Eur. Phys. J. B **34**, 275–280 (2003)
DOI: 10.1140/epjb/e2003-00222-4

THE EUROPEAN PHYSICAL JOURNAL B

Pre-formed superconducting and quadrupolar fluctuations and heavy electron mass in an exactly solvable model

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Received 19 May 2003 / Received in final form 26 June 2003
Published online 11 August 2003 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2003

Abstract. We present the Bethe ansatz solution for the two-channel non-magnetic hybridization impurity model of electrons with spin and orbital degrees of freedom. It is shown that a small concentration of such impurities enhances the effective mass of electrons. A large concentration of impurities results in a pre-formation of superconducting and quadrupolar-order fluctuations and in the co-existence of them for some range of parameters.

PACS. 75.30.Mb Valence fluctuation, Kondo lattice, and heavy-fermion phenomena – 71.27.+a Strongly correlated electron systems; heavy fermions

There has recently been a renewed interest in heavy fermions. While the nature of many effects for Ce- and Yb-based heavy fermion systems with $4f^1$ (or $4f^{13}$) configuration of $4f$ localized electrons is often understood, the one for Pr-based compounds (with $4f^2$ configuration of localized electrons) remains to be clarified. As an example, one can consider the heavy fermion behavior of normal phases, superconductivity and quadrupolar ordering in Pr-based heavy fermion compounds with the filled skutterudite structure ($PrMe_4Pn_{12}$, where Me is a transition metal and Pn is a pnictogen) [1]. There are many experimental evidences [1] that in all these compounds the main effect is connected with the low-lying non-Kramers (non-magnetic) doublet Γ_3 (or similar non-magnetic states, like Γ_1 singlet which, together with $\Gamma_{4,5}$ triplets, are splitted from the 9-fold degenerate multiplet of the localized Pr^{3+} due to the cubic crystalline electric field (CEF) of ligands [2]). Some authors mentioned non-Fermi-liquid-like effects in such systems [3]. Moreover, several experiments reported the unconventional strong-coupling superconductivity in $PrOs_4Sb_{12}$, the onset of which is due to pre-formed pairs at temperatures higher than T_c, caused by the hybridization of non-magnetic localized Pr states with conduction electrons [4]. Also, it was pointed out that in $PrOs_4Sb_{12}$ the quadrupolar ordering can take place [5].

Motivated by these experimental facts, in this work we study an exactly solvable model. Our goal is to describe some of important effects caused by the hybridization of low-lying non-magnetic states [6] of $4f^2$ electrons with conduction electrons. The experiments [1,3–5] suggest that two low-energy configurations of the localized Pr^{3+} may be important: the doublet Γ_3, or the singlet Γ_1. This is why, in our simplified model we consider two almost degenerate low-lying non-magnetic states hybridized with itinerant electrons. Then a mixed valence behavior of f orbitals results. We point out, however, that our model is too simplified to describe the real behavior of Pr-based compounds, and reveals only some (but not all) of their main features. The hybridization Hamiltonian is

$$\mathcal{H}^j_{hyb} = V \sum_{m,\sigma,q\tau} \delta(x - x_j) \times \left(a^\dagger_{m,\sigma}(x)|Q,q,\tau\rangle\langle Q',q'\tau| + \text{h.c.}\right), \quad (1)$$

where $a^\dagger_{m,\sigma}(x)$ are creation operators for conduction electrons (σ denotes a spin projection of a conduction electron), bra and kets denote low-energy states of localized electrons of N_i f-orbitals (situated at x_j positions) with quantum numbers $Q \geq 0$, which describe quadrupolar degree of freedom, their projections q and spin projections τ. It turns out that here different bra and kets pertain to different values of a valence of a f-orbital. m describe degrees of freedom of conduction electrons which interact with quadrupolar moments of a localized electrons. V are hybridization elements, here supposed to be site-independent. We also suppose the Coulomb repulsion of electrons at the same orbital to be very large to exclude a multiple occupancy of each orbital [8]. Thus, each impurity has to satisfy the completeness condition $\sum_{q,\tau} |Q,q,\tau\rangle\langle Q,q,\tau| + \sum_{q',\tau} |Q',q',\tau\rangle\langle Q',q'\tau| = 1$. The

