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One-Particle Properties of an Inhomogeneous Interacting Electron Gas*

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In previous publications (especially by Hohenberg, Kohn, and Sham), a theory of the ground state of an inhomogeneous interacting electron gas was developed, in which the electronic density $n(\mathbf{r})$ played a dominant role. The present paper extends this approach to the one-particle Green's function and physical properties related to it, such as single-particle-like excitations and, in the case of metals, the Fermi surface. The Dyson mass operator Σ is studied as a function of its spatial arguments and as a functional of $n(\mathbf{r})$, and, in both senses, it is found to have important short-range properties. An approximation for Σ, which is exact for systems of slowly varying density, is proposed. This leads to simple, explicit, Schrödinger-like equations for the single-particle-like excitations, whose solution determines their energies and lifetimes. In particular, we show how to apply this procedure to metals.

I. INTRODUCTION

In this paper we shall be concerned with the one-particle Green's function[1] $G(\mathbf{r},\mathbf{r}';E)$ associated with the ground state of a system of interacting electrons moving in an external potential $v(\mathbf{r})$. As is well known, the Green's function determines a number of important physical properties of the system, in particular its single-particle-like excitations and, in the case of a metal, the Fermi surface. We shall give special attention to these properties.

The Green's function is a solution of the Dyson equation

$$(-E-\tfrac{1}{2}\nabla^2)G(\mathbf{r},\mathbf{r}';E)+\int d\mathbf{r}''\,\Sigma(\mathbf{r},\mathbf{r}'';E)\times G(\mathbf{r}'',\mathbf{r}';E)=-\delta(\mathbf{r}-\mathbf{r}''),\quad(1.1)$$

where Σ is the so-called mass operator. The same mass operator appears also in a Schrödinger-type equation, whose solution determines the spectrum of the one-particle elementary excitations (see Sec. II). Recently, Hohenberg and Kohn[2] have shown that any property of a system of electrons is a unique functional of the density $n(\mathbf{r})$ of the ground state. In particular then, Σ is such a functional. This fact by itself, however, is not yet useful for a practical determination of G and of the elementary excitations.

In Sec. III and the Appendix of this paper we show explicitly, in some simple cases, the following two more specific properties:

(a) $\Sigma(\mathbf{r},\mathbf{r}';E)$ is a *short-range* kernel, with a range of the order $|\mathbf{r}-\mathbf{r}'|\sim\lambda_F$ $(=2\pi/k_F)$, where k_F is the Fermi momentum corresponding to the local density.

(b) Let us write Σ in the form

$$\Sigma(\mathbf{r},\mathbf{r}';E)=\varphi(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')+M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0)),\quad(1.2)$$

where $\varphi(\mathbf{r}_0)$ is the electrostatic potential at $\mathbf{r}_0=\frac{1}{2}(\mathbf{r}+\mathbf{r}')$. Then the functional form of M depends only on the density $n(\mathbf{s})$ *in the vicinity* of $\mathbf{r}$ and $\mathbf{r}'$, in the sense of $|\mathbf{s}-\mathbf{r}_0|\sim\mathrm{Max}(\lambda_F,\lambda_{TF})$. (Here λ_F is the Fermi wavelength and λ_{TF} is the Thomas-Fermi screening length.) This property is a consequence of the Ward identities.[3] Such short-range properties would be expected on intuitive grounds. Although we shall formally establish them only in special cases, we believe that they have general validity. Inasmuch as the Green's function describes single-particle propagation, Eq. (1.1) combined with properties (a) and (b) then leads to a picture of particles propagating in the medium with an effective energy $E-\varphi(\mathbf{r})$, where φ is the local electrostatic potential, and under the influence of nonlocal forces which depend however only on the density distribution $n(\mathbf{s})$ in the vicinity of $\mathbf{r}$.

In Sec. IV. we make the simplest approximation consistent with (b), namely that M is the mass operator of a uniform electron gas with the local density $n(\mathbf{r}_0)$. This leads to a simple calculational scheme for G and thus for the single-particle-like excitations of the system.

In Sec. V we apply this method to electrons in metals and discuss quasiparticles, the Fermi surface, and the specific heat.

In a future publication we plan to present the results of using this theory for specific atomic and solid-state systems. In the meantime, we would like to draw attention to the rather encouraging numerical results obtained for ground-state energies and densities of atoms and ions,[4] using similar approximations.

II. THE GREEN'S FUNCTION AND ELEMENTARY EXCITATIONS

In this section we review briefly the formal connection between properties of the one-particle Green's function and elementary excitations in a form useful for inhomogeneous systems.

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* Supported in part by the U. S. Office of Naval Research.

[1] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Method of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963); J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960).

[2] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[3] P. Nozières and J. M. Luttinger, Phys. Rev. **127**, 1423 (1962); P. Nozières, *Theory of Interacting Fermi Systems* (W. A. Benjamin, Inc., New York, 1964).

[4] B. Y. Tong and L. J. Sham, Phys. Rev. **144**, 1 (1966).

