

# Generalization of Band Theory to Include Self-Energy Corrections\*

G. W. PRATT, JR.

*Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts*

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A one-particle Schrödinger-like equation is found whose eigenvalues in certain cases are identical with the energies of the many electron states of a semiconductor or insulator including self energy corrections. The one particle Hamiltonian is expressed in terms of the Coulomb interaction as modified by polarization processes. The relation is given between the modified Coulomb interaction and the dielectric function which is the generalization of the classical dielectric constant. Suggestions are made as to how the one-particle equation including self-energy effects might be solved in practice.

## I. INTRODUCTION

IN recent years very significant progress has been made in the experimental measurements in solids of the effective masses of holes and electrons and in the determination of the energy gaps between bands. The measurement of the direct gap in Ge to three significant figures illustrates the degree of present day capabilities.<sup>1</sup> These developments lead one to ask how closely ordinary energy band theory can be expected to be in agreement with experiment. In what we term ordinary energy band theory one writes the many electron wave function as a single determinant of one particle Bloch functions  $b_{nk}(\mathbf{r})$  labelled by a band index  $n$  and propagation vector  $k$ . At symmetry points in  $k$  space the Bloch functions have the transformation properties dictated by the crystalline symmetry and ideally they would be self-consistent solutions of the Hartree-Fock equations. Such a self-consistent solution has never been carried out because of the great computational difficulties involved. However, there are reasons to believe that even a true solution of the Hartree-Fock equations would not provide satisfactory values for effective masses and energy gaps in many cases.

The one-particle equations of which the  $b_{nk}(\mathbf{r})$  are solutions contain none of the dielectric properties of the solid. However, static dielectric constants can be very large, e.g., about 16 in Ge and 12 in Si—two materials which have been the subject of the most refined experimental studies. In such cases one can expect the Coulomb interaction between electrons to be considerably modified. A single electron moving through the crystal in the conduction band will induce a polarization of the electrons in the valence band. This polarization will react back on the conduction electron thereby making a contribution to the periodic potential which in general will depend on the velocity of the conduction electron because of the electronic inertia of the solid. Speaking classically, the larger the

dielectric constant, the more important will be the effects of such polarization processes.

The purpose of this paper is to investigate the corrections to ordinary band theory due to dielectric effects. Our ultimate goal is to find from first principles a one particle equation which is a generalization of the Hartree-Fock equation for a single  $b_{nk}(\mathbf{r})$  and in which the dielectric properties of the solid appear explicitly.

In Sec. II a brief discussion is given of how the bare Coulomb interaction becomes modified by polarization processes leading to an effective Coulomb interaction. A dielectric function, rather than a constant, is defined in terms of the effective Coulomb interaction by analogy with the classical Poisson equation in a dielectric. In Sec. III the problem of finding the energy of a single electron in the conduction band of a solid whose lower lying bands are filled is set up using time dependent perturbation theory, and the self-energy corrections to the unperturbed energy are discussed. By an appropriate choice of the electronic potential appearing in the unperturbed Hamiltonian, the self energy corrections to the eigenvalues of the unperturbed problem can be made to vanish. This leads to a one particle equation which is the desired generalization of the Hartree-Fock equations. The form of equation obtained is in agreement with a result obtained some time ago by Schwinger<sup>2</sup> from considerations of the Green's functions of field theory. The summary and conclusion appears in Sec. IV.

## II. THE MODIFIED COULOMB INTERACTION AND THE DIELECTRIC FUNCTION

In a many-body system the interaction between pairs of particles is influenced by the presence of the other particles. As is well known, important corrections to the bare Coulomb interaction between electrons arise in solids due to the excitation of virtual hole-electron pairs. This is discussed in this section from the standpoint of time dependent perturbation theory.

Let the total electronic Hamiltonian be written as the sum of two terms  $H_0$  and  $H_1$ .  $H_0$  represents a fictitious noninteracting many electron system and is

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<sup>1</sup> S. Zwerdling, B. Lax, L. Rott, and K. Button, Phys. Rev. 114, 80 (1959).

