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RAMAN SCATTERING BY A MOLECULE ADSORBED AT THE SURFACE OF A THIN METALLIC FILM

Iowa State University PH.D. 1980

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Raman scattering by a molecule adsorbed at
the surface of a thin metallic film

by

Mark Francis Wright

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>A. Electromagnetic Fields in Metals</td>
<td>1</td>
</tr>
<tr>
<td>B. Raman Scattering Theories</td>
<td>4</td>
</tr>
<tr>
<td>II. THE ELECTROMAGNETIC FIELDS INSIDE A THIN METALLIC FILM</td>
<td>11</td>
</tr>
<tr>
<td>A. RPA Conductivity Tensor</td>
<td>13</td>
</tr>
<tr>
<td>B. Solution of the Wave Equation</td>
<td>25</td>
</tr>
<tr>
<td>C. Display of Fields</td>
<td>30</td>
</tr>
<tr>
<td>D. Point of Clarification</td>
<td>35</td>
</tr>
<tr>
<td>III. RAMAN SCATTERING THEORY</td>
<td>40</td>
</tr>
<tr>
<td>A. S Matrix Development</td>
<td>40</td>
</tr>
<tr>
<td>B. The Resonance Diagram</td>
<td>45</td>
</tr>
<tr>
<td>C. Electron Scattering</td>
<td>48</td>
</tr>
<tr>
<td>D. The Differential Cross Section</td>
<td>51</td>
</tr>
<tr>
<td>E. Molecule-Electron Interaction</td>
<td>54</td>
</tr>
<tr>
<td>IV. RESULTS AND CONCLUSIONS</td>
<td>59</td>
</tr>
<tr>
<td>A. Frequency Dependence of $\frac{d\sigma}{d\Omega}$</td>
<td>59</td>
</tr>
<tr>
<td>B. Effects of Higher Electron Density</td>
<td>61</td>
</tr>
<tr>
<td>C. Roughness</td>
<td>65</td>
</tr>
<tr>
<td>D. Epilogue</td>
<td>68</td>
</tr>
<tr>
<td>V. APPENDIX A: CURRENT-CURRENT RESPONSE FUNCTION</td>
<td>69</td>
</tr>
<tr>
<td>VI. APPENDIX B: $\mathbf{k}$ SPACE INTEGRATIONS</td>
<td>72</td>
</tr>
<tr>
<td>VII. APPENDIX C: TRIGONOMETRIC INTEGRATIONS</td>
<td>74</td>
</tr>
<tr>
<td>VIII. REFERENCES</td>
<td>76</td>
</tr>
<tr>
<td>IX. ACKNOWLEDGEMENTS</td>
<td>79</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

Beginning in 1974 (1), and on several occasions since (2,3,4), Surface Enhanced Raman scattering (SER) has been observed for molecules adsorbed to metallic substrates such as silver, copper, and gold. The cross section is found to be four or more magnitudes larger than the isolated molecule cross section. A great amount of theoretical work arose in an attempt to explain this phenomenon. This chapter will briefly describe the work of past authors who have treated topics relevant to my research problem. Since the problem of electromagnetic fields in thin films comprises most of Chapter II, I will first review the research in this area, and then explore the array of current theories of SER. Chapter II will detail the calculation of the vector potential. Chapter III will use those calculations to determine the Raman scattering cross section in the manner prescribed by Loudon (5). Results and conclusions will be presented in Chapter IV.

A. Electromagnetic Fields in Metals

In a local calculation of electromagnetic fields in the presence of a boundary, electric fields normal to the surface are discontinuous. Local calculations treat the current density at a point in space as being linearly related to the electric field at the same point. In real physical situations, however, all field are continuous. A variety of authors perform nonlocal calculations for electromagnetic fields in metals. Nonlocal calculations have the currents at a point in the
metal depend on the values of the field at all other points in the metal. For problems which possess translational invariance the preceding statement can also simply mean that the response functions depend on the wavelength of the excitation as well as the frequency. Without translational invariance the response functions do not assume such a simple form. Van Gelder (6) uses linear response theory in the density matrix formulation, with electronic wavefunctions which vanish at the surface, to treat a metallic film. He performs a nonlocal calculation for normally incident light and examines the difference in the surface impedance for this calculation versus a classical solution arrived at from the Boltzmann equation. Melynk and Harrison (7) neglect the single particle excitation contribution to the quantum mechanical nonlocal dielectric functions and inspect the reflectance and transmittance of thin metallic films. They concern themselves primarily with excitation of plasmons. Kliewer and Fuchs (8) assume specular reflection of the electrons at the boundary of a semi-infinite metal and derive expressions for the displacement vector. Explicit use is made of the Lindhard dielectric functions in a subsequent publication (9), rather than the dielectric functions derived from the Boltzmann equation (8). Jones, Kliewer and Fuchs (10) assume specular reflection conditions for a thin metal film and expand the fields in Fourier series with a periodicity of twice the film thickness. They calculate and display the absorption for the film. Langbein (11) develops a theory for the electromagnetic modes of a metallic slab. He treats the electrons as moving in a rectangular well. The electronic
wavefunctions die out exponentially beyond the well and are sine waves inside. However, no calculations are performed. Feibelman (12) calculates and displays the vector potential in the limit of long wavelength for the half-space jellium bounded by vacuum. He divides space into three regions; vacuum, surface and bulk metal. He solves Maxwell's equations with the random phase approximation (RPA) conductivity tensor using the single particle energies and wavefunctions of Lang and Kohn (13). Since his interest is an application to photo-emission he examines photon energies in the 7-20 eV range for various bulk electron densities. Mukhopadhyay and Lundqvist (14) develop a procedure similar to that of Feibelman and concentrate on the semi-infinite classical barrier problem. They show that the Fuchs-Kliwer specular reflection model is equivalent to representing electron wavefunctions by sine waves which terminate at the boundary and subsequently neglecting 'interference' terms in the response functions. Apell (15) extends their results and calculates the real and imaginary parts of the vector potential at various frequencies of the incident light. (Refs. (14) and (15) incorrectly treat the integral relations for the vector potential and this will be discussed in Chapter II.) Bagchi (16) looks at the conductivity tensor relevant to a semi-infinite barrier problem. He uses single particle wavefunctions for the electrons which are solutions of the Schroedinger equation in the presence of a finite step potential. He plots the difference of the diagonal components of the conductivity tensor integrated over one coordinate in one case, and for one coordinate evaluated at the surface of the
metal in another case. Bagchi, Barrera and Rajagopal (17) use Green's function techniques to treat the differential reflectance of a metal surface with chemisorbed impurities. Here also a nonlocal formalism is used but it is assumed the fields are constant over distances in which the conductivity varies.

None of the above calculations embody realistic representations for electronic wavefunctions in a formalism tractable and simple enough to calculate the vector potential at any frequency, wavelength and angle of incidence of the incident light.

B. Raman Scattering Theories

An organized and systematic review of the theoretical explanations for Surface Enhanced Raman (SER) scattering is provided by Furtak and Reyes (18). I will here divide the present theories into three categories: those implying a shift of the resonance frequency of the molecule; those relying on electroreflectance theory; and finally those which incorporate the geometry of the substrate to explain SER.

King, Van Duyne and Schatz (19) have suggested that the dipole field of the molecule interacts with its image in the metal to create an infinite effective polarizability and an infinite dipole moment. The infinity occurs at a specific molecule-metal separation which depends on the polarizability of the free molecule and the local dielectric functions of the external medium and metal. The real vulnerability of the theory lies in using the far field approximations for distances on the order of the size of the molecule. Eesley and Smith
include coverage dependent effects and claim that molecule-
molecule interactions can actually diminish the enhancement for mono-
layer coverages larger than 0.1. The local field which polarizes the 
molecule takes into account the scattered light, the image field, and the 
field of all other molecules. The local field is said to depend on the 
polarizability and can be enhanced by a factor of seven, which in their 
approach leads to a cross section for Raman scattering \( 7^3 \) larger than 
that for an isolated molecule. Efrima and Metiu (21,22,23), in a series 
of papers, develop a classical theory for light scattering by a molecule 
neal a metal surface. In a more sophisticated treatment of the image 
field the authors claim that the local field which polarizes the 
molecule is a primary plus a secondary field. The primary field is the 
incident plus reflected wave and is evaluated from the Fresnel equa-
tions. The secondary field is the field which results from dipole 
emission, subsequent reflection from the surface, and then interaction 
with the same dipole. The dipole is taken to exist only at a point. 
In this model the polarizability also becomes resonant for specific 
molecule metal distances. The frequency dependence of the cross sec-
tion does not appear resonance-like, however, because molecules are at 
different separations and the complete spectrum is smeared by contribu-
tions from different resonances.

Ford and Weber (24) adopt a semi-classical approach similar to 
Efrima and Metiu. They make explicit use, however, of the nonlocal 
dielectric functions of Lindhard with a finite relaxation time. Large 
enhancements are possible only over variations of molecule metal
distances less than $10^{-3}$ Å. The authors dislike the image enhancement and claim that finite molecular sizes and variations in molecule metal spacing diminish this image effect by $10^3$. Philpott (25) developed a formalism which allows a molecule located near a metal surface to interact with surface plasmons. If the molecule has an excited state near the energy of a surface plasmon the molecular energy level can shift and broaden. The adsorbed molecule can consequently display a resonance Raman effect at a frequency where the isolated molecule would not. Hexter and Albrecht (26) propose the same mechanism. Pettinger and others (27) claim that the anodic roughening cycle necessary for SER in all electrochemical environments does not roughen the metal but creates a surface complex exhibiting resonance Raman. He says the proof lies in the fact that pyridine must be in solution during the cycle. Billmann and others (28) achieve SER for cyanide upon adding cyanide after the cycle is completed. Birke, Lombardi and Gerstein (29) propose that dynamic equilibrium is achieved in the molecule metal system between photoionization of a molecular electron to a level of the metal substrate, and metal to molecule electron tunneling. The resonance energy of the molecule is shifted due to the equilibrium mechanism. The Fermi level is adjusted by the dynamic equilibrium process such that resonance conditions are maintained over a wide range of photon frequencies. However, a metal adsorbate system, when subjected to laser light at different frequencies, displays enhancement for both frequencies (30). This would not be possible if the Fermi level shifted for one or the other laser frequencies.
All of the above theories obtain enhancement through a shift of the resonance energy of the polarizability to an energy which coincides with visible light. The argument is less than compelling for a number of reasons. Since a wide variety of molecules display SER at similar frequencies this induced resonance explanation requires rather different energy shifts for different molecules. Molecules which are resonant in an isolated state would not be expected to display SER in an adsorbed state when subjected to light at the resonance energy of the isolated molecule. The contrary is observed (2,31). Resonant molecules in an isolated condition show even larger cross sections when placed into an adsorbed state (1). It is also somewhat unclear what the total effect of the resonance shift might be on the enhancement. Explicit calculations for the new molecular energy lifetimes, including the new decay modes, might show sufficient broadening to effectively quash the enhancement. Furthermore, except for Pettinger et al. (27), almost all experimenters agree that some degree of roughness is required to observe SER. None of the theories requiring a resonance shift take this empirical fact into account. Ford and Weber (24) claim that roughness could provide a method for conversion of electron-hole pairs into scattered Raman photons. This process would be inefficient but combined with the image field effect could yield a total enhancement of $10^6$-$10^7$. I will further examine the effects of roughness on theoretical calculations in Chapter IV.

Another class of theories, Otto (32) and McCall and Platzmann (33), approach SER through the theory of electroreflectance. Otto proposes
that the adsorbate molecules form a square lattice and interact with each other and with the substrate via Van der Waals forces. The lattice vibrations of the adsorbate are at a frequency essentially equal to the vibrational frequency of a free molecule. This occurs because for small photon wavevectors only the optical modes are excited. Otto's development incorporates the features of a treatment by Delanaye, Lucas and Mahan (34) of the modes of such a system. The optical modes create an oscillating electric field which modulates the surface charge density and hence the reflectance (see, e.g., McIntyre (35)). By utilizing empirical parameters of electroreflectance Otto can obtain a $10^3$ enhancement over a free molecule for Raman scattering. He claims that roughness would allow coupling of the light to larger Fourier components of the oscillating electric field and hence yield another $10^3$ enhancement. McCall and Platzmann require charge transfer from molecule to metal and rely more explicitly on the theory of reference (35) to provide connection with needed parameters of electroreflectance to obtain $10^5$ enhancement. The basic problem with both approaches is that the frequency dependence of electroreflectance and of SER are quite different.

Other existing theories rely on the large fields, which arise from collective oscillations of the electrons in the substrate, to obtain enhanced Raman scattering. Creighton, Blatchford and Albrecht (4) examine pyridine molecules adsorbed on silver and gold aqueous sol particles. The authors display a correspondence between the absorption frequency of Mie theory (36) and the frequency dependence of the Raman
scattering intensity. Moskovits (37) uses effective medium theory and the results of Goad and Moskovits (38) to claim that the effective dielectric constant of a film of colloidal metal particles on top of a metal substrate displays a resonance in its imaginary part at wavelengths different from those of the ordinary surface plasmon. He explains the dissimilarity in frequency dependence of SER observed by two different groups (Fleischmann et al. (1) and Creighton et al. (39)) by stating that their volume filling fractions (volume of colloidal particles divided by total volume they encompass) are quite different and hence exhibit resonances at different exciting frequencies. Moskovits (40) also uses a model of metal spheres half-way embedded in a substrate and covered with adsorbate (41) to examine the differential reflectance and frequency dependence of the Raman scattering intensity for a metal adsorbate system. He takes the data of Pettinger et al. (27) for differential reflectance and by fitting parameters in his theory to match this data he calculates the imaginary part of the effective dielectric constant. He is able to correlate the frequency dependence of the Raman scattering intensity with the imaginary part of the effective dielectric constant multiplied by 1.58.