A solution of the Dyson equation (1.1) can be constructed as follows.[5] We define the right and left eigenfunctions $\chi_n(\mathbf{r},E)$ and $\chi_n^\dagger(\mathbf{r},E)$ of the (energy-dependent) operator $-\frac{1}{2}\nabla^2+\Sigma$ belonging to the eigenvalue $\mathcal{E}_n(E)$ as follows:

$$(-\mathcal{E}_n(E)-\tfrac{1}{2}\nabla^2)\chi_n(\mathbf{r},E)+\int d\mathbf{r}'\times\Sigma(\mathbf{r},\mathbf{r}';E)\chi_n(\mathbf{r}',E)=0, \quad (2.1)$$

and

$$(-\mathcal{E}_n(E)-\tfrac{1}{2}\nabla^2)\chi_n^\dagger(\mathbf{r},E)+\int d\mathbf{r}'\times\chi_n^\dagger(\mathbf{r}',E)\Sigma(\mathbf{r}',\mathbf{r};E)=0. \quad (2.2)$$

Note that in general $\chi^\dagger$ is not the complex conjugate of χ. For every E, the χ_n, $\chi_n^\dagger$ satisfy the orthonormality relations

$$\int d\mathbf{r}\,\chi_n^\dagger(\mathbf{r},E)\chi_{n'}(\mathbf{r},E)=\delta_{nn'}. \quad (2.3)$$

In terms of these functions G is given by

$$G(\mathbf{r},\mathbf{r}';E)=\sum_n\frac{\chi_n(\mathbf{r},E)\chi_n^\dagger(\mathbf{r}',E)}{E-\mathcal{E}_n(E)}. \quad (2.4)$$

If the equation

$$E-\mathcal{E}_n(E)=0 \quad (2.5)$$

has a solution for some n and E, which we denote by E_n, then $G(\mathbf{r},\mathbf{r}';E)$ has a pole at E_n. It then follows from the spectral representation of G, that the $N+1$ or N-1 particle system has an eigenstate with this energy. Very often G does not have rigorous poles but there exist values of E for which, with a given value of n,

$$|E-\mathcal{E}_n(E)|=\text{local minimum}. \quad (2.6)$$

Such values of E signify approximate eigenstates of the $N+1$ or $N-1$ particle systems. In general, the values of E satisfying (2.6) are complex, in which case the real part should be associated with a physical energy and the imaginary part with a decay rate.

In the following sections we shall study the structure of the mass operator Σ and derive some simple approximations for it which allow us to solve the Schrödinger-type equation (2.1) and hence to obtain the (in general complex) energies of the single-particle excitations.

III. SHORT-RANGE PROPERTIES OF THE MASS OPERATOR

In this section we illustrate the short-range properties (a) and (b) of the mass operator Σ which were described in the Introduction.

For a homogeneous gas, the first-order exchange contribution to the mass operator is given by

$$M_1(\mathbf{r},\mathbf{r}';E)=-\frac{1}{|\mathbf{r}-\mathbf{r}'|}\times\left[\frac{\sin(k_F|\mathbf{r}-\mathbf{r}'|)-k_F|\mathbf{r}-\mathbf{r}'|\cos(k_F|\mathbf{r}-\mathbf{r}'|)}{2\pi^2|\mathbf{r}-\mathbf{r}'|^3}\right]. \quad (3.1)$$

This is an oscillatory function whose amplitude falls off as $|\mathbf{r}-\mathbf{r}'|^{-3}$ and whose scale is $1/k_F$. For large values of E, a term of just this kind, with the factor in brackets replaced by the exact one-particle density matrix, is the dominant part of the complete M. Graphical considerations lead us to believe that for all values of E the range of the actual mass operator is $1/k_F$.

We now turn to property (b) of the operator M defined in Eq. (1.2); i.e., that its functional form depends only on the density $n(\mathbf{s})$ in the vicinity of the points $\mathbf{r}$ and $\mathbf{r}'$.

We first note that by extracting from Σ the electrostatic potential term $\varphi(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$ and by writing the energy argument of the remaining part M as $E-\varphi(\mathbf{r}_0)$, the functional form of M is independent of any uniform shift of the electrostatic potential. This is a prerequisite for showing that M depends only on the electronic charge density near $\mathbf{r}$ and $\mathbf{r}'$.

We now demonstrate the asserted property for an electronic system of almost constant density,

$$n(\mathbf{r})=n_0+n_1(\mathbf{r}), \quad (3.2)$$

where n_1 is small and has zero spatial average.

We shall compare the mass operator of the system under consideration with that of a homogeneous electron gas with density n_0. Where necessary, quantities of the latter system will be distinguished by the subscript h. We shall show that

$$M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0))=M_h(\mathbf{r}-\mathbf{r}';E-\varphi(\mathbf{r}_0))+\int d\mathbf{s}\,M^{(1)}(\mathbf{r},\mathbf{r}';\mathbf{r}_0-\mathbf{s};E-\varphi(\mathbf{r}_0))n_1(\mathbf{s}), \quad (3.3)$$

where $M^{(1)}$ is a short-range function of $\mathbf{r}_0-\mathbf{s}$.

Imagine that the spatially varying density $n_1(\mathbf{r})$ is caused by a small external potential $v(\mathbf{r})$ acting on the homogeneous electron gas. By perturbation theory,

$$\Sigma(\mathbf{r},\mathbf{r}';E)=\Sigma_h(\mathbf{r},\mathbf{r}';E)+\frac{1}{(2\pi)^6}\int\int d\mathbf{k}\,d\mathbf{q}\times\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')+i\mathbf{q}\cdot\mathbf{r}_0]\Lambda(\mathbf{k},\mathbf{q};E)v(\mathbf{q}), \quad (3.4)$$

where Λ is the vertex function and $v(\mathbf{q})$ is the Fourier transform

$$v(\mathbf{q})=\int d\mathbf{r}\,e^{-i\mathbf{q}\cdot\mathbf{r}}v(\mathbf{r}). \quad (3.5)$$

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[5] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, p. 884; A. J. Layzer, Phys. Rev. **129**, 897 (1963).

