On the theory of superconductivity: the one-dimensional case

By H. Fröhlich, F.R.S.

Department of Theoretical Physics, University of Liverpool

(*Received* 1 *December* 1953)

The one-dimensional case of free electrons interacting with lattice displacements is solved by a self-consistent method. It is found that for a certain range of the interaction parameter a single sinusoidal lattice displacement is strongly excited in the lowest level of the system. Its wave-length is such as to create an energy gap in the single-electron energy spectrum with all states below it filled, and all above it empty. This periodic lattice displacement plays the role of an 'inner field' and leads to periodic fluctuation in the electronic density in such a way that the two stabilize each other. In an infinite medium described by a periodic boundary condition they are not fixed absolutely in space, but only relative to each other. Excitation of electrons across the gap leads to a decrease in both the electronic density fluctuations and the width of the gap.

The whole system, electrons plus lattice displacements, can move through the lattice without being disturbed provided the velocity v is sufficiently small. The inertia of this system is equal to that of all electrons augmented by a term due to the lattice displacements. Elastic scattering of individual electrons which normally leads to the residual resistance is impossible if v is sufficiently small. The linear specific heat of normal electrons is eliminated and replaced by an exponential term.

1. Introduction and discussion

The conjecture that the interaction between electrons coupled through the field of lattice displacements is responsible for superconductivity (Fröhlich 1950) has been strongly supported by the discovery of the isotope effect (Maxwell 1950; Reynolds, Serin, Wright & Nesbitt 1950; Bär, Mendelssohn, Olsen, Allen & Dawton 1950; Lock, Pippard, Shoenberg, Allen & Dawton 1950). Subsequent discussion has shown, however, that the theoretical methods usually employed in field theory are unsatisfactory in the present case (Bardeen 1951; Fröhlich 1952, 1953). Owing to these difficulties it has not been possible so far to deal theoretically with the main properties of superconductors such as specific heat and electromagnetic behaviour. Pending the development of new methods it seemed desirable, therefore, to show in a simple way and on a simple model how some of the properties of superconductors can arise from just such an interaction, even though this may involve, in the first place, the use of a somewhat unrealistic model.

It is the purpose of the present paper to show that in the one-dimensional free-electron model the interaction with lattice displacements can be treated in a fairly satisfactory way, and that such a model has properties as might be expected from a superconductor if extrapolated to one dimension. Such a model is, of course, rather unrealistic because magnetic fields cannot exist in one dimension. Even so, one should expect the electrons to behave as a superfluid. The elastic scattering of electrons by impurities which normally leads to the residual resistance should thus be absent at the absolute zero of temperature T. Moreover, the electronic specific heat which is linear in T in the absence of interaction should be replaced by a term

proportional to $\exp(-\text{const.}/T)$ as $T \to 0$. It is just these two properties which will be derived here.

The solutions leading to these properties can be described in terms of simple physical concepts. Remember, first, that an external sinusoidal potential of given amplitude leads to an energy gap in the one-dimensional single-electron energy spectrum. It also leads to a decrease of the total energy of the electrons. In the ground state the magnitude of this decrease is largest if the number of electrons (in each spin direction) equals the number of levels below the gap. This requires the period of the potential to correspond to a wave number $2k_0$, where k_0 is the largest wave number of occupied free-electron levels in a Fermi distribution at $T = 0$. Through the influence of the interaction, the electron density is periodic with the same period as the potential. It will be seen that in our case for a fair range of the interaction constant (cf. (2·54)) the lattice displacement of wave number $2k_0$ is very highly excited in the lowest level of the whole system (electrons and lattice displacements); and an equilibrium is reached in which the ensuing periodic fluctuation of the electron density is such as to maintain the periodic displacement of the lattice and vice versa. At first sight it might seem, therefore, that the interaction transforms the metal into an insulator as $T \to 0$. In fact, however, in an infinite lattice described by a periodic boundary condition (circle) the periodic density fluctuations of electrons and lattice are fixed only relative to each other, but not within the lattice. It will be seen that states exist where both move with a certain velocity v through the lattice provided v is small enough. These states are of such a nature that the $N_{\text{el.}}$ electrons are moved bodily through the lattice and thus carry an electric current. The movement of the lattice displacement, however, leads to a fluctuation of each ion around its average position (as in an elastic wave) and thus does not contribute to the current. The inertia of this moving system is then equal to the inertia of all the electrons augmented by the inertia due to the motion of the lattice displacement. Thus the electrons are hinged on the periodic positions of the ions in an insulator, but on their periodic displacements in the present case.

