Energy of N Cooper Pairs by Analytically Solving the Richardson-Gaudin Equations for Conventional Superconductors

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(Received 22 March 2011; published 22 December 2011)

This Letter provides the solution to a yet unsolved basic problem of solid state physics: the ground state energy of an arbitrary number of Cooper pairs interacting via the Bardeen-Cooper-Schrieffer potential. We here break a 50 yr old math problem by analytically solving Richardson-Gaudin equations which give the exact energy of these N pairs via N parameters coupled through N nonlinear equations. Our result fully supports the standard BCS result obtained for a pair number equal to half the number of states feeling the potential. More importantly, it shows that the interaction part of the N-pair energy depends on N as $N(N-1)$ only from $N=1$ to the dense regime, a result which evidences that Cooper pairs interact via Pauli blocking only.

DOI: 10.1103/PhysRevLett.107.267001 PACS numbers: 74.20.Fg, 03.75.Hh, 67.85.Jk

Superconductivity [1–4] is one of the most fascinating phenomena of solid state physics. Its physical understanding stayed a major problem for half a century [5]. The first step towards this understanding came from H. Fröhlich [6] who pointed out that two electrons with opposite spins can attract each other via the ion motion. A few years later, L. Cooper showed [7] that, no matter how weak this attraction is, two electrons with opposite spins can form a bound state when added to a Fermi sea in an energy layer where a small attracting potential acts—we will call this layer "potential layer" in the following. To handle more than one pair is difficult because this imposes control over Pauli blocking between paired fermions. A way to overcome this difficulty is to turn to the grand canonical ensemble, with a nonfixed pair number, as proposed by Bardeen, Cooper and Schrieffer (BCS). Using a wave function ansatz—based on the idea that electron pairs are bosonic particles, so that they are likely to condense into the same state—they derived [8], through a minimization of the Hamiltonian mean value, the condensation energy for electrons filling half the potential layer.

A few years after BCS work, R. W. Richardson [9–11] and M. Gaudin [12,13], made an important step in showing that the BCS Hamiltonian leads to one of the very few exactly solvable Schrödinger equations. Indeed, the *exact* energy of N up spin and N down spin electrons paired by the so-called "reduced BCS potential,"

$$V_{\rm BCS} = -V \sum w_{\mathbf{p}'} w_{\mathbf{p}} a^\dagger_{\mathbf{p}'\uparrow} a^\dagger_{-\mathbf{p}'\downarrow} a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow}, \tag{1}$$

with $w_{\mathbf{p}} = 1$ for $\varepsilon_{F_0} < \varepsilon_p < \varepsilon_{F_0} + \Omega$, reads as a sum of N complex quantities R_j solution of N algebraic equations. Although this is a significant advance compared to solving a second order differential equation for N-body wave function, the resolution of these N equations still is a formidable math problem which, over the past half century, stayed unsolved for arbitrary N and potential strength. Through an elegant electrostatic analogy [14], Richardson succeeded in recovering the BCS condensation energy in the large N limit. For small enough N, these equations are commonly approached numerically to understand the physics of superconductor granules [15–17].

Cooper pairs are composite bosons quite different from the semiconductor excitons we extensively studied over the last decade [18]. Through our exciton studies, we however understood that the many-body physics of composite bosons is driven by the Pauli exclusion principle between the particle fermionic components. To microscopically control the effect of Pauli blocking when the Cooper pair number increases, we must stay in the canonical ensemble with both, the number of pairs and the number of states available for pairing, fixed. This is why we decided to tackle these Richardson-Gaudin equations again in order to solve them analytically for arbitrary N.