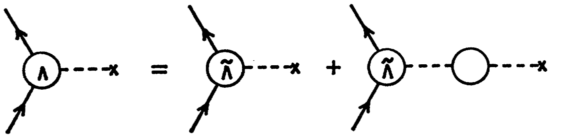

FIG. 1. The total vertex function and the proper vertex part. ——— Coulomb interaction; ——>—— Fermion propagator; >—X external potential.

The external potential is related to the density change by the linear polarizability[2] α:

$$v(\mathbf{q})=-(4\pi/q^2)(1/\alpha(\mathbf{q}))n_1(\mathbf{q})\,. \tag{3.6}$$

This polarizability also enters into the relation between the vertex function Λ and the proper vertex part $\tilde{\Lambda}$

$$\Lambda(\mathbf{k},\mathbf{q};E)=\tilde{\Lambda}(\mathbf{k},\mathbf{q};E)(1-\alpha(\mathbf{q}))\,. \tag{3.7}$$

(see Fig. 1.)

The electrostatic potential is, to first order, given by

$$\varphi(\mathbf{q})=(1-1/\alpha(\mathbf{q}))(4\pi/q^2)n_1(\mathbf{q})\,. \tag{3.8}$$

Substituting (3.7) into Eq. (3.4) and subtracting (3.8) from it gives

$$M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0))=M_h(\mathbf{r}-\mathbf{r}';E)+\frac{1}{(2\pi)^6}\int d\mathbf{k}\,d\mathbf{q}$$
$$\times\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')+i\mathbf{q}\cdot\mathbf{r}_0]\{\tilde{\Lambda}(\mathbf{k},\mathbf{q},E)-1\}$$
$$\times\left\{1-\frac{1}{\alpha(\mathbf{q})}\right\}\frac{4\pi}{q^2}n_1(\mathbf{q})\,. \tag{3.9}$$

To determine the function M_1 in Eq. (3.3) we must change the argument of M_h in Eq. (3.9) to $E-\varphi(\mathbf{r}_0)$:

$$M_h(\mathbf{r}-\mathbf{r}';E)=M_h(\mathbf{r}-\mathbf{r}';E-\varphi(\mathbf{r}_0))$$
$$+\varphi(\mathbf{r}_0)\partial M_h(\mathbf{r}-\mathbf{r}';E)/\partial E\,. \tag{3.10}$$

Substitution of (3.10) in Eq. (3.9) and comparison with Eq. (3.3) gives

$$M^{(1)}(\mathbf{r},\mathbf{r}';\mathbf{r}_0-s;E)=\frac{1}{(2\pi)^6}\int d\mathbf{k}\,d\mathbf{q}$$
$$\times\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')+i\mathbf{q}\cdot(\mathbf{r}_0-\mathbf{s})]M^{(1)}(\mathbf{k},\mathbf{q};E)\,, \tag{3.11}$$

where

$$M^{(1)}(\mathbf{k},\mathbf{q};E)=\left\{\frac{\partial M_h(\mathbf{k},E)}{\partial E}+\tilde{\Lambda}(\mathbf{k},\mathbf{q};E)-1\right\}$$
$$\times\left(1-\frac{1}{\alpha(\mathbf{q})}\right)\frac{4\pi}{q^2}\,. \tag{3.12}$$

For small q we have the Ward identity[3]

$$\alpha(q)\sim1-(q^2/4\pi)d\mu_h/dn_0\,, \tag{3.13}$$

where μ_h is the chemical potential of a uniform gas of density n_0 and $\varphi=0$. This leads to a cancellation of the $1/q^2$ singularity in (3.12) and guarantees the short range of $M^{(1)}$ as function of $(\mathbf{r}_0-\mathbf{s})$.[6]

A second Ward identity[3] states that

$$\lim_{q\to0}M^{(1)}(\mathbf{k},\mathbf{q},E)=1-\frac{\partial M_h(\mathbf{k},E)}{\partial E}-\frac{\partial M_h(\mathbf{k},E)}{\partial\mu_h}\,. \tag{3.14}$$

Hence

$$\lim_{q\to0}M^{(1)}(\mathbf{k},\mathbf{q},E)=\frac{\partial M_h(\mathbf{k},E)}{\partial\mu_h}\frac{d\mu_h}{dn_0}=\frac{\partial M_h(\mathbf{k},E)}{\partial n_0}\,. \tag{3.15}$$

This result, combined with the previously demonstrated short-range property of $M^{(1)}$ as function of $(\mathbf{r}_0-\mathbf{s})$, implies that the mass operator depends only on the local density distribution even if the mean density (or total number of electrons) is altered.

The same conclusions are also obtained if, instead of considering small modifications of a uniform electron gas, one takes the case of a nearly perfectly periodic lattice. This case is worked out in the Appendix.

IV. APPROXIMATE FORMS OF THE MASS OPERATOR M

Let us assume that the density $n(\mathbf{r})$ of the ground state has been determined, for example by the methods of Refs. 2 and 7. In view of the fact that $M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0))$ depends only on the density near the point $\mathbf{r}_0$, the simplest approximation is

$$M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0))\approx M_h(\mathbf{r}-\mathbf{r}';E-\varphi(\mathbf{r}_0);n(\mathbf{r}_0))\,, \tag{4.1}$$

where M_h is the mass operator of a uniform electron gas of density $n(\mathbf{r}_0)$. Clearly this will be the leading term of a gradient expansion in the case of a system of slowly varying density. We hope that it will also be a reasonably good approximation for actual electronic systems in which, in fact, n sometimes varies rather rapidly. Let us here recall that M represents only the nonlocal (exchange and correlation) part of Σ; the local part $\varphi(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$ which is usually dominant, is treated exactly.[8]