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energy of localized at the f-orbital electrons is described by the Hamiltonian

$$\mathcal{H}_{orb} = \epsilon_Q \sum_{q,\tau} |Q,q,\tau\rangle\langle Q,q,\tau| + \epsilon_{Q'} \sum_{q',\tau} |Q',q',\tau\rangle\langle Q',q',\tau|, \quad (2)$$

where $\epsilon_{Q,Q'}$ are energies of two considered multiplets, so that f-level energies can be parametrized by one parameter $\theta = \epsilon_Q - \epsilon_{Q'} - \mu$ (μ is the chemical potential). We write the Hamiltonian of conduction electrons in the long-wave form (the Fermi velocity is equal to 1)

$$\mathcal{H}_{cond} = -\sum_{m,\sigma} \int dx a^\dagger_{m\sigma}(x) \times \left(i\partial_x + (1/\Lambda)[\partial_x^2 - V(x)] \right) a_{m\sigma}(x), \quad (3)$$

where $V(x) = \sum_j^{N_i} \delta(x-x_j)(x/|x|)[\delta'(x+0)+\delta'(x-0)]$ [7]. The parameter Λ measures the curvature scale of the spectrum [9,10]. Actually this Hamiltonian is very similar to the Hamiltonian of reference [10] (for the isotropic hybridization), with spin and channel (quadrupolar) degrees of freedom (the latters are denoted here by m, Q and q) interchanged. Notice, that the special case, "exactly" reminiscent of the situation of reference [10] corresponds to the case $Q = 0$. We can also take into account a possible direct interaction of electrons between $4f$ orbitals of neighboring localized $4f$ electrons, which causes quadrupole-quadrupole interactions. To model the latter we can add a direct hopping of $4f$ electrons between neighboring localized orbitals (with the hopping element being much less than the inter-shell Coulomb repulsion, hence, in the first nonzero approximation it produces a direct antiferroquadrupolar coupling between neighboring localized electrons). (However, here we study only impurities which do not cause reflections, hence, we only model standard Ruderman-Kittel-Kasuya-Yoshida interaction between impurities, which is caused by reflections.) We shall consider such a possible coupling [11] in the long-wave limit. We emphasize that we shall consider the direct interaction between quadrupoles chosen in such a form to keep the exact integrability of the system, *i.e.* that (maybe not very realistic from the experimental viewpoint) Hamiltonian to use the exact solvability of the total system, see below. The total Hamiltonian is $\mathcal{H} = \sum_j (\mathcal{H}^j_{hyb} + \mathcal{H}_{orb}) + \mathcal{H}_{cond} + \mathcal{H}_{int}$ [12]. The Hamiltonian of this direct impurity-impurity quadrupolar interaction between the nearest-neighboring f-orbitals has a complicated form which follows from the fact that two-particle scattering matrices (TPSM) of electrons localized on orbitals satisfy Yang-Baxter relations (YBR) mutually and with the TPSM of conduction and localized orbitals, see below. In the simplest case of all electrons being localized on orbitals it has the form of a Takhtajan-Babujian SU(2)-symmetric Hamiltonian of effective quadrupolar moments Q [13].

The TPSM of conduction and f electron is diagonal in the spin subspace. In the quadrupolar subspace it has the form (for $\Lambda \gg 1$)

$$\hat{S}^{m,m'}_{q,q'}(k) = \delta_{m,m'}\delta_{q,q'} + (q,m|q+m)\,(q',m'|q'+m') \times \left\{ iV^2(2Q+1)/\left[k - \theta - iV^2\left(Q+\tfrac{1}{2}\right)\right]\right\} \hat{P}^{m,m'}_{q,q'}, \quad (4)$$

where k is the quasimomentum. Here $\hat{P}^{m,m'}_{q,q'} = \delta_{m,m'}\delta_{q,q'} + \delta_{-m,m'}\delta_{q',q+2m}$, $|q| \le Q$ and the Clebsch-Gordan coefficient $(q,m|q+m) = \left(Q,q;\tfrac{1}{2},m|Q\tfrac{1}{2},(Q+\tfrac{1}{2}),(q+m)\right)$ selects the way the impurity hybridizes to "quadrupolar" degrees of freedom of itinerant electrons [8]. The impurity (we call it "attractive") can temporarily absorb one conduction electron to form an effective quadrupolar moment $Q' = Q + \frac{1}{2}$, *i.e.* the impurity is mixed-valent and its wave function is a linear superposition of two different non-magnetic (quadrupolar) configurations. (The case with "repulsive" impurities which mix states with Q and $Q' = Q - \frac{1}{2}$, is also integrable. For that case the TPSM differs from Eq. (4) by the sign of the second term.) Those TPSM satisfy the YBR mutually, with the TPSM between conduction electrons and with the (possible) TPSM between localized neighboring f electrons. The situation here is reminiscent of three possible TPSM of the Takhtajan-Babujian model.

