PHYSICS

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1958

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Abstract

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ON THE THERMODYNAMICS OF SUPERCONDUCTIVITY

(Presented by Academician N. N. Bogolyubov on 24 VI 1958)

In a recent work by N. N. Bogolyubov, D. N. Zubarev, and Yu. A. Tserkovnikov ([1]), a theory of the phase transition of superconductors was considered on the basis of a model Hamiltonian. The thermodynamics of superconductivity was also constructed by Bardeen, Cooper, and Schrieffer ([2]) by means of an approximate variational method. In papers ([3]) the possibility was investigated of applying the variational principle to a model Hamiltonian of a more general form, and results were obtained confirming ([1], [2]). Below it will be shown that the variational principle makes it possible to obtain, in a more general form, the results of the works mentioned, if one starts directly from the Fröhlich Hamiltonian.

Bearing in mind the calculation of the statistical sum for an ensemble described by the grand Gibbs distribution, we introduce the chemical potential λ and consider the Hamiltonian

$$H = \sum_{k,\sigma} (E(k) - \lambda) a^+_{k,\sigma} a_{k,\sigma} + \sum_q \hbar\omega_q b^+_q b_q +$$

$$+g \sum_{\substack{k,q,\sigma \\ q=k'-k}} \left(\frac{\hbar\omega_q}{2V}\right)^{1/2} a^+_{k,\sigma} a_{k',\sigma} b^+_q + \text{complex conjugate}, \tag{1}$$

where $E(k)$ is the electron energy; $\hbar\omega_q$ is the phonon energy; g is the coupling constant, V is the volume of the system.

For calculating the statistical sum of the system

$$Z = \operatorname{Sp} e^{-\beta H}, \qquad \beta = \frac{1}{k_0 T}, \tag{2}$$

we shall use Feynman’ s operator calculus ([4]) and eliminate the phonon amplitudes, after which we obtain

$$Z = X\ \mathrm{Sp}\exp\left\{-\int_0^\beta H_e\,ds + \sum_{q\neq 0}(1+\bar{n}_q)\int_0^\beta ds\int_0^s dp\,\gamma_{qs}^+\gamma_{qp}e^{-\hbar\omega_q(s-p)}\right.$$

$$\left. + \sum_{q\neq 0}\bar{n}_q\int_0^\beta ds\int_0^s dp\,\gamma_{qs}^+\gamma_{qp}e^{\hbar\omega_q(s-p)}\right\}. \tag{3}$$

Here H_e is the first term of operator (1),

$$\gamma_q = g\left(\frac{\hbar\omega_q}{2V}\right)^{1/2}\sum_{k,\sigma}a_{k,\sigma}^+ a_{k+q,\sigma},$$

$$X = \prod_{q\neq 0}(1+\bar{n}_q)$$

is the statistical sum of the free lattice;

$$\bar{n}_q = (e^{\beta\hbar\omega_q}-1)^{-1};$$

s, p are ordering indices.

Let us note that if in (3) one drops the ordering indices s, p on the operators $H_e, \gamma_q, \gamma_q^+$ and carries out the integration, then in the exponent of this expression there appears the fourth form of the model Hamiltonian, derived earlier in paper ([5]).

Returning to the consideration of (3), we shall use the variational principle for the statistical sum ([6])

$$Z \geqslant Z_0 e^{-\beta S}, \tag{4}$$

where

$$Z_0 = \mathrm{Sp}\,e^{-\beta H_0}, \qquad S = \frac{1}{Z_0\beta}\,\mathrm{Sp}\left[\int_0^\beta (\widetilde{H} - H_0)_s\,ds\,\exp\left(-\int_0^\beta H_0\rho\,d\rho\right)\right]. \tag{5}$$

By $-\int_0^\beta \widetilde{H}_s ds$ is meant the expression contained in the braces in (3); H_0 is the trial Hamiltonian operator. (5) takes into account that the trace (3) is taken of a T-ordered exponential.

It is easy to see that in the case when $(\widetilde{H} - H_0)_s$ depends only on a single ordering index, (5) goes over into the corresponding expression of paper ([6a]). At the same time, the variational theorem (4), (5) is equivalent to the general variational theorem ([6b]), presented in Lagrangian form.

For the choice of H_0, following the basic idea of N. N. Bogoliubov ([7]), we pass to new Fermi amplitudes α_{f0}, α_{f1} by means of the canonical transformation*

$$\alpha_{f0} = u_f a_{f,\,1/2} - v_f a^+_{-f,\,-1/2}, \qquad \alpha_{f1} = u_f a_{-f,\,-1/2} + v_f a^+_{f,\,1/2}, \qquad u_f^2 + v_f^2 = 1. \tag{6}$$

