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Bose–Einstein Condensation of Collective Electron Pairs

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Abstract Among quantum phenomena in solids at low temperatures, the superconductivity and Bose–Einstein condensation (BEC) are representatives of arising from coherent macroscopic quantum states. In this article, we discuss possible correlations between these two phenomena. It is well known that the Cooper pairs are not true bosons and then, we introduce the concept of collective electron pairs (CEP) through a unitary transformation of electron pairs. The CEP accomplish bosonic commutation relations at the dilute limit, being able to accumulate many of them at a single quantum state, in contrast to the standard Cooper pairs. An exact solution of all single CEP eigenstates is found by means of the Richardson's equation within a multishell model. The obtained energy spectrum is used to determine the BEC temperature of CEP. In addition, we present an alternative approach to calculate the superconducting critical temperature by using the BEC formalism for a system composed by ground-state CEP, excited pairs and unpaired electrons.

Keywords Superconductivity · Bose–Einstein condensation · Collective electron pairs

1 Introduction

The viewpoint of superconductivity as a Bose–Einstein condensation (BEC) has renewed interests since the discovery of high-temperature superconductors [1] and

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the finding of BEC in a wide range of systems, such as ^{4}He superfluid [2], atomic gases of rubidium [3], sodium [4] and lithium [5], as well as exciton-polaritons in microcavities [6,7]. However, the Cooper pairs are not true bosons, as pointed out by J. Bardeen, L.N. Cooper and J.R. Schrieffer (BCS) in 1957 [8]. In fact, Cooper pair creation ($\hat{b}^\dagger_{\mathbf{k}} \equiv \hat{c}^\dagger_{\mathbf{k}\uparrow}\hat{c}^\dagger_{-\mathbf{k}\downarrow}$) and annihilation ($\hat{b}_{\mathbf{k}} \equiv \hat{c}_{-\mathbf{k}\downarrow}\hat{c}_{\mathbf{k}\uparrow}$) operators have the following commutation relations,

$$\begin{cases} \left[\hat{b}^\dagger_{\mathbf{k}}, \hat{b}^\dagger_{\mathbf{k}'}\right] \equiv \hat{b}^\dagger_{\mathbf{k}}\hat{b}^\dagger_{\mathbf{k}'} - \hat{b}^\dagger_{\mathbf{k}'}\hat{b}^\dagger_{\mathbf{k}} = 0, \quad \left[\hat{b}_{\mathbf{k}}, \hat{b}_{\mathbf{k}'}\right] = 0 \\ \left[\hat{b}_{\mathbf{k}}, \hat{b}^\dagger_{\mathbf{k}'}\right] = (1 - \hat{n}_{-\mathbf{k}\downarrow} - \hat{n}_{\mathbf{k}\uparrow})\delta_{\mathbf{k}\mathbf{k}'} \end{cases}, \tag{1}$$

where $\hat{n}_{\mathbf{k}\sigma} = \hat{c}^\dagger_{\mathbf{k}\sigma}\hat{c}_{\mathbf{k}\sigma}$ is the number operator of electrons, $\hat{c}^\dagger_{\mathbf{k}\sigma}$ and $\hat{c}_{\mathbf{k}\sigma}$ are the creation and annihilation operators of a single electron with linear momentum $\mathbf{k}$ and spin σ, respectively. Moreover, it is easy to prove that $\hat{b}^\dagger_{\mathbf{k}}\hat{b}^\dagger_{\mathbf{k}} = \hat{b}_{\mathbf{k}}\hat{b}_{\mathbf{k}} = 0$, which avoids to place more than one Cooper pair on any quantum state, making impossible a BEC of Cooper pairs.

Recently, we have shown [9] that linear combinations of Cooper pairs, named in this paper collective electron pairs (CEP), could have bosonic nature at the dilute limit, due to their diffuse character over the Cooper pairs allowing the accumulation of many of them at a single quantum state. The creation operator of such CEP ($\hat{a}^\dagger_\alpha$) can be obtained as a unitary transformation of Cooper pairs [10]

$$\hat{a}^\dagger_\alpha \equiv \sum_{l=1}^{M} A_\alpha(l)\,\hat{b}^\dagger_{\mathbf{k}_l} = \frac{1}{\sqrt{M}}\sum_{l=1}^{M} \exp\left(\frac{i2\pi l\alpha}{M}\right)\hat{b}^\dagger_{\mathbf{k}_l}, \tag{2}$$

where $\alpha = 0$ for ground-state CEP and $\alpha = 1, 2, \cdots, M-1$ for excited pairs, being M the total number of available pairing states.