Pettinger, Tadjeddine and Kolb (42) using the attenuated total reflection technique (ATR) show that surface plasmons can at most account for enhancements of 10-100. Furthermore, without the ATR configuration, momentum conservation dictates that large scale roughness is needed for surface plasmon creation and it is generally agreed that although some roughness is needed for SER it is not of a large scale.
This evidence seems to diminish the attractiveness of the previous theories of Moskovits and Creighton et al. The roughness required for the proposals of Moskovits (37,40), however, is not large scale. In addition, the geometric resonances, which occur in such small particles as spheres, are not entirely analogous to surface plasmons at a plane interface. I believe, therefore, that these theories have a great deal of validity and will examine their relationship to the theory of this thesis in Chapter IV.

The final group of mechanisms proposed for SER require coupling of the incident and scattered photons to single particle excitations in the metal. Burstein and co-workers (43) list four separate types of interactions between single particle excitations and the adsorbed molecule. In this thesis I take mechanism b) of Reference (43) to describe the molecule metal interaction. I view Raman scattering as a three step process. In the first stage the incident photon creates an electron-hole pair inside the metal. In the second step the electron scatters inelastically off the molecule putting the molecule into an excited vibrational state. Finally, the electron recombines with the hole to create the scattered photon. The entire process takes place through third order perturbation theory. I describe the details of the Raman scattering theory in Chapter III and in the next chapter I calculate the vector potential which will be used in the electron-photon matrix elements.
II. THE ELECTROMAGNETIC FIELDS INSIDE A THIN METALLIC FILM

The purpose of this section is to determine the vector potential inside a thin metallic film upon which a photon is incident. The photon is assumed to be p-polarized and the lattice is treated as a uniform positive background. I take $\phi = 0$, but $\nabla \cdot \hat{A}$ is not zero inside the film. The vector potential outside the film is represented by incident and reflected plane waves on one side and by a transmitted plane wave on the other side (see Fig. 1). The plane of incidence is taken to be the x-z plane and translational invariance in the x-y plane allows the vector potential inside the film to take the form

$$\hat{A}(\vec{r},t) = \hat{A}_{K_0}(z)e^{i(1/k_x)x - i\omega t}$$

(2.1)

with $\vec{k}_0$ being the wave vector of the incident light, having x and z but no y component, and $\omega$ being the frequency of the incident light. The dependence of the vector potential on the z coordinate is not assumed to be of a plane wave nature due to the asymmetry in the z direction. The film is assumed to have infinite potential barriers at the metal vacuum interfaces. The treatment is semi-classical. That is, the electrons are treated quantum mechanically but the fields are not quantized. Combining Maxwell's equations we can write the wave equation

$$\nabla^2 \hat{A}(\vec{r},t) - \frac{1}{c^2} \frac{\partial^2 \hat{A}(\vec{r},t)}{\partial t^2} - \nabla (\nabla \cdot \hat{A}(\vec{r},t)) = -\frac{4\pi}{c} j(\vec{r},t)$$

(2.2)
Figure 1. Electromagnetic radiation incident at boundary of thin metallic film. $E_{in}$ is the magnitude of the electric vector of the incident light and $R$ and $T$ denote reflection and transmission. The radiation incident from below the film facilitates separation into even and odd parity fields with respect to the center of the film, its total contribution, however, is zero.
The current density $\mathbf{j}$ is determined from linear response theory in the random phase approximation. We assume $e^{-i\omega t}$ dependence for all observables and write the resulting two equations from (2.2).

\begin{align}
\frac{d^2}{dz^2} A^x_{k_0,\omega}(z) + \frac{\omega^2}{c^2} A^x_{k_0,\omega}(z) - ik_0 \frac{d}{dz} A^z_{k_0,\omega}(z) &= - \frac{4\pi}{c} j^x(z,\omega) \\
- k_0^2 A^z_{k_0,\omega}(z) + \frac{\omega^2}{c^2} A^z_{k_0,\omega}(z) - ik_0 \frac{d}{dz} A^x_{k_0,\omega}(z) &= - \frac{4\pi}{c} j^z(z,\omega)
\end{align}

Henceforth, we will write $A^z(z)$ for $A^z_{k_0,\omega}(z)$. The next section will show how the current density is evaluated.

A. RPA Conductivity Tensor

The current density in equations (2.3) is taken to be the quantum mechanical average of $\mathbf{j}_{\text{op}}(\mathbf{r},t)$, i.e.,

$$\mathbf{j}(\mathbf{r},t) = \langle \psi(t) | \mathbf{j}_{\text{op}}(\mathbf{r},t) | \psi(t) \rangle$$

(2.4)

with

$$\mathbf{j}_{\text{op}}(\mathbf{r},t) = \frac{e}{2m} \sum_i \left[ \left[ \mathbf{p}_i - \frac{e}{c} \mathbf{A}(\mathbf{r}_i,t) \right] \delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i) \left[ \mathbf{p}_i - \frac{e}{c} \mathbf{A}(\mathbf{r}_i,t) \right] \right]$$

(2.5)

and with $|\psi(t)\rangle$ the wave function of the electron gas in the presence of the photon. The subscript op denotes quantum mechanical operator and the sum over the index $i$ is over all electrons in the film. The Hamiltonian for the electron gas in an electromagnetic field is

$$H = \sum_i \frac{1}{2m} \left( \mathbf{p}_i - \frac{e}{c} \mathbf{A}(\mathbf{r}_i,t) \right)^2 + \sum_{i<j} U(\mathbf{r}_i - \mathbf{r}_j) = H_0 + H'$$

(2.6a)
with \( U(\mathbf{r}_i - \mathbf{r}_j) \) the Coulomb interaction and with

\[
H_0 = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} U(\mathbf{r}_i - \mathbf{r}_j) \quad ; \quad H' = -\frac{e}{2mc} \sum_i (\mathbf{p}_i \cdot \mathbf{A}(\mathbf{r}_i, t) + \mathbf{A}(\mathbf{r}_i, t) \cdot \mathbf{p}_i) . \tag{2.6b}
\]

I keep only first order terms in the vector potential in accord with linear response theory. For the Schroedinger picture the wave function takes the form to first order (44)

\[
|\psi(t)\rangle = e^{-iHt/\hbar} |\psi_H(0)\rangle - i\hbar^{-1} e^{-iHt/\hbar} \int_{t_0}^{t} dt' H'_H(t') |\psi_H(0)\rangle \tag{2.7}
\]

The subscript \( H \) denotes Heisenberg picture. \( |\psi_H(0)\rangle \) is the interacting ground state of the electron gas in the absence of the perturbation. Henceforth, \( |\psi_H(0)\rangle \) will simply be written \( |\psi\rangle \). The lower limit of integration, \( t_0 \), marks the onset of the perturbation and insures causality.

\( \mathcal{J}_{op} \) may be written

\[
\mathcal{J}_{op}(\mathbf{r}) = \frac{e}{2m} \sum_i (\mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{p}_i) \tag{2.8}
\]

and therefore

\[
\mathcal{J}(\mathbf{r}, t) = \langle \psi(t) | \mathcal{J}_{op}(\mathbf{r}, t) | \psi(t) \rangle = \langle \psi(t) | \mathcal{J}_{op}(\mathbf{r}) | \psi(t) \rangle - \frac{e^2}{mc} \mathbf{A}(\mathbf{r}, t) \langle \psi(t) | n(\mathbf{r}) | \psi(t) \rangle \tag{2.9}
\]

with
the electron density operator. I employ the formalism of Fetter and Walecka (44) to write

\[ \langle \psi(t)|\hat{J}_{\text{op}}(\mathbf{r})|\psi(t)\rangle = i\hbar^{-1} \int_{t_0}^{t} dt' \langle \psi_0| [H_0(t'), \hat{J}_{\text{op}}(\mathbf{r},t)] \psi_0 \rangle . \quad (2.11) \]

Consequently, I may write to first order in \( \hat{A} \)

\[ \hat{J}(\mathbf{r},t) = \frac{i\hbar^{-1}}{c} \int_{t_0}^{t} dt' \int d^3r' \langle \psi_o| [\hat{J}_{\text{op}}(\mathbf{r},t), J_{\text{op}}^\beta(\mathbf{r},t)] \psi_o \rangle \hat{A}^\beta(\mathbf{r}',t') \]

\[ - \frac{e^2}{mc} \hat{A}(\mathbf{r},t)n_o(\mathbf{r}) \quad (2.12) \]

with

\[ \hat{J} \cdot \hat{A} = J^\beta A^\beta \quad \text{ and } \quad n_o(\mathbf{r}) = \langle \psi_0| n(\mathbf{r})|\psi_0\rangle . \]

In accord with the notation of Mukhopadhyay and Lundqvist (14) I write with \( \hbar \) now equal to 1

\[ \hat{J}(\mathbf{r},t) = \frac{i\omega}{c} \int d^3r' \delta(\mathbf{r},\mathbf{r}',t,t') \cdot \hat{A}(\mathbf{r}',t') dt' \quad (2.13) \]

and

\[ \hat{J}(\mathbf{r},\omega) = \frac{ik}{c} \int d^3r' \delta(\mathbf{r},\mathbf{r}',\omega) \hat{A}(z') e^{ik \cdot x'} \quad (2.14) \]

with
\[ o^{\alpha \beta}(\mathbf{r}, \mathbf{r}', \omega) = \frac{i e^2 n_o(r)}{m(\omega + i\epsilon)} \delta(\mathbf{r} - \mathbf{r}') \delta^{\alpha \beta} + \frac{1}{(\omega + i\epsilon)} c^{\alpha \beta}(\mathbf{r}, \mathbf{r}', \omega) \quad (2.15) \]

where

\[ c^{\alpha \beta}(\mathbf{r}, \mathbf{r}', \omega) = \sum_n \left[ \frac{\langle \psi_o | J^{\alpha}(\mathbf{r}) | \psi_n \rangle \langle \psi_n | J^{\beta}(\mathbf{r}') | \psi_o \rangle}{\omega + i\epsilon - \omega_n} \right. \]

\[ \left. - \frac{\langle \psi_o | J^{\beta}(\mathbf{r}') | \psi_n \rangle \langle \psi_n | J^{\alpha}(\mathbf{r}) | \psi_o \rangle}{\omega + i\epsilon - \omega_n} \right] \]

((\omega + i\epsilon) in the denominators of (2.15) is explained in Appendix A).

This may be derived from Eq. (2.12) by replacing \( t_0 \) by \( -\infty \) and the integrand for the \( \alpha \)th component by

\[-\delta(t-t') \sum_n \left[ \langle \psi_o | J^{\alpha}(\mathbf{r}, t) | \psi_n \rangle \langle \psi_n | J^{\beta}(\mathbf{r}', t') | \psi_o \rangle \right. \]

\[- \langle \psi_o | J^{\beta}(\mathbf{r}', t') | \psi_n \rangle \langle \psi_n | J^{\alpha}(\mathbf{r}, t) | \psi_o \rangle \]

and performing the time integrations. I use the integral representation for the step function

\[ \delta(t-t') = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega(t-t')}}{\omega + i\epsilon} \quad . \quad (2.16) \]

Also \( \omega_n = E_n - E_o \), where \( E_n \) is the energy of the \( n \)th excited state and \( E_o \) is the ground state energy. I write for clarity

\[ H_o |\psi_n\rangle = E_n |\psi_n\rangle \]

so that it may be remembered the ground state \( |\psi_o\rangle \) and the excited states \( |\psi_n\rangle \) are eigenstates of the interacting electron gas.
I am now going to use the RPA. The RPA is seen in almost all treatments of the Coulomb interaction in metals. It can be regarded as a method of screening the applied fields and usually is put into words by saying that each Fourier component of the Coulomb potential is treated independently. It may also be seen in the equation of motion of an electron-hole pair. It is usually invoked there by keeping only the Fourier component of the Coulomb potential which corresponds to the momentum of the electron-hole pair. In analyzing the response of an electron gas to a time dependent scalar potential, the RPA takes the form of treating the electron gas as noninteracting but replacing the external potential by the total potential. That is, it includes in the external potential the effect of screening by the electron gas (45). In the present context it will mean that the interacting states, e.g., \( |\psi_o> \), will be replaced by the noninteracting states, e.g., \( |\phi_o> \). \( |\phi_o> \) and \( |\phi_n> \) will be the ground state and \( n^{th} \) excited state, respectively, of the noninteracting electron gas. For example, we can write

\[
H_0^0 = \sum_i p_i^2 / 2m \quad \text{and} \quad H_0^0 |\phi_n> = E_n^0 |\phi_n>
\]

with \( E_n^0 \) simply being a sum of single particle kinetic energies. The RPA will also mean that \( \hat{A}(r,t) \) will be regarded as the total potential, i.e., \( \hat{A}(r,t) \) contains the applied field plus the field induced by the screening action of the electrons.

