# Generalized Self-Consistent Field Theory and the Dielectric Formulation of the Many-Body Problem*

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(Received 26 December 1962)

A generalized self-consistent field (SCF) theory of many-particle systems is developed by modifying the usual functional relationship between energy and wave function. A parameter $\xi$, $0 \leq \xi \leq 1$, is thus introduced into the energy so that for $\xi = 0$, the particles interact only with a self-consistent field, for $\xi = 1$ the particles interact dynamically among themselves with the correct field, and for intermediate values of $\xi$ both SCF and dynamical interactions occur. A systematic development of the theory is given for time-independent and time-dependent problems, for finite temperatures, and for both uniform and nonuniform systems. The derivative with respect to $\xi$ of the total energy, or free energy, is expressed in terms of the dielectric function and an improved version of the dielectric formulation of the many-body problem thereby obtained. A brief discussion of the advantages of the method, possible applications, and further generalizations or extensions is included.

## I. INTRODUCTION

TWO recent contributions to the literature on the many-body problem[1,2] are noteworthy in that exact theorems are derived in an elementary way without recourse to perturbation theory. Nozières and Pines[1] prove that the total energy $E_0(e^2)$ of a gas of $N$ electrons in volume $\Omega$ is given by

$$E_0(e^2) = E_0(0) - \int_0^{e^2} \frac{d\lambda}{\lambda}$$

$$\times \sum_q \left[ \frac{\hbar}{2\pi} \int_0^{\infty} d\omega \, \text{Im} \frac{1}{\epsilon(q,\omega;\lambda)} - \frac{Nv_q}{2} \right], \quad (I.1)$$

where $E_0(0)$ is the free-electron energy; $\epsilon(q,\omega;\lambda)$ is the dielectric function of the electron gas for wave number $q$, frequency $\omega$, and value $\lambda$ of electron charge squared; and where $v_q$ is the Fourier transform of the interaction, $4\pi e^2/q^2\Omega$. The theorem holds for any velocity-independent central interaction between the particles provided only that the Fourier transform exists (no hard core). Englert and Brout[2] have generalized (I.1) to finite temperature:

$$F(e^2) = F(0) - \left[ \int_0^{e^2} \frac{d\lambda}{\lambda} \sum_q \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega \right.$$

$$\left. \times \left( \frac{1}{1-e^{-\hbar\omega/kT}} \right) \text{Im} \frac{1}{\epsilon(q,\omega;\lambda,T)} - \frac{Nv_q}{2} \right], \quad (I.2)$$

where $F$ is now the free energy, and the dielectric function $\epsilon$ depends on temperature. The only assumption implicit in the derivation of (I.1) is that the formal derivative of $E_0(\lambda)$,

$$\frac{dE_0(\lambda)}{d\lambda} = \left( \Psi_0(\lambda), \tfrac{1}{2} \sum_{i,j}' \frac{1}{r_{ij}} \Psi_0(\lambda) \right), \quad (I.3)$$

is integrable, and similarly for (I.2). In (I.3), $\Psi_0(\lambda)$ is the ground state for charge squared equal to $\lambda$. Once this restriction is made, (I.1) or (I.2) is a direct consequence of a quite general fluctuation-dissipation theorem. On the surface, at least, assuming integrability appears less restrictive than requiring the existence of one form or another of perturbation theory.

Equations (I.1) and (I.2) furnish a rapid means of approximate calculation of the energy once an approximate dependence of the dielectric constant on charge is established. However, despite the appearance in the integral over $\lambda$ of small values of $\lambda$, the charge squared can never be treated as small, and it is necessary to go to infinite order of perturbation theory to obtain the lowest satisfactory approximation to the dielectric function.[1] But then all distinction from perturbation theory is lost, and the analysis has no advantage over the beautiful work of Hubbard,[3-5] who established an equation equivalent to (I.1) by perturbation theory[3] before Nozières and Pines, obtained explicit results for the energy of an electron gas,[4] and treated electrons in a crystal as well.[5] An approximation to the dielectric function can be obtained simply from an analysis of the equations of motion of the creation and destruction operators[6,7] or, more simply still, from self-consistent-field (SCF) theory.[8,9] Further, Hubbard[5] has found it convenient, if not essential, to start his perturbation analysis of the crystal from the Hartree problem. We, therefore, propose to derive exact formulas equivalent to (I.1) and (I.2) *and holding for nonuniform systems as well* by starting out from a SCF approximation rather than the free-particle problem.

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[1] P. Nozières and D. Pines, Nuovo Cimento **9**, 470 (1958).
[2] F. Englert and R. Brout, Phys. Rev. **120**, 1085 (1960).
[3] J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957).
[4] J. Hubbard, Proc. Roy. Soc. (London) **A243**, 336 (1958).
[5] J. Hubbard, Proc. Roy. Soc. (London) **A244**, 199 (1958). This is only a formal solution of the problem. The possibility of basing an actual calculation on it is remote if lattice effects in the dielectric function are to be included. This was not done in references 22 and 23.
[6] R. Brout, Phys. Rev. **108**, 515 (1957).
[7] H. Suhl and N. R. Werthamer, Phys. Rev. **122**, 359 (1961).
[8] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, 8 (1954).
[9] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

The essential point of the Nozières-Pines theory[1] is that a simple expression is found for $dE_0(\lambda)/d\lambda$ which is then integrated from $\lambda=0$, i.e., the free-electron case, to $\lambda=e^2$, i.e., the actual problem. The resulting expression (I.1) thus depends on this particular starting point and the path of integration chosen. One might also parametrize the energy by means of some parameter $\xi$ different from $e^2$ in such a way that for $\xi=0$ the parametrized energy reduces to that of an approximate problem nearer to the actual problem than the free-electron case and for $\xi=1$ becomes the actual energy. Constructing an expression for $dE_0/d\xi$ and then integrating would mean calculating a smaller correction by a more rapidly converging process. As already mentioned, the starting point we choose is a SCF approximation; the formal problem we solve in this paper is how to construct in a systematic way an approximate theory which passes continuously over to the exact theory as a parameter $\xi$ varies from 0 to 1. This parameter $\xi$ can then be used as an ordering parameter alternative to $r_s$, the radius of a sphere containing one electron, usually employed.[10]

Accordingly, in Sec. II we introduce a generalized SCF formalism in its simplest guise, that for the ground state of a uniform system of fermions, and derive a formula alternative to (I.1). In Sec. III, we derive the corresponding formula for the ground-state energy of a collection of atoms with fixed nuclei; however, a more complex analysis of the dielectric function is required. In Sec. IV, the SCF formalism is generalized to temperature-dependent problems, and we derive formulas alternative to (I.2) or its generalizations. A general discussion of possible applications is given in Sec. V.

The detailed study of SCF theory carried out here for the first time is of considerable interest in its own right, as are the exact formulas derived for the ground-state energy or the free energy. These same techniques can, for example, be applied to superconductors or to Bose fluids, after the Bogoliubov transformation[11] has been made, in order to construct a theory valid in a wider domain. It is even possible to allow for a hard-core interaction systematically, provided the excluded volume is small. However, these possibilities do not give rise to the primary motivation of the present work, which is to provide the basis for an approximate theory of real metals valid to reasonable accuracy at normal metallic densities. It is with this in mind that the paper should be read.

