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Superconducting correlations in metallic nanoparticles: Exact solution of the BCS model by the algebraic Bethe ansatz

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Superconducting pairing of electrons in nanoscale metallic particles with discrete energy levels and a fixed number of electrons is described by the reduced Bardeen, Cooper, and Schrieffer model Hamiltonian. We show that this model is integrable by the algebraic Bethe ansatz. The eigenstates, spectrum, conserved operators, integrals of motion, and norms of wave functions are obtained. Furthermore, the quantum inverse problem is solved, meaning that form factors and correlation functions can be explicitly evaluated. Closed form expressions are given for the form factors and correlation functions that describe superconducting pairing.

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Due to recent advances in nanotechnology it has become possible to fabricate and characterize individual metallic grains with dimensions as small as a few nanometers.[1] They are sufficiently small that the spacing, d, of the discrete energy levels can be determined. A particularly interesting question concerns whether superconductivity can occur in a grain with d comparable to Δ, the energy gap in a bulk system. If $d \ll \Delta$, the superconducting correlations are well described by a mean-field solution to the reduced pairing Hamiltonian [Eq. (1) below] due to Bardeen, Cooper, and Schrieffer (BCS) in the grand canonical ensemble with a variable number of electrons. However, if $d \sim \Delta$ recent numerical calculations have shown that when the number of electrons is fixed (as in the canonical ensemble) the superconducting fluctuations become large and approximate treatments become unreliable.[1,2] Thus, exact calculations of physical quantities are highly desirable. It has only recently been appreciated that the exact eigenstates and spectrum of the BCS model were found in the 1960s by Richardson, in the context of nuclear physics.[1,3] The model has subsequently been found to have a rich mathematical structure: it is integrable (i.e., has a complete set of conserved operators),[4] has a connection to conformal field theory,[5] and is related to Gaudin's inhomogeneous spin-1/2 models.[6–9]

In this Communication we show how the BCS model can be solved using the algebraic Bethe ansatz (ABA) method. This result can be deduced from the observation that the conserved operators obtained in Ref. 4 were also obtained in Ref. 9 via the ABA, but in another context. This observation has been made in Ref. 8. However, the approach we adopt here is slightly different from Ref. 9, which facilitates the solution of the quantum inverse problem[10–13] to explicitly evaluate form factors (i.e., one point functions) and correlation functions. This completes the agenda recently set out by Amico *et al.*[8] We also readily obtain known results for eigenstates, the spectrum, and conserved operators. Our treatment is also applicable to superconductivity in fermionic atom traps[14,15] and can also be extended to a solvable model for condensate fragmentation in boson systems.[16,17]

The Hamiltonian for the reduced BCS model consists of a kinetic energy term and an interaction term which describes the attraction between electrons in time reversed states,

$$H_{BCS} = \sum_{\substack{j=1 \\ \sigma=+,-}}^{\Omega} \epsilon_j c_{j\sigma}^{\dagger} c_{j\sigma} - g \sum_{j,j'=1}^{\Omega} c_{j+}^{\dagger} c_{j-}^{\dagger} c_{j'-} c_{j'+}, \quad (1)$$

where $j = 1, \ldots, \Omega$ labels a shell of doubly degenerate single particle energy levels with energies ϵ_j and $c_{j\sigma}$ the annihilation operators; $\sigma = +,-$ labels the degenerate time reversed states; g denotes the BCS pairing coupling constant. Using the pseudospin realization of electron pairs: $S_j^z = (c_{j+}^{\dagger} c_{j+} + c_{j-}^{\dagger} c_{j-} - 1)/2$, $S_j^+ = c_{j+}^{\dagger} c_{j-}^{\dagger}$ and $S_j^- = c_{j-} c_{j+}$, the BCS Hamiltonian (1) becomes (up to a constant term)

$$H_{spin} = \sum_{j=1}^{\Omega} 2\epsilon_j S_j^z - \frac{g}{2} \sum_{j,k=1}^{\Omega} (S_j^+ S_k^- + S_k^+ S_j^-). \quad (2)$$

