Chapter 25

# SUPERCONDUCTIVITY IN ULTRASMALL METALLIC PARTICLES

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**Abstract** Recent single electron transport experiments in nanometer size samples renewed the question about the lower limits of the size of superconductors, and the crossover from superconducting to normal state. In order to give answers to these questions, a pairing Hamiltonian for fixed number of particles is studied including the degeneracy of levels around the Fermi energy. For $d$-fold degenerate states we find that the ratio of two successive parity parameters $\Delta_p$ is nearly $1 + 1/d$.

## 1. INTRODUCTION

Back in the year of 1959, Anderson [1] proposed that for a small metallic particle superconductivity should disappear as the mean level spacing $\delta$ becomes of the order of bulk gap $\Delta$. Since the level spacing is related to the size of the material as $\delta \sim 1/\text{Vol}$, according to Anderson's criterion, superconductivity would disappear in ultrasmall grains.

Interest in superconductivity in ultrasmall grains recently renewed with a series of experiments by Black, Ralph and Tinkham (BRT) [2, 3] (and more recently by Davidović and Tinkham [4, 5]). BRT accomplished in fabricating a single Al particle of nanometer size connected to two separate metal leads by tunnel junctions. They obtain the current-voltage $(I - V)$ curve with discrete steps corresponding to tunneling via individual electronic states in the sample, providing the first spectroscopic measurement of these states. BRT observe that the spectroscopic gap parameter vanishes as the size of the sample decreases. For estimated level spacing $\delta \sim 0.02$ meV (corresponding sample size is $r \sim 10$ nm) a gap is observed, while for $\delta \sim 0.7$ meV ($r \sim 2.5$ nm) gap disap-



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pears. Since $\Delta \sim 0.34$ meV for Al, BRT conclude that their experimental results are in qualitative agreement with Anderson's criterion. BRT also observed that the gap parameter persists for smaller samples with even number of electrons than those with odd number of electrons.

These experiments raised questions about the crossover from superconducting to normal state in ultrasmall grains with level spacing $\delta \sim \Delta$. Standard BCS theory gives a good description of the phenomenon of superconductivity for large samples. However one should expect that the quantum fluctuations of the order parameter grows as $\delta$ reaches $\Delta$. Matveev and Larkin (ML)[6] show that the corrections to the mean field results which are small in large grains ($\delta \ll \Delta$), become important in the opposite limit ($\delta \gg \Delta$). ML [6] introduce a parameter for parity effect:

$$\begin{aligned} \Delta_p &= E_g^{2n+1} - \frac{1}{2}\left(E_g^{2n} + E_g^{2n+2}\right) , \\ \tilde{\Delta}_p &= -E_g^{2n} + \frac{1}{2}\left(E_g^{2n+1} + E_g^{2n-1}\right) . \end{aligned} \tag{25.1}$$

Although with standard BCS calculations it vanishes, ML show that, if the quantum fluctuations are properly taken into account, the parity parameter does not vanish for $\delta \gg \Delta$. They obtain the following asymptotic results

$$\begin{aligned} \frac{\Delta_p}{\Delta} &= 1 - \frac{\delta}{2\Delta} , \frac{\delta}{\Delta} \ll 1, \\ \frac{\Delta_p}{\Delta} &= \frac{\delta}{\Delta}\frac{1}{2\ln\frac{\delta}{\Delta}}, \quad \frac{\delta}{\Delta} \gg 1 , \end{aligned} \tag{25.2}$$

In scope of these asymptotic results, ML conclude $\Delta_p/\Delta$ has a minimum about $\delta \sim \Delta$. Note that this value corresponds to the crossover in question, that is transition from superconducting to normal state.

Mastellone, Falci and Fazio [7], and Berger and Halperin [8] solve the problem numerically by exact diagonalization. Both groups obtain similar results suggesting a minimum in $\Delta_p/\Delta$ for $\delta \sim \Delta$, in agreement with ML's predictions. Braun and von Delft [9] approach the problem within a fixed-N picture of superconductivity. Instead of grand canonical ensemble, they solve the problem by using a canonical ensemble. Their results confirm the minimum predicted by ML.

