Mixed valence in a generalized Hubbard model

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A generalized Hubbard model involving two kinds of spinless fermions with different masses is proposed to explain the properties of mixed-valence compounds. An equivalence between the proposed model and an effective anisotropic antiferromagnetic Heisenberg model with external field is established in the strong-interaction limit. The ground-state energy and partition function are obtained analytically using generalized mean field theory which, for bipartite lattices, allows the system to be reduced to an equivalent two-site problem. The analytic behavior of the valence and compressibility under variation of pressure and the phase diagram in the ground state and at finite temperature are investigated. The conditions for a first-order transition depending on the position of the f band are obtained, taking into account the effect of local hybridization between the s and f states. The known anomalies in the behavior of n_f and χ in mixed-valence systems are interpreted in analogy with the magnetization and susceptibility in the corresponding pseudospin model.

Many phenomena in heavy-fermion compounds, high-T_c superconductors, quantum crystals, etc. have been modeled either with a single-band Hubbard model[1] or a spinless Falicov–Kimball (FK) (or closely related) model.[2–4] These models are also often used to explain phase diagram anomalies and interesting valence behavior in mixed-valence compounds under change of temperature and pressure (see, e.g., Ref. 5). Aside from some details of electron structure these two models can be studied together as particular cases of a more general model (GM),

$$H_{\mathrm{GM}}=-t_1\sum_{\langle ij\rangle} c_{i\uparrow}^{+}c_{j\uparrow}-t_2\sum_{\langle ij\rangle} c_{i\downarrow}^{+}c_{j\downarrow}+U\sum_i c_{i\uparrow}^{+}c_{i\uparrow}c_{i\downarrow}^{+}c_{i\downarrow}$$
$$-\frac{H}{2}\sum_i (c_{i\uparrow}^{+}c_{i\uparrow}-c_{i\downarrow}^{+}c_{i\downarrow}), \tag{1}$$

which includes hopping terms and intrasite repulsion ($U>0$) for two different kinds of particles. For $t_1=t_2$ it is, of course, a Hubbard model with an applied magnetic field. Although Eq. (1) is written in the language of electron creation operators with spin indices, an equivalent Hamiltonian could be written using band or orbital indices, as in the FK model. In other words, the $c_\uparrow^+, c_\downarrow^+$ operators in Eq. (1) can be replaced with creation operators f^+, a^+ representing spinless fermions in the f and s bands. The field strength H in this case represents the energy difference between the centers of the two bands, which in mixed-valence materials can be changed with pressure. For $t_1=0$, this is equivalent to the FK model. In the strong interaction limit $U\to\infty$ the GM reveals some interesting relations between the two models, and helps to explain the connections between such phenomena as superfluity and excitonic insulators, antiferromagnetism (or charge-density waves) and valence-density waves, ferromagnetism, and pure integer valency. In addition, viewed as a generalization of the FK model there are significant advantages to using Eq. (1) for describing mixed-valence compounds. In the pure FK model, for example, mixed-valence states can appear only as a spatially periodic lattice of ions,[4] with $n_f=0$ or 1, a kind of orbital antiferromagnetism. The generalized model, however, also permits a liquidlike state of uniform, noninteger valence, as has been seen experimentally,[5] and it correctly predicts the first-order transitions seen in those materials under change of temperature and pressure.

It is convenient to rewrite the GM Hamiltonian, replacing the creation operators by Hubbard operators[1] so that $c_{i\sigma}^{+}=X_i^{\sigma 0}+\sigma X_i^{2-\sigma}$ and the Hamiltonian takes the symmetrized form $H_{\mathrm{GM}}=\Sigma_{i,\Delta}H(i,i+\Delta)+H(i+\Delta,i)$, where Δ is summed over the lattice vectors, and $H(i,j)$ can be written in terms of two-site operators as follows:

$$\begin{aligned}H(i,j)=&-t_1(X_i^{\uparrow 0}X_j^{0\uparrow}+X_i^{2\downarrow}X_j^{\downarrow 2})-t_2(X_i^{\downarrow 0}X_j^{0\downarrow}+X_i^{2\uparrow}X_j^{\uparrow 2})\\&-t_1(X_i^{\uparrow 0}X_j^{\downarrow 2}+X_i^{2\downarrow}X_j^{0\uparrow})+t_2(X_i^{\downarrow 0}X_j^{\uparrow 2}+X_i^{2\uparrow}X_j^{0\downarrow})\\&+U/2(X_i^{22}+X_j^{22})-H/4(X_i^{\uparrow\uparrow}+X_j^{\uparrow\uparrow}-X_i^{\downarrow\downarrow}-X_j^{\downarrow\downarrow}).\end{aligned} \tag{2}$$