To grasp the trend induced by Pauli blocking on the pair binding energy, we first considered two pairs: even this $N=2$ problem had no known solution although this definitely is the next problem to tackle after $N=1$ studied by Cooper. A year ago, we showed [19] that the *exact* energy for two pairs reads as

$$E_2 = 2E_1 + \frac{2}{\rho}\left(1 + \frac{2\sigma}{1-\sigma}\right)\frac{\tan\theta/2}{\theta/2}, \tag{2}$$

with θ such that

$$\frac{2\theta \sin\theta}{1 - 2\sigma\cos\theta + \sigma^2} = \frac{2}{\rho\Omega\sigma} \equiv \gamma. \tag{3}$$

$E_1 = 2\varepsilon_{F_0} - \varepsilon_c$ is the single-pair energy found by Cooper. ε_{F_0} is the Fermi energy of the electrons which do not feel the potential. $2\sigma/(1-\sigma) = \varepsilon_c/\Omega$ is the single-pair binding energy in units of the potential extension Ω. The parameter $\sigma = \exp(-2/\rho V)$, with ρ being the density of states taken as constant in the potential layer, is sample volume free, ρ and $1/V$ linearly increasing with volume.

This 2-pair energy gives hints to understanding the effects of Pauli blocking on Cooper pairs. In a large sample, $\rho \to \infty$, so $\theta \to 0$. Difference between the energies of two correlated pairs E_2 and two single pairs $2E_1$ has a naive contribution $2/\rho$ which comes from the fact that the second pair must occupy the up and down states $(\varepsilon_{F_0} + 1/\rho)$ just above the ε_{F_0} Fermi level. $E_2 - 2E_1$ also has a more subtle contribution $2\varepsilon_c/N_\Omega$ where $N_\Omega = \rho\Omega$ is the number of states in the potential layer from which paired electrons are formed. This $2\varepsilon_c/N_\Omega$ contribution brings the 2-pair correlation energy from the two single-pair value $2\varepsilon_c$ down to $2\varepsilon_c(1 - 1/N_\Omega)$. This decrease is induced by the *moth-eaten effect* coming from the Pauli exclusion principle between composite bosons [18]. It is better understood by writing ε_c as $N_\Omega\varepsilon^*$ where $\varepsilon^* = 2\sigma/(1-\sigma)\rho$ is the contribution of each of the N_Ω empty pair states in the potential layer. When a second pair is added, the number of states available for pairing decreases from N_Ω to $N_\Omega - 1$; so the binding energy must decrease, due to Pauli blocking, from $N_\Omega\varepsilon^*$ to $(N_\Omega - 1)\varepsilon^*$, as we find.

The purpose of this Letter is to see how this microscopic understanding of the Cooper pair correlation energy extends to $N > 2$. We here present an analytical solution of Richardson-Gaudin equations for the energy of an arbitrary number of up and down spin electrons paired by the BCS potential. We find that the N-pair energy takes a remarkably compact form

$$E_N = NE_1 + \frac{N(N-1)}{\rho}\frac{1+\sigma}{1-\sigma}, \tag{4}$$

within terms in $(N/\rho)^n$ free from sample volume and thus negligible in the thermodynamic limit, in front of the two volume linear terms of E_N.

This result reduces not only to Eq. (2) for $N = 2$ but also to the energy obtained by Bardeen, Cooper and Schrieffer for $N_{\mathrm{BCS}} = N_\Omega/2$ which corresponds to a potential extending symmetrically on both sides of the normal electron Fermi sea. Indeed, Eq. (4) gives the condensation energy as

$$E_N^{(0)} - E_N = N\varepsilon_c\left[1 - \frac{N-1}{N_\Omega}\right], \tag{5}$$

where $E_N^{(0)} = 2[N\varepsilon_{F_0} + N(N-1)/2\rho]$ is the energy of N "normal" electrons added above ε_{F_0}, for a constant density of states ρ. This condensation energy reduces to $\varepsilon_c N_{\mathrm{BCS}}/2$ for half-filling which is the BCS value, $\rho\Delta^2/2$, the excitation gap reading as $\Delta \simeq \Omega\sigma^{1/2}$ for small σ.