## II. UNIFORM FERMION SYSTEM; GROUND STATE

We consider a system of $N$ identical fermions within a volume $\Omega$ interacting via pairwise central interactions

$v(r_{ij})=v_{ij}$. The Hamiltonian for the system is

$$\mathcal{H}=\sum_i \frac{p_i^2}{2m}+\tfrac{1}{2}\sum_{ij}{}' v_{ij}. \tag{II.1}$$

Following Bohm and Pines,[12] we may simplify the writing of $\mathcal{H}$ by setting

$$v(\mathbf{r})=\sum_q v_q e^{i\mathbf{q}\cdot\mathbf{r}}, \quad v_q=\frac{1}{\Omega}\int d^3r\, v(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}, \tag{II.2}$$

$$\rho_q\equiv\sum_j e^{-i\mathbf{q}\cdot\mathbf{r}_j}\rightarrow\sum_k a_k^\dagger a_{k+q}$$

$$\text{in second quantization,} \tag{II.3}$$

$$K\equiv\sum_i p_i^2/2m. \tag{II.4}$$

$\mathcal{H}$ then becomes

$$\mathcal{H}=K+\tfrac{1}{2}\sum_q v_q\{\rho_q\rho_{-q}-N\}. \tag{II.5}$$

The ground-state energy $E_0$ is the expectation of (II.5) with the ground-state wave function, $|0\rangle$

$$E_0=\langle 0|K|0\rangle+\tfrac{1}{2}\sum_q v_q\{\langle 0|\rho_q\rho_{-q}|0\rangle-N\}, \tag{II.6}$$

$$\langle 0|0\rangle=1. \tag{II.7}$$

$E_0$ is, of course, a minimum with respect to variation of $|0\rangle$,

$$\delta E_0=0, \quad \delta\langle 0|0\rangle=0, \tag{II.8}$$

or, equivalently, $|0\rangle$ satisfies the Schrödinger equation

$$\mathcal{H}|0\rangle=E_0|0\rangle \tag{II.9}$$

with $E_0$ the lowest eigenvalue. If $v_q$ has a strength $\lambda$ ($e^2$ for Coulomb interactions), it follows from the stationarity of $E_0$, Eq. (II.8), that

$$\frac{dE_0(\lambda)}{d\lambda}=\frac{1}{\lambda}\frac{1}{2}\sum_q v_q\{\langle 0|\rho_q\rho_{-q}|0\rangle-N\}. \tag{II.10}$$

This equation may be regarded as the starting point of the Nozières-Pines formulation.

### II.1 Generalized SCF Theory of the Ground State

The integration of (II.10) over $\lambda$ carries one from the free-particle problem ($\lambda=0$) to the actual problem. The free-particle problem is not usually a good starting, nor is the convergence rapid along this path or integration. The familiar Hartree approximation suggests itself as, in general, a better starting approximation for the energy with possibly more rapid convergence along the path of integration. The way the Hartree approximation is usually derived is to replace the exact wave function in the variational principle (II.6)-(II.8) by a product of one-particle wave functions. Such an

[10] K. A. Brueckner and M. Gell-Mann, Phys. Rev. **106**, 364 (1957).
[11] S. T. Beliaev, in *The Many Body Problem*, edited by C. De Witt and P. Nozieres (John Wiley & Sons, Inc., New York, 1959), p. 433.
[12] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

unsymmetric form for the wave function can never be reached continuously from the actual problem by variation of a parameter; moreover, the resulting equations for the one-electron functions are not Hermitian. It is necessary to modify the usual Hartree theory somewhat before it can serve our purposes. In particular, instead of restricting the form of the wave function and leaving the functional relation between wave function and energy unchanged, we modify the functional relation between energy and wave function by the factorization[9]

$$\langle 0|\rho_q\rho_{-q}|0\rangle \rightarrow \langle 0|\rho_q|0\rangle\langle 0|\rho_{-q}|0\rangle,$$

and leave the wave function unrestricted. To distinguish the resulting theory from the usual Hartree or the Hartree-Fock theory, we call it simply the SCF theory.[9]

We thus replace the form (II.6) by

$$E_0=\langle 0|K|0\rangle+\tfrac{1}{2}\sum_q v_q\langle 0|\rho_q|0\rangle\langle 0|\rho_{-q}|0\rangle. \quad (II.11)$$

Applying the variational principle (II.8) yields the SCF equation

$$(K+V_S^{(0)})|0\rangle=\mathcal{E}_0|0\rangle, \quad (II.12)$$

where

$$V_S^{(0)}=\sum_q v_q\langle 0|\rho_q|0\rangle\rho_{-q} \quad (II.13)$$

is the total self-consistent potential. Equation (II.12) is separable into a set of Hermitian single-particle equations, even though $|0\rangle$ remains a determinant of the single-particle wave functions satisfying these equations. They differ from the Hartree equations in that the potential is the same in each and contains the interaction of a one-particle state with itself. Consequently, one would expect the SCF theory to provide a good starting approximation only for extended systems. The sum of the one-particle eigenvalues gives $\mathcal{E}_0$, and the total energy is

$$E_0=\mathcal{E}_0-\tfrac{1}{2}\sum_q v_q\langle 0|\rho_q|0\rangle\langle 0|\rho_{-q}|0\rangle$$
$$=\mathcal{E}_0-\tfrac{1}{2}\langle 0|V_S^{(0)}|0\rangle. \quad (II.14)$$

Because of the translational invariance of the system, $\langle 0|\rho_q|0\rangle$ vanishes unless $q=0$, but that is a simplification we need not make at this stage.

It should be emphasized that despite the occurrence of a determinantal wave function, there is no exchange in the SCF theory. This is an advantage in many problems, e.g., the electron gas, in which exchange and correlation must be introduced on the same footing.[13]

Suppose now that we consider a somewhat more general functional relation between the energy and the wave function than (II.11) as the starting point of a *generalized* SCF theory, that obtained by multiplying (II.11) with $1-\xi$ and (II.6) with $\xi$, where $0\leqslant\xi\leqslant1$:

$$E_0(\xi)=\langle 0\xi|K|0\xi\rangle+\tfrac{1}{2}\sum_q v_q\langle 0\xi|\rho_q|0\xi\rangle\langle 0\xi|\rho_{-q}|0\xi\rangle$$
$$+\tfrac{1}{2}\xi\sum_q v_q\{\langle 0\xi|\rho_q\rho_{-q}|0\xi\rangle$$
$$-\langle 0\xi|\rho_q|0\xi\rangle\langle 0\xi|\rho_{-q}|0\xi\rangle-N\}. \quad (II.15)$$

[13] J. Bardeen, Phys. Rev. **50**, 1098 (1936); E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

Thus $E_0(0)$ is the SCF energy and $E_0(1)$ the exact ground-state energy. Further, wherever $\xi$ is introduced in this paper, the formalism reduces to the conventional one for $\xi=1$. If we impose the variational principle (II.8) on our $\xi$-dependent function $|0\xi\rangle$, we get a generalized SCF equation

$$\mathfrak{K}_S^0|0\xi\rangle=\{K+(1-\xi)V_S^{(0)}(\xi)$$

$$+\frac{\xi}{2}\sum_q v_q(\rho_q\rho_{-q}-N)\}|0\xi\rangle=\mathcal{E}_0(\xi)|0\xi\rangle, \quad (II.16)$$

where

$$V_S^{(0)}(\xi)=\sum_q v_q\langle 0\xi|\rho_q|0\xi\rangle\rho_{-q}, \quad (II.17)$$

and

$$E_0(\xi)=\mathcal{E}_0(\xi)-\tfrac{1}{2}(1-\xi)\langle 0\xi|V_S^{(0)}(\xi)|0\xi\rangle. \quad (II.18)$$

If $|0\xi\rangle$ satisfies (II.16), then $E_0(\xi)$ is stationary, and

$$\frac{dE_0(\xi)}{d\xi}=\tfrac{1}{2}\sum_q v_q\{\langle 0\xi|\rho_q\rho_{-q}|0\xi\rangle$$
$$-\langle 0\xi|\rho_q|0\xi\rangle\langle 0\xi|\rho_{-q}|0\xi\rangle-N\}. \quad (II.19)$$

