Magnetism and Phase Separation in Polymeric Hubbard Chains

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We study a class of one-dimensional chains whose topology leads to flatbands in the electronic spectrum. Using the Hubbard model, we find that these materials should exhibit ferrimagnetic ordering for a half-filled band, in agreement with a theorem by Lieb. Away from half filling the system displays a very rich magnetic phase diagram. Possible experimental realizations are suggested.

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The possibility that the single-orbital version of the Hubbard model might exhibit, under any circumstance, a ferromagnetic ground state has been a longstanding highly controversial issue [1]. Recently, Lieb presented [2] the first proven example of unsaturated itinerant-electron ferromagnetism based on the repulsive Hubbard model, thus taking a significant step forward. He showed that a bipartite lattice at *half-filled* band has total ground-state spin $2S_T = ||B| - |A||$, where $|B|$ ($|A|$) is the number of sites in the B (A) sublattice. The theorem holds in all dimensions without even the need of a periodic structure. Extensions of these ideas have been put forward by Mielke and Tasaki [3], who showed that such lattices, whether bipartite or not, might, in fact, exhibit a multiband structure containing a flatband, i.e., a highly (bulk) degenerate single-electron state. The mechanism for ferromagnetism works most effectively when this flatband is nearly "saturated" but becomes ineffective when the electron filling factor is too small. Specific examples of two- and three-dimensional lattices have been given on which ferromagnetism is sustained in a finite range of electron filling factor. Notice that on "symmetric" bipartite lattices having $|A| = |B|$, ferromagnetism might only be found *away* from half filling. In this case the so-called Nagoaka theorem [4] asserts that the ground state on square and cubic finite lattices with one hole in a half-filled band is a *fully aligned* ferromagnetic state (Nagoaka state) in the infinite on-site Hubbard-Coulomb repulsion (U) limit. Several studies and attempts to verify and to extend Nagoaka's theorem to finite values of hole density, Coulomb repulsion, and temperature have recently been reported [5].

In this work we study the very interesting possibility of the existence of unsaturated ferromagnetic ground states in complex polymeric organic and inorganic chains. Two of the possible structures leading to highly degenerate one-particle states are depicted in Figs. 1(a) and 1(b): The model polymer of Fig. 1(a) is a well-known structure in inorganic chemistry [6], where M and L represent, respectively, a metal atom and a suitable ligand, and Fig. 1(b) shows one example of an organic conjugated polymer designed to possess aligned spins due to the presence of molecular radicals R^*.

Organic conjugated polymers have been extensively studied since the discovery that some of these materials undergo a dramatic change in conductivity on doping [7]. However, very few examples of organic ferromagnets have been reported in the literature [8,9]. The synthesis and characterization of metal-free poly(m-aniline), a conjugated polymer that reacts with acids (proton doping), have recently been reported [8]. ESR and magnetic susceptibility measurements on this material are consistent with ferrimagnetic interaction between unpaired π electrons.

We focus our attention on the bipartite lozenge chain shown in Fig. 1(c) on which the unit cell contains two sublattices A and B, the sites of A being connected by hopping t to four sites of B, whereas the sites of B have only two nearest-neighbor sites of A. On-site Hubbard-Coulomb repulsion U is assumed on every site.

The tight-binding (TB) energy spectrum is composed of two distinct level structures: The first one has nondegenerate levels at $\varepsilon = \pm 2\sqrt{2}t$ and twofold degenerate levels at $\varepsilon = \pm 2\sqrt{2}t\cos(3\nu\pi/N)$, $\nu = 1, 2, 3 \ldots, (N/3 - 1)/2$, for N odd, and an extra twofold degenerate level at $\varepsilon = 0$ ($\nu = N/6$), for N even. The second level structure is an $(N/3)$-fold degenerate

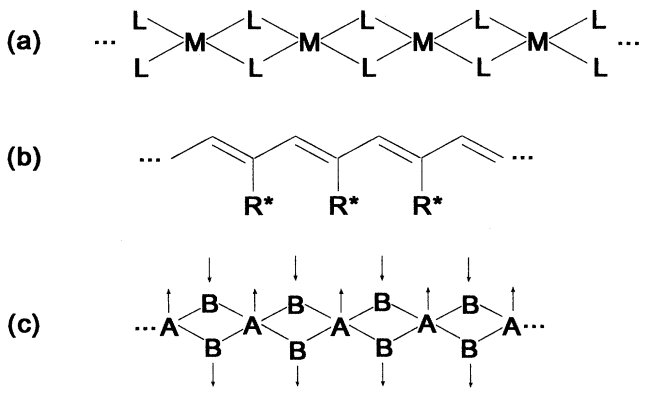

FIG. 1. (a) Bipartite inorganic metal (M)–ligand (L) chain; (b) substituted polyacetylene with lateral radical R^*; (c) bipartite AB_2 chain and spin configuration for a half-filled band.

