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SOLITON-LIKE DOPING OF THE HALF-FILLED HUBBARD CHAIN

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A recent random field approximation to the half-filled band Hubbard model is discussed. Attention is focused on the magnetic polarons occurring in this picture which within the static approximation lead to bound states in the Hubbard gap. It is argued that it is favorable for the half-filled system to initially accommodate added charges through the formation of such soliton-like defects which when the static approximation is relaxed propagate along the chain.

I. INTRODUCTION

In reduced dimensional and/or narrow banded solids the effects of electron-electron or electron-phonon interactions are usually enhanced leading to the possibility of such interesting phenomena as nonmetal-metal "transitions" as a function of temperature, antiferromagnetism and charge density waves.

Recently Su, Schrieffer and Heeger[1] have studied in detail the ground and soliton excited states of a half-filled band one-dimensional (1-D) Peierls-type model as well as the effects on this system associated with light doping. Su, Schrieffer and Heeger (SSH) applied the results of their studies to *trans*-$(CH)_x$ and it was shown that a number of the model predictions were consistent with experiment. Included in this experimental support is (i) the observation of *cis* to *trans* isomerization induced free radicals which are highly mobile[2] and (ii) a decrease in the Curie-law contribution to the spin susceptibility with doping.[3]

In the work of SSH there is no explicit inclusion of Coulomb interactions between electrons in the model band

which is evidently a correct starting assumption for trans-$(CH)_x$. Here we will consider a complementary problem. Explicitly, the model we will treat is described by the Hubbard Hamiltonian

$$H = \sum_{i\sigma} \varepsilon_o n_{i\sigma} + \sum'_{ij\sigma} V_{ij} a^{+}_{i\sigma} a_{j\sigma} + U\sum_i n_{i\uparrow} n_{i\downarrow}, \qquad (1)$$

where the sites $\{i\}$ form a 1-D chain and the number of electrons per site is taken to be one (half-filled band). The operators $a^{+}_{i\sigma}$ and $a_{i\sigma}$ are the usual creation and annihilation operators for an electron of spin σ in the Wannier state centered at the site i; $|i\sigma\rangle$. The first two terms entering the right-hand-side of Eq. 1 describe a tight-binding band where for simplicity V_{ij} will be taken as V for i,j nearest neighbors and zero otherwise. The last term includes electron-electron repulsive interactions between opposite spin electrons in the same Wannier state. Note in (1) interactions such as $U_{ij} n_{i\sigma} n_{j\sigma}$ $(i \neq j)$ etc. are neglected, an approximation which will become less satisfactory with increasing V. Also, in writing (1) no distortive terms were included.

Partial justification for neglecting the distortive (reconstructing) interactions in favor of the Coulomb interactions as in the Hubbard model or vice-versa as in the SSH model can be provided within the context of a Peierls-Hubbard model which explicitly takes into account both effects. Indeed for this model assuming a half-filled band Mertsching[4] has shown by using a mean-field like approach that it is not favorable for a composite antiferromagnetic-Peierls distorted state to exist except for the special case where the pure Peierls state and pure antiferromagnetic state are degenerate in energy. Hence, in view of these results it is reasonable depending on what regime one is operating in to explicitly neglect either the distortive or Hubbard terms. These terms can be thought of as being taken into account implicitly, however, through a renormalization of the electron-electron or electron-phonon couplings respectively.

The Hubbard Hamiltonian provides a prototype model for studying the effects of electron-electron interactions in narrow banded systems and of course is not restricted to 1-D. As such it has been applied to a wide range of physical systems such as impurity bands in crystalline semiconductors,[5] transition-metal oxides,[6] and certain charge-transfer-salts.[7]

In the next section we review a recently developed[8-11] static, binary-alloy, random-field approximation scheme for

treating the half-filled Hubbard model which includes self-consistently the possibility of magnetic ordering. We then show in Section III that it is favorable for the half-filled 1-D system to accommodate an additional charge through the formation of a soliton-like π-phase kink formed by improperly joining two semi-infinite antiferromagnetic chains. Finally in Section IV we relate the results of these studies to a 1-D reconstruction model where the electron-phonon coupling appears in the diagonal part of the effective Hamiltonian.

