PHYSICAL REVIEW B **81**, 174514 (2010)

Two-Cooper-pair problem and the Pauli exclusion principle

Walter V. Pogosov,[1,2] Monique Combescot,[1] and Michel Crouzeix[3]
[1]*Institut des NanoSciences de Paris, Université Pierre et Marie Curie–CNRS, Campus Boucicaut, 140 rue de Lourmel, 75015 Paris, France*
[2]*Institute for Theoretical and Applied Electrodynamics, Russian Academy of Sciences, Izhorskaya 13, 125412 Moscow, Russia*
[3]*Institut de Recherche Mathématiques de Rennes, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France*

(Received 16 November 2009; revised manuscript received 12 April 2010; published 13 May 2010)

While the one-Cooper-pair problem is now a textbook exercise, the energy of two pairs of electrons with opposite spins and zero total momentum has not been derived yet, the exact handling of Pauli blocking between bound pairs being not that easy for $N=2$ already. The two-Cooper-pair problem however is quite enlightening to understand the very peculiar role played by the Pauli exclusion principle in superconductivity. Pauli blocking is known to drive the change from 1 to N pairs but no precise description of this continuous change has been given so far. Using Richardson's procedure, we here prove that Pauli blocking increases the free part of the two-pair ground-state energy but decreases the binding part when compared to two isolated pairs—the excitation gap to break a pair however increasing from one to two pairs. When extrapolated to the dense BCS regime, the decrease in the pair binding while the gap increases strongly indicates that at odd with common belief, the average pair binding energy cannot be on the order of the gap.

DOI: 10.1103/PhysRevB.81.174514 PACS number(s): 74.20.Fg, 03.75.Hh, 67.85.Jk

I. INTRODUCTION

The first step toward understanding the microscopic grounds of superconductivity was made by Fröhlich[1] who has realized that electrons in metals can form bound pairs due to their weak interaction with the ion lattice, which results in an effective electron-electron attraction. A few years later, Cooper has considered[2] a simplified quantum-mechanical problem of two electrons with opposite spins and zero total momentum added to a "frozen" Fermi sea, i.e., a sea of noninteracting electrons. Within the Cooper model, an attractive interaction between these two electrons is introduced, this interaction being localized in a finite-width layer above the frozen Fermi sea. Cooper has shown that such an attraction, no matter how weak, leads to the appearance of a bound state for the two additional electrons. This result was demonstrated for a single pair although it was fully clear that conventional superconductivity takes place in a macroscopic system of electrons paired by such an attraction.

One year later, Bardeen, Cooper, and Schrieffer[3] (BCS) have proposed an approximate solution of the quantum many-body problem for electrons with opposite spins attracting each other. A very important result of the BCS theory is the existence of a gap in the excitation spectrum above the ground state. In the BCS model, the potential layer, in which an attraction between electrons with opposite spins acts, extends symmetrically on both sides of the Fermi level. This implies that indeed a macroscopic number of electrons interact with each other. In order to avoid the difficult problem associated with the Pauli exclusion principle between a given number of same spin electrons, the grand canonical ensemble was used. The original formulation of BCS theory is also based on a variational ansatz for the ground-state wave function: The wave function is taken with all the electrons feeling the attraction, paired, i.e., "condensed" into the *same* quantum-mechanical state.

It was, however, emphasized by Schrieffer that electron pairs are not elementary bosons because they are constructed from two elementary fermions[4] so that their creation and destruction operators do not obey simple bosonic commutation relations. Schrieffer also claimed that the large overlap which exists between pairs in the dense BCS configuration cuts any link with the two-body Cooper model, the isolated pair picture thus having little meaning in the dense regime.[4] In spite of this claim, it is rather obvious that the many-electron BCS configuration can be reached from the one-Cooper-pair limit by simply adding more and more electron pairs into the layer where the attraction acts, until the layer becomes half filled. A canonical procedure of this kind would allow one to see the evolution of correlated electron pairs from the dilute to the dense regime and to understand deeper the role of the Pauli exclusion principle in fermion pairing. Notice that such an approach can also be considered as a useful and well-defined toy model for the crossover between local and extended pairs of attracting fermions, which in the present time attracts large attention within the field of ultracold gases.[5–7] The crossover problem is still open even for the simplest case of the "reduced" BCS potential for fermion-fermion interaction: a variational solution has only been proposed long-time ago by Eagles[8] and also by Leggett.[9] It also uses a BCS-type ansatz for the ground-state wave function.

A possible way to tackle the problem in the canonical ensemble, i.e., for a fixed number of electron pairs, is to use the procedure developed by Richardson.[10,11] It allows us to write the form of the *exact* N-pair eigenstate of the Schrödinger equation in the case of the so-called reduced BCS potential which is the simplest formulation of the electron-electron interaction mediated by the ion motion. The eigenstate, as well the energy of N pairs, read in terms of N parameters $R_1,\dots,R_N$, which are solutions of N nonlinear algebraic equations. Although Richardson's approach greatly simplifies the problem by avoiding a resolution of a N-body Schrödinger equation, the solution of these equations for $R_1,\dots,R_N$ in a compact form for general N remains an open problem. One of the difficulties is due to the fact that N is not a parameter in these equations but only enters through the number of equations. This is rather unusual and makes the N dependence of the system energy quite uneasy to extract. Nowadays, Richardson's equations are tackled numerically for small-size superconducting granules containing countable numbers of electron pairs.[12] We wish to add that the canonical approach has also been used in the form of a variational fixed-N projected BCS-type theories, see, e.g., Ref. 13.

The goal of the present paper, is to extend the original Cooper's work for one-electron pair to *two* pairs: we *analytically* solve the two Richardson's equations in the large sample limit. Our work can be considered as an initial step toward the establishing of the precise link which exists between dilute and dense regimes of pairs since it indicates a general trend for the evolution of the ground-state energy with the increase of pair number, i.e., overlap between pairs. Richardson's equations are here solved by three methods. They of course give identical results but shine different light on these equations. The approaches to tackle Richardson's equations, proposed in this paper, in fact constitute perspectives for the extension to a larger number of pairs and hopefully to the thermodynamical limit.

The solution we obtain shows that the average pair binding energy is *smaller* in the two-pair configuration than for one pair. This result can be physically understood by noting that electrons which are paired are fermions; therefore, by increasing the number of pairs, we decrease the number of states in the potential layer available to form these paired states. The energy decrease we here find is actually quite general for composite bosons.[14]

However, extrapolation of this understanding to the dense BCS configuration faces difficulty within the common understanding of BCS results. Indeed, it is generally believed[15,16] that the pair binding energy in the dense BCS limit is on the order of the superconducting gap Δ. At the same time, this gap is found as exponentially larger than the single-pair binding energy obtained by Cooper. According to the tendency we here revealed, the average pair binding energy in the dense regime should be smaller than that in the one-pair problem.

