Falicov-Kimball model and the problem of electronic ferroelectricity

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Abstract

The density matrix renormalization group method is used to examine possibilities of electronic ferroelectricity in the spinless Falicov-Kimball model. The model is studied for a wide range of parameters including weak and strong interactions as well as the symmetric and unsymmetric case. In all examined cases the $< d^+ f >$-expectation value vanishes for vanishing hybridization $V$, indicating that the spinless Falicov-Kimball model does not allow for a ferroelectric ground state with a spontaneous polarization.

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The Falicov-Kimball model (FKM) has become, since its introduction [1] in 1969, one of the most popular examples of a system of interacting electrons with short-range interactions. It has been used in the literature to study a great variety of many-body effects in metals, of which metal-insulator transitions, mixed-valence phenomena, and charge-density waves are the most common examples [2]. In the last few years the FKM is extensively studied in connection with the exciting idea of electronic ferroelectricity [3, 4, 5, 6, 7]. It is generally supposed that the ferroelectricity in mixed-valent compounds is of purely electronic origin, i.e., it results from an electronic phase transition, in contrast to the conventional displacive ferroelectricity due to a lattice distortion. Since the FKM is probably the simplest model of electronic phase transitions in rare-earth and transition-metal compounds it was natural to start to examine possibilities of electronic ferroelectricity just on this model. An important milestone on this way was the recent work by Portengen at al. [3, 4]. They studied the FKM with a k-dependent hybridization in Hartree-Fock approximation and found, in particular, that the Coulomb interaction $U$ between the itinerant $d$-electrons and the localized $f$-electrons gives rise a non-vanishing excitonic $< d^+ f >$-expectation value even in the limit of vanishing hybridization $V \to 0$. As an applied (optical) electrical field provides for excitations between d- and f-states and thus for a polarization expectation value $P_{df} = < d^+_i f_i >$, the finding of a spontaneous $P_{df}$ (without hybridization or electric field) has been interpreted as evidence for electronic ferroelectricity. This result motivated further theoretical studies of the model. Analytical calculations within well controlled approximation (for $U$ small) performed by Czycholl [3] in infinite dimensions do not confirm the existence of electronic ferroelectricity. In contrast to results obtained by Portengen et al. [3, 4] he found that the FKM in the symmetric case ($E_f = 0, n_f = n_d = 0.5$) does not allow for a ferroelectric ground state with a spontaneous polarization, i.e., there is no non-vanishing $< d^+ f >$-expectation value in the limit of vanishing hybridization. The
same conclusion has been also obtained independently by extrapolation of small-cluster exact-diagonalization calculations in the one dimension for both intermediate and strong interactions [3]. In these regions the finite-size effects are negligible and thus the results can be satisfactory extrapolated to the thermodynamic limit. Very recently Zlatić et. al. [7] analysed the static susceptibility for spontaneous polarization in the ordinary FKM ($V = 0$) using the exact solution of the model in infinite dimensions. They found, in particular, that the spontaneous hybridization susceptibility diverges at $T \to 0$ for $U = 0$ and probably for nonzero $U$ too, indicating a possibility of a nonzero $\langle d^+ f \rangle$-expectation value in the ground state.

In order to shed some light on these controversial results we perform an exhaustive study of the model for a wide range of model parameters. While in our previous paper the possibilities for the electronic ferroelectricity have been studied only in the symmetric case and intermediate and strong interactions [3] we extend here calculations also to the unsymmetric case and small interactions. To suppress the finite-size effects in the weak-coupling limit one has to consider much larger clusters than can be treat numerically within the exact-diagonalization calculations ($L \sim 12$). For this reason we have decided to use in numerical computations the density matrix renormalization group (DMRG) method [8] that allows to treat several times larger clusters and still to keep the high accuracy of computations.

As mentioned above the FKM is based on the coexistence of two different types of electronic states in a given material: localized, highly correlated ionic-like states and extended, uncorrelated, Bloch-like states. It is accepted that insulator-metal transitions result from a change in the occupation numbers of these electronic states, which remain themselves basically unchanged in their character. Taking into account only the intra-atomic Coulomb interaction between the two types of states, the Hamiltonian of the spinless FKM with hybridization can be written as the sum of four terms:
\[
H = \sum_{ij} t_{ij} d_i^+ d_j + U \sum_i f_i^+ f_i d_i^+ d_i + E_f \sum_i f_i^+ f_i + V \sum_i d_i^+ f_i + h.c.,
\]
where \( f_i^+ \), \( f_i \) are the creation and annihilation operators for an electron in the localized state at lattice site \( i \) with binding energy \( E_f \) and \( d_i^+ \), \( d_i \) are the creation and annihilation operators of the itinerant spinless electrons in the \( d \)-band Wannier state at site \( i \).