The YBR are the necessary and sufficient conditions for the integrability [14]. To remind, the TPSM $\hat{S}$ satisfies the following YBR:

$$\hat{R}_{12}(k_1-k_2)\hat{S}_{1,imp}(k_1-\theta)\hat{S}_{2,imp}(k_2-\theta) = \hat{S}_{2,imp}(k_2-\theta)\hat{S}_{1,imp}(k_1-\theta)\hat{R}_{12}(k_1-k_2), \quad (5)$$

where $\hat{R}(k)$ is the TPSM of conduction electrons, and indices for the matrices S show which particles scatter. Matrices $\hat{R}$ also satisfy the YBR

$$\hat{R}_{12}(k_1-k_2)\hat{R}_{13}(k_1-k_3)\hat{R}_{23}(k_2-k_3) = \hat{R}_{23}(k_2-k_3)\hat{R}_{13}(k_1-k_3)\hat{R}_{12}(k_1-k_2), \quad (6)$$

where indices enumerate scattering conduction electrons. There is no direct coupling between conduction electrons in our model [7]. However, the naive choice of the diagonal scattering matrices for the TPSM of conduction electrons does not satisfy the YBR. Correlations between conduction electrons are induced *via* the hybridization with localized electrons. The two-electron wave function (WF) of conduction electrons can be written as a product of a coordinate WF, a spin WF, and an "quadrupolar" WF. The WF has to be antisymmetric under the exchange of two particles. Hence, if spin and "quadrupolar" parts have the same symmetry, the coordinate WF is antisymmetric and vanishes if the coordinates of electrons coincide, so that electrons cannot interact. Conducting electrons then necessarily form a spin singlet and "quadrupolar" triplet or a spin triplet and "quadrupolar" singlet. When applied to a triplet (either in the spin or quadrupolar sector) WF the corresponding TPSM yields one, while if it acts on a singlet it gives rise to a phase shift. For the case of spin and "quadrupolar" singlets the two phase factors cancel

and there is no effective interaction between conduction electrons. Hence the hybridization of conduction electrons with the (interacting) electrons in $4f$ orbitals *dynamically correlates* the motion of formers. That is why the TPSM between conduction electrons obtains the form, *cf.* references [10,15]

$$\hat{R}(k) = \frac{\left[k\hat{I}_\sigma + iV^2\hat{P}_\sigma\right]\left[k\hat{I}_m - iV^2\hat{P}_m\right]}{[k^2+V^4]}, \qquad (7)$$

where $\hat{I}_{m(\sigma)}$ and $\hat{P}_{m(\sigma)}$ are the identity and permutation operators in the "quadrupolar" (spin) subspace.

The integrability of the model demands restrictions on the values of quadrupole-quadrupole couplings, as discussed above. In fact, it is possible to show (*cf.* Refs. [10,16]) that the Hamiltonian of the direct interaction between localized electrons $\mathcal{H}_{int}$ has to be proportional to θ^2, to preserve the exact integrability. The TPSM between conduction electrons have to satisfy the YBR with $\hat{S}$ (and mutually) also to preserve the integrability. They also factorize in spin and quadrupolar subspaces, and in each subspace their form is similar to the Takhtajan-Babujian TPSM, with opposite signs of interaction in those subspaces, like for $\hat{R}$.