## 2. THE MODEL

Although it is supposed that these ultrasmall samples are irregular in shape, it has been argued [10] that spatial symmetry may exist no matter how small the sample is. In case such a symmetry exists, for

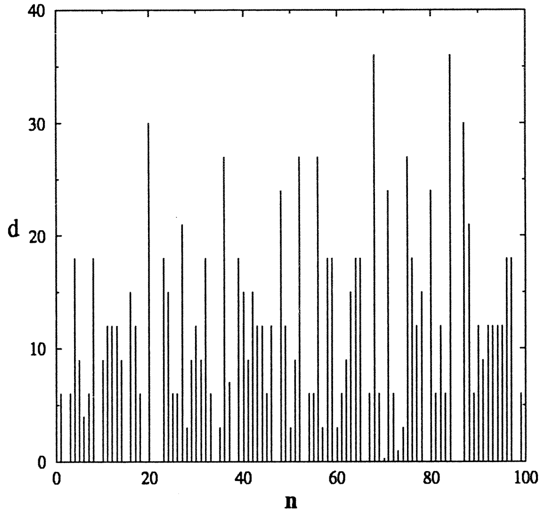


*Figure 25.1* Degeneracy of energy levels for a parabolic dispersion, where $E_n = \frac{\hbar^2\pi^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$. The number of solutions $d$ satisfying $n^2 = n_1^2 + n_2^2 + n_3^2$ for a range of energies about the Fermi energy is shown as vertical lines for each channel.

a parabolic dispersion, degeneracy is of the order of $k_F L$ where $k_F$ is the Fermi momentum and $L$ is the particle size, and typical distance between levels is of the order of $\hbar^2/mL^2$. Fig. 25.1 shows the degeneracy of energy levels in such a parabolic dispersion. If we assume that there is no spatial symmetry in the grain, then the only degeneracy is due to the time reversal symmetry. In order to understand the effect of time reversal symmetry, let us consider the standard BCS theory. For a grain where eigenstates are labeled by crystal momentum $\mathbf{k}$, time reversed states are $|\mathbf{k}\downarrow\rangle$ and $|-\mathbf{k}\uparrow\rangle$. Note that there is another similar but different pair between $|\mathbf{k}\uparrow\rangle$ and $|-\mathbf{k}\downarrow\rangle$. Since in usual BCS reduced Hamiltonian there is a summation over $\mathbf{k}$, both pairs are properly taken into account in calculations. However, when we sum over energy levels rather than the individual states we must be careful in including both pairs [11]. Nevertheless, the model without double degeneracy can still be considered to describe superconductivity in systems with real wave functions e.g. one dimensional infinite quantum well.

We address the question of ultrasmall superconducting grains within a pairing Hamiltonian

$$H = \sum_{f,\sigma} \epsilon_f c^\dagger_{f,\sigma} c_{f,\sigma} - g \sum_{f,f' \in S} c^\dagger_{f,\sigma} c_{f,\sigma} c^\dagger_{f',-\sigma} c_{f',-\sigma}, \tag{25.3}$$

where $c^\dagger_{f,\sigma}$ and $c_{f,\sigma}$ are fermion creation and annihilation operators which satisfy the anti-commutation relation

$$[c_{f,\sigma}, c_{f',\sigma'}]_+ = \delta_{ff'}\delta_{\sigma\sigma'}, \tag{25.4}$$

and $f$ denotes the single particle quantum numbers including degeneracy, $\epsilon_f$ denotes the single particle energy levels, $\sigma = \pm 1$ denotes the states with up and down spin, which are conjugate with respect to time reversal symmetry, $g$ is the pair-pair coupling term. The second summation is over a convenient set of levels $S$. For the BCS model this set is the collection of levels lying within a shell which has a width of $2\omega_D$ about the Fermi level. Hence, in the second sum we impose this restriction and consider only the states

$$f, f' \in S = \{-n_c, ...., n_c\}, \tag{25.5}$$

where $n_c = [\omega_D/\delta]$ (where $[\ldots]$ denotes integer part of the argument).

