\mathbf{k}+\mathbf{G}}^{(i)} \cdot \mathbf{g}_j = \hat{\alpha}_{\mathbf{k}}^{(i)} \cdot \mathbf{g}_j + \mathbf{G} \quad (111.30)
\]
Eqs. (11.27) and (11.30) provide the means for determining the plane-wave coefficients at any point in $\overline{k}$-space, provided they are known in the irreducible zone. It may be pointed out that the assumption of completeness for the set of recips is never rigorously met in practice. However, if the value of $\overline{q}$ is not taken to be too large, the error introduced is small.

Using the above procedure the matrix elements were evaluated in a region of $\overline{k}$-space defined by $0 \leq k_x \leq 2\pi/a$, $-2\pi/a \leq k_y \leq 2\pi/a$, $0 \leq k_z \leq \pi/a$. These matrix elements were then stored on magnetic tape.

Once the energy eigenvalues and matrix elements are known, $\varepsilon_{\tau} (\overline{q}, \omega)$ can be easily evaluated by application of Eq. (11.25). After the sum is performed, the result has to be multiplied by a statistical weight factor. This weight factor is proportional to the number of states in each small cell in $\overline{k}$-space and can be evaluated in the following way.

Let $N$ be the number of unit cells in the crystal, and let $v$ be the volume. Then the volume of a unit cell $v_c = v/N$, and the Brillouin zone volume is $8\pi^2/v_c$. Now, the number of $\overline{k}$-vectors inside the Brillouin is equal to the total number of unit cells in the crystal. Hence, the volume occupied by a single wave vector in $\overline{k}$-space is

$$\frac{1}{N} \frac{8\pi^3}{v_c}.$$
Therefore the number of wave vectors per unit volume of \( \mathbf{k} \)-space is

\[ N_{v}/8\pi^3 = v/8\pi^3 \].

Since there are 2 spin states corresponding to each \( \mathbf{k} \)-vector, the number of states per unit volume of \( \mathbf{k} \)-space is \( 2v/8\pi^3 \).

For a mesh size of \( M_s \) points in the Brillouin zone, the volume of each small cell in \( \mathbf{k} \)-space is

\[ \frac{1}{M_s} \frac{8\pi^3}{v_c} \].

Then the total number of states \( N_s \) in each small cell is

\[ N_s = \frac{1}{M_s} \frac{8\pi^3}{v_c} \times \frac{2v}{8\pi^3} = \frac{1}{M_s} \frac{2v}{v_c} \].

Fig. 7 shows the volume in \( \mathbf{k} \)-space to be summed over when \( \mathbf{q} \) is taken in the symmetry direction \( \Delta(\Gamma-H) \). This volume is \( \frac{1}{2}(2\pi/a)^3 \) and is \( 1/4 \)th the Brillouin-zone volume. Hence the required statistical weight is

\[ \text{Statistical weight} = 4 \times N_s = \frac{16v}{M_s a^3} \].

When \( \mathbf{q} \) is taken along the symmetry direction \( \Sigma(\Gamma-N) \), (see Fig. 5), the volume in \( \mathbf{k} \)-space to be summed over is twice the volume shown in Fig. 7. Consequently, for this case the statistical weight is given by

\[ \text{Statistical weight} = 2 \times N_s = \frac{8v}{M_s a^3} \].
The effectiveness of the mesh summation was put to test by calculating the free-electron Lindhard dielectric function for finite electron life-times. This was accomplished by comparing the Lindhard dielectric function as given by the closed form expression in Eq. (11.27) with the results of mesh summation. The results are presented in Figs. 8, 9, and 10. It can be seen from Figs. 8 and 9, that although the results of Eq. (11.27) vary considerably from the mesh summation results at small values of $\Omega$, the agreement is considerably better at higher values of $\Omega$. It can also be seen from Figs. 8 and 10, that the peak in $\text{Im}(-1/\varepsilon_{\omega})$, which, according to the definition in this work, locates the plasmon, occurs at the high $\Omega$ side where $\text{Re}(\varepsilon_{\omega})$ crosses the axis. In this region the mean deviation between the results of Eq. (11.27) and those of the mesh calculation for $\text{Re}(\varepsilon_{\omega})-1$ is $\sim 5\%$. It can be seen from Fig. 8 that in $\text{Re}(\varepsilon_{\omega})$ the results for $M_5 = 128,000$ do not differ very much from the results for $M_5 = 1024,000$. This can also be seen from Fig. 10 where the peak positions for both mesh sizes are almost identical. It therefore seems reasonable to use $M_5 = 128,000$ in the calculations. Peak positions depend very sensitively on the location of the zero of $\text{Re}(\varepsilon_{\omega})$. Slight deviations in this quantity can cause the position of the plasmon peak to shift significantly.

The $5\%$ deviation in the values of $\text{Re}(\varepsilon_{\omega})-1$ between the results of Eq. (11.27) and those of the mesh calculation were found to persist for higher values of $Q$ in the frequency region where $\text{Re}(\varepsilon_{\omega}) \sim 0$. Hence, the mesh summation introduces a $5\%$ error in the value of $\text{Re}(\varepsilon_{\omega})-1$. 

Fig. 8. $\text{Re}[\epsilon_\Omega (Q, \Omega)]$ as a function of $\Omega$ at $Q = 60.67$, evaluated from the closed form expression for the free-electron Lindhard dielectric function as given by Eq. (11.27), and by summing over a mesh of 128,000 points and 1,024,000 points in the Brillouin zone. Parameters used are for sodium.
Fig. 9. $\text{Im}[\epsilon_j(Q, \Omega)]$ as a function of $\Omega$ at $Q = 60.67$, evaluated from the closed form expression for the free-electron Lindhard dielectric function as given by Eq. (II.27), and by summing over a mesh of 128,000 points and 1024,000 points in the Brillouin zone. Parameters used are for sodium.
Fig. 10. $\text{Im}\left(-\frac{1}{\varepsilon_{ij}}(Q,\Omega)\right)$ as a function of $\Omega$ at $Q = 60.67$, evaluated from the closed form expression for the free-electron Lindhard dielectric function as given by Eq. (II.27) and by summing over a mesh of 128,000 and 1,024,000 points in the Brillouin zone. Parameters used are for sodium.
CHAPTER IV. RESULTS AND DISCUSSION

Potassium

The APW energy bands for potassium along high-symmetry directions are shown in Fig. 11. The free-electron energy bands for an empty BCC lattice are shown in Fig. 12. Comparing these two figures we see that the crystal potential removes the degeneracies from all the free-electron bands except \( \Delta_5 \). The effect of band splitting, along the symmetry directions \( \Delta \) and \( \Sigma \), on the plasmon dispersion curve, will be discussed later in this section.

In the calculation of the dielectric function we have ignored the presence of the core levels, since the highest core level in potassium, \( M_{\text{II}, \text{III}} \), is \( 17.8 \pm 0.4 \text{ eV} \) below the Fermi level. The plasma frequency for potassium is \( \sim 4 \text{ eV} \), and we shall not be interested in transitions involving energies \( \gtrsim 8 \text{ eV} \).

For the highest value of the wave vector \( (q \sim 6\pi/4a) \) used in the calculation of the dielectric function, it was found that the sum in Eq. (11.25) converged to within the limits of the desired accuracy by using the six bands presented in Table 4. No change was observed in the position of the plasmon peak when nine bands were used. The bands presented in Table 4 correspond roughly to the bands shown in Fig. 11 for energies up to \( \sim 800 \text{ rydbergs} \).

The lattice constant for potassium at \( 5^\circ\text{K} \), as quoted by Pearson, is \( 9.874 \text{ (a.u.)} \). This value has been used in our calculations. The change in molar volume in going from \( 0^\circ\text{K} \) to \( 80^\circ\text{K} \) is \( \sim 1\% \).
Fig. 11. Energy bands for potassium along high-symmetry directions. Energies are measured with respect to the constant potential in the interstitial region, $V_{\text{int}} = -0.401$ rydbergs. Lattice constant $= 9.874$ (atomic units)
Fig. 12. Free-electron energy bands for an empty BCC lattice
Table 4. First six APW energy bands for potassium. Energies are given in rydbergs with respect to $V_{\text{int}} = -0.401$ ryd. Lattice constant = 9.874 (a.u.)

<table>
<thead>
<tr>
<th>$(4a/\pi)^{\Gamma} \kappa$</th>
<th>Band 1</th>
<th>Band 2</th>
<th>Band 3</th>
<th>Band 4</th>
<th>Band 5</th>
<th>Band 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>0.031</td>
<td>0.558</td>
<td>0.558</td>
<td>0.558</td>
<td>0.625</td>
<td>0.625</td>
</tr>
<tr>
<td>(0 0 0)</td>
<td>0.039</td>
<td>0.545</td>
<td>0.545</td>
<td>0.563</td>
<td>0.587</td>
<td>0.633</td>
</tr>
<tr>
<td>(1 0 0)</td>
<td>0.062</td>
<td>0.522</td>
<td>0.522</td>
<td>0.522</td>
<td>0.578</td>
<td>0.655</td>
</tr>
<tr>
<td>(2 0 0)</td>
<td>0.098</td>
<td>0.461</td>
<td>0.495</td>
<td>0.495</td>
<td>0.602</td>
<td>0.684</td>
</tr>
<tr>
<td>(3 0 0)</td>
<td>0.146</td>
<td>0.409</td>
<td>0.478</td>
<td>0.478</td>
<td>0.603</td>
<td>0.635</td>
</tr>
<tr>
<td>(4 0 0)</td>
<td>0.200</td>
<td>0.368</td>
<td>0.469</td>
<td>0.469</td>
<td>0.533</td>
<td>0.673</td>
</tr>
<tr>
<td>(5 0 0)</td>
<td>0.256</td>
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<td>0.467</td>
<td>0.467</td>
<td>0.485</td>
<td>0.713</td>
</tr>
<tr>
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<td>0.467</td>
<td>0.467</td>
<td>0.467</td>
<td>0.667</td>
</tr>
<tr>
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<td>0.315</td>
<td>0.469</td>
<td>0.469</td>
<td>0.469</td>
<td>0.636</td>
</tr>
<tr>
<td>H</td>
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<td></td>
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<td></td>
</tr>
<tr>
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<td>0.571</td>
<td>0.604</td>
<td>0.615</td>
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<tr>
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<td>0.566</td>
<td>0.587</td>
<td>0.643</td>
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<td>0.488</td>
<td>0.525</td>
<td>0.611</td>
<td>0.678</td>
</tr>
<tr>
<td>(3 1 0)</td>
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<td>0.473</td>
<td>0.492</td>
<td>0.620</td>
<td>0.643</td>
</tr>
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<td>0.463</td>
<td>0.466</td>
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<td>0.491</td>
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<td>Band 2</td>
<td>Band 3</td>
<td>Band 4</td>
<td>Band 5</td>
<td>Band 6</td>
</tr>
<tr>
<td>-----------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
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<td>0.615</td>
<td>0.660</td>
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<tr>
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<td>0.507</td>
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<td>0.615</td>
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<td>0.462</td>
<td>0.556</td>
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<td>0.615</td>
<td>0.659</td>
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<td>0.399</td>
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<td>0.304</td>
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<td>0.679</td>
</tr>
<tr>
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<td>0.308</td>
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<td>0.534</td>
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<tr>
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<tr>
<td>((\frac{4a}{\pi})^k)</td>
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<td>Band 2</td>
<td>Band 3</td>
<td>Band 4</td>
<td>Band 5</td>
<td>Band 6</td>
</tr>
<tr>
<td>----------------------</td>
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<td>0.418</td>
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<td>0.646</td>
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<td>0.612</td>
<td>0.687</td>
</tr>
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<td>0.354</td>
<td>0.595</td>
<td>0.595</td>
<td>0.650</td>
</tr>
<tr>
<td>((6 2 2))</td>
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<td>0.291</td>
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<td>0.584</td>
<td>0.636</td>
</tr>
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<td>0.544</td>
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<td>0.691</td>
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</tr>
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<td>0.697</td>
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<td>0.686</td>
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<td>0.681</td>
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<td>0.290</td>
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</tr>
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<td>((4 4 3))</td>
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<td>0.343</td>
<td>0.472</td>
<td>0.693</td>
<td>0.702</td>
</tr>
<tr>
<td>(P)</td>
<td>0.309</td>
<td>0.309</td>
<td>0.309</td>
<td>0.444</td>
<td>0.703</td>
<td>0.703</td>
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</table>
The energy eigenvalues were calculated by solving the determinant obtained from the APW matrix (Eq. (11.30)). The computer program used for this calculation was designed to compute the roots of this secular determinant by an iterative procedure, which yielded energy eigenvalues that converged to within .001 rydbergs. To achieve a certain measure of confidence in these calculated bands, a comparison was made with the calculations of Yamashita, Wakoh, and Asano, in which the APW bands for potassium were computed using Callaway's potential with a lattice parameter of 9.826 (a.u.). Observe that the lattice parameter used in Ref. 33 is lower than the one used in this work. The energy eigenvalues calculated in the present work are listed in Table 5, along with those of Ref. 33, for certain symmetry points. It can be seen from this table that the agreement, considering the fact that different lattice parameters and potentials were used, is excellent. Since most of the energy eigenvalues used in the computation of the dielectric function are the spline-interpolated energies, it was necessary to obtain an estimate of the error introduced by the interpolation scheme. This was accomplished by comparing the spline-interpolated energies with those obtained from the APW matrix for a random sample of points in \( \mathbf{k} \)-space. The maximum error was 0.004 rydbergs. We consider this to be the accuracy to which the energy eigenvalues are known. In performing the spline interpolation no account was taken of band-crossings along high symmetry directions. The error introduced by this procedure is expected to be small, since band-crossings are few in number and take place only along high-symmetry directions.
Table 5. Energy bands for potassium at some symmetry points from Ref. 33 and from the present work. Energies are in rydbergs with respect to $\Gamma_1$.

<table>
<thead>
<tr>
<th>(4a/$\pi$)R</th>
<th>Energy (rydbergs)</th>
<th>Yamashita et al.</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$ (0 0 0)</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>$\Gamma_{25}$ (0 0 0)</td>
<td>0.500</td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>$\Gamma_{12}$ (0 0 0)</td>
<td>0.569</td>
<td>0.594</td>
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<td>$N'_1$ (4 4 0)</td>
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<tr>
<td>$P_4$ (4 4 4)</td>
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<td>0.279</td>
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</table>
The Fermi energy $E_F$ was determined using the first method described in Chapter III, i.e., from the density of states, and is $E_F = 0.167$ rydbergs, where the zero of energy is taken at $\Gamma_1$. This value of $E_F$ was fed into the APW matrix to determine the Fermi wavevector $k_F$ and the nature of the Fermi surface. Within the limits of error to which the energy eigenvalues are known, the Fermi surface of potassium was found to be spherical and $k_F$ was found to correspond to the free electron value of 0.395 in atomic units, or 0.746 $\text{Å}^{-1}$.

