PHYSICAL REVIEW B VOLUME 34, NUMBER 3 1 AUGUST 1986

Nonperturbative theory of exchange and correlation in one-electron quasiparticle states

R. K. Nesbet
IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099
(Received 21 March 1986)

A nonperturbative argument is used to derive a one-electron Hamiltonian whose eigenfunctions are in one-to-one correspondence with electron or hole quasiparticles of an N-electron system. Nonlocal exchange is included exactly, and self-energy terms due to electronic correlation are included at the level of approximation of a given N-electron wave function. When parametrized by quasiparticle occupation numbers, this one-electron Hamiltonian is the functional derivative of an exact N-electron energy functional, as in the Landau theory of interacting fermion systems. The present nonperturbative derivation extends the Landau theory to ordered or localized systems for which many-body perturbation theory is not directly applicable. Analysis of the Bardeen-Cooper-Schrieffer (BCS) reduced Hamiltonian for superconductors leads to a temperature-dependent energy gap and a transition temperature in good agreement with the BCS theory, in a formalism that conserves the number of electrons.

I. INTRODUCTION

Many-body perturbation theory runs into difficulties in treating electronic interactions in condensed matter with significant ordered or localized electronic structure. In particular, ordered states that do not develop adiabatically from corresponding unperturbed states cannot be represented by the theory. The present paper approaches many-body theory from a new point of view, in order to develop a formalism that does not depend on perturbation theory. Applications of current interest for such a theory include materials in which both magnetic ordering and superconductivity are possible, and narrow-band systems in general.

For localized systems, or for localized states in extended systems, any quantitative theory must exclude the nonphysical Coulomb self-interaction of a single electron. This is done trivially in the Hartree-Fock approximation, by explicit use of nonlocal exchange. Using antisymmetric N-electron variational wave functions, nonlocal exchange and correlation energies are computed quantitatively in current molecular theory.[1-3] This direct approach is not feasible for extended systems. In solid-state physics, the formalism of many-body perturbation theory is highly developed and widely used.[4,5] The natural model of an unperturbed system is the free-electron gas. Because the Hartree-Fock approximation is inaccurate for the free-electron gas, exchange and correlation must be taken into account at a common level of approximation, usually represented by an effective local potential. Such an approximation can be inaccurate for localized states, because the removal of one-electron Coulomb self-energy is not exact.

In many-body perturbation theory, one-electron energy levels are defined as roots of a Dyson equation, giving the poles of the one-electron Green function.[4-6] This formalism has been used in recent calculations[7] of band-gap parameters in Si, implementing the theory at the lowest physically consistent level of perturbation terms.[8] These calculations resolve serious discrepancies in standard band theory calculations using the local-density approximation (LDA).[9,10] While clearly more difficult than LDA calculations, the work of Hybertsen and Louie[7] shows the importance of including nonlocal electron self-energy, with dynamical dielectric screening, in the Dyson equation.

It will be shown here that an effective one-electron Hamiltonian is uniquely defined for a given eigenstate of any N-electron system. Nonlocal exchange is included exactly, eliminating the one-electron Coulomb self-energy, but other self-energy terms due to electronic correlation are included at the level of approximation of the given N-electron wave function.

The concept behind the formalism developed here is that the correlated N-electron ground state is real and tangible, while the point of departure of perturbation theory, the so-called normal unperturbed state, is a nonphysical artifact. The present theory is based on universal properties of correlated wave functions. Two basic principles are exploited, and the apparatus of many-body theory is derived from these principles. An effective one-electron Hamiltonian is derived whose eigenvalues are Landau one-electron energies,[11] derivatives of an exact energy functional with respect to occupation numbers. The eigenfunctions of this one-electron Hamiltonian are in one-to-one correspondence with quasiparticle operators appropriate to the Fermi-liquid model.[11] These operators are explicitly constructed. Their properties make it possible to construct the one-electron Green function. Dyson energies, defined as poles of this Green function, are equal to the Landau one-electron energies in the case of normal solids, whose one-electron functions are Bloch waves, but not for finite or localized systems, for which the addition or removal of one electron causes a finite change in the one-electron Hamiltonian.

The first basic principle used here is that an exact energy expression for any N-electron eigenstate can be parameterized in terms of coefficients that are amplitudes for virtual electron-pair excitation. The second basic principle is that any given N-electron eigenstate determines a unique orbital function basis, through the condition that the overlap between the N-electron wave function and a single Slater determinant should be maximized. These orbital basis functions are eigenfunctions of a uniquely defined one-electron Hamiltonian.

A novel aspect of the present formalism, which supplants the adiabatic switching-on of standard perturbation theory, is to represent the second-quantized Hamiltonian of the interacting N-electron system in the orbital basis adapted to a particular eigenstate. The explicit construction of quasiparticle operators and development of a Landau energy functional is carried out in this representation.

Section II here reviews the basic definitions of one-electron energies in many-body perturbation theory and in the Landau theory of interacting fermions (Fermi liquids). Section III derives the one-electron Hamiltonian of the present theory and shows that it is compatible with energy levels derived from a Landau energy functional. Section IV constructs quasiparticle operators defined by addition or removal of one electron from a given N-electron eigenstate, and shows that they are in one-to-one correspondence with the eigenfunctions of the one-electron Hamiltonian appropriate to this state. Section V shows how to construct the one-electron Green function. To demonstrate that this formalism really moves onto new ground, application to the BCS Hamiltonian is discussed in Sec. VI. A summary and discussion is given in Sec. VII.

II. ONE-ELECTRON ENERGIES

One-electron energies can be defined in terms of electron and hole quasiparticles, using many-body perturbation theory.[4-6] If the N-electron ground state is

$$\Psi = | N \rangle \ , \tag{1}$$

with energy $E(N)$, then eigenstates of $N-1$ electrons, with energies $E(N-1,i)$ can be denoted by

$$\Psi_i = | N-1,i \rangle = \eta_i \Psi \ . \tag{2}$$

Eigenstates of $N+1$ electrons, with energies $E(N+1,a)$, can be denoted by

$$\Psi^a = | N+1,a \rangle = \eta_a^\dagger \Psi \ . \tag{3}$$

A one-to-one correspondence between orbital basis functions $\{\phi_i;\phi_a\}$ and the quasiparticle operators $\eta_i,\eta_a^\dagger$ will be established in Sec. IV, below. Because of this correspondence, Eq. (2) refers to a selected subset of N eigenstates of the $(N-1)$-electron Hamiltonian. For consistency of notation, the indexing of states $| N+1,a \rangle$ starts with $a=N+1$.

In Eq. (2), η_i is a fermion quasiparticle annihilation operator, such that

$$\begin{gathered}([\eta_i,H]-E_i\eta_i)\,|N\rangle = 0 \ , \\ \eta_1^\dagger\,|N\rangle = 0 \ , \\ E(N-1,i) = E(N)-E_i, \quad i=1,2,\ldots,N \ .\end{gathered} \tag{4}$$

Here, E_i is the energy of an occupied electron quasiparticle state in the N-electron state $|N\rangle$. In Eq. (3), $\eta_a^\dagger$ is a fermion quasiparticle creation operator such that

$$\begin{gathered}([H,\eta_a^\dagger]-E_a\eta_a^\dagger)\,|N\rangle = 0 \ , \\ \eta_a\,|N\rangle = 0 \ , \\ E(N+1,a) = E(N)+E_a, \quad a>N \ .\end{gathered} \tag{5}$$

Here, E_a is the energy of an unoccupied electron quasiparticle state.

The fermion property requires the anticommutator relations

$$\{\eta_p,\eta_q^\dagger\} = \delta_{pq}, \quad \text{all } p,q \ . \tag{6}$$

Orthonormality of the wave functions requires, using Eqs. (2) and (3),

$$\langle N \,|\, \eta_i^\dagger\eta_j \,|\, N\rangle = \langle N-1,i \,|\, N-1,j\rangle = \delta_{ij} \ , \tag{7a}$$

$$\langle N \,|\, \eta_a\eta_b^\dagger \,|\, N\rangle = \langle N+1,a \,|\, N+1,b\rangle = \delta_{ab} \ . \tag{7b}$$

If Eqs. (4) and (5) are valid, mean values of mixed operators such as $\eta_a^\dagger\eta_i$, with $i \le N < a$, vanish in state $|N\rangle$. Hence, Eqs. (6) are valid in this state, and the quasiparticles have fermion properties.

