

## Localized single-particle excitations for a normal-metal sphere in a superconducting host

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We calculate the single-particle excitation spectrum of a spherical normal-metal particle embedded in an infinite superconducting host by solving the Bogoliubov equations, assuming that the electron and hole amplitudes are proportional. The pair potential is modeled by a step function which vanishes in the normal metal and takes on the bulk superconductor value in the host. With these assumptions, bands of bound states are found with energies lower than the superconductor pair potential. These states will fill up the gap for large enough particle size. The effects of these bound states on measurable physical quantities are briefly discussed.

The excitation spectrum of a normal metal in contact with a superconductor has long been a subject of interest.<sup>1,2</sup> This spectrum is well suited to calculation via the Bogoliubov equations, which describe such excitations in terms of coupled electronlike and holelike amplitudes.<sup>3</sup> As pointed out by de Gennes and Saint-James,<sup>1</sup> the result of this calculation is that there is no energy gap in the excitation of a slab of normal metal deposited on an infinite superconducting substrate. Similar results for a normal-metal-superconductor bilayer have recently been obtained by Zaitlin,<sup>2</sup> who also discussed the effect of these excitations on the discontinuity in the heat capacity at the transition temperature.

The purpose of this Brief Report is to work out the excitation of a simple geometry that has not been previously considered: a single sphere of normal metal embedded in a superconducting host. This geometry is of interest because of the considerable current work on random composites of normal metal and superconductor, which have numerous unusual properties.<sup>4</sup> The particular case of normal metal in superconductor is relevant because of recent predictions, based on classical arguments that the normal metal will absorb electromagnetic radiation below the energy gap of the superconductor.<sup>5</sup> Here, it will be shown that there is always a finite density of single-particle excitations within a spherical inclusion of normal metal, and that the bottom of the band of excitations approaches zero energy as the sphere becomes larger. This result suggests that there will be substantial electromagnetic absorption within the energy gap by such inclusions, and also implies changes in the specific heat and  $I$ - $V$  characteristics of such materials from the usual behavior of bulk superconductors.

We consider a normal-metal sphere ( $N$ ) of radius  $a$  embedded in an infinite superconducting host ( $S$ ). For simplicity, we assume that the Fermi energy is the same for both. The pair potential  $\Delta$  is approximated by

$$\Delta(\mathbf{r}) = \Delta(r) = \begin{cases} 0 & r < a \text{ in } N \\ \Delta_0 & r > a \text{ in } S \end{cases} \quad (1)$$

In principle, the pair potential should be computed self-consistently from the quasiparticle wave functions obtained from the Bogoliubov equations, but this calculation is quite difficult and will not be attempted here.  $\Delta_0$  is thus the bulk energy gap of the superconductor. Although (1) is only approximate, we believe that the spectrum resulting from it

should give the most important features in systems of physical interest.

The excitation spectrum of the system can be obtained by solving the Bogoliubov equations:

$$\begin{aligned} \left( -\frac{\hbar^2}{2m} \nabla^2 - E_F \right) u + \Delta v &= \epsilon u, \\ \left( \frac{\hbar^2}{2m} \nabla^2 + E_F \right) v + \Delta u &= \epsilon v. \end{aligned} \quad (2)$$

Here,  $u$  and  $v$  are the electron and hole amplitudes of the quasiparticle wave function and  $\epsilon$  is the energy eigenvalue. We shall seek solutions in which the energies  $\epsilon$  of the excitations are less than the pair potential  $\Delta_0$  in the superconductor. We make the additional assumption that the amplitudes  $u$  and  $v$  are proportional. This ansatz will certainly give some solutions to Eqs. (2), but we have not succeeded in proving that there are no additional solutions. Nevertheless, given the boundary conditions, a self-consistency condition for the energies  $\epsilon$  can be obtained. From this equation, the energies and the corresponding density of states can then be determined. The resulting density of states is found to depend on only two parameters:  $k_F a$ , the product of the Fermi wave vector and particle radius; and  $\Delta_0/E_F$ , the ratio of the pair potential to the Fermi energy.