<sup>2</sup> J. Schwinger, Proc. Natl. Acad. Sci. U. S. 37, 452 (1951).

given by

$$H_0 = \sum_{i=1}^N h(x_i) = \sum_i [T_i + V_n(x_i) + V(x_i)]. \quad (1)$$

$T_i$  is the kinetic energy of the  $i$ th electron,  $V_n(x_i)$  is the potential energy of an electron at  $x_i$  due to the periodic lattice of nuclear charge, and  $V(x_i)$  is an approximate potential which attempts to represent the interactions of an electron at  $x_i$  with all of the remaining electrons of the solid. The eigenfunctions and eigenvalues of  $H_0$  define the unperturbed or bare system.  $H_1$  is the difference between  $H$  and  $H_0$ ,

$$H_1 = \sum_{i < j} \frac{e^2}{r_{ij}} - \sum_{i=1}^N V(x_i), \quad (2)$$

and is treated in the following as a perturbation.

Our discussion of the interacting system will be based on the Feynmann<sup>3</sup> method drawing heavily on the recent work of Hubbard<sup>4</sup> who applies these techniques to the many electron problem. The starting point is to assume that at  $t = -\infty$ ,  $H = H_0$ , so that the system is in one of the unperturbed stationary states  $\phi$ . The perturbation is switched on adiabatically by writing it as

$$H_1(\alpha, t) = H_1 e^{-\alpha|t|},$$

and the temporal development is described by the unitary operator  $U_\alpha(t, -\infty)$

$$\psi(t) = \lim_{\alpha \rightarrow 0} U_\alpha(t, -\infty) \phi. \quad (3)$$

$U_\alpha(t, -\infty)$  is given in terms of  $H_1(\alpha, t)$  by the well-known expansion

$$U_\alpha(t, -\infty) = \sum_{n=0}^{\infty} \left( \frac{-i}{\hbar} \right)^n \frac{1}{n!} \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_n \\ \times P[H_1(\alpha, t_1) H_1(\alpha, t_2) \cdots H_1(\alpha, t_n)], \quad (4)$$

$P$  being the chronological operator which orders the factors in the product such that time increases from right to left.

A statement of the method for carrying out a diagrammatic analysis of the  $U$  operator can be found

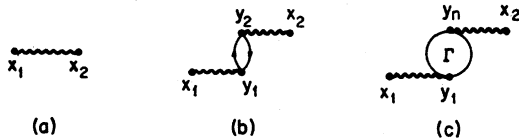


FIG. 1. The instantaneous Coulomb interaction is represented in (a) as a wavy line between  $x_1$  and  $x_2$ . A simple example of how a polarization process can contribute to the interaction between two electrons at space-time points  $x_1$  and  $x_2$  is shown in (b). The general polarization diagram is shown in (c).

<sup>3</sup> R. P. Feynmann, Phys. Rev. **76**, 749, 769 (1949).

<sup>4</sup> J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957); **A243**, 336 (1958); **A244**, 199 (1958).

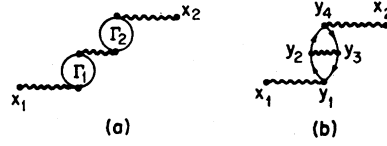


FIG. 2. (a) illustrates an improper polarization diagram; (b) illustrates a proper polarization diagram.

in Hubbard's paper.<sup>4</sup> Of particular interest here is the modified Coulomb interaction  $\mathcal{V}(x, x')$  for which Hubbard derives an integral equation. The instantaneous Coulomb interaction

$$v(x_1 - x_2) = e^2 \delta(t_1 - t_2) / |x_1 - x_2|$$

is represented in the diagrams as a wavy line drawn between the points  $x_1$  and  $x_2$  as shown in Fig. 1(a). In the evaluation of the  $U$  operator one finds that more complicated couplings than  $v(x_1 - x_2)$  can occur between the points  $x_1$  and  $x_2$ . For example instead of the direct interaction of Fig. 1(a), the process shown in Fig. 1(b) is possible. In Fig. 1(b) a hole-electron pair is created at  $y_1$  due to  $v(x_1 - y_1)$  and it recombines at  $y_2$ . The effective interaction between  $x_1$  and  $x_2$  is found by integrating over the intermediate variables  $y_i$  as is explained by Hubbard.

