

Intermediate Coupling Theory of Electronic Ferroelectricity

C. D. Batista,¹ J. E. Gubernatis,¹ J. Bonča,² and H. Q. Lin³

¹Center for Nonlinear Studies and Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

²Department of Physics, FMF, University of Ljubljana and J. Stefan Institute, Ljubljana, Slovenia

³Department of Physics, The Chinese University of Hong Kong, Hong Kong, China

(Received 4 August 2003; published 6 May 2004)

We calculate the quantum phase diagram of an extended Falicov-Kimball model for one- and two-dimensional systems in the intermediate coupling regime. Even though some features of the phase diagram are obtained analytically, the main results are calculated with a constrained path Monte Carlo technique. We find that this regime is dominated by a Bose-Einstein condensation of excitons with a built-in electric polarization. The inclusion of a finite hybridization between the bands removes the condensate but reinforces the ferroelectricity.

DOI: 10.1103/PhysRevLett.92.187601

PACS numbers: 77.80.-e, 71.27.+a, 71.28.+d

In a recent Letter [1], one of us demonstrated that a novel ferroelectric state, originally proposed by Portengen *et al.* [2], is present in the strong-coupling and mixed-valence regime of an extended Falicov-Kimball model (FKM) [3]. In contrast to the traditional ferroelectric (FE) transitions, which are a subgroup of the structural phase transitions, the new FE state is caused by a purely electronic mechanism of an essential *quantum* nature. Its electronic origin and the strong interplay between the orbital and the spin flavors of the electronic degrees of freedom make this novel state suitable for new technological applications. For example, it opens the possibilities of faster switching ferroelectrics and controlling their optical properties with magnetic fields. Accordingly, it is important to define more clearly the conditions for the experimental observation of this novel state.

Our extended FKM model consists of two dispersive bands plus an interband local Coulomb interaction. In the absence of interband hybridization, the half-filled model exhibits a FE state that is a Bose-Einstein (BE) condensate of excitons. The electric polarization is the result of a spontaneous phase-coherent hybridization between the two local orbitals with opposite parity under inversion. The FE moment is proportional to the real part of the $U(1)$ order parameter of the condensate. These conclusions were based on a strong-coupling treatment of the model. An accompanying perturbative analysis suggested that, if hybridization between the bands were included, the BE condensate (BEC) would be replaced by a distinguishing Ising-like FE state [1].

To resolve this point, we will now step way beyond the original work by moving away from the strong-coupling limit and from the perturbative treatment of the hybridization and focus on the intermediate coupling regime. We find that ferroelectricity remains robust. In particular, it possesses the same phases as the strong and weak coupling regimes, even though the nature of the condensate changes continuously from BCS-like in the weak coupling limit to a BEC of hard-core bosons in the strong coupling regime [4]. We will in fact report the complete

one- (1D) and two-dimensional (2D) quantum phase diagrams of the extended FKM in the intermediate coupling regime. The results are obtained from a scaling analysis of the numerical data produced with the constrained path Monte Carlo (CPMC) technique [5]. When we include a finite hybridization between the bands, we find as predicted by the perturbation analysis a very large FE (or antiferroelectric) region for the mixed-valence regime which is no longer a BEC of excitons but an Ising-like state with a spontaneously broken inversion symmetry.

There are two recent experiments to which our results might apply. Moro *et al.* observed a FE state in free Nb clusters [6]. The experiment shows that cold clusters may attain an anomalous component with very large electric dipole moments. It is clear that in pure Nb the FE moment cannot be produced by a lattice distortion. Therefore, the ferroelectricity must have an *electronic origin*. In addition, *ab initio* calculations [7] in pure Nb indicate that the valence electron has the same amount of *s* and *p* character. This observation makes the present theory a candidate to explain the FE state of the free Nb clusters.

Another relevant experiment is the phase-coherent state observed by Spielman *et al.* [8]. The two bands are provided by two parallel 2D electron systems interacting through an interlayer Coulomb interaction. There is also an applied magnetic field whose value is such that the Landau level filling factor of each layer is $1/2$. From the results obtained in Ref. [1] and the theory that we include below, we will propose an experiment to observe electronic ferroelectricity in these bilayer systems.