We emphasize that all four possible cases of the generalized hybridization repulsive or attractive impurities with spins S or quadrupolar moments Q in the free conduction electron host are integrable, because TPSM between conduction electrons for a repulsive spin impurity, an attractive spin impurity, a repulsive quadrupolar impurity and an attractive quadrupolar impurity can be chosen in such a way to satisfy YBR with the TPSM between conduction and localized electrons for all these four cases. Naturally, YBR also imply that TPSM between neighboring localized electrons can be constructed for all four cases, see, *e.g.*, [10,17] Our Bethe ansatz solution is similar to the situation of impurities in a host with the Hund-like exchange interaction between conduction electrons [17]. Earlier we studied the special case of $S = 0$ repulsive impurity in the spin subspace in [10]. The general integrable case (in which we consider any number of spin and quadrupolar degrees of freedom of conduction electrons, and possible multiple occupancies of orbitals) will be reported elsewhere [18].

To determine the spectrum and the eigenfunctions of our model, we impose periodic boundary conditions and solve the corresponding Schrödinger equations by means of Bethe's ansatz. The procedure is standard and we skip details. The energies and eigenstates of our model are parameterized by three sets of *rapidities*: charge rapidities $\{k_j\}_{j=1}^{N}$ (with N the number of electrons), spin rapidities $\{\lambda_\alpha\}_{\alpha=1}^{M^*}$ (with M^* the number of down spins), and "quadrupole" rapidities $\{\xi_\beta\}_{\beta=1}^{n^*}$ (with n^* the number of electrons in the first orbital state). A magnetic field, H, and a lower-symmetric CEF, D, can lift the degeneracy of orbitals, the latters becoming unequally populated. Eigenstates correspond to solutions of the Bethe ansatz equations (BAE), obtained on a periodic interval of length N_a:

$$\begin{aligned}
e_{2Q+1}^{N_i}\left(\Lambda f_j - \theta'\right) e^{ik_j N_a} &= \prod_{\gamma=1}^{M^*} e_1^{-1}(f_j - \lambda_\gamma) \\
&\times \prod_{q=1}^{n^*} e_1(f_j - \xi_q),\ j = 1,\ldots,N, \\
\prod_{j=1}^{N} e_1(\lambda_\alpha - f_j) &= -\prod_{\delta=1}^{M^*} e_2(\lambda_\alpha - \lambda_\delta),\ \alpha = 1,\ldots,M^*, \\
e_{2Q}^{N_i}\left(\xi_\beta - \theta'\right) \prod_{j=1}^{N} e_1(\xi_\beta - f_j) &= -\prod_{\gamma=1}^{n^*} e_2\left(\xi_\beta - \xi_\gamma\right), \qquad (8)
\end{aligned}$$

where $f_j = k_j/V^2\Lambda$, $\theta' = \theta/V^2$, $e_n(y) = (2y - in)/(2y + in)$, and $\beta = 1,\ldots,n^*$. The energy is given by

$$\begin{aligned}
E = \sum_{j=1}^{N}\left[k_j\left(1 + V^2 f_j\right) + 2x\pi a_{2Q+1}\left(k_j - \theta\right)\right] \\
- 2x\pi\sum_{\beta=1}^{n^*} a_{2Q}\left(\xi_\beta - \theta\right), \qquad (9)
\end{aligned}$$

where $a_n(y)$ is the Fourier transform of $\exp(-n|p|V^2/2)$. The last two terms (with $x = N_i/N_a$ being the concentration of $4f$ impurities) are caused by the added direct coupling between quadrupolar moments of neighboring $4f$ electrons (and vanish if such a coupling is zero). Without direct interaction between impurities the energy of the system does not explicitly depend on the characteristics of impurities (θ, Q and N_i), *i.e.* terms, proportional to x in equation (9) vanish. The fact that energies and eigenstates are blind to the spatial positions of impurities is an artifact of the integrability. However, real systems often exhibit a large quasi-degeneracy of the states as function of the distribution of hybridization impurities for stoichiometric compounds.

In the thermodynamic limit ($N_a, N, M^*, n^* \to \infty$ with N/N_a, M^*/N_a and n^*/N_a kept fixed) the solutions of the BAE can be classified as: real charge rapidities corresponding to unbound itinerant electrons; pairs of complex conjugated charge rapidities representing spin-triplet quadrupolar-singlet pairs; spin bound states (λ-strings); and quadrupolar bound states (ξ-strings) with the density functions ($\rho(k)$ for unbound electrons, $\sigma'(\xi)$ for pairs, $\sigma_n(\lambda)$ for spin strings, and $\phi_n(\xi)$ for quadrupolar strings of length n). The thermal equilibrium is characterized by the *dressed energies* of excitations. These functions satisfy thermodynamic Bethe ansatz equations (TBAE), which follow from equations (8, 9). TBAE satisfied by the density distributions (but not those for dressed energies) are linear, so that contributions of conduction electrons and localized electrons can always be separated. Integral equations for dressed energies are linear only in the ground state. The number of electrons is