The free-electron plasma frequency $\omega_p$ as determined from the free-electron Fermi wave vector and the free-electron mass $m_e$ is

$$\omega_p = 4.394 \text{ eV}.$$ 

This plasma frequency will be used to scale the free-electron plasmon dispersion curves for potassium. Fig. 13 shows the plasmon dispersion curves and the single-particle excitation regions in a free-electron gas of density corresponding to that of potassium. The curve labeled Lindhard was obtained using the finite lifetime Lindhard dielectric function, Eq. (11.27). The curve labeled Boltzmann was obtained using the Boltzmann dielectric function, Eq. (11.30). The single-particle excitation region shown in Fig. 13 between the curves

$$\Omega = (\hbar \omega_p / 2m_e c^2)(Q^2 + 2 k_F Q)$$

is that for the SCF description. It was shown in Chapter II that in the semi-classical, i.e., the Boltzmann description of the electron gas, plasmons could propagate without Landau damping for $\Omega > v_F/Q$. This boundary is also shown in
Fig. 13. Plasmon dispersion relations for a free-electron gas with parameters for potassium. The region between the two parabolas,

$$\Omega = \frac{\hbar \omega}{2m_e c} \left( Q^2 + 2k_F Q \right),$$

defines the region in which single-particle excitations can occur in the SCF description. The line

$$\Omega = \frac{\nu_F}{c} Q$$

denotes the boundary to the right of which Landau damping can occur in the semi-classical or the Boltzmann limit. The dotted line

$$\Omega^2 = 1 + \frac{3}{5} \left( \frac{\nu_F}{c} \right)^2 Q^2,$$

is the extension of the small $Q$ behavior of the Lindhard and the Boltzmann plasmon dispersion relations.
\[ \Omega^2 = 1 + \frac{3}{5} (V_F/c)^2 q^2 \]

\[ \Omega = \frac{\hbar \omega_p}{2 m_e c^2} (q^2 - 2K_F q) \]

\[ \Omega = \frac{V_F}{c} q \]

\[ \Omega = \frac{\hbar \omega_p}{2 m_e c^2} (q^2 + 2K_F q) \]
Fig. 13. Note that in the Boltzmann description, the single-particle excitation region corresponds to $\Omega \leq v_F/c$ Q. A damping factor, $\gamma = 3.0 \times 10^{-3}$, corresponding to a moderately pure sample has been used in calculating these dispersion curves. The absence of Landau damping in the free-electron Boltzmann curve is clearly demonstrated. It can also be seen that for small wave vectors, $Q \leq 120$, the Lindhard and the Boltzmann curves are essentially the same. This segment of the plasmon dispersion curve can be written as

$$\omega^2 = \omega_p^2 + \frac{2}{5} v_F^2 q^2.$$  \hspace{1cm} (IV.1)

Eq. (IV.1) includes the first two terms in the expansion of the free-electron plasmon frequency as a power series in $q^2$ (see Ref. 3). In terms of dimensionless units as defined by Eq. (II.1'), Eq. (IV.1) becomes

$$\Omega^2 = 1 + \frac{2}{5} (v_F/c)^2 Q^2.$$  \hspace{1cm} (IV.1')

Eq. (IV.1') is also plotted in Fig. 13. It is evident that for large values of $Q$ neither the Boltzmann nor the Lindhard curve is adequately represented by this equation.

We now present the plasmon dispersion curves as obtained from a multi-band calculation of the SCF dielectric function (Eq. (11.24)). In these calculations, the six lowest bands as given in Table 4 were used. A phenomenological damping factor given by $\gamma = 3.0 \times 10^{-3}$
was included, and a mesh of 128,000 points in the Brillouin zone was employed in performing the sum over $\mathbf{k}$-space. Plasmon positions were located by scanning $\text{Im}(-1/\epsilon_{\mathbf{q}})$ in frequency at fixed values of the wave vector $\mathbf{q}$, to obtain its peak position.

In a thin film experiment (see Chapter II), the wave vector of the plasmon has two components. Using the dimensionless units employed in Chapter II, there is one component $Q_\parallel$ parallel to the surface of the film, and a component $Q_\perp$ perpendicular to the surface. It can be seen from Eq. (II.1'), that for frequencies at which plasmon peaks occur, i.e., for $1 < \Omega < 1.6$, $Q_\parallel = q c/\omega_p = \Omega \sin \theta \sim 1$. However, $Q_\perp = q c/\omega_p = q c/\omega_p = \frac{n \pi c}{n_{p}^d}$, where $n = 1, 3, 5, \text{etc.}$ For a film as thick as 100 $\AA$, the smallest value of $Q_\perp \sim 30$. Hence $Q_\perp \gg Q_\parallel$. In our calculations we have obtained the plasmon dispersion curve for two wave-vector directions. In comparing our calculations with the experimental results, we will assume that the direction of plasmon propagation is perpendicular to the film surface. In view of the numbers displayed above, such an approximation is clearly justified.

Since the plasmon wave vector $\mathbf{q}$ has to be commensurate with the chosen grid of points, the components of $\mathbf{q}$ will be integral multiples of $\pi/20a$ along each of the axis, $k_x, k_y, k_z$, shown in Fig. 5. As was mentioned in Chapter III, the matrix elements, $M_{k \mathbf{q}, k+\mathbf{q}}$, were known only for a coarse mesh of 1024 points in the Brillouin zone. Therefore, if we calculate the matrix element for a $\mathbf{q}$ whose components are other than integral multiples of $\pi/4a$ (corresponding to the coarse mesh of 1024 points), the matrix elements will either be overestimated or
underestimated. We have therefore usually used those values of \( q \) whose components are integral multiples of \( \pi/4a \).

In Fig. 14 we present the plasmon dispersion curve for potassium with \( q \) along the (110) direction. In this particular plot we have taken the plasma frequency to have the free-electron value \( \omega_p = 4.394 \text{ eV} \). The points shown in the plot have wave vectors whose magnitudes are given by \( q = \sqrt{2} h(\pi/4a) \), where the \( h \)-values are given in Fig. 14. \( \Omega \) is known to a precision of \( \pm 0.005 \). To within the accuracy of the calculation, the points on Fig. 14 fall on a straight line. The best straight line (in the least-squares sense) fitted to these points was then extrapolated to obtain the plasma frequency

\[
\omega_p^B = 3.58 \pm 0.02 \text{ eV}.
\]

The plasma frequency for potassium as obtained by several experimenters are given below in Table 6.

Table 6. List of some experimentally determined plasma frequencies for potassium

<table>
<thead>
<tr>
<th>Author</th>
<th>Type of Experiment</th>
<th>Plasma Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>N. V. Smith(^{35})</td>
<td>Optical ellipsometry</td>
<td>3.8 ( \pm ) 0.1 eV</td>
</tr>
<tr>
<td>R. E. Palmer and S. E. Schnatterly(^{36})</td>
<td>Optical ellipsometry</td>
<td>3.8 ( \pm ) 0.1 eV</td>
</tr>
<tr>
<td>C. Kunz(^{37})</td>
<td>Electron energy loss</td>
<td>3.72 eV</td>
</tr>
<tr>
<td>M. Anderegg, B. Feuerbacher, and B. Fitton(^{1})</td>
<td>Photoemission</td>
<td>3.55 eV</td>
</tr>
</tbody>
</table>
Fig. 14. Plasmon dispersion curve for potassium with wave vector along the (110) direction as obtained by the multi-band calculation.

\[ \Omega = \omega \psi_p, \quad q = \sqrt{2} \frac{\hbar}{4a}. \]

The straight line intersects the \( \Omega^2 \)-axis at \( \Omega^2 = 0.664 \).
In an ellipsometry experiment, the quantities measured are the relative amplitudes and phase shifts of the reflectivity for s- and p-polarized light. This data is then used to calculate a local dielectric function, \( \varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega) \), and the plasma frequency is obtained by determining the frequency for which \( \varepsilon_1(\omega) = 0 \). In Smith's experiment, the reflectivity data was obtained for frequencies ranging from 0.5 eV to 4.0 eV. Palmer and Schnatterly obtained data from 1.75 eV to 4.5 eV. In both experiments, the upper limit of the frequency range was well above the plasma frequency, and an analysis in terms of a local dielectric function is clearly not satisfactory in this region.

The electron energy-loss experiment of Kunz is a direct measurement of the plasma frequency. The experiment of Anderegg et al. will be discussed below.

In Fig. 15 we compare the free-electron Lindhard and Boltzmann dispersion curves with the multi-band calculation of the present work for \( \vec{q} \) along the (110) direction. For the free-electron curves we used the dimensionless units \( \Omega = \nu / \nu_p \), and \( Q = q_c / \nu_p \), where \( \nu_p = 4.394 \) eV. The dimensionless scale used for the multi-band curve is \( \Omega_B = \nu / \nu_p^B \), \( Q_B = q_c / \nu_p^B \), where \( \nu_p^B = 3.58 \) eV. Fig. 15 indicates that for \( Q_B \leq 110 \), the multi-band dispersion curve has the same shape as the free-electron curves.

A word of caution should be inserted at this point. The plasmon dispersion curve was calculated only for \( q \geq 0.213 \, \text{Å}^{-1} \), and it is in this region alone that we can state that \( \Omega_B^2 \) varies linearly with \( q^2 \). This is an unfortunate restriction imposed by the computational technique. In the strictest sense, there is no a priori reason to justify a linear extrapolation of this straight line for smaller values of \( q \).
Fig. 15. Comparison of the calculated plasmon dispersion relation for potassium (wave vector along the (110) direction) with the free-electron Lindhard and Boltzmann dispersion relations. The dashed line, representing the dispersion relation including band effects, involves

$$\Omega_B = \frac{\omega}{\omega_p}$$

and

$$Q_B = \frac{q_c}{\omega_p}$$.

The solid lines, representing the free-electron curves, involve

$$\Omega = \frac{\omega}{\omega_p}$$

and

$$Q = \frac{q_c}{\omega_p}$$.
down to $q = 0$. Hence, any conclusion on the shape of the dispersion curve for $q < 0.213 \, \text{Å}^{-1}$, as well as the value of the plasma frequency remains open to question until accurate determinations can be made in this region.

The plasmon dispersion relation for potassium was also calculated for wave vector $\mathbf{q}$ along the symmetry direction (100). The result, along with the free-electron curves, is shown in Fig. 16. As before, the calculated multi-band dispersion curve is scaled to $\omega_p = 3.58 \, \text{eV}$, whereas the free-electron curves are scaled to $\omega_p = 4.394 \, \text{eV}$. The dispersion relation could not be obtained for $Q < 165$ with the computational procedure we used. Comparing Fig. 16 with Fig. 15, it is immediately apparent that this dispersion curve is very different from that for $\mathbf{q}$ along the (110) direction. For wave vector along the (100) direction the multi-band dispersion curve appears to have roughly the shape of the free-electron Lindhard curve for $Q_b < 300$. For higher values of $Q_b$, the shape of the curve changes drastically, and shows a behavior almost like the free-electron Boltzmann curve. In the (110) direction the deviation from the free-electron behavior sets in at a much lower value of $Q_b$, i.e., $Q_b \geq 110$.

A qualitative understanding of this anomalous behavior of the plasmon dispersion relation can be found in the band structure for potassium. Fig. 12 shows the energy bands for an empty BCC lattice with lattice parameters for sodium. Let us first consider the (100) direction, from $\Gamma$ to $H$, and confine our attention to the five lowest bands, $\Delta_1, \Delta_1, \Delta_2$, and $\Delta_5$. Comparing Fig. 11 with Fig. 12 we find
Fig. 16. Plasmon dispersion curves for potassium. The dashed line, representing the results of the multi-band calculation with the wave vector along the (100) direction, involves
\[ \Omega_B = \omega / \omega_p^B, \quad \text{and} \quad Q_B = q_c / \omega_p^B. \]
The solid lines, representing the free-electron dispersion relations, involve
\[ \Omega = \omega / \omega_p, \quad Q = q_c / \omega_p. \]
that the crystal potential splits up the four-fold degenerate free-electron band, $\Delta_1\Delta_2\Delta_3$, into the singly-degenerate bands $\Delta_1$ and $\Delta_2$, and a doubly-degenerate band $\Delta_3$. This splitting causes the density of states in the APW bands to be very different from that of the free-electron bands.

Electrons, making transitions from filled states below the Fermi surface to empty states above it, are affected by this difference, for wave vectors $\mathbf{q}$ which are large enough such that the final state is near or beyond the Brillouin zone boundary. In the (100) direction, the magnitude of the wave vector from the Fermi surface to the zone edge $H$ is given by $q \sim 3(\pi/4a)$ or $q_B \sim 250$. Fig. 16 shows that the anomalous behavior in the plasmon dispersion starts for $q_B \sim 300$.

Consider now the bands in the (110) direction, from $\Gamma$ to $N$. Here the first two bands, $\Sigma_1$ and $\Sigma_2$, remain reasonably free-electron-like except for the introduction of a band gap at $N$. However, the critical value of $q$ needed to take electrons out of the first Brillouin zone is $\sim 0.5(\pi/4a)$, or $q_B \sim 41.4$. The lowest value of $q_B$ at which we calculated a plasmon peak in this direction is $\sim 112$, at which value important transitions to higher bands will have already commenced. The next set of bands in the free-electron model is the four-fold degenerate set, $\Sigma_1\Sigma_2\Sigma_3\Sigma_4$. The crystal potential splits these up into four singly-degenerate bands as can be seen in Fig. 11. The critical energy at which the electrons will begin to see the change in the density of states from the free-electron density of states is roughly the energy difference between the top of the Fermi surface and the
bottom of $\Sigma_2$ at $N_2$. This energy is ~ 0.25 rydbergs, or 3.4 eV. However, the plasma frequency for potassium is 3.58 eV. Hence, for potassium in the (110) direction, deviations from the free-electron behavior may be expected for $q$ large enough to excite interband transitions.

