Letters to the Editor

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New Method in the Theory of Superconductivity

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(Received February 24, 1958)

PREVIOUS work[1] has shown that plasmon effects play an important, if hidden, role in the Bardeen-Cooper-Schrieffer theory[2] of superconductivity: they are essential for understanding the zero-momentum pairing condition. For this reason, at least, a deeper justification of the B.C.S. theory must be good enough to treat plasmon (long-range Coulomb) effects correctly.

Our method obtains the ground state and elementary excitations of the B.C.S. superconductor while including the Coulomb forces and the higher-order corrections from the phonon forces by a method equivalent to the Sawada-Brout theory of correlation energy[3] (which is exact in the high-density limit).

One way of expressing the Sawada-Brout theory is to write down the full equation of motion of the quantity[4]

$$\rho_{\mathrm{k},\sigma}{}^{\mathrm{Q}}=c_{\mathrm{k+Q},\sigma}{}^{*}c_{\mathrm{k},\sigma}, \tag{1}$$

which is, with only Coulomb interactions,

$$\begin{aligned}[H,\rho_{\mathrm{k},\sigma}{}^{\mathrm{Q}}]&=(\epsilon_{\mathrm{k+Q}}-\epsilon_{\mathrm{k}})\rho_{\mathrm{k},\sigma}{}^{\mathrm{Q}}+4\pi e^2\hbar^2\Omega^{-1}\\&\times\textstyle\sum_{q\neq0}q^{-2}\sum_{\mathrm{k}',\sigma'}(\rho_{\mathrm{k}',\sigma'}{}^{\mathrm{q}})^*(\rho_{\mathrm{k},\sigma}{}^{\mathrm{Q-q}}-\rho_{\mathrm{k+q},\sigma}{}^{\mathrm{Q-q}}).\end{aligned} \tag{2}$$

In the sum almost all of the terms are products of two $\rho_{\mathrm{k}}{}^{\mathrm{Q}}$; terms which are not involve products $c_{\mathrm{k},\sigma}{}^*c_{\mathrm{k},\sigma}=n_{\mathrm{k},\sigma}$, and are of two types: the terms $\mathbf{q}=\mathbf{Q}$, and exchange terms. Sawada shows the exchange and nonlinear terms to be negligible in the high-density limit (this is the random-phase approximation) by comparing with the Gell-Mann—Brueckner theory,[5] so that the equation of motion simplifies to

$$\begin{aligned}[H,\rho_{\mathrm{k},\sigma}{}^{\mathrm{Q}}]&=(\epsilon_{\mathrm{k+Q}}-\epsilon_{\mathrm{k}})\rho_{\mathrm{k},\sigma}{}^{\mathrm{Q}}\\&+4\pi e^2\hbar^2Q^{-2}\Omega^{-1}\rho^{\mathrm{Q}}(n_{\mathrm{k},\sigma}-n_{\mathrm{k+Q},\sigma}),\end{aligned} \tag{3}$$

where $\rho^{\mathrm{Q}}=\sum_{\mathrm{k},\sigma}\rho_{\mathrm{k},\sigma}{}^{\mathrm{Q}}$.

This leads to the plasma oscillations as well as giving the Coulomb corrections to the energies of the individual particle modes. An observation which is trivial here but will not be in our generalization is the presence of nonphysical modes, for example $|\mathbf{k}|$, $|\mathbf{k+Q}|>k_F$, for which (3) gives the correct energy but which, when applied to the Fermi sea or to anything derived via (3) from it, are zero identically. The absence of these modes is a subsidiary condition on the theory.

Our method generalizes this by observing that in the B.C.S. ground state of the superconductor not only the $n_{\mathrm{k},\sigma}$ have finite averages, but also the quantities

$$b_{\mathrm{k}}{}^0=c_{-\mathrm{k}\downarrow}c_{\mathrm{k}\uparrow}\cong b_{\mathrm{k}}{}^{0*}=c_{\mathrm{k}\uparrow}{}^*c_{-\mathrm{k}\downarrow}{}^*. \tag{4}$$

