VI. CONCLUSIONS

The primary purpose of this paper has been to generalize the Ginzburg-Landau phenomenological theory to include the Josephson effect, and in this way develop a tool which will be useful in dealing with problems difficult to handle with existing microscopic theories. The primary contribution of this paper has been to show that self-consistent solutions do exist to the equations of the model, provided that the current does not exceed a certain critical current identified with the maximum Josephson current.

There are several other treatments of the Josephson effect in existence all of which have two important points in common: The properties of the oxide are lumped into a single number, the transmission coefficient; and the type of configuration which can be handled conveniently is limited to the one-dimensional problem treated in Sec. III. The present approach, being based on a phenomenological theory, differs from the earlier models in just these respects. This tends to give the present model, if not a fundamental, at least a very distinct practical advantage. For it is applicable to more complex configurations, as shown in Sec. IV; and the description of the oxide in terms of an effective potential, as pointed out in Sec. V, leads to an estimate of the effective current carrying area of the junction.

The present model, in addition, leads to a useful physical interpretation of the Josephson effect: In certain respects, a nonsuperconducting gap placed between two superconductors behaves like a weak superconductor, allowing small nondissipative currents to pass; the maximum Josephson current being associated with the critical current for the weak superconductors.

Finally, it must be stated that the development of the model suggested by Maki[2] is far from complete. There remain several problems which need to be investigated, of which only two will be mentioned. First, there needs to be an accurate determination of the effective potential. Until this is done, it will only be possible to make order-of-magnitude calculations for the quantities of interest. Second, it is essential to be able to include in a self-consistent manner the effect of both electric and magnetic external fields. Work is now in progress on both of these problems.

ACKNOWLEDGMENT

The author is grateful to Dr. Sylvan Katz for many illuminating discussions throughout the course of this work.

PHYSICAL REVIEW VOLUME 138, NUMBER 4A 17 MAY 1965

Collective Oscillations in a Dense Electron Gas Containing a Fixed Point Charge*

EDWARD A. SZIKLAS
United Aircraft Corporation Research Laboratories, East Hartford, Connecticut
(Received 23 December 1964)

The collective excitations of a dense electron gas containing a fixed point charge with neutralizing positive background are investigated. A dielectric formulation, evaluated in a self-consistent-field approximation, yields a single-particle Schrödinger equation describing the collective modes. This equation has solutions belonging to the continuous spectrum (free plasmons) and to the discrete spectrum (bound plasmons). A cross section is derived for scattering of free plasmons by the point charge. The bound plasmon, representing a density wave trapped at the impurity site, has no counterpart in the uniform gas; it exists only for negative impurity charge and has an excitation frequency lying in the range $\omega_p/\sqrt{2} \leq \omega < \omega_p$, where ω_p is the plasma frequency. The bound plasmon appears to be a reasonably well-defined excitation with a lifetime $\sim 10^{-15}$ sec in metals. A simple hydrodynamical model provides further physical insight. The experimental detection of bound and free plasmons in metals and the relationship between surface plasmons, experimentally observed in many metals, and the predicted bound plasmon are discussed.

1. INTRODUCTION

IN modern many-body theory attention has been confined almost exclusively to uniform systems. This may be attributed, first, to the mathematical difficulties associated with nonuniform systems and, secondly, to the hope that most important many-body effects are exhibited by uniform and nonuniform systems alike, and the treatment of the latter would add only mathematical complexity. Nevertheless, while the uniform system serves as a useful model for many problems, it is desirable to have at least a qualitative understanding of the effects that may be introduced by nonuniformities. The present paper is devoted to that end.

As a simple departure from a uniform system, we consider a dense electron gas immersed in a static electric field due to the presence of a single fixed point charge. A uniform background of positive charge provides over-all electrostatic neutrality. This ideal model is not without practical interest. The point charge

* This work is based on a Ph.D. dissertation submitted to Yale University and was supported in part by the U. S. Air Force Office of Scientific Research.

represents roughly an impurity atom or ion in a metal.

In a previous study Layzer[1] has investigated the quasiparticle excitations of this system. He finds for a positive point charge a discrete spectrum of bound holes, finite in number, which vanishes at sufficiently high electron densities. In contrast, we examine the collective excitations of the system. For a uniform electron gas the dispersion relation for collective oscillations is given by[2]

$$\omega^2=\omega_p{}^2+\tfrac{3}{5}v_F{}^2k^2+O(k^4), \tag{1}$$

where ω_p is the usual free-electron plasma frequency,

$$\omega_p=(4\pi e^2n/m)^{1/2}, \tag{2}$$

n is the electron number density, and v_F is the Fermi velocity. In brief, we wish to determine how Eq. (1) is modified by the presence of the point charge.

Our approach is an adaptation of the work of Ehrenreich and Cohen,[3] later generalized by Cohen.[4] In the former study a time-dependent self-consistent field (SCF) is employed in a dielectric formulation of the many-electron problem. The SCF theory provides a simple means for calculating the longitudinal, wave-vector and frequency-dependent dielectric constant for a uniform gas, and from this the properties of the system may be deduced. In the subsequent study by Cohen this treatment is generalized to include nonuniform systems.

We apply a modified version of the Cohen-Ehrenreich theory to the particular system under consideration. In Sec. 2 a brief description of the SCF approximation is given, and the linearized dielectric response of the system to a weak external perturbation is computed in this approximation. In the absence of external perturbations, the dielectric response furnishes the desired condition for self-sustained oscillations or normal modes of the system.

In Sec. 3 the results of the microscopic theory are considered in the light of a crude hydrodynamical model, and experiments in solids relevant to the theory are briefly discussed.

2. SCF THEORY AND DIELECTRIC FORMULATION

We treat a system of N electrons contained in a large volume Ω. An external static field due to a uniform positive charge density $[(N-z)/\Omega]e$ and a single fixed point charge ze, located at the origin of coordinates, acts on each electron. Since $\Omega\to\infty$ implies $N\to\infty$ for fixed electron number density N/Ω, it is clear that $N\gg z$ for finite z.

The Hamiltonian for the system may be written

$$H=\sum_{i=1}^{N}\frac{p_i{}^2}{2m}-z\sum_{\mathbf{q}\neq0}v_{\mathbf{q}}\rho_{-\mathbf{q}}+\tfrac{1}{2}\sum_{\mathbf{q}\neq0}v_{\mathbf{q}}[\rho_{\mathbf{q}}\rho_{-\mathbf{q}}-N], \tag{3}$$

where $v_{\mathbf{q}}$ and $\rho_{\mathbf{q}}$ are the Fourier transforms of the Coulomb potential and the electron number density, i.e.,

$$v_{\mathbf{q}}=4\pi e^2/\Omega q^2, \tag{4}$$

$$\rho_{\mathbf{q}}=\sum_{i=1}^{N}\exp(-i\mathbf{q}\cdot\mathbf{r}_i). \tag{5}$$

The $\mathbf{q}=0$ terms, missing from Eq. (3), cancel exactly against the term containing the uniform background of positive charge.

SCF Approximation and Linear Response

Following Ehrenreich and Cohen[3] and Cohen,[4] we define a self-consistent field (SCF) approximation to the true Hamiltonian. The time-independent SCF Hamiltonian is given by

$$H_s{}^0=\sum_i\frac{p_i{}^2}{2m}-\sum_{\mathbf{q}\neq0}v_{\mathbf{q}}[z-\langle\varphi_0|\rho_{\mathbf{q}}|\varphi_0\rangle]\rho_{-\mathbf{q}} \tag{6}$$

and satisfies the time-independent Schrödinger equation

$$H_s{}^0|\varphi_n\rangle=\mathcal{E}_n|\varphi_n\rangle.$$

Equation (6) is obtained from Eq. (3) by means of a variational principle in which the approximate factorization

$$\langle\varphi_0|\rho_{\mathbf{q}}\rho_{-\mathbf{q}}|\varphi_0\rangle\cong\langle\varphi_0|\rho_{\mathbf{q}}|\varphi_0\rangle\langle\varphi_0|\rho_{-\mathbf{q}}|\varphi_0\rangle$$

is made. Since $H_s{}^0$ can be written as the sum of identical single-particle operators, the eigenstates $|\varphi_n\rangle$ are Slater determinants.

Having defined a set of SCF states, we wish to examine the linear response of the system to a weak external time-dependent field. First, a simple generalization of Eq. (6) is required to incorporate time dependence into the formalism:

$$H_s(t)=\sum_i\frac{p_i{}^2}{2m}-\sum_{\mathbf{q}\neq0}v_{\mathbf{q}}[z-\langle\psi|\rho_{\mathbf{q}}|\psi\rangle]\rho_{-\mathbf{q}}. \tag{7}$$

Here,

$$H_s|\psi\rangle=i\hbar\frac{\partial}{\partial t}|\psi\rangle. \tag{8}$$

Eq. (7), called the time-dependent SCF Hamiltonian, follows from a time-dependent formulation of the variational principle.[4]

The following time-dependent perturbation is considered:

$$H_1(t)=\textstyle\sum_{\mathbf{q}}U_{\mathbf{q}}(t)\rho_{-\mathbf{q}}, \tag{9}$$

where for all $\mathbf{q}$

$$U_{\mathbf{q}}(t)\sim e^{(-i\omega+\alpha)t}. \tag{10}$$

Here, we depart from Cohen, who considered a perturbation having a single spatial Fourier component. This modification will prove necessary in the subsequent analysis. The parameter α is a positive infinitesimal

[1] A. J. Layzer, Phys. Rev. **129**, 908 (1963).
[2] D. Bohm and D. Pines, Phys. Rev. **82**, 625 (1951); **85**, 338 (1952); **92**, 609, 626 (1953).
[3] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).
[4] M. H. Cohen, Phys. Rev. **130**, 1301 (1963).

which serves to turn on the perturbation adiabatically and to ensure that the response of the system is causal.