We now present the comparison of our results with the experimental results of Anderegg et al.\textsuperscript{1} First we give a brief review of the method used in Ref. 1 to fit the experimental data to a theoretical curve. In this experiment, the wave-length modulated photoelectric yield spectra of potassium was measured for three different film thicknesses. For very thin films the photoelectric yield is proportional to the absorption. The frequencies at which plasmon resonances occurred were measured, but no measurements were made of the absolute value of the film thickness. Only the relative film thickness was monitored by a quartz-crystal microbalance. Since it is known that plasmon resonances occur when the wave vector $q$ normal to the surface of the film is equal to $n \pi / d$, where $d$ is the film thickness, and $n$ is an odd integer, the absolute value of the thickness of the thickest film as well as the $n$-value for the lowest resonance of this film were obtained by fitting the experimentally observed points to the curve given by Eq. (IV.1) with $v_F = 8.5 \times 10^7$ cm/sec. The lowest resonance was identified as having $n = 11$, and the film thickness they obtained was 100 Å. The thicknesses for the other two films were then found to be 58 Å and 27 Å.
The plasmon dispersion curve for potassium with wave vector along the (110) direction as obtained from the multi-band calculation can be expressed as:

\[ \omega^2 = (\omega_p B)^2 + (\alpha_{110}^2) q^2, \]  

(IV.2)

where \( \alpha_{110}^2 = (6.28 \pm 0.04) \times 10^7 \text{ cm/sec}. \)

There is, however, no reason to assume, as was done by Anderegg et al. \(^1\), that \( \alpha_{110}^2 = \frac{3}{5} v_F^2 \). The equation \( \omega^2 = \omega_p^2 + \frac{3}{5} v_F^2 q^2 \) is the small \( q \) expansion of the free-electron dispersion relation as obtained from the Boltzmann or the Lindhard dielectric functions. As is shown in Fig. 13, this equation does not represent the free-electron plasmon dispersion curve in either the Lindhard or the Boltzmann formulation of \( Q > 215 \text{ or } q > 0.48 \text{ Å}^{-1} \). We emphasize here that the representation Eq. (IV.2) for the (110) plasmon dispersion curve for potassium is obtained from the calculated results using a multi-band model. The fact that it has the same form as the small \( q \) expansion of the free-electron plasmon frequency is simply fortuitous.

Since the experimentally determined dispersion curve \(^1\) appears to have the same shape as our band-calculated curve for wave vector along the (110) direction, we have fitted the experimental data for the thickest film to Eq. (IV.2) by varying the film thickness and the

\( \Delta \text{Eq. (IV.2) may also be expressed in dimensionless units as} \)

\[ \Omega_B^2 = 1 + (A_{110}^1)^2 Q_B^2, \]  

(IV.3)

where \( A_{110}^1 = (2.095 \pm 0.005) \times 10^{-3} \).
n-value assigned to the lowest resonance. The best fit (in the least-squares sense) was obtained by assigning \( n = 11 \) to the lowest resonance for a film 124 Å thick. The other two films were then found to be 72 Å and 33 Å thick. \( n = 7 \) was assigned to the lowest resonance for the 72 Å film, whereas \( n = 3 \) was assigned to the lowest resonance for the 33 Å film. The results are shown in Fig. 17. The excellent agreement between the experimental results and our calculations suggests that the film was very probably deposited with its normal directed along the (110) axis. This conclusion is tentative until further calculations are performed for more general directions of the wave vector and the character of the film is understood.

Consider now the damping characteristics of the plasmons. Fig. 18 shows a profile of the loss-functions near the plasmon peaks when the wave vector \( \mathbf{q} \) is along the (100) direction. Comparison with the free-electron peak in Fig. 10 immediately shows that these peaks are considerably broader than the free-electron peak, and that additional structure exists around the plasmon peak. The frequency range within which \( \text{Re}(\varepsilon) \) passes through zero is also shown in Fig. 18. As was mentioned in Chapter 11, the plasmon peaks were selected principally on the basis of prominence. The proximity to \( \text{Re}(\varepsilon) = 0 \) was used as an additional criterion. The source of plasmon broadening was traced to interband transitions by expressing

\[
\text{Im}(\varepsilon) = \varepsilon_2^{\text{intra}} + \varepsilon_2^{\text{inter}}, \tag{IV.4}
\]
Fig. 17. Fit of the experimentally determined plasmon frequencies of Anderegg et al. for potassium to the calculated dispersion curve of the present work. Solid line represents the theoretically calculated plasmon dispersion curve for potassium with wave vector in the (110) direction. Frequency

$$\Omega_b = \omega \sqrt{\frac{B}{\omega_p}}$$.
Fig. 18. Profiles of the multi-band calculated loss function near the plasmon peaks for potassium with wave vector along the (100) direction.

\[ \Omega_B = \omega/\omega_p \]

\( \Omega_p \) is the frequency at which plasmon peak is identified. The bars extending upwards from the abscissa indicate the frequency region within which \( \text{Re}(\varepsilon) \) passes through zero.
where $\epsilon_2^{\text{intra}}$ is the intraband contribution to $\Im(\epsilon_2)$, and $\epsilon_2^{\text{inter}}$ is the interband contribution. In Table 7 are shown these two contributions separately at the position of the plasmon peak for wave vectors along (100). It is readily seen that $\epsilon_2^{\text{inter}} \gg \epsilon_2^{\text{intra}}$. Since $\Im(\epsilon_2)$ is a reasonable indication of the amount of damping, the above observation leads to the conclusion that most of the plasmon damping is being caused by interband transitions.

Fig. (18f) shows a plasmon peak which is well within the free-electron single-particle excitation region. We can see here that the peak is so broad that it is scarcely possible to identify the plasmon. In this region the plasmon exhibits Landau damping.

The half-width of the plasmon peak is a good criterion for estimating the amount of damping. However, due to the presence of secondary peaks, it has not been possible to generate a procedure for uniquely determining these half-widths from Fig. 18. For a free-electron gas $\Im(-1/\epsilon_2)$ satisfies the following sum rule,\(^3\)

$$\int_0^\infty d\Omega [\Im(-1/\epsilon_2(Q,\Omega))] = \frac{\pi}{2}.$$  

This sum rule is a direct consequence of a longitudinal version of the Thomas-Reiche-Kuhn sum rule, which is also valid for Bloch states.\(^3\)

From this equation we see that the product of the peak height of $\Im(-1/\epsilon_2)$ with $\Omega$, which we call $H$, should decrease as the width of the peak increases. This assumption is reasonable since the peak in the loss-function is primarily being caused by the excitation of a plasmon.
Table 7. The intraband and interband contributions to \( \text{Im}(\varepsilon_f) \) at plasmon peak positions for potassium with wave vector along the (100) direction and \( \gamma = 3.0 \times 10^{-3} \). The frequency at the plasmon peak is denoted by \( \Omega_0 \).

<table>
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<th>( \Omega_0 )</th>
<th>( Q_B )</th>
<th>( \varepsilon_2^{\text{intra}} )</th>
<th>( \varepsilon_2^{\text{inter}} )</th>
</tr>
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<tr>
<td>1.043</td>
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<td>( 2.00 \times 10^{-1} )</td>
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<tr>
<td>1.166</td>
<td>248.41</td>
<td>( 3.776 \times 10^{-3} )</td>
<td>( 4.071 \times 10^{-1} )</td>
</tr>
<tr>
<td>1.350</td>
<td>331.21</td>
<td>( 1.594 \times 10^{-3} )</td>
<td>( 4.370 \times 10^{-1} )</td>
</tr>
<tr>
<td>1.497</td>
<td>414.01</td>
<td>( 7.521 \times 10^{-4} )</td>
<td>( 4.419 \times 10^{-1} )</td>
</tr>
</tbody>
</table>
with secondary structures superposed on it. In this work we have chosen $H$ as an indicator of plasmon damping since the peak height is a much less ambiguous quantity in the curves of Fig. 18 than the corresponding half-widths.

In Fig. 19 we show plasmon damping, as given by $H$, as a function of $Q_B$ for plasmon propagation along the symmetry directions ((100) and (110). We notice that although there is a general trend towards increased damping as $Q_B$ increases, details in the damping characteristics are different for the two different directions of plasmon propagation. Such differences are to be expected, since the primary source of plasmon damping are interband transitions, and the density of states of the bands vary along different symmetry directions.

The secondary structures (peaks and shoulders) around the plasmon peak (Fig. 18) are most probably due to interband transitions involving local areas of high density of states in the bands. This could be verified by a careful examination of the structure of the bands and their associated density of states for regions where such transitions are expected to occur. It can be seen from Fig. 18 that the secondary structures are superpositions on a primary peak in the loss-function, which has been identified as the plasmon peak.

Sodium

The APW energy bands for BCC sodium with lattice constant $7.984$ (a.u.) at $5^\circ K$ as calculated by Gupta, are shown along certain high-symmetry directions in Fig. 20. As in the case of potassium, it
Fig. 19. Product of plasmon peak height with $\Omega_B$, given by $H$, measured in units of $\Omega_B/\epsilon_\omega$, as a function of $Q_B$ for wave vector along the symmetry directions (100) and (110) in potassium.
Fig. 20. Energy bands for sodium along high-symmetry directions from the calculations of Gupta. Energies are measured with respect to constant potential in the interstitial region, \( V_{\text{int}} = -0.989 \) rydbergs. Lattice constant = 7.984 (atomic units).
ENERGY, RYDBERGS
was found that the six lowest energy bands were sufficient for the computation of the dielectric function. These six bands are listed in Table 8, and correspond roughly to the ones shown in Fig. 20 for energies up to ~ 1.500 rydbergs. The highest core level in sodium, $L_{\text{III,III}}$, lies $31.1 \pm 0.4$ eV below the Fermi level. Since the plasma frequency for sodium is $~6$ eV, transitions from the core states will not play any part in our calculations. A set of 26 recip was used in the energy band calculations, and consequently the crystal wavefunction was expanded in a set of 26 plane waves. The set of recips used for sodium are the first 26 listed in Table 2. The energies are accurate to within 0.001 rydbergs.

The Fermi energy was calculated in exactly the same manner as in the case of potassium and was found to be $E_F = 0.244$ rydbergs, measured from $\Gamma$. However, since the APW matrix was not available, the Fermi wave-vector could not be determined, nor could the sphericity of the Fermi surface be verified. It was therefore assumed throughout the calculations that the Fermi surface was a perfect sphere with the Fermi wave-vector $k_F$ having the free-electron value

$$k_F = 0.923 \text{Å}^{-1}.$$ 

This is a reasonable assumption since sodium is known to be a very free-electron-like metal. The free-electron plasma frequency as obtained from the free electron $k_F$ and free-electron mass is
Table 8. First six APW energy bands for sodium from the calculations of Gupta. Energies are given in rydbergs with respect to $V_{\text{int}} = -0.989$ rydbergs. Lattice constant = 7.984 (a.u.)

<table>
<thead>
<tr>
<th>$(4a/\pi)\overline{R}$</th>
<th>Band 1</th>
<th>Band 2</th>
<th>Band 3</th>
<th>Band 4</th>
<th>Band 5</th>
<th>Band 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>0.011</td>
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<th>Band 3</th>
<th>Band 4</th>
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Table 8 (continued)

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<th>Band 2</th>
<th>Band 3</th>
<th>Band 4</th>
<th>Band 5</th>
<th>Band 6</th>
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<td>0.697</td>
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<td>1.095</td>
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<td>0.750</td>
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<td>0.451</td>
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<td>1.500</td>
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\[ \omega_p = 6.044 \text{ eV}. \]

The calculated plasmon dispersion curve for sodium with the wave vector along the (110) direction is shown in Fig. 21. The plasma frequency at \( q = 0 \) with band effects included was determined by assuming the calculated dispersion curve to have the same slope as the free-electron Lindhard or Boltzmann curve for \( Q \leq 90 \). This assumption was suggested by the very close agreement between the shape of the free-electron Lindhard curve and the calculated multi-band curve, for \( 90 \leq Q \leq 270 \). The plasma frequency thus calculated is

\[ \omega_p^B = 5.80 \pm 0.03 \text{ eV}. \]

Some experimentally determined plasma frequencies for sodium are presented in Table 9.

Table 9. List of some experimentally determined plasma frequencies for sodium

<table>
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<tr>
<th>Author</th>
<th>Type of Experiment</th>
<th>Plasma Frequency</th>
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<tr>
<td>N. V. Smith(^{35})</td>
<td>Optical ellipsometry</td>
<td>5.65 \pm 0.1 eV</td>
</tr>
<tr>
<td>R. E. Palmer and S. E. Schnatterly(^{36})</td>
<td>Optical ellipsometry</td>
<td>5.4 \pm 0.2 eV</td>
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<tr>
<td>C. Kunz(^{37})</td>
<td>Electron energy loss</td>
<td>5.72 eV</td>
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Fig. 21 Plasmon dispersion relations for sodium for wave vector along (110) direction. Solid lines representing free-electron curves involve

$$\Omega = \omega / \omega_p, \quad Q = qc / \omega_p.$$ 

Dashed line representing the results of the multi-band calculation involves

$$\Omega_B = \omega / \omega_p^B, \quad Q_B = qc / \omega_p^B.$$
Smith's experiment\textsuperscript{35} covered the frequency range 0.5 to 4.0 eV, while that of Palmer and Schnatterly\textsuperscript{36} was in the frequency range 1.75 to 4.5 eV. Both of these frequency ranges fall considerably short of the plasma frequency which was obtained by extrapolating $\varepsilon_1(\omega)$ to zero. The electron energy-loss experiment,\textsuperscript{37} which is a direct measurement of the plasma frequency, is much closer to our calculated value.

A qualitative understanding of the apparently free-electron-like behavior of the multi-band dispersion curve for sodium, when the wave vector is along the (110) direction, can be found in the energy bands in the symmetry direction $\Sigma(\Gamma \rightarrow N)$. If we compare the APW bands (Fig. 20) with the free-electron bands (Fig. 12), we find that the APW bands along $\Sigma$ remain very free-electron-like, except for the presence of the energy gap at $N$, up to the point $N_2$ at $\sim 0.840$ rydbergs. This is the point where the density of states in the APW bands begin to differ significantly from those of the free-electron bands, since the four-fold degenerate band $\Sigma_1\Sigma_2\Sigma_3\Sigma_4$ in the free-electron case is now split by the crystal potential into four singly-degenerate bands, $\Sigma_1$, $\Sigma_2$, $\Sigma_3$, and $\Sigma_4$. The energy difference between $N_2$ and the Fermi level is 0.59 rydbergs or 8.02 eV. The plasma frequency for sodium being 5.80 eV, we expect the dispersion curve in the (110) direction to be very free-electron-like for $\Omega_b \lesssim 1.38$. Going back to Fig. 21 we find this to be the case.
The small $q$ expansion of the calculated plasmon dispersion relation for the (110) direction may be expressed as

\[ \omega^2 = (\omega_p B)^2 + (\alpha_{Na}^{110})^2 q^2, \]  

(IV.5)

where $\alpha_{Na}^{110} = (7.02 \pm 0.04) \times 10^7$ cm/sec. Note that Eq. (IV.5) is valid only for $q \leq 0.26 \text{Å}^{-1}$ or $Q_B \leq 90$. 