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level at $\varepsilon = 0$. In the thermodynamic limit, the resulting density of states (DOS) for one spin species is given by $\rho(\varepsilon) = \frac{1}{3}\delta(\varepsilon) + \frac{2}{3}N\sum_k \delta(\varepsilon - \varepsilon_k)$, where $\varepsilon_k = -2\sqrt{2}t\cos ka$, $ka = (0, \pi)$, and a is the lattice parameter. We thus easily obtain $\rho(\varepsilon) = \frac{1}{3}\delta(\varepsilon) + (2/3\pi)\,[1/(8t^2 - \varepsilon^2)^{1/2}]$. It is clear that the presence of the "off" sites, added to a linear chain in order to build the bipartite lattice structure of Fig. 1(c), leads to the formation of a highly degenerate energy level at the center of the band [see Fig. 2(a)], containing 1/3 of the levels.

In the Hartree-Fock (HF) approximation, the Hubbard Hamiltonian is written as

$$H = -t\sum_{i,\sigma}\{c^{\dagger}_{i,\sigma}c_{i+1,\sigma} + c^{\dagger}_{i+1,\sigma}c_{i,\sigma}\} + U\sum_{i,\sigma} n_{i,-\sigma}c^{\dagger}_{i,\sigma}c_{i,\sigma}\,, \tag{1}$$

where $c^{\dagger}_{i,\sigma}$ ($c_{i,\sigma}$) are electron operators and $n_{i,\sigma}$ is the mean electron density of spin σ at site i. Periodic boundary conditions are applied, resulting in the following band structure:

$$\varepsilon_{\pm}(k,\sigma) = (U/2t)\,(n_{A,-\sigma} + n_{B,-\sigma}) \pm \sqrt{\Delta^2_{-\sigma} + 8\cos^2(ka/2)}\,, \tag{2}$$

$$\varepsilon_{\rm loc}(k,\sigma) = (U/t)n_{B,-\sigma}\,, \tag{3}$$

$$\Delta_{\sigma} = (U/2t)\,(n_{A,\sigma} - n_{B,\sigma})\,. \tag{4}$$

In the above expressions, the subscripts A and B refer to the corresponding atoms of Fig. 1(c). The dispersionless band $\varepsilon_{\rm loc}(k,\sigma)$ arises from the topology of this polymer and corresponds to states localized on B atoms *only*. Equations for the densities $n_{A,\sigma}$ and $n_{B,\sigma}$ are found by application of the standard variational procedure and are solved self-consistently. For electronic densities such that the flatband is occupied, the equation for $n_{B,\sigma}$ is increased by a factor of $f/2$, where f is the fraction of occupied states of the appropriate spin. The total energy per unit cell can be evaluated by

$$E = (a/\pi)\sum_{\sigma}\int^{k_F}\varepsilon(k,\sigma)dk - U\sum_{i\,\in\,\text{cell}} n_{i,\sigma}n_{i,-\sigma}\,. \tag{5}$$

At half filling, the HF DOS is shown in Fig. 2(b) for $U = 2t$. The system is insulating, the gap given by $\Delta(U) = \varepsilon_+(\pi/a,\uparrow) - \varepsilon_-(\pi/a,\downarrow)$ (>0 for *any* $U > 0$); the fulfilled localized level lies on the top of the $\varepsilon_-(k,\uparrow)$ band, i.e., $\varepsilon_{\rm loc}(k,\uparrow) = \varepsilon_-(\pi/a,\uparrow)$. We then find $2S_A = n_{A\uparrow} - n_{A\downarrow} = -0.36$ and $2S_B = n_{B\uparrow} - n_{B\downarrow} = 0.68$, and thus an *average* total spin per unit cell $2S = 4S_B - |2S_A| = 1$, in fact, valid for *any* $U > 0$, as required by Lieb's theorem. A salient feature here is that the spin magnitudes on sites A and B are unequal, indicating a quit general *ferrimagnetic* ordering.

