

Interaction of electrons with lattice vibrations

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Using methods of modern field theories a canonical transformation of the Hamiltonian of free electrons in the field of the lattice vibrations is performed. This transformation takes account of the bulk of the interaction of the electrons with the vibrational field and leads to a renormalization of the velocity of sound and of the interaction parameter F . An objection of Wentzel's against the use of large F is removed in this way. Even in the case of weak interaction the transformed Hamiltonian contains already in zero order terms which require a modification of the usual procedure in the theory of metals, and which at low temperatures lead to an increase of the effective mass of the electrons. Treatment of strong interaction requires the development of a new method.

1. INTRODUCTION

In the theory of metals in its simplest form electrons are treated as free, apart from their interaction with the lattice vibrations. Bloch (1928) has described this interaction in terms of absorption or emission of vibrational quanta. Recently, it has been noticed by the author (Fröhlich 1950, quoted as I) that this implies also the possibility of virtual emission and absorption of quanta and in this way gives rise to an interaction between electrons. In fact, the situation is best described in terms of a field theory in which the electrons are the sources of the vibrational field. Discussion with the help of perturbation theory led to the introduction of an interaction parameter F . It was found that if F is larger than a critical value F_0 then the electron distribution in momentum space differs in the ground state from the normal distribution. This new state was tentatively identified with the superconductive state which led to a prediction of the isotope effect. Starting from a knowledge of this effect, Bardeen (1950) has developed a theory on similar lines.

Further development of the theory has been hindered so far by mathematical difficulties. For the condition $F > F_0$ implies that perturbation theory can no longer be usefully applied to calculate details of the energy spectrum, although it should be expected to lead to the correct magnitude of the energy of the ground state.

The case of normal metals for which $F < F_0$ shows also some points of interest. Thus, as Buckingham (1951) has pointed out, the density of energy levels is altered by the interaction. This may lead to anomalies in the specific heat. Also, as was first suggested by Cooke (1951), certain anomalies in the soft X-ray emission spectrum of Na observed by Skinner (1940) might find their explanation in this way. The only explanation that was available at the time would require an overlapping of energy bands which is very unlikely in Na.

The major part (E_1) of the interaction energy between the electrons and the lattice vibrations is due to an adjustment of the electronic density in the potential field of the lattice vibrations and follows them adiabatically. It is this part which gives rise to the (negative) self energy of a vibrational quantum calculated by

Wentzel (1951), as has been suggested by Huang (1951). All the interesting effects mentioned above are, however, due to a second part (E_2) of the interaction which is dynamic in nature; its ratio to E_1 is very small, of the order of the ratio of the velocity of sound to the velocity of the electrons. Wentzel has pointed out that the first part E_1 would lead to a breakdown of the lattice if $F > F_0$.

It is the main object of the present paper to perform a more satisfactory separation of E_1 from E_2 than by ordinary perturbation theory. This will be done by a canonical transformation, using methods of modern field theories. It will lead to a renormalization of the velocity of sound and of the interaction parameter. Wentzel's objection to the possibility of choosing F larger than F_0 will then be found to hold no longer.

2. A CANONICAL TRANSFORMATION

Consider a Hamiltonian which consists of three parts,

$$H' = H_{\text{el.}} + H_{\text{f}} + H_{\text{int.}} \quad (2.1)$$

due to free electrons, field, and interaction. Let $\mathbf{P}(\mathbf{r}, t)$ be a longitudinal displacement of the lattice and assume

$$H_{\text{f}} = \frac{1}{2} \int (M\mathbf{P}^2 + Ms'^2(\text{div } \mathbf{P})^2) n \, d\mathbf{r}, \quad \text{curl } \mathbf{P} = 0, \quad (2.2)$$

where M is the mass of an ion of the lattice, n their number per unit volume and s' the velocity of sound in the absence of ion-electron interaction.† It is useful to introduce here a complex function \mathbf{B} instead of the real \mathbf{P} by

$$\text{div } \mathbf{B} = \text{div } \mathbf{P} + i\dot{\mathbf{P}}\mathbf{w}/sw', \quad \text{curl } \mathbf{B} = 0. \quad (2.3)$$

