Understanding BCS Theory

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New calculation reveals that \( E \) is constant in a thin layer across the Fermi surface, befitting the definition of energy gap parameter, \( \Delta \) varies dramatically. The BCS self-consistent equation has a simple and exact solution, showing that the well-known ratio 3.5 must be replaced by 4. A simple formula is found to estimate energy gap from first principles with reasonable accuracy, useful to the current research into high \( T_c \) superconductivity.

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According to Bardeen, Schrieffer and Cooper (BCS) the superconducting energy gap is measured by the minimum value of \( E \). In the original approximation \( \Delta \) is a constant that equals the minimum value of \( E \). In the literature \( 2\Delta \) has become synonymous with energy gap. However, we find that \( E \) is constant in a thin layer across the Fermi surface, befitting the definition of energy gap parameter, \( \Delta \) varies dramatically. Since \( \Delta \) has played such a pivoting role in the current study of superconductivity, this matter appears to be serious enough to warrant attention.

While the BCS theory is deep and fundamental, specific results from this theory could be improved, because these results arise from approximations employed to ease mathematical difficulties. In particular the BCS self-consistent equation at \( T > 0 \) has a simple and exact solution which can be proved by simple inspection. This exact solution leads to a rather surprising conclusion that the well-known BCS ratio 3.5 must be replaced by 4.

Furthermore, we believe that the BCS theory has significant power of prediction which was unnoticed previously. We use the well-established method of iteration to solve the BCS self-consistent equation. We use the Mott-Jones assumption as our first approximation which can be proved by simple inspection. This exact solution leads to a rather surprising conclusion that \( \Delta(k + q) \approx \Delta(k) \) and \( E(k + q) \approx E(k) \), which lead through Eq. (1) to

\[
E = E_0 \tanh \left( \frac{E}{2k_B T} \right) \tag{2}
\]

where

\[
E_0 = \sum_q V(k, q) \tag{3}
\]

which is just the value of \( E \) at \( T = 0 \): \( \tanh(E/2k_B T) \to 1 \) when \( T \to 0 \) in Eq. (2).

The iteration method was not used by BCS to solve Eq. (1). Instead, they assumed \( V = \text{const.} \) in that equation, and converted the summation there into integration, giving

\[
\frac{1}{N(0) V} = \int_0^{\hbar \omega} \tanh \left( \frac{E}{2k_B T} \right) \frac{d\epsilon}{E} \tag{4}
\]

which is one of the key equations of the BCS theory, where \( N(0) \) is the density of state near the Fermi surface, \( \omega \) an unspecified phonon frequency. Further approximation was applied to find the well-known ratio \( 2\Delta/k_B T_c = 3.5 \). However, it is interesting that \( E \) from Eq. (2) is also the exact solution of Eq. (1), provided that \( \hbar \omega N(0) V = E_0 \); approximation is not necessary. This can be checked easily by simple inspection. Since \( \tanh(E/2k_B T) \leq E/2k_B T \), we find from Eq. (3) \( T \leq E_0/2k_B \) which means \( T_c = E_0/2k_B \) and therefore

\[
\frac{2E_0}{k_B T_c} = 4 \tag{5}
\]

which reduces to \( 2\Delta/k_B T_c = 4 \) when \( \epsilon = 0 \). Therefore the ratio 3.5 must be replaced by 4, regardless of whether Eq. (1) is solved via the original BCS approximation or
not. Indeed, the ratio 3.5 does not appear to have much advantage: we find from 23 superconducting elements in the literature that on average \( 2E_0/k_BT_c \) is 3.8 with standard deviation 0.597. The deviation is 0.627 from the ratio 4.0, compared with 0.672 from ratio 3.5.

Now we evaluate \( E_0 \) in Eq. (3) quantitatively. We have

\[
V(k, q) = \sum_{\ell=1}^{3} \frac{2\hbar \omega_l(q) M^2_l(k, q)}{[\hbar \omega_l(q)]^2 - [\epsilon(k + q) - \epsilon(k)]^2} \tag{6}
\]

where \( \omega_l \) is the phonon frequency, \( l \) identifies phonon branch (excluding transverse phonons, which do not interact with electrons in N-processes) \(^3\). Eq. (6) is slightly different from that in \(^2\) where phonon polarization is neglected. The matrix element

\[
\mathcal{M}_l(k, q) = \hat{q}_l \left[ \frac{\hbar N}{2M \omega_l(q)} \right]^{1/2} \int \psi^*_\ell(r) \delta V(r) \psi_\ell(r) \, dr \tag{7}
\]

measures the strength of electron-phonon interaction. Here \( \psi \) is the electron wave function, \( \sigma \) spin \( \uparrow \) or \( \downarrow \), \( M \) mass of an atom, \( N \) number of atoms in unit volume, \( r \) coordinates in real space, \( \Omega \) a volume surrounding the atom, \( \Gamma_0 \) its boundary, and \( \delta V(r) = V(r) - V(\Gamma_0) \), \( V \) being the potential field. We define \( \hat{q}_l \) as the \( l \)-th component of \( U \), \( U \) being the \( 3 \times 3 \) unitary matrix found when solving the classical equation of motion for the atom. Mott and Jones found matrix elements when \( \Omega_0 \) is the Wigner-Seitz cell \(^3\). We find Eq. (7) when \( V(\Gamma_0) \) is constant (this defines \( \Omega_0 \) in a natural manner).