We write above model of many-fermion system (25.3) as an Hamiltonian of fermion pairs interacting via pairing forces in second quantized form

$$H = \sum_f 2\epsilon_f \hat{N}_f - g \sum_{f,f' \in S} b^\dagger_f b_{f'}, \tag{25.6}$$

where

$$\hat{N}_f = \frac{1}{2}\left(c^\dagger_{f,\sigma} c_{f,\sigma} + c^\dagger_{f,-\sigma} c_{f,-\sigma}\right), \tag{25.7}$$

and

$$b_f = c_{f,-\sigma} c_{f,\sigma}. \tag{25.8}$$

Since the second term of $H$ defines interaction between pairs only, unpaired particles do not interact. Therefore, singly occupied levels are taken out from the set $S$. This is the so-called "blocking effect". Moreover, with the shift of chemical potential, levels included in $S$ will also change. Fig. 25.2 shows both of these effects.

We first calculate ground state energies for three successive states with number of particles being equal to $l$, $l+1$ and $l+2$. Since we also consider degeneracy in the system, we obtain $2 \times d$ ($d$ being the level degeneracy) different $\Delta_p$ values. We use the following labeling scheme

$$\Delta_p^{(m)} = (-1)^m \left[E_g^{(2N+m-1)} - \frac{1}{2}\left(E_g^{(2N+m-2)} + E_g^{(2N+m)}\right)\right], \tag{25.9}$$

where $N = n_c d$ (total number of levels within the shell below Fermi energy and above). Hence, for example, for $m = 1$

$$\Delta_p^{(1)} = -E_g^{(2N)} + \frac{1}{2}\left(E_g^{(2N-1)} + E_g^{(2N+1)}\right), \tag{25.10}$$

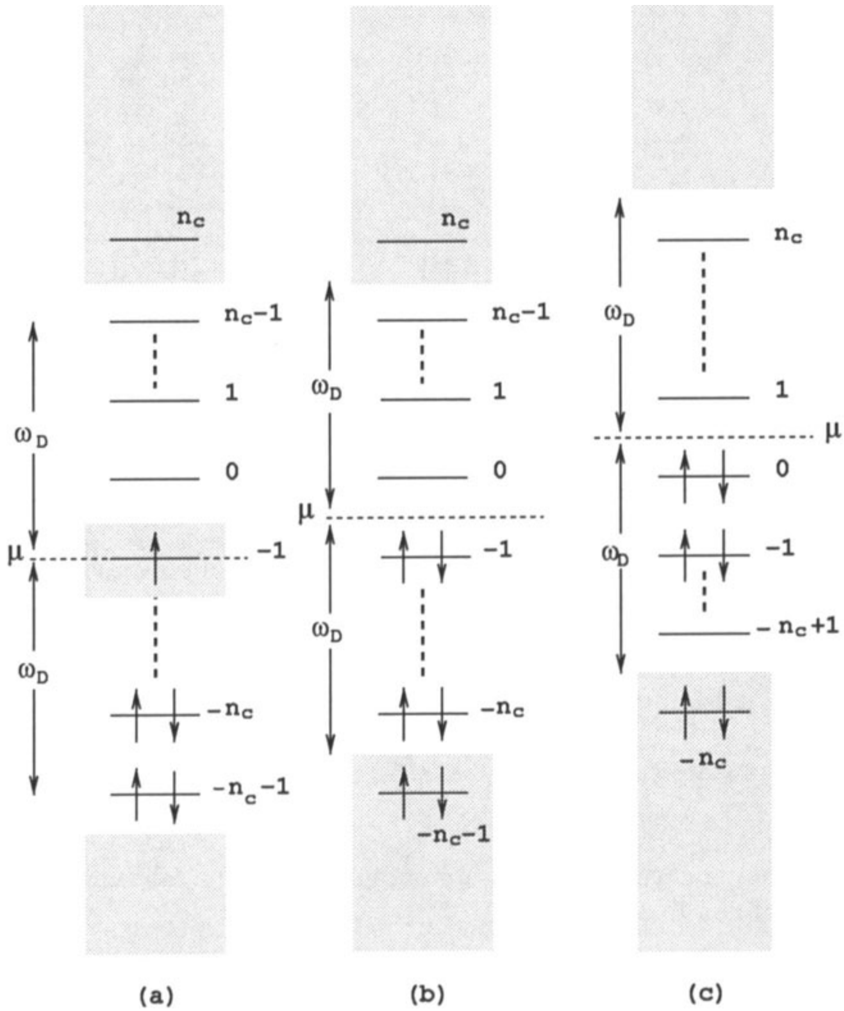


*Figure 25.2* Levels included in the set $S$. The pair-pair interaction is assumed to be restricted to pairs with energy within the $2\omega_D$ shell about Fermi level. When Fermi level shifts, the levels which should be included in the set $S$ change. In addition to this, singly occupied levels are taken out from the set $S$, which is the so called "blocking effect". Here, the shaded regions correspond to the levels which are occupied by non-interacting particles

which is schematically presented in Fig. 25.3.

