Self-Consistent Field Approach to the Many-Electron Problem*

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The self-consistent field method in which a many-electron system is described by a time-dependent interaction of a single electron with a self-consistent electromagnetic field is shown to be equivalent for many purposes to the treatment given by Sawada and Brout. Starting with the correct many-electron Hamiltonian, it is found, when the approximations characteristic of the Sawada-Brout scheme are made, that the equation of motion for the pair creation operators is the same as that for the one-particle density matrix in the self-consistent field framework. These approximations are seen to correspond to (1) factorization of the two-particle density matrix, and (2) linearization with respect to off-diagonal components of the one-particle density matrix. The complex, frequency-dependent dielectric constant is obtained straightforwardly from the self-consistent field approach both for a free-electron gas and a real solid. It is found to be the same as that obtained by Noziéres and Pines in the random phase approximation. The resulting plasma dispersion relation for the solid in the limit of long wavelengths is discussed.

THE electromagnetic properties of crystals have long been studied by considering the time-dependent interaction of a single particle with a self-consistent electromagnetic field.[1] This procedure seems plausible for studying the response of electrons to any external perturbation, and Bardeen,[2] Wolff,[3] Lindhard,[4] Frölich and Pelzer,[5] Ferrell,[6] and others[7] have used this or a closely related approach with considerable success in discussing such phenomena as the electron-phonon interaction, the frequency and wave-number dependence of the dielectric constant, plasma oscillations, and characteristic energy losses in solids. These, and similar phenomena, have also been studied on the basis of more sophisticated treatments of the many-body problem[8–13] with largely identical results. The explicit relationship of the self-consistent field approach (e.g., Lindhard[4]) to the many-body approach (e.g., Sawada and Brout[10,11]) has not been stated. It is the purpose of this note to examine this relationship and to show that for many problems the two approaches may be regarded as rigorously equivalent. We do so by showing that the approximations introduced by Sawada and Brout are in fact sufficient to deduce the equation of the self-consistent field approach.

1. SELF-CONSISTENT FIELD, OR SCF, METHOD

We begin with a convenient formulation of the SCF method. We consider the single-particle Liouville equation

$$i\hbar(\partial\rho/\partial t)=[H,\rho],\qquad(1)$$

as describing the response of any particle of the system to the self-consistent potential $V(x,t)$, where ρ is the operator represented by the single-particle density matrix. The single-particle Hamiltonian in (1) is

$$H=H_0+V(x,t),\qquad(2)$$

where $H_0=p^2/2m$ is the Hamiltonian of a free electron satisfying Schrödinger's equation $H_0|\mathbf{k}\rangle=E_\mathbf{k}|\mathbf{k}\rangle$, and $|\mathbf{k}\rangle=\Omega^{-\frac{1}{2}}e^{i\mathbf{k}\cdot\mathbf{x}}$, Ω being the volume of the system. We expand the operator ρ in the form $\rho=\rho^{(0)}+\rho^{(1)}$. The unperturbed (Dirac or von Neumann) density matrix has the property $\rho^{(0)}|\mathbf{k}\rangle=f_0(E_\mathbf{k})|\mathbf{k}\rangle$, where $f_0(E_\mathbf{k})$ is the distribution function. Use of the von Neumann density matrix permits us to treat systems at finite temperatures. We now Fourier-analyze $V(x,t)$ in the form

$$V(x,t)=\sum_{\mathbf{q}'}V(q',t)e^{-i\mathbf{q}'\cdot\mathbf{x}},\qquad(3)$$

and linearize Eq. (1) by neglecting products of the type $V\rho^{(1)}$. This approximation is equivalent to first-order self-consistent perturbation theory. Taking