We account for electron correlations by means of the exact diagonalization (ED) of finite clusters and by Monte Carlo (MC) simulation using periodic boundary conditions (PBC). The spatial ordering is studied by calculating the longitudinal spin correlation functions $L_\delta = (1/N)\sum_i \langle S^s_i S^z_{i+\delta}\rangle$, where $S^z_i + \frac{1}{2}(n_{i\uparrow} - n_{i\downarrow})$ and δ defines the order of neighborhood of the thermodynamic correlation function. Our MC data are shown in Fig. 3 for a cluster of three unit cells using PBC, $U = 2t$, and half-filled band. At the lowest temperature one can reach, the *local* moment L_0 is already about 70% of the value for a completely localized spin, $L_0 = 0.25$. This result is consistent with the estimated value of $L_0 \approx 0.2$ at $T = 0$ found by ED of a cluster of two unit cells. Note also that the system sustains some degree of short-range magnetic correlations up to temperatures of about $kT \approx 5.0t$. As $L_1 < 0$, $L_2 > 0$, and $L_3 < 0$ for all temperatures investigated, we conclude that in the ground state each sublattice is, on the average, ferromagnetically

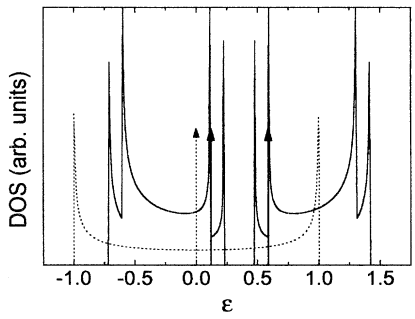

FIG. 2. Densities of states (DOS) for the AB_2 chain: (a) TB (dotted lines) and (b) HF (full lines) for $U = 2t$ at half filling. Vertical arrows indicate localized bands (energies in units of $2\sqrt{2}t$).

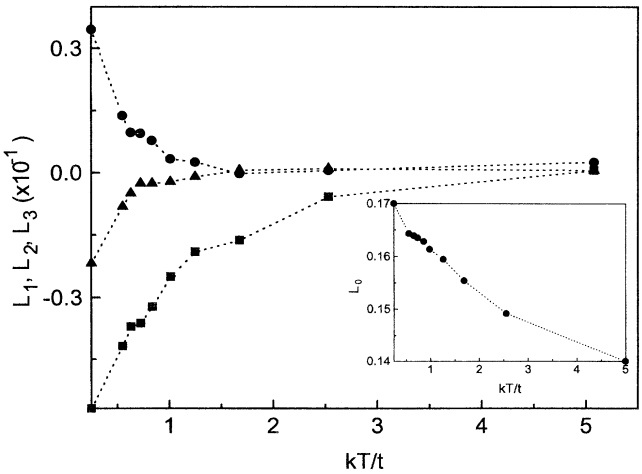

FIG. 3. Monte Carlo data for the temperature dependence of the first (L_1,■), second (L_2,●), and third (L_3,▲) neighbor correlation functions. The inset shows the average site local moment.

ordered but in opposite directions, thus confirming the ferrimagnetic ordering found in the HF approximation.

We now turn to investigate the rich and complex behavior of the system away from half filling and for the three limiting cases of interest, namely, $U \ll t$, $U \sim t$, and $U \gg t$. The HF predictions are as follows. For $U/t \to 0$ (TB limit) the HF dispersive bands are degenerate, and we find $n_{A\uparrow} = n_{A\downarrow} \cong k_F/2\pi$, $n_{B\uparrow} \cong k_F/4\pi$, and $n_{B\downarrow} \cong k_F/4\pi + f/2$, resulting in $2S \cong f$, where f is the fraction of occupied orbital states in the $\varepsilon_{\rm loc}(k,\uparrow)$ level. The total spin per unit cell is nonzero for $2/3 < n \leq 1$, as shown by the full straight line in Fig. 4(a). Figure 4(b) shows the TB energy per unit cell ($U \to 0$) and evidences the *flat* portion for $2/3 \leq n \leq 1$, corresponding to states of zero energy on the $\varepsilon_{\rm loc}(k,\uparrow)$ level. It suggests that for $2/3 < n < 1$ the system phase separates into a rich ferrimagnetic region, characterized by a *completely filled* $\varepsilon_{\rm loc}(k,\uparrow)$ level, and a hole-rich paramagnetic region with an *empty* $\varepsilon_{\rm loc}(k,\uparrow)$ level.

