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Dimerization in the two-dimensional Hubbard model

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We have used both an exact diagonalization method for finite-size systems and a perturbation technique to study the lattice instability due to dimerization in a two-dimensional Hubbard model in the large-U limit. We show that a critical electron-phonon coupling strength is required to form a dimerized state, in contrast to the one-dimensional system. Our calculations suggest the phase transition to the dimerized state is of first order. The relevance to high-T_c superconductor materials is discussed.

I. INTRODUCTION

We study the stability of the antiferromagnetic (AFM) ground state of a square-lattice Hubbard model against a lattice dimerization due to electron-lattice interactions. In particular we look at the limit of large Coulomb repulsion for the half-filled case. We treat the phonon mode adiabatically. Two different methods are used: exact diagonalization of the finite-size systems and an analytic perturbation technique. In contrast to the results in a one-dimensional (1D) system, we find that a critical electron-lattice coupling is required for lattice dimerization. Furthermore, our small-system calculations strongly suggest that the phase transition from AFM to the dimerized state is first order.

The competing effects of the electron-electron repulsion and the electron-lattice interaction on a 1D system have been studied by many authors.[1] It has been shown that an infinitesimal electron-lattice coupling leads to lattice distortion. This subject, however, has not been investigated in 2D systems, especially not in the large-U case.

Our work was motivated by the recent discovery of high-T_c superconductivity in Cu oxide compounds.[2] Many of the proposed models for the superconductivity are based on the 2D Hubbard model.[3] The copper-copper dimerization phonon mode has been considered in some theoretical proposals. The weak coupling limit is discussed by Barisic, Batistic, and Friedel.[4] In the large-U limit, Kivelson, Rokhsar, and Sethna[5] have proposed a variant of Anderson's "resonant valence bond" (RVB) theory[6] in which the dimerization phonon mode plays a central role. On the other hand, based on the results in 1D, Hirsch[7] has conjectured the square lattice in the half-filled Hubbard model to be inherently unstable against dimerization, forming a "bond charge-density-wave" state. The present work examines the large-U case.

II. MODEL HAMILTONIAN

We consider a single half-filled electron band in a square lattice within the tight-binding approximation. The influence of the dimerization mode is to change the electron hopping integral. We treat the lattice displacements classically, and neglect the quantum fluctuations. Within this approximation, the lattice displacements enter in the problem as parameters, and the system can be described by the Hamiltonian

$$H=-\sum_{\langle ij\rangle\sigma}(t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+\text{H.c.})+\sum_{i}Un_{i\uparrow}n_{i\downarrow}+\frac{K}{2}\sum_{i}u_i^2 \ . \tag{1a}$$

In Eq. (1a) the hopping is between the nearest-neighbor sites i and j, and the hopping integral t_{ij} is given by

$$t_{ij}=t_0-\alpha u_{ij} \ , \tag{1b}$$

with α the electron-phonon coupling, and u_{ij} the length change between the two sites, whereas t_0 is the hopping integral without dimerization. The third term in Eq. (1a) describes the elastic energy due to lattice displacements and K is the elastic constant.

The classical approximation we adopt in Eqs. (1) has been used to study 1D systems by Soos and Ramasesha.[8] Quantum-fluctuation effects on dimerization have been studied by Su,[9] and the qualitative features of the classical solution of the phonon mode survive.

In the limit $t_0/U \ll 1$, the half-filled Hubbard model of Eqs. (1) maps onto an antiferromagnetic Heisenberg Hamiltonian:

$$H=\sum_{\langle ij\rangle}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+\frac{K}{2}\sum_{i}u_i^2 \ , \tag{2a}$$

with the exchange constant

$$J_{ij}=4t_{ij}^2/U \ . \tag{2b}$$

Without electron-phonon coupling, the ground state of the antiferromagnetic Heisenberg model in a square lattice is believed to be the antiferromagnetic ordered state with a doubled unit cell. In the presence of the electron-lattice coupling, the spin coupling favors the dimerization, but the elastic energy opposes it.