I return now to Eq. (2.14)
which is a nonlocal equation for $\mathbf{A}(z)$. This means that $\mathbf{J}(z)$, which through equations (2.3) is related to $\mathbf{A}(z)$, depends on $\mathbf{A}(z')$ for all points $z'$ over which the conductivity tensor is nonzero. I now proceed to examine the RPA conductivity tensor for the thin film. It is first necessary to put the current-current response function $C^\alpha\beta$ and the electron density $n_0(\mathbf{r})$ in more tractable forms. In the formalism of second quantization I may write

$$
\mathbf{J}_\text{op}^\alpha(\mathbf{r}) = \frac{e}{2m} \sum \frac{1}{\mathbf{p}} \left( \delta(\mathbf{r} - \mathbf{r}_1) + \delta(\mathbf{r} - \mathbf{r}_1) \mathbf{p}_1^\alpha \right)
$$

$$
= \frac{e}{2im} \left[ \psi^+(\mathbf{r}) \nabla_a \psi(\mathbf{r}) - (\nabla_a \psi^+(\mathbf{r})) \psi(\mathbf{r}) \right] \quad (2.17)
$$

with

$$
\psi(\mathbf{r}) = \sum_{k,N} \psi^{\dagger}_{k,N}(\mathbf{r}) C_{k,N} \quad (2.18)
$$

Under the assumption that the electrons are confined by infinite potential barriers at the surface but are otherwise free, the single particle wavefunctions $\psi_{k,N}^\dagger(\mathbf{r})$ take the form

$$
\psi_{k,N}^\dagger(\mathbf{r}) = \frac{e^{i\mathbf{k} \cdot \mathbf{r}^\dagger}}{2\pi} \psi_N(z) = \frac{e^{i\mathbf{k} \cdot \mathbf{r}^\dagger}}{2\pi \sqrt{a}} \sin \frac{N\pi}{2a} (z + a) \quad (2.19)
$$

where $\mathbf{r}^\dagger$ is a vector in the $x$-$y$ plane and the film has thickness $2a$ with center at $z=0$. $C_{k,N}^\dagger$ is an annihilation operator for electrons. It is quite clear then that $\langle \psi_n^\dagger | \mathbf{J}_\text{op}^\alpha(\mathbf{r}) | \psi_n \rangle$, which in the RPA becomes
$\langle \phi_\alpha \mid J_{\alpha \beta}^\pi(r) \mid \phi_n \rangle$, is a matrix element between states which differ by an electron-hole pair. I write

$$\langle \phi_\alpha \mid J_{\alpha \beta}^\pi(r) \mid \phi_n \rangle = \phi_n^\alpha(r)$$

and therefore $\phi_n^\alpha$ is found to be

$$\phi_n^\alpha(r) = \frac{e}{2m} (2\pi)^2 \cdot \left[ \Theta(\epsilon_F - \epsilon_{k,N}) \cdot (1 - \Theta(\epsilon_F - \epsilon_{k',N})) \right]$$

$$\cdot \left[ \psi_N^*(z) e^{-\frac{\mathbf{k' \cdot r}}{2m}} \nabla_a \psi_N(z) e^{\frac{\mathbf{i \mathbf{k' \cdot r}}}{2m}} - (\nabla_a \psi_N^*(z) e^{\frac{-\mathbf{i \mathbf{k' \cdot r}}}{2m}}) \psi_N(z) e^{\frac{\mathbf{i \mathbf{k' \cdot r}}}{2m}} \right]$$

(2.20)

with $\epsilon_{k,N} = \frac{\mathbf{k}^2}{2m} + \frac{N^2 \pi^2}{8ma^2}$ and $\epsilon_F$ the Fermi energy. It is shown in Appendix A that

$$C^{\alpha \beta}(r, r', \omega) = \int \frac{d^2 \mathbf{k}}{(2\pi)^2} e^{\mathbf{i \mathbf{k} \cdot (r - r')}} C^{\alpha \beta}(k, z, z', \omega)$$

(2.21)

with

$$C^{\alpha \beta}(k, z, z', \omega) = 2 \int \frac{d^2 \mathbf{k'}}{(2\pi)^2} \sum_{N, N'} \left\{ \frac{\Theta(\epsilon_F - \epsilon_{k', N'}) - \Theta(\epsilon_F - \epsilon_{k', N})}{\omega + i\epsilon - (\epsilon_{k', N'} - \epsilon_{k + k', N})} \right\}$$

$$\cdot j_{NN'}^\alpha(z) \cdot j_{NN'}^\beta(z')$$

(2.22)

and

$$j_{NN'}^x(z) = \frac{e(2k' + k)^x}{2m} \psi_N(z) \psi_N(z)$$

(2.23a)
\[ j_{NN}'(z) = \frac{e}{24m} \left[ \psi_N'(z) \frac{d}{dz} \psi_N(z) - (\frac{d}{dz} \psi_N'(z)) \psi_N(z) \right]. \tag{2.23b} \]

The factor of two in front of the integral accounts for spin. It may be shown, by placing (2.21) into (2.14) and performing the integrations over the x-y plane, that the only \( \hat{k} \) vector which will be relevant in Eq. (2.21) is \( \hat{k} = \hat{k}_0^x \) where \( \hat{x} \) is a unit vector in the x-direction.

Since \( n(\mathbf{r}) = \sum_{\mathbf{r}} \delta(\mathbf{r}_i - \mathbf{r}) = \hat{\psi}(\mathbf{r}) \hat{\psi}(\mathbf{r}) \), in the RPA we find the electron density

\[ n_o(\mathbf{r}) = 2 \sum_N \int \frac{d^2k}{(2\pi)^2} \Theta(\varepsilon_F - \varepsilon_{k,N}) |\psi_N(z)|^2 . \tag{2.24} \]

The factor of two in front accounts for spin. This may easily be shown to be

\[ n_o(\mathbf{r}) = \frac{2\pi}{4\pi^2} \sum_{N=1}^{IF} \frac{\pi^2(F^2 - N^2)}{a \cdot 4a^2} \cdot \sin^2 \frac{2\pi N}{2a} (z + a) \tag{2.25} \]

where \( \varepsilon_F = F^2/8ma^2 \) and \( IF \) is the largest integer less than \( F \). The number of electrons in an area \( A \) of the film is

\[ N = \int d^3r n_o(\mathbf{r}) = \frac{A \cdot 2^3}{16a^3} \sum_{N=1}^{IF} (F^2 - N^2) \int_{-a}^{a} dz \sin^2 \frac{2\pi N}{2a} (z + a) \]

\[ = \frac{A \cdot 2\pi}{16a^2} \sum_{N=1}^{IF} (F^2 - N^2) \tag{2.26} \]

If each electron occupies a volume \( \frac{4}{3} \pi r_0^3 \) where \( r_0 = r_s \cdot a_0 \) and \( a_0 \) is the Bohr radius, then the bulk electron density may be written as \( \frac{3}{(4\pi r_s^3 a_0^3)} \). I set the average electron density equal to the bulk
electron density, i.e.,

\[
\frac{N}{(2a \cdot A)} = \frac{\pi}{16a^3} \sum_{N=1}^{\infty} \left( F^2 - N^2 \right) = \frac{3}{4r_s^3a_0^3} \pi
\]

\[
= \frac{\pi}{16a^3} \left[ IF \cdot F^2 - IF \cdot (IF + 1) \cdot (IF + 2)/6 \right] . (2.27)
\]

I define \( T = 2a/a_0 \) and find

\[
T^3 = \frac{2}{3} \pi^2 r_s^3 IF[IF \cdot F^2 - (IF + 1)(IF + 2)/6] . (2.28)
\]

I can choose an \( r_s \) value, say 4.86 for potassium, and a film thickness \( 2a \) of say 11.5 Å and solve for \( F \) from Eq. (2.28). For these choices \( F = 3.0325 \) and \( IF = 3 \). The plasma frequency \( \omega_o = (4\pi Ne^2/2a \cdot A)^{1/2} \) may be written as

\[
\omega_o = \left( \frac{3}{3} \right)^{1/2} \cdot \left[ \frac{1}{ma_0^2} \right] . (2.29)
\]

For \( r_s = 4.86 \) this gives a plasma energy of 4.3 eV, equivalent to the energy of a 2880 Å photon. In \( \mathbf{k} \) space the filled Fermi sea (ground state of electron gas) will appear as a half-sphere of radius \( 3.0325\pi/2a \) and there will be 3 discrete levels parallel to the \( k^x-k^y \) plane filled with electrons out to the boundary of the half-sphere (see Fig. 2).

I now return to Eq. (2.22) and proceed to further evaluate the response functions \( C^{\alpha\beta} \). By consulting Appendix A it is quite clear I may write

\[
C^{xz}(k^x_o, z, z', \omega) = -C^{zx}(k^x_o, z', z, \omega) \quad (2.30)
\]
Figure 2. Fermi Sea for three energy level film $k_F = 3.0325\pi/2a$
where I have made explicit use of the relevant $\mathbf{k}$ vectors from Eq. (2.21)
which will occur in the development. I now evaluate the integrations in Eq. (2.22) for $C^{xx}(k_o^x, z, z', \omega)$, $C^{xz}(k_o^x, z, z', \omega)$ and $C^{zz}(k_o^x, z, z', \omega)$.
To simplify the notation I drop $k_o^x$ and $\omega$ from the response functions and write from (2.21) with $\alpha = \beta = \chi$

$$C^{xx}(z, z') = \frac{2e^2}{4\alpha^2} \int \frac{d^2 k}{(2\pi)^2} \left[ \gamma_{NN}(z) \gamma_{NN'}(z') \right]$$

(2.31)

with

$$\gamma_{NN}(z) = \sin \frac{N\pi}{2a} (z + a) \sin \frac{N'\pi}{2a} (z + a) \quad . (2.32)$$

I make the following substitutions in the integrand of (2.31):

$$k^x = \frac{\pi}{2a} s; \quad k^y = \frac{\pi}{2a} t; \quad k^z = \frac{\pi}{2a} q_o$$

and in the first term make the replacement $k^x = k^x - k_o^x$. This yields

$$C^{xx}(z, z') = \frac{\pi e^2}{16\alpha^4} \int r dr d\theta \sum_{NN'} \left[ \frac{\Theta(F^2 - N^2 - r^2)(2r \cos \theta - q_o)^2}{8\alpha^2 (\omega + i\epsilon) - (N^2 - r^2 - q_o^2 - 2r q_o \cos \theta)^2} \right] \gamma_{NN}(z) \gamma_{NN'}(z')$$

(2.33)

with $s = r \cos \theta$ and $t = r \sin \theta$. In the second term I interchange $N \leftrightarrow N'$ remembering that $\gamma_{NN'} = \gamma_{N'N'}$. I define
\[ X(N, N', q_0^2) = 8ma^2(\omega + i\epsilon) + (N^2 - N'^2 - q_0^2)\pi^2 \quad (2.34) \]

and find

\[ C^{XX}(z, z') = \frac{\pi e^2}{16ma} \int \int \int \frac{\theta(F^2 - N^2 - r^2)}{X(N, N', q_0^2) + 2rq_o \cos \theta \pi^2} \left( \frac{(2r \cos \theta - q_o)^2}{X(N', N, q_0^2) + 2rq_o \cos \theta \pi^2} \right) \cdot \gamma_{NN'}(z) \gamma_{NN'}(z') \cdot \right) \]

I now define the following three integrals \( I_1, I_2 \) and \( I_3 \) with

\[ I_1 = \int_0^{\sqrt{F^2 - N^2}} dr \int_0^{2\pi} \cos^2 \theta d\theta \left[ \frac{1}{X(N, N', q_0^2) + 2rq_o \cos \theta \pi^2} \right. \right. \]

\[ - \frac{1}{X(N', N, q_0^2) + 2rq_o \cos \theta \pi^2} \left. \right) \cdot \right) \]

(2.35)

\( I_2 \) is gotten from \( I_1 \) by replacing in the numerator, \( r^3 \) by \( r^2 \), \( \cos^2 \theta \) by \( \cos \theta \), and the minus in front of the second term by a plus. \( I_3 \) is obtained from \( I_1 \) by replacing in the numerator, \( r^3 \) by \( r \), \( \cos^2 \theta \) by \( 1 \).

With these definitions I find

\[ C^{XX}(z, z') = \frac{\pi e^2}{16ma} \sum_{NN'} \theta(F^2 - N^2) [4I_1 - 4q_o I_2 + q_o^2 I_3] \cdot \gamma_{NN'}(z) \gamma_{NN'}(z') \cdot \right) \]

(2.36)

The integrals \( I_1, I_2 \) and \( I_3 \) are done in Appendix B. Similar techniques produce the following representations of the other response functions

\[ C^{Xz}(z, z') = \frac{\pi e^2}{16ma} \sum_{NN'} \theta(F^2 - N^2) [2I_2 - q_o I_3] \gamma_{NN'}(z) \cdot \beta_{NN'}(z') \quad (2.37) \]
and

\[ C^{zz}(z, z') = \frac{\pi e^2}{16m^2} \sum_{NN'} \theta(P^2 - N^2) I_3 \beta_{NN'}(z) \cdot \beta_{N'N}(z') \]  

(2.38a)

with

\[ \beta_{NN'}(z) = [N \sin \frac{N'\pi}{2a} (z+a) \cos \frac{N\pi}{2a} (z+a) - N' \sin \frac{N\pi}{2a} (z+a) \cos \frac{N'\pi}{2a} (z+a)] . \]

(2.38b)

The sum over \( N \) is from 1 to \( \infty \), but the sum over \( N' \) is from 1 to \( \infty \).

**B. Solution of the Wave Equation**

I now return to consideration of Eqs. (2.3), which may be written as

\[
\begin{align*}
\frac{d^2}{dz^2} A^x(z) + \frac{\omega^2}{c^2} A^x(z) - ik_o^x \frac{d}{dz} A^z(z) &= \frac{4\pi e^2}{mc^2} n_o(z) A^x(z) \\
&+ \frac{4\pi}{c^2} \int dz' C^{x'x} A^y(z')
\end{align*}
\]

(2.3a)

and

\[
\begin{align*}
-k_o^x A^z(z) + \frac{\omega^2}{c^2} A^z(z) - ik_o^x \frac{d}{dz} A^x(z) &= \frac{4\pi e^2}{mc^2} n_o(z) A^z(z) \\
&+ \frac{4\pi}{c^2} \int dz' C^{x'z} A^y(z')
\end{align*}
\]

(2.3b)

These are coupled equations for \( A^x \) and \( A^z \) in a nonlocal formalism. I consider there to be fields incident from below the film in a symmetric fashion with respect to the actual incident wave, and polarized in opposite directions with respect to their mutual wave vector so as to
give zero contribution to the overall vector potential (see Fig. 1).