Our extended FKM for spinless fermions on a D -dimensional hypercubic lattice is

$$H = \sum_{\mathbf{i}, \nu} \epsilon_{\nu} n_{\mathbf{i}}^{\nu} + \sum_{\mathbf{i}, \eta, \nu, \nu'} t_{\nu\nu'} (f_{\mathbf{i}\nu}^{\dagger} f_{\mathbf{i}+\hat{\mathbf{e}}_{\eta}\nu'} + f_{\mathbf{i}+\hat{\mathbf{e}}_{\eta}\nu'}^{\dagger} f_{\mathbf{i}\nu}) + U^{ab} \sum_{\mathbf{i}} (n_{\mathbf{i}}^a - 1/2)(n_{\mathbf{i}}^b - 1/2), \quad (1)$$

where $\nu = \{a, b\}$ is the orbital index, $\hat{\mathbf{e}}_{\eta}$ is a vector in the

η direction ($\eta = \{x_1, x_2, \dots, x_D\}$), and $n_i^\nu = f_{i\nu}^\dagger f_{i\nu}$ is the occupation number of each orbital. Note that $t_{ab} = -t_{ba}$ because the two orbitals have opposite parity under spatial inversion.

This Hamiltonian can be rewritten as an asymmetric Hubbard model if the orbital flavor is represented by a pseudospin variable [1]: $c_{i\uparrow}^\dagger = f_{ia}^\dagger$, $c_{i\uparrow} = f_{ia}$, $c_{i\downarrow}^\dagger = f_{ib}^\dagger$, and $c_{i\downarrow} = f_{ib}$. The pseudospin components are given by $\tau_i^\alpha = \frac{1}{2} \sum_{\nu, \nu'} f_{i\nu}^\dagger \sigma^{\nu\nu'} f_{i\nu'}$, with $\alpha = \{x, y, z\}$. The new expression for H is an asymmetric Hubbard model with a Zeeman term:

$$H = e_d \sum_{i,\sigma} n_{i\sigma} + \sum_{\langle i,j \rangle, \sigma, \sigma'} t_{\sigma\sigma'} (c_{i\sigma}^\dagger c_{j\sigma'} + c_{j\sigma'}^\dagger c_{i\sigma}) + U^{ab} \sum_i n_{i\uparrow} n_{i\downarrow} + B_z \sum_i \tau_i^z, \quad (2)$$

where $e_d = \frac{1}{2}(\epsilon_a + \epsilon_b)$, $t_{\uparrow\uparrow} = t_{aa}$, $t_{\downarrow\downarrow} = t_{bb}$, $t_{\uparrow\downarrow} = t_{ab}$, $t_{\downarrow\uparrow} = t_{ba}$, and $B_z = \epsilon_a - \epsilon_b$. If there is no hybridization between the bands, there is a remaining $U(1)$ symmetry generated by the total magnetization along the z axis $M^z = \sum_i \tau_i^z$. In the original language, this $U(1)$ symmetry corresponds to the conservation of the difference between the total number of particles in each band.

We will consider from now on only the half-filled case, i.e., one particle per site. The ground state of H exhibits two possible magnetic orderings in the strong-coupling limit: Ising-like antiferromagnetism and xy -like ferromagnetism (antiferromagnetism) for $\gamma = -t_{\uparrow\downarrow}/t_{\uparrow\uparrow} > 0$ ($\gamma < 0$) [1]. In terms of the original variables, the Ising-like phase corresponds to staggered orbital ordering (SOO), and for $D \geq 2$ the xy -like ferromagnetism corresponds to a BEC of excitons with a built-in electric polarization [2]:

$$\mathbf{P} = \frac{\boldsymbol{\mu}}{\Omega} \sum_i (f_{ia}^\dagger f_{ib} + f_{ia} f_{ib}^\dagger) = \frac{2\boldsymbol{\mu}}{\Omega} M^x, \quad (3)$$

where $\boldsymbol{\mu}$ is the interband dipole matrix element and Ω is the volume of the system. The electrical polarization is then proportional to the real part of the $U(1)$ order parameter of the BEC.