While the first two terms in Eq. (2) represent simple hopping, the second two are interconfiguration fluctuation terms and can be removed by a suitable unitary transformation as in Ref. 6. In the strong interaction limit the transformed Hamiltonian can be expanded to any order in powers of $t_{1,2}/U$. Projecting the transformed Hamiltonian onto the subspace of singly occupied states, exactly at half-filling ($n_\uparrow+n_\downarrow=1$) gives, to lowest order, an effective Hamiltonian

$$H_{\mathrm{eff}}=-\frac{t_1^2+t_2^2}{2U}\sum_{\langle ij\rangle}(X_i^{\uparrow\uparrow}X_j^{\downarrow\downarrow}+X_i^{\downarrow\downarrow}X_j^{\uparrow\uparrow})+\frac{t_1t_2}{U}\sum_{\langle ij\rangle}(X_i^{\uparrow\downarrow}X_j^{\downarrow\uparrow}$$
$$+hc)-\frac{H}{2}\sum_i (X_i^{\uparrow\uparrow}-X_i^{\downarrow\downarrow}). \tag{3}$$

Since the Hubbard operators $X^{\alpha\beta}$ generate an $SU(2)$ algebra, and their commutation relations are isomorphic to those of the pseudospin operator L ($2L^z=X^{\uparrow\uparrow}-X^{\downarrow\downarrow}$ and $L^+=X^{\uparrow\downarrow}$), the effective Hamiltonian above can be written in the form

$$H_{\mathrm{eff}}=J_\parallel\sum_{\langle ij\rangle}(2L_i^zL_j^z-\tfrac{1}{2})+J_\perp\sum_{\langle ij\rangle}(L_i^+L_j^-+hc)-H\sum_i L_i^z, \tag{4}$$

with $J_\parallel=(t_1^2+t_2^2)/2U$ and $J_\perp=t_1t_2/U$. Thus, to lowest order, the GM is strictly equivalent to an anisotropic antiferromagnet with external field. Using analogies of this kind one may advantageously translate the substantial existing knowledge about spin systems to mixed-valence systems.

The transformed Hamiltonian is valid for all t_1, t_2, and in earlier work[7] the case $t_1\ll t_2$ was described. It is also easy

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to show that taking $t_1=t_2$ (Hubbard model) gives a spin analog equivalent to Anderson superexchange,[8] H_{An}. Here we examine in greater detail the FK-like case $t_1 \to 0$. Expanding the resulting effective Hamiltonian to fourth order gives

$$H_{Is}=\frac{t_2^2}{U}\sum_{nn} L_i^z L_j^z+\frac{t_2^4}{U^3}\sum_{nnn} L_i^z L_j^z - H\sum_i L_i^z + \text{const} \quad (5)$$

so that any exact results from the Ising model can be easily transferred to the FK model in the strong interaction limit. In particular, one expects the appearance of a spatially ordered phase in the GM in two dimensions, similar to results described earlier[4] about the appearance of a chessboard structure of f fermions in $D \geq 2$ in the symmetric case ($H=0$). We show below, however, that even with $H \neq 0$, there is a region where the chessboard structure is stabile. Higher-order corrections as in Eq. (5) are important for their implications regarding additional spatially ordered phases for $H \neq 0$.

Comparing the Anderson Hamiltonian H_{An} with H_{Is} above, we see that the difference between the Hubbard and FK models in the strong interaction limit is no more than that between a classical Ising system and a quantum antiferromagnet. Thus, exactly at half-filling the FK model can be considered to be a classical analog of the Hubbard model. Below we show that, in spite the fact that $J_\parallel \geq J_\perp$, the inclusion of a finite, small bandwidth for the f states changes the character of the phase transition from second to first order and stabilizes the quantum-liquid (QL) state with strong excitonic correlations.

