Gate-induced band ferromagnetism in an organic polymer

Ryotaro Arita, Yuji Suwa1, Kazuhiko Kuroki2, and Hideo Aoki
Department of Physics, University of Tokyo, Hongo, Tokyo 113-0033, Japan
1 Advanced Research Laboratory, Hitachi Ltd., Higashi Kogakubo, Kokubunji, Tokyo 185-8601, Japan
2 Department of Applied Physics and Chemistry, University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

We propose that a chain of five-membered rings (polyaminotriazole) should be ferromagnetic with an appropriate doping that is envisaged to be feasible with an FET structure. The ferromagnetism is confirmed by a spin density functional calculation, which also shows that ferromagnetism survives the Peierls instability. We explain the magnetism in terms of Mielke and Tasaki’s flat-band ferromagnetism with the Hubbard model. This opens a new possibility of band ferromagnetism in purely organic polymers.

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Since the discovery of conducting organic polymers, a great variety of studies have been performed to pave a new way to further employ polymers or oligomers in realizing various functions, such as field-effect transistors (FETs) or electroluminescent diodes. This is most recently highlighted by a series of works by Batlogg and coworkers, where they have demonstrated that some molecular crystals (anthracene etc) and polymers (polythiophene) can not only be metallized, but even exhibit superconductivity.

If a gate-induced superconducting plastic is possible, a gate-induced ferromagnetic plastic is of no less interests. Ferromagnetism, usually a feature of d or f electron systems, taking place in π electron systems has indeed been a theoretical and experimental challenge, for which an enormous amount of studies have been carried out. In particular, purely organic ferromagnets are interesting. A theoretical proposal was made by Shima and one of the present authors, where they have demonstrated that some molecular crystals (anthracene etc) and polymers (polythiophene) can not only be metallized, but even exhibit superconductivity.

Here we propose a novel possibility for a band ferromagnetism in a purely organic polymer that realizes another class of flat-band ferromagnetism due to Mielke and Tasaki mechanism. We first find that a chain of five-membered rings with a right choice of the functional group (polyaminotriazole) has a flat band. When this band is made half-filled, where the doping is envisaged to be realized in an FET structure, we then show that the ground state is ferromagnetic with a spin density functional calculation, which also shows that the magnetism survives the Peierls instability. We finally confirm that this really has to do with the Mielke-Tasaki mechanism by mapping the π-orbital system to a tight-binding model with the Hubbard repulsion. This way we end up with a gate-induced ferromagnetic plastic.

The problem of ferromagnetism in the Hubbard model, despite a long history since the 1960s, is still some way from a full understanding. One sensible way to study the problem is to take some characteristic situation where ferromagnetism may be rigorously proved. In fact, Mielke and independently Tasaki have proposed some classes of models where a flat band exists at the bottom, and have proved rigorously for the Hubbard model that the ground state is fully spin-polarized when the flat band is half-filled. When the flat band lies in between dispersive bands, the rigorous proof becomes inapplicable, but ferromagnetism is still expected when what is called the local connectivity condition for the basis vectors in the flat band is satisfied. This amounts to a condition that adjacent “Wannier” orbitals have to overlap, despite the flat dispersion, no matter how they are combined to minimize the orbit size, which is why spins tend to align due to Pauli’s principle. The case of a middle flat-band is actually studied in the context of a model atomic quantum wire, where the ferromagnetism is shown to be realized unless the repulsive interaction is below a critical value.

Mielke-Tasaki flat bands are usually constructed from interferences between nearest-neighbor and second neighbor transfers, which requires special lattice structures especially in spatial dimensions greater than two. On the other hand, in quasi-one-dimensional chains we can conceive lattices having flat bands relatively easily, since it is easier to make Wannier orbitals which satisfy the connectivity condition in a chain than in a network. This is why we first look for some organic polymers. Although we will have to consider weak three-dimensional couplings to estimate the actual Tc, the possibility of band ferromagnetism in organic polymers should be an intriguing avenue to explore. Here we propose that one such system has a flat band. We then show from both a band structure calculation and an exact diagonalization for the Hubbard model that the system should be ferromagnetic when the band is made half-filled with
a gate-induced doping in an FET (field-effect transistor) structure recently developed by Batlogg et al. [5,6].