Fig. 22 shows the dispersion curve for the (100) direction. It has roughly the same behavior as the potassium curve in the (100) direction (see Fig. 16). This is because the energy bands for sodium and potassium in the symmetry direction $\Delta$ are very similar for energies up to $\sim 1.65 \omega_p B$, where the energies are measured from the Fermi level.

Fig. 23 shows the profiles of the loss-function near the plasmon peak for wave vector along the (100) direction. It can be seen that although these peaks are broad and include significant structure compared to the free-electron peak (Fig. 10), they are sharper than the corresponding peaks for potassium (Fig. 18). Fig. 23f shows the structure of $\text{Im}(-1/e_j^*)$ when the plasmon is inside the free-electron single-particle excitation region. It clearly exhibits very strong Landau damping.

Fig. 24 shows $H$ as a function of $Q$ for plasmon propagation along

\[ \Omega_B^2 = 1 + (A_{Na}^{110})^2 Q_B^2, \]  

(IV.6)

where $A_{Na}^{110} = (2.342 \pm 0.005) \times 10^{-3}$. 

---

\(^a\)Eq. (IV.5) may also be expressed in the dimensionless form
Fig. 22. Plasmon dispersion curves for sodium. Dashed line representing the results of the multi-band calculation with wave vector along the (100) direction involves
\[ \Omega_B = \frac{\omega}{m_p B}, \quad Q_B = \frac{q c}{m_p B}. \]

Solid lines representing the free-electron dispersion relations involve
\[ \Omega = \frac{\omega}{m_p}, \quad Q = \frac{q c}{m_p}. \]
Fig. 23. Profiles of the multi-band calculated loss-functions near the plasmon peaks for sodium with wave vector along the (100) direction.

\[ \Omega_b = \frac{\omega}{\omega_p} B \]

\( \Omega_b \) is the frequency at which plasmon peak is identified. The bars extending upwards from the abscissa indicate the frequency region within which \( \text{Re}(\varepsilon) \) passes through zero.
Fig. 24. Product of the plasmon peak height with $\Omega_0$, given by $H$, measured in units of $\Omega_B/\epsilon_f$, as a function of $Q_B$ for wave vector along the symmetry directions (100) and (110) in sodium.
the two symmetry directions, (100) and (110). As in the case of potassium, there is a definite trend towards increased damping as the wave vector increases, but the detailed shapes for the two different symmetry directions differ.
CHAPTER V. CONCLUSIONS

The modification of the plasmon dispersion relations of sodium and potassium from the free-electron values when band-structure effects are included indicates that the collective behavior of conduction electrons in a metal is significantly affected by the periodic potential of the lattice, even in these free-electron-like metals. Although the detailed quantitative relationship between the band structure of these metals and the plasmon dispersion relations is not at the moment understood, we have attained some knowledge of certain broad features of this relationship. They are as follows.

1. The shape of the dispersion curve depends very sensitively on the direction of plasmon propagation. This can be seen immediately by comparing the dispersion curves for either sodium or potassium in the two symmetry directions, (100) and (110).

2. Deviations from the free-electron behavior are brought about principally by the change in the density of states of the bands when the crystal potential is introduced.

3. The presence of interband transitions depresses the plasma frequency \( \nu_p \) below its free-electron value.

4. Interband transitions give rise to significant plasmon damping resulting in rather broad plasmon peaks. The dependence of damping on wave vector is different for sodium and potassium and depends on the direction of plasmon propagation. The loss-function in general involves additional structure in the neighborhood of the plasmon peak,
presumably resulting from density of states effects. The presence of these structures makes the determination of plasmon peak half-widths difficult.

5. Interband transitions alter the coefficient of the $q^2$-dependent term in the small wave-vector expansion of the plasmon dispersion relation. (See Eqs. (IV.2) and (IV.5).)

6. Plasmon dispersion relations for neither sodium nor potassium follow the behavior of the free-electron curves (Lindhard or Boltzmann). However, sodium is in general more free-electron-like in its behavior than potassium. This can be seen from the following considerations. (a) The plasma frequency for sodium is lowered by 4% from its free-electron value, whereas the plasma frequency for potassium is lowered by 19%. (b) For plasmon propagation in the (110) direction, the dispersion curve for sodium has essentially the same shape as that resulting from the Lindhard dielectric function. The dispersion curve for potassium in this direction deviates considerably from that of the free-electron theory.

In the calculations that we have performed in this work, there are four general areas in which improvements are desirable.

1. Inclusion of local-field corrections. It has been shown by Wiser, that in the long-wavelength (zero wave-vector) limit, the longitudinal dielectric function of a real solid can be separated into a core part (resulting from the polarization of the ion cores), and an acceleration part (resulting from the polarization of the itinerant electrons), and that local-field corrections are confined to the core
polarization terms. For simple alkali metals like sodium and potassium, whose electronic structure consists of s- and p-like bands, it is reasonable to assume that local-field corrections are not very significant in the small wave-vector region. The largest wave vector that we have been dealing with in this work is comparable in size to the reciprocal lattice vectors, and hence, the consequences of the neglect of local-field corrections should be examined. The inclusion of such effects requires a revision of the theory of the optical properties of thin films. The simple closed form expression for the surface impedance as given by Eq. (11.1) will no longer be valid.

2. In our calculations, we have approximated the wavefunction throughout the entire unit cell by a linear combination of a limited number of plane waves (26 for sodium and 43 for potassium). Strictly speaking, this form is valid only in the interstitial region between the muffin-tin spheres. For a more satisfactory calculation, the correct solutions to the Schrödinger equation with the muffin-tin potential should be used for the region inside the muffin-tin spheres.

3. We have used the matrix elements for 1024 points in the Brillouin zone in performing a sum over a considerably finer mesh of 128,000 points. Consequently, the number of wave vectors at which we could reliably obtain the plasma frequency was somewhat limited, especially in the (110) direction. This limitation can be overcome by obtaining the energy eigenvalues and the plane-wave coefficients for a finer mesh than 1024 points in the Brillouin zone. This would involve a great deal of labor and a vast amount of computer time, but
now that there are clear indications that very interesting effects appear in the plasmon dispersion curves and the associated damping, such an effort appears worthwhile.

4. We obtained the plasma frequency by extrapolating our calculated curve to $q = 0$. Even though this was the method employed by the experimentalists to determine the plasma frequency, and the assumptions required to make such an extrapolation appear to be reasonable, the method is not really satisfactory. The plasma frequency should be determined from an explicit evaluation of $\epsilon_{\omega}^\infty(0,\omega)$.

Finally, we comment on the interpretation of Anderegg et al. of their potassium data. The behavior of the plasmon dispersion curve for potassium cannot be obtained from the solution to the Boltzmann equation. At small wave vectors ($Q < 110$) the shape agrees with those of the free-electron curves (Boltzmann or Lindhard), but the parameters involved in the approximate dispersion relation $\omega^2 = \omega_p^2 + \alpha^2 q^2$, (which, it should be noted is valid, in general, only for small $q$) are entirely different. At higher $Q$-values even the shape of the free-electron Boltzmann curve deviates from the actual dispersion curve. The behavior of the experimentally determined dispersion curve agrees well with that calculated from the SCF dielectric function into which the structure of the electronic energy bands has been incorporated. Note that the Lindhard dielectric function is the SCF dielectric function evaluated for free-electron bands.
PART II. MAGNETIC FIELD EFFECTS ON THE DIELECTRIC RESPONSE OF AN ELECTRON GAS
CHAPTER I. INTRODUCTION

The object of this work is to develop a theory for the properties of a bounded medium of free-electron gas in the presence of an external static magnetic field, for frequency regions where non-local effects are of importance. Alternatively, we are interested in developing dielectric functions to describe such a situation.

The presence of an external static magnetic field affects the dynamics of electrons in two ways. In one, the electron motion becomes the classical cyclotron motion of electrons about the magnetic field. In the other, which becomes important for strong magnetic fields, the allowed orbits are those commonly described as Landau levels. For magnetic fields weak enough such that \( \omega_c \tau < 1 \), the consequences of the former effect may be investigated by a semi-classical formulation of the problem in terms of a linearized Boltzmann equation. Here \( \omega_c \) is the frequency of rotation of the electron about the static magnetic field, and \( \tau \) is the electron life-time.

Kliwer and Fuchs\(^9\) have explicitly demonstrated, for a semi-infinite medium in which the electrons are assumed to be specularly reflected at the surface, that the response of an electron gas to an external perturbing field, as obtained from the solution of the linearized Boltzmann equation, can be represented by the corresponding infinite-medium dielectric functions. In this work, the semi-classical aspects of the dielectric response will be obtained in terms of a non-local conductivity tensor for an infinite medium.
Considerable literature exists in which the semi-classical conductivity tensor, in the presence of an external static magnetic field, has been obtained from the solution of the linearized Boltzmann equation. In all these investigations, the effect of electron collisions with impurities is treated by invoking the relaxation-time ansatz, in which the relaxation of the perturbed distribution towards equilibrium is assumed to be to the uniform, unperturbed distribution. In this work, the Boltzmann equation will be solved without the benefit of the relaxation-time approximation. This more rigorous treatment of the collision process introduces additional terms in the conductivity tensor when charge density fluctuations associated with excitations such as longitudinal acoustic waves and plasmons are present in the electron gas.

For magnetic fields which are strong enough to make the effect of Landau quantization important, the semi-classical results break down, and a more rigorous quantum-mechanical formulation is required. The quantum-mechanical treatment of the conductivity tensor for an infinite medium in the presence of a strong magnetic field has also been thoroughly investigated. However, as has been recently demonstrated by Beck, et al., and by Newns, a correct quantum-mechanical formulation of the dielectric response cannot be fully described by the infinite-medium conductivity tensor alone, even for specular scattering of electrons at the boundaries. These authors have shown that the inhomogeneity of space, incorporated into the structure of the electron wavefunction by means of correct boundary conditions, introduces
additional response near the surface. This can be of great importance in the investigation of excitations close to the surface. This effect has been explicitly taken into account in this work.

Chapter II gives the semi-classical formulation. The problem is set up for a general orientation of the static magnetic field with respect to the wave vector of the response. The results for two special cases, magnetic field parallel to the wave vector and magnetic field perpendicular to the wave vector, are also presented. Chapter III gives the quantum-mechanical formulation. Differences from the infinite medium response are explicitly displayed.
CHAPTER II. SEMI-CLASSICAL FORMULATION

General Conductivity Tensor

Consider a gas of free electrons in the presence of an external static magnetic field $\mathbf{B}_o$, and an electromagnetic disturbance which goes as $\exp[i\mathbf{q} \cdot \mathbf{r} - i\omega t]$. $\mathbf{B}_o$ does not include the fields arising from the internal configuration of the system. We choose the coordinate axes such that $\mathbf{B}_o$ is along the z-axis and the wave vector $\mathbf{q}$ lies in some arbitrary direction in the $(x, z)$ plane, making an angle $\theta$ with the z-axis. The single-particle distribution function for an electron in state $\mathbf{k}$, $f_{\mathbf{k}}(\mathbf{r}, \mathbf{v}, t)$, satisfies the Boltzmann equation,

$$\frac{\partial f_{\mathbf{k}}}{\partial t} + \mathbf{v} \cdot \nabla f_{\mathbf{k}} = \frac{e}{\hbar} (\mathbf{E}^\perp + \frac{1}{c} \nabla \times \mathbf{B}_o) \cdot \mathbf{v} f_{\mathbf{k}} - \frac{\partial f_{\mathbf{k}}}{\partial t_{\text{coll}}},$$  \hspace{1cm} (11.1)

where $\mathbf{v} = \hbar \mathbf{k}/m$, is the velocity of the electrons of mass $m$, and $\mathbf{E}^\perp$ is the perturbing electric field. We have neglected magnetic field components of the electromagnetic disturbance since it is $\sim (v/c)$ smaller than $\mathbf{E}^\perp$. $(\partial f_{\mathbf{k}}/\partial t)$ stands for the rate of change of the distribution function due to collision from impurities, lattice defects, etc., and is given by

$$\frac{\partial f_{\mathbf{k}}}{\partial t_{\text{coll}}} = \sum_{\mathbf{k}'} [W_{\mathbf{k} \mathbf{k}'}, f_{\mathbf{k}'} (1 - f_{\mathbf{k}}) - W_{\mathbf{k} \mathbf{k}'} f_{\mathbf{k}} (1 - f_{\mathbf{k}'})],$$  \hspace{1cm} (11.2)

where $W_{\mathbf{k} \mathbf{k}'}$ is the transition rate for electrons scattered from state $\mathbf{k}'$ to a state $\mathbf{k}$ via collision with impurities, lattice defects, etc.
If we now impose the condition, that the collision process consists of elastic scattering events, then \( W_{kk'} = W_{kk'} \), and Eq. (11.2) assumes the form given by Ziman, and consequently,

\[
\frac{\partial f_k}{\partial t}_{\text{coll}} = \frac{1}{\tau(e_k)} f_k + \sum_{k'} W_{kk'} f_{k'}^k,
\]

(11.3)

where we define the scattering time \( \tau(e_k) \) by

\[
\frac{1}{\tau(e_k)} \equiv \sum_{k'} W_{kk'}.
\]

(11.4)

If we now confine our attention to the linear response of the system, we can write

\[
f_k = f_0 + f_1(v) \exp[iq \cdot r - i\omega t] + O(E^2),
\]

(11.5)

where we have assumed that the response of the system has the same spatial and time variation as the oscillating electromagnetic disturbance. \( f_0 \) is the equilibrium distribution of the electron gas given by a Fermi-Dirac distribution function,

\[
f_0 = \{\exp[\beta(e_k - \mu) + 1]\}^{-1},
\]

(11.5a)

where \( \beta = (k_B T)^{-1} \), and \( \mu \) is the chemical potential. The \( B_0 \)-dependent term in Eq. (11.1) can be written as
where \( \omega_c \) is the cyclotron frequency and is given by

\[
\omega_c = \frac{eB_0}{mc},
\]

and the wave vector \( \vec{k} \) has been written in terms of the spherical components, \( \vec{k} = (k, \theta_k, \phi_k) \). If we now write

\[
\vec{E}(\vec{r}, t) = \vec{E}(q, \omega) \exp[i(q \cdot \vec{r} - \omega t)]
\]

and substitute Eqs. \((\text{II}-5a)\) and \((\text{II}-5b)\) into Eq. \((\text{II}-1)\), we obtain the linearized Boltzmann equation,

\[
\frac{\partial f}{\partial \phi} + \frac{\xi}{\omega_c} f = \frac{e\vec{E}}{\omega_c} \cdot \vec{\nabla} f + \frac{1}{\omega_c} \sum_{k^l} W_{kk^l} f_{k^l}(\vec{v}'),
\]

where

\[
\xi = \frac{1}{\tau(\omega_c) + i(\vec{q} \cdot \vec{v} - \omega)}.
\]

A general solution for Eq. \((\text{II}-6)\) can be written in the form

\[
f_{k^l}(\vec{v}) = \exp(-ia \sin \theta_k - ib \phi_k)[F(v, \theta_k) + \frac{1}{\omega_c} \frac{\partial f_0}{\partial \omega_c}]
\]

\[
\left[ e \vec{E} \int_{0}^{\alpha_k} d \alpha_{k^l} \vec{\nabla} \exp(ia \sin \theta_{k^l} + ib \phi_{k^l}) \right] 
\]

\[
+ \sum_{j} \int_{0}^{\alpha_k} \exp(ia \sin \theta_k + ib \phi_k) d \phi_k.
\]

where

\[ a = \frac{q_x v}{\omega_c} \sin \theta_k, \quad (11.9a) \]

\[ b = \frac{1}{\omega_c} \left[ q_z v \cos \theta_k - \omega - \frac{i}{\tau} \right], \quad (11.9b) \]

\[ q_x = q \sin \theta, \quad (11.9c) \]

and

\[ q_z = q \cos \theta. \quad (11.9d) \]

It can be verified that Eq. (11.8) is a solution to Eq. (11.6) by substituting \( f_1(v) \) from Eq. (11.8) into Eq. (11.6).