Equation (4) is very astonishing at first because it looks like the first two terms of the small N expansion of the N-pair energy: Higher order N terms seem missing! We have already reached these two terms in a previous work [20] in which we analytically solved Richardson-Gaudin equations in the very dilute limit $N \ll N_c$ where $N_c = \rho\varepsilon_c$ is the pair number over which single Cooper pairs would start to overlap. Since this number is far smaller than the BCS pair number $N_\Omega/2$, the procedure we have used to extract the R_j's from these equations is definitely not valid in the dense BCS limit. Moreover, it is so demanding that there was no hope to use it for higher order N terms in order to at least check that they do cancel exactly.

To prove that these higher order terms do not exist in the large volume limit, we have constructed a totally different procedure. We have found a way to reach the sum of R_j's directly, without calculating these parameters separately, as we have done in our previous work. This is somehow necessary because the R_j's are 2 by 2 complex conjugate—with one R_j real for N odd. When N increases, these R_j's run away from the real axis which prevents their convergence for large N. By contrast, $\sum_j(R_j - E_1)/N\eta$ where

$$\eta \equiv i\sqrt{N\gamma} = i\sqrt{2N/\rho\Omega\sigma} \tag{6}$$

reduces to a degree-one η polynomial due to a set of fundamental cancellations somewhat magic at first [21].

Since the analytical resolution of Richardson-Gaudin equations for arbitrary N and V is a formidable math problem which stayed open for 50 years, some readers may wish to see the major steps of our procedure. These are given in a separate section, to be skipped by a more general audience ready to accept that we have proved Eq. (4).

This very nice solution for a model Hamiltonian widely used in the literature brings some interesting new light in a field commonly considered as fully understood: it provides a direct link between condensation energy and Pauli blocking, out of reach when using the usual BCS ansatz in the grand canonical ensemble because N, then, is not a free parameter. By rewriting the condensation energy for N pairs given in Eq. (5) as $N\varepsilon_c(N) = E_N^{(0)} - E_N$, we find that the average condensation energy per pair in the N-pair configuration, is proportional to the number of states available for pairing. Indeed, for a total number of pairs N_Ω in this layer and $(N-1)$ pair states occupied the average condensation energy simply reads

$$\varepsilon_c(N) = [N_\Omega - (N-1)]\varepsilon^*. \tag{7}$$

This evidences that the unique consequence of increasing the number of pairs in the potential layer is to block more and more states in this layer, until all states are occupied: the correlation energy then reduces to zero. In the Cooper problem, $N = 1$ and $\varepsilon_c(1) = N_\Omega\varepsilon^*$, while in the usual BCS configuration $N = N_\Omega/2$ and the average condensation energy reduces to one half the single-pair value. Equation (7) shows that Cooper pairs only "interact" through Pauli blocking. They can thus overlap without breaking, in contrast to excitons which dissociate into an electron-hole plasma through a Mott transition when overlap starts.

One important consequence of Eq. (7) is that the average pair energy cannot be identified, as is commonly done [2], with the excitation gap much larger than the single-pair value. The gap is the energy to break a pair. In the dense regime, this energy is far larger than just the energy of the broken pair due to Pauli induced many-body effects between the broken pair and the $(N-1)$ unbroken pairs.

Mathematical resolution of Richardson-Gaudin equations.— The energy of N up spin and N down spin electrons interacting via the BCS potential of Eq. (1), reads [9,12,22] as $\sum_{j=1}^{N} R_j$ where the R_j's are coupled through

$$1=\sum_{\mathbf{p}}\frac{Vw_{\mathbf{p}}}{2\varepsilon_{\mathbf{p}}-R_j}+\sum_{k\neq j}\frac{2V}{R_j-R_k}. \tag{8}$$

We now list the major steps of our resolution.

