where one exponential factor is due to the shrinking and the other due to the phase-factor effect. We can conclude in this case that (1) the shrinking and the phase-factor effects contribute the same order of magnitude to the magnetoresistance even in an extremely strong field, (2) the dependence of the magnetoresistance coefficient on the average donor separation changes from an R^3 dependence in the weak and moderately strong field case to an R^2 dependence, and (3) the dependence of the magnetoresistance on the magnetic field changes from an H^2 to an H dependence.

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Projected Wave-Field Approach to the Many-Electron Problem in Solids*

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The orthogonalized plane wave (O. P. W.) method for treating electrons in solids is generalized to the many-body problem. The core electrons are assumed to be dynamically independent of the valence electrons. Using a field-theoretical approach, a model wave field is introduced whose valence projection is the valence wave field of the physical system. When an appropriate choice is made for the model Hamiltonian, the rapid convergence of the O. P. W. method is incorporated in the many-body perturbation expansion.

An attractive feature of the scheme is that the perturbation expansion can be carried out using zero-order Green's functions appropriate to free electrons. The single-particle self-energy to low order is the sum of the one-body O. P. W. contribution and a screened exchange energy similar to that obtained in the case of the uniform electron gas.

The theory is expected to be most useful for metals and valence crystals for which the single-particle O. P. W. method is known to be appropriate.

I. INTRODUCTION

IN the past few years a great deal of progress has been made in the study of the gas of interacting electrons. We do not want to summarize the results obtained, but we rather refer the reader to some relevant papers on the subject.[1]

Different formalisms have been developed for this problem according to the aspect emphasized. The collective approach of Bohm and Pines is best suited to the study of the plasma oscillations. A perturbation theory was developed by Brueckner, Goldstone, Hubbard, and others for the study of the ground-state correlation energy. An alternative approach to plasma effects has been based on linearization of the Heisenberg equation of motion (Sawada, Fukuda, Brueckner, and Brout; Suhl and Werthamer). This method gives, in principle, also one-particle excitation energies and the ground-state energy.

The powerful Green's function formalism of field theory has been adapted to the many-body problem by Galitski and Migdal[2] and in a more general form by Martin and Schwinger.[3] Klein has shown that within this formalism a one-body model potential can be constructed and made self-consistent to all orders.[4]

In the present paper, we use the Green's function formalism to derive perturbation expressions for valence and conduction states of electrons in a covalent crystal, including correlation effects which are neglected in ordinary band theory. In most recent studies of

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[1] David Pines, *The Many-Body Problem* (W. A. Benjamin Inc., New York, 1961); D. Bohm and D. Pines, Phys. Rev. **92**, 608 (1953); P. Nozières and D. Pines, *ibid.* **111**, 442 (1958); K. Brueckner and M. Gell-Mann, *ibid* **106**, 364 (1957); J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957); J. Hubbard, *ibid* **A240**, 539 (1957); **A243**, 336 (1957); D. F. Du Bois, Ann. Phys. (New York) **7**, 174 (1959); A. Klein and P. Prange, Phys. Rev. **112**, 994 (1958); K. Sawada, N. Fukuda, K. Brueckner, and R. Brout, *ibid* **108**, 507 (1957); W. Kohn and J. Luttinger, *ibid* **118**, 41 (1960); J. M. Luttinger and J. C. Ward, *ibid* **118**, 1417 (1960); J. M. Luttinger, *ibid* **121**, 942 (1961); H. Suhl and N. Werthamer, *ibid.* **122**, 359 (1961).

[2] V. M. Galitski and A. B. Migdal, Soviet Phys.—JETP 7, 96 (1958).

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

[4] A. Klein, Phys. Rev. **121**, 950 (1961).

correlation energies in real crystals the basis wave functions employed are the solutions of the Hartree-Fockpr oblem.[5] These have led to formal extensions of the free electron gas results, which however seem to be of little use as a basis for numerical calculations. We will consider the Hartree-Fock potential and the remaining two-body interactions jointly as the perturbation Hamiltonian on the symmetrized plane wave states of a constant potential (empty lattice states) with the additional condition that the core states be known and unchanged by the dynamics of the valence electrons. Essentially, we extend the orthogonalized plane wave (O. P. W.) method.[6] The quasi-particle energies we obtain reduce in the one electron approximation to the energies of valence and conduction states of the O. P. W. method.

In Sec. II a simplified Heisenberg equation of motion is obtained for the valence projection of the electron wave field. The one-particle Green's function for this valence projection is introduced in Sec. III. In Sec. IV we introduce an auxiliary wave field ψ_0 by requiring explicitly that the core projection of the valence wave field vanish. A self-adjoint effective Hamiltonian and an equation of motion for ψ_0 is derived. In Sec. V we relate the Green's function for the valence wave field to that for the auxiliary wave field. In Sec. VI we show that the O. P. W. method results from our more general treatment upon neglecting correlation terms. In Sec. VII we give a perturbation expansion for the self-energy including correlation terms.

II. HAMILTONIAN FORMULATION FOR THE VALENCE ELECTRON WAVE FIELD

We work in the Heisenberg picture and write the second quantized Hamiltonian for the electrons as

$$H=\int dxdx'\,\psi^\dagger(x,t)\langle x|H_1-U|x'\rangle\psi(x',t) +\frac{1}{2}\int dxdx'\,\psi^\dagger(x,t)\psi^\dagger(x',t) \times V_2(x,x')\psi(x',t)\psi(x,t). \quad (2.1)$$

The variable x represents the spacial and spin coordinates $\mathbf{r}$ and s. The operator H_1-U is the kinetic energy operator $p^2/2m$ plus the interaction with the fixed nuclei. By choosing U appropriately the Hartree-Fock terms arising from the Columb interaction between electrons, $V_2(x,x')$, can be canceled and in this way H_1 can be arranged to include electron-electron interactions within the Hartree-Fock approximation. This possibility has been discussed in detail by Goldstone[1] and Hubbard.[5] In general, H_1 is not diagonal in the x representation.

[5] J. Hubbard, Proc. Roy. Soc. (London) **A244**, 199 (1958).
[6] C. Herring, Phys. Rev. **57**, 1163 (1940). T. O. Woodruff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4.

Our basic approximation is to treat the valence electrons as being dynamically independent of the core electrons. By this we mean that all terms in the Hamiltonian which couple valence and core electrons will be treated in the Hartree-Fock approximation. The validity of this assumption is insured by two conditions:

(a) In a perturbation treatment of the correlation energy, the important excitation energies involved in core-valence interactions are large compared to those entering valence-valence interactions.

(b) The spacial overlap of core and valence wave functions is small so that matrix elements involving core and valence electrons tend to be smaller than those involving core or valence electrons alone.