To determine the linear response, we consider a classical test charge located at the position $\mathbf{r}$. The potential $V(\mathbf{r},t)/-e$ measured by this test charge is given by Poisson's equation. Fourier transformation in space gives

$$V_{\mathbf{q}}(t)=v_{\mathbf{q}}[\langle\psi|\rho_{\mathbf{q}}|\psi\rangle-z]+U_{\mathbf{q}} \quad \mathbf{q}\neq 0. \tag{11}$$

The change in $V_{\mathbf{q}}$ when the perturbation H_1 is turned on constitutes the response of the system. At $t=-\infty$ the system is assumed to be in the SCF ground state $|\varphi_0\rangle$.

$$\Delta V_{\mathbf{q}}=V_{\mathbf{q}}(t)-V_{\mathbf{q}}(-\infty)=v_{\mathbf{q}}\Delta\langle\rho_{\mathbf{q}}\rangle+U_{\mathbf{q}} \tag{12}$$

$$\Delta\langle\rho_{\mathbf{q}}\rangle=\langle\psi|\rho_{\mathbf{q}}|\psi\rangle-\langle\varphi_0|\rho_{\mathbf{q}}|\varphi_0\rangle. \tag{13}$$

Equation (12) relates the response $\Delta V_{\mathbf{q}}$ to the applied potential $U_{\mathbf{q}}$. To proceed further, we must express $\Delta\langle\rho_{\mathbf{q}}\rangle$ in terms of $U_{\mathbf{q}}$.

Application of first-order, time-dependent perturbation theory (equivalent to the use of a linearized density matrix) gives

$$\sum_{\mathbf{q}'\neq 0}[\delta_{\mathbf{q}\mathbf{q}'}-\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)v_{\mathbf{q}'}]\Delta\langle\rho_{\mathbf{q}'}\rangle=\sum_{\mathbf{q}'}\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)U_{\mathbf{q}'}, \quad \mathbf{q}\neq 0 \tag{14}$$

where

$$\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)=\sum_{n\neq 0}\frac{1}{\hbar}\left[\frac{\langle\varphi_0|\rho_{\mathbf{q}}|\varphi_n\rangle\langle\varphi_n|\rho_{-\mathbf{q}'}|\varphi_0\rangle}{\omega-\omega_{n0}+i\alpha}-\frac{\langle\varphi_0|\rho_{-\mathbf{q}'}|\varphi_n\rangle\langle\varphi_n|\rho_{\mathbf{q}}|\varphi_0\rangle}{\omega+\omega_{n0}+i\alpha}\right] \tag{15}$$

and

$$\hbar\omega_{n0}=\mathcal{E}_n-\mathcal{E}_0. \tag{16}$$

For a uniform gas $\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)$ is "diagonal" since for such a system the states $|\varphi_n\rangle$ are momentum as well as energy eigenstates.

The formal solution of Eq. (14) for $\Delta\langle\rho_{\mathbf{q}}\rangle$ may be written in matrix notation

$$\boldsymbol{\Delta\varrho}=\mathfrak{M}\mathfrak{D}\mathbf{U}, \tag{17}$$

where $\boldsymbol{\Delta\varrho}$ and $\mathbf{U}$ are vectors whose components are $\Delta\langle\rho_{\mathbf{q}}\rangle$ and $U_{\mathbf{q}}$; $\mathfrak{D}$ is a matrix whose components are $\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)$; and $\mathfrak{M}$ is a matrix whose inverse is defined by

$$(\mathfrak{M}^{-1})_{\mathbf{q}\mathbf{q}'}=\delta_{\mathbf{q}\mathbf{q}'}-\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)v_{\mathbf{q}'}. \tag{18}$$

Similarly, Eq. (12) can be written using Eq. (17)

$$\boldsymbol{\Delta V}=\boldsymbol{\varepsilon}^{-1}\mathbf{U}, \tag{19}$$

where the inverse dielectric matrix $\boldsymbol{\varepsilon}^{-1}$ is defined

$$\boldsymbol{\varepsilon}^{-1}=\mathbf{I}+\mathbf{v}\mathfrak{M}\mathfrak{D}. \tag{20}$$

Here, $\mathbf{I}$ is the unit matrix, and $\mathbf{v}$ is a diagonal matrix with components $v_{\mathbf{q}}\delta_{\mathbf{q}\mathbf{q}'}$. Equation (19) is easily inverted with the use of Eqs. (18) and (20). The result is

$$\mathbf{U}=\boldsymbol{\varepsilon}\boldsymbol{\Delta V} \tag{21}$$

which defines the dielectric matrix

$$\boldsymbol{\varepsilon}=\mathbf{I}-\mathbf{v}\mathfrak{D}. \tag{22}$$

In component form Eqs. (21) and (22) are written

$$U_{\mathbf{q}}=\sum_{\mathbf{q}'}\epsilon(\mathbf{q},\mathbf{q}';\omega)\Delta V_{\mathbf{q}'} \tag{23}$$

$$\epsilon(\mathbf{q},\mathbf{q}';\omega)=\delta_{\mathbf{q}\mathbf{q}'}-v_{\mathbf{q}}\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega). \tag{24}$$

The physical significance of Eq. (23) is this: An applied potential U with single wave vector $\mathbf{q}$ gives rise to a response ΔV having many Fourier components $\Delta V_{\mathbf{q}}$. In other words, an input wave is scattered by the nonuniform gas. For a uniform gas $\epsilon(\mathbf{q},\mathbf{q}';\omega)$ is diagonal, and the wave vector of the response is identical to that of the input. The need to include all Fourier components in the perturbation, Eq. (9), follows from the fact that in deriving the dielectric matrix, we solve first for a *single* Fourier component of the response, $\Delta V_{\mathbf{q}}$. For a nonuniform gas this necessarily involves *all* Fourier components of the applied potential.

Of paramount importance are the conditions under which a response exists in the absence of a perturbation. Such conditions describe the normal modes of the system. Normal modes exist for certain frequencies ω such that

$$\sum_{\mathbf{q}'}\epsilon(\mathbf{q},\mathbf{q}';\omega)\Delta V_{\mathbf{q}'}=0. \tag{25}$$

This expression, with $\epsilon(\mathbf{q},\mathbf{q}';\omega)$ defined by Eq. (24), yields a dispersion relation for ω whose form we seek for the collective modes of the system.

Equation (25) is in general complex. If the collective modes are assumed to be reasonably well defined, i.e., $\omega_2\ll\omega_1$, ω_1 and ω_2 being the real and imaginary parts of ω, then a Taylor series expansion of Eq. (25) is permissible:

$$\sum_{\mathbf{q}'}\left\{\epsilon_1(\mathbf{q},\mathbf{q}';\omega)+i\left[\epsilon_2(\mathbf{q},\mathbf{q}';\omega)+\omega_2\frac{\partial\epsilon_1(\mathbf{q},\mathbf{q}';\omega)}{\partial\omega}\right]\right\}\Delta V_{\mathbf{q}'}\approx 0. \tag{26}$$

Here, ϵ_1 and ϵ_2 are the real and imaginary parts of ϵ. First-order perturbation theory gives

$$\sum_{\mathbf{q}'}\epsilon_1(\mathbf{q},\mathbf{q}';\omega)\Delta V_{\mathbf{q}}{}^{(0)}=0 \tag{27}$$

and

$$\omega_2=-\left[\sum_{\mathbf{q},\mathbf{q}'}\Delta V_{\mathbf{q}}{}^{(0)*}\epsilon_2(\mathbf{q},\mathbf{q}';\omega)\Delta V_{\mathbf{q}'}{}^{(0)}\right]\Big/\left[\sum_{\mathbf{q},\mathbf{q}'}\Delta V_{\mathbf{q}}{}^{(0)*}\frac{\partial\epsilon_1(\mathbf{q},\mathbf{q}';\omega)}{\partial\omega}\Delta V_{\mathbf{q}'}{}^{(0)}\right], \tag{28}$$

where $\Delta V_{\mathbf{q}}{}^{(0)}$ is the zeroth-order approximation to $\Delta V_{\mathbf{q}}$. Equation (27) determines the normal modes $\omega\approx\omega_1$, and Eq. (28) the lifetime $\tau\sim 1/|\omega_2|$ of these modes.

Evaluation of the Dielectric Matrix

Further progress can be made only by detailed examination of ϵ_1 and ϵ_2 for the system in question. For this purpose we evaluate $\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)$, defined by Eq. (15).

Since the eigenstates $|\varphi_n\rangle$ are Slater determinants in the SCF approximation and $\rho_{\mathbf{q}}$ is the sum of single-particle operators, the N-particle matrix element $\langle\varphi_0|\rho_{\mathbf{q}}|\varphi_n\rangle$ reduces to a single-particle matrix element. The single-particle states satisfy the following Schrödinger equation

$$\left\{-\frac{\hbar^2}{2m}\nabla^2-\sum_{\mathbf{q}\neq 0} v_{\mathbf{q}}[z-\langle\varphi_0|\rho_{\mathbf{q}}|\varphi_0\rangle]\exp(i\mathbf{q}\cdot\mathbf{r})\right\}u_i(\mathbf{r}) = \epsilon_i u_i(\mathbf{r}). \quad (29)$$

In terms of these states $\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)$ becomes

$$\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega) = 2\sum_{i,j}\frac{\langle u_i|\exp(-i\mathbf{q}\cdot\mathbf{r})|u_j\rangle\langle u_i|\exp(-i\mathbf{q}'\cdot\mathbf{r})|u_j\rangle^*}{\hbar\omega+\epsilon_i-\epsilon_j+i\hbar\alpha} \times(f_i-f_j), \quad (30)$$

where

$$\langle u_i|\exp(-i\mathbf{q}\cdot\mathbf{r})|u_j\rangle = \int d\mathbf{r}u_i^*(\mathbf{r})\exp(-i\mathbf{q}\cdot\mathbf{r})u_j(\mathbf{r}), \quad (31)$$

f_i is a Fermi factor defined by

$$\begin{aligned} f_i &= 1 \quad \epsilon_i < \epsilon_F \\ &= 0 \quad \epsilon_i > \epsilon_F, \end{aligned} \quad (32)$$

and ϵ_F is the Fermi level of the states ϵ_i. The factor 2 appearing in Eq. (30) accounts for spin degeneracy.

As written, Eq. (29) must be solved self-consistently for the lowest $N/2$ ($\sim 10^{23}$) states in order to determine the SCF ground state $|\varphi_0\rangle$. Fortunately, this tedious task can be avoided by virtue of a simple physical argument.