An alternative definition of one-electron energies is made in the phenomenological Fermi-liquid theory of Landau.[5,11] An energy functional that depends only on quasiparticle occupation numbers n_p is postulated to exist. Since these numbers are treated as continuous variables, a grand canonical ensemble is assumed. For variations that conserve total particle number

$$N = \sum_p n_p \ , \tag{8}$$

a chemical potential μ is defined such that $E-\mu N$ is stationary. Given N, the ground state corresponds to the absolute minimum of $E-\mu N$ subject to the fermion conditions

$$0 \le n_p \le 1, \quad \text{all } p \ . \tag{9}$$

One-electron energies at $T=0$ are defined by

$$\varepsilon_p = \frac{\partial E}{\partial n_p} \ . \tag{10}$$

Hence, for the ground state, with $i \le N < a$,

$$n_i = 1, \quad \varepsilon_i < \mu \ ; \tag{11a}$$

$$0 < n_p < 1, \quad \varepsilon_p = \mu \ ; \tag{11b}$$

$$n_a = 0, \quad \varepsilon_a > \mu \ . \tag{11c}$$

The chemical potential (Fermi level) μ is $\partial E/\partial N$, determined so that all quasiparticle states are occupied in order of increasing energy until Eqs. (8) and (11) are satisfied. At nonzero temperature T, the entropy is

$$S = -k \sum_p [n_p \ln n_p + (1-n_p)\ln(1-n_p)] \ . \tag{12}$$

Free energy $E-\mu N-TS$ is minimized to determine the occupation numbers for nonzero T,

$$n_p = \{\exp[(\varepsilon_p-\mu)/kT]+1\}^{-1} \ . \tag{13}$$

Equations (4), (5), and (10) must be recognized as different definitions of one-electron energies. To emphasize this point, E_i or E_a, defined by Eqs. (4) or (5), respectively, can be referred to as Dyson energies, and ε_i or ε_a of Eqs. (10) and (11) as Landau energies. For the same physical model, they must be related by

$$E_i=\int_0^1 \varepsilon_i\, dn_i,\ \ i\le N\ , \tag{14a}$$

$$E_a=\int_0^1 \varepsilon_a\, dn_a,\ \ a>N\ . \tag{14b}$$

For localized systems, the Landau and Dyson energies are clearly different. Since N is quantized, the Landau definition requires a statistical definition of nonintegral occupation numbers. In standard many-body theory, occupation numbers $\{n_p\}$ are defined for quasiparticles represented in the orbital basis that diagonalizes the unperturbed Hamiltonian. The present formalism differs by constructing a particular basis $\{\phi_i;\phi_a\}$ that is determined by a true eigenstate of N electrons. The basis orbitals are in one-to-one correspondence with states $|N-1,i\rangle$ and $|N+1,a\rangle$ of $N-1$ and $N+1$ electrons, respectively. By requiring finite or periodic boundary conditions, it can be assumed that energy levels are discrete. In this case, occupation numbers in a pure quantum state will be shown to be quantized, having values 0 or 1 only, except for possible degeneracies exactly at the Fermi level. Fractional occupation numbers $\{n_p\}$ are defined only statistically. Values of an energy functional interpolating between integral $\{n_p\}$, as postulated in the Landau theory, can be chosen for analytical convenience, so long as the values for integral $\{n_p\}$ are correct. This argument shows that discontinuities in $\partial E/\partial n$ at integral $\{n_p\}$ are not a necessary consequence of the underlying quantum theory, despite recent emphasis on such discontinuities in the Kohn-Sham formalism.[12,13] An energy functional will be considered here that is based on an exact formula for the N-electron energy, for any N. This functional is a polynomial function of occupation numbers. Hence the Landau energies given in Eq. (10) are continuous at integral $\{n_p\}$.

III. DERIVATION OF THE ONE-ELECTRON HAMILTONIAN

The present discussion is concerned with ground-state properties and low-lying excitations of N-electron systems. Theorems of Hohenberg and Kohn[9] establish for fixed N that the ground-state energy E_0 is a functional of the one-electron density, and that E_0 is minimized by the true ground-state one-electron density function. Low-lying excitations of the ground state can be considered in terms of eigenstates of $N-1$ and $N+1$ electrons in the same external potential.[4,5] As discussed in detail by Nozieres,[5] many-body perturbation theory can be used to justify the Landau Fermi-liquid model, in which the N-electron energy is treated as a function of occupation numbers in a particular one-electron orbital basis.

The present argument differs from previous developments of this theory by defining an orbital basis that is determined by the true N-electron wave function. This basis is transformed as the wave function varies. This eliminates the functional derivatives with respect to basis variation of the exact formula for N-electron energy used here, which becomes a function of occupation numbers as postulated in the Landau theory. Internal consistency requires that the equations that determine the orbital basis should also determine Landau energies in agreement with Eq. (10). This will be demonstrated here.

The Hamiltonian operator for N electrons is of the form

$$H=\sum_i h(\mathbf{x}_i)+\sum_{i,j} v(\mathbf{x}_i,\mathbf{x}_j)\ , \tag{15}$$

where $i,j=1,\ldots,N$ and ij denotes distinct index pairs with $i>j$. In second-quantized notation,

$$H=\sum_p\sum_q (p\,|\,h\,|\,q)a_p^\dagger a_q +\tfrac{1}{2}\sum_p\sum_q\sum_r\sum_s (pq\,|\,v\,|\,sr)a_p^\dagger a_q^\dagger a_r a_s\ , \tag{16}$$

where $a_p^\dagger$ is an electron creation operator for orbital state $\phi_p(\mathbf{x})$, and the adjoint a_p is the corresponding annihilation operator. Equation (16) is valid for arbitrary N. The indices run over an assumed complete orthonormal set of basis orbitals, with specific spin indices suppressed. The basis is assumed to be discretized by imposing periodic boundary conditions on a macroscopic cell boundary, or by confining the system to a finite volume. The one-electron operator h includes all external potentials, and v is the unscreened Coulomb interaction.

It is convenient to subdivide the orthonormal orbital basis for N-electron wave functions into two subsets: N orbitals $\{\phi_i\}$ that are occupied in a reference Slater determinant Φ_0, and the residual set of unoccupied orbitals $\{\phi_a\}$. A normalized Slater determinant can be denoted by $\Phi_{ij\cdots}^{ab\cdots}$, indicating that orbitals $\phi_i,\phi_j,\ldots$, occupied in Φ_0, are replaced, in the order given by $\phi_a,\phi_b,\ldots$. By convention here $i,j,k,\ldots\le N<a,b,c,\ldots$. In second-quantized notation,

$$\Phi_0=a_N^\dagger\cdots a_1^\dagger\,|\,\mathrm{vac}\rangle\ . \tag{17}$$

The determinantal basis is generated in the form

$$\begin{aligned}\Phi_i^a&=a_a^\dagger a_i\Phi_0\ ,\\ \Phi_{ij}^{ab}&=a_a^\dagger a_b^\dagger a_j a_i\Phi_0\ ,\\ &\ \ \cdots\ .\end{aligned} \tag{18}$$

An N-electron wave function is expanded as

$$\Psi=c_0\left[\Phi_0+\sum_i\sum_a\Phi_i^a c_i^a+\sum_{i,j}\sum_{ab}\Phi_{ij}^{ab}c_{ij}^{ab}+\cdots\right]. \tag{19}$$

It will be assumed here that the orbital basis maximizes the weight of reference determinant Φ_0 in a given wave function Ψ. It has been shown[14,15] that this condition eliminates single-excitation functions Φ_i^a from the expansion of Ψ. Wave functions of this structure are said to satisfy the Brueckner condition.[16,17] From Eq. (19),

$$c_0=(\Phi_0\,|\,\Psi)\ . \tag{20}$$

Orbital variations of Φ_0 are of the form

$$\delta\Phi_0=\sum_i \sum_a \Phi_i^a \delta c_i^a , \tag{21}$$

since Φ_0 is invariant under unitary transformation of its occupied orbitals $\{\phi_i\}$. It follows from Eq. (21) that stationary $|c_0|^2$ implies

$$(\Phi_i^a|\Psi)=c_0c_i^a=0, \quad i\le N<a , \tag{22}$$

which is the Brueckner condition.

If all coefficients c_i^a vanish in Eq. (19), and if Ψ is an eigenfunction of H, the energy eigenvalue is given exactly[1] by

$$E=\sum_i (i|h|i)+\sum_{i,j}(ij|\bar{v}|ij)+\sum_{i,j}\sum_{a,b}(ij|\bar{v}|ab)c_{ij}^{ab} . \tag{23}$$

Here, $\bar{v}$ denotes the Coulomb-exchange operator $v(1-P)$, where P exchanges electron coordinates. Equation (23) is exact because there are no terms involving more than two electrons in the electronic Hamiltonian. Since Φ_0 is assumed to be the Slater determinant of greatest weight in the expansion of Ψ,

$$|c_{ij}^{ab}|\le 1, \quad i,j\le N<a,b \tag{24}$$

by construction. The wave function Ψ is invariant under separate unitary transformation of the occupied orbitals $\{\phi_i\}$ and the unoccupied orbitals $\{\phi_a\}$, and Eq. (23) is also invariant to such transformations. Since $(ij|\bar{v}|ab)$ is separately antisymmetric in the index pairs ij and ab, the coefficients can be assumed to have the same antisymmetry, corresponding to matrix elements of an effective operator $\bar{u}$,

$$c_{ij}^{ab}=(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)^{-1}(ab|\bar{u}|ij) . \tag{25}$$

This form is exhibited in the lowest order of perturbation theory,

$$c_{ij}^{ab}=(E-D_{ij}^{ab})^{-1}(ab|\bar{v}|ij) , \tag{26}$$

where the energy denominator depends on the particular perturbation formalism. Equation (26) is consistent with treating $\bar{u}$ in Eq. (25) as an operator.

From the Hohenberg-Kohn theorems, if Ψ is the electronic ground state for fixed N, the effective operator $\bar{u}$ can be considered to be a functional of electron density, since the orbital basis $\{\phi_i;\phi_a\}$ and the coefficients c_{ij}^{ab} are determined by Ψ. The coefficients c_{ij}^{ab} will be treated here as parameters to be computed or estimated by detailed perturbation or variational calculations. In principle, they are determined by a stationary variational condition. Quantitative results have been obtained for electronic pair correlation in calculations on atoms and molecules.[1,2,3,15] Values of c_{ij}^{ab} in a particular basis can be abstracted from such calculations. For an extended system, large molecule or solid, calculations within an atomic cell could be considered to give matrix elements of an effective operator $\bar{u}$, as in Eq. (25). This matrix of $\bar{u}$ can be converted to a basis of Bloch waves in a solid by simple linear transformation. This procedure is justified if the operator $\bar{u}$ can be considered to be independent of one-electron occupation numbers, for ground-state functions with the same external potential but different boundary conditions. Since $\bar{u}$ is a functional of electron density, such an approximation is plausible.