For then if \mathbf{B} is developed into plane waves (V = total volume)

$$\mathbf{B} = \frac{\mathbf{w}}{w} \left(\frac{2\hbar}{nVMws'} \right)^{\frac{1}{2}} \sum_{\mathbf{w}} b_{\mathbf{w}} e^{i\mathbf{w}\mathbf{r}}, \quad (2.4)$$

one finds
$$H_{\text{f}} = \frac{1}{2} nMs'^2 \int |\text{div } \mathbf{B}|^2 d\mathbf{r} = \frac{1}{2} \sum_{\mathbf{w}} \hbar ws' (b_{\mathbf{w}}^+ b_{\mathbf{w}} + b_{\mathbf{w}} b_{\mathbf{w}}^+). \quad (2.5)$$

Quantization according to Bose-Einstein statistics requires the commutation rules

$$(b_{\mathbf{w}}, b_{\mathbf{v}}) = b_{\mathbf{w}} b_{\mathbf{v}} - b_{\mathbf{v}} b_{\mathbf{w}} = 0, \quad (b_{\mathbf{w}}, b_{\mathbf{v}}^+) = \delta_{\mathbf{v}, \mathbf{w}}. \quad (2.6)$$

The electronic part will be based on wave functions

$$\psi = V^{-\frac{1}{2}} \sum_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}, \quad (2.7)$$

where to satisfy the Pauli principle

$$a_{\mathbf{k}} a_1 + a_1 a_{\mathbf{k}} = 0, \quad a_{\mathbf{k}}^+ a_1 + a_1 a_{\mathbf{k}}^+ = \delta_{1, \mathbf{k}}. \quad (2.8)$$

Thus

$$H_{\text{el.}} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}}, \quad (2.9)$$

with

$$\epsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m. \quad (2.10)$$

† A slightly more general formulation would be obtained by replacing $(\text{div } \mathbf{P})^2$ by $\sum_{i, k} (\partial P_i / \partial x_k)^2$.

Finally the interaction will be written as

$$H_{\text{int.}} = C' \int \psi^+ \psi \operatorname{div} \mathbf{P} \, d\mathbf{r} = i \sum_{\mathbf{w}, \mathbf{k}} D_w (b_{\mathbf{w}} a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} - b_{\mathbf{w}}^+ a_{\mathbf{k}-\mathbf{w}}^+ a_{\mathbf{k}}), \quad (2.11)$$

where C' is a constant with dimension of an energy. Note that the $a_{\mathbf{k}}$ commute with the $b_{\mathbf{w}}$ and that

$$\rho_{\mathbf{w}} = \sum_{\mathbf{k}} a_{\mathbf{k}-\mathbf{w}}^+ a_{\mathbf{k}} = \rho_{-\mathbf{w}}^+ \quad (2.12)$$

is the Fourier coefficient of the electronic density operator. The constants D_w are real, and given by

$$D_w^2 = \frac{C'^2 \hbar w s'}{2nVMs'^2} = \frac{4F'\zeta}{3nV} \hbar w s', \quad (2.13)$$

if
$$F' = \frac{3}{8} \frac{C'^2}{\zeta M s'^2}. \quad (2.14)$$

Thus F' becomes identical with the interaction constant F introduced in I (2.9), if we replace there C^2 and s by $9C'^2/8$ and s' respectively. ζ is the Fermi energy as defined in I (2.2).

From (2.1), (2.5), (2.6), (2.9), (2.11) and (2.12) one obtains

$$H' = \sum_{\mathbf{k}} \epsilon_k a_{\mathbf{k}}^+ a_{\mathbf{k}} + \sum_{\mathbf{w}} \hbar w s' (b_{\mathbf{w}}^+ b_{\mathbf{w}} + \frac{1}{2}) + i \sum_{\mathbf{w}, \mathbf{k}} D_w (b_{\mathbf{w}} \rho_{\mathbf{w}}^+ - b_{\mathbf{w}}^+ \rho_{\mathbf{w}}). \quad (2.15)$$

We now wish to perform a canonical transformation which removes the interaction term as completely as possible. Let S be an operator satisfying

$$S^+ = -S, \quad (2.16)$$

so that e^S is unitary. Then

$$H = e^{S^+} H' e^S = H' - (S, H') + \frac{1}{2}(S, (S, H')) + \dots, \quad (2.17)$$

where the brackets represent the commutators similar to the notation in (2.6). S will be assumed of the form

$$S = \sum_{\mathbf{w}} S_{\mathbf{w}}, \quad S_{\mathbf{w}} = -\gamma_{\mathbf{w}} b_{\mathbf{w}} + \gamma_{\mathbf{w}}^+ b_{\mathbf{w}}^+ = -S_{\mathbf{w}}^+, \quad (2.18)$$

where
$$\gamma_{\mathbf{w}} = \sum_{\mathbf{k}} \phi(\mathbf{k}, \mathbf{w}) a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}}, \quad \gamma_{\mathbf{w}}^+ = \sum_{\mathbf{k}} \phi^*(\mathbf{k}, \mathbf{w}) a_{\mathbf{k}-\mathbf{w}}^+ a_{\mathbf{k}}, \quad (2.19)$$

and $\phi(\mathbf{k}, \mathbf{w})$ is a c -number which will be discussed below.