This discrepancy motivated us to focus on what is called pair binding energy and more generally "Cooper pair" in the various understanding of the BCS theory. Usually, pairs are said to have a binding energy on the order of Δ. However, such pairs are introduced not *ab initio* but to provide a physical understanding of the BCS result for the ground-state energy.[16,17] Pairs with energy on the order of the gap are called "virtual pairs" by Schrieffer.[4] They represent couples of electrons *excited* above the normal Fermi level for noninteracting electrons, as a result of the attraction between up- and down-spin electrons. Since the Fermi level is smeared out on a scale of Δ by the attraction, the number of such pairs is much smaller than the total number of electron pairs feeling the attraction. The latter were named "superfluid pairs" by Schrieffer.[4] By construction, the concept of "virtual pair" breaks a possible continuity between the dilute and dense regimes of pairs in a somewhat artificial way. By contrast, staying within the framework of superfluid pairs greatly facilitates the physical understanding of the role of Pauli blocking in superconductivity as well as in the BEC-BCS crossover problem (BEC standing for Bose-Einstein condensation). Our results in fact demonstrate the importance of a clear separation between the various concepts of Cooper pair found in the literature.

We wish to mention that the results presented in this paper do not have straightforward experimental applications. The main goal of this paper is to reveal the general trend for the evolution of energy spectrum when changing the number of pairs and to make a first step toward a fully controllable resolution of the N-pair problem. However, even a two-pair configuration has a relation to real materials having correlated pairs of fermions because this configuration corresponds to a dilute regime of pairs, realized in some systems. Conceptually, the overlap between pairs can be tuned either by changing fermion-fermion interaction or total number of pairs. We here show that by increasing the overlap between pairs, we block more and more states available for the construction of paired states. For the first time, a dilute regime of pairs was addressed by Eagles[8] in the context of superconducting semiconductors having a low-carrier concentration. In particular, it was shown in this paper that the excitation spectrum in the dilute regime is controlled by the binding energy of an isolated pair (in agreement with our results) rather than by a more cooperative gap which appears when pairs start to overlap. Thus, this picture is quite similar to the isolated pair model considered by Cooper.

There also is a variety of unconventional superconductors which are characterized by rather short coherence length that implies pairs not overlapping so strongly as in conventional low-T_c materials. For instance, it was argued in Ref. 18 that the BEC-BCS crossover might be relevant for high-T_c cuprates. Some experiments seem to support this idea, for example, Ref. 19 where experimental data on the dependence of the superconducting transition temperature on Fermi temperature are collected for various superconducting materials. This analysis indicates that conventional low-T_c superconductors stay apart from short coherence length materials, including heavy fermion superconductors. Thus, it was argued that to understand these unconventional materials, it is appropriate to focus on the most basic aspect, i.e., on the short coherence length, rather than to introduce more exotic and less generic concepts.[20] It was also shown that the very recently discovered Fe-based pnictides, which constitute a new class of high-T_c superconductors, should be understood as low-carrier density metals resembling underdoped cuprates[21] so that it is possible that the BEC-BCS crossover phenomenon is relevant for these materials as well. Quite recently, it was demonstrated in Ref. 22 that size quantization in nanowires made of conventional superconductors can result in a dramatic reduction in the coherence length bringing superconducting state to the BEC-BCS crossover regime. We finally would like to mention that the two correlated pair problem has received great attention within the ultracold gas field, see, e.g., Ref. 5. All these examples demonstrate that, paradoxically, the Cooper problem seems to be more relevant to modern physics than several decades ago. It is also worth mentioning that BCS Hamiltonian, which only includes interaction between the up- and down-spin electrons with zero pair momentum, is oversimplified. Nevertheless, fermionic pairs in the BEC-BCS transition regime have not been described yet in a fully controlled manner even within this Hamiltonian. *One* of the possible strategies to tackle this crossover therefore is to find a precise solution of the problem for the simplest Hamiltonian and only after that, to turn to more elaborate Hamiltonians.

The paper is organized as follows. In Sec. II, we briefly recall the one-Cooper-pair problem to settle notations. In Sec. III, we present two solutions to the two-pair ground state, as well as a discussion of the possible excited states. We conclude in Sec. IV. In Appendix, we give another exact solution to the two-pair Richardson's equations which shines a different light to the problem.

II. ONE-COOPER-PAIR PROBLEM

Let us briefly recall the one-Cooper-pair problem. We consider a Fermi sea $|F_0\rangle$ made of electrons with up and down spins. An attractive potential between electrons with opposite spins and opposite momenta acts above the Fermi level ε_{F_0}. This potential is taken as constant and separable to allow analytical calculations. In terms of free-pair-creation operators $\beta^\dagger_{\mathbf{k}}=a^\dagger_{\mathbf{k}\uparrow}a^\dagger_{-\mathbf{k}\downarrow}$, it reads as

$$\mathcal{V} = -V\sum_{\mathbf{k}',\mathbf{k}} w_{\mathbf{k}'}w_{\mathbf{k}}\beta^\dagger_{\mathbf{k}'}\beta_{\mathbf{k}}. \tag{1}$$

V is a positive constant and $w_{\mathbf{k}}=1$ for $\varepsilon_{F_0}<\varepsilon_k<\varepsilon_{F_0}+\Omega$.

We add a pair of electrons with opposite spins to the frozen sea $|F_0\rangle$. When the pair has a nonzero momentum, it is trivial to see that $a^\dagger_{\mathbf{p}\uparrow}a^\dagger_{-\mathbf{p}'\downarrow}|F_0\rangle$ with $\mathbf{p}\neq\mathbf{p}'$ is eigenstate of $H=H_0+\mathcal{V}$, where $H_0=\Sigma_{\mathbf{k},s}\varepsilon_k a^\dagger_{\mathbf{k}s}a_{\mathbf{k}s}$, its energy being $(\varepsilon_p+\varepsilon_{p'})$. If the pair has a zero total momentum, the H eigenstates are linear combinations of $\beta_{\mathbf{k}}|F_0\rangle$. We look for them as

$$|\psi_1\rangle = \sum_{\mathbf{k}} G(\mathbf{k})\beta^\dagger_{\mathbf{k}}|F_0\rangle. \tag{2}$$

The Schrödinger equation $(H-\mathcal{E}_1)|\psi_1\rangle=0$ imposes $G(\mathbf{k})$ to be such that

$$[2\varepsilon_{\mathbf{k}}-\mathcal{E}_1]G(\mathbf{k}) - Vw_{\mathbf{k}}\sum w_{\mathbf{k}'}G(\mathbf{k}') = 0. \tag{3}$$

For $2\varepsilon_{\mathbf{k}}\neq\mathcal{E}_1$, the eigenfunction $G(\mathbf{k})$ depends on $\mathbf{k}$ as $w_{\mathbf{k}}/(2\varepsilon_{\mathbf{k}}-\mathcal{E}_1)$ so that $|\psi_1\rangle$ is only made of pairs within the potential layer, as physically expected. The eigenvalues such that $2\varepsilon_{\mathbf{k}}\neq\mathcal{E}_1$ for all $\mathbf{k}$ within the potential layer then follows from Eq. (3) as

$$1 = V\sum_{\mathbf{k}}\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-\mathcal{E}_1} \simeq \frac{V\rho_0}{2}\int_{\varepsilon_{F_0}}^{\varepsilon_{F_0}+\Omega}\frac{2d\varepsilon}{2\varepsilon-\mathcal{E}_1}. \tag{4}$$