The problem of determining the eigenstates of the pairing-force Hamiltonian was solved by R. W. Richardson and N. Sherman in 1964 [12]. However, this solution was forgotten for a long time despite of its importance in application to BCS theory of superconductivity. And only

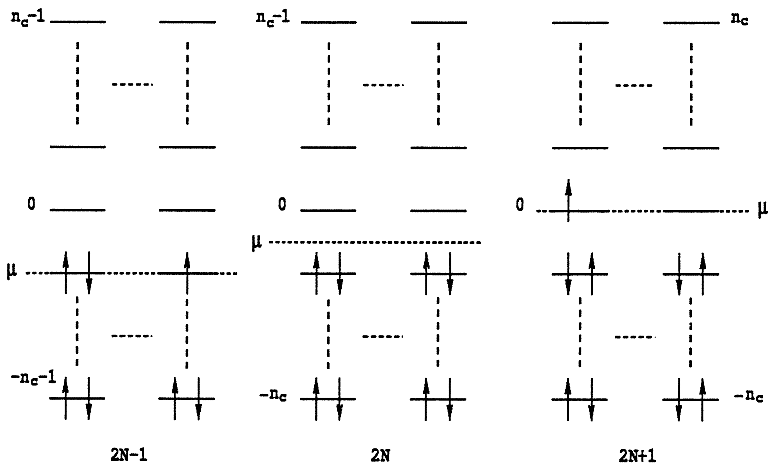


*Figure 25.3* Three consecutive configurations for different number of electrons. Here, the three consecutive configurations whose ground state energies are used to calculate $\Delta_p^{(1)}$, are shown schematically. Note the shift of chemical potential for different number of electrons. Below each configuration, number of electrons are written for clarity.

recently, it has been "re-discovered" by the condensed matter community [13].

Ground state energy of the model is given by

$$E = E_1 + \ldots + E_N, \tag{25.11}$$

where the pair parameters $E_i$ are obtained from the following coupled system of non-linear equations

$$\frac{d}{\lambda\delta} + 2\sum_{j\neq i}^{N} \frac{1}{E_j - E_i} - \sum_{n=1}^{M} \frac{\Omega(n)}{2\epsilon_n - E_i} = 0; \quad i = 1, \ldots N, \tag{25.12}$$

where we introduced the dimensionless coupling parameter $\lambda = gd/\delta$. Here $\Omega(n)$ is the pair degeneracy of the level corresponding to energy $\epsilon_n = n\delta$, $N$ is the total number of pairs, and $M$ is the total number of levels in the set $S$. The roots $E_i$ of (25.12) are required to be distinct. However, the domain of validity of the solution can be extended by letting $E_i$'s to be complex [14]. Complex roots $E_i$ occur in complex conjugate pairs. This preserves the reality of $E$ which is the sum of all roots (25.11). Such complex conjugate roots of the system also preserves the reality of the wave function for the model [12]. Nevertheless, the existence of complex roots of (25.12) depend upon the state of the system and can not easily be treated in a general way.