At this stage it should be remembered that the theory of metals contains the hypothesis that the elastic waves can be considered as harmonic. This means that in the Hamiltonian terms containing $b_{\mathbf{w}}^2$, $b_{\mathbf{w}} b_{\mathbf{v}}$, $b_{\mathbf{w}}^+ b_{\mathbf{v}}$ ($\mathbf{w} \neq \mathbf{v}$), and similar combinations, should be negligible after the observed velocity of sound s has been introduced. This is not yet obvious from (2.15) because s' is not the observed velocity of sound. Following this hypothesis we can neglect terms with $S_{\mathbf{w}} S_{\mathbf{v}}$ if $\mathbf{w} \neq \mathbf{v}$. Then from (2.17) and (2.18)

$$H = H' + \sum_{\mathbf{w}} \{-(S_{\mathbf{w}}, H') + \frac{1}{2}(S_{\mathbf{w}}, (S_{\mathbf{w}}, H'))\} + \dots \quad (2.20)$$

Let now
$$H' = H_0 + H_1 + H_2, \quad (2.21)$$

where
$$H_0 = \sum_{\mathbf{k}} \epsilon_k a_{\mathbf{k}}^+ a_{\mathbf{k}} + \sum_{\mathbf{w}} \hbar w s b_{\mathbf{w}}^+ b_{\mathbf{w}} + \sum_{\mathbf{w}} \frac{1}{2} \hbar w s', \quad (2.22)$$

$$H_1 = \sum_{\mathbf{w}} H_{1\mathbf{w}}, \quad H_{1\mathbf{w}} = i D_w (b_{\mathbf{w}} \rho_{\mathbf{w}}^+ - b_{\mathbf{w}}^+ \rho_{\mathbf{w}}), \quad (2.23)$$

$$H_2 = \sum_{\mathbf{w}} H_{2\mathbf{w}}, \quad H_{2\mathbf{w}} = \hbar w (s' - s) b_{\mathbf{w}}^+ b_{\mathbf{w}}. \quad (2.24)$$

The velocity s will be defined below so as to approach the velocity of sound as closely as possible. Then arranging terms in rising order of $b_{\mathbf{w}}$ (except for $\hbar w s b_{\mathbf{w}}^+ b_{\mathbf{w}}$),

$$H = H_0 - \sum_{\mathbf{w}} \{ (S_{\mathbf{w}}, H_0) + H_{1\mathbf{w}} \} + \sum_{\mathbf{w}} \{ (S_{\mathbf{w}}, \frac{1}{2}(S_{\mathbf{w}}, H_0) - H_{1\mathbf{w}}) + H_{2\mathbf{w}} \} + \dots \quad (2.25)$$

This expression can be evaluated with the help of (2.6) and (2.8). For then

$$(a_{\mathbf{k}}^+ a_{\mathbf{l}}, a_{\mathbf{q}}^+ a_{\mathbf{r}}) = \delta_{\mathbf{lq}} a_{\mathbf{k}}^+ a_{\mathbf{r}} - \delta_{\mathbf{kr}} a_{\mathbf{q}}^+ a_{\mathbf{l}}, \quad (2.26)$$

and hence with (2.19),

$$(\gamma_{\mathbf{w}}, a_{\mathbf{k}}^+ a_{\mathbf{k}}) = -\phi(\mathbf{k}, \mathbf{w}) a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} + \phi(\mathbf{k} + \mathbf{w}, \mathbf{w}) a_{\mathbf{k}+\mathbf{w}}^+ a_{\mathbf{k}}, \quad (2.27)$$

$$(\gamma_{\mathbf{w}}, a_{\mathbf{k}-\mathbf{w}}^+ a_{\mathbf{k}}) = -\phi(\mathbf{k}, \mathbf{w}) (n_{\mathbf{k}-\mathbf{w}} - n_{\mathbf{k}}), \quad n_{\mathbf{k}} = a_{\mathbf{k}}^+ a_{\mathbf{k}}, \quad (2.28)$$

$$(\gamma_{\mathbf{w}}, a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}}) = -\phi(\mathbf{k} - \mathbf{w}, \mathbf{w}) a_{\mathbf{k}}^+ a_{\mathbf{k}-2\mathbf{w}} + \phi(\mathbf{k} + \mathbf{w}, \mathbf{w}) a_{\mathbf{k}+\mathbf{w}}^+ a_{\mathbf{k}-\mathbf{w}}. \quad (2.29)$$