From Poisson's equation the Fourier transform of the induced electron density due to the presence of a fixed weak point charge ze is given by

$$\langle\rho_{\mathbf{q}}^{\text{ind}}\rangle = z\{1-[\epsilon(\mathbf{q},0)]^{-1}\}, \quad (33)$$

where $\epsilon(\mathbf{q},0)$ is the static form of the wave vector and frequency-dependent dielectric constant for a *uniform* electron gas. The expectation-value symbol is used here to denote a thermal average over the states of the system in the presence of the point charge. In the SCF approximation for a dense electron gas, we may take

$$\langle\rho_{\mathbf{q}}^{\text{ind}}\rangle \approx \langle\varphi_0|\rho_{\mathbf{q}}|\varphi_0\rangle \quad \mathbf{q}\neq 0. \quad (34)$$

Thus, Eq. (29) becomes approximately

$$\left[-\frac{\hbar^2}{2m}\nabla^2-z\sum_{\mathbf{q}\neq 0}\frac{v_{\mathbf{q}}}{\epsilon(\mathbf{q},0)}\exp(i\mathbf{q}\cdot\mathbf{r})\right]u_i(\mathbf{r}) = \epsilon_i u_i(\mathbf{r}). \quad (35)$$

In effect, the Coulomb potential of the fixed point charge is shielded by the dielectric constant of the electron gas. This could have been written down on physical grounds at the outset. It is more reassuring to find, however, that it follows directly from the SCF approximation of Cohen and Ehrenreich.

The static dielectric constant for the uniform gas is well known in the SCF approximation[5]

$$\epsilon(\mathbf{q},0) = 1+\frac{k_{\text{FT}}^2}{q^2}\left[\frac{1}{2}+\frac{k_{\text{FT}}}{2q}\left(1-\frac{q^2}{4k_{\text{F}}^2}\right)\ln\left|\frac{q+2k_{\text{F}}}{q-2k_{\text{F}}}\right|\right]. \quad (36)$$

Here k_{F} and k_{FT} are the Fermi and Fermi-Thomas wave vectors, the latter defined by

$$k_{\text{FT}} = (4k_{\text{F}}/\pi a_0)^{1/2}, \quad (37)$$

where a_0 is the Bohr radius.

The potential appearing in Eq. (35) becomes a Yukawa potential with shielding length $1/k_{\text{FT}}$ if the long-wavelength approximation to $\epsilon(\mathbf{q},0)$ is employed, viz.,

$$\epsilon(\mathbf{q},0) \underset{\mathbf{q}\to 0}{=} 1+k_{\text{FT}}^2/q^2. \quad (38)$$

Equation (35) has a finite number of bound states. One can show by means of a WKB calculation[6] that for metallic densities z must be greater than about 2 if bound states are to exist at all. In the high-density limit, the number of bound states drops to zero for finite z.

In evaluating $\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)$ to determine the collective modes, we will find that the bound-state solutions of Eq. (35), even if present, can be ignored. Hence, we may confine attention to the scattering (continuum) states of this Schrödinger equation.

Roughly speaking, the first Born approximation to a scattering state is valid throughout the entire continuous spectrum if the scattering potential is too weak to support a bound state. In the high-density limit this condition is satisfied by the potential in Eq. (35). For the intermediate densities characteristic of metals, the validity of the Born approximation is not assured for all $\epsilon_i > 0$. Nevertheless, this approximation is made here with the hope that results will be at least qualitatively correct in the intermediate density region.

In the first Born approximation, we find for the matrix element

$$\langle u_{\mathbf{k}}|\exp(-i\mathbf{q}\cdot\mathbf{r})|u_{\mathbf{k}'}\rangle = \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}}-z\frac{v_{\mathbf{k}'-\mathbf{k}-\mathbf{q}}}{\epsilon(\mathbf{k}'-\mathbf{k}-\mathbf{q},0)}(1-\delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}}) \times[(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'-\mathbf{q}}-i\beta)^{-1}-(\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}'}-i\beta)^{-1}], \quad (39)$$

where $|u_{\mathbf{k}}\rangle$ denotes a scattering state of Eq. (35) labeled by the incident wave vector $\mathbf{k}$, and the limit $\beta\to 0^+$ is implied. Substitution of Eq. (39) and an analogous expression for $\langle u_{\mathbf{k}}|\exp(-i\mathbf{q}'\cdot\mathbf{r})|u_{\mathbf{k}'}\rangle$ into Eq. (30) gives to first order in z (with neglect of contributions from possible bound states)

$$\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega) = \mathfrak{D}(\mathbf{q},\omega)\delta_{\mathbf{q},\mathbf{q}'}+\mathfrak{N}(\mathbf{q},\mathbf{q}';\omega)(1-\delta_{\mathbf{q}\mathbf{q}'}), \quad (40)$$

[5] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, 30 (1954).

[6] W. G. Holladay, J. B. Thomas, and C. R. Smith, Am. J. Phys. **31**, 16 (1963).

where $\mathfrak{D}(\mathbf{q},\omega)$ and $\mathfrak{N}(\mathbf{q},\mathbf{q}';\omega)$ denote the diagonal and nondiagonal components, respectively, of $\mathfrak{D}(\mathbf{q},\mathbf{q}';\omega)$.

$$\mathfrak{D}(\mathbf{q},\omega)=2\sum_{\mathbf{k}}\frac{f_{\mathbf{k}}-f_{\mathbf{k}+\mathbf{q}}}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}}+\epsilon_{\mathbf{k}}+i\hbar\alpha}, \tag{41}$$

$$\mathfrak{N}(\mathbf{q},\mathbf{q}';\omega)=-2z\frac{v_{\mathbf{q}-\mathbf{q}'}}{\epsilon(\mathbf{q}-\mathbf{q}',0)}\sum_{\mathbf{k}}\left\{\frac{f_{\mathbf{k}}-f_{\mathbf{k}+\mathbf{q}}}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}}+\epsilon_{\mathbf{k}}+i\hbar\alpha}[(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}-\mathbf{q}'}+i\beta)^{-1}-(\epsilon_{\mathbf{k}+\mathbf{q}'}-\epsilon_{\mathbf{k}+\mathbf{q}}+i\beta)^{-1}]\right.$$
$$\left.+\frac{f_{\mathbf{k}}-f_{\mathbf{k}+\mathbf{q}'}}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}'}+\epsilon_{\mathbf{k}}+i\hbar\alpha}[(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}'-\mathbf{q}}-i\beta)^{-1}-(\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}+\mathbf{q}'}-i\beta)^{-1}]\right\}. \tag{42}$$

For a uniform gas only the diagonal components $\mathfrak{D}(\mathbf{q},\omega)$ appear. These have poles for $\hbar\omega\approx\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}}$ corresponding to quasiparticle excitations. The nondiagonal components $\mathfrak{N}(\mathbf{q},\mathbf{q}';\omega)$ have, in addition, poles corresponding to elastic scattering of quasiparticles by the fixed point charge.

If consideration is restricted to the plasmon region defined by $\hbar\omega$ greater than both $\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}}$ and $\epsilon_{\mathbf{k}+\mathbf{q}'}-\epsilon_{\mathbf{k}}$, the infinitesimal α may be omitted from Eqs. (41) and (42). Within this region, where collective effects dominate, $\mathfrak{D}(\mathbf{q},\omega)$ is real and $\mathfrak{N}(\mathbf{q},\mathbf{q}';\omega)$ separates into the following real and imaginary parts:

$$\mathfrak{N}_1(\mathbf{q},\mathbf{q}';\omega)=-2z\frac{v_{\mathbf{q}-\mathbf{q}'}}{\epsilon(\mathbf{q}-\mathbf{q}',0)}\sum_{\mathbf{k}}\left\{\frac{f_{\mathbf{k}}-f_{\mathbf{k}+\mathbf{q}}}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}}+\epsilon_{\mathbf{k}}}P[(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}-\mathbf{q}'})^{-1}-(\epsilon_{\mathbf{k}+\mathbf{q}'}-\epsilon_{\mathbf{k}+\mathbf{q}})^{-1}]\right.$$
$$\left.+\frac{f_{\mathbf{k}}-f_{\mathbf{k}+\mathbf{q}'}}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}'}+\epsilon_{\mathbf{k}}}P[(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}'-\mathbf{q}})^{-1}-(\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}+\mathbf{q}'})^{-1}]\right\}, \tag{43}$$

$$\mathfrak{N}_2(\mathbf{q},\mathbf{q}';\omega)=2\pi z\frac{v_{\mathbf{q}-\mathbf{q}'}}{\epsilon(\mathbf{q}-\mathbf{q}';0)}\sum_{\mathbf{k}}\left\{\frac{f_{\mathbf{k}}-f_{\mathbf{k}+\mathbf{q}}}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}}+\epsilon_{\mathbf{k}}}[\delta(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}-\mathbf{q}'})-\delta(\epsilon_{\mathbf{k}+\mathbf{q}'}-\epsilon_{\mathbf{k}+\mathbf{q}})]\right.$$
$$\left.+\frac{f_{\mathbf{k}}-f_{\mathbf{k}+\mathbf{q}'}}{\hbar\omega-\epsilon_{\mathbf{k}+\mathbf{q}'}+\epsilon_{\mathbf{k}}}[\delta(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}'-\mathbf{q}})-\delta(\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}+\mathbf{q}'})]\right\}. \tag{44}$$

Here, P denotes principal value. Strictly speaking, P has meaning only if the $\mathbf{k}$ sum is transformed to an integral sign. Note that $\mathfrak{N}_1$ and $\mathfrak{N}_2$ are symmetric and antisymmetric in $\mathbf{q}$ and $\mathbf{q}'$, respectively.

The sums in Eqs. (43) and (44) may be transformed to integrals and evaluated in the limit $\mathbf{q}, \mathbf{q}'\to 0$. An order-of-magnitude argument shows that the resultant contribution from possible single-particle bound states is negligible. A surprisingly simple result for $\mathfrak{N}_1$ is found. Details are given in the Appendix.

$$\mathfrak{N}_1(\mathbf{q},\mathbf{q}';\omega)\underset{\mathbf{q},\mathbf{q}'\to 0}{=}\left\{\frac{\mathbf{q}\cdot\mathbf{q}'}{m\omega^2}z[1-(\epsilon(\mathbf{q}-\mathbf{q}',0))^{-1}]+\cdots\right\}. \tag{45}$$

A comparison of Eqs. (45) and (33) immediately gives

$$\mathfrak{N}_1(\mathbf{q},\mathbf{q}';\omega)\underset{\mathbf{q},\mathbf{q}'\to 0}{=}\frac{\mathbf{q}\cdot\mathbf{q}'}{m\omega^2}\langle\rho_{\mathbf{q}-\mathbf{q}'}{}^{\mathrm{ind}}\rangle+\cdots. \tag{46}$$

A generalization can be made for an arbitrary impurity-charge distribution. Because of the linear approximation with respect to z in Eq. (33), the induced density due to a collection of point charges can be written as the sum

$$\langle\rho_{\mathbf{k}}{}^{\mathrm{ind}}\rangle=\textstyle\sum_i\langle\rho_{\mathbf{k}}{}^{\mathrm{ind}}\rangle_i,$$

where $\langle\rho_{\mathbf{k}}{}^{\mathrm{ind}}\rangle_i$ is the linearized contribution of the ith charge. Hence, Eq. (46), derived for a point charge, is valid for nonuniform gases, in general, provided that the nonuniformity is sufficiently weak. Later we shall use this fact and show that it leads to an experimentally observed result.