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matrix elements between states $\mathbf{k}$ and $\mathbf{k+q}$, we thus obtain

$$i\hbar(\partial/\partial t)\langle\mathbf{k}|\rho^{(1)}|\mathbf{k+q}\rangle$$
$$=\langle\mathbf{k}|[H_0,\rho^{(1)}]|\mathbf{k+q}\rangle+\langle\mathbf{k}|[V,\rho^{(0)}]|\mathbf{k+q}\rangle$$
$$=(E_\mathbf{k}-E_\mathbf{k+q})\langle\mathbf{k}|\rho^{(1)}|\mathbf{k+q}\rangle$$
$$+[f_0(E_\mathbf{k+q})-f_0(E_\mathbf{k})]V(q,t),\quad(4)$$

where $\langle\mathbf{k}|V|\mathbf{k+q}\rangle=V(q,t)$. The potential V consists of an external potential V_0 plus the screening potential V_s, which is related to the induced change in electron density,

$$n=\text{Tr}\{\delta(\mathbf{x}_e-\mathbf{x})\rho^{(1)}\}$$
$$=\Omega^{-1}\sum_q e^{-i\mathbf{q}\cdot\mathbf{x}}\sum_{\mathbf{k}'}\langle\mathbf{k}'|\rho^{(1)}|\mathbf{k}'+\mathbf{q}\rangle,\quad(5)$$

by Poisson's equation:

$$\nabla^2 V_s=-4\pi e^2 n.\quad(6)$$

Here $\delta(\mathbf{x}_e-\mathbf{x})$ is the charge density operator, $\mathbf{x}_e$ being the position operator and $\mathbf{x}$ referring to a specific point in space. We thus find

$$V_s(q,t)=v_q\sum_{\mathbf{k}'}\langle\mathbf{k}'|\rho^{(1)}|\mathbf{k}'+\mathbf{q}\rangle,\quad(7)$$

where $v_q=4\pi e^2/q^2\Omega$. By substituting the above expression giving V_s for V in Eq. (4) we obtain the Loiuville-Poisson equation determining $\langle\mathbf{k}|\rho^{(1)}|\mathbf{k+q}\rangle$ in the absence of an external perturbation:

$$i\hbar(\partial/\partial t)\langle\mathbf{k}|\rho^{(1)}|\mathbf{k+q}\rangle$$
$$=(E_\mathbf{k}-E_\mathbf{k+q})\langle\mathbf{k}|\rho^{(1)}|\mathbf{k+q}\rangle$$
$$+v_q[f_0(E_\mathbf{k+q})-f_0(E_\mathbf{k})]\sum_{\mathbf{k}'}\langle\mathbf{k}'|\rho^{(1)}|\mathbf{k}'+\mathbf{q}\rangle.\quad(8)$$

We have derived Eq. (8) in order to provide an explicit basis for comparison of the SCF method with the Sawada-Brout scheme. In solving problems by the SCF method, however, one can usually avoid the explicit expression of V_s in terms of $\rho^{(1)}$ within the equation of motion by making an *Ansatz* concerning the time dependence of $V(q,t)$. To illustrate this point, we calculate the frequency and wave-number dependence of the longitudinal dielectric constant $\epsilon(\omega,q)$. We imagine that the external potential $V_0(q,t)$ acts on the system with time dependence $e^{\alpha t}e^{i\omega t}$, where $\alpha\to 0$ corresponds to an adiabatic turning on of the perturbation. This potential polarizes the system. It follows from the definition of the dielectric constant and the Fourier analysis prescribed by Eq. (3) that

$$P(q,t)=(4\pi)^{-1}[\epsilon(\omega,q)-1]\mathcal{E}(q,t).\quad(9a)$$

The polarization $P(q,t)$ is related to the induced change in electron density by $\nabla\cdot\mathbf{P}=en$ or

$$-iqP(q,t)=en(q,t),\quad(9b)$$

and the electric field $\mathcal{E}(q,t)$ is given by

$$e\mathcal{E}(q,t)=-iqV(q,t).\quad(9c)$$

Equation (4) is readily solved for $\langle\mathbf{k}|\rho^{(1)}|\mathbf{k+q}\rangle$ by assuming that $\langle\mathbf{k}|\rho^{(1)}|\mathbf{k+q}\rangle$ and $V_s(q,t)$ have the same

time dependence as $V_0(q,t)$. The induced change in electron density $n(q,t)$ may then be calculated from (5) and $\epsilon(\omega,q)$ deduced from the field equations (9a, b, c). We find

$$\epsilon(\omega,q)=1-\lim_{\alpha\to 0}v_q\sum_\mathbf{k}\frac{f_0(E_\mathbf{k+q})-f_0(E_\mathbf{k})}{E_\mathbf{k+q}-E_\mathbf{k}-\hbar\omega+i\hbar\alpha}.\quad(10)$$

This result was first obtained by Lindhard[4] with the SCF method and later by Nozières and Pines[13] using a many-particle approach based on the random-phase approximation for a Fermi gas at zero temperature.