2 BEC in an Ideal Gas of Collective Electron Pairs

Let us start from the BCS Hamiltonian [8],

$$\hat{H}_{BCS} = \sum_{\mathbf{k},\sigma} \varepsilon(\mathbf{k})\hat{c}^\dagger_{\mathbf{k},\sigma}\hat{c}_{\mathbf{k},\sigma} - V\sum_{\mathbf{k},\mathbf{k}'} \hat{b}^\dagger_{\mathbf{k}}\hat{b}_{\mathbf{k}'} \tag{3}$$

where $\varepsilon(\mathbf{k})$ is the single electron energy and $V > 0$ is the electron–electron interaction potential constant. The single pair energies (E_ν) of this Hamiltonian can be obtaining by solving the Richardson's equation [11]

$$\sum_{\mathbf{k}} \frac{1}{2\varepsilon(\mathbf{k}) - E_\nu} = \frac{1}{V}, \tag{4}$$

and the corresponding eigenfunctions can be written as

$$|\nu\rangle \equiv \left\{ \sum_{\mathbf{k}} \frac{1}{[2\varepsilon(\mathbf{k}) - E_\nu]^2} \right\}^{-1/2} \sum_{\mathbf{k}} \frac{1}{2\varepsilon(\mathbf{k}) - E_\nu} \hat{b}^\dagger_{\mathbf{k}} |0\rangle \, . \tag{5}$$

It is well known [11] that if $\varepsilon(\mathbf{k})$ is non-degenerate such that $\varepsilon(\mathbf{k}_\nu) < \varepsilon(\mathbf{k}_{\nu+1})$ for $\nu = 1, 2, \cdots, M$, there is one and only one solution of Eq. (4) with

$$2\varepsilon(\mathbf{k}_\nu) < E_\nu < 2\varepsilon(\mathbf{k}_{\nu+1}) \tag{6}$$

and its ground-state energy (E_0) located at

$$E_0 < 2\varepsilon(\mathbf{k}_1). \tag{7}$$

For systems with degenerate $\varepsilon(\mathbf{k})$, we use a multishell model in $\mathbf{k}$ space, in which each shell s has M_s available pairing $\mathbf{k}$-states with the same energy ε_s. From Eq. (6) we can conclude that in each shell s there are $M_s - 1$ eigenstates ($|s, \nu\rangle$) of Hamiltonian (3) with the same energy $E_{s,\nu} = 2\varepsilon_s$ for $\nu = 1, 2, \cdots, M_s - 1$, whose eigenfunctions are

$$|s, \nu\rangle = \hat{a}^\dagger_{s,\nu} |0\rangle = \frac{1}{\sqrt{M_s}} \sum_{l=1}^{M_s} \exp\left(\frac{i2\pi l \nu}{M_s} \right) \hat{b}^\dagger_{k_l} |0\rangle \, , \tag{8}$$

where $\mathbf{k}_l \in \Omega_s \equiv \{\mathbf{k} \, | \varepsilon(\mathbf{k}) = \varepsilon_s\}$. For a system with N_S shells, the rest N_S energies ($E_{s,0}$) can be determined by solving Eq. (4) rewritten as

$$\sum_{s'=1}^{N_S} \frac{M_{s'}}{2\varepsilon_{s'} - E_{s,0}} = \frac{1}{V} \tag{9}$$

with eigenfunctions given by Eq. (5). It is important to stress that states (5) and (8) are CEP and they are bosons at the dilute limit [10].

Within the formalism of grand canonical ensembles, the average number of bosons in an ideal system is $N = \sum_E [e^{\beta(E-\mu)} - 1]^{-1}$, where $\beta \equiv 1/k_B T$, the chemical potential $\mu < \min(E)$ and the summation is carried over all single boson energies. For a multishell model of CEP, this average number can be expressed as a summation of the average ground-state occupation number (N_0) plus the excited one (N_{exc}), *i.e.*,

$$N = N_0 + N_{exc} = \frac{1}{e^{\beta(E_{1,0}-\mu)} - 1} + \sum_{s=2}^{N_s} \frac{1}{e^{\beta(E_{s,0}-\mu)} - 1} + \sum_{s=1}^{N_s} \frac{M_s - 1}{e^{\beta(2\varepsilon_s-\mu)} - 1}, \tag{10}$$