$$N = N_a\left[\int dk\rho(k) + 2\int d\xi\sigma'(\xi)\right], \qquad (10)$$

while the quadrupolar moment and magnetization are given by

$$\mathcal{Q} = N_i Q + N_a \left[\tfrac{1}{2} \int dk \rho(k) - \sum_{n=1}^{\infty} n \int d\xi \phi_n(\xi) \right],$$
$$M^z = N_a \left[\tfrac{1}{2} \int dk \rho(k) + \int d\xi \sigma'(\xi) - \sum_{n=1}^{\infty} n \int d\lambda \sigma_n(\lambda) \right], \quad (11)$$

respectively. Then one can obtain the valence, magnetic and quadrupolar moment of localized electrons. To save the space we shall not present here TBAE, referring to the forthcoming report [18]. The most interesting case for this kind of models is the ground state and low temperature ($T \ll 1$) behavior. The inspection of the TBAE reveals that in the ground state only five kinds of excitations have Dirac seas (*i.e.* states with negative energies), namely, unbound electrons, spin-triplet quadrupolar-singlet pairs, spin strings of lengths 1 and 2, and quadrupolar strings of length $2Q$. The latters have their Dirac sea only for a system with a direct coupling between neighboring f-orbitals, *i.e.* their Dirac seas vanish for $x \to 0$.

Let us first consider the case of a small concentration of impurities, which is related to the limit $x \to 0$ ($N_i = 1$) and $\Lambda \to \infty$ [10]. In this case the host has the properties of the gas of noninteracting electrons, and each impurity can be considered as isolated. In the case $H = 0$ we have $m^z_{imp} = 0$, and, hence, the Dirac seas for spin strings of lengths 1 and 2 are totally filled. Then the latters can be eliminated from equations for densities *via* a Fourier transformation. It is the *fusion* procedure [9,10]. For $D = 0$ the impurity valence is (we used the regularization scheme as, *e.g.*, in [8] with the Fermi points $\pm B$ of the dressed energy of pairs, $\Psi(\pm B) = 0$, related to μ) $n_{imp} = (1/\pi)(\tan^{-1}[(B-\theta)/V^2(Q+1)] + \tan^{-1}[(B+\theta)/V^2(Q+1)])$, *i.e.* it varies from zero to 1. For an empty band the impurity valence is zero and it grows monotonically with B. θ measures the coupling to the host, *i.e.* for $|\theta| \ll B$ the impurity is on resonance with the host, while if $|\theta| \gg B$ it is off-resonance. Hence, n_{imp} decreases monotonically with increasing $\theta > 0$. Also n_{imp} decreases with increasing Q. For $Q > \frac{1}{2}$ the quadrupolar susceptibility (it is connected [2] with the nonlinear magnetic susceptibility, defined as the third derivative of the magnetization with respect to the applied magnetic field) diverges as $D \to 0$. In the "non-magnetic Kondo" limit of large $|\theta|$ ($T_K \sim \exp(-\pi|\theta|) \sim D \ll B/V^2$) we have

$$\mathcal{Q}_{imp} = Q_0 \left[1 \pm (\mathcal{LD})^{-1} - \ln(\mathcal{LD})/(\mathcal{LD})^2 + \dots \right], \quad (12)$$