The quantitative development of these ideas will be carried out with the use of a self-consistent method using the magnitude of the amplitude of the lattice displacement with wave number $2k_0$ as a parameter—denoted by β in appropriate units. If x_j is the spatial co-ordinate of the jth electron and b_w a co-ordinate describing the lattice displacement of wave number w, then the wave function Ψ of the whole system in one of the states described above can be written as (cf. § 2)

$$\Psi = \exp\{\mathrm{i}(mv/\hbar)\sum_j x_j\}\,\Phi(\ldots x_j \ldots; \ldots b_w \ldots; \beta(v^2)), \tag{1·1}$$

where v is quantized according to (2·18). Furthermore, if v^2 is sufficiently small (cf. (2·52))

$$\beta(v^2) = \beta_0 + \beta_1 v^2/s^2, \tag{1·2}$$

where β_0 and β_1 are of equal order of magnitude, and s is the velocity of sound. This wave function represents a state carrying an electric current

$$J = eN_{\text{el.}}v. \tag{1·3}$$

Its total momentum is given by

$$P = N_{\text{el.}}(m+m_1)\,v, \tag{1·4}$$

and its energy is (again if v^2 is sufficiently small)

$$E = N_{\text{el.}}(\tfrac{1}{3}\zeta - \tfrac{1}{3}F\nu\tfrac{1}{2}m_1 s^2 + \tfrac{1}{2}(m+m_1)\,v^2). \tag{1·5}$$

Here

$$\zeta = \frac{\hbar^2 k_0^2}{2m}, \tag{1·6}$$

i.e. $\frac{1}{3}\zeta N_{\text{el.}}$ is the energy of the ground state in the absence of interaction. The mass m_1 is defined in terms of an interaction parameter $F\nu$ by equation (2·52). It is connected with the above-mentioned gap of width W (cf. (2·53)) in the single-electron energy spectrum by

$$W^2 = \tfrac{4}{3}F\nu\zeta m_1 s^2 \tag{1·7}$$

if $v = 0$.

From (1·1) and (1·5) it follows that the function $\Phi(\ldots x_j \ldots; \ldots b_w \ldots; \beta_0)$ describes the system in the ground state ($v = 0$) as discussed above; i.e. it represents a periodic lattice displacement (wave number $2k_0$) giving rise to an energy gap in the single-electron spectrum with all levels below the gap occupied, and all above it empty. Clearly, apart from the states $v \neq 0$ there are other low-lying levels of the whole system whereby single electrons are lifted across the gap although $v = 0$, so that the lattice displacement and the bulk of electrons do not move through the lattice. If, however, the total momentum of the two states are required to be equal then it follows that the energy of the states described in (1·1) to (1·5) (above the ground state) is vanishingly small compared with the other type of states. For to lift an electron across the gap requires an energy of at least W, while the gain of momentum is at best of the order $2\hbar k_0$. A state of type (1·1) having the same momentum must, according to (1·4), have a velocity $v = 2\hbar k_0/N_{\text{el.}}(m+m_1)$, and an energy above the ground state which according to (1·5) is $\frac{1}{2}N_{\text{el.}}(m+m_1)\,v^2 = 2\hbar^2 k_0^2/N_{\text{el.}}(m+m_1)$ which vanishes as $N_{\text{el.}} \to \infty$ and thus is certainly smaller than W.

The existence of the energy gap W in the single-electron spectrum eliminates the possibility of elastic scattering of single electrons provided v is sufficiently small. Since collective motion is possible, however, it follows that at $T = 0$ an electric current can exist showing no residual resistance.† Also in view of the energy gap the electronic specific heat varies as $\exp(-W/2kT)$ as $T \to 0$.

With rising temperature, electrons are excited across the gap. Their wave functions lead to electronic densities which reduce the periodic fluctuations in total electronic density. This in turn must reduce the periodic lattice displacement and hence also reduce the width of the gap. A situation thus arises which formally resembles that in systems showing second-order transitions.

It is not intended here to treat the case $T \neq 0$ in a quantitative way mainly because of the unrealistic features of the one-dimensional model. In fact, the main feature of this model, namely, the interaction of all electrons through a single 'internal field' (i.e. a single sinusoidal type of lattice displacement) cannot in

† The energy of such a state, showing a frictionless current, is by $\frac{1}{2}J^2(m+m_1)/e^2N_{\text{el.}}$ above the ground state (cf. (1·5) and (1·3)).

a simple way be generalized to three dimensions where no doubt an appropriate superposition of a very great number of simple sinusoidal lattice displacements will be required to produce an energy gap in the one-electron spectrum. In fact, this feature, preventing too simple a generalization of the one-dimensional case, is desirable because the one-dimensional case does not show the isotope effect (since $m_1 \propto 1/s^2$, cf. (2·52)). This is not unduly disconcerting, and it may be expected that the interplay between various types of lattice displacements and other differences between the one- and the three-dimensional case should lead back to this effect as already indicated in the treatment by perturbation theory.

