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Analytical determination of the Cooper pair condensation using linearized solutions of the BCS Hamiltonian

Carlos Ramírez [a], Vicenta Sánchez [a], Chumin Wang [b,*]

[a] Departamento de Física, Facultad de Ciencias, Universidad Nacional Autónoma de México, Apartado Postal 70-542, 04510 D.F., Mexico
[b] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, 04510 D.F., Mexico

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ABSTRACT

In this paper, we find analytically the first order solutions of the Bardeen, Cooper and Schrieffer (BCS) Hamiltonian with degenerated single-electron energy levels. The results are compared to the Richardson exact solutions calculated numerically, showing good agreement in the weak interaction limit. Using this first-order solution, we further calculate the number of pairs at the ground state as a function of temperature. In particular, the Bose–Einstein condensation (BEC) temperature is found when the population of ground-state pairs starts growing. This study provides a BEC analysis of the superconductivity for weak coupling regime, which traditionally belongs to the BCS side of the BCS–BEC *crossover* picture.

1. Introduction

The study of superconductivity has fascinated many physicists since its discovery. It consists of a lack of electrical resistance and a total expulsion of magnetic fields inside a material. The first microscopic explanation was given by Bardeen, Cooper and Schrieffer (BCS) in 1957 [1] as a consequence of the appearance of electron pairs, named Cooper pairs, given rise from an effective attraction between electrons. The pairing Hamiltonian proposed by BCS with a constant interaction has been also applied in fields like nuclear physics, to find the first nuclear energies of many atoms [2]. However, the BCS theory is not suitable for systems in which the separation between single-electron energy levels is large enough to be considered as a continuum, such as granular or nanostructured superconductors [3,4]. In particular, when the system dimension is reduced below the superconducting coherence length, a critical regime is appeared above the bulk critical temperature where a superconducting gap is measured by scanning tunneling microscopy on individual Pb nanoparticles [5].

In 1963, R.W. Richardson achieved to transform the many-particle Schrödinger problem into a series of coupled non-linear algebraic equations, whose solutions are the exact eigenstates of the BCS Hamiltonian [6]. Such coupled equations are as follows:

$$\sum_{s=1}^{L} \frac{M_s}{2\varepsilon_s - E_n} - \sum_{n' \neq n}^{N_P} \frac{2}{E_{n'} - E_n} = \frac{1}{V}, \tag{1}$$

where it is assumed that there are L different values of the single-electron energy (ε_s) with a degeneracy M_s and $n = 1, 2, \cdots, N_P$, being N_P the number of pairs in the system. Using the solutions E_n, the energy of the system is given by

$$E = \sum_{n=1}^{N_P} E_n, \tag{2}$$

with corresponding eigenfunction proportional to

$$\prod_{n=0}^{N_P} \left[\sum_{\mathbf{k}} \frac{\hat{c}_{\mathbf{k},\uparrow}^{\dagger} \hat{c}_{-\mathbf{k},\downarrow}^{\dagger}}{2\varepsilon_{\mathbf{k}} - E_n} \right] |0\rangle, \tag{3}$$

where $\varepsilon_{\mathbf{k}}$ is the single-electron energy, $\hat{c}_{\mathbf{k},\sigma}^{\dagger}$ and $\hat{c}_{\mathbf{k},\sigma}$ are respectively the creation and annihilation operators of an electron with crystal momentum $\mathbf{k}$ and spin σ in a crystalline solid. This Richardson's solution has helped to determine the energy spectrum of systems with few pairs [2] and to analyze the spin susceptibility of a superconducting ultra-small grain [7], even though the ignorance of a general analytical expression of the many-pair energy. Thermodynamical properties of small systems with a fixed particle number have been addressed by a variation after projection approach [8] and an additional perturbative procedure is also proposed [9]. Moreover, quantum Monte Carlo simulations are performed to study the nuclear pairing model [10].

On the other hand, the superconductivity viewed as a Bose–Einstein condensation (BEC) has been recurrently suggested through the years [11,12]. It is widely accepted the BCS–BEC *crossover* viewpoint, which identifies two limiting behaviors. In the BCS limit, Cooper pairs overlap due to their large size or high

density, while the BEC limit shows opposite conditions producing molecular Cooper pairs which interact with each other like bosons [13–15]. In fact, we have shown that creation and annihilation operators of collective Cooper pairs accomplish bosonic commutation relations in the dilute limit, corresponding to the BEC side [16]. Additionally, we have found recently a coincidence between BCS and BEC theories in the narrow-band limit [17].