where $\mathcal{LD} = |\ln D/AT_K|$ (A is a constant). Here, for $D \ll T_K$ the upper sign and $Q_0 = Q$ are to be selected, while $T_K \ll D \ll B/V^2$ corresponds to the lower sign and $Q_0 = Q + \frac{1}{2}$. Notice that for large enough T_K one needs to take into account charge (mixed-valence) fluctuations, too. For the lowest $4f^2$ doublet (Γ_3), $Q = \frac{1}{2}$ (which seems to be the case for $PrOs_4Sb_{12}$ [1]), the ground state is a singlet and the zero-field quadrupolar susceptibility is finite, *i.e.* for small fields it is $\mathcal{Q}_{imp} \propto DT_K^{-1}$ (plus corrections due to the mixed-valence), reminiscent of the Fermi-liquid-like behavior with the heavy mass. The expansion of the free energy and the dressed energies yields for $Q = \frac{1}{2}$ the Curie-like quadrupolar susceptibility for $T \gg T_K$ (with usual logarithmic corrections), but for $T \ll T_K$ it is finite. For $Q > \frac{1}{2}$, the quadrupolar susceptibility is Curie-like with a Curie constant corresponding to an effective moment Q at low T and to a free moment $Q+\frac{1}{2}$ at high T. The specific heat of the non-magnetic impurity for $Q = \frac{1}{2}$ is Fermi-liquid like at low T, $C_{imp} = \pi T/3T_K$. For higher T in this case and for $Q > \frac{1}{2}$ at $T \sim D$ the degeneracy of the impurity gives rise to Schottky anomalies [19].

Next, consider the finite concentration of impurities (*i.e.* we keep x and Λ finite). Pairs, pre-formed due to the hybridization, are related to superconducting fluctuations. For $D = 0$ the band of strings is completely filled and yields zero total quadrupolar moment, *i.e.* the impurity quadrupolar moments are all compensated due to the antiferroquadrupolar correlations. The dressed energy of quadrupolar strings $\kappa_{2Q}(\xi)$ is negative (*i.e.* occupied) for all ξ if $x > 0$, but identically zero and, hence, empty for $x \to 0$. The point $x \to 0$ is then singular. The behavior of the model in the dilute limit $x \to 0$ is completely different to that for finite concentrations. Observe that if impurities do not directly interact with each other, they are not compensated and the limit $x \to 0$ is not singular. For $D \neq 0$ the large $|\xi|$ tails of $\kappa_{2Q}(\xi)$ are positive and not occupied, giving rise to a finite quadrupolar moment. For $H = D = 0$ the quadrupolar and magnetic susceptibilities are constant. Quadrupolar fluctuations renormalize dressed energies for pairs and unpaired electrons, increasing the respective energies. The value of the gap for unbound electrons, Δ, *i.e.* one-half of the smallest energy required to destroy a pair, is:

$$\Delta = [\Psi_0(B) - 2\pi x a_{2Q+2}(B-\theta)] \left[\tfrac{1}{2} - G_0(0) \right] + 2\pi x a_{2Q+2}(\theta) - G_0 * [\Psi_0(\xi) + 2\pi x a_{2Q+2}(\xi - \theta)], \quad (13)$$

where $*$ denotes convolution, $2\Lambda\Psi_0(\xi) = 2(4\xi + \Lambda)^2 - \Lambda^2$, and

$$G_n(x) = (2\pi)^{-1} \int dp \frac{\exp\left(-ipx - n|p|V^2/2\right)}{2\cosh\left(V^2 p/2\right)}. \quad (14)$$

The gap implies the critical CEF value $D_c = 2\Delta$ (and, thus, the related critical H) at which the gap is closed. The effect of impurities on the gap depends on the value of θ: For a given B/V^2 the gap decreases for small θ/V^2 and increases for larger values of θ/V^2. The gap increases with x when the impurities are off-resonance, being weakly coupled to itinerant electrons. Here impurity quadrupolar moments compensate each other, so that they do not have a destructive influence on pairs. The increase of Δ with x is the consequence of an enhanced density of states of electrons due to the presence of impurities. For small θ, *i.e.* on-resonance case, the coupling between impurities and host is strong, reducing the gap with x until a critical concentration x_{cr} at which the gap is closed.

There is a reminiscence of co-existence of superconducting and quadrupolar fluctuations. For $x < x_{cr}$ pairs

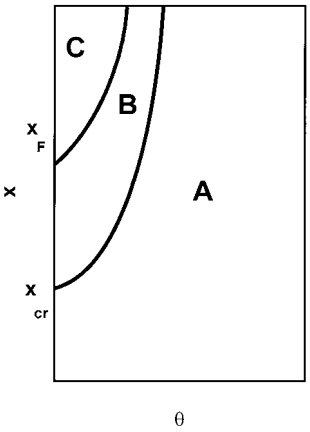

Fig. 1. The low concentration part of the ground state phase diagram θ–x of the considered system with the finite concentration of impurities.

coexist with antiferroquadrupolar fluctuations. On the other hand, for $x > x_{cr}$ the gap is closed and the band of unpaired electrons is gradually populated, but the quadrupolar spontaneous moment of unpaired electrons is compensated by a weak quadrupolar component of the impurity $2Q$-string band. For $x > x_F > x_{cr}$ the large $|\xi|$ tails of the dressed energy κ_{2Q} are positive. This introduces holes into the $2Q$-string band and, hence, induces a ferroquadrupolar component into the system.