We use free electron energy to evaluate Eq. (6). This means that the Fermi surface is spherical, our assumption when solving Eq. (6). As a result, the denominator of Eq. (6) becomes \( 4\epsilon_F c_l \delta^2_l = (\zeta + \cos \theta)^2 \), \( \epsilon_F = (\hbar^2/2m)k_F^2 \) is the Fermi energy (we study \( k \) near the Fermi surface), \( \epsilon_l = (\hbar^2/2m)|q|^2, \delta^2_l = (m/2)^2/\epsilon_F, v_l = \omega_l(q)/q \) the sound velocity. In the Debye approximation \( \delta_l = (Z/6)^{1/3} \Theta_D/\Theta_F \approx 10^{-3} \) in all superconducting metals, where \( Z \) is the valency, \( \Theta_D \) and \( \Theta_F \) the Debye and Fermi temperatures. It is apparent that \( V(k, q) \gg 0 \) (condition to have an energy gap) holds in Eq. (6) only when \( \zeta + \cos \theta \approx 0, \zeta = |q|/2k \), \( \theta \) being the angle between \( k \) and \( q \), so that \( |k|^2 + |q|^2 + 2|k||q| \cos \theta \approx |k|^2 \). Thus \( \epsilon(k + q) \approx \epsilon(k) \): electrons change momentum but not energy in scattering, the assumption by Mott and Jones \(^2\).

We substitute Eq. (6) into Eq. (3) and replace the summation over \( q \) with an integration over \( (4\pi/3)|k|_p^2 \) (volume of the first Brillouin zone), which exists in the sense of the Cauchy principal value (used by Kuper to verify the BCS theory) \(^2\) \(^3\), i.e. positive and negative contributions of \( V(k, q) \), if finite, are cancelled on a series of spherical surface, the singular point ignored. We are entitled to do so, because Eq. (6) is defined on a grid of \( k \) and \( q \), which may not be in precise combinations to let \( V(k, q) = \infty \). We can also avoid such combinations by suppressing a few phonons with little physical consequence. This principal value varies little among phonon branches, allowing us to use \( \sum q_l^2 = q^2/|U|^2 = |q|^2/|U|^2 \) (|U| unitary) to simplify the result. We use the expression for metal resistivity \(^3\) to calibrate \( \delta V \) in Eq. (6) and find

\[
E_0 = \frac{\hbar e^2}{k_B T_p} \eta n \rho v^2 \tag{8}
\]

where \( \epsilon \) and \( n \) are electron charge and density, respectively, \( k_B \) the Boltzmann constant, \( \rho \) the resistivity at temperature \( T_p \) (not necessarily low), \( v = k_B \Theta_D/hk_D \) the Debye sound velocity, \( k_D \) being the phonon cut-off wavenumber, and

\[
\eta = \frac{1}{\pi} \int_0^{(4\zeta)^{-1/3}} F^2(x) \frac{c^2 d\zeta}{1 - \zeta^2} \int_0^{(4\zeta)^{-1/3}} F^2(x) \zeta^3 d\zeta \approx 1 \tag{9}
\]

Here \( F(x) = 3(x \cos x - \sin x)/x^3 \) is the overlap integral function, \( x = 3.84\alpha^{1/3}Z^{1/3} \), \( \alpha = N\Theta_0/\Omega \) the fraction of \( \Omega_0 \) in a primitive cell, and \( \Omega \) the unit volume. We assume \( |q|/2k = \zeta < (4\zeta)^{-1/3} < 1 \), because Eq. (8) arises from a canonical transformation \(^3\) where operator commutation requires \( q \neq \pm 2k \).

\[\text{FIG. 1. (A) Extended solution of the BCS self-consistent equation, } E_k = E \text{ or } -\epsilon, \text{ when } -E < \epsilon < E \text{ or } \epsilon < -E, \text{ respectively. (B) } \Delta = (E^2 - \epsilon^2)^{1/2} \text{ which varies dramatically when } -E < \epsilon < E. \text{ } \Delta \approx E \text{ only when } \epsilon \approx 0.\]

It is apparent from Eqs. (3) and (8) that \( E \) and \( E_0 \) are constant. In contrast \( \Delta = (E^2 - \epsilon^2)^{1/2} \) varies dramatically when \(-E < \epsilon < E\). Beyond this range Eq. (6) does not have non-trivial solution in first iteration. This justifies the approach of BCS to integrate Eq. (6) only in a thin layer across the Fermi surface \(^3\). However Eq. (6) has an extended solution (Fig. 1)

\[
E_k = \begin{cases} E & : -E < \epsilon < E \\ -\epsilon & : \epsilon < -E \end{cases} \tag{10}
\]

where \( E_k = -\epsilon \) arises from the trivial solution \( \Delta = 0 \) of Eq. (6). The pair occupancy (Fig. 2)

\[
h_k = \frac{1}{2} \left( 1 - \frac{\epsilon}{E_k} \right) \tag{11}
\]
varies linearly when $-E < \epsilon < E$, but equals 1 when $\epsilon < -E$. This also justifies the BCS approach to integrate Eq. (8) only in a thin layer; otherwise we have $h_k > 1$ or $< 0$. The over-all probability of occupancy at $T > 0$ is given by $h_k(1 - 2f_k)$. Here

$$f_k = 1 / \left[1 + \exp \left(\frac{E_k}{k_B T}\right)\right]$$

is the probability of excitation which, unlike the Fermi-Dirac distribution, drops towards the interior of the Fermi sea (Fig. 2) where electrons are apparently more difficult to excite. Curves in Figs. 1 and 2 all have a kink at $\epsilon = -E$, which is likely to be smoothed out after further iterations.

In conclusion the BCS theory has significant power of prediction when evaluated via the well-established method of iteration. This could be of current interest, because some novel theories for high $T_c$ superconductors resemble the BCS theory quite closely [8, 9]. These theories are often phenomenological, but nonetheless detailed enough for one to evaluate the matrix element [9]. Therefore a formula similar to Eq. (8) might arise, which could be useful when comparing the theory with experiments.

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