For  $r > a$  (i.e., in  $S$ ), the assumption that  $u$  and  $v$  are proportional allows Eqs. (2) to be decoupled. Requiring that the two equations are consistent with each other leads to

$$\left( \frac{\hbar^2}{2m} \nabla^2 + E_F + \epsilon - \Delta_0 \alpha \right) u = 0, \quad (3)$$

where  $\alpha$  can take on the two values  $\alpha_1, \alpha_2$ :

$$\begin{aligned} \alpha_1 &= \frac{\epsilon}{\Delta_0} + \left[ \left( \frac{\epsilon}{\Delta_0} \right)^2 - 1 \right]^{1/2} = \frac{\epsilon}{\Delta_0} + i \left[ 1 - \left( \frac{\epsilon}{\Delta_0} \right)^2 \right]^{1/2}, \\ \alpha_2 &= \frac{\epsilon}{\Delta_0} - \left[ \left( \frac{\epsilon}{\Delta_0} \right)^2 - 1 \right]^{1/2} = \frac{\epsilon}{\Delta_0} - i \left[ 1 - \left( \frac{\epsilon}{\Delta_0} \right)^2 \right]^{1/2}. \end{aligned} \quad (4)$$

In (4) the second forms of the solutions are valid for bound states with energies  $\epsilon < \Delta_0$ .

The general solution of Eq. (3) (in  $S$ ) is

$$\begin{pmatrix} u(\vec{r}) \\ v(\vec{r}) \end{pmatrix} = \sum_{lm} \left[ A_{lm} \begin{pmatrix} h_l^{(1)}(k_1 r) \\ \alpha_1 h_l^{(1)}(k_1 r) \end{pmatrix} + B_{lm} \begin{pmatrix} h_l^{(1)}(k_2 r) \\ \alpha_2 h_l^{(1)}(k_2 r) \end{pmatrix} \right] Y_{lm}(\theta, \phi), \quad (5)$$

where spherical coordinates have been used and  $h_l^{(1)}(x)$  is the spherical Hankel function of order  $l$ .  $A_{lm}$  and  $B_{lm}$  are coefficients to be determined and the  $Y_{lm}(\theta, \phi)$  are spherical harmonics. In writing Eq. (5), use has been made of the requirement that  $u$  and  $v$  remain finite at large  $r$ . The wave vectors  $k_1$  and  $k_2$  are complex and are given by

$$k_1 = - \left\{ E_F - i\Delta_0 \left[ 1 - \left( \frac{\epsilon}{\Delta_0} \right)^2 \right]^{1/2} \right\}^{1/2} \left( \frac{2m}{\hbar^2} \right)^{1/2}$$

and

$$k_2 = \left\{ E_F + i\Delta_0 \left[ 1 - \left( \frac{\epsilon}{\Delta_0} \right)^2 \right]^{1/2} \right\}^{1/2} \left( \frac{2m}{\hbar^2} \right)^{1/2}. \quad (6)$$

For  $r < a$  (i.e., in  $N$ ) Eq. (2) reads

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - E_F \right) u = \epsilon u, \quad \left( \frac{\hbar^2}{2m} \nabla^2 + E_F \right) v = \epsilon v. \quad (7)$$

$$\frac{\alpha_1}{\alpha_2} = \frac{kk'h_l^{(1)}(k_1 a)h_l^{(1)}(k_2 a)j_{l-1}(ka)j_{l-1}(k'a) - k_1 k' h_l^{(1)}(k_2 a)h_{l-1}^{(1)}(k_1 a)j_{l-1}(k'a)j_l(ka) - kk_2 h_l^{(1)}(k_1 a)h_{l-1}^{(1)}(k_2 a)j_{l-1}(ka)j_l(k'a) + k_1 k_2 h_{l-1}^{(1)}(k_1 a)h_l^{(1)}(k_2 a)j_l(ka)j_l(k'a)}{kk'h_l^{(1)}(k_1 a)h_l^{(1)}(k_2 a)j_{l-1}(ka)j_{l-1}(k'a) - k_2 k' h_l^{(1)}(k_1 a)h_{l-1}^{(1)}(k_2 a)j_{l-1}(k'a)j_l(ka) - kk_1 h_l^{(1)}(k_2 a)h_{l-1}^{(1)}(k_1 a)j_{l-1}(ka)j_l(k'a) + k_1 k_2 h_{l-1}^{(1)}(k_1 a)h_l^{(1)}(k_2 a)j_l(ka)j_l(k'a)} \quad (10)$$

Equation (10) is an implicit transcendental equation determining the excitation energies  $\epsilon$ . Both sides of Eq. (10) are complex but can be shown to have absolute value unity. The equation can be solved numerically for each  $l$  and, hence, the density of states can be obtained numerically. The required input parameters are properties of the materials, namely,  $k_F a$  and  $\Delta_0/E_F$ , the ratio of the pair potential to the Fermi energy. For  $l=0$ , one obtains by the same procedure the condition

$$\frac{\alpha_1}{\alpha_2} = \frac{[k \cot(ka) - ik_1][k' \cot(k'a) - ik_2]}{[k \cot(ka) - ik_2][k' \cot(k'a) - ik_1]} \quad (11)$$

