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Polaronic effects in fluctuating-valence solids: A renormalization-group study

W. Hanke and D. Schmeltzer

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

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The influence of critical quantum (phonon) fluctuations on a one-dimensional model of fluctuating-valence electrons locally coupled to dispersionless phonons at $T=0$ K is studied. Near the insulator-metal transition of the half-filled band case the electronic correlation length diverges and induces long-range fluctuations of the boson field. These fluctuations suppress the standard polaronic effects, i.e., the relaxation shift and lifetime enhancement. For these results scaling is essential, which is treated within a real-space renormalization-group scheme.

Recently, the electronic theory of fluctuating-valence (FV) solids has been a subject of considerable investigation.[1,2] One challenging difficulty in these solids stems from the simultaneous presence of both extremely localized f electronic states and delocalized band (d) states in the vicinity of the Fermi level. Besides strong interactions between local f (≈ 10 eV) and f and d band (≈ 1 eV) electrons, large degeneracies prohibit the application of standard perturbation theory. Important progress has, therefore, recently been achieved in studies of the single-impurity Anderson model by use of the Brillouin-Wigner perturbation theory[3-5] and nonperturbative renormalization-group (RG) methods.[6,7] Finite-cell simulations of the periodic Anderson model,[8,9] as well as renormalization-group studies of a spinless model containing, however, additionally the f-d Coulomb interaction, and of a Kondo lattice model,[10] have revealed significant differences, if the concentrated case of interacting impurities is considered.

This Rapid Communication deals with the second characteristic difficulty of FV: The energy splitting between the quasidegenerate f^n and f^{n-1} ionic configurations is of the order of phonon energies. Therefore strong and nonadiabatic electron-lattice coupling may arise and the relatively slow valence fluctuations may influence the local lattice distortions. This can considerably reduce the frequency of valence fluctuations and thus effectively increase the lifetime of the individual configurations. Additionally, it can introduce a relaxation shift in the f level. This level, which is usually assumed to be very close to the Fermi level E_F, has recently been found in several FV systems to be a few eV below E_F.[11,12] The nonadiabatic electron-phonon coupling so far has mostly been dealt with within the small polaron model[13,14] and for the single-impurity limit.[15]

In this Rapid Communication we want to discuss a one-dimensional (1D) FV model in which a concentrated model of f and d electrons is locally coupled to a boson field of Einstein oscillators. Particular attention is paid to the question of how the electronic properties of this FV model are affected by coupling to the lattice at $T=0$, where quantum fluctuations come into play.

For a rough estimate of the consequences of (f) electron-lattice coupling, the two limiting cases of adiabatic and "antiadiabatic" coupling may be considered[14]. In the adiabatic limit the frequency ω_0, and therefore the isotropic "breathing" motion of the surrounding ions, is low. Here the lattice cannot respond to the hopping of an f electron into the band and its immediate recapture. The charge fluctuation rate or effective width Γ of the f level, from Fermi's golden rule, is just proportional to the square of the hybridization V. On the other hand, in the antiadiabatic limit ($\omega_0 >> \Gamma$), the lattice can follow the electronic configurations. Here, one expects the electron-lattice coupling to favor a positive radial displacement of neighboring atoms in the FV lattice, if the f level is occupied.[14] This argument is consistent with a polaronically reduced hybridization and charge fluctuation rate and a band shift. Our primary result is that, near the vanishing Coulomb gap (i.e., when the Coulomb interaction U between f and d electrons goes to zero), the long-range electronic correlations and the related phonon quantum fluctuations, in fact, suppress the standard polaronic effects. Hence, near $U=0$ in our RG study, no reduction of the FV frequency with accompanying lifetime enhancement and no relaxation shift occur. It is shown that this suppression crucially depends on scaling and would not appear for finite-sized cells. Implications for other FV electronic models and possible extensions to higher dimensions are discussed.

Our Hamiltonian is of the form

$$H = H_{\rm el} + H_{\rm ph} \ , \tag{1}$$

with the electronic part

$$H_{\rm el} = E_d \sum_i d_i^\dagger d_i - t \sum_i (d_i^\dagger d_{i+1} + \text{H.c.}) + E_f \sum_i f_i^\dagger f_i + V \sum_i (f_i^\dagger d_i + \text{H.c.}) + U \sum_i n_{d_i} n_{f_i} \ . \tag{2}$$

Here $d_i^\dagger$ denotes the creation operator of the band (d) states with hopping matrix element $-t$ and $f_i^\dagger$ the creation operator for a localized f electron at site i.

The ground state and gap properties of this 1D spinless model of FV have previously been studied employing a real-space RG block method.[10,16] For the half-filled band situation the ground state has been found to be insulating for all nonzero values of U. That the Coulomb interaction between the f electrons probably plays a similar role may be inferred from recent 1D finite-cell studies of the periodic Anderson model[9]: These studies also display the existence

of the insulating gap which increases with the Hubbard U.