In this paper, we use the BCS Hamiltonian given by [18]

$$\hat{H} = \sum_{\mathbf{k},\sigma} \varepsilon(\mathbf{k}) \hat{c}_{\mathbf{k},\sigma}^\dagger \hat{c}_{\mathbf{k},\sigma} - V \sum_{\mathbf{k},\mathbf{k}'} \hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}'} \tag{4}$$

where $\hat{b}_{\mathbf{k}}^\dagger = \hat{c}_{\mathbf{k},\uparrow}^\dagger \hat{c}_{-\mathbf{k},\downarrow}^\dagger$ and $\hat{b}_{\mathbf{k}} = \hat{c}_{-\mathbf{k},\downarrow} \hat{c}_{\mathbf{k},\uparrow}$ are respectively the creation and annihilation operators of Cooper pairs. In the next sections, we give analytically the complete energy spectrum of Hamiltonian (4) at first order in V and consequently determine its condensation properties.

2. First order solutions of the BCS Hamiltonian

Let us consider that all the single-electron energies $\varepsilon(\mathbf{k})$ can be grouped in sets Ω_s with a constant energy ε_s and M_s elements in each set. Then, Hamiltonian (4) can be rewritten as

$$\hat{H} = \sum_{s=1}^{L} \hat{H}_s - V \sum_{\substack{s,s'=1 \\ -t(s' \neq s)}}^{L} \hat{B}_s^\dagger \hat{B}_{s'}, \tag{5}$$

where

$$\hat{H}_s = \varepsilon_s \sum_{\mathbf{k} \in \Omega_s} \hat{c}_{\mathbf{k},\sigma}^\dagger \hat{c}_{\mathbf{k},\sigma} - V \sum_{\mathbf{k},\mathbf{k}' \in \Omega_s} \hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}'}, \tag{6}$$

$$\hat{B}_s^\dagger = \sum_{\mathbf{k} \in \Omega_s} \hat{b}_{\mathbf{k}}^\dagger, \text{ and } \hat{B}_s = \sum_{\mathbf{k} \in \Omega_s} \hat{b}_{\mathbf{k}}. \tag{7}$$

Hamiltonian $\hat{H}_s$ can be solved analytically and the solutions are composed by Q_s unpaired electrons, P_s ground-state pairs and X_s excited pairs, having energy [17]

$$E_{Q_s,P_s,X_s} = (Q_s + 2P_s + 2X_s)\varepsilon_s - P_s V(M_s - Q_s - P_s - 2X_s + 1) \tag{8}$$

and the corresponding eigenfunction given by

$$|Q_s\{\mathbf{k}_i,\sigma_i\}, P_s, X_s(i)\rangle \equiv \hat{c}_{\mathbf{k}_1,\sigma_1}^\dagger \cdots \hat{c}_{\mathbf{k}_{Q_s},\sigma_{Q_s}}^\dagger \left[\sum_{\mathbf{k} \in \Omega_s} \hat{b}_{\mathbf{k}}^\dagger \right]^{P_s}$$
$$\sum_{\{\mathbf{q}_1,\cdots,\mathbf{q}_{X_s}\} \subset \tilde{\Omega}_s} A_i(\mathbf{q}_1,\cdots,\mathbf{q}_{X_s}) \hat{b}_{\mathbf{q}_1}^\dagger \cdots \hat{b}_{\mathbf{q}_{X_s}}^\dagger |0\rangle, \tag{9}$$

where $\tilde{\Omega}_s \equiv \Omega_s - \{\mathbf{k}_1, \cdots, \mathbf{k}_{Q_s}\}$. The degeneration of the energy is

$$D_{Q_s,P_s,X_s} = \frac{2^{Q_s} M_s! (M_s - Q_s - 2X_s + 1)}{Q_s! X_s! (M_s - Q_s - X_s + 1)!} \tag{10}$$

and the parameters are subject to the constriction of

$$Q_s + P_s + 2X_s \leq M_s. \tag{11}$$

Based on the solution (9) and a straightforward calculation, it can be shown that

