Thermodynamical properties of small superconductors with a fixed number of particles

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The variation after projection approach is applied for the first time to the Richardson pairing Hamiltonian to describe the thermodynamics of small superconductors with a fixed number of particles. The minimization of the free energy is made by a direct diagonalization of the entropy. The variation after projection applied at finite temperature provides a perfect reproduction of the exact canonical properties of odd or even systems from very low to high temperatures.

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I. INTRODUCTION

Recent progress in single-electron tunneling spectroscopy has revealed the persistence of a pairing effect even at a very small number of particles [1]. The tremendous experimental work in ultrasmall metallic grains [2] has enabled the systematic investigation of the transition from large systems, the bulk limit, up to very small systems. By varying the number of particles, careful analysis has been made of thermal excitations or of the action of an external magnetic field. The smearing of the superfluid-to-normal phase transition, the survival of pairing correlations, odd-even staggering [3,4], and possible reentrant effects [5] have also been analysed. These studies have underlined the importance of finite size effect on pairing correlations and the necessity to develop theories beyond the Bardeen-Cooper-Schrieffer (BCS) or the Hartree-Fock-Bogoliubov (HFB) ones that properly account for particle number conservation. Some of these studies are at the crossroad with nuclear physics where systems contain very few to several hundreds of nucleons [6] and some of the approaches that are used nowadays to deal with particle number conservation, such as projection techniques [7,8], have been imported in condensed matter [1]. In this case, improvement beyond the BCS and/or HFB is obtained by considering a state with a good particle $|\Psi_N\rangle = P_N|\Phi_0\rangle$, where P_N is the projector on N particles while $|\Phi_0\rangle$ denotes a quasiparticle (BCS or HFB) state. The explicit breaking of the symmetry, U(1) in the present case, allows one to grasp the physics of pairing while its restoration is required to describe the onset of pairing in very small systems (see, for instance, Fig. 1 of Ref. [9]).

A natural extension of this approach, proposed some time ago in Ref. [10], is able to provide a canonical description of a finite system at thermal equilibrium by considering a many-body projected density $\hat{D}_N$ written as (see also Ref. [11])

$$\hat{D}_N = \frac{1}{Z}\hat{P}_N \exp(-\beta\hat{h})\hat{P}_N, \tag{1}$$

where $Z = \mathrm{Tr}[\hat{P}_N \exp(-\beta\hat{h})\hat{P}_N]$, $\beta = 1/(k_B T)$, and $\hat{h}$ is the quasiparticle effective BCS or HFB Hamiltonian. In view of the complexity of this approach, approximations or alternative theories have been proposed. In Ref. [12], a general projection formalism was developed and largely applied in the static-path approximation. The problem of particle number projection at finite temperature was also addressed in the context of thermofield dynamics [13] but no applications have been done till now. Starting from a mean-field plus pairing description in the grand-canonical ensemble, several improvements of increasing complexity have been proposed to correct from particle number explicit nonconservation. Along this line, a modified BCS theory [14] has been introduced where part of the statistical fluctuation is directly incorporated in the quasiparticle transformation. This approach has been further improved by extending the Lipkin-Nogami approach to finite temperature, projecting onto the good particle number after variation [15]. Note, however, that the internal consistency and applicability of the modified BCS, especially at high temperature, has been questioned [16]. Other extensions have been proposed by adding quantum fluctuation associated with RPA modes described on top of a BCS plus Lipkin-Nogami projection approach [17] or in the static-path approximation [18]. On the other hand, starting from a functional integral formulation and treating approximately the collective fluctuations around the mean-field path is shown to provide a suitable tool over a wide range of temperatures but breaks down at very low temperature [19]. An approximate scheme to deal with quantal fluctuations consists of the use of a grand-canonical plus a parity-projected technique [4,5,20] which allows one to describe qualitatively odd-even effects but still suffers from abrupt and/or spurious phase transitions [2]. Even in very schematic models [21], unless an exact treatment is made either by direct diagonalization [22] or by quantum Monte-Carlo techniques [23], a canonical finite-T method based on mean-field theory and valid at arbitrary small or high temperatures remains problematic and appears as a challenge in this field [2].