Since the energy E is determined in Eq. (23) by the parameters c_{ij}^{ab}, in an orbital basis for which all coefficients c_i^a vanish, the corresponding one-electron Hamiltonian $\mathscr{H}$ must also depend on these parameters. The form of $\mathscr{H}$ compatible with Eq. (23) will be derived here. Stability of Eq. (22), the Brueckner condition, or independence of time in a time-dependent formalism, requires that matrix elements of H should vanish for virtual single excitations. This stability condition defines an effective one-electron Hamiltonian $\mathscr{H}$ such that

$$(a|\mathscr{H}|i)=(\Phi_i^a|H|\Psi)=0, \quad i\le N<a . \tag{27}$$

These equations imply that the form of Eq. (23) is preserved under first-order variations of the orbital basis.

In the Hartree-Fock approximation, the effective one-electron Hamiltonian,

$$\mathscr{H}_0=h+\sum_{j=1}^{N}(j|\bar{v}|j) , \tag{28}$$

is invariant under unitary transformation of the occupied orbital set $\{\phi_i\}$ and is not affected by transformation of the unoccupied set $\{\phi_a\}$. Hence a canonical basis can be constructed in which $\mathscr{H}_0$ is diagonalized.[1] A similar situation holds for the operator $\mathscr{H}$ to be considered here, which includes electronic correlation.

The matrix elements in Eq. (27) are well known[15,16] for Ψ expanded through virtual triple excitations:

$$\Psi=\Phi_0+\sum_{i,j}\sum_{a,b}\Phi_{ij}^{ab}c_{ij}^{ab}+\sum_{i,j,k}\sum_{a,b,c}\Phi_{ijk}^{abc}c_{ijk}^{abc}+\cdots . \tag{29}$$

Since terms of quadratic or higher order in the coefficients c_{ij}^{ab} are absent from Eq. (23), it is consistent to omit terms of this order from $(a|\mathscr{H}|i)$ derived from Eq. (27), which becomes, for $i\le N<a$,

$$(a|\mathscr{H}|i)=(a|\mathscr{H}_0|i)+\sum_j\sum_{c,b}(aj|\bar{v}|cb)c_{ij}^{cb} -\sum_{k,j}\sum_b (kj|\bar{v}|ib)c_{kj}^{ab}=0 . \tag{30}$$

The residual terms in Eq. (27) can be considered to determine the coefficients c_{ijk}^{abc} through linear equations

$$\sum_j\sum_b (j|\mathscr{H}_0|b)c_{ij}^{ab}+\sum_{j,k}\sum_{b,c}(jk|\bar{v}|bc)c_{ijk}^{abc}=0 , \quad i\le N<a , \tag{31}$$

from which coefficients c_{ijk}^{abc} can be constructed by antisymmetrizing products $c_{ij}^{ab}\gamma_k^c$ if the coefficients γ_k^c satisfy equations

$$(j|\mathscr{H}_0|b)+\sum_k\sum_c (jk|\bar{v}|bc)\gamma_k^c=0, \quad j\le N<b . \tag{32}$$

The sum of Eqs. (30) and (31) gives Eq. (27) exactly, with unrestricted sums as indicated. This form is obtained[16] by transferring certain "exclusion principle violating" terms between the originally derived last two terms of Eq. (30) and the first term of Eq. (31). Because elements

$(j\,|\mathscr{H}_0|\,b)$, for $j \le N < b$, vanish in the Hartree-Fock approximation, they are of order c_{ij}^{ab}. Hence, both terms in Eq. (31) are essentially of second order in these coefficients. If the orbital basis is determined by Eq. (30), solution of Eqs. (31) is required for consistent solution of the N-electron Schrödinger equation, following Eq. (27). Since coefficients c_{ijk}^{abc} are not needed for energy-level calculations, Eqs. (31) can be assumed without actually being solved.

Since total wave function and energy are invariant under separate unitary transformation of occupied and unoccupied orbitals, Eq. (30) determines the orbital basis up to such transformations and ensures that the energy is stationary with respect to orbital variations. Consistent definition of an operator $\mathscr{H}$ in the subspace of occupied orbitals, $i,l \le N$ is given by

$$(l\,|\mathscr{H}|\,i)=(l\,|\mathscr{H}_0|\,i)+\sum_{j}\sum_{c,b}(lj\,|\bar{v}|\,cb)c_{ij}^{cb} -\sum_{k,j}\sum_{b}(kj\,|\bar{v}|\,ib)c_{kj}^{lb}\;. \tag{33a}$$

In the unoccupied subspace, $a,d > N$,

$$(a\,|\mathscr{H}|\,d)=(a\,|\mathscr{H}_0|\,d)+\sum_{j}\sum_{c,b}(aj\,|\bar{v}|\,cb)c_{dj}^{cb} -\sum_{k,j}\sum_{b}(kj\,|\bar{v}|\,db)c_{kj}^{ab}\;. \tag{33b}$$

Coefficients c_{kj}^{lb} in Eq. (33a) are defined by electronic correlation in state $|\,N-1,l\,\rangle$. Similarly, coefficients c_{dj}^{cb} in Eq. (33b) are defined in state $|\,N+1,d\,\rangle$.

While the present derivation is not dependent on perturbation theory, it is important to show that the formalism is correct when perturbation theory is valid. This is demonstrated most directly by comparing Eqs. (33) with the graphical representation of the electron self-energy, given in particular by Thouless[6] (Fig. 19, p. 68). When first-order perturbation formulas are valid for the coefficients c_{ij}^{ab}, the three terms of Eqs. (33) correspond to the first- and second-order connected self-energy diagrams shown by Thouless.

Because of the antisymmetry of coefficients c_{ij}^{ab}, for both upper and lower index pairs, the internal sums in Eqs. (30) and (33) are invariant under unitary transformation separately of the occupied and unoccupied basis orbitals. Hence $\mathscr{H}$ is defined as an operator, independent of representation. Unlike the Dyson equation in perturbation theory, the effective Schrödinger equation involving $\mathscr{H}$ is linear, since $\mathscr{H}$ does not depend on the eigenvalues. The coefficients c_{ij}^{ab} are of course dependent on total energy and on the total eigenstate, but they are treated as given numerical parameters here. In applications of this formalism, this implies an outer self-consistency loop, in which coefficients c_{ij}^{ab} are determined for a given representation of the orbital basis, followed by redefinition of $\mathscr{H}$ for these parameters, and solution of the orbital eigenvalue equations with the current parameterized operator $\mathscr{H}$.

Equation (23) is an exact energy formula for N electrons. It depends only on numerical values of the coefficients c_{ij}^{ab} in a particular orbital basis. If the operator form of c_{ij}^{ab} is assumed, as in Eq. (25), then the sums in Eq. (23) are invariant under separate unitary transformations of the occupied orbitals $\{\phi_i\}$ and the unoccupied orbitals $\{\phi_a\}$. The procedure followed here is to construct this orbital basis so that E is stationary with respect to transformations that mix occupied and unoccupied orbitals. Then the functional derivatives of the energy with respect to orbital variations vanish, and E given by Eq. (23) acts as a functional of occupation numbers, as postulated in the Landau theory. The implied energy functional is

$$E(\{n\})=\sum_{i} n_i(i\,|h|\,i)+\sum_{i,j} n_i n_j(ij\,|\bar{v}|\,ij) +\sum_{i,j} n_i n_j \sum_{a,b}(1-n_a)(1-n_b)(ij\,|\bar{v}|\,ab)c_{ij}^{ab}\;. \tag{34}$$

The sums here are unrestricted in range, but indexes are chosen to correspond to Eq. (23) for the ground state energy when $i,j \le N < a,b$. The coefficients c_{ij}^{ab} are assumed to be defined for all index values. Equation (34) acts as a functional of occupation numbers in the vicinity of the ground state of N electrons, or of whatever other state is used to determine the orbital basis, which is assumed to vary with the N-electron state. The coefficients c_{ij}^{ab} also vary with the N-electron state, but are determined variationally.

By construction here, the N-electron energy is stationary with respect to variations of the orbital basis and of the pair-excitation coefficients c_{ij}^{ab}. The Rayleigh quotient, which can be expressed as Eq. (34) plus a second more complicated term that vanishes for an exact N-electron eigenfunction, is stationary with respect to all variations with specified occupation numbers. This second term can be expressed as a functional of the N-electron wave function Ψ and of the reference state Φ_0. It does not depend explicitly on occupation numbers. Its functional derivatives with respect to the orbital basis and partial derivations with respect to the coefficients c_{ij}^{ab} do not vanish, but they cancel exactly the explicit derivatives of Eq. (34). Hence, although the orbital basis and pair coefficients are implicit functions of the occupation numbers, the chain rule for partial derivatives implies that variations of total energy with respect to occupation numbers are given by the explicit partial derivatives of Eq. (34) with respect to these numbers.

