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Quantum fluctuations and the ground-state phase diagram of the strong-coupling Holstein-Hubbard model

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Abstract. – A Grassmann functional integration technique is applied to the anisotropic pseudospin Hamiltonian derived from the Holstein-Hubbard model with strong electron-phonon coupling. It is found that in those regions of the low-temperature phase diagram where superconductivity and the charge-density wave coexist already the static and homogeneous saddle point solution of the resulting field theory yields a ground-state energy which is *lower* than the classical result corresponding to the usual mean-field solution. This is due to the presence of quantum fluctuations and leads to new ground-state phase boundaries quantitatively different from those obtained in previous work by conventional operator decoupling schemes.

The interaction between conduction electrons and the lattice vibrations in a solid is of importance for the low-temperature properties of a great variety of materials. Strongly correlated electron systems with electron-phonon coupling [1]-[4] have been studied especially in the context of different variants of the Holstein model [5]-[8], which describes itinerant fermions interacting with purely local phonon modes. The Holstein-Hubbard [9]-[11] and the Holstein-t-J [12]-[14] models are of particular interest for these systems, because they display competing low-temperature instabilities against the formation of charge-density wave (CDW) and superconducting (SC) ordering. Anharmonicity of the phonon potential [11] developing a double-well structure indicates bipolaronic pairing already at moderate electron-phonon coupling strength of the Holstein-Hubbard Hamiltonian, and superlattice ordering of polarons [13] is found in large regions of the phase diagram of the Holstein-t-J model.

In the limit of strong electron-phonon interaction, the Holstein Hamiltonian is equivalent to the anisotropic spin-1/2 Heisenberg model [15], albeit with an additional constraint which relates the magnetization with the band-filling. The phase diagram of this anisotropic pseudospin model exhibits a rich structure depending on doping and temperature [16], including pure superconducting and charge-ordered phases and a mixed (M) phase where both types of

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order coexist. The properties of these low-temperature phases which meet in a tetracritical point have been widely explored utilizing conventional decoupling techniques of the mean-field and RPA type and classical ground-state analysis [17]-[19]. More recently, the Holstein model has also been studied intensively in the limit of infinite spatial dimensions [20], [21] where the problem is reduced to a purely local one retaining its full dynamics and where the mean-field phase diagram is expected to become exact. The identification of the "correct" mean-field solution therefore deserves renewed interest.

Here we present a field-theoretic formulation of the Holstein-Hubbard model with strong electron-phonon coupling, applying a Grassmann functional integration technique to the effective pseudospin Hamiltonian derived perturbatively for large bipolaronic pairing energy. This results in a representation of the model in terms of unconstrained bosonic fields which fully accounts for quantum fluctuations. As a consequence, already the static and homogeneous saddle point solution of this field theory, which can be identified with a large-n limit of the underlying effective Hamiltonian, yields a ground-state energy which for the mixed phase is *lower* than the corresponding result of the classical ground-state and the conventional $T=0$ mean-field solution. This stabilization of the mixed phase due to quantum effects results in phase boundaries which are quantitatively different from those obtained by the usual mean-field decoupling approximation. Despite the mean-field–like nature of the saddle point result which neglects spatial fluctuations, quantum fluctuations are present in the corresponding action due to the independence of the bosonic order parameter decoupling fields which are not constrained to fixed total length of the local pseudospin.

The Holstein-Hubbard model is given by the Hamiltonian

$$\mathcal{H} = \sum_{\mathbf{r}\mathbf{r}'\sigma} t_{\mathbf{r}\mathbf{r}'}\, c^\dagger_{\mathbf{r}\sigma} c_{\mathbf{r}'\sigma} + U_0 \sum_{\mathbf{r}} n_{\mathbf{r}\uparrow} n_{\mathbf{r}\downarrow} + \Omega \sum_{\mathbf{r}} b^\dagger_{\mathbf{r}} b_{\mathbf{r}} + g \sum_{\mathbf{r}\sigma} n_{\mathbf{r}\sigma}(b^\dagger_{\mathbf{r}} + b_{\mathbf{r}}) - \mu_0 \sum_{\mathbf{r}\sigma} n_{\mathbf{r}\sigma}, \tag{1}$$