All these effects can be derived analytically using a generalized mean field approximation (GMFA) for bipartite systems, i.e., those consisting of two sublattices A and B. Taking the most general decoupling scheme for Hubbard operators in Eq. (3) the Hamiltonian can be reduced to the two-site form,

$$H_{\text{eff}}^{MF}=(-J_\parallel z\bar{n}_{2a}-H/2)X_1^{\uparrow\uparrow}+(-J_\parallel z\bar{n}_{2f}-H/2)X_1^{\downarrow\downarrow}+(-J_\parallel z\bar{n}_{1a}-H/2)X_2^{\uparrow\uparrow}+(-J_\parallel z\bar{n}_{1f}-H/2)X_2^{\downarrow\downarrow}+J_\perp z\Delta_2(X_1^{\uparrow\downarrow}+X_1^{\downarrow\uparrow})$$
$$+J_\perp z\Delta_1(X_2^{\uparrow\downarrow}+X_2^{\downarrow\uparrow})+J_\parallel z(\bar{n}_{1f}\bar{n}_{2a}+\bar{n}_{1a}\bar{n}_{2f})-2J_\perp z\Delta_1\Delta_2, \quad (6)$$

where z is the coordination number of the lattice, and we have introduced the order parameters $\Delta_{1,2}=\langle X_{1,2}^{\sigma-\sigma}\rangle$ for the excitonic correlations (orbital mixing) in xy plane and $\eta=\langle X_1^{\sigma-\sigma}-X_2^{\sigma-\sigma}\rangle$ for the spatial orbital ordering in z plane. The number of particles n_1 and n_2 on the A and B sites is then $n_1=\bar{n}_{1f}+\bar{n}_{1a}$ and $n_2=\bar{n}_{2f}+\bar{n}_{2a}$ and the total number of particles on the two sublattices, exactly at half-filling, is $n_1+n_2=2$.

After diagonalization of Eq. (6) one can find eigenstates $E_{1,2}^{\pm}$ and the partition function Z depending on Δ, η, and $m=2\bar{n}_f-1$. The analysis of self-consistent equations for these gives the dependence of the valence $\bar{n}_f$ on the position of the f level H,

$$h=\frac{H}{2J_\parallel z}=mg+\sqrt{m^2+(g^2-1)\eta^2(m)}. \quad (7)$$

Analysis of Eq. (7) reveals many phases, which are shown in Fig. 1. In a strong magnetic field we have ferromagnetic ordering or integer valence (IV) states $\bar{n}_f=0$ or 1. On decreasing the magnitude of h, the system undergoes a transition into an excitonic insulator at $h^*=1+1/g$. In this region $\bar{n}_f$ changes linearly with h, $\bar{n}_f=h/h^*$. This phase most closely resembles a uniform QL with strong hole-particle correlations, and with $(2m_0+1)/2<\bar{n}_f<1$, where $m_0=\sqrt{[(g-1)/(g+1)]}$. For h between $\pm\sqrt{(g^2-1)}\,\bar{n}_f$ is multivalued until some critical field $\pm h_0$ where the system undergoes a first-order transition from a mixed state with $\eta \neq 0$, $\Delta \neq 0$, in which valence-density waves (VDW) coexist with the QL, into a pure spatially ordered phase with VDW. When the mass of the f fermions goes to infinity we obtain at $T=0$ two consecutive jumps from IV states into VDWs with $\bar{n}_f=\bar{n}_s=1/2$, as shown in Fig. 1. It is also possible to obtain such a transition in systems with short-range electron-phonon interactions.[10] The transition, however, becomes continuous at any finite temperature. Thus, the stabilized excitonic phase is ruled out in the ground state whenever we exclude a finite bandwidth for f states, and there is no possibility to obtain a first-order transition in the FK model at finite temperatures. From Eq. (7) one can easily find the compressibility $\chi=-d\bar{n}_f/dp$, which is small in IV configurations and in spatially ordered phases ($\bar{n}_f=1/2$), but in the QL phase becomes constant $\chi=1/h^*$. The value increases with pressure, and reaches a maximum near the transition into the mixed state. Such behavior has been seen in experiments in SmS under pressure.[5,10]