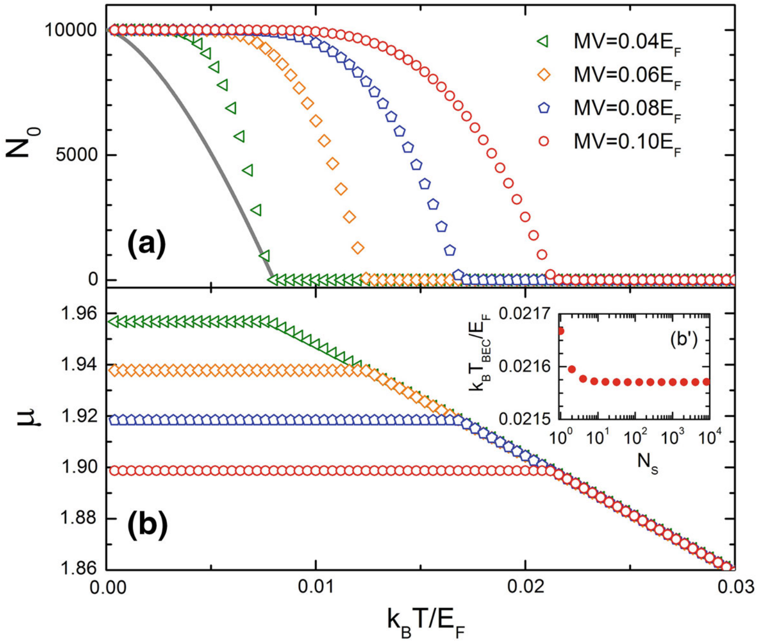

Fig. 1 (**a**) Ground state occupation number (N_0) and (**b**) the chemical potential (μ) as function of the temperature (T) for a system with $N = 10^4$ bosons, $N_S = 10^3$ shells, $M_s = 10^3$ available pairing states in each shell and ε_s uniformly distributed in $[0.99E_F, 1.01E_F]$. The *gray line* indicates N_0 for an ideal gas of 3D free bosons, rescaling its BEC critical temperature and the total number of bosons. *Inset* (**b′**) Bose–Einstein condensation temperature (T_{BEC}) as a function of the number of shells (N_S) for the same system with $MV = 0.01E_F$ (Color figure online)

where $\mu < E_{1,0}$. The BEC consists of a macroscopic occupation of the ground state [12], which starts when $T = T_{BEC}$, $\mu = E_{1,0}$ and $N = N_{exc}$. In Fig. 1(a) N_0 and (b) μ are plotted as functions of temperature (T) by using Eq. (10) for a system with $N = 10^4$ bosons, $N_S = 10^3$ shells, $M_s = 10^3$ available pairing states in each shell, $M = N_S M_s = 10^6$ total pairing states, ε_s uniformly distributed in $[0.99E_F, 1.01E_F]$ and four values of interaction constant V. In inset 1(b′), asymptotical variation of the BEC temperature (T_{BEC}) is illustrated when N_s increases and then, $N_s = 10^3$ is taken for the calculations of Fig. 1. Observe in Fig. 1(a) that almost all CEP are accumulated on the ground state at finite temperatures, when μ approaches to the ground-state energies as shown in Fig. 1(b). Notice also that Fig. 1(a, b) are signatures of a BEC [13], which suggests that CEP are able to condensate at the dilute limit. Nevertheless, in contrast to the standard BEC of 3D free bosons [12], whose ground-state population (N_0) is illustrated by a gray line in Fig. 1(a), the N_0 of CEP is almost a constant for temperatures below the half of the critical temperature.

It is worth to emphasize that in the dilute limit the CEP wavefunctions have a minimum overlap, which can be visualized as a non-interacting system of molecular bosons, corresponding to the BEC side of the BCS-BEC crossover. In the next section, the possibility of breaking these electron pairs will be included in an analytical study of a single-shell system, which would approach the BCS side.

3 BEC Formalism of Superconductivity

In this section, we consider a system with a single shell of energy ε and M available pairing states, containing U unpaired electrons, P pairs at the ground state, and X pairs on excited states. The Hamiltonian of such system is given by Eq. (3) and its energy spectrum can be analytically calculated as following.

3.1 Energy Spectrum

The presence of U unpaired electrons contributes to (a) reducing the number of available pairing states to $\tilde{M} \equiv M - U$, known as the blocking effect, (b) adding an energy of $U\varepsilon$ to the total one, and (c) increasing the number of configurations by a factor of

$$D_U = \frac{2^U M!}{U!(M-U)!}, \tag{11}$$

since U unpaired electrons may be placed in Mpossible states. In Eq. (11), 2^U comes from the spin degree of freedom.