The R matrix. An essential ingredient of the ABA, which follows from the quantum inverse scattering method (QISM), is the construction of the R matrix solving the quantum Yang-Baxter equation,

$$R_{12}(u_1 - u_2) R_{13}(u_1 - u_3) R_{23}(u_2 - u_3)$$
$$= R_{23}(u_2 - u_3) R_{13}(u_1 - u_3) R_{12}(u_1 - u_2),$$

where the u_j are spectral parameters. Here R_{jk} denotes the matrix on $V \otimes V \otimes V$ (where V is the two-dimensional Hilbert space on which the pseudospin operators act) acting on the jth and kth spaces and as an identity on the remaining space. The R matrix may be viewed as the structural constants for the Yang-Baxter algebra generated by the monodromy matrix $T(u)$,

$$R_{12}(u_1 - u_2) T_1(u_1) T_2(u_2) = T_2(u_2) T_1(u_1) R_{12}(u_1 - u_2). \quad (3)$$

There are two kinds of realizations of the Yang-Baxter algebra which are relevant to our construction. One is operator valued given by the R matrix $R_{0j}(u)$ and the other is a c-number representation G which does not depend on the spectral parameter u. In the latter case, we have $[R(u), G \otimes G] = 0$. The comultiplication behind the Yang-Baxter algebra allows us to construct a representation of the monodromy matrix through

$$T_0(u) = G_0 R_{0\Omega}(u - \epsilon_\Omega) \cdots G_0 R_{01}(u - \epsilon_1).$$

Defining the transfer matrix via $t(u)\equiv tr_0 T_0(u)$ it follows that $[t(u),t(v)]=0$ for all values of the parameters u, v. If the R matrix possesses the regularity property $R_{jk}(0)=P_{jk}$ with P being the permutation operator, then it is easily verified that

$$t(\epsilon_j)=G_jR_{jj-1}(\epsilon_j-\epsilon_{j-1})\cdots G_jR_{j1}(\epsilon_j-\epsilon_1)G_jR_{j\Omega}(\epsilon_j-\epsilon_\Omega)\cdots G_jR_{jj+1}(\epsilon_j-\epsilon_{j+1})G_j.$$

Let us now assume that the R matrix is quasiclassical, i.e., it admits a series expansion $R(u)=I+\eta r(u)+\cdots$, for an appropriate parameter η. If we can also choose G such that $G=1+\eta\Gamma+\cdots$, then the expansion of $t(\epsilon_j)$ in terms of η takes the form,

$$t(\epsilon_j)=I+\eta\tau_j+\cdots. \tag{4}$$

An immediate consequence from the commutativity of the transfer matrices is $[\tau_j,\tau_k]=0$. Therefore an integrable model is obtained by taking the set $\{\tau_i\}$ as the conserved operators and a Hamiltonian given as a function of the τ_j.

We apply the procedure described above to the $su(2)$ invariant R matrix $R(u)=b(u)I+c(u)P$, with entries that are rational functions: $b(u)=u/(u+\eta)$ and $c(u)=\eta/(u+\eta)$. Note that the regularity property $R(0)=P$ is present. For this case, we can choose G as any element of the $su(2)$ algebra. We claim that the BCS model corresponds to the special choice

$$G_j=\exp(-2\eta S_j^z/g\Omega). \tag{5}$$

This can be viewed as a generalized inhomogeneous six-vertex model. Expanding this and the R matrix to first order in η and substituting in Eq. (4) we find from Eq. (4) that

$$\tau_j=-\frac{2}{g}S_j^z+2\sum_{k\neq j}^{\Omega}\frac{\mathbf{S}_j\cdot\mathbf{S}_k}{(\epsilon_j-\epsilon_k)}$$

where we have discarded a constant term. These operators are the isotropic Gaudin Hamiltonians in a nonuniform magnetic field.[9] Their relevance to the spin realization of the BCS model (2) is that the latter is expressible (up to a constant) as

$$H_{spin}=-g\sum_{j=1}^{\Omega}(\epsilon_j-g/2)\tau_j+\frac{g^3}{4}\sum_{j,k=1}^{\Omega}\tau_j\tau_k.$$

Although the above expressions for the conserved operators only apply to the case when all ϵ_j's are distinct, our construction can be adapted to accommodate the cases when some of ϵ_j's are the same.

