Mechanisms for the superconducting state from a one-particle derivation of the BCS gap equations.

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The BCS results for the superconducting gap $\Delta$ and $T_C$ are obtained from a one-particle model. Superconductivity appears when the electronic energy gains of the band structure surpass the energy needed for atomic vibrations or magnetic moment oscillations. The vibration/oscillation amplitudes determine the superconducting gap, and the Fermi surface is important for the $q$-dependence. This permits for complementary interpretations of the parameters for superconductivity and modeling of density-of-state effects. It also makes the superconducting mechanism less exotic.

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I. INTRODUCTION.

The Bardeen-Cooper-Schrieffer (BCS) theory is the basis for a microscopic understanding of superconductivity \[1\]. It has, together with band theory, been successful for an understanding of the correlation between the superconducting (SC) $T_C$ and material parameters like phonon frequency, electron-phonon coupling, $\lambda$, and the electronic density-of-states (DOS) at the Fermi energy, $N(E_F)$ \[2, 3\]. The good understanding of the “gap ratio”, the ratio between the SC gap, $\Delta$, at $T=0$ and $k_BT_C$, is another example of the success of the BCS theory. The observation of isotope effects are often in good agreement with the predictions from BCS, which confirms the dependence on lattice stiffness. Although the variations of $T_C$ with pressure can be complex they are usually understood from lattice hardening and the behavior of the matrix elements for electron-phonon coupling \[4\]. However, there are complications \[5\]: Competition with magnetism and electron-electron correlation is reducing $T_C$. High-$T_C$ cuprates are not understood, since their $\lambda$s are not very large. The isotope effect is sometimes very complex, even in elementary metals. Other shortcomings might be that the many-body BCS formula does not allow for an intuitive comprehension of the superconducting mechanism and there is no direct explanation of the Meissner effect \[6\].

Here is presented a simple one-electron like derivation of the BCS gap equation. Many assumptions are the same as in BCS, but some interpretations are different. The many-body formulation of BCS gap equation is based on exchange of virtual phonons and the SC state appears ”when the energy difference between the electrons involved is less than the phonon energy” \[4\]. In the present one-particle derivation the gain in electronic energy is caused by dynamic changes of the band structure. A one-particle band will have a gap because of a periodic potential perturbation, as in the appearance of a gap for semiconductors \[6\]. A spontaneous lattice vibration creates the perturbation and the electronic states at $\vec{k}$ and $-\vec{k}$ are affected equally (but there is no exchange of phonons). Also states on nearby $k$-points are involved as can be found from the band dispersion. Only phonons which modifies electronic states around the Fermi surface (FS) are of interest, since changes of the bands far from the Fermi energy ($E_F$) make no change in the total kinetic energy. This puts a constraint on the $q$-vectors of the phonons. The difference between the present derivation and original BCS is that the energy gain is calculated from all one-particle states near $E_F$, and the SC state appears as soon as this gain is larger than the vibrational energy. This allows for further insight to the mechanism of SC pairing, since the parameters can be understood in a simple way from the band structure.

II. ONE-ELECTRON MODEL AT $T=0$.

Phonons and spin fluctuations in the normal (non-SC) state are excited thermally following the thermal Bose-Einstein occupation, $g(T, \omega)$, of the phonon- or spin wave DOS, $F(\omega)$ or $F_m(\omega)$, respectively. The averaged atomic displacement amplitude for phonons, $u$, can be calculated as function of $T$ \[6, 7\]. Approximate results for Debye like spectra make $u^2 \sim 3\hbar \omega D/2K$ at low $T$ and $3k_BT/K$ at high $T$, where $K$ is an effective force constant, which can be calculated from $K = M\omega^2 = d^2E/du^2$ ($E$ is the total energy), where $M_A$ is an atomic mass. The corresponding relations for averaged fluctuation amplitudes of the magnetic moments, $m$, are the same, but without the polarization factor 3 and with replacement of $K$ with $K_m = d^2E/dm^2$, which is constant for harmonic dependence of the total energy as function of $m$ \[8\]. Thus, for the normal state, one can estimate $u$ and $m$ at any given $T$ from these relations, if the ‘force’ factors $K$ and $K_m$ can be calculated or are known from experiment.

