

# High-Frequency Conductivity of Degenerate Semiconductors\*

AMIRAM RON†‡

*Plasma Physics Laboratory, Princeton University, Princeton, New Jersey*

AND

NARKIS TZOAR

*Bell Telephone Laboratories, Whippany, New Jersey*

(Received 29 April 1963)

The problem of high-frequency conductivity of a degenerate semiconductor is investigated by a kinetic description. The finite duration of encounters is taken into account in a self-consistent fashion which properly includes collective effects. This treatment is an extension for quantum plasmas of the Dawson-Oberman method given for classical plasmas.

## I. INTRODUCTION

RECENTLY Dawson and Oberman<sup>1,2</sup> developed a method for obtaining the absorption of electromagnetic waves in *classical* plasmas, taking into account collective effects. They have used an elementary model for the classical plasma, where the ions are infinitely heavy and randomly distributed<sup>1</sup> or in thermal equilibrium with the electrons.<sup>2</sup> Their results are in accord with a complete treatment given by Oberman, Ron, and Dawson.<sup>3</sup>

The purpose of the present work is to calculate the absorption of electromagnetic waves in heavily doped semiconductors. This system is approximately described by an elementary model, where randomly distributed fixed ions are embedded in a dense electron gas.<sup>4</sup> Our treatment is a generalization of the Dawson-Oberman work to a quantum system. For the derivation of the absorption coefficient one may use more sophisticated methods, e.g., Green's function approach,<sup>5</sup> which although having the advantage of being rigorous, are rather elaborate. We feel that for the sake of simplicity it is advantageous to derive the absorption coefficient by employing an elementary model thereby obtaining a simple physical interpretation.

We approach the problem using a quantum-mechanical kinetic equation for the electrons taking into account their collisions with the ions, without carrying the usual time-scale restriction inherent in the well-known transition *probability* approach to transport phenomena.<sup>6</sup> It is clear that for applied fields changing rapidly in time, one cannot use the Dirac time-depend-

ent perturbation theory in the infinite time limit for the calculations of collisions if the frequency of the driving field is higher than the collision frequency.

In Sec. II we introduce our model and derive the basic equations. Section III is devoted to the numerical calculation of the resistivity and to the discussion of the results.

## II. MODEL AND BASIC EQUATIONS

In our model of the degenerate semiconductor, the appropriate Hamiltonian is

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum'_{ij} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,l} \frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_l|}, \quad (1)$$

where the  $\mathbf{r}_i$  and  $\mathbf{R}_l$  are, respectively, the electron and ion coordinates,  $e$  and  $m$  are, respectively, the effective charge and mass of the electrons while embedded in the crystal (for a detailed discussion of the physical assumptions, see Wolff<sup>4</sup>). In Eq. (1),  $\mathbf{p}_i$  represents the electron's momentum and  $Ze$  the charge of the ions. The presence of a prevailing spatially uniform electric field  $\mathbf{E}$ , oscillating in time at the frequency  $\omega$ , adds to the Hamiltonian

$$H_F = - \sum_i e\mathbf{E} \cdot \mathbf{r}_i e^{-i\omega t}. \quad (2)$$

This field represents an electromagnetic wave in the limit where the wavelength is much longer than the Bohr radius of the electrons. We also restrict ourselves to frequencies much greater than the collision frequency.

We now introduce the one-electron density matrix

$$F(\mathbf{r}_1, \mathbf{r}_1', t) = \langle \psi^\dagger(\mathbf{r}_1', t) \psi(\mathbf{r}_1, t) \rangle, \quad (3)$$

where  $\psi(\mathbf{r}t)$  and  $\psi^\dagger(\mathbf{r}t)$  are the annihilation and creation Heisenberg operators for the electrons. For any operator  $A$  we define

$$\langle A \rangle = \text{Tr}\{\rho A\}, \quad (4)$$

where  $\rho$ , the many-electron density matrix, is constant in time. The Wigner distribution function for the

\* This work was accomplished under the auspices of the U. S. Atomic Energy Commission.

† On leave of absence from Technion-Israel Institute of Technology, Haifa, Israel.