\( F(v, \theta_k) \) is a constant of integration to be determined from the boundary condition

\[ f_1(\omega_k) = f_1(\omega_k + 2\pi). \quad (11.9e) \]

\( G \) will be determined from the self-consistency requirement

\[ \left( \frac{\partial f}{\partial \varepsilon} \right)_K = \sum_{k'} W_{kk'} f_1(\tilde{v}'). \quad (11.10) \]

Having determined \( F(v, \theta_k) \) from condition (11.9), we can finally write
Knowing the distribution function, we can now calculate the current density and hence the conductivity tensor. The Fourier transform of the current density is given by

\[ j(q, w) = -2e(h^3) \int f_1(\vec{v}) d^3\vec{v}. \]  

Now, \( \frac{\partial f_0}{\partial \epsilon_k} = \frac{1}{m} \frac{\partial f_0}{\partial \omega} \). Also, at very low temperatures \( \frac{\partial f_0}{\partial \omega} \sim -\delta(\omega - \omega_F) \), where \( \omega_F \) is the Fermi velocity. Hence

\[ j(x, y, z) = \frac{2e}{4\pi} \frac{\sigma_0}{\omega_c \tau_0} \int d\phi_k \left( \begin{array}{c} \sin \theta_k \\ \cos \theta_k \\ \end{array} \right) \frac{\sin \theta_k}{(\exp(2\pi i \omega_F) - 1)} \frac{\sin \theta_k}{\cos \theta_k} \]

\[ = \int_{\phi_k + 2\pi} d\phi_k' \exp(i\phi_F \sin \theta_k' + i\phi_k \phi_k') \{ E_x \sin \theta_k \cos \theta_k \\
+ E_y \sin \theta_k \sin \theta_k' + E_z \cos \theta_k + \frac{G}{e\nu_F} \}, \]  

\[ (11.13) \]
where

\[ \tau_0 = \tau(\varepsilon_F) , \]  
\[ \sigma_0 = \frac{ne^2}{m} \tau_0 , \]  
\[ a_F = a(v = v_F) \]  
\[ b_F = b(v = v_F) \]  
\[ n = \text{mean electron density} , \]  
and

\[ \varepsilon_F = \text{Fermi energy} . \]

Performing the necessary integrations in Eq. (11.13) and using

\[ j_j(q, \omega) = \sigma_{ij}(q, \omega) \varepsilon_j(q, \omega) \]  

as the definition of the conductivity tensor \( \sigma_{ij}(q, \omega) \), where \( i,j \) denote \( x, y, \) or \( z \), we obtain, after some algebraic manipulations, the following expressions for \( \sigma_{ij} \):

\[ \sigma_{xx} = \frac{3}{8} \frac{\sigma_0}{i \hbar c \tau_0} \sum_{q} \frac{1}{2} \tau_0 \tau_0 r_{x}^2 + \sum_{n=-\infty}^{\infty} d \theta_k \frac{\sin^3 \theta_k}{b_F + n} [\Lambda_{n+1, n-1}(X \sin \alpha_k)]^2 , \]  

(11.16)
\[ \sigma_{xy} = -\sigma_{yx} = -\frac{3}{8} \frac{\sigma_o}{\omega_c \tau_o} [2i \omega_c \tau_o \Gamma g_x g_y \]
\[ + \sum_{n=-\infty}^{\infty} \int_0^{\pi} d\theta_k \frac{\sin^3 \theta_k}{b_F + n} \Lambda_{n+1, n+1} (x \sin \theta_k) J_n (x \sin \theta_k) ] \] (11.17)

\[ \sigma_{yy} = \frac{3}{8} \frac{\sigma_o}{i \omega_c \tau_o} [2i \omega_c \tau_o \Gamma g_y^2 + \sum_{n=-\infty}^{\infty} \int_0^{\pi} d\theta_k \frac{\sin^3 \theta_k}{b_F + n} \Lambda_{n+1, n+1} (x \sin \theta_k)] \] (11.18)

\[ \sigma_{yz} = -\sigma_{zy} = \frac{3}{4} \frac{\sigma_o}{i \omega_c \tau_o} [2i \omega_c \tau_o \Gamma g_x g_z \]
\[ + \sum_{n=-\infty}^{\infty} \int_0^{\pi} d\theta_k \frac{\sin^2 \theta_k \cos \theta_k}{b_F + n} \Lambda_{n+1, n+1} (x \sin \theta_k) J_n (x \sin \theta_k) ] \] (11.19)

and

\[ \sigma_{zz} = \frac{3}{2} \frac{\sigma_o}{i \omega_c \tau_o} [2i \omega_c \tau_o \Gamma g_z^2 + \sum_{n=-\infty}^{\infty} \int_0^{\pi} d\theta_k \frac{\sin \theta_k \cos^2 \theta_k}{b_F + n} J_n^2 (x \sin \theta_k) ] \] (11.20)

where

\[ \Gamma = 1 - \frac{1}{2i \omega_c \tau_o} \int_0^{\pi} d\theta_k \sin \theta_k \sum_{n=-\infty}^{\infty} \frac{J_n^2 (\theta_k)}{b_F + n} \] (11.21)
\( g_x, g_y, \) and \( g_z \) are defined by the equation

\[
G = e v_F \left[ \frac{i}{2} E_x g_x + \frac{1}{2i} E_y g_y + E_z g_z \right],
\]  
(11.22)

and can be obtained from the self-consistency requirement, Eq. (11.10), (see Appendix 1),

\[
J_{n,m}^\pm(x) = J_n(x) \pm J_m(x),
\]  
(11.23)

where the \( J_n(x) \) are Bessel functions, and

\[
x = q_x v_F / \omega_c.
\]  
(11.24)

These expressions then comprise the conductivity tensor of a free-electron gas in the semi-classical formulation for an arbitrary relative orientation of \( \vec{q} \) and \( \vec{H}_0 \). Consider now two special cases.

**Conductivity Tensor for \( \vec{q} \) parallel to \( \vec{B}_0 \)**

In the special geometry when \( \vec{q} \) is parallel to \( \vec{B}_0 \) and both lie along the \( z \)-axis, we have from Eq. (11.9)

\[
q_x = 0, \quad (11.25a)
\]

\[
q_z = q, \quad (11.25b)
\]

\[
a_F = 0, \quad (11.25c)
\]
and
\[
\beta_F = \frac{1}{\omega_c} (q \nu_F \cos \theta_k - \omega - \frac{i}{\tau_0}).
\]

Also, since \(x_F = 0\), \(x = 0\) and the only non-vanishing Bessel function which occurs in the expressions for the conductivity tensor is \(J_0(0) = 1\). From Appendix I we then have

\[
g_x = g_y = 0,
\]

and
\[
g_z = \frac{1}{2\pi} \int_0^{\pi} d\theta_k \frac{\sin \theta_k \cos \omega_k}{1 + i(q \nu \cos \theta_k - \omega \tau_0)},
\]

where \(\nu_0 = \nu_F \tau_0\).

It is shown in Appendix I that the \(g\)'s are non-vanishing when electron relaxation is assumed to be towards local states of equilibrium. Eq. (11.26) shows that if such effects are properly included, only the longitudinal response, which in this particular geometry happens to be in the \(z\)-direction, is affected.

If we now define the quantity
\[
\lambda_n = \frac{1}{2\pi} \int_0^{\pi} \frac{\sin \theta_k \cos \omega_k}{1 + i(q \nu \cos \theta_k - \omega \tau_0)},
\]

then from Eq. (11.21) we find
\[ r = 1 - \frac{1}{2} \int_{0}^{\pi} \sin \theta_k \frac{d\theta_k}{1 + i(q \omega_o \cos \theta_k - \omega_o)} = 1 - \lambda_o , \]

and

\[ g_z = \frac{\lambda_1}{1 - \lambda_o} . \tag{11.28} \]

From Eq. (11.20), the expression for \( \sigma_{zz} \) becomes

\[ \sigma_{zz} = 3 \sigma_o \int_{0}^{\pi} \sin \theta_k \cos \theta_k \left[ \frac{\lambda_1}{1 - \lambda_o} + \cos \theta_k \right] \]

\[ \times \frac{1}{1 + i(q \omega_o \cos \theta_k - i\omega_o)} , \]

or

\[ \sigma_{zz} = 3\sigma_o \left[ \frac{\lambda_1^2}{1 - \lambda_o} + \lambda_2 \right] . \tag{11.29} \]

In Eq. (11.29) we notice that \( \sigma_{zz} \) is independent of the magnetic field since the electron dynamics are not influenced by the magnetic field in the direction parallel to the field. Eq. (11.29) is nothing more than the longitudinal conductivity of a free-electron gas. Had we made the relaxation time approximation, we would have had \( g_z = 0 \) and, consequently, the first term in the square brackets in Eq. (11.29) would not have appeared. This term results from charge density fluctuations in the electron gas and is very important when longitudinal excitations are under consideration.
From Eq. (11.16) - (11.19), we see that for \( \vec{q} \) parallel to \( \vec{B}_0 \),

\[
\sigma_{xx} = \sigma_{yy} = \frac{3}{8} \sigma_0 \int_0^{\pi} d\theta_k \sin^3 \theta_k \left[ \frac{1}{1 + iq \tau_0 \cos \theta_k - i(\omega - \omega_c)\tau_0} \right.
\]
\[
+ \left. \frac{1}{k + i q \tau_0 \cos \theta_k - i(\omega + \omega_c)\tau_0} \right],
\]

(11.30)

\[
\sigma_{xy} = -\sigma_{yx} = \frac{3}{8} \sigma_0 \int_0^{\pi} d\theta_k \sin^3 \theta_k \left[ \frac{1}{1 + iq \tau_0 \cos \theta_k - i(\omega + \omega_c)\tau_0} \right.
\]
\[
- \left. \frac{1}{1 + iq \tau_0 \cos \theta_k - i(\omega - \omega_c)\tau_0} \right],
\]

(11.31)

\( \sigma_{xz} = \sigma_{zx} = 0 \), and \( \sigma_{yz} = \sigma_{zy} = 0 \). In the limit of zero magnetic field, \( \sigma_{xy} = 0 \) and \( \sigma_{xx} = \sigma_{yy} = \sigma_t \), where \( \sigma_t \) is the transverse conductivity of a free-electron gas.

3. Conductivity Tensor for \( \vec{q} \) Perpendicular to \( \vec{B}_0 \)

In this geometry the magnetic field \( \vec{B}_0 \) is along the z-direction and the wave vector \( \vec{q} \) is along x. Thus

\[
a_F = \frac{q_F \sin \theta_k}{\omega_c}
\]

(11.32)

and

\[
b_F = \frac{1}{i \omega_c \tau_0} (1 - i \omega \tau_0).
\]

Also, \( g_z = 0 \), but \( g_x \) and \( g_y \) are in general non-zero. To compare our results with those of Cohen, Harrison, and Harrison, we introduce their notation in which we define the following quantities:

\[
g_n(x) = \int_0^{\pi/2} J_n^2(\kappa \sin \theta_k) \sin \theta_k \, d\theta_k,
\]

(11.33)
The properties of these functions are discussed in Ref. 44. We can now write the expressions for the components of the conductivity tensor as

\[ \sigma_{xx} = \frac{3}{4} \sigma_o \kappa g_x^2 + \frac{3\sigma_o}{q \tau_o} \sum_{n=-\infty}^{\infty} \frac{(1-i\omega \tau_o)g_n(x)}{1+i(n\omega_c-\omega)\tau_o}, \quad (11.37) \]

\[ \sigma_{yy} = \frac{3}{4} \sigma_o \kappa g_y^2 + 3\sigma_o \sum_{n=-\infty}^{\infty} \frac{S_n(x)}{1+i(n\omega_c-\omega)\tau_o}, \quad (11.38) \]

\[ \sigma_{xy} = -\sigma_{yx} = \frac{3}{4i} \sigma_o \kappa g_x g_y + \frac{\sigma_o}{2q \tau_o} \sum_{n=-\infty}^{\infty} \frac{(1-i\omega \tau_o)g_n^*(x)}{1+i(n\omega_c-\omega)\tau_o}, \quad (11.39) \]

\[ \sigma_{zz} = 3\sigma_o \sum_{n=-\infty}^{\infty} \frac{r_n(x)}{1+i(n\omega_c-\omega)\tau_o}, \quad (11.40) \]
\[
\sigma_{xz} = \sigma_{zx} = \sigma_{yz} = \sigma_{zy} = 0. \tag{11.41}
\]

We also have
\[
g_x = \frac{2}{\Gamma q \tau_0} \left[ 1 - \sum_{n=-\infty}^{\infty} \frac{(1 - i \omega \tau_o) g_n(x)}{1 + i (n \omega_c - \omega) \tau_o} \right] \tag{11.42}
\]

and
\[
g_y = \frac{1}{\Gamma} \sum_{n=-\infty}^{\infty} \frac{g_n^*(x)}{1 + i (n \omega_c - \omega) \tau_o}. \tag{11.43}
\]

where
\[
\Gamma = 1 - \sum_{n=-\infty}^{\infty} \frac{g_n(x)}{1 + i (n \omega_c - \omega) \tau_o}. \tag{11.44}
\]

Eq. (11.40) is identical to the corresponding expression for \(\sigma_{zz}\) in Ref. 44. If we make the relaxation-time approximation, i.e., \(g_x = g_y = 0\), then the rest of the conductivity tensor components are identical to those given in Ref. 44.
CHAPTER III. QUANTUM MECHANICAL TREATMENT

We shall derive here the free-electron dielectric response of a semi-infinite medium in the presence of a static magnetic field directed perpendicular to the surface of the medium, by the self-consistent-field (SCF) method of Ehrenreich and Cohen. Our main objective in this particular calculation is to examine the effect of the boundary and the presence of the static magnetic field on the response of the system. Hence, to avoid complications in the algebra not related to these two effects, we shall treat electron collisions with impurities, lattice defects, etc. by invoking the simple relaxation-time approximation. In this approximation, the relaxation of the electrons towards a uniform equilibrium distribution is assumed. We shall assume the electrons to be scattered specularly at the surface of the medium, and the presence of the boundary will be taken into account by imposing an infinite potential barrier at the surface. The interaction of the electron spin with the static magnetic field will be explicitly included.