$$\langle Q_s, P_s, X_s | -V \sum_{s,s'=1,(s' \neq s)}^{N_s} \hat{B}_s^\dagger \hat{B}_{s'} | Q_s, P_s, X_s \rangle = 0, \tag{12}$$

and then the wavefunctions of Hamiltonian (5) can be written as

$$|Q_1, P_1, X_1, \cdots, Q_{N_s}, P_{N_s}, X_{N_s}\rangle = |Q_1, P_1, X_1\rangle$$
$$\otimes \cdots \otimes |Q_{N_s}, P_{N_s}, X_{N_s}\rangle \tag{13}$$
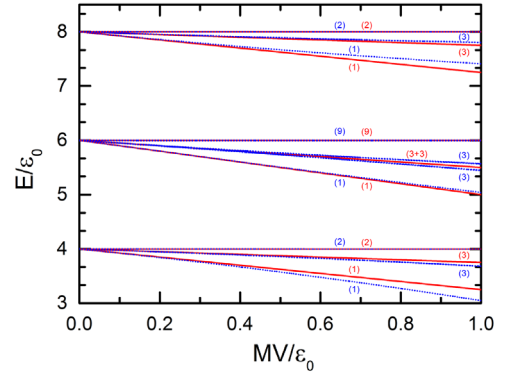

Fig. 1. (Color online) Energy spectrum of Hamiltonian (5) as a function of the interaction strength (V) calculated from the exact Richardson equations (blue dotted lines) and the first order solution in V (red solid lines). The degeneracy of each line is indicated between parentheses.

with corresponding energy and degeneration at a first order in V given by

$$E_{Q_1,P_1,X_1,\cdots,Q_{N_s},P_{N_s},X_{N_s}} = \sum_{s=1}^{N_s} E_{Q_s,P_s,X_s}$$

and $$D_{Q_1,P_1,X_1,\cdots,Q_{N_s},P_{N_s},X_{N_s}} = \prod_{s=1}^{N_s} D_{Q_s,P_s,X_s}. \tag{14}$$

Fig. 1 shows the linear solutions (red solid lines) of Hamiltonian (5) given in Eq. (14) as functions of the interaction (V) in comparison to the exact solutions obtained from the Richardson equations (blue dotted lines) for the case of $L = 2$, $\varepsilon_1 = \varepsilon_0$, $\varepsilon_2 = 2\varepsilon_0$, $M_1 = M_2 = 4$, $M = M_1 + M_2 = 8$ and $N_P = 2$. Notice the agreement between both solutions for small V, as expected for a first order perturbation solution. Moreover, the degeneracy (14) of first-order solutions is the same of the exact solutions. In particular, the degeneracy (3+3) indicates two configurations, $[P_1, X_1; P_2, X_2] = [1, 0; 0, 1]$ and $[0, 1; 1, 0]$, both with the same linearized energy.

It would be worth mentioning that this approximation could be obtained by making $\lambda a_\nu \ll 1$ in Eq. (13) of reference [19] developed for the case of non-degenerated systems.

3. Statistical analysis for the weak coupling limit

For the weak coupling regime, the energy spectrum given in Eq. (14) allows us to write the grand canonical partition function as

$$\Xi(\mu, T) = \prod_{s=1}^{L} \Xi_s(\mu, T) \tag{15}$$

where μ is the chemical potential, T is the temperature and Ξ_s is the partition function of each set Ω_s, i.e.

$$\Xi_s(\mu, T) = \sum_{Q_s=0}^{M_s} \sum_{P_s=0}^{M_s-Q_s} \sum_{X_s=0}^{(M_s-Q_s-P_s)/2} \Theta(Q_s, P_s, X_s, \mu, \beta), \tag{16}$$

where limits of summations come from constriction (11) and

$$\Theta(Q_s, P_s, X_s, \mu, \beta) = D_{Q_s,P_s,X_s} e^{-\beta [E_{Q_s,P_s,X_s} - \mu(Q_s+2P_s+2X_s)]}. \tag{17}$$

It can be noticed that [12]

$$\ln[\max \Theta(Q_s, P_s, X_s, \mu, \beta)] \leq \ln[\Xi_s(\mu, T)]$$
$$\leq \ln[\max \Theta(Q_s, P_s, X_s, \mu, \beta)] + 3 \ln M_s. \tag{18}$$