Algebraic Bethe ansatz. In the ABA, the integrals of motion are obtained by finding the eigenfunctions of the transfer matrix which is given by the trace of the monodromy matrix. The monodromy matrix is written in the form

$$T(u)=\begin{pmatrix}A(u) & B(u)\\ C(u) & D(u)\end{pmatrix},$$

which is the quantum equivalent of the scattering coefficients of the classical inverse scattering problem. Then from the Yang-Baxter algebra (3), we may derive the fundamental commutation relations (FCR) between the entries of the monodromy matrix. Choosing the state $|0\rangle=\otimes_{j=1}^{\Omega}|\uparrow\rangle_j$ as the pseudovacuum, then we have the pseudovacuum eigenvalues $a(u)$ and $d(u)$ of $A(u)$ and $D(u)$: $a(u)=\exp(-\eta/g), d(u)=\exp(\eta/g)\Pi_j b(u-\epsilon_j)$. Following the standard procedure,[10,18] we choose the Bethe state

$$\Psi(v_1,\ldots,v_N)=\prod_{\alpha=1}^{N}B(v_\alpha)|0\rangle. \tag{6}$$

Then we may derive the off-shell Bethe ansatz equations using the FCR,[18,19] which, in the quasiclassical limit, take the form

$$\frac{1}{2}\tau_j\psi=\lambda_j\psi-\sum_{\alpha=1}^{N}\frac{f_\alpha S_j^-}{\epsilon_j-v_\alpha}\psi'_\alpha, \tag{7}$$

where

$$\lambda_j=-\frac{1}{2g}-\frac{1}{2}\sum_{\alpha}\frac{1}{\epsilon_j-v_\alpha}+\frac{1}{4}\sum_{i\neq j}\frac{1}{\epsilon_j-\epsilon_i},$$

$$f_\alpha=\frac{1}{g}+\sum_{\beta\neq\alpha}\frac{1}{v_a-v_\beta}-\frac{1}{2}\sum_j\frac{1}{v_\alpha-\epsilon_j},$$

$$\psi\equiv|v_1,\ldots,v_N\rangle=\prod_{\alpha=1}^{N}\sum_{j=1}^{\Omega}\frac{S_j^-}{v_\alpha-\epsilon_j}|0\rangle.$$

In (7) we defined ψ'_α by

$$\psi=\sum_{j=1}^{\Omega}\frac{S_j^-}{v_\alpha-\epsilon_j}\psi'_\alpha.$$

Imposing $f_\alpha=0$, one immediately sees that ψ becomes the eigenvector of the conserved operator τ_j with λ_j as the eigenvalue. The constraint $f_\alpha=0$ is then equivalent to Richardson's equations,[3]

$$\frac{2}{g}+\sum_{\beta\neq\alpha}^{N}\frac{2}{v_\alpha-v_\beta}=\sum_{j=1}^{\Omega}\frac{1}{v_\alpha-\epsilon_j}. \tag{8}$$

Here $\Omega-N$ may be interpreted as the number of time-reversed pairs of electrons. The energy eigenvalue of the Hamiltonian (2) is

$$E_{spin}=\sum_{j=1}^{\Omega}\epsilon_j-2\sum_{\alpha=1}^{N}v_\alpha+g(2N-\Omega). \tag{9}$$