Equation (II.19) may be taken as the starting point of an analysis similar to that of Nozières and Pines.[1] It differs from the Nozières-Pines expression (II.10) only through the presence of $\langle 0\xi|\rho_q|0\xi\rangle\langle 0\xi|\rho_{-q}|0\xi\rangle$ in (II.19). Since, however, these vanish for uniform systems apart from $q=0$, the advantage of introducing the generalized SCF theory is not yet apparent and will not become so until we express (II.19) in terms of the dielectric constant. To do that we must first develop a time-dependent SCF formalism. The explicit dependence of the SCF $(1-\xi)V_S^{(0)}$ in the Hamiltonian (II.16) on $\xi$ provides a considerable advantage over the fixed SCF usually introduced.[5]

## II.2 Time-Dependent SCF Theory

In ordinary quantum mechanics one treats time-dependent problems essentially by starting out from the Schrödinger equation

$$i\hbar\partial\Psi/\partial t=\mathfrak{K}\Psi, \quad (II.20)$$

which reduces to (II.9) for the time-independent problem. However, in the problems involving a self-consistent field, we have no energy operator to insert into (II.20), only an expression such as (II.15) for the energy itself. In the time-independent problem just discussed, that energy expression was used to derive a wave equation by insertion into the variational principle of ordinary quantum mechanics. For time-dependent problems, one can do the same.

The variational principle of which (II.20) is the Euler equation is

$$\delta\int_{-\infty}^{\infty} dt\left[(\Psi,\mathfrak{K}\Psi)-i\hbar(\Psi,\partial\Psi/\partial t)\right]=0. \quad (II.21)$$

To obtain the time-dependent SCF equation, we

substitute for $(\Psi, \mathcal{3C}\Psi)$ in (II.21) the SCF energy

$$E(\Psi) = (\Psi, K\Psi) + \tfrac{1}{2}\sum_q v_q(\Psi, \rho_q\Psi)(\Psi, \rho_{-q}\Psi)$$
$$+ \tfrac{1}{2}\xi \sum_q v_q\{(\Psi, \rho_q\rho_{-q}\Psi)$$
$$- (\Psi, \rho_q\Psi)(\Psi, \rho_{-q}\Psi) - N\} \quad (II.22)$$

and carry out the variation. We get, as might be expected,

$$i\hbar\partial\Psi/\partial t = \mathcal{3C}_S\Psi, \quad (II.23)$$

where

$$\mathcal{3C}_S = K + (1-\xi)V_S(\Psi) + \tfrac{1}{2}\xi\sum_q v_q\{\rho_q\rho_{-q} - N\} \quad (II.24)$$

$$V_S(\Psi) = \sum_q v_q(\Psi, \rho_q\Psi)\rho_{-q}. \quad (II.25)$$

Although $\langle 0\xi | \rho_q | 0\xi \rangle$ must vanish, $(\Psi, \rho_q\Psi)$ need not. The advantage for uniform systems of the SCF procedure over the procedure of Nozières and Pines, in fact, resides in this difference between time-dependent problems, e.g., in which $\Psi$ is a mixed state or an external perturbation acts.

We now define the density matrix P (read "capital rho") as the direct product of $\Psi$ with $\Psi^*$ as usual; its equation of motion is, from (II.23),

$$i\hbar\partial P/\partial t = [\mathcal{3C}_S, P]. \quad (II.26)$$

For its representation we need a complete set of functions. The eigenfunctions $|m\xi\rangle$ of $\mathcal{3C}_S{}^0$ are most convenient,

$$\mathcal{3C}_S{}^0|m\xi\rangle = \mathcal{E}_m|m\xi\rangle. \quad (II.27)$$

To emphasize the diagonal character of $\mathcal{3C}_S{}^0$ in this representation, we write for it $\mathcal{E}$, a diagonal matrix the elements of which are the $\mathcal{E}_m$. Thus (II.26) becomes

$$i\hbar\partial P/\partial t = [\mathcal{E}, P] + (1-\xi)[\Delta V_S, P], \quad (II.28)$$

where

$$\Delta V_S \equiv V_S(\Psi) - V_S{}^0. \quad (II.29)$$

Equation (II.28) must be solved self-consistently with

$$V_S(\Psi) = \sum_q v_q(\mathrm{Tr}P\rho_q)\rho_{-q}. \quad (II.25')$$

## II.3 The Dielectric Function

We now suppose that an external potential acts on the system, adding to the Hamiltonian a term $\mathcal{3C}_1$ which is a sum of one electron operators depending on position as $e^{-i\mathbf{q}\cdot\mathbf{r}}$ and not on momentum,[14] and depending on time as $\exp[(i\omega + \alpha)t]$, $\alpha \to 0^+$,

$$\mathcal{3C}_1 = A_q\rho_{-q}, \quad A_q \propto e^{i\omega t}e^{\alpha t}, \quad \alpha \to 0^+. \quad (II.30)$$

Initially, at $t = -\infty$, the system is in the ground state with

$$P_{nm} = P_{nm}{}^0 = \delta_{m0}\delta_{n0}. \quad (II.31)$$

As the system evolves, a term of order $\mathcal{3C}_1$ appears in P, $P^{(1)}$, so that $\Delta V_S$ is also of order $\mathcal{3C}_1$. Linearizing the

[14] It is a simple matter to generalize this to momentum-dependent potentials; *vid.* the following note: P. Pascual and L. M. Falicov, Phys. Rev. **129**, 1310 (1963).

equation of motion (II.28), we get

$$i\hbar\partial P/\partial t^{(1)} = [\mathcal{E}, P^{(1)}] + (1-\xi)[\Delta V_S, P^0] + [\mathcal{3C}_1, P^0]. \quad (II.32)$$

Putting (II.32) into component form and integrating, we obtain for the nonvanishing elements

$$P_{0n}{}^{(1)} = \frac{[(1-\xi)\langle 0\xi|\Delta V_S|n\xi\rangle + \langle 0\xi|\mathcal{3C}_1|n\xi\rangle]}{\hbar[(\omega-\omega_{n0}) - i\alpha]},$$
$$n \neq 0, \quad (II.33)$$

where

$$\hbar\omega_{n0} = \mathcal{E}_n - \mathcal{E}_0. \quad (II.34)$$

The change produced in the expectation value of $\rho_{q'}$ by $\mathcal{3C}_1$ is

$$\Delta\langle\rho_{q'}\rangle = \sum_n{}' P_{0n}{}^{(1)}\langle n\xi|\rho_{q'}|0\xi\rangle$$
$$+ \sum_n{}' P_{n0}{}^{(1)}\langle 0\xi|\rho_{q'}|n\xi\rangle. \quad (II.35)$$

Substituting (II.28), (II.25'), and (II.30) into (II.35), we obtain for $\Delta\langle\rho_{q'}\rangle$

$$\Delta\langle\rho_{q'}\rangle - \sum_{q''}[\mathfrak{D}(q',q'')(1-\xi)v_{q''}]\Delta\langle\rho_{q''}\rangle$$
$$= \mathfrak{D}(q',q)A_q, \quad (II.36)$$

where

$$\mathfrak{D}(q',q'') = \frac{1}{\hbar}\sum_n{}'\left\{\frac{\langle 0\xi|\rho_{q'}|n\xi\rangle\langle n\xi|\rho_{-q''}|0\xi\rangle}{-(\omega+\omega_{n0}) + i\alpha}\right.$$
$$\left. + \frac{\langle 0\xi|\rho_{-q''}|n\xi\rangle\langle n\xi|\rho_{q'}|0\xi\rangle}{(\omega-\omega_{n0}) - i\alpha}\right\}, \quad (II.37)$$

and the primed sum means exclusion of the $n=0$ term.