Phonons and spin waves have an influence on the electronic state and its DOS \[8\], and may cause a pseudo gap close to $E_F$ in the normal state of high-$T_C$ copper oxides \[10\]. Phonons make a periodic potential perturbation along a chain of atoms,

$$V(x) = V_0 e^{-ix\cdot\vec{q}}$$

(1)

if the phonon propagation is along $\vec{x}$ with wave vector $\vec{q}$ \[6, 10\]. A spin wave makes an analogous perturbation.
within the spin polarized part of the potential. The potentials for opposite spins are the same except for a phase shift of \( \pi \). The result is an anti-ferromagnetic (AFM) spin configuration with wave length given by \( 2\pi/q \). Phonons and spin waves can be considered separately, but several works have shown that an important spin-phonon coupling (SPC) exists in the cuprates, which also can explain many of their unusual properties \([11,12,13,14]\).

The following development is based on phonon excitations, but later it will be seen how things will change with spin waves and SPC.

At very low \( T \) there are practically no occupation of phonons. The Fermi-Dirac occupation \( f(\epsilon,T) = 1/(e^{\epsilon/k_B T} + 1) \) is essentially a step function at \( E_F \) (here \( E_F \) is put at zero). The simple nearly free-electron (NFE) model, with the periodic potential, leads to a gap \( E_g = 2V_0 \) in the free electron band at a new ”zone-boundary” \( k = G/2 \[8,10]\), and the general band dispersion as function of \( k \) is

\[
\varepsilon = \frac{1}{2}(k^2 + (k - G)^2 \pm \sqrt{(k^2 - (k - G)^2)^2 + 4V_0^2})
\]

If the gap appears at \( E_F \) for this particular value of \( k \) there is a gain in kinetic energy, \( E \).

For band energies near the gap it is convenient to express the \( k \)-dispersion in terms of a linear \( \epsilon \) measured from \( E_F = 0 \), so that \( \epsilon = const. \cdot k \), where \( k \) is measured from the zone boundary at \( G/2 \). The approximation of a linear \( \epsilon \) as function of \( k \) is valid for \( \epsilon \ll W \), the band width from the bottom of the band to \( E_F \). Thus,

\[
\varepsilon = \pm \sqrt{\epsilon^2 + V_0^2}
\]

The normal free electron dispersion, \( \varepsilon = \epsilon \), is recovered for \( V_0 = 0 \), and \( N(\epsilon) = N|d\epsilon/d\epsilon| \), becomes constant and equal to \( N \). The gapped \( \tilde{N} \) is zero for energies within \( \pm V_0 \) around \( E_F \).

The electron-phonon coupling \( \lambda \) will enhance the electronic DOS for energies \( \pm \hbar \omega \) around \( E_F \), where it can be written \( N M^2/K [6] \). The matrix element \( M \) is zero outside the interval \( \pm \hbar \omega \). Inside the interval it can be evaluated as \( \langle \Psi^*(E_F,r) dV(r)/d\epsilon \Psi(E_F,r) \rangle \), which is the first order change in energy caused by the perturbation \( dV(r) \) for \( du \rightarrow 0 \). For a finite value of \( u \) the change in energy will be finite and equal to the gap \( V_0 \), since \( V_0/u \) is constant for harmonic vibrations. Thus, instead of calculating \( M \) as a matrix element it is possible to take the value directly from the band gap, and \( M \) can be written \( V_0/u \) for energies close to \( E_F \). The separate values of \( V_0 \) and \( u \) are important variables, and later it can be verified that the band gap \( V_0 \) is linked to the SC gap \( \Delta \).