An additional particle-hole transformation on one of the spin flavors maps Eq. (2) into a negative U asymmetric Hubbard model with the Zeeman term replaced by a chemical potential. Under this transformation, the xy -like ferromagnetism is mapped into a superconducting state. This establishes a formal connection between the BEC of excitons and a superconductor. The BEC of electron-hole pairs in the weak coupling regime is mapped into a BCS-like superconductor.

One-dimensional case.—From now on, we will set $\gamma > 0$ and $t_{\uparrow\uparrow}$ as the unit of energy. We start by considering the simplest case of zero hybridization between the bands: $t_{\uparrow\downarrow} = t_{\downarrow\uparrow} = 0$. In Fig. 1, we present the 1D quantum phase diagram of H as a function of γ and B_z . Most of the phase diagram was calculated with the unbiased CPMC technique [5]. The diagram shows the same three phases which were obtained in the strong-coupling limit [1].

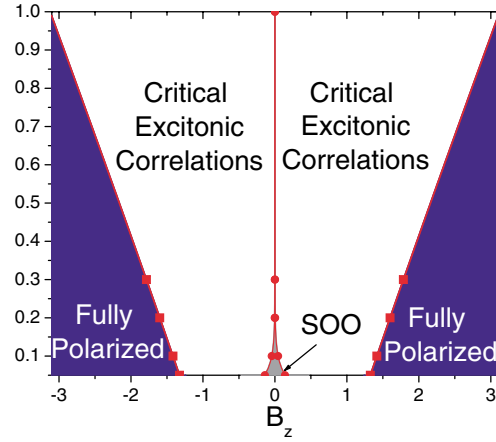


FIG. 1 (color online). One-dimensional quantum phase diagram of the extended FKM $U^{ab} = 1$ ($t_{\uparrow\downarrow} = t_{\downarrow\uparrow} = 0$) [9]. The circles are the calculated points for B_z^{c1} and the full line is an exponential fit. The error bars are smaller than the symbol sizes. The squares are numerical results for B_z^{c2} and the full line is the analytical calculation.

For $B_z = 0$, the ground state is an Ising-like antiferromagnet (SOO). At a critical value of $|B_z| = B_z^{c1}$, there is a transition from the orbitally ordered gapped phase to a critical (gapless) phase with dominating pseudospin-pseudospin correlations in the xy plane. This second phase is also characterized by a nonzero uniform magnetization along the z axis. When $|B_z|$ reaches a second critical value, B_z^{c2} , M^z saturates and a new gap opens. In terms of our original language, this is the transition from a mixed-valence to nonmixed valence regime in which one band is full and the other one is empty. This is also a transition from an excitonic to a band insulator.

The value of B_z^{c2} is exactly obtained by solving the one particle problem of flipping one pseudospin in a fully saturated system. To show that this value is not altered by a discontinuous change of the magnetization, we also include the numerical calculation of B_z^{c2} based on the computation of $E_m(M^z, B^z = 0)$, minimum energy for the subspace with a given magnetization M^z . Note that this can be done because M^z is a good quantum number of $H(t_{\uparrow\downarrow} = t_{\downarrow\uparrow} = 0)$. B_z^{c1} is the critical value of B^z which is required to change the total magnetization M^z of the ground state, i.e., it is the minimum value of $[E_m(M^z, B^z = 0) - E_{\text{GS}}(B^z = 0)]/M^z$, where E_{GS} is the ground state energy. To calculate B_z^{c1} in the thermodynamic limit, we scaled this minimum value for different chain sizes up to $N_s = 100$ (N_s is the number of sites). A typical scaling is shown in Fig. 2(a) for two different values of γ . The finite extrapolated value of B_z^{c1} implies a finite gap Δ_f for the Ising-like (SOO) phase. The case $\gamma = 1$ corresponds to the $SU(2)$ critical point for which the pseudospin correlations along the three different axis are the same. For the strong-coupling limit [1], it is known that the gap of the Ising-like (SOO) phase closes exponentially (Kosterlitz-Thouless transition) when γ gets close to 1 (see Fig. 1).