It is then possible to separate the problem into even and odd symmetries about the center of the film. The same technique is seen in Refs. (8,46). I therefore write for \(-a \leq z \leq a\)

\[
A^x(z) = \sum_{n=0}^{\infty} A^x_o(n)(-1)^n \cos \frac{n\pi z}{a} + \sum_{n=1}^{\infty} A^x_e(n)(-1)^n \sin \frac{(2n-1)\pi z}{2a}.
\] (2.39a)

and

\[
A^z(z) = \sum_{n=1}^{\infty} A^z_o(n)(-1)^n \sin \frac{n\pi z}{a} + \sum_{n=1}^{\infty} A^z_e(n)(-1)^n \cos \frac{(2n-1)\pi z}{2a}.\] (2.39b)

The subscripts label the parity of the \(A^z\) field, \(o\) for odd and \(e\) for even. I ask the reader to imagine placing (2.39) into (2.3). The odd and even parts separate and will be considered separately. For the odd fields we multiply (2.3a) by \(\int_{-a+\delta}^{a-\delta} dz \cos \frac{n\pi z}{a}\) (\(\delta\) is an infinitesimal distance) and (2.3b) by \(\int_{-a}^{a} dz \sin \frac{n\pi z}{a}\) to obtain for the \(n^{th}\) equation from (2.3a)

\[
2H_o^y(a-\delta) \cdot a + A^x_o(n)\left[\frac{\omega a^2}{c^2} - \frac{2}{n\pi^2}\right] - ik_o n\pi a A^z_o(n) =
\]

\[
\sum_{N=1}^{\infty} \sum_{m=0}^{\infty} (-1)^m A^x_o(m) [D(N)k^o(N,m,n) + \sum_{N'=1}^{\infty} C^{xx}(N,N',m,n)]
\]

\[
+ \sum_{N=1}^{\infty} \sum_{m=1}^{\infty} \sum_{N'=1}^{\infty} (-1)^m A^z_o(m) C^{xx}(N,N',m,n)\] (2.40)

and from (2.3b)
\[ \begin{align*}
A^z_o(n) &= \left( \frac{\omega^2 a^2}{c^2} - k^2_o a^2 \right) + i k_a \alpha \pi A^x_o(n) = \\
&= \frac{\omega^2 a^2}{c^2} A^x_o(n) + i k_a \alpha \pi A^x_o(n) \\
&\quad \text{IF} \sum_{N=1}^\infty \sum_{m=0}^{\infty} (-1)^m A^x_o(m) [D(N)L_o^0(N,m,n) + \sum_{n'=1}^\infty C^{zz}(N,N')L^1(N,N',m,n)] \\
&\quad - \frac{\omega^2 a^2}{c^2} A^x_o(n) C^{xx}(N,N')L^1(N,N',m,n) \\
&\quad \text{IF} \sum_{N=1}^\infty \sum_{m=0}^{\infty} \sum_{N'=1}^\infty (-1)^m A^x_o(m) C^{xz}(N,N')L^1(N,N',m,n) \\
&\quad \text{with the following definitions} \\
D(N) &= \frac{4 e^2}{(\omega + i\epsilon)}(F^2 - N^2) \\
C^{xx}(N,N') &= \frac{4\pi e^3 \omega^2}{16c^2(\omega + i\epsilon) ma} [4I_1 + q_o^2 I_3 - 4q_o I_2] \\
C^{xz}(N,N') &= \frac{i4\pi e^3 \omega^2}{16c^2(\omega + i\epsilon) ma} [2I_2 - q_o I_3] \\
C^{zz}(N,N') &= -C^{xz}(N,N') \\
K^0(N,m,n) &= \int_{-a}^a dz \sin^2 \frac{N\pi}{2a} (z+a) \cos \frac{\nu z}{a} \cos \frac{\mu z}{a} \\
L^0(N,m,n) &= \int_{-a}^a dz \sin^2 \frac{N\pi}{2a} (z+a) \sin \frac{\nu z}{a} \cos \frac{\nu z}{a} \\
K^1(N,N',m,n) &= \left[ \int_{-a}^a dz \gamma_{NN'}(z) \cos \frac{\nu z}{a} \right] \left[ \int_{-a}^a dz \gamma_{NN'}(z') \cos \frac{\nu z'}{a} \right]
\end{align*} \]
\[ K^2(N,N',m,n) = \left[ \int_{-a}^{a} dz \, \gamma_{NN'}(z) \cos \frac{n \pi z}{a} \right] \cdot \left[ \int_{-a}^{a} dz' \, \beta_{N,N'}(z') \sin \frac{m \pi z'}{a} \right] \]  

(2.50)

\[ L^1(N,N',m,n) = \left[ \int_{-a}^{a} dz \, \beta_{NN'}(z) \sin \frac{n \pi z}{a} \right] \cdot \left[ \int_{-a}^{a} dz' \, \gamma_{NN'}(z') \cos \frac{m \pi z'}{a} \right] \]  

(2.51)

\[ L^2(N,N',m,n) = \left[ \int_{-a}^{a} dz \, \beta_{NN'}(z) \sin \frac{n \pi z}{a} \right] \cdot \left[ \int_{-a}^{a} dz' \, \beta_{N,N'}(z') \sin \frac{m \pi z'}{a} \right] \]  

(2.52)

The integrals over trigonometric functions are performed in Appendix C. The term \( 2H^Y_o(a-\delta) \) arises from representing \( A_z \) and \( \frac{dA}{dz} \) by functions which are discontinuous at the metal surfaces. Equations (2.40) and (2.41) can further be written in the form

\[ 2a H^Y_o(a-\delta) = \sum_{m=0}^{\infty} G^{xx}(n,m)A^x_o(m) + \sum_{m=1}^{\infty} G^{xz}(n,m)A^z_o(m) \]  

(2.42)

and

\[ 0 = \sum_{m=0}^{\infty} G^{zx}(n,m)A^x_o(m) + \sum_{m=1}^{\infty} G^{zz}(n,m)A^z_o(m) \]  

(2.43)

with

\[ G^{xx}(n,m) = \left( \frac{\omega}{c} \right)^2 \left( -n^2 \pi^2 \right) \delta_{nm} + \sum_{N=1}^{\infty} \frac{1}{i} (-1)^m [D(N)K^O(N,m,n) + \sum_{N'=1}^{\infty} C^{xx}(N,N')K^{N'}(N,N',m,n)] \]  

(2.44)
\[ G^{XX}(n,m) = -\frac{i k}{c} a_0 \delta_{nm} + \sum_{N=1}^{\infty} \sum_{N'=1}^{\infty} (-1)^m C^{XX}(N,N')K^2(N,N',m,n) \] (2.45)

\[ G^{ZC}(n,m) = - G^{ZX}(n,m) \] (2.46)

\[ G^{ZZ}(n,m) = \left( \frac{\omega^2 a^2}{c^2} - k^2 a^2 \right) \delta_{nm} + \sum_{N=1}^{\infty} \sum_{N'=1}^{\infty} \frac{IF}{[D(N)L^0(N,m,n)]} \] (2.47)

where \( \delta_{nm} \) is the Kronecker delta and is zero for \( n \neq m \). Equations (2.42) and (2.43) may be combined in symbolic matrix form

\[ \begin{pmatrix} G^{XX} & G^{XZ} \\ G^{ZX} & G^{ZZ} \end{pmatrix} \begin{pmatrix} A^X_o \\ A^Z_o \end{pmatrix} = \begin{pmatrix} 2a H^Y_0(a-\delta) \\ 0 \end{pmatrix} \] (2.48)

The \( G \) matrix is terminated at some cutoff number and the matrix Eq. (2.48) is solved on a computer to yield the coefficients \( A^X_o(n) \) and \( A^Z_o(n) \). The equations for the even coefficients are quite similar and are solved in the same way. \( H^Y_0(a-\delta) \) may be written in its form on the outside of the film as it is continuous across the surface

\[ a \cdot H^Y_0(a-\delta) = a \cdot H^Y_0(a+\delta) = -\frac{i \omega}{c} E_{in} e^{-ik a} [1 + R_o e^{i2k a}] \] (2.49)

with \( E_{in} \) the amplitude of the incident plane wave and \( R_o \) the reflection coefficient for the odd fields. The reflection coefficient \( R_o \) may be written
\[ R_{o} = e^{-2ikz_{o}} \left[ \frac{E^{x}(a-\delta)}{H^{y}_{o}(a-\delta)} + \cos \theta \right] / \left[ \cos \theta - \frac{E^{x}_{o}(a-\delta)}{H^{y}_{o}(a-\delta)} \right] \]  \hspace{1cm} (2.50)

with \( \theta \) the angle of incidence. I define \( A^{x}_{o}(n)' = A^{x}_{o}(n)/(H^{y}_{o}(a-\delta) \cdot a) \) and therefore find

\[ R_{o} = e^{-2ikz_{a}} \left[ \frac{i\omega a}{c} \sum_{n=0}^{\infty} A^{x}_{o}(n)' + \cos \theta \right] / \left[ \cos \theta - \frac{i\omega a}{c} \sum_{n=0}^{\infty} A^{x}_{o}(n)' \right] \]  \hspace{1cm} (2.51)

The even fields have similar expressions. After recombining even and odd fields I find for the transmission

\[ T = \frac{1}{4} |R_{o} - R_{e}|^2 \]  \hspace{1cm} (2.52)

reflection

\[ R = \frac{1}{4} |R_{o} + R_{e}|^2 \]  \hspace{1cm} (2.53)

and absorption

\[ A = 1 - T - R = 1 - (|R_{o}|^2 + |R_{e}|^2)/2 \]  \hspace{1cm} (2.54)

C. Display of Fields

The solution of Eq. (2.48) for the Fourier coefficients of the odd fields, and the solution of the similar matrix equation for the even fields, allows explicit display of the fields through Eqs. (2.39a) and (2.39b). Figure 3 shows the real and imaginary parts of \( E^{z}(z) \) as a function of distance within the film. The \( E^{x} \) component of the field
Figure 3. Real and imaginary parts of $E^z = i\omega/c A^z$ for 46 Å potassium film
is almost a constant and will not be shown. If a cutoff is imposed, the Fourier representation of the $A^Z$ field is zero at the film surfaces and therefore not continuous with the field in vacuum. Since the series in (2.39b) are terminated at some finite number of terms, the usual Gibbs phenomenon would occur if I simply plotted Eq. (2.39b) as it stands. The Gibbs phenomenon makes the Fourier representation of the $A^Z$ field invalid at the surface. The Gibbs phenomenon can be eliminated by adding a sawtooth and subtracting its Fourier series and by adding a square wave and subtracting its Fourier series to (2.39b). That is, we add to Eq. (2.39b)

$$A^Z_0(a+\delta) \left( \frac{Z}{a} + \sum_{n=1}^{\infty} \frac{2}{\pi n} (-1)^n \sin \frac{n\pi z}{a} \right) + A^Z_e(a+\delta) \left( 1 + \sum_{n=1}^{\infty} \frac{4(-1)^n}{\pi(2n-1)} \cos \left( \frac{2n-1}{2a} \pi z \right) \right) = 0 . \quad (2.55)$$

Since all series must be terminated at some finite value, in order to evaluate (2.39b), the preceding technique makes the fields behave at the surfaces as they should.

The key features of Fig. 3 are that the fields match up to their external values at the surfaces and that there are characteristic oscillations inside the film. Figure 3 is for a 46 A, potassium film ($r_s = 4.86$) at a frequency of the incident light of half the plasma frequency. The angle of incidence is taken to be 75°.

Figures 4 and 5 display the absorption for 11.5 and 46.0 A potassium films, respectively. The angle of incidence is again taken to be 75°. The dotted line is the result of a local calculation where the current density $J$ is taken to be
Figure 4. Absorption for 11.5 Å potassium film
Figure 5. Absorption for 46 Å potassium film
\[ \vec{f}(\vec{r}, \omega) = - \frac{\omega \omega}{4 \pi c (\omega + i \varepsilon)} \cdot \vec{A}(\vec{r}, \omega). \quad (2.56) \]

Figure 6 shows the real part of the \( \vec{E}^z \) field for the 11.5 Å film at the plasma resonance \( (\omega = 1.169 \omega_p) \). Figure 7 shows the real part of the \( \vec{E}^z \) field for the 46.0 Å film at the first plasma resonance peak \( (\omega = 1.055 \omega_p) \). Figures 6 and 7 display the nature of the plasma resonances for the thin metallic films. The frequency of a plasma resonance is such that an odd number of half-wavelengths of the plasmon fit exactly inside the film. That is, the resonance condition

\[ \frac{n \lambda}{2} = 2a \quad n = 1, 3, 5, \ldots \quad (2.57) \]

is satisfied. Figures 6 and 7 are for \( n = 3 \).

D. Point of Clarification

It is worth discussing at this point several comments in the literature concerning the continuity of the \( \Lambda^z \) field at the surface of a semi-infinite metal in the Fuchs-Kliewer model (8). On three separate occasions various authors have claimed that the \( \Lambda^z \) field is discontinuous at the surface (14,15,47). It is shown in a very simple argument by Johnson and Rimbey (48) that for a simple function \( f(z) \) with finite discontinuity at \( z = 0 \) but otherwise 'well-behaved',

\[ f(0^+) - f(0^-) = i \lim_{q^z \to 0} q^z F(q^z) \quad (2.58) \]

where

\[ F(q^z) = \int_{-\infty}^{\infty} f(z) e^{-iq^zz} dz. \quad (2.59) \]
Figure 6. Real part of $E^z = i\omega/c A^z$ for plasma resonance condition $n = 3$ in 11.5 Å potassium film (see Eq. (2.57))
Figure 7. Real part of $\text{Re}(E^Z) = i\omega/c A^2$ for plasma resonance condition $n = 3$ in 46 Å potassium film (see Eq. (2.57))
Under the specular reflection assumptions the fields in vacuum take the form

\[ A^x(z) = A^x(-z) \quad \text{and} \quad A^z(z) = -A^z(-z) \quad (\text{see (9)}) \]

so that

\[ A^z(0^+) = -A^z(0^-) \quad (2.60) \]

and it is readily found that

\[ A^z(0^+) = i \lim_{q^z \to \infty} \frac{q^z}{2} A^z(q^z) \quad (2.61) \]

If I apply this to \( A^z(q^z) \) given in Appendix B of Ref. (14) I find

\[ A^z(0^+) = i \tilde{H}^y(0^+) \cdot \frac{2k^x c^2}{\omega} \lim_{q^z \to \infty} \frac{1}{\varepsilon(q, \omega)} = i \tilde{H}^y(0^+) \frac{c}{\omega} \sin \theta \quad (2.62) \]

where \( \theta \) is the angle of incidence and \( k^x \) is the x component of the incident wave vector. One can easily show that outside the metal in vacuum

\[ A^z(0^+) = |E| \frac{c}{\omega} \sin \theta (1 + R) \quad (2.63) \]

where \( R \) is the reflection coefficient and \( |E| \) the magnitude of the electric vector of the incident wave. Since it is also true that

\[ \tilde{H}^y(0) = - |E|(1 + R) \]

\( A^z(z) \) is continuous at the surface in the Fuchs-Kliewer model. It is quite obvious that the neglect of the contribution of the other branch
cuts involved in the integral B.12 of Ref. 14 is responsible for the author's conclusion that \( A^z(z) \) is discontinuous.