The phonon and electron-phonon contribution $H_{\rm ph}$ is

$$H_{\rm ph}=\omega_0\sum_i(a_i^\dagger a_i+\tfrac{1}{2})+\lambda\sum_i(a_i^\dagger+a_i)n_{f_i} \ , \tag{3}$$

where $a_i^\dagger$ creates a local phonon of frequency ω_0, coupled to f charge fluctuations only.[14] t defines our scale of energies and is set $\equiv 1$ from now on. Thus the Hamiltonian is characterized by the energies (U,V,ω_0) and the polaron binding energy $E_B=\lambda^2/\omega_0$, as a measure of the coupling strength. For simplicity, we consider in the following $E_d\equiv E_f$ in Eq. (2).

First, we introduce the scaling equations of the electronic model for small U and V. This follows closely our earlier RG work for general U and V.[10] To this, the chain is dissected into blocks of $N=3$ sites, which are coupled via the hopping term $(-t)$. The Hamiltonian is then diagonalized for each block making use of the conserved quantities, i.e., parity and number of particles. Since we are working in the half-filled band case, only the $(N-1)$- $(=2)$, N-, and $(N+1)$-particle subspaces have to be considered. Only the four lowest-energy states of the 4^N block states are retained to reexpress the Hamiltonian. They are denoted by $|0'\rangle$, $|+'\rangle$, $|-'\rangle$, $|+-'\rangle$ and are the lowest states in the $(N-1)$- and $(N+1)$-particle subspaces, and the two lowest states in the N-particle subspace. In momentum-space description they are given by[10,16]

$$\begin{aligned}&|0'\rangle=\prod_{l=1}^{N-1}\alpha_{k_l}^\dagger|0\rangle \ , \quad |-'\rangle=\alpha_{k_N}^\dagger|0'\rangle \ ,\\ &|+'\rangle=\beta_{k_1}^\dagger|0'\rangle \ , \quad |+-'\rangle=\beta_{k_1}^\dagger\alpha_{k_N}|0'\rangle \ ,\end{aligned} \tag{4}$$

where $\alpha_{k_1}^\dagger$ $(\beta_{k_1}^\dagger)$ with $k_l=\pi l/(N+1)$, $1\le l\le N$, denotes the creation operator of a lower (upper) band state of the diagonalized Hamiltonian $(U=0)$ of Eq. (2).[10,16] The renormalization of the interaction

$$H_1=U\sum_i n_{di}n_{fi} \tag{5}$$

follows for small $U<t$ from perturbation theory, i.e., from

$$\begin{aligned}U'=&\langle+-'|H_1|+-'\rangle+\langle 0'|H_1|0'\rangle\\ &-\langle+'|H_1|+'\rangle-\langle-'|H_1|-'\rangle \ .\end{aligned} \tag{6}$$

Similarly, the change in the hybridization V due to U is

$$\Delta V=(\langle+'|H_1|+'\rangle-\langle-'|H_1|-'\rangle)/2 \ . \tag{7}$$

Adding this to the change in V, which is already due to the new block states in Eq. (4), we arrive, after tedious but straightforward calculations, at the scaling relations of the purely electronic $H_{\rm el}$ for small U and V:

$$V'/t'=c-d(U/t) \ , \tag{8.1}$$

$$U'/t'=U/t+\epsilon(U/t)^2 \ , \tag{8.2}$$

$$U'=\tfrac{3}{4}U(V/t)^2 \ . \tag{8.3}$$

The coefficients c, d, and ϵ are computed for the case $N=3$. For the Bose system we closely follow our earlier work on the RG method for the polaron effect in the Hubbard Hamiltonian.[17] The renormalized harmonic oscillator (HO) in the $N=3$ sites block is constructed, making use of the equivalence between three independent 1D HO's and the isotropic 3D HO. Keeping the two lowest block Bose states and building the complete Fermi-plus-Bose block states out of the direct-product states, we can now also compute the renormalized phonon coupling with respect to these states, and obtain[17]

$$\lambda'=N^y\lambda \tag{9}$$

and

$$\omega_0'=\omega_0 \ . \tag{10}$$

Here $N^y=1/\sqrt{3}$.

Equations (8), together with (9) and (10), then constitute the complete scaling relations.

From Eq. (8.1) follows the integrated relation

$$V(l)+dU(l)=ct(l) \ , \tag{11}$$

where l denotes the continuous scale change.[17] The correlation length is a function of (U/t), and solving Eq. (8.2) is given by

$$L=\exp(l_0)\sim\exp[\epsilon/(U/t)] \ . \tag{12}$$

Here l_0 is the final length of the RG iterations and is related to the final block size by $(N=3)^{n_0}=\exp(l_0)$.

In particular, we can infer from (12) that scaling is towards localized behavior for any nonzero value of U, and hence the hopping $t(l=l_0)$ goes to zero. This will enable us, in the following, to *always* make use of the standard small polaron results if we just replace the usual polaron parameters by their scaled counterparts.