While the results presented in Ref. [10] were very promising, this method has never been applied due to its complexity. Here, we apply for the first time the method proposed in Ref. [10] to the Richardson Hamiltonian at thermal equilibrium and show that this approach provides a proper description of both thermal and quantal fluctuations from very low to high temperatures. The canonical description of a quantum finite system can be obtained by minimizing the Helmholtz free energy F

$$\delta F = \delta(\mathrm{Tr}[\hat{H}\hat{D}_N] - TS) = 0, \tag{2}$$

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where S denotes the entropy associated with the projected density (1), i.e., $S = -k_B \mathrm{Tr}(\hat{D}_N \ln \hat{D}_N)$. The approach is applied to the pairing Hamiltonian written as [21]

$$\hat{H} = \sum_{i,\sigma=\pm} (\varepsilon_i - \sigma \mu_B B)\hat{c}^\dagger_{i\sigma}\hat{c}_{i\sigma} - G \sum_{i,j} \hat{c}^\dagger_{i,+}\hat{c}^\dagger_{i,-}\hat{c}_{i,-}\hat{c}_{i,+}, \quad (3)$$

where B is an external magnetic field. For not too big systems, thermodynamic quantities can be studied in different statistical ensembles without approximation by direct diagonalization of the Hamiltonian in different seniority spaces [22].

The results discussed below are obtained for a system of $\Omega = 10$ doubly folded equidistant levels whose energies are

$$\varepsilon_i = \left(i - \tfrac{1}{2}(\Omega+1)\right)\Delta\varepsilon, \quad i = 1, \ldots, \Omega, \quad (4)$$

and a pairing strength $G = 0.4\Delta\varepsilon$. In the following, the total energy, pairing gap, and temperature are given in units of $\Delta\varepsilon$. To take advantage of the U(1) symmetry breaking, the Hamiltonian $\hat{h}$ is written as a sum of quasiparticle excitations $\hat{h} = \sum_k E_k \hat{\alpha}^\dagger_k \hat{\alpha}_k$, where the E_k denotes the eigenvalues of the underlying HFB Hamiltonian, while the quasiparticle creation operators are written as

$$\hat{\alpha}^\dagger_k = u_k \hat{c}^\dagger_{k,+} - v_k c_{k,-}, \quad \hat{\alpha}^\dagger_{\bar{k}} = u_k \hat{c}^\dagger_{k,-} + v_k c_{k,+}. \quad (5)$$

Similar to what is done in nuclear physics, two levels of complexity exist in the application of projection techniques. The projection can be made either before [variation after projection (VAP)] or after [projection after variation (PAV)] variation [6]. The latter is much less demanding since it only requires one to solve finite temperature BCS (FT-BCS) equations and make projection without minimizing Eq. (2). As an illustration, the temperature dependence of the energy $\langle E \rangle$ and the associated heat capacity defined through $C_V = \partial\langle E\rangle/\partial T$ obtained with FT-BCS (dashed line) and FT-PAV (dotted line) are compared to the exact result (thick line) in Fig. 1 for $N = 10$ particles. The exact solution is obtained following Ref. [22].

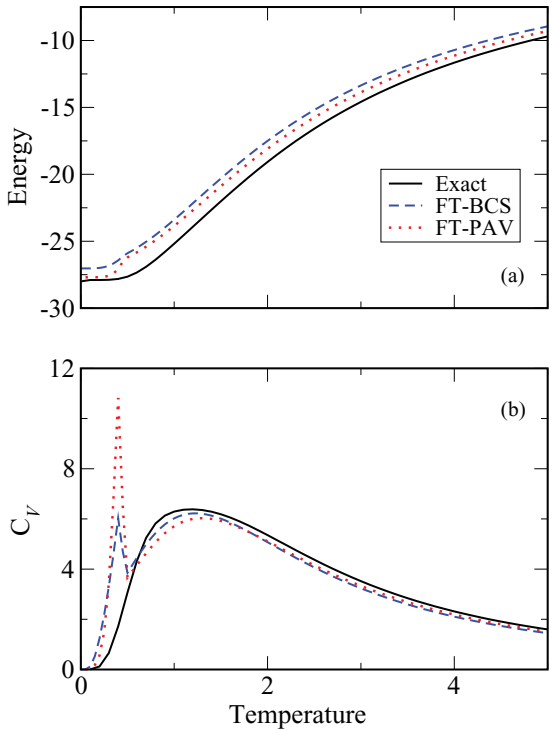

FIG. 1. (Color online) Evolution of the energy (a) and heat capacity (b) obtained with the FT-BCS (dashed line), PAV (dotted line), and exact solution (thick line) for a system of $N = 10$ particles.