An interesting similarity in form between the diagonal and nondiagonal components of $\mathfrak{D}_1(\mathbf{q},\mathbf{q}';\omega)$ may be deduced. The wave vector and frequency-dependent dielectric constant for a uniform gas $\epsilon(\mathbf{q},\omega)$ has been evaluated by Lindhard in the SCF approximation.[5] Use of Eq. (24) then gives for the diagonal components of $\mathfrak{D}_1(\mathbf{q},\mathbf{q}';\omega)$ in the long-wavelength limit

$$\mathfrak{D}(\mathbf{q},\omega)\underset{\mathbf{q}\to 0}{=}\frac{q^2N}{m\omega^2}\left(1+\frac{3}{5}\frac{v_F{}^2}{\omega^2}q^2+\cdots\right). \tag{47}$$

Since $N=\langle\varphi_0|\rho_0|\varphi_0\rangle$, we may write

$$\mathfrak{D}(\mathbf{q},\omega)\delta_{\mathbf{q}\mathbf{q}'}\underset{\mathbf{q}\to 0}{=}\frac{\mathbf{q}\cdot\mathbf{q}'}{m\omega^2}\langle\varphi_0|\rho_{\mathbf{q}-\mathbf{q}'}|\varphi_0\rangle\times\left(1+\frac{3}{5}\frac{v_F{}^2}{\omega^2}q^2+\cdots\right)\delta_{\mathbf{q}\mathbf{q}'}. \tag{48}$$

This should be compared with Eq. (46) where $\langle\rho_{\mathbf{q}-\mathbf{q}'}{}^{\mathrm{ind}}\rangle$ is replaced by $\langle\varphi_0|\rho_{\mathbf{q}-\mathbf{q}'}|\varphi_0\rangle$. One sees that the diagonal and nondiagonal components of $\mathfrak{D}_1(\mathbf{q},\mathbf{q}';\omega)$ have *identical* form in the limit $\mathbf{q}, \mathbf{q}'\to 0$, a fact which is not apparent on cursory inspection of Eqs. (41) and (42).

For the complete matrix $\mathfrak{D}_1(\mathbf{q},\mathbf{q}';\omega)$ we have from Eqs. (40), (46), and (48)

$$\mathfrak{D}_1(\mathbf{q},\mathbf{q}';\omega) \underset{\mathbf{q},\mathbf{q}'\to 0}{=} \frac{\mathbf{q}\cdot\mathbf{q}'}{m\omega^2}\langle\varphi_0|\rho_{\mathbf{q}-\mathbf{q}'}|\varphi_0\rangle \times\left[1+\frac{3}{5}\frac{v_F^2}{\omega^2}q^2\delta_{\mathbf{q}\mathbf{q}'}+\cdots\right], \quad (49)$$

where for the present system

$$\langle\varphi_0|\rho_{\mathbf{q}-\mathbf{q}'}|\varphi_0\rangle = N\delta_{\mathbf{q}\mathbf{q}'}+z[1-(\epsilon(\mathbf{q}-\mathbf{q}',0))^{-1}](1-\delta_{\mathbf{q}\mathbf{q}'}). \quad (50)$$

The real part of the dielectric matrix may now be inferred from Eq. (24) and the above expressions. In the long-wavelength limit

$$\epsilon_1(\mathbf{q},\mathbf{q}';\omega) \underset{\mathbf{q},\mathbf{q}'\to 0}{=} \delta_{\mathbf{q}\mathbf{q}'}\left[1-\frac{\omega_p^2}{\omega^2}\left(1+\frac{3}{5}\frac{v_F^2}{\omega^2}q^2+\cdots\right)\right] -(1-\delta_{\mathbf{q}\mathbf{q}'})\left\{\frac{z}{N}\frac{\omega_p^2}{\omega^2}\frac{\mathbf{q}\cdot\mathbf{q}'}{q^2}[1-(\epsilon(\mathbf{q}-\mathbf{q}',0))^{-1}]+\cdots\right\}. \quad (51)$$

Equation (51) shows that the ratio of nondiagonal to diagonal components of $\epsilon_1(\mathbf{q},\mathbf{q}';\omega)$ is of order z/N ($\ll 1$). Also, the "width" or departure from diagonal form in momentum space is seen with the aid of Eq. (38) to be of order k_{FT}.

Collective-Mode Dispersion Relation

If for all collective modes, $\Delta V_{\mathbf{q}}^{(0)}$ is different from 0 only when $q \lesssim k_{\mathrm{FT}}$, we may use $\epsilon_1(\mathbf{q},\mathbf{q}';\omega)$ as evaluated in the long-wavelength limit in Eq. (27). This will be the case if the collective modes are well defined. For, if $\Delta V_{\mathbf{q}}^{(0)}$ overlaps the quasiparticle spectrum, rapid decay of collective modes into single-particle excitations is to be expected. Under this assumption substitution of Eq. (51) into Eq. (27) gives the following homogeneous integral equation. (The summation sign and Kronecker deltas are replaced by an integral sign and delta functions in accordance with the usual prescription.)

$$\left(q^2-\frac{2M}{\hbar^2}E\right)\varphi(\mathbf{q}) = -\Lambda\int d\mathbf{q}'K(\mathbf{q},\mathbf{q}')\varphi(\mathbf{q}'). \quad (52)$$

Here,

$$\varphi(\mathbf{q}) = q\Delta V_{\mathbf{q}}^{(0)} \quad (53)$$

$$\frac{2M}{\hbar^2}E = \frac{5}{9}\frac{\omega^2}{\omega_p^2}\left(\frac{\omega^2}{\omega_p^2}-1\right)k_{\mathrm{FT}}^2 \quad (54)$$

$$\Lambda = \frac{z}{(N/\Omega)(2\pi)^3}\frac{5}{9}\frac{\omega^2}{\omega_p^2}k_{\mathrm{FT}}^2 \quad (55)$$

$$K(\mathbf{q},\mathbf{q}') = \frac{\mathbf{q}\cdot\mathbf{q}'}{qq'}[1-(\epsilon(\mathbf{q}-\mathbf{q}',0))^{-1}]. \quad (56)$$

The form of Eq. (52) is deliberately chosen to resemble a single-particle Schrödinger equation in the momentum representation. The kernel $K(\mathbf{q},\mathbf{q}')$ is symmetric (a consequence of the fact that $\mathfrak{D}_1(\mathbf{q},\mathbf{q}';\omega)$ is symmetric) which means that the eigenvalue E is real. Since $K(\mathbf{q},\mathbf{q}')$ depends on both $\mathbf{q}$ and $\mathbf{q}'$ rather than on their difference, the "potential" seen by the effective single particle is velocity- as well as position-dependent.

The identification of Eq. (52) as a Schrödinger equation is indicative of the particle character of a collective mode or plasmon. In effect, we have reduced the N-particle problem to a single-particle problem describing the collective modes of the system.

We recall that the origin of Eq. (52) is a statement of Poisson's equation [Eq. (11)] for *classical electrostatics*. Quantum mechanics enters only in the calculation of the expectation value $\Delta\langle\rho_{\mathbf{q}}\rangle$.

As a check on the valdity of Eq. (52), we consider the special case of a uniform gas ($z=0$). For this system the coupling constant Λ vanishes, and a free-particle Schrödinger equation results with the solution

$$\varphi(\mathbf{q}) = \delta(\mathbf{q}-\mathbf{k}), \quad (57)$$

where

$$k^2 = \frac{5}{9}\frac{\omega^2}{\omega_p^2}\left(\frac{\omega^2}{\omega_p^2}-1\right)k_{\mathrm{FT}}^2. \quad (58)$$

Straightforward manipulation of Eq. (58) reproduces Eq. (1), the known dispersion relation for collective modes in a uniform gas. Moreover, Eq. (57) when transformed to coordinate space gives the required plane wave with wave vector $\mathbf{k}$.

Continuous Spectrum Solutions

For nonvanishing z the solutions of Eq. (52) are not trivial. The possibility exists for solutions belonging to both the discrete spectrum ($E<0$) and to the continuous spectrum ($E>0$). The latter solutions, called free plasmons, are similar in character to those of the uniform gas. We treat this case first.

The excitation spectrum for a free plasmon in the presence of a fixed point charge is identical to that obtained above, viz., Eq. (58), from which Eq. (1) follows. We find that the only effect of the point charge is to act as a scattering center for free plasmons. To deduce the scattering cross section, Eq. (52) is recast in the form of a Lippman-Schwinger equation

$$|\Phi\rangle = |\mathbf{k}\rangle+\lim_{\epsilon\to 0}(E_{\mathbf{k}}-H_0+i\epsilon)^{-1}V|\Phi\rangle, \quad (59)$$

where $|\mathbf{k}\rangle$ is a free-particle eigenvector with eigenvalue $E_{\mathbf{k}}=\hbar^2k^2/2M$, H_0 is the free-particle Hamiltonian, and the following identification is made:

$$\langle\mathbf{q}|\Phi\rangle = \varphi(\mathbf{q}) \quad (60)$$

$$\langle\mathbf{q}|V|\mathbf{q}'\rangle = \Lambda K(\mathbf{q},\mathbf{q}')\frac{\hbar^2}{2M}. \quad (61)$$

In the first Born approximation Eq. (59), written in the coordinate representation, reduces to

$$\langle \mathbf{r}|\Phi\rangle \approx \frac{1}{(2\pi)^{3/2}}\left\{\exp(i\mathbf{k}\cdot\mathbf{r}) + \Lambda\int d\mathbf{q}\,\exp(i\mathbf{q}\cdot\mathbf{r})\frac{K(\mathbf{q},\mathbf{k})}{k^2-q^2+i\epsilon}\right\}.$$

The integral appearing above can be evaluated in the limit $r\to\infty$.

$$\langle \mathbf{r}|\Phi\rangle \underset{r\to\infty}{\approx} \frac{1}{(2\pi)^{3/2}}\left\{\exp(i\mathbf{k}\cdot\mathbf{r}) + f(\hat{r}k)\frac{e^{ikr}}{r}\right\}. \quad (62)$$

Here,

$$f(\hat{r}k) = -2\pi^2\Lambda K(\hat{r}k,\mathbf{k}) \quad (63)$$

and $\hat{r}k$ denotes a vector a magnitude k oriented in the $\mathbf{r}$ direction.