‡ Present address: Department of Physics, University of California, San Diego, La Jolla, California.

<sup>1</sup> J. Dawson and C. Oberman, *Phys. Fluids* **5**, 517 (1962).

<sup>2</sup> J. Dawson and C. Oberman, *Phys. Fluids* **6**, 394 (1963).

<sup>3</sup> C. Oberman, A. Ron, and J. Dawson, *Phys. Fluids* **5**, 1514 (1962).

<sup>4</sup> P. A. Wolff, *Phys. Rev.* **126**, 405 (1962).

<sup>5</sup> A. Ron and N. Tzoar, *Phys. Rev. Letters* **10**, 45 (1963) and *Phys. Rev.* **131**, 12 (1963).

<sup>6</sup> R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), Chap. VI.

electrons<sup>7</sup> is given in terms of  $F(\mathbf{r}_1, \mathbf{r}_1', t)$  by

$$\tilde{F}(\mathbf{x}, \mathbf{p}, t) = \int d\mathbf{r} e^{i\mathbf{p}\cdot\mathbf{r}} F(\mathbf{x} + \mathbf{r}/2, \mathbf{x} - \frac{1}{2}\mathbf{r}, t). \quad (5)$$

In the high-density limit, where the number of electrons in the Bohr sphere is large, we obtain the following equations for  $\tilde{F}(\mathbf{x}, \mathbf{p}, t)$  in the rest frame of the ions

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial}{\partial \mathbf{x}} - e\mathbf{E}e^{-i\omega t} \cdot \frac{\partial}{\partial \mathbf{p}} \right) \tilde{F}(\mathbf{x}, \mathbf{p}, t) \\ &= -ie \int d\mathbf{r} e^{-i\mathbf{p}\cdot\mathbf{r}} [\Phi(\mathbf{x} + \mathbf{r}/2) - \Phi(\mathbf{x} - \frac{1}{2}\mathbf{r})] \\ & \quad \times \int \frac{d\mathbf{p}'}{(2\pi)^3} e^{i\mathbf{p}'\cdot\mathbf{r}} \tilde{F}(\mathbf{x}, \mathbf{p}', t), \quad (6) \end{aligned}$$

where

$$\begin{aligned} \Phi(\mathbf{x}, t) = & -e \int d\mathbf{x}' d\mathbf{p}' |\mathbf{x} - \mathbf{x}'|^{-1} \tilde{F}(\mathbf{x}', \mathbf{p}', t) \\ & + Ze \sum_i |\mathbf{x} - \mathbf{R}_i|^{-1} \quad (7) \end{aligned}$$

is the self-consistent field of the electrons and the field due to the ions and  $\hbar$  is taken to be one.

Equations (6) and (7) were obtained under the assumption that the electron-electron correlations, including their exchange effects, are *systematically* neglected. The validity of this neglect has been borne out by the more general treatments of Refs. 3 and 5. This amounts to the fact that the electron-electron correlation and exchange contribute only to effects of second order, while we restrict ourselves to effects of the first order only.

To facilitate the solution of the coupled Eqs. (6) and (7) we perform the following transformations:

$$\begin{aligned} \boldsymbol{\rho} &= \mathbf{x} - \boldsymbol{\varepsilon}e^{-i\omega t}, \\ \mathbf{q} &= \mathbf{p} + i\omega m \boldsymbol{\varepsilon}e^{-i\omega t}, \\ t &= t, \end{aligned} \quad (8)$$

where

$$\boldsymbol{\varepsilon} = (e/m\omega^2)\mathbf{E}. \quad (9)$$

Equations (6) and (7) become

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \frac{\mathbf{q}}{m} \cdot \frac{\partial}{\partial \boldsymbol{\rho}} \right) \tilde{f}(\boldsymbol{\rho}, \mathbf{q}, t) \\ &= -ie \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} [\tilde{\Phi}(\boldsymbol{\rho} + \mathbf{r}/2, t) - \tilde{\Phi}(\boldsymbol{\rho} - \mathbf{r}/2, t)] \\ & \quad \times \int \frac{d\mathbf{q}'}{(2\pi)^3} e^{i\mathbf{q}'\cdot\mathbf{r}} \tilde{f}(\boldsymbol{\rho}, \mathbf{q}', t), \quad (10) \end{aligned}$$