Another approximate form for M can be derived from (4.1) in which the electrostatic potential $\varphi(\mathbf{r})$ does not explicitly appear. For this purpose we use the relation,[2] valid for a gas of slowly varying density,

$$\mu=\varphi(\mathbf{r})+\mu_h(n(\mathbf{r}))\,, \tag{4.2}$$

where μ is the chemical potential and $\mu_h(n)$ is the

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[6] Consideration of representative graphs leads to the conclusion that the effective range is the larger of the two lengths λ_F and λ_{TF} defined in the Introduction. Because of the logarithmic singularity of the first derivative of $M^{(1)}$ at $q=2k_F$, which may be seen, for example, in the quantity $\alpha(q)$, $M^{(1)}$ considered as function of $(\mathbf{r}_0-\mathbf{s})$ exhibits Friedel-type oscillations and thus falls off rather slowly, as $|\mathbf{r}_0-\mathbf{s}|^{-3}$.

[7] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[8] This approximation scheme is analogous to the method of Ref. 7, for calculating total energy and density in the ground state. In both cases only exchange and correlation effects are approximated by the leading term of a gradient expansion.

chemical potential of a uniform gas of density n with $\varphi=0$. With this further approximation we obtain from (4.1), the alternative form

$$M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0)) \approx M_h[\mathbf{r}-\mathbf{r}';E-\mu+\mu_h(n(\mathbf{r}_0));n(\mathbf{r}_0)]. \quad (4.3)$$

Finally, M can be approximately replaced by a local operator. We begin by writing the Schrödinger-type equation (3.1) in the form

$$(-\mathcal{E}(E)-\tfrac{1}{2}\nabla^2+\varphi(\mathbf{r}))\chi(\mathbf{r},E)+\int d\mathbf{r}' \times M(\mathbf{r},\mathbf{r}';E)\chi(\mathbf{r}',E)=0, \quad (4.4)$$

where the subscript n has been suppressed. The last term in this equation we now estimate on the assumption that the density of the system is slowly varying.[8] This allows us, first of all, to use for M the approximation (4.3). Further, in such a situation $\chi(\mathbf{r},E)$ is a superposition of locally plane waves, $e^{i\mathbf{p}(\mathbf{r})\cdot\mathbf{r}}$, with

$$\tfrac{1}{2}p^2+M_h(p,\,E-\mu+\mu_h(n);n)=E-\mu+\mu_h(n), \quad (4.5)$$

where n is the local density. (This is quite analogous to the situation encountered in applications of the WKB method.) When operating on such a plane wave the mass operator (4.3) is equivalent to the local operator $u(\mathbf{r};E)\delta(\mathbf{r}-\mathbf{r}')$, where

$$u(\mathbf{r};E)=M_h[p(\mathbf{r}),\,E-\mu+\mu_h(n(\mathbf{r}));n(\mathbf{r})] \quad (4.6)$$

and $p(\mathbf{r})$ is determined from (4.5). With this definition Eq. (4.4) now acquires the simple form

$$(-\mathcal{E}(E)-\tfrac{1}{2}\nabla^2+\varphi(\mathbf{r})+u(\mathbf{r};E))\chi(\mathbf{r},E)=0. \quad (4.7)$$

For an elementary excitation at the Fermi level $\mathcal{E}(E)=E=\mu$ and (4.5) simplifies to

$$\tfrac{1}{2}p^2+M_h(p,\,\mu_h(n);n)=\mu_h(n). \quad (4.8)$$

This equation is satisfied by $p=k_{\mathrm{F}}$ and hence u becomes simply

$$u(\mathbf{r};\mu)=(\mu_h(n)-\tfrac{1}{2}k_{\mathrm{F}}^2(n)) \equiv\mu_{xc}(n), \quad (4.9)$$

where $\mu_{xc}(n)$ is the exchange and correlation portion of the chemical potential which has played a dominant role in our theory of the ground state.[7] (See Ref. 4 for a numerical estimate of this quantity and for further references.)

As an illustration let us construct the $u(\mathbf{r},E)$ which includes the effects of exchange but not correlation. For this case

$$u=M_h(p,\,E-\mu+\mu_h(n),\,n) =-\frac{k_{\mathrm{F}}}{\pi}\left[1+\frac{k_{\mathrm{F}}^2-p^2}{2pk_{\mathrm{F}}}\ln\left|\frac{k_{\mathrm{F}}+p}{k_{\mathrm{F}}-p}\right|\right], \quad (4.10)$$

where

$$k_{\mathrm{F}}=(3\pi^2n)^{1/3}, \quad (4.11)$$

$$\mu_h(n)=\tfrac{1}{2}k_{\mathrm{F}}^2-k_{\mathrm{F}}/\pi, \quad (4.12)$$

and p is determined by

$$\tfrac{1}{2}p^2-\frac{k_{\mathrm{F}}}{\pi}\left[1+\frac{k_{\mathrm{F}}^2-p^2}{2pk_{\mathrm{F}}}\ln\left|\frac{k_{\mathrm{F}}+p}{k_{\mathrm{F}}-p}\right|\right] =E-\mu+\tfrac{1}{2}k_{\mathrm{F}}^2-\frac{k_{\mathrm{F}}}{\pi}. \quad (4.13)$$

In the eventuality that u is required for such a large negative value of $(E-\mu)$ that (4.13) does not have a real solution for p, the correct imaginary p is found by solving (4.13) with the replacement

$$\ln\left|\frac{k_{\mathrm{F}}+p}{k_{\mathrm{F}}-p}\right|\to\ln\left(\frac{k_{\mathrm{F}}+p}{k_{\mathrm{F}}-p}\right) \quad (4.14)$$

and making the same replacement in the expression for u. The resulting value of u will be real.