The creation and annihilation of the hole-electron pair in Fig. 1(b) is termed a polarization process  $\Gamma$ , these processes being defined in general as a part  $\Gamma$  of the complete diagram connected to it by two interaction lines and with  $\Gamma$  having no external lines. In general we represent a polarization diagram as shown in Fig. 1(c), where  $\Gamma$  contains  $n$  vertices. By summing over all possible polarization parts  $\Gamma$  and by integrating over all intermediate vertices  $y_i$  one finds the modified Coulomb interaction  $\mathcal{V}(x_1, x_2)$ .

Hubbard has shown that  $\mathcal{V}(x_1, x_2)$  satisfies the integral equation

$$\mathcal{V}(x_1, x_2) = v(x_1 - x_2) + \int \mathcal{V}^*(x_1, x') \mathcal{V}(x', x_2) d^4 x', \quad (5)$$

$\mathcal{V}^*(x_1, x')$  represents the sum of all proper polarization processes  $\Gamma'$ . If a polarization process can be decomposed into two or more parts connected to each other by a single interaction line, the process is called improper. Otherwise one has a proper polarization process. Examples of each type are shown in Figs. 2(a) and 2(b).

We now proceed to introduce the dielectric function in terms of the modified Coulomb interaction. In the ordinary Coulomb interaction  $v(x_1 - x_2)$  is a Green's function such that the electrostatic potential at  $x_1$  due to a charge density  $\rho(x_2)$  is

$$\phi(x_1) = \int v(x_1 - x_2) \rho(x_2) dx^3.$$

This corresponds to a relation between Fourier transforms which in the case of a classical dielectric of

dielectric constant  $\epsilon$  is

$$\phi(k, \lambda) = \epsilon^{-1} v(k) \rho(k, \lambda), \quad (6)$$

where  $k$  refers to the spatial dependence and  $\lambda$  allows for a time dependence. The effective potential at  $x_1$  due to  $\rho(x_2)$  in a many electron system as modified by polarization processes is

$$\phi_{\text{eff}}(x_1) = \int \mathcal{V}(x_1, x_2) \rho(x_2) d^4 x_2, \quad (7)$$

and where  $t_1 \geq t_2$  because of causality. Replacing  $\mathcal{V}(x_1, x_2)$  in Eq. (7) and by Eq. (5) and Fourier analyzing the result using

$$\mathcal{V}^*(k, k', \lambda) = v(k) \mathcal{V}'(k, k', \lambda),$$

one finds

$$\begin{aligned} \phi_{\text{eff}}(k, \lambda) = v(k) & \left[ \int (2\pi)^3 \delta(k'' - k) \right. \\ & \left. + \int \frac{dk'}{2\pi^3} \mathcal{V}'(k, -k', -\lambda) \mathcal{V}(k', -k'', +\lambda) \right] \\ & \times \frac{\rho(k'', \lambda)}{(2\pi)^3} dk''. \quad (8) \end{aligned}$$

By analogy with the classical Poisson's equation (6) we define the dielectric function  $\epsilon^{-1}(k, k'', \lambda)$  as

$$\begin{aligned} \epsilon^{-1}(k, k'', \lambda) = (2\pi)^3 \delta(k'' - k) & + (2\pi)^{-3} \int dk' \\ & \times \mathcal{V}'(k, -k', -\lambda) \mathcal{V}(k', -k'', +\lambda). \quad (9) \end{aligned}$$

Thus we arrive at a generalized form of Poisson's equation

$$\phi_{\text{eff}}(k, \lambda) = v(k) (2\pi)^{-3} \int \epsilon^{-1}(k, k'', \lambda) \rho(k'', \lambda) dk''. \quad (10)$$