As is well known, in addition to the systematic overestimation of the energy, the FT-BCS theory suffers from the sharp superfluid to normal phase transition as the temperature increases. In contrast, the exact solution displays a much smoother behavior. It is clearly seen in this figure that, except in the very small temperature case, the FT-BCS + PAV does even a worse job and does not cure the threshold effect.

Extrapolating the improvement generally observed at $T = 0$ [9] to the finite temperature case, one can anticipate a much better description if VAP is performed. In that case, the variational principle (2) should be minimized by both varying the components (u_k, v_k) and the energy E_k consistently [10]. While in principle possible, such minimization has never been performed because the Hamiltonian $\hat{h}$ and the operator $\hat{P}_N \exp(-\beta\hat{h})\hat{P}_N$ do not commute and therefore cannot be diagonalized simultaneously. As a consequence, while a guideline of practical implementation was proposed long ago in Ref. [10], except in the case of the two-level degenerate system, the predictive power of VAP at finite temperature (called hereafter FT-VAP) has never been attested.

In the present work, we applied the FT-VAP following the strategy proposed in Ref. [10]. In practice, the variational principle is minimized by writing first the energy in terms of the one- and two-body density of the projected density, both of them written as a nontrivial function of u_k, v_k, and E_k [see Eq. (36) in Ref. [10]]. The minimization is carried out via a sequential quadratic programming method by using the v_k and E_k as variational parameters. To compute the free energy without approximation, at each iteration of the minimization, the entropy is calculated by

$$S = -k_B \sum_i D^N_i \ln D^N_i, \quad (6)$$

where D^N_i are the eigenvalues of the statistical operator $\exp(-\beta\hat{h})/Z$ in the Fock space composed by all the many-body configurations with N particles. Each configuration is characterized by η pairs and I unpaired particles, with $2\eta + I = N$. Moreover, since states with a different number of unpaired particles cannot be connected by the operator $\exp(-\beta\hat{h})$, the problem is reduced to the diagonalization of block matrices for each allowed seniority I. The required computational cost is thus given essentially by two operations, i.e., the calculation of the matrix elements of the statistical operators and the diagonalization itself. For the latter, a standard QR algorithm is used. The calculation of the matrix elements is done by using the bit representation of the many-body states (see, for example, Ref. [24]). Each configuration is identified by an integer word whose bits correspond to the single-particle levels and have value 1 or 0 depending on whether the level is occupied or empty. In such a way all the

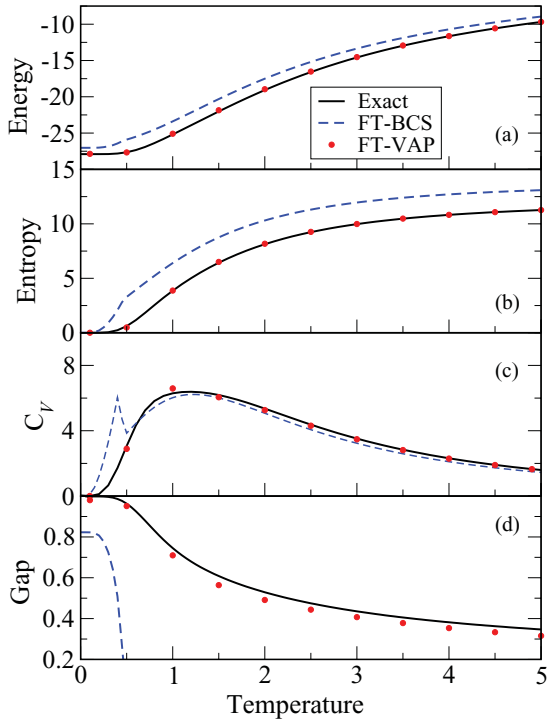

FIG. 2. (Color online) Predictive power of the FT-VAP. The energy $\langle H \rangle$ (a), entropy (b), heat capacity (c), and the average gap (d) obtained with the FT-VAP (filled circles) are compared to the exact (thick line) and FT-BCS case (dashed line) for a system of $N = 10$ particles.

matrix elements can be obtained by using very simple logical operations which allow us to perform calculations much faster.