Equations (4.5)–(4.14) are convenient for extensive systems, such as metals (see Sec. V). However, for finite systems, such as atoms, the concept of a chemical potential, first introduced in Eq. (4.2), is somewhat artificial and arbitrary. It may therefore be preferable to use the approximate form (4.1) for M, which has the effect of replacing, in Eqs. (4.5)–(4.13), μ by $\mu_h(n)+\varphi$.

V. APPLICATION TO METALS

As an illustration of the use of the simple approximation (4.6) for M, we now consider the case of metals. Here the solutions of Eq. (2.1), which includes all electron-electron effects, have the same translation symmetry properties as single-particle Bloch waves and so we shall denote them by $\chi_{\mathbf{k}}$ with the crystal momentum $\mathbf{k}$ being unrestricted (extended zone scheme). We assume that the density $n(\mathbf{r})$ of the ground state has been obtained. We must then solve the following equation

$$\{-\mathcal{E}_{\mathbf{k}}(E)-\tfrac{1}{2}\nabla^2+\varphi(\mathbf{r})+u(\mathbf{r},E)\}\chi_{\mathbf{k}}(\mathbf{r},E)=0, \quad (5.1)$$

where u is, through Eq. (4.6), entirely determined by the density $n(\mathbf{r})$.

Let us first consider this equation for $E=\mu$, which by (4.9), becomes

$$\{-\mathcal{E}_{\mathbf{k}}(\mu)-\tfrac{1}{2}\nabla^2+\varphi(\mathbf{r})+\mu_{xc}(n)\}\chi_{\mathbf{k}}(\mathbf{r},\mu)=0. \quad (5.2)$$

The solutions of this equation with eigenvalue

$$\mathcal{E}_{\mathbf{k}}(\mu)=\mu \quad (5.3)$$

are the single-particle excitations at the Fermi surface and therefore Eq. (5.3) determines the location of the Fermi surface in k space. The correct value of μ must be self-consistently determined by the requirement that the volume enclosed by the Fermi surface corresponds correctly to the total number of electrons.[9]

We would like to remark that Eq. (5.2) is identical to Eq. (2.8) in Ref. 7, which was used to determine the density and total energy of the ground state. The present considerations show therefore that μ and the Fermi surface are already correctly determined by the ground-state calculation of Ref. 7. However, solutions of Eq. (2.8) in Ref. 7, with eigenvalues $\epsilon_{\mathbf{k}}\neq\mu$, must *not* be interpreted as corresponding to elementary excitations, to which we now turn.

For the general elementary excitation, we must go back to Eq. (5.1) with its energy-dependent and complex effective potential $u(\mathbf{r},E)$. The most important excitations have energies near μ. To obtain these we need to develop $u(\mathbf{r},E)$ near the value $E=\mu$. From Eq. (4.5) we find

$$p-k_{\mathrm{F}}=(E-\mu)\left[\frac{1-\partial M_h(p,E;n)/\partial E}{p+\partial M_h(p,E;n)/\partial k}\right]_{E=\mu,\,p=\mathbf{k}_{\mathrm{F}}}$$

$$=(E-\mu)\frac{m^*(n)}{k_{\mathrm{F}}(n)}, \tag{5.4}$$

where $m^*(n)$ is the density-of-states mass of the uniform gas of density n.[10] Substituting into (4.6) gives after a little rearrangement

$$u(\mathbf{r},E)=\mu_{xc}(n)+(E-\mu)(1-m^*(n))+\cdots. \tag{5.5}$$

We notice that the first-order correction is real; the imaginary part of $u(\mathbf{r},E)$ is of the form $-ic(n)(E-\mu)^2$, with $c>0$.[11] By virtue of (5.5), the eigenvalues of (5.1) will differ from the eigenvalues $\mathcal{E}_{\mathbf{k}}(\mu)$ of (5.2) by terms of order $(E-\mu)$. First-order perturbation theory gives

$$\mathcal{E}_{\mathbf{k}}(E)=\mathcal{E}_{\mathbf{k}}(\mu)+(E-\mu)\int[1-m^*(n(\mathbf{r}))]\times|\chi_{\mathbf{k}}(\mathbf{r},\mu)|^2\,d\mathbf{r}. \tag{5.6}$$

We can now solve Eq. (2.5) for the quasiparticle energies $E_{\mathbf{k}}$:

$$E_{\mathbf{k}}=\mu+\frac{\mathcal{E}_{\mathbf{k}}(\mu)-\mu}{\int m^*(n(\mathbf{r}))|\chi_{\mathbf{k}}(\mathbf{r},\mu)|^2d\mathbf{r}}. \tag{5.7}$$

From these energies we can obtain the density of states $g(\mu)$, which determines the specific heat;

$$g(\mu)=\frac{1}{N}\sum\nolimits_{\mathbf{k}}\delta(\mathcal{E}_{\mathbf{k}}(\mu)-\mu)\int m^*(n(\mathbf{r}))|\chi_{\mathbf{k}}(\mathbf{r},\mu)|^2d\mathbf{r}. \tag{5.8}$$

This may be shown to agree, to the accuracy of our approximation, with Eq. (3.17) of Ref. 7,

$$g(\mu)=g_s(\mu)+\frac{1}{N}\int n(\mathbf{r})\{g_h(\mu_h(n))-g_0(\mu_0(n))\}d\mathbf{r}, \tag{5.9}$$

where the subscripts s, h, 0 denote, respectively, the inhomogeneous single-particle system with potential $\varphi(\mathbf{r})+u(\mathbf{r},\mu)$; the homogeneous interacting electron gas; and the homogeneous noninteracting gas.

