PHYSICAL REVIEW VOLUME 123, NUMBER 2 JULY 15, 1961

Generalized Koopmans' Theorem*

J. C. Phillips
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago 37, Illinois

(Received February 24, 1961)

Koopmans' theorem states that if the wave function of a many-electron system is approximated by a Slater determinant of Hartree-Fock one-electron wave functions, with one-electron energies defined as the difference in energy of $(N+1)$- and N-particle systems, then these one-electron energies are given by the expectation value of the Hartree-Fock Hamiltonian with respect to the one-electron wave functions. Koopmans' theorem is here generalized to include correlation effects by using Hubbard's expression for the total energy of a free-electron gas. The resulting one-electron Hamiltonian contains in first-order screened exchange. Hubbard's lowest polarization diagram gives, in addition, part of the screened second-order Coulomb interactions, which is small for metallic densities. Collective terms are also obtained. Comparison with the Bohm-Pines Hamiltonian shows a one-to-one correspondence, but with different cutoff functions in each term. Following Hubbard, we extend the method to include the effects of a periodic potential to first order. The resulting one-electron Hamiltonian provides a convenient and accurate basis for self-consistent energy band calculations including exchange and correlation in metals and semiconductors.

1. INTRODUCTION

IT has been apparent for some time that in spite of the success of the Hartree-Fock scheme for molecules, neglect of screening of the exchange interaction can lead to serious errors in one-electron energies in crystals. The way in which correlation removes singularities in the momentum dependence of the single-particle energy for the free-electron gas has been described by Quinn and Ferrell[1] in terms of self-energies of quasi-particles. The quasi-particle formalism has also recently been extended by Pratt[2] to the periodic potential problem, using the general methods of Hubbard[3–5] to treat the screening of Coulomb interactions through electron correlation.

It is our opinion that in spite of the elegance of the method, the quasi-particle formalism often tends to obscure rather than clarify the relationship between many-electron and one-electron wave functions.[6–8] For this reason we present here an alternative approach to effective single-particle Hamiltonians based on an extension of Koopmans' derivation[9] of the Hartree-Fock Hamiltonian.

A simple definition of one-electron energies is given by the following procedure. Construct a complete set of one-electron wave functions $\psi_i(\mathbf{x})$. If perturbation theory converges starting with these functions, we may calculate the total energy E^N of an N-particle system, as a function of occupation numbers N_i of the $\psi_i(\mathbf{x})$. Similarly, neglect resonant processes and calculate the (real) energy E_k^{N-1} of an $(N-1)$-particle system with one electron removed from state k. The one-electron energy ϵ_k is

$$\epsilon_k = E^N - E_k^{N-1}. \tag{1.1}$$

Koopmans[9] showed that (1.1) led to particularly simple results when the system wave function Ψ was approximated by a Slater determinant of the one-electron wave functions ψ_i. Then the total energy of the N-electron system is

$$\begin{aligned} E_{\mathrm{HF}} &= \int \Psi^* \mathcal{H} \Psi d\tau \\ &= \sum_i N_i \int \psi_i^*(r_1)\left[-\frac{\hbar^2}{2m}\nabla_1^2 + V(\mathbf{r}_1)\right]\psi_i(\mathbf{r}_1) d\tau_1 \\ &\quad + \tfrac{1}{2}e^2 \sum_{i,j}{}' N_i N_j \left[\int \frac{\rho_{ii}^*(\mathbf{r}_1)\rho_{jj}(\mathbf{r}_2)}{r_{12}} d\tau_{12} \right. \\ &\quad \left. - \tfrac{1}{2}\int \frac{\rho_{ij}^*(\mathbf{r}_1)\rho_{ij}(\mathbf{r}_2)}{r_{12}} d\tau_{12}\right]. \end{aligned} \tag{1.2}$$