Since interactions which involve virtual excitations of core electrons to valence states are to be neglected, it follows that the core electrons are treated in the single-particle approximation. The single-particle core wave functions satisfy the equations

$$\int dx'\,\langle x|H_1|x'\rangle u_{n_c}(x')=E_{n_c}u_{n_c}(x). \quad (2.2)$$

It is convenient to use these core wave functions to decompose $\psi(x,t)$ into core and valence projections:

$$\psi(x,t)=\psi_c(x,t)+\psi_v(x,t), \quad (2.3)$$

where

$$\psi_c(x,t)=\int dy\,\langle x|\mathbf{P}_c|y\rangle\psi(y,t)\equiv\mathbf{P}_c\psi(x,t),$$
$$\psi_v(x,t)=\int dy\,\langle x|\mathbf{P}_v|y\rangle\psi(y,t)\equiv\mathbf{P}_v\psi(x,t). \quad (2.4)$$

The projection operator $\mathbf{P}_c$ is defined by

$$\mathbf{P}_c=\textstyle\sum_{n_c}|u_{n_c}\rangle\langle u_{n_c}|, \quad (2.5)$$

where n_c represents a set of quantum numbers labeling the core states. The valence projection operator $\mathbf{P}_v$ is defined by

$$\mathbf{P}_v+\mathbf{P}_c=1.$$

Note the relations:

$$\mathbf{P}_c^2=\mathbf{P}_c,\quad \mathbf{P}_v^2=\mathbf{P}_v,\quad \mathbf{P}_v\mathbf{P}_c=\mathbf{P}_c\mathbf{P}_v=0,$$
$$[\mathbf{P}_c,H_1]=[\mathbf{P}_v,H_1]=0. \quad (2.6)$$

Thus, if ψ is expressed in terms of the complete set of eigenstates of H_1, ψ_c, and ψ_v are of the form

$$\psi_c(x,t)=\textstyle\sum_{n_c}u_{n_c}(x)a_{n_c}(t),$$
$$\psi_v(x,t)=\textstyle\sum_{n_v}u_{n_v}(x)a_{n_v}(t). \quad (2.7)$$

The functions $u_{n_v}(x)$ include all eigenfunctions of H_1 except those occupied by core electrons. The operators a_n are destruction operators for electrons in states labeled by n.

The anticommutation relations for ψ,

$$\{\psi(x,t),\psi^\dagger(x',t)\}=\delta(x-x'),$$
$$\{\psi(x,t),\psi(x',t)\}=\{\psi^\dagger(x,t),\psi^\dagger(x',t)\}=0, \quad (2.8)$$

lead to the following anticommutation relations for ψ_c and ψ_v:

$$\begin{aligned}&\{\psi_c(x,t),\psi_c^\dagger(x',t)\}=\langle x|\mathbf{P}_c|x'\rangle,\\&\{\psi_v(x,t),\psi_v^\dagger(x',t)\}=\langle x|\mathbf{P}_v|x'\rangle,\\&\{\psi_v(x,t),\psi_v(x',t)\}=\{\psi_v^\dagger(x,t),\psi_v^\dagger(x',t)\}=0,\\&\{\psi_c(x,t),\psi_c(x',t)\}=\{\psi_c^\dagger(x,t),\psi_c^\dagger(x',t)\}=0.\end{aligned} \quad (2.9)$$

With these relations, the equations of motion for ψ_c and ψ_v can be obtained from

$$i(\partial/\partial t)\psi_c(x,t)=[\psi_c(x,t),H], \quad (2.10a)$$
$$i(\partial/\partial t)\psi_v(x,t)=[\psi_v(x,t),H]. \quad (2.10b)$$

Since the core electrons are treated in the single-particle approximation, the time dependence of ψ_c is given directly by the one-electron energies of the core electrons. Therefore, we concentrate on the equation of motion for the valence wave field

$$\begin{aligned}i\frac{\partial}{\partial t}\psi_v(x,t)=&\int dx'dx''\,\langle x|\mathbf{P}_v|x'\rangle\langle x'|H_1-U|x''\rangle\psi(x'',t)\\&+\int dx'dx''\,\langle x|\mathbf{P}_v|x'\rangle\psi^\dagger(x'',t)\\&\times V_2(x',x'')\psi(x'',t)\psi(x',t).\end{aligned} \quad (2.11)$$

On substituting $\psi=\psi_c+\psi_v$ in the two-body term of (2.11), one obtains eight terms. In accordance with our Hartree-Fock treatment of the core electrons, we retain only the terms

$$\int dx'dx''\langle x|\mathbf{P}_v|x'\rangle\psi_v^\dagger(x'',t)\psi_v(x'',t)\times V_2(x',x'')\psi_v(x',t), \quad (2.12a)$$

$$\int dx'dx''\langle x|\mathbf{P}_v|x'\rangle\langle\psi_c^\dagger(x'',t)\psi_c(x'',t)\rangle_c\times V_2(x',x'')\psi_v(x',t), \quad (2.12b)$$

$$\int dx'dx''\langle x|\mathbf{P}_v|x'\rangle\langle\psi_c^\dagger(x'',t)\psi_c(x',t)\rangle_c\times V_2(x',x'')\psi_v(x'',t), \quad (2.12c)$$

where $\langle\sigma\rangle_c$ denotes the expectation value of σ with respect to the core states which are fully occupied. Term (2.12a) leads to the Coulomb interaction between valence electrons while terms (2.12b) and (c) give the direct and exchange interactions, respectively, between the core and valence electrons within the Hartree-Fock approximation. Since by construction U contains the interaction of the core and valence electrons within the Hartree-Fock approximation, terms (2.12b) and (c) are canceled by the corresponding terms in U. Thus, we obtain an equation of motion involving ψ_v alone

$$\begin{aligned}i\frac{\partial}{\partial t}\psi_v(x,t)=&\int dx'\langle x|H_1-\mathbf{P}_vU_v|x'\rangle\psi_v(x',t)\\&+\int dx'dx''\,\psi_v^\dagger(x'',t)\psi_v(x'',t)\langle x|\mathbf{P}_v|x'\rangle\\&\times V_2(x',x'')\psi_v(x',t).\end{aligned} \quad (2.13)$$

Here, U_v represents that part of the two-body interactions between valence electrons which we wish to include in H_1. If we choose $U_v=0$, all the interactions between valence electrons are represented by the last term on the right-hand side of (2.13). However, U_v can be chosen to be the Hartree-Fock approximation for the two-body interaction so that H_1 is the Hartree-Fock Hamiltonian. As we shall see in Sec. VII the most convenient choice is $U_v=$const, since approximate self-consistency can be obtained by a screening of the one-body potential as pointed out by Cohen and Phillips.[7] The equation of motion (2.13) can be derived from an effective Hamiltonian:

$$\begin{aligned}H_v=&\int dxdx'\,\psi_v^\dagger(x,t)\langle x|H_1-\mathbf{P}_vU_v|x'\rangle\psi_v(x',t)\\&+\frac{1}{2}\int dxdx'\,\psi_v^\dagger(x,t)\psi_v^\dagger(x',t)\\&\times V_2(x',x)\psi_v(x',t)\psi_v(x,t),\end{aligned} \quad (2.14)$$

since by direct calculation, the expression

$$i(\partial/\partial t)\psi_v(x,t)=[\psi_v(x,t),H_v] \quad (2.15)$$

agrees with (2.13).

III. ONE-PARTICLE GREEN'S FUNCTIONS FOR THE VALENCE FIELD

The space- and time-dependent one-particle Green's function is

$$G(x,x',\tau)=i\langle 0|T\{\psi(x,\tau)\psi^\dagger(x,0)\}|0\rangle, \quad (3.1)$$

where $|0\rangle$ stands for the exact Heisenberg ground state of the interacting system and T is the usual time-ordering operator for fermions. Introducing some complete set of one-particle states $|\alpha\rangle$ for expansion of the field operators and a Fourier time inversion, we obtain

$$\begin{aligned}G(x,x';\tau)=&\sum_{\alpha,\alpha'}\langle x|\alpha\rangle G_{\alpha\alpha'}(\tau)\langle\alpha'|x'\rangle\\=&\sum_{\alpha,\alpha'}\langle x|\alpha\rangle\left\{\int\frac{dp_0}{2\pi}e^{-ip_0\tau}G_{\alpha\alpha'}(p_0)\right\}\langle\alpha'|x'\rangle,\end{aligned} \quad (3.2)$$

with the understanding that

$$G_{\alpha\alpha'}(\tau)=\langle 0|T\{a_\alpha(\tau)a_{\alpha'}^\dagger(0)\}|0\rangle$$

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

and

$$a_\alpha(\tau)=\int\langle\alpha|x\rangle\psi(x,\tau)dx$$

is the destruction operator for an electron in the state $|\alpha\rangle$.