ρ_0 is the mean density of states in the potential layer. This leads for a weak potential, i.e., a dimensionless parameter $v=\rho_0 V$ small compared to 1, to

$$\mathcal{E}_1 \simeq 2\varepsilon_{F_0} - \varepsilon_c, \tag{5}$$

$$\varepsilon_c \simeq 2\Omega e^{-2/v}. \tag{6}$$

As seen below, it will be physically enlightening to rewrite this one-Cooper-pair binding energy as

$$\varepsilon_c \simeq (\rho_0\Omega)(2e^{-2/v}/\rho_0) = N_\Omega\varepsilon_V. \tag{7}$$

$N_\Omega=\rho_0\Omega$ is the number of empty pair states in the potential layer Ω from which the Cooper pair bound state is constructed, these states being all empty in the one-Cooper-pair problem. $\varepsilon_V=2e^{-2/v}/\rho_0$ appears as a binding-energy unit induced by *each* of the empty pair states in the potential layer. ε_V only depends on the potential amplitude V and the density of states ρ_0 in the potential layer.

Equation (7) already shows that the wider the potential layer Ω, the larger the number of empty states feeling the potential from which the Cooper pair is made and, ultimately, the larger the binding energy ε_c. We can also note that the pair binding energy depends *linearly* on the number of states available to form a bound state. This remark is actually crucial to grasp the key role played by Pauli blocking in superconductivity: Indeed, this blocking makes the number of empty states available to form a bound state decrease when the pair number increases—or when one pair is broken as in the case of excited states.

III. TWO-COOPER-PAIR PROBLEM

We now add two pairs having opposite spin electrons and zero total momentum to the Fermi sea $|F_0\rangle$ and we look for the eigenstates $(H-\mathcal{E}_2)|\psi_2\rangle=0$ as

$$|\psi_2\rangle = \sum G(\mathbf{k}_1,\mathbf{k}_2)\beta^\dagger_{\mathbf{k}_1}\beta^\dagger_{\mathbf{k}_2}|F_0\rangle. \tag{8}$$

The bosonic character of fermion pairs which leads to $\beta^\dagger_{\mathbf{k}_1}\beta^\dagger_{\mathbf{k}_2}=\beta^\dagger_{\mathbf{k}_2}\beta^\dagger_{\mathbf{k}_1}$, allows us to enforce $G(\mathbf{k}_1,\mathbf{k}_2)=G(\mathbf{k}_2,\mathbf{k}_1)$ without any lost of generality. The Schrödinger equation fulfilled by $G(\mathbf{k}_1,\mathbf{k}_2)$ is somewhat more complicated than for one pair. To get it, it is convenient to note that

$$\mathcal{V}\beta^\dagger_{\mathbf{k}_1}\beta^\dagger_{\mathbf{k}_2}|F_0\rangle = -V(1-\delta_{\mathbf{k}_1\mathbf{k}_2})(w_{\mathbf{k}_1}\beta^\dagger_{\mathbf{k}_2}+w_{\mathbf{k}_2}\beta^\dagger_{\mathbf{k}_1})\sum w_{\mathbf{p}}\beta^\dagger_{\mathbf{p}}|F_0\rangle, \tag{9}$$

the factor $(1-\delta_{\mathbf{k}_1\mathbf{k}_2})$ being necessary for both sides of the above equation to cancel for $\mathbf{k}_1=\mathbf{k}_2$. When used into $(H-\mathcal{E}_2)|\psi_2\rangle=0$ projected upon $\langle F_0|\beta_{\mathbf{k}_1}\beta_{\mathbf{k}_2}$, we get

$$\begin{aligned}0 = (1-\delta_{\mathbf{k}_1\mathbf{k}_2})\Bigg[&(2\varepsilon_{\mathbf{k}_1}+2\varepsilon_{\mathbf{k}_2}-\mathcal{E}_2)G(\mathbf{k}_1,\mathbf{k}_2)\\ &- V\Bigg(w_{\mathbf{k}_1}\sum_{\mathbf{k}\neq\mathbf{k}_2}w_{\mathbf{k}}G(\mathbf{k},\mathbf{k}_2)+(\mathbf{k}_1\leftrightarrow\mathbf{k}_2)\Bigg)\Bigg].\end{aligned} \tag{10}$$

The above equation makes $G(\mathbf{k}_1,\mathbf{k}_1)$ undefined. This however is unimportant since the $\mathbf{k}_1=\mathbf{k}_2$ contribution to $|\psi_2\rangle$ anyway cancels due to the Pauli exclusion principle. For $\mathbf{k}_1\neq\mathbf{k}_2$, the equation fulfilled by $G(\mathbf{k}_1,\mathbf{k}_2)$ follows from the cancellation of the above bracket. With probably in mind a $(\mathbf{k}_1,\mathbf{k}_2)$ decoupling, Richardson suggested to split $\mathcal{E}_2$ as

$$\mathcal{E}_2 = R_1 + R_2 \tag{11}$$

with $R_1\neq R_2$, a requirement mathematically crucial as seen below. We can then note that

$$\frac{2\varepsilon_{\mathbf{k}_1}+2\varepsilon_{\mathbf{k}_2}-\mathcal{E}_2}{(2\varepsilon_{\mathbf{k}_1}-R_1)(2\varepsilon_{\mathbf{k}_2}-R_2)}=\frac{1}{2\varepsilon_{\mathbf{k}_1}-R_1}+\frac{1}{2\varepsilon_{\mathbf{k}_2}-R_2} \tag{12}$$

with (R_1,R_2) possibly exchanged. This probably led Richardson to see that the symmetrical function constructed on the left-hand side (LHS) of the above equation, namely,

$$G(\mathbf{k}_1,\mathbf{k}_2)=\frac{1}{(2\varepsilon_{\mathbf{k}_1}-R_1)(2\varepsilon_{\mathbf{k}_2}-R_2)}+(R_1\leftrightarrow R_2) \tag{13}$$

is an exact solution of the Schrödinger equation provided that R_1 and R_2 are such that

$$1=V\sum\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-R_1}+\frac{2V}{R_1-R_2}=(R_1\leftrightarrow R_2) \tag{14}$$

as obtained by inserting Eq. (13) into $(H-\mathcal{E}_2)|\psi_2\rangle=0$. Note that the denominator in the above equation clearly shows why (R_1,R_2) are required to be different. The fundamental advantage of Richardson's procedure is to replace the resolution of a two-body Schrödinger equation for $G(\mathbf{k}_1,\mathbf{k}_2)$ by a problem far simpler, namely, the resolution of two nonlinear algebraic equations.

This procedure nicely extends to N pairs, the equations for $R_1,\ldots,R_N$ reading as Eq. (14), with all possible R differences. However, to the best of our knowledge, the analytical resolution of these equations for arbitrary N has stayed an open problem, even when $N=2$. We now show how we can tackle this resolution analytically, first through a perturbative approach, and then through two exact procedures.