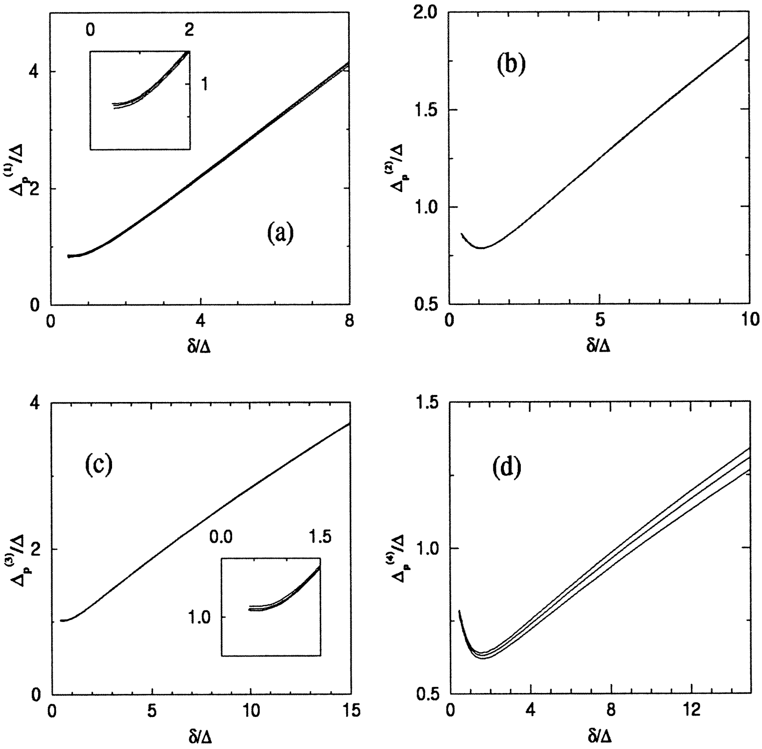


*Figure 25.4* Dependence of parity effect parameter upon level spacing for doubly degenerate energy levels. $M = 41, 51, 61$ from top to bottom in (c), while from bottom to top in (a), (b) and (d).

## 3. RESULTS

We plot $\Delta_p^{(m)}/\Delta$ versus $\delta/\Delta$ for double degeneracy in Fig. 25.4. For higher degeneracy, such as $d = 4$, we obtain similar results. It is seen that in the region $\delta \sim \Delta$, the curves have different behaviors. While $\Delta_p^{(odd)}/\Delta$ decreases steadily towards 1, $\Delta_p^{(even)}/\Delta$ makes a minimum at $\delta \sim \Delta$. A similar behavior is observed for the non-degenerate case [11].

As it has been mentioned earlier that for certain energy spectra and more generally for lattice symmetries, energy levels are strongly degenerate near the Fermi energy. Eq. 25.12 has an analytic solution for a single $d-$fold degenerate level[12]. In this case with our notation $n_c = 0$ and the ground state energy measured from the Fermi level is given by

$$E^{(2n)} = 2n\epsilon - \frac{\lambda\delta}{d} n[d - n + 1],$$

$$E^{(2n+1)} = 2n\epsilon - \frac{\lambda\delta}{d}n[(d-1) - n + 1], \tag{25.13}$$

where $n$ is the number of hardcore bose particles, and $\epsilon$ is the energy measured from the Fermi level. Blocking effect is taken into consideration in the second equation of (25.13). We calculate the following parity parameters

$$\Delta_p^{(even)} = E^{(2n+1)} - \frac{1}{2}[E^{(2n)} + E^{(2n+2)}]$$
$$\Delta_p^{(odd)} = -E^{(2n)} + \frac{1}{2}[E^{(2n-1)} + E^{(2n+1)}]. \tag{25.14}$$

By substituting (25.13) into (25.14), we obtain

$$\Delta_p^{(even)} = \frac{\lambda\delta}{2}, \quad \Delta_p^{(odd)} = \frac{\lambda\delta}{2} + \frac{\lambda\delta}{2d}, \tag{25.15}$$

so that

$$\frac{\Delta_p^{(odd)}}{\Delta_p^{(even)}} = 1 + \frac{1}{d}. \tag{25.16}$$

These results suggest that the parity parameter remains non-zero for an infinitely degenerate single level. Comparing Figs. 25.4-(b) and (c), for example at $\delta/\Delta = 0.99$, we find that $\Delta_p^{(3)}/\Delta_p^{(2)} = 1.04/0.78 \sim 1.33$ which is quite close to 1.50 that we would obtain from (25.16). Moreover for some larger $\delta/\Delta$ value ($\delta/\Delta = 10.36$), we obtain $\Delta_p^{(3)}/\Delta_p^{(2)} = 2.90/1.91 \sim 1.51$ which is even closer to corresponding value for single level spectrum. Table 25.1 shows $\Delta_p^{(odd)}/\Delta_p^{(even)}$ ratios for 2-fold and 4-fold degenerate cases. Note that the ratio (25.16) is applicable for three