Up to this point we have not made explicit use of the translation invariance of the system, in order to lay the ground work for a later treatment of nonuniform systems. Restricting ourselves to the uniform case, translation invariance arguments applied to the matrix elements in (II.37) quickly show us that $\mathfrak{D}(q',q'')$ vanishes unless $q' = q''$. Thus $\Delta\rho_{q'}$ vanishes unless $q = q'$, and

$$\Delta\langle\rho_q\rangle = \frac{\mathfrak{D}_q(\omega)}{1 - (1-\xi)v_q\mathfrak{D}_q(\omega)}A_q, \quad (II.38)$$

where $\mathfrak{D}(q,q)$ has been abbreviated to $\mathfrak{D}_q$ and the frequency dependence made explicit.

Consider now a test particle at $\mathbf{r}_0$ which interacts both with all the particles in the system and the external potential as well. The total potential acting on the test particle is thus

$$\mathcal{U} = \sum_i v(|\mathbf{r}_0 - \mathbf{r}_i|) + A_q e^{i\mathbf{q}\cdot\mathbf{r}_0}. \quad (II.39)$$

The change in the average $\mathcal{U}$ induced by the external potential is, recalling (II.2) and (II.3),

$$\Delta\langle\mathcal{U}\rangle = [v_q\Delta\langle\rho_q\rangle + A_q]e^{i\mathbf{q}\cdot\mathbf{r}_0}. \quad (II.40)$$

But this, according to (II.38), is proportional to $A_q$

itself,

$$\Delta\langle\mathcal{U}\rangle=\frac{A_q e^{i\mathbf{q}\cdot\mathbf{r}_0}}{\epsilon(\mathbf{q},\omega;\,\xi)},\qquad(\text{II.41})$$

where

$$\epsilon(\mathbf{q},\omega;\,\xi)=1-\frac{v_q\mathcal{D}_q(\omega)}{1+\xi v_q\mathcal{D}_q(\omega)}.\qquad(\text{II.42})$$

We now appeal to analogy with the longitudinal electromagnetic case. There the interaction is the Coulomb interaction, and the total Coulomb acting on a test charge equals that from the external charge distribution divided by the dielectric constant, or preferably dielectric function, considering the frequency and wave number dependence. Thus $\epsilon(\mathbf{q},\omega;\,\xi)$ is a kind of frequency and wave number dependent dielectric function. We note that for $\xi=1$, i.e., the actual problem, Eq. (II.42) reduces to the result of Nozières and Pines[1]

$$\epsilon(\mathbf{q},\omega;\,1)=\frac{1}{1+v_q\mathcal{D}_q(\omega)}.\qquad(\text{II.43})$$

However, for $\xi=0$, the dielectric function does not reduce to one as it would in the Nozières-Pines theory for $\lambda=0$, but instead to the Hartree dielectric function first given by Lindhard[8,9]

$$\epsilon(\mathbf{q},\omega;\,0)=1+v_q\sum_{\mathbf{k}}\frac{f_{\mathbf{k}}-f_{\mathbf{k}+\mathbf{q}}}{(E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}})-\hbar\omega-i\hbar\alpha}.\qquad(\text{II.44})$$

We get a nontrivial dielectric constant even for $\xi=0$ because we have never assumed the electric charge, or its equivalent, to vanish.

## II.4 The Ground-State Energy

From the definition (II. 37) of $\mathcal{D}(\mathbf{q}',\mathbf{q}'')$, it follows that[15]

$$\frac{\hbar}{\pi}\int_0^\infty \text{Im}\mathcal{D}_q(\omega)d\omega$$

$$=\sum_n{}'\langle 0\xi|\rho_{-\mathbf{q}}|n\xi\rangle\langle n\xi|\rho_{\mathbf{q}}|0\xi\rangle$$

$$=[\langle 0\xi|\rho_{\mathbf{q}}\rho_{-\mathbf{q}}|0\xi\rangle-\langle 0\xi|\rho_{\mathbf{q}}|0\xi\rangle\langle 0\xi|\rho_{-\mathbf{q}}|0\xi\rangle]$$

$$=\langle 0\xi|\rho_{\mathbf{q}}\rho_{-\mathbf{q}}|0\xi\rangle(1-\delta_{\mathbf{q},0}),\qquad(\text{II.45})$$

where the last line holds only in the uniform case. Comparing (II.45) with (II.19), we see that

$$\frac{dE_0(\xi)}{d\xi}=\frac{\hbar}{2\pi}\sum_{\mathbf{q}}\int_0^\infty v_q\,\text{Im}\mathcal{D}_q(\omega)d\omega-\frac{N}{2}\sum_{\mathbf{q}}v_q.\qquad(\text{II.46})$$

Inverting (II.42) to get $v_q\mathcal{D}_q(\omega)$ and inserting the

result into (II.46), we obtain

$$E_0(1)=E_0(0)-\frac{\hbar}{2\pi}\int_0^1 d\xi\sum_{\mathbf{q}}\int_0^\infty d\omega$$

$$\times\text{Im}\left\{\frac{\epsilon(\mathbf{q},\omega;\,\xi)-1}{1+\xi[\epsilon(\mathbf{q},\omega;\,\xi)-1]}\right\}-\sum_{\mathbf{q}}\frac{Nv_q}{2}\quad(\text{II.47})$$

for the ground-state energy. The $\mathbf{q}=0$ term absent in the last line of (II.45) is either already included in the Hartree energy $E_0(0)$ or cancelled altogether, as for an electron gas.

There are significant differences between (II.47) and (I.1). The parameter $\xi$ enters explicitly into (II.47) in such a way that it is possible to use $\epsilon(\mathbf{q},\omega;\,0)$ as a $\xi$-independent approximation to the dielectric constant and get a meaningful result. Writing

$$\epsilon(\mathbf{q},\omega;\,0)=1+A+i\Sigma\qquad(\text{II.48})$$

gives

$$\text{Im}\frac{\epsilon-1}{1+\xi(\epsilon-1)}=\frac{\Sigma}{(1+\xi A)^2+(\xi A)^2}.\qquad(\text{II.49})$$

Supposing that $\Sigma$ and $A$ are independent of $\xi$ gives

$$\int_0^1 d\xi\,\text{Im}\frac{\epsilon-1}{1+\xi(\epsilon-1)}=\tan^{-1}\frac{\Sigma}{1+A}.\qquad(\text{II.50})$$

Inserting (II.50) into (II.47) after interchanging the integration on $\xi$ with those on $\mathbf{q}$ and $\omega$ gives Hubbard's first result[4] when the $\xi=0$ limit, i.e., the Hartree approximation, is taken for $\epsilon$. This result was established by Hubbard by use of perturbation theory and could be recaptured by Nozières and Pines from Eq. (I.1) only after an equivalent perturbation analysis of $\epsilon$. In contrast, the result follows trivially out of the present theory.

Hubbard[4] has pushed beyond Eq. (II.50) by a rough evaluation of higher diagrams in the perturbation theory, and Suhl and Werthamer[7] have also by an equation of motion analysis. In both treatments there is no self-evident convergence parameter other than $r_s$, which is a doubtful one. Questions of convergence and criteria for the selection of terms are difficult; indeed there are objections to Hubbard's results.[16] In the present theory, $\xi$ itself is a natural convergence parameter. Preliminary investigations show that a modification of the Martin-Schwinger theory[17] based on the present formalism appears to be a promising way to get at the higher order $\xi$ dependence of $\epsilon$.