Here $V(\mathbf{r})$ is the external (lattice) potential, N_i is the one-electron occupation number for the Hartree-Fock orbital ψ_i,

$$\rho_{ij}(\mathbf{r}) = \psi_i^*(\mathbf{r})\psi_j(\mathbf{r}), \tag{1.3}$$

and we have assumed that each orbital state is occupied equally by electrons of up and down spin. A short calculation gives

$$\epsilon_k = \frac{\partial E_{\mathrm{HF}}}{\partial N_k} = \int \psi_k^*(\mathbf{r}_1)\mathcal{H}^F \psi_k(\mathbf{r}_1) d\tau_1, \tag{1.4}$$

$$\mathcal{H}^F = -\frac{\hbar^2}{2m}\nabla_1^2 + V(r_1) + e^2 \sum_i{}' N_j \int \frac{\rho_{jj}(\mathbf{r}_2)}{r_{12}} d\tau_2 + A, \tag{1.5}$$

where A is the exchange operator:

$$A\psi_i(\mathbf{r}_1) = -\tfrac{1}{2}e^2 \sum_i{}' N_j \int \frac{\rho_{ji}(\mathbf{r}_2)}{r_{12}} d\tau_2 \, \psi_j(\mathbf{r}_1). \tag{1.6}$$

---

* Research supported in part by the Office of Naval Research.

[1] J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

[2] G. W. Pratt, Jr., Phys. Rev. **118**, 462 (1960).

[3] J. Hubbard, Proc. Roy. Soc. (London) **A240**, 539 (1957).

[4] J. Hubbard, Proc. Roy. Soc. (London) **A243**, 336 (1958).

[5] J. Hubbard, Proc. Roy. Soc. (London) **A244**, 199 (1958).

[6] Cf. the controversy concerning the appearance of effective charges e^* in the articles by Falicov, Luttinger, and Stern in references 7 and 8.

[7] *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

[8] J. M. Luttinger, Phys. Rev. **121**, 1251 (1961).

[9] T. Koopmans, Physica **1**, 104 (1933).

If the one-electron wave functions $\psi_i(\mathbf{x})$ are now chosen as self-consistent eigenfunctions of H^F, then H^F is just the Hartree-Fock Hamiltonian.

In deriving (1.4) it is assumed in the usual discussions[10] that $\psi_i(\mathbf{x})$ is unchanged by the ionization of electron k if $\psi_i(\mathbf{x})$ is of the extended (Bloch) type. For the free-electron gas this is easily seen to be the case, but this conclusion is not valid in general. In the presence of an external potential the lowest energy E_k^{N-1} will be obtained by modifying each $\psi_{k'}{}^n(x)$ by the admixture of $\psi_{k'}{}^{n'}(\mathbf{x})$, where n and n' are band indices. Each wave function is changed by an amount of order $1/N$, but since N-wave functions change, the perturbed energy of the $(N-1)$-particle system will be changed by an amount

$$\frac{1}{N}\sum_{k'}\frac{(\delta V_{nn'})^2}{E_n-E_{n'}}\simeq\frac{1}{N}\sum_{k'}\frac{V_{nn'}{}^4}{(E_F)^3} \tag{1.7a}$$

$$\simeq\frac{1}{N}\sum_{k'}\frac{V_{nn'}{}^2}{E_F}. \tag{1.7b}$$

In practice we are concerned with one-electron excitations that preserve the neutrality of the crystal, so that δV in (1.7) refers to the nonconstant part of the perturbing potential. For the magnitude of δV in the case that V is weak, there are two possibilities, depending on whether the state k is quasi-degenerate with another state or not:

(a) If it is not (and this is the case for most states in metals) then δV is of order V^2/E_F.

(b) If it is (this applies to a few states of high symmetry in metals, and to all the states near the energy gap in semi-conductors) then δV is of order V. Since ϵ_k is of order E_F, we conclude from (1.7a) and (1.7b) that Koopmans' theorem is valid to fourth or second order, respectively, depending on ψ_k.