*Table 25.1* $\Delta_p^{(odd)}/\Delta_p^{(even)}$ ratios. As $\delta/\Delta$ increases, the ratio $\Delta_p^{(odd)}/\Delta_p^{(even)}$ approaches the value $1+1/d$ as can be predicted by using the solution due to Richardson and Sherman, for d-fold degenerate single level.

| | At $\frac{\delta}{\Delta} \sim 1$ | At $\frac{\delta}{\Delta} \sim 10$ |
|---|---|---|
| 2-fold degeneracy; $d = 2$ | | |
| $\frac{\Delta_p^{(odd)}}{\Delta_p^{(even)}} = 1 + \frac{1}{d} = 1.5$ | $\frac{\Delta_p^{(3)}}{\Delta_p^{(2)}} \sim 1.33$ | $\frac{\Delta_p^{(3)}}{\Delta_p^{(2)}} \sim 1.51$ |
| 4-fold degeneracy; $d = 4$ | | |
| $\frac{\Delta_p^{(odd)}}{\Delta_p^{(even)}} = 1 + \frac{1}{d} = 1.25$ | $\frac{\Delta_p^{(3)}}{\Delta_p^{(4)}} \sim 1.17$ | $\frac{\Delta_p^{(3)}}{\Delta_p^{(4)}} \sim 1.24$ |

successive configurations where chemical potential does *not* shift. Thus, we conclude that, existence of degeneracy can be observed in experiments via the ratio of $\Delta_p$ values. If there is large difference in all successive $\Delta_p$, then this is most probably a sign of non-degeneracy. However, if there is not such a difference for any $\Delta_p$ values, this can be interpreted as a sign of degeneracy. Moreover, level degeneracy can be predicted by observing these $\Delta_p$'s.

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## References

[1] P. W. Anderson, Theory of dirty superconductors, J. Phys. Chem. Solids **11**, 26 (1959).

[2] D. C. Ralph, C. T. Black, and M. Tinkham, Spectroscopic measurements of discrete electronic states in single metal particles, Phys. Rev. Lett. **74**, 3241 (1995).

[3] D. C. Ralph, C. T. Black, and M. Tinkham, Gate-voltage studies of discrete electronic states in aluminum nanoparticles, Phys. Rev. Lett. **78**, 4087 (1997).

[4] D. Davidović and M. Tinkham, Unconventional clustering of discrete energy levels in an ultrasmall Au grain, Appl. Phys. Lett. **73**, 3959 (1998).

[5] D. Davidović and M. Tinkham, Spectroscopy, interactions, and level splittings in Au nano-particles, cond-matt/990543 (1999).

[6] K. A. Matveev and A. I. Larkin, Parity effect in ground state energies of ultrasmall superconducting grains, Phys. Rev. Lett. **78**, 3749 (1997).

[7] A. Mastellone, G. Falci and Rosario Fazio, A small superconducting grain in the canonical ensemble, Phys. Rev. Lett. **80**, 4542 (1998). [cond-matt/9801179]

[8] S. D. Berger and B. I. Halperin, Parity effect in a small superconducting particle, Phys. Rev. B **58**, 5213 (1998). [cond-matt/9801286]

[9] F. Braun and J. von Delft, Superconductivity in ultrasmall metallic grains, Phys. Rev. B **59**, 9527 (1999).

[10] U. Landman, Clusters, dots, dot-molecules and Wigner crystallization, NATO Advanced Study Institute on "*Quantum Mesoscopic Phenomena and Mesoscopic Devices in Microelectronics*", Ankara/Antalya, 1999.

[11] H. Boyaci, Z. Gedik, and I. O. Kulik, Superconductivity in mesoscopic metal particles: The role of degeneracy, cond-mat/9909386.
[12] R. W. Richardson and N. Sherman, Exact eigenstates of the pairing-force Hamiltonian, Nuclear Physics **52**, 221 (1964).
[13] F. Braun and J. von Delft, Fixed-N Superconductivity: The Exact Crossover from the Bulk to the Few-Electron Limit, Advances in Solid State Physics **39**, 341 (Vieweg Braunschweig/Wiesbaden 1999). [cond-matt/9907402]
[14] R. W. Richardson, Numerical study of the 8-32-particle eigenstates of the pairing Hamiltonian, Phys. Rev. **141**, 949 (1966).