where $c^\dagger_{\mathbf{r}\sigma}$ ($c_{\mathbf{r}\sigma}$) creates (destroys) an electron with spin σ at site $\mathbf{r}$ and with chemical potential μ_0, $b^\dagger_{\mathbf{r}}$ ($b_{\mathbf{r}}$) creates (destroys) a vibrational quantum of the local (Einstein) phonon modes with frequency Ω, $t_{\mathbf{r}\mathbf{r}'}$ introduces hopping of the conduction electrons between neighboring lattice sites, U_0 is the on-site Hubbard interaction, and g describes the coupling between the electronic degrees of freedom and the lattice vibrations. This coupling term can be eliminated by the well-known polaron transformation $\tilde{b}_{\mathbf{r}} = b_{\mathbf{r}} - (g/\Omega)\sum_\sigma n_{\mathbf{r}\sigma}$ and $\tilde{c}_{\mathbf{r}\sigma} = c_{\mathbf{r}\sigma} \exp\left[-(g/\Omega)(b^\dagger_{\mathbf{r}} - b_{\mathbf{r}})\right]$, which results in a Hubbard model in terms of the operators $\tilde{c}_{\mathbf{r}\sigma}$, with the polaron binding energy $U = U_0 - 2g^2/\Omega$, and where the hopping term involves the excitation of local vibrational quanta. For sufficiently strong attractive coupling, $|U| \gg t$, the hopping of electrons can be treated as a perturbation around the highly degenerate ground state consisting of tightly bound electron pairs of bipolaronic origin. To second order in t, this yields an effective anisotropic (XXZ) Heisenberg model,

$$\mathcal{H} = J \sum_{\langle \mathbf{r}\mathbf{r}'\rangle} \left(\frac{1}{4} \sum_{\sigma\sigma'} c^\dagger_{\mathbf{r}\sigma} c_{\mathbf{r}\sigma} c^\dagger_{\mathbf{r}'\sigma'} c_{\mathbf{r}'\sigma'} - \lambda\, c^\dagger_{\mathbf{r}\uparrow} c^\dagger_{\mathbf{r}\downarrow} c_{\mathbf{r}'\downarrow} c_{\mathbf{r}'\uparrow} \right) - \mu_0 \sum_{\mathbf{r}\sigma} n_{\mathbf{r}\sigma}, \tag{2}$$

when the pseudospin operators $\hat{S}^z_{\mathbf{r}} = \frac{1}{2}(n_{\mathbf{r}\uparrow} + n_{\mathbf{r}\downarrow} - 1)$, $\hat{S}^+_{\mathbf{r}} = c^\dagger_{\mathbf{r}\uparrow} c^\dagger_{\mathbf{r}\downarrow}$, and $\hat{S}^-_{\mathbf{r}} = c_{\mathbf{r}\downarrow} c_{\mathbf{r}\uparrow}$ are introduced. The pseudospin interaction J and the easy-axis anisotropy λ are strongly dependent [15] on the polaron band-narrowing parameter $S = g^2/\Omega^2$. If one considers only temperatures which are small compared to the phonon energy scale, $T \ll \Omega$, thermal excitations of the vibrational modes may be neglected. For weak electron-phonon coupling or large phonon frequency, $S \to 0$, the interaction between electrons is instantaneous and one recovers the ordinary negative-U Hubbard model, so that $J = 2t^2/|U|$ and the effective Heisenberg Hamiltonian becomes isotropic, $\lambda \to 1$. In the static limit of large S, only the

z-components of the pseudospins interact, with $J = t^2/|U|$, and the XY-type interaction is suppressed, $\lambda \to 0$. The spin Hamiltonian corresponding to (2) has been studied in the context of a variety of problems in magnetism and liquid helium. Its special character for the present system lies in the additional constraint which relates the (pseudo)magnetization with the band-filling, $\langle \hat{S}^z \rangle = \nu - 1/2$, with $\nu = \langle n_\uparrow n_\downarrow \rangle$, and which is responsible for several peculiar features of the phase diagram [16].