In general, the eigenfunction of W pairs can be written as

$$|W\rangle \equiv \sum_{\mathbf{k}_1,\cdots,\mathbf{k}_W \in \tilde{\Omega}} A(\mathbf{k}_1, \cdots, \mathbf{k}_W)\, \hat{b}^\dagger_{\mathbf{k}_1} \cdots \hat{b}^\dagger_{\mathbf{k}_W} \left|\tilde{0}\right\rangle, \tag{12}$$

where $\tilde{\Omega}$ is the set of $\tilde{M}$ available pairing states and $|\tilde{0}\rangle$ is the empty state of pairs. Given that the second term of Hamiltonian (3) has null effects on the energy of a single excited pair as discussed in section two, this fact persists for the case of X purely excited pairs ($|X\rangle$), which is a subset of (12). In other words, we have $\sum_{\mathbf{k},\mathbf{k}'\in\tilde{\Omega}} \hat{b}^\dagger_{\mathbf{k}} \hat{b}_{\mathbf{k}'} |X\rangle = \hat{a}^\dagger_0 \hat{a}_0 |X\rangle = 0$, where $\hat{a}^\dagger_0 \equiv \sum_{\mathbf{k}\in\tilde{\Omega}} \hat{b}^\dagger_{\mathbf{k}}$ is the creation operator of a ground-state pair. Hence,

$$\hat{H}_{BCS} |X\rangle = 2X\varepsilon |X\rangle . \tag{13}$$

Given that $|X\rangle$ has no ground-state pair, it leads to $\hat{a}_0 |X\rangle = 0$, which implies

$$\sum_{\mathbf{k}_X \neq \mathbf{k}_1,\cdots,\mathbf{k}_{X-1}} A(\mathbf{k}_1, \cdots, \mathbf{k}_X) = 0. \tag{14}$$

Equation (14) represents a system of linear equations of variables $A(\mathbf{k}_1, \cdots, \mathbf{k}_X)$. The number of equations and the number of variables are respectively equal to the number of ways to build sets $\{\mathbf{k}_1, \cdots, \mathbf{k}_{X-1}\} \subset \tilde{\Omega}$ and $\{\mathbf{k}_1, \cdots, \mathbf{k}_X\} \subset \tilde{\Omega}$. Thus, the number of different linearly independent solutions of (14) is the difference of the number of variables and the number of equations, and it is given by

$$D_X = \frac{\tilde{M}!}{X!\,(\tilde{M}-X)!} - \frac{\tilde{M}!}{(X-1)!\,(\tilde{M}-X+1)!}$$
$$= \frac{\tilde{M}!}{X!\,(\tilde{M}-X+1)!}(\tilde{M}-2X+1). \tag{15}$$

In Eq. (15), the conditions of $D_X > 0$ and $\frac{\tilde{M}!}{X!\,(\tilde{M}-X+1)!} > 0$ imply

$$2X \leq \tilde{M}. \tag{16}$$

In general, the states (12) accomplish

$$\hat{H}_{BCS}\,|W\rangle = E\,|W\rangle\,, \tag{17}$$

and it can be shown by straightforward calculation that

$$\hat{H}_{BCS}\hat{a}_0^\dagger\,|W\rangle = [E + 2\varepsilon - V(\tilde{M} - 2W)]\,\hat{a}_0^\dagger\,|W\rangle\,. \tag{18}$$

Equations (17) and (18) prove that if $|W\rangle$ is an eigenfunction of Hamiltonian (3), $|W\rangle$ plus a ground-state pair is also an eigenfunction. From Eqs. (13) and (18), it can be proven by mathematical induction that state $|P, X\rangle$ with P ground-state pairs and X excited pairs is also an eigenfunction of Hamiltonian (3) with energy

$$E_{P,X} = (2P + 2X)\varepsilon - P(\tilde{M} - 2X - P + 1)V, \tag{19}$$

and condition (16) becomes

$$2X \leq \tilde{M} - P, \tag{20}$$

because the ground-state pairs reduce the available space for the excited pairs.