When the equations of motion (3) are generalized to include terms which are linear when the b's as well as n's are finite, they involve the quantities

$$b_{\mathrm{k}}{}^{\mathrm{Q}*}=c_{\mathrm{k+Q}\uparrow}{}^*c_{-\mathrm{k}\downarrow}{}^*,\quad b_{\mathrm{k}}{}^{\mathrm{Q}}=c_{-\mathrm{k-Q}\downarrow}c_{\mathrm{k}\uparrow}; \tag{5}$$

and including the extended form of the attractive phonon interaction used by B.C.S.,[1,2] the equations of motion are

$$\begin{aligned}[H,\rho_{\mathrm{k}\uparrow}{}^{\mathrm{Q}}]&=(\epsilon_{\mathrm{k+Q}}-\epsilon_{\mathrm{k}})\rho_{\mathrm{k}\uparrow}{}^{\mathrm{Q}}\\&+4\pi e^2\hbar^2Q^{-2}\Omega^{-1}\rho^{\mathrm{Q}}(n_{\mathrm{k}\uparrow}-n_{\mathrm{k+Q}\uparrow})\\&-\textstyle\sum_{\mathrm{k}'}(\frac{1}{2}V-2\pi e^2\hbar^2\Omega^{-1}|\mathbf{k}-\mathbf{k}'|^{-2})\\&\times[b_{\mathrm{k}'}{}^0(b_{\mathrm{k}}{}^{\mathrm{Q}}-(b_{-\mathrm{k}'-\mathrm{Q}}{}^{-\mathrm{Q}})^*)\\&\qquad+b_{\mathrm{k}}{}^0(b_{-\mathrm{k}'-\mathrm{Q}}{}^{-\mathrm{Q}})^*-b_{\mathrm{k+Q}}{}^0b_{\mathrm{k}'}{}^{\mathrm{Q}}],\end{aligned} \tag{6}$$

(where we neglect $\mathbf{Q}$ relative to $\mathbf{k}-\mathbf{k}'$ wherever permissible) and

$$\begin{aligned}[H,b_{\mathrm{k}}{}^{\mathrm{Q}}]&=-(\epsilon_{\mathrm{k+Q}}+\epsilon_{\mathrm{k}})b_{\mathrm{k}}{}^{\mathrm{Q}}-2\pi e^2\hbar^2\Omega^{-1}Q^{-2}\\&\times(b_{\mathrm{k}}{}^0\rho_{\uparrow}{}^{\mathrm{Q}}+b_{\mathrm{k+Q}}{}^0\rho_{\downarrow}{}^{\mathrm{Q}})-\textstyle\sum_{\mathrm{k}'}(\frac{1}{2}V-2\pi e^2\hbar^2\Omega^{-1}|\mathbf{k}-\mathbf{k}'|^{-2})\\&\times[b_{\mathrm{k}'}{}^0(\rho_{\mathrm{k}\uparrow}{}^{\mathrm{Q}}+\rho_{-\mathrm{k-Q}\downarrow}{}^{\mathrm{Q}})+b_{\mathrm{k}'}{}^{\mathrm{Q}}(n_{\mathrm{k}}+n_{-\mathrm{k-Q}})].\end{aligned} \tag{7}$$

There are additional equations for the deviations $\delta b_{\mathrm{k}}{}^0$ and $\delta n_{\mathrm{k},\sigma}$ of the b^0's and n's from their ground state values. These contain constant terms unless a certain condition for equilibrium is satisfied, which for $V=0$ leads trivially to the Fermi sea but in the superconducting case is the B.C.S. integral equation determining the ground state. The linear terms then give equations similar to (6) and (7) with $Q^{-2}\rho^{\mathrm{Q}}$ terms absent.

Equations (6) and (7) become manageable only when the auxiliary conditions which eliminate nonphysical modes (single-particle excitations which do not jump the energy gap) are used. In this step it was necessary to use Bogoliubov's description of the ground state in terms of a transformed set of fermions.[6] We find the following types of excitations:

I. A set of individual particle modes displaced by an amount of order Ω^{-1} from the continuous spectrum with energy gap of the Bardeen theory.

II. A set of plasma modes with a dispersion relation very like that of Bohm and Pines.[4] In the absence of the plasma (Q^{-2}) terms, these occupy the energy gap and obey some of the relationships given in reference 1, but have a phonon-like dispersion law.[7]

III. A single $Q=0$ mode at $\omega=0$ which corresponds to a coordinate conjugate to the total number of electrons N. The zero-point motion of this mode automatically fixes N; this feature is what allows us to work with the b operators, which do not conserve this number.

From this the following conclusions may be drawn:

(1) By calculating the zero-point energies and motions of these modes as in reference 3, the next higher-order corrections to the B.C.S. theory could be obtained. We justify this theory in that we show that these reasonably large corrections do not change the excitation spectrum in essentials.