The partition function of the effective Hamiltonian (2) is now written as a functional integral over Grassmann fields, $Z = \int \prod_{\mathbf{r}\sigma\tau} \mathcal{D}\overline{\psi}_{\mathbf{r}\sigma}(\tau)\mathcal{D}\psi_{\mathbf{r}\sigma}(\tau)\ \exp[\mathcal{S}\{\overline{\psi}_{\mathbf{r}\sigma}(\tau), \psi_{\mathbf{r}\sigma}(\tau)\}]$, with the action

$$\mathcal{S}\{\overline{\psi}_{\mathbf{r}\sigma}(\tau), \psi_{\mathbf{r}\sigma}(\tau)\} = \int_0^\beta \mathrm{d}\tau \left[\sum_{\mathbf{r}\sigma} \overline{\psi}_{\mathbf{r}\sigma}(\tau)\partial_\tau \psi_{\mathbf{r}\sigma}(\tau) - \mathcal{H}\left(\overline{\psi}_{\mathbf{r}\sigma}(\tau), \psi_{\mathbf{r}\sigma}(\tau)\right)\right]. \qquad (3)$$

The fermionic Hilbert space constraint for the pseudospin Hamiltonian (2) which rules out singly occupied sites, imposes the periodicity conditions $\psi_{\mathbf{r}\sigma}(\beta) = i\sigma\psi_{\mathbf{r}\sigma}(0)$, with $\sigma = \pm 1$, resulting in a shift of the corresponding fermionic Matsubara frequency spectrum, $z_{n\sigma} = \pi T(2n + 1 + \sigma/2)$ [22]. By means of the Hubbard-Stratonovitch transformation, the quartic terms in (3) can now be decoupled, so that one arrives at the effective action for the bosonic pair fields,

$$\mathcal{S}\{\Delta_{q,m}, Q_{q,m}\} = -\beta \sum_m \int \mathrm{d}^d q \frac{1}{J_q}\left(\frac{1}{\lambda}\overline{\Delta}_{q,m}\Delta_{q,m} + Q_{q,m}Q_{-q,-m}\right) + \sum_{\mathbf{r}} \ln\det \mathcal{M}_{\mathbf{r}}. \qquad (4)$$

The (complex) field Δ corresponds to the order parameter in the XY-sector (superconductivity), whereas the (real) field Q is related to the Ising magnetization (charge-density wave or uniform filling). The fermion determinant in (4) contains the matrix kernel

$$\beta^{-1}(\mathcal{M}_{\mathbf{r}})_{n+m,n} = (iz_{n\sigma}\,\rho_z + \mu_0\,\rho_0)\delta_{m,0} + (-1)^{\mathbf{r}} Q_{\mathbf{r},m}\,\rho_0 - \Delta_{\mathbf{r},m}\,\rho_+ + \overline{\Delta}_{\mathbf{r},-m}\,\rho_-, \qquad (5)$$

where the ρ are Pauli matrices in Nambu space. Assuming only static and homogeneous contributions of the decoupling fields from the (momentum dependent) components Q_0, Q_π, and Δ_0, one may now evaluate the fermion determinant with the corresponding $\mathcal{M}_0$ and identify the saddle point action,

$$\mathcal{S}_{\text{s.p.}} = -\frac{\beta}{J_0}\left(Q_0^2 - Q_\pi^2 + \frac{1}{\lambda}|\Delta_0|^2\right) + \frac{1}{2}\ln(\cosh\beta R_+ \cosh\beta R_-) \qquad (6)$$

with the local one-particle energies $R_\pm = \sqrt{|\Delta_0|^2 + (\mu \pm Q_0)^2}$ which are dependent on the sublattice, and the modified chemical potential $\mu = \mu_0 + Q_\pi$.

Minimization of the corresponding free energy then yields the saddle point self-consistency equations for the order parameters of superconductivity,

$$\frac{1}{J_0\lambda} = \frac{\tanh\beta R_+}{4R_+} + \frac{\tanh\beta R_-}{4R_-}, \qquad (7)$$

and of the charge-density wave,

$$\frac{Q_0}{J_0} = (\mu + Q_0)\frac{\tanh\beta R_+}{4R_+} - (\mu - Q_0)\frac{\tanh\beta R_-}{4R_-}. \qquad (8)$$

These equations also follow from the usual many-body theoretical relations $\langle c^\dagger_{\mathbf{r}\sigma} c_{\mathbf{r}\sigma}\rangle = T\sum_n G_{\mathbf{r}}(z_{n\sigma})$ and $\langle c_{\mathbf{r}\downarrow} c_{\mathbf{r}\uparrow}\rangle = T\sum_n F_{\mathbf{r}}(z_{n\sigma})$, involving the electronic sublattice propagators $\mathcal{G} = (\mathcal{M}_0)^{-1}$ which in Nambu notation are given by

$$(\mathcal{G}_{\mathbf{r}\mathbf{r}'})_{n+m,n} = \delta_{\mathbf{r},\mathbf{r}'}\,\delta_{m,0}\begin{pmatrix} G(z_{n\sigma}) & F(z_{n\sigma}) \\ -F(z_{n\sigma}) & G^*(z_{n\sigma}) \end{pmatrix} = \frac{-iz_{n\sigma}\,\rho_z + (\mu \pm Q_0)\rho_0 + i|\Delta_0|\,\rho_y}{z_{n\sigma}^2 + (\mu \pm Q_0)^2 + |\Delta_0|^2}. \qquad (9)$$