For the weakly periodic potentials that obtain in metals and semiconductors[11–13] the correction estimated in (1.7) is generally small, even in case b. Heine[13a] has suggested that in Al the states at W (case b) may be affected by as much as 0.1 rydberg by "exciton" formation. According to (1.7), with $\delta V\sim 0.1$ ry, $E_F\sim 1$ ry, as in Al, $\delta E\sim 0.01$ ry, which is too small to affect the order of levels appreciably.

2. SCREENED ONE-ELECTRON POTENTIALS

According to Hubbard,[4] the exchange and correlation energy of a free-electron gas is given by

$$E_H=\frac{\hbar}{4\pi}\sum_{\mathbf{q}}\int d\omega\,\tan^{-1}\frac{\mathcal{E}_2}{\mathcal{E}_1}-N\sum_{\mathbf{q}}\frac{2\pi e^2}{q^2}, \tag{2.1}$$

where $\mathcal{E}=\mathcal{E}_1+i\mathcal{E}_2$. If only the lowest-order polarization diagram, resulting from one Fourier component q of the Coulomb interaction, is retained,

$$\mathcal{E}_1=1+\eta_1,\quad \mathcal{E}_2=\eta_2+\eta_3, \tag{2.2}$$

$$\eta_1(\mathbf{q},\omega)=\frac{4\pi e^2}{q^2}\sum_{\mathbf{k}'}N_{\mathbf{k}'}\left[\frac{P}{E_{\mathbf{k}'+\mathbf{q}}-E_{\mathbf{k}'}+\hbar\omega}+\frac{P}{E_{\mathbf{k}'-\mathbf{q}}-E_{\mathbf{k}'}-\hbar\omega}\right], \tag{2.3}$$

$$\eta_2(\mathbf{q},\omega)=\frac{4\pi^2e^2}{\hbar q^2}\sum_{\mathbf{k}'}N_{\mathbf{k}'}\left[\delta\left(\frac{E_{\mathbf{k}'+\mathbf{q}}-E_{\mathbf{k}'}}{\hbar}-\omega\right)+\delta\left(\frac{E_{\mathbf{k}'+\mathbf{q}}-E_{\mathbf{k}'}}{\hbar}+\omega\right)\right], \tag{2.4}$$

$$\eta_3(\mathbf{q},\omega)=-\frac{4\pi^2e^2}{\hbar q^2}\sum_{\mathbf{k}'}N_{\mathbf{k}'}N_{\mathbf{k}'+\mathbf{q}}\left[\delta\left(\frac{E_{\mathbf{k}'+\mathbf{q}}-E_{\mathbf{k}'}}{\hbar}-\omega\right)+\delta\left(\frac{E_{\mathbf{k}'+\mathbf{q}}-E_{\mathbf{k}'}}{\hbar}+\omega\right)\right]. \tag{2.5}$$

Our one-electron energy is now given by

$$\epsilon_{\mathbf{k}}=\partial E_H/\partial N_{\mathbf{k}}=\frac{\hbar}{4\pi}\sum_{\mathbf{q}}\int d\omega\,\frac{\mathcal{E}_1(\partial\eta_2/\partial N_k+\partial\eta_3/\partial N_k)-(\eta_2+\eta_3)\partial\eta_1/\partial N_k}{\mathcal{E}_1{}^2+\mathcal{E}_2{}^2}-\sum_{\mathbf{q}}\frac{2\pi e^2}{q^2}. \tag{2.6}$$

The most important term in (2.6) is

$$\epsilon_k{}^{(1)}=\frac{\hbar}{4\pi}\sum_{\mathbf{q}}\int d\omega\,\frac{\mathcal{E}_1\partial\eta_3/\partial N_{\mathbf{k}}}{\mathcal{E}_1{}^2+\mathcal{E}_2{}^2}=\sum_{\mathbf{q}}\frac{2\pi e^2}{q^2}N_{\mathbf{k}+\mathbf{q}}\sigma^{-1}(\mathbf{q},\,(E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}})/\hbar),\quad \sigma^{-1}(\mathbf{q},\omega)=\frac{\mathcal{E}_1(\mathbf{q},\omega)}{\mathcal{E}_1{}^2(\mathbf{q},\omega)+\mathcal{E}_2{}^2(\mathbf{q},\omega)}. \tag{2.7}$$

---

[10] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[11] We assume that core effects have been removed by orthogonalization; then the effective potential for valence electrons is weak. See references 12 and 13.