The first term of (1) is the kinetic energy corresponding to quantum-mechanical hopping of the itinerant \( d \) electrons between sites \( i \) and \( j \). These intersite hopping transitions are described by the matrix elements \( t_{ij} \), which are \(-t\) if \( i \) and \( j \) are the nearest neighbors and zero otherwise (in the following all parameters are measured in units of \( t \)). The second term represents the on-site Coulomb interaction between the \( d \)-band electrons with density \( n_d = 1 \sum_i d_i^+ d_i \) and the localized \( f \) electrons with density \( n_f = 1 \sum_i f_i^+ f_i \), where \( L \) is the number of lattice sites. The third term stands for the localized \( f \) electrons whose sharp energy level is \( E_f \). The last term represents the hybridization between the itinerant and localized states.

In order to test the convergence of the DMRG method for the FKM with hybridization let us first consider the case \( U = 0 \) \((E_f = 0) \). In this case the Hamiltonian (1) can be diagonalized exactly yielding the following expressions for the ground-state energy and the \( P_{df} \) expectation value

\[
E_g = \frac{1}{2L} \sum_k (\epsilon_k - (\epsilon_k^2 + 4V^2)^{1/2}),
\]
\[
P_{df} = -\frac{V}{L} \sum_k \frac{1}{(\epsilon_k^2 + 4V^2)^{1/2}},
\]
where \( \epsilon_k = \frac{1}{L} \sum_{ij} t_{ij} e^{ik(R_i - R_j)} \). These expressions are valid for arbitrary \( L \) and thus they can be used directly for comparison with DMRG results obtained on finite clusters. Such a comparison shows that the DMRG results reproduce the exact
results with high accuracy ($\sim 10^{-5}$) even if a relatively small number of states is kept ($m = 128$), thereby the clusters up to 100 sites become accessible for numerical studies. This is illustrated in Fig. 1a where the difference $\Delta E = E^\text{exact}_g - E^\text{DMRG}_g$ is plotted as a function of $L$ for $m = 128$ and two values of $V$. It is seen that the difference $\Delta E$ is smaller than $10^{-5}$ for all clusters of size $L \leq 100$. One can expect that the finite-size effects will be considerably reduced for such cluster sizes and thus the DMRG results could be satisfactory extrapolated to the thermodynamic limit also for weak interactions. Numerical results obtained for the ground-state energy $E_g$ (Fig. 1b) and the $P_{df}$ expectation value (Fig. 2a) fully confirm this conjecture.

It is seen that the finite-size effects are small for both $E_g$ and $P_{df}$ and so the most important feature, and namely the behavior of $P_{df}$ for $V \to 0$ can be reliably deduced from these results. In all cases the $\langle d^+ f \rangle$-expectation value vanishes in the limit $V \to 0$, so there is no spontaneous polarization in the one-dimensional spinless FKM with nearest-neighbor hopping $\hbar \omega$ for $U = 0$. Using the expression (3) one can show immediately that the same behavior holds in any dimension. In Fig. 2b we have displayed numerical results for $P_{df}$ obtained in the thermodynamic limit for $d = 1, 2$ and $d = \infty$ (Bethe lattice). In all cases $P_{df}$ vanishes continuously for $V \to 0$, which seems to contradict recent results obtained by Zlatić et. al. [7] for the ordinary FKM ($V = 0$) in infinite dimensions. Indeed, a comparison of our $d = \infty$ results for the $\langle d^+ f \rangle$-expectation value with $d = \infty$ results obtained by Zlatić et. al. [7] for the spontaneous hybridization susceptibility $\chi_{hyb}$ leads to very interesting observation.

While the hybridization susceptibility $\chi_{hyb}$ diverges for $V = 0$, the $P_{df}$ expectation value goes to zero in the limit of vanishing $V$. This can be shown also analytically using the explicit expression (Eq. 3) for the $P_{df}$ expectation value. Replacing the summation in Eq. 3 by integration over the energy and taking the constant density of states, for simplicity, one can easily show that the $P_{df}$ expectation value (in the limit of vanishing $V$) behaves like $V \ln V$. Thus $P_{df}$ vanishes at $V = 0$, although $\chi_{hyb}$
diverges at this point. This shows that one has to be very careful in doing conclusions about the $P_{df}$ behavior from the spontaneous hybridization susceptibility.

The same behavior of the model we expect also for nonzero $U$. To verify this we perform an exhaustive study of the model for a wide range of the model parameters. In addition to the half-filled band case $n = 1$ we examine here in detail also the case $n = 0.5$, $E_f < 0$, where Zlatić et. al. [7] found a numerical evidence for a spontaneous polarization (the divergence of the spontaneous hybridization susceptibility).