In general, $G_{\alpha\alpha'}$ cannot be made diagonal for all times in the presence of both the lattice potential and the two-body interaction, in contrast to the familiar case of a uniform background. If at time $t=0$ a particle is added to the system in state α, the probability amplitude that the system is in the same state at time τ is given by

$$G_{\alpha\alpha}(\tau).$$

A similar interpretation holds for the off-diagonal elements.

It has been shown by Galitski and Migdal[2] that if the analytic continuation of $G_{\alpha\alpha}(p_0)$ has poles near the real axis they give the excitation energies and lifetimes of the quasi-particles obtained by adding an electron or a hole to the many-electron system.

We expect that for systems where the O. P. W. method is applicable, e.g., valence crystals and metals, these conditions are satisfied for the low-lying excited states of the system.

Introducing core and valence fields via (2.3) into the expression (3.1) for G, we obtain four terms. As a consequence of our assumption of the dynamical independence of the core and valence electrons it follows that the cross terms vanish, leaving

$$G(x,x';\tau)=i\langle0|T\{\psi_c(x,\tau)\psi_c^\dagger(x',0)\}|0\rangle+i\langle0|T\{\psi_v(x,\tau)\psi_v^\dagger(x',0)\}|0\rangle. \quad (3.4)$$

Henceforth, we shall be concerned only with the valence field Green's function,

$$G_v(x,x';\tau)=i\langle0|T\{\psi_v(x,\tau)\psi_v^\dagger(x',0)\}|0\rangle. \quad (3.5)$$

In a representation α the time Fourier transform of $G_{v\alpha\alpha}$ is

$$G_{v\alpha}(p_0)=\int e^{ip_0\tau}G_{v\alpha\alpha}(\tau)d\tau. \quad (3.6)$$

IV. INTRODUCTION OF THE AUXILIARY WAVE FIELD

It is basic to this formalism that we impose explicitly the condition

$$\mathbf{P}_c\psi_v(x,t)\equiv0.$$

In analogy to the O. P. W. method for the one-electron valence states we introduce an auxiliary electron wave field $\psi_0(x,t)$ by writing

$$\psi_v(x,t)=\mathbf{P}_v\psi_0(x,t)=\psi_0(x,t)-\mathbf{P}_c\psi_0(x,t). \quad (4.1)$$

The core projection $\mathbf{P}_c\psi_0(x,t)$ is at our disposal. On substituting (4.1) into (2.10b), we have

$$\begin{aligned}i(\partial/\partial t)\psi_0(x,t)&=H_1\psi_0(x,t)+[i(\partial/\partial t)-H_1]\mathbf{P}_c\psi_0(x,t)-\mathbf{P}_vU_v\mathbf{P}_v\psi_0(x,t)\\&+\int dx'dx''[\mathbf{P}_v\psi_0(x',t)]^\dagger[P_v\psi_0(x',t)]\langle x|P_v|x'\rangle\\&\times V_2(x',x'')[P_v\psi_0(x'',t)],\end{aligned} \quad (4.2)$$

where $\mathbf{P}_v$ and H_1 are understood to be nonlocal operators. We note again the important point that Eq. (4.2) is unchanged by the addition of an arbitrary core field $\mathbf{P}_c\Phi_0$ to ψ_0, so that only $\mathbf{P}_v\psi_0$ is really determined.

Although $\mathbf{P}_c\psi_0(x,t)$ is not determined dynamically by H_v or by (4.2), it will nevertheless be restricted. Since we will treat the ψ_0 field by a Green's function scheme, it is essential to require that ψ_0 satisfy the anticommutation relations:

$$\begin{aligned}\{\psi_0(x,t),\psi_0^\dagger(x',t)\}&=\delta^3(x-x'),\\\{\psi_0(x,t),\langle\psi_0(x',t)\}&=\{\psi_0^\dagger(x,t),\psi_0^\dagger(x',t)\}=0.\end{aligned} \quad (4.4)$$

The projected form of the above relations is

$$\begin{aligned}\{\mathbf{P}_c\psi_0(x,t),(\mathbf{P}_c\psi_0(x',t))^\dagger\}&=\langle x|\mathbf{P}_c|x'\rangle,\\\{\mathbf{P}_c\psi_0(x,t),\psi_v(x',t)\}&=\{\mathbf{P}_c\psi_0(x,t),\psi_v^\dagger(x',t)\}=0,\\\{\mathbf{P}_c\psi_0(x,t),\mathbf{P}_c\psi_0(x',t)\}&=0.\end{aligned} \quad (4.5)$$

The time dependence of $\mathbf{P}_c\psi_0(x,t)$ must maintain these relations. In the absence of the time derivative on the right-hand side of (4.2) all the time derivatives of the field anticommutators would be expressible in terms of the original anticommutators. If then these have the canonical values at $t=0$, all their time derivatives would vanish and they would be independent of time. To preserve the relations (4.5) at all time in the presence of the time derivative term in (4.2) it is necessary that the equal-time anticommutators satisfy

$$\{\mathbf{P}_c\dot\psi_0,(\mathbf{P}_c\psi_0)^\dagger\}+\{\mathbf{P}_c\psi_0,(\mathbf{P}_c\dot\psi_0)^\dagger\}=0, \quad (4.6a)$$

$$\{\mathbf{P}_c\dot\psi_0,\mathbf{P}_c\psi_0\}=0, \quad (4.6b)$$

$$\{\mathbf{P}_c\dot\psi_0,\psi_v\}+\{\mathbf{P}_c\psi_0,\dot\psi_v\}=0, \quad (4.6c)$$

$$\{\mathbf{P}_c\dot\psi_0,\psi_v^\dagger\}+\{\mathbf{P}_c\psi_0,\psi_v^\dagger\}=0. \quad (4.6d)$$

The derivatives of ψ_v are expressible in terms of ψ_v, so that $\{\mathbf{P}_c\psi_0,\dot\psi_v$ or $\dot\psi_v^\dagger\}$ also vanishes at $t=0$. Thus, (c) and (d) become

$$\{\mathbf{P}_c\dot\psi_0,\psi_v\}=0, \quad (4.6c')$$

$$\{\mathbf{P}_c\dot\psi_0,\psi_v^\dagger\}=0. \quad (4.6d')$$

These conditions (and also those on higher derivatives) are satisfied if

$$\begin{aligned}i(\partial/\partial t)\mathbf{P}_c\psi_0(x,t)&=\mathbf{P}_cg\mathbf{P}_c\psi_0(x,t)\\&=\int d^3x'\langle x|\mathbf{P}_cg\mathbf{P}_c|x'\rangle\mathbf{P}_c\psi_0(x,t),\end{aligned} \quad (4.7)$$

where g is any self-adjoint operator. A particular choice of g will determine the core projection $\mathbf{P}_c\psi_0$ by means of Eq. (4.7).

Accordingly, we can replace Eq. (4.2) by

$$i(\partial/\partial t)\psi_0(x,t) = H_1\psi_0(x,t)+\mathbf{P}_c A\mathbf{P}_c\psi_0(x,t)-\mathbf{P}_v U_v\mathbf{P}_v\psi_0(x,t) + \int dx'dx''[\mathbf{P}_v\psi_0(x',t)]^\dagger[\mathbf{P}_v\psi_0(x',t)]\langle x|\mathbf{P}_v|x''\rangle \times V_2(x',x'')[\mathbf{P}_v\psi_0(x'',t)]. \quad (4.8)$$

For compactness we have written

$$\mathbf{P}_c g\mathbf{P}_c - H_1\mathbf{P}_c = \mathbf{P}_c(g-H_1)\mathbf{P}_c = \mathbf{P}_c A\mathbf{P}_c, \quad (4.9)$$

using the relation (2.6). The self-adjoint effective Hamiltonian for the auxiliary field is

$$H_{\text{eff}} = \int dxdx'\,\psi_0^\dagger(x',t)\{\langle x'|H_1|x\rangle+\langle x'|\mathbf{P}_c A\mathbf{P}_c|x\rangle\}\psi_0(x,t)+\frac{1}{2}\int dxdx'[\mathbf{P}_v\psi_0(x',t)]^\dagger[\mathbf{P}_v\psi_0(x,t)]^\dagger \times V_2(x,x')[\mathbf{P}_v\psi_0(x,t)][\mathbf{P}_v\psi_0(x',t)]-\int dxdx'\,\psi_0^\dagger(x',t)\langle x'|\mathbf{P}_v U_v\mathbf{P}_v|x\rangle\psi_0(x,t). \quad (4.10)$$

This Hamiltonian manifestly gives back the equation of motion (4.8) whose core projection is (4.7). Equations (4.9)–(4.10), together with the commutation rules (4.4) and (4.5), provide the Hamiltonian formulation for the auxiliary field $\psi_0(x,t)$.