Equation (62) has the familiar asymptotic form of an ingoing plane wave plus an outgoing spherical wave, i.e., the free plasmon is scattered by the impurity charge. The function $f(\hat{r}k)$ is the usual scattering amplitude. In the long-wavelength limit

$$f(\hat{r}k) \underset{k\to 0}{\approx} -\frac{zr_s^2a_0}{(9\pi/4)^{1/6}}\frac{10}{9\pi^{1/2}}\cos\theta, \quad (64)$$

where θ is the scattering angle and r_s is the interparticle spacing parameter.

$$r_s = \left(\frac{3\Omega}{4\pi a_0^3 N}\right)^{1/3}. \quad (65)$$

Thus, the differential cross section $|f(\hat{r}k)|^2$ for plasmon scattering has dipole character as $\mathbf{k}\to 0$.

The total cross section is of order $z^2r_s^4a_0^2$ which is comparable to the cross-sectional area of the induced density distribution. This result suggests that the free plasmon is scattered by the nonuniform density rather than directly by the impurity charge itself.

Discrete-Spectrum Solutions

We now seek solutions of Eq. (52) belonging to the discrete spectrum. These have no counterpart in the uniform gas. They correspond to a plasmon bound to the impurity site and are analogous to the trapping of phonons at lattice defect sites.

Since E is negative, we set

$$\gamma^2 = -\frac{2M}{\hbar^2k_{\mathrm{FT}}^2}E. \quad (65')$$

Eq. (52) may be written in nondimensional form

$$(x^2+\gamma^2)\varphi(\mathbf{x}) = -\frac{5}{9}z\left[1+\left(1-\frac{36}{5}\gamma^2\right)^{1/2}\right]\frac{r_s^{3/2}}{\pi^3}\int d\mathbf{x}'K(\mathbf{x},\mathbf{x}')\varphi(\mathbf{x}'), \quad (66)$$

where

$$\mathbf{x} = \mathbf{q}/k_{\mathrm{FT}} \quad (67)$$

and use has been made of the fact that γ^2 and ω are related through Eq. (54).

$$\omega^2/\omega_p^2 = \{1+[1-(36/5)\gamma^2]^{1/2}\}/2. \quad (68)$$

A second root of the quadratic equation yielding Eq. (68) is rejected as unphysical.

One notes in Eq. (66) that the coupling constant depends on the eigenvalue γ^2. Since γ^2 is positive and ω must be real, we conclude from Eq. (68) that solutions belonging to the discrete spectrum are possible only in the range

$$0<\gamma^2\leq 5/36, \quad (69)$$

corresponding to

$$1>\omega/\omega_p\geq 1/\sqrt{2}. \quad (70)$$

The original many-particle Hamiltonian, Eq. (3), is invariant under rotations. Hence, the eigenfunctions $\varphi(\mathbf{x})$ transform according to the full rotation group, i.e.,

$$\varphi(\mathbf{x}) \to \varphi_{lm}(x,\theta,\phi) = F_l(x)Y_l^m(\theta,\phi). \quad (71)$$

Substitution of Eq. (71) reduces Eq. (66) to a one-dimensional integral equation,

$$(x^2+\gamma^2)f_l(x) = \lambda\int_0^\infty dx'K_l(x,x')f_l(x'), \quad (72)$$

where

$$f_l(x) = xF_l(x) \quad (73)$$

$$K_l(x,x') = xx'\int_{-1}^{1} d\mu\,\mu P_l(\mu) \times[1-(\epsilon(x^2+x'^2-2xx'\mu,0))^{-1}], \quad (74)$$

$$\lambda = -z\frac{10}{9}\left[1+\left(1-\frac{36}{5}\gamma^2\right)^{1/2}\right]\frac{r_s^{3/2}}{\pi^2}. \quad (75)$$

Here, $P_l(\mu)$ is the Legendre polynomial of order l.

In the long-wavelength approximation, we have from Eq. (38)

$$1-[\epsilon(x^2+x'^2-2xx'\mu,0)]^{-1} \approx (x^2+x'^2-2xx'\mu+1)^{-1}.$$

With this approximation Eq. (74) can be integrated exactly,[7]

$$K_l(x,x') = Q_1\left(\frac{x^2+x'^2+1}{2xx'}\right) \qquad l=0$$

$$= \left(\frac{x^2+x'^2+1}{2xx'}\right)Q_l\left(\frac{x^2+x'^2+1}{2xx'}\right) \qquad l\neq 0, \quad (76)$$

where $Q_l(z)$ is the lth order Legendre function of the

[7] Use is made of the usual recurrence relations for Legendre polynomials and an integral formula given by E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, Cambridge, England, 1962), 4th ed., p. 320.

second kind. The lowest three orders of $K_l(x,x')$ are

$$K_0(x,x')=\left(\frac{x^2+x'^2+1}{4xx'}\right)\ln\left(\frac{(x+x')^2+1}{(x-x')^2+1}\right)-1, \quad (77)$$

$$K_1(x,x')=\left(\frac{x^2+x'^2+1}{2xx'}\right)\left[\left(\frac{x^2+x'^2+1}{4xx'}\right)\times\ln\left(\frac{(x+x')^2+1}{(x-x')^2+1}\right)-1\right], \quad (78)$$

$$K_2(x,x')=\left(\frac{x^2+x'^2+1}{2xx'}\right)\left\{\frac{1}{4}\left[3\left(\frac{x^2+x'^2+1}{2xx'}\right)^2-1\right]\times\ln\left(\frac{(x+x')^2+1}{(x-x')^2+1}\right)-\frac{3}{2}\left(\frac{x^2+x'^2+1}{2xx'}\right)\right\}. \quad (79)$$

Equation (72) with $l=0$ was solved numerically on an IBM 7090 computer. The method employed is an adaptation of a numerical iteration scheme described by Salpeter.[8] In this procedure, it is convenient to regard λ as the eigenvalue and γ^2 as a known parameter. In other words, the binding energy is prescribed, and the problem is to deduce the coupling constant. The method is suitable for finding the lowest eigenvalue λ, corresponding to an eigenfunction without nodes.

Numerical solutions were obtained for five values of γ^2 (0.02, 0.06, 0.10, 0.12, 5/36). These values encompass nearly the entire permissible range of γ^2 as indicated by Eq. (69). The computed eigenfunctions and eigenvalues are plotted in Figs. 1 and 2. As assumed, $\Delta V_q^{(0)}\to f(q)/q^2$ lies mainly in the plasmon region. Over its full range λ varies nearly linearly with γ^2 and deviates from a constant value (≈ 3.0) by less than 4 percent. Since λ is positive, z must be negative in accordance with Eq. (75).

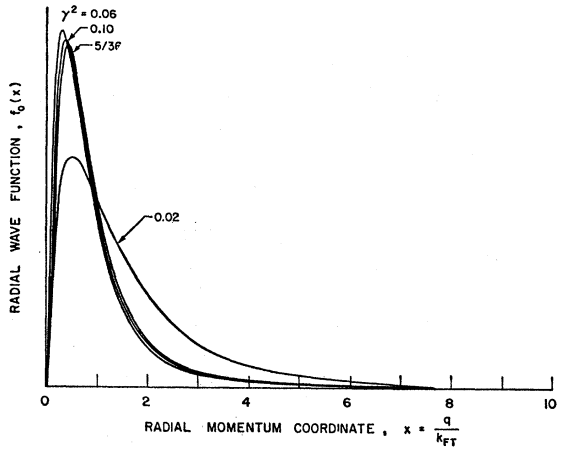

FIG. 1. Radial wave functions for bound S-state plasmon.

[8] E. E. Salpeter, Phys. Rev. 84, 1226 (1951).

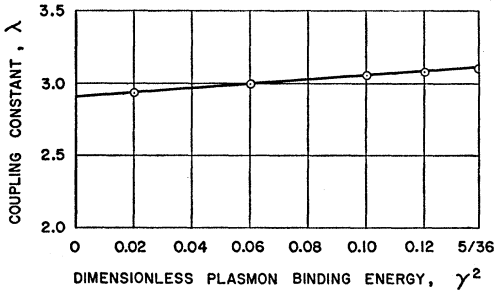

FIG. 2. Eigenvalues for bound S-state plasmon.

Thus, bound S-state plasmons exist only for negative impurity charge.

From Eq. (75) the product $-zr_s^{3/2}$ is fixed once λ and γ^2 are known. For metals r_s has the approximate range

$$1.8\lesssim r_s<5.5.$$

These limits are indicated in Fig. 3 where the impurity charge $-z$ is plotted as a function of binding energy γ^2. In low-density metals ($r_s\approx 5.5$), an impurity charge of $z=-1$ appears to be just sufficient to support a bound plasmon. At higher densities larger values of $-z$ are required.

In Eq. (72) the binding energy appears in nondimensional form. Its magnitude in energy units can be deduced from Eq. (65′) if the effective mass M of a plasmon is known. If the usual formula for effective

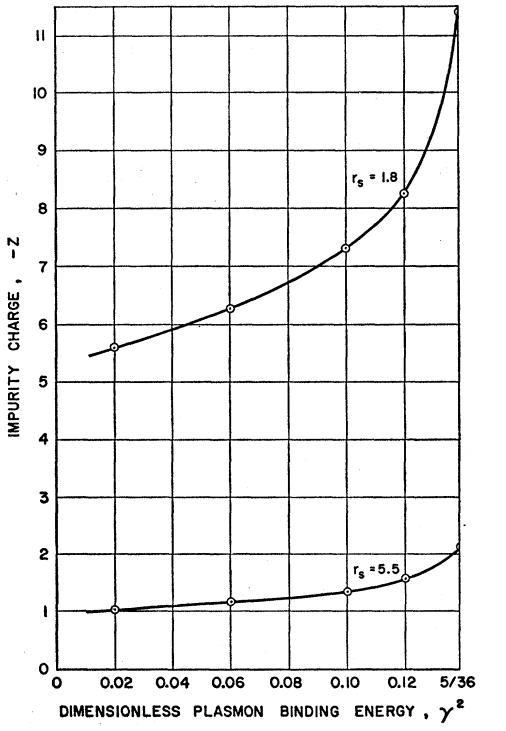

FIG. 3. Magnitude of impurity charge required to support a bound S-state plasmon.

mass is assumed to hold

$$M=\hbar(\partial^2\omega/\partial k^2)^{-1}, \tag{80}$$

we have from Eq. (1)

$$M=(5/9)(\hbar k_{\mathrm{FT}}{}^2/\omega_p) \tag{81}$$

and

$$-E=(9/10)\hbar\omega_p\gamma^2. \tag{82}$$

Since γ^2 has the maximum value 5/36, the binding energy of a bound plasmon must lie in the range

$$0<-E\leq\hbar\omega_p/8. \tag{83}$$

For metals $\hbar\omega_p/8\sim 1$ eV.