Figure 1 shows the dependence of the energies of the  $l=0$  states on particle size for  $\Delta_0/E_F=0.001$ , as obtained by solving Eq. (11) for various values of  $k_F a$ . The variation of the  $l=0$  state is of particular interest because, as will be seen, this state forms the bottom of "bands" in the density of states for  $\epsilon < \Delta_0$ . For small  $k_F a$ , the energy of the  $l=0$  bound state approaches  $\Delta_0$ . However, there always exists an  $l=0$  solution with  $\epsilon < \Delta_0$  no matter how small  $k_F a$  may be. This result is different from the analogous result for a square well potential in single-particle quantum mechanics, in which a bound state exists only for a sphere of radius greater than a minimum size. In the present case, however, the assumption of a discontinuous change in the gap parameter at  $r=a$  may be inaccurate for a small particle, and when this assumption is corrected, the results may be quite different. As the particle size increases,  $\epsilon/\Delta_0$  decreases for

Since the solutions must remain finite at the origin, the coefficients of the spherical Neumann function solutions must vanish and the most general solution is

$$\begin{pmatrix} u(\vec{r}) \\ v(\vec{r}) \end{pmatrix} = \sum_{lm} \begin{pmatrix} C_{lm} j_l(kr) \\ D_{lm} j_l(k'r) \end{pmatrix} Y_{lm}(\theta, \phi), \quad (8)$$

$j_l(x)$  being a spherical Bessel function, and  $C_{lm}$  and  $D_{lm}$  coefficients to be determined. The wave vectors  $k$  and  $k'$  are given by

$$k = (E_F + \epsilon)^{1/2} \left( \frac{2m}{\hbar^2} \right)^{1/2}, \quad (9)$$

$$k' = (E_F - \epsilon)^{1/2} \left( \frac{2m}{\hbar^2} \right)^{1/2}.$$

With Eqs. (5) and (8), we determine the unknown coefficients and allowed energies by matching boundary conditions at  $r=a$ , requiring that both the wave functions and their first derivatives be continuous at the surface. These requirements give four homogeneous conditions for the four unknown coefficients  $A$ ,  $B$ ,  $C$ , and  $D$  for fixed  $l$  and  $m$ . To have nontrivial coefficients, for  $\epsilon < \Delta_0$ , the following condition must hold valid for  $l \geq 1$ :

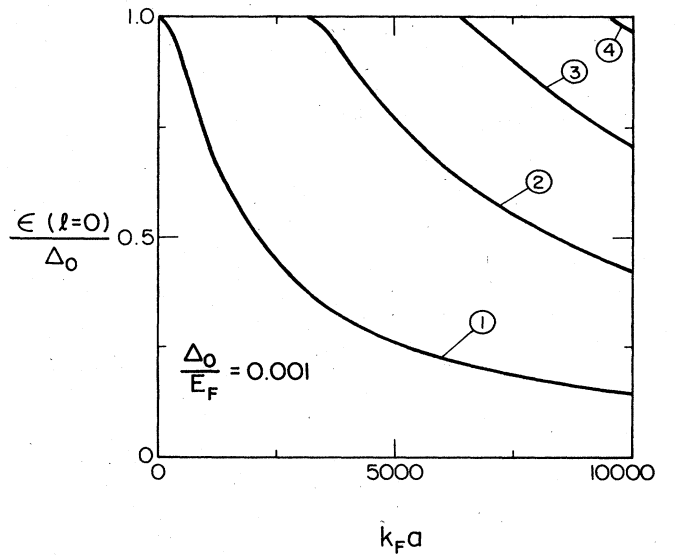


FIG. 1. Energy  $\epsilon$  of  $l=0$  states as a function of  $k_F a$  for  $\Delta_0/E_F=0.001$ . The figure shows the first four bands up to  $k_F a = 10000$ . Here,  $k_F$  is the Fermi wave number,  $a$  the particle radius,  $\Delta_0$  the superconductor pair potential, and  $E_F$  the Fermi energy.

the first  $l=0$  state, and for  $k_F a$  greater than a critical value of about 3200 (corresponding to about 3200 Å for Pb), a second  $l=0$  solution develops with energy very close to  $\Delta_0$ . Further increases in particle size give rise to third or higher  $l=0$  solutions, and the first  $l=0$  state moves to lower and lower energy. The positions of the  $l=0$  states prove to depend on  $k_F a$  and  $\Delta_0/E_F$  only in the combination  $(k_F a)(\Delta_0/E_F)$ .