The conditions for the existence of the integral over $\xi$ in (II.49) are of great interest, but unfortunately we have no idea what they are. One cannot investigate the existence of the integral by interchanging the $\xi$ integra-

[15] Provided $\mathcal{E}_n>\mathcal{E}_0$, which is true for uniform systems from (II.18). For nonuniform systems, a deeper discussion is required and is given in Sec. III.

[16] The higher approximation to the dielectric function given by Hubbard in reference 4 is unsatisfactory. See L. M. Falicov and V. Heine, Advan. Phys. 10, 57 (1961).

[17] P. C. Martin and J. Schwinger, Phys. Rev. 115, 1342 (1959).

tion with the **q** and $\omega$ integrations as has been done. Whatever the domain of validity of (II.49), it is probably larger than that of (I.1). However, the low-density electron gas probably cannot be described with the present theory without elimination from the beginning of the interaction of each electron with its own average charge distribution present in the SCF theory. This consideration suggests that although iteration by use of $\xi$ may give more rapid convergence than expansion in $r_s$, the densities at which both break down are comparable.

One can, with reason, object to the introduction of (II.47) as an essentially new result on the following grounds. For the uniform case $V_S^0$ vanishes so that $\mathcal{K}_S^0$ is the same as the actual $\mathcal{K}$ but for a reduction of the strength of the interaction by the factor $\xi$. Thus, the integrand in (II.47) must be the same function of $\xi$ as the integrand in (I.1) is of $\lambda$, and (II.47) can indeed be derived from (I.1) by reordering the perturbation expression for $\mathfrak{D}_q(\omega)$ (obtained without self-consistent field) in terms of its "proper parts."[18] However, such a derivation is to some tastes more cumbersome than the present one, makes use of perturbation theory, provides no natural expansion parameter, gives no physical interpretation of the proper part of $\mathfrak{D}_q(\omega)$ as a SCF dielectric function, and provides no particular basis for going on to nonuniform systems.

### III. NONUNIFORM SYSTEMS: THE MANY-ELECTRON GROUND STATE ENERGY

The particular nonuniform system we consider here as a specific example is that of a collection of $N$ electrons (index $i$, $j$) and nuclei (index $a$, $b$ and charges $Z_a$, $\sum_a Z_a = N$) fixed in as yet unspecified positions. The general kind of theory developed here is of interest also in connection with finite nuclei, atoms, or molecules, but a variety of special problems encountered there make it unprofitable to make the discussion general enough for both types of systems. The many-electron Hamiltonian is

$$\mathcal{K} = \sum_i \frac{P_i^2}{2m} + \frac{1}{2}\sum_{ij}' \frac{e^2}{r_{ij}} - \sum_{ia} \frac{Z_a e^2}{R_{ia}} + \frac{1}{2}\sum_{ab}' \frac{Z_a Z_b e^2}{R_{ab}}. \quad \text{(III.1)}$$

By defining

$$S_q \equiv -\sum_a Z_a e^{-i q \cdot R_a} \quad \text{(III.2)}$$

and recalling from Eqs. (II.2) and (II.3) that $v(r) = e^2/r$ so that $v_q = 4\pi e^2/q^2\Omega$, (III.1) may be written

$$\mathcal{K} = K + \frac{1}{2}\sum_q v_q\{(\rho_q + S_q)(\rho_{-q} + S_{-q}) - N - \sum_a Z_a^2\}, \quad \text{(III.3)}$$

where $K$, $\rho_q$, and $\Omega$ have their previous meanings [Eqs. (II.3) and (II.4)]. The ground state $|01\rangle$ has

the energy $E_0(1)$

$$E_0(1) = \langle 01|\mathcal{K}|01\rangle = \langle 01|K|01\rangle + \frac{1}{2}\sum_q v_q\{\langle 01|\rho_q\rho_{-q}|01\rangle + S_q\langle 01|\rho_{-q}|01\rangle + \langle 01|\rho_q|01\rangle S_{-q} + S_q S_{-q} - N - \sum_a Z_a^2\}. \quad \text{(III.4)}$$

Variation of (III.4) with respect to $|01\rangle$ of course produces the Schrödinger equation, but we go on instead to a generalized SCF theory like that of Sec. II.

The SCF approximation to (III.4) is

$$E_0(0) = \langle 00|K|00\rangle + \frac{1}{2}\sum_q v_q\{(\langle 00|\rho_q|00\rangle + S_q) \times (\langle 00|\rho_{-q}|00\rangle + S_{-q}) - \sum_a Z_a^2\}. \quad \text{(III.5)}$$

The linear combination $(1-\xi)E_0(0) + \xi E_0(1)$ produces, as before, the generalized SCF expression for the energy

$$E_0(\xi) = \langle 0\xi|K|0\xi\rangle + \frac{1}{2}\sum_q v_q\{(\langle 0\xi|\rho_q|0\xi\rangle + S_q) \times (\langle 0\xi|\rho_{-q}|0\xi\rangle + S_{-q}) - \sum_a Z_q^2\} + \frac{1}{2}\xi\sum_q v_q\{\langle 0\xi|\rho_q\rho_{-q}|0\xi\rangle - \langle 0\xi|\rho_q|0\xi\rangle\langle 0\xi|\rho_{-q}|0\xi\rangle - N\}. \quad \text{(III.6)}$$

Varying (III.6) leads to

$$\mathcal{K}_S^0|0\xi\rangle = \mathcal{E}_0(\xi)|0\xi\rangle, \quad \text{(III.7)}$$

$$\mathcal{K}_S^0 = K + V_S^0 + \frac{1}{2}\xi\sum_q v_q\{\rho_q\rho_{-q} - N\}, \quad \text{(III.8)}$$

$$V_S^0 = \sum_q v_q\{(1-\xi)\langle 0\xi|\rho_q|0\xi\rangle + S_q\}\rho_{-q}, \quad \text{(III.9)}$$

$$E_0(\xi) = \mathcal{E}_0(\xi) + \frac{1}{2}\sum_q\{-(1-\xi)\langle 0\xi|\rho_q|0\xi\rangle \times \langle 0\xi|\rho_{-q}|0\xi\rangle + S_q S_{-q} - \sum_a Z_a^2\}, \quad \text{(III.10)}$$

$$\frac{dE_0(\xi)}{d\xi} = \frac{1}{2}\sum_q v_q\{\langle 0\xi|\rho_q\rho_{-q}|0\xi\rangle - \langle 0\xi|\rho_q|0\xi\rangle\langle 0\xi|\rho_{-q}|0\xi\rangle - N\}. \quad \text{(III.11)}$$

Note that $dE_0(\xi)/d\xi$ is formally the same as for the uniform case.

For an arbitrary, time-dependent wave function $\Psi$, the energy $E(\Psi)$ to be inserted into the variational principle (II.21) is obtained from (III.6) by substituting $\Psi$ for $|0\xi\rangle$. There results

$$i\hbar\partial\Psi/\partial t = \mathcal{K}_S\Psi, \quad \text{(III.12)}$$

$$\mathcal{K}_S = \mathcal{K}_S^0 + \Delta V_S(\Psi), \quad \text{(III.13)}$$

$$\Delta V_S(\Psi) = (1-\xi)\sum_q v_q\Delta\langle\rho_q\rangle\rho_{-q}, \quad \text{(III.14)}$$

$$\Delta\langle\rho_q\rangle = (\Psi,\rho_q\Psi) - \langle 0\xi|\rho_q|0\xi\rangle. \quad \text{(III.15)}$$

Comparison of Eqs. (III.12)–(III.15) with Eqs. (II.23)–(II.25) shows that the development of Sec. (II.2) from Eq. (II.26) on and the development of Sec. (II.3) up through Eqs. (II.36) and (II.37) for $\Delta\langle\rho_q\rangle$ can be carried over unchanged.