On the other hand, for $U = 2t$, say, holes first appear in the dispersive band $\varepsilon_-(k,\downarrow)$, causing a major decrease of the local spin on site A and thus an increase of the total spin per unit cell, as shown in Fig. 4(a). This spin increase persists until holes appear in the $\varepsilon_{\rm loc}(k,\uparrow)$ level. For values of n leading to a partially filled $\varepsilon_{\rm loc}(k,\uparrow)$ level the charge compressibility, $\kappa^{-1} = n^2\,\partial\mu/\partial n$, is negative, where μ is the chemical potential whose n dependence is displayed in Fig. 4(b). It also predicts phase separation, as confirmed by the Maxwell construction shown in Fig. 5, devised to fix the wrong upward convexity of the energy exhibited in Fig. 5(b). It should be noticed, however, that now there is a *finite* range of doping, near the half-filled band, for which *itinerant* ferrimagnetism persists in the system before phase separation takes place for higher values of doping.

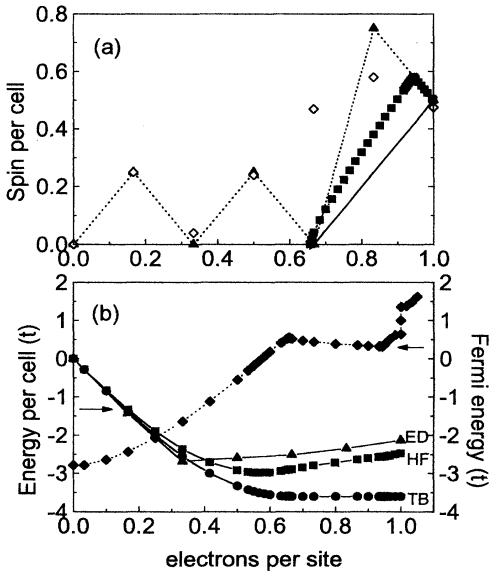

FIG. 4. (a) Average spin per unit cell [TB results (—), HF (■), and exact diagonalization (ED) (▲)], and (b) total energies per unit cell (left axis) and Fermi energy (right axis), of the AB_2 chain, for $U = 2t$, as a function of site electronic density. Local spin per cell from ED indicated by (◊). Energies in units of t.

Finally, we study the limit $U \gg t$ for which double occupancy of sites is avoided. In this case care must be taken for $n \cong 1$, since now there are two competing mechanisms: the one leading to antiferromagnetic ordering between sublattices A and B (and also to Lieb's theorem at $n = 1$) and that of Nagaoka forcing the system to fully polarize. If the former mechanism dominates, we find from Eqs. (2) and (4) the simple band structure $\varepsilon_-(k,\uparrow) = \varepsilon_-(k,\downarrow) \cong -8(t^2/U)\cos^2 ka/2$, $\varepsilon_+(k,\uparrow) = \varepsilon_+(k,\downarrow) \cong U + 8(t^2/U)\cos^2 ka/2$, and $\varepsilon_{\rm loc}(k,\uparrow) = \varepsilon_{\rm loc}(k,\downarrow) - U = 0$. Similarly to the case $U/t \to 0$, the dispersive bands are spin degenerate, but, in contrast, a strong narrowing effect occurs together with the expected Hubbard splitting. We also have $n_{A\uparrow} = n_{B\downarrow} \cong 0$, $n_{A\downarrow} \cong k_F/\pi$, $n_{B\uparrow} \cong k_F/2\pi + f/2$, and $2S = f$, thus resulting in phase separation for $2/3 < n < 1$ because the $\varepsilon_{\rm loc}(k,\uparrow)$ level is partially filled. If, on the other hand, Nagaoka's mechanism dominates, the band structure is TB-like with strong spin splitting U. For $\alpha(1 - n) > t/U$, where α is of the order of unity, we expect full polarization, though the argument of Nagaoka, and extensions of it, cannot ensure a unique ground state (see Tasaki, Ref. [5]).