The requirement of causality is satisfied by prescribing the contour of integration. For a translationally invariant system  $\mathcal{V}(x_1, x_2)$  depends only on  $x_1 - x_2$  so so that the only nonzero Fourier components of  $\epsilon^{-1}$  are of the form  $\epsilon^{-1}(k, -k, \lambda)$ . Under these conditions (10) reduces to

$$\phi_{\text{eff}}(k, \lambda) = \epsilon^{-1}(k, -k, \lambda) v(k) \rho(k, \lambda), \quad (11)$$

a result already obtained for the free electron gas.<sup>5</sup> The relation between the effective potential and the dielectric function  $\epsilon^{-1}$  is found from (7) to be

$$\mathcal{V}(k, -k'', \lambda) = \epsilon^{-1}(k, k'', \lambda) v(k). \quad (12)$$

Furthermore, in order that a periodic charge density set up a periodic potential,  $k$  and  $k''$  in  $\epsilon^{-1}(k, k'', \lambda)$  can only differ by a reciprocal lattice vector.

<sup>5</sup> J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

In view of Eq. (12) and (5) one can write an integral equation for  $\epsilon^{-1}$ . This equation or the integral equation for  $\mathcal{V}(x_1, x_2)$  is readily solved in the case of translational invariance where  $\mathcal{V}$  is a function of  $x_1 - x_2$  only. Hubbard<sup>4</sup> obtains the solution

$$\begin{aligned} \mathcal{V}(k, -k, \lambda) &= \frac{v(k)}{1 - \mathcal{V}^*(k, -k, \lambda)}, \\ \text{giving} \\ \epsilon^{-1}(k, -k, \lambda) &= \frac{1}{1 - \mathcal{V}^*(k, -k, \lambda)}. \end{aligned}$$

It is much more difficult to solve the integral equations for the periodic potential problem and this case has been investigated by Falk.<sup>6</sup> Falk has shown the relation between  $\epsilon^{-1}$  and the inverse dielectric operator  $K$  of the Martin-Schwinger theory.<sup>7</sup>

It may be noted that the effective Coulomb interaction satisfies an integral equation of much the same form as that satisfied by the reaction matrix of the Brueckner theory. The reaction matrix describes the interaction of a pair of particles where there is a negligible probability that this pair interaction will be affected by other excited pairs. Iteration of the integral equation for the reaction matrix leads to the Brueckner ladder diagrams.<sup>8</sup> The Coulomb interaction in contrast is modified principally by polarization processes where the interaction of a pair is affected by the presence of other excited pairs. This is due to the long range character of the Coulomb force. Iteration of the integral equation for  $\mathcal{V}(x_1, x_2)$  leads to the polarization diagrams described in the text.

### III. THE ONE PARTICLE EQUATIONS

In this section a one particle equation including dielectric effects is found by examining the expression for the energy of the interacting system. Our remarks will be directed to the problem of a solid whose description in terms of the one electron picture is that of  $2N$  electrons filling the atomic core states and the valence band. These states are eigenfunctions of the one particle Hamiltonian  $h(x)$  defined in (1). This  $2N$  particle state will be taken as the unperturbed vacuum state  $\phi_0$ . In addition let there be an electron in the next highest band, the conduction band, which will be taken to be nondegenerate and to be separated from the valence band by an energy gap  $\mathcal{E}_g(k)$ . This bare  $2N+1$  electron state is denoted by  $\phi_{nk}$  where  $n$  specifies the band and  $k$  the propagation vector of the single electron in the conduction band  $n$ . In order that the dressed state  $\psi_{nk}$  corresponding to  $\phi_{nk}$  be stationary there must be no bare state of the same net  $k$  with energy lower than or equal to  $\mathcal{E}_{nk}$  the energy of  $\phi_{nk}$ . Momentum conserva-

<sup>6</sup> D. S. Falk, Phys. Rev. **118**, 105 (1960).