The advantage of introducing the ψ_0 field is twofold: (1) If the ψ_v field is expanded in plane waves, the operator expansion coefficients cannot satisfy the canonical anticommutation relations so that the conventional Green's function approach cannot be employed. The ψ_0 field does not suffer this defect. (2) The ψ_0 field is the analog of the effective wave function introduced by Phillips and Kleinman[8] in the single-particle O. P. W. scheme. As Bassani and Celli have pointed out,[9] this artifice allows the one-body potential to be readily treated by perturbation theory.

These circumstances suggest that one attempt to treat the lattice potential and the two-body interaction in a joint perturbation expansion based on zero-order Green's functions appropriate to symmetrized plane waves.

V. GREEN'S FUNCTION FOR THE AUXILIARY FIELD

The excitation energies of the valence electron system are given by the poles of the time Fourier transform of G_v. We expand ψ_0 in symmetrized plane wave states

$$\psi_0(x,t)=\sum_{\mathbf{p},\alpha} S_{\mathbf{p}\alpha}(x)c_{\mathbf{p}\alpha}(t),$$

where $S_{\mathbf{p},\alpha}(x)$ represents a plane wave of momentum $\mathbf{p}$ in the extended zone scheme and at symmetry points is a symmetrized combination of plane waves belonging to the irreducible representation α. For convenience α also labels the spin state. In terms of the operators $c_{\mathbf{p}\alpha}$, from (3.1) and (4.5) we obtain

$$G_v(x,x';\tau)=\sum_{\mathbf{p}\mathbf{p}'\alpha\alpha'}\langle 0|T\{c_{\mathbf{p}\alpha}(\tau)c_{\mathbf{p}'\alpha}^\dagger(0)\}|0\rangle \times[\mathbf{P}_v S_{\mathbf{p}\alpha}(x)][\mathbf{P}_v S_{\mathbf{p}'\alpha'}(x')]^*. \quad (5.1)$$

Thus, an expansion of ψ_0 in symmetrized plane waves leads to an expansion of G_v in orthogonalized plane waves.

It would have been possible to expand ψ_v directly in orthogonalized plane waves

$$\psi_v(x,t)=\sum_{\mathbf{p}\alpha}[\mathbf{P}_v S_{\mathbf{p}\alpha}(x)]c_{\mathbf{p}\alpha}(t),$$

where $c_{\mathbf{p},\alpha}$ have the conventional anticommutation rules. This, however, does not completely specify the $c_{\mathbf{p},\alpha}$ because the $\mathbf{P}_v S_{\mathbf{p},\alpha}(x)$ are not an orthogonal set. The role of ψ_0 and H_{eff} is to allow a complete specification of the $c_{\mathbf{p},\alpha}$. The term $i\langle 0|T\{c_{\mathbf{p}\alpha}(\tau)c_{\mathbf{p}'\alpha}^\dagger(0)\}|0\rangle$ is just the Green's function of the auxiliary field $\psi_0(x,t)$ in the symmetrized plane-wave representation. Since we will be interested in the excitation energies we will consider only the diagonal terms,

$$G_0(\mathbf{p}\alpha,\tau)=i\langle 0|T\{c_{\mathbf{p}\alpha}(\tau)c_{\mathbf{p}\alpha}^\dagger(0)\}|0\rangle. \quad (5.2)$$

It is important to recognize that the ground state of the auxiliary system corresponding to ψ_0 and H_{eff} is not identical with the ground state of H_v. Nevertheless, the ground state of the auxiliary system may be used in Eq. (5.2) and henceforth we will understand $|0\rangle$ in this sense. This may be seen from Eq. (4.10) in that H_{eff} differs from H_v by the addition of arbitrary core part which commutes with H_v. The ground state of H_{eff} differs from that of the valence electron system in a factor on which ψ_v does not operate.

The effective Hamiltonian (4.12) can be written in terms of the operators $c_p=c_{\mathbf{p}\alpha}$:

$$H_{\text{eff}}=\sum_{pp'}\{\epsilon_p^{(0)}\delta_{pp'}+\langle S_{p'}|[V(x)-V_0]|S_p\rangle+\langle S_{p'}|\mathbf{P}_c A\mathbf{P}_c|S_p\rangle\}c_{p'}^\dagger(t)c_p(t) + \tfrac{1}{2}\sum_{p_1p_1'p_2p_2'}\langle \mathbf{P}_v S_{p_1'},\mathbf{P}_v S_{p_2'}|V_2|\mathbf{P}_v S_{p_1},\mathbf{P}_v S_{p_2}\rangle c_{p_1'}^\dagger(t)c_{p_2'}^\dagger(t)c_{p_2}(t)c_{p_1}(t)-\sum_{pp'}\langle \mathbf{P}_v S_{p'}|U_v|\mathbf{P}_v S_p\rangle c_{p'}^\dagger(t)c_p(t), \quad (5.3)$$

[8] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).
[9] F. Bassani and V. Celli, Nuovo cimento **11**, 805 (1959). F. Bassani and V. Celli, J. Phys. Chem. Solids **20**, 64 (1961).

where

$$\epsilon_p^{(0)}=p^2/2m+V_0 \tag{5.4}$$

and V_0 is a constant which can be chosen in the most convenient way. We write $H_{\text{eff}}=H_0+H'$ and for the unperturbed part take

$$H_0=\sum_p \epsilon_p^{(0)} c_p^\dagger(t)c_p(t). \tag{5.5}$$

The time Fourier transform of the Green's function of the unperturbed system in the symmetrized plane wave representation can be written as

$$\begin{aligned} G_0^{(0)}(p,p_0)&=\frac{(-)}{p_0-\epsilon_p^{(0)}+i\eta_p^{(0)}};\\ \eta_p^{(0)}&=(0+) \quad \text{for} \quad \epsilon_p^{(0)}>\epsilon_F^{(0)},\\ &=(0-) \quad \text{for} \quad \epsilon_p^{(0)}<\epsilon_F^{(0)}. \end{aligned} \tag{5.6}$$

For the perturbed system the diagonal part of the Green's function will have the Dyson equation form,

$$G_0(p,p_0)=\frac{(-)}{p_0-\epsilon_p^{(0)}-\Sigma(p,p_0)}, \tag{5.7}$$

where $\Sigma(p,p_0)$ is the diagonal irreducible self-energy, which may have an imaginary part. The poles of $G_0(p,p_0)$ are the solutions in the p_0 plane of the equation,

$$p_0\equiv\epsilon_p^{(0)}+\Sigma(p,p_0). \tag{5.8}$$

VI. CHOICE OF THE ARBITRARY OPERATOR g AND REDUCTION TO THE O. P. W. METHOD

We now return to the arbitrary self-adjoint operator g (or A) first introduced in Sec. IV. Only the core projection of g is of concern to us, and this is completely specified by the matrix elements $\langle kn_c|g|k'n_c'\rangle$ between core states, which are now labeled by a reduced zone vector and a band index. We must choose g to be diagonal in k, since everything else is, and can choose it diagonal in n_c. Nothing new can result from taking g nondiagonal in the $|kn_c\rangle$. Then we have

$$\mathbf{P}_c g\mathbf{P}_c=\sum_{kn_c} g_{kn_c}\mathbf{P}_{kn_c},$$

with

$$\begin{aligned} g_{kn_c}&=\langle kn_c|g|kn_c\rangle,\\ \mathbf{P}_{kn_c}&=|kn_c\rangle\langle kn_c|. \end{aligned} \tag{6.1}$$

The g_{kn_c} constitute a finite set of adjustable parameters. We note that their number is equal to the number of core states, so that the arbitrariness at our disposal while considerable is nevertheless limited. In our selection of the g_{kn_c} we are guided by the choice appropriate to a system of electrons in the external lattice potential but without two-body interactions and here first describe the analysis for that case.

