A Possible Mechanism of Quartet Condensation for Room Temperature Superconductivity

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We seek a possible room temperature superconductivity beyond the Cooper pairing mechanism through quartet condensation. A quartet consists of two kinds of electron pairs of a spin singlet with total momenta zero belonging to two different bands. We calculate the ground state energy, the energy gap, the excited state energy and the transition temperature by extending the BCS theory for pairing condensation to quartet condensation for a possible room temperature transition to superconductivity. We do this for a two-band electron system rather than for the ordinary superconductor of a single-band electron, because the effective interaction is larger in this case than in the case of the pairing interaction. We conjecture that the idea of the quartet condensation may be applicable to superfluid \textsuperscript{4}He.

\section{Introduction}

We have investigated the superconductivity of MgB\textsubscript{2},\textsuperscript{1} where we consider an effective two-band electron system by adopting the order parameter $\Delta_\parallel$ in the (B\textsubscript{2})-plane and the perpendicular order parameter $\Delta_\perp$ transversing to the Mg layer. Akimitsu\textsuperscript{2} attempted to obtain a transition temperature higher than that of MgB\textsubscript{2} by replacing the metallic layer of Mg with other kinds of metals, but had no success. One of the authors (T. S.) proposed to him the quartet condensation mechanism after hearing his talk on this topic without suggesting to him a new synthesis of alloys. The next day we heard a talk by Miyake\textsuperscript{4} concerning the quartet superfluidity of a fermionic atomic gas and later obtained a preprint\textsuperscript{5} of his paper with Kamei after one week.

We read Ref. 5) and grasped a clear understanding of how the quartet condensation appears in a superconducting two-band electron system. They mainly treated the extreme dilute gas case by using a Feynman-type variational principle, but they hinted at a prescription for obtaining a condensed quartet state in terms of the BCS theory at the end of their paper. The transition temperature of quartet condensation in nuclear matter has been discussed by Röpke et al.,\textsuperscript{8} who found that a transition from the normal state to four particle condensation can occur, but it is overwhelmed by weak coupling Cooper pairing at sufficiently high density in the case of nuclear matter existing in the form of a strongly coupled quantum liquid. They obtained this result by investigating the pole of a four-particle Green function. A model system in a large spin $S$ system was investigated by Stepanenko and Gunn.\textsuperscript{9} They demonstrated that the instability of the Fermi sea with respect to the condensation of a bound baryonic composition containing $2S + 1$ atoms and the gap in the excitation
spectrum can be calculated using a BCS-type variational method. The problem of a one-dimensional system has been discussed by Schlottmann,\(^{10}\) who found that a one-dimensional \(N\)-component Fermi gas with repulsive and attractive \(\delta\)-function interactions can be solved exactly and behaves like a Luttinger liquid in the repulsive case (while there appear spin gaps in the excitation spectrum and the ground state in the absence of an external field) and consists of bound states of \(N\) particles in the attractive case. Wu\(^{11}\) studied competing orders in one-dimensional spin \(3/2\) fermion systems with a constant potential and found that a gapless Luttinger liquid phase and two spin gap phases can be identified at incommensurate filling, and a four-fermion clustering (quartet) instability dominates in the one spin gap phase, while the other spin gap phase is characterized by a single Cooper pairing in the purely repulsive interaction regime.

In this paper, we treat a quartet condensation by the BCS method\(^7\) and apply it to a two-band electron superconductor. We obtain various physical properties and suggest the possibility of synthesizing a thin layer made of an insulator which ejects two electrons into conductive superconducting layers. We conjecture that the idea of quartet condensation can be applied to superfluid \(^4\)He.