and

$$\begin{aligned} \tilde{\Phi}(\boldsymbol{\rho}, t) &= \Phi(\boldsymbol{\rho} + \boldsymbol{\varepsilon}e^{-i\omega t}) \\ &= -e \int d\boldsymbol{\rho}' d\mathbf{q}' |\boldsymbol{\rho} - \boldsymbol{\rho}'|^{-1} \tilde{f}(\boldsymbol{\rho}', \mathbf{q}', t) \\ & \quad + Ze \sum_i |\boldsymbol{\rho} + \boldsymbol{\varepsilon}e^{-i\omega t} - \mathbf{R}_i|^{-1}, \quad (11) \end{aligned}$$

with

$$\tilde{f}(\boldsymbol{\rho}, \mathbf{q}, t) = \tilde{F}(\boldsymbol{\rho} + \boldsymbol{\varepsilon}e^{-i\omega t}, \mathbf{q} - i\omega m \boldsymbol{\varepsilon}e^{-i\omega t}, t). \quad (12)$$

We shall now assume that the right-hand side of Eq. (10) causes only a small perturbation on the equilibrium solution of that equation,

$$f_0(\mathbf{p}) = [\exp\beta(p^2/2m - \mu) + 1]^{-1}, \quad (13)$$

where  $\beta$  is the inverse temperature in energy units and  $\mu$  is the chemical potential of the noninteracting electrons. In other words, we assume that the discrete nature of the ions causes only a small effect, and that the electron motion in the region of frequencies under consideration is largely inertia-dominated (the conductivity is mainly reactive). The equations for  $f$  and  $\psi$ , the small departure from equilibrium are

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \frac{\mathbf{q}}{m} \cdot \frac{\partial}{\partial \boldsymbol{\rho}} \right) f(\boldsymbol{\rho}, \mathbf{q}, t) = -ie \int \frac{d\mathbf{q}'}{(2\pi)^3} f_0(q') \\ & \quad \cdot \int d\mathbf{r} e^{-i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{r}} [\psi(\boldsymbol{\rho} + \frac{1}{2}\mathbf{r}) - \psi(\boldsymbol{\rho} - \frac{1}{2}\mathbf{r})], \quad (14) \end{aligned}$$

and

$$\begin{aligned} \psi(\boldsymbol{\rho}, t) &= -e \int d\boldsymbol{\rho}' d\mathbf{q}' |\boldsymbol{\rho} - \boldsymbol{\rho}'|^{-1} f(\boldsymbol{\rho}', \mathbf{q}', t) \\ & \quad + Ze \sum_i |\boldsymbol{\rho} + \boldsymbol{\varepsilon}e^{-i\omega t} - \mathbf{R}_i|^{-1}. \quad (15) \end{aligned}$$

If we denote the Fourier transform of a function  $f(\boldsymbol{\rho})$  by

$$f(\mathbf{k}) = \frac{1}{(2\pi)^3} \int d\boldsymbol{\rho} \exp(i\mathbf{k}\cdot\boldsymbol{\rho}) f(\boldsymbol{\rho}), \quad (16)$$

and Fourier-analyze Eqs. (14) and (15), we obtain

$$\begin{aligned} & \left( \frac{\partial}{\partial t} - \frac{i}{m} \mathbf{q}\cdot\mathbf{k} \right) f(\mathbf{k}, \mathbf{q}, t) \\ &= -ie\psi(\mathbf{k}, t) [f_0(\mathbf{q} + \frac{1}{2}\mathbf{k}) - f_0(\mathbf{q} - \mathbf{k}/2)], \quad (17) \end{aligned}$$

and

$$\begin{aligned} \psi(\mathbf{k}, t) &= -\frac{4\pi e}{k^2} \int d\mathbf{q} f(\mathbf{k}, \mathbf{q}, t) \\ & \quad + \frac{4\pi e Z}{(2\pi)^3 k^2} \sum_i \exp[i\mathbf{k}\cdot(\mathbf{R}_i - \boldsymbol{\varepsilon}e^{-i\omega t})]. \quad (18) \end{aligned}$$

<sup>7</sup> E. Wigner, Phys. Rev. **40**, 749 (1932), and for more details see Yu L. Klimontovich and V. P. Silin, Usp. Fiz. Nauk **70**, 247 (1960) [translation: Soviet Phys.—Usp. **3**, 84 (1960)].