I point this out at this time to further stress the issue that the \( A^z(z) \) field in (2.39b) is continuous when an infinite number of terms in the series is used. Equations similar to (2.61) and (2.62) could be derived at this time but the limits are not easily taken as the form of the Fourier coefficients for \( n \to \infty \) cannot readily be written down.
III. RAMAN SCATTERING THEORY

The theoretical formalism for first order Raman scattering is developed in third order time dependent perturbation theory by Loudon (5). The final state is assumed to be a scattered photon together with the adsorbed molecule in an excited vibrational state. The initial state consists of an incident photon and the molecule in its vibrational ground state. (In Loudon's case the excitation was a phonon.) I assume also that the electrons in the substrate are in the ground state, |$\phi_0>$, for both the initial and the final state.

A. S Matrix Development

I proceed with the formalism in the language of second quantization. The final state is written

$$|f> = |k'>|1>|FS>$$  \hspace{1cm} (3.1)

where $k'$ denotes the wave vector of the scattered photon, $|1>$ denotes a single vibrational excitation in the adsorbed molecule, and $|FS>$ denotes the filled Fermi sea. (I use the notation of Sakurai (49) to denote occupation number states.) The initial state is written

$$|i> = |k|0>|FS>$$  \hspace{1cm} (3.2)

where $k$ is the wave vector of the incident photon and $|0>$ denotes the vibrational ground state of the molecule. Ultimately we seek the differential cross section for the Raman scattering event. The transition probability per unit time is written

$$P = \lim_{\epsilon \to 0} \lim_{t \to 0} \frac{d}{dt} |<f|U_{\epsilon}(t,-\infty)|i>|^2$$  \hspace{1cm} (3.3)
where \( U(t, \omega) \) is the S-matrix in the adiabatic approximation. In order to determine \( U \) I write the Hamiltonian for the photon-molecule-thin metal film system as

\[
H = \sum_i \left( \frac{\hat{p}_i^2}{2m} - \frac{e}{c} \hat{A}(\hat{r}_i) \right)^2 \cdot \frac{1}{2m} + H_{\text{ME}} + H_{\text{FIELD}} \quad . \tag{3.4}
\]

I neglect the \( \hat{A} \cdot \hat{A} \) term, and comment on its contribution later in the chapter, so that \( H \) may be written

\[
H = H_0 + H_{\text{FIELD}} + H_1 \quad . \tag{3.5}
\]

with

\[
H_0 = \sum_i \frac{\hat{p}_i^2}{2m} \quad ; \quad H_1 = -\frac{e}{2mc} \sum_i \left( \hat{p}_i \cdot \hat{A}(\hat{r}_i) + \hat{A}(\hat{r}_i) \cdot \hat{p}_i \right) + H_{\text{ME}}
\]

where \( H_{\text{ME}} \) is the molecule-electron interaction and \( H_{\text{FIELD}} \) is the electromagnetic energy stored in the fields. I define

\[
H_{\text{PE}} = -\frac{e}{2mc} \sum_i \left( \hat{p}_i \cdot \hat{A}(\hat{r}_i) + \hat{A}(\hat{r}_i) \cdot \hat{p}_i \right) \quad . \tag{3.6}
\]

so that I may write

\[
H_1 = H_{\text{PE}} + H_{\text{ME}} \quad . \tag{3.7}
\]

and \( H_1 \), the perturbation, will be regarded as composed of a photon-electron and a molecule-electron interaction. I work in the interaction representation and apply the adiabatic hypothesis by multiplying \( H_1 \) by \( e^{-\omega |t|} \). The time dependence of \( H_1 \) in the interaction representation is then written
In accord with normal procedures for quantizing the electromagnetic field (49) I write

\[ A(t) = c \left( \frac{2\pi \hbar}{V} \right)^{1/2} \sum \frac{1}{k \omega}^{1/2} \left[ a_{k \gamma}^+ e^{ikx} e^{iky} A_{k, \omega}^e(z, \gamma) + a_{k \gamma}^+ e^{-ikx} e^{-iky} A_{k, \omega}^e(z, \gamma) \right] \]  

(3.9)

where the \( a_{k \gamma}^+ \)'s and \( a_{k \gamma} \)'s are annihilation and creation operators, respectively, for photons. \( V \) is the traditional volume of the large box used in plane wave normalization and \( A_{k, \omega}^e(z, \gamma) \) is the vector potential inside the thin film in the presence of a photon of wave vector \( k \), frequency \( \omega = c|k| \), and polarization \( \gamma \). For \( \gamma \) corresponding to p-polarization \( A_{k, \omega}^e(z, \gamma) \), with \( k = \vec{k} \), is the solution of Eqs. (2.3a) and (2.3b) of Chapter II. In the absence of the thin film, replacement of \( A_{k, \omega}^e(z, \gamma) \) by \( \vec{e}_\gamma e^{ikz} \) would yield the traditional form of the quantized vector potential in (3.9). \( \vec{e}_\gamma \) is the polarization vector. \( \vec{k} \cdot \vec{e}_\gamma \) is zero but \( \vec{k} \cdot A_{k, \omega}^e \neq 0 \). The electron photon interaction is then given by (44)

\[ H_{PE} = -2 \frac{e}{2m} \left( \frac{2\pi \hbar}{V} \right)^{1/2} \sum \frac{1}{k \omega}^{1/2} \sum \frac{a_{k \gamma}^+}{|k|} <k|N| \hat{p} \cdot \hat{a}_{k \gamma} > - \frac{m}{2} \frac{e^2}{\hbar} \left( \frac{2\pi \hbar}{V} \right)^{1/2} \sum \frac{a_{k \gamma}^+}{|k|} <k|N| \hat{p} \cdot \hat{a}_{k \gamma} > + \text{complex conjugate} \]  

(3.10)

The leading factor 2 accounts for spin and
\[
\langle k N | \hat{p} \cdot \hat{a}_{kY} + \hat{a}_{kY} \cdot \hat{p} | k' N' \rangle = \int_{-a}^{a} \frac{dz}{a} \int \frac{dxdy}{(2\pi)^2} e^{-i \hat{p} \cdot \hat{r}} \sin \frac{N\pi}{2a} (z+a) 
\cdot \left[ \hat{p} \cdot (e^{i \hat{p} \cdot \hat{r}} \hat{a}_{k,\omega} (z,\gamma) + (e^{i \hat{p} \cdot \hat{r}} \hat{a}_{k,\omega} (z,\gamma)) \cdot \hat{p} \right] 
\cdot e^{i \hat{p} \cdot \hat{r}} \sin \frac{N'\pi}{2a} (z+a) .
\]

(3.11)

\( \hat{c}_{j,j} \) and \( \hat{c}_{j,j'} \) are creation and annihilation operators, respectively, for electrons. \( \hat{H}_{\text{ME}} \) will be assumed to have the form

\[
\hat{H}_{\text{ME}} = 2K \sum_{\vec{k},\vec{k}' \in N} \sum_{\vec{k},\vec{k}' \in N'} \hat{c}_{\vec{k},\vec{k}'} \hat{c}_{\vec{k}',\vec{k}} + \text{complex conjugate}
\]

(3.12)

where \( \hat{d}_\xi \) annihilates the quantum of vibration of frequency \( \xi \). The details of this approximation and the precise meaning of \( K \) will be deferred until later in the chapter.

From Fetter and Walecka (44) \( U_\varepsilon \) may be written

\[
U_\varepsilon (t,-\infty) = 1 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' \hat{H}_\varepsilon (t') U_\varepsilon (t',-\infty) .
\]

(3.13)

This equation may be iterated to obtain \( U_\varepsilon \) to any desired order. In examining Eqs. (3.1) and (3.2) it is evident that in order to create the photon \( \vec{k}' \) and the molecular vibration as well as annihilate the incoming photon we need two \( \hat{H}_{\text{PE}} \) and one \( \hat{H}_{\text{ME}} \). That is, we need \( U_\varepsilon \) to third order to get a nonzero matrix element for \( \langle f | U_\varepsilon | i \rangle \) (unless I use the \( \vec{A} \cdot \vec{A} \) term which will be addressed later). I write for \( U_\varepsilon \), therefore,
$$U_\varepsilon(t, -\infty) = \left(-\frac{i}{\hbar}\right)^3 \int_{-\infty}^{t} dt' H_1(t') \int_{-\infty}^{t'} H_1(t'') \int_{-\infty}^{t''} H_1(t''') dt''' \quad (3.14)$$

so that

$$\langle f | U_\varepsilon(t, -\infty) | i \rangle = \left(-\frac{i}{\hbar}\right)^3 \sum_{LM} \langle f | H_1 | L \rangle \langle L | H_1 | M \rangle \langle M | H_1 | i \rangle$$

\[\cdot \int_{-\infty}^{t} dt' e^{i(E_f-E_L)t'/\hbar} e^{iEt'} \int_{-\infty}^{t'} dt'' e^{i(E_L-E_M)t''/\hbar} e^{iEt''} \int_{-\infty}^{t''} dt''' e^{i(E_M-E_i)t'''/\hbar} e^{iEt'''} \quad . \quad (3.15)\]

The states $|l\rangle$ and $|\varepsilon\rangle$ are products of a molecular vibration state and excited states of the noninteracting electron gas, e.g., $|\phi_n\rangle$ of Chapter II. The meaning of Eq. (3.3) is now apparent. I wish to observe the probability that the final state may be observed at $t = 0$ in a fully interacting system given that at $t = -\infty$ the system was in the initial state with no perturbation present. Since all interactions (e.g., $H_1$) become full at $t = 0$, I take the limit as $t$ goes to zero along with the convergence preserving limit as $\varepsilon$ goes to zero. (As mentioned in Appendix A $\varepsilon$ is assigned a definite number in the energy denominators which follow.) The integrals in (3.14) may be easily performed, and yield

$$P = \lim_{\varepsilon \rightarrow 0} \lim_{t \rightarrow 0} \frac{1}{\hbar} \frac{d}{dt} \left\{ \sum_{LM} \frac{\langle f | H_1 | L \rangle \langle L | H_1 | M \rangle \langle M | H_1 | i \rangle}{i \left( \frac{E_M-E_i}{\hbar} - i\varepsilon \right) \left( \frac{E_L-E_i}{\hbar} - 2i\varepsilon \right)} \right\}$$

\[\cdot \exp \left( \frac{i}{\hbar} \frac{E_f-E_i}{\hbar} - 3i\varepsilon \right) \left( \frac{E_f-E_i}{\hbar} - 3i\varepsilon \right)^{t/2} \quad . \quad (3.16)\]
where I have used

\[ \int_{-\infty}^{t} dt' \; e^{i(E-i\epsilon)t'} = \frac{1}{i} \frac{e^{i(E-i\epsilon)t}}{(E-i\epsilon)} \quad . \]  

(3.17)

Using

\[ \lim_{t \to 0} \lim_{\epsilon \to 0} \frac{d}{dt} \left[ \frac{e^{6\epsilon t}}{(E_f-E_i)^2 + 9\epsilon^2} \right] = 2\pi\delta(E_f-E_i) \quad . \]  

(3.18)

I find

\[ P = \frac{2\pi}{h^6} \sum_{LM} \left| \langle f | H_1 | L \rangle \langle L | H_1 | M \rangle \langle M | H_1 | i \rangle \right|^2 \delta(E_f-E_i) \]  

(3.19)

where I replace $2\epsilon$ by $\epsilon$ and now consider $\epsilon$ to be a finite real number to simulate damping.

B. The Resonance Diagram

I point out once more that Eq. (3.19) demands that of the three $H_1$'s which appear there, I need two $H_{PE}$'s and one $H_{ME}$. However, there are six different ways of permuting the two $H_{PE}$'s and one $H_{ME}$ in order to go from $|i\rangle$ to $|f\rangle$ via the intermediate states $|L\rangle$ and $|M\rangle$. The six types of terms can be represented diagrammatically as shown in Fig. 8. Events toward the bottom of a diagram occur before those at the top. In diagram (a) I describe the order of events as first the absorption of the incident photon occurs, then the molecular vibration is excited and finally the scattered photon is emitted. At each step an electron (hole) is scattered. For diagram (a) $E_M$ and $E_L$ are written
Figure 8. Third order diagrams involving $p \cdot \hat{A}$ perturbation

Figure 9. Diagrams from $\hat{A} \cdot \hat{A}$ perturbation
and of course $E_i = \hbar \omega$. Conservation of energy dictates (6($E_f - E_i$) in (3.19)) that $\omega = \omega' + \xi$. $\varepsilon_{eh}$ denotes the energy of an electron-hole pair. That is,

$$\varepsilon_{eh} = \frac{\hbar^2}{2m} \left( \frac{k_e^2}{k_h^2} + \frac{\pi^2}{4a^2} (N_e^2 - N_h^2) \right)$$  \hspace{1cm} (3.20)

where the subscripts $e$ and $h$ stand for electron and hole, respectively.