<sup>7</sup> P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

<sup>8</sup> See for example, R. Prange and A. Klein, Phys. Rev. **112**, 1008 (1959).

tion assures that  $\phi_{nk}$  is decoupled from all states  $\phi_{nk}'$  degenerate with it. So long as  $\mathcal{E}_{nk}$  does not rise above the bottom of the conduction band by an amount equal to or exceeding  $\mathcal{E}_g(0)$  it will be possible to construct a stationary dressed state the energy of which will be denoted by  $E_{nk}$ .  $E_{nk}$  is given as the unperturbed energy  $\mathcal{E}_{nk}$  plus the level shift  $\Delta E_{nk}$

$$E_{nk} = \mathcal{E}_{nk} + \Delta E_{nk}. \quad (13)$$

$\Delta E_{nk}$  can be shown to be<sup>9,10</sup>

$$\Delta E_{nk} = \Delta E_0 + \text{S.E.}(nk), \quad (14)$$

where  $\Delta E_0$  is the level shift of the vacuum state  $\phi_0$  and  $\text{S.E.}(nk)$  is the self-energy of the state  $\phi_{nk}$ . If  $\epsilon_{nk}$  is the energy of the one-electron Schrödinger equation

$$h(x)u_{nk}(x) = \epsilon_{nk}u_{nk}(x), \quad (15)$$

then  $E_{nk}$  measured from the energy  $\mathcal{E}_0 + \Delta E_0$  of the dressed vacuum state is

$$E_{nk} = \epsilon_{nk} + \text{S.E.}(nk). \quad (16)$$

The term  $\text{S.E.}(nk)$  represents a correction to  $\epsilon_{nk}$  due to the dielectric properties of the system. It will be shown that the one particle Hamiltonian  $h(x)$  can be chosen so that the self energy corrections vanish and the correct energy is given directly as in eigenvalue of

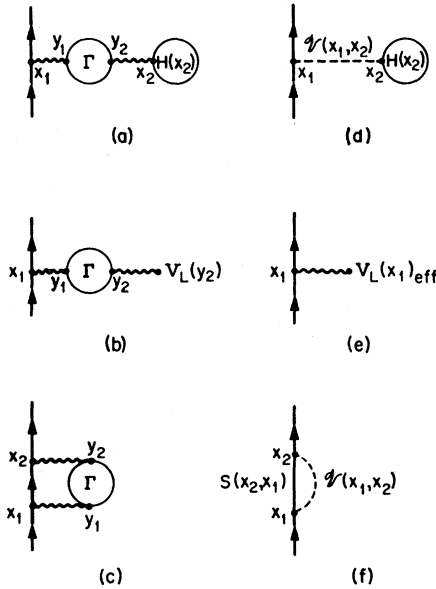


FIG. 3(a) represents a self-energy diagram where an electron in the conduction band interacts with the vacuum through a polarization part  $\Gamma$ . The self-energy diagram resulting from a summation of diagrams of the type (a) over all  $\Gamma$  is shown in (d). The self-energy diagram where an electron interacts with the assumed local potential  $V_L$  through a polarization part  $\Gamma$  is shown in (b). The sum of such diagrams over all  $\Gamma$  is shown in (e). The self-energy diagram resulting purely from polarization processes is shown in (c) and the total contribution of these diagrams is given in (f).

<sup>9</sup> N. M. Hugenholtz, *Physica* 23, 481 (1957).

<sup>10</sup> C. Bloch and J. Horowitz, *Nuclear Phys.* 8, 91 (1958).

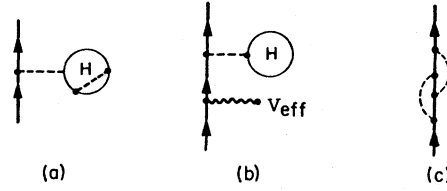


FIG. 4. In parts (a), (b), and (c) are shown typical processes that are neglected when the theory is cut off at the first order in the modified Coulomb interaction.

$h(x)$ . To do this we develop  $\text{S.E.}(nk)$  in terms of the modified Coulomb interaction  $\mathcal{U}(x, x')$  or equivalently by (12) in terms of the dielectric function  $\epsilon^{-1}$ . This development is carried out here to first order in  $\mathcal{U}(x, x')$  although it could be taken to higher orders if necessary.