In Fig. 2, the result obtained in FT-VAP is compared to the exact solution for a system of $N = 10$ particles at various temperatures. In FT-VAP, the gap is given by Eq. (42) of Ref. [10] while in the exact case it is computed through

$$\Delta = \sqrt{-G(E - E_0)}, \tag{7}$$

where E is the total exact energy and E_0 is given by

$$E_0 = \sum_i \left(\varepsilon_i - \frac{G}{2} n_i\right) n_i, \tag{8}$$

containing both the single-particle and the self-energy terms, n_i being the occupation numbers. In this figure, we see that except for the small systematic difference observed for the gap, the FT-VAP approach provides a perfect description of the thermodynamics of a system with a fixed particle number in any range of temperatures. None of the limitations [15,19] appearing in other mean-field-based theories are seen. In particular, the entropy, which is an approximation in FT-VAP, perfectly matches the exact one. The same quality of agreement is found also at higher temperatures (up to $T = 10$).

We further investigated the applicability of FT-VAP for an odd number of particles. Taking advantage of the fact that the FT-BCS density mixes up odd and even parities as soon as a nonzero temperature is applied, we used the same technique as in the even case. The only difference is that now the projector entering in the density Eq. (1) corresponds to an odd number

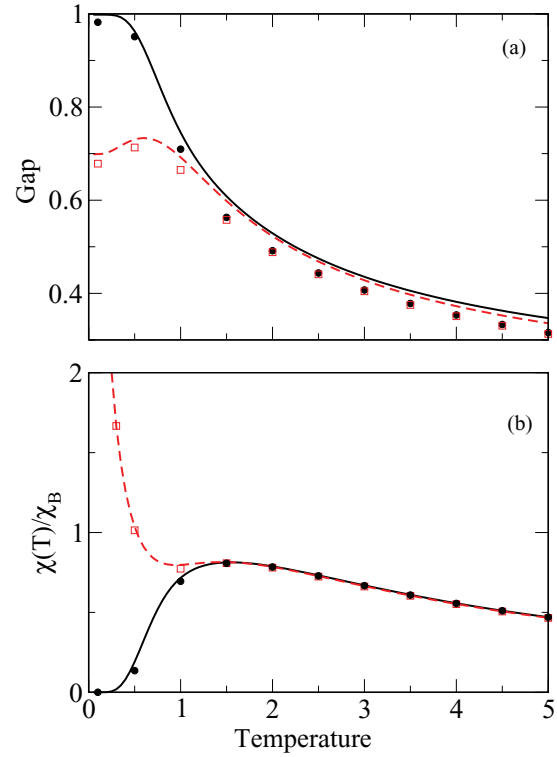

FIG. 3. (Color online) Evolution of the mean gap (a) and spin susceptibility (b) for $N = 10$ (filled circles) and $N = 11$ (open squares) particles as a function of T obtained with the FT-VAP. The corresponding exact result for the even and odd systems are presented respectively with solid and dashed lines. In this figure, the spin susceptibility is normalized by the bulk high temperature value $\chi_B = 2\mu_B^2/\Delta\varepsilon$.

of particles. In Fig. 3(a), the pairing gap obtained in FT-VAP for $N = 10$ and $N = 11$ particles is compared to the exact case. In Fig. 3(b), the spin susceptibility χ, defined as [5]

$$\chi(T) = -T \left.\frac{\partial^2 \ln Z}{\partial B^2}\right|_{B=0}, \tag{9}$$

is shown for the two cases.

In the limit of a small magnetic field, the susceptibility identifies with the fluctuation of the magnetization $\hat{M} = -\mu_B \sum_{\sigma,i} \sigma \hat{c}^\dagger_{i,\sigma} \hat{c}_{i,\sigma}$ [23], i.e.,

$$\chi(T) = -\frac{1}{T}(\langle \hat{M}^2 \rangle - \langle \hat{M} \rangle^2). \tag{10}$$

In small systems, large differences are observed in the thermodynamics of odd and even systems [2]. This is clearly seen especially at low temperatures for the gap. The spin susceptibility further underlines the differences. The FT-VAP perfectly grasps the thermodynamics of odd systems and one cannot distinguish its result from the exact solution.

In conclusion, we applied for the first time the variation after projection approach to describe the canonical properties of a nondegenerate superconducting system. The minimization of the free energy is made with no approximation on the entropy. The FT-VAP provides a perfect reproduction of the exact result in the Richardson Hamiltonian case both in the low and high

temperature limits and does not have the limitation of other mean-field-based approaches. Due to the necessity to make use of explicit diagonalization for the entropy, the present approach is still restricted to a rather small number of particles. Approximated methods to evaluate the projected entropy are thus necessary for the study of larger systems. In this regard, an attempt was made in Ref. [25] where an approximated way to calculate the entropy, based on the Peierls inequality, was used. However, although the critical temperature shifts up with respect to the grand-canonical case, this method still suffers from a sharp phase transition that is washed out when the projected entropy is exactly evaluated. The investigation and development of new methods to evaluate the entropy in an approximated way allowing one at the same time to describe properly both low and high temperature properties are needed. Work in this direction is in progress.