For arbitrary occupation numbers, matrix elements of the one-electron Hamiltonian $\mathscr{H}(\{n\})$, given by Eq. (30), take the form

$$(p\,|\mathscr{H}(\{n\})|\,q)=(p\,|h|\,q)+\sum_{j} n_j(pj\,|\bar{v}|\,qj)+\sum_{j} n_j\sum_{a,b}(1-n_a)(1-n_b)(pj\,|\bar{v}|\,ab)c_{qj}^{ab} -\sum_{i,j} n_i n_j\sum_{b}(1-n_b)(ij\,|\bar{v}|\,qb)c_{ij}^{pb}\;. \tag{35}$$

Correspondence with the Landau theory is demonstrated by evaluating the partial derivatives of $E(\{n\})$ with respect to occupation numbers, defining, from Eq. (34),

$$\begin{aligned}\varepsilon_p=\frac{\partial E}{\partial n_p}&=(p\,|\,h\,|\,p)+\sum_j n_j(pj\,|\,\bar{v}\,|\,pj)\\&\quad+\sum_j n_j\sum_{a,b}(1-n_a)(1-n_b)(pj\,|\,\bar{v}\,|\,ab)c_{pj}^{ab}\\&\quad-\sum_{i,j}n_in_j\sum_b(1-n_b)(ij\,|\,\bar{v}\,|\,pb)c_{ij}^{pb}\ . \end{aligned}\tag{36}$$

In a diagonal representation of $\mathscr{H}(\{n\})$, Eqs. (35) and (36) are identical, showing that Eq. (34) defines a Landau functional. The Landau energies are

$$\varepsilon_i=\frac{\partial E}{\partial n_i}=(i\,|\,\mathscr{H}\,|\,i),\quad i\le N\ ,\tag{37a}$$

$$\varepsilon_a=\frac{\partial E}{\partial n_a}=(a\,|\,\mathscr{H}\,|\,a),\quad a>N\ ,\tag{37b}$$

for the N-electron ground state. Equations (35) define the operator $\mathscr{H}$ as a functional of occupation numbers.

IV. QUASIPARTICLE STATES AND ENERGIES

Because of electronic interaction, the quasiparticle operators are not elementary one-electron operators. In the equations-of-motion[18] or excitation operator[19] method, the structure of these operators is deduced by substituting a linear combination of elementary operators a, $aaa^\dagger$, etc., into Eqs. (4) that define the quasiparticle operator η_i, and similarly for $\eta_a^\dagger$ defined by Eqs. (5). The basic commutator required is

$$[a_p,H]=\sum_s(p\,|\,h\,|\,s)a_s+\sum_q\sum_r\sum_s(pq\,|\,v\,|\,sr)a_q^\dagger a_r a_s\ .\tag{38}$$

The resulting hierarchy of operator equations is closed and reduced to numerical equations for the coefficients by using mean values or anticommutator relations.

As an example, the Hartree-Fock approximation is obtained by allowing the operator $[a_p,H]$ to act on the single-determinant state Φ_0 of Eq. (17). The hierarchy of equations is closed by replacing all operator products by their mean values in state Φ_0,

$$a_p^\dagger a_s\cong n_p\delta_{sp},\quad a_p^\dagger a_q^\dagger a_r a_s\cong n_pn_q(\delta_{ps}\delta_{qr}-\delta_{pr}\delta_{qs})\ ,\tag{39}$$

where n_p,n_q are occupation numbers in Φ_0. Then, using Eqs. (39),

$$a_i^\dagger[a_a,H]\cong(a\,|\,\mathscr{H}_0\,|\,i)=0,\quad i\le N<a\ ,\tag{40}$$

if Eq. (27) is applied to the Hartree-Fock operator defined by Eq. (28). In a diagonal representation of $\mathscr{H}_0$,

$$([a_i,H]-\varepsilon_i^0a_i)\Phi_0\cong 0\tag{41}$$

if the orbital basis satisfies Eq. (40) and ε_i^0 is an eigenvalue of $\mathscr{H}_0$. Since $a_i^\dagger\Phi_0$ is identically zero, Eqs. (4) are satisfied, and a_i acts on Φ_0 as a quasiparticle annihilation operator.

If Eqs. (4) and (5) are approximately satisfied, then

$$[H,\eta_i^\dagger]\,|\,N\rangle=0,\quad i\le N\ ,\tag{42a}$$

$$[\eta_a,H]\,|\,N\rangle=0,\quad a>N\ ,\tag{42b}$$

to the same level of approximation. These equations provide consistency conditions for an orbital basis compatible with an assumed form of the quasiparticle operators. Since $a_a^\dagger\Phi_0$ is not identically zero for $a>N$ and $a_i\Phi_0$ is not identically zero for $i<N$, Eqs. (42) are equivalent to definitions of a one-electron Hamiltonian $\mathscr{H}$ such that

$$(a\,|\,\mathscr{H}\,|\,i)=\langle\Phi_0\,|\,a_a[H,\eta_i^\dagger]\,|\,N\rangle=0,\quad i\le N<a\ ,\tag{43a}$$

or

$$(a\,|\,\mathscr{H}\,|\,i)=\langle\Phi_0\,|\,a_i^\dagger[\eta_a,H]\,|\,N\rangle=0,\quad i\le N<a\ .\tag{43b}$$

In the Hartree-Fock approximation, using Eq. (40) and the corresponding expression for $a_a[H,a_i^\dagger]$, Eqs. (43) both reduce to

$$(a\,|\,\mathscr{H}_0\,|\,i)=0,\quad i\le N<a\ ,\tag{44}$$

for $\eta_i^\dagger=a_i^\dagger$ and $\eta_a=a_a$. Thus Eqs. (43) are compatible with Eq. (27) in the Hartree-Fock case. It should be noted that Eq. (44) determines the determinantal wave function Φ_0, invariant under unitary transformation of its occupied orbitals, whether or not the operator $\mathscr{H}_0$ is diagonalized within the set of occupied orbitals.

An unnormalized N-electron wave function subject to the Brueckner condition can be expressed as

$$\Psi=\Phi_0+\sum_{i,j}\sum_{a,b}\Phi_{ij}^{ab}c_{ij}^{ab}+\cdots\ ,\tag{45}$$

which implies the exact energy formula given by Eq. (23). Unnormalized quasiparticle operators will be assumed to have a form in one-to-one correspondence with the orbital basis functions,

$$\begin{aligned}\eta_p^\dagger&=a_p^\dagger+\tfrac{1}{2}\sum_q\sum_r\sum_s a_qa_r^\dagger a_s^\dagger c_{pq}^{rs}+\cdots\ ,\\ \eta_p&=a_p+\tfrac{1}{2}\sum_q\sum_r\sum_s a_sa_ra_q^\dagger(c_{pq}^{rs})^*+\cdots\ ,\end{aligned}\tag{46}$$

where, if Eq. (25) is valid,

$$(c_{pq}^{rs})^*=-c_{rs}^{pq}\ .\tag{47}$$

This ansatz, Eqs. (46), will be shown to be consistent with Eqs. (4) and (5) and with Eq. (45) if coefficients c_{ij}^{ab} with $i,j\le N<a,b$ are equal to the corresponding coefficients in Eq. (45). As in Eqs. (33), coefficients in which one pair of indices are of mixed range, such as c_{ij}^{lb} with $i,j,l\le N<b$, are defined in states $|\,N-1,l\rangle$. Similarly, coefficients c_{dj}^{ab}, with $j\le N<d,a,b$ are defined in state $|\,N+1,d\rangle$. Coefficients for which $r\le N<s$ or $s\le N<r$ in Eqs. (46) are not determined by the present argument, and will be assumed to vanish. Certain coefficients with repeated indices occur and cannot be assumed to be zero. Thus, $c_{ij}^{ib}=c_j^b$, evaluated in state $|\,N-1,i\rangle$ when expanded in the orbital basis appropriate to state $|\,N\rangle$. Similarly, $c_{aj}^{ab}=c_j^b$, evaluated in state $|\,N+1,a\rangle$ in the orbital basis for state $|\,N\rangle$.

The orbital basis must satisfy Eqs. (43). It will be shown that with the assumed form of the quasiparticle operators, Eqs. (43) are compatible with the Brueckner condition, which implies Eq. (27) and defines an effective one-electron Hamiltonian operator. An implication of these results is that Ψ takes the form of a "quasideterminant," constructed in analogy to Φ_0, Eq. (17), but with bare electron creation operators $a_i^\dagger$ replaced by $\eta_i^\dagger$, for $i \leq N$,

$$\Psi = |N\rangle = \eta_N^\dagger \cdots \eta_1^\dagger |\mathrm{vac}\rangle \ . \tag{48}$$

The number operators $\eta_p^\dagger \eta_p$ are quantized in this state, with occupation number eigenvalues

$$n_i = 1, \ \ n_a = 0, \ \ i \leq N < a \ . \tag{49}$$

The product of operators $\eta_i^\dagger$ and $\eta_j^\dagger$, with $i,j \leq N$, as defined by Eqs. (46) with the assumed coefficient values, reduces to

$$\eta_i^\dagger \eta_j^\dagger = a_i^\dagger a_j^\dagger + \sum_{a,b} \sum_k (a_k a_j^\dagger c_{ik}^{ab} - a_i^\dagger a_k c_{kj}^{ab}) a_a^\dagger a_b^\dagger + \cdots \ , \tag{50}$$

if terms quadratic in the coefficients are neglected. Operator products that annihilate the vacuum state are neglected. Then, for the term in parentheses,

$$\sum_k (a_k a_j^\dagger c_{ik}^{ab} - a_i^\dagger a_k c_{kj}^{ab}) |\mathrm{vac}\rangle = (1 - n_i - n_j) c_{ij}^{ab} |\mathrm{vac}\rangle$$
$$= c_{ij}^{ab} |\mathrm{vac}\rangle \ . \tag{51}$$

Hence, Eq. (50) is approximated by

$$\eta_i^\dagger \eta_j^\dagger \cong a_i^\dagger a_j^\dagger + \sum_{a,b} a_a^\dagger a_b^\dagger c_{ij}^{ab} + \cdots \ , \tag{52}$$

and Eq. (48) gives precisely the terms included in Eq. (45).