Since the conductivity is defined by the limit  $\boldsymbol{\varepsilon} \rightarrow 0$ , we shall expand the second term on the right-hand side

of Eq. (18):

$$\sum_l \exp[i\mathbf{k} \cdot (\mathbf{R}_l - \boldsymbol{\varepsilon} e^{-i\omega t})] \approx \sum_l e^{i\mathbf{k} \cdot \mathbf{R}_l} [1 - i\mathbf{k} \cdot \boldsymbol{\varepsilon} e^{-i\omega t}]. \quad (19)$$

(See Ref. 1, Appendix A for the justification of this expansion.) With this linearization we can decompose the solutions of Eqs. (17) and (18) into two parts corresponding to the two source terms on the right-hand side of Eq. (19):

$$\begin{aligned} f(\mathbf{k}, \mathbf{q}, t) &= f_s(\mathbf{k}, \mathbf{q}) + f(\mathbf{k}, \mathbf{q}, \omega) e^{-i\omega t}, \\ \psi(\mathbf{k}, t) &= \psi_s(\mathbf{k}) + \psi(\mathbf{k}, \omega) e^{-i\omega t}. \end{aligned} \quad (20)$$

The solution for the static part is

$$\psi_s(\mathbf{k}) = \frac{4\pi e^2 Z}{k^2} \frac{1}{(2\pi)^3} \frac{1}{\mathcal{E}(k, 0)} \sum_l e^{i\mathbf{k} \cdot \mathbf{R}_l}, \quad (21)$$

and for the dynamic part

$$\psi(\mathbf{k}, \omega) = \frac{4\pi e^2 Z}{k^2} \frac{1}{(2\pi)^3} \frac{i\mathbf{k} \cdot \boldsymbol{\varepsilon}}{\mathcal{E}(k, \omega)} \sum_l e^{i\mathbf{k} \cdot \mathbf{R}_l}, \quad (22)$$

where  $\mathcal{E}(k, \omega)$  is the dielectric function given by

$$\mathcal{E}(k, \omega) = 1 - \frac{4\pi e^2}{k^2} \int \frac{d\mathbf{p}}{(2\pi)^3} \frac{f_0(\mathbf{p} + \mathbf{k}/2) - f_0(\mathbf{p} - \frac{1}{2}\mathbf{k})}{\mathbf{p} \cdot \mathbf{k}/m - \omega - i\delta}. \quad (23)$$

Following Dawson and Oberman<sup>1</sup> we obtain the average field on the ions due to the electrons:

$$\begin{aligned} \langle \mathbf{E}(\omega) \rangle_{av} &= \frac{4\pi e Z}{(2\pi)^3} \int \frac{d\mathbf{k}}{k^2} \mathbf{k} \cdot \boldsymbol{\varepsilon} \\ &\times \left[ \frac{1}{\mathcal{E}(k, 0)} - \frac{1}{\mathcal{E}(k, \omega)} \right] \left\langle \frac{1}{N} \sum_{ij} e^{-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \right\rangle, \end{aligned} \quad (24)$$

where  $\langle \dots \rangle$  stands for the ensemble average over the ion positions. In our case where the ions are randomly distributed, the averaging over the ion positions in Eq. (24) gives one.

From the equation of motion of the electrons, in the ion's rest frame we obtain

$$-i\omega \mathbf{j} = (e^2 n/m) [\mathbf{E} + \langle \mathbf{E}(\omega) \rangle_{av}], \quad (25)$$

where  $\mathbf{j}$  is the average current density. Here we use the fact that the force acting on the ions, due to the electrons, is equal and opposite to the force which is exerted on the electrons due to the ions, and that this force is invariant under the frame transformation.