II. APPROXIMATION AND RESULTS FOR THE HALF-FILLED CASE

Random Binary Alloy Approximation

In the self-consistent random binary alloy approximation[9,12] the motion of a σ-spin electron in the half-filled band Hubbard model is described by the effective Hamiltonian

$$H_\sigma = \sum_{i\sigma} (\varepsilon_o + \varepsilon_{i\sigma}) n_{i\sigma} + \sum_{ij} V_{ij} a^+_{i\sigma} a_{j\sigma}, \tag{2}$$

where the potentials $\{\varepsilon_{i\sigma}\}$ are taken as random variables obeying the binary (A-B) alloy probability density

$$P(\varepsilon_{i\uparrow}\varepsilon_{i\downarrow}) = \frac{1}{2}\sum_{\alpha=A,B} \delta(\varepsilon_{i\uparrow}-\varepsilon^\alpha_\uparrow)\delta(\varepsilon_{i\downarrow}-\varepsilon^\alpha_\downarrow), \tag{3}$$

with $\varepsilon^A_\uparrow = \varepsilon^B_\downarrow = \frac{1}{2}U(1-\mu_o)$ and $\varepsilon^A_\downarrow = \varepsilon^B_\uparrow = \frac{1}{2}U(1+\mu_o)$.

The quantity μ_o is determined self-consistently from the equation

$$\mu_o = \langle \bar{n}_{i\uparrow} \rangle_{i=\mu_o} - \langle \bar{n}_{i\downarrow} \rangle_{i=\mu_o}, \tag{4}$$

where the bar denotes a quantum mechanical average and the symbol $\langle\ \rangle_{i=\mu_o}$ indicates an average over the random variables $\{\varepsilon_{i\sigma}\}$ with the exception of $\varepsilon_{i\uparrow}$ and $\varepsilon_{i\downarrow}$ which are held fixed at $U(1-\mu_o)/2$ and $U(1+\mu_o)/2$ respectively. The quantity $\tilde{\mu}_o \equiv |\mu_o|$ can be interpreted as the magnitude of a local moment. The binary-alloy approximation has been motivated within the Gaussian random fields formation of the Hubbard model.[9,12] Furthermore, at zero temperature it is exact in both the atomic ($V\to 0$) and metallic ($U/V\to 0$) limits of the model and hence interpolates between these two limits.

Magnetic Ordering

In a series of papers[8-11] the binary alloy approximation was generalized to include self-consistently the possibility of magnetic ordering. This was achieved by introducing a parameter P giving the probability of finding an A-type site which has the potentials $(\varepsilon^A_{i\uparrow}, \varepsilon^A_{i\downarrow})$ given that a nearest neighboring site is of B-type, i.e. exhibits the potentials $(\varepsilon^B_{i\uparrow}, \varepsilon^B_{i\downarrow})$. The quantity P represents a short range order parameter and is determined self-consistently by requiring that the effective free-energy be a minimum with respect to its variations. This way of introducing magnetic ordering is equivalent to a nearest-neighbor Ising coupling. Indeed in 1-D it was shown[10] that the condition $(\partial F/\partial P)_{\mu_o} = 0$ is equivalent to defining an Ising J_o as

$$J_o = \frac{1}{2}(\partial F_{el}/\partial P)_{\mu_o}, \tag{5}$$

where F_{el} is given in Ref. 10 and this result was subsequently generalized[9,11] to higher dimensions.