Consider now the itinerant ferroquadrupolar component for x slightly larger than x_{cr}. Then the square root dependence $\sqrt{x - x_{cr}}$ arises from the van Hove singularity of the 1D band. On the other hand, the zero-field quadrupolar moment is proportional to $x - x_F$. The effect of the CEF is to gradually break up the antiferroquadrupolar frustration, weaken the pairs, and introducing this way a hole population in the band of $2Q$-strings and, hence, a nonzero quadrupolar moment.

The low concentration part of the ground state phase diagram of the considered system can be sketched as follows, see Figure 1. At low values of θ (in resonance) and x and for large θ (out of resonance) for any concentration the Dirac sea of $2Q$-strings is totally filled, and there exists the Dirac sea of pairs (the filling of which depends on the number of electrons in the system). In this phase (A in Fig. 1) superconducting and antiferroquadrupolar fluctuations co-exist, and there are no unbound electron excitations. This phase is divided from other phases by a line of the second order quantum phase transition. On the other hand, for small values of θ and $x_{cr} < x < x_F$ there appears a phase (B in Fig. 1) in which Dirac sea for unbound electron excitations appears together with the totally filled Dirac sea for $2Q$-strings and pairs. It turns out that in this phase the total quadrupolar moment of the system is zero. For in-resonance values of θ, but for $x_F < x$ the system is in the phase (C in Fig. 1) with co-existing superconducting and ferroquadrupolar fluctuations, *i.e.* spontaneous quadrupolar moment appears. All lines of quantum phase transitions are connected with the van Hove singularities of one-dimensional bands of low-lying excitations (here unbound electron excitations and $2Q$-strings).

In conclusion, in this paper we have studied the model of localized $4f^2$ interacting electrons with low-energy non-magnetic multiplets, which hybridize with conduction electrons. Our exact solution reveals several remarkable properties. For a small concentration of non-magnetic, but related to a quadrupolar moment, impurities the enhancement of the effective electron mass persists, while the hybridization with the finite concentration of such impurities dynamically induces the creation of spin-triplet quadrupolar-singlet pairs, a spin gap of unbound conduction electrons, and quadrupolar moments. As the concentration increases for strong quasi-degeneracy of the mixed configurations of $4f$ orbitals, the gap can be closed, signaling a quantum phase transition to a uncompensated quadrupolar-ordered phase (coexisting with superconducting fluctuations). Hence, our study describes how the hybridization between two almost degenerate non-magnetic (but related to quadrupolar moments) configurations of $4f^2$ orbitals and conduction electrons can produce *both* heavy electron mass and pre-formation of superconducting fluctuations of conduction electrons and quadrupolar ordering. Notice that the pairing between conduction electrons is caused by the hybridization between them and localized $4f^2$ electrons. The 3D interaction must produce superconducting and/or quadrupolar ordering of these pre-formed fluctuations. It turns out that a fully non-perturbative analysis of the relevant physics of heavy electrons and pre-formation of superconducting and quadrupolar ordering is allowed from the grounds of *the same* model. However, we emphasize again that our exact solution has only several features, reminiscent of Pr-based skutterudites, and cannot, naturally, describe their total behaviour.

This study was supported by the Swedish Foundation for International Cooperation in Research and Higher Education (STINT).