[12] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[13] M. H. Cohen and V. Heine, Phys. Rev. (to be published).

[13a] V. Heine, Proc. Roy. Soc. (London) **A240**, 361 (1957).

From (2.7) it can be seen that $\epsilon_{\mathbf{k}}^{(1)}$ is just a screened exchange energy. The spatial representation of the one-electron operator B corresponding to (2.7) is

$$B\psi_i(\mathbf{r}_1)=-\tfrac{1}{2}e^2\sum_j N_j\int\frac{\rho_{ji}(\mathbf{r}_2)}{\sigma_{ji}(\mathbf{r}_{12})r_{12}}\psi_j(\mathbf{r}_1),\quad (2.8);\qquad \frac{1}{r\sigma_{ji}(\mathbf{r})}=\frac{1}{(2\pi)^3}\int d^3q\,\frac{e^{i\mathbf{q}\cdot\mathbf{r}}\mathcal{E}_1(\mathbf{q},\,(E_j-E_i)/\hbar)}{(\mathcal{E}_1^2+\mathcal{E}_2^2)q^2},\quad (2.9)$$

in direct correspondence with (1.6). It is often a good approximation to put $\sigma(\mathbf{q},\omega)\simeq\sigma(\mathbf{q},0)=\mathcal{E}_1(\mathbf{q},0)$. Then (2.8) states that the Coulomb interaction in (1.6) should be screened by the static dielectric constant of the medium.

Let us now consider the remaining terms in (2.6). The terms proportional to $\eta_1\partial\eta_2/\partial N_{\mathbf{k}}-\eta_2\partial\eta_1/\partial N_{\mathbf{k}}$ give

$$\epsilon_{\mathbf{k}}^{(2)}=\tfrac{1}{4}\sum_{\mathbf{q}}\left(\frac{4\pi e^2}{q^2}\right)^2\left\{\sum_{\mathbf{k}'}\frac{2N_{k'}}{E_{\mathbf{k}'+\mathbf{q}}+E_{\mathbf{k}-\mathbf{q}}-E_{\mathbf{k}'}-E_{\mathbf{k}}}\left(\frac{1}{|\mathcal{E}(\mathbf{q},\,(E_{\mathbf{k}-\mathbf{q}}-E_{\mathbf{k}})/\hbar)|^2}+\frac{1}{|\mathcal{E}(\mathbf{q},\,(E_{\mathbf{k}'+\mathbf{q}}-E_{\mathbf{k}'})/\hbar)|^2}\right)\right\},\quad (2.10)$$

while the terms proportional to $\eta_3\partial\eta_1/\partial N_{\mathbf{k}}$ give

$$\epsilon_{\mathbf{k}}^{(3)}=-\tfrac{1}{4}\sum_{\mathbf{q}}\left(\frac{4\pi e^2}{q^2}\right)^2\sum_{\mathbf{k}'}2N_{\mathbf{k}'}\frac{2N_{\mathbf{k}'+\mathbf{q}}}{E_{\mathbf{k}'+\mathbf{q}}+E_{\mathbf{k}-\mathbf{q}}-E_{\mathbf{k}'}-E_{\mathbf{k}}}\,\frac{1}{|\mathcal{E}(\mathbf{q},\,(E_{\mathbf{k}'+\mathbf{q}}-E_{\mathbf{k}'})/\hbar)|^2}.\quad (2.11)$$