In order to implement the approximation scheme described above, one must have a way of calculating both the totally and partially averaged density of states of a random binary alloy exhibiting short-range correlations. This poses no problem in 1-D where exact[13] as well as accurate approximate schemes exist.[14]

Ground State Properties

For the half-filled band 1-D case it can be shown that in the ground state P = 1. Thus, the effective moment at the site j is expressible as $\mu_j = (-1)^j\tilde{\mu}_o$ and the set of moments $\{\mu_j\}$ arrange themselves antiferromagnetically. When P = 1 the present scheme reduces to a mean-field-like approximation with perfect magnetic ordering provided $\mu_o \neq 0$. Furthermore the self-consistency condition (4) becomes equivalent to determining μ_o by requiring $[\partial E(\mu;P=1)/\partial\mu]_{\mu=\mu_o} = 0$, where E is the total energy of the system. The energy $E(\mu)$ is obtained as a function of μ by taking $\varepsilon^A_\uparrow = U(1-\mu)/2$ etc. If more than one stationary point of $E(\mu)$ is found one should pick the one corresponding to the lowest energy.

For P = 1 and $U \neq 0$ it is easily seen that $E(\mu;P=1)$ is symmetric around $\mu = 0$ and exhibits two minima at $\mu = \pm\tilde{\mu}_o \neq 0$. These two minima are degenerate in energy and correspond to the two stable antiferromagnetic arrangements

that can be drawn. Note that one pattern can be simply transformed to the other by shifting it one site along the chain. Also note that the existence of this double minimum behavior in $E(\mu;P=1)$ for any U/V depends on the 1-D nature of the system. In higher dimensional alternate lattice systems there exists[15] a $U_c>0$ such that when $U<U_c$ there is only a single minimum in $E(\mu;P=1)$ occurring at $\tilde{\mu}_o = 0$. Hence in higher dimensions, unlike 1-D, the antiferromagnetic ground state is not always favored.

Due to the perfect periodicity of the ground state various quantities of interest can be calculated explicitly.[10] Results, within the static approximation, for the magnitude of the effective local moment, $\tilde{\mu}_o$, and the ground state energy, E_G, are shown in Figs. 1 and 2 respectively.

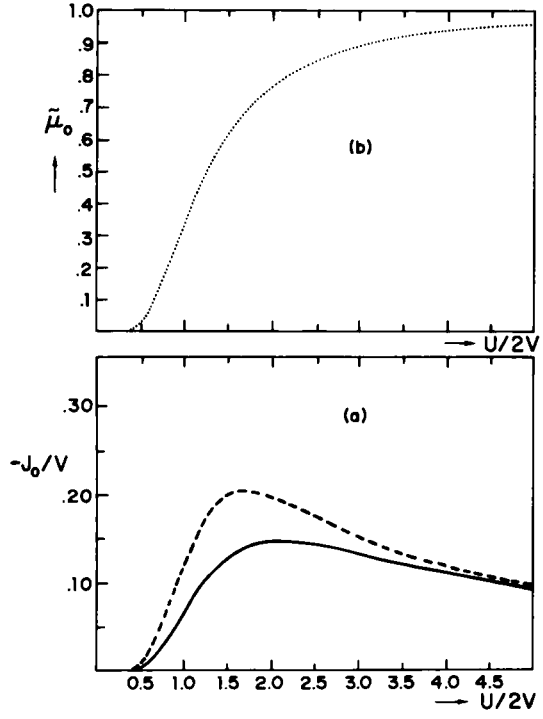

FIGURE 1 (a) Magnitude of the zero-temperature magnetic coupling J_o vs U/2V (dashed line) in the static approximation. The solid line represents the same quantity modified by dynamical processes, (b) Magnitude of the zero temperature moment vs. U/2V in the static approximation.