References

1. See E.D. Bauer, N.A. Frederick, P.C. Ho, V.S. Zapf, M.B. Maple, Phys. Rev. B **65**, 100506(R) (2002); Y. Aoki, T. Namiki, T.D. Matsuda, K. Abe, H. Sugawara, H. Sato, Phys. Rev. B **65**, 064446 (2002) and references therein
2. K.R. Lea, M.J.K. Leask, W.P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962)
3. H. Mitamura, N. Takeshita, Y. Uwatoko, H. Mori, A. Yamaguchi, T. Tomita, H. Wada, N. Mori, H. Ishimoto, T. Goto, Physica B **281** & **282**, 150 (2000)
4. H. Kotegawa, M. Yogi, Y. Imamura, Y. Kawasaki, G.-q. Zheng, Y. Kitaoka, S. Ohsaki, H. Sugawara, Y. Aoki, H. Sato, Phys. Rev. Lett. **90**, 027001 (2003); D.E. MacLaughlin, J.E. Sonier, R.H. Heffner, O.O. Bernal, Ben-Li Young, M.S. Rose, G.D. Morris, E.D. Bauer, T.D. Do, M.B. Maple, Phys. Rev. Lett. **89**, 157001 (2002); Y. Aoki, T. Namuki, S. Ohsaki, S.R. Saha, H. Sugawara, H. Sato, J. Phys. Soc. Jpn **71**, 2098 (2002); K. Tenya,

N. Oeschler, P. Gegenwart, F. Steglich, Acta Phys. Polon. B **34**, 995 (2003)
5. N. Oeschler, P. Gegenwart, F. Steglich, N.A. Frederick, E.D. Bauer, M.B. Maple, Acta Phys. Pol. B **34**, 959 (2003); Y. Aoki, T. Namiki, T. Kanayama, S. Ohsaki, S.R. Saha, H. Sugawara, H. Sato, *ibid.* **34**, 1145 (2003); R. Vollmer, A. Faisst, C. Pleiderer, H.V. Löhneysen, E.D. Bauer, M.B. Maple, *ibid.* **34**, 1185 (2003)
6. For the review of the non-magnetic Kondo effect use D.L. Cox, A. Zawadowski, Adv. Phys. **47**, 599 (1998)
7. The counterterm (with $V(x)$) is necessary to preserve the integrability at the positions of impurities. The inclusion of this term does not principally affect physical properties of a single impurity (*cf.* Ref. [9,10]). Pairs cannot be created due to that term in the dense localized $4f$-states case
8. P. Schlottmann, Phys. Rep. **181**, 1 (1989)
9. N. Andrei, C. Destri, Phys. Rev. Lett. **52**, 364 (1984)
10. A.A. Zvyagin, Phys. Rev. B **63**, 014503 (2001)
11. It is not necessary to include this direct interaction between neighboring impurities for the integrability of the model. Though, a nonzero coupling constant has to be related to the value of the hybridization, *cf.* [10]
12. In the limit of a small concentration of impurities our model is three-dimensional (3D). In the dense limit of impurities, on the other hand, our model is 1D, which is non-realistic for filled Pr skutterudites. Nonetheless, we believe that our model can describe the nature of pre-formation of superconducting and quadrupolar orderings, together with the enhancement of the effective electron mass stemmed from these non-magnetic hybridization impurities. The advantage of 1D models is the possibility of exact solutions *via* non-perturbative methods, which are difficult to obtain in higher dimensions. Our 1D calculations may serve as a testing ground for perturbative or numerical methods for more realistic situations
13. L.A. Takhtajan, Phys. Lett. A **87**, 479 (1982); H.M. Babujian, Nucl. Phys. B **215**, 317 (1983)
14. V.E. Korepin, N.M. Bogoliubov, A.G. Izergin, *Quantum Inverse Scattering Method and Correlation Functions* (Cambridge University Press, 1993)
15. A. Jerez, N. Andrei, G. Zaránd, Phys. Rev. B **58**, 3814 (1998)
16. A.A. Zvyagin, J. Phys. A **34**, R21 (2001)
17. A.A. Zvyagin, P. Schlottmann, Nucl. Phys. B [FS] **586**, 686 (2000); *ibid.* **565**, 555 (2000)
18. A.A. Zvyagin, unpublished
19. For the lowest $4f^2$ singlet (Γ_1) one has $Q = 0$. This implies the leading dependence of the impurity quadrupolar moment to be $\mathcal{Q}_{imp} \sim -D\mathcal{LD}$, *i.e.* the quadrupolar susceptibility to have a logarithmic divergence which persists for low T ($D = 0$): $\chi(T) \propto -\ln(T/T_K)$, while the low-$T$ specific heat to be $C_{imp} \propto -T\ln(T/T_K)$. It seems to contradict the data of experiments for $PrOs_4Sb_{12}$ [1,3–5]