Let us first discuss the DMRG results obtained for $P_{df}$ in the half-filled band case and small but finite $U$. This case was not discussed in our previous paper [6] since small-cluster exact-diagonalization calculations were not able to give reliable answers due to large finite-size effects in this region. As mentioned above within the DMRG method much large clusters can be treated numerically, thereby the finite-size effects are considerably reduced. The weak-coupling numerical results for $P_{df}$ are displayed in Fig. 3 for $U = 0.5$ and several values of $E_f$. Obviously the one-dimensional FKM does not exhibit a ferroelectric ground state with a spontaneous polarization in the weak-coupling limit. For all examined values of $E_f$ the $< d^+ f >$-expectation value vanishes for $V \to 0$, and it is demonstrated that this result is independent of $L$.

The same calculations are performed also for $n = 0.5$ and $E_f < 0$. Since the numerical results obtained by Zlatić et. al. [7] show on the possibility of a spontaneous polarization in this region a very detailed analysis of the model is done in this parameter space for both weak and strong interactions. The typical behaviors obtained by numerical simulations are presented in Fig. 4. Again there is no spontaneous polarization, neither for weak nor for strong interactions. In all cases $P_{df} \to 0$ for $V \to 0$. The finite-size effects are small for both weak and strong interactions and thus these results can be satisfactory extrapolated to the thermodynamic limit.

Thus we can summarize our results. The numerical studies of the spinless FKM by density matrix renormalization group method did not confirm a possibility of
a ferroelectric ground state with a spontaneous polarization in this model. In all examined cases (weak and strong interactions, the symmetric and unsymmetric case) the $P_{df}$ expectation value vanishes for $V \to 0$, in contrast to what is expected from the behavior of the spontaneous hybridization susceptibility [7]. This fact considerably reduces (although does not exclude definitively) the possibility for the existence of a ferroelectric ground state with a spontaneous polarization in the spinless FKM.

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References

[1] L.M. Falicov and J.C. Kimball, Phys. Rev. Lett. 22, 997 (1969).

[2] D.L. Khomskii, Quantum Theory of Solids, edited by I.M. Lifshitz (Mir, Moscow 1982).

[3] T. Portengen, T. Östreich, L.J. Sham, Phys. Rev. Lett. 76, 3384 (1996).

[4] T. Portengen, T. Östreich, L.J. Sham, Phys. Rev. B 54, 17452 (1996)

[5] G. Czycholl, Phys. Rev. B 59, 2642 (1999)

[6] P. Farkašovský, Phys. Rev. B 59, 9707 (1999).

[7] V. Zlatić, J.K. Freericks, R. Lemanski, G. Czycholl, cond-mat/0107040.

[8] S.R. White, Phys. Rev. Lett. 69, 2863 (1992); Phys. Rev. B 48, 10345 (1993).

[9] Note that $P_{df}$ can be finite for some special (unfortunately, physically not very interesting) types of hopping. For example, $P_{df}(V = 0)$ is finite in the atomic limit $t_{ij} = 0$ ($\epsilon_k = 0$) as well as in the case of unconstrained hopping $t_{ij} = -t$, for all $i,j$ ($\epsilon_k = -tL\delta_{k,0}$).
Figure Caption

Fig. 1. (a) The difference $\Delta E = E_{g}^{exact} - E_{g}^{DMRG}$ as a function of $L$ calculated for $U = 0$, $m = 128$ and two different values of $V$. (b) The ground-state energy as a function of hybridization for $U = 0$ and $m = 128$. Numerical curves corresponding to $L = 12, 24$ and 48 are calculated by DMRG method, while the exact analytical solution in the thermodynamic limit $L = \infty$ is obtained from Eq. 2.

Fig. 2. (a) Hybridization dependence of the $\langle d^+ f \rangle$-expectation value calculated for finite clusters (DMRG results) and in the thermodynamic limit (from Eq. 3) for $U = 0$. (b) Hybridization dependence of the $\langle d^+ f \rangle$-expectation value calculated in the thermodynamic limit (from Eq. 3) for $d = 1, 2$ and $d = \infty$.

Fig. 3. Hybridization dependence of the $\langle d^+ f \rangle$-expectation value calculated for $U = 0.5$ and several values of $E_f$ (DMRG results) at half-filling ($n = 1$). To reveal the finite-size effects the calculations have been performed for several finite clusters.

Fig. 4. Hybridization dependence of the $\langle d^+ f \rangle$-expectation value calculated for $U = 0.5$ (a) and $U = 5$ (b) and several values of $E_f$ (DMRG results) at quarter-filling ($n = 1/2$).
Hybridization $V$

(a) $L=12$
- $L=24$
- $L=48$
- $L=\infty$

(b) $d=1$
- $d=2$
- $d=\infty$

$\langle d^f \rangle$ expectation value
Hybridization V

\[ E_f = -2 \]
\[ E_f = 0 \]
\[ E_f = -0.8 \]

<\text{d}f^\dagger> - expectation value

Hybridization V

- L=16
- L=24
- L=32
Hybridization $V$ - expectation value

- $E_f = 0$
- $E_f = -0.4$
- $E_f = -0.8$

$L = 16$
$L = 24$
$L = 32$