A. Perturbative approach

A simple way to tackle the Richardson's equations analytically is to note that Eq. (4) allows to replace 1 in the LHS of Eq. (14) by the same sum with R_1 replaced by $\mathcal{E}_1$. If we now add and substract the two Richardson's equations, we get two equations in which the potential V has formally disappeared, namely,

$$\sum\left(\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-R_1}+\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-R_2}\right)=2\sum\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-\mathcal{E}_1}, \tag{15}$$

$$\sum\left(\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-R_1}-\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-R_2}\right)=-\frac{4}{R_1-R_2}. \tag{16}$$

V is in fact hidden into $\mathcal{E}_1$. This is a wise way to put the singular V dependence of Cooper pairs into the problem, at minimum cost.

In view of Eq. (15), we are led to expand the sums appearing in Richardson's equations as

$$\sum_{\mathbf{k}}\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-R_1}=\sum_{\mathbf{k}}\frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}}-\mathcal{E}_1+\mathcal{E}_1-R_1}$$

$$=\sum_{n=0}^{\infty}J_n(R_1-\mathcal{E}_1)^n, \tag{17}$$

where $J_0=1/V$ while $J_{n>0}$ is a positive constant given by

$$J_n=\sum_{\mathbf{k}}\frac{w_{\mathbf{k}}}{(2\varepsilon_{\mathbf{k}}-\mathcal{E}_1)^{n+1}}=\frac{\rho_0}{2}\frac{I_n}{n\varepsilon_c^n}, \tag{18}$$

$$I_n\simeq 1-e^{-2n/v} \tag{19}$$

for v small. For this expansion to be valid, we must have $|R_i-\mathcal{E}_1|<2\varepsilon_{\mathbf{k}}-\mathcal{E}_1$ for all k. This condition is going to be fulfilled for large samples, as possible to check in the end.

It is convenient to look for R_i through $C_i=(R_i-\mathcal{E}_1)/\varepsilon_c$ with $i=(1,2)$. Equations (15) and (16) then give

$$\sum_{n=1}^{\infty}\frac{I_n}{n}(C_1^n+C_2^n)=0, \tag{20}$$

$$(C_1-C_2)\sum_{n=1}^{\infty}\frac{I_n}{n}(C_1^n-C_2^n)=-2\gamma_c. \tag{21}$$

The above formulation evidences that the Richardson's equations contain a small dimensionless parameter, namely,

$$\gamma_c=4/N_c, \tag{22}$$

where $N_c=\rho_0\varepsilon_c$. Indeed, N_c is just the pair number from which pairs start to overlap. This makes N_c large, and consequently γ_c small compared to 1, in the large sample limit.

For $\gamma_c=0$, the solution of the above equations reduces to $C_1=C_2=0$, i.e., $\mathcal{E}_2=2\mathcal{E}_1$. The fact that the two-pair energy $\mathcal{E}_2$ differs from the energy of two single pairs $2\mathcal{E}_1$ is physically due to Pauli blocking but mathematically comes from a small but nonzero value of γ_c.

To solve Eqs. (20) and (21) in the small γ_c limit, it is convenient to set $C_1=S+D$ and $C_2=S-D$. This allows us to rewrite Eqs. (20) and (21) as

$$-D^2=\frac{\gamma_c/2}{\left[I_1+\dfrac{I_3}{2}(D^2+3S^2)+\cdots\right]+S[I_2+I_4(D^2+S^2)+\cdots]}, \tag{23}$$

$$-S=\frac{\dfrac{I_2}{2}(D^2+S^2)+\dfrac{I_4}{4}(D^4+6D^2S^2+S^4)+\cdots}{I_1+\dfrac{I_3}{3}(3D^2+S^2)+\cdots}. \tag{24}$$

Their solution at lowest order in γ_c reads $\gamma_c/2I_1\simeq -D^2\simeq 2SI_1/I_2$. When inserted into $R_1+R_2=2\mathcal{E}_1+(C_1+C_2)\varepsilon_c$, this gives the two-pair energy as

$$\mathcal{E}_2\simeq 2\mathcal{E}_1+\gamma_c\frac{I_2}{2I_1^2}\varepsilon_c$$

$$\simeq 2\mathcal{E}_1+\frac{2}{\rho_0}(1+2e^{-2/v}). \tag{25}$$

Using the expression of $\mathcal{E}_1$ given in Eqs. (5) and (6), we can rewrite this energy as

$$\mathcal{E}_2\simeq 2\left[\left(2\varepsilon_{F_0}+\frac{1}{\rho_0}\right)-\varepsilon_c\left(1-\frac{1}{N_\Omega}\right)\right]$$

$$\simeq 2\left[\left(2\varepsilon_{F_0}+\frac{1}{\rho_0}\right)-\varepsilon_V(N_\Omega-1)\right]. \tag{26}$$

Compared to the energy of two single pairs $2\mathcal{E}_1=2(2\varepsilon_{F_0}-\varepsilon_c)$, we see that Pauli blocking has two quite different effects. (i) It first increases the normal part of this energy as reasonable since the Fermi level for free electrons increases. The first term in Eq. (26) is nothing but $2\varepsilon_{F_0}+2(\varepsilon_{F_0}+\frac{1}{\rho_0})$: one pair has a kinetic energy $2\varepsilon_{F_0}$ while the second pair has a slightly larger kinetic energy $2(\varepsilon_{F_0}+\frac{1}{\rho_0})$, the Fermi level increase when one electron is added, being $1/\rho_0$. (ii) Another less obvious effect of the Pauli exclusion principle is to *decrease* the average pair binding energy. Indeed due to Pauli blocking, $(N_\Omega-1)$ pair states only are available to form a bound state in the two-pair configuration while all the N_Ω pair states are available in the case of a single Cooper pair.

B. Exact approach

The perturbative approach developed above, through the $(R_i-\mathcal{E}_1)$ expansion of the sum appearing in the Richardson's equations, helped us to easily get the effect of Pauli blocking on the ground state of two Cooper pairs. It is in fact possible to avoid this γ_c expansion as we now show.

Through the perturbative calculation, we have found that the difference R_1-R_2 is imaginary at first order in γ_c. It is possible to prove that this difference is imaginary at any order in γ_c: The Richardson's procedure amounts to add an imaginary part to the two-pair energy, in order to escape into the complex plane and avoid poles in sums like the one of Eq. (4), the two "Richardson's energies" then reading as $R_1=R+iR'$ and $R_2=R-iR'$, with R and R' real.