Using (6.1), the solution of (4.7) is

$$\mathbf{P}_c\psi_0(x,t)=\sum_{kn_c}\exp(-ig_{kn_c}t)\mathbf{P}_{kn_c}\psi_0(x,0). \tag{6.2}$$

We can isolate the arbitrary time dependence in $G_0(x,x',\tau)$ by writing via (4.1)

$$\begin{aligned} G_0(x,x';\tau)=&\,i\langle 0|T\{\psi_v(x,\tau)\psi_0^\dagger(x',0)\}|0\rangle\\ &+i\langle 0|T\{[\mathbf{P}_c\psi_0(x,\tau)\psi_0^\dagger(x',0)\}|0\rangle. \end{aligned} \tag{6.3}$$

In an extended zone scheme we write $p=k+h$, $S_p=S_{kh}$, $c_p=c_{kh}$, where h indicates a reciprocal lattice vector. Due to the second term on the right-hand side of (6.3), $G_0(kh,p_0)$ contains the terms:

$$\sum_{n_c}\left\{\frac{(-)}{p_0-g_{kn_c}+i\eta}\sum_{h'}\langle kh|\mathbf{P}_{kn_c}|kh'\rangle\langle 0|c_{kh'}(0)c_{kh}^\dagger(0)|0\rangle+\frac{(-)}{p_0-g_{kn_c}-i\eta}\sum_{h'}\langle kh|\mathbf{P}_{kn_c}|kh'\rangle\langle 0|c_{kh}^\dagger(0)c_{kh'}(0)|0\rangle\right\}.$$

Accordingly, the g_{kn_c} appear as arbitrary frequencies in the auxiliary field and arbitrary poles of $G_0(kh,p_0)$. To circumvent this difficulty, we choose

$$g_{kn_c}=E_{kh}$$

for all n_c, where E_{kh} is the solution of the Dyson equation, that is the physical excitation energy of the valence electrons. In this way the nonphysical poles associated with g_{kn_c} are made to coincide with the physical pole. Thus, the parameters g_{kn_c} are independent of n_c but differ for different valence states kh. This choice is identical to that of the conventional O. P. W. method.

While this choice is a convenient one, it is also a necessary choice if perturbation theory is to be used. It is shown in the appendix that for any other choice of g_{kn_c} the core projection of the one particle eigenstates of the ψ_0 field for valence state kh vanishes. Therefore, this eigenstate would be exactly the Hartree-Fock valence state wave function and the advantage of the O. P. W. method would be lost.

Remembering that we expand ψ_0 in plane waves, the point of practical importance for the convergence of the procedure is that the one-body effective potential $(V+\mathbf{P}_cA\mathbf{P}_c)$ with the O. P. W. selection for A behaves like a very smooth potential for crystals with covalent bondings. Accordingly, although the repulsive part of the potential $\mathbf{P}_cA\mathbf{P}_c$ is nonlocal and eigenvalue dependent, various simplifications have been attempted. Phillips and Kleinman,[8] and Antončik[10] approximate $\mathbf{P}_cA\mathbf{P}_c$ with a local potential, which can be useful for

[10] E. Antončik, J. Chem. Phys. Solids **10**, 314 (1959). Czech. J. Phys. **10**, 22 (1960); **4**, 439 (1954).

qualitative considerations and interpolation schemes. Cohen and Heine[11] suggest a nonlocal but eigenvalue-independent expression of the form $(-\mathbf{P}_c V)$ which is not Hermitian. The Hermitian expression $(-\mathbf{P}_c V \mathbf{P}_c)$ could be chosen, which would correspond to choosing for the arbitrary operator g in our case the kinetic energy operator $p^2/2m$. The errors involved in these approximations are eigenvalue dependent and are expected to be larger for higher energy states.

The problem of choosing the arbitrary part of the Hamiltonian when two-body correlation terms are present is not as simple as in the one-body case. A reasonable generalization of the consistency requirement which we have there suggests that in the more general case we choose for g the real part of the pole which gives the excitation energy of a given quasi-particle state. When the solution of the Dyson equation is $E_{kh}+i\Gamma_{kh}$ we require $g_{kn_c}=E_{kh}$.

A more general formulation could be made by stipulating that the arbitrary core-space operator of (4.7) which determines $\mathbf{P}_c\psi_0$ include two-body terms in $\mathbf{P}_c\psi_0$. An arbitrary self-adjoint two-body operator which has no valence projection could be included in H_{eff} without affecting the valence field or invalidating the commutation rules. The arbitrary poles as well as the physical pole of $G_0(p,p_0)$ would then be complex. The core-state matrix elements of this two-body operator would provide an additional parameter set which presumably could then be adjusted to make the arbitrary poles coincide with the physical pole in the imaginary as well as the real part. Detailed specification of such a two-body core operator is, however, quite a complicated matter.

We follow the simpler prescription of requiring consistency in the excitation energy only, since $\Gamma_{kh}\ll E_{kh}$ and it is generally a good approximation to assume that $\Sigma(E_{kh}+i\Gamma_{kh}, kh)\simeq\Sigma(E_{kh},kh)$.

VII. EXCITATION ENERGIES AND LIFETIMES FROM THE PERTURBATION EXPANSION ON THE GREEN'S FUNCTION

The quasi-particle energies and lifetimes of our system can be evaluated from a perturbation expansion on the unperturbed Green's function $G_0^{(0)}(p,p_0)$. As indicated in Secs. IV and V we go to the interaction representation with the perturbing Hamiltonian

$$H'=\sum_{p_1',p_1}\langle S_{p_1'}|\{V-V_0\}|S_{p_1}\rangle c_{p_1'}^{\dagger}(t)c_{p_1}(t)+\sum_{p_1'p_1}\langle S_{p_1'}|\mathbf{P}_c\{g-H_1\}\mathbf{P}_c|S_{p_1}\rangle c_{p_1'}^{\dagger}(t)c_{p_1}(t)$$
$$+\tfrac{1}{2}\sum_{p_1'p_2'p_1p_2}\langle\mathbf{P}_v S_{p_2'},\mathbf{P}_v S_{p_1'}|V_2|\mathbf{P}_v S_{p_2},\mathbf{P}_v S_{p_1}\rangle c_{p_1'}^{\dagger}(t)c_{p_2'}^{\dagger}(t)c_{p_2}(t)c_{p_1}(t)$$
$$-\sum_{p_1'p_1}\langle\mathbf{P}_v S_{p_1'}|U_v|\mathbf{P}_v S_{p_1}\rangle c_{p_1'}^{\dagger}(t)c_{p_1}(t). \quad (7.1)$$

The first two terms on the right-hand side of Eq. (7.1) represent a one-body effective potential while the last two terms together represent the residual interactions. The one-body effective potential is the lattice potential plus a nonlocal repulsive potential which depends on the excitation energies, as discussed in Sec. VI.