2. PROOF OF EQUIVALENCE

In this section, we show that the approximations required to obtain (1) or (8) from the many-electron Hamiltonian are just those characteristic of the Sawada-Brout scheme. It proves useful to consider the total second-quantized Hamiltonian in the coordinate representation:

$$\mathcal{3C}=-\left(\frac{\hbar^2}{2m}\right)\int\psi^\dagger(\mathbf{x})\nabla^2\psi(\mathbf{x})d\mathbf{x}$$
$$+\frac{1}{2}\int\left(\frac{e^2}{|\mathbf{x-y}|}\right)\psi^\dagger(\mathbf{y})\psi^\dagger(\mathbf{x})\psi(\mathbf{x})\psi(\mathbf{y})d\mathbf{x}d\mathbf{y}.\quad(11)$$

The operator $\psi(\mathbf{x})=\sum_\mathbf{k}a_\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{x}}$ develops in time according to

$$i\hbar(\partial/\partial t)\psi(\mathbf{x})=[\psi,\mathcal{3C}],\quad(12)$$

where $a_\mathbf{k},a_\mathbf{k}^\dagger$ are, respectively, annihilation and creation operators referring to the state k and satisfy the usual commutation rules for Fermi particles. Performing the commutation indicated in (12), we find the Schrödinger-like equation

$$i\hbar(\partial/\partial t)\psi(\mathbf{x})=H_{\text{op}}(\mathbf{x})\psi(\mathbf{x}),\quad(13)$$

with

$$H_{\text{op}}(\mathbf{x})=-\left(\frac{\hbar^2}{2m}\right)\nabla_x^2+\int d\mathbf{y}\,\rho(\mathbf{y},\mathbf{y})\frac{e^2}{|\mathbf{x-y}|}$$
$$\equiv H_0(\mathbf{x})+V_{\text{op}}(\mathbf{x}).\quad(14)$$

The density matrix operators $\rho_{\text{op}}(\mathbf{x},\mathbf{x}')$ and $\rho_{\text{op}}(\mathbf{k},\mathbf{k}')$ in the x and k representations, respectively, are defined by

$$\rho_{\text{op}}(\mathbf{x},\mathbf{x}')=\psi^\dagger(\mathbf{x}')\psi(\mathbf{x})$$
$$=\Omega^{-1}\sum_{\mathbf{kk}'}\rho_{\text{op}}(\mathbf{k},\mathbf{k}')\exp[i(\mathbf{k}\cdot\mathbf{x}-\mathbf{k}'\cdot\mathbf{x}')],\quad(15)$$

and satisfy the equations of motion

$$i\hbar(\partial/\partial t)\rho_{\text{op}}(\mathbf{x},\mathbf{x}')=H_{\text{op}}(\mathbf{x})\rho_{\text{op}}(\mathbf{x},\mathbf{x}')$$
$$-\rho_{\text{op}}(\mathbf{x},\mathbf{x}')H_{\text{op}}(\mathbf{x}'),\quad(16)$$

$$i\hbar(\partial/\partial t)\rho_{\text{op}}(\mathbf{k},\mathbf{k+q})=(E_\mathbf{k}-E_\mathbf{k+q})\rho_{\text{op}}(\mathbf{k},\mathbf{k+q})$$
$$+\sum_{\mathbf{k}'q'}v_{q'}[\rho_{\text{op}}(\mathbf{k}',\mathbf{k}'+\mathbf{q}')$$
$$\times\rho_{\text{op}}(\mathbf{k+q}',\mathbf{k+q})$$
$$-\rho_{\text{op}}(\mathbf{k},\mathbf{k+q-q}')\rho_{\text{op}}(\mathbf{k}',\mathbf{k}'+\mathbf{q}')].\quad(17)$$

In Eq. (16), $H_{op}(x)$ operates only on x, and $H_{op}(x')$ operates only on x'. Equations (16) and (17) are exact.