It may be worth noting that the propagators (9) can be identified with the Green's functions in the large-n limit of an n-orbital generalization for the Hamiltonian (2). From the above relations an additional equation for the chemical potential follows:

$$\nu - 1/2 = (\mu + Q_0)\frac{\tanh \beta R_+}{4R_+} + (\mu - Q_0)\frac{\tanh \beta R_-}{4R_-}. \tag{10}$$

This equation (10) together with the extremal condition for the action also implies $Q_\pi = -J_0(\nu - 1/2)$ for the uniform filling of the system. From (7) and (8) one derives the filling dependent critical temperatures for the pure phases, $T_c^{SC} = J_0\lambda\,(2\nu - 1)/\ln\frac{\nu}{1-\nu}$ and $T_c^{CDW} = 2J_0\,\nu(1-\nu)$, which agree with the usual mean-field results [17], [18]. At $T = 0$, and for the pure superconducting phase, where $Q_0 \equiv 0$, one finds $|\Delta_0| = J_0\lambda\sqrt{\nu(1-\nu)}$ and $\mu = \frac{1}{2}J_0\lambda(2\nu - 1)$. In the mixed phase, where both superconductivity and charge-ordering are present, the field theoretic zero-temperature saddle point solution is given by

$$\begin{aligned} |\Delta_0|^2 &= \frac{J_0^2\lambda^2}{4}\frac{|2\nu-1|}{\sqrt{1-\lambda}}\left(1 - |2\nu - 1|\sqrt{1-\lambda}\right), \\ Q_0^2 &= \frac{J_0^2}{4}\left(1 - |2\nu - 1|\sqrt{1-\lambda}\right)\left(1 - \frac{|2\nu-1|}{\sqrt{1-\lambda}}\right), \\ \mu &= \frac{J_0}{2}\sqrt{1-\lambda}\left(1 - |2\nu - 1|\sqrt{1-\lambda}\right)\,\mathrm{sgn}(2\nu - 1). \end{aligned} \tag{11}$$

At precisely half band-filling, the superconducting order parameter vanishes and one finds a purely charge-ordered phase. The corresponding ground-state energies of these SC and M phases are

$$E_{SC} = -\frac{J_0}{4}\left(\lambda + (1+\lambda)|2\nu - 1|^2\right) \qquad \text{and} \quad E_M = -\frac{J_0}{4}\left(1 + \lambda|2\nu - 1|^2\right), \tag{12}$$

from which it follows that in the vicinity of the half-filled band the mixed phase is favored and a continuous transition SC $\to$ M takes place upon approaching the center of the electronic band,

$$E_M < E_{SC} \qquad \text{for} \quad |2\nu - 1| < \sqrt{1-\lambda}. \tag{13}$$

For low but finite temperatures the boundary between the mixed and the pure superconducting region of the phase diagram is given by $|2\nu - 1| \simeq \sqrt{1-\lambda}\,(1 + (\beta J_0\lambda)\exp[-\beta J_0\lambda])$, whereas the mixed and the pure charge-ordered phase are separated by the line $|2\nu - 1| \simeq \exp[-\beta J_0\lambda]$. The transition line (13) is in agreement with the result obtained by an expansion of (8) for small Q_0 in the SC phase, and with the corresponding instability condition for Gaussian charge-density fluctuations around the purely superconducting saddle point solution.