In Fig. 6 are plotted HF data of a site-to-site simulation for a chain of 150 sites using PBC and $U = 10^3 t$. Indeed, we find that the *average* total spin per cell is saturated down to $n = 0$. The n dependence of the energy exhibits a quite symmetric curve, except very near $n = 1$ where Lieb's theorem is valid. Both features characterize the behavior of a collection of noninteracting TB spinless fermions. Notice that for $1/3 < n < 2/3$ the energy curve is flat, suggesting phase separation for doping in this interval. Moreover, for $n < 1/3$ and $2/3 < n < 1$ we find very small (of the order of 0.3 %–0.7 %) modulation of the unit-cell spin distribution on top of the average fully polarized ferromagnetic background.

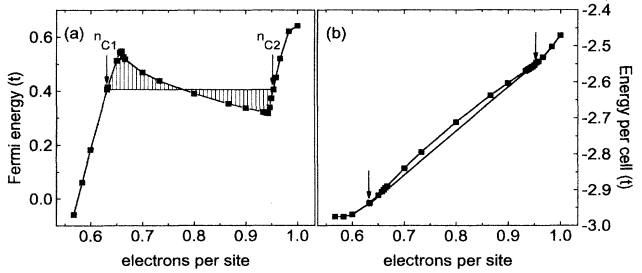

FIG. 5. Maxwell construction of HF results for $U = 2t$: (a) Fermi energy, and (b) total energy. Densities n_{c1} and n_{c2} define the range in which phase separation is predicted.

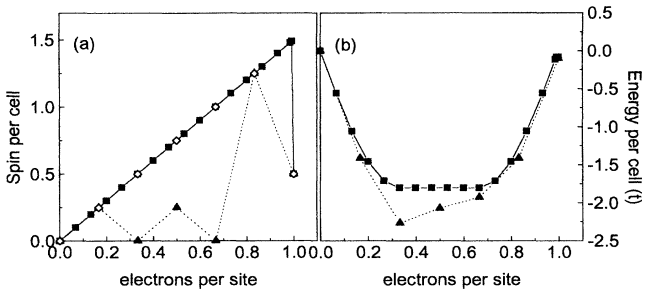

FIG. 6. (a) Average spin per unit cell versus electronic density: HF results for $U = 10^3 t$ (■) and ED for $U = 10^2 t$ (▲). Local spin per cell from ED indicated by (◊). (b) Total energy per unit cell from HF calculation (■) and ED (▲).

In Fig. 4 we compare the HF results with those from ED of a cluster containing two unit cells and $U = 2t$. The n dependence of the total spin and energy per unit cell follows the same trends found in HF approximation. In particular, for $n < 2/3$ the total spin has the minimum possible value. We also calculate the *local* value of the spin per unit cell (notice that quantum fluctuation effects are present) and find that its n dependence suggests that for $n < n_{c2}$ the unit cells are *antiferromagnetically* coupled, leading to a singlet ($S = 0$) ground state. In the HF approximation this configuration has energy only 1% higher than that with unit cells ferromagnetically coupled. For such a small system we find no indication of phase separation instabilities for $U \sim t$.

For $U = 100t$, we see from Fig. 6 that Nagaoka's condition is satisfied for one hole and, furthermore, that each unit cell is *fully polarized* down to $n = 0$. For $n < n_{c2}$ the spin arrangement is again such as to attain the minimum total spin value. In the HF approximation this configuration has energy about 20% higher than that with full polarization. The energy curve has similar trends, except in the region where HF predicts phase separation. For higher values of U we find numerical instabilities for $1/3 < n < 2/3$, which might indicate a region of phase separation. However, we cannot exclude the possibility that in the bulk system the formation of a more complex spiral spin density wave is realized and that, in the high doping regime, the destruction of long-range order occurs.

In summary, we have studied the magnetic properties of a class of one-dimensional Hubbard chains whose topology produces flatbands in the electronic spectrum. It has been found that this class of materials should exhibit ferrimagnetic order at half filling, for any $U > 0$, in agreement with Lieb's theorem [2]. The above reported results also point to the possibility of producing metal-free, fully organic polymers having a rich magnetic behavior. This could be experimentally monitored by electrochemical techniques, or by fixing pH conditions, in the same way that conductivity can be controlled in conventional conjugated polymers.

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