We observe that the right-hand member of Eq. (16) is just the commutator of $H_{op}(x)$ and $\rho_{op}(x,x')$ in a mixed representation. In complete operator form, (16) becomes

$$i\hbar\dot{\rho}_{op} = [H_{op}, \rho_{op}]. \tag{18}$$

Equation (18) is just the formal analog of Eq. (1) in second quantization. For a single system in the state Ψ at time t, we have

$$\rho = (\Psi, \rho_{op}\Psi), \tag{19}$$

for the value of ρ at time t. For an ensemble of systems, (19) is replaced by its ensemble average. We denote either average by $\langle\rho_{op}\rangle_{Av}$. Without loss of generality we may average (18) and obtain

$$i\hbar\langle\dot{\rho}_{op}\rangle_{Av} = \langle[H_{op}, \rho_{op}]\rangle_{Av}. \tag{20}$$

On the other hand, (1) is evidently

$$i\hbar\langle\dot{\rho}_{op}\rangle_{Av} = [\langle H_{op}\rangle_{Av}, \langle\rho_{op}\rangle_{Av}], \tag{21}$$

because $V_s = \langle V_{op}\rangle_{Av}$ and therefore $H = \langle H_{op}\rangle_{Av}$ according to (2) and (14). Thus the approximation required for obtaining (1) from (18) is the replacement of the expectation value of a product of density matrices by the product of the expectation values, e.g.,

$$\langle\rho_{op}(y,y)\rho_{op}(x,x')\rangle_{Av} \rightarrow \langle\rho_{op}(y,y)\rangle_{Av}\langle\rho_{op}(x,x')\rangle_{Av}. \tag{22}$$

The approximation in (22) will be designated as "Hartree factorization." In order to arrive at the equation corresponding to (1) which contains exchange, we would have to replace the right side of (22) by the appropriately antisymmetrized combination (Hartree-Fock factorization).

In deriving Eqs. (4) and (8) the further approximation of linearization has been made. Without linearization, Eq. (8) would have been the factorized form of Eq. (17):

$$i\hbar(\partial/\partial t)\langle k|\rho|k+q\rangle$$
$$= (E_k - E_{k+q})\langle k|\rho|k+q\rangle$$
$$+ \sum_{k'q'} v_{q'}[\langle k'|\rho|k'+q'\rangle\langle k+q'|\rho|k+q\rangle$$
$$- \langle k|\rho|k+q-q'\rangle\langle k'|\rho|k'+q'\rangle], \tag{23}$$

where

$$\langle k|\rho|k+q\rangle = \langle\rho_{op}(k, k+q)\rangle_{Av}. \tag{24}$$

By neglecting all terms $q' \neq q$ in (23), which corresponds to the random phase approximation[8] (RPA), we find

$$i\hbar(\partial/\partial t)\langle k|\rho|k+q\rangle = (E_k - E_{k+q})\langle k|\rho|k+q\rangle$$
$$+ v_q[\langle k+q|\rho|k+q\rangle$$
$$- \langle k|\rho|k\rangle]\sum_{k'}\langle k'|\rho|k'+q\rangle. \tag{25}$$

Equations (25) and (8) are seen to be almost identical. The correspondence with the formulation of the SCF method given in Sec. 1 is established completely by identifying $\langle k|\rho|k\rangle$ in (25) with $f_0(E_k)$ in (8) and

$\langle k|\rho|k+q\rangle$ with $\langle k|\rho^{(1)}|k+q\rangle$. The RPA is therefore seen to be equivalent to treatment of the off diagonal elements of ρ as perturbations with respect to the diagonal components.

Sawada and Brout have derived an approximate equation of motion of the electron-hole pair creation operator $a_{k+q}^\dagger a_k = \rho_{op}(k, k+q)$. The approximations they employ are (1) the RPA and (2) the replacement of diagonal components $\rho_{op}(k,k)$ by their expectation values for the free-electron gas. The resulting equation for $\rho_{op}(k, k+q)$,

$$i\hbar(\partial/\partial t)\rho_{op}(k, k+q)$$
$$= (E_k - E_{k+q})\rho_{op}(k, k+q) + v_q[f_0(E_{k+q}) - f_0(E_k)]$$
$$\times \sum_{k'}\rho_{op}(k', k'+q), \tag{26}$$