In fact, by applying the Stirling formula to Eq. (10) we obtain that

$$\ln\left[\max\left\{D_{Q_s,P_s,X_s} e^{-\beta[E_{Q_s,P_s,X_s} - \mu(Q_s+2P_s+2X_s)]}\right\}\right] \gg 3 \ln M_s. \tag{19}$$

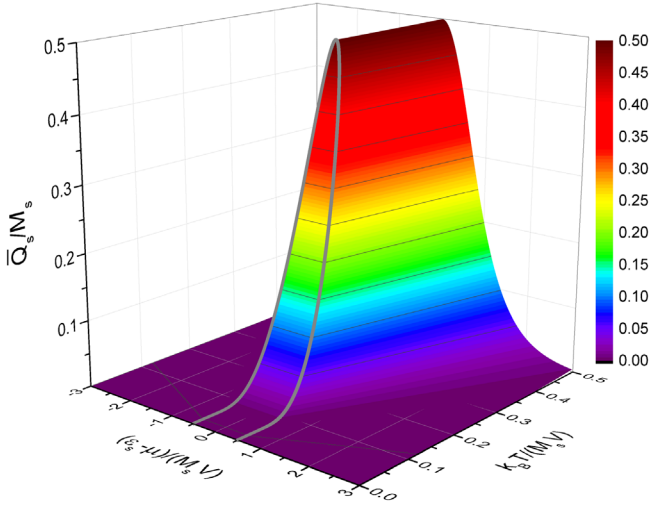**Fig. 2.** Number of unpaired electrons at shell s (Q_s) as a function of the temperature (T) and the single-electron energy (ε_s).
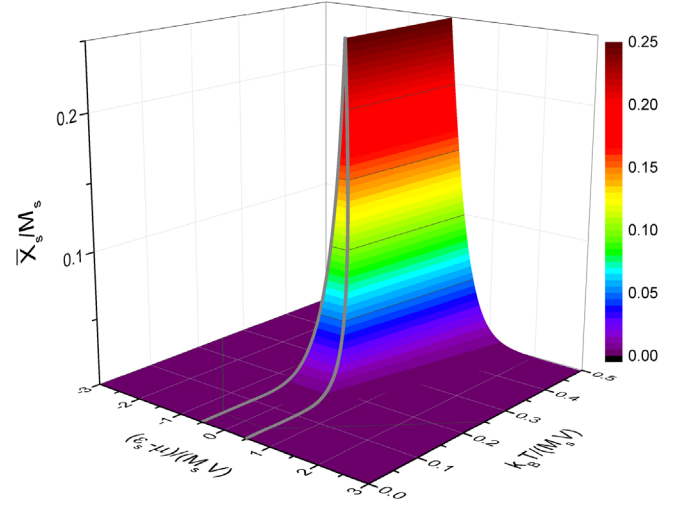

Fig. 4. Number of excited pairs at shell s (X_s) as a function of the temperature (T) and the single-electron energy (ε_s).
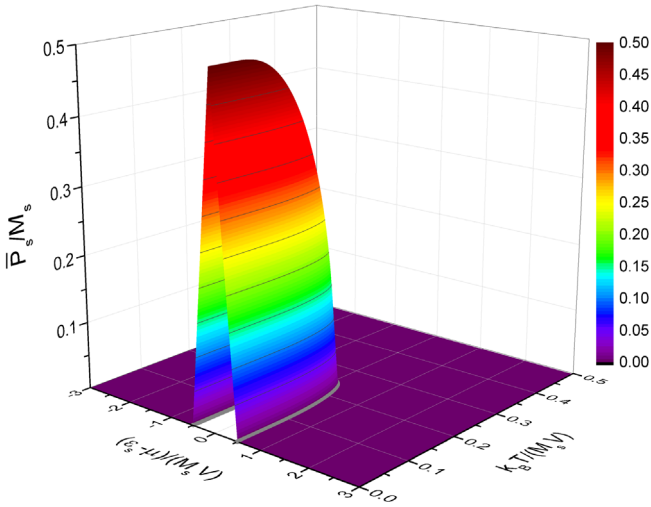

Fig. 3. Number of ground-state pairs at shell s (P_s) as a function of the temperature (T) and the single-electron energy (ε_s).

Fig. 5. Heat capacity (C) as a function of temperature (T) obtained from Eq. (25).