In Fig. 8 only two of the six terms (diagrams) have the potential to let both energy denominators get very small. Diagram (a) has

$E_M - E_i = \varepsilon_{eh} - \hbar \omega$ and $E_L - E_i = \varepsilon_{eh}' - \hbar \omega'$. Diagram (e) has

$E_M - E_i = \varepsilon_{eh}$ but $E_L - E_i = \varepsilon_{eh}' - \hbar \xi$. Given the selection rules in the numerator of (3.18), which arise from the trigonometric integrations of Appendix C, there is no accessible region of phase space for which $\varepsilon_{eh} = \hbar \xi$. That is, $N_h$ cannot equal $N_e$ and for typical $\hbar \xi$ this alone precludes the equivalence as

$$\frac{\hbar^2 \pi^2}{8ma^2} (N_e^2 - N_h^2) \gg \hbar \xi$$  \hspace{1cm} (3.21)

I consequently keep only the terms corresponding to diagram (a) in Eq. (3.19). This diagram is traditionally referred to as the resonance diagram.

Figure 9 displays the diagrams which would have arisen if the $\hat{A} \cdot \hat{A}$ term had been kept in Eq. (3.6). Each diagram has only a single energy difference denominator. Diagram (i) has the energy denominator
\( \varepsilon_{eh} + \hbar \xi \) and diagram (ii) has the denominator \( \varepsilon_{eh} - \hbar \xi \). For reasons previously mentioned these two diagrams contribute negligibly to the total transition probability.

C. Electron Scattering

The approximation of keeping only the resonant diagram yields the following expression for \( P \).

\[
P = \frac{2\pi}{\hbar^6} \left| \sum_{JJ'} \frac{\langle FS| H_{PE}'| J \rangle \langle J| H_{ME}'| J' \rangle \langle J'| H_{PE}'| FS \rangle}{((\varepsilon_{eh} - \hbar \omega)/\hbar - i\epsilon)(\varepsilon_{eh} - \hbar \omega')/\hbar - i\epsilon)} \right|^2 \delta(E_{E} - E_{I}) \quad (3.22)
\]

\( |J\rangle \) and \( |J'\rangle \) are now excited states of the noninteracting electron gas. They differ from the ground state by an electron-hole pair. I also define

\[
H_{PE}' = -\frac{2e}{2m} \left( \frac{2\pi \hbar}{\omega V} \right)^{1/2} \sum_{\vec{k}\vec{k}'} \sum_{NN'} \langle \vec{k}N'| \vec{p} \cdot \hat{a}_{\vec{k}'}^* + \hat{a}_{\vec{k}}^* \cdot \vec{p} | \vec{k}'N' \rangle c_{\vec{k}N}^+ c_{\vec{k}'N'}^\dagger
\]
\quad (3.23)

and

\[
H_{PE}' = -\frac{e^2}{2m} \left( \frac{2\pi \hbar}{\omega V} \right) \sum_{\vec{k}\vec{k}'} \sum_{NN'} \langle \vec{k}N'| \vec{p} \cdot \hat{a}_{\vec{k}'}^* + \hat{a}_{\vec{k}}^* \cdot \vec{p} | \vec{k}'N' \rangle c_{\vec{k}N}^+ c_{\vec{k}'N'}^\dagger \quad (3.24)
\]

and

\[
H_{ME} = 2K \sum_{\vec{k}\vec{k}'} \sum_{NN'} c_{\vec{k}N}^+ c_{\vec{k}'N'}^\dagger \quad (3.25)
\]

The polarization index has been dropped and both incident and scattered photons are assumed p-polarized. In obtaining (3.22) I have used
\[ \langle \hat{k}' | \hat{a}^+_k | \Omega \rangle = \langle 0 | \hat{a}^+_k | \hat{k} \rangle = \langle 1 | \hat{q}^+_\xi | 0 \rangle = 1 \quad . \] (3.26)

The terms in (3.22) may be viewed according to the following scheme. \( \hat{H}^E_{PE} \) scatters an electron out of the Fermi sea to create the state \( | J' \rangle \). \( \hat{H}^E_{ME} \) then scatters either the electron or the hole to create the state \( | J \rangle \). Finally, \( \hat{H}^E_{PE} \) scatters the remaining electron back into the remaining hole. The sum over \( J \) and \( J' \) allows for all possible scatterings which can occur given that one begins and ends with the Fermi Sea. It is then seen that (3.22) can be further divided into two groups. The matrix element \( \langle J | \hat{H}^E_{ME} | J' \rangle \) can be viewed either as electron scattering or as hole scattering. Hole scattering is pictured schematically in Fig. 10. Events proceed from bottom to top. As remarked in Chapter II the Fermi Sea for the thin film appears as a half-sphere with discrete levels parallel to the \( k_x - k_y \) plane. Electron scattering involves replacing pictures (b) and (c) of Fig. 10 by (b') and (c'), respectively, of Fig. 11. It is worth noting that only the condition \( \omega = \omega' + \xi \) must be observed. It is not required to have energy conserved at each step in the overall process. For this reason, hole scattering as portrayed in Fig. 10 is possible even though the hole falls in energy as the molecular vibration occurs.

I assume at this point that electron scattering dominates and defer justification of this assumption until I take up discussion of the \( \hat{H}^E_{ME} \) later in the chapter.
Figure 10. Hole scattering

Figure 11. Electron scattering
D. The Differential Cross Section

I now write explicitly the transition probability $P$ from (3.22)

$$P = \frac{2\pi}{\hbar^6} \frac{K^* K}{V^2} \frac{e^4}{4} \hbar^2 \left| \sum_{n_1/2n_1} \Theta(\epsilon_F - \epsilon_{F_1}^{1/2}, N_1) \Theta(\epsilon_{F_1}^{1/2} + k', N_2 - \epsilon_F) \right|

\cdot \Theta(\epsilon_{F_2}^{1/2}, N_3 - \epsilon_F) \cdot \Theta(\epsilon_{F_4}^{1/2}, N_5 - \epsilon_F) \cdot \Theta(\epsilon_{F_2}^{1/2}, k, N_6)

\cdot \left< \hat{\rho}_{1/2} N_1 | \rho \cdot a_{k'}^* + a_k^* | \hat{\rho}_{1/2} + \hat{k}' N_2 < \hat{\rho}_{4/5} N_5 | \rho \cdot a_{k'}^* + a_k^* | \hat{\rho}_{4/5} - \hat{k}, N_6 > \right|^2

\frac{\delta_k^{2, 3} \delta_{k', k} \cdot \delta_{k_2, k} \cdot \delta_{k_4, k} \cdot \delta_{N_2, N_3} \cdot \delta_{k_3, k} \cdot \delta_{N_4, N_5} \cdot \delta_{k_5, k} \cdot \delta_{N_6, N_6}}{(e_2^{1/2} - e_2^{1/2} - \hbar(\omega + i\epsilon))(e_2^{1/2} - e_2^{1/2} - \hbar(\omega' + i\epsilon))} \cdot (3.27)

The Kronecker $\delta_{k_2, k_1}^{1/2}, k_1 + k'$ for the p-polarized photon $k'$ means

$\delta_{k_1, k}^x \delta_{k_1, k}^y$. There are some matrix elements in (3.27) that can be readily evaluated. Summations over $k$ in (3.27) are performed by writing

$$\frac{1}{A} \sum_{k} = \int \frac{dk_x dk_y}{(2\pi)^2} \ , \ (3.28)$$

where $A$ is the area of the film. I regard $k^x$ and $k'^x$ as small with respect to $\frac{\pi}{2a}$ and write

$$P = \frac{2\pi}{\hbar^6} \frac{K^* K}{V^2} \frac{2 e^4}{4} \hbar^2 \left| \sum_{n_1/2n_1} \Theta(\epsilon_F - \epsilon_{F_1}^{1/2}, N_1) \Theta(\epsilon_{F_1}^{1/2} + k', N_2 - \epsilon_F) \right|

\cdot \Theta(\epsilon_{F_2}^{1/2}, N_3 - \epsilon_F) \cdot \Theta(\epsilon_{F_4}^{1/2}, N_5 - \epsilon_F)

\frac{(\frac{\hbar^2}{8ma^2} (N_3^2 - N_1^2) - \hbar(\omega + i\epsilon))(\frac{\hbar^2}{8ma^2} (N_2^2 - N_1^2) - \hbar(\omega' + i\epsilon))}{(\frac{\hbar^2}{8ma^2} (N_3^2 - N_1^2) - \hbar(\omega + i\epsilon))(\frac{\hbar^2}{8ma^2} (N_2^2 - N_1^2) - \hbar(\omega' + i\epsilon))}$$
\[
\cdot \pi^2 [2 \ k^X <N_1 | A^X(z) | N_2> + \frac{\pi}{z a i} (N_1 <N_1 | A^X(z) | N_2> - N_2 <N_1 | A^X_2(z) | N_2>)]
\]
\[
\cdot [2 \ k^X <N_3 | A^X_2(z) | N_1> + \frac{\pi}{z a i} (N_3 <N_3 | A^X_2(z) | N_1> - N_1 <N_3 | A^X_2(z) | N_1>)]
\]
\[
(3.29)
\]

\[
|N_1> \text{ in coordinate representation could be written}
\]
\[
<N_1 | z > = \frac{1}{a^{1/2}} \sin \frac{N \pi}{2a} (z + a)
\]
\[
(3.30)
\]

and \( |N_1> \) in coordinate representation would appear

\[
<N_1 | z > = \frac{1}{a^{1/2}} \cos \frac{N \pi}{2a} (z + a)
\]

\[
(3.31)
\]

The integrals of the form \( <N_1 | A^| N_2> \) are done in Appendix C. Since

\[
\int d^{2}k k^k = 0,
\]

P may be written

\[
P = \frac{2\pi K^k}{\hbar \omega} (\frac{2\pi \hbar}{m}) \frac{M^k}{h^k} \left[ \sum_{N_1 N_2 N_3} \frac{\theta(\epsilon_F - \epsilon_F, N_1) \theta(\epsilon_F, N_2 - \epsilon_F)}{(2\pi)^2 \frac{\hbar^2}{2m} \frac{\hbar^2}{2} (N_3^2 - N_1^2)} - \hbar(\omega + i\epsilon) \right]
\]

\[
\cdot \frac{\Theta(\epsilon_F - \epsilon_F, N_3 - \epsilon_F)}{\frac{\hbar^2}{2m} (N_2^2 - N_1^2)} - \hbar(\omega + i\epsilon)
\]

\[
- \frac{\pi^2}{4a} (N_1 <N_1 | A^X_2(z) | N_2> - N_2 <N_1 | A^X_2(z) | N_2>) \cdot (N_3 <N_3 | A^X_2(z) | N_1>)
\]

\[
- N_1 <N_3 | A^X_2(z) | N_1>)^2 \]

(3.32)

In view of the fact that \( A^X, A^Z \) are both Fourier series involving even and odd terms, (3.32) is a rather formidable expression. It is quickly
simplified to a certain extent by examining the $d^2k$ integration in correspondence with the three theta functions. $N_1$ must always designate a level inside the Fermi half sphere. $N_2$ and $N_3$ must always be bigger than $N_1$ but can lie on levels which are parallel with filled levels. Such a situation is pictorially shown in Fig. 11. The area of the $\hat{k}$ space integration is set by the level position of either $N_2$ or $N_3$. The theta function for the higher of the two numbers $N_2$, $N_3$ may be ignored as its restrictions are already included by the theta function of the lower number. There are, therefore, three kinds of $\hat{k}$ space integrations.

(i) For $N_2$, $N_3$ both greater than $F$

$$\int d^2k \Theta(\epsilon_F - \epsilon_{\hat{k}N_1}) = \frac{\pi \frac{2}{4a}}{2} (F^2 - N_1^2) \ ; \ \int d^2k k^2 \Theta(\epsilon_F - \epsilon_{\hat{k}N_1}) = \frac{\pi \frac{2}{4a}}{2} (F^2 - N_1^2)^2.$$

(ii) For $N_1 < N_2 \leq F$ and $N_2 < N_3$

$$\int d^2k \Theta(\epsilon_F - \epsilon_{\hat{k}N_1}) \Theta(\epsilon_{\hat{k}N_2} - \epsilon_F) = \frac{\pi \frac{2}{4a}}{2} \pi (N_2^2 - N_1^2)$$

$$\int d^2k k^2 \Theta(\epsilon_F - \epsilon_{\hat{k}N_1}) \Theta(\epsilon_{\hat{k}N_2} - \epsilon_F) = \frac{\pi \frac{2}{4a}}{2} ((F^2 - N_1^2)^2 - (F^2 - N_2^2)^2).$$

(iii) For $N_1 < N_3 \leq F$ and $N_3 < N_2$ merely replace $N_2$ by $N_3$ in (ii). Eq. (3.32) is still a complicated mesh of Kronecker delta's but is a tractable expression.

The desired quantity is the differential cross section $\frac{d\sigma}{d\Omega}$. $d\Omega$ is the element of solid angle in which the exiting photon lies. $\frac{d\sigma}{d\Omega}$ is obtained by multiplying the transition probability per unit time by
the number of states available to the emitted photon and dividing by
the incident intensity c/V (44).

\[ \frac{d\sigma}{d\Omega} = \frac{P \cdot V \omega' \omega}{(2\pi)^3 \hbar c^3} . \]  

(3.35)

In Chapter IV \( \frac{d\sigma}{d\Omega} \) is examined over a wide range of the frequency of the
incident photon and for different electron densities and film thick­
nesses. It should be noted by the reader that I have declared the
polarization of both the incident and the scattered photons. For
s-polarized photons \( \Lambda^z \) is zero, and it is the \( \Lambda^z \) terms which dominate
the cross section for p-polarization. Consequently I do not include
photons of s-polarization as they do not significantly contribute to
the differential cross section.