From Eqs. (24) and (25) we obtain

$$\sigma = \sigma_0 \left\{ 1 - \frac{2}{3\pi} \frac{e^2}{m\omega^2} I(\omega) \right\}, \quad (26)$$

where

$$\sigma_0 = i\omega_p^2 / 4\pi\omega. \quad (27)$$

$\omega_p = (4\pi e^2 n/m)^{1/2}$  is the plasma frequency, and

$$I(\omega) = \int dk k^2 \left[ \frac{1}{\mathcal{E}(k, 0)} - \frac{1}{\mathcal{E}(k, \omega)} \right]. \quad (28)$$

Equations (26), (27), and (28) are our final results for the high-frequency and long-wavelength conductivity for a degenerate semiconductor.

### III. ASYMPTOTIC VALUES AND NUMERICAL CALCULATION

In this section we are concerned with explicit evaluation of the resistivity given by

$$\begin{aligned} R(\omega) &= \text{Re} 1/\sigma(\omega) \\ &= \frac{1}{6\pi^2} \frac{e^2}{m\omega_p^2} \frac{1}{\omega} \int dk k^2 \frac{\mathcal{E}_i(k, \omega)}{[\mathcal{E}_r(k, \omega)]^2 + [\mathcal{E}_i(k, \omega)]^2}, \end{aligned} \quad (29)$$

where  $\mathcal{E}_r$  and  $\mathcal{E}_i$  stand for the real and imaginary parts of  $\mathcal{E}(k, \omega)$ . In the following calculation we approximate  $\mathcal{E}(k, \omega)$  by its zero-temperature value (see, e.g., Glick and Ferrell<sup>8</sup>).  $R(\omega)$  is explicitly evaluated in the Appendix for the limits  $\omega/\omega_F \ll 1$  and  $\omega/\omega_F \gg 1$ , where  $\omega_F$  is the Fermi frequency, and given by

$$R(\omega) = (2\pi/\omega_F) \alpha r_s \left[ \ln \frac{2\pi}{\xi \alpha r_s} - 1 \right]; \quad \begin{matrix} \omega/\omega_F \ll 1, \\ r_s \ll 1 \end{matrix} \quad (30)$$

and

$$R(\omega) = (8\pi/3) \alpha r_s \omega_F^{1/2} \omega^{-3/2}; \quad \omega/\omega_F \gg 1. \quad (31)$$

Here  $r_s = r_0/a_0$ , where  $r_0$  is the mean radius per particle and  $a_0 = \hbar^2/m e^2$  is the Bohr radius;  $\alpha = (4/9\pi)^{1/3}$  and  $\xi \gtrsim 1$  is a numerical factor (see Appendix). In order to evaluate Eq. (29), one must consider separately the contribution from the pole arising when both  $\mathcal{E}_i$  and  $\mathcal{E}_r$  are zero. The estimate of the pole contribution is obtained in the Appendix and is given by

$$R_p(\omega) = \frac{16\pi}{3} \left( \frac{5}{12} \right)^{3/2} \frac{1}{\omega_F} \frac{[(\omega/\omega_p)^2 - 1]^{1/2}}{(\omega/\omega_p)^2}. \quad (32)$$

One should notice that  $R_p(\omega)$  has its maximum at  $\omega = \sqrt{2}\omega_p$ , and that for this value of  $\omega, k \ll k_F$ ; and therefore, the approximation for

$$\mathcal{E}_r = 1 - \frac{\omega_p^2}{\omega^2} - \frac{3}{5} \left( \frac{2\omega_F}{\omega_p} \right)^2 \left( \frac{k}{k_F} \right)^2$$

is consistent. However, for  $\omega \gg \omega_p$ ,  $R_p(\omega)$  behaves like  $1/\omega$ , which is an overestimate of the contribution from the pole. One should therefore place a cutoff frequency on  $\omega$ . We have no easy way to calculate this cutoff and we merely choose it to be at  $\omega_c = 2.5\omega_p$ .

The rest of Eq. (29) has been computed on an IBM-7094 for a degenerate semiconductor and is displayed

<sup>8</sup> A. J. Glick and R. A. Ferrell, Ann. Phys. (N. Y.) 2, 359 (1960).