It appears then that two aspects of the interaction between electrons and lattice displacements have been investigated: perturbation theory points to the importance of the dynamic part of the interaction and indicates the isotope effect; it neglects, however, the interaction between the electrons arising from an 'internal field' (also due to lattice displacements) which in the one-dimensional case, at least, leads to the expected co-operative behaviour. This suggests that a combination of the two aspects might lead to the derivation of all the main properties of superconductors.

2. Calculations

Consider a one-dimensional system of $N_{\text{el.}}$ electrons interacting with lattice displacements. Then (factor 2 for spin)

$$N_{\text{el.}} = 2 \sum_{k=-k_0}^{k_0}{}', \tag{2·1}$$

where k is the wave number attributed to free-electron states. The Hamiltonian of the system is essentially the same as used previously (Fröhlich 1952, equation (2·1)), restricted to one dimension. In the present paper, however, electrons will be described by their co-ordinates x_j in configurational space. Thus if Ψ is the wave function of the whole system depending on x_j and on the co-ordinates describing the lattice displacements, b_w,

$$H = \int \Psi^+ \mathscr{H} \Psi \tag{2·2}$$

$$\int \Psi^+ \Psi = 1, \tag{2·3}$$

with
$$\mathscr{H} = \sum_{j=1}^{N_{\text{el.}}} \frac{p_j^2}{2m} + \sum_{w>0} \hbar w s (b_w^+ b_w + b_{-w}^+ b_{-w}) + \mathscr{H}_{\text{int.}} \tag{2·4}$$

and
$$\mathscr{H}_{\text{int.}} = \mathrm{i} \sum_{w>0} D_w \{(b_w + b_{-w}^+) \sum_j \mathrm{e}^{\mathrm{i}wx_j} - (b_w^+ + b_{-w}) \sum_j \mathrm{e}^{-\mathrm{i}wx_j}\}, \tag{2·5}$$

where $w > 0$ is the wave number of a lattice displacement, $p_j = -\mathrm{i}\hbar\partial/\partial x_j$, and the b_w's satisfy

$$b_w b_u - b_u b_w = (b_w, b_u) = 0; \quad (b_w, b_u^+) = \delta_{uw}, \quad (b_w, b_{-u}) = 0, \text{etc.} \tag{2·6}$$

All spatial functions $\mathrm{e}^{\mathrm{i}kx}$ and $\mathrm{e}^{\mathrm{i}wx}$ satisfy a periodic boundary condition with unit length as period, so that e.g., $k = 2\pi n/L$ with integer n and $L = 1$ cm. The integration in (2·2) and (2·3) extends over all x_j's (unit length) and over all co-ordinates describing the lattice oscillators. They are understood in a sufficiently

general way, i.e. if the b_w's are represented by matrices then the appropriate sums are to be taken. The interaction constants D_w can be written as previously (Fröhlich 1952, equation (2·13))

$$D_w^2 = \frac{4}{3}\frac{F}{N}\zeta\hbar w s = \frac{4}{3}\frac{F\nu}{N_{\text{el.}}}\zeta\hbar w s, \tag{2·7}$$

where $\nu = N_{\text{el.}}/N$ is the number of free electrons per atom and the velocity of sound s of the ionic system was previously denoted by s'.

If the interaction parameter F (previously denoted by F') is sufficiently small then one might think that $\mathscr{H}_{\text{int.}}$ can be treated as a small perturbation. This is not true, however, as can easily be seen by calculating the self-energy $-\hbar w\Delta s$ of a vibrational quantum of wave number w. Thus if in zero order the electrons are described by plane waves, with all states up to wave number $\pm k_0$ filled, and if the oscillator w is in the first excited state then its interaction with the electrons leads to a self-energy (assuming $w \leqslant 2k_0$)

$$-\hbar w\Delta s = 2\sum_{k=k_0-w}^{k_0}\frac{D_w^2}{\epsilon_k - \epsilon_{k+w} + \hbar w s} + 2\sum_{-k_0}^{-k_0+w}\frac{D_w^2}{\epsilon_k - \epsilon_{k-w} - \hbar w s}$$

$$= -\frac{F\nu}{3}\hbar k_0 s \ln\frac{(2k_0+w)^2 - (2ms/\hbar)^2}{(2k_0-w)^2 - (2ms/\hbar)^2}, \tag{2·8}$$

where

$$\epsilon_k = \hbar^2 k^2/2m. \tag{2·9}$$

Now if $w \ll 2k_0$, using $k_0 \gg ms/\hbar$, development of the logarithm in (2·8) shows that $\Delta s < s$ as long as