Then, the free energy (F) of the system can be written as

$$F(\mu,T) = -k_B T \ln\left[\Xi(\mu,T)\right] \approx -k_B T \sum_s$$
$$\ln\left[\max\left\{D_{Q_s,P_s,X_s} e^{-\beta\left[E_{Q_s,P_s,X_s} - \mu(Q_s + 2P_s + 2X_s)\right]}\right\}\right]. \tag{20}$$

Eq. (20) means that in the thermodynamic equilibrium the most probable values of Q_s, P_s and X_s are those that maximize the free energy.

The parameters Q_s, P_s and X_s are limited by the condition (11) and $Q_s, P_s, X_s \geq 0$, delimiting the feasible region of the solution. By a direct maximization process of Eq. (17), it can be shown that if the solution is strictly in the interior of the feasible region, the parameters $\overline{Q}_s$, $\overline{P}_s$ and $\overline{X}_s$ that maximize F are solutions of

$$\begin{cases} 2E_s = V\left(M_s - \overline{Q}_s - 2\overline{X}_s\right) \\ \overline{Q}_s = 2\sqrt{\overline{X}_s M_s} - 2\overline{X}_s \\ 1 = M_s V \tan h\left(E_s/2k_B T\right)/2E_s \end{cases}, \tag{21}$$

where $E_s \equiv V\overline{P}_s + \varepsilon_s - \mu$. In general, $\overline{Q}_s$, $\overline{P}_s$ and $\overline{X}_s$ are numerically determined by maximizing Eq. (17) within the feasible region including its boundaries and the results are respectively shown
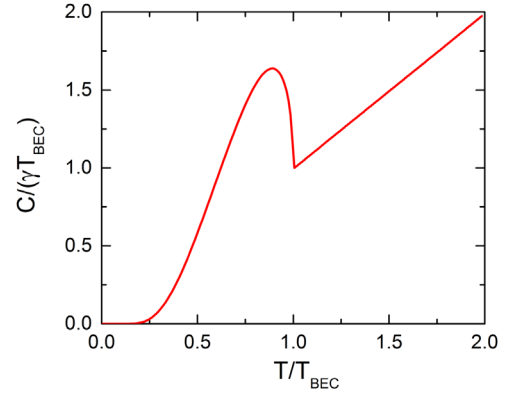
in Figs. 2–4 as functions of the temperature (T) and the single-electron energy (ε_s). For shells with $\varepsilon_s < \mu$, the quantities $\overline{Q}_s$, $\overline{P}_s$ and $\overline{X}_s$ represent unpaired, ground-state pairs and excited pairs of holes, respectively. It is worth mentioning that these figures are independent from specific values of M_s and V. Observe that for $\overline{P}_s \rightarrow 0^+$, we have from Eq. (21)

$$\frac{k_B T}{M_s V} = \frac{z}{\ln\left(\frac{1+2z}{1-2z}\right)}, \tag{22}$$

$$\frac{\overline{X}_s}{M_s} = \frac{1}{4}(1-2z)^2, \tag{23}$$

and

$$\frac{\overline{Q}_s}{M_s} = \frac{1}{2} - 2z^2, \tag{24}$$

where $z \equiv |\varepsilon_s - \mu|/(M_s V)$. Eqs. (22)–(24) are represented by gray lines in Figs. 2–4.

Observe in Fig. 3 that the population of pairs at the ground state, $\overline{P}_s$, becomes zero for temperatures above $M_s V/(4k_B)$, hence we can define the BEC temperature as $k_B T_{BEC} = MV/4$.

Now, we calculate the average energy ($\overline{E}$) as a function of temperature (T) by using Eqs. (8) and (14), i.e.

$$\overline{E}(T) = \sum_{s=1}^{N_s} \left[\overline{Q}_s(T) + 2\overline{P}_s(T) + 2\overline{X}_s(T)\right]\varepsilon_s - \overline{P}_s(T)V\left[M_s - \overline{Q}_s(T) - \overline{P}_s(T)\right.$$
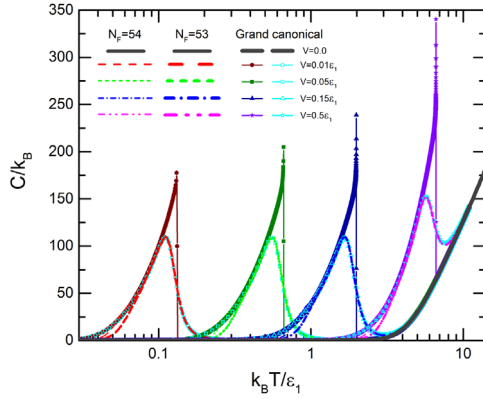$$\left. - 2\overline{X}_s(T) + 1\right], \tag{25}$$