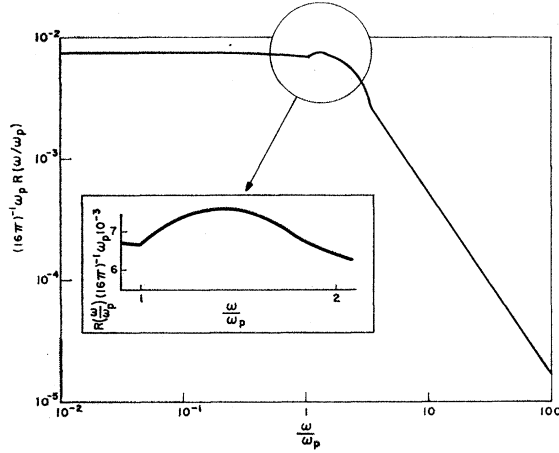


FIG. 1. Plot of the function  $(16\pi)^{-1}\omega_p R(\omega/\omega_p)$ .

in Fig. 1. We have chosen the effective electron mass and charge to be  $m/100$  and  $e/(10)^{1/2}$ , respectively (see, e.g., Ref. 4), and the electron density (for convenience)  $1.03 \times 10^{18}$  electrons/cm<sup>3</sup>.

The resistivity  $R(\omega)$  show a bump of order 15% just above the plasma frequency. This enhancement of the resistivity is due to the generation of a longitudinal plasma oscillation and it arises from the pole of the integrand. For classical plasmas, Dawson and Oberman<sup>1</sup> have found the same effect; however, numerically it is a very small effect.

#### ACKNOWLEDGMENTS

We would like to thank Dr. C. Oberman, Dr. J. Dawson, and Dr. P. A. Wolff for helpful discussion, and to Miss V. Rogers of the Whippany Laboratories for the numerical computation.

#### APPENDIX

We wish now to evaluate  $R(\omega)$  for the limits  $\omega/\omega_F \gg 1$ ,  $\omega/\omega_F \ll 1$  and find also the contribution from the plasma pole to  $R(\omega)$ .

We rewrite Eq. (29) as

$$R(\omega) = \frac{16\pi}{\omega_F} \frac{1}{\Omega} \int dq q^2 \frac{\mathcal{E}_i(q\Omega)}{[\mathcal{E}_r(q\Omega)]^2 + [\mathcal{E}_i(q\Omega)]^2}, \quad (\text{A1})$$

where

$$\Omega = \omega/\omega_F, \quad q = k/2k_F,$$

and

$$\begin{aligned} \mathcal{E}_i(q\Omega) &= \frac{\alpha r_s}{4} \frac{1}{q^3} \Omega = \mathcal{E}_i^I(q\Omega); \quad \frac{\Omega}{4q} < 1 - q \\ &= \alpha r_s \frac{1}{8q^3} \left[ 1 - \left( \frac{\Omega}{4q} - q \right)^2 \right] = \mathcal{E}_i^{II}(q\Omega); \\ & \quad |1 - q| < \frac{\Omega}{4q} < 1 + q \\ &= 0 \text{ elsewhere,} \end{aligned} \quad (\text{A2})$$

$$\begin{aligned} \mathcal{E}_r(q\Omega) &= 1 + \frac{\alpha r_s}{\pi} \frac{1}{q^2} \\ &+ \frac{1}{8q} \left[ 1 - \left( \frac{\Omega}{4q} - q \right)^2 \right] \ln \left| \frac{(\Omega/4) - q^2 - q}{(\Omega/4) - q^2 + q} \right| \\ &+ \frac{1}{8q} \left[ 1 - \left( \frac{\Omega}{4q} + q \right)^2 \right] \ln \left| \frac{(\Omega/4) + q^2 + q}{(\Omega/4) + q^2 - q} \right|. \end{aligned} \quad (\text{A3})$$