We first note that polymers comprising five-membered rings should be promising. This is because we find it empirically easier to realize flat bands in chains of odd-membered rings. Intuitively, odd-membered rings incorporate frustrations for electron transfers, while even-membered (i.e., bipartite) rings have an obvious disadvantage of a tendency toward antiferromagnetism when the electron-electron repulsion is turned on, which should compete with ferromagnetism. The tight-binding model on the connected five-membered rings has indeed dispersionless bands in appropriate, realistic conditions, where the eigenstate on the flat band indeed satisfies the local connectivity condition (i.e., overlapping orbitals, see Fig. 1).

So we start with a search for the case of flat bands by scanning various five-membered polymers, i.e., polypyrrole, polythiophene, polytriazole, polyaminotriazole, etc. The band structure is obtained with first principles calculations within the framework of the generalized gradient approximation based on the density functional theory (which we call GGA-DFT). [16] We adopt the exchange-correlation functional introduced by Perdew, Burke and Wang [16] and ultra-soft pseudo-potentials [17,18] in a separable form. The wave functions are expanded by plane waves up to a cut-off energy of 20.25Ry. As for the unit cell, five-membered rings usually alternate their directions in a chain (see Fig. 2), so that there are two rings in a unit cell with the Brillouin zone folded. We take a repeated-chain model along directions perpendicular to the chain with a sufficiently large repeat distance. The atomic configuration as well as the unit cell size along the chain are optimized to minimize the ground state energy with the conjugate gradient scheme [15].

It turns out that the flat band is rather hard to realize even for five-membered chains, which is not too surprising since an odd-membered ring is by no means a sufficient condition for a flat band. However, attaching some functional group to each ring helps since this changes site energies and transfer integrals, and we have found that among the polymers investigated here polyaminotriazole (poly(4-amino 1,2,4triazole) to be precise, see inset of Fig. 2) hits the right condition. Figure 2 shows that the top valence band (with two branches due to the above-mentioned band folding) has little dispersion (∼O(0.1eV)) there.

To induce the flat-band ferromagnetism, this band has to be half-filled, while the band is fully filled when undoped. To assess the possibility of the spin polarization in hole-doped polyaminotriazole, we have carried out the GGA including the spin degrees of freedom based on the spin density functional theory (which we call GGA-SDFT). [16] We have focused on the situation where the highest valence band is hole doped to make its upper branch empty. Figure 3 shows the band structure in which we have taken a polarized state as the initial state. The optimized state remains to be polarized, where the splitting between the majority-spin and the minority-spin bands is ∼1 eV. This is the same order of the exchange splitting estimated in [24] for the atomic quantum wire.

We have to be careful when we dope the band, since one-dimensional metals are in general unstable against the Peierls distortion, where the electronic energy is lowered at the cost of the lattice distortion. So we have checked whether the energy gained due to the spin polarization overcomes the Peierls transition. The left panel of Fig. 4 is the band structure of the Peierls-distortion allowed, spin-unpolarized state obtained by the GGA-DFT. We can see that the Peierls-splitting at X is negligibly small. Physically, this should be because σ-electrons which form the backbone of the structure have a rigid enough bonding that can cope with the Peierls instability here. The total energy of the global minimum in the GGA-DFT calculation is higher than that of the polarized optimized state in the GGA-SDFT calculation by ∼400 meV.

If we allow the spatial distributions of up and down spins to be different in the GGA-SDFT starting from an initially unpolarized state, the resulting band structure has a wide gap at the Fermi level (right panel of Fig. 4), which we attribute to an antiferromagnetic gap. Although the total energy of the antiferromagnetic state is lower than that for the uniformly zero spin density (the left panel of Fig. 4), the energy is higher than that of the optimized polarized state (Fig. 1) by ∼50 meV. Thus we can conclude that the true ground state in the GGA-SDFT is the polarized state, so that we can expect that polyaminotriazole becomes, when appropriately doped, ferromagnetic at sufficiently low temperature.