The energy of an atomic oscillation consists of elastic and kinetic contributions, but its time dependence, \( 2U(t) = Ku^2\cos^2(\omega t) + M_0\omega^2\sin^2(\omega t) \), is a constant in the harmonic approximation. For \( t = 0 \) all the energy is of elastic origin so the cost in energy to generate an atomic vibration can be written \( U = \frac{1}{2}Ku^2 \), where \( u \) refers to the maximal atomic displacement. Totally there will be a gain in energy if \( |U| \leq |E| \). The system will spontaneously generate phonons in such a case, and this is the condition for the SC state. Both \( U \) and \( E \) are the energies per unit cell for which the DOS of the normal state is \( N \). The condition \( |U| = |E| \) is written

\[
\frac{1}{2}Ku^2 = \int_{-\hbar\omega}^{0} \epsilon(N(\epsilon) - \tilde{N}(\epsilon))d\epsilon
\]

for \( T = 0 \), where \( \tilde{N}(\epsilon) \) is the DOS with the gap and \( N(\epsilon) \), the DOS of the normal state, is assumed constant within \( \hbar \omega \) around \( E_F \). The integration is only to \( \hbar \omega \) since \( \lambda \), which will appear later in the equation, is zero for energies larger than \( \pm \hbar \omega \).

With a substitution \( \epsilon^2 = \epsilon^2 + \Delta^2 \) we obtain \( \tilde{N} = N\epsilon/\sqrt{\epsilon^2 - V_0^2} \) and,

\[
\frac{1}{2}Ku^2 = \int_{-\hbar\omega}^{0} N e d\epsilon - \int_{-\hbar\omega}^{-\Delta} \frac{N\epsilon^2}{\sqrt{\epsilon^2 - V_0^2}} d\epsilon
\]

With \( \Delta \) replacing \( V_0 \) this gives

\[
Ku^2 = N(\hbar \omega)^2 + 2N\Delta^2 \ln(2\hbar \omega/\Delta) - N(\hbar \omega)^2
\]

and

\[
\Delta = 2\hbar \omega e^{-1/\lambda}
\]

since \( \lambda = N\Delta^2/Ku^2 \[8 \] \) when the gap at \( T = 0 \) is \( \Delta \).

Therefore, on one hand it can be argued that \( V_0 \) has to be equal to \( \Delta \), the SC gap, since this derivation then reproduces the BCS result. But the equivalence between \( \Delta \) and \( V_0 \) can also be understood from the fact that \( V_0 \) is a measurable band gap in the superconductor. Further, a constant \( \lambda \) implies that the phonon amplitude \( u \) is proportional to \( \Delta \), so that \( u \) is largest at \( T = 0 \), and \( u \rightarrow 0 \) when \( \Delta \rightarrow 0 \) at \( T \rightarrow T_C \).

The integral and the interpretations look a bit different from BCS \[11,12\], but the final result for \( \Delta \) is the same. Any system will generate phonons as soon as the gain in electronic energy generated by the phonon is larger than the energy needed for the phonon. In reality other more subtle effects, electron-electron correlation energy and potential terms will be added to the energy costs and those terms will prevent a SC gap in many systems.

A numerical solution needs some care for the diverging part of \( \tilde{N} \), but models with non-constant \( N \) and with larger ratios of \( \Delta/\hbar \omega \) can be studied.