(1) The first step is to note that the one pair energy, $E_1=R_1$, fulfills the above equation without the k sum. By subtracting this equation from Eq. (8), we get

$$0=\sum_{\mathbf{p}}w_{\mathbf{p}}\frac{R_j-E_1}{(2\varepsilon_{\mathbf{p}}-E_1)(2\varepsilon_{\mathbf{p}}-R_j)}+\sum_{k\neq j}\frac{2}{R_j-R_k}. \tag{9}$$

We then set $R_j-E_1=\varepsilon_c z_j$ and expand the sum over $\mathbf{p}$ as a z_j infinite series. By setting

$$\frac{2\varepsilon_c^n}{\rho(1-\sigma)}\sum_{\mathbf{p}}\frac{w_{\mathbf{p}}}{(2\varepsilon_{\mathbf{p}}-E_1)^{n+1}}=\frac{1-\sigma^n}{n(1-\sigma)}\equiv a_n, \tag{10}$$

we find, for γ defined in Eq. (3), that the z_j's fulfill

$$0=\sum_{n=1}^{\infty}a_n z_j^n+\gamma\sum_{k\neq j}\frac{1}{z_j-z_k}. \tag{11}$$

(2) In a second step, we multiply the above equation by z_j^{ℓ} with $\ell=(0,1,2,\ldots)$ and we sum over j. This gives

$$0=\sum_{n=1}^{\infty}a_n Z_{n+\ell}+\gamma D_{\ell}, \tag{12}$$

where the sums Z_m and D_m are defined as

$$Z_m=\sum_{j=1}^{N}z_j^m,\qquad D_m=\sum\sum_{j\neq k}\frac{z_j^m}{z_j-z_k}. \tag{13}$$

The N-pair energy follows from Z_1. Through the replacement of z_j^m by $(z_j^m-z_k^m)/2$ in D_m, it is easy to show that $D_0=0$, $D_1=N(N-1)/2$, $D_2=(N-1)Z_1$, $D_3=(N-3/2)Z_2+Z_1^2/2$, and so on... As $Z_0=N$, the general expression of D_m actually reads

$$D_{m\geq 1}=\frac{1}{2}\sum_{r=0}^{m-1}Z_rZ_{m-1-r}-\frac{m}{2}Z_{m-1}. \tag{14}$$

(3) The third step is to rescale Z_m as $Z_m=N\eta^m X_m$ with η defined in Eq. (6). Equations (12)–(14) then give the set of equations fulfilled by the X_m's as

$$\sum_{n=1}^{\infty}a_n\eta^{n-1}X_{n+\ell}=\frac{1}{2}\sum_{r=0}^{\ell-1}X_rX_{\ell-1-r}-\frac{\ell}{2N}X_{\ell-1}, \tag{15}$$

for $\ell\geq 1$, with the right-hand side equal to zero for $\ell=0$. This shows that the X_m's are η series. We write them as $X_m=\sum_{q\geq 0}x_{m,q}\eta^q$. Since $X_0=1$, we get $x_{0,0}=1$ and $x_{0,q\neq 0}=0$. The other $x_{m,q}$'s follow from identification of the η^q terms in Eq. (15). A tedious but straightforward calculation shows that X_1 is an odd function of η

$$X_1=-\eta\left(1-\frac{1}{N}\right)\frac{1+\sigma}{4}+\frac{1}{N}X_1', \tag{16}$$

where X_1' depends on $(\eta, 1/N, \sigma)$ as

$$X_1'=\left(1-\frac{1}{N}\right)(1+\sigma)(1-\sigma)^2\left\{y_{3,0}\eta^3+\left(y_{5,0}-\frac{y_{5,1}}{N}\right)\eta^5+\left(y_{7,0}-\frac{y_{7,1}}{N}+\frac{y_{7,2}}{N^2}\right)\eta^7+\cdots\right\}, \tag{17}$$

the $y_{m,k}$'s depending on σ only. This leads to

$$E_N=\sum_{j=1}^{N}R_j=NE_1+\epsilon_c N\eta X_1=NE_1+\frac{N(N-1)}{\rho}\frac{1+\sigma}{1-\sigma}+\epsilon_c\eta X_1'. \tag{18}$$

Since the last term scales as $(\eta^4,\eta^6,\eta^8,\cdots)$, it gives volume free contributions to E_N in $(N/\rho)^n$ with $n=(2,3,\cdots)$, in agreement with Eq. (4).