As H_0 we take the expression

$$H_0 = \sum_k \Omega(k)\left(\alpha^+_{k0}\alpha_{k0} + \alpha^+_{k1}\alpha_{k1}\right), \tag{7}$$

where $\Omega(k)$ is the energy of the new elementary excitations. The functions $\Omega(k), u_k, v_k$ will be determined with the aid of the variational principle from the condition of a maximum of the right-hand side of (4), or of a minimum of the thermodynamic potential of the system. As a result of the calculations we obtain for S the expression

$$\begin{aligned} S = 2\sum (E(k)-\lambda)v_k^2 + 2\sum_k \left[(E(k)-\lambda)(u_k^2 - v_k^2) - \Omega_k\right] N_k \\ - \frac{g^2}{2V}\sum_k\sum_{k'}\hbar\omega_q \Bigg\{ (u_k v_{k'} + u_{k'} v_k)^2 \Bigg[\frac{(1+\bar{n}_q)(1-\bar{N}_{k'}-\bar{N}_k) + \bar{N}_k\bar{N}_{k'}}{\hbar\omega_q + \Omega_k + \Omega_{k'}} \\ + \frac{\bar{N}_k\bar{N}_{k'} - \bar{n}_q(1-\bar{N}_{k'}-\bar{N}_k)}{\hbar\omega_q - \Omega_{k'} - \Omega_k} \Bigg] \\ + (u_k u_{k'} - v_k v_{k'})^2 \Bigg[\frac{\bar{n}_q(\bar{N}_{k'}-\bar{N}_k) + \bar{N}_{k'} - \bar{N}_k\bar{N}_{k'}}{\hbar\omega_q + \Omega_k - \Omega_{k'}} \\ + \frac{\bar{n}_q(\bar{N}_k - \bar{N}_{k'}) + \bar{N}_k - \bar{N}_k\bar{N}_{k'}}{\hbar\omega_q + \Omega_{k'} - \Omega_k} \Bigg] \Bigg\}, \end{aligned} \tag{8}$$

where

$$\bar{N}_k = \left(1 + e^{\beta\Omega_k}\right)^{-1}.$$

The thermodynamic potential of the system has the form

$$\Psi = S - \frac{1}{\beta} \ln Z_0, \tag{9}$$

where S is defined by formula (8),

$$Z_0 = \prod_k \left(1 + e^{-\beta \Omega_k}\right)^2 .$$

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* The transformation (6) is effected by the unitary operator

$$S = \exp\left[\sum_k w_k \left(a^+_{k,\,1/2} a^+_{-k,\,-1/2} - a_{-k,\,-1/2} a_{k,\,1/2}\right)\right], \qquad u_k = \cos w_k, \quad v_k = \sin w_k.$$

The condition of a minimum of the thermodynamic potential leads to the equations

$$\frac{\partial \Psi}{\partial v_k} = 0; \tag{10}$$

$$\frac{\partial \Psi}{\partial \Omega_k} = 0; \tag{10a}$$

$$u_k^2 + v_k^2 = 1. \tag{10 }$$

From (10) we obtain the following expressions for u_k, v_k:

$$u_k^2 = \frac{1}{2}\left(1 + \frac{\xi(k)}{\sqrt{\xi^2(k) + c^2(k)}}\right), \qquad v_k^2 = \frac{1}{2}\left(1 - \frac{\xi(k)}{\sqrt{\xi^2(k) + c^2(k)}}\right), \tag{11}$$

where

$$\xi(k) = E(k) - \lambda - \operatorname{cth}\frac{\beta\Omega_k}{2} \sum_{k'} (J(kk') - H(kk'))(u_{k'}^2 - v_{k'}^2),$$

$$c(k) = 2 \operatorname{cth}\frac{\beta\Omega_k}{2} \sum_{k'} (J(k,k') - H(k,k')) u_{k'} v_{k'},$$

$$J(k,k') =$$

$$= \frac{g^2}{2V}\hbar\omega_q \frac{\hbar\omega_q[1+2\overline{N}_k\overline{N}_{k'}-\overline{N}_k-\overline{N}_{k'}]+(\Omega_k+\Omega_{k'})\,\mathrm{cth}\,\frac{\beta\hbar\omega_q}{2}(\overline{N}_k+\overline{N}_{k'}-1)}{[\hbar^2\omega_q^2-(\Omega_k+\Omega_{k'})^2]}, \tag{12}$$

$$H(k,k') = \frac{g^2}{2V}\hbar\omega_q \frac{\hbar\omega_q[\overline{N}_k+\overline{N}_{k'}-2\overline{N}_k\overline{N}_{k'}]+(\Omega_{k'}-\Omega_k)\,\mathrm{cth}\,\frac{\beta\hbar\omega_q}{2}(\overline{N}_{k'}-\overline{N}_k)}{[\hbar^2\omega_q^2-(\Omega_k-\Omega_{k'})^2]}.$$