Hence if c.c. indicates the conjugate complex of the previous expression,

$$-(S_{\mathbf{w}}, H_0) + H_{1\mathbf{w}} = b_{\mathbf{w}} \sum_{\mathbf{k}} [(\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s) \phi(\mathbf{k}, \mathbf{w}) + i D_w] a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} + \text{c.c.} \quad (2.30)$$

Also, since $b_{\mathbf{w}}^2$ terms will be neglected,

$$\begin{aligned} (S_{\mathbf{w}}, b_{\mathbf{w}} a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}}) &= -(\gamma_{\mathbf{w}}, a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}}) b_{\mathbf{w}}^2 + (\gamma_{\mathbf{w}}^+ b_{\mathbf{w}}^+, a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} b_{\mathbf{w}}) \\ &\simeq b_{\mathbf{w}}^+ b_{\mathbf{w}} (\gamma_{\mathbf{w}}^+, a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}}) - a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} \gamma_{\mathbf{w}}^+, \end{aligned} \quad (2.31)$$

so that

$$\begin{aligned} (S_{\mathbf{w}}, \frac{1}{2}(S_{\mathbf{w}}, H_0) - H_{1\mathbf{w}}) + H_{2\mathbf{w}} &= b_{\mathbf{w}}^+ b_{\mathbf{w}} \{ \hbar w (s' - s) \\ &\quad - \sum_{\mathbf{k}} [(\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s) |\phi(\mathbf{k}, \mathbf{w})|^2 + i D_w (\phi^*(\mathbf{k}, \mathbf{w}) - \phi(\mathbf{k}, \mathbf{w})) (n_{\mathbf{k}-\mathbf{w}} - n_{\mathbf{k}})] \\ &\quad - \sum_{\mathbf{k}} \{ [\frac{1}{2}(\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s) \phi(\mathbf{k}, \mathbf{w}) + i D_w] a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} \gamma_{\mathbf{w}}^+ + \text{c.c.} \} \}. \end{aligned} \quad (2.32)$$

We shall now choose $\phi(\mathbf{k}, \mathbf{w})$ such that the interaction term in the transformed Hamiltonian, i.e. expression (2.30), becomes as small as possible. Let

$$\phi(\mathbf{k}, \mathbf{w}) = \frac{-i D_w}{\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s} (1 - \Delta(\mathbf{k}, \mathbf{w})), \quad (2.33)$$

$$\text{where} \quad \Delta(\mathbf{k}, \mathbf{w}) \equiv \Delta^2(\mathbf{k}, \mathbf{w}) = \begin{cases} 1 & \text{if } (\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s)^2 < \Gamma_w^2 \\ 0 & \text{if } (\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s)^2 > \Gamma_w^2 \end{cases} \quad (2.34)$$

The function Δ has to be introduced to prevent $\phi(\mathbf{k}, \mathbf{w})$ from becoming infinite which would prevent the development indicated in (2.17) and (2.25). The energy Γ_w has to be chosen such as to make this series converge.

As a next step the velocity s should be determined such that the term $b_{\mathbf{w}}^+ b_{\mathbf{w}} \hbar w s$ in H_0 is the only term of the Hamiltonian H containing $b_{\mathbf{w}}^+ b_{\mathbf{w}}$. This requires that in (2.32) the term proportional to $b_{\mathbf{w}}^+ b_{\mathbf{w}}$ must vanish. Since $n_{\mathbf{k}}$ (cf. 2.28) is an operator this would make s an operator. Therefore $n_{\mathbf{k}}$ will be replaced by its expectation value $\bar{n}_{\mathbf{k}}$, and hence from (2.32)

$$\hbar w (s' - s) = \sum_{\mathbf{k}} \{ (\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s) |\phi(\mathbf{k}, \mathbf{w})|^2 + i D_w (\phi^*(\mathbf{k}, \mathbf{w}) - \phi(\mathbf{k}, \mathbf{w})) \} (\bar{n}_{\mathbf{k}-\mathbf{w}} - \bar{n}_{\mathbf{k}}), \quad (2.35)$$

$$\text{or using (2.33)} \quad \hbar w (s' - s) = \sum_{\mathbf{k}} \frac{D_w^2 (1 - \Delta(\mathbf{k}, \mathbf{w}))}{\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s} (\bar{n}_{\mathbf{k}} - \bar{n}_{\mathbf{k}-\mathbf{w}}). \quad (2.36)$$

Thus s may depend on w .