The theory of the dielectric constant, however, is substantially different in the nonuniform case.[19-21] Although Eq. (II.39) still furnishes the starting point,

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[18] We are indebted to Dr. F. Englert for discussion of this point.

[19] D. S. Falk, Phys. Rev. **118**, 105 (1960).
[20] S. L. Adler, Phys. Rev. **126**, 413 (1962).
[21] N. Wiser, Phys. Rev. **129**, 62 (1963).

Eq. (II.40) must be generalized to

$$\Delta\langle \mathcal{V}\rangle = \sum_{\mathbf{q}'}[v_{\mathbf{q}'}\Delta\langle\rho_{\mathbf{q}'}\rangle + A_{\mathbf{q}}\delta_{\mathbf{q}\mathbf{q}'}]e^{i\mathbf{q}'\cdot\mathbf{r}_0}. \quad \text{(III.16)}$$

The proportionality of $\Delta\langle\rho_{\mathbf{q}'}\rangle$ to $A_{\mathbf{q}}$ permits us to rewrite (III.16) as

$$\Delta\langle \mathcal{V}\rangle = \sum_{\mathbf{q}'} \epsilon^{-1}(\mathbf{q}',\mathbf{q};\omega;\xi)A_{\mathbf{q}}e^{i\mathbf{q}'\cdot\mathbf{r}_0}, \quad \text{(III.17)}$$

where $\epsilon^{-1}(\mathbf{q}',\mathbf{q})$ is an element of the inverse dielectric function, now in the form of a matrix. Solving Eq. (II.36) formally for $\Delta\langle\rho_{\mathbf{q}'}\rangle$ and inserting into (III.16), we obtain

$$\epsilon^{-1}(\mathbf{q}',\mathbf{q};\omega;\xi) = \delta_{\mathbf{q}'\mathbf{q}} + \sum_{\mathbf{q}''} v_{\mathbf{q}'}\mathfrak{M}_{\mathbf{q}'\mathbf{q}''}\mathfrak{D}(\mathbf{q}'',\mathbf{q}), \quad \text{(III.18)}$$

$$(\mathfrak{M}^{-1})_{\mathbf{q}'\mathbf{q}''} = \delta_{\mathbf{q}'\mathbf{q}''} - (1-\xi)\mathfrak{D}(\mathbf{q}',\mathbf{q}'')v_{\mathbf{q}''}. \quad \text{(III.19)}$$

We need $v_{\mathbf{q}}\mathfrak{D}(\mathbf{q},\mathbf{q})$. It is easiest to solve (III.18) and (III.19) for this quantity symbolically, defining $\boldsymbol{\varepsilon}^{-1}$ as the matrix with elements $\epsilon^{-1}(\mathbf{q}',\mathbf{q})$, $\boldsymbol{v}$ as the matrix with elements $v_{\mathbf{q}}\delta_{\mathbf{q}\mathbf{q}'}$, etc. The result is

$$\boldsymbol{v}\cdot\mathfrak{D} = -(\boldsymbol{\varepsilon}-\mathbf{I})\cdot[\mathbf{I}+\xi(\boldsymbol{\varepsilon}-\mathbf{I})]^{-1}. \quad \text{(III.20)}$$

Proceeding as in Eqs. (II.45)–(II.47), we obtain

$$E_0(1) = E_0(0) - \frac{\hbar}{2\pi}\int_0^1 d\xi \sum_{\mathbf{q}} \int_0^\infty d\omega \, \mathrm{Im}\{(\boldsymbol{\varepsilon}-\mathbf{I})$$
$$\cdot[\mathbf{I}+\xi(\boldsymbol{\varepsilon}-\mathbf{I})]^{-1}\}_{\mathbf{q}\mathbf{q}} - \sum_{\mathbf{q}}\frac{Nv_{\mathbf{q}}}{2} \quad \text{(III.21)}$$

for the ground-state energy of the system of electrons and nuclei under consideration. The only difference in form between (III.21) and (II.47) is the appearance of $\boldsymbol{\varepsilon}$ as a matrix in the former and $\epsilon$ as a number in the latter. The formula (III.21) should be compared with the corresponding formula developed by Hubbard from perturbation theory.[5]

In the derivation of (III.21), the tacit assumption was made that the wave function $|0\xi\rangle$ corresponding to the minimum possible value of $E(\xi)$, $E_0(\xi)$, is also the ground state of the Hamiltonian $\mathcal{H}_s^0$, i.e., that $\mathcal{E}_0(\xi)$ in (III.7) is the lowest eigenvalue of $\mathcal{H}_s^0$. The integration over frequency in (III.21) would otherwise extend over negative frequencies. Further, if $\mathcal{E}_0(\xi)$ were not the lowest eigenvalue of $\mathcal{H}_s^0$, the statistical mechanics of the next section would not give the state of lowest total energy, $|0\xi\rangle$, as the only occupied state at zero temperature. Thus, it is essential for the success of the present theories that $\mathcal{E}_0(\xi)$ be the lowest eigenvalue of $\mathcal{H}_s^0$.

To explore this question we first define the total energy associated with an arbitrary wave function $\Psi$, $E(\Psi)$, by substituting $\Psi$ for $|0\xi\rangle$ in (III.6). Similarly we define

$$\mathcal{E}(\Psi) = (\Psi,\mathcal{H}_s^0\Psi).$$

It is easy to prove that

$$E(\Psi) - E_0 = \mathcal{E}(\Psi) - \mathcal{E}_0$$
$$+ \frac{1-\xi}{2}\sum_{\mathbf{q}} v_{\mathbf{q}}|(\Psi,\rho_{\mathbf{q}}\Psi) - \langle 0\xi|\rho_{\mathbf{q}}|0\xi\rangle|^2$$

by use of (III.10). Suppose now that $\mathcal{E}_0$ is the lowest eigenvalue of $\mathcal{H}_s^0$ and that $v_{\mathbf{q}}$ is repulsive. It immediately follows that $E(\Psi) \geq E_0$ from the above equation. Since $\Psi$ is arbitrary, it follows in turn that $E_0$ is the lowest possible value of the energy. We have thus proved that the self-consistent solution of (III.7), $|0\xi\rangle$, which is the ground state of its own self-consistent Hamiltonian $\mathcal{H}_s^0$, gives the minimum total energy for repulsive interactions. For attractive interactions, no such general proof appears possible, and an internally consistent generalized SCF theory may exist only conditionally. We do not intend to search for the required conditions on the attractive potential, as we are concerned primarily with applications to the electron theory of metals where the interactions are repulsive. We may speculate, however, that the potential must be such as not to admit either collective or few-particle bound states. Inasmuch as the uniform system with attractive interactions may show instability against collective or few-particle bound states, the reservations concerning the present theory expressed here for nonuniform systems probably should be extended also to uniform systems. The local increases, however, in particle density occurring in nonuniform systems can be expected to enhance such tendencies toward instability.