The meaning of $\epsilon_{\mathbf{k}}^{(2)}$ and $\epsilon_{\mathbf{k}}^{(3)}$ can be seen by comparing (2.10) and (2.11) with the second-order Coulomb term in the total energy; according to Macke,[14]

$$E^{(2)}=\sum_q\left(\frac{4\pi e^2}{q^2}\right)^2 2\sum_{\mathbf{k}'}\sum_{\mathbf{k}''}\frac{N_{\mathbf{k}'}N_{\mathbf{k}''}(1-N_{\mathbf{k}'+\mathbf{q}})(1-N_{\mathbf{k}''-\mathbf{q}})}{E_{\mathbf{k}'+\mathbf{q}}+E_{\mathbf{k}''-\mathbf{q}}-E_{\mathbf{k}'}-E_{\mathbf{k}''}}.\quad (2.12)$$

Thus $\epsilon_{\mathbf{k}}^{(2)}$ and $\epsilon_{\mathbf{k}}^{(3)}$ represent the functional derivative of the N^2 and part of the N^3 terms in (2.12), multiplied by $\frac{1}{4}$ and screened by the dielectric constant. If we neglect the frequency dependences, the effective interactions in (2.10) and (2.11) are

$$\frac{4\pi e^2}{\mathcal{E}(\mathbf{q})q^2}\,\frac{4\pi e^2}{\mathcal{E}^*(\mathbf{q})q^2}.\quad (2.13)$$

This is a characteristic result of the Hubbard theory, as has been pointed out by Nozières and Pines.[15] In practice, the second-order terms are negligible since, compared to first-order exchange, they are of order

$$\lesssim\frac{1}{4}\,\frac{e^2/\mathcal{E}(\mathbf{r}_s)r_sa_0}{E_F}\lesssim\frac{r_s}{16\mathcal{E}(\mathbf{r}_s)},\quad (2.14)$$

where $\frac{4}{3}\pi r_s^3$ is the mean volume per electron in Bohr units and $\mathcal{E}(\mathbf{r})$ is defined as in (2.9). For metallic densities $r_s=3$, $\mathcal{E}(\mathbf{r}_s)\gtrsim 5$ and (2.14) is of order 0.05.

A fourth term remains from $\partial\eta_2/\partial N_{\mathbf{k}}$ and the last term in (2.6):

$$\epsilon_{\mathbf{k}}^{(4)}=-2\pi e^2\sum_{\mathbf{q}}\frac{1}{q^2}\left[1-\frac{1}{|\mathcal{E}(\mathbf{q},\,(E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}})/\hbar)|^2}\right].\quad (2.15)$$

For large q, $\mathcal{E}\longrightarrow 1$ so that (2.15) does not diverge.

The fifth and last term comes from the zero-point energy of plasma oscillations E_p. This is contained implicitly in (2.1) and according to Hubbard[4] gives a contribution to E_H of the form

$$E_p=\sum_{\mathbf{q}}\frac{\hbar}{2}\int_{\varepsilon_1+i\varepsilon_2=0}\delta(\omega-\omega_p)\omega d\omega.\quad (2.16)$$

As a first approximation assume a constant plasma frequency; then the sum on $\mathbf{q}$ in (2.16) cuts off at q_1, where

$$\hbar\omega_p=(\hbar^2/2m)(q_1^2+2q_1k_F),\quad (2.17)$$

so that

$$E_p\simeq\sum_{|\mathbf{q}|<q_1}\tfrac{1}{2}\hbar\omega_p.\quad (2.18)$$

The plasma energy acts to shift the zero of energy. If we use a second approximation popularized by Nozières and Pines,[16] that

$$q_1=\gamma r_s^{\frac{1}{2}}k_F\sim r_s^{-\frac{1}{2}},$$

where γ is a constant, then

$$\omega_pq_1^3\sim N_1^{\frac{1}{2}}(N^{1/6})^3\sim N$$

so that we can add E_p to our one-electron energy in the form

$$\epsilon_{\mathbf{k}}^{(5)}=\partial E_p/\partial N=(1/N)E_p.\quad (2.19)$$

The meaning of $\epsilon_{\mathbf{k}}^{(4)}$ and $\epsilon_{\mathbf{k}}^{(5)}$ can be seen by comparing them with the collective terms in the Bohm-Pines

---

[14] W. Macke, Z. Naturforsch. **5a**, 192 (1959).