$$\tfrac{2}{3}F\nu < 1. \tag{2·10}$$

This condition is essentially equal to one derived by Wentzel (1951) and ensures stability of the lattice. If, however, $w \simeq 2k_0$, then perturbation theory cannot be applied, however small F, because (2·8) diverges (e.g. when $\frac{1}{2}w = k_0 - ms/\hbar$). Thus perturbation theory can only be applied if the largest value w_m of w is sufficiently smaller than $2k_0$. In the following it will be assumed, however, that $w_m > 2k_0$, though (2·10) should hold. The interaction of the electrons with the lattice displacement of wave number $2k_0$ will then be treated by a self-consistent field method, omitting interaction with lattice displacements of all other wave numbers in the hope that these can later be treated by perturbation. This leads to the establishment of a gap W in the single-electron spectrum. Applying then perturbation theory for the remaining interaction clearly the energy denominators in the expression for the second-order perturbation energy can no longer vanish whatever the value of w ($< w_m$) (contrary to (2·8)) provided

$$W > \hbar w_m s. \tag{2·11}$$

This inequality is hence a condition for the convergence of the present approximation. It will be seen to lead to a lower limit for F compatible with the upper limit given by (2·10).

Consider thus the Hamiltonian density $\mathscr{H}$ to be split into

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}'_{\text{int.}}, \tag{2·12}$$

where $\mathscr{H}'_{\text{int.}}$ is given by (2·5), omitting in the summation, however, the term $w = w_0 \equiv 2k_0$ which is included in $\mathscr{H}_0$. Let Ψ_0 be a wave function of the system described by $\mathscr{H}_0$. Then equations (2·2) and (2·3) hold if $\mathscr{H}$ and Ψ are replaced by $\mathscr{H}_0$ and Ψ_0 respectively. The wave equation for Ψ_0 can thus be derived by a variational method, i.e.

$$\delta \int \Psi_0^+ (\mathscr{H}_0 - \mu)\, \Psi_0 = 0, \tag{2·13}$$

where μ is a Lagrangian parameter. However, the operator of the momentum of the whole system (i.e. $\hbar$ times the total wave number)

$$P_{\text{op.}} = \sum_j p_j + \sum_{w>0} \hbar w (b_w^+ b_w - b_{-w}^+ b_{-w}) \tag{2·14}$$

commutes with $\mathscr{H}_0$ (and with $\mathscr{H}$),

$$P_{\text{op.}}\, \Psi_0 = P \Psi_0 \quad \text{or} \quad \int \Psi_0^+ P_{\text{op.}}\, \Psi_0 = P, \tag{2·15}$$

where P is a constant of motion. Hence equation (2·13) is equivalent to

$$\delta \int \Psi_0^+ (\mathscr{H}_0 - \mu - v P_{\text{op.}})\, \Psi_0 = 0, \tag{2·16}$$

where v is another parameter, and ($D_{w_0} = D$; c.c. denotes a conjugate term)

$$\mathscr{H}_0 - \mu - v P_{\text{op.}} = \sum_j \left(\frac{p_j^2}{2m} - v p_j \right) + \sum_{w>0} \{ \hbar w (s - v)\, b_w^+ b_w + \hbar w (s + v)\, b_{-w}^+ b_{-w} \} + \mathrm{i} D \{ (b_{w_0} + b_{-w_0}^+) \sum_j \mathrm{e}^{\mathrm{i} w_0 x_j} - \text{c.c.} \} - \mu. \tag{2·17}$$

Equation (2·16) can be considered as solving (2·13) with (2·15) as a further condition. The variational equation will be useful in this form for selecting solutions with given momentum P.

Introducing now a new wave function Φ by†

$$\Psi_0 = \mathrm{e}^{\mathrm{i}(mv/\hbar) \Sigma x_j}\, \Phi, \quad \text{with} \quad mv/\hbar = 2\pi n / L, \tag{2·18}$$

equation (2·16) is found to be equivalent to

$$\delta \int \Phi^+ G \Phi = 0, \tag{2·19}$$

with
$$G = \sum_j \frac{p_j^2}{2m} + \sum_{w>0} \{ \hbar w (s - v)\, b_w^+ b_w + h w (s + v)\, b_{-w}^+ b_{-w} \} + \mathrm{i} D \{ (b_{w_0} + b_{-w_0}^+) \sum_j \mathrm{e}^{\mathrm{i} w_0 k_j} - \text{c.c.} \} - \mu - \tfrac{1}{2} N_{\text{el.}} m v^2. \tag{2·20}$$