There are three types of self energy diagrams of first order in  $\mathcal{U}(x, x')$  which arise from the perturbation  $H_1$  defined in (2). Examples are shown in Figs. 3(a), 3(b), and 3(c). In Fig. 3(a), a free particle in the conduction or higher band interacts with the vacuum at  $x_1$  via a polarization part  $\Gamma$  and an  $H$  part which is that part of the diagram joined to the complete structure by a single interaction line.  $H$  parts arise from the  $\sum_{i < j} e^2 / r_{ij}$  part of  $H_1$  and after summing over all possible  $\Gamma$  and  $H(x)$  they represent the modified Coulomb interaction of a particle in a band above the valence band with the valence and atomic core electrons.<sup>11</sup> The result of summing over all  $\Gamma$  for a given  $H$  part is shown in Fig. 3(d).

The second type of self energy diagram is shown in Fig. 3(b); this being due to the  $\sum_i V(x_i)$  part of  $H_1$ . Summing over all  $\Gamma$  and integrating over internal vertices leads to the replacement of  $V(x)$  by  $V_{\text{eff}}(x)$ .  $V_{\text{eff}}(x)$  is readily shown to satisfy the integral equation

$$V_{\text{eff}}(x) = V(x) + \int \mathcal{U}^*(x, x') V_{\text{eff}}(x') d^4 x'. \quad (17)$$

If  $V(x)$  is said to arise from the charge density  $\rho_V(x')$ , then  $V_{\text{eff}}(x)$  is given by

$$V_{\text{eff}}(x) = \int \mathcal{U}(x, x') \rho_V(x') d^4 x'. \quad (18)$$

Figure 3(e) shows the interaction of a particle outside of the vacuum with  $V_{\text{eff}}$ .

The final type of self energy diagram to be considered here is shown in Fig. 3(c) where an electron arriving at  $x_1$  is scattered into an intermediate state between  $x_1$  and  $x_2$  by its interaction with the system through  $\Gamma$ . At  $x_2$  it is scattered again (back to its original state in the self-energy process). The totality of these processes is shown in Fig. 3(f).

Some examples of self-energy diagrams not included in this first order in  $\epsilon^{-1}$  discussion are shown in Fig. 4.

<sup>11</sup> We are using the notation of Hubbard whose paper may be consulted for more details. J. Goldstone, *Proc. Roy. Soc. (London)* A239, 267 (1957) also has discussed these  $H$ -part diagrams.

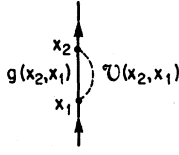


FIG. 5. This represents the self-energy diagram resulting from the inclusion of the nonlocal potential given in Eq. (23) in the unperturbed Hamiltonian.

From Fig. 4(a) it is seen that  $H$  parts containing internal interaction lines are neglected. The only  $H$  part that will be included in the following is

$$H(x) = \rho_H(x) = \sum_i^{\text{occupied}} u_i^*(x) u_i(x), \quad (19)$$

where the sum is over the filled levels of the unperturbed vacuum state  $\phi_0$ .

The necessary freedom required in order to choose  $h(x)$  so that the self energy corrections to  $\epsilon_{nk}$  cancel is provided by the potential  $V(x)$  which appears in (1) and (2). First, however, we note that, as in the Hartree-Fock case,  $V(x)$  will in general have a local and a nonlocal part

$$V(x) = V_L(x) + \int V_{NL}(x, x') P(x, x') d^4x' \delta(t_x). \quad (20)$$

$P(x, x')$  has the property that

$$V(x) u_p(x) = V_L(x) u_p(x) + \int V_{NL}(x, x') u_p(x') d^4x' \delta(t_x). \quad (21)$$

Thus  $H_1$  is

$$H_1 = \sum_{i < j} e^2 / |x_i - x_j| - \sum_i [V_L(x_i) + \int V_{NL}(x_i, x) P(x_i, x) d^4x] \delta(t_{x_i}), \quad (22)$$

and  $H_0$  is amended by adding the nonlocal term. Let the nonlocal part of  $V(x)$  be defined in terms of  $\mathcal{U}(x, x')$  as

$$\int \mathcal{U}(x, x') g(x, x') P(x, x') d^4x' \delta(t_x) \quad (23)$$

with the function  $g(x, x')$  as yet unspecified. Including a nonlocal term of this form in  $V(x)$  gives rise to only one new self-energy diagram of first order in  $\mathcal{U}(x, x')$ . This is shown in Fig. 5. Thus  $S.E.(nk)$  is found by evaluating the contributions of Figs. 3(d), 3(e), 3(f) and Fig. 5.  $V_{\text{eff}}$  appearing in Fig. 3(e) and defined in (17) comes from  $V_L(x)$ .