(2) Collective and plasma effects indeed reinforce the B.C.S. theory in the way predicted in reference 1, even though the exact matrix elements in B.C.S. are incorrect because of the neglect of collective effects.

I am indebted to H. Suhl for help with some of the calculations and for many conversations. A more complete description of the method will be published later.

1 P. W. Anderson, Phys. Rev. **110**, 985 (1958), this issue.
2 Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957). This is called B.C.S. hereafter.
3 K. Sawada, Phys. Rev. **106**, 372 (1957); Sawada, Brueckner, Fukuda, and Brout, Phys. Rev. **108**, 507 (1957); R. Brout, Phys. Rev. **108**, 515 (1957).
4 This is related to a method used by D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953), Appendix II.
5 M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).
6 N. N. Bogoliubov, J. Exptl. Theoret. Phys. U.S.S.R. (to be published). Similar relations were also derived by J. G. Valatin (private communication via J. Bardeen).
7 By Feynman's argument [see reference 1; also Phys. Rev. **94**, 262 (1954)], this implies that zero-point motions greatly reduce the long-range correlation in the Bardeen theory.

Sign of the Cubic Field Splitting for Mn^{++} in ZnS

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(Received April 1, 1958)

The electron spin resonance of Mn^{++} in cubic ZnS has been studied by Matarrese and Kikuchi.[1] They report that in the spin Hamiltonian

$$H=g\beta\mathbf{H}\cdot\mathbf{S}+\tfrac{1}{6}a(S_x^4+S_y^4+S_z^4)+A\mathbf{I}\cdot\mathbf{S},$$

one has $a=-8.35\mp0.06$ gauss and $A=+68.4\mp0.1$ gauss. Actually, since the measurements were made at room temperature, a change of sign for both the cubic field splitting constant a and the hyperfine interaction constant A would also produce the same spectrum. In order to distinguish between the two possibilities, it is necessary to measure the relative intensities of the transitions at low temperature.[2] We have made such a measurement[3] at 4°K and at a frequency of 20 kMc/sec, and find that the signs reported were in error. They should be $a=+8.35\mp0.06$ gauss, $A=-68.4\mp0.1$ gauss.

This is of interest because of a recent theoretical treatment of Mn^{++} in cubic fields by Watanabe.[4] He concludes that a should be positive regardless of the sign of D in the cubic potential $-eV=D(x^4+y^4+z^4-\frac{3}{5}r^4)$. Most measurements for manganese have been in solids where the ion is surrounded by six negative ions in approximate octahedral symmetry. In these solids D is positive, and the sign of a has been found to be positive also.[5] In ZnS, the ion is presumed to be surrounded by a tetrahedron of four negative sulfur ions and the sign of D would therefore be negative. As a result, this system provides an important test for the theory, and the positive sign for a appears to confirm Watanabe's result. Similar agreement has been found for manganese in germanium, where the sign of a has also been determined to be positive.[6]

However, the crystalline model does not predict the correct sign of the g shift in these substantially covalent solids. Watanabe's result states that the g value should always be less than the free electron value (2.0023). The measured values are 2.0025 ∓ 0.0002 in ZnS [1] and 2.0061 ∓ 0.0002 in germanium.[6] Positive g shifts are also indicated in powders of CdS, ZnSe, and CdTe.[7] As a result, the agreement in the sign of a does not necessarily indicate that the crystalline field model can be successfully applied to such highly covalent solids.

1 L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids **1**, 117 (1956).
2 See, for instance, W. Low, Phys Rev. **105**, 793 (1957).
3 The crystal used for this measurement was kindly supplied by Professor Kikuchi.
4 H. Watanabe, Progr. Theoret. Phys. Japan **18**, 405 (1957).
5 K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 342.
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Rate Processes and Low-Temperature Electrical Conduction in *n*-Type Germanium

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(Received March 17, 1958)

The low-temperature electrical conduction of *n*-type germanium as a function of applied electric field is characterized by an ohmic region for fields less than ~0.2 v/cm, a region of steadily increasing conductivity, and finally a critical "breakdown" field at which the current rises "vertically" with the applied electrical field.[1] The large variation of conductivity is due mainly to an increase in carrier density as, with increasing electric field, the mean carrier energy increases from its equilibrium value. The breakdown is associated, in a general way, with ionization of neutral donors by the impact of "hot" electrons.[1] In Fig. 1, data obtained by pulse techniques are presented to illustrate the behavior at high current densities.[2] The essential feature to be noted is that after a significant "vertical" rise the j-E curve becomes concave downwards.