It will be noticed that, in terms of Φ, energy and momentum are given by

$$E = \int \Psi_0^+ \mathscr{H}_0 \Psi_0 = \int \Phi^+ \Big\{ \sum_j \left(\frac{p_j^2}{2m} + v p_j \right) + \tfrac{1}{2} N_{\text{el.}} m v^2 + \sum_{w>0} \hbar w s (b_w^+ b_w + b_{-w}^+ b_{-w}) + \mathrm{i} D [(b_{w_0} + b_{-w_0}^+) \sum_j \mathrm{e}^{\mathrm{i} w_0 x_j} - \text{c.c.}] \Big\} \Phi, \tag{2·21}$$

and
$$P = \int \Psi_0^+ P_{\text{op.}}\, \Psi_0 = \int \Phi^+ \{ \sum_j p_j + N_{\text{el.}} m v + \sum_{w>0} \hbar w (b_w^+ b_w - b_{-w}^+ b_{-w}) \} \Phi, \tag{2·22}$$

respectively.

† Equation (2·18) can, of course, also be considered as introducing a canonical transformation.

It will now be assumed that Φ can be written in the form

$$\Phi = \psi(x_1, \ldots, x_j, \ldots)\,\chi, \tag{2·23}$$

where ψ depends on the electronic co-ordinates only, and χ on the oscillator co-ordinates. χ can be written as a product,

$$\chi = \prod_w \chi_w \chi_{-w}, \tag{2·24}$$

where all $\chi_{\pm w}$'s represent free oscillator wave functions, except when $w = w_0$. The electron wave function can (for each spin system) be written in determinantal form, built up of one-electron wave functions $\psi_k(x_j)$. Introduction of (2·23) into (2·19) yields immediately

$$\frac{p_j^2}{2m} + 2\mathrm{i}\zeta(\beta\,\mathrm{e}^{\mathrm{i}w_0 x_j} - \beta^*\,\mathrm{e}^{-\mathrm{i}w_0 x_j}), \psi_k(x_j) = \eta_k \psi_k(x_j), \tag{2·25}$$

$$\hbar w_0(s-v)\,b_{w_0}^+ b_{w_0} + \mathrm{i}N_{\mathrm{el.}} D(b_{w_0}\,\overline{\mathrm{e}^{\mathrm{i}w_0 x}} - b_{w_0}^+\,\overline{\mathrm{e}^{-\mathrm{i}w_0 x}}), \chi_{w_0} = \lambda_+ \chi_{w_0}, \tag{2·26}$$

$$\hbar w_0(s+v)\,b_{-w_0}^+ b_{-w_0} + \mathrm{i}N_{\mathrm{el.}} D(b_{-w_0}^+\,\overline{\mathrm{e}^{\mathrm{i}w_0 x}} - b_{-w_0}\,\overline{\mathrm{e}^{-\mathrm{i}w_0 x}}), \chi_{-w_0} = \lambda_- \chi_{-w_0}, \tag{2·27}$$

where

$$\beta = (\overline{b_{w_0}} + \overline{b_{-w_0}^+})\frac{D}{2\zeta} \tag{2·28}$$

is a dimensionless c-number,

$$\overline{b_{w_0}} = \int \chi_{w_0}^+ b_{w_0} \chi_{w_0}, \text{ etc.} \tag{2·29}$$

and

$$N_{\mathrm{el.}}\,\overline{\mathrm{e}^{\mathrm{i}w_0 x}} = \sum_k \int \psi_k^*(x)\,\mathrm{e}^{\mathrm{i}w_0 x}\,\psi_k(x)\,\mathrm{d}x. \tag{2·30}$$

Here $\sum_k$ goes over all occupied electron levels (counted twice if occupied by two electrons with opposite spin), and η_k, λ_+ and λ_- are the eigenvalues of equations (2·25) to (2·27) respectively. Since (2·26) and (2·27) represent wave equations of displaced oscillators it follows immediately that

$$\overline{b_{w_0}} = \frac{\mathrm{i}DN_{\mathrm{el.}}}{\hbar w_0(s-v)}\,\overline{\mathrm{e}^{-\mathrm{i}w_0 x}}, \quad \overline{b_{-w_0}} = -\frac{\mathrm{i}DN_{\mathrm{el.}}}{\hbar w_0(s+v)}\,\overline{\mathrm{e}^{\mathrm{i}w_0 x}}, \text{ etc.} \tag{2·31}$$

