Fractionally Charged Polarons and Phase Separation in an Extended Falicov-Kimball Model

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We present the first numerical study of the Falicov-Kimball model extended by an on-site hybridization away from the particle-hole symmetry point. Stable polaronic distortions of the charge-density wave (CDW) phase are observed when doping with a single hole. For moderate hole-doping, we find phase separation between a hole-rich homogeneous state and the usual CDW state. Excitonic order is enhanced around the hole-rich region, locally manifesting the global competition between this and the CDW phase. Associated with the hole-doping is a fractionalization of the electron density between the itinerant and localized electrons. The calculated local density of states at the polaron centre reveals this fractionalization to be the result of charge fluctuations induced by the hybridization. We propose a scanning tunneling microscope experiment to test our results.

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The Falicov-Kimball model (FKM) has found use far beyond its original role as a minimal model for valence transitions 1. The FKM describes itinerant d-electrons interacting via a repulsive contact potential U with localized f-electrons of energy ϵf; this simple physical picture is a useful starting point for more complex models of mixed-valence (MV) phenomenon 2, heavy fermions 3, electronic ferroelectricity 4, 5, 6 and unconventional superconductivity 7. The “bare” form of the FKM has also attracted much interest: it exhibits a charge density wave (CDW) instability at half-filling in any dimension D and is considered a basic model of binary alloys 8.

Apart from the extreme limits D = 1 9 and D → ∞ 10, very little is known about the FKM away from half-filling. The numerical results of Lemański et al. suggest a rich 2D phase diagram, with phase separated coexistence of many different orderings 11: it would clearly be very interesting to assess the stability of these states within the context of a more realistic model. The effect of dilute hole doping on the CDW is also of interest: in related models displaying density-wave instabilities (e.g. the Hubbard model) hole-doping away from perfect nesting produces polarons 12. Yin et al. have studied polarons in the strong-coupling FKM with a weak f-electron hopping term, obtaining non-trivial modifications of the usual t-J model results 13. Of greater relevance, Liu and Ho have proposed that polarons form in a FKM with hybridization, as a precursor to a valence transition between states with integral and fractional occupation of the f-orbitals 14.

In this Letter we extend our previous study of the FKM with d-f hybridization away from the particle-hole symmetry point 15. We perform a Hartree-Fock (HF) decoupling of the interaction and exactly diagonalize the resulting real-space Bogoliubov-de Gennes (BdG) eigenequations. We work exclusively in the limit of zero temperature where the HF approach is known to be most accurate. Doping with a single hole produces a local polaronic distortion of the CDW phase. Unique to our model, we find a fractional partitioning of the electron density between the two orbitals localized at the doped hole; this is revealed by the local density of states (LDOS) spectra at the polaron centre. We discuss the origin of the fractionalization and a proposed experimental approach to observing this novel electronic state. For a moderate hole-doping, we find that phase separation between a hole-rich homogeneous phase and the usual half-filled CDW phase is the ground state. The global competition between these phases is manifested as a local enhancement of excitonic ordering.

We consider an extended FKM for spinless fermions:

\[ \mathcal{H} = - \sum_{i,j} t_{ij} d^\dagger_i d_j - \sum_{i,j} t^\prime_{ij} f^\dagger_i f_j + \epsilon_f \sum_j n^f_j + V \sum_j \left\{ d^\dagger_i f_j + \text{H.c.} \right\} + U \sum_j n^f_j n^d_j. \]  

(1)

In addition to the usual FKM terms, we include a hopping \( t^\prime_{ij} \) for the f-electrons and an on-site hybridization \( V \) between the d- and f-orbitals 14. Here we concentrate on the case \( V \neq 0 \) and \( t^\prime_{ij} = 0 \); we consider also a finite \( t^\prime_{ij} \) with \( V = 0 \) for comparison with previous work 15, 16. The hopping integrals \( t_{ij} \) and \( t^\prime_{ij} \) are, respectively, t and \( t^\prime \) for nearest neighbours, vanishing otherwise.