An interesting connection between Schrödinger equations for a plasmon and for the hydrogen atom is worth mentioning. If in Eq. (72) for $l=0$ we take the limit $k_{\mathrm{FT}}\rightarrow 0$, corresponding to the absence of shielding, the resultant equation becomes identical with the $l=1$ radial equation for the hydrogen atom.[9]

A large portion of the preceding analysis is predicated on the assumption that the plasmon, whether bound or free, is a reasonably well-defined excitation. The validity of this assumption is known for the free plasmon in the long-wavelength limit. We must show that the bound plasmon is also well defined. For this purpose we turn to Eq. (28).

The linewidth of an S-state bound plasmon is given by

$$\omega_2=-\frac{\int d\mathbf{q}\int d\mathbf{q}'\dfrac{f_0(q)}{q^2}\epsilon_2(\mathbf{q},\mathbf{q}';\omega_0)\dfrac{f_0(q')}{q'^2}}{\int d\mathbf{q}\int d\mathbf{q}'\dfrac{f_0(q)}{q^2}\dfrac{\partial\epsilon_1(\mathbf{q},\mathbf{q}';\omega_0)}{\partial\omega}\dfrac{f_0(q')}{q'^2}}, \tag{84}$$

where ω_0 denotes the S-state eigenfrequency. An order-of-magnitude evaluation of Eq. (84) will suffice. Consequently, we include only the diagonal portions of $\boldsymbol{\epsilon}_1$ and $\boldsymbol{\epsilon}_2$.

$$\omega_2\approx-\frac{\int d\mathbf{q}\dfrac{|f_0(q)|^2}{q^4}\epsilon_2(\mathbf{q},\omega_0)}{\int d\mathbf{q}\dfrac{|f_0(q)|^2}{q^4}\dfrac{\partial\epsilon_1(\mathbf{q},\omega_0)}{\partial\omega}}. \tag{85}$$

The real and imaginary parts of the uniform-gas dielectric constant have been evaluated elsewhere in the SCF approximation.[5] For example, we find

$$\partial\epsilon_1/\partial\omega|_{\omega=\omega_0}\sim 2/\omega_p,$$

which may be substituted into Eq. (85). The remaining integrals were performed numerically for the particular solution $\gamma^2=0.02$ illustrated in Fig. 1. The result obtained is

$$\omega_2/\omega_p\sim -0.1, \tag{86}$$

which indicates that the bound plasmon is a fairly well-defined excitation. (The negative sign signifies damping [See Eq. (10)].) Finally, the lifetime of the excitation is given approximately by

$$\tau\sim 1/|\omega_2|\sim 1/0.1\omega_p, \tag{87}$$

or for metallic densities

$$\tau\sim 10^{-15}\ \text{sec}. \tag{88}$$

3. DISCUSSION

We have seen that in the presence of an impurity charge two distinct types of plasmons may exist. The first, called a free plasmon, has the same excitation spectrum found for the uniform gas. The nonuniformity acts as a scattering center for free plasmons.

In contrast, the bound plasmon has no counterpart in the uniform gas. It exists (at least for $l=0$) only if the impurity charge is negative. Furthermore, it belongs to the discrete spectrum with an excitation frequency less than the plasma frequency of the surrounding uniform gas.

The detailed microscopic theory sheds little light on the physical mechanism responsible for the existence of bound plasmons. Seeking an explanation, we consider an idealized model of the nonuniform gas in which the induced density distribution due to the point charge is replaced by a simple step-function approximation. Inside a radius $r_0(\sim 1/k_{\mathrm{FT}})$ centered at the impurity site, the electron density is treated as a constant N_1; outside this region the density N_2 is also constant. Clearly, for positive z, the quantity $N_1>N_2$ while for negative z, the quantity $N_1<N_2$. Since the density is uniform, we may apply uniform-gas results to either region. For the moment we overlook the fact that certain matching conditions must be satisfied at the interface $r=r_0$ in order for a valid solution to exist.

The dispersion relation for free-plasmon excitation in regions 1 ($r<r_0$) and 2 ($r>r_0$) is

$$\omega^2=\omega_p{}^{(\alpha)2}+\tfrac{3}{5}v_F{}^{(\alpha)2}k_\alpha{}^2, \quad \alpha=1,2 \tag{89}$$

where $\omega_p{}^{(\alpha)}=(4\pi e^2N_\alpha/m)^{1/2}$, etc. It is important to note that for fixed frequency ω the wave vector $\mathbf{k}_\alpha$ is, in general, different in the two regions.

If z is negative, we may consider solutions in the frequency range $\omega_p{}^{(1)}<\omega<\omega_p{}^{(2)}$. By virtue of Eq. (89) $\mathbf{k}_1$ is then real and $\mathbf{k}_2$ pure imaginary. This means that a propagating wave in region 1 must be matched to a damped wave in region 2, resulting in a wave trapped at the impurity site, i.e., a bound plasmon. Conversely, if z is positive, no trapping is possible. Only propagating waves, i.e., free plasmons, may then be constructed.

[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 38.

Hydrodynamical Model

The validity of the preceding argument rests on the assumption that a progapating plasma wave may be matched to a damped plasma wave at the interface $r=r_0$. To investigate this assumption, a simple hydrodynamical theory patterned after the work of Bloch[10] and Jensen[11] is constructed. In this theory the electron gas is treated as a fluid whose pressure is related to the zero-point energy of the particles.

The linearized Bloch equations for irrotational flow (with neglect of retardation) are

$$\frac{\partial u}{\partial t}+\frac{e}{m}\varphi-\frac{4\pi e^2}{mk_{\mathrm{FT}}{}^2}n=0, \tag{90}$$

$$\frac{\partial n}{\partial t}=\nabla\cdot n_0\nabla u, \tag{91}$$

$$\nabla^2\varphi=4\pi en. \tag{92}$$

Here, u is the velocity potential, φ the electric field potential, and n the electron number density. These three quantities are regarded as perturbations on the steady-state flow field, and n_0 is the steady-state number density. Equation (90) originates from the equation of motion of a fluid; Eq. (91) from the continuity equation; and Eq. (92) is Poisson's equation.

With the choice

$$\begin{aligned} n_0&=N_1, \quad r<r_0\\ &=N_2, \quad r>r_0, \end{aligned} \tag{93}$$

Eqs. (90), (91), and (92) may be combined to give

$$(\partial^2 n^{(\alpha)}/\partial t^2)+\omega_p{}^{(\alpha)2}[n^{(\alpha)}-(k_{\mathrm{FT}}{}^{(\alpha)})^{-2}\nabla^2 n^{(\alpha)}]=0. \tag{94}$$

Solutions of the following form are sought:

$$\begin{aligned} n^{(\alpha)}(\mathbf{r},t)&=N^{(\alpha)}(\mathbf{r})e^{i\omega t}\\ u^{(\alpha)}(\mathbf{r},t)&=U^{(\alpha)}(\mathbf{r})e^{i\omega t}\\ \varphi^{(\alpha)}(\mathbf{r},t)&=\Phi^{(\alpha)}(\mathbf{r})e^{i\omega t}. \end{aligned} \tag{95}$$

Equation (94) reduces to a Helmholtz equation

$$\nabla^2 N^{(\alpha)}+k_\alpha{}^2 N^{(\alpha)}=0, \tag{96}$$

where

$$k_\alpha{}^2=k_{\mathrm{FT}}{}^{(\alpha)2}[(\omega^2-\omega_p{}^{(\alpha)2})/\omega_p{}^{(\alpha)2}]. \tag{97}$$

Since Eq. (96) constitutes two equations, a total of four boundary conditions are required. Two of these are conditions at 0 and ∞. The remaining two are matching conditions at the interface $r=r_0$. When use is made of Eq. (90), these may be written

$$\left[\Phi^{(1)}-\frac{4\pi e}{k_{\mathrm{FT}}{}^{(1)2}}N^{(1)}\right]_{r=r_0}=\left[\Phi^{(2)}-\frac{4\pi e}{k_{\mathrm{FT}}{}^{(2)2}}N^{(2)}\right]_{r=r_0}, \tag{98}$$

$$N_1\left[\frac{\partial\Phi^{(1)}}{\partial r}-\frac{4\pi e}{k_{\mathrm{FT}}{}^{(1)2}}\frac{\partial N^{(1)}}{\partial r}\right]_{r=r_0}=N_2\left[\frac{\partial\Phi^{(2)}}{\partial r}-\frac{4\pi e}{k_{\mathrm{FT}}{}^{(2)2}}\frac{\partial N^{(2)}}{\partial r}\right]_{r=r_0}. \tag{99}$$

Equations (98) and (99) express the irrotational character of the velocity flow field and conservation of mass flow across the interface. For application to Eq. (96) these must be expressed in terms of $N^{(\alpha)}$.

The electric potential satisfies the equation

$$\Phi(\mathbf{r})=-e\int d\mathbf{r}'\frac{N^{(\alpha)}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{100}$$

In the absence of any surface charge or dipole layer, Φ and its radial derivative are continuous across the interface. Thus, the matching conditions, Eqs. (98) and (99), are

$$(k_{\mathrm{FT}}{}^{(1)})^{-2}N^{(1)}|_{r=r_0}=(k_{\mathrm{FT}}{}^{(2)})^{-2}N^{(2)}|_{r=r_0} \tag{101}$$

$$(N_1-N_2)\int d\mathbf{r}'N^{(\alpha)}(\mathbf{r}')\frac{\partial}{\partial r}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\Big|_{r=r_0}+4\pi\left[\frac{N_1}{k_{\mathrm{FT}}{}^{(1)2}}\frac{\partial N^{(1)}}{\partial r}-\frac{N_2}{k_{\mathrm{FT}}{}^{(2)2}}\frac{\partial N^{(2)}}{\partial r}\right]_{r=r_0}=0. \tag{102}$$

As predicted, if the charge z is negative, bound solutions of Eq. (96) subject to Eqs. (101) and (102) may be found in the frequency range $\omega_p{}^{(1)}<\omega<\omega_p{}^{(2)}$. Since k_2 is pure imaginary, we set $k_2=i\kappa_2$. The required well-behaved solutions are

$$\begin{aligned} N(\mathbf{r})&=A_l j_l(k_1 r)Y_l{}^m(\theta,\phi), \quad r<r_0\\ &=B_l h_l{}^{(1)}(i\kappa_2 r)Y_l{}^m(\theta,\phi), \quad r>r_0 \end{aligned} \tag{103}$$

where $j_l(z)$ and $h_l{}^{(1)}(z)$ are spherical Bessel and Hankel functions.