The inclusion of local hybridization in the GM $V(c_\uparrow^+ c_\downarrow+c_\downarrow^+ c_\uparrow)$ would be the same as considering the GM in presence of a transverse magnetic field $V(L^++L^-)$. This factor is of an excitonic type and increases the tendency toward a first-order transition from a spatially ordered phase into QL state with strong excitonic correlations.

If we consider the Ising-type interaction ($t_1 \to 0$) to all orders in t/U, which includes the antiferromagnetic long-range interactions with all neighbors (analogous to a classical gas with Coulomb repulsion,[11] then an infinite number of incommensurate modulated phases is found between the ferromagnetic and the VDW "antiferromagnetic" ordered phases in the one-dimensional case. This means that the FK model at $U \to \infty$ can be converted into an Ising model with long-range antiferromagnetic interactions. The crystallization of f particles into a periodic structure and dielectric splitting of the f band has been found in the 1D case.[12] The similarity between the ground-state energy and the partition functions of the FK model and the classical lattice gas has also been found recently for the 1D case.[13]

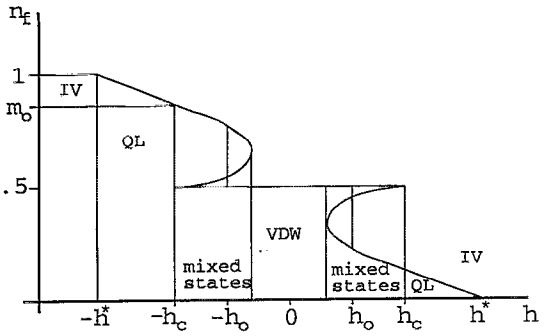

FIG. 1. The occupation number $\bar{n}_f$ as a function of h in a generalized Hubbard model at $0<1/g<1$.

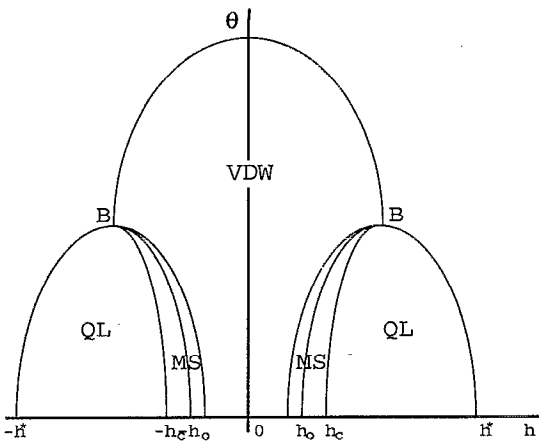

FIG. 2. The predicted h-T phase diagram for the generalized model for $D \geqslant 3$.

The thermodynamic behavior of our system can be analyzed easily. From analysis of these equations one can easily find the thermodynamic characteristics, and investigate the phase diagram at finite temperatures. The schematic phase diagram of critical temperatures versus magnetic field (or pressure) of the GM in the strong interaction limit is shown in Fig. 2. In some cases[14] the transition from the VDW to the QL state can be realized through an intermediate mixed state (MS), where the first-order transition line is split into two lines terminating in tetracritical point B. One first order phase transition from the QL into the VDW state is also possible by increasing the temperature at constant field (pressure) (see Fig. 2). Physically, this result is connected with the fact that excitonic effects, which are absent at high temperatures, become important at low temperatures. The phase boundary between the QL and VDW states indicates an increase of entropy for the spatially ordered phase with temperature. The bicritical point T_{bc} and spinodals, which are characteristic of the first-order transition, are also seen in Fig. 2. We expect that in the 3D case only a finite number of commensurate crystalline ordered phases exists at finite temperatures and can survive near the equilibrium line in the VDW region. At high pressures, near the IV phase the transition from QL into normal state is smooth, and its dependence on the magnetic field is logarithmic $T_c = -J_\perp/\ln(h-h^*)$. This result means that the excitonic effect by itself cannot give rise to a first-order transition and is possible only near the boundary of a spatially ordered phase. The high-temperature compressibility in the normal paramagnetic phase behaves as predicted in mean field theory, $\chi = d\bar{n}_f/dP = C/(T-T_c^*)$, where T_c^* and C are the Curie–Weiss temperature and the Curie constant. Thus, all anomalies in the behavior of n_f and χ in mixed-valence systems can be interpreted in analogy with the temperature dependence of the magnetic moment and susceptibility of a Heisenberg–Ising system under variation of external field.