APPENDIX

We now consider the functional dependence on density of the mass operator in a nearly perfect metallic crystal. In this case the procedure follows in outlines similar to Sec. III. We write the density $n_a(\mathbf{r})$ as

$$n_a(\mathbf{r})=n(\mathbf{r})+n_1(\mathbf{r}), \tag{A1}$$

where $n(\mathbf{r})$ has the perfect crystal symmetry and $n_1(\mathbf{r})$ is the small deviation averaged to zero. We compare the mass operators of these two systems with densities $n_a(\mathbf{r})$ and $n(\mathbf{r})$. From Sec. III, we see that we need to express the difference of the two mass operators in terms of a vertex part and to establish the long-range behavior (or the low-momentum-transfer behavior) by two Ward identities. To avoid the objection of Kohn and Luttinger[12] to the Goldstone perturbation theory in the case of a metallic crystal, we use the finite-temperature formalism[1] for the Green's function to establish the Ward identities and then take the zero-temperature limit. These identities enable us to prove our conjecture for this special case. Therefore, it seems, quite generally, that the short-range density dependence of the mass operator is just a physical manifestation of the Ward identities.

Consider the periodic lattice, in which the potential can, by virtue of the lattice translational symmetry, be Fourier-analyzed as

$$v(\mathbf{r})=\sum\nolimits_{\mathbf{Q}}e^{i\mathbf{Q}\cdot\mathbf{r}}v(\mathbf{Q}), \tag{A2}$$

$\mathbf{Q}$ denoting the reciprocal lattice vector. Similarly, the vertex part due to a static perturbation can be written as

$$\Lambda(\mathbf{r},\mathbf{r}';\mathbf{r}_0-\mathbf{s};iE_n+\mu)=\Omega^{-2}\sum_{\mathbf{kk}'\mathbf{q}}\exp[i\mathbf{k}\cdot\mathbf{r}-i\mathbf{k}'\cdot\mathbf{r}'+i\mathbf{q}\cdot(\mathbf{r}_0-\mathbf{s})]\times\Lambda(\mathbf{k},\mathbf{k}';\mathbf{q};iE_n+\mu), \tag{A3}$$

where $E_n=(2n+1)\pi k_{\mathrm{B}}T$ at a finite temperature T, μ is the chemical potential of the perfect crystal, and Ω the volume. By crystal symmetry,

$$\mathbf{k}'=\mathbf{k}+\mathbf{K} \tag{A4}$$

for some reciprocal lattice vector $\mathbf{K}$.

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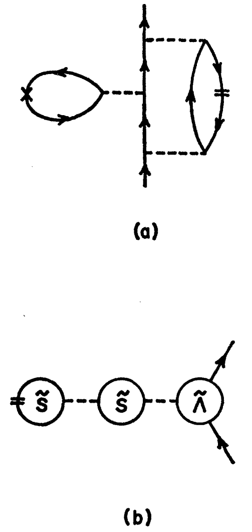

FIG. 2(a) A proper cut diagram. (b) An improper cut diagram. —×— lattice potential $v(\mathbf{Q})$; —‖— cut.

For the first Ward identity, we evaluate $\partial\Sigma(\mathbf{k},\mathbf{k}'; iE_n+\mu)/\partial\mu$. Differentiation with respect to μ is equivalent to cutting in turn each fermion line in the diagrams of the mass operator.[3] There result two classes of diagrams: (a) so-called proper cut diagrams, typified by Fig. 2(a), in which the cut is not separated from the external fermion line of Σ by a single-interaction line, and (b) improper cut diagrams, typified by Fig. 2(b), in which $\tilde{S}$ represents the sum of all proper static polarization graphs. The contribution to $\partial\Sigma/\partial\mu$ from proper cut diagrams is

$$\delta_{\mathbf{k}\mathbf{k}'}-\tilde{\Lambda}(\mathbf{k},\mathbf{k}'; q=0; iE_n+\mu), \tag{A5}$$

where $\tilde{\Lambda}$ ls the proper vertex part; and from improper cut diagrams

$$\sum_{\mathbf{Q},\mathbf{Q}'} \tilde{\Lambda}(\mathbf{k}-\tfrac{1}{2}\mathbf{Q}, \mathbf{k}'+\tfrac{1}{2}\mathbf{Q}; \mathbf{Q}; iE_n+\mu)\epsilon^{-1}(\mathbf{Q},\mathbf{Q}') \times v_c(\mathbf{Q})\tilde{S}(\mathbf{Q}',0), \tag{A6}$$

where the $\mathbf{Q}$'s are reciprocal lattice vectors, $v_c(\mathbf{Q})$ represents Coulomb interaction matrix elements

$$\begin{aligned} v_c(\mathbf{Q})&=0, & \mathbf{Q}&=0; \\ v_c(\mathbf{Q})&=4\pi/Q^2, & \mathbf{Q}&\neq 0, \end{aligned} \tag{A7}$$

and ϵ is the static dielectric function,

$$\epsilon(\mathbf{Q},\mathbf{Q}')=\delta_{\mathbf{Q},\mathbf{Q}'}+v_c(\mathbf{Q})\tilde{S}(\mathbf{Q},\mathbf{Q}'). \tag{A8}$$

Adding (A5) and (A6), we get

$$\partial\Sigma(\mathbf{k},\mathbf{k}'; iE_n+\mu)/\partial\mu = \delta_{\mathbf{k},\mathbf{k}'}-\sum_{\mathbf{Q}} \tilde{\Lambda}(\mathbf{k}-\tfrac{1}{2}\mathbf{Q}, \mathbf{k}'+\tfrac{1}{2}\mathbf{Q}; \mathbf{Q}; iE_n+\mu)\epsilon^{-1}(\mathbf{Q},0). \tag{A9}$$