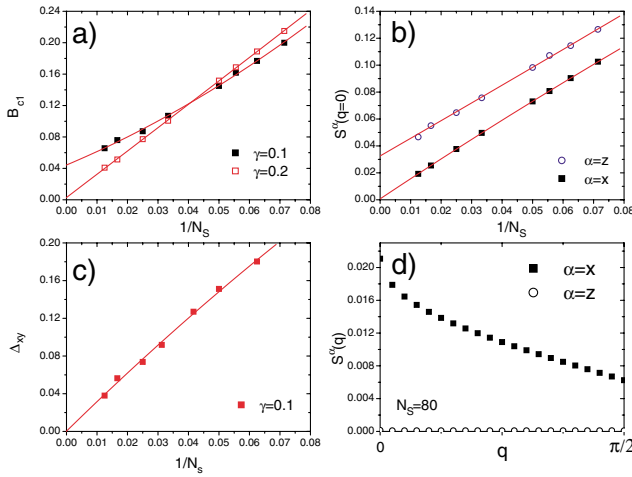


FIG. 2 (color online). $U = 1$; $t_{\parallel} = t_{\perp} = 0$. (a) Scaling of B_z^{c1} calculated with the CPMC method in chains of length N_s . (b) Scaling of $S^x(0)$ and $S^z(\pi)$ for $B_z = 0$ and $\gamma = 0.1$. As expected, $S^z(\pi)$ has a finite value in the thermodynamic limit indicating that the ground state has long-range staggered orbital ordering. (c) Scaling of the energy gap Δ_{xy} for $M^z/N_s = 1/4$. The scaling function is a second order polynomial expression in $1/N_s$. (d) Pseudospin-pseudospin correlation function for $M^z/N_s = 1/4$.

The different phases were identified by computing the pseudospin-pseudospin correlation function:

$$S^\alpha(\mathbf{q}) = \frac{1}{N_s^2} \sum_{i,j} (\tau_i^\alpha \tau_j^\alpha - \langle \tau_i^\alpha \rangle \langle \tau_j^\alpha \rangle) e^{iq \cdot (\mathbf{r}_i - \mathbf{r}_j)}. \quad (4)$$

In Fig. 2(b), we show the scaling of $S^x(0)$ and $S^z(\pi)$ calculated with the CPMC for $B_z = 0$ and $\gamma = 0.1$. As expected, $S^z(\pi)$ has a finite value in the thermodynamic limit indicating that the ground state has long-range staggered orbital ordering.

In Fig. 2(c), we show the scaling of the energy gap of the xy -like phase, Δ_{xy} , for $M^z/N_s = 1/4$. Δ_{xy} scales to zero in the thermodynamic limit as expected from the critical nature of this phase. Figure 2(d) shows that the pseudospin-pseudospin correlation function [see Eq. (4)] in the x (or y) direction is much larger than the corresponding correlation along the z axis. This shows the xy -like nature of this phase.

Two-dimensional case.—The main qualitative difference between the 1D (Fig. 1) and the 2D (Fig. 3) quantum phase diagrams of $H(t_{\parallel} = t_{\perp} = 0)$ is that the excitonic condensate is critical in one dimension, as required by the Mermin-Wagner theorem [11], and has long-range order in two dimensions. In the pseudospin language, this means that the 2D system has a finite in-plane magnetization \mathbf{M}^\perp (see Fig. 4). In addition, Eq. (3) shows that this state has built-in electric polarization proportional to the x component of \mathbf{M}^\perp or the real part of the complex order parameter of the excitonic condensate [1].

As in the 1D case, $B_z^{c2}(\gamma)$ was computed exactly, and the transition from the SOO to the ferroelectric BEC of excitons is simultaneously a first order valence transition because the relative population between the two bands, M^z , changes discontinuously. Note that, in the intermediate coupling regime, the extension of the ferroelectric

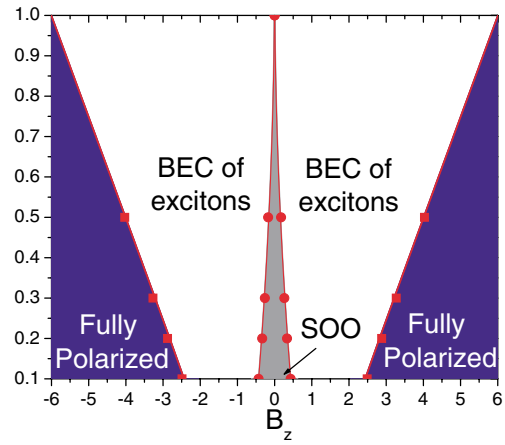


FIG. 3 (color online). Two-dimensional phase diagram of the extended FKM for $U = 2$ ($t_{\parallel} = t_{\perp} = 0$). The circles are the calculated points for B_z^{c1} and the full line is a guide to the eye. The error bars are smaller than the symbol sizes. The squares are numerical results for B_z^{c2} and the full line is the analytical calculation.

phase for γ not very close to zero is of the order of the bandwidth, while in the strong-coupling regime the size of this region is proportional to $t_{aa}t_{bb}/U^{ab}$.