E. Molecule-Electron Interaction

I now consider the molecule-electron interaction. From the
prescription for second quantization, the matrix element \( K \) of (3.12)
should be written

\[ K = \langle \frac{1}{A^{\cdot a}} \int_0^a \int_{-a}^a d^2p d^2r \ e^{i(k_3 \cdot \hat{r} - k_2 \cdot \hat{r})} V(\hat{r}, q) \sin \frac{N}{2a} (z+a) \]

\[ \cdot \sin \frac{N}{2a} (z+a) |0\rangle . \]  

(3.36)

\( V(\hat{r}, q) \) is the interaction between the electron in the film and the
adsorbed molecule. It is assumed to depend on both the electron
coordinate \( \hat{r} = (\hat{r}, z) \) and the vibrational coordinate \( q \) of the molecule.
It should also be remembered that because of momentum conservation in the x-y plane \( \mathbf{k}_3 - \mathbf{k}_2 = (k^x - k^{x'}) \), which is negligible since the photon wave vectors are very small. The approximation of (3.12) amounts to neglecting the dependence of \( K \) on the energies of the electrons. That is, \( K \) is taken independent of \( N_2 \) and \( N_3 \). This is in accord with a viewpoint that for relatively low-energy electrons, whatever the form of \( V(r, q) \), \( K \) would be constant over the range of electron energies available in Eq. (3.22). This is the case for the treatment of \( K \) performed in this thesis calculation. The real space integral in (3.36) is viewed as yielding some function \( g(\lambda) \) with \( \lambda = q - q^0 \) where \( q^0 \) is the equilibrium position of the normal coordinate \( q \) involved in the vibration. For small \( \lambda \)

\[
g(\lambda) \approx g(q^0) + \lambda g'(q^0)
\]

and therefore (50)

\[
\langle l | g(\lambda) | 0 \rangle = g'(q^0) \langle 1 | \lambda | 0 \rangle = g'(q^0)(\frac{2\hbar}{M(w-w')})^{1/2} \cdot \frac{1}{2}
\]

with \( M \) the reduced mass of the atoms involved in the vibration. Consequently Eq. (3.36) yields

\[
K = \frac{(\text{Energy} \cdot \text{Volume})}{2A \cdot a} g'(q^0)(\frac{2\hbar}{M(w-w')})^{1/2}
\]

with an as yet unspecified \( (\text{Energy} \cdot \text{Volume}) \) arising from the integral.

An estimate of the magnitude of the matrix element of (3.36) may be arrived at from empirical data for electron-polar molecule scattering. Realizing that in actuality the electrons in the film have a
negative energy and must overcome the work function to assume a positive energy, it is not hard to visualize a situation in which the electrons may 'tunnel' outside the film to interact with or scatter off the molecule. Given this picture, one might suppose that replacing sine waves by plane waves in (3.36) would make little difference as to the magnitude of the matrix element. A Fermi Golden Rule calculation of the vibrational cross section for electron polar molecule scattering treating the incident and scattered electrons as plane waves would yield

\[
\frac{d\sigma}{d\Omega} \bigg|_{\text{el-mol}} = \frac{2\pi}{\hbar} \left| \langle \psi' \| H_{\text{ME}} \| \psi \rangle \right|^2 \frac{vk' dk' \delta(E' - E)}{(2\pi)^3 (\hbar k/m) \cdot (1/V)}
\]  

(3.39)

It turns out that experimental work shows such scattering to be isotropic and that a conservative estimate for the magnitude of this cross section is \(2.5 \times 10^{-18} \text{ cm}^2/\text{steradian}\) \((51,52,53)\). Reference \((51)\) quotes cross sections from the crossed beam technique, which is reliable for absolute cross sections, and Reference \((52)\) concerns electron scattering off CO adsorbed to platinum. A theoretical calculation \((53)\) is performed for the experiment described in \((52)\) and shows that if the CO were not adsorbed to a metal surface a factor of 4 reduction would result. The above quoted cross section is an average over 1-3 eV electrons and in no way represents the cross section near the resonance energy of the vibration which may be a factor of 10 larger. I find then
\[ K(A \cdot a)^2 = \frac{\text{d} \sigma}{\text{d} \omega} \left|_{\text{vib}} \right. \left|_{\text{el-mol}} \right. (2\pi)^2 \frac{4}{m} \]

\[ K = \frac{a^2}{A \cdot a} (2.5 \times 10^{-18} \text{ cm}^2)^{1/2} \cdot (2\pi) \cdot 2 \cdot (13.58 \text{ eV}) \]

It is worthwhile to mention the consequences of alternative methods for calculating \( K \). A point dipole exterior to the metal Coulomb interacting with an electron inside the metal, gives an integration over the spatial coordinates which yields a result independent of the vibration coordinate. For a thin film, if one takes the point dipole a distance \( z_0 = q_0 + \lambda \) above the film and inserts

\[ V(\mathbf{r}, z_0) = \frac{Q z_0 \cdot z}{(z_0 + \rho)^{3/2}} \]

into (3.36) and integrates over a few angstroms at the top of the film, the spatial integral yields a result independent of \( z_0 \) if \( \mathbf{k}_3 - \mathbf{k}_2 \) is taken to be zero. (The format of the potential and the range of integration is in accord with metallic screening theories.) Therefore, the previously mentioned \( g(\lambda) \) is independent of \( \lambda \) and no transition between ground and vibrational levels of the molecule is possible. A nonzero result would occur only if \( \mathbf{k}_3 - \mathbf{k}_2 \) is taken nonzero which is reasonable only for very large photon energies or for roughness at the film surfaces.

Another possibility would be to represent the electron-molecule interaction as a spherical square well. The electron would be allowed to tunnel out and overlap with the well. The problem is that no valid
estimates of the depth of such a well currently exist. Inelastic electron tunneling experiments (54) can fit the tunneling data to the Brailsford and Davis (55) theory of the double step potential in order to obtain values for the strengths of such a spherical square well. Tsang and Kirtley (54) predict no Raman enhancement for molecules whose inelastic electron tunneling data may be fit by a well depth of greater than 1.0 eV. One would expect the Raman scattering cross section formulated in this chapter to increase with the strength of the interaction and not vice versa. In addition, the Brailsford Davis theory is not easily applied to a localized molecule.

In conclusion of Chapter III I address the previously posed question of the hole-scattering contribution to the Raman scattering cross section. Since hole-scattering involves electrons below the Fermi energy, the probability of these electrons tunneling out to interact with the molecule is negligible compared to electron scattering which involves electrons above the Fermi energy. For this reason hole-scattering is neglected in (3.22).
IV. RESULTS AND CONCLUSIONS

The Fourier coefficients $A^X_0(n)$ and $A^Z_0(n)$ in Eqs. (2.39) for the incident photon, and also the coefficients for the scattered photon, can be determined by solving the symbolic matrix eq. (2.38). Given the initial conditions of the incident radiation, i.e. frequency $\omega$ and angle of incidence $\theta$, and also given frequency $\omega' = \omega - \xi$ and angle of collection $\theta'$ of the scattered radiation, (2.48) is solved separately for first the incident radiation and then again for the scattered radiation. These results can be entered into Eq. (3.32) for the transition probability per unit time $P$, which can then be placed into (3.35) to yield the differential cross section $d\sigma/d\Omega$.

This chapter examines how well the values for $d\sigma/d\Omega$ compare to experiment and attempts to detail how roughness might actually lead to even larger differential cross sections for Raman scattering.

A. Frequency Dependence of $d\sigma/d\Omega$

Figure 12 displays the Raman scattering cross section as a function of the frequency of the incident photon for a 46Å potassium film. The frequency of the vibration is taken to be 2000 cm\(^{-1}\) and the angle of incidence is 75° with the scattered photon also collected at 75°. The horizontal scale is the frequency of incident light in relation to the plasma frequency of potassium. In the vicinity of $\omega = .58\omega_p$ (5000Å) the differential cross section is approximately $30 \times 10^{-28}$ cm\(^2\)/str. This is a factor of 30 over generally accepted differential cross sections for free molecules (56). (The reader
Figure 14. Raman cross section for 46 Å potassium film
may express some skepticism over generalizing such a cross section as though no differences in the magnitude of the quoted cross section would result in examining different molecules. Benzene and pyridine, however, have Raman cross sections for the isolated state equivalent up to an order of magnitude. No significant changes would occur in Fig. 12 upon taking the vibrational frequency to be 1000 cm$^{-1}$.

Beyond $\omega = \omega_p$, is seen the influence of the plasmons on $\partial \sigma / \partial \Omega$. The enormous peak values correspond to scattering cross sections on the order of $10^{-23}$ cm$^2$/str. Figure 13 shows similar results to those of Figure 12 and the only difference is that Fig. 13 is for an 11.5 Å potassium film instead of a 46 Å potassium film. Exempting the structure below the plasma frequency, the differential cross section obeys an $\omega^4$ law between $\omega = .4$ and $.9\omega_p$. This structure is due to the effect of single particle excitations which match the incident or scattered photon in energy. Actually, one might expect single particle resonances to show up in an even more pronounced fashion. For frequencies in the vicinity of single particle resonances, however, the Fourier coefficients in the numerator of (3.32) are also changed markedly. Examining eq. (2.39) of Chapter II leads one to suggest that the changes in the Fourier coefficients near resonance energies for single particle excitations diminish the effect of making the denominators in (3.22) very small.

B. Effects of Higher Electron Density

Potassium in real physical situations exhibits properties that
Figure 13. Raman cross section for 11.5 Å potassium film

\[ \sigma(\omega) \propto \frac{d\sigma}{d\Omega} \times 10^{-27} \text{ (cm}^2\text{)} \]

\[ \omega/\omega_p \]

--- marks 5000 Å incident light
closely parallel a free electron metal. As such, it is an excellent choice for this calculation given the assumptions of Chapters II and III. Potassium, however, has never been examined for surface enhanced Raman scattering. As mentioned in the initial chapter, silver, copper and gold lead the list of substrates associated with SER. Silver has a plasma frequency which is less than half the value predicted by strictly free electron calculations. Interband transitions are responsible for this condition and interband effects are not easily incorporated into the framework of Chapters II and III. Even with these comments in mind, I believe it somewhat informative to examine the results of a calculation for \( r_s = 3.02 \) (Ag) for the differential cross section of Raman scattering.

Figure 14 is a coarse plot of \( d\sigma/d\Omega \) for both potassium and silver verses the relative frequency \( \omega/\omega_p \). (The reader should realize that the horizontal scale is not absolute in Fig. 14. On an absolute scale silver would 'beat' potassium at the far left, potassium would dominate in the visible wavelengths, and the two would somewhat coalesce in the ultraviolet and beyond.) The results seem to suggest that the frequency dependence of this calculation is not an absolute one and that the ratio of the absolute frequency to the plasma frequency is the more relevant number to follow.

Reasons have already been given in Chapter I as to why this calculation was performed for a thin film rather than a semi-infinite medium. I reiterate that for a thin film the electronic wave functions are straightforward and simple and the calculation itself quite
Figure 14. Raman scattering cross section for 46 Å silver x and potassium o films. The frequency scale is not absolute as the frequency for silver is more than twice that of potassium.
tractable. A semi-infinite sample creates difficulties in regard to
a credible choice for the electron wavefunctions. (It should be
remembered by the reader that terminating the series in (2.39)
does not correctly treat the vector potential at the surface. If
the electronic wavefunctions terminate at the surface, however,
one might expect the effects of series termination to be minimal.)
I expect, however, that the only difference in the results for \( \frac{d\sigma}{d\Omega} \)
for a thin film verses a semi-infinite medium, would be the absence
of the plasma peaks beyond the plasma frequency.

C. Roughness

Typical experiments are performed in the neighborhood of
4880 Å and yield cross sections that are enhanced \( 10^4 \) - \( 10^6 \) rather
than the somewhat meager factor of 30 previously stated. As noted
in the introduction, roughness plays a key role in SER according
to an overwhelming majority of experimentalists. This thesis
calculation assumes a smooth surface. This assumption forces
momentum conservation parallel to the surface of the film and
drastically simplifies \( k \) space integrations. Elimination of the
constraint of a smooth surface would conceivably make an already
difficult task impossible. It is interesting, however, to speculate
on how abrogation of the smooth surface restriction might effect
the differential cross section results.

The bold lines in Fig. 15 mark transitions of electrons which
are currently allowed under the confines of a smooth surface.
Figure 15. Electron transitions out of Fermi Sea; bold lines are allowed, dashed lines are not allowed for a smooth surface

Figure 16. Concept of Moskovits
Electrons are forced to jump levels in order to undergo an energy change via photon absorption. The momentum of the photon is not large enough to kick an electron to a position outside the Fermi sea and yet keep the electron on the same discrete level. \( k_x^* \) can change only by \( k_x^o \) or \( k_x^o' \) and \( k_y^* \) cannot change at all due to momentum conservation parallel to the smooth surface. Small scale roughness, irregularities on the order of angstroms, would allow transitions such as the ones shown by the dashed lines of Figure 15. Such transitions would increase the Raman scattering cross section in two ways. Presently the selection rules embodied in the integrals of Appendix C preclude use of the rather large Fourier coefficient of \( A_x^x, A_o^x(0) \). This is just a statement that the only transitions possible for a smooth surface involve momentum changes in the \( k^2 \) direction. \( A_o^x(0) \) possesses no momentum at all. Roughness would allow \( A_o^x(0) \) to be used in (3.32). Furthermore small scale roughness would dramatically increase the amount of phase space available for the \( k \) space integrations in Eqs. (3.33) and (3.34).

Another way in which small scale roughness might significantly augment the Raman scattering cross section parallels the development of Moskovits (40). As stated in the introduction, Ref. (40) models the metal surface in accord with Fig. 16, i.e. small metallic spheres embedded in a smooth metal surface. Metallic spheres display enhanced fields characterized as plasma resonances at frequencies near \( \omega_p/\sqrt{3} \) where \( \omega_p \) is the frequency at a bulk plasmon. (Analogously, the peaks in the absorption or \( d\sigma/d\Omega \) for the thin film beyond \( \omega_p \).)
arise from large electromagnetic fields at the peak frequencies.) As mentioned earlier in this chapter, the differential cross section for Raman scattering calculated in this thesis can be as large as $10^{-23}\text{ cm}^2$ in the vicinity of the plasma resonances. For small spheres embedded in a smooth substrate it is not implausible to suggest that such large cross sections might result at frequencies more closely attune to the 4880Å argon laser line.