Because the coefficients c_{ij}^{ab} are antisymmetric with respect to index pair (i,j), both leading terms of Eq. (52) vanish when $i = j$, in agreement with the anticommutator relations. This verifies the second of Eqs. (4). The effect of $\eta_a, a > N$, operating on Ψ can be found from

$$\eta_a \eta_i^\dagger \eta_j^\dagger \cong \left[a_a + \sum_{i,j} \sum_b a_i a_j a_b^\dagger c_{ij}^{ab} + \cdots \right]$$
$$\times \left[a_i^\dagger a_j^\dagger + \sum_{a,b} a_a^\dagger a_b^\dagger c_{ij}^{ab} + \cdots \right]$$
$$= \left[\sum_b a_b^\dagger c_{ij}^{ab} - \sum_b a_b^\dagger c_{ij}^{ab} + \cdots \right] = 0 \ . \tag{53}$$

Neglecting terms quadratic in the coefficients c_{ij}^{ab}, this verifies the second of Eqs. (5).

With quasiparticle operators approximated as in Eqs. (46), it must be verified that Eqs. (27) and (43) are compatible, so that the one-electron Hamiltonian $\mathscr{H}$ is uniquely defined. A diagonalized representation of $\mathscr{H}$ is assumed. Expressed in second-quantized notation, Eq. (27) is

$$\langle \Phi_0 | a_i^\dagger a_a H | N \rangle = 0, \ \ i \leq N < a \ . \tag{54}$$

Using Eqs. (4) and (5), Eqs. (43) reduce to

$$-\langle \Phi_0 | a_a \eta_i^\dagger H | N \rangle = 0, \ \ i \leq N < a \ , \tag{55a}$$

$$\langle \Phi_0 | a_i^\dagger \eta_a H | N \rangle = 0, \ \ i \leq N < a \ . \tag{55b}$$

From Eqs. (46), for $\eta_i^\dagger$, products $a_j a_a^\dagger a_b^\dagger$ annihilate $\langle \Phi_0 | a_a$ when operating to the left in the first of Eqs. (55), and nonvanishing terms in $a_b a_j^\dagger a_i^\dagger$ are quadratic in c_{ij}^{ab}. Hence, $\eta_i^\dagger$ can be replaced by $a_i^\dagger$ in this equation, which becomes identical to Eq. (54). Similarly, in the second of Eqs. (55), η_a can be replaced by a_a, and this equation also reduces to Eq. (54). Hence, to the accuracy of terms retained in Eqs. (46), Eqs. (27) and (43) are consistent.

Equation (43a) cannot be extended to define matrix elements $(l | \mathscr{H} | i)$ for $i,l \leq N$ within the occupied basis set, because $a_l^\dagger \Phi_0$ vanishes identically. However, an effective operator $\mathscr{H}_l$ can be defined in the eigenstate $|N-1,l\rangle$ by its matrix elements in the orbital basis that diagonalizes $\mathscr{H}$ for state $|N\rangle$. This gives

$$(l | \mathscr{H}_l | i) = \langle a_l \Phi_0 | a_l [H, \eta_i^\dagger] | N-1, l \rangle$$
$$= \langle \Phi_0 | [H, \eta_i^\dagger] \eta_l | N \rangle = E_i \delta_{li}, \ \ i,l \leq N \ . \tag{56}$$

The Dyson energy E_i occurs here, as required by Eqs. (4), rather than the Landau energy ε_i. Nondiagonal elements can be evaluated, using Eqs. (46) and neglecting terms quadratic in coefficients c_{ij}^{ab},

$$(l | \mathscr{H}_l | i) = (l | \mathscr{H} | i) = 0, \ \ l \neq i, \ \ i,l \leq N \ , \tag{57}$$

which verifies the assumed form of operators $\eta_p^\dagger$ in Eqs. (46).

Similarly, from Eq. (43b), matrix elements of an effective operator $\mathscr{H}^d$ can be defined in the orbital basis that diagonalizes $\mathscr{H}$ for state $|N\rangle$,

$$(d | \mathscr{H}^d | d) = \langle a_d^\dagger \Phi_0 | a_d^\dagger [\eta_a, H] | N+1, d \rangle$$
$$= \langle \Phi_0 | [\eta_a, H] \eta_d^\dagger | N \rangle = E_a \delta_{ad}, \ \ a,d > N \ . \tag{58}$$

Nondiagonal elements, evaluated using Eqs. (46), are

$$(a | \mathscr{H}^d | d) = (a | \mathscr{H} | d) = 0, \ \ d \neq a, \ \ a,d > N \ . \tag{59}$$

Equations (43), (57), and (59) establish a one-to-one correspondence between the basis orbitals $\{\phi_i ; \phi_a\}$ that diagonalize the effective one-electron Hamiltonian $\mathscr{H}$ and quasiparticle operators with the same indices. The Dyson energies that occur in Eqs. (56) and (58) can be computed by integrating Eqs. (14), using Landau energies ε_i and ε_a that are eigenvalues of the operator functional $\mathscr{H}(\{n\})$ given by Eq. (35). In principle, the orbital basis should be recomputed for each set of occupation numbers. A simple approximation is obtained by expanding the operator $\mathscr{H}$ in the Taylor series of occupation number displacements about the N-electron ground state. In particular, suppressing indication of occupation numbers that retain their ground state values,

$$\mathscr{H}(n_i) = \mathscr{H}(1) - \frac{\partial \mathscr{H}}{\partial n_i}(1)(1 - n_i) + \cdots \ , \ \ i \leq N \ , \tag{60a}$$

$$\mathscr{H}(n_a) = \mathscr{H}(0) + \frac{\partial \mathscr{H}}{\partial n_a}(0) n_a + \cdots \ , \ \ a > N \ . \tag{60b}$$

Hence, from Eqs. (14), for $i \leq N$,

$$E_i=\int_0^1 \left(i \left| \mathscr{H}(1)-(1-n_i)\frac{\partial \mathscr{H}}{\partial n_i}(1)+\cdots \right| i \right) d(1-n_i)$$

$$\cong \varepsilon_i-\frac{1}{2}\frac{\partial \varepsilon_i}{\partial n_i}\ , \tag{61}$$

evaluated for $n_i=1$. From Eq. (36) this approximation gives

$$E_i \cong \varepsilon_i+\sum_j n_j \sum_b (1-n_b)(ij\,|\,\bar{v}\,|\,ib)c_{ij}^{ib},\ \ i \leq N\ . \tag{62}$$

Similarly, for $a>N$,

$$E_a=\int_0^1 \left(a \left| \mathscr{H}(0)+n_a\frac{\partial \mathscr{H}}{\partial n_a}(0)+\cdots \right| a \right) dn_a$$

$$\simeq \varepsilon_a+\frac{1}{2}\frac{\partial \varepsilon_a}{\partial n_a}\ , \tag{63}$$

evaluated for $n_a=0$. From Eq. (36),

$$E_a \cong \varepsilon_a-\sum_j n_j \sum_b (1-n_b)(aj\,|\,\bar{v}\,|\,ab)c_{aj}^{ab},\ \ a>N\ . \tag{64}$$

The coefficients c_{ij}^{ib} and c_{aj}^{ab} in Eqs. (62) and (64) reduce to one-electron virtual excitation coefficients c_j^b, which vanish in state $|N\rangle$ by construction (the Brueckner condition). However, in Eqs. (60), the orbital basis appropriate to state $|N\rangle$ is used in states $|N-1,i\rangle$ and $|N+1,a\rangle$. The Brueckner condition no longer holds in these states for this basis. The extra terms in Eqs. (62) and (64) vanish if $\mathscr{H}$ does not change when one electron is added or removed. In a normal periodic solid the addition or removal of one Bloch wave can have only an infinitesimal effect on $\mathscr{H}$, so that Landau and Dyson energies can be identified. In contrast, finite effects are expected for finite systems or for localized states in solids.

To illustrate the points made in this formal argument, consider the He atom as an extreme example of a finite system. The ${}^1S$ ground-state wave function can be represented in a natural orbital expansion, which satisfies the Brueckner condition, for $N=2$,

$$|N\rangle=1s^2+\sum_a \phi_a^2 c_{1s^2}^{a^2}\ . \tag{65}$$

The two occupied orbitals are $1s\alpha$ and $1s\beta$, with identical radial wave functions. The ${}^2S$ ground state of He^+ is degenerate. The spin-up substate is indexed by $1s\beta$, the orbital removed from the reference determinant of the state $|N\rangle$, if the orbital basis were not changed. However, the basis must change in this case, and the eigenstate is

$$|N-1,1s\beta\rangle=1s_0\alpha\ . \tag{66}$$

The hydrogenic $1s_0$ orbital of He^+ is distinctly more compact than the occupied $1s$ natural orbital of He, since the two electrons of the neutral atom mutually screen each other. The Landau energies $\varepsilon_{1s\beta}$ must differ in these two states, Eqs. (65) and (66), because the appropriate orbital basis changes. Neither of these Landau energies equals the Dyson energy $E_{1s\beta}$, which is defined as the difference between total energy eigenvalues.