(4) The last step is to prove that *all* corrections to the first two terms of E_N are indeed volume free; i.e., X_1 reduces to $X_1^{(0)}=-\eta(1+\sigma)/4$ for large volume. To do it, we reconsider Eq. (15) without its last term

$$a_1X_{\ell+1}^{(0)}+a_2\eta X_{\ell+2}^{(0)}+a_3\eta^2X_{\ell+3}^{(0)}+\cdots=\frac{1}{2}\sum_{r=0}^{\ell-1}X_r^{(0)}X_{\ell-1-r}^{(0)}. \tag{19}$$

The $X_m^{(0)}$'s, solution of this equation, are η polynomials

$$X_m^{(0)}=x_{m,0}^{(0)}+x_{m,1}^{(0)}\eta+\cdots+x_{m,m}^{(0)}\eta^m, \tag{20}$$

the $x_{m,k}^{(0)}$ coefficients, defined for $0\leq k\leq m$ and nonzero for even $m+k$ only, being just the ones appearing in

$$P_n(t,\sigma)=\frac{1}{2^n(n+1)!}\frac{d^n}{dt^n}[(t-\sigma)^n(t-1)^n] \tag{21}$$

$$=x_{n,n}^{(0)}+x_{n+1,n-1}^{(0)}t+\cdots+x_{2n,0}^{(0)}t^n. \tag{22}$$

From $P_1(t,\sigma)=-(1+\sigma)/4+t/2$, we then find $X_1^{(0)}=x_{1,1}^{(0)}\eta=-\eta(1+\sigma)/4$ as we want.

The first key to check that the solution of Eq. (19) is given by Eq. (20) is to note that $P_n(t,\sigma)$is related to the Legendre polynomial $L_n(t)$ through

$$P_n(t,\sigma) = \left(\frac{1-\sigma}{2}\right)^n \frac{1}{n+1} L_n\left(\frac{2t-1-\sigma}{1-\sigma}\right). \quad (23)$$

The orthogonality of Legendre polynomials [23] then gives

$$0 = \frac{1}{1-\sigma}\int_\sigma^1 t^k P_n(t,\sigma)dt, \quad (24)$$

for $0 \leq k \leq n-1$. By writing $P_n(t,\sigma)$ as in Eq. (22), it follows from this equation that $0 = x^{(0)}_{n,n}a_{k+1} + x^{(0)}_{n+1,n-1}a_{k+2} + \cdots + x^{(0)}_{2n,0}a_{k+1+n}$, where a_n is just the scalar appearing in Eq. (10).

The second key also follows from the link between $P_n(t,\sigma)$ and $L_n(t)$. We can show that

$$\frac{1}{1-\sigma}\int_\sigma^1 \frac{P_n(u,\sigma) - P_n(t,\sigma)}{u-t}du = \frac{1}{2}\sum_{r=0}^{n-1} P_r(t,\sigma)P_{n-1-r}(t,\sigma), \quad (25)$$

the right-hand side reducing to zero for $n = 0$. Equation (22) inserted into the left-hand side of Eq. (25) gives this left-hand side as a t polynomial $G_n(t) = x^{(0)}_{n+1,n-1}g_1(t) + \cdots + x^{(0)}_{2n,0}g_n(t)$ where $g_m(t)$ depends on the a_j scalars of Eq. (10) as $g_m(t) = \sum_{j=1}^m a_j t^{m-j}$. For $n = 1$, this, in particular, gives $G_1(t) = a_1 x^{(0)}_{2,0} = 1/2$ since $P_0(t,\sigma) = 1$.

Using Eqs. (24) and (25), it becomes possible to show by identification that Eq. (20) fulfills Eq. (19). Details will be given in an extended version of this Letter.