§2. The ground state and the energy gap of a quartet

We begin by briefly summarizing Ref. 5\). The creation operator of a quartet with 0 total momentum is given by

\[
\alpha_0^\dagger = \sum_{k_1} \cdots \sum_{k_4} \delta(k_1 + k_2 + k_3 + k_4) \Phi(k_1, k_2, k_3, k_4) a_{k_1,\sigma_1}^A a_{k_2,\sigma_2}^A a_{k_3,\sigma_3}^B a_{k_4,\sigma_4}^B, \tag{1}
\]

where \(a_{k,\sigma}^I\) is the creation operator of the one-particle state whose wave function is of the form \(\phi^I(k, \sigma)\) belonging to the band \(I = A\) or \(B\). The wave function \(\Phi\) is given by a product of one-particle states:

\[
\Phi(k_1^A, k_2^A, k_3^B, k_4^B) = \prod_{i=1,2,I=A,B} \phi^I(k_i, \sigma_i). \tag{2}
\]

Then, the many-body quartet condensed state \(|\Psi_{QC}\rangle\) can be written

\[
|\Psi_{QC}\rangle = P_{N/4} \exp \left( \sqrt{\frac{N}{4}} \alpha_0^\dagger \right) |\text{vac}\rangle, \tag{3}
\]

where \(N\) is the total number of fermions, the projection operator \(P_{N/4}\) projects out the \(N/4\)-quartet state, and \(|\text{vac}\rangle\) denotes the vacuum. The state (3) is equivalent to

\[
|\Psi_{QC}\rangle = P_{N/4} \prod_{\{k_1,k_2,k_3,k_4\}} \prod_{i=1,2,I=A,B} \left( u^I(\{k_i\}) + v^I(\{k_i\}) a_{k_1,\sigma_1}^A a_{k_2,\sigma_2}^A a_{k_3,\sigma_3}^B a_{k_4,\sigma_4}^B \right) |\text{vac}\rangle, \tag{4}
\]

where the factor \(\delta(k_1 + k_2 + k_3 + k_4)\) has been omitted from the product \(\prod_{i=1,2,I=A,B}^\dagger\), and the relation \(\phi^I(k) = u^I(\{k_i\})/u^I(\{k_i\})\) and the normalization condition \(|u^I(\{k_i\})|^2 + |v^I(\{k_i\})|^2 = 1\) must be satisfied.
The Hamiltonian of our system is given by

\[ H = H_0 + H_1, \]  

(5)

where

\[ H_0 = \sum_k \epsilon_k a_k^\dagger a_k, \]  

(6)

\[ H_1 = \frac{1}{2} \sum_{p,p',k,\sigma,k',\sigma'} V_{k,p+k\sigma}^I a_{p+k\sigma}^I a_{p'+k\sigma'}^\dagger a_{p'\sigma'}^\dagger a_{p\sigma}. \]  

(7)

As in the BCS theory, we assume the following reduced model quartet Hamiltonian, which connects the part with net momentum 0 in the original Hamiltonian (5) by introducing the quartet creation operator \( \alpha_{k,p}^\dagger \) as

\[ \alpha_{k,p}^\dagger = a_k^A \dagger a_{-k}^A \dagger a_p^B \dagger a_{-p}^B \dagger, \]  

(8)

\[ H_{\text{red}} = H'_0 + H'_1, \]  

(9)

where

\[ H'_0 = \sum_{k^A > k_F^A, p^B > p_F^B} (\epsilon_{k^A} + \epsilon_{p^B}) \alpha_{k^A,p^B}^\dagger \alpha_{k^A,p^B} + 2 \sum_{k^A < k_F^A, p^B < p_F^B} (|\epsilon_{k^A}| + |\epsilon_{p^B}|) \alpha_{k^A,p^B}^\dagger \alpha_{k^A,p^B}, \]  

(10a)

and

\[ H'_1 = \sum_{(k^A,p^B), (k'^A,p'^B)} V_{(k^A,p^B), (k'^A,p'^B)} \alpha_{k^A,p^B}^\dagger \alpha_{k'^A,p'^B} = \sum_{K,K'} V_{K,K'} \alpha_{K}^\dagger \alpha_{K'}. \]  

(10b)