We conjecture that the three-dimensional (3D) quantum phase diagram of H should be similar to the 2D one since the quantum fluctuations are smaller in the first case. Moreover, we expect the quantum phase diagram to have the same topology for the weak and intermediate coupling regimes in any dimension $D \geq 2$. The main expected difference between $D = 2$ and $D = 3$ occurs at finite temperatures due to the Mermin-Wagner theorem [11]. The transition temperature associated to the BE condensation is finite only for the 3D case. The BEC of electron-hole pairs undergoes a Kosterlitz-Thouless phase transition in a 2D system.

From Eq. (3), we see that the electric polarization is the consequence of a spontaneous phase-coherent hybridization between the two bands. The $U(1)$ phase must have a real component in order to produce a finite electric polarization. We can ask the physical consequence of a pure imaginary phase $\phi = \pm\pi/2$ ($\tan\phi = M^x/M^y$), i.e., the planar magnetization pointing in the y direction. In this case, instead of ferroelectricity, the phase-coherent state contains an ordering of atomic currents. Since the two atomic orbitals have opposite parity, these currents do not produce a net local magnetic dipole, but they can have a net quadrupolar magnetic moment. Therefore, the y direction in the pseudospin space corresponds to ferroquadrupolar or antiferroquadrupolar magnetic ordering.

As predicted in [1], we will now show that the inclusion of an explicit hybridization between the bands breaks explicitly the $U(1)$ symmetry which is spontaneously broken in the condensate and removes the degeneracy associated with all the possible orientations of \mathbf{M}^\perp . Along with this, the natural question to answer is: What is the particular orientation favored by a nonzero hybridization.

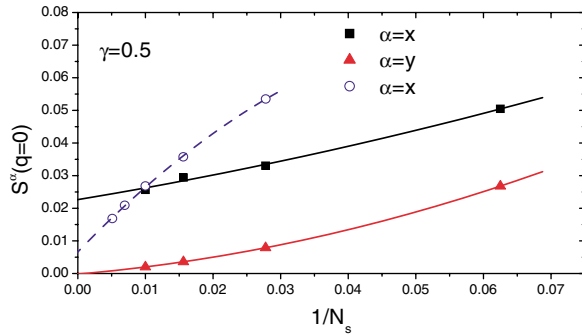


FIG. 4 (color online). Scaling of $S^x(0)$ and $S^y(0)$ for a 2D system: $U = 4$, $t_{\parallel} = -t_{\perp} = 0.2$, and $B_z = 1$ (full lines); $U = 2$, $t_{\parallel} = -t_{\perp} = 0$ and $M^z/N_s = 1/4$ (dashed line). The scaling function is a second order polynomial expression in $1/N_s$.

Inclusion of hybridization.—In addition to the trivial $U(1)$ symmetry associated with the conservation of the total number of particles, the remaining symmetries of H for nonzero hybridization are the spatial (\hat{I}) and the temporal (\hat{T}) inversions. Since the two orbitals have opposite parities, the signs of t_{\parallel} and t_{\perp} are interchanged under the application of \hat{I} . For the pseudospin components, we have $\hat{I}\tau_i^x\hat{I} = -\tau_i^x$, $\hat{I}\tau_i^y\hat{I} = -\tau_i^y$, and $\hat{I}\tau_i^z\hat{I} = \tau_i^z$. The temporal inversion (complex conjugation) leaves τ_i^x and τ_i^z invariant and changes the sign of τ_i^y . The ferroelectric state occurs when \hat{I} is spontaneously broken. The ordering of atomic currents occurs if both \hat{I} and \hat{T} are spontaneously broken. Note that the product $\hat{I}\hat{T}$ is still a symmetry of this second state.