We proceed by analyzing a symmetry-preferred dimerized state with the displacements along one square axis, e.g., $\mathbf{u}_i = \pm u_0/2$ (1,0), where the sign ± corresponds to the two sublattices. Another dimerized state with the displacements along diagonal $\mathbf{u}_i = \pm u_0/\sqrt{8}$ (1,1) is found to be not favored energetically, and will only be discussed briefly. In the symmetry-preferred dimerized state, the couplings in the direction transverse to the dimers remain essentially unaffected $J_T = J = 4t_0^2/U$, because the displacements are very small in units of the lattice constant. The longitudinal couplings (along the dimers) become $J_{L\pm} = 4(t_0 \pm a u_0)^2/U$. Introducing dimensionless displacements $x = a u_0/t_0$, and the dimensionless coupling constant $\lambda = 32a^2/KU$, Eqs. (2) can be rewritten as

$$H/J = \sum_{\langle ij\rangle} \tilde{J}_{ij}\mathbf{S}_i\cdot\mathbf{S}_j + Nx^2/\lambda \ , \tag{3a}$$

with the dimensionless exchange coupling

$$\tilde{J}_{ij} = J_{ij}/J = (1 - x\eta_{ij})^2 \ , \tag{3b}$$

where $\eta_{ij} = 1$ for the longitudinal pair $\langle ij\rangle$ and zero for the transverse one. N is the number of electrons.

III. EXACT SMALL SYSTEM CALCULATIONS

The Hamiltonian of Eqs. (3) can be diagonalized exactly for finite-size systems with appropriate periodic boundary conditions. In the absence of the dimerization, this has been done by Oitmaa and Betts.[10] Their results are important to understanding the ground state of the undistorted system. In the dimerized lattice the finite super cells of 8 and 10 sites are shown in Fig. 1. Hamiltonian (3) can be regarded as a function of the displacement x for a given coupling constant λ. The true ground state corresponds to the lowest energy with respect to x. The energy per site, E, as a function of the displacement obtained from the 8-sites system is plotted in Fig. 2 for several values of λ. The results of the 10-sites system are essentially the same except for an overall energy shift. Our results show that a critical electron-lattice coupling strength is required for the dimerization. In cases $\lambda < \lambda_c \simeq 1.175$, the dimerized state is not energetically favored. This means that the AFM state remains stable at weak electron-lattice coupling. We also find that the displacement just beyond the critical coupling constant λ_c is finite: $x_c \simeq 0.6$. This suggests a first-order phase transition between AFM and the dimerized state. To demonstrate this further, we expand the energy per site at zero temperature in terms of a Taylor series in the displacement x:

$$E = E_0 + (a_2 + 1/\lambda)x^2 + f(x) \ , \tag{4a}$$

where

$$f(x) = a_4x^4 + a_6x^6 + \cdots \ . \tag{4b}$$

In Eqs. (4), E_0 is the energy in the absence of dimerization, which agrees with the results of Oitmaa and Betts.[10] From Eqs. (3), all the coefficients a_n, hence $f(x)$, are independent of λ. We find numerically, $a_2 = -0.7919$ and -0.7922 for the 8- and 10-site systems, respectively. The function $f(x)$ is the dimerization energy minus the quadratic term. A necessary condition for a second-order phase transition is that $a_4 > 0$ or $f(x) > 0$ for small values of x. However, the small-system calculations show that a_4 is negative, although the value is still system-size dependent, and it is difficult to extrapolate to the infinite system. The function $f(x)$ is found to have a pronounced minimum as shown in Fig. 3.

If the transition were second order, the critical coupling λ would be $-1/a_2$. At that value of λ, the actual energy gain due to the dimerization with the finite displacement is about 0.02 J per site. This strongly indicates that the transition is of first order.

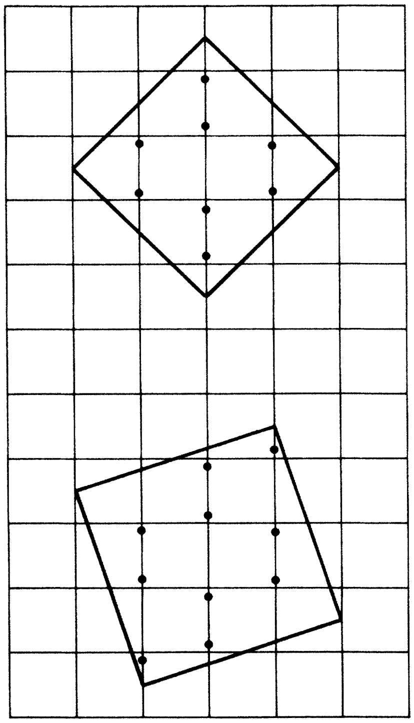

FIG. 1. Finite cells of 8 and 10 sites on the square lattice, in which the infinite lattice is filled by periodic repetition of the cells. The displacements of the ions are $\pm u_0/2$.