Equation (2·25) describes an electron in a sinusoidal field. Its solution is simplified if $\beta\beta^* < 1$ is assumed. According to Peierls (1930) if $2k \simeq w_0$, i.e. $k \simeq k_0$, it is solved by

$$\psi_{0k\pm}(x) = a_{1\pm}\,\mathrm{e}^{\mathrm{i}kx} + a_{2\pm}\,\mathrm{e}^{\mathrm{i}(k-w_0)x} \quad (k>0), \tag{2·32}$$

with

$$\eta_{0k\pm} = 2\zeta\{\tfrac{1}{2}y^2 - y + 1 \pm \sqrt{(\beta\beta^* + (y-1)^2)}\}, \tag{2·33}$$

$$y = k/k_0 > 0. \tag{2·34}$$

Also

$$a_{2\pm} = a_{1\pm}\frac{\mathrm{i}\beta^*}{y - 1 \mp \sqrt{\{\beta\beta^* + (y-1)^2\}}} \quad \text{and} \quad |a_{1\pm}|^2 = \mp\frac{1}{2}\frac{y - 1 \mp \sqrt{\{\beta\beta^* + (y-1)^2\}}}{\sqrt{\{\beta\beta^* + (y-1)^2\}}}. \tag{2·35}$$

These solutions can be extended beyond the region near $k \simeq k_0$ and discussed in terms of zero-order solutions ($\beta = 0$) represented by plane waves with wave number

say q ($q \gtrless 0$) and energy ϵ_q (cf. (2·9)). Then outside the region in which $(y-1)^2 < \beta\beta^*$ (i.e. $k \simeq k_0$) one of the factors a_1 or a_2 is always predominant, leading to a zero-order solution except for terms of order $|\beta|^2$. For η_- the ranges $0 < q < k_0$ and $-k_0 < q < 0$ correspond to $0 < y < 1$ and $1 < y < 2$ respectively. For η_+ the same y regions correspond to $-2k_0 < q < -k_0$ and $k_0 < q < 2k_0$ respectively. The energy gap occurs at $y = 1$, and is of width $2|\beta|\zeta$; deviations from zero-order solution remain linear in $|\beta|$, approximately, when $(y-1)^2 < \beta\beta^*$. The total number of electrons equals the number of levels below the gap. Assuming all these levels to be occupied, a fraction $|\beta|$ of all states show linear energy terms in $|\beta|$ making a contribution of order $|\beta|^2$ to the total energy. This requires that for the majority of states, for which $(y-1)^2 > \beta\beta^*$, the energy be accurate up to the order $\beta\beta^*$. Perturbation theory will give good results in this region, and development of η_0 or ψ_{0k} in powers of β leads in fact to terms occurring in perturbation theory. For η_- they correspond to the transitions $q \rightleftharpoons q - w_0$, and $q \rightleftharpoons q + w_0$ in the two regions $0 < y < 1$ and $1 < y < 2$ (i.e. $0 < q < k_0$ and $-k_0 < q < 0$) respectively. These terms must be supplemented by others corresponding to transitions $q \rightleftharpoons q + w_0$ and $q \rightleftharpoons q - w_0$ in the two regions respectively. Thus when $(y-1)^2 > \beta\beta^*$ the solutions which are correct up to second order in $|\beta|$ are

$$\eta_{k\pm} = \eta_{0k\pm} + \Delta\eta_{k\pm}, \quad \psi_{k\pm} = \psi_{0k\pm} + \Delta\psi_{k\pm}, \tag{2·36}$$

where
$$\Delta\eta_{k-} = -\frac{\zeta\beta\beta^*}{y+1}, \quad \Delta\psi_{k-} = -\frac{\mathrm{i}}{2}\frac{a_1}{|a_1|}\frac{\beta}{y+1}\mathrm{e}^{\mathrm{i}(k+w_0)x} \quad \text{if } 0 < y < 1, \tag{2·37}$$

and
$$\Delta\eta_{k-} = -\frac{\zeta\beta\beta^*}{3-y}, \quad \Delta\psi_{k-} = \frac{\mathrm{i}}{2}\frac{a_2}{|a_2|}\frac{\beta^*}{3-y}\mathrm{e}^{\mathrm{i}(k-2w_0)x} \quad \text{if } 1 < y < 2. \tag{2·38}$$

These solutions can also be used in the region where $(y-1)^2 < \beta\beta^*$ containing a fraction $|\beta|$ of electrons. For since the $\Delta\eta$'s are of the order $\beta\beta^*$ (the denominators never vanish) they yield a negligible contribution of order $|\beta|^3$ to the total energy. Thus the solutions (2·36) are of sufficient accuracy in the region $0 < y < 2$ corresponding to $-2k_0 < q < 2k_0$ in zero order.