3. THE RENORMALIZED HAMILTONIAN

From (2.25) making use of (2.22), (2.23), (2.30), (2.33) and of the fact that in view of (2.36) the $b^\dagger b$ term of (2.32) can be neglected,

$$H = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \sum_{\mathbf{w}} \hbar \omega_s b_{\mathbf{w}}^\dagger b_{\mathbf{w}} + \sum_{\mathbf{w}} \frac{1}{2} \hbar \omega_s' + i \sum_{\mathbf{w}, \mathbf{k}} D_{\mathbf{w}} (b_{\mathbf{w}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}-\mathbf{w}} - b_{\mathbf{w}}^\dagger a_{\mathbf{k}-\mathbf{w}}^\dagger a_{\mathbf{k}}) \Delta(\mathbf{k}, \mathbf{w}) + H_s, \quad (3.1)$$

$$\text{where } H_s = -\frac{1}{2} \sum_{\mathbf{w}, \mathbf{k}, \mathbf{q}} \frac{D_{\mathbf{w}}^2 (1 + \Delta(\mathbf{k}, \mathbf{w})) (1 - \Delta(\mathbf{q}, \mathbf{w}))}{\epsilon_{\mathbf{q}-\mathbf{w}} - \epsilon_{\mathbf{q}} + \hbar \omega_s} (a_{\mathbf{k}}^\dagger a_{\mathbf{k}-\mathbf{w}} a_{\mathbf{q}-\mathbf{w}}^\dagger a_{\mathbf{q}} + \text{c.c.}). \quad (3.2)$$

In this Hamiltonian the physical meaning of the quantities $a_{\mathbf{k}}$ and $b_{\mathbf{w}}$ is different from that introduced in § 2. However, since they were defined by the commutation rules (2.6) and (2.8), which still hold, it is not necessary to use a new notation. As a consequence, for instance, the Fourier component of the electronic density is no longer given by (2.12), but by

$$\rho_{\mathbf{w}} = e^{S^\dagger} \sum_{\mathbf{k}} a_{\mathbf{k}-\mathbf{w}}^\dagger a_{\mathbf{k}} e^S, \quad (3.3)$$

which can be calculated in a similar way as H has been obtained in § 2. The quantity $\sum_{\mathbf{k}} a_{\mathbf{k}-\mathbf{w}}^\dagger a_{\mathbf{k}}$, on the other hand, now represents the Fourier component of the density of particles described by plane waves with amplitudes $a_{\mathbf{k}}$ satisfying Fermi statistics. These particles are electrons, carrying with them some lattice deformation. The $b_{\mathbf{w}}$'s on the other hand, are now the amplitudes of oscillations of the ions of the lattice carrying with them oscillations in the electronic density which lead to the renormalized velocity of sound.

The various terms in the Hamiltonian H , equation (3.1), have thus the following meaning. The first two terms represent the energy of the free particles and the free vibrations described by $a_{\mathbf{k}}$ and $b_{\mathbf{w}}$ respectively. The third term leads to absorption or emission of vibrational quanta by the particles; but in view of the factor Δ it vanishes unless energy is conserved within a range Γ_w , as follows from (2.34). The fourth term H_s represents an interaction between the particles.

In the derivation of (3.1) it was assumed that Γ_w must be chosen such that the terms indicated by dots in (2.25) can be neglected. Clearly if Γ_w is very large then H , equation (3.1), becomes identical with H' , equation (2.15). To make the best use of the transformation Γ_w should therefore be chosen as small as possible. The first of the neglected terms in (2.25) which contains S_w in third order has therefore been calculated. This term is certainly negligible if

$$\Gamma_w^2 \sim (\hbar \omega (s' - s))^2, \quad (3.4)$$

and it might even be smaller. From this it follows that in good approximation (error $\sim \hbar \omega s' / \zeta$) equation (2.36), determining the renormalized velocity of sound, becomes

$$\hbar \omega (s' - s) \simeq \sum_{\mathbf{k}}' \frac{D_{\mathbf{w}}^2 (\bar{n}_{\mathbf{k}} - \bar{n}_{\mathbf{k}-\mathbf{w}})}{\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}}} = 2 \sum_{\mathbf{k}}' \frac{D_{\mathbf{w}}^2 \bar{n}_{\mathbf{k}}}{\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}}}, \quad (3.5)$$

where the dash indicates the principal value for the integral which replaces the sum by

$$\sum_{\mathbf{k}}' \rightarrow \frac{V}{(2\pi)^3} 2 \int d\mathbf{k}. \quad (3.6)$$