In this example, the exact quasiparticle operator defined by

$$|N\rangle=\eta_{1s\beta}^{\dagger}\,|N-1,1s\beta\rangle \tag{67}$$

is

$$\eta_{1s\beta}^{\dagger}=\left[a_{1s\beta}^{\dagger}a_{1s\alpha}^{\dagger}+\sum_a a_{a\beta}^{\dagger}a_{a\alpha}^{\dagger}c_{1s^2}^{a^2} \right] a_{1s_0\alpha}\ , \tag{68}$$

defined in a mixed basis. The representation of $a_{1s_0\alpha}$ in the orthonormal basis for state $|N\rangle$, as assumed in Eqs. (46), is

$$a_{1s_0\alpha}=a_{1s\alpha}+\sum_a a_{a\alpha}c_{a\alpha}^{1s\alpha}\ , \tag{69}$$

neglecting terms quadratic in the coefficients defined by Eq. (69). When substituted into Eq. (68), using $a_{1s\alpha}^{\dagger}a_{1s\alpha}\cong 1$, again neglecting quadratic terms, this gives

$$\eta_{1s\beta}^{\dagger}=a_{1s\beta}^{\dagger}+\sum_a a_{1s\alpha}a_{a\beta}^{\dagger}a_{a\alpha}^{\dagger}c_{1s^2}^{a^2}$$

$$+\sum_a a_{a\alpha}a_{1s\beta}^{\dagger}a_{1s\alpha}^{\dagger}c_{a\alpha}^{1s\alpha}+\cdots\ . \tag{70}$$

This agrees with Eqs. (46) if

$$c_{1s\beta a\alpha}^{1s\beta 1s\alpha}=c_{a\alpha}^{1s\alpha}\ , \tag{71}$$

and identifies terms in Eqs. (46) whose coefficients have repeated indices, like c_{ia}^{ij}, with transformations of the orbital basis.

Studies of the infinite uniform interacting free-electron gas[4,8,20] indicate that electronic exchange and correlation must be considered together when electrons interact through the unscreened Coulomb potential. Rapid dependence on momentum transfer of the exchange potential is largely compensated by a corresponding variation of the correlation potential. The full effective exchange-correlation potential is accordingly much more localized (independent of momentum transfer) than either of its separate unscreened components. In Eq. (23), which is exact for total energy, there must be substantial cancellation between the last two terms, in a basis of Bloch waves for a solid. To exploit this cancellation, due to dielectric screening, approximations in the two terms must be consistent. The most systematic approach is to replace the bare Coulomb potential by a dynamically screened potential, which can be obtained either by canonical transformation or by constructing the residual intrinsic electronic Hamiltonian after decoupling collective plasma excitations.[19,21] As a practical alternative, calculations within a neutral translational cell could simply omit all effects of external potentials, retaining only a screened Madelung potential, thus assuming that dielectric screening confines the Coulomb interaction to the range of a lattice spacing. The error in this model could be estimated and corrected by a perturbation calculation of the dynamical screening effect, starting from wave functions computed in the strictly localized model. The method suggested here for estimating coefficients c_{ij}^{ab} in a basis of Bloch waves could be used for such calculations.

V. THE SINGLE-PARTICLE GREEN FUNCTION

If a complete set of quasiparticle operators are known, the single-particle Green function[4–6] can be constructed. Following Hedin and Lundqvist,[4] the zero-temperature one-electron Green function is

$$G(\mathbf{x},\mathbf{x}',\varepsilon)=\sum_{I}\frac{f_I(\mathbf{x})f_I^{*}(\mathbf{x}')}{\varepsilon-E_I-i\eta}+\sum_{a}\frac{f_A(\mathbf{x})f_A^{*}(\mathbf{x}')}{\varepsilon-E_A+i\eta}\,, \tag{72}$$

in the limit $\eta\rightarrow 0+$, in coordinate-energy representation. The functions $f_I(\mathbf{x})$ and $f_A(\mathbf{x})$ will be defined below. The sums here are over complete sets of states of $N-1$ and $N+1$ electrons, respectively, for indices I and A. When imposed finite or periodic boundary conditions are relaxed, the sums in Eq. (72) are replaced by integrals over a continuous energy range, weighted by density-of-states factors, and the total excitation energies E_I or E_A take on complex values. The resulting contour integrals have complex values.

The orbital basis set constructed here is in one-to-one correspondence with a set of quasiparticle operators. Although the orbital set can be assumed to be complete (and orthogonal), this cannot be true for the states $|N-1,i\rangle$ and $|N+1,a\rangle$ identified in terms of the quasiparticle operators η_i and $\eta_a^\dagger$, respectively, acting on state $|N\rangle$. A complete manifold of states of $N-1$ electrons must include all orders of excitation, represented by operators

$$\eta_I=\eta_i,\eta_i\eta_j\eta_b^\dagger,\ldots \tag{73}$$

acting on $|N\rangle$. Similarly, for $N+1$ electrons, a complete manifold requires operators

$$\eta_A^\dagger=\eta_a^\dagger,\eta_j\eta_a^\dagger\eta_b^\dagger,\ldots \tag{74}$$

acting on $|N\rangle$.

The functions in Eq. (72) are defined by[4]

$$\begin{aligned}f_I(\mathbf{x})&=\left\langle N-1,I\left|\sum_p\phi_p(\mathbf{x})a_p\right|N\right\rangle\,,\\ f_A(\mathbf{x})&=\left\langle N\left|\sum_p\phi_p(\mathbf{x})a_p\right|N+1,A\right\rangle\,.\end{aligned} \tag{75}$$

In the orbital basis constructed here for state $|N\rangle$, the bare electron annihilation operators can be expanded by inversion of Eqs. (46),

$$a_p=\eta_p+\tfrac{1}{2}\sum_q\sum_r\sum_s\eta_s\eta_r\eta_q^\dagger c_{rs}^{pq}+\cdots\,, \tag{76}$$

with nonzero coefficients determined as in Eqs. (46). Using Eqs. (7), matrix elements of the bare electron operators are, from Eq. (76),

$$\langle N-1,i\,|\,a_p\,|\,N\rangle=\langle N\,|\,\eta_i^\dagger a_p\,|\,N\rangle=\delta_{ip},\quad i\le N\,, \tag{77a}$$

$$\langle N\,|\,a_p\,|\,N+1,a\rangle=\langle N\,|\,a_p\eta_a^\dagger\,|\,N\rangle=\delta_{pa},\quad a>N\,. \tag{77b}$$

Higher-order states, as indicated in Eqs. (73) and (74), also produce matrix elements of the bare electron operators a_p. The operator a_i has a component in state

$$|N+1,(j;ab)\rangle=\eta_j\eta_a^\dagger\eta_b^\dagger\,|\,N\rangle\,. \tag{78}$$

Using Eq. (76), the amplitude coefficient is

$$\langle N\,|\,a_i\eta_j\eta_a^\dagger\eta_b^\dagger\,|\,N\rangle=-c_{ij}^{ab*},\quad i,j\le N<a,b\,. \tag{79}$$

Similarly, operator a_a has a component in state

$$|N-1,(ij;b)\rangle=\eta_i\eta_j\eta_b^\dagger\,|\,N\rangle\,. \tag{80}$$

The amplitude coefficient is

$$\langle N\,|\,\eta_b\eta_j^\dagger\eta_i^\dagger a_a\,|\,N\rangle=-c_{ij}^{ab},\quad i,j\le N<a,b\,. \tag{81}$$

The energy of the higher-order state defined by Eq. (78) is estimated by $E(N)+E_{j;ab}$, where

$$E_{j;ab}=E_a+E_b-E_j\,. \tag{82}$$

Similarly, the energy of the state defined by Eq. (80) is estimated by $E(N)-E_{ij;b}$, where

$$E_{ij;b}=E_i+E_j-E_b\,. \tag{83}$$

Since the orbital basis is chosen to diagonalize the single quasiparticle Landau energies ε_i and ε_a, respectively, it cannot be assumed that the energies of states $I=(ij;b)$ or $A=(j;ab)$ are exactly diagonalized at the same level of approximation. Hence, Eqs. (82) and (83) are mean values in approximate eigenstates. Energy shifts due to interactions among these states could be estimated by direct calculations of the relevant $(N-1)$ or $(N+1)$-electron eigenstates.

The present argument shows, for interacting fermions, that the set of quasiparticle operators η_i or $\eta_a^\dagger$ must be augmented by higher-order operators, as in Eqs. (73) or (74). From Eqs. (75), (77), and (81), functions $f_I(\mathbf{x})$ at successive orders of excitation of the $(N-1)$-electron manifold are

$$\begin{aligned}&f_i(\mathbf{x})=\phi_i(\mathbf{x}),\quad i\le N\,,\\ &f_{ij;b}(\mathbf{x})=-\sum_a\phi_a(\mathbf{x})c_{ij}^{ab},\quad i,j\le N<a,b\,,\\ &\ldots\,.\end{aligned} \tag{84}$$

Similarly, from Eqs. (75), (77), and (79), the functions $f_A(\mathbf{x})$ at successive orders of excitation of the $(N+1)$-electron manifold are

$$\begin{aligned}&f_a(\mathbf{x}),\quad N<a\,,\\ &f_{j;ab}(\mathbf{x})=-\sum_i\phi_i(\mathbf{x})c_{ij}^{ab*},\quad i,j\le N<a,b\,,\\ &\ldots\,.\end{aligned} \tag{85}$$

These functions, with energy mean values given by Eqs. (82) and (83), should be used in Eq. (72) to construct the one-electron Green function.