Scalar products and norms. Directly evaluating the norms of Bethe wave functions can be tedious, if not impossible. However, using the QISM they can be represented as determinants.[10,20] Since this representation only depends on the R matrix, the derivation presented previously for different models can be readily applied to our (generalized) inhomogeneous six-vertex model. In the QISM construction, the determinant representation for scalar products

$$\langle 0|\prod_{\beta=1}^{N}C(w_\beta)\prod_{\alpha=1}^{N}B(v_\alpha)|0\rangle$$

play a crucial role; especially, when one of the sets of parameters, for example $\{v_a\}$, is a solution of the Bethe equations.[10,11,21] In the quasiclassical limit, the leading term of the scalar product for the inhomogeneous six-vertex model gives rise to the scalar product

$$\langle w_1,\ldots,w_N|v_1,\ldots,v_N\rangle=\frac{\prod_{\beta=1}^{N}\prod_{\substack{\alpha=1\\ \alpha\neq\beta}}^{N}(v_\beta-w_\alpha)}{\prod_{\beta<\alpha}(w_\beta-w_\alpha)\prod_{\alpha<\beta}(v_\beta-v_\alpha)}\times\det{}_N J(\{v_\alpha\},\{w_\beta\}), \qquad (10)$$

where the matrix elements of J are given by

$$J_{ab}=\frac{v_b-w_b}{v_a-w_b}\left(\sum_{j=1}^{\Omega}\frac{1}{(v_a-\epsilon_j)(w_b-\epsilon_j)}-2\sum_{\alpha\neq a}\frac{1}{(v_a-v_\alpha)(w_b-v_\alpha)}\right). \qquad (11)$$

Here $\{v_\alpha\}$ are a solution to Richardson's equations (8), whereas $\{w_\beta\}$ are arbitrary parameters. Richardson's expression[22] for the square of the norm of the Bethe state follows from Eqs. (10) and (11) by taking the limit $w_\alpha \to v_\alpha$.

Solution of the quantum inverse problem. In order to calculate the form factors and correlation functions, we need to solve this problem for the generalized inhomogeneous six-vertex model. This then allows the reconstruction of local quantum spin operators in terms of the quantum monodromy matrix. A general procedure for doing this has recently been presented[11,12] for the so-called *fundamental* models. A model is said to be fundamental whenever the local Lax operator in the transfer matrix is the same as the R matrix. In our case, where the model is not fundamental, due to the inclusion of the operators G_i, we find

$$S_i^-=\prod_{\alpha=1}^{i-1}t(\epsilon_\alpha)K^{-i+1}B(\epsilon_i)K^{i-1}\prod_{\alpha=1}^{i}t^{-1}(\epsilon_\alpha),$$

$$S_i^+=\prod_{\alpha=1}^{i-1}t(\epsilon_\alpha)K^{-i+1}C(\epsilon_i)K^{i-1}\prod_{\alpha=1}^{i}t^{-1}(\epsilon_\alpha),$$

$$S_i^z=\prod_{\alpha=1}^{i-1}t(\epsilon_\alpha)K^{-i+1}\frac{(A(\epsilon_i)-D(\epsilon_i))}{2}K^{i-1}\prod_{\alpha=1}^{i}t^{-1}(\epsilon_\alpha),$$

with $K\equiv\prod_{j=1}^{\Omega}G_j=\exp(-2\eta\sum_{j=1}^{\Omega}S_j^z/g\Omega)$. The above construction is one of our main results. The appearance of the powers of K arises from the c-number matrix realization of the Yang-Baxter algebra G which is peculiar to our construction. Following Ref. 11, one can obtain the representation of the correlation functions in terms of pseudovacuum eigenvalues $a(u)$ and $d(u)$.

