Letters to the Editor

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Bound Electron Pairs in a Degenerate Fermi Gas*

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IT has been proposed that a metal would display superconducting properties at low temperatures if the one-electron energy spectrum had a volume-independent energy gap of order $\Delta \simeq kT_c$, between the ground state and the first excited state.[1,2] We should like to point out how, primarily as a result of the exclusion principle, such a situation could arise.

Consider a pair of electrons which interact above a quiescent Fermi sphere with an interaction of the kind that might be expected due to the phonon and the screened Coulomb fields. If there is a net attraction between the electrons, it turns out that they can form a bound state, though their total energy is larger than zero. The properties of a noninteracting system of such bound pairs are very suggestive of those which could produce a superconducting state. To what extent the actual many-body system can be represented by such noninteracting pairs will be discussed in a forthcoming paper.

Because of the similarity of the superconducting transition in a wide variety of complicated and differing metals, it is plausible to assume that the details of metal structure do not affect the qualitative features of the superconducting state. Thus, we neglect band and crystal structure and replace the periodic ion potential by a box of volume V. The electrons in this box are free except for further interactions between them which may arise due to Coulomb repulsions or to the lattice vibrations.

In the presence of interaction between the electrons, we can imagine that under suitable circumstances there will exist a wave number q_0 below which the free states are unaffected by the interaction due to the large energy denominators required for excitation. They provide a floor (so to speak) for the possible transitions of electrons with wave number $k_i > q_0$. One can then consider the eigenstates of a pair of electrons with k_1, $k_2 > q_0$.

For a complete set of states of the two-electron system we take plane-wave product functions, $\varphi(\mathbf{k}_1,\mathbf{k}_2;\ \mathbf{r}_1,\mathbf{r}_2) = (1/V)\exp[i(\mathbf{k}_1\cdot\mathbf{r}_1+\mathbf{k}_2\cdot\mathbf{r}_2)]$ which satisfy periodic boundary conditions in a box of volume V, and where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of electron one and electron two. (One can use antisymmetric functions and obtain essentially the same results, but alternatively we can choose the electrons of opposite spin.) Defining relative and center-of-mass coordinates, $\mathbf{R}=\frac{1}{2}(\mathbf{r}_1+\mathbf{r}_2)$, $\mathbf{r}=(\mathbf{r}_2-\mathbf{r}_1)$, $\mathbf{K}=(\mathbf{k}_1+\mathbf{k}_2)$ and $\mathbf{k}=\frac{1}{2}(\mathbf{k}_2-\mathbf{k}_1)$, and letting $\mathcal{E}_K+\epsilon_k=(\hbar^2/m)(\frac{1}{4}K^2+k^2)$, the Schrödinger equation can be written

$$(\mathcal{E}_K+\epsilon_k-E)a_{\mathbf{k}}+\textstyle\sum_{\mathbf{k}'} a_{\mathbf{k}'}(\mathbf{k}|H_1|\mathbf{k}') \times\delta(\mathbf{K}-\mathbf{K}')/\delta(0)=0 \quad (1)$$

where

$$\Psi(\mathbf{R},\mathbf{r})=(1/\sqrt{V})e^{i\mathbf{K}\cdot\mathbf{R}}\chi(\mathbf{r},K), \qquad \chi(\mathbf{r},K)=\textstyle\sum_{\mathbf{k}}(a_{\mathbf{k}}/\sqrt{V})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (2)$$

and

$$(\mathbf{k}|H_1|\mathbf{k}')=\left(\frac{1}{V}\int d\mathbf{r}e^{-i\mathbf{k}\cdot\mathbf{r}}H_1 e^{i\mathbf{k}'\cdot\mathbf{r}}\right)_{0\text{ phonons}}.$$

We have assumed translational invariance in the metal. The summation over $\mathbf{k}'$ is limited by the exclusion principle to values of k_1 and k_2 larger than q_0, and by the delta function, which guarantees the conservation of the total momentum of the pair in a single scattering. The K dependence enters through the latter restriction.

Bardeen and Pines[3] and Fröhlich[4] have derived approximate formulas for the matrix element $(\mathbf{k}|H_1|\mathbf{k}')$; it is thought that the matrix elements for which the two electrons are confined to a thin energy shell near the Fermi surface, $\epsilon_1\simeq\epsilon_2\simeq\epsilon_F$, are the principal ones involved in producing the superconducting state.[2-4] With this in mind we shall approximate the expressions for $(\mathbf{k}|H_1|\mathbf{k}')$ derived by the above authors by

$$(\mathbf{k}|H_1|\mathbf{k}')=-|F| \quad \text{if} \quad k_0\lesssim k,\ k'\lesssim k_m \qquad =0 \quad \text{otherwise}, \quad (3)$$

where F is a constant and $(\hbar^2/m)(k_m{}^2-k_0{}^2)\simeq 2\hbar\omega\simeq 0.2$ ev. Although it is not necessary to limit oneself so strongly, the degree of uncertainty about the precise form of $(\mathbf{k}|H_1|\mathbf{k}')$ makes it worthwhile to explore the consequences of reasonable but simple expressions.