[15] P. Nozières and D. Pines, Nuovo cimento **9**, 470 (1958).

[16] P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).

energy[17]:

$$\frac{1}{N}E_{\mathrm{coll}}=\frac{1}{N}\sum_{|\mathbf{q}|<q_c}\left(\frac{\hbar\omega_p}{2}-\frac{2\pi Ne^2}{q^2}\right). \tag{2.20}$$

Thus $\epsilon_{\mathbf{k}}^{(4)}$ is just the self-energy correction to the plasma energy, which is represented in the Bohm-Pines theory by the last term in (2.20). We note that in the Bohm-Pines formalism a universal cutoff (q_c) is used, whereas according to Hubbard the cutoff for $\epsilon_{\mathbf{k}}^{(5)}$ is q_1, while that for $\epsilon_{\mathbf{k}}^{(4)}$ is given by the brackets in (2.15), which are weakly k dependent. Detailed analysis of $\mathcal{E}(\mathbf{q},\omega)$ for a free-electron gas[4] or model semiconductor[18] shows, however, that $\epsilon_{\mathbf{k}}^{(4)}$ is nearly constant for $E_{\mathbf{k}}$ near E_F. (Physically this is a consequence of the separation of single-particle frequencies from plasma frequencies.) Thus, as suggested by (2.20), we can group $\epsilon_{\mathbf{k}}^{(4)}$ with $\epsilon_{\mathbf{k}}^{(5)}$ and regard both as contributing an over-all constant to the one-electron Hamiltonian.

We note that our screened exchange energy $\epsilon_{\mathbf{k}}^{(1)}$ is similar to the Bohm-Pines screened exchange, except that here the cutoff factor is also different $[\mathcal{E}_1/(\mathcal{E}_1^2+\mathcal{E}_2^2)]$. In second order still another cutoff factor $(1/|\mathcal{E}|)$ appears, but by now the correspondence is breaking down, since $\epsilon_{\mathbf{k}}^{(2)}$ and $\epsilon_{\mathbf{k}}^{(3)}$ represent only part of the second-order Coulomb energy. Higher-order polarization diagrams are not expected to supply the remaining parts. This means that no significance can be attached to attempts[19] to carry the Bohm-Pines theory beyond first order.

3. WEAKLY PERIODIC POTENTIAL

The general theory of correlation effects in crystals has also been developed by Hubbard,[5] using Hartree functions as a basis for perturbation theory. Pratt[2] has shown that for constructing effective single-particle Hamiltonians Hubbard's procedure with minor modifications can be carried out with self-consistent basis functions. Following Hubbard and Pratt we now consider valence-valence exchange and correlation.

We assume that self-consistent calculations have been carried out with the screened exchange potential derived below, and one-electron energies E_i and wave functions $\psi_i(\mathbf{x})$ have been obtained. Then following Hubbard's notation, and retaining only the lowest-order polarization diagram,

$$\bar{V}(\mathbf{x}',\mathbf{x})=\bar{W}(\mathbf{x}',\mathbf{x})=(i/\hbar)S(\mathbf{x}',\mathbf{x})S(\mathbf{x},\mathbf{x}'), \tag{3.1}$$

$$\begin{aligned}S(\mathbf{x}',\mathbf{x})=\mathcal{E}(t'-t)\sum(1-N_i)\psi_i(\mathbf{x}')\psi_i^*(\mathbf{x})e^{(i/\hbar)E_i(t-t')}\\-\mathcal{E}(t-t')\sum N_i\psi_i(\mathbf{x}')\psi_i^*(\mathbf{x})e^{(i/\hbar)E_i(t-t')}.\end{aligned} \tag{3.2}$$