In the zero-temperature limit, Eq. (A9) becomes

$$\left(\frac{\partial}{\partial E}+\frac{\partial}{\partial\mu}\right)\Sigma(\mathbf{k},\mathbf{k}'; E)=\delta_{\mathbf{k},\mathbf{k}'} -\sum_{\mathbf{Q}} \tilde{\Lambda}(\mathbf{k}-\tfrac{1}{2}\mathbf{Q}, \mathbf{k}'+\tfrac{1}{2}\mathbf{Q}, \mathbf{Q}; E)\epsilon^{-1}(\mathbf{Q},0). \tag{A10}$$

The second Ward identity is derived from (A9) by closing the external fermion line, giving

$$\partial n(\mathbf{Q})/\partial\mu=\sum_{\mathbf{Q}'} \tilde{S}(\mathbf{Q},\mathbf{Q}')\epsilon^{-1}(\mathbf{Q}',0)=S(\mathbf{Q},0), \tag{A11}$$

$S(\mathbf{Q},\mathbf{Q}')$ being the sum of all proper and improper static polarization diagrams. It is also easy to see that for $\mathbf{Q}'\neq 0$,

$$\partial\Sigma(\mathbf{k},\mathbf{k}'; E)/\partial v(\mathbf{Q}') =\sum_{\mathbf{Q}} \tilde{\Lambda}(\mathbf{k}-\tfrac{1}{2}\mathbf{Q}, \mathbf{k}'+\tfrac{1}{2}\mathbf{Q}; \mathbf{Q}; E)\epsilon^{-1}(\mathbf{Q},\mathbf{Q}'), \tag{A12}$$

and

$$\partial n(\mathbf{Q})/\partial v(\mathbf{Q}')=-S(\mathbf{Q},\mathbf{Q}'). \tag{A13}$$

Equations (A10)–(A13) form the extension of the Ward identities (3.13) and (3.14) to the case of a perfect crystal, since

$$\lim_{q\to 0} \tilde{S}(\mathbf{q}+\mathbf{Q}, \mathbf{q}+\mathbf{Q}')=\tilde{S}(\mathbf{Q},\mathbf{Q}') \tag{A14}$$

and

$$\lim_{q\to 0} \tilde{\Lambda}(\mathbf{k}, \mathbf{k}-\mathbf{q}+\mathbf{Q}'; \mathbf{q}+\mathbf{Q}; iE_n+\mu) =\tilde{\Lambda}(\mathbf{k}, \mathbf{k}+\mathbf{Q}'; \mathbf{Q}; iE_n+\mu). \tag{A15}$$

From the same type of reasoning as above, we also have

$$\partial\varphi(\mathbf{Q})/\partial\mu=-\epsilon^{-1}(\mathbf{Q},0) \tag{A16}$$

and

$$\partial\varphi(Q)/\partial v(\mathbf{Q}')=\epsilon^{-1}(\mathbf{Q},\mathbf{Q}'), \quad \mathbf{Q}'\neq 0, \tag{A17}$$

which we shall use later.

Now we are ready to consider the mass operator of the system whose lattice symmetry is slightly disturbed by a small potential $v_1(\mathbf{r})$ which creates the deviation in density $n_1(\mathbf{r})$ from the periodic $n(\mathbf{r})$.

$$\Sigma_a(\mathbf{r},\mathbf{r}'; E)=\Sigma(\mathbf{r},\mathbf{r}'; E)+\Omega^{-1} \sum_{\mathbf{k},\mathbf{K},\mathbf{q}} \exp[i\mathbf{k}\cdot\mathbf{r}-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}'+i\mathbf{q}\cdot\mathbf{r}_0]\Lambda(\mathbf{k}, \mathbf{k}+\mathbf{K}; \mathbf{q}; E)v_1(\mathbf{q}), \tag{A18}$$

and

$$v_1(\mathbf{q})=\Omega^{-1}\int d\mathbf{r}\, e^{-i\mathbf{q}\cdot\mathbf{r}}v_1(\mathbf{r}). \tag{A19}$$

The change in the electrostatic potential is

$$\varphi_1(\mathbf{r})=\varphi_a(\mathbf{r})-\varphi(\mathbf{r})=\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\{v_1(\mathbf{q})+v_c(\mathbf{q})n_1(\mathbf{q})\}, \tag{A20}$$

in terms of which, (A18) becomes

$$\Sigma_a(\mathbf{r},\mathbf{r}';E)-\Sigma(\mathbf{r},\mathbf{r}';E)=\Omega^{-1}\sum_{\mathbf{k},\mathbf{K},\mathbf{q}}\exp[i\mathbf{k}\cdot\mathbf{r}-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}'+i\mathbf{q}\cdot\mathbf{r}_0]\tilde{\Lambda}(\mathbf{k},\,\mathbf{k}+\mathbf{K};\,\mathbf{q};\,E)\varphi_1(\mathbf{q})\,. \tag{A21}$$