Here $d\mathbf{k}$ is the volume element in \mathbf{k} -space, and the factor 2 takes care of the two possibilities for electronic spin. In the same approximation in which Γ_w and $\hbar w s$ have been neglected $\bar{n}_{\mathbf{k}}$ can be replaced by a Fermi distribution at the absolute zero of temperature. In all cases of interest this involves an error of less than 1%. The integration is straightforward and leads to

$$\frac{s' - s}{s'} = 2\nu g F' \quad (3.7)$$

(ν = number of electrons per ion) in agreement with Wentzel (1951). Here g is a numerical factor; $g = 1$ if $w \ll k_0$; $g = \frac{1}{2}$ if $w = k_0$, where k_0 is the wave number of the highest occupied level.

The term H_s , equation (3.2), can be simplified by introducing an operator $s_{\text{op.}}$ by

$$\begin{aligned} \hbar w(s' - s_{\text{op.}}) &= - \sum_{\mathbf{k}} \frac{D_w^2(1 - \Delta(\mathbf{k}, \mathbf{w}))}{\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar w s} (n_{\mathbf{k}-\mathbf{w}} - n_{\mathbf{k}}) \\ &= \sum_{\mathbf{k}, \mathbf{q}} \frac{D_w^2(1 + \Delta(\mathbf{k}, \mathbf{q}))(1 - \Delta(\mathbf{q}, \mathbf{w}))}{\epsilon_{\mathbf{q}-\mathbf{w}} - \epsilon_{\mathbf{q}} + \hbar w s} (a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} a_{\mathbf{q}-\mathbf{w}}^+ a_{\mathbf{q}}), \end{aligned} \quad (3.8)$$

making use of $\Delta^2 \equiv \Delta$, and of (cf. 2.26)

$$(a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} a_{\mathbf{q}-\mathbf{w}}^+ a_{\mathbf{q}}) = \delta_{\mathbf{kq}} (n_{\mathbf{k}} - n_{\mathbf{k}-\mathbf{w}}). \quad (3.9)$$

Thus according to (2.36), s is the expectation value of $s_{\text{op.}}$. Also, with the help of (3.8), one finds

$$\begin{aligned} & -\frac{1}{2} \sum_{\mathbf{w}} \left\{ D_w^2 \sum_{\mathbf{k}, \mathbf{q}} \frac{(1 + \Delta(\mathbf{k}, \mathbf{w}))(1 - \Delta(\mathbf{q}, \mathbf{w}))}{\epsilon_{\mathbf{q}-\mathbf{w}} - \epsilon_{\mathbf{q}} + \hbar w s} a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} a_{\mathbf{q}-\mathbf{w}}^+ a_{\mathbf{q}} - \hbar w(s' - s_{\text{op.}}) \right\} \\ &= -\frac{1}{2} \sum_{\mathbf{w}} \left\{ D_w^2 \sum_{\mathbf{k}, \mathbf{q}} \frac{(1 + \Delta(\mathbf{k}, \mathbf{w}))(1 - \Delta(\mathbf{q}, \mathbf{w}))}{\epsilon_{\mathbf{q}-\mathbf{w}} - \epsilon_{\mathbf{q}} + \hbar w s} a_{\mathbf{q}-\mathbf{w}}^+ a_{\mathbf{q}} a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} \right\} \\ &= -\frac{1}{2} \sum_{\mathbf{w}} \left\{ D_w^2 \sum_{\mathbf{k}, \mathbf{q}} \frac{(1 + \Delta(\mathbf{k} - \mathbf{w}, -\mathbf{w}))(1 - \Delta(\mathbf{q} - \mathbf{w}, -\mathbf{w}))}{\epsilon_{\mathbf{q}} - \epsilon_{\mathbf{q}-\mathbf{w}} + \hbar w s} a_{\mathbf{q}}^+ a_{\mathbf{q}-\mathbf{w}} a_{\mathbf{k}-\mathbf{w}}^+ a_{\mathbf{k}} \right\}. \end{aligned} \quad (3.10)$$