R is by construction real since $R_1+R_2=2R$ is the energy of the two Cooper pairs. In order to show that R' also is real, let us go back to Eq. (16). In terms of (R,R'), this equation reads

$$\sum\frac{w_{\mathbf{k}}}{X_{\mathbf{k}}^2+R'^2}=\frac{1}{R'^2}, \tag{27}$$

where $X_{\mathbf{k}}=2\varepsilon_{\mathbf{k}}-R$ is real. We then note that this equation also reads

$$\sum\frac{w_{\mathbf{k}}X_{\mathbf{k}}^2}{|X_{\mathbf{k}}^2+R'^2|^2}=R'^{*2}\left[\frac{1}{|R'|^4}-\sum\frac{w_{\mathbf{k}}}{|X_{\mathbf{k}}^2+R'^2|^2}\right]. \tag{28}$$

From it, we readily see that since the LHS and the bracket are both real, R'^{*2} must be real. R'^{*2} can then either be positive or negative, i.e., R' can be real or imaginary, which produces (R_1,R_2) either both real or complex conjugate.

To show that (R_1,R_2) cannot be both real, we go back to Eq. (16). By noting that $\Sigma w_{\mathbf{k}}$ is nothing but the number N_Ω of pairs in the potential layer, we can rewrite this equation as

$$0=\sum w_{\mathbf{k}}\left[\frac{1}{2\varepsilon_{\mathbf{k}}-R_1}-\frac{1}{2\varepsilon_{\mathbf{k}}-R_2}+\frac{4}{N_\Omega(R_1-R_2)}\right] \tag{29}$$

$$=\frac{1}{R_1-R_2}\sum w_{\mathbf{k}}\frac{A_{\mathbf{k}}}{(2\varepsilon_{\mathbf{k}}-R_1)(2\varepsilon_{\mathbf{k}}-R_2)}, \tag{30}$$

where

$$A_{\mathbf{k}}=(R_1-R_2)^2+\frac{4}{N_\Omega}(2\varepsilon_{\mathbf{k}}-R_1)(2\varepsilon_{\mathbf{k}}-R_2). \tag{31}$$

It is possible to rewrite the second term of $A_{\mathbf{k}}$ using $4ab=(a+b)^2-(a-b)^2$. This leads to

$$A_{\mathbf{k}}=\left(1-\frac{1}{N_\Omega}\right)(R_1-R_2)^2+\frac{1}{N_\Omega}(4\varepsilon_{\mathbf{k}}-R_1-R_2)^2. \tag{32}$$

Since the number of pairs N_Ω in the potential layer is far larger than 1, $A_{\mathbf{k}}$ would be positive if (R_1,R_2) were both real. For (R_1,R_2) outside the potential layer over which the sum over $\mathbf{k}$ is taken, the sum in Eq. (30) would be made of terms with a given sign so that this sum cannot cancel. Consequently, solutions outside the potential layer must be complex conjugate whatever γ_c.

For (R_1,R_2) complex conjugate, i.e., R' real, the sum over $\mathbf{k}$ in Eq. (27), performed within a constant density of states, leads to

$$\frac{1}{R'^2}=\frac{\rho_0}{2}\int_{\varepsilon_{F_0}}^{\varepsilon_{F_0}+\Omega}\frac{2d\varepsilon_{\mathbf{k}}}{X_{\mathbf{k}}^2+R'^2}$$

$$=\frac{\rho_0}{2R'}\left(\arctan\frac{2\Omega+X_{F_0}}{R'}-\arctan\frac{X_{F_0}}{R'}\right), \tag{33}$$

where $X_{F_0}=2\varepsilon_{F_0}-R$. If we now take the tangent of the above equation, we find

$$\tan\frac{2}{\rho_0R'}=\frac{2\Omega R'}{R'^2+X_{F_0}(2\Omega+X_{F_0})}. \tag{34}$$

Turning to Eq. (15), we find that it reads in terms of (R,R') as

$$\sum\frac{X_{\mathbf{k}}}{X_{\mathbf{k}}^2+R'^2}=\frac{1}{V}. \tag{35}$$

If we again perform the integration over $\mathbf{k}$ with a constant density of states, this equation gives

$$\frac{X_{F_0}^2+R'^2}{(2\Omega+X_{F_0})^2+R'^2}=e^{-4/v}. \tag{36}$$

R and R' then appear as the solutions of two algebraic equations, namely, Eqs. (34) and (36). Unfortunately, they do not have compact form solutions.

It is however possible to solve these equations analytically in the large sample limit. ρ_0 then goes to infinity so that N_Ω and N_c are both large. In this limit $\tan(2/\rho_0R')\simeq 2/\rho_0R'$ to lowest order in $(1/\rho_0)$. Equation (34) then gives $R'^2\simeq X_{F_0}(2\Omega+X_{F_0})/N_\Omega$.

For ρ_0 infinite, i.e., N_Ω infinite, R' reduces to zero so that, due to Eq. (36), $z=X_{F_0}/(2\Omega+X_{F_0})$ reduces to $e^{-2/v}$. Equation (36) can then be rewritten as

$$z^2 \simeq e^{-4/v}\frac{1+z/N_\Omega}{1+1/zN_\Omega}. \tag{37}$$

Since $e^{-2/v}N_\Omega = N_c/2$ is also large compared to 1, this gives the first-order correction in $1/\rho_0$ to $z \simeq e^{-2/v}$ as $z \simeq e^{-2/v}[1+(e^{-2/v}-e^{2/v})/2N_\Omega]$. From $X_{F_0}=2\Omega z/(1-z)$ which for z small reduces to $X_{F_0}\simeq 2\Omega(z+z^2)$, we end by dropping terms in $e^{-4/v}$, with R at first order in $1/\rho_0$ given by

$$R \simeq 2\epsilon_{F_0} - 2\Omega e^{-2/v}\left(1-\frac{1}{N_c}-\frac{1}{N_\Omega}\right)$$

$$\simeq 2\epsilon_{F_0} + \frac{1}{\rho_0} - \epsilon_c\left(1-\frac{1}{N_\Omega}\right). \tag{38}$$

Since $\mathcal{E}_2 = 2R$, this result is just the one obtained from the perturbative approach given in Eq. (26).

The major advantage of this exact procedure is to clearly show that the above result corresponds to the dominant term in both, the large sample limit by dropping terms in $(1/\rho_0)^2$ in front $1/\rho_0$, *and* the small potential limit by dropping terms in $e^{-4/v}$ in front of $e^{-2/v}$. As seen from the first expression of R in Eq. (38), the Pauli exclusion principle induces a double correction, in $1/N_c$ and in $1/N_\Omega$ to the one-pair binding energy $\epsilon_c = 2\Omega e^{-2/v}$. However, the corrections in $1/N_c$ ends by giving a potential free correction to the two-pair energy $\mathcal{E}_2$ because, in a nonobvious way, it in fact comes from a simple change in the free-electron Fermi sea filling, as seen from the second expression of R in Eq. (38).