In the high-frequency limit, i.e.,  $\omega/\omega_F \gg 1$  we approximate  $\mathcal{E}_r$  to be  $\mathcal{E}_r \approx 1$  and need to consider only the contribution from  $\mathcal{E}_i^{II}(q\Omega) \ll 1$ . Thus, we obtain

$$\begin{aligned} R^{(\infty)}(\omega) &= R(\omega \gg \omega_F) = \lim_{\omega \gg \omega_F} \frac{16\pi}{\omega_F} \frac{1}{\Omega} \int dq q^2 \mathcal{E}_i(q\Omega) \\ &= \lim_{\omega \gg \omega_F} \frac{16\pi}{\omega_F} \frac{1}{\Omega} \frac{\alpha r_s}{8} \\ & \quad \times \int_{\frac{1}{2}[(\Omega+1)^{1/2}-1]}^{\frac{1}{2}[(\Omega+1)^{1/2}+1]} \frac{dq}{q} \left[ 1 - \left( \frac{\Omega}{4q} - q \right)^2 \right] \\ &= \frac{8\pi}{3} (\omega_F)^{1/2} \alpha r_s \omega^{-3/2}. \end{aligned} \quad (\text{A4})$$

This is our final result for  $R^{(\infty)}(\omega)$  given in Eq. (30).

For the calculation of  $R^{(0)}(\omega) = \lim_{\omega \ll \omega_F} R(\omega)$ , we write

$$\begin{aligned} R^{(0)}(\omega) &= \lim_{\omega \ll \omega_F} \frac{16\pi}{\omega_F} \frac{1}{\Omega} \int_0^1 dq q^2 \frac{\mathcal{E}_i^I(q\Omega)}{[\mathcal{E}_r(q\Omega)]^2} \\ &= \frac{16\pi}{\omega_F} \frac{1}{4} \int_0^1 \frac{dq}{q} \left\{ 1 + \frac{\alpha r_s}{2\pi} \frac{1}{q^2} [1 + f(q)] \right\}^{-2}, \end{aligned} \quad (\text{A5})$$

where

$$f(q) = \frac{1 - q^2}{2q} \ln \frac{1 + q}{1 - q}. \quad (\text{A6})$$

The integral in Eq. (A5) is very difficult to evaluate. However since  $f(q) \lesssim 1$ , we now evaluate  $R^{(0)}(\omega)$  to be

$$R^{(0)}(\omega) = \frac{16\pi}{\omega_F} \frac{1}{4} \int_0^1 \frac{dq}{q} \left( 1 + \frac{\xi \alpha r_s}{2\pi} \frac{1}{q^2} \right)^{-2}, \quad (\text{A7})$$

where  $1 < \xi < 2$  as can be found from more elaborate calculations in the case of interest where  $\alpha r_s/2\pi \ll 1$ . The integral in Eq. (A7) can be evaluated analytically and we obtain

$$\begin{aligned} R^{(0)}(\omega) &= \frac{2\pi}{\omega_F} \alpha r_s \left[ \ln \left( 1 + \frac{2\pi}{\xi \alpha r_s} \right) - 1 + \left( 1 + \frac{2\pi}{\xi \alpha r_s} \right)^{-1} \right] \\ &\cong \frac{2\pi}{\omega_F} \alpha r_s \left[ \ln \left( 1 + \frac{2\pi}{\xi \alpha r_s} \right) - 1 \right] \text{ for } \alpha r_s \ll 1, \end{aligned} \quad (\text{A8})$$

which is our final result as it is given by Eq. (30).

We finally wish to calculate the contribution from the pole. Here we write

$$R_p(\omega) = 16\pi \frac{1}{\omega} \int dq q^2 \frac{\mathcal{E}_i(q\omega)}{[\mathcal{E}_r(q\omega)]^2 + [\mathcal{E}_i(q\omega)]^2}$$

$$= -16\pi^2 \frac{1}{\omega} \int dq q^2 \delta[\mathcal{E}_r(q\omega)]. \quad (A9)$$

In order to evaluate the integral in Eq. (A9), we shall

approximate  $\mathcal{E}_r$  by

$$\mathcal{E}_r(q\omega) = 1 - \frac{\omega_p^2}{\omega^2} - \frac{12}{5} \left( \frac{\omega_F}{\omega_p} \right)^2 q^2. \quad (A10)$$