Hubbard has shown that if  $V_L(x)$  is chosen as the Hartree-like potential

$$V_L(x) = \int v(x - x') \rho_H(x') dx', \quad (24)$$

with  $\rho_H$  given in Eq. (19), then the contributions of Figs. 3(d) and 3(e) will cancel. Making this choice and

evaluating Fig. 3(f) according to the rules in Hubbard's paper  $E_{nk}$  computed from the vacuum energy  $\mathcal{E}_0 + \Delta E_0$  becomes

$$\begin{aligned} E_{nk} = & + \int u_{nk}^*(x_1) h(x_1) u_{nk}(x_1) d^4x_1 \\ & + \int d_4x_1 d_4x_2 u_{nk}^*(x_2) u_{nk}(x_1) S(x_2, x_1) \\ & \quad \times \mathcal{U}(x_2, x_1) \delta(t_1) \\ & - \int d_4x_1 d_4x_2 u_{nk}^*(x_2) u_{nk}(x_1) g(x_2, x_1) \\ & \quad \times \mathcal{U}(x_2, x_1) \delta(t_1). \end{aligned} \quad (25)$$

Here  $S(x_2, x_1)$  is the propagator

$$S(x_2, x_1) = \epsilon(t_2 - t_1) \sum_i^{\text{unoccupied}} u_i(x_2) u_i^*(x_1) - \epsilon(t_1 - t_2) \sum_i^{\text{occupied}} u_i(x_2) u_i^*(x_1), \quad (26)$$

and where  $\epsilon(t)$  is zero for  $t < 0$ , unity for  $t > 0$ , and  $\frac{1}{2}$  for  $t = 0$ . The occupied and unoccupied orbitals are those filled or empty in the bare vacuum state  $\phi_0$ . The first term in Eq. (25) is the single particle energy  $\epsilon_{nk}$ , the second term is the contribution of Fig. 3(f), and the last term of Fig. 5 with the negative sign stemming from the sign with which  $V_{NL}$  enters  $H_1$  in Eq. (22).

If  $g(x_2, x_1)$  is taken equal to  $S(x_2, x_1)$ , the self-energy corrections to first order in  $\mathcal{U}(x, x')$  vanish and  $E_{nk}$  is simply

$$E_{nk} = + \epsilon_{nk}.$$

Thus the eigenvalue  $\epsilon_{nk}$  of  $h(x)$  already contains the dielectric properties of the system to first order in  $\epsilon^{-1}$ . The above choices for  $V_L$  and  $V_{NL}$  give  $h(x)$  the form

$$\begin{aligned} h(x_1) = & (-\hbar^2/2m) \nabla_1^2 + V_n(x_1) + \sum_i^{\text{occupied}} \\ & \times \int v(x_1 - x_2) u_i^*(x_2) u_i(x_2) d^3x_2 \\ & + \int d^4x_2 S(x_2, x_1) \mathcal{U}(x_2, x_1) \delta(t_1) P(x_1, x_2). \end{aligned} \quad (27)$$

The last term on the right of (27) is the approximation to the mass operator to first order in the modified Coulomb interaction. The one particle Hamiltonian is of the same form as the one particle equation derived by Schwinger<sup>2</sup> in quantum electrodynamics from much more general considerations. All of the one particle functions  $u_i(x)$  defining the vacuum as well as the orbital  $u_{nk}(x)$  associated with the conduction band satisfy

$$h(x) u_j(x) = \epsilon_j u_j(x). \quad (28)$$

However, if  $\mathcal{U}(x_2, x_1)$  in (27) is replaced by the instantaneous Coulomb interaction, only the case of  $j = nk$  in (28) reduces to the proper Hartree-Fock equation. Unlike the Hartree-Fock method which is

based on the variational principle, the approach here is that of perturbation theory. Consequently it is a necessary assumption for the unperturbed system that all electrons experience the same local and the same nonlocal potential in order that the unperturbed total Hamiltonian  $H_0$  in (1) be the sum of energy operators for the separate particles.