If in Eq. (102) $1/|\mathbf{r}-\mathbf{r}'|$ is expanded in terms of spherical harmonics, Eqs. (101), (102), and (103) combine to form

$$\left(\frac{R_1}{R_2}\right)^2\frac{\eta h_l{}^{(1)}(i\eta)}{\xi j_l(\xi)}=\left\{\frac{(1-\epsilon)l\eta^{l-1}\int_\eta^\infty\frac{h_l{}^{(1)}(ix)}{x^{l-1}}dx+i\left(\frac{\eta}{R_2}\right)^2[lh_{l-1}{}^{(1)}(i\eta)-(l+1)h_{l+1}{}^{(1)}(i\eta)]}{(1-\epsilon)\frac{l+1}{\xi^{l+2}}\int_0^\xi x^{l+2}j_l(x)dx+\epsilon\left(\frac{\xi}{R_1}\right)^2[lj_{l-1}(\xi)-(l+1)j_{l+1}(\xi)]}\right\}, \tag{104}$$

[10] F. Bloch, Z. Physik **81**, 363 (1933).
[11] H. Jensen, Z. Physik **106**, 620 (1937).

where

$$\begin{aligned}\xi&=k_1r_0\\ \eta&=\kappa_2r_0\\ \epsilon&=N_1/N_2\\ R_\alpha&=k_{\mathrm{FT}}{}^{(\alpha)}r_0.\end{aligned}\tag{105}$$

The quantities ξ and η are related through Eq. (97)

$$\frac{\xi^2}{[(1-\epsilon)/\epsilon^{2/3}]R_2^2}+\frac{\eta^2}{(1-\epsilon)R_2^2}=1.\tag{106}$$

To compare with the microscopic theory, we consider the special case $l=0$. Equation (104) then reduces to

$$\frac{\cot\xi}{\xi}-\frac{1}{\xi^2}=\epsilon^{-1/3}\left[\frac{1}{\eta}+\frac{1}{\eta^2}\right].\tag{107}$$

Equations (106) and (107) must be solved simultaneously by graphical or numerical means. These relations bear a striking resemblance to equations appearing in the well-known problem in quantum mechanics, first treated by Margenau,[12] of a particle bound in a three-dimensional square well. It is particularly interesting to note that in this analog the same disparity between l values exists as in the microscopic theory. Equation (107) corresponds to the $l=1$ equation in the quantum-mechanical analog.[13]

A graphical solution of Eqs. (106) and (107) is illustrated in Fig. 4. Two intersections occur at the values $(\xi,\eta)=(3.36, 2.46)$ and $(6.29, 0.25)$. Their corresponding eigenfrequencies are deduced from Eq. (97) to be $\omega/\omega_p{}^{(2)}=0.60$ and 0.997.

Further details of the solution are relatively uninteresting. We have seen that solutions corresponding to bound plasmons are found in the hydrodynamical theory when the charge z is negative. It is easy to show that propagating-wave solutions or free plasmons also exist. In short, the hydrodynamical theory provides a qualitative check on the predictions of the microscopic theory as well as physical insight into the nature of these predictions.

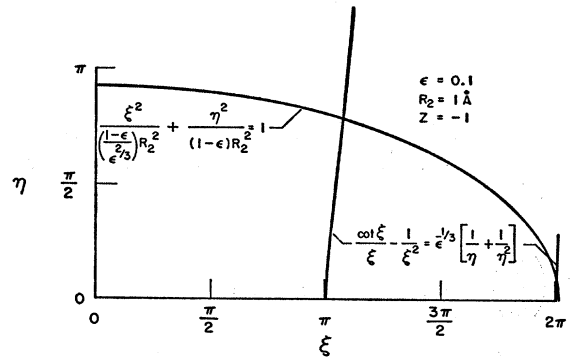

FIG. 4. Sample graphical solution of Eqs. (106) and (107).

Experimental Detection of Bound and Free Plasmons

It is well known that plasmons may be excited in metals by fast electrons. In the Born approximation the transition rate for inelastic collisions of fast, charged particles with a uniform electron gas is readily obtained.[14] We wish here to indicate briefly how the results of such an analysis are modified for a nonuniform gas.

We consider a high-velocity particle with charge z_0e moving through the electron gas. Since the velocity is large, a classical path approximation is permissible,

$$\mathbf{R}=\mathbf{v}_0t;\quad \mathbf{v}_0=\mathrm{const},\tag{108}$$

where $\mathbf{R}$ and $\mathbf{v}_0$ are the position and velocity of the particle.

The interaction Hamiltonian is

$$H_{\mathrm{int}}=-z_0\textstyle\sum_{\mathbf{k}\neq0}v_{\mathbf{k}}(\rho_{\mathbf{k}}-z)\exp(i\mathbf{k}\cdot\mathbf{R}).\tag{109}$$

Applying Fermi's golden rule of time-dependent perturbation theory

$$w_{0\to n}(\omega)=\frac{2\pi}{\hbar^2}|\langle\varphi_0|H_{\mathrm{int}}(\omega)|\varphi_n\rangle|^2\delta(\omega-\omega_{n0}),\tag{110}$$

where $H_{\mathrm{int}}(\omega)$ is the Fourier component in time of H_{int}, we obtain for the full transition probability due to H_{int}

$$w=\textstyle\sum_{\mathbf{k}}w(\mathbf{k},\mathbf{k}\cdot\mathbf{v}_0).\tag{111}$$

Here,

$$\begin{aligned}w(\mathbf{k},\mathbf{k}\cdot\mathbf{v}_0)=&\frac{2\pi z_0^2}{\hbar^2}v_{\mathbf{k}}\sum_{\mathbf{k}'\neq0}v_{\mathbf{k}'}\delta_{\mathbf{k}\cdot\mathbf{v}_0,\mathbf{k}'\cdot\mathbf{v}_0}\\&\times\sum_{n\neq0}\langle\varphi_0|\rho_{\mathbf{k}}|\varphi_n\rangle\langle\varphi_n|\rho_{-\mathbf{k}'}|\varphi_0\rangle\delta(\mathbf{k}\cdot\mathbf{v}_0+\omega_{n0})\end{aligned}\tag{112}$$

gives the transition probability for momentum transfer $-\hbar\mathbf{k}$ and energy transfer $-\hbar\mathbf{k}\cdot\mathbf{v}_0$ to the nonuniform gas. For a uniform gas Eq. (112) reduces to the known result[14]

$$\begin{aligned}w(\mathbf{k},\mathbf{k}\cdot\mathbf{v}_0)=&\frac{2\pi z_0^2}{\hbar^2}v_{\mathbf{k}}{}^2\sum_{n\neq0}|\langle\varphi_0|\rho_{\mathbf{k}}|\varphi_n\rangle|^2\\&\times\delta(\mathbf{k}\cdot\mathbf{v}_0+\omega_{n0}).\end{aligned}\tag{113}$$

In the analysis beginning with Eq. (110), it is important to recognize that the states $|\varphi_n\rangle$ are eigenstates of the true Hamiltonian, Eq. (3). Past convention has been to use this notation for the eigenstates of the SCF Hamiltonian, Eq. (6). Since the distinction will soon become important, hereafter we use $|\varphi_n{}^s\rangle$ for SCF eigenstates and $|\varphi_n\rangle$ for true Hamiltonian eigenstates.

[12] H. Margenau, Phys. Rev. **46**, 613 (1934).

[13] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 79.

[14] See, e.g., D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), pp. 126–128.

In the new notation Eq. (24) is written

$$\epsilon^{\mathrm{SCF}}(\mathbf{k},\mathbf{k}';\omega)=\delta_{\mathbf{k}\mathbf{k}'}-v_{\mathbf{k}}\mathfrak{D}^{\mathrm{SCF}}(\mathbf{k},\mathbf{k}';\omega), \quad (114)$$

provided

$$\mathfrak{D}^{\mathrm{SCF}}(\mathbf{k},\mathbf{k}';\omega)=\sum_{n\neq 0}\frac{1}{\hbar}\left[\frac{\langle\varphi_0{}^s|\rho_{\mathbf{k}}|\varphi_n{}^s\rangle\langle\varphi_n{}^s|\rho_{-\mathbf{k}'}|\varphi_0{}^s\rangle}{\omega-\omega_{n0}{}^{(s)}+i\alpha}-\frac{\langle\varphi_0{}^s|\rho_{-\mathbf{k}'}|\varphi_n{}^s\rangle\langle\varphi_n{}^s|\rho_{\mathbf{k}}|\varphi_0{}^s\rangle}{\omega+\omega_{n0}{}^{(s)}+i\alpha}\right]. \quad (115)$$

In contrast, Cohen[4] finds for the inverse of the true dielectric matrix

$$\epsilon^{-1}(\mathbf{k},\mathbf{k}';\omega)=\delta_{\mathbf{k}\mathbf{k}'}+v_{\mathbf{k}}\mathfrak{D}(\mathbf{k},\mathbf{k}';\omega), \quad (116)$$

where $\mathfrak{D}(\mathbf{k},\mathbf{k}';\omega)$ is given by Eq. (115) with the superscript s omitted throughout.

Inspection of Eqs. (112) and (116) shows that

$$w(\mathbf{k},\mathbf{k}\cdot\mathbf{v}_0)=-\frac{2z_0{}^2}{\hbar}\sum_{\mathbf{k}'\neq 0}{}'v_{\mathbf{k}'}\delta_{\mathbf{k}\cdot\mathbf{v}_0,\mathbf{k}'\cdot\mathbf{v}_0}\times\mathrm{Im}\epsilon^{-1}(\mathbf{k},\mathbf{k}';-\mathbf{k}\cdot\mathbf{v}_0), \quad (117)$$

where the prime on the summation sign restricts $\mathbf{k}'$ to values for which $\mathbf{k}'\cdot\mathbf{v}_0$ and hence $\mathbf{k}\cdot\mathbf{v}_0$ are negative. For uniform gas Eq. (117) reduces to

$$w(\mathbf{k},\mathbf{k}\cdot\mathbf{v}_0)=-(2z_0{}^2/\hbar)v_{\mathbf{k}}\,\mathrm{Im}[\epsilon(\mathbf{k},-\mathbf{k}\cdot\mathbf{v}_0)]^{-1}, \quad (118)$$

where $\epsilon(\mathbf{k},\omega)$ is the frequency and wave-vector dependent dielectric constant for the uniform gas.

