

Adiabatic Approximations and Superconductivity Theories

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In a number of recent suggestions for a theory of superconductivity a variant of the conventional perturbation theory was used to treat the lattice-electron interaction in crystals and to obtain apparently new results which were different from the theory proposed earlier by Fröhlich. It is demonstrated here that the variant theory, which uses the same matrix elements as Fröhlich, gives identically the same correction to the energy of the crystal as does the Fröhlich theory and that the apparently new results stem from erroneous neglect of the renormalization of the sound frequencies and of the zero-point motion.

IN an early attempt at a theory of superconductivity Fröhlich¹ treated the electron-nucleus interaction term of the conventional Hamiltonian in the manner of conventional perturbation theory. This constituted a correction to the lowest order Born-Oppenheimer approximation for the system of electrons and nuclei in the lattice. A later development was the BCS theory² which was selective as regards the interaction term in the Hamiltonian and was also nonperturbational; here we are not concerned with this theory at all. We are concerned, however, with a number of suggestions for a theory of superconductivity, which use a variant of the conventional perturbation theory to treat the conventional Hamiltonian and exhibit apparently new results; some of these suggestions³⁻⁵ date before, another⁶ after, the BCS theory. The new results are regarded by their authors as favorable for a theory of superconductivity as well as an improvement on, and different from the theory proposed earlier by Fröhlich. It is shown here that what really happens is that a term is left out of sight right at the beginning; if one attends to this term, one gets back to the starting point of the Fröhlich theory.

The starting point of the Fröhlich theory is essentially the second-order energy correction for the state characterized by the single electron wave vector \mathbf{k} and occupation numbers n_f of the f normal mode of lattice vibration

$$\Delta E(\mathbf{k}, n_f) = - \sum_{f, \mathbf{k}'} \frac{|\langle n_f \pm 1, \mathbf{k}' | \mathbf{q}_f \cdot \nabla_{\mathbf{q}_f} V | n_f, \mathbf{k} \rangle|^2}{E_{\mathbf{k}'} - E_{\mathbf{k}} \pm \hbar \omega_f}. \quad (1)$$

V is an effective potential of interaction between the nuclei and electrons. The derivatives are evaluated at the equilibrium positions of the nuclei, $\mathbf{q}_f = 0$. The order of magnitude of this correction compared to the zero-order energy is given by the ratio of the velocity of sound to the velocity of the electrons at the Fermi surface, or equivalently by the square root of the ratio of electronic and nuclear masses. To this order, the

¹ H. Fröhlich, *Phys. Rev.* **79**, 845 (1950).

² J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

³ J. M. Ziman, *Proc. Camb. Phil. Soc.* **51**, 707 (1955).

⁴ A. Haug, *Z. Physik* **146**, 75 (1956).

⁵ H. Stumpf, *Z. Naturforsch.* **11a**, 259 (1956).

⁶ R. K. Nesbet, *Phys. Rev.* **126**, 2014 (1962); **128**, 139 (1962).

total decrease of the energy of the crystal is given by the sum of all these corrections, with each term of the sum (1) multiplied by the factor $2f_{\mathbf{k}}(1-f_{\mathbf{k}'})$, required by the exclusion principle and the multiplicity of the spin states. The resulting double sum is given also (with the modification that $n_f=0$ in the zero-order states) in Peierls' book.⁷ It is there pointed out that when the summation is carried out over a continuous energy range, the singularity is to be treated by introducing an imaginary quantity in the denominator of (1).

We shall now make a *formal* expansion of (1), in powers of $\hbar\omega(E_{\mathbf{k}'}-E_{\mathbf{k}})$ (henceforth we shall drop the suffix f on n, ω, \mathbf{q}) which is nominally of the order of the ratio of typical phonon and electron velocities and therefore small. (It is, in fact, the expansion parameter of the perturbation theory.) The first three terms of the expansion, when simplified by making use of the known matrix elements of the harmonic oscillator, become

$$- \sum_{f, \mathbf{k}'} \langle n | q^2 | n \rangle \frac{|\langle \mathbf{k}' | \nabla_{\mathbf{q}} V | \mathbf{k} \rangle|^2}{(E_{\mathbf{k}'} - E_{\mathbf{k}})}, \quad (2)$$

$$\sum_{f, \mathbf{k}'} \frac{1}{2M_f} \frac{|\langle \mathbf{k}' | \nabla_{\mathbf{q}} V | \mathbf{k} \rangle|^2}{(E_{\mathbf{k}'} - E_{\mathbf{k}})^2},$$

(M_f = effective mass of f mode) (3)

$$- \sum_{f, \mathbf{k}'} \frac{|\langle n \pm 1 | \mathbf{q} | n \rangle|^2 |\langle \mathbf{k}' | \nabla_{\mathbf{q}} V | \mathbf{k} \rangle|^2}{(E_{\mathbf{k}'} - E_{\mathbf{k}})^3} (\hbar\omega)^2. \quad (4)$$