Standard perturbation theory is based on an adiabatic time development starting from noninteracting bare particle states.[4,5] Roots of the one-electron Dyson equation, as usually defined, are indexed by a single orbital index. This corresponds to the first order of the quasiparticle states with operators η_i or $\eta_a^\dagger$. The present argument shows that additional states, corresponding to higher-order excitations of the $(N-1)$- and $(N+1)$-electron manifolds, are required for a complete representation of the one-electron Green function. Such states are considered by Hedin and Lundqvist.[4] In discussing the electron self-energy, they show that the one-electron Dyson equation at given **k** has multiple solutions. One solution corresponds to a quasiparticle, $\eta_{\mathbf{k}}^{\dagger}$ for an electron state, including virtual plasmons and particle-hole excitations. Another solution corresponds to an electron plus real plasmons, described here by operators at the second order of excitation in Eq. (74). As mentioned above, interactions between these higher-order excitations, resulting in energy-shift corrections to Eq. (82), should be taken into account by variational or perturbation calculations on states of the $(N-1)$- or $(N+1)$-electron manifolds.

It should be noted that the energy range of these higher-order states will in general overlap the spectrum of eigenvalues E_i or E_a. By construction, the quasiparticle operators η_i and $\eta_a^{\dagger}$ are decoupled from higher-order quasiparticles, but in the overlapping energy range the energy density of states must take such quasiparticle states into account.

VI. RELATION TO BARDEEN-COOPER-SCHRIEFFER THEORY

An important practical goal of the present analysis is to provide a common formalism for treating normal solids and superconductors. It will be shown here, in outline, how this formalism might be applied to the electronic interaction Hamiltonian postulated in the BCS theory.[22] A more detailed analysis will be published separately.

The basic mechanism of BCS theory is a selective interaction between electrons in time-reversed states $(\mathbf{k}\uparrow)$ and $(-\mathbf{k}\downarrow)$, where the arrow denotes spin direction. It was shown by Cooper[23] that an attractive interaction between electrons just above the Fermi surface in a metal leads to a collective bound state below the single-particle energy continuum. As shown in the BCS theory, the result is to disrupt the continuous distribution of one-electron energies across the Fermi level and to form an energy gap. The interaction mechanism is a net attraction due to virtual emission and reabsorption of phonons.

The special nature of this interaction is emphasized in discussions by March *et al.*[24] and by Weisskopf.[25] The postulated electronic interaction is only weakly dependent on momentum transfer, in contrast to the Coulomb interaction, but is confined to a narrow energy shell of width 2δ at the Fermi surface. For the phonon-induced interaction, δ is of magnitude $\hbar\omega$, where ω is a Debye frequency, such that $\hbar\omega \sim 0.05$ eV. For Bloch waves or quasiparticles indexed by momenta $\mathbf{k}_i, \mathbf{k}_j$, the sums over index pairs$_{ij}$ that occur in the total electronic energy, Eq. (23) here, can be expressed as double sums over $\mathbf{Q}_{ij}$ and $\mathbf{q}_{ij}$, where the total momentum of a pair ij is

$$\mathbf{Q}_{ij} = \mathbf{k}_i + \mathbf{k}_j \tag{86}$$

and the momentum transfer is

$$\mathbf{q}_{ij} = \mathbf{k}_i - \mathbf{k}_j \; . \tag{87}$$

For an interaction that is weakly dependent on **q**, the effective strength of the interaction depends on the number of values of **q** that are compatible with given total **Q**. A geometrical argument[24] shows that in the limit of small δ the measure of the sum over **q** is one dimensional unless $\mathbf{Q}=0$, but two dimensional (half the area of the Fermi surface) for $\mathbf{Q}=0$. Hence the interaction is selective for pairs $(\mathbf{k}, -\mathbf{k})$.

The physical basis for $\mathbf{Q}=0$ selectivity is elucidated in the discussion by Weisskopf.[25] A traveling electron, envisaged as a wave packet, with momentum **k**, leaves behind it a tube of inward ion displacements. A second electron, following the same path, finds a region of attractive potential in this tube, and its energy is lowered. The effect is negligible unless the paths are parallel, and is maximized if the momenta are equal and opposite. Since spatial wave functions can be identical only in relative singlet states, the interaction is maximized for opposite spin pairs $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$.

The BCS model can be described in terms of a reduced Hamiltonian of the form

$$H_{\mathrm{BCS}} = \sum_{\pm K} E_K^0 a_K^{\dagger} a_K + \tfrac{1}{2} \sum_{K} \sum_{K'} V_{KK'} a_K^{\dagger} a_{-K}^{\dagger} a_{-K'} a_{K'} \; , \tag{88}$$

where K denotes $(\mathbf{k},\uparrow)$ and $-K$ denotes $(-\mathbf{k}\downarrow)$. The unperturbed creation operators $a_K^{\dagger}$ can be postulated to refer to quasiparticles of a normal metal. The screened Coulomb interaction is already contained in the effective one-electron energies E_K^0. The model two-electron interaction $V_{KK'}$ is assumed to be attractive and to act only if E_K^0 and $E_{K'}^0$ both lie within an energy shell of width 2δ at the Fermi surface, $E^0 = \mu$.

In the present formalism, the point of departure is the *correlated* N-electron ground state, which is not required to have any simple relationship to a noninteracting system. The two basic principles used here, the exact energy formula, Eq. (23), and the stability condition, Eq. (27), which determines an effective one-electron Hamiltonian, are universally valid. This argument leads directly to the energy functional given by Eq. (34), in the orbital basis that diagonalizes the one-electron Hamiltonian of Eq. (35). Applied to the BCS model Hamiltonian, Eq. (34) for the energy functional is

$$E_{\mathrm{BCS}} = \sum_{\pm K} n_K E_K^0 + \sum_K n_K n_{-K} V_{KK} + \sum_K n_K n_{-K} \sum_L (1-n_L)(1-n_{-L}) V_{KL} C_{LK} \; . \tag{89}$$

Exchange integrals do not occur here because the reduced Hamiltonian, Eq. (88), does not couple electrons of parallel spin. The coefficients C_{LK} can be assumed to be of the form given by Eq. (25). Their magnitudes are bounded by Eq. (24).

The Landau energies, which are eigenvalues of the effective one-electron Hamiltonian, are given by Eqs. (36). When applied to Eq. (89) this gives

$$\varepsilon_P = \frac{\partial E}{\partial n_P} = E_P^0 + n_{-P} V_{PP} + n_{-P} \sum_L (1-n_L)(1-n_{-L}) V_{PL} C_{LP} - (1-n_{-P}) \sum_K n_K n_{-K} V_{KP} C_{PK} \; . \tag{90}$$

The occupation numbers here refer to quasiparticle states that include the BCS interaction. Hence, Eq. (48) is valid, and quasiparticle levels are occupied in sequence of increasing Landau energies. A Fermi level or chemical potential μ is defined such that at zero temperature

$$n_I = n_{-I} = 1, \quad \varepsilon_I < \mu , \tag{91a}$$

and

$$n_A = n_{-A} = 0, \quad \varepsilon_A > \mu . \tag{91b}$$

In the BCS theory, V_{PP} is of order Ω^{-1}, if Ω is the system volume, so V_{PP} can be neglected in Eq. (90). The sums in Eq. (90) are symmetrical about the Fermi level if matrix elements $V_{KK'}$ are approximately constant, equal to $-V\Omega^{-1}$ within the interacting shell of width 2δ. A simplified treatment of temperature dependence is possible when these sums can be assumed to be approximately equal and independent of temperature. Then

$$\begin{gathered}\sum_L (1-n_L)(1-n_L)V_{PL}C_{LP} \cong -D , \\ \sum_K n_K n_{-K} V_{KP} C_{PK} \cong -D .\end{gathered} \tag{92}$$

These sums are negative, representing ground-state correlation energies, regardless of the sign of V. Equations (92) should be valid in the strong-coupling limit,[26] when the dimensionless product of V and the density of states at the Fermi level is relatively large. In this limit a greater proportion of electronic states within the energy width 2δ are maintained in their $T=0$ condition ($n_K = 1$ or $n_L = 0$) for $T > 0$.