Consider then a free-electron gas, filling the half-space \( z > 0 \), in the presence of a static magnetic field \( B_0 \hat{z} \). In the SCF method, the many-body interactions of the electrons in the gas are replaced by the interactions of a single electron with a self-consistent field. Let this self-consistent field be described by the vector potential \( \mathbf{A}(\mathbf{r}, t) \). We choose the Landau gauge to describe the static magnetic field by the vector potential \( \mathbf{A}_0 = (0, B_0 x, 0) \).
The Hamiltonian of a single electron of charge $-e$ and mass $m$ in the presence of the electromagnetic field $\mathbf{B}_0$ is

$$H(t) = H_0 + H_1(t), \quad (III.1)$$

where

$$H_0 = \frac{1}{2m} \left( \mathbf{p} + \frac{e}{c} \mathbf{A}_0 \right)^2 + \mu_B \mathbf{B}_0 \sigma_z, \quad (III.2)$$

$$H_1(t) = \frac{e}{2c} \left( \mathbf{\nabla} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{\nabla} \right), \quad (III.3)$$

with the velocity operator $\mathbf{\nabla}$ given by

$$\mathbf{\nabla} = \frac{1}{m} \left( \mathbf{p} + \frac{e}{c} \mathbf{A}_0 \right), \quad (III.4)$$

$\mu_B = e\hbar / 2mc$ is the Bohr magneton, $\sigma_z$ is the z-component of the spin operator, and $\mathbf{p}$ is the free-electron momentum operator given by $\mathbf{p} = -i\hbar \mathbf{\nabla}$. Ref. 48 gives a complete set of states of the unperturbed Hamiltonian $H_0$ for an infinite medium without the spin-interaction term. This is given by

$$\psi_{\mathbf{k}, n}(\mathbf{x}) = \mathbf{1}_{\mathbf{k}, n} = (\Omega^*)^{-\frac{1}{2}} e^{i(k_yy + k_zz)} U_n(x + \frac{\hbar k_y}{m_B c}), \quad (III.4')$$
where the states are normalized inside a box of volume $Q'$, and $U_n(x)$ are normalized simple-harmonic-oscillator states, \(^{20}\) with $n = 0, 1, 2, \ldots$, $\omega_C = eB_0/mc$ is the cyclotron frequency. The presence of the spin-interaction in the Hamiltonian in Eq. (111.2) can be taken into account by multiplying $\psi_{k,n}(x)$ by the spin wave-function, $\chi^\pm$, for a particle of spin $1/2$. \(^{20}\) The $+$ sign denotes the spin-up, whereas the $-$ sign denotes the spin-down state. The presence of the infinite potential barrier at the boundary requires that $\psi_{k,n}(x)|_{z=0} = 0$. If we now normalize our states inside a box of volume $\Omega = (2L_x, 2L_y, L_z)$, the complete set of states of the unperturbed Hamiltonian $H_0$ (Eq. (111.2)) for half-space is given by

$$\psi_{k,n,\pm}(x) = |k,n,\pm\rangle = |k\rangle = \frac{1}{(L_y L_z)^{\frac{3}{2}}} e^{ik_y y} \sqrt{\frac{\hbar k_y}{m\omega_C}} U_n(x + \frac{y}{m\omega_C}) \chi^\pm \text{sink}_z. \quad (111.5)$$

The eigenvalues corresponding to these states are \(^{48}\)

$$E(n,k_z,\pm) = E_\alpha = (n + \frac{\Delta}{2})\hbar \omega_C + \frac{\hbar k_z^2}{2m} \pm \frac{\Delta}{2} \hbar \omega_C, \quad (111.6)$$

where we have introduced the last term in Eq. (111.6) because of the spin-interaction term in $H_0$.

Having obtained the eigenvalues and eigenstates of the unperturbed Hamiltonian, we now proceed to evaluate the response of the system under the influence of the perturbing Hamiltonian $H_1(t)$. The response
will be obtained from the single-particle density matrix, whose corresponding operator \( \rho \) satisfies the equation of motion

\[
\frac{\partial \rho}{\partial t} + \frac{i}{\hbar} [H, \rho] = \frac{\partial \rho}{\partial t}_{\text{coll}} ,
\]

(\ref{eq:coll_term})

where the term \( \frac{\partial \rho}{\partial t}_{\text{coll}} \) has been introduced to represent the time rate of change of the density matrix due to electron collisions with impurities, lattice defects, etc. In the simple relaxation-time approximation this collision term is given by

\[
\frac{\partial \rho}{\partial t}_{\text{coll}} = - \frac{\rho - \rho_0(H_0)}{\tau} ,
\]

(\ref{eq:collision_term})

where \( \rho_0(H_0) \) is the density operator for the system in the equilibrium state so that \( \rho_0(H_0) |\alpha\rangle = f_0(\alpha) |\alpha\rangle \), where \( f_0(\alpha) \) is Fermi-Dirac distribution given by Eq. (\ref{eq:fermi_dirac}) and \( \tau \) is a phenomenological electron lifetime.

Then, linearizing Eq. (\ref{eq:coll_term}) by writing

\[
\rho = \rho_0 + \delta \rho ,
\]

where \( \delta \rho \) is a small change in \( \rho \) from its equilibrium value \( \rho_0 \) brought about by the presence of the self-consistent field, we have

\[
\langle \alpha | \delta \rho | \alpha' \rangle = \Delta_{\alpha'\alpha} \langle \alpha | H_1 | \alpha' \rangle ,
\]

(\ref{eq:linearized_term})
where

\[ \Delta^{\alpha \alpha'} = \frac{f^\alpha(x) - f^\alpha(x')}{E^\alpha - E^\alpha' + \hbar (\omega + i/\tau)} \quad (111.10) \]

The induced current density at point \( \vec{x} \) at time \( t \) is given by

\[ \vec{J}(\vec{x}, t) = \text{Tr}\{\rho \vec{J}_{op}\} \quad (111.11) \]

where

\[ \vec{J}_{op} = -\frac{\hbar}{2} e [ (\nabla + \frac{e}{mc} \vec{A}(\vec{x}_0, t)) \delta(\vec{x} - \vec{x}_0) + \delta(\vec{x} - \vec{x}_0)(\nabla + \frac{e}{mc} \vec{A}(\vec{x}_0, t))] \quad (111.12) \]

and \( \text{Tr}(x) \) denotes the trace of the matrix \( x \).

Substituting Eq. (111.12) into Eq. (111.11) and dropping all terms higher than the linear terms in the self-consistent field, we obtain

\[ \vec{J}(\vec{x}, t) = \vec{J}_1(\vec{x}, t) + \vec{J}_2(\vec{x}, t) \quad (111.13) \]

where

\[ \vec{J}_1(\vec{x}, t) = -\frac{e}{2} \sum_\alpha \langle \alpha | [\nabla \delta(\vec{x} - \vec{x}_0) + \delta(\vec{x} - \vec{x}_0) \nabla] \delta_\beta | \alpha \rangle \quad (111.14) \]

and
\[ j_2(x, t) = -\frac{e}{2mc} \sum_{\alpha} \langle \alpha | A(\vec{x}_0, t) \delta(\vec{x} - \vec{x}_0) \rho_0 | \alpha \rangle . \quad (111.15) \]

Since we have assumed the electrons to be scattered specularly at the surface \( z = 0 \), we can define fields for \( z < 0 \) by the following conditions,

\[ E_{x, y}(z) = E_{x, y}(-z) , \quad (111.16a) \]

and

\[ E_z(z) = -E_z(-z) . \quad (111.16b) \]

Since

\[ \overline{E}(\vec{x}, t) = -\frac{1}{c} \frac{\partial A}{\partial t} (\vec{x}, t) , \quad (111.17) \]

it follows immediately that the \( x \)- and \( y \)-components of the vector potential have even parity about \( z = 0 \), whereas the \( z \)-component has odd parity. We can then define the Fourier transforms of the components of \( \overline{A}(\vec{x}) \) in the following way:

\[ A_{x, y}(\vec{q}) = \int_{-L_x}^{L_x} \int_{-L_y}^{L_y} \int_{-\infty}^{\infty} e^{-iq_y y} A_{x, y}(\vec{x}) , \quad (111.18) \]

and
\[ A_z(q) = \int_{-L_x}^{L_x} dx \int_{-L_y}^{L_y} dy \int_0^L dz \, e^{-iq_y y} \sin q_z A_z(x) . \quad (11.19) \]

Recall that in our reference frame \( q_x = 0 \). The inverse Fourier transforms are then given by

\[ A_{x,y}(\vec{x}) = \frac{2}{\Omega} \sum_{q_y} \sum_{q_z} A_{x,y}(q) \, e^{iq_y y} \cos q_z z , \quad (11.20) \]

and

\[ A_z(\vec{x}) = \frac{2}{\Omega} \sum_{q_y} \sum_{q_z} A_z(q) \, e^{iq_y y} \sin q_z z , \quad (11.21) \]

where \( q_y = n_y \pi/L_y \), with \( n_y = 0, \pm 2, \pm 4, \ldots \), and \( q_z = n_z \pi/L_z \), with \( n_z = 0, 2, 4, \ldots \), for the cosine series and \( n_z = 2, 4, \ldots \), for the sine series.

Going back to the expression for current density, we can write Eq. (11.14) as

\[ j_1(\vec{x}, t) = -\frac{e}{2} \sum_{\alpha \alpha'} \langle \alpha | \nabla \delta(\vec{x}-\vec{x}_o) + \delta(\vec{x}-\vec{x}_o) \nabla | \alpha' \rangle A_{\alpha \alpha'} \langle \alpha' | H_1 | \alpha \rangle , \quad (11.22) \]

where we have used Eq. (11.9) to obtain the expression for \( \langle \alpha' | \delta_p | \alpha \rangle \). Here \( \vec{x}_o = (x_o, y_o, z_o) \) refer to the coordinates of the electron, and \( \vec{x} = (x, y, z) \) refer to the coordinates of the point at
which the current density is being evaluated. If we now define the quantity \( \mathbb{V}(\mathbf{q}) \) by

\[
\mathbb{V}(\mathbf{q}) = \mathbf{v}_x, y \cdot e^{iq\cdot y_0 \cos(q_zz_0)} + e^{iq\cdot y_0 \cos(q_zz_0)} \mathbf{v}_x, y ,
\]

and

\[
\mathbb{V}_z(\mathbf{q}) = \mathbf{v}_z \cdot e^{iq\cdot y_0 \sin(q_zz_0)} + e^{iq\cdot y_0 \sin(q_zz_0)} \mathbf{v}_z ,
\]

we can write

\[
\langle \alpha' | H_1 | \alpha \rangle = \frac{e}{2c} \Omega \sum_q \langle \alpha' | \mathbb{V} | \alpha \rangle \cdot \mathbb{A}(\mathbf{q}) ,
\]

where \( \mathbb{A}(\mathbf{q}) \) is defined by Eqs. (III.18) and (III.19), and \( \mathbf{v}_x, \mathbf{v}_y, \text{ and } \mathbf{v}_z \) are the three components of the velocity operator defined by Eq. (III.4).

Substituting Eq. (III.25) into Eq. (III.22) and Fourier transforming \( \mathbb{j}_1(\mathbf{x},t) \) in space and time, we obtain

\[
\mathbb{j}_1(q_y, q_z, \omega) = -\frac{e}{2\omega c} \sum_q \sum_{\alpha \alpha'} \Delta_{\alpha \alpha'} \langle \alpha' | \mathbb{V}(q_y, q_z) | \alpha \rangle^* \langle \alpha' | \mathbb{V}(q_y, q_z) | \alpha \rangle \cdot \mathbb{A}(\mathbf{q}, \omega)
\]

Similarly, by Fourier transforming \( \mathbb{j}_2(\mathbf{x},t) \) from Eq. (III.15), we obtain
\[ j_{2x,y}(q_y,q_{1z}) = - \frac{2}{\Omega m c} \sum_{q_z} A_{x,y}(q_y,q_z)[\{\delta(q_z+q_{1z}) + \delta(q_z-q_{1z})\}N \]
\[ - \frac{\beta}{\bar{\omega}} \sum_{\alpha} f_{\alpha}(E_\alpha)[\delta(2k_z+q_z+q_{1z}) + \delta(2k_z-q_z-q_{1z}) \]
\[ + \delta(2k_z+q_z-q_{1z}) + \delta(2k_z-q_z+q_{1z})] \], \quad (111.27) \]

and

\[ j_{2z}(q_y,q_{1z}) = - \frac{2}{\Omega m c} \sum_{q_z} A_{z}(q_y,q_z)[\{\delta(q_z-q_{1z}) - \delta(q_z+q_{1z})\}N \]
\[ - \frac{\beta}{\bar{\omega}} \sum_{\alpha} f_{\alpha}(E_\alpha)[\delta(2k_z+q_z-q_{1z}) + \delta(2k_z-q_z+q_{1z}) \]
\[ - \delta(2k_z+q_z+q_{1z}) - \delta(2k_z-q_z-q_{1z})] \], \quad (111.28) \]

where \( N \) is the total number of electrons in volume \( \Omega \).