Expression (4) may be rewritten as

$$- \sum_{f, \mathbf{k}'} \frac{\hbar^4 |\langle n \pm 1 | \nabla_{\mathbf{q}} | n \rangle|^2 |\langle \mathbf{k}' | \nabla_{\mathbf{q}} V | \mathbf{k} \rangle|^2}{M_f^2 (E_{\mathbf{k}'} - E_{\mathbf{k}} \pm \hbar\omega)(E_{\mathbf{k}'} - E_{\mathbf{k}})^2}. \quad (5)$$

This rewriting of (4) is admissible to the extent of our approximation. Our purpose with it is to demonstrate in what follows that the authors of references 3-6, by taking their starting point with expression (5), do, in fact, disregard quantities which are orders of magnitude higher. Now, actually (3) is considered and is shown to be unimportant, which it is, since it is diagonal

⁷ R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), p. 144.

and essentially constant for all occupied states. In contrast, the term (2) contains off-diagonal matrix elements and could cause the lowering of the total energy by the occupation of states outside the Fermi sphere, in the same way but, being of higher order of magnitude, to a greater extent than (5).

We shall now follow reference 3 to derive the result obtained there. The Hamiltonian

$$H = \sum \frac{1}{2m} p^2 + \sum \frac{1}{2M} P^2 + U(X) + V(X, x)$$

consists of the kinetic energies of the electrons, of those of the nuclei and of terms denoting, generically, the interactions between the ions and between the ions and electrons. In the usual manner the electronic wave functions $\Psi_X(x)$, depending parametrically on the nuclear coordinates X , are the solutions of

$$\left[\sum \frac{1}{2m} p^2 + U(X) + V(X, x) \right] \Psi_X(x) = [E_X + U(X)] \Psi_X(x).$$

In the next step, operating with the total Hamiltonian on the complete wave function $\Psi_X(x)\phi(X)$ gives

$$H\Psi_X(x)\phi(X) = \Psi_X(x) \left[\sum \frac{P^2}{2M} + E_X + U(X) \right] \phi(X) + \frac{\hbar^2}{M} \nabla_X \Psi_X(x) \cdot \nabla_X \phi(X) - \frac{\hbar^2}{2M} \phi(X) \nabla_X^2 \Psi_X(x). \quad (6)$$

The square brackets may be rewritten as

$$[E_{X_0} + (n + \frac{1}{2})\hbar\omega]$$

provided $\phi(X) \equiv \phi_n(X)$ is the solution of the harmonic oscillator problem. In this case, the second term will induce transitions to the $(n \pm 1)$ th oscillator. The other factor may be evaluated by approximating

$$\Psi_X(x) \simeq \Psi_{X_0} + (X - X_0) \nabla_{X_0} \Psi_{X_0}(x),$$

so that

$$\nabla_X \Psi_X(x) - \nabla_{X_0} \Psi_{X_0}(x) \cong - (H_{X_0} - E_{X_0})^{-1} \nabla_{X_0} [V(X_0, x) - E_{X_0}] \Psi_{X_0}(x) \quad (7)$$

from the original Schrödinger equation. The second-

order correction to a state a , n is (writing E_a for E_{X_0})

$$\begin{aligned} \Delta E(a, n) &= - \frac{1}{M^2} \sum_b \frac{(n+1, n)\hbar\omega M}{2(E_b - E_a \pm \hbar\omega)} \\ &\times |\langle b | (H_{X_0} - E_a)^{-1} (\nabla_{X_0} [V(X_0, x) - E_{X_0}]) | a \rangle|^2 \quad (8) \\ &= - \sum_b \frac{(n+1, n)\hbar\omega}{2M(E_b - E_a \pm \hbar\omega)} \frac{|\langle b | \nabla_{X_0} V | a \rangle|^2}{(E_b - E_a)^2}. \end{aligned}$$

It will be easily seen that apart from the differing notation, which we use for the purpose of the next section, (8) is equal to (5). The last term in (6) gives, in the lowest order, (3) on using (7) and the anti-Hermitian property of ∇ . The important question is, where does (2) come from in this theory? The answer is that the frequency which arises from (6) depends also on the electronic state and so does, through the frequency or at zero temperature through the zero-point motion, the energy of the crystal.

In fact,

$$E_X^a = E_a - (X - X_0)^2 \sum_b \frac{|\langle b | \nabla_{X_0} V | a \rangle|^2}{(E_b - E_a)},$$

which accounts for (2).

The conclusions are that, on one hand, it is unjustified *a priori* to consider the term given by (8) and to neglect the electronic contribution to the frequency, and that on the other hand, when this term is considered, the expression (1) of the Fröhlich theory is regained. It is *unnecessary* to consider the contribution of this term to the energy, since this is just the *difference* between corresponding expressions in the Fröhlich theory and the theory based on (8) alone (providing that the modes of approximation are valid and no arithmetical mistakes are made). Insomuch that the claim is made, in reference 6 in particular, that new results are obtained, one must conclude that these are due to the erroneous neglect of (2).