Fig. 6. Heat capacity (C) of correlated electrons on a spherical surface as a function of temperature (T) for interaction strengths $V = 0.01\varepsilon_1$ (circles), $0.05\varepsilon_1$ (squares), $0.15\varepsilon_1$ (triangles) and $0.5\varepsilon_1$ (stars), in comparison with those obtained in Ref. [21] (dashed lines).

and then, the heat capacity (C) defined as $\partial \overline{E}/\partial T$ is showed in Fig. 5. Notice that there is a linear behavior for $T > T_{BEC}$, i.e., $C = \gamma T$ corresponding to a free electron system [20]. For $T \ll T_{BEC}$, the heat capacity has an exponential behavior as occurs in the BCS theory [18]. Moreover, for temperatures just below T_{BEC} the heat capacity has a smooth decay, which is due to the different null-P_s temperature for each shell s. This is a consequence of the decoupling of shells caused by the first order approximation.

4. Application to electrons on a spherical surface

The approach presented in this paper can be applied to the case of non-uniform angular-momentum energy levels of electrons on a spherical surface, given by [21]

$$\varepsilon_l = \frac{\hbar^2}{2m_e R^2} l(l+1) \tag{26}$$

with a constant radio R and a degeneration of $2(2l+1)$. For the case of a fixed average number of particles, the chemical potential (μ) is adjusted accordingly. In Fig. 6, the heat capacity (C) is showed for electrons on a sphere with the Fermi angular-momentum level at $L_F = 26$, $N_F = 54$ electrons in such level and interaction strength $V = 0.01\varepsilon_1$ (solid circles), $0.05\varepsilon_1$ (solid squares), $0.15\varepsilon_1$ (solid triangles) and $0.5\varepsilon_1$ (solid stars). Beyond the thermodynamic limit given by Eq. (20), i.e., performing all the summations of Eq. (16), the corresponding heat capacities are also illustrated in Fig. 6 by open symbols within the grand-canonical ensemble analysis. These results can be compared with those obtained by means of the canonical ensemble approach [21], illustrated as dashed lines in Fig. 6. It is worth mentioning that the abrupt fall of heat capacity is due to the large separation of energy levels in comparison to the temperature energy ($k_B T$), which leads to a heat capacity originated from the single Fermi energy level, in contrast to the case analyzed in Fig. 5. On the other hand, the macroscopic approximation of Eq. (20) seems to be far from the exact evaluation (open symbols), since this system have only $L_F = 26$ levels occupied.

5. Conclusions

In this paper, we have obtained an analytical first-order perturbation solution of the BCS Hamiltonian for systems with degenerated single-electron energies, which has a good agreement with the exact numerical solution obtained from Richardson's equations at the weak coupling limit. This first-order solution decouples the shells in the momentum space, where each shell has a constant single-electron energy, and then allows an analytical study of the BEC for systems with a macroscopic degree of freedom, in contrast to the small systems addressable by Richardson's solution. This study was carried out by considering three essential components in superconductors: unpaired electrons, ground-state and excited electron-pairs. It would be important to stress that there is an universal behavior of $\overline{Q}_s$, $\overline{P}_s$ and $\overline{X}_s$ shown in Figs. 2–4, since it is independent from the model parameters M_s and V. The results further show the existence of ground-state pairs only in a limited number of shells around the Fermi energy, as illustrated in Fig. 2. The present work supports the viewpoint that superconductivity in the weak coupling can also be interpreted as a BEC of Cooper pairs, because the number of ground state pairs increases when the temperature falls below the superconducting critical temperature. This solution is particularly valuable for granular superconductors, where quantum size effects discretize the energy levels, making useless the BCS theory. Finally, the smooth decay of the electronic heat capacity observed in Fig. 5 is due to the decoupling of shells originated by the first order approximation, which could be improved by considering higher orders of approximation in spite of losing analytical results.

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