Form factors. For the BCS model the pair correlator

$$C_m^2\equiv\langle c_{m+}^\dagger c_{m+}c_{m-}^\dagger c_{m-}\rangle-\langle c_{m+}^\dagger c_{m+}\rangle\langle c_{m-}^\dagger c_{m-}\rangle \qquad (12)$$

is of particular interest.[1,23] (We use the notation that $\langle\chi\rangle \equiv\langle v_1,\ldots v_N|\chi|v_1,\ldots,v_N\rangle/\langle v_1,\ldots v_N|v_1,\ldots,v_N\rangle$ for any operator χ). C_m^2 can be interpreted as the probability enhancement of finding a pair of electrons in level m, instead of two uncorrelated electrons. (It is zero for $g=0$). In the pseudospin representation $C_m^2=\langle S_m^-S_m^+\rangle\langle S_m^+S_m^-\rangle=1/4-\langle S_m^z\rangle^2$. In general, form factors such as

$$F^z(m,\{w_\beta\},\{v_\alpha\})\equiv\langle 0|\prod_{\beta=1}^{N}C(w_\beta)S_m^z\prod_{\alpha=1}^{N}B(v_\alpha)|0\rangle$$

can be calculated for the generalized inhomogeneous six-vertex model. In the quasiclassical limit, they reduce to the form factors of the BCS model,

$$\langle w_1,\ldots,w_{N+1}|S_m^-|v_1,\ldots,v_N\rangle=\langle v_1,\ldots,v_N|S_m^+|w_1,\ldots,w_{N+1}\rangle=\frac{\prod_{\beta=1}^{N+1}(w_\beta-\epsilon_m)}{\prod_{\alpha=1}^{N}(v_\alpha-\epsilon_m)}\frac{\det_{N+1}\mathcal{T}(m,\{w_\beta\},\{v_\alpha\})}{\prod_{\beta>\alpha}(w_\beta-w_\alpha)\prod_{\beta<\alpha}(v_\beta-v_\alpha)},$$

$$\langle w_1,\ldots,w_N|S_m^z|v_1,\ldots,v_N\rangle=\prod_{\alpha=1}^{N}\frac{(w_\alpha-\epsilon_m)}{(v_\alpha-\epsilon_m)}\frac{\det_N\left(\frac{1}{2}\tilde{\mathcal{T}}(\{w_\beta\},\{v_\alpha\})-Q(m,\{w_\beta\},\{v_\alpha\})\right)}{\prod_{\beta>\alpha}(w_\beta-w_\alpha)\prod_{\beta<\alpha}(v_\beta-v_\alpha)},$$

with the matrix elements of $\mathcal{T}$ given by

$$\mathcal{T}_{ab}(m)=\prod_{\substack{\alpha=1\\ \alpha\neq a}}^{N+1}(w_\alpha-v_b)\left(\sum_{J=1}^{\Omega}\frac{1}{(v_b-\epsilon_j)(w_a-\epsilon_j)}-2\sum_{\alpha\neq a}\frac{1}{(v_b-w_\alpha)(w_a-w_\alpha)}\right),\quad b<N+1,$$

$$\mathcal{T}_{aN+1}(m)=\frac{1}{(w_a-\epsilon_m)^2},\quad Q_{ab}(m)=\frac{\prod_{\alpha\neq b}(v_\alpha-v_b)}{(w_a-\epsilon_m)^2}.$$

Above, $\tilde{\mathcal{T}}$ is the $N\times N$ matrix obtained from $\mathcal{T}$ by deleting the last row and column and replacing $N+1$ by N in the matrix elements. Here we assume that both $\{v_\alpha\}$ and $\{w_b\}$ are solutions to Richardson's Bethe equations (8). However, the results are still valid for $S_m^\pm$ if only $\{w_b\}$ satisfy the Bethe equations.