Hereafter, we regroup the combination of indices \((k^A,p^B)\) into the single index \(K\), as shown in the last equality of Eq. (10b), and we also write \( \alpha_{k,p}^A,B^\dagger \) as \( \alpha_{k}^A,B^\dagger \). Here, in the sum over \(K\), we take the sum of the momenta \(k^A\) from the pair of electron momenta \(k^A\) and \(-k^A\) and the momenta \(p^B\) from the pair of electron momenta \(p^B\) and \(-p^B\) belonging to each respective band, \(A\) and \(B\). Hereafter, a summation over \(K\) is understood to be over the momenta \(k\) and \(p\) from pairs \((k, -k)\) and \((p, -p)\). We approximate the attractive interaction \(V_{K,K'}\) as

\[ V_{K,K'} = \begin{cases} -U, & \epsilon_F^A - \Delta E < \epsilon_k^A < \epsilon_F^A + \Delta E, \ 
\epsilon_F^B - \Delta E < \epsilon_k^B < \epsilon_F^B + \Delta E \\
0, & \text{otherwise} \end{cases} \]  

(11)

where \(\Delta E\) is the energy width around \(\epsilon_F\) and is of the order of the Debye energy or the Fermi energy (depending on the interaction scheme), and is taken to be the same for the two bands. We assume that interactions are the same for an \(A\) band pair and a \(B\) band pair, and therefore we set \(u(\{k_l\}) = u_K\) and \(v(\{k_l\}) = v_K\).

The ground state energy \(E_0\) is the expectation value of \(H\) with respect to \(|\Psi_{QC}\rangle\), given in (4):

\[ E_0 = \langle KE \rangle + \langle PE \rangle, \]  

(12)
where

\[ \langle KE \rangle = 2 \sum_{k,p} (\epsilon^A_k + \epsilon^B_k) |v_K|^2, \quad (13) \]

and

\[ \langle PE \rangle = -4 \sum_{K,K'} U(u_K v_K)(u_{K'} v_{K'}). \quad (14) \]

We next carry out a variational calculation of \( E_0 \) with respect to \( v_K \) under the condition \( |u_K|^2 + |v_K|^2 = 1 \). This yields

\[ \frac{\partial E_0}{\partial v_K} = 0 = 2(\epsilon^A_k + \epsilon^B_k)v_K - 2U \left(u_K - \frac{v_K^2}{u_K}\right) \sum_{K'} u_{K'} v_{K'}. \quad (15) \]

Then, from Eq. (15), we find

\[ (\epsilon^A_k + \epsilon^B_k)v_K = \varepsilon_0 \left(u_K - \frac{v_K^2}{u_K}\right), \quad (16) \]

where \( \varepsilon_0 \) is defined as the energy gap

\[ \varepsilon_0 = U \sum_{k',p'} u_{K'} v_{K'}. \quad (17) \]

Hereafter, we assume the kinetic energies \( \epsilon^A_k \) and \( \epsilon^B_p \) of the respective bands to be the same, i.e. \( \epsilon^A_k = \epsilon^B_p = \epsilon_k \). Then, if we solve Eq. (16), we obtain the following solution:

\[ u_K^2 = \frac{1}{2} \left( 1 + \frac{\epsilon_k}{\sqrt{\epsilon_k^2 + \varepsilon_0^2}} \right), \quad (18a) \]

and

\[ v_K^2 = \frac{1}{2} \left( 1 - \frac{\epsilon_k}{\sqrt{\epsilon_k^2 + \varepsilon_0^2}} \right). \quad (18b) \]

The gap equation (17) can be rewritten with the help of Eqs. (18a) and (18b) as

\[ \varepsilon_0 = U \sum_k \frac{\varepsilon_0}{\sqrt{\epsilon_k^2 + \varepsilon_0^2}}, \quad (19) \]

which is solved through the integral

\[ 1 = U \rho_{CQ} \int_{-\Delta E}^{\Delta E} \frac{1}{\sqrt{\epsilon_k^2 + \varepsilon_0^2}} d\epsilon_k, \quad (20) \]

by assuming the energy range to be that given in Eq. (11). From this, we obtain \( \varepsilon_0 \) as

\[ \varepsilon_0 = 2\Delta E \exp \left(-\frac{1}{\rho_{CQ}U}\right), \quad (21) \]
where $\rho_{\text{CQ}}$ is the density of states of the condensed quartet state at the fermi energy $\epsilon_F$.