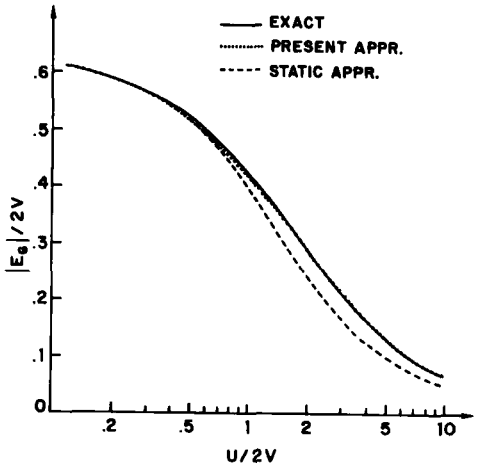

FIGURE 2 Ground state energy per electron for the half-filled 1-D Hubbard model. The exact results according to Ref. 17.

As $U/V \to \infty$ $\tilde{\mu}_o \to 1$ while as $U/V \to 0$, $\tilde{\mu}_o \to 0$. This reduction of $\tilde{\mu}_o$ with decreasing U/V is due to a motional narrowing effect. The density of states (DOS) exhibits a gap, $E_G(=U\tilde{\mu}_o)$, with the fermi-level lying at the center of this gap.

One can show that J_o defined by Eq. (5) approaches $-\Delta\tilde{H}/2m$ as $T \to 0$ where $\Delta\tilde{H}$ represents the change in energy of the system when m local moments are turned over. We plot $-J_o$ in Fig. 1a obtained by improperly joining two semi-infinite antiferromagnetic chains. As $U/V \to \infty$, $J_o \to -V^2/U$, which is the standard result from 2nd order perturbation theory. As $U/V \to 0$, $J_o \to 0^-$ in an exponential way. In order for J_o to be well defined it is necessary that $-J_o$ given by $\Delta\tilde{H}/2m$ be independent of m. This question has been studied in detail by Economou and Mihas[16] and will not be treated here. Suffice it to say that when the static approximation is relaxed as described below this condition, although not exactly, is approximately obeyed.

Finite Temperatures

The finite temperature behavior of the half-filled band 1-D Hubbard model within the present scheme is complicated and will not be extensively discussed. Rather we summarize

some of the results pertinent to our present development and refer the reader to Ref. 10 for further details.

At any finite temperature, T, P is no longer equal to one and approaches .5 for high $k_B T/V$ (k_B is Boltzmann's constant). For very low $k_B T/V$ the perfect magnetic order in the ground state is disrupted by occasional defects. The lowest lying in energy of these defects results from the improper joining of two semi-infinite antiferromagnetic chains. The next lowest defect is formed by simply changing $\mu_o \rightarrow -\mu_o$ at one site, etc. Such defects produce occupied and unoccupied bound states in the Hubbard gap and the resulting complex entity has been termed[8] a magnetic polaron (MP). In the phase-kink language the two aforementioned defects correspond to the π and 2π kinks respectively. Note, as we shall see below, the electronic structure of the π-kink defect here is very different from that of the corresponding defect discussed by SSH.

With increasing T(decreasing P) the concentration of MP levels in the gap increases and the bound states broaden into impurity bands which eventually merge with the main subbands. Simultaneously, $\tilde{\mu}_o$ will decrease and this together with the decrease in P can lead to a metal-nonmetal transition (not a phase transition) depending on the value of U/V.

Dynamic Processes

The static approximation neglects the time dependence of the random potential; however, this potential actually changes in time. Within the present approximate framework this means that the configuration of A and B type sites over the lattice is not frozen but changes in time so that an A-site becomes a B-type and vice-versa. As pointed out by Economou and White such dynamic processes (DP) can be incorporated *a posteriori* by adding to the self-consistent static random Hamiltonian a term of the form $\Delta H = \sum_{ij} t_{ij} \sigma_i^+ \sigma_j^-$ where σ_i^+ is the usual Pauli matrix which changes a down local moment to at the site i to up or equivalently a B site to an A site. This addition will transform the Ising part of the self-consistent Hamiltonian into an isotropic Heisenberg one, where in obtaining this result the isotropic nature of the Hubbard model has been used which requires that $t_{ij} = +2J_{ij}$. Thus the time dependent nature of the problem is equivalent to changing the magnetic excitations from Ising-like to Heisenberg-like. This replacement of the Ising by the Heisenberg Hamiltonian will modify such quantities as J_o and the ground state energy