From (11), the hybridization gap is given by $V(l=l_0)$:

$$V(l=l_0)=-dU(l=l_0)=-d\Delta \ , \tag{13}$$

where Δ denotes the Coulomb gap.

Using Eqs. (8.3) and (11), we further obtain

$$dU/dl=-zU \ , \tag{14}$$

and, therefore,

$$\Delta=U(l=l_0)=U\exp(-zl_0)\sim A\exp[-z_e/(U/t)] \ . \tag{15}$$

with $z=\ln 4/c^2\ln 3$ and the constant A slightly depending on U and V. The constant (z) is of the order of 1.

Equation (9) gives for the scaled coupling

$$\lambda(l=l_0)=\lambda\exp(-yl_0)=\lambda L^{-y} \ . \tag{16}$$

Now, making use of the fact that scaling is always such that the interblock hopping $t(l_0)$ vanishes, we have for the scaled Hamiltonian the local form

$$H(l=l_0)=\sum_i[E(l_0)(c_{d,i}^\dagger c_{d,i}+c_{f,i}^\dagger c_{f,i})+\lambda(l_0)(b_i^\dagger+b_i)n_{f,i}+V(l_0)(c_{d,i}^\dagger c_{f,i}+\text{H.c.})+U(l_0)n_{d,i}n_{f,i}+\omega_0 b_i^\dagger b_i] \ . \tag{17}$$

The usual displaced oscillator transformation, with $H'=U^{-1}HU$ and $U=\exp[-(\lambda/\omega_0)(b^\dagger-b)n_f]$ eliminates the phonon coupling, i.e.,

$$H'(l=l_0)=\sum_i\left[\left[E(l_0)-\frac{4\lambda^2(l_0)}{\omega_0}\right]c_{f,i}^{\dagger}c_{f,i}+E(l_0)c_{d,i}^{\dagger}c_{d,i}+V(l_0)\exp\left[-\frac{\lambda(l_0)}{\omega_0}(b_i^{\dagger}-b_i)\right](c_{d,i}^{\dagger}c_{f,i}+\text{H.c.})+\omega_0 b_i^{\dagger}b_i+U(l_0)n_{d,i}n_{f,i}\right]. \tag{18}$$

In H' we can perform the local phonon averages, since the hopping term is missing, and obtain for the effective hybridization

$$\begin{aligned}V_{\text{eff}}(l_0)&=\langle\exp-\lambda(l_0)(b^{\dagger}-b)/\omega_0\rangle\, V(l_0)\\&=V(l_0)\exp\left[-\frac{2\lambda^2(l_0)}{\omega_0^2}\right]\\&=V(l_0)\exp\left[-\frac{2\lambda^2}{\omega_0^2}L^{-2y}\right],\end{aligned} \tag{19}$$

where L^{-2y} is close to L^{-1} ($y\approx 0.5$).

Thus we have all the standard results of previous polaron studies, however, with the crucial difference being that the polaronic reduction of the hybridization energy V and the relaxation shift $\lambda^2(l_0)/\omega_0$ depend on the correlation length L.

Hence, near the insulator-metal transition, i.e., when U goes to zero, the diverging correlation length L suppresses the polaronic effect. On the other hand, for larger U, L tends to one and we recover the small polaron result.

At this point arises the question of the relevance of this result for other models of FV and for higher dimensions: Apart from the fact that our model Hamiltonian is rather idealized in that it is only local in the coupling and spinless, it is, of course, limited to the half-filled band case and to one dimension.

This clearly puts limits on any direct application to experimental observations. Nevertheless, we believe that our model calculation demonstrates the importance of quantum fluctuations for the low-temperature critical behavior of correlated fermion systems, like FV systems, coupled to a boson field: Whenever the system undergoes an insulator-metal transition the correlation length will diverge. This will change the local and dispersionless character of the electron-phonon coupling in Eq. (3), and long-ranged phonon quantum fluctuations can affect ground-state and low-excitational properties. We have just considered an oversimplified model which demonstrates this in a special case. Other 1D models in the half-filled case, like the Anderson model[9] or the Kondo-lattice model,[10] give also an insulating gap as a result of the coherence of states on different sites in a periodic system. Here, similar results for the electron-lattice coupling are to be expected. These results certainly cannot be directly extended to higher dimensions where, even in the half-filled case, one expects the gap to vanish for a certain range of parameters (example: Hubbard model). However, also in higher dimensions, the phonon quantum fluctuations near an insulator-metal transition should strongly influence any type of local Fermi-Bose coupling. The importance of critical quantum fluctuations in one, two, and three dimensions has recently been asserted in a specific example of a noninteracting electron version of the small polaron.[18]

[1]For various review, particularly on theory, see *Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981).

[2]For recent reviews see, also, *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam, 1982); N. Grewe, H. J. Leder, and P. Entel, in *Festkörperprobleme XX,* edited by J. Treusch (Vieweg, Braunschweig, 1980).

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