Now using (2·32) to (2·38),

$$\int \psi^*_{k-}(x)\,\mathrm{e}^{\mathrm{i}w_0 x}\,\psi_{k-}(x)\,\mathrm{d}x = \frac{\mathrm{i}\beta^*}{2}\left(\frac{1}{\sqrt{\{\beta\beta^* + (y-1)^2\}}} + \begin{matrix}1/(y+1)\\ 1/(3-y)\end{matrix}\right) \quad \text{if} \quad \begin{matrix}0<y<1,\\ 1<y<2,\end{matrix} \tag{2·39}$$

and hence from (2·30) and (2·31) a condition for the determination of β (2·28) can be derived which depends on the occupation of electronic levels. In the lowest state all levels below the gap (η_-) are filled, and all above it are empty. In this case the sum in (2·30) can be written as

$$\sum_k \ldots = \frac{N_{\mathrm{el.}}}{2}\int_0^2 \ldots \mathrm{d}y, \tag{2·40}$$

and hence from (2·39) and (2·30),

$$\begin{aligned}\overline{\mathrm{e}^{\mathrm{i}w_0 x}} &= \frac{\mathrm{i}\beta^*}{2}\frac{1}{2}\left\{\int_0^2 \frac{\mathrm{d}y}{\sqrt{\{\beta\beta^* + (y-1)^2\}}} + \int_0^1 \frac{\mathrm{d}y}{y+1} + \int_1^2 \frac{\mathrm{d}y}{3-y}\right\} \\ &= \frac{\mathrm{i}\beta^*}{4}\left(\ln\frac{\sqrt{(1+\beta\beta^*)}+1}{\sqrt{(1+\beta\beta^*)}-1} + 2\ln 2\right) \simeq \frac{\mathrm{i}\beta^*}{2}\ln\frac{4}{|\beta|},\end{aligned} \tag{2·41}$$

using $\beta\beta^* < 1$ in the last step. Equations (2·31), (2·41) and (2·28), and their conjugates using (2·7), thus yield

$$\beta = 0 \quad \text{or} \quad \tfrac{2}{3}Fv\frac{1}{1-v^2/s^2}\ln\frac{4}{|\beta|} = 1. \tag{2·42}$$

It will be seen (2·50) that $\beta = 0$ leads to a higher energy than the other solution so that

$$\beta\beta^* = 16\exp\left[-\frac{3}{Fv}(1-v^2/s^2)\right]. \tag{2·43}$$

The total energy E is now obtained from (2·21) using (2·23) to (2·27),

$$E = \sum_k \eta_k + v\sum_j \overline{p_j} + \tfrac{1}{2}N_{\text{el.}}mv^2 + \sum_w \hbar w s(\overline{b_w^+ b_w} + \overline{b_{-w}^+ b_w}). \tag{2·44}$$

Here

$$\overline{p_j} = \frac{\hbar}{\mathrm{i}}\int\psi^+\frac{\partial}{\partial x_j}\psi, \quad \overline{b_{\pm w}^+ b_{\pm w}} = \int\chi_{\pm w}^+ b_{\pm w}^+ b_{\pm w}\chi_{\pm w}. \tag{2·45}$$

Clearly, using (2·26) and (2·27),

$$\overline{b_{\pm w_0}^+ b_{\pm w_0}} = \overline{b_{\pm w_0}^+}\,\overline{b_{\pm w_0}} + n_{\pm w_0}, \quad \text{also} \quad \overline{b_{\pm w}^+ b_{\pm w}} = n_{\pm w} \quad (w \neq w_0), \tag{2·46}$$

where the n_w are positive integers or zero. In the lowest state of the system $n_{\pm w} = 0$ for all w. Furthermore, if all the states below the gap are filled, $\Sigma\overline{p_j} = 0$. Thus from (2·44), using (2·36) to (2·38), (2·40), (2·33) and (2·28),

$$\begin{aligned} E = {} & N_{\text{el.}}\zeta\int_0^2 (\tfrac{1}{2}y^2 - y + 1 - \sqrt{\{\beta\beta^* + (y-1)^2\}})\,\mathrm{d}y + \tfrac{1}{2}N_{\text{el.}}mv^2 \\ & - \tfrac{1}{2}N_{\text{el.}}\zeta\beta\beta^*\left(\int_0^1 \frac{\mathrm{d}y}{y+1} + \int_1^2 \frac{\mathrm{d}y}{3-y}\right) + \hbar w_0 s\,(\overline{b_{w_0}^+}\,\overline{b_{w_0}} + \overline{b_{-w_0}^+}\,\overline{b_{-w_0}}). \end{aligned} \tag{2·47}$$

From (2·31) and its conjugates,

$$\overline{b_{-w_0}^+} = \overline{b_{w_0}}(s-v)/(s+v), \text{ etc.} \tag{2·48}$$

and hence with (2·28) after carrying out the integrations,

$$\begin{aligned} E = N_{\text{el.}}\zeta\Big\{ & \tfrac{4}{3} - \sqrt{(1+\beta\beta^*)} - \tfrac{1}{2}\beta\beta^*\ln\frac{\sqrt{(1+\beta\beta^*)}+1}{\sqrt{(1+\beta\beta^*)}-1} \\ & - \beta\beta^*\ln 2 + \frac{3}{2Fv}(1+v^2/s^2)\,\beta\beta^*\Big\} + \tfrac{1}{2}N_{\text{el.}}mv^2. \end{aligned} \tag{2·49}$$