In summary, we have found that a system with U unpaired electrons, P ground-state pairs and X excited pairs has energy of

$$E_{U,P,X} = (2P + 2X + U)\varepsilon - P(M - U - 2X - P + 1)V, \tag{21}$$

with a constriction of $2X \leq M - U - P$. The different solutions of excited pairs and different ways to place the unpaired electrons, makes energy (21) to have a degeneracy of

$$D_{U,P,X} = D_U D_X = \frac{2^U M!(M - U - 2X + 1)}{U!X!(M - U - X + 1)!}, \tag{22}$$

according to Eqs. (11) and (15). Notice that the energies given by Eq. (21) have been firstly obtained by reference [11] and together with the degeneracy (22) are necessary for the statistical analysis, as carried out in the next subsection.

3.2 Grand-Canonical Treatment

In order to achieve the problem solved by BCS [8], let us consider a single shell with a single electron energy $\varepsilon = \mu$ and the grand-canonical partition function (Ξ) can be written from Eqs. (20) to (22) as [12]

$$\Xi = \sum_{U=0}^{M} \sum_{P=0}^{M-U} \sum_{X=0}^{(M-P-U)/2} \Theta(U, P, X), \tag{23}$$

where

$$\Theta(U, P, X) = \frac{2^U M!(M - U - 2X + 1)}{U!\, X!\, (M - U - X + 1)!}\, e^{\beta\, (M-U-2X-P+1)PV}. \tag{24}$$

Because $\Theta(U, P, X) \geq 0$ and Ξ contains the term of max $[\Theta(U, P, X)]$, hence

$$\max\,[\Theta(U, P, X)] \leq \Xi \leq (M + 1)^3 \max\,[\Theta(U, P, X)]\,. \tag{25}$$

By taking the logarithm of inequalities (25) and $\ln M \ll \ln\{\max\,[\Theta(U, P, X)]\}$ as occurs in the two-dimensional Ising model [14], we have

$$\ln \Xi \approx \max\,[\ln \Theta(U, P, X)] = \ln \Theta(U_0, P_0, X_0), \tag{26}$$

where $U_0,\ P_0$ and X_0 are the corresponding occupation numbers at the equilibrium state and maximize $\Theta(U, P, X)$. In general, the thermodynamic properties of a system can be derived from the logarithm of Ξ, which is obtained by maximizing $\Theta(U, P, X)$ as a function of temperature from Eq. (24). Following the standard derivative procedure of maximization, we obtain that these equilibrium occupation numbers satisfy the following equations

$$P_0(T) = \frac{M - U_0(T) - 2X_0(T) + 1}{2} \tag{27}$$

$$U_0(T) = 2\left[\sqrt{X_0(T)(M + 1)} - X_0(T)\right] \tag{28}$$

and

$$k_B T = \frac{V\ P_0(T)}{\ln\left[\frac{M+2P_0(T)}{M-2P_0(T)}\right]}. \tag{29}$$

In particular, at zero temperature these occupation numbers become $P_0(0) = M/2,\ X_0(0) = U_0(0) = 0,$ i.e., the system is uniquely composed by ground-state pairs. From Eq. (29) the BEC temperature (T_{BEC}), above which the number of ground-state pairs becomes negligible [12], can be determined by

$$k_B T_{BEC} = \lim_{P_0 \to 0} \frac{V\, P_0}{\ln\left(\frac{M+2P_0}{M-2P_0}\right)} = \frac{MV}{4}, \tag{30}$$

where the L'Hôpital's rule has been used.

3.3 From BEC to BCS Results

The superconducting energy gap (2Δ) at zero temperature is defined as the energy difference between the superconducting ground state and the lowest excited state [8] and it can be calculated as the energy required to break a ground-state pair and form two unpaired electrons, i.e.,

$$2\Delta(T) \equiv \frac{E_{U_0+2, P_0-1, X_0} - E_{U_0, P_0, X_0}}{2} = [M - U_0(T) - 2X_0(T)]\, V \approx 2P_0(T)\, V, \tag{31}$$

where $M \gg 1$ is considered and Eqs. (21) and (27) are used. From Eqs. (29) and (31), $\Delta(T)$ can be determined by

$$k_B T = \frac{\Delta(T)}{\ln\left(\frac{\Delta(0)+\Delta(T)}{\Delta(0)-\Delta(T)}\right)}. \tag{32}$$