Having found the one particle Hamiltonian (27) the goal of the paper has been achieved at least in a formal sense. Although the theory given here has been limited to first order effects in the modified Coulomb interaction, this is not a fundamental limitation. The local and nonlocal potentials could be chosen so as to eliminate the self-energy corrections to any desired order in  $\mathcal{U}$ .

#### IV. CONCLUSIONS

Even though it has been shown here that one can find the corrected energies  $E_{nk}$  as solutions of a one particle equation, the practical possibility of solving this equation is certainly rather remote. Both  $S(x_2, x_1)$  and  $\mathcal{U}(x_2, x_1)$  in Eq. (27) depend on a complete set of one electron orbitals leading to an insurmountable self-consistent field problem. If this complete set were replaced by a rather small number of functions, a problem would result at least as difficult as the self-consistent Hartree-Fock case which has never been carried out for a solid. Other alternatives must be sought.

It might prove reasonable in some cases to evaluate the nonlocal potential for a free electron gas by the type of approximation used by Hubbard<sup>4</sup> in his discussion of the free electron gas correlation energy. From this point one might proceed much as Slater has done in his treatment of exchange in the Hartree-Fock method.<sup>12</sup> This is merely to suggest a type of alternative to the full self-consistent problem.

Another approach would be to use the single particle equation with a phenomenological form of the local and nonlocal potentials whose defining parameters are to be determined from experiment. This amounts to a carry over of the ideas behind crystal field theory to the periodic potential problem. Phillips<sup>13</sup> has already

introduced an energy band interpolation scheme using a local potential with parameters chosen to fit experiment. His pseudopotential method has been very successful in fitting a considerable amount of data in Ge and Si.

Although Phillips used only a local potential, he was aware that a nonlocal potential must also be included to account for exchange and correlation (dielectric) effects. Kane<sup>14</sup> has shown how the effective mass depends on a nonlocal potential. Using Kane's results Phillips<sup>15</sup> has concluded that the experimental effective mass constants for Ge and Si as found by cyclotron resonance cannot be obtained from theory unless nonlocal effects are included.

A nonlocal potential can readily be incorporated into Phillips' pseudopotential method. This would lead to a set of equations for the Fourier coefficients  $v_{nk}(K)$  of the periodic part of the Bloch function  $b_{nk}(r)$  of the form

$$[\epsilon_{nk} - (\hbar^2/2m)(k+K_i)^2]v_{nk}(K_i) - \sum (K_j)[V_L(K_i - K_j) + V_{NL}(k+K_i, -k-K_j)] \times v_{nk}(K_j) = 0. \quad (29)$$

Here  $V_L(K)$  and  $V_{NL}(k, -k+K)$  are Fourier coefficients of the local and nonlocal parts of the pseudopotential. If the nonlocal part  $V_{NL}(r_1, r_2)$  is taken to depend only on  $r_1 - r_2$ , then (29) becomes

$$[\epsilon_{nk} - (\hbar^2/2m)(k+K_i)^2 - V_{NL}(k+K_i, -k-K_i)] \times v_{nk}(K_i) - \sum (K_j)V_L(K_i - K_j)v_{nk}(K_j) = 0. \quad (30)$$

Approximating  $V_{NL}(k+K_i, -k-K_i)$  as  $A_0 + A_2(k+K_i)^2$  would be equivalent to making  $\hbar^2/2m$  a disposable parameter in addition to the disposable Fourier coefficients of the local part of the pseudopotential used by Phillips. Thus it might be that a satisfactory representation of nonlocal effects could be achieved in the pseudopotential method by the addition of only a single extra parameter.

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<sup>14</sup> E. O. Kane, J. Phys. Chem. Solids **6**, 236 (1958).

<sup>15</sup> J. C. Phillips, J. Phys. Chem. Solids **7**, 52 (1958).