For a crystal, where the nuclei are periodically arranged, translation symmetry forces all matrix elements $\mathbf{q}\mathbf{q}'$ of $\mathfrak{D}$ or $\boldsymbol{\varepsilon}$ to vanish unless $\mathbf{q}'=\mathbf{q}+\boldsymbol{\kappa}$, where $\boldsymbol{\kappa}$ is $2\pi$ times a reciprocal lattice vector. Equation (III.20) simplifies to

$$v_{\mathbf{q}}\mathfrak{D}(\mathbf{q},\mathbf{q}) = -\sum_{\kappa}[\epsilon(\mathbf{q},\mathbf{q}+\kappa) - \delta_{\kappa,0}]W_{\kappa+q,q}, \quad \text{(III.22)}$$

$$(W^{-1})_{\kappa+q,q} = \delta_{\kappa,0} + \xi[\epsilon(\kappa+\mathbf{q},\mathbf{q}) - \delta_{\kappa,0}], \quad \text{(III.23)}$$

and Eq. (II.21) simplifies correspondingly. A simple approximation to (III.21) can be developed by using the $\xi=0$ approximation and neglecting all terms with $\kappa\neq0$ in (III.22). In this way one gets an expression identical to (II.47), with $\epsilon(\mathbf{q},\mathbf{q})$ from (III.22) and (III.23) replacing $\epsilon(\mathbf{q})$ from (II.42). For small $\mathbf{q}$, this is tantamount to neglecting local-field corrections to the dielectric constant[19]; for large $\mathbf{q}$ the simple concept of a local field loses its meaning. A still simpler approximation, of course, is to use the free-electron dielectric constant in (III.21); this has been shown to be reasonably accurate for atoms with small cores.[22] Thus Eq. (III.21) or Hubbard's theory[5] can be made to provide the basis for accurate band-structure calculations in

[22] M. H. Cohen and J. C. Phillips, Phys. Rev. 124, 1818 (1961).

crystals containing small cores, as Phillips and Kleinman have shown in detail for silicon.[23,24] In principle, all the elements necessary for the band structure calculations were already provided by Hubbard[23,24]; the present work, however, provides a much simpler basis for carrying them out.

## IV. STATISTICAL MECHANICS

We wish to derive an expression for the free energy of a uniform system analogous to Eq. (I.2). To do this it is necessary to generalize our SCF methods to finite temperature. We do so by replacing the expression (II.15) for the ground-state energy by

$$U = \mathrm{Tr}P_0 K + \tfrac{1}{2} \sum_q v_q [\mathrm{Tr}P_0\rho_q][\mathrm{tr}P_0\rho_{-q}]$$
$$+ \tfrac{1}{2}\xi \sum_q v_q \{ [\mathrm{tr}P_0\rho_q\rho_{-q}]$$
$$- [\mathrm{tr}P_0\rho_q][\mathrm{tr}P_0\rho_{-q}] - N \} \quad \text{(IV.1)}$$

for the average total energy in thermal equilibrium $U$, where $P_0$ is now the density matrix for thermal equilibrium. We define the free energy to be

$$F = U + kT[\mathrm{tr}P_0 \ln P_0]. \quad \text{(IV.2)}$$

We now apply the variation principle

$$\delta F = 0, \quad \text{(IV.3)}$$

subject to

$$\delta \, \mathrm{tr}P_0 = 0, \quad P_0^\dagger = P_0 \quad \text{(IV.4)}$$

to (IV.1) and (IV.2), and obtain for $P_0$

$$P_0 = \exp[(\psi - \mathcal{3C}_S^0)/kT], \quad \text{(IV.5)}$$

where

$$\mathcal{3C}_S^0 = K + (1-\xi)V_S^0 + \tfrac{1}{2}\xi \sum_q v_q\{\rho_q\rho_{-q} - N\}, \quad \text{(IV.6)}$$

$$V_S^0 = \sum_q v_q[\mathrm{tr}P_0\rho_q]\rho_{-q}, \quad \text{(IV.7)}$$

$$\psi = F + \frac{1-\xi}{2} \sum_q v_q[\mathrm{tr}P_0\rho_q][\mathrm{tr}P_0\rho_{-q}]. \quad \text{(IV.8)}$$

To obtain a convenient representation for $P_0$, we diagonalize $\mathcal{3C}_S^0$:

$$\mathcal{3C}_S^0 |m\rangle = \mathcal{E}_m |m\rangle. \quad \text{(IV.9)}$$

The eigenfunction $|m\rangle$ and eigenvalues $\mathcal{E}_m$ of $\mathcal{3C}_S^0$ are now, in principle, temperature dependent because of the presence of $V_S^0$ in $\mathcal{3C}_S^0$. In this representation, we have

$$(P_0)_{mn} = \exp[(\psi - \mathcal{E}_m)/kT]\delta_{mn} \equiv p_m\delta_{mn}. \quad \text{(IV.10)}$$

Equations (IV.9) and (IV.10) form the basis of the self-consistent determination of $P_0$. Alternatively, $P_0$ can be approximately determined by variation of parameters in (IV.1).

We retain in the present theory the probabilistic interpretation of the density matrix, so that $(P_0)_{mm}$ is the probability of the system being in the state $m$. More explicitly, we imagine that we are dealing with an ensemble of systems, each with a wave function $\Psi$, the time development of which is governed by the

[23] J. C. Phillips, Phys. Rev. **123**, 420 (1961).
[24] J. C. Phillips and L. Kleinman, Phys. Rev. **128**, 2098 (1962).

Hamiltonian $\mathcal{3C}_S^0$. The density matrix must be the ensemble average of the direct product of $\Psi$ and $\Psi^*$. Expanding $\Psi$ in the $|m\rangle$,

$$\Psi = \sum_m a_m |m\rangle, \quad \text{(IV.11)}$$

we have

$$(P_0)_{mn} = \langle a_m a_n^* \rangle_{\mathrm{av}}^0, \quad \text{(IV.12)}$$

where $\langle \ \rangle_{\mathrm{av}}^0$ means averaging over an equilibrium ensemble. For the nonequilibrium, time-dependent ensemble, the density matrix $P$ is still the ensemble average of the direct product of $\Psi$ with $\Psi^*$, but the time evolution of $\Psi$ is governed by $\mathcal{3C}_S$ obtained by substituting $P$ for $P_0$ in (IV.6) and (IV.7),

$$i\hbar\partial\Psi/\partial t = \mathcal{3C}_S\Psi. \quad \text{(IV.13)}$$

Thus, the probabilistic interpretation of $P$ leads directly to

$$i\hbar\partial P/\partial t = [\mathcal{3C}_S, P] \quad \text{(IV.14)}$$

for the equation of motion of $P$.[25]

From this point on, because in Eq. (IV.14) we have recaptured Eq. (II.26), the development closely parallels that of Sec. II. Here $\Delta\langle\rho_{q'}\rangle$ is defined as

$$\Delta\langle\rho_{q'}\rangle = \mathrm{Tr}[(P - P_0)\rho_{q'}] \quad \text{(IV.15)}$$

and still is given by Eq. (II.36), but with $\mathfrak{D}(q,q'')$ now defined as

$$\mathfrak{D}(\mathbf{q'},\mathbf{q''}) = \frac{1}{\hbar} \sum_m p_m \sum_n{}' \left\{ \frac{\langle m|\rho_{q'}|n\rangle\langle n|\rho_{-q''}|m\rangle}{-(\omega+\omega_{nm})+i\alpha} \right.$$
$$\left. + \frac{\langle m|\rho_{-q''}|n\rangle\langle n|\rho_{q'}|m\rangle}{(\omega-\omega_{nm})-i\alpha} \right\}. \quad \text{(IV.16)}$$

Invoking now, for the first time, the translation invariance of the system, $\mathfrak{D}(\mathbf{q'},\mathbf{q''})$ vanishes unless $\mathbf{q'} = \mathbf{q''}$, so we set $\mathfrak{D}(\mathbf{q},\mathbf{q}) = \mathfrak{D}_q(\omega)$. Further, it may be shown by simple manipulation[2] that

$$\mathrm{Im}\mathfrak{D}_q(\omega) = [1 - e^{-\hbar\omega/kT}]\frac{\pi}{\hbar}\sum_m p_m \sum_n{}' \langle m|\rho_{-q}|n\rangle$$
$$\times \langle n|\rho_q|m\rangle\delta(\omega_{nm} - \omega). \quad \text{(IV.17)}$$