Nevertheless, we believe that the result obtained here is sufficiently promising that in the near future, an effort should be made to promote the FT-VAP and make it more versatile. It should be mentioned finally that the present method provides a natural extension of the FT-BCS or FT-HFB theory presently used to describe nuclei within the energy density functional framework applied at finite temperature [26].

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[1] F. Braun and J. von Delft, Phys. Rev. Lett. **81**, 4712 (1998).
[2] J. von Delft and D. C. Ralf, Phys. Rep. **345**, 61 (2001).
[3] F. Braun and J. von Delft, Phys. Rev. B **59**, 9527 (1999).
[4] R. Balian, H. Flocard, and M. Véneroni, arXiv:cond-mat/9802006v1.
[5] A. Di Lorenzo, R. Fazio, F. W. J. Hekking, G. Falci, A. Mastellone, and G. Giaquinta, Phys. Rev. Lett. **84**, 550 (2000).
[6] P. Ring and P. Schuck, *The Nuclear Many-Body Problem* (Springer-Verlag, Berlin, 1980).
[7] M. Bender, P.-H. Heenen, and P.-G. Reinhard, Rev. Mod. Phys. **75**, 121 (2003).
[8] M. A. Fernández and J. L. Egido, Phys. Scr., T **125**, 87 (2006).
[9] G. Hupin and D. Lacroix, Phys. Rev. C **83**, 024317 (2011).
[10] C. Esebbag and J. L. Egido, Nucl. Phys. A **552**, 205 (1993).
[11] R. Balian, H. Flocard, and M. Véneroni, Phys. Rep. **317**, 251 (1999).
[12] R. Rossignoli and P. Ring, Ann. Phys. (NY) **235**, 350 (1994).
[13] K. Tanabe and H. Nakada, Phys. Rev. C **71**, 024314 (2005).
[14] N. D. Dang and A. Arima, Phys. Rev. C **68**, 014318 (2003).
[15] N. D. Dang, Phys. Rev. C **76**, 064320 (2007), and references therein.
[16] V. Yu. Ponomarev and A. I. Vdovin, Phys. Rev. C **72**, 034309 (2005).
[17] N. Q. Hung and N. D. Dang, Phys. Rev. C **81**, 057302 (2012)
[18] R. Rossignoli, N. Canosa, and P. Ring, Ann. Phys. (NY) **275**, (1999)
[19] R. Rossignoli and N. Casona, Phys. Lett. B **394**, 242 (1997); R. Rossignoli, N. Casona, and J. L. Egido, Nucl. Phys. A **605**, 1 (1996).
[20] J. von Delft, A. D. Zaikin, D. S. Golubev, and W. Tichy, Phys. Rev. Lett. **77**, 3189 (1996).
[21] R. W. Richardson and N. Sherman, Nucl. Phys. **52**, 221 (1964); R. W. Richardson, Phys. Rev. **141**, 949 (1966); J. Math. Phys. **9**, 1327 (1968).
[22] A. Volya, B. A. Brown, and Z. Zelevinsky, Phys. Lett. B **509**, 37 (2001); T. Sumaryada and Alexander Volya, Phys. Rev. C **76**, 024319 (2007).
[23] K. Van Houcke, S. M. A. Rombouts, and L. Pollet, Phys. Rev. E **73**, 056703 (2006).
[24] E. Caurier, G. Martnez-Pinedo, F. Nowacki, A. Poves, and A. P. Zuker, Rev. Mod. Phys. **77**, 427 (2005).
[25] H. Nakada and K. Tanabe, Phys. Rev. C **74**, 061301 (2006).
[26] V. Martin, J. L. Egido, and L. M. Robledo, Phys. Rev. C **68**, 034327 (2003); E. Khan, N. Van Gian, and N. Sandulescu, Nuclear Phys. A **789**, 94 (2007); A. F. Fantina, J. Margueron, P. Donati, and P. M. Pizzochero, J. Phys. G: Nucl. Part. Phys. **38**, 025101 (2001).