**III. THE LIMIT \( \Delta \rightarrow 0. \)**

The model for finding \( T_C \) is obtained from eq. \[4 \] but with the Fermi-Dirac function as the \( T \)-dependent weight factor for \( \tilde{N}(\epsilon) \) and \( N(\epsilon) \), and with the integration in
the interval \([-\hbar \omega, \hbar \omega]\). Thus, at \(T_C\) it is required that the phonon energy is equal to the difference between the kinetic energy of the gapped and the normal electronic DOS, but with the constraint that \(\Delta \to 0\). This is solved numerically from

\[ Ku^2 \approx NI(h\omega, \Delta, T) \]  

(8)

or

\[ 1/\lambda \approx I(h\omega, \Delta, T)/\Delta^2 \]

(9)

where

\[ I = \int_{-h\omega}^{h\omega} e f de - \int_{-h\omega}^{h\omega'} e|e|/\sqrt{(e^2 - \Delta^2)}f de \]

(10)

for \(\Delta \to 0\). The ‘ in the first integral means that the energies where \(|e| < \Delta\) are excluded. A factor of \(\Delta^2\) is extracted from the right hand side of eq. (8) and combined with \(N\) and \(Ku^2\) on the left hand side to give \(\lambda\) as before.

The original BCS expression for \(T_C\), which is derived from

\[ 1/gN = \int_0^{h\omega} de/tanh(e/2k_B T) \]

(11)

(where \(gN\) is the coupling constant \([13]\)) is independent of \(\Delta\). Here, we solve this equation numerically with the same precision as the one-particle expression for very small \(\Delta\). The results, shown in Fig. 1, tend towards the analytic solution of eq. (11), i.e., the numerical BCS result for \(h\omega=0.1\) eV. The thin and broken lines show the corresponding result from eqs. (9) for 5 different \(\Delta\)'s (0.5, 1, 2, 4 and 8 meV). The result for the smallest \(\Delta\) is indistinguishable from the BCS result over this temperature range.

IV. SPIN-PHONON COUPLING.

As was mentioned above, typical atomic displacements and magnetic moments from phonons and spin waves in the normal state can be determined from thermal excitations via the effective force constants \(K\) and \(K_m\). Magnetic moments, with a tendency for a pseudogap in the DOS, are driven by thermal excitations, but the left hand side of eq. (5) is larger than the right hand side. However, the situation might be reversed at lower \(T\), when \(m\) is supported by the SC gap. In the SC state \(u\) and \(m\) are proportional to the SC gap; \(u = \sqrt{(N/K}\lambda)\Delta\) and \(m = \sqrt{(N/K_m}\lambda_{sf})\Delta\), respectively. Increasing amplitudes of \(u\) in superconductors at low \(T\) should be measurable, but their values are small in conventional superconductors. For example, in Nb, with \(\lambda \approx 1.2\), \(N \approx 0.7(eVatonspin)^{-1}\), \(K \approx 6\) eV/\(\AA^2\) \([2]\) and \(\Delta \approx 3\) meV, \(u/a_0\) (\(a_0\) the lattice constant) will be less than one order of magnitude smaller than \(u\) from zero-point motion. The complex FS of d-band superconductors implies a multitude of active q-vectors. Lithium, which under pressure can have a high \(T_C\) and a simple free electron FS, should be more promising for detection of \(u\) for a few q-vectors.

Copper oxides with high \(T_C\) and relatively simple 2-dimensional FS, should have sizable amplitudes of the magnetic moments (assuming that spin fluctuations are responsible for superconductivity), and simple q-dependence. Both the superconducting gap and the pseudogap for \(T > T_C\) are sensitive to spin waves (or phonons) with the same q-vectors. For instance, fluctuations in form of spin waves and SPC in the cuprates are thermally excited at large \(T\) and contribute to a pseudogap for \(T \leq T^*\) \([12]\). The fact that \(m\) (or \(u\)) is proportional to \(\Delta\) shows that these magnetic fluctuations will reappear.
in the SC state and become stronger as \( T \to 0 \). This is in line with the observations of increasing peak intensity of spin waves at or below \( T_C \) in experiments of inelastic neutron scattering on underdoped YBCO [17]. Theoretical estimates of \( m \), in the range 0.1-0.2 \( \mu_B/Cu \) in the SC state and in the normal state at large \( T \), are not very precise because of uncertainties in density functional calculations. However, the \( q \)-dependence is not expected to change as \( T \) goes below \( T_C \), so the results for spin excitations calculated for the normal state in ref. [18] can be carried over to the SC state.