We perform the standard HF decomposition 2 of the Coulomb repulsion term: \( n^f_j n^d_j = \langle n^f_j \rangle n^d_j + \langle n^d_j \rangle n^f_j - \Delta_j d^\dagger_j f_j - \Delta^*_j f^\dagger_j d_j \). Here \( \Delta_j = \langle f^\dagger_j d_j \rangle \) is the excitonic average at site \( j \). In the absence of a hybridization potential \( V \), \( \Delta_j \neq 0 \) indicates the excitonic insulator phase 15; Portengen et al. interpreted such a “spontaneous” excitonic average as evidence of electronic ferroelectricity 4. The resulting HF Hamiltonian is diagonalized by the canonical transform, \( \gamma_n = \sum_j (u^2_n d_j + v^2_n f_j) \). The quasiparticle wavefunction amplitudes, \( u^2_n \) and \( v^2_n \), are derived.
by solving the associated BdG eigenequations:

$$\sum_j \left( \mathcal{H}_{ij}^{dd} H_{ij}^{df} H_{ij}^{ff} \right) \left( \begin{array}{c} u_j^n \\ v_j^n \end{array} \right) = E_n \left( \begin{array}{c} u_j^n \\ v_j^n \end{array} \right),$$

(2)

where the components of the Hamiltonian matrix are defined as $\mathcal{H}_{ij}^{dd} = -t_{ij} + U(n_j^f)\delta_{ij}$, $H_{ij}^{df} = -t_{ij} + (\epsilon_f + U(n_j^d))\delta_{ij}$ and $H_{ij}^{ff} = (V - U\Delta_j)\delta_{ij}$. In terms of the diagonal basis the order parameters at site $j$ are given by $\langle n_j^f \rangle = \sum_{n=1}^{N_{tot}} |u_j^n|^2$, $\langle n_j^d \rangle = \sum_{n=1}^{N_{tot}} |v_j^n|^2$ and $\Delta_j = \sum_{n=1}^{N_{tot}} v_j^n u_j^n$. We also define the $d$- and $f$-electron CDW order parameters $\delta_j^d = (-1)^j(\langle n_j^d \rangle - \frac{1}{2})$ and $\delta_j^f = (-1)^j(\langle n_j^f \rangle - \frac{1}{2})$. Note that in the CDW phase $\text{sgn}(\delta_j^d) = -\text{sgn}(\delta_j^f)$. Our calculations are performed in the canonical ensemble at zero temperature and thus the sum over $n$ extends over the first $N_{tot}$ occupied quasiparticle states.

We solve the BdG eigenequations self-consistently using a numerical iteration scheme. Commencing with an initializing set of order parameters, we exactly diagonalize Eq. (2) and hence compute new order parameters using the obtained quasiparticle wavefunctions. These values are then used as an input for the next iteration; this procedure is repeated until a desired accuracy is reached. The calculations are performed for a $N = 24 \times 24$ lattice with periodic boundary conditions. To calculate the quasiparticle LDOS we use the converged $24 \times 24$ lattice as a supercell in a $10 \times 10$ array. The $d$-electron hopping integral $t$ defines our energy scale. The results presented below correspond to $\epsilon_f = 0$ and $U = 2.0$; for the case of a single hole we take $V = 0.1$ ($t_f = -0.1$), while $V = 0.2$ ($t_f = -0.2$) for the case of moderate hole-doping.

Limit of a single hole: We dope a single hole into the CDW state by computing the order parameters for $N_{tot} = N - 1$ (note $N_{tot} = N$ corresponds to half filling); the converged results are presented in Fig. 1. The hole appears as a localized vacancy in the occupied $f$-electron sub-lattice [see Fig. 1(a)]. This defect in the periodic HF potential $U(n_j^f)$ experienced by the $d$-electrons produces a distortion of the $d$-electron CDW state which extends over several lattice constants [Fig. 1(b,c)], defining the spatial extent of a polaron. Near the polaron, the excitonic average $\Delta_j$ [Fig. 1(d)] shows a Friedel-like oscillation with its tails extending along the diagonals. The enhancement of $|\Delta_j|$ about the $f$-hole indicates that the polaron in the FKM is a local manifestation of the competition between the global excitonic ordering and CDW states.

Away from the polaron $\delta_j^f$ is uniform to within the accuracy of the convergence, indicating the expected single $d$-electron per unit cell in the CDW bulk. Overall, however, we find a total $d$-electron population $N_d = 288.1084$, as against the case of $N_{d0} = 288$ $d$-electrons in the usual half-filled CDW state. A “fraction” $\Delta N_d = N_d - N_{d0} = 0.1084$ of a $d$-electron is associated with the polaron. Correspondingly, the total $f$-electron population $N_f = 286.8916$ such that $\Delta N_f = N_f - N_{f0} = -1.1084$, showing the transfer of charge from the $f$- to the $d$-orbitals. Although the formation of a polaron about the $f$-hole is indicated by Liu and Ho’s work [9], their method did not allow them to observe the fractionalization. Our result also differs from the homogeneous distribution of fractional charge in the traditional MV state [2]; we find the fractional charge localized at the polaron.