has the same form as Eq. (25) for $\langle k|\rho|k+q\rangle$ which corresponds to Eq. (8) in the SCF method. *Thus the SCF equation is simply the average of the Sawada-Brout equation.* Both schemes involve the RPA as well as a form of factorization. The extra generality of the scheme of Sawada and Brout resulting from their partial averaging is unnecessary for calculating properties of the system associated with one-electron operators only. Such a one-electron operator O has the form $O_{op} = tr\{O_{op}\rho_{op}\}$ in second quantization. Its expectation value $\langle O_{op}\rangle_{Av} = (\Psi, O_{op}\Psi) = tr\{O\rho\}$ involves only $\langle\rho_{op}\rangle_{Av} = \rho$. The same value of $\langle O_{op}\rangle_{Av}$ clearly obtains whether we solve the SCF equation for ρ or use the Sawada-Brout scheme. Therefore, the simplicity and ease of interpretation of the SCF method commend it for such problems as the calculation of the dielectric constant (Sec. 1) and the response of the system to a general external perturbation.

The SCF method does not yield by itself results depending on two-electron operators such as those entering the correlation energy. The more general Sawada-Brout equation (26), however, can be used in such problems. Nevertheless, the SCF calculation of the dielectric constant can be used in conjunction with an elegant formula due to Nozières and Pines[13] which exactly relates the correlation energy of the electron gas to its dielectric constant. Nozières and Pines obtain in this way the result of Sawada[10] and Hubbard[12] for the correlation energy.

A normal-mode analysis of the SCF equation, (8) or (25), can be performed following the procedure used by Brout[11] in connection with the Sawada-Brout equation, (26). The formal similarity of the two equations ensures that the condition for the existence of plasma oscillations and the corresponding dispersion relation is the same in both cases, namely the vanishing of the dielectric constant of Eq. (10). This normal mode analysis also affords a rigorous justification of the *Ansatz* for the time dependence of V_s used in obtaining (10).

Particular advantages of the present formulation of the SCF method are (1) the Liouville equation reduces

in the classical limit to the ordinary Boltzmann equation used in transport theory and (2) the method applies to systems at finite temperatures. These features are not shared by formulations using the Hartree equation as the point of departure.[3,4] As a direct consequence of the normal-mode analysis already mentioned, one finds that at finite temperature the imaginary part of the dielectric constant does not vanish. Thus plasma oscillations do not exist as independent excitations of the system at finite temperature, and the plasma resonance is broadened. Further, the method is readily generalized to real crystals, as described in the next section.

3. APPLICATIONS TO REAL SOLIDS

To illustrate the simplicity and utility of the SCF method, we calculate the dielectric constant for a real solid and examine the plasma dispersion relation for plasma oscillations characterized by $q \cong 0$. We make the simplifying assumption that the core states of the atoms composing the solid are sufficiently tightly bound and the valence or conduction bands are sufficiently broad that local field corrections and hence umklapp processes may be neglected. The results obtained in elementary fashion by the SCF method agree with those previously obtained by Adams,[14] Wolff,[3] Nozières and Pines,[13] and others.

The generalization of the SCF method as presented in Sec. 1 is obtained by replacing the Hamiltonian H_0 by that for an electron in the unperturbed periodic lattice and the wave functions $|k\rangle$ by $|kl\rangle = \Omega^{-\frac{1}{2}} u_{kl}(\mathbf{x}) e^{i\mathbf{k}\cdot\mathbf{x}}$. Here $u_{kl}(\mathbf{x})$ is the spatially periodic part of the wave function corresponding to wave vector $\mathbf{k}$ and band l. In terms of the integral

$$(kl | k+q, l') \equiv v_a^{-1} \int_0 u_{kl}^*(\mathbf{x}) u_{k+q,l'}(\mathbf{x}) d\mathbf{x}, \quad (27)$$

which extends over the unit cell, we find the generalizations of Eqs. (4), (5), and (8) to be, respectively,

$$i\hbar(\partial/\partial t)\langle kl | \rho^{(1)} | k+q, l'\rangle$$
$$= (E_{kl} - E_{k+q,l'})\langle kl | \rho^{(1)} | k+q, l'\rangle$$
$$+ [f_0(E_{k+q,l'}) - f_0(E_{kl})] V(q,t)(kl | k+q, l'), \quad (28)$$