The integration in Eq. (A9) is straightforward and we obtain

$$R_p(\omega) = 4\pi^2 \left( \frac{5}{12} \right)^{3/2} \frac{1}{\omega_F} \left( \frac{\omega_p}{2\omega_F} \right)^2 \frac{[(\omega/\omega_p)^2 - 1]^{1/2}}{(\omega/\omega_p)^2}$$

$$= \frac{16\pi}{3} \left( \frac{5}{12} \right)^{3/2} \frac{1}{\omega_F} \frac{[(\omega/\omega_p)^2 - 1]^{1/2}}{(\omega/\omega_p)^2}, \quad (A11)$$

which is our final result given in Eq. (32).

### Many-Electron Perturbation Theory for Nonmetallic Low-Density Systems

W. J. CARR, JR.

*Westinghouse Research Laboratories,\* Pittsburgh, Pennsylvania*

(Received 10 April 1963)

A perturbation theory is developed to second order for the energy of a system of weakly interacting atoms. For a large uniform system the expression is correctly proportional to the number of atoms  $N$ . The result is given as the sum of electrostatic and Van der Waals terms plus exchange effects. The exchange energy is described first in the pair approximation, followed by corrections due to electron exchange among three or more atoms in both the first and second orders of the perturbation series. The second-order exchange term is due to the effect on exchange produced by the first-order perturbation on the wave function caused by Van der Waals forces.

The zeroth-order term is the energy of the isolated atoms so that in the ground state all other terms are successive corrections to the smaller binding energy.

In the case where the unperturbed atoms have an angular momentum, use of degenerate perturbation theory leads to a spin-wave type of solution, with coupling between the atoms.

**A**LTHOUGH the perturbation treatment developed here has some general features, the specific formulation is for the case of electrons in a nonmetallic solid, where the solid is not dense and the individual atoms are well separated. This case does not lend itself well to treatment with the usual many-body theory based in zeroth order upon noninteracting electrons.

In the limit of zero density the electrons on different atoms are distinguishable, being associated with the various atomic sites, and the problem is to calculate the binding energy as the density is increased and interatomic exchange of electrons begins to occur.

One obvious choice for an unperturbed Hamiltonian is

$$H_0 = \sum_{i=1}^N h_i(\mathbf{R}_i), \quad (1)$$

which describes a collection of  $N$ , noninteracting atoms, with  $h_i(\mathbf{R}_i)$  the Hamiltonian of the  $i$ th atom having

\* Most of the work reported here was done while the author was at the Atomic Energy Research Establishment (Theoretical Physics Division) Harwell, England.

nuclear coordinates  $\mathbf{R}_i$ . The eigenfunctions of  $H_0$  are

$$\psi_J = \psi_{j_1}(\mathbf{R}_1) \cdots \psi_{j_N}(\mathbf{R}_N) \quad (2)$$

and the eigenvalues

$$\epsilon_J = \epsilon_{j_1} + \epsilon_{j_2} + \cdots + \epsilon_{j_N}, \quad (3)$$

where  $\psi_{j_i}(\mathbf{R}_i)$  is centered about  $\mathbf{R}_i$  and is an eigenfunction of  $h_i(\mathbf{R}_i)$  (antisymmetric in the space and spin coordinates of those electrons about  $\mathbf{R}_i$ ) with eigenvalue  $\epsilon_{j_i}$ . Here we have arbitrarily assigned particular electrons to particular atoms and  $\psi(\mathbf{R}_1)$  indicates  $\psi(\mathbf{R}_1; 1, 2, \cdots)$  where the electrons 1, 2,  $\cdots$  are assigned to the atom at  $\mathbf{R}_1$ .

The  $\Psi_J$  form a complete orthogonal set and, therefore, it might seem that the set  $\alpha\Psi_J$  would be convenient for the expansion of an antisymmetric function of all electrons, where

$$\alpha = \sum_{\nu} (\pm) P_{\nu}, \quad (4)$$

the sum being over all permutations  $P_{\nu}$  of electronic space and spin coordinates, and the sign being given by the parity. However, the  $\alpha\Psi_J$  are no longer eigen-