Correlation functions. We find that the correlation functions of the BCS model take the same form as the underlying $su(2)$ spin 1/2 Gaudin model, with the parameters v_j satisfying Richardson's Bethe ansatz equations (8) instead of Gaudin's ones. Here we present explicitly the two-point correlation function

$$\langle w_1,\ldots,w_N|S_m^- S_n^+|v_1,\ldots,v_N\rangle = \sum_{\alpha=1}^{N} \frac{1}{v_\alpha-\epsilon_n}\langle w_1,\ldots,w_N|S_m^-|v_1,\ldots,\hat{v}_\alpha,\ldots,v_N\rangle - \sum_{\alpha\neq\beta}\frac{1}{(v_\alpha-\epsilon_n)(v_\beta-\epsilon_n)} \times\langle w_1,\ldots,w_N|S_m^- S_n^-|v_1,\ldots,\hat{v}_\alpha,\ldots,\hat{v}_\beta,\ldots,v_N\rangle. \tag{13}$$

Here the hat denotes that the corresponding parameter is not present in the set. Since $\{w_a\}$ is a solution of the Bethe equations, $\langle w_1,\ldots,w_N|S_m^-|v_1,\ldots,\hat{v}_\alpha,\ldots,v_N\rangle$ is the form factor given before, while

$$\langle w_1,\ldots,w_N|S_m^- S_n^-|v_1,\ldots,v_{N-2}\rangle = \frac{\prod_{\beta=1}^{N}(w_\beta-\epsilon_m)(w_\beta-\epsilon_n)}{\prod_{\alpha=1}^{N-2}(v_\alpha-\epsilon_m)(v_\alpha-\epsilon_n)} \frac{\det_N \mathcal{T}(m,n,\{w_\beta\},\{v_\alpha\})}{\prod_{\beta>\alpha}(w_\beta-w_\alpha)\prod_{\beta<\alpha}(v_\beta-v_\alpha)}, \tag{14}$$

with

$$\mathcal{T}_{ab}(m,n)=\prod_{\substack{\alpha=1\\ \alpha\neq a}}^{N}(w_\alpha-v_b)\left(\sum_{j=1}^{\Omega}\frac{1}{(v_b-\epsilon_j)(w_a-\epsilon_j)} -2\sum_{\alpha\neq a}\frac{1}{(v_b-w_\alpha)(w_a-w_\alpha)}\right), \qquad b<N-1,$$

$$\mathcal{T}_{aN-1}(m,n)=\frac{2w_a-\epsilon_m-\epsilon_n}{[(w_a-\epsilon_m)(w_a-\epsilon_n)]^2},$$

$$\mathcal{T}_{aN}(m,n)=\frac{1}{(w_a-\epsilon_m)^2},$$

In Eq. (14) $m\neq n$ is assumed, with the convention that it is zero when $m=n$. Such a determinant representation of the correlation function will be computationally more accessible than a previous proposal[7] relying on the generating function associated with the Gaudin algebra. The above results constitute the building blocks of the Penrose-Onsager-Yang off-diagonal long-range order (ODLRO) parameter Δ_{OD},[24]

$$\Delta_{OD}\equiv\frac{1}{\Omega}\sum_{mn}\langle S_n^+ S_m^-\rangle. \tag{15}$$

The small grain behavior of this parameter and its connection with the pair correlator (12) was recently discussed in Ref. 25.

Further applications. Our work is also relevant to proposals to observe BCS superconductivity in gases of fermionic atoms such as spin-polarized ^{6}Li.[14] Quantum degeneracy of ^{6}Li at temperatures of about 240 nK has recently been observed in an atom trap with frequencies, $\omega\sim1$ kHz,[15] corresponding to an energy level spacing of the order of 10^{-12} eV. The estimated BCS transition temperature is of the order of 20 nK,[14] corresponding to an energy gap of the order of 4×10^{-12} eV. Hence, these systems are in a regime where the physics considered here will be important.

Dukelsky and Schuck[16] recently introduced a solvable model for condensate fragmentation in finite boson systems. The model they solved follows from the construction used above when the Yang-Baxter algebra is realized in terms of the generators of the Lie algebra $su(1,1)$. The model also provides a new mechanism for the enhancement of sd dominance in interacting boson models in the context of nuclear physics.[26]

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