This fractional charge arises from the mixing of the orbital wavefunctions by the hybridization. As a result of this mixing, the number of $d$- and $f$-electrons are not separately conserved. (Note that the total number of electrons, $\hat{N} = \hat{N}_d + \hat{N}_f$, remains constant.) The hybridization allows electrons in the $d$-orbitals to tunnel into the $f$-orbitals and $\text{vice versa}$; this implies charge fluctuations between the two orbitals leading to the observed fractional populations. Although true also in the half-filled CDW state, it is only with the introduction of the inhomogeneities by hole-doping (i.e. the polarons) that the fractional charge can be directly observed. Fractionally charged polarons are therefore unique to multi-orbital models such as the FKM considered here; there is no analogous effect in single-orbital systems.

We find that the fractional $d$-electron $\Delta N_d$ (or $f$-electron $\Delta N_f$) is strongly dependent upon $U$ and $V$: $\Delta N_d$ increases with both these parameters, although it decreases as $V$ is raised above the critical value that destabilizes the global CDW phase. According to our HF decomposition the excitonic average enters into the equations as an effective hybridization potential $-U\Delta_j$. In the CDW state, however, this is only non-zero in the presence of a finite on-site hybridization [12]. As the magnitude of $\Delta_j$ is directly proportional to both $U$ and $V$, the observed behaviour of $\Delta N_d$ is easily understood.

FIG. 1: (color online) The variation of the $f$-electron density (a), the $d$-electron density (b), the $d$-electron CDW order parameter (c), and the excitonic order parameter (d) in the vicinity of a single hole.
The fractionalization can be explicitly visualized by computing the LDOS both at the polaron site and in the CDW bulk. From our converged solutions for the computing the LDOS both at the polaron site and in time broadening characterized by the parameter $\alpha$ our plots of the LDOS spectra we always take the off-diagonal terms $\mathcal{H}^{df}_{ij}$ Eq. 2 produce quasiparticles with mixed nature, as evidenced by the coincidence of the peaks in the $d$- and $f$-electron spectra. The effect of the hybridization on the waves can be clearly appreciated in Fig. 2(a).

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Using Eq. 3 we calculate the variation of $\rho_i^f(\omega)$ across the lattice for $\omega = -0.131$ and $\omega = 0.168$. In (c) and (d) we plot the $f$-electron DOS $\rho_i^f(\omega)$ for the energies corresponding to (a) and (b).

Finite hole doping. To study the effects of moderate hole-doping, we solve the BdG eigenequations for $N_{tot} = N - 10$. The results for $V = 0$ suggest a large variety of possible charge-orderings [11]; to find the ground state we therefore consider a number of different initial order parameter sets. These sets range from vertical and diagonal stripe orderings to a random distribution of quasiparticle weight across the lattice. Since we work in the zero temperature limit, we test the relative stability of the converged results by calculating the total energy $E = \sum_n E_n - U \sum_j (|n_j^d|^2 - |\Delta_j|^2)$. We present the variations of $\delta_j^d$ for a representative sample of these initializations in Fig. 4(a-d); these figures are labelled with decreasing energy from $E/N = -1.5554$ for Fig. 4(a) to $E/N = -1.5586$ for Fig. 4(d). Fig. 4(e) gives the varia-
Our observation of clustering again confirms the relevance of the V in the f-hole results, we find enhancement of the excitonic order parameter $|\Delta_f|$ mainly at the boundary of the f-hole cluster [Fig. 4(e)]. This again locally evidences the competition between the excitonic and CDW orders.

In conclusion, we have investigated the FKM extended by the d-f hybridization away from the half-filling symmetry point. Throughout this report, we have compared and contrasted our results with the extended FKM proposed in [5]. We have studied the formation of polarons when a single hole is doped into the CDW state. Associated with the polaron, we have discovered a fractional partitioning of the electron density between the excitonic and CDW states is energetically favorable. In both doping limits, enhancement of the excitonic ordering is found around the hole-rich region, locally manifesting the global competition between the two phases [13].

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