etc. which were determined self-consistently by employing an Ising-type picture. Furthermore, the perfect long-range-order of the ground state will now be reduced to short-range-order. The renormalization of J_o, E_G etc. can be approximately determined using methods described elsewhere.[9,10] The renormalization of J is most significant around U/2V = 1.5 as shown in Fig. 1 while E_G, now calculated taking into account DP as described above, is found to be in excellent agreement for the exact results of Lieb and Wu[17] for all U/V (see Fig. 2). The MP appearing for T > 0 will not be localized any more but rather propagate in the system. Such propagation arises because of ΔH and is hence characterized by a transfer matrix element 2J. We will return to this question below.

III. SOLITON-LIKE DOPING

So far within our approximate approach we have reviewed some of the properties of the half-filled Hubbard chain. In what follows we consider within the present picture the effects at zero T of adding an electron or hole to the system. For definiteness we treat the case of an added electron noting in passing that similar results are obtained in the case of an added hole.

Let us first consider the consequences of an added electron within the framework of the static approximation. If we suppose that P maintains its half-filled value of one then the energy required to add this electron when referenced to the half-filled case is simply $\Delta E_1 \equiv x = U\tilde{\mu}_o/2$ where $\tilde{\mu}_o$ in terms of U/V is displayed in Fig. 1 of the text and given by Eq. 3 of Ref. 10. On the other hand one can suppose that this added electron induces a π-kink soliton-like MP. Due to the presence of this π-kink defect the total DOS of the system is changed by an amount $\sum_{i\sigma} \delta\rho_{i\sigma}$. The quantity $\sum_{\sigma i} \delta\rho_{i\sigma}$ can be calculated explicitly using Green function techniques.[10] In this way it is found that two states are removed from both the occupied and unoccupied Hubbard subbands. Assuming, without loss of generality that $\varepsilon_o = -U/2$, two of these states appear symmetrically about the center of the Hubbard gap at $E_p^{\mp} = \pm[(V^2+x^2)^{\frac{1}{2}}-V]$. The remaining two states also appear symmetrically around midgap but now outside the Hubbard subbands at $\pm[(V^2+x^2)^{\frac{1}{2}}+V]$. The additional charge in the system results in occupation in the upper isolated state in the Hubbard gap. For this case the change in energy of the system measured with respect to the half-filled case is

$$\Delta E_2 = \sum_{i\sigma} \int_{-\infty}^{E_p^+} E\delta\rho_{i\sigma} dE = -2J_o + \sqrt{V^2+x^2} - V. \qquad (6)$$

If $\Delta E_1 - \Delta E_2 \equiv \Delta > 0$ the system will accommodate the additional charge through an induced π-kink MP. A plot of Δ vs. U/V is displayed in Fig. 3 and we see this inequality is in fact obeyed for all finite U/V.

Within the static approximation the MP level which becomes occupied is localized in the Hubbard gap and hence the system would be insulating. However, as mentioned in Section II relaxing the static approximation allows such MPs to propagate. Since this propagation is described by a hopping matrix +2J, the effective mass of this quasiparticle, m*, is such that $m^* \propto 1/|J_o|$. Note, relaxing the static approximation also renormalizes J_o so that the energy required to create the π-kink MP is slightly smaller than that obtained from Eq. 6 while m* will be slightly larger than that found by using J_o.