$$n = \Omega^{-1} \sum_q e^{-i\mathbf{q}\cdot\mathbf{x}} \sum_{k,l,l'} (k+q, l' | kl)$$
$$\times \langle kl | \rho^{(1)} | k+q, l'\rangle, \quad (29)$$

and

$$i\hbar(\partial/\partial t)\langle kl | R | k+q, l'\rangle$$
$$= (E_{kl} - E_{k+q,l'})\langle kl | R | k+q, l'\rangle$$
$$+ v_q |(kl | k+q, l')|^2 [f_0(E_{k+q,l'}) - f_0(E_{kl})]$$
$$\times \sum_{k'} \sum_{nn'} \langle k'n | R | k'+q, n'\rangle, \quad (30)$$

where

$$\langle kl | R | k+q, l'\rangle = (k+q, l' | kl)\langle kl | \rho^{(1)} | k+q, l'\rangle. \quad (31)$$

[14] E. N. Adams, Phys. Rev. **85**, 41 (1952).

The longitudinal frequency and wave-number dependent dielectric constant again is obtained straightforwardly from the relationship $\nabla \cdot \mathbf{P} = en$. We find

$$\epsilon(\omega,q) = 1 - \lim_{\alpha \to 0} v_q \sum_{k,l,l'} |(kl | k+q, l')|^2$$
$$\times \frac{f_0(E_{k+q,l'}) - f_0(E_{kl})}{E_{k+q,l'} - E_{kl} - \hbar\omega + i\hbar\alpha}. \quad (32)$$

The Liouville-Poisson equation (30) and the expression for the dielectric constant (32) differ from that for the free electron case in that v_q is replaced by $v_q |(k | k+q, l')|^2$ and the summation over wave number is replaced by one extending over the band indices as well.

It is interesting to exhibit explicit expressions for the real and imaginary parts, $\epsilon_1(\omega,q)$ and $\epsilon_2(\omega,q)$, of the dielectric constant, which are easily given in the limit $q \to 0$. Perturbation theory in this limit yields

$$|(kl | k+q, l')|^2 = \delta_{ll'} + (1 - \delta_{ll'})(q/m\omega_{ll'})^2 |P_{ll'}^\mu|^2, \quad (33)$$

where

$$P_{ll'}^\mu = v_a^{-1} \int_0 u_{kl'}^* p^\mu u_{kl} d^3x,$$

p^μ being the momentum operator associated with the direction of propagation of the wave $\mathbf{q}$, and $\hbar\omega_{l'l} = E_{kl'} - E_{kl}$. After expanding other quantities depending on q about $q=0$, we find to lowest order

$$\epsilon_1(\omega,0) = 1 - (e/\pi\hbar\omega)^2 \sum_l \int d^3k\, f_0(E_{kl}) \partial^2 E_{kl}/\partial k_\mu^2$$
$$+ m^{-1}(e/\pi)^2 \sum_{ll'}' \mathcal{P} \int d^3k$$
$$\times f_0(E_{kl}) f_{l'l}^\mu (\omega_{l'l}^2 - \omega^2)^{-1}, \quad (34)$$

$$\epsilon_2(\omega,0) = (e^2/q^2\pi) \sum_l \int d^3k\, f_0(E_{kl})$$
$$\times [\delta(E_{k+q,l} - E_{kl} - \hbar\omega) - \delta(E_{k-q,l} - E_{kl} + \hbar\omega)]$$
$$+ \pi^{-1}(e/m\omega)^2 \sum_{ll'}' \int d^3k [f_0(E_{kl}) - f_0(E_{kl'})]$$
$$\times |P_{ll'}^\mu|^2 \delta(E_{kl'} - E_{kl} - \hbar\omega). \quad (35)$$

Here $\mathcal{P}$ denotes that principal parts of the corresponding integrals are to be taken and the prime on the summations that terms $l=l'$ are to be excluded. Further the oscillator strength

$$f_{l'l}^\mu = (2/\hbar\omega_{l'l}m) |P_{l'l}^\mu|^2$$

has been introduced.