Because $\epsilon^{-1}(\mathbf{k},\mathbf{k}';\omega)$ is the inverse of an infinite dimensional matrix, Eq. (117) is difficult to analyze quantitatively. Nevertheless, its essential features are clear. As a reasonable approximation $\epsilon^{-1}(\mathbf{k},\mathbf{k}';\omega)$ may be replaced by $[\epsilon^{\mathrm{SCF}}(\mathbf{k},\mathbf{k}';\omega)]^{-1}$. We have seen that the matrix $\epsilon^{\mathrm{SCF}}(\mathbf{k},\mathbf{k}';\omega)$ has the eigenvalue zero for frequencies ω corresponding to the collective modes of the system. Hence, Eq. (117) will have resonances when $-\mathbf{k}\cdot\mathbf{v}_0$ approaches a collective mode. These absorption peaks correspond to the excitation of plasmons within the electron gas. Thus, both bound and free plasmons can be excited by fast electrons, the presence of the former depending, of course, on the existence of negative impurity sites.

If the preceding argument is correct, existing experimental data should show evidence for bound as well as free plasmons in solids. A noteworthy feature of the early (prior to about 1959) measurements of characteristic electron energy losses in solids is the frequent disagreement in results reported by different observers and even by the same observer at different times.[15] Often a main resonance peak is found by all observers at the predicted plasma frequency, but there the similarity in results ends. Additional satellite peaks are frequently observed which defy identification. Marton[16] has attributed such anomalies to certain instrumental difficulties and/or impurities (volume or surface) in the solid specimen.

The latter explanation accords with the present analysis. Satellite peaks in the frequency range $\omega_p/\sqrt{2}\leq\omega<\omega_p$ may well represent the excitation of bound plasmons at negative impurity sites. Once created, a bound plasmon in the ground state may be further excited to higher bound states or even ionized (i.e., transformed into a free plasmon). Hence, bound plasmon effects are not confined to the range $\omega_0/\sqrt{2}\leq\omega<\omega_p$. The complete plasmon excitation spectrum may have a richness comparable to that of the hydrogen atom.

In more recent experiments (since about 1959), great care has been taken to obtain pure samples and to avoid effects of surface oxidation and contamination by the specimen support.[17] With certain notable exceptions this care has led to a marked diminution in the number of satellite peaks observed. These exceptions have been positively identified as surface effects of one of two types: (1) a modified plasma loss due to the presence of an oxide layer on the surface, and (2) a plasma loss at the frequency $\omega=\omega_p/\sqrt{2}$ representing the excitation of a "surface" plasmon.

Surface plasmons were first predicted theoretically by Ritchie[18] who used a hydrodynamical model applied to a finite metal foil. In classical terms a surface plasmon represents an electron density wave trapped at the surface and hence bears a close resemblance to a bound plasmon. To investigate this connection, we suppose, as previously argued, that Eq. (46) is valid for nonuniform gases in general and apply it to a system consisting of a semi-infinite metallic slab. The lattice potential is approximated by a uniform background of positive charge which terminates in a plane. The resultant electric field appears to an electron as a distribution of *negative* charge at the surface. The induced electron density distribution may be calculated in some suitable approximation and substituted in Eq. (46). Equation (27) then yields a one-dimensional Schrödinger equation by virtue of the symmetry of the system. The exact form of this Schrödinger equation is relatively unimportant. What matters is that its energy eigenvalue is again given by Eq. (54), and as we have seen, bound-state solutions ($E<0$) are limited by Eq. (54) to the range $\omega_p>\omega\geq\omega_p/\sqrt{2}$. Furthermore, the limiting value $\omega=\omega_p/\sqrt{2}$ is obtained for sufficiently large, applied, negative, surface charge.

Thus, the surface plasmon, experimentally observed in many different solids at the excitation frequency

[15] For a review of the experimental methods, results, and difficulties up to 1955, see: L. Marton, L. B. Leder, and H. Mendlowitz, *Advances in Electronics and Electron Physics* (Academic Press Inc., New York, 1955), Vol. 7.

[16] L. Marton, Rev. Mod. Phys. **28**, 172 (1956).

[17] See, e.g., C. J. Powell, Proc. Phys. Soc. (London) **76**, 593 (1960).

[18] R. H. Ritchie, Phys. Rev. **106**, 874 (1957).

$\omega_p/\sqrt{2}$, and the impurity bound plasmon appear to be different manifestations of the same phenomena. Generalizing, one may conclude that any induced deficiency in electron density, if sufficiently large, may support a bound plasmon.

ACKNOWLEDGMENTS

The author wishes to express his deep gratitude to Professor Henry Margenau and Professor Michael J. Stephen for their advice and many helpful comments throughout the preparation of this work.

APPENDIX

We wish to evaluate the sum appearing in Eq. (43) in the limit $\mathbf{q}, \mathbf{q}' \to 0$. Equation (43) may be rewritten

$$\mathfrak{N}_1(\mathbf{q},\mathbf{q}';\omega)=-\frac{4zv_{\mathbf{q}-\mathbf{q}'}}{\epsilon(\mathbf{q}-\mathbf{q}',0)}P\sum_{\mathbf{k}} f_{\mathbf{k}}\left\{\frac{\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}}}{(\hbar\omega)^2-(\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}})^2}\left[(\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}+\mathbf{q}'})^{-1}-(\epsilon_{\mathbf{k}+\mathbf{q}-\mathbf{q}'}-\epsilon_{\mathbf{k}})^{-1}\right]\right.$$
$$\left.+\frac{\epsilon_{\mathbf{k}+\mathbf{q}'}-\epsilon_{\mathbf{k}}}{(\hbar\omega)^2-(\epsilon_{\mathbf{k}+\mathbf{q}'}-\epsilon_{\mathbf{k}})^2}\left[(\epsilon_{\mathbf{k}+\mathbf{q}'}-\epsilon_{\mathbf{k}+\mathbf{q}})^{-1}-(\epsilon_{\mathbf{k}+\mathbf{q}'-\mathbf{q}}-\epsilon_{\mathbf{k}})^{-1}\right]\right\}. \quad \text{(A1)}$$

In the long-wavelength limit

$$\mathfrak{N}_1(\mathbf{q},\mathbf{q}';\omega)\underset{\mathbf{q},\mathbf{q}'\to 0}{\approx}-\frac{4zv_{\mathbf{q}-\mathbf{q}'}}{\epsilon(\mathbf{q}-\mathbf{q}',0)(\hbar\omega)^2}P\sum_{\mathbf{k}} f_{\mathbf{k}}\left[1-\frac{\epsilon_{\mathbf{k}+\mathbf{q}}-\epsilon_{\mathbf{k}}}{\epsilon_{\mathbf{k}+\mathbf{q}'-\mathbf{q}}-\epsilon_{\mathbf{k}}}-\frac{\epsilon_{\mathbf{k}+\mathbf{q}'}-\epsilon_{\mathbf{k}}}{\epsilon_{\mathbf{k}+\mathbf{q}-\mathbf{q}'}-\epsilon_{\mathbf{k}}}\right]. \quad \text{(A2)}$$

With the replacement

$$\sum_{\mathbf{k}}\to\frac{\Omega}{(2\pi)^3}\int d\mathbf{k}$$

Eq. (A2) becomes

$$\mathfrak{N}_1(\mathbf{q},\mathbf{q}';\omega)\underset{\mathbf{q},\mathbf{q}'\to 0}{\approx}-\frac{4zv_{\mathbf{q}-\mathbf{q}'}}{\epsilon(\mathbf{q}-\mathbf{q}',0)(\hbar\omega)^2}\frac{\Omega}{(2\pi)^3}\int_{k<k_F} d\mathbf{k}\left[1-\frac{2\mathbf{k}\cdot\mathbf{q}+q^2}{2\mathbf{k}\cdot(\mathbf{q}-\mathbf{q}')+|\mathbf{q}-\mathbf{q}'|^2}-\frac{2\mathbf{k}\cdot\mathbf{q}'+q'^2}{2\mathbf{k}\cdot(\mathbf{q}'-\mathbf{q})+|\mathbf{q}-\mathbf{q}'|^2}\right]. \quad \text{(A3)}$$

The first integral yields

$$\int_{k<k_F} d\mathbf{k}=\tfrac{4}{3}\pi k_F^2.$$

The second and third integrals are identical if the interchange $\mathbf{q}, \mathbf{q}' \to \mathbf{q}', \mathbf{q}$ is made. Straightforward evaluation gives

$$\int_{k<k_F} d\mathbf{k}\frac{2\mathbf{k}\cdot\mathbf{q}+q^2}{2\mathbf{k}\cdot(\mathbf{q}-\mathbf{q}')+|\mathbf{q}-\mathbf{q}'|^2}=\frac{2\pi}{|\mathbf{q}-\mathbf{q}'|}\left\{\tfrac{2}{3}k_F^3\frac{\mathbf{q}\cdot(\mathbf{q}-\mathbf{q}')}{|\mathbf{q}-\mathbf{q}'|}+\frac{\mathbf{q}\cdot\mathbf{q}'}{4}\left[|\mathbf{q}-\mathbf{q}'|k_F+\left(k_F^2-\frac{|\mathbf{q}-\mathbf{q}'|^2}{4}\right)\ln\left|\frac{2k_F+|\mathbf{q}-\mathbf{q}'|}{2k_F-|\mathbf{q}-\mathbf{q}'|}\right|\right]\right\}.$$

Finally, substitution into Eq. (A3) yields

$$\mathfrak{N}_1(\mathbf{q},\mathbf{q}';\omega)=\frac{zv_{\mathbf{q}-\mathbf{q}'}\mathbf{q}\cdot\mathbf{q}'}{\epsilon(\mathbf{q}-\mathbf{q}',0)(\hbar\omega)^2}\frac{\Omega k_F}{2\pi^2}\left[1+\frac{(k_F^2-|\mathbf{q}-\mathbf{q}'|^2/4)}{|\mathbf{q}-\mathbf{q}'|k_F}\ln\left|\frac{2k_F+|\mathbf{q}-\mathbf{q}'|}{2k_F-|\mathbf{q}-\mathbf{q}'|}\right|\right]. \quad \text{(A4)}$$

On comparison with Eq. (36), this result assumes the surprisingly simple form revealed by Eq. (45).