We can expand the exact $G_0(p,p_0)$ in a perturbation series whose terms are classified by the linked cluster expansion.[1] All terms appearing in this expansion can be represented by Feynman diagrams in which a solid line indicates a zero-order Green's function $G_0^{(0)}(p,p_0)$ while wavy and dotted lines represent one-body and two-body interaction matrix elements, respectively. A two-body interaction line will connect two solid lines, while a one-body interaction will have only one end attached to a solid line. Detailed rules for such diagrams are given in standard reference books.[12] We here call a diagram irreducible if it cannot be separated into two disconnected parts by breaking a single solid line of momentum p and frequency p_0. The self-energy Σ appearing in Eq. (5.7) contains only irreducible diagrams. The pole $E(p)+i\Gamma(p)$ of the analytic continuation of $G_0(p,p_0)$ into the lower (upper) p_0 half-plane for $p_0>\mu$ ($p_0<\mu$) gives the excitation energy $E(p)$ and the damping rate $\Gamma(p)$ of the quasi-particles of momentum $\mathbf{p}$, where μ is the Fermi energy. This pole is the solution in the complex p_0 plane of the Dyson equation,

$$-p_0+\epsilon_p^{(0)}+\Sigma(p,p_0)=0. \quad (7.2)$$

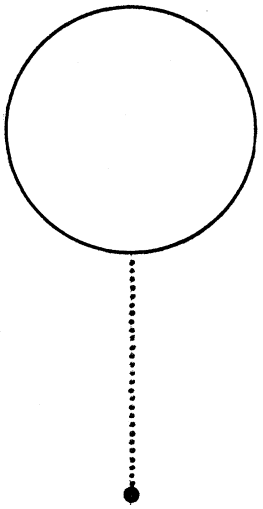

FIG. 1. First-order Coulomb self-energy diagram.

[11] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

[12] J. M. Jauch and F. Rohrlich, *The Theory of Photons and Electrons* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1955). H. Bethe, S. Schweber, and F. D. DeHoffmann, *Mesons and Fields* (Row, Peterson and Company, Evanston, Illinois, 1955), Vol. I.

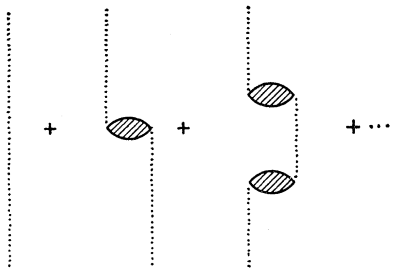

FIG. 2. Diagrams giving screening of two-body interaction lines. All bare interaction lines carry the same momentum q.

The irreducible diagrams include terms to all orders and can be separated for convenience into those which include only one-body interactions, those which include only two-body interactions, and those which include both. Without loss of generality we consider the relevant self-energy diagrams in a plane wave representation. When the symmetrized combinations of plane waves are used a linear combination of such contributions is obtained.

Before specifying which diagrams we shall retain as contributing to $\Sigma(p,p_0)$, we must settle the choice of U_v, the screening of interaction lines, and the choice of V_0.

It is most convenient to choose U_v so as to cancel the divergent part of the Hartree term represented by the diagram in Fig. 1. The divergent contribution of this diagram is

$$V_2(0)[1-\langle p|\mathbf{P}_c|p\rangle]\times\left\{N-\int\frac{d^3p'}{(2\pi)^3}\langle p'|\mathbf{P}_c|p'\rangle f_{p'}{}^{(0)}\right\}, \quad (7.3)$$

where N is the total number of electrons in the auxiliary system, and $f_p{}^{(0)}$ is the Fermi function for the unperturbed system. The term in curly brackets is just the number N_v of valence electrons. There is also a finite contribution from the diagram of Fig. 1 which is, however, of second order in matrix elements of $\mathbf{P}_c$ and we shall neglect it in our discussion. Taking U_v constant, the first-order contribution of the last term of (7.1) is

$$-\langle p|\mathbf{P}_vU_v\mathbf{P}_v|p\rangle=-U_v[1-\langle p|\mathbf{P}_c|p\rangle]. \quad (7.4)$$

The Hartree divergence is canceled by choosing

$$U_v=V_2(0)N_v. \quad (7.5)$$

On physical grounds we expect that all interactions should be screened by the two-body interactions. The mathematical expressions for this screening are more complicated than in the case of the uniform Fermi gas because of the projection operators which appear in the two-body interaction of Eq. (7.1). By using a small-core approximation, which consists in neglecting integrals of the type $\langle u_{n_c}(1),p'(2)|V_2|u_{n_v}(1),p(2)\rangle$ as in Sec. II, the two-body operator in (7.1) becomes

$$\tfrac{1}{2}\sum_{p_1'p_2'p_1p_2q}V_2(q)\langle p_2'-q|\mathbf{P}_v|p_2\rangle\langle p_1'+q|\mathbf{P}_v|p_1\rangle c_{p_1'}{}^\dagger c_{p_2'}{}^\dagger c_{p_2}c_{p_1}. \quad (7.6)$$

The difference of (7.6) from the case of the uniform Fermi gas is entirely contained in the $\mathbf{P}_v$ matrix elements, and these can be associated with the vertices at ends of two-body interaction lines. The selection rules arising from these vertex factors are, for example,

$$\langle p'-q|\mathbf{P}_v|p\rangle=\delta_{p'-q,p+h}\langle p+h|\mathbf{P}_v|p\rangle,$$

where h is any reciprocal lattice vector. Setting $\mathbf{P}_v=1$ would give the usual uniform-gas case delta function. On using these selection rules, (7.6) can be written

$$\tfrac{1}{2}\sum_{p_1'p_2h_1h_2q}V_2(q)\langle p_1'+q|\mathbf{P}_v|p_1'+q+h_1\rangle\times\langle p_2+h_2|\mathbf{P}_v|p_2\rangle c_{p_1'}{}^\dagger c_{p_2+q+h_2}{}^\dagger c_{p_2}c_{p_1'+q+h_1}. \quad (7.7)$$

Let us consider a two-body interaction line screened as shown in Fig. 2, where the shaded circles represent the sum of irreducible polarization parts and all bare interaction lines carry the momentum q. We call irreducible polarization parts all diagrams which cannot be separated into two diagrams by cutting a single interaction line of momentum q. They are displayed in Fig. 3. The dominant contribution to the irreducible polarization parts is given by the first bubble of Fig. 3 as in the case of the uniform high-density electron gas (see Gell-Mann and Brueckner).[1] The series in Fig. 2 then has a simple sum and gives for the screened interaction $\mathcal{V}_2$:

$$\mathcal{V}_2(q)=V_2(q)/\{1+iV_2(q)P^v(q,q_0)\}. \quad (7.8)$$

The denominator in Eq. (7.8) is the dielectric function $\epsilon(q,q_0)$. The polarization propagator is given by

$$P^v(q,q_0)\equiv P_{q,q}{}^v(q_0)=2\sum_h\int\frac{d^4p}{(2\pi)^4}G_0{}^{(0)}(p,p_0)G_0{}^{(0)}(p+h+q,\,p_0+q_0)\times\langle p+h|\mathbf{P}_v|p\rangle\langle p+q|\mathbf{P}_v|p+q+h\rangle. \quad (7.9)$$

If we neglect terms of second order in matrix elements of $\mathbf{P}_c$ we retain only the $h=0$ term in the summation in (7.9). Since the integration over p_0 introduces the factor $f_p(1-f_{p+q+h})$, the orthogonality coefficients are nearly constant over the range of integration and can be taken out from under the integral sign. We can,