Using Eq. (1.2) in Eq. (A21), we obtain

$$M_a(\mathbf{r},\mathbf{r}';E-\varphi_a(\mathbf{r}_0))-M(\mathbf{r},\mathbf{r}';E-\varphi_a(\mathbf{r}_0))$$
$$=\Omega^{-1}\sum_{\mathbf{k},\mathbf{K},\mathbf{q}}\exp[i\mathbf{k}\cdot\mathbf{r}-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}'+i\mathbf{q}\cdot\mathbf{r}_0]\left[\tilde{\Lambda}(\mathbf{k},\,\mathbf{k}+\mathbf{K};\,\mathbf{q};\,E)-\delta_{\mathbf{K},0}+\frac{\partial\Sigma(\mathbf{k},\,\mathbf{k}+\mathbf{K};\,E)}{\partial E}\right]\varphi_1(\mathbf{q})\,. \tag{A22}$$

We have to express φ_1 in terms of the change in density n_1. The latter is related to the perturbing potential v_1 by

$$n_1(\mathbf{q})=-\sum_{\mathbf{Q},\mathbf{Q}'}\tilde{S}(\mathbf{q},\,\mathbf{q}+\mathbf{Q})\epsilon^{-1}(\mathbf{q}+\mathbf{Q},\,\mathbf{q}+\mathbf{Q}')v_1(\mathbf{q}+\mathbf{Q}'). \tag{A23}$$

Provided $\mathbf{q}\neq 0$, the inversion to express v_1 in terms of n_1 must be possible by the general theory of Hohenberg and Kohn.[2] Thus, Eq. (A22) becomes

$$M_a(\mathbf{r},\mathbf{r}';E-\varphi_a(\mathbf{r}_0))-M(\mathbf{r},\mathbf{r}';E-\varphi_a(\mathbf{r}_0))=\int d\mathbf{s}\,M^{(1)}(\mathbf{r},\mathbf{r}';\mathbf{r}_0-\mathbf{s};E-\varphi(\mathbf{r}_0))n_1(\mathbf{s})\,, \tag{A24}$$

with

$$M^{(1)}(\mathbf{r},\mathbf{r}';\mathbf{r}_0-\mathbf{s};E-\varphi(\mathbf{r}_0))=\Omega^{-2}\sum_{\mathbf{k},\mathbf{K},\mathbf{q}}\exp[i\mathbf{k}\cdot\mathbf{r}-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}'+i\mathbf{q}\cdot(\mathbf{r}_0-\mathbf{s})]M^{(1)}(\mathbf{k},\,\mathbf{k}+\mathbf{K};\,\mathbf{q};\,E) \tag{A25}$$

and

$$M^{(1)}(\mathbf{k},\,\mathbf{k}+\mathbf{K};\,\mathbf{q};\,E)=\sum\nolimits_{\mathbf{Q}}\left[\delta_{\mathbf{K},-\mathbf{Q}}-\frac{\partial\Sigma(\mathbf{k}-\frac{1}{2}\mathbf{Q},\,\mathbf{k}+\mathbf{K}+\frac{1}{2}\mathbf{Q};\,E)}{\partial E}-\tilde{\Lambda}(\mathbf{k}-\tfrac{1}{2}\mathbf{Q},\,\mathbf{k}+\mathbf{K}+\tfrac{1}{2}\mathbf{Q},\,\mathbf{q}+\mathbf{Q};\,E)\right]\tilde{S}_{\mathbf{q}}^{-1}(\mathbf{Q},0), \tag{A26}$$

where $\tilde{S}_{\mathbf{q}}^{-1}$ is given by,

$$\sum\nolimits_{\mathbf{Q}'}\tilde{S}_{\mathbf{q}}^{-1}(\mathbf{Q},\mathbf{Q}')\tilde{S}(\mathbf{q}+\mathbf{Q}';\,\mathbf{q}+\mathbf{Q}'')=\delta_{\mathbf{Q},\mathbf{Q}''}\,. \tag{A27}$$

So far, all the results are valid for a perfect crystal, be it an insulator or a conductor. In the zero-temperature limit, the behavior of $\tilde{S}_{\mathbf{q}}^{-1}$ as $\mathbf{q}\rightarrow 0$ differs depending on whether it is a conductor or an insulator. For an insulator

$$\tilde{S}(\mathbf{Q},0)\equiv 0 \tag{A28}$$

and hence $\tilde{S}(\mathbf{q}+\mathbf{Q},\,\mathbf{q}+\mathbf{Q}')$ does not have an inverse as defined by (A27) when $\mathbf{q}=0$. By contrast, for a conductor, $\tilde{S}(\mathbf{Q},\mathbf{Q}')$ has an inverse $\tilde{S}_0^{-1}(\mathbf{Q},\mathbf{Q}')$. Applying Eqs. (A10), (A12), and (A16)–(A26), we deduce that

$$\lim_{q\rightarrow 0}M^{(1)}(\mathbf{k},\,\mathbf{k}+\mathbf{K};\,\mathbf{q};\,E)=M^{(1)}(\mathbf{k},\,\mathbf{k}+\mathbf{K};\,0;\,E)\,, \tag{A29}$$

and

$$\lim_{q\rightarrow 0}\Omega^{-1}\sum_{\mathbf{k},\mathbf{K}}\exp[i\mathbf{k}\cdot\mathbf{r}-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}']M^{(1)}(\mathbf{k},\,\mathbf{k}+\mathbf{K};\,\mathbf{q};\,E)$$
$$=\frac{\partial M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0))}{\partial\mu}S_0^{-1}(0,0)-\sum_{\mathbf{Q}\neq 0}\frac{\partial M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0))}{\partial v(\mathbf{Q})}S_0^{-1}(\mathbf{Q},0)=\frac{\partial M(\mathbf{r},\mathbf{r}';E-\varphi(\mathbf{r}_0))}{\partial n(\mathbf{Q}=0)}\,, \tag{A30}$$

the last step being true by virtue of Eqs. (A11) and (A13). This leads us to the same conclusion as in Sec. III.