The quantities \( \langle \alpha' | V | \alpha \rangle \) are evaluated in Appendix II and are given by

\[ \langle \alpha' | V | \alpha \rangle = i \left( -\frac{\hbar}{2m} \right)^{\frac{3}{2}} \sum_{s,s'} \delta(k_y+q_y-k_{1y})[\delta(q_z+k_{1z}-k_z) + \delta(q_z-k_{1z}+k_z) \]
\[ - \delta(q_z+k_{1z}+k_z) - \delta(q_z-k_{1z}-k_z)] \chi^{(-)}_{n' n}(q_y) \], \quad (111.29) \]

\[ \langle \alpha' | V | \alpha \rangle = \delta(s,s') \delta(k_{1z}-k_z-q_y)[\delta(q_z+k_{1z}-k_z) + \delta(q_z-k_{1z}+k_z) - \delta(q_z+k_{1z}+k_z) \]
\[ - \delta(q_z-k_{1z}+k_z)] \left( \frac{\hbar q_y}{\mu} \right) _{n' n}(q_y) + \left( \frac{\hbar \omega_c}{2m} \right) \chi^{(+)}_{n' n}(q_y) \], \quad (111.30) \]
\[ \langle \alpha' | V_z | \alpha \rangle = - \frac{ih}{m} \delta_{s',s} \delta(q_y + k - k') \{ [q_z/2 - k] \delta(q_z + k') - [q_z/2 + k] \delta(q_z - k') \} \]
\[ + (q_z/2 + k_z) \delta(q_z - k' + k_z) - (q_z/2 + k_z) \delta(q_z + k' + k_z) \]
\[ - (q_z/2 - k_z) \delta(q_z - k' - k_z) \} f_{n',n}(q_y), \]  
\[ (111.31) \]

where \( s \) and \( s' \) refer to the spin quantum numbers in \( \alpha \) and \( \alpha' \),

\[ \chi_{n',n}^{(+)}(q) = (n+1)^{\frac{1}{2}} f_{n',n+1}(q) \pm n^{\frac{1}{2}} f_{n',n-1}(q), \]
\[ (111.32) \]

and

\[ f_{n',n}(q) = \int_{-\infty}^{\infty} dx \ U_{n',n}(x + \frac{\hbar q}{m_0 c}) U_n(x). \]
\[ (111.33) \]

From Eq. (111.17) we have

\[ E(q, \omega) = \frac{i \omega}{c} \mathcal{R}(q, \omega). \]
\[ (111.34) \]

Using Eq. (111.34) in Eqs. (111.26), (111.27), and (111.28), for the current density, we can see that the current density can be written in the form

\[ j_i(q, \omega) = \sum_{j=1}^{3} \sum_{q^i} \sigma_i j(q,q^i,\omega) E_j(q^i,\omega), \]
\[ (111.35) \]
where 1, 2, 3, stand for \( x, y, z \) respectively, and the conductivity tensor components are now given by

\[
\sigma_{ij}(q, q', \omega) = \delta_{q_x} \delta_{q_y} \delta_{q_z} \left[ D_{ij}(q, q', \omega) q_x' q_y' q_z' + S_{ij}(q, q', \omega) \right]
\]  

The dielectric response thus consists of a diagonal part \( D_{ij}(q, \omega) \), which, as is given below, is the usual infinite-medium response, and a non-diagonal part \( S_{ij}(q, q', \omega) \), which results from the imposition of the infinite potential barrier at the boundary. We shall refer to the first as the bulk contribution, and to the second as the surface contribution. These terms are given by

\[
D_{xx} = \frac{i e^2}{2 \Omega_m \omega} \left[ 2N + \frac{\hbar \omega}{\Omega_m} \frac{\hbar}{\omega} \sum_{n, n'} \sum_{k_y, k_z} \frac{2}{1} \left\{ \chi^{(-)}_{n n'} \left( \frac{\hbar \omega}{2m} \right) f_{n' n}(q_y) \right\} \Delta(n, k_z + q_z s; n, k_z, s) \right],
\]

\[
D_{xy} = D_{xy} = \frac{i e^2}{2 \Omega_m \omega} \frac{\hbar \omega}{\Omega_m} \frac{\hbar}{\omega} \sum_{n, n'} \sum_{k_y, k_z} \frac{2}{1} \left\{ \chi^{(+)}_{n n'}(q_y) \right\} \Delta(n, k_z + q_z s; n, k_z, s),
\]

\[
D_{yy} = \frac{i e^2}{2 \Omega_m \omega} \left[ 2N + 2m \sum_{n, n'} \sum_{k_y, k_z} \frac{2}{1} \left\{ \frac{\hbar \omega}{2m} f_{n' n}(q_y) \right\} \Delta(n, k_z + q_z s; n, k_z, s) \right],
\]

\[
D_{yz} = \frac{i e^2}{2 \Omega_m \omega} \frac{\hbar \omega}{\Omega_m} \frac{\hbar}{\omega} \sum_{n, n'} \sum_{k_y, k_z} \frac{2}{1} \left\{ \chi^{(+)}_{n n'}(q_y) \right\} \Delta(n, k_z + q_z s; n, k_z, s),
\]

\[
D_{xz} = \frac{i e^2}{2 \Omega_m \omega} \frac{\hbar \omega}{\Omega_m} \frac{\hbar}{\omega} \sum_{n, n'} \sum_{k_y, k_z} \frac{2}{1} \left\{ \chi^{(+)}_{n n'}(q_y) \right\} \Delta(n, k_z + q_z s; n, k_z, s),
\]

\[
D_{zx} = \frac{i e^2}{2 \Omega_m \omega} \frac{\hbar \omega}{\Omega_m} \frac{\hbar}{\omega} \sum_{n, n'} \sum_{k_y, k_z} \frac{2}{1} \left\{ \chi^{(+)}_{n n'}(q_y) \right\} \Delta(n, k_z + q_z s; n, k_z, s),
\]

\[
D_{zy} = \frac{i e^2}{2 \Omega_m \omega} \frac{\hbar \omega}{\Omega_m} \frac{\hbar}{\omega} \sum_{n, n'} \sum_{k_y, k_z} \frac{2}{1} \left\{ \chi^{(+)}_{n n'}(q_y) \right\} \Delta(n, k_z + q_z s; n, k_z, s),
\]

\[
D_{zz} = \frac{i e^2}{2 \Omega_m \omega} \frac{\hbar \omega}{\Omega_m} \frac{\hbar}{\omega} \sum_{n, n'} \sum_{k_y, k_z} \frac{2}{1} \left\{ \chi^{(+)}_{n n'}(q_y) \right\} \Delta(n, k_z + q_z s; n, k_z, s),
\]
\[ D_{xx} = D_{zx} = -\frac{\text{i} e^2}{\Omega_0} \left( \frac{\hbar \omega_c}{2m} \right)^{\frac{1}{2}} \sum_{n, n'} k_y k_z \sum_{s=1}^{2} x^{(-)}(n, n') f_{n'} n(q_y) f_{n} n(q_z + 2k_z) \left( \Delta(n', k_z + q_z, s; n, k_z, s) \right), \] (111.40)

\[ D_{yz} = -D_{zy} = \frac{\hbar}{\Omega_0} \sum_{n, n'} k_y k_z \sum_{s=1}^{2} (q_z + 2k_z) f_{n'} n(q_y) f_{n} n(q_y) \left( \Delta(n', k_z + q_z, s; n, k_z, s) \right) \] (111.41)

\[ D_{zz} = \frac{\text{i} e^2}{2\Omega_0} \left[ 2N + 2m \left( \frac{\hbar \omega_c}{2m} \right)^{\frac{1}{2}} \sum_{n, n'} k_y k_z \sum_{s=1}^{2} (q_z + 2k_z) f_{n'} n(q_y) f_{n} n(q_y) \left( \Delta(n', k_z + q_z, s; n, k_z, s) \right) \right], \] (111.42)

\[ S_{xx}(\vec{q}', q_x, \omega) = -\frac{\text{i} e^2}{2\Omega_0} \sum_{n, n'} k_y \sum_{s=1}^{2} \left[ f_{n} (n, \frac{q_z - q_z'}{2}, s) + f_{n} (n, -\frac{q_z - q_z'}{2}, s) \right] \] (111.43)

\[ S_{xx}(\vec{q}', q_x, \omega) = -S_{yx}(\vec{q}', q_x, \omega) \]

\[ = -\frac{\hbar \omega_c}{\Omega_0} \frac{1}{2m} \sum_{n, n'} k_y \sum_{s=1}^{2} x^{(-)}(n, n') f_{n'} n(q_y) f_{n} n(q_y) \left( \Delta(n', n_z + q_z, s; n, n_z - q_z, s) \right) \] (111.44)
\( S_{yy}(q', \vec{q}_s, \omega) = -\frac{ie^2}{2\Omega m \omega} \sum_{s=1}^{\infty} \sum_{n, k_y} \left\{ f_0(n, \frac{q_z + q'_z}{2}, s) + f_0(n, \frac{q_z - q'_z}{2}, s) \right\} \)
\[ - \frac{ie^2}{\Omega \omega} \sum_{s=1}^{\infty} \sum_{n, n'} k_y \left\{ \frac{\hbar q_y}{2m} f_{n'} n(q_y) + \frac{\hbar \omega_c}{2m} \chi^+(q_y) \right\}^2 \]
\[ \times \left[ \Delta(n', \frac{q_z + q'_z}{2}, s; n, \frac{q_z - q'_z}{2}, s) \right] \]
\[ + \Delta(n', \frac{q_z - q'_z}{2}, s; n, \frac{q_z + q'_z}{2}, s) \right\} , \quad (111.45) \]

\( S_{xz}(q', q_s, \omega) = S_{zx}(q', q_s, \omega) \)
\[ = \frac{ie^2}{\Omega \omega} \left( \frac{\hbar}{2m} \right) \left( \frac{\hbar \omega_c}{2m} \right)^{\frac{1}{2}} \sum_{s=1}^{\infty} \sum_{n, n'} k_y \left\{ \frac{\hbar q_y}{2m} f_{n'} n(q_y) + \frac{\hbar \omega_c}{2m} \chi^+(q_y) \right\} \left( \frac{q_z + q'_z}{2}, s; n, \frac{q_z - q'_z}{2}, s \right) \]
\[ - \Delta(n', \frac{q_z - q'_z}{2}, s; n, \frac{q_z + q'_z}{2}, s) \right\} , \quad (111.46) \]

\( S_{yz}(q', \vec{q}_s, \omega) = -S_{zy}(q', \vec{q}_s, \omega) = \frac{ie^2}{\hbar \omega m} \sum_{s=1}^{\infty} \sum_{n, n'} k_y \left\{ \frac{\hbar q_y}{2m} f_{n'} n(q_y) + \frac{\hbar \omega_c}{2m} \chi^+(q_y) \right\} \left( \frac{q_z + q'_z}{2}, s; n, \frac{q_z - q'_z}{2}, s \right) \]
\[ - \Delta(n', \frac{q_z - q'_z}{2}, s; n, \frac{q_z + q'_z}{2}, s) \right\} , \quad (111.47) \]
and

\[ S_{zz}(\tilde{q}', \tilde{q}, \omega) = -\frac{i e^2}{2\hbar m_0} \sum_{s=1}^{\Sigma} \left\{ f_0(n, \frac{q_z+q'_z}{2}, s) + f_0(n, \frac{q_z-q'_z}{2}, s) \right\} \]

\[ -\frac{i e^2}{\omega} \left( \frac{\hbar}{2m} \right)^2 q_z q'_z \sum_{n', n, k_y} f_{n'n}^2(q_y) \]

\[ \left\{ \Delta(n', \frac{q_z+q'_z}{2}, s; n, \frac{q_z-q'_z}{2}, s) \right\} \]

\[ + \Delta(n', \frac{q_z-q'_z}{2}, s; n, \frac{q_z+q'_z}{2}, s) \}. \quad (111.48) \]

Note that the surface contributions are non-diagonal in \( q_z \), a consequence of the inhomogeneity of space in the z-direction. From these results, we can make the following observations on the nature of the response of a semi-infinite medium.

1. A single Fourier component of the response can no longer be obtained from the corresponding Fourier component of the exciting field, as is the case for a spatially homogeneous system in the RPA description. The presence of a boundary surface at \( z = 0 \) destroys the homogeneity of space along the z-direction, which results in a mixing among the z-components of the momentum of the response between various states. As a result, each component of the conductivity tensor is no longer a scalar quantity but a matrix.

2. The surface contribution \( S \) is purely quantum mechanical. It has been demonstrated, for zero magnetic fields, that in the semi-classical limit (\( \hbar \to 0 \)), the response of the semi-infinite medium
is given entirely by the semi-classical limit of the bulk contribution $\mathcal{D}$. This can also be seen from the calculation of Kliewer and Fuchs who obtained a semi-classical expression for the dielectric function (zero magnetic field) of a semi-infinite slab from the solutions of the Boltzmann equation. They found, by assuming the electrons to be specularly scattered at the surface, that the response could be expressed in terms of the infinite-medium dielectric functions.

3. It can be seen from the expressions that we have obtained that the surface contribution $S$ is non-local, and that it does not exist in the zero wave-vector limit. Hence, the local theory of optical properties is unchanged by the inclusion of such effects.

Thus, we have obtained general expressions for the response of a bounded medium in the presence of a static magnetic field. As can be seen from Eqs. (111.37) - (111.48), the general formulation of the problem is somewhat complex and mathematically involved.

As a first step in examining the nature of the surface contributions, we examined the effect of a static disturbance on the charge density of the electron gas. For further simplification, we assumed that the disturbance was represented by a one-dimensional self-consistent potential $V(q)$ inside the electron gas. The wave-vector of the response also has a single component $q$, perpendicular to the surface. We then found that the change in the charge density, $\delta \rho_e(q)$, due to the disturbance, was given by

\[
\delta \rho_e(q) = \sum_{q'} \left[ \mathcal{D}(q') \delta_{q,q'} + S(q,q') \right] V(q'),
\]  

(111.49)
where $D(q')$ is the usual bulk response for an infinite medium, and $S(q,q')$ is the analog of the surface contribution in Eq. (111.36).