The ground state energy $E_0$ is calculated as

$$E_0 = \sum_k 2\epsilon_k v_K^2 - U \sum_{K,K'} u_K v_{K'} u_{K'} v_K,$$

$$= 4 \sum_k \left( \epsilon_k - \frac{\epsilon_k}{\sqrt{\epsilon_k^2 + \epsilon_0^2}} \right) \frac{1}{4} - \frac{\epsilon_0^2}{2U},$$

$$= -\frac{1}{2} \rho_{\text{CQ}} \epsilon_0^2.$$  (24)

The density of states $\rho_{\text{CQ}}$ is equal to the density of states $\rho_F$ of an ordinary conduction electron Fermi sphere, because there are 2 (spin) $\times$ 2 (band) (=4) degrees of freedom, but this is divided by the number of constituents of a quartet, 4. The magnitude of the quartet interaction $U$ via a phonon or a direct interaction is twice the pairing interaction, $V_{\text{pair}}$, because each electron can interact with its partner in the same band, or with an electron in another band, as shown in Fig. 1, where the fermi momentum and energy are the same for each band, and therefore an electron in one band can crossover into the other band. Therefore the magnitude of the effective interaction $\rho_{\text{CQ}}U$ is twice the Cooper pair effective interaction if $U$ is $2V_{\text{pair}}$.

Thus the magnitude of the energy gap $\epsilon_0$ as well as the ground state energy $E_0$ is larger in absolute magnitude than in the Cooper pairing case if the quartet interaction magnitude $U$ is assumed to be twice the pairing interaction $V_{\text{pair}}$. That the quartet ground state energy is lower than the pairing ground state energy is also guaranteed by the theorem proved by Nagaoka and Usui,\textsuperscript{6) which asserts that a more symmetric ground state wave function gives a lower ground state energy.

§3. Excited state, free energy and transition temperature

Proceeding as in BCS theory,\textsuperscript{7) the excited state wave function is given by

$$|\Psi_e\rangle = \prod_K (u_K + v_K \alpha^+_K \prod_{K'} (v_{K'} - u_{K'} \alpha^+_K) \prod_{k''} b^{\Lambda k''}_{k''} b^{\Lambda k''}_{k''} \prod_{k''' \sigma} a^{\Lambda} k'''_{\sigma} |\text{vac}\rangle,$$
and a pair of particles as \( s_k + p_k = (S_k + P_k)/n_k \) and that of the quartet occupancy as \( q_k = Q_k/n_k \), where there are \( S_k \) single particles, \( P_k \) pairs of particles and \( Q_k \) quartets, and \( n_k \) is the total number of states of occupancy with momenta \( k \). If we set \( n_k = a_{k\sigma}^\dagger a_{k\sigma} \), the expectation values of \( n_k \) and \( 1 - n_k \) with respect to \( |\Psi_e\rangle \) are given by

\[
\langle \Psi_e | n_k | \Psi_e \rangle = \frac{1}{2} s_k + p_k + q_k u_K^2 + \left( 1 - \frac{1}{2} s_k - p_k - q_k \right) v_K^2, \quad \epsilon > 0, \quad (26)
\]

\[
\langle \Psi_e | (1 - n_k) | \Psi_e \rangle = \frac{1}{2} s_k + p_k + q_k v_K^2 + \left( 1 - \frac{1}{2} s_k - p_k - q_k \right) u_K^2, \quad \epsilon < 0, \quad (27)
\]

with

\[
u_K(-\epsilon) = v_K(\epsilon). \quad (28)
\]

Thus, we find that the expectation value \( W_{KE} \) of \( H_0 \) with respect to \( |\Psi_e\rangle \) is given by

\[
W_{KE} = \sum_K |\epsilon_k| \left[ s_k + 2p_k + 2q_k + 2(1 - s_k - 2p_k + 2q_k) v_K(|\epsilon_k|^2) \right]. \quad (29)
\]

Hereafter, a sum over \( K \) is understood to be a sum over \( k^A \) and \( p^B \), as in §2.