With these matrix elements, the eigenvalue equation becomes

$$1=-|F|\int_{\epsilon_0}^{\epsilon_m}\frac{N(K,\epsilon)d\epsilon}{E-\epsilon-\mathcal{E}_K}, \quad (4)$$

where $N(K,\epsilon)$ is the density of two-electron states of total momentum K, and of energy $\epsilon=(\hbar^2/m)k^2$. To a very good approximation $N(K,\epsilon)\simeq N(K,\epsilon_0)$. The resulting spectrum has one eigenvalue smaller than $\epsilon_0+\mathcal{E}_K$, while the rest lie in the continuum. The lowest eigenvalue is $E_0=\epsilon_0+\mathcal{E}_K-\Delta$, where Δ is the binding energy of the pair

$$\Delta=(\epsilon_m-\epsilon_0)/(e^{1/\beta}-1), \quad (5)$$

where $\beta=N(K,\epsilon)|F|$. The binding energy, Δ, is independent of the volume of the box, but is strongly dependent on the parameter β.

Following a method of Bardeen,[5] by which the coupling constant for the electron-electron interaction, which is due to phonon exchange, is related to the high-temperature resistivity which is due to phonon absorption, one gets $\beta\simeq\rho n\times10^{-6}$, where ρ is the high-temperature resistivity in esu and n is the number of valence electrons per unit volume. The binding energy displays a sharp change of behavior in the region $\beta\simeq1$ and it is just this region which separates, in almost every case, the superconducting from the nonsuperconducting metals.[5] (Also it is just in this region where the attractive interaction between electrons, due to the phonon field, becomes about equal to the screened Coulomb repulsive interaction.)

The ground-state wave function,

$$\chi_0(r,K)=(\text{const})\int\frac{e^{i\mathbf{k}\cdot\mathbf{r}}N(K,\epsilon(k))}{\mathcal{E}_K+\epsilon(k)-E}\left(\frac{d\epsilon}{dk}\right)d\mathbf{k}, \quad (6)$$

represents a true bound state which for large values of r decreases at least as rapidly as const/r^2. The average extension of the pair, $[\langle r^2\rangle_{\text{Av}}]^{\frac{1}{2}}$, is of the order of 10^{-4} cm for $\Delta\simeq kT_c$. The existence of such a bound state with nonexponential dependence for large r is due to the exclusion of the states $k<k_0$ from the unperturbed spectrum, and the concomitant degeneracy of the lowest energy states of the unperturbed system. One would get no such state if the potential between the electrons were always repulsive. All of the excited states $\chi_{n>0}(\mathbf{r},K)$ are very nearly plane waves.

The pair described by $\chi_0(r)$ may be thought to have some Bose properties (to the extent that the binding energy of the pair is larger than the energy of interaction between pairs).[6] However, since $N(K,\epsilon)$ is strongly dependent on the total momentum of the pair, K, the binding energy Δ is a very sensitive function of K, being a maximum where $K=0$ and going very rapidly to zero where $K\simeq k_m-k_0$. Thus the elementary excitations of the pair might correspond to the splitting of the pair rather than to increasing the kinetic energy of the pair.

In either case the density of excited states (dN/dE) would be greatly reduced from the free-particle density and the elementary excitations would be removed from the ground state by what amounted to a small energy gap.

If the many-body system could be considered (at least to a lowest approximation) a collection of pairs of this kind above a Fermi sea, we would have (whether or not the pairs had significant Bose properties) a model similar to that proposed by Bardeen which would display many of the equilibrium properties of the superconducting state.

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[2] See also, for further references and a general review, J. Bardeen, *Theory of Superconductivity Handbuch der Physik* (Springer-Verlag, Berlin, to be published), Vol. 15, p. 274.
[3] J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).
[4] H. Fröhlich, Proc. Roy. Soc. (London) **A215**, 291 (1952).
[5] John Bardeen, Phys. Rev. **80**, 567 (1950).
[6] It has also been suggested that superconducting properties would result if electrons could combine in even groupings so that the resulting aggregates would obey Bose statistics. V. L. Ginzburg, Uspekhi Fiz. Nauk **48**, 25 (1952); M. R. Schafroth, Phys. Rev. **100**, 463 (1955).

Magnetic Resonance in Manganese Fluoride

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NUCLEAR magnetic resonance of the fluorine nuclei in MnF_2 has recently been observed by Shulman and Jaccarino,[1] who found a much greater "paramagnetic shift" of the resonance field than would be expected from simple magnetic dipole fields of the manganese ions. Electronic paramagnetic resonance of Mn^{2+} ions present as impurities in the isomorphous crystal ZnF_2 has previously been observed by Tinkham,[2] who made detailed measurements of the fluorine hyperfine structure which results from overlap of the magnetic electrons onto the fluorine ions. The purpose of this note is to point out that the shift of the nuclear resonance can be estimated from Tinkham's data, and that good agreement with the measured value is found.

With an obvious extension of Tinkham's nomenclature, the Hamiltonian for the system can be written as

$$\mathcal{H}=-g_N\beta_N\mathbf{H}\cdot\mathbf{I}+\sum_N\mathbf{I}\cdot A^N\cdot\mathbf{S}^N, \quad (1)$$

where $\mathbf{I}$ is the spin operator for a fluorine nucleus, A^N is the hyperfine structure constant for interaction between this nucleus and the Nth manganese ion whose spin operator is $\mathbf{S}^N$. Owing to the rapid change of spin orientation for the manganese ions, we must take a weighted mean of the different values of the projection M of $\mathbf{S}^N$ on the direction of the applied field. This mean is

$$\bar{M}=\sum_M M\exp(-W_M/kT)/\sum_M\exp(-W_M/kT),$$

which cannot be evaluated from first principles in a substance such as MnF_2 where strong internal fields are acting. However, we may relate it to the measured susceptibility, since, per mole,

$$\chi=Ng\beta\bar{M}/H.$$

Hence we have, for the quantum of energy required to