where $\Delta(0) = P_0(0)V = MV/2$. According to the BCS theory, the superconducting critical temperature (T_c) is reached when $\Delta(T)$ approaches to zero. In addition, Eq. (31) ensures that $P_0(T)$ and $\Delta(T)$ becomes zero at the same temperature. Therefore $T_c = T_{BEC}$. In Fig. 2, the number of ground-state pairs (P_0) and the superconducting gap (Δ) as a function of temperature is shown by using Eqs. (29) and (32). The populations of unpaired electrons (U_0) and excited pairs (X_0) versus the temperature (T) are respectively shown in insets 2(a) and 2(b) obtained from Eqs. (27) and (28). It is worth to mention that the gap Eq. (32) can alternatively be obtained from the BCS theory [8] by taking $N(\varepsilon) = M\delta(\varepsilon)$ instead of $N(\varepsilon) = N(0)$, since a single shell model is used in this analysis. Finally, from $\Delta(0) = MV/2$ and Eq. (30) we obtain $2\Delta(0) = 4k_B T_C$, which is close to the BCS result of $2\Delta(0) = 3.5k_B T_C$ [8].

4 Conclusions

In this article, an alternative viewpoint of the superconductivity based on the BEC is discussed. Firstly, we proven that a dilute ideal gas of CEP can condensate at a finite temperature, due to the bosonic nature of CEP and the existence of an energy gap between the ground state and the first exited one. We further extended the analysis beyond the single-pair approximation to determine the energy spectrum and included

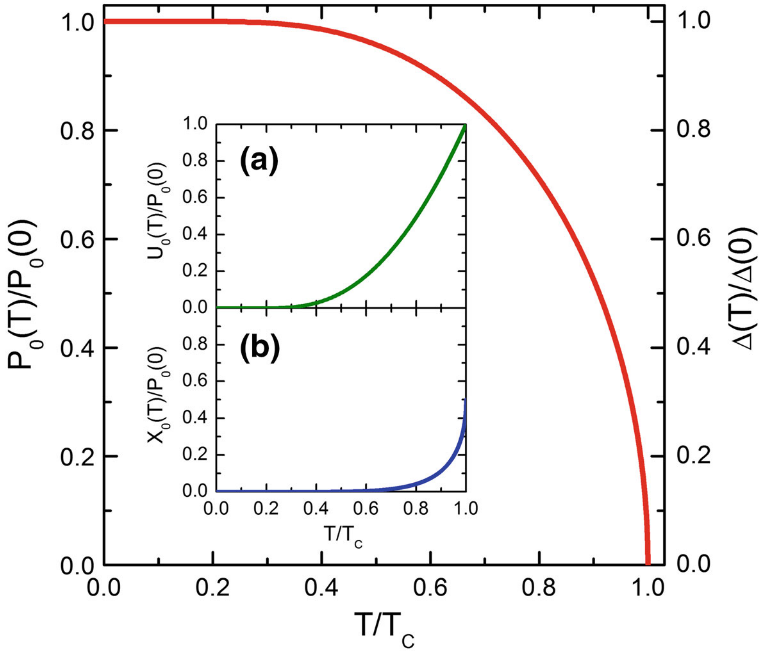

Fig. 2 Number of ground-state pairs (P_0) and superconducting gap (Δ) are plotted as a single function of temperature (T) normalized by the critical temperature ($T_c = T_{BEC}$). *Insets* Populations of (**a**) unpaired electrons (U_0) and (**b**) excited pairs (X_0) versus the temperature (T) (Color figure online)

also unpaired electrons to quantify the grand canonical partition function as well as the BEC temperature. Moreover, based on the concept of superconducting energy gap we found that the superconducting critical temperature of BCS is equal to the BEC temperature, since this analysis is developed beyond the BEC of ideal gases allowing the overlap of Cooper wavefunctions as in the BCS theory. Within the crossover scheme [15], the BEC of CEP at the dilute limit based on single CEP energy spectra is situated in the BEC side, while the BEC analysis including ground-state pairs, excited pairs and unpaired electrons, in parallel to the BCS original approach [8], allows to address the superconductivity at the BCS side. In addition, the temperature dependence of the CEP ground-state population (N_0) in Sect. 2 shows its difference from the well-known BEC of 3D free bosons due to the presence of a constant energy gap between the ground state and the first excited one. Actually, such gap varies with the temperature as in a superconductor, which leads to a qualitatively different behavior around the critical temperature as shown in Fig. 2. This gap variation is originated from the many-pair solution including the blocking effect. Finally, it is worth mentioning that the present study was developed in an essentially analytic form and a further numerical study could include an anisotropic interaction potential in a multishell model to address the d-wave superconductivity observed in cuprate ceramic superconductors.

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