To obtain a full excitation spectrum below the gap, we need to solve Eq. (10) for all  $l$  and determine the energies of the states with  $\epsilon < \Delta_0$ . This may be done numerically by repeated use of the recursion relations for spherical Bessel and Hankel functions to generate functions of higher order. We have carried out this procedure for  $k_F a = 300$  and  $k_F a = 450$  with  $\Delta_0/E_F = 0.01$ . This choice of parameters has a  $l=0$  state deep in the gap so that the distribution of higher  $l$  states can be clearly seen. (For  $k_F a = 300$  and  $\Delta_0/E_F = 0.001$ , the  $l=0$  state falls at  $\epsilon/\Delta_0 = 0.959$ ; there are approximately  $k_F a$  bound states with energies below  $\Delta_0$  distributing themselves between 0.959 and  $\epsilon/\Delta_0 = 1.00$ .) The total number of states in a given energy interval can be computed by counting the number of allowed  $l$  values and taking into account the  $(2l+1)$  degeneracy of each  $l$ . The resulting densities of states are shown as histograms in Figs. 2 and 3.

Figure 2 ( $k_F a = 300$ ) represents the case in which only a single band of allowed  $l$  values is present. The number of allowed  $l$  values in this first band is around  $k_F a$ , so that the total number of states  $N$  in the band is

$$N = \sum_{l=0}^{k_F a} (2l+1) \sim \int_0^{k_F a} (2l+1) dl \sim (k_F a)^2. \quad (12)$$

The lowest band is found always to be "complete" in the sense that the cutoff value of  $l$  is around  $k_F a$ . By using the

large argument expansions of  $j_l(x)$  and  $h_l(x)$  for  $l \ll k_F a$ , it can be shown that the form of Eq. (10) is identical for any small even  $l$ . The same is true for different small odd  $l$ 's. The equations obtained are, in fact, approximately the same for both cases (even and odd small  $l$ 's), and hence the energies of all small  $l$  states ( $l \ll k_F a$ ) are approximately the same. This results in the peak shown in Fig. 2 at the bottom of the band. For larger  $l$ 's, the energy difference between neighboring  $l$  states becomes larger, and the number of states per unit energy interval therefore decreases. From the pattern of Fig. 2, the density of states is large at energy near the bottom of the band, decreases as  $\epsilon/\Delta_0$  increases, and finally rises slightly as  $\epsilon$  approaches  $\Delta_0$ . Figure 3 shows a case ( $k_F a = 450$ ) such that the particle is large enough for the presence of a second band. The example shown here represents an "incomplete" second band in the sense that the particle size puts a cutoff other than  $k_F a$  on  $l$ . That is, the size is still not large enough for the second band to develop into a "complete" band. If the particle size is further increased, the second band develops fully and additional bands will start forming in similar fashion.

The existence of bound states in the gap will certainly affect physical quantities that depend on the density of states.<sup>6</sup> The heat capacity, for example, can be computed for a given density of states and for low enough temperatures. At such temperatures, we expect the dominant contributions to come from states in the gap. Tunneling measurements can also give the density of states,<sup>6,7</sup> and the presence of unusual structure in the density of states will produce corresponding structure in the  $I$ - $V$  characteristic for tunneling from a superconductor into a normal metal. Finally, the presence of states in the gap will produce additional far infrared absorption below the gap in the composite superconductor, arising from the influence of the localized states. The magnitude of the optical absorption so produced, however, will

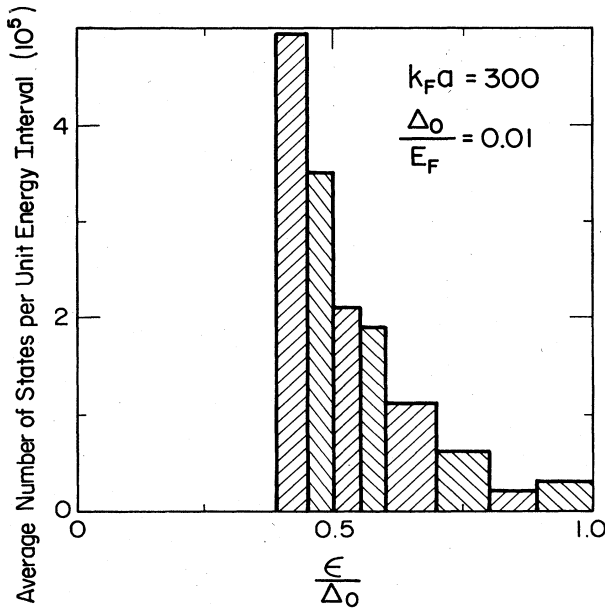


FIG. 2. Distribution of allowed energy states for a sphere of normal metal embedded in a superconductor. Only the first band is present in this case. The shaded area in each energy interval gives the number of states. Notation as in Fig. 1.