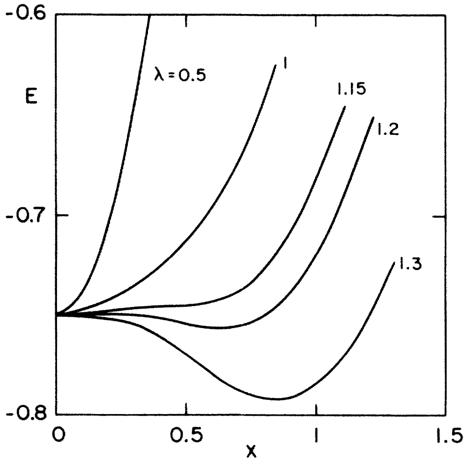

FIG. 2. Energy per site as functions of the dimensionless displacements x for several values of the dimensionless electron-phonon coupling constant λ in 8-site systems.

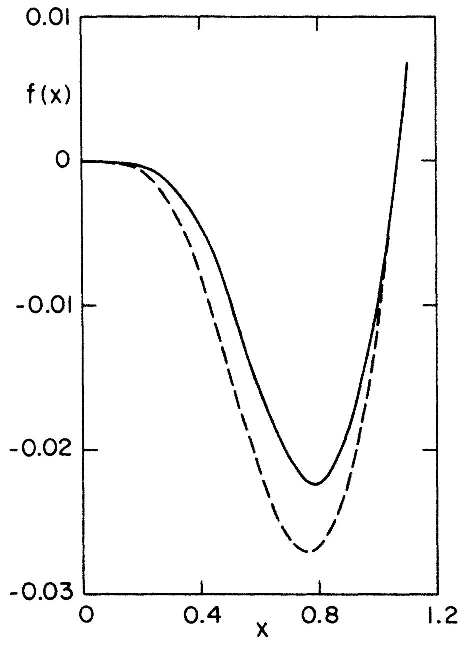

FIG. 3. Dimerization energy per site $f(x)$ as functions of the displacements x in 8 sites systems (dashed curve) and in 10 sites systems (solid curve). The quadratic terms have been subtracted out in $f(x)$.

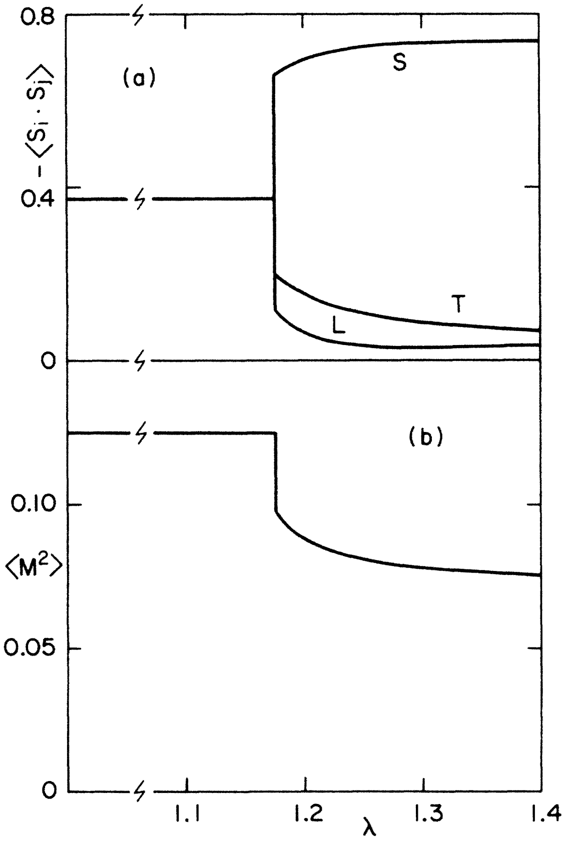

FIG. 4. (a) Nearest-neighbor spin-spin correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ as functions of the coupling constant λ. The curves S, T, and L are for the shorter bond, the longer bond, and the transverse bond $\langle ij \rangle$, respectively. (b) Magnetization as functions of λ.

We have computed the ground-state expectation values of the spin-spin correlation of the two nearest-neighbor sites $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$. This value is about -0.33 from the estimate of Oitmaa and Betts,[10] for an infinite system in the absence of dimerization. For the dimerized lattice, the values of $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ are different for the shorter bond, the longer bond, and the transverse bond. The shorter bond has much stronger spin-spin correlation than the other bonds when $\lambda > \lambda_c$. In Fig. 4(a) we plot the correlations as functions of the coupling constant λ. The sudden changes of the correlation functions at λ_c are in accordance with the first-order phase transition.