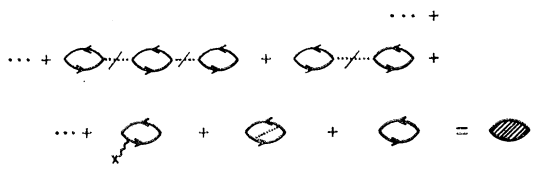

FIG. 3. Irreducible polarization diagrams. A slash in an interaction line indicates that the momentum transfer carried by that line differs from q by a nonzero reciprocal lattice vector.

accordingly, use for the polarization propagator the simple expression

$$P^v(q,q_0)=\langle p|\mathbf{P}_v|p\rangle_{\rm av}\langle p+q|\mathbf{P}_v|p+q\rangle_{\rm av}P^0(q,q_0). \quad (7.10)$$

The quantity $P^0(q,q_0)$ is the polarization propagator in the random phase approximation (r. p. a.) for the uniform electron gas; its explicit expression was given first by Lindhard.[13] The subscript av indicates an average over values of p within the Fermi sea. Because the matrix elements of $\mathbf{P}_c$ are nearly constant with p we could equally well replace this average by the value of the matrix element at any p so long as it is not too far above the Fermi momentum. It can be shown that diagrams similar to those of Fig. 2 but in which the final bare-interaction line carries momentum transfer $q'\neq q$ give rise to contributions which are of second order in matrix elements of $\mathbf{P}_c$. Therefore, we will use (7.8) for the contribution of a fully screened two-body interaction line, which we will represent by a double-dash line.

For $q=k_q+h_q$ lying on the surface or outside of the first Brillouin zone $V_2(k_q)\gg V_2(q)$ will appear in the slashed interaction lines in the strings of bubbles indicated in Fig. 3. The dominant contributions of these terms are those for which $V_2(k_q)$ appears in every slashed interaction line. The resulting correction to the polarization propagator (7.9) is

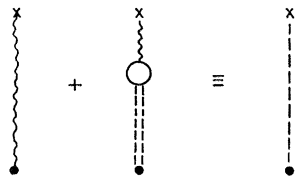

FIG. 4. Screening of one-body interactions.

$$-iP_{q,k_q}{}^vV_2(k_q)P_{k_q,q}{}^v\{1+iV_2(k_q)P_{k_q,k_q}{}^v\}^{-1},$$

where $P_{k_q,q}{}^v$ is the contribution of a bubble which does not conserve momentum and $P_{k_q,k_q}{}^v$ is the contribution of a bubble which preserves momentum. The term $P_{q,k_q}{}^v$ is first-order small compared to $P_{k_q,k_q}{}^v$ so that this correction is second-order small with respect to the polarization propagator (7.9) and can be neglected.

The one-body potential will also be screened by the two-body interactions. Cohen and Ehrenreich[14] have shown that such screening is, to first order in the external field, equivalent to self-consistency in the Hartree-Fock approximation. A general expression for the screening of the one-body potential in the r. p. a. can be obtained by summing the two diagrams of Fig. 4, where on any interaction line the energy transfer is zero and the three-momentum is a reciprocal lattice vector. To first order in both V and $\mathbf{P}_c$ the screened one-body interaction is

$$\langle p+q|\mathcal{U}|p\rangle\equiv\langle p+q|V|p\rangle_{\rm screened}=\langle p+q|V_1|p\rangle-i\frac{V_2(q)}{\epsilon(q,0)}\langle p|\mathbf{P}_v|p\rangle 2\int\frac{d^4p'}{(2\pi)^4}G_0{}^{(0)}(p',p_0')$$

$$\times G_0{}^{(0)}(p'+q,p_0')\langle p'+q|\mathbf{P}_v|p'+q\rangle\langle p'+q|V_1|p'\rangle. \quad (7.11)$$

We can remove the $\mathbf{P}_v$ matrix element from under the integral sign just as in deriving (7.10). For the local part $\mathcal{U}^L$ of $\mathcal{U}$ we then find, for $q\neq 0$

$$\mathcal{U}^L(q)\equiv\langle p+q|\mathcal{U}^L|p\rangle=V^L(q)/\epsilon(q,0). \quad (7.12)$$

The simplified screening contained in (7.12) has the same form as that obtained by Cohen and Phillips[7] by imposing self-consistency to first order in the O. P. W. method and approximating the one-body interaction by a local potential.

We choose the constant V_0 to be the space average of the local part $\mathcal{U}^L$ of the lattice potential. This removes from the perturbation the term $\mathcal{U}^L(0)$, which cannot be obtained from formula (7.12). The computation of this term is discussed by Herman[15] and by Woodruff,[6] who also include exchange in the local part of the potential by using the Slater approximation.

In applying the screening described above to the effective one-body potential we must use some caution. The effective potential in first quantization form is

$$V+\mathbf{P}_c(g-H_1)\mathbf{P}_c,$$

and all terms should be screened according to formula (7.11). However the repulsive potential is determined by the choice of core-state eigenfunctions and eigenvalues and all screening is included if these are chosen self-consistently. In practical calculations Hartree-Fock results, when available, are used for the core states.

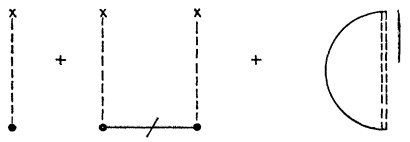

FIG. 5. Low-order irreducible self-energy diagrams. The slash on the particle line indicates that the momentum carried differs from that carried by the incoming line by a reciprocal lattice vector.

[13] J. Lindhard, Kgl. Danske Videnskab, Selskab, Mat.-fys. Medd. 28, 8 (1954)

[14] H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).

[15] F. Herman, Phys. Rev. 93, 1214 (1954).

With the above definition of the one-body and two-body interaction matrix elements one can, in principle, compute all the irreducible self-energy terms and solve Eq. (7.2) for the excitation energies. In practice, we are limited to a few terms in the self-energy and an approximate solution of the Dyson equation. We propose to consider the diagrams in Fig. 5 only; this is an extension of the usual energy band theory to include correlation effects within the r. p. a. and to first order in matrix elements of $\mathbf{P}_c$. Equation (7.2) in this case is

$$E(p)+i\Gamma(p)=\epsilon_p{}^{(0)}+\langle S_p|(\mathcal{U}-V_0)|S_p\rangle+\sum_{nc}[E(p)-E_{n_c}]\langle S_p|u_{n_c}\rangle\langle u_{n_c}|S_p\rangle$$
$$+\sum_{p'\neq p}{}'\frac{|\langle S_p|(\mathcal{U}-V_0)|S_{p'}\rangle+\sum_{n_c}[E(p)-E_{n_c}]\langle S_p|u_{n_c}\rangle\langle u_{n_c}|S_{p'}\rangle|^2}{E(p)-\epsilon_{p'}{}^{(0)}}$$
$$-i\int\frac{d^4q}{(2\pi)^4}G_0{}^{(0)}(p+q,E(p)+q_0)\mathcal{U}_2(q,q_0)\langle p|\mathbf{P}_v|p\rangle\langle p+q|\mathbf{P}_v|p+q\rangle. \quad (7.13)$$

Equation (7.13) can be solved by iteration by replacing $E(p)$ with a perturbation expansion $E(p)=E^{(0)}(p)+E^{(1)}(p)+\cdots$ and considering, as usual, matrix elements of V and $\mathbf{P}_c$ first-order small. The first four terms on the right-hand side of Eq. (7.13) will give the perturbation expansion obtained by Bassani and Celli[9] from the O. P. W. method, while the last term is a correction due to exchange and correlation between the valence electrons. The main contribution to this last term is just the free electron self energy for $p_0=E_p$ with modifications involving matrix elements of $\mathbf{P}_c$. The magnitude of this correction has to be assessed by an explicit calculation.