Expand the exchange charge density in a Fourier series:

$$\begin{aligned}\rho^{ij}(\mathbf{x})&=\psi_i^*(\mathbf{x})\psi_j(\mathbf{x})\\&=\exp[-i(\mathbf{k}'-\mathbf{k}'')\cdot\mathbf{x}]\sum_{\boldsymbol{\kappa}} g_\kappa^{ij}\exp(-i\boldsymbol{\kappa}\cdot\mathbf{x})\end{aligned} \tag{3.3}$$

(where $\mathbf{k}'$ refers to the largest Fourier component of ψ_i, and similarly for $\mathbf{k}''$ and ψ_j); then

$$\begin{aligned}\bar{W}(\mathbf{x}',\mathbf{x},\omega)=\frac{2\pi}{i\hbar}\bigg[\sum_i\sum_j N_i(1-N_j)\rho_{ij}^*(\mathbf{x}')\rho_{ij}(\mathbf{x})\delta_-\left(\frac{E_j-E_i}{\hbar}+\omega\right)\\+\sum_i\sum_j N_j(1-N_i)\rho_{ij}^*(\mathbf{x}')\rho_{ij}(\mathbf{x})\delta_+\left(\frac{E_j-E_i}{\hbar}+\omega\right)\bigg],\end{aligned} \tag{3.4}$$

after Fourier-transforming $\bar{W}$ with respect to t. We now neglect the terms in $\rho_{ij}^*(\mathbf{x}')\rho_{ij}(\mathbf{x})$ which do not depend on $(\mathbf{x}'-\mathbf{x})$:

$$\rho_{ij}^*(\mathbf{x}')\rho_{ij}(\mathbf{x})\simeq\exp[i(\mathbf{k}'-\mathbf{k}'')\cdot(\mathbf{x}'-\mathbf{x})]\sum_{\boldsymbol{\kappa}}|g_\kappa^{ij}|^2\exp[i\boldsymbol{\kappa}\cdot(\mathbf{x}'-\mathbf{x})]. \tag{3.5}$$

We must now see why this approximation is justified in the weakly periodic case.

In the case of first-order exchange the terms neglected by (3.5) integrate to zero. According to Sec. 2, however, the correct first-order potential is exchange screened by $\sigma(\mathbf{q},\omega)\simeq\mathcal{E}(\mathbf{q},0)$. The important point now is that screening is a property of the entire system of electrons, and in a weakly periodic potential where band gaps are small compared to the plasma energy, $\mathcal{E}_1$ will be essentially the same as in a free-electron gas. It is necessary to retain the oscillatory terms in $\partial\eta_3/\partial N_{\mathbf{k}}$ since these depend explicitly on the interference between $N_{\mathbf{k}}\psi_{\mathbf{k}}$ and $N_{\mathbf{k}+\mathbf{q}}\psi_{\mathbf{k}+\mathbf{q}}$, but not in $\mathcal{E}_1$. We are, in effect, arguing that local field corrections to the dielectric constant are small in the weakly periodic case; this has been known for some time from the success of the free-electron formula for the plasma frequency in many crystals.[17]

From (3.4) and (3.5),

$$\begin{aligned}1-\mathcal{E}(\mathbf{q},\omega)=V^*(\mathbf{q},\omega)=\bigg\{-\frac{4\pi e^2}{q^2}\sum_i N_i\frac{P(E_j-E_i)}{(E_j-E_i)^2-(\hbar\omega)^2}\\-i\frac{4\pi^2e^2}{q^2}\sum_i N_i(1-N_j)[\delta(E_j-E_i-\hbar\omega)+\delta(E_j-E_i+\hbar\omega)]\bigg\}\sum_{\boldsymbol{\kappa}}|g_\kappa^{ij}|^2\delta(\mathbf{k}'-\mathbf{k}''+\boldsymbol{\kappa}-\mathbf{q}),\end{aligned} \tag{3.6}$$

---

[17] D. Pines, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1.