Turning to relation (10a), let us note that in calculating the derivatives of Ψ with respect to Ω_k one should not alter the energy denominators of this expression, since this may lead to a substantial overestimation of the accuracy of the theory. It is not difficult to see that condition (10a), together with the above restriction, is equivalent to the equations

$$\frac{\partial\Psi_0}{\partial\Omega_k} = 2\overline{N}_k, \qquad \frac{\partial}{\partial\overline{N}_k}\frac{1}{\beta}\frac{\mathrm{Sp}\left[\int_0^\beta \widetilde{H}_s\,ds\,\exp\left(-\int_0^\beta H_0\,dt\right)\right]}{Z_0} = 2\Omega_k, \quad (10\ )$$

where

$$\Psi_0 = -\frac{1}{\beta}\ln Z_0.$$

The right-hand sides of equations (10) are doubled, since the energies of elementary excitations of the two kinds of quasiparticles 0 and 1 are identical. After some simplifications, (10) leads to the following results:

$$\Omega_k = \sqrt{(1-\eta(k))^2\xi^2(k)+c^2(k)}, \tag{13}$$

where

$$\eta(k) = -\frac{g^2}{2V}\sum_{k'}\hbar\omega_q\left\{\frac{2\hbar\omega_q\Omega_{k'}\left[\mathrm{cth}\,\frac{\beta\Omega_k}{2}(u_k^2-v_k^2)(u_{k'}^2-v_{k'}^2)+\mathrm{th}\,\frac{\beta\Omega_{k'}}{2}\right]}{[\hbar\omega_q^2-(\Omega_k+\Omega_{k'})^2][\hbar\omega_q^2-(\Omega_k-\Omega_{k'})^2]}-\right.$$

$$\left.-\frac{[\hbar\omega_q^2-\Omega_k^2+\Omega_{k'}^2]\left[\mathrm{cth}\,\frac{\beta\hbar\omega_q}{2}\,\mathrm{th}\,\frac{\beta\Omega_{k'}}{2}\,\mathrm{cth}\,\frac{\beta\Omega_k}{2}(u_k^2-v_k^2)(u_{k'}^2-v_{k'}^2)+\mathrm{cth}\,\frac{\beta\hbar\omega_q}{2}\right]}{[\hbar\omega_q^2-(\Omega_k+\Omega_{k'})^2][\hbar\omega_q^2-(\Omega_k-\Omega_{k'})^2]}\right\}. \tag{14}$$

On the basis of (11) and (12) we obtain the following integral equation for determining the magnitude of the gap $c(\mathbf{k})$ in the spectrum of elementary excitations of the superconductor (13):

$$c(\mathbf{k}) = \operatorname{cth} \frac{\beta\Omega_k}{2} \sum_{\mathbf{k}'} (J(\mathbf{k},\mathbf{k}') - H(\mathbf{k},\mathbf{k}')) \frac{c(\mathbf{k}')}{\sqrt{\xi^2(\mathbf{k}') + c^2(\mathbf{k}')}}. \tag{15}$$

Equation (15) always has the trivial solution $c(\mathbf{k}) = 0$. A nontrivial solution of (15) exists only at temperatures $T < T_c$. The critical temperature T_c can be determined from the following exact equation, obtained by linearizing (15):

$$\gamma(k) = \operatorname{cth} \frac{\beta\Omega_n(k)}{2} \sum_{k'} (J_n(\mathbf{k},\mathbf{k}') - H_n(\mathbf{k},\mathbf{k}')) \frac{\gamma(k')}{|\xi_n(k')|}, \tag{15a}$$

where the index n means that the corresponding quantities are taken in the normal state of the metal, when $c = 0$.

A very simplified equation for estimating T_c is obtained by setting the trace of the kernel of equation (15a) equal to unity. As a result we have (for $k_m \leqslant 2k_F$):

$$k_0 T_c = 1.14\hbar\omega_{\text{cp}} e^{-1/\rho}, \qquad \rho = \frac{mk_{Fg}^2}{2\pi^2\hbar^2} \left(\frac{k_m}{2k_F}\right)^2, \tag{16}$$

$$\omega_{\text{cp}} = 0.303\,\omega_D, \tag{17}$$

where k_F is the Fermi momentum, $\omega_D = \omega(k_m)$ is the Debye frequency. (It is possible that the true value of T_c differs somewhat from the one given.)

On the basis of equations (10) it is easy to show that at the critical point there is no first-order phase transition; however, at this point there is a nonzero jump in the heat capacity of the metal, $\Delta\sigma$:

$$\Delta\sigma = -\beta^3 \sum_p \left[\frac{\partial v_p}{\partial\beta} \frac{\partial}{\partial v_p} \left(\frac{\partial\Psi}{\partial\beta}\right) + \frac{\partial\Omega_p}{\partial\beta} \frac{\partial}{\partial\Omega_p} (\partial\Psi) \right]_{T_c}. \tag{18}$$

Both terms in (18) give a nonzero contribution to $\Delta\sigma$; however, in modeling the second term proves to be the more significant.

Note. The thermodynamics of superconductivity in the Fröhlich model was considered independently by D. N. Zubarev and Yu. A. Tserkovnikov by means of the thermodynamic theory of perturbations, taking account of the renormalization of the velocity of sound ([8]).

The author takes this opportunity to express deep gratitude to Acad. N. N. Bogolyubov, and also to D. N. Zubarev, I. A. Kvasnikov, V. V. Tolmachev, and Yu. A. Tserkovnikov for valuable advice and discussion of the results.

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Received
20 VI 1958

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Note: Figure translations are in progress. See original paper for figures.