We have also computed the ground-state expectation values of the squares of the staggered magnetization $M_z = \sum_i \varepsilon_i S_i^z$, where $\varepsilon_i = \pm 1$, depending on which sublattice i is on. The expectation values are given by

$$\langle M^2 \rangle = \frac{1}{N^2} \sum_{i,j} \varepsilon_i \varepsilon_j \langle S_i^z S_j^z \rangle \ ,$$

where the sum runs over all the sites. The results are shown in Fig. 4(b). The staggered magnetization has a sudden drop when the electron-lattice coupling λ reaches λ_c as a result of the first-order phase transition.

In the above calculations, we have neglected the length changes of the transverse bonds. Inclusion of this produces an additional term H' in Eqs. (3), and

$$H' = \sum_{\langle ij \rangle \in T} (J_T - J) \mathbf{S}_i \cdot \mathbf{S}_j + \frac{N}{8} K [(a_0^2 + u_0^2)^{1/2} - a_0]^2 \ ,$$

where the first and second terms are the shift of the spin-spin correlation and the elastic energy of the transverse bonds respectively. a_0 is the lattice parameter. Since $a_0 \gg u_0$, we can neglect higher-order terms in u_0/a_0, and

$$J_T = J(1 - x^2/y + x^4/4y^2) \ ,$$

with $y = \alpha a_0/t_0 \gg x$.

Using the exact solution of the Hamiltonian in Eqs. (3), and treating H' perturbatively, we can examine the effect of H'. The energy correction per site due to H' is given by $E'(x) = \langle \psi(x) | H' | \psi(x) \rangle / N$ in first-order perturbation theory, where $\psi(x)$ is the lowest-energy state of the Hamiltonian in Eqs. (3) for a fixed x. In analogy with E, we may expand E' in terms of a Taylor series: $E' = a_2' x^2 + a_4' x^4 + \cdots$. We find that $a_2' \approx 0.32/y$ and $a_4' < 0$. Since y is very large (about 10 if we use the parameter values $a_0 = 4$ Å, $t_0 = 0.5$ eV, $\alpha = 1 \sim 2$ eV/Å), a_2' is very small in comparison with $a_2 \simeq -0.79$. The negative value of a_4' is to further enhance the first-order phase transition. Thus the qualitative results we obtained from Eqs. (3) remain the same.

IV. RESULTS OF THE ANALYTIC PERTURBATION THEORY

We now study the Hamiltonian of Eqs. (3) using an analytic perturbation method. In the square lattice, we expect that the ground state of (3) will show a doubled unit cell either due to AFM order or due to dimerization. The reciprocal wave vectors of the new lattice are $Q_{1,2} = \pi/a_0\,(1, \pm 1)$. In the new cell we denote two sites as 1,2. The

Eqs. (3) can be rewritten as

$$H/J=\sum_{\mathbf{q}}\tilde{J}_q\mathbf{S}_q\cdot\mathbf{S}_{-q}+Nx^2/\lambda\ , \tag{5a}$$

$$\tilde{J}_q=\frac{1}{N}\sum_{\langle ij\rangle}\tilde{J}_{ij}\exp(i\mathbf{q}\cdot\mathbf{R}_{ij})\ , \tag{5b}$$

$$\tilde{J}_{ij}=J_{ij}/J\ , \tag{5c}$$

where $\mathbf{S}_q$ is the Fourier transform of the spin operator $\mathbf{S}_i$. Note that $\tilde{J}_q$ is not real in general due to the lack of inversion symmetry, but still $\tilde{J}_{-\mathbf{q}}=\tilde{J}^*_{\mathbf{q}}$. Using Eq. (3b), we find

$$\tilde{J}_{\mathbf{q}}=2[(1+x^2)\cos(q_xa_0)+\cos(q_ya_0)+2ix\sin(q_xa_0)]\ .$$

The AFM state was shown to be stable at $T=0$, $u_0=0$ in Ref. 8, in agreement with the spin-wave theory result. We use the latter approach to investigate analytically the stability of the AFM state at finite u_0. Assuming the Néel state $S_{1,z}=-S_{2,z}=S=\frac{1}{2}$, we expand Eq. (5a) to lowest order in spin-wave fluctuations. In terms of boson operators b and $b^\dagger$, the spin part can be written as

$$\frac{H_s}{J}=\frac{N}{2}S^2\tilde{J}_0+S\sum_{\mathbf{q}}\{\tilde{J}_0(b^\dagger_{1,\mathbf{q}}b_{1,\mathbf{q}}+b^\dagger_{2,\mathbf{q}}b_{2,\mathbf{q}}) + \tilde{J}^*_{\mathbf{q}}b_{1,\mathbf{q}}b_{2,-\mathbf{q}}+\tilde{J}_{\mathbf{q}}b^\dagger_{1,\mathbf{q}}b^\dagger_{2,-\mathbf{q}}\}\ , \tag{6}$$

with $\tilde{J}_0=\tilde{J}_{\mathbf{q}=0}$. A diagonalization of H_s yields an approximate ground-state energy per site of the system

$$\frac{E}{J}=\frac{S}{N}\sum_{\mathbf{q}}[(\tilde{J}_0^2-|\tilde{J}_q|^2)^{1/2}-\tilde{J}_0]+x^2/\lambda\ . \tag{7}$$