Introduction of this equation and of (3.8) into (3.2) leads to

$$H_s = - \sum_{\mathbf{w}} \left\{ \frac{1}{2} \hbar w(s' - s_{\text{op.}}) + \frac{4}{3} \frac{F \zeta}{n V} \sum_{\mathbf{k}, \mathbf{q}} \psi(\mathbf{q}, \mathbf{w}) a_{\mathbf{q}}^+ a_{\mathbf{q}-\mathbf{w}} a_{\mathbf{k}-\mathbf{w}}^+ a_{\mathbf{k}} \right\}, \quad (3.11)$$

where we have defined

$$\begin{aligned} \psi(\mathbf{q}, \mathbf{w}) &= \frac{1}{2} \hbar w s \left\{ \frac{(1 + \Delta(\mathbf{k}, \mathbf{w}))(1 - \Delta(\mathbf{q}, \mathbf{w}))}{\epsilon_{\mathbf{q}-\mathbf{w}} - \epsilon_{\mathbf{q}} + \hbar w s} \right. \\ &\quad \left. - \frac{(1 + \Delta(\mathbf{k} - \mathbf{w}, -\mathbf{w}))(1 - \Delta(\mathbf{q} - \mathbf{w}, -\mathbf{w}))}{\epsilon_{\mathbf{q}-\mathbf{w}} - \epsilon_{\mathbf{q}} - \hbar w s} \right\}. \end{aligned} \quad (3.12)$$

Use has been made of (2.13) according to which

$$\frac{D_w^2}{\hbar w s} = \frac{4}{3} \frac{\zeta}{n V} \frac{F' s'}{s}, \quad (3.13)$$

and with the help of (3.7) the renormalized interaction parameter F has been defined by

$$F = \frac{F' s'}{s} = \frac{F'}{1 - 2\nu g F'}. \quad (3.14)$$

4. DISCUSSION

The final Hamiltonian is obtained from (3.1) and (3.2) using (3.11) and (3.13) as

$$\begin{aligned}
 H = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} + \sum_{\mathbf{w}} \left\{ \hbar \omega s b_{\mathbf{w}}^+ b_{\mathbf{w}} + \frac{1}{2} \hbar \omega s_{\text{op.}} \right. \\
 + i \left(\frac{4}{3} \frac{\zeta F}{nV} \right)^{\frac{1}{2}} (\hbar \omega s)^{\frac{1}{2}} \sum_{\mathbf{k}} (b_{\mathbf{w}} a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}} - b_{\mathbf{w}}^+ a_{\mathbf{k}-\mathbf{w}}^+ a_{\mathbf{k}}) \Delta(\mathbf{k}, \mathbf{w}) \\
 \left. - \frac{4}{3} \frac{\zeta F}{nV} \sum_{\mathbf{k}, \mathbf{q}} \psi(\mathbf{q}, \mathbf{w}) a_{\mathbf{q}}^+ a_{\mathbf{q}-\mathbf{w}} a_{\mathbf{k}-\mathbf{w}}^+ a_{\mathbf{k}} \right\}. \quad (4.1)
 \end{aligned}$$

Since in good approximation $s_{\text{op.}}$ can be replaced by s the renormalization of the velocity of sound can be considered as completed. According to (3.7) to make s positive the original interaction parameter F' must satisfy the condition

$$2\nu F'g < 1, \quad (4.2)$$

as was found by Wentzel (1951). The transformed Hamiltonian contains, however, no longer an F' but the renormalized interaction parameter F which, according to (3.14), can have any positive value, however large, in spite of Wentzel's condition (4.2). Wentzel's objection against large F thus no longer holds.

In the approximation in which the particles are treated as free the Hamiltonian (4.1) gives already in zero order the bulk of the results previously obtained by perturbation theory in second order. In this case

$$\overline{a_{\mathbf{k}}^+ a_{\mathbf{k}}} = \bar{n}_{\mathbf{k}} = 0 \text{ or } 1, \quad \overline{a_{\mathbf{k}}^+ a_{\mathbf{k}-\mathbf{w}}} = 0 \quad \text{if } \mathbf{w} \neq 0. \quad (4.3)$$