Roughness also clouds the distinction between s and p-polarized light. SER has been seen for s-polarized light, and this calculation predicts no enhancement for s-polarized light on a smooth surface. Roughness mixes up s and p-polarized light so that s-polarized light has some component perpendicular to the surface in the presence of roughness. As mentioned in Chapter III, it is the component of Å normal to the surface which is most important in (3.22) and therefore SER for s-polarized light on a rough surface is consistent with the predictions of this thesis.

D. Epilogue

The contents of this thesis do not lay to rest the conflicting explanations for SER outlined in Chapter I. I believe, however, that the merits of this thesis lie in the simplicity of the model and the first principles nature of the approach. It is my hope that future theoretical work on SER will take note of these results in order to develop a consistent, cogent explanation for the large cross sections found in SER experiments.
V. APPENDIX A: CURRENT-CURRENT RESPONSE FUNCTION

In the RPA we have

$$C_{\alpha\beta}^{\alpha}(\vec{r},\vec{r}',\omega) = \sum_{n} \left[ \frac{\phi_{n}\phi_{n}^{*}(\vec{r})}{\omega + i\varepsilon - \omega_{n}} - \frac{\phi_{n}\phi_{n}^{*}(\vec{r}')}{\omega + i\varepsilon + \omega_{n}} \right] \tag{A.1}$$

but from the form of $\phi_{\alpha}^{\alpha}(\vec{r})$ given in Chapter II it is obvious that the summation index $n$ is substantially more complex than is represented by the single index $n$. $\phi_{\alpha}^{\alpha}(\vec{r})$ may be written

$$\phi_{n}^{\alpha}(\vec{r}) = \frac{1}{(2\pi)^{2}} e^{i(\vec{k}-\vec{k}') \cdot \vec{p}}[\theta(\vec{e}_{F}^{N'} - \vec{e}_{F}^{N}) \cdot \theta(\vec{e}_{F}^{N'} - \vec{e}_{F}^{N})] j_{NN'}^{\alpha}(z) \tag{A.2}$$

with $j_{NN'}^{\alpha}(z)$ given as

$$j_{NN'}^{\alpha}(z) = \frac{\sqrt{\vec{r} \cdot \vec{r}'}}{2ma} \sin \frac{N_{\alpha} \pi}{2a} \sin \frac{N_{\alpha}' \pi}{2a} \tag{A.3}$$

and

$$j_{NN'}^{\beta}(z) = \frac{e^{\pi}}{4ima} \left[ N \sin \frac{N_{\beta} \pi}{2a} (z+a) \cos \frac{N_{\beta} \pi}{2a} (z+a) - N' \sin \frac{N_{\beta} \pi}{2a} (z+a) \right. \tag{A.4}$$

$$\left. \cdot \cos \frac{N_{\beta} \pi}{2a} (z+a) \right].$$

I note the following identities

$$j_{NN'}^{\alpha}(z) = - j_{N'N}^{\alpha}(z) = j_{N'N}^{\alpha}(z) \quad j_{NN'}^{\alpha}(z) = j_{N'N}^{\alpha}(z) = j_{NN}^{\alpha}(z). \tag{A.5}$$

I then write
The factor of two in front accounts for the two possible spin states the excited electron may take. If we interchange \( \mathbf{k} \leftrightarrow \mathbf{k}' \) and \( N \leftrightarrow N' \) in the second term of (A.6) we see that it is the same as the first except for changing the step functions. This is done with impunity as \( \mathbf{k}, \mathbf{k}', N, N' \) are all dummy variables. Since \( \Theta(-a) = 1 - \Theta(a) \) we may combine terms in (A.6) through the relation

\[
 \Theta(a) \cdot \Theta(-b) - \Theta(b) \Theta(-a) = \Theta(a) - \Theta(b) .
\]

It is then seen that

\[
 C^{\alpha \beta}(\mathbf{r}, \mathbf{r}', \omega) = 2 \left[ \int \frac{d^2 k d^2 k'}{(2\pi)^4} \right] \frac{e^{i(\mathbf{k} - \mathbf{k}')} \cdot \mathbf{p}^\alpha \mathbf{p}^\beta}{\omega + i\epsilon - (\epsilon_{\mathbf{k}', N} - \epsilon_{\mathbf{k}, N})} \sum_{NN'} \left[ \Theta(\epsilon_F - \epsilon_{\mathbf{k}, N}) - \Theta(\epsilon_F - \epsilon_{\mathbf{k}', N'}) \right] \cdot j_{NN'}^\alpha(z) j_{NN'}^\beta(z') .
\]

(A.7)

I now put \( Q = \mathbf{k} - \mathbf{k}' \) so that \( \mathbf{k} = Q + \mathbf{k}' \). This yields

\[
 C^{\alpha \beta}(\mathbf{r}, \mathbf{r}', \omega) = 2 \left[ \int \frac{d^2 Q}{(2\pi)^2} e^{iQ \cdot (\mathbf{r} - \mathbf{r}')} \right] \frac{d^2 \mathbf{k}'}{(2\pi)^2} \sum_{NN'} \left[ \Theta(\epsilon_F - \epsilon_{\mathbf{k}', N}) \cdot j_{NN'}^\alpha(z) j_{NN'}^\beta(z') \right.

- \Theta(\epsilon_F - \epsilon_{\mathbf{k}, N}) \cdot \frac{j_{NN'}^\alpha(z) j_{NN'}^\beta(z)}{\omega + i\epsilon - (\epsilon_{\mathbf{k}', N} - \epsilon_{\mathbf{k}, N})} \right] .
\]

(A.8)
With the substitution $Q = \mathbf{k} - \mathbf{k}'$, $j^X$ must be written

$$j_{NN'}^X(z) = \frac{e}{2ma} (2\mathbf{k}' + \mathbf{Q})^X \sin \frac{N\pi}{2a} (z+a) \sin \frac{N'\pi}{2a} (z+a) \quad (A.9)$$

and this is precisely the form for $C^{\alpha\beta}(r, r',\omega)$ quoted in Chapter II.

To simulate damping, $\epsilon/\omega_p$ is taken to be $10^{-3}$ and is retained in all response functions. The inclusion of $\epsilon$ in the denominator of Eq. (2.15) is also intended to more realistically represent collisions in the electron gas. Although such an approximation does not allow the electron density to relax to its local equilibrium value (see, e.g., Mermin (57)), I do not feel the results for the fields and absorption suffer to any significant extent. When the more correct finite relaxation dielectric functions of Mermin (57) are used in Ref. (10), no significant difference is seen in the results there quoted.
VI. APPENDIX B: \( \vec{k} \) SPACE INTEGRATIONS

I address now the integrals \( I_1, I_2 \) and \( I_3 \) of Chapter II. For conciseness I make the following substitutions

\[
R = (F^2 - N^2)^{1/2}; \quad X^+ = X(N,N',q_o^2); \quad X^- = X(N',N,-q_o^2).
\]

\( I_1 \) may then be written

\[
I_1 = \int_0^R \int_0^{2\pi} r^3 dr \cos^2 \theta \ d\theta \ \frac{1}{X^+ + 2rq_o \cos \theta \frac{\pi}{2}} - \frac{1}{X^- + 2rq_o \pi^2 \cos^2 \theta}.
\]

(B.1)

Examining the \( \theta \) integration it may be seen to take the form

\[
\int_0^{2\pi} \frac{\cos^2 \theta}{a + b \cos \theta} = \frac{4}{a} \int_0^{\pi/2} \frac{\sin^2 \theta \ d\theta}{\cos \theta + (1 - b^2/a^2) \sin^2 \theta}.
\]

(B.2)

from standard tables (58) this may be written as

\[
\frac{2\pi}{a} \frac{1}{(1 - b^2/a^2)^{1/2}(1 + (1 - b^2/a^2)^{1/2})}.
\]

(B.3)

The \( r \) integration then takes the form

\[
\int_0^R \frac{r^3 dr}{(1 - cr^2)^{1/2}(1 + (1 - cr^2)^{1/2})}
\]

(B.4)

with \( b^2/a^2 = c \). The substitution \( y = (1 - cr^2)^{1/2} \) yields

\[
\frac{1}{c^2} (1 - \frac{c}{2} R^2 - (1 - cR^2)^{1/2})
\]

(B.5)

for the value of the integral. \( I_1 \) may then be written
\[ I_1 = \frac{2\pi}{2\pi} \left( \frac{\pi}{16q_o^2} \right) \left( X^+ \right)^3 \left( 1 - \left( \frac{4q_o^2 \pi^2 R^2}{(X^+)^2} \right)^{1/2} \right) - \left( X^- \right)^3 \left( 1 - \left( \frac{4q_o^2 \pi^2 R^2}{(X^-)^2} \right)^{1/2} \right) \]

\[ - \frac{2\pi R^2}{8q_o^2 \pi^2} (X^- - X^+) \]  

(B.6)

\[ I_2 \text{ and } I_3 \text{ may be evaluated in the same manner as } I_1. \text{ In evaluating } I_3 \text{ the } \theta \text{ integration appears as} \]

\[ \int_{0}^{2\pi} \frac{d\theta}{a + b \cos \theta} = \frac{2\pi}{a - \left(1 - b^2/a^2\right)^{1/2}} \]  

(B.7)

\[ \text{from standard reference tables (58). } I_2 \text{ is found to be} \]

\[ I_2 = -2q_o \pi^2 \left( \frac{2\pi}{16q_o^2 \pi^2} \right) \left[ (X^+)^2 \left( 1 - \left( 1 - \frac{4q_o^2 \pi^2 R^2}{(X^+)^2} \right)^{1/2} \right) \right] \]

\[ + (X^-)^2 \left( 1 - \left( 1 - \frac{4q_o^2 \pi^2 R^2}{(X^-)^2} \right)^{1/2} \right) \]  

(B.8)

\[ \text{and } I_3 \text{ may be written} \]

\[ I_3 = \frac{2\pi}{4q_o^2 \pi^2} \left[ \left( 1 - \left( 1 - \frac{4q_o^2 \pi^2 R^2}{(X^+)^2} \right)^{1/2} \right) - X^- \left( 1 - \left( 1 - \frac{4q_o^2 \pi^2 R^2}{(X^-)^2} \right)^{1/2} \right) \right]. \]  

(B.9)
VII. APPENDIX C: TRIGONOMETRIC INTEGRATIONS

I now list and evaluate the integrals which occur in Eq. (2.47-2.52) as well as other integrals which occur in consideration of the even parity fields. In all integrals I make the substitution $y = 2\pi/2a$ and $x = y + \pi/2$ and make use of the following identities

\[
\cos ny \cos my = 1/2(\cos(m + n)y + \cos(m - n)y)
\]
\[
\sin ny \sin my = 1/2(\cos(m - n)y - \cos(m + n)y)
\]
\[
\sin^2 ny = 1/2(1 - \cos 2ny); \sin my \cos ny = 1/2(\sin(m + n)y + \sin(m - n)y).
\]

\[
K^0(m,n,N) = a(-1)^{m+n}[1/2\delta_{mn} - 1/4\delta_{N,m+n} - 1/4\delta_{N,|m-n|}]
\]

\[
L^0(m,n,N) = a(-1)^{m+n}[1/2\delta_{mn} + 1/4\delta_{N,m+n} - 1/4\delta_{N,|m-n|}]
\]

\[
J^0(m,n,N) = \frac{2a}{\pi}(-1)^{m+n} \int_0^\pi \cos(2n-1)x \cdot \cos(2m-1)x \cdot \sin^2 N x \, dx
\]

\[
= a(-1)^{m+n}[1/2\delta_{mn} - 1/4\delta_{N,m+n-1} - 1/4\delta_{N,|m-n|}]
\]

\[
H^0(m,n,N) = \frac{2a}{\pi}(-1)^{m+n} \int_0^\pi \sin(2n-1)x \cdot \sin(2m-1)x \cdot \sin^2 N x \, dx
\]

\[
= a(-1)^{m+n}[1/2\delta_{mn} + 1/4\delta_{N,m+n-1} - 1/4\delta_{N,|m-n|}]
\]

\[
\int_{-a}^{a} dz_{NN}(z) \cos \frac{\nu_2 z}{a} = \frac{a(-1)^n}{2} [\delta_{2n,|N-N'|} - \delta_{2n,N+N'}]
\]
\[ \int_{-a}^{a} d\tilde{z} \beta_{N'}^{(z)} \sin \frac{nz \pi z}{a} = a \frac{(-1)^n}{2} \left[ N(\delta_{2n,N,N'} + \delta_{2n,N'-N} - \delta_{2n,N-N'}) 
\right. \\
\left. - N'(\delta_{2n,N+N'} + \delta_{2n,N-N'} - \delta_{2n,N'-N}) \right] \] (C.6)

\[ \int_{-a}^{a} d\tilde{z} \gamma_{NN'}^{(z)} \sin \frac{2n-1\pi z}{2a} = a(-1)^{n+1} \left[ \frac{\delta_{2n-1,N-N'}}{2} - \delta_{2n-1,N+N'} \right] \] (C.7)

\[ \int_{-a}^{a} d\tilde{z} \delta_{NN'}^{(z)} \cos \frac{2n-1\pi z}{2a} = \left[ (N-N')\delta_{2n-1,N+N'} + (N+N')\delta_{2n-1,N'-N} \right. \\
\left. - \delta_{2n-1,N-N'} \right] \] (C.8)
VIII. REFERENCES


30. This has been observed by R. P. Van Duyne (Northwestern University) and A. Z. Genack (Exxon Research and Engineering Co.).
42. B. Pettinger, A. Tadjeddine and D. M. Kolb (to be published).
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