We note that the terms in ϵ_1 and ϵ_2 consist of intra-band and interband contributions. In ϵ_2 the first term, corresponding to one-electron intraband excitations, has not been approximated in order to exhibit its close relationship to the free electron case. The second term is associated with interband optical absorption. This is not surprising since for $q=0$ the transverse dielectric constant, which describes the interaction of the solid with electromagnetic waves, can be shown to equal the longitudinal dielectric constant which is associated with collective motion of the electrons. This leads to the result first pointed out by Wolff[3] and by Fröhlich and Pelzer[5] that the plasma frequency of infinite wavelength and the damping of these oscillations in the solid may be deduced from optical data. Further it is seen that even for q very small, with the exception of semiconductors or semimetals, ϵ_2 does not vanish for solids having any reasonable structure of the conduction bands so that plasma oscillations are always damped and cannot strictly exist as normal modes of the system. The plasma frequency in the limit of small q is obtained from $\epsilon_1(\omega,0)=0$.

In the case of insulators, for which all bands $l\leqslant L$ are filled and those for which $l>L$ are empty, the second term of Eq. (34) vanishes. Because of the relationship $f_{l'l}{}^{\mu}=-f_{ll'}{}^{\mu}$, the double sum in the third term of (34) may be written in the following two alternative forms: (i) $\sum_{l\leqslant L,\, l'>L}$ and (ii) $\sum_{l\leqslant L,\, l'}$. The first form immediately leads to the theorem that the plasma frequency of an insulator cannot fall inside the band gap. The second form permits the deduction of the plasma frequency in the limiting case that $\omega\ll\omega_{cv}$, where $\hbar\omega_{cv}$ is the energy difference between the valence and core bands, and that $\omega\gg\omega_{l'v}$ for all bands l' that contribute appreciably to the f-sum rule

$$\sum_l f_{l'v}{}^{\mu}=1-(m/\hbar^2)\partial^2 E_{kv}/\partial k_{\mu}{}^2.$$

In that case the plasma frequency is given by $\omega_p{}^2=4\pi n_v e^2/\epsilon_c m$ where n_v is the density of valence electrons, ϵ_c is the dielectric constant due to the core, and m is the free electron mass. We note also that the condition $\omega\gg\omega_{l'v}$ insures that ϵ_2 is small so that the plasma oscillations are only weakly damped.

For a "free-electron" metal with spherical surfaces of constant energy and a single partly occupied con-duction band l, the second term of (34) becomes $-4\pi n_l e^2/\omega^2 m^*$ where m^* is the isotropic effective mass of the conduction band and n_l is the electron density in the band. The third term gives rise to a shift of the plasma frequency due to the presence of interband transitions. In the limit that this term is small, the shift agrees with that calculated by Adams.[14] The shift may be neglected in the limit that $\omega_p\ll\omega_{l'l}$ for all bands l' contributing appreciably to the f-sum rule. This is properly true only in semiconductors and possibly semimetals. On the other hand, in the case of a metal having a number of close-lying valence bands v in addition to the conduction band l, well separated from the core states, for which $\omega_p\gg\omega_{l'v}$ for all bands l' contributing appreciably to the f-sum rule, we find again that $\omega_p{}^2=4\pi n_{vl}e^2/\epsilon_c m$. Here n_{vl} is the density of valence plus conduction electrons. This shows that the plasma frequency is the same for metals and insulators provided that the plasma frequency is sufficiently large.

Finally, in the case of simple intrinsic semiconductors or semimetals, where the plasma frequency is sufficiently small, the interband term in Eq. (34) gives rise to a real dielectric constant ϵ due to the filled core and almost completely filled valence band. Collective motions can therefore exist as independent normal modes. Here, however, we have the simultaneous presence of an electron and a hole plasma. As first pointed out by Pines,[15] the normal modes of these interacting plasmas correspond to "optical" and "acoustical" vibrations just as in the case of lattice vibrations of a solid containing two atoms per unit cell. From Eq. (34) it is immediately seen that the optical mode frequency for infinite wavelength is $\omega_p{}^2=(4\pi n e^2/\epsilon)(m_n{}^{*-1}+m_p{}^{*-1})$, where $m_n{}^*$ and $m_p{}^*$ are the effective masses associated, respectively, with the conduction and valence band. The acoustic frequencies vanish at infinite wavelengths and are obtained only if the intraband terms in Eq. (32) are expanded to a higher order in q. If this is done, the results agree with those of Nozières and Pines.[13]

[15] D. Pines, Can. J. Phys. 34, 1379 (1956).