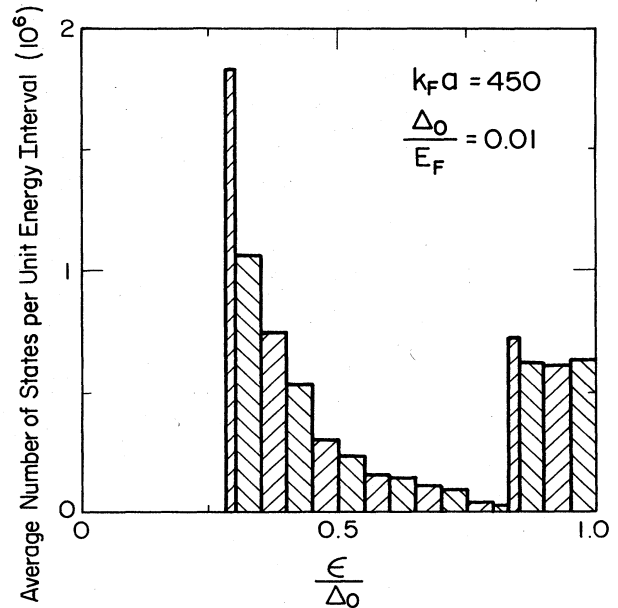


FIG. 3. Distribution of allowed energy states. In this case, the first band starts at  $\epsilon/\Delta_0 = 0.285$  and the second band enters at  $\epsilon/\Delta_0 = 0.830$ .

be difficult to determine because local (depolarization) field effects will cause the local electric field within the  $N$  grains to differ from that of the bulk superconductor.

In actual measurements, we are dealing with a system of many particles, possibly of different sizes, embedded in a host. If the interactions between these particles can be ignored, the structure in the  $I$ - $V$  characteristic, and other properties, will be a superposition of those of single particles with different sizes. The interaction range can be estimated from the wave functions calculated above. For  $r > a$ , the wave functions (5) are exponentially decaying functions with a decay length  $\xi$  given by the inverse of the imaginary part of the wave number (6):

$$\xi = \frac{\hbar v_F}{\Delta_0} \frac{1}{[1 - (\epsilon/\Delta_0)^2]^{1/2}}, \quad (13)$$

where we have used the approximation  $\Delta_0 \ll E_F$ , and  $v_F$  is the Fermi velocity. This length is of the order of the superconducting coherence length for states well within the gap but becomes arbitrarily large for states near the gap edge. The overlap between bound states could thus become signi-

ficant at fairly low concentrations of inclusions.

To summarize, we have shown that in a superconducting composite containing spherical normal-metal inclusions, there exist bound states with energies below the superconducting energy gap which are solutions to the Bogoliubov equations. These bound states form into bands which have a substantial nonzero density of states and which may influence various measurable properties of superconducting composites. We have not been able to prove uniqueness, i.e., to prove that there exist no other bound states besides the ones we have calculated. Nevertheless, we expect such bound states to influence the properties not only of superconductors containing spherical inclusions, but also other geometries (such as superconductors with disklike normal-metal inclusions), where the explicit calculation of the density of states may be more difficult.

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<sup>1</sup>P. G. de Gennes and D. Saint-James, *Phys. Lett.* **4**, 151 (1963); see also D. Saint-James, *J. Phys. (Paris)* **25**, 899 (1964).

<sup>2</sup>M. P. Zaitlin, *Solid State Commun.* **41**, 317 (1982); *Phys. Rev. B* **25**, 5729 (1982).

<sup>3</sup>See, for example, P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).

<sup>4</sup>See, for example, *Inhomogeneous Superconductors—1979*, edited by

D. U. Gubser, T. L. Francavilla, J. R. Leibowitz, and S. A. Wolf, *AIP Conf. Proc. No. 58* (AIP, New York, 1979).

<sup>5</sup>J. Garner and D. Stroud, *Phys. Rev. B* **28**, 2447 (1983).

<sup>6</sup>See, for example, M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975), pp. 36–59.

<sup>7</sup>W. L. McMillan, *Phys. Rev.* **175**, 559 (1968).