C. Excited state

We now consider the two-pair excited states with a broken pair having a nonzero total momentum, as possibly obtained by photon absorption. Such a pair does not feel the BCS potential so that it stays uncorrelated. These excited states thus read

$$|\psi_{1;\mathbf{k},\mathbf{k}'}\rangle = \sum F(\mathbf{k}_1)\beta^\dagger_{\mathbf{k}_1}a^\dagger_{\mathbf{k}\uparrow}a^\dagger_{-\mathbf{k}'\downarrow}|F_0\rangle. \tag{39}$$

To derive the equation fulfilled by $F(\mathbf{k}_1)$, it is convenient to note that, for $\mathbf{k}\neq\mathbf{k}'$,

$$\beta_{\mathbf{p}}\beta^\dagger_{\mathbf{k}_1}a^\dagger_{\mathbf{k}\uparrow}a^\dagger_{-\mathbf{k}'\downarrow}|F_0\rangle$$

$$=\delta_{\mathbf{k}_1\mathbf{p}}(1-\delta_{\mathbf{k}_1\mathbf{k}}-\delta_{\mathbf{k}_1\mathbf{k}'})a^\dagger_{\mathbf{k}\uparrow}a^\dagger_{-\mathbf{k}'\downarrow}|F_0\rangle \tag{40}$$

the bracket insuring cancellation for $\mathbf{k}_1=\mathbf{k}$ or $\mathbf{k}'$, as necessary due to the LHS. It is then easy to show, from the Schrödinger equation $(H-\mathcal{E}_{1,\mathbf{kk}'})|\psi_{1;\mathbf{k},\mathbf{k}'}\rangle=0$ projected upon $\langle F_0|a_{-\mathbf{k}'\downarrow}a_{\mathbf{k}\uparrow}\beta_{\mathbf{p}}$ that

$$0=(1-\delta_{\mathbf{pk}}-\delta_{\mathbf{pk}'})\Bigg[(2\varepsilon_{\mathbf{p}}+\varepsilon_{\mathbf{k}}+\varepsilon_{\mathbf{k}'}-\mathcal{E}_{1,\mathbf{kk}'})F(\mathbf{p})$$

$$-Vw_{\mathbf{p}}\sum_{\mathbf{q}\neq\mathbf{k},\mathbf{k}'}w_{\mathbf{q}}F(\mathbf{q})\Bigg]. \tag{41}$$

This makes $F(\mathbf{p})$ undefined for $\mathbf{p}=\mathbf{k}$ or $\mathbf{k}'$. This is unimportant since the corresponding contribution in $|\psi_{1;\mathbf{k},\mathbf{k}'}\rangle$ cancels due to the Pauli exclusion principle. For $\mathbf{p}\neq(\mathbf{k},\mathbf{k}')$, the equation fulfilled by $F(\mathbf{p})$ is obtained by enforcing the bracket of the above equation to cancel. Following the one-Cooper-pair procedure, we get the eigenvalue equation for one broken pair $(\mathbf{k},-\mathbf{k}')$ plus one Cooper pair as

$$\frac{1}{V}=\sum_{\mathbf{p}\neq\mathbf{k},\mathbf{k}'}\frac{w_{\mathbf{p}}}{2\varepsilon_{\mathbf{p}}+\varepsilon_{\mathbf{k}}+\varepsilon_{\mathbf{k}'}-\mathcal{E}_{1,\mathbf{kk}'}}. \tag{42}$$

A first possibility is to have the two free electrons in the two lowest states of the potential layer, namely, $\varepsilon_{\mathbf{k}}=\varepsilon_{F_0}$ and $\varepsilon_{\mathbf{k}'}=\varepsilon_{F_0}+1/\rho_0$. The $\mathbf{p}$-state energy in the above equation must then be larger than $\varepsilon^{(2)}_{F_0}$ with $\varepsilon^{(n)}_{F_0}=\varepsilon_{F_0}+n/\rho_0$ so that Eq. (39) merely gives

$$\frac{1}{V}=\frac{\rho_0}{2}\int_{\varepsilon^{(2)}_{F_0}}^{\varepsilon_{F_0}+\Omega}\frac{2d\varepsilon}{2\varepsilon+2\varepsilon_{F_0}+1/\rho_0-\mathcal{E}_{1,\mathbf{kk}'}}. \tag{43}$$

By writing $\varepsilon_{F_0}+\Omega$ as $\varepsilon^{(n)}_{F_0}+\Omega^{(n)}$ with $\Omega^{(n)}=\Omega-n/\rho_0$, Eqs. (4) and (5) for the single-pair energy readily give

$$\mathcal{E}_{1,\mathbf{kk}'}-\left(2\varepsilon_{F_0}+\frac{1}{\rho_0}\right)\simeq 2\left(\varepsilon_{F_0}+\frac{2}{\rho_0}\right)-2\left(\Omega-\frac{2}{\rho_0}\right)e^{-2/v}. \tag{44}$$

Another possibility is to put the two free electrons in the second and third lowest states of the potential layer, namely, $\varepsilon_{\mathbf{k}}=\varepsilon_{F_0}+1/\rho_0$ and $\varepsilon_{\mathbf{k}'}=\varepsilon_{F_0}+2/\rho_0$. The $\mathbf{p}$-state energy in Eq. (39) can then be equal to ε_{F_0} or larger than $\varepsilon^{(3)}_{F_0}$. In this case, Eq. (39) gives

$$\frac{1}{V}=\frac{1}{2\varepsilon_{F_0}-E}+\frac{\rho_0}{2}\int_{\varepsilon^{(3)}_{F_0}}^{\varepsilon_{F_0}+\Omega}\frac{2d\varepsilon}{2\varepsilon-E} \tag{45}$$

in which we have set $E=\mathcal{E}_{1,\mathbf{kk}'}-2\varepsilon_{F_0}-3/\rho_0$. By writing E as $2\varepsilon^{(3)}_{F_0}-2\Omega^{(3)}e^{-2/v}x$, the above equation gives x through

$$\frac{2}{xN''_c-3}=\log\frac{x}{1+xe^{-2/v}}, \tag{46}$$

where $N''_c=2\Omega^{(3)}e^{-2/v}\rho_0$ is close to N_c, i.e., large compared to 1 in the large sample limit. This gives $x\simeq 1+2/N''_c$ so that the energy $\mathcal{E}_{1,\mathbf{kk}'}$ would then be equal to

$$\mathcal{E}'_{1,\mathbf{kk}'}\simeq 4\varepsilon_{F_0}+\frac{7}{\rho_0}-2\left(\Omega-\frac{3}{\rho_0}\right)e^{-2/v}. \tag{47}$$

This energy is larger than the one given in Eq. (44) with the broken pair in the two lowest-energy levels of the potential layer.

Such a conclusion stays valid for broken pair electrons in higher states: the minimum energy for a broken pair plus a correlated pair is given by $\mathcal{E}_{1,\mathbf{kk}'}$ in Eq. (44). The excitation gap to break one of the two Cooper pairs into two free electrons $\Delta=\mathcal{E}_{1,\mathbf{kk}'}-\mathcal{E}_2$, thus appears to be

$$\Delta=\varepsilon_c+\frac{3}{\rho_0}=\varepsilon_c\left(1+\frac{3}{N_c}\right). \tag{48}$$

We can then remember that the excitation gap for a single pair is equal to $[\varepsilon_{F_0}+(\varepsilon_{F_0}+\frac{1}{\rho_0})]-(2\varepsilon_{F_0}-\varepsilon_c)$, i.e., $\varepsilon_c+\frac{1}{\rho_0}$: The broken pair being again in the *two* lowest states of the potential layer, this brings an additional $\frac{1}{\rho_0}$ contribution to the average pair binding energy ε_c. Equation (48) thus shows that the gap increases when going from one to two pairs. This increase in fact comes from a mere kinetic energy increase induced by Pauli blocking. It is worth noting that, while Pauli blocking induces an *increase* of the gap, it produces a *decrease* from ε_c to $\varepsilon_c(1-1/N_\Omega)$ of the average pair binding energy when going from one to two correlated pairs. Since $N_\Omega=\rho_0\Omega$ is far larger than $N_c=\rho_0\varepsilon_c$, the gap increase however is far larger than the binding energy decrease.