Conclusion.— We here derive the energy of N Cooper pairs by solving Richardson-Gaudin equations analytically for arbitrary N and potential strength. We prove that, for large samples, the interaction part of the N Cooper pair energy depends on N as $N(N-1)$ only: higher order N terms do not exist. As a result, the average Cooper pair binding energy $(E^{(0)}_N - E_N)/N$ linearly decreases with pair number from $N = 1$ to the dense regime, [see Eq. (5)], this energy being simply proportional to the number of empty states available for pairing in the potential layer. As a result, the pair binding energy cannot be identified with the gap, as commonly done.

Our result fully supports the BCS result for the ground state energy obtained in the grand canonical ensemble when the potential layer extends symmetrically on both sides of the normal electron Fermi sea. One puzzling question still remains: Why does the BCS ansatz lead to the *exact* ground state energy for N equal to half-filling since its projection onto the N-pair subspace corresponds to $|\psi_N^{(\mathrm{BCS})}\rangle = (B^\dagger)^N|F_0\rangle$ with *all* pairs condensed into the *same* state, while the exact Richardson-Gaudin wave function reads as $|\psi_N\rangle = B^\dagger(R_1)\cdots B^\dagger(R_N)|F_0\rangle$ where

$$B^\dagger(R_j) = \sum_{\mathbf{k}} \frac{w_{\mathbf{k}}}{2\varepsilon_{\mathbf{k}} - R_j} a^\dagger_{\mathbf{k}\uparrow}a^\dagger_{-\mathbf{k}\downarrow}, \quad (26)$$

the R_j's being *all different* due to Pauli blocking, as seen from the last term of Eq. (8)? Is this N-pair energy agreement also valid for correlation functions? We hope that this Letter will stimulate more works in connection with the effects of the Pauli exclusion principle on paired electrons, in a field, BCS superconductivity, commonly considered as fully understood.

We wish to thank Tony Leggett, Walter Pogosov, and Guojun Zhu for numerous discussions.

[1] J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964).
[2] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (Dover Publications, New York, 2003).
[3] M. Tinkham, *Introduction to Superconductivity* (Dover Publications, New York, 2004).
[4] A. J. Leggett, *Quantum Liquids: Bose Condensation and Cooper Pairing in Condensed Matter Systems* (Oxford Univ. Press, Oxford, 2006).
[5] K. Onnes, Comm. Phys. Lab. Univ. Leiden **122** (1911).
[6] H. Frohlich, Phys. Rev. **79**, 845 (1950).
[7] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).
[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[9] R. W. Richardson, Phys. Lett. **3**, 277 (1963).
[10] R. W. Richardson and N. Sherman, Nucl. Phys. **52**, 221 (1964).
[11] R. W. Richardson, J. Math. Phys. (N.Y.) **9**, 1327 (1968).
[12] M. Gaudin, J. Phys. (Paris) **37**, 1087 (1976).
[13] For a review, see M. Gaudin, Modèles Exactement Résolus (Les Editions de Physique, Paris, 1995).
[14] R. W. Richardson, J. Math. Phys. (N.Y.) **18**, 1802 (1977).
[15] F. Braun and J. von. Delft, Phys. Rev. Lett. **81**, 4712 (1998).
[16] J. M. Roman, G. Sierra, and J. Dukelsky, Nucl. Phys. **B634**, 483 (2002).
[17] J. Dukelsky, S. Pittel, and G. Sierra, Rev. Mod. Phys. **76**, 643 (2004).
[18] M. Combescot, O. Betbeder-Matibet, and F. Dubin, Phys. Rep. **463**, 215 (2008).
[19] W. V. Pogosov, M. Combescot, and M. Crouzeix, Phys. Rev. B **81**, 174514 (2010), Eq. (2) follows from the appendix.
[20] W. Pogosov and M. Combescot, JETP Lett. **92**, 484 (2010).
[21] M. Combescot, T. Cren, M. Crouzeix, and O. Betbeder-Matibet, Eur. Phys. J. B **80**, 41 (2011).
[22] M. Combescot and G. Zhu, Eur. Phys. J. B **79**, 263 (2011).
[23] L. S. Gradstein and I. M. Ryzhik, *Tables of Integrals, Series and Products* (Academic Press, New York, 2000).