At absolute zero temperature, $D(q)$ was found to be given by

$$D(q) = -\frac{8m_0 c}{\pi^2 a_0} \frac{1}{\hbar q} \sum_{n=0}^{\infty} \left| \frac{1+q/2K_n}{1-q/2K_n} \right|,$$

where

$$K_n = \left( \frac{\hbar^2}{\pi} \right) [E_F - (n+\frac{1}{2})\hbar \omega_c]^{\frac{1}{2}},$$

$n_o$ is the largest integer which is less than or equal to $E_F/(\hbar \omega_c) - \frac{1}{2}$, and $a_o = \hbar^2/(me^2)$ is the Bohr radius.

Similarly,

$$S(q,q') = \frac{32}{\pi L_z} \frac{\hbar \omega_c}{\hbar a_o} \frac{(n_- - n_+) / (qq')}{(qq')},$$

where $n_\pm$ is the largest integer less than or equal to

$$\frac{1}{\hbar \omega_c} \left( \frac{2m}{\hbar} \right)^{\frac{1}{2}} \left[ k_F^2 - (\frac{q+q'}{2})^2 \right] - \frac{1}{2},$$

with $k_F^2 = 2m E_F/\hbar^2$. In these calculations we have ignored the spin-interaction term in the Hamiltonian [Eq. (111.2)].

Upon examining the definition of $n_\pm$ closely we find for $q' > q$, 

\begin{equation}
S(q,q') = \begin{cases}
0, & q' \geq 2k_F + q,
\frac{32}{\pi L_z} \frac{m_0 c}{\hbar a_0} \frac{n_-}{qq'}, & 2k_F - q < q' < 2k_F + q,
\frac{32}{\pi L_z} \frac{m_0 c}{\hbar a_0} \frac{n_- - n^+}{qq'}, & q' < 2k_F + q, 2k_F - q,
\end{cases}
\tag{111.52a}
\end{equation}

From Eqs. (111.52) and (111.53) it is clear that a potential \( V(q) \) cannot give rise to a response \( \delta \rho_e(q') \) for \( q' \) outside the region

\[ 0 < q' < 2k_F + q. \]

As an illustration, the charge density in real space, \( \delta \rho_e(x) \), which is given by

\[ \delta \rho_e(x) = \frac{2}{L_z} \sum_q \cos q' x \delta \rho_e(q), \]

was calculated for the simple one-dimensional potential

\[ V(x) = V(0) \cos qx. \]
The computed value of the charge density showed that the contribution resulting from the surface term $S(q,q')$, was significant for distances $\sim 1/k_F$ from the surface. Hence, it is reasonable to conclude that the contributions from $S(q,q')$ are localized near the surface, and may be neglected for studying effects associated with the bulk response of the medium.

The formalism that has been developed in this work may be used to calculate the optical properties (reflection, transmission, absorption) of a thin film in the presence of a static magnetic field. The absorptance, for p-polarized incident light and frequencies $\omega \geq \omega_p$, may be studied to see what effect the magnetic field has on the resonant characteristics in the absorptance, brought upon by excitation of bulk plasmons. The effect of static magnetic fields on the collective excitations of an electron gas has been studied in several theoretical investigations. A calculation of the optical properties can demonstrate the extent to which these effects might be observed experimentally.

The static magnetic field, whose presence is manifested by the Landau levels (see Eq. (111.6)), affects plasmon modes significantly for $\omega_c \sim \omega_p$, where $\omega_p$ is the plasma frequency. Plasmons can bring about single-particle excitations between Landau levels, and such excitations can significantly affect plasmon modes when the above-mentioned condition is met. For most metals, $\omega_p \sim 5 - 15 \text{ eV}$. Hence, it would require extremely strong magnetic fields, $\sim 100$ kilogauss, to
affect the plasmon modes in a metal. In degenerate semiconductors, where the density of free-carriers is much smaller than that in metals, these effects may be observed for much weaker magnetic fields.

As mentioned earlier, the effect of a magnetic field on excitations localized near the surface may also be investigated by the formalism developed in this work. For such effects, the non-diagonal components, $S(q,q')$, of the dielectric response will also have to be included.
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APPENDIX 1

The quantity $G$, which appears in Eq. (II.11) of Part II for $f_1(\nu)$, has to be evaluated from the self-consistency requirement

$$\frac{\partial f}{\partial \varepsilon_k} G = \sum_{\nu'} W_{\kappa \nu'} f_1(\nu') . \tag{A1.1}$$

Summing both sides of Eq. (A1.1) over $\kappa$, we have

$$- \frac{4\pi}{m} v_F G = \sum_{\kappa'} \frac{1}{\tau(\varepsilon_{\kappa'})} f_1(\nu') , \tag{A1.2}$$

where the definition of $\tau(\varepsilon_{\kappa'})$ from Eq. (II.4) of Part II has been used.

Substituting the expression for $f_1(\nu')$ from Eq. (II.11) of Part II into Eq. (A1.1) and performing the necessary integrations and algebraic manipulations, we obtain

$$G = \frac{e v_F}{2i m \tau_0} \int_0^\pi d\theta_k \sin\theta_k \sum_{n=-\infty}^\infty J_n(\chi \sin\theta_k) \left[ \frac{\chi}{2} \sin\theta_k \right] + \frac{J_{n+1}(x \sin\theta_k)}{b_F + n + 1} + \frac{J_{n-1}(x \sin\theta_k)}{b_F + n - 1} + \frac{E_F}{2} \sin\theta_k \left[ \frac{J_{n+1}(x \sin\theta_k)}{b_F + n + 1} \right] + E_z \cos\theta_k \frac{J_n(x \sin\theta_k)}{b_F + n} , \tag{A1.3}$$

where

$$\Gamma = 1 - \frac{1}{2i m \tau_0} \int_0^\pi d\theta_k \sin\theta_k \sum_{n=-\infty}^\infty \frac{J_n^2(x \sin\theta_k)}{b_F + n} . \tag{A1.4}$$
Thus, $G$ can be written as

$$G = eV_F \left[ \frac{1}{2} E g_x + \frac{1}{2i} E g_y + E g_z \right], \quad \text{(A1.5)}$$

where

$$g_x = \frac{1}{2i \omega_c \tau_0 \Gamma} \sum_{n=-\infty}^{\infty} \int_0^\pi d\theta_k \sin^2 \theta_k \frac{J_n(x \sin \theta_k)}{b_F + n},$$

$$\Lambda_{n+1, n-1}^+(x \sin \theta_k), \quad \text{(A1.6)}$$

$$g_y = \frac{1}{2i \omega_c \tau_0 \Gamma} \sum_{n=-\infty}^{\infty} \int_0^\pi d\theta_k \sin^2 \theta_k \frac{J_n(x \sin \theta_k)}{b_F + n},$$

$$\Lambda_{n-1, n+1}^-(x \sin \theta_k), \quad \text{(A1.7)}$$

and

$$g_z = \frac{1}{2i \omega_c \tau_0 \Gamma} \sum_{n=-\infty}^{\infty} \int_0^\pi d\theta_k \sin \theta_k \cos \theta_k \frac{J_n^2(x \sin \theta_k)}{b_F + n}. \quad \text{(A1.8)}$$

$\Lambda_{n, m}^+(x)$ is defined in Eq. (11.23) for Part II.

In the relaxation-time approximation, all perturbed states are assumed to relax towards the unperturbed state of uniform equilibrium $f_0$ given by the Fermi-Dirac distribution, in a time $\tau_0$. In this case the collision term is given by
\[
\frac{\partial f_k}{\partial t} \bigg|_{\text{coll}} = -\frac{f_{k} - f_0}{\tau_0},
\]

and the term

\[
\sum_{k} W_{kk'} f_1(\mathbf{v}')
\]

does not exist. Consequently, \( G \) does not exist. In this work, the relaxation-time limit will be made by setting \( g_x = g_y = g_z = 0 \).
APPENDIX II

Using the definition of $V(q)$ from Eqs. (111.23) and (111.24) of Part II and the velocity operator $v$ from Eq. (111.4) of Part II, we can write

$$\langle \alpha' | x(q) | \alpha \rangle = -\frac{i\hbar}{m} \langle \alpha' | \frac{\partial}{\partial x} e^{iq_y y} \cos q_z z + e^{iq_y y} \cos q_z z \frac{\partial}{\partial x} | \alpha \rangle$$

$$= -\frac{2i\hbar}{m} \langle \alpha' | e^{iq_y y} \cos q_z z \frac{\partial}{\partial x} | \alpha \rangle .$$

$$= -\frac{2i\hbar}{m} \frac{1}{L_y L_z} \int_{-L_y}^{L_y} dy \ e^{-ik_y y} e^{iq_y y} e^{ik_y y} \int_{0}^{L_z} dz \ \sin k_z z \ \cos q_z z \ \sin k_z z$$

$$= \left( ky + \frac{\hbar k_y}{m\omega_c} \right) \frac{\hbar}{m} \ U_n(x + \frac{\hbar k_y}{m\omega_c}) , \quad (A11.1)$$

where we have used Eq. (111.5) from Part II for $|\alpha\rangle$.

The integrations over $y$ and $z$ are straightforward and yield

$$\int_{-L_y}^{L_y} dy \ e^{-ik_y y} e^{iq_y y} e^{ik_y y} \int_{0}^{L_z} dz \ \sin k_z z \ \cos q_z z \ \sin k_z z$$

$$= \frac{L_y L_z}{2} \delta(k_y + q_y - k_y') [\delta(q_z + k_z - k_z') + \delta(q_z - k_z' + k_z')$$

$$- \delta(q_z + k_z' + k_z) - \delta(q_z - k_z' - k_z)] . \quad (A11.2)$$

The remaining integral,
can be expressed as

\[ I = \int_{-\infty}^{\infty} dx \ U_{n}^{i}(x + \frac{\hbar k_{y}^{i}}{m_{0} c}) \frac{\partial}{\partial x_{0}} U_{n}(x + \frac{\hbar k_{y}}{m_{0} c}), \]

by invoking the condition \( k_{y}^{i} = k_{y} + q_{y} \) from the previous integral.

The functions \( U_{n}(x) \) are given by

\[ U_{n}(x) = N_{n} H_{n}(\xi x) e^{-\frac{1}{2} \xi^{2} x^{2}}, \quad (A11.3) \]

where

\[ N_{n} = \left( \frac{\xi}{\pi^{1/4} 2^{n} n!} \right)^{1/2}, \quad (A11.4) \]

\[ \xi = \left( \frac{m_{0} c}{\hbar} \right)^{1/2}, \quad (A11.5) \]

and the \( H_{n}(x) \) are Hermite polynomials which satisfy the recursion relations,

\[ H_{n}^{i}(x) = 2n H_{n-1}(x), \quad (A11.6) \]

and
\[ H_{n+1}(x) = 2x H_n - 2n H_{n-1}(x), \quad (A11.7) \]

where the prime denotes differentiation with respect to the argument.

Using the definition of \( U_n(x) \) from Eq. (A11.3) and the recursion relations, Eqs. (A11.6) and (A11.7), we have

\[ 1 = - \left( \frac{m \omega_c}{2 \hbar} \right)^{\frac{1}{2}} \chi_n^{(+)}(q_y), \quad (A11.8) \]

where \( \chi_n^{(+)} \) is defined by Eq. (III.32) of Part II. Thus, combining Eqs. (A11.1), (A11.2), and (A11.8) we find

\[ \langle \alpha' | V_x(q) | \alpha \rangle = i \left( \frac{\hbar \omega_c}{2m} \right)^{\frac{1}{2}} \mathbf{\delta}(k_z + k_x - k_y) \left[ \mathbf{\delta}(q_z + k_z + k_x) + \mathbf{\delta}(q_z - k_z - k_x) \right] \chi_n^{(+)}(q_y) \]. \quad (A11.9)

Similarly, we can write

\[ \langle \alpha' | V_y(q) | \alpha \rangle = \langle \alpha' | V_y e^{i q_y y} \cos q_z z + e^{i q_y y} \cos q_z z v_y | \alpha \rangle \]

\[ = \langle \alpha' | \left( - \frac{i \hbar}{m} \frac{\partial}{\partial y} + \omega_c \right) e^{i q_y y} \cos q_z z + e^{i q_y y} \cos q_z z \]

\[ \left( - \frac{i \hbar}{m} \frac{\partial}{\partial y} + \omega_c \right) | \alpha \rangle \]

\[ = \langle \alpha' | e^{i q_y y} \cos q_z z \left( \frac{\hbar q_y}{m} + 2 \left( - \frac{i \hbar}{m} \frac{\partial}{\partial y} + \omega_c \right) \right) | \alpha \rangle . \]
Integrating, we obtain

\[
\langle \alpha' | V_y(q) | \alpha \rangle = \delta(k_y' - k_y - q_y) \left[ \delta(q_z + k_z - k_z') + \delta(q_z - k_z + k_z') - \delta(q_z + k_z + k_z') \right] \\
- \delta(q_z - k_z - k_z') \left[ \left( \frac{\hbar q_y}{2m} \right) n_{n'}(q_y) \right] \\
+ \left( \frac{\hbar \omega_c}{2m} \right)^{1/2} n_{n'}(q_y) \right] .
\]

Finally, for the matrix element of \( V_z(q) \), we have

\[
\langle \alpha' | V_z(q) | \alpha \rangle = \langle \alpha' | V_z e^{iq_y y} \sin q_z z + e^{iq_y y} \sin q_z z V_z | \alpha \rangle \\
= -\frac{i\hbar}{m} \langle \alpha' | e^{iq_y y} \left[ \frac{\partial}{\partial z} \sin q_z z + \sin q_z z \frac{\partial}{\partial z} \right] | \alpha \rangle \\
= -\frac{i\hbar}{m} \langle \alpha' | e^{iq_y y} \left[ q_z \cos q_z z + 2 \sin q_z z \frac{\partial}{\partial z} \right] | \alpha \rangle
\]

or

\[
\langle \alpha' | V_z(q) | \alpha \rangle = -\frac{i\hbar}{m} \delta(q_y + k_y - k_y') \left[ (q_z / 2 - k_z) \delta(q_z + k_z') - (q_z / 2 + k_z) \delta(q_z + k_z) \right] \\
+ (q_z / 2 + k_z) \delta(q_z - k_z + k_z') - (q_z / 2 + k_z) \delta(q_z + k_z + k_z') \\
- (q_z / 2 - k_z) \delta(q_z - k_z - k_z') \left[ \frac{\partial}{\partial z} \right] n_{n'}(q_y) .
\]

(A11.11)