The changes we obtain in the excitation gap and in the average pair binding energy when going from one to two pairs, are a strong indication that the gap in the dense BCS configuration cannot be simply linked to the pair binding energy, as commonly said. Indeed, the pair binding energy is going to stay smaller than $\varepsilon_c=2\Omega e^{-2/v}$ due to Pauli blocking in the potential layer while the experimental gap in the dense regime is known to be on the order of $\Omega e^{-1/v}$ which is far larger than ε_c.

We wish to stress that, in addition to the excited states considered in this section, in which the broken pair ends by having a nonzero momentum, there also are excited states, not included into the present work. In these excited states, the two pairs still have a zero momentum but correspond to R's located somewhere in the quasicontinuum spectrum of the one-electron states, i.e., in between two one-electron levels. For such R's, it is not possible to straightforwardly replace summation by integration in the Richardson's equations as we did throughout the present paper.

IV. CONCLUSION

We here extend the well-known one-pair problem, solved by Cooper, and consider two correlated pairs of electrons added to a Fermi sea of noninteracting electrons. The Schrödinger equation for the two-pair ground state has been reduced by Richardson to a set of two coupled algebraic equations. We here give three different methods to solve these two equations analytically in the large sample limit, providing a unique result. These methods are perspective for the extension to an arbitrary number of pairs in order to hopefully cover the crossover between dilute and dense regimes of Cooper pairs, as well as to apply them to nanoscopic superconductors. Although the two-pair problem we here solve, is only a first step toward the resolution of this quite fundamental problem, it already allows us to understand more deeply the role of Pauli blocking between electrons from which pairs are constructed. We show that this blocking leads to a *decrease* in the average pair binding energy in the two-pair system compared to the one-pair configuration. This decrease is due to the fact that by increasing the number of pairs, we decrease the number of available states to form bound pairs.

This two-pair problem actually has some direct relation to real physical systems, where correlated pairs are more local than in conventional BCS superconductors. We can mention underdoped cuprates, heavy fermion superconductors, pnictides, and ultracold atomic gases. It was shown long-time ago,[8] in the context of superconducting semiconductors with low-carrier density, that the excitation spectrum of such dilute system of pairs is controlled by the binding energy of an isolated pair rather than by a cooperative BCS gap. Hence, this picture is very similar to the classical Cooper model. Within the two-pair configuration that we here solve using Richardson's procedure, we reach the same conclusion for the excitation spectrum. We also reveal how the composite nature of correlated pairs affects their binding energies through the Pauli exclusion principles for elementary fermions from which the pairs are constructed.

The extrapolation of the tendency we find to the dense BCS regime of pairs, indicates that the average pair binding energy in this regime must be smaller than that of an isolated pair. At the same time, it is generally believed that the pair binding energy in the BCS configuration is on the order of the superconducting gap, which is much larger than the isolated pair binding energy. To understand this discrepancy, we must note that there are two rather different concepts of "pairs" in the many-particle BCS configuration. Those with energy on the order of the gap are introduced not *ab initio* but enforced to have a gap energy in order to provide a qualitative understanding for the expression for the ground-state energy, found within the BCS theory. These entities, called virtual pairs by Schrieffer,[4] correspond to pairs of electrons *excited* above the Fermi sea of noninteracting electrons. These virtual pairs have to be contrasted with what Schrieffer calls superfluid pairs,[4] made of *all* the electrons with opposite momenta feeling the attracting BCS potential, the number of these pairs being much larger than the number of virtual pairs. Staying within the framework of superfluid pairs greatly helps to understand the dilute and dense regimes of pairs on the same footing.

ACKNOWLEDGMENTS

W.V.P. acknowledges supports from the French Ministry of Education, RFBR (Project No. 09-02-00248), and the Dynasty Foundation.

APPENDIX

In this appendix, we propose another exact approach to Richardson's equations which may turn more convenient for problems dealing with a pair number larger than 2.

We start with Eq. (14) and calculate the sum by again assuming a constant density,

$$\frac{2}{v}=\int_{\varepsilon_{F_0}}^{\varepsilon_{F_0}+\Omega}\frac{2d\varepsilon}{2\varepsilon-R_1}+\frac{4}{\rho_0(R_1-R_2)} \tag{A1}$$

with R_1 possibly complex. Instead of R_i, we are going to look for $a_i=(2\Omega+2\varepsilon_{F_0}-R_i)/(2\varepsilon_{F_0}-R_i)$ with $i=(1,2)$. Since $R_i=2\varepsilon_{F_0}-2\Omega/(a_i-1)$, the above equation yields

$$\frac{2}{v}=\mathrm{Log}\ a_1+\frac{2}{N_\Omega}\frac{(a_1-1)(a_2-1)}{a_1-a_2}, \tag{A2}$$

where Log denotes the principal value of the complex logarithmic function, i.e., the one that satisfies $-\pi<\mathrm{Im}(\mathrm{Log}\ a_1)\leq\pi$

By adding the same equation with indices (1) and (2) exchanged, we readily get

$$a_1 a_2 = e^{4/v}. \tag{A3}$$

This equation is nothing but Eq. (36) since for $R_1 = R + iR'$, we do have $a_1 = (2\Omega + X_{F_0} - R - iR')/(X_{F_0} - R - iR')$, with i changed into $-i$ for (R_1, a_1) changed into (R_2, a_2). From Eq. (A3), we conclude that $a_1 = e^{2/v} t$ while $a_2 = e^{2/v}/t$.

Next, we note that since the two-pair energy $\mathcal{E}_2 = R_1 + R_2$, which also reads

$$\mathcal{E}_2 = 4\varepsilon_{F_0} - 2\Omega \frac{a_1 + a_2 - 2}{e^{4/v} + 1 - (a_1 + a_2)} \tag{A4}$$

is real, $(a_1 + a_2)$ must be real. This implies $t + 1/t = t^* + 1/t^*$ or equivalently $(t - t^*)(tt^* - 1) = 0$. Consequently, t is either real or such that $|t| = 1$, i.e., $t = e^{i\varphi}$. To choose between these two possibilities, we consider the difference of the two Richardson's equations as written in Eq. (A2). This difference which first appears as

$$0 = \mathrm{Log}\frac{a_1}{a_2} + \frac{4}{N_\Omega}\frac{(a_1 - 1)(a_2 - 1)}{a_1 - a_2} \tag{A5}$$

reads in terms of t as

$$e^{2/v} + e^{-2/v} = t + \frac{1}{t} - \frac{N_\Omega}{2}\left(t - \frac{1}{t}\right)\mathrm{Log}\, t. \tag{A6}$$

For t real, $(t - t^{-1})\mathrm{Log}\, t$ is always positive, except for $t = 1$ where it cancels. This shows that the right-hand side (RHS) of Eq. (A6), equal to 2 for $t = 1$, stays essentially smaller than 2 for N_Ω far larger than 1. Since $e^{2/v} + e^{-2/v}$ is far larger than 2 for v small, we conclude that Eq. (A6) cannot be fulfilled for t real.