VIII. CONCLUSIONS

We have developed a formalism in which the O. P. W. method is generalized to deal with many-electron problems in solids. The basic assumption is that core states are dynamically independent of the valence electrons and are adequately treated in the one-electron approximation. In consequence a model wave field has been introduced whose valence projection is the valence wave field of the physical system, but whose core projection can be chosen to facilitate the use of low-order perturbation theory. A major advantage of the scheme is that one can work with field-theoretic techniques using in zero order the Green's functions for plane waves. One- and two-body interactions enter on the same footing in a joint perturbation expansion of the single-particle Green's function. This allows some flexibility in the choice of the one-body interaction.

The formalism is adapted to practical computations in that efficient use can be made of experience gained both in O. P. W. calculations and in calculations on the uniform electron gas. For example in (7.13) one can use electron gas results in computing the screened exchange term and existing O. P. W. results in the one-body terms.

With respect to previous work the present approach offers a twofold practical advantage. On the one hand, we can improve band structure calculations by including some dynamical correlations between valence electrons. On the other hand, we include effects of the crystal structure on the dielectric function, e.g., (7.10), and on plasmon frequencies.

APPENDIX

We give here two different proofs of our assertions in Sec. VI regarding the choice of the arbitrary parameters g_{kn_c}. In the presence of only the external one-body interactions the operator which gives the irreducible self-energy as defined in Sec. VII is

$$\Sigma(p_0|kh)=V_e[1+G^{(0)}(p_0)(1-\mathbf{P}_{kh})V_e]^{-1}$$
$$=V_e-V_eG^{(0)}(p_0)(1-\mathbf{P}_{kh})\Sigma(p_0|kh). \quad (A1)$$

We have written

$$V_e=V-V_0+\mathbf{P}_c(g-H_1)\mathbf{P}_c, \quad (A2)$$
$$G^{(0)}(p_0)=(-)[p_0-H_0+i\eta(1-2\mathbf{P}_F{}^{(0)})]^{-1}, \quad (A3)$$
$$\eta=0+,$$
$$\mathbf{P}_{kh}=|kh\rangle\langle kh|, \quad (A4)$$
$$\mathbf{P}_F{}^{(0)}=\sum_{kh}\mathbf{P}_{kh} \quad \text{for} \quad \epsilon_{kh}{}^{(0)}<\epsilon_F{}^{(0)}.$$

From (A2) and (6.1) we have

$$\partial V_e/\partial g_{kn_c}=\mathbf{P}_{kn_c}. \quad (A5)$$

On differentiating (A1) and using (A5) we obtain

$$\partial\Sigma(p_0|kh)/\partial g_{kn_c}=[1+V_e(1-\mathbf{P}_{kh})G^{(0)}(p_0)]^{-1}$$
$$\mathbf{P}_{kn_c}[1+G^{(0)}(p_0)(1-\mathbf{P}_{kh})V_e]^{-1}. \quad (A6)$$

The full effective one-body Hamiltonian is

$$H=H_0+V_e=\mathbf{P}_vH_1\mathbf{P}_v+\mathbf{P}_cg\mathbf{P}_c, \quad (A7)$$

and its appropriately normalized eigenstates are

$$|v_{kh}\rangle=[1+G^{(0)}(p_0)(1-\mathbf{P}_{kh})V_e]^{-1}|kh\rangle,$$
$$\langle kh|v_{kh}\rangle=1. \quad (A8)$$

The energy shift, or irreducible self-energy, is just

$$\Sigma(kh,p_0)\equiv\langle kh|\Sigma(p_0|kh)|kh\rangle=\langle kh|V_e|v_{kh}\rangle. \quad (A9)$$

Accordingly, (A9), (A8), and (A6) show that

$$\partial\Sigma(kh,p_0)/\partial g_{kn_c}=|\langle kn_c|v_{kh}\rangle|^2. \tag{A10}$$

We obtain another expression for the derivative of the energy shift by differentiating the Dyson equation and the full Green's operator corresponding to H. The full Green's operator is

$$G(p_0)=(-)[p_0-H+i\eta(1-2\mathbf{P}_F)]^{-1}, \tag{A11}$$

where $\mathbf{P}_F$ refers to the Fermi surface of the perturbed system. Since

$$H|kn_c\rangle=g_{kn_c}|kn_c\rangle, \tag{A12}$$

we have

$$G(p_0)|kn_c\rangle=\frac{(-)}{p_0-g_{kn_c}}|kn_c\rangle. \tag{A13}$$

Differentiation of the identity

$$G(p_0)G^{-1}(p_0)=1$$

then gives

$$\begin{aligned}\partial G(p_0)/\partial g_{kn_c}&=-G(p_0)[\partial G^{-1}(p_0)/\partial g_{kn_c}]G(p_0),\\&=-G(p_0)\mathbf{P}_{kn_c}G(p_0),\\&=-(p_0-g_{kn_c})^{-2}\mathbf{P}_{kn_c}.\end{aligned} \tag{A14}$$

Hence,

$$\partial G(kh,p_0)/\partial g_{kn_c}=-|\langle kh|kn_c\rangle|^2/(p_0-g_{kn_c})^2. \tag{A15}$$

Differentiation of the Dyson equation now yields

$$\begin{aligned}&\partial\Sigma(kh,p_0)/\partial g_{kn_c}\\&\quad=-[G(kh,p_0)]^{-2}[\partial G(kh,p_0)/\partial g_{kn_c}]\\&\quad=\left[\frac{\epsilon_{kh}{}^{(0)}+\Sigma(kh,p_0)-p_0}{g_{kn_c}-p_0}\right]^2|\langle kh|kn_c\rangle|^2.\end{aligned} \tag{A16}$$

Now take $g_{kn_c}\neq E_{kh}$ and let p_0 go to the root E_{kh} of the Dyson equation. According to (A16) and (A10) the energy shift $\Sigma(kh,E_{kh})$ is independent of g_{kn_c} and the eigenstate $|v_{kh}\rangle$ is orthogonal to $|kn_c\rangle$. We have thus substantiated our statements in Sec. VI, essentially by explicit construction to all orders of perturbation theory.

A succinct nonperturbative demonstration follows upon expanding the auxiliary field operator ψ_0 in a complete set of eigenfunctions of H_0+V_e. We write

$$\begin{aligned}\psi_0(x,t)&=\sum_{kr}\langle x|v_{kr}\rangle b_{kr}(t),\\(H_0+V_e)|v_{kr}\rangle&=\epsilon_{kr}|v_{kr}\rangle,\\b_{kr}(t)&=e^{-it\epsilon_{kr}}b_{kr}(0).\end{aligned} \tag{A17}$$

The solution (6.2) of Eq. (4.7) gives, in this representation,

$$\mathbf{P}_{kn_c}\psi_0(x,t)=\exp(-itg_{kn_c})\Sigma_r\langle x|\mathbf{P}_{kn_c}|v_{kr}\rangle b_{kr}(0). \tag{A18}$$

On the other hand, projection of (A17) gives

$$\mathbf{P}_{kn_c}\psi_0(x,t)=\sum_r e^{-it\epsilon_{kr}}\langle x|\mathbf{P}_{kn_c}|v_{kr}\rangle b_{kr}(0). \tag{A19}$$

Since the $b_{kr}(0)$ are independent operators we equate coefficients in (A18) and (A19). Therefore, we see that for each kn_c either

$$\langle kn_c|v_{kr}\rangle=0 \text{ for all } r, \tag{A20}$$

or for some one r'

$$\begin{aligned}g_{kn_c}&=\epsilon_{kr'},\\\langle kn_c|v_{kr'}\rangle&\neq 0,\\\langle kn_c|v_{kr}\rangle&=0 \text{ if } r'\neq r.\end{aligned} \tag{A21}$$

In consequence, the O. P. W. choice of the g_{kn_c} is a consistency condition, necessary if the expansion of ψ_0 is to contain any smooth functions. As indicated by (A21), the desired smoothness can be secured for one band index at a time.