The matrix elements of \( H'_1 \) for the quartet interaction can be calculated by computing the occupied states of the quartet state as

\[
\Psi_{KK'} = \beta_{11}\varphi_{11}(\cdots 1K \cdots 1K' \cdots) + \beta_{10}(\cdots 1K \cdots 0K' \cdots) + \beta_{01}(\cdots 0K \cdots 1K' \cdots) + \beta_{00}(\cdots 0K \cdots 0K' \cdots), \quad (30)
\]

where \( 1K \) and \( 0K \) represent the occupancy and nonoccupancy, respectively, of the quartet state with total momentum \( K \). If we denote the ground quartet by + and the excited quartet by −, we have \((+,+), (-,-), (+,-) \) and \((-,+))\). The surviving matrix elements of \( H'_1 \) with respect to \( \Psi_{KK'} \) in (30) come from \( \beta_{11}, \beta_{10}, \beta_{01} \) and \( \beta_{00} \) for each case, and they are given by

\[
\begin{align*}
u_K u_K u_{K'} v_{K'} \{ & (1 - s_k - 2p_k - q_k) (1 - s_k' - 2p_k' - q_k') + q_k q_k' \\
& - (1 - s_k - 2p_k - q_k) q_k' - q_k (1 - s_k' - 2p_k' - q_k') \} \\
& = u_K v_K u_{K'} v_{K'} (1 - s_k - 2p_k - 2q_k) (1 - s_k' - 2p_k' - 2q_k'). \quad (31)
\end{align*}
\]

If we introduce the four-body distribution function \( F_K \), which gives the overall probability of quartet occupancy, then \( s_k + 2p_k \) and \( q_k \) are given by

\[
s_k + 2p_k = 4F_K(1 - F_K) \quad \text{and} \quad q_k = F_K^2. \quad (32)
\]

Then the entropy is given by

\[
-TS = 2k_B T \sum_K [F_K \ln F_K + (1 - F_K) \ln(1 - F_K)]. \quad (33)
\]

The expectation value of \( H_0 \) with respect to the excited state wave function is given by

\[
W_{KE} = 2 \sum_K |\epsilon_k| \left\{ [2F_K(1 - F_K)] + 2(1 - 2F_K(1 - F_K) - 2F_K^2) \right\} |v_K|^2. \quad (34)
\]
The free energy $F$ is now given by

$$F = 2\sum_K |\epsilon_K|[F_K + (1 - 2F_K)|v_K|^2] - \sum_{K,K'} u_K v_K u_{K'} v_{K'} (1 - 2F_K)(1 - 2F_{K'}) - 2k_B T \sum_K [F_K \ln F_K + (1 - F_K) \ln(1 - F_K)].$$

(35)

If we minimize $F$ with respect to $v_K$ under the condition $|u_K|^2 + |v_K|^2 = 1$, we obtain the following:

$$\frac{\partial F}{\partial v_K} = 2 \left\{ 2(1 - 2F_K)|\epsilon_k|v_K - \left[ \sum_{K'} u_{K'} v_{K'} (1 - 2F_{K'}) \right] \left( u_K - \frac{|v_K|^2}{u_K} \right)(1 - 2F_K) \right\} = 0.$$  

(36)

Next, if we define the energy gap $\epsilon_0(T)$ for finite temperatures as

$$\epsilon_0 = U \sum_{k,p} u_K v_K (1 - 2F_K),$$

(37)

then identifying $\epsilon^A_k = \epsilon^B_k = \epsilon_k$ as $\epsilon_k$ in §2, we get the solutions for $u_K$ and $v_K$ as

$$u^2_K = \frac{1}{2} \left( 1 + \frac{\epsilon_k}{\sqrt{\epsilon_k^2 + \epsilon_0^2}} \right),$$

(38a)

and

$$v^2_K = \frac{1}{2} \left( 1 - \frac{\epsilon_k}{\sqrt{\epsilon_k^2 + \epsilon_0^2}} \right).$$

(38b)