Using again $\beta\beta^* < 1$,

$$E \simeq \tfrac{1}{3}N_{\text{el.}}\zeta - \beta\beta^* N_{\text{el.}}\zeta\left(\tfrac{1}{2} + \ln\frac{4}{|\beta|} - \frac{3}{2Fv}(1+v^2/s^2)\right) + \tfrac{1}{2}N_{\text{el.}}mv^2. \tag{2·50}$$

In a similar way (2·22) leads to

$$vP = N_{\text{el.}}\left(mv^2 + \beta\beta^*\zeta\frac{3}{Fv}\frac{v^2}{s^2}\right). \tag{2·51}$$

In neither (2·50) nor (2·51) has use been made of the equilibrium value (2·42) for $\beta\beta^*$. In fact this value can be derived again from $\delta(E - Pv) = 0$ which follows from (2·19), using $\beta\beta^*$ as available parameter.

Inserting now $\beta\beta^*$ from (2·42), and developing into powers of v^2/s^2 using terms up to v^2/s^2 only, leads to expressions (1·4) and (1·5) for P and E, if m_1 is given by

$$\tfrac{1}{3}Fvm_1s^2 = 16\zeta e^{-3/vF}, \tag{2·52}$$

and if $\frac{v^2}{s^2}\frac{3}{vF} < 1$. Also, equation (1·7) follows since the gap width at $v = 0$ is

$$W = 2\,|\,\beta\,|\,\zeta = 8\zeta e^{-3/2vF}. \tag{2·53}$$

It will be noticed that replacement of w_0 by another value of w increases the total energy because then $N_{\text{el.}}$ is no longer equal to the number of states below the gap.

As pointed out previously the consideration of the terms $\mathscr{H}'_{\text{int.}}$ by perturbation theory is now possible if (2·10) and (2·11) are satisfied. Together with $\beta\beta^* < 1$, (2·11) requires, using (2·53) and (2·43), that

$$1 > 4e^{-3/2Fv} > \hbar w_m s/2\zeta. \tag{2·54}$$

It will be noticed that in this case (2·10) is also fulfilled. (2·54) gives a fair range for Fv if $\hbar w_m s/2\zeta \ll 1$ (in the three-dimensional case the ratio is of the order 10^{-2} or 10^{-3}). In this case Ψ_0 is a good approximation to the wave function Ψ, i.e. (1·1) holds,† and (1·5) is a good approximation to the energy.

It should finally be observed that the change in electronic density due to the interaction with the lattice displacements leads also to a change (increase) in the Coulomb energy. This could also be treated within the scope of the self-consistent method and would essentially result in a change of the value for m_1, and in condition (2·54). It would not alter the main result of the present investigation, namely, (i) that electrons with energy of order ζ (per electron) may be contained within a certain energy region by an interaction which is very weak, i.e. which leads only to a small change of total energy, and (ii) that the whole configuration may move through the lattice, exhibiting a single degree of freedom only.

References

Bär, M., Mendelssohn, K., Olsen, J. L., Allen, W. D. & Dawton, R. H. 1950 *Nature, Lond.*, **166**, 1071.

Bardeen, J. 1951 *Rev. Mod. Phys.* **23**, 261.

Fröhlich, H. 1950 *Phys. Rev.* **79**, 845; *Proc. Phys. Soc.* A, **63**, 778.

Fröhlich, H. 1952 *Proc. Roy. Soc.* A, **215**, 291.

Fröhlich, H. 1953 *Physica*, **19**, 755.

Lock, J. M., Pippard, A. B., Shoenberg, D., Allen, W. D. & Dawton, R. H. 1950 *Nature, Lond.*, **166**, 1071.

Maxwell, E. 1950 *Phys. Rev.* **78**, 477.

Peierls, R. 1930 *Ann. Phys., Lpz.*, **4**, 121.

Reynolds, C. A., Serin, B., Wright, W. H. & Nesbitt, L. B. 1950 *Phys. Rev.* **78**, 487.

Wentzel, G. 1951 *Phys. Rev.* **83**, 168.

† It should also be noticed that replacement of x_j by $x_j + c$ (c = constant) for all x_j leads to multiplication of Ψ by a constant whose magnitude is unity. This follows from (2·18), (2·23), (2·35) to (2·38), (2·32) with the use of (2·28), (2·31) and (2·30).