These phase boundaries, however, are at variance with the results obtained from a purely classical ground-state analysis and the usual mean-field–like treatment of the Hamiltonian [17], [18]. Considering the classical mean-field version of the pseudospin Hamiltonian (2),

$$H = \frac{J_0}{4}\big(\cos\theta_1\,\cos\theta_2 - \lambda\sin\theta_1\,\sin\theta_2\big) - \frac{\mu_0}{2}\big(\cos\theta_1 + \cos\theta_2\big) \tag{14}$$

with the constraint $\cos\theta_1 + \cos\theta_2 = 2(2\nu - 1)$, minimization of the energy with respect to the orientations of the sublattice magnetization θ_1 and θ_2 yields a SC $\to$ M transition line given by $|2\nu - 1| = \sqrt{(1-\lambda)/(1+\lambda)}$. The difference of this classical phase boundary from the result (13) is due to a lowering of the ground-state energy of the mixed phase by quantum fluctuations, which are captured in the field-theoretical treatment. While the $T = 0$

saddle point solution for the pure SC phase reproduces the classical ground-state energy, $E_{\mathrm{SC}} = E_{\mathrm{SC}}^{\mathrm{classical}}$, for the mixed phase one finds a result which is lower than the classical value,

$$\Delta E_{\mathrm{M}} = E_{\mathrm{M}} - E_{\mathrm{M}}^{\mathrm{classical}} = -\frac{J_0 \lambda}{4} |2\nu - 1|^2, \tag{15}$$

thus extending the region of stability of the mixed phase beyond the classical phase boundary. The effect of quantum fluctuations can also be seen in the $T = 0$ saddle point results for the mean length of the local magnetization. While $|\langle \mathbf{S} \rangle| = 1/2$ retains its classical value in the pure SC phase, when both superconductivity and charge-ordering are present one finds a reduction of the total pseudospin length, indicating the role of quantum effects,

$$|\langle \mathbf{S} \rangle|^2 \equiv \frac{|\Delta_0|^2}{J_0^2 \lambda^2} + \frac{Q_0^2}{J_0^2} + \left(\nu - 1/2\right)^2 = \frac{1}{4} \left(1 - |2\nu - 1| \left(\sqrt{1-\lambda} - |2\nu - 1|\right)\right). \tag{16}$$

It may seem surprising that in the framework of the saddle point solution, in which the contribution of spatial fluctuations of the order parameter fields is suppressed, quantum corrections can be present. However, the effective action (4) is the complete quantum action of the system with the order parameter fields as independent and unconstrained variables of functional integration. The extremal conditions for the action therefore lead to independent self-consistency equations for these fields, even when one considers only the static and homogeneous solution. Thus, also with spatial and dynamical fluctuations being absent, the saddle point values for the fields can include corrections to the purely classical result which imposes a fixed-length constraint on the pseudospin. Accordingly, these quantum corrections are present only in the mixed phase which is really characterized by two independent order parameters, while they do not occur in the pure phases where one has only a single self-consistency equation.

Quantum corrections have also been claimed to be included in the RPA type treatment of the present problem [19]. In contrast to the results found here, the RPA predicts a stabilization of the pure SC phase against the M phase by quantum fluctuations. As a consequence, this leads to a qualitative change of the ground-state phase diagram in which the SC $\to$ M transition line now asymptotically approaches a finite filling ν for large anisotropy, $\lambda \to 0$. However, as can be shown in the n-orbital generalization of the effective pseudospin Hamiltonian (2), the RPA mixes non-systematically contributions which are leading in powers of $1/n$ with some of those in next higher order [22]. Therefore, at least in the $n \to \infty$ limit where the Green's functions (9) become exact, the effect of quantum fluctuations is correctly described by the field-theoretic approach presented above.

Besides these purely static results, the field-theoretic representation also allows to obtain the dynamics of the system around the saddle point. Extracting the dynamical contributions to the action by the decomposition $\mathcal{M}_{n+m,n} = \mathcal{M}_0 \, \delta_{m,0} + \Phi_{n+m,n}$, and expanding (4) to second order in the fluctuation fields Φ, yields the dynamical Gaussian corrections of the action. From these one can immediately deduce the excitation spectra, which for nonvanishing superconducting order parameter Δ_0 exhibit a gapless branch with linear dispersion $\omega \sim q$ characteristic for superfluidity. From the dynamical contributions one also finds the Gaussian corrections to the energy, which do not alter the $T = 0$ phase boundary (13), however.

In summary, a field-theoretic representation has been formulated for the strong-coupling Holstein-Hubbard model, which takes into account the effect of quantum fluctuations already in the mean-field–like saddle point approximation. This appears to be a consequence of the fact that the order parameter fields are independent of each other and are not subject to constraining conditions. The resulting ground-state energy for the coexistence phase of charge-ordering and superconductivity is found to be reduced below the corresponding classical value by quantum effects. This stabilization of the mixed phase leads to a ground-state phase diagram which differs quantitatively from the conventional mean-field solution.

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