The standard propositions for higher \( T_C \) is to increase \( \omega \) (through isotope shifts) and/or \( \lambda \) (through higher absolute value of the DOS [19]). It is seen that \( \lambda \) can remain constant and lead to larger \( \Delta \) if \( m \) (or \( u \)) is increased. This might be achieved through anharmonicity so the maximum \( m \) are increased without large changes of \( K_m \). Another possibility is to modify the way \( \omega \) (through isotope shifts) and/or \( \lambda \) (through higher absolute value of the DOS [19]) can be carried over to the SC state.

V. FIELD DEPENDENCE.

From the discussion about selective \( q \)-dependence there is a possible reason to why a weak magnetic field is expelled in a superconductor. As mentioned, one particular phonon, \( \vec{q}_i \), is responsible for the gap on the para-

\[ E_0 = 2(f(-\Delta, T)(-\Delta) + f(\Delta, T)(\Delta)) \]  

A field puts the states asymmetrically around \( E_F \) and the kinetic energy for the two spin states ("up" or "down") will be

\[ E_H^\pm = f(-\Delta \pm h, T)(-\Delta \pm h) + f(\Delta \pm h, T)(\Delta \pm h) \]  

where \( h = \mu_B H \). The result is that \( E_0 < E_H^- + E_H^+ \) for most \( T > 0 \) (but for \( k_B T \) and \( h \) being small in comparison to \( \Delta \)), i.e., the symmetric state with no field has the lowest energy.

The increasing kinetic energy can also be demonstrated for the approximation of a constant DOS by adding and subtracting the field \( h \) in the Fermi-Dirac function. Figure 2 shows the energy difference, \( D(h, T) \), of kinetic energy for the gapped superconducting DOS with and without field, which is calculated as:

\[ \text{FIG. 2: The full, broken and semi-broken lines show the values of the energy integral } D(h, T) \text{ (see eq. 13) as function of } h \text{ for low, intermediate, and high temperature, respectively. The values are normalized to 1 for } h = 0. \text{ These calculations are made with } \Delta = 5mRy \text{ and } h\omega = 50mRy. \]
\[ D(h, T) = \int_{-\hbar \omega'}^{\hbar \omega'} e^{\tilde{N}(e)(f(e+h, T)+f(e-h, T)−2f(e, T))} de \] (15)

when \( h < \Delta \) for low and high \( T \) (\( \approx \Delta \)). The increase of \( D \) as function of the field \( h \) is because the thermal occupation can be made more efficiently if \( E_F \) is closer to the DOS peak (on \( \tilde{N} \)) above the gap in the "majority" and closer to the DOS peak below the gap in the "minority" states, than if \( E_F \) is in the middle of the gap. Thus, the gapped state with \( \mu_B H = 0 \) has the lowest kinetic energy. This state will be preferred by the system as long as screening of an external field can be made through superconducting currents. The model shows that the minimum at \( h = 0 \) is less profound for large \( T \), or when \( k_B T \) exceeds about \( 5\Delta \). The feedback from the transfer of minority to majority spin states and effects of a non-constant DOS are not included in the model.

VI. CONCLUSION.

The BCS formulas for \( \Delta \) at \( T = 0 \) and \( T_C \) at \( \Delta = 0 \) are derived directly from the one-particle DOS functions of the gapped and normal state band structures. This allows for an easy comprehension and further interpretations of the SC mechanism. While phonons and/or spin waves are excited thermally in the normal state, they are generated via the electronic band gap in the superconducting state. Atomic displacements of harmonic vibrations and magnetic moments of harmonic spin fluctuations are proportional to the SC gap. Since the SC gap is closely related to the gap of the perturbed band structure, it will be interesting to consider DOS functions in materials with impurities and other defects via supercell calculations.

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