From (IV.17) it follows that

$$\frac{\hbar}{\pi} \int_{-\infty}^{\infty} d\omega \, [1 - e^{-\hbar\omega/kT}]^{-1} \mathrm{Im}\mathfrak{D}_q(\omega)$$
$$= \mathrm{Tr}(P_0\rho_q\rho_{-q}) - \sum p_m\langle m|\rho_q|m\rangle\langle m|\rho_{-q}|m\rangle$$
$$= \mathrm{Tr}P_0\rho_q\rho_{-q}(1 - \delta_{q,0}). \quad \text{(IV.18)}$$

For a uniform system $\langle m|\rho_q|m\rangle$ vanishes except for $\mathbf{q} = 0$. Further, because of the stationarity of $F$ with respect to $P_0$,

$$dF/d\xi = \tfrac{1}{2}\sum_q v_q\{\mathrm{Tr}(P_0\rho_q\rho_{-q}) - (\mathrm{Tr}P_0\rho_q)(\mathrm{Tr}P_0\rho_{-q}) - N\}$$
$$= \tfrac{1}{2}\sum_q v_q\{\mathrm{Tr}(P_0\rho_q\rho_{-q})(1 - \delta_{q0}) - N\}. \quad \text{(IV.19)}$$

[25] The above theory can be readily generalized to hold for open systems. $P$ then has the grand canonical form, and $\mathcal{3C}_S - \mu N$ everywhere replaces $\mathcal{3C}_S$ in the formalism, where $\mu$ is the chemical potential.

Comparing (IV.18) with (IV.19) and noting that the relation between $\mathfrak{D}_q(\omega)$ and the dielectric constant is unchanged by the introduction of a finite temperature, we obtain the SCF analog of Eq. (I.2)

$$F(1)=F(0)-\frac{\hbar}{2\pi}\int_0^1 d\xi \sum_q \left[\int\int_{-\infty}^{\infty} d\omega \frac{1}{1-e^{-\hbar\omega/kT}}\right.$$

$$\left.\times \mathrm{Im}\left\{\frac{\epsilon-1}{1+\xi(\epsilon-1)}\right\}\right]-\sum_q \frac{Nv_q}{2}. \quad (IV.20)$$

Again, the advantages of this formula over that of Englert and Brout, Eq. (I.2), are a more rapid convergence of the integral over $\xi$ than of the integral over $\lambda$ and a wider regime of existence of the integral. For $\xi=0$, the dielectric constant is given by Eq. (II.44) where the $f_k$ are now the temperature-dependent Fermi factors.[12] It would provide an approximation to (IV.20) equivalent to (II.50).

We now turn to the generalization to finite temperature of Eq. (III.21) for nonuniform systems. The development of the statistical mechanics proceeds as in the earlier part of this section, that development being sufficiently general. Further, the relationship between $v_q\mathfrak{D}(\mathbf{q},\mathbf{q})$, as defined in (IV.16), and the dielectric function remains the same as in Sec. II. The only novel element arises in relating $\mathfrak{D}(\mathbf{q},\mathbf{q})$ to $dF/d\xi$.

Equation (IV.18) holds, before its final simplification for the nonuniform system as well,

$$\frac{\hbar}{\pi}\int_{-\infty}^{\infty} d\omega \left[1-e^{-\hbar\omega/kT}\right]^{-1} \mathrm{Im}\mathfrak{D}(\mathbf{q},\mathbf{q})$$

$$=\mathrm{Tr}(P_0\rho_q\rho_{-q})-\sum_m p_m\langle m|\rho_q|m\rangle\langle m|\rho_{-q}|m\rangle, \quad (IV.18')$$

and so does (IV.19),

$$dF/d\xi=\tfrac{1}{2}\sum_q v_q\{\mathrm{Tr}(P_0\rho_q\rho_{-q})$$

$$-(\mathrm{Tr}P_0\rho_q)(\mathrm{Tr}P_0\rho_{-q})-N\}. \quad (IV.19')$$

Comparing these two equations we see that the desired formula can be constructed only if

$$(\mathrm{Tr}P_0\rho_q)(\mathrm{Tr}P_0\rho_{-q})=\sum_m p_m\langle m|\rho_q|m\rangle\sum_n p_n\langle n|\rho_{-q}|n\rangle$$

can be shown to equal

$$\sum_m p_m\langle m|\rho_q|m\rangle\langle m|\rho_{-q}|m\rangle.$$

Let $X_m+iY_m$ stand for $\langle m|\rho_q|m\rangle$. We must show that $\langle X^2+Y^2\rangle_{av}$ in (IV.18') is a sufficiently good approximation to, or equals, $\langle X\rangle_{av}^2+\langle Y\rangle_{av}^2$ in (IV.19'). For the condensed systems to be considered here, crystals, liquid metals, etc., $X_m$ is a macroscopic variable for the important states in the average, ranging from $N^{1/2}$ to $N$ in its order. We may, therefore, invoke the Einstein theory of the fluctuations of a macroscopic variable as presented, for example, in Tolman's book[26] to argue

that the relative difference between $\langle X^2+Y^2\rangle_{av}$ and $\langle X\rangle_{av}^2+\langle Y\rangle_{av}^2$ is of order $kT/N$. It follows that

$$F(1)=F(0)-\frac{\hbar}{2\pi}\int_0^1 d\xi \sum_q \int_{-\infty}^{\infty} d\omega \frac{1}{1-e^{-\hbar\omega/kT}} \mathrm{Im}\{(\boldsymbol{\varepsilon}-\mathbf{I})$$

$$\cdot [\mathbf{I}+\xi(\boldsymbol{\varepsilon}-\mathbf{I})]^{-1}\}_{qq}-\sum_q \tfrac{1}{2}Nv_q. \quad (IV.21)$$

## V. THE GENERAL CASE

The following general theorem emerges from the analysis of the preceding sections:

*If* the Hamiltonian can be written in the form

$$\mathfrak{IC}=\mathfrak{IC}_0+\sum_q v_q O_q\cdot O_{-q}, \quad (V.1)$$

where $\mathfrak{IC}_0$ need not be spatially invariant and may contain interactions, e.g., the hard-core part of a potential, and where $O_q$ may be any operator, scalar, tensor, spin-dependent, or whatever, *then* a formula like (IV.21) holds with $\boldsymbol{\varepsilon}$ replaced by an appropriately generalized response function. In the course of proving the theorem by the methods of this paper, one establishes a generalized fluctuation-dissipation theorem relating $\langle O_q\cdot O_{-q}\rangle$ to the response function. Further, one can establish an equation of motion for $O_q$ or for $\langle O_q\rangle$, solve it by iteration, using $\xi$ as an ordering parameter for the iteration, and thus arrive at a power series expansion of the response function in $\xi$ to insert into the formula for the free energy.

One can obtain rapidly, clearly, and elegantly with the above method results already known for many-body problems, e.g., the electron gas,[3-5] Heisenberg ferromagnetism,[27-30] classical statistical mechanics,[31] and others. However, we have not yet obtained any essentially new results in the cited problems. We do expect to be able to obtain essentially new results by the introduction of our generalized SCF methods into the theory of thermodynamic Green's functions and its attendant approximation schemes.[17,32] Further, we have found the method perspicuous and very convenient for a development of the theory of real metals to be presented in later publications.[33]

[26] R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, New York, 1938), p. 636 ff.

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