[18] J. C. Phillips and L. Kleinman (to be published).

[19] J. G. Fletcher and D. C. Larson, Phys. Rev. **111**, 455 (1958).

which is analogous to Hubbard's equation (II, 24). The interference terms are represented by the last factor in (3.6).

According to the foregoing argument we may approximate the real part of (3.6) by

$$-\frac{4\pi e^2}{q^2}\sum_i N_i \frac{P}{E_j - E_i}, \tag{3.7}$$

where we have taken $\omega = 0$. Then we obtain a screened exchange operator which in the space representation is

$$B\psi_{\mathbf{k},\alpha}{}^n(\mathbf{r}_1) \simeq -\tfrac{1}{2}e^2 \sum_{\mathbf{k}'} \int d^3r_2\, \psi_{\mathbf{k}'}{}^*(\mathbf{r}_2) \frac{1}{\mathcal{E}(\mathbf{r}_{12})r_{12}} \psi_{\mathbf{k},\alpha}{}^n(\mathbf{r}_2)\psi_{\mathbf{k}'}(\mathbf{r}_1). \tag{3.8}$$

Here α labels irreducible representations and n is a band index. Since B has the full symmetry of the crystal it has no matrix elements between different irreducible representations. The operator B in (3.8) is a natural generalization of the exchange operator A in (1.6) which includes screening.

The operator B can be calculated self-consistently in metals and semiconductors without prohibitive effort. A number of matrix elements of A and B for valence-valence exchange have been calculated for silicon; the results will be published elsewhere.

As one would expect, there is little screening ($\mathcal{E} \simeq 1$) of valence-core exchange. This can be seen explicitly from (2.7), since valence-core energy differences are generally of order 10 ry$\gg \hbar\omega_p$. For d electrons this inequality often does not hold, and quite complicated correlations are possible, e.g., in the noble metals.

We conclude by comparing our approach with the quasi-particle viewpoint, as formulated generally by Hugenholtz[20] and applied to the electron gas by Pratt.[2] Hugenholtz shows that the excited state energy $E_{\mathbf{k}}{}^{N-1}$ is in general complex. The one-electron energy $\epsilon_{\mathbf{k}}$ in (1.1) should therefore be taken as $\mathrm{Re}(E^N - E_{\mathbf{k}}{}^{N-1})$. Hubbard shows that the exchange and correlation energy is proportional to $i/\mathcal{E}$; by computing changes in $\mathrm{Im}(1/\mathcal{E})$ we have implicitly applied Hugenholtz's prescription to our case. It follows that if the approximations that we have made are applied to Pratt's Eq. (27), similar one-electron operators should result. From Pratt's derivation it is not evident when such approximations are valid; on the other hand, Koopmans' method leads quite simply to accurate one-electron Hamiltonians for weakly periodic crystals.

Note added in proof. The connection between Koopmans' method and the quasi-particle approach is clarified by comparing our results with the elegant extension of the random-phase approximation by Suhl and Werthamer [Phys. Rev. **122**, 359 (1961)]. They calculate quasi-particle interactions and so find in lowest order in Eqs. (21) and (22) screened exchange. When the quasi-particle energy ω_k in their (21) is replaced by $E_k + i\eta(\eta \rightarrow 0+)$ it can be shown that the real part of the interaction reduces to our (2.7), but with exchange omitted from ϵ_2 (i.e., $\eta_3 = 0$). Pines and Hubbard have emphasized that it is essential to include exchange in the dielectric function in each order to obtain results valid at intermediate densities (where the expansion parameter is $|\epsilon(r_s)|^{-1}$) rather than high densities (expansion parameter r_s).

ACKNOWLEDGMENT

I am grateful to Professor M. H. Cohen for several stimulating conversations.

---

[20] N. M. Hugenholtz, Physica **23**, 481 (1957).