The above analysis indicates that it is favorable for doping of the isolated infinite half-filled chain to initially proceed through the formation of π-kink defects

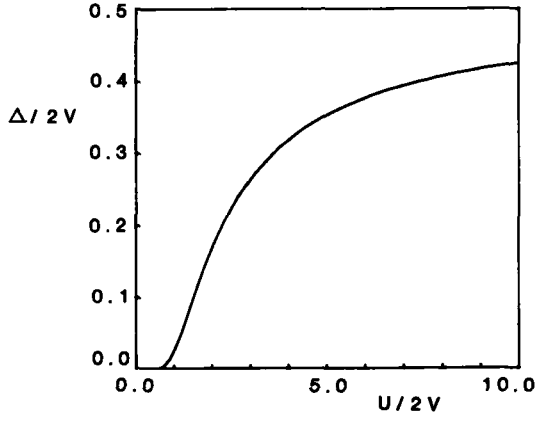

FIGURE 3 The difference within the static approximation in energy between introducing an added charge at the edge of the upper Hubbard band and accommodating this charge by formation of a π-kink MP.

However, in an actual physical system this may not always be the case. This follows because in such a system it is expected that the two minima in the $E(\mu)$ (occurring in the ideal case at $\mu = \pm\tilde{\mu}_\rho$) would probably not be strictly degenerate due to interchain or other external interactions, finite length effects etc. This lifting of the degeneracy due to constraints would at the very least give rise to barriers to the formation of π-kink MPs. Such is the case since for these quasi-particles to be at all defined requires flipping of fairly large regions of the chain. In the extreme the removal of the degeneracy could prohibit dopant induced π-kinks altogether, favoring the less global (in terms of boundary conditions) 2π-kinks.

Considerations along the above lines lead us to the following qualitative picture. If the dopant concentration is such that (i) the average separation between dopants is distant enough such that each π-kink associated with a dopant molecule interacts only weakly with a neighboring dopant induced π-kink and (ii) not so low that flipping the chain in the region intervening between two dopants costs too much energy, then the π-kink doping/compensation picture is applicable. On the other hand if (ii) is strongly violated the dopants are expected to induce 2π-kinks in contrast to π-kinks. Situations intermediate between the π-2π extremes can be envisioned. For example, the system may favor 2π-kink doping but because the degeneracy between the two arrangements is only weakly removed this 2π-kink could have a resolvable internal structure in terms of two π-kinks. One of these would be charged and the other not. These two kinks would be bound together with an interaction energy which could increase with distances. These and related points have been developed in some detail by White and Brant[18] for the corresponding problem in trans-$(CH)_x$. As an aside it is noteworthy that some of the same effects which resist doping induced π-kinks could generate them in the undoped material.

IV. CONCLUDING REMARKS

Here we have discussed the half-filled 1-D Hubbard model and the MP defects that can be induced in this system through light doping. It should be clear from the above that these soliton-like defects are distinctly different from those discussed by SSH. On the other hand, within the static approximation the present analyses can be related to a problem involving electron-distortive interactions. More explicitly, if one considers the half-filled band

Holstein-Anderson type model described by the Hamiltonian

$$H = \sum_{i\sigma} (\varepsilon_o + \lambda X_i) n_{i\sigma} + \sum_{ij\sigma} V_{ij} a^+_{i\sigma} a_{j\sigma} + \frac{1}{2} C \sum_i X_i^2 + \sum_i P_i^2/2M \qquad (7)$$

a close mathematical analogy can be drawn. This model within a mean-field-like approach exhibits a charge-density-wave ground state. In this system π-kink excitations can occur which when considered in well separated pairs lead to an effective DOS mathematically similar to what we have obtained for π-kink MPs in the static approach to the Hubbard model. The physical interpretation of these results however are of course different and further details of this analysis will be presented elsewhere.

The Hamiltonian (7) differs from the Hamiltonian of SSH in that it leads to an effective electronic Hamiltonian with the distortion terms occurring in the diagonal part of this Hamiltonian as opposed to the off-diagonal part. Physically such a model as (7) arises when there are present some internal degrees of freedom which principally lead to shifts in the site orbitals and not the hopping matrix elements. I know of no concrete example of this behavior in 1-D; however, in 2-Ds a very good example is provided by models that have been used to describe the 2x1 reconstruction of freshly cleaved Si <111> surfaces.[15]

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