Equations (90) and (92) imply

$$\varepsilon_P \cong E_P^0 + (1-2n_{-P})D . \tag{93}$$

Since occupation numbers are determined by Eqs. (91), the Landau energies differ below and above the Fermi level. At zero temperature,

$$\varepsilon_I = \varepsilon_{-I} = E_I^0 - D, \quad \varepsilon_I < E_I^0 \le \mu , \tag{94a}$$

$$\varepsilon_A = \varepsilon_{-A} = E_A^0 + D, \quad \mu \le E_A^0 < \varepsilon_A . \tag{94b}$$

This gives an energy gap of magnitude $2D$ at the Fermi level. Equation (93) indicates that the energy gap depends on temperature through the occupation numbers n_{-P}. The gap vanishes in the high-temperature limit because $n_{-P} \rightarrow \frac{1}{2}$ at the Fermi level. Evaluated at $E_P^0 = \mu$, Eq. (13) is an implicit equation for occupation number as a function of T,

$$n = F(n) = \{\exp[(1-2n)D/kT]+1\}^{-1} . \tag{95}$$

At $T=0$ this equation has three solutions, $n=0, \frac{1}{2}, 1$, compatible with Eqs. (91) for the ground state. Three solutions exist for $F'(\frac{1}{2}) > 1$, but coalesce into a unique solution, $n=\frac{1}{2}$, for $F'(\frac{1}{2}) \le 1$. Hence the transition temperature T_c is determined by $F'(\frac{1}{2}) = 1$, or

$$2D/kT_c = 4 , \tag{96}$$

in agreement with the exact result in the strong-coupling limit.[26]

When the temperature dependence of the occupation numbers in Eqs. (92) cannot be neglected, Eq. (90) can still be simplified by assuming constant interaction

$$V_{KK'} \cong -V/\Omega . \tag{97}$$

If Eq. (47) is valid for the coefficients $C_{K'K}$, the two sums in Eq. (90) can be combined to give Eq. (93) with a temperature-dependent parameter D defined for $E_K^0 \cong \mu$ by

$$D = \frac{1}{2\Omega}\sum_{K'}(1-2n_{K'})VC_{K'} . \tag{98}$$

Comparing with BCS theory[22] at $T=0$, the coefficients can be assumed to have the form

$$C_K = D/E_K , \tag{99}$$

where

$$E_K = [(E_K^0-\mu)^2 + D^2]^{1/2}\,\mathrm{sgn}(E_K^0-\mu) . \tag{100}$$

As required by the present formalism, the coefficients C_K have magnitude ≤ 1. Parameter D is nonnegative. For nonzero D, Eq. (98) is the consistency condition of the BCS theory at $T=0$. Replacing the sum by an integral over the shell of interacting electrons, for density of states ρ at the Fermi level,

$$\frac{2}{\rho V} = \int_{-\delta}^{+\delta}\frac{d\varepsilon}{(\varepsilon^2+D^2)^{1/2}} . \tag{101}$$

Hence, at $T=0$, the energy gap is $2D$, where

$$D = \delta\,\mathrm{csch}\frac{1}{\rho V} \cong 2\delta e^{-1/\rho V} . \tag{102}$$

At T_c, the Landau energies ε_K reduce to E_K^0, and occupation numbers are given by the normal Fermi-Dirac function. Hence, for $T \lesssim T_c$, Eq. (98) becomes

$$D(T) = \frac{V}{2\Omega}\sum_{K'}\frac{D(T)}{\varepsilon_{K'}}\tanh\left[\frac{\varepsilon_{K'}}{2kT}\right] . \tag{103}$$

Unless $D(T)$ is identically zero, the limit $T \rightarrow T_c$ requires a consistency condition, expressed as an integral over the shell of interacting electrons,

$$\frac{2}{\rho V} = \int_{-\delta}^{+\delta} d\varepsilon\frac{1}{\varepsilon}\tanh\left[\frac{\varepsilon}{2kT_c}\right] . \tag{104}$$

This equation determines T_c in the BCS theory.[22,24] In the weak-coupling limit ($kT_c \ll \delta$),

$$kT_c \cong 1.14\delta e^{-1/\rho V} . \tag{105}$$

From Eqs. (102) and (105), using $D(T=0)$,

$$2D/kT_c = 3.52 , \tag{106}$$

which is the BCS result in the weak-coupling limit. Experimental values of this ratio,[27] from thermodynamic measurements, lie generally between 3.5 and 4.0, while tunneling measurements give a larger spread of data. Detailed analysis of the temperature dependence of the energy gap, as determined by the present theory, will be given in a separate publication.

Evaluation of the coefficients C_{LK} in Eqs. (89) amounts to solution of the secular equation for a Cooper pair.[23] The difference from the BCS theory is that the present formalism starts from a parametrized representation of the correlated N-electron ground state, not from a postulated noninteracting electron system. The coefficients C_{LK} are of magnitude near unity for $\mathbf{k}$ and $\mathbf{l}$ near the Fermi surface, since they are elements of the ground-state eigenvector of a Hamiltonian matrix with many near-degenerate diagonal elements, corresponding to virtual pair excitations of the unperturbed system. Details of this analysis will be published elsewhere.

A crucial physical question is why the present analysis does not lead to an energy gap in normal metals. The answer is that the gap structure is built into the postulated BCS Hamiltonian, by the unique pairing between orbital states $(\mathbf{k},\uparrow)$ and $(-\mathbf{k},\downarrow)$. For the normal Coulomb or screened Coulomb interaction, matrix elements depend primarily on momentum transfer q, so the sum over index pairs ij in Eq. (34) cannot be reduced to a single term. The result is that the second term in Eq. (93) becomes a sum over states above and below the Fermi level, and the average value goes to zero.

VII. DISCUSSION

An electron added or removed from a quasiparticle state carries with it all the energy and momentum associated with it in the interacting N-electron system.[11] As discussed by Nozieres,[5] the concept of a quasiparticle is justified by many-particle perturbation theory only if, starting from a noninteracting particle, identity is maintained through a process of switching on the particle interaction. The lifetime must be longer than the switching time. Hence, quasiparticle theory would appear to be valid only for small deviations from the N-electron ground state. In contrast, the present derivation is time independent and appears to be universally applicable to N-electron systems. Quasiparticle lifetimes appear only at the final stage of analysis, when confining boundary conditions that discretize energy levels are relaxed.

In applying this formalism to finite or localized systems a distinction must be made between Landau and Dyson one-electron energy levels. The former are derivatives of an energy functional with respect to an occupation number, while the latter are energy differences between eigenstates of N and $N \pm 1$ electrons. The Landau and Dyson one-electron energies are shown to be equal only when the one-electron Hamiltonian defined here is unaffected by adding or removing one electron from a given N-electron eigenstate.

This one-electron Hamiltonian, which contains nonlocal exchange and correlation operators, is uniquely defined for any given N-electron eigenstate. The eigenvalues of this one-electron Hamiltonian are equal to Landau energies. The eigenfunctions provide an orbital basis for representation of the system Hamiltonian. Quasiparticle operators can be explicitly constructed in this basis.

The total energy functional defined here depends on a particular choice of orbital basis and on values of virtual pair excitation coefficients as well as on occupation numbers. The pair coefficients are assumed to be exact, satisfying a stationary variational principle for the total energy, so functional derivatives of the energy with respect to these coefficients can be assumed to vanish. Functional derivatives with respect to the orbital basis vanish by construction since this condition defines the one-electron Hamiltonian. Hence, variations of the residual energy expression depend only on the occupation numbers, as postulated in the Landau theory. The present derivation shows that this result is valid in a neighborhood of the occupation-number values for the N-electron state used to define the pair-excitation coefficients and one-electron Hamiltonian or orbital basis. The one-electron Hamiltonian is parametrized by occupation numbers. Its eigenfunctions and eigenvalues should be recomputed as occupation numbers change in a finite or localized system.

The virtual pair-excitation coefficients are considered here as basic parameters, to be computed separately from the one-electron Hamiltonian and quasiparticle operators. Since calculations can be carried out accurately for localized systems, a practical computational procedure might be to compute pair-excitation coefficients in a localized representation by a cellular calculation, then to transform to a Bloch wave representation for an extended system, assuming that Eq. (25) is valid. Analysis of the BCS Hamiltonian, given in Sec. VI here, indicates that the present formalism is valid for systems for which perturbation theory is generally considered to be inapplicable.

ACKNOWLEDGMENTS

The author is grateful, for helpful discussion and critical comments, to F. Herman, H. Morawitz, J. A. Barker, W. Kohn, and J. R. Schrieffer.

---

[1] R. K. Nesbet, Adv. Chem. Phys. **9**, 321 (1965); **14**, 1 (1969).

[2] I. Shavitt, in *Methods of Electronic Structure Theory,* edited by H. F. Schaefer III (Plenum, New York, 1977), p. 189.

[3] W. Meyer, in *Methods of Electronic Structure Theory,* edited by H. F. Schaefer III (Plenum, New York, 1977), p. 413.

[4] L. Hedin and S. Lundqvist, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 1.

[5] P. Nozieres, *Theory of Interacting Fermi Systems* (Benjamin, New York, 1964).

[6] D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic, New York, 1961).

[7] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985).

[8] L. Hedin, Phys. Rev. **139**, A796 (1965).

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

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

[11] L. D. Landau, Zh. Eksp. Teor. Fiz. **30**, 1058 (1956) [Sov. Phys.—JETP **3**, 920 (1956)]; **32**, 59 (1957) [**5**, 101 (1957)].

[12] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[13] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[14] W. Brenig, Nucl. Phys. **4**, 363 (1957).

[15] W. Kutzelnigg, in *Methods of Electronic Structure Theory,* edited by H. F. Schaefer III (Plenum, New York, 1977), p. 129.

[16] R. K. Nesbet, Phys. Rev. **109**, 1632 (1958).

[17] K. A. Brueckner and W. Wada, Phys. Rev. **103**, 1008 (1956).

[18] D. J. Rowe, Rev. Mod. Phys. **40**, 153 (1968).

[19] R. K. Nesbet, J. Math. Phys. **6**, 621 (1965).

[20] A. W. Overhauser, Phys. Rev. B **2**, 874 (1970); **3**, 1888 (1971).

[21] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, New York, 1963).

[22] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[23] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).

[24] N. H. March, W. H. Young, and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (Cambridge University Press, New York, 1967).

[25] V. F. Weisskopf, Contemp. Phys. **22**, 375 (1981).

[26] D. J. Thouless, Phys. Rev. **117**, 1256 (1960).

[27] R. Meservey and B. B. Schwartz, in *Superconductivity,* edited by R. D. Parks (Dekker, New York, 1964), Vol. 1, p. 117.