The last term in (4.1) thus contributes to the energy in zero order only if $\mathbf{k} = \mathbf{q}$. Using (3.12), (2.34) and (2.36) this contribution can be written as

$$\begin{aligned}
 - \sum_{\mathbf{w}} \frac{4F\zeta}{3nV} \sum_{\mathbf{k}} \frac{1}{2} \hbar \omega s \left(\frac{1 - \Delta(\mathbf{k}, \mathbf{w})}{\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar \omega s} - \frac{1 - \Delta(\mathbf{k} - \mathbf{w}, -\mathbf{w})}{\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} - \hbar \omega s} \right) \bar{n}_{\mathbf{k}} (1 - \bar{n}_{\mathbf{k}-\mathbf{w}}) \\
 = - \sum_{\mathbf{w}} \left(\frac{4F\zeta}{3nV} \sum_{\mathbf{k}} \frac{\hbar \omega s (1 - \Delta(\mathbf{k}, \mathbf{w}))}{\epsilon_{\mathbf{k}-\mathbf{w}} - \epsilon_{\mathbf{k}} + \hbar \omega s} \bar{n}_{\mathbf{k}} (1 - \bar{n}_{\mathbf{k}-\mathbf{w}}) + \frac{1}{2} \hbar \omega (s' - s) \right). \quad (4.4)
 \end{aligned}$$

In the limiting case that $\Gamma_w \rightarrow 0$ the factors $(1 - \Delta)$ imply that principle values have to be taken in the sums (integrals). From the left-hand side of (4.4) it is seen then that the last term of (4.1) is nearly identical with the energy E_2 obtained in I from perturbation theory if the renormalized values of s and F are used. It will be remembered that this term forms the basis of the discussions in I. Also, since the first term on the right-hand side of (4.4) becomes formally identical with the total energy obtained in perturbation theory, $E_1 + E_2$, it follows that the energy E_1 of I represents essentially the energy change $\Sigma \frac{1}{2} \hbar \omega (s - s')$ of the zero point energy of the oscillators due to renormalization of the velocity of sound.

With growing Γ_w the factors $(1 - \Delta)$ require a choice of the limits of integration which eliminates from the energy a finite range Γ_w near the values at which the denominator vanishes. At the same time the third term of (4.1) makes a contribution ΔE which, in view of the factor $\Delta(\mathbf{k}, \mathbf{w})$, just arises from the energy regions eliminated in the last term by the factors $(1 - \Delta(\mathbf{k}, \mathbf{w}))$. This third term is connected with

transitions between states of nearly equal energy; it thus lifts a degeneracy due to the possibility of emission and absorption processes which conserve energy within a range Γ_w . For a Fermi distribution f_0 at the absolute zero of temperature, therefore, $\Delta E = 0$ if $\Gamma_w \leq \hbar\omega$. If a single electron is lifted into a state \mathbf{k} outside this distribution then

$$\Delta E = - \left[\sum_{\mathbf{w}} D_w^2 \Delta(\mathbf{k}, \mathbf{w}) (1 - \bar{n}_{\mathbf{k}-\mathbf{w}}) \right]^{\frac{1}{2}} \quad (4.5)$$

is found. If $\Gamma_w = \hbar\omega$ is chosen then Bardeen's (1950, equation (4.3)) expression is obtained which, as he has shown, leads to nearly the same results as obtained in I (i.e. $\Gamma_w \rightarrow 0$ and use of principle values). Thus in the present approximation the value of Γ_w has no great influence on the results.

The free particle approximation used here may be hoped to lead to reasonably good results if F is sufficiently small, i.e. for normal metals as discussed in §1. Even in this case, however, the usual procedure in the theory of metals must be modified so as to include the last term in the Hamiltonian (4.1) because it contributes to the energy already in zero order. At low temperatures this term leads to a change of the dependence of electronic energy on wave number in a small energy region near the Fermi surface as follows from figure 1*a* of I. This modification can be expressed in terms of an increase of the effective mass of electrons over the high temperature value. It is probably responsible for the effects mentioned in §1 and should also alter the theoretical ratio of high to low temperature electrical conductivity which, as pointed out by Bhatia (1952), cannot be considered as satisfactory at present.

For large F (superconductors) the free particle approximation would lead to the results found in I. For dimensional reasons it may be hoped to yield a correct magnitude of the energy of the ground state, a view supported experimentally by the isotope effect of superconductors. The free particle approximation cannot, however, be expected to be applicable to the calculation of details of the energy spectrum, and hence of the specific heats and the electro-magnetic properties of superconductors. Theoretical treatment of these effects must wait, therefore, for the development of new methods to deal with equation (4.1).

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