The other possibility is $t = e^{i\varphi}$ with $0 < |\varphi| < \pi$ so that $\log t = i\varphi$. We then have $a_1 = a_2^*$, i.e., $R_1 = R_2^*$. This shows that the two Richardson's energies are complex conjugate, as found by the other exact approach. When used into Eq. (A6), this t leads to

$$\varphi \sin \varphi + \frac{2}{N_\Omega}\cos \varphi = \delta_c \tag{A7}$$

with $\delta_c = \frac{e^{2/v} + e^{-2/v}}{N_\Omega} \simeq \frac{2}{N_c}$. Once Eq. (A7) for φ is solved, the two-pair energy given in Eq. (A4) follows from:

$$\mathcal{E}_2 = 4\varepsilon_{F_0} - 4\Omega \frac{e^{2/v}\cos \varphi - 1}{e^{4/v} + 1 - 2e^{2/v}\cos \varphi}. \tag{A8}$$

The solutions of Eq. (A7) cannot be expressed in a compact form in terms of classical functions. We however see that the two dimensionless terms in Eq. (A7), namely, $2/N_\Omega$ and δ_c, are small. Furthermore, $2/N_\Omega$ is smaller than δ_c. The function in the LHS of Eq. (A7) is increasing from $2/N_\Omega$ up to a maximum $\simeq 1.82$, then decreasing down to $-2/N_\Omega$ as φ runs in $[0, \pi]$, and still decreasing on $[\pi, 2\pi]$. This shows that Eq. (A7) admits exactly one solution in the interval $(0, \pi/2)$, another one in the interval $(\pi/2, \pi)$ but no solution in $[\pi, 2\pi]$. Changing φ in $-\varphi$ would provide also two solutions on $(-\pi, 0)$ but this just corresponds to exchange a_1 and a_2 so that they cannot be considered as distinct solutions. For these solutions, $\varphi \sin \varphi$ stays close to zero so that φ is close to 0 or to π. For $\varphi = 0$, the RHS of the above equation reduces, for v small, to $4\varepsilon_{F_0} - 4\Omega e^{-2/v}$ which is just twice the energy of a single Cooper pair as given in Eq. (6). The effect of Pauli blocking on this two single-pair energy results from a large but finite number of pair states N_Ω in the potential layer, as physically expected. We can note that, by contrast, $\varphi = \pi$ would lead to $\mathcal{E}_2$ close to $4\varepsilon_{F_0} + 4\Omega e^{-2/v}$. This solution has to be sorted out because it corresponds to R_1 and R_2 located in the complex plane very close to the real axis where the one-electron levels are positioned so that the distance between them and this real axis is on the order of $1/\rho_0$. This prevents substitution of discrete summation by integration, in Eq. (A1), as discussed above.

For φ close to zero, Eq. (A7) gives the leading term in $1/N_\Omega$ as $\varphi^2 \simeq (e^{1/v} - e^{-1/v})^2/N_\Omega$. The ratio in Eq. (A8) then reads for φ small as

$$\frac{1}{e^{2/v} - 1}\left[1 - \frac{\varphi^2}{2}\frac{e^{2/v}(e^{2/v} + 1)}{(e^{2/v} - 1)^2}\right]$$

$$\simeq \frac{1}{e^{2/v} - 1} - \frac{e^{2/v}}{2N_\Omega}\frac{e^{4/v} - e^{2/v} - 1 + e^{-2/v}}{(e^{2/v} - 1)^3}. \tag{A9}$$

When inserted into Eq. (A8), we end with

$$\mathcal{E}_2 \simeq 4\varepsilon_{F_0} - 4\Omega e^{-2/v} + \frac{2\Omega}{N_\Omega}(1 + 2e^{-2/v}) \tag{A10}$$

which is nothing but Eq. (26).

The main advantage of this second exact method is to have the two-pair energy reading in terms of φ which follows from a single equation, namely, Eq. (A7). By contrast, to get $\mathcal{E}_2$ through $X_{F_0} = 2\varepsilon_{F_0} - \mathcal{E}_2$, as in the other exact method, we must solve two coupled equations, namely, Eqs. (34) and (36).

[1] H. Fröhlich, Phys. Rev. **79**, 845 (1950).

[2] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).

[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[4] J. R. Schrieffer, *Theory of Superconductivity* (Perseus, Massachusetts, 1999).

[5] R. Combescot, X. Leyronas, and M. Y. Kagan, Phys. Rev. A **73**, 023618 (2006).

[6] I. Bloch, J. Dalibard, and W. Zwerger, Rev. Mod. Phys. **80**, 885 (2008).

[7] S. Giorgini, L. P. Pitaevskii, and S. Stringari, Rev. Mod. Phys. **80**, 1215 (2008).

[8] D. M. Eagles, Phys. Rev. **186**, 456 (1969).

[9] A. J. Leggett, J. Phys. Colloq. **41**, C7 (1980).

[10] R. W. Richardson, Phys. Lett. **3**, 277 (1963).

[11] R. W. Richardson and N. Sherman, Nucl. Phys. **52**, 221 (1964).

[12] J. Dukelsky, S. Pittel, and G. Sierra, Rev. Mod. Phys. **76**, 643 (2004).

[13] F. Braun and J. von Delft, Phys. Rev. Lett. **81**, 4712 (1998).

[14] M. Combescot, O. Betbeder-Matibet, and F. Dubin, Phys. Rep. **463**, 215 (2008).

[15] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics, Part 2* (Pergamon, Oxford, 1980).

[16] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Dover, New York, 2003).

[17] M. Tinkham, *Introduction to Superconductivity* (Dover, New York, 2004).

[18] M. Randeria, in *Bose-Einstein Condensation*, edited by A. Griffin, D. Snoke, and S. Stringari (Cambridge University Press, Cambridge, 1995), pp. 355–392.

[19] Y. J. Uemura, Physica C **282-287**, 194 (1997).

[20] Q. Chen, J. Stajic, S. Tan, and K. Levin, Phys. Rep. **412**, 1 (2005).

[21] D. J. Singh and M.-H. Du, Phys. Rev. Lett. **100**, 237003 (2008); L. Craco, M. S. Laad, S. Leoni, and H. Rosner, Phys. Rev. B **78**, 134511 (2008).

[22] A. Shanenko, M. Croitoru, A. Vagov, and F. Peeters, arXiv:0910.2345 (unpublished).