In Fig. 4, we plot $S^x(0)$ and $S^y(0)$ as a function of the size of a two-dimensional system. The largest system has $N_s = 100$ sites. The scaling clearly shows that the ferroelectric state ($M_x \neq 0$) is stabilized in the thermodynamic limit. This agrees with a perturbative analysis which is valid only in the strong-coupling limit [1].

The BEC of excitons is thus replaced by an Ising-like ferroelectric state when a finite hybridization is included. This result has important physical consequences since most real systems have an explicit hybridization between the two bands, and for this reason a BEC of excitons is extremely hard to observe. For the bilayer system that we mentioned in the introduction [8], the interband hybridization is reduced to a very small value by increasing the distance between layers. According to our results, this bilayer system must exhibit the phenomenon of electronic ferroelectricity if the two layers are made of bands with opposite parity (such as “ s ” and “ p ”) instead of being identical. Then, the $d|\mathbf{P}|/dE$ response as a function of the uniform electric field E should show the same resonant behavior observed in the tunneling conductance as a function of the interlayer voltage [8].

In summary, we derived the quantum 1D and 2D phase diagrams of the extended FKM in the intermediate coupling regime. In the absence of hybridization, we found that the insulating phase obtained at half filling has a

transition from a nonmixed valence to a mixed-valence regime as a function of the energy difference between the centers of both bands. At this transition, the system changes from a band to an excitonic insulator which is a BEC of electron-hole pairs. Additionally, we showed that this condensate contains two different orderings which are degenerate: *ferroelectric order* and *chiral order*. The chiral state is a spontaneous ordering of local atomic currents. Since the two bands have opposite parity under spatial inversion, these currents can produce only a non-zero quadrupolar magnetic moment. For bands with the same parity, the chiral state can produce orbital magnetism and the ferroelectric state is replaced by quadrupolar electric ordering. If the distance between both bands is further decreased, there is a first order valence transition from the BEC of excitons to a state with staggered orbital ordering.

We also showed that the $U(1)$ degeneracy associated with the BEC is lifted by the interband hybridization, and the degenerate ground state is replaced by an Ising-like FE state (broken Z_2 symmetry). This result is valid even beyond the perturbative regime. It is crucial for applications of the present theory to systems such as the free Nb clusters [6] which are most likely in the intermediate coupling regime and have a considerable hybridization between the s and the p valence bands.

We wish to thank M. P. Lilly, J. P. Eisenstein, and R. Moro for stimulating discussions. This work was sponsored by the U.S. DOE under Contract No. W-7405-ENG-36. J.B. acknowledges the financial support of Slovene Ministry of Education, Science and Sports. H.Q. Lin is partly supported by RGC Project No. CUHK 4037/02P.

- [1] C. D. Batista, Phys. Rev. Lett. **89**, 166403 (2002).
- [2] T. Portengen, Th. Östreich, and L. J. Sham, Phys. Rev. Lett. **76**, 3384 (1996); Phys. Rev. B **54**, 17452 (1996).
- [3] L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. **22**, 997 (1969).
- [4] P. Nozieres and S. Scmitt-Rink, J. Low Temp. Phys. **59**, 195 (1985).
- [5] S. Zhang *et al.*, Phys. Rev. Lett., **74**, 3652 (1995).
- [6] R. Moro *et al.*, Science **300**, 1265 (2003).
- [7] G. B. Grad *et al.*, Phys. Rev. B **62**, 12743 (2000).
- [8] I. B. Spielman *et al.*, Phys. Rev. Lett. **84**, 5808 (2000).
- [9] The excitonic phase disappears at $\gamma = 0$ due to the localization of the pseudospin down electrons. For $D = 1$ and $\gamma = 0$, this phase should undergo a transition to the most homogeneous array of down electrons or to a phase segregated metallic state if B_z is close to B_z^{c2} and $U \lesssim 1.2$ [10]. A similar behavior is expected for the 2D case [10]. Our results indicate that these transitions occur for $\gamma < 0.05$ in $D = 1$ and $\gamma < 0.1$ in the 2D case.
- [10] P. Farkašovsky, Eur. Phys. J. B **20**, 209 (2001).
- [11] N. D. Mermin and H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966).