Using analogies between the FK model at $U \to \infty$ and the antiferromagnetic Ising or classical lattice-gas model, we can predict spatial ordering (VDW). In addition the long-range interactions for the Ising model (see Ref. 11) give rise to numerous other modulated long-range-ordered phases and, similarly, using an analogy with the classical lattice-gas model, one can predict an infinite number of phase transitions with charge-density wave states under change of pressure in the FK model. Thus, the thermodynamic behavior as well as the value of all critical exponents for FK model can be obtained using analogies with exactly solvable one- and two-dimensional Ising or lattice gas models. Even a small bandwidth causes a the appearance of a valence fluctuation term (or spin-flop terms in the effective Heisenberg Hamiltonian), and drastically changes the properties of the system. In spite of the fact that the exact solution of the 2D Heisenberg–Ising model is not known, it is possible to reach some conclusions about the ground-state properties and correlation function behavior even in this case.[15] For example, at low temperatures the bounds obtained in Ref. 16 rule out the possibility of excitonic condensation in 2D lattices, but allow power-law-like decay for excitonic correlations in the GM, which can be of the Kosterlitz–Thouless type, whenever t_1 or t_2 is different from zero.

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[1] J. Hubbard, Proc. R. Soc. London Sect. A **277**, 273 (1964).
[2] L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. **22**, 997 (1969).
[3] V. L. Emery, Phys. Rev. B **14**, 2989 (1976); A. N. Kocharian and D. I. Khomskii, Sov. Phys. JETP **44**, 404 (1976); Solid State Commun. **18**, 985 (1976); N. Sh. Izmailian, A. N. Kocharian, P. S. Ovnanian, and D. I. Khomskii, Fiz. Tverd. Tela **23**, 2977 (1981).
[4] U. Brandt and R. Schmidt, Z. Phys. B **63**, 45 (1986); B **67**, 43 (1987); B **75**, 365 (1989); B **79**, 295 (1990); T. Kennedy and E. H. Lieb, Physica A **138**, 320 (1986); A **140**, 240 (1986); Q. Si, G. Kotliar, and A. Georges, Phys. Rev. B **2**, 1261 (1992); J. K. Freericks, *ibid.* B **48**, 14 797 (1993).
[5] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981); C. M. Varma, Rev. Mod. Phys. **48**, 219 (1976).
[6] A. N. Kocharian and P. S. Ovnanian, Z. Phys. B **83**, 161 (1991).
[7] A. N. Kocharian and A. S. Saakian, Physica B **199&200**, 582 (1994).
[8] P. W. Anderson, Phys. Rev. **115**, 2 (1959).
[9] H. Matsuda and T. Matsubara, Prog. Theor. Phys. **17**, 19 (1957).
[10] D. I. Khomskii, Sov. Phys. Usp. **22**, 879 (1979).
[11] V. L. Pokrovsky and G. V. Uimin, J. Phys. C **11**, 3535 (1978).
[12] R. Lyzwa, Phys. Lett. A **164**, 323 (1992).
[13] C. Gruber, J. L. Lebowitz, and N. Macris, Phys. Rev. B **48**, 4312 (1993).
[14] M. Fisher and D. Nelson, Phys. Rev. Lett. **32**, 1350 (1974).
[15] T. Kennedy, E. Lieb, and B. Siram Shastry, Phys. Rev. Lett. **61**, 2583 (1988).
[16] A. N. Kocharian and A. G. Sogomonian, Physica B **194–196**, 445 (1994)