{To check this conclusion, I have calculated the chemical potential function according to the method of Nesbet [reference 6, second paper, Eqs. (15), (16)]. It is found that whereas his result, arising from our Eq. (8), is $\arctan[2v(k - k_F)/sk_F]$ [his Eq. (19)], the neglected term gives $\ln[4(k - k_F)^2/k_F^2 + s^2/v^2]$, with a coefficient of the same order. Consequently, we find essentially an infinite drop (with $s/v \sim 0$) as the Fermi surface is approached, instead of the finite zig-zag as supposed. This result invalidates the conclusions of that paper, and confirms our conclusion.}

Having demonstrated the consistency of different perturbational approaches, we might let matters rest here. However, it may not be quite clear whether expression (1), is, indeed, as its form suggests, the correct second-order perturbational correction to the energy of the electron-lattice system or is it merely an "acci-

dental" sum, correct to three orders, of the three terms due to (6) of the previous section? In particular, it is not clear whether the vibrational frequency appearing in the denominator in (1) is, or is not, the renormalized frequency? We shall, therefore, deduce an expression, based on some assumptions, which can be used as a starting point for perturbational investigations of the effects of the lattice-electron interaction on the population of the electronic states. The expression is formally equivalent to (1).

It is evident that, because of the operation of the exclusion principle, lattice-electron interaction will only affect the population of the states at a small distance, of the order of the quantity: the Fermi momentum times the ratio of the phonon and electron velocities, from the Fermi surface. Let the crystal be stripped of such of its electrons which might be in these states in the neighborhood of the Fermi surface, and let it be *assumed* that the lattice remains stable and, that moreover, the ions retain *exactly* their previous distances and *approximately* their vibrational frequencies. The interionic interaction term, including the shielding by the *available* electrons, will be denoted by $U(X)$. Let the removed electrons be replaced now *anywhere* in the sensitive region about the Fermi surface and let it be further *assumed* that the interaction term between *these* electrons and the screened ions, $V(X,x)$ is not changed in its form when the electrons occupy different states in the narrow strip about the Fermi surface. (This assumption means that the shielding effect of the "core" electrons is insensitive to the relatively narrow choice of states of the removed electrons. Any current theory of screening, e.g., Bardeen and Pines⁸ or Migdal's,⁹ is consistent with this assumption.)

These assumptions are likely to be valid approximately, but not true exactly. It is not easy to give even an order-of-magnitude estimate of the quantitative extent of their validity—but this does not matter for us. What we want to establish here is an exact result, or at least a safe approximation procedure, under stated assumptions, so that an alternative result may be known to depend *critically* on the absence of such assumptions, or to be wrong. The value of such a clear-cut criterion is evident from the previous section.

The Hamiltonian of the previous section now applies

⁸ J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

⁹ A. Migdal, Soviet Phys.—JETP **7**, 996 (1958).

for the system of screened ions (coordinate X) and the removed (and replaced) electrons (x). The set of wave functions $\Psi_{X_0}(x)\phi_n(X)$ is the exact solution of the following equations:

$$\begin{aligned} \left[\sum \frac{1}{2m} p^2 + U(X) + V(X_0, x) \right] \Psi_{X_0}(x) &= [E_{X_0} + U(X)] \Psi_{X_0}(x), \\ \left[\sum \frac{1}{2M} P^2 + U(X) + E_{X_0} \right] \phi_n(X) &= [E_{X_0} + (n + \frac{1}{2})\hbar\omega_0] \phi_n(X). \end{aligned}$$

Here the second equation actually refers (apart from a constant in the energy of the solution) to the condition in which the metal is depleted of some of its electrons, so that the frequency ω_0 is independent of the occupation or otherwise of the states near the Fermi surface. The effect of the lattice-electron interaction may now be found by applying perturbation theory to the difference between the original Hamiltonian and that differential expression whose solutions are $\Psi_{X_0}(x)\phi_n(X)$, namely,

$$\Delta H = V(X,x) - V(X_0,x) \sim (X - X_0) \nabla_{X_0} V(X_0,x).$$

The lowest order nondiagonal correction is clearly

$$\begin{aligned} \Delta E(a,n) &= - \sum_b \frac{|\langle n \pm 1, b | (X - X_0) \nabla_{X_0} V(X_0,x) | n, a \rangle|^2}{E_b - E_a \pm \hbar\omega_0}, \quad (9) \end{aligned}$$

where the summation is subject to the exclusion principle.

There is some slight difference, but no inconsistency, between this last result and the corresponding result of Bardeen and Pines.⁸ The frequency ω_0 which appears in our Eq. (9) occupies an intermediate stage between their Ω (the bare ion-ion frequency) and the fully renormalized ω . We introduced a number of assumptions in order to avoid using Ω , which might be imaginary. ω_0 , which is the renormalized frequency through all but the depleted electrons, is nearly equal to ω . It is ω_0 which should appear in the lowest order perturbational correction due to ΔH ; the authors of reference (8) used a canonical transformation, and not a step by step perturbation expansion, so they have ω in place of ω_0 .