The results can be represented in terms of Taylor series in x as in Eqs. (4). The $\mathbf{q}$ integrals yield $E_0=-0.657$, $a_2=-0.619$, $a_4=0.051$. E_0 represents the usual spin-wave results for an undeformed Heisenberg model.[11] The value of a_2 is close to that we find in small-system calculations. The two different methods give the same conclusion: A critical electron-lattice coupling is required to form a dimerized state.

Since $a_4>0$, the perturbation analysis would indicate a second-order transition to a dimerized state at $\lambda=\lambda_c=1.62$. Considering the uncertainty of the perturbative approximation for the strong coupling systems as well as the smallness of the value a_4 (one order of magnitude smaller than a_2), we feel that the qualitative results from the exact calculations of the small systems are more reliable.

The above results are for the longitudinal dimerized state. We have also considered the state with the displacements along the diagonal. In that case, Eqs. (5), (6), and (7) hold, but $\tilde{J}_{\mathbf{q}}$ is given by

$$\tilde{J}_{\mathbf{q}}=2\left\{\left(1+\frac{x^2}{2}\right)[\cos(q_xa_0)+\cos(q_ya_0)] +i\sqrt{2}x[\sin(q_xa_0)-\sin(q_xa_0)]\right\}\ .$$

And we find $a_2=-0.387$. The diagonal dimerization is thus not favored. This can be understood by noting that in the large-λ limit, the diagonal dimerization does not lead to a state of ordered singlets, while the longitudinal dimerization does. The Cu displacement degree of freedom tends to favor the singlet pairing as discussed in Ref. 5.

V. DISCUSSION

Within the adiabatic approximation, we have studied the Hubbard model in the large-U limit on a square lattice including the dimerization phonon mode at the half-filled case. The model is equivalent to an antiferromagnetic Heisenberg model with a spin-lattice interaction. The most firm conclusion we can draw is that the AFM state is stable against weak electron-lattice interaction. The critical coupling $\lambda_c=32\alpha_c^2/KU$ to form a dimer solid is found to be order of 1 in both the small-system exact calculations and the analytical perturbation method. This result is qualitatively different from that in 1D case. In 1D chain, the ground state of the system in the absence of electron-phonon interaction is a singlet without an AFM order. The lattice is unstable against arbitrary weak electron-phonon coupling.[1] However, the ground state in a square lattice appears to be an ordered AFM state, which makes it much more stable. Each site in a square lattice has four bonds to connect with. Dimerization favors one bond, but weakens the other three bonds in exchange energy. This explains the dimensionality dependence of the problem.

Our small system calculations strongly suggest that the transition between AFM state and the dimer solid is first-order. A finite displacement is thus expected at the transition point.

We now discuss the possible effect of a finite phonon frequency. It has been proposed[5] that finite-frequency phonons may favor the RVB dimer liquid due to the quantum tunneling in La-Cu-O materials. Since the transition is of first order, it seems very difficult to have a state between AFM and the dimer solid at the half-filled system. When doped, however, the liquid state gains more kinetic energy,[12] a possible dimer liquid state cannot be excluded.

Finally, we estimate the electron-lattice coupling parameter for the Cu–O plane in La_2CuO_4. The elastic constant can be estimated from the Raman scattering measurements, $K\simeq10$ eV/Å^2. The Coulomb energy is approximately $U=5$ eV. The electron-lattice coupling constant α' of the copper and oxygen ions is related to the deformation potential energy V found in band-structure calculations,[13] where $V=1.6$–3.9 eV/Å. Note that the Coulomb interaction U is partly included in a Haretree-Fock-type interaction in the band-structure calculation. Taking this into account, we have

$$\alpha'=\left[\left(\frac{V}{4}\right)^2+\frac{UK}{16}\right]^{1/2}\ .$$

The electron-lattice coupling constant α of the copper-copper ions is related to α'. But the former one is related to the second-order hopping process (copper to copper via oxygen ion), so α must be less than α'. An accurate estimate of α seems difficult at the moment. Experimentally, however, the copper displacement has not been observed yet.

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