Furthermore, the minimization of $F$ with respect to $F_K$ yields

$$\frac{\partial F}{\partial F_K} = \left\{ |\epsilon_k|(u^2_K - v^2_K) + 2u_K v_K \sum_{K'} u_{K'} v_{K'} (1 - 2F_{K'}) - 2k_B T \ln \frac{F_K}{1 - F_K} \right\} = 0.$$  

(39)

The vanishing of the quantity inside the curly brackets of Eq. (39) yields the following:

$$2 \left\{ \frac{\epsilon_k^2}{\sqrt{\epsilon_k^2 + \epsilon_0^2}} + \frac{\epsilon_k^2}{\sqrt{\epsilon_k^2 + \epsilon_0^2}} - k_B T \ln \frac{F_K}{1 - F_K} \right\} = 0.$$  

(40)

Then we get

$$F_K = 1 / \left( 1 + e^{\beta \sqrt{\epsilon_k^2 + \epsilon_0^2}} \right).$$

(41)
If we insert Eq. (41) into Eq. (37) and assume the energy ranges for $\epsilon^A_k$ and $\epsilon^B_k$ (that is, $\epsilon_k$) as given in Eq. (11), we obtain the energy gap equation for finite temperatures as

$$1 = \rho_{\text{CQ}} U \int \frac{\tanh \frac{\beta}{2} \sqrt{\epsilon_k^2 + \epsilon_0^2}}{2 \sqrt{\epsilon_k^2 + \epsilon_0^2}} d\epsilon_k,$$  \hspace{1cm} (42)

and the expression for $T_C$ from Eq. (42) by setting $\epsilon_0 = 0$ as

$$T_C = 1.14 \Delta E \exp \left( -\frac{1}{\rho_{\text{CQ}} U} \right).$$  \hspace{1cm} (43)

We can now discuss the value of $T_C$ considering the following three points. First, $U$ is twice as large as the Cooper pair interaction $V_{\text{pair}}$, because the partners forming the quartet can be $2 \times 2 = 4$, in comparison with 2 for the case of Cooper pairing. Second, the density of states $\rho_{\text{CQ}}$ is equal to $\rho_F$ for the pairing case, because we have to divide the number four of the contributions of the quartet in comparison with two for the pairing case. Therefore, we conclude that the effective interaction is twice as large as that in the pairing interaction case from the above considerations:

$$\rho_{\text{CQ}} U = 2 \rho_F V_{\text{pair}}.$$  \hspace{1cm} (44)

Third, the range of the interaction $\Delta E$ can be the Debye energy for phonon mediated superconductivity or the Fermi energy $\epsilon_F$ if the interaction between quartets is of electronic origin, as in the case of infrared divergence associated with heavy particles, studied by Kondo,\textsuperscript{12} and as in the case of a plasmon mediated superconductivity, studied by Takada.\textsuperscript{13}

To form a quartet superconductor, we need two bands of conduction electrons, as in MgB$_2$, and we may have to replace the Mg layer in the case of MgB$_2$ by another thin insulating layer, which requires that two electrons be supplied to the base plane B$_2$ in order for $T_C$ to reach room temperature.

§4. Conclusion and discussion

We have investigated the possibility of quartet condensation in a two-band superconductor in order to obtain a higher $T_C$, which is believed to be near room temperature, by extending pair condensation to quartet condensation and using a variational method. We obtained the ground state energy, the quartet energy gap, the excited state energy, the entropy, the free energy and the transition temperature $T_C$ of the quartet condensation. The larger effective interaction causes $T_C$ to be higher than that in the case of pair condensation, because the magnitude of the quartet interaction is thought to be twice that of the pairing interaction.

We made a suggestion about how to obtain a quartet superconductor experimentally. We also studied the stability of the quartet state by calculating the decay and the recombination rates of the quartet state.

We may be able to extend our idea concerning quartet condensation to superfluid $^4$He, in which the spin and isotropic spin degrees of freedoms of the nucleons
allow formation of the quartet state. We conjecture that superfluid $^4$He is formed through quartet condensation, because the fact that the roton minimum energy is four times $T_\lambda$ suggests quartet formation. The phonon part of the excitation spectrum of superfluid $^4$He is believed to be due to the collective excitation of the quartet state.

References

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