Now we come to the key question of whether the ferromagnetism obtained in the band calculation can be identified as the flat-band ferromagnetism for the Hubbard model a l’a Mielke-Tasaki. To do so we have first to map the π-electron system to a tight-binding model (see the right panel of Fig. 5), with a Hamiltonian, $H_0 = -\sum_{ij,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i \epsilon_i n_i$ in the standard notation. We have estimated the values of transfer integrals by first identifying π bands, then characterizing the wave functions as bonding or anti-bonding at Brillouin zone center and edges. The site energies are estimated from the energy levels of isolated atoms. The obtained figures are: $t_{\text{CC}} \simeq t_{\text{CN}} \simeq t_{\text{t}} = 2.5$ eV, $t_{\text{NN}} = 3 \sim 4$ eV, $\epsilon_o \simeq \epsilon_1 = -1 \sim -2$ eV. The band structure for this tight-binding model, depicted in the left panel of Fig. 5, indeed reproduces the features of that for π-electrons in polyaminotriazole (Fig. 4). If we turn to wave functions in Fig. 5 the wave functions at Γ on the flat band in the tight-binding model also reproduce the features of those on the flat band in the GGA-DFT result for polyaminotriazole.
We have indeed a ferromagnetic phase unless the repulsion satisfies the above equations throughout. We can draw a phase diagram by noting that a flat band arises when a set of equations,

\[
\epsilon - \epsilon_1 = (1 - \epsilon) (t_{NN}^2 - (\epsilon - \epsilon_1)^2) - t_{NN}, \\
(\epsilon - \epsilon_1 + t_{NN})/(1 - \epsilon) = -t_{NN}/(\epsilon_0 - \epsilon) - t_{NN}(\epsilon - \epsilon_0),
\]

are satisfied, where \(\epsilon\) is the eigenenergy of the flat band and \(t_{CN} = t_{CC} = t_0 (= 1\) here) is assumed for simplicity. In Fig. 7 we show the phase diagram against \(U\) and \(\epsilon_1\) obtained with an exact diagonalization calculation for a 12-site (2 unit cell) Hubbard model for \(t_0 = 2.5\) eV and various values of \(t_{NN} = 3.0 - 4.0\) eV, where \(\epsilon_0\) is chosen to satisfy the above equations throughout. We can see that we have indeed a ferromagnetic phase unless the repulsion is not too strong (i.e., \(U < U_c\) with \(U_c = 2 \sim 5\) eV). The presence of a \(U_c\) is as expected from the above discussion for a flat band lying in between dispersive ones. Our preliminary quantum Monte Carlo calculation suggests that two unit cell is sufficient to roughly determine the ferromagnetic phase boundary.

Let us finally comment on the robustness of the flat-band ferromagnetism. First, the one-electron dispersion does not have to be exactly flat to realize ferromagnetism, as confirmed from a number of studies. Also, electron-electron interactions extending beyond the on-site do not necessarily degrade the ferromagnetism. This has been shown for the extended Hubbard model where the off-site repulsion \(V\) does not degrade, or in some situation even induces, the ferromagnetism. As for the doping dependence, a numerical calculation has indicated that the ferromagnetism survives when the flat band is shifted away from the half-filling. Therefore, we may expect that the appropriate polymers as exemplified by polyaminotriazole should have ferromagnetic instabilities at low temperatures when the system is sufficiently doped in e.g. an FET geometry. In view of a quite recent finding that polythiophene may be doped with this geometry to realize superconductivity, we expect the gate-induced band ferromagnetism in purely organic polymers conceived here should be within experimental feasibility.

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FIG. 1. The connected five-membered rings, where the shading indicates a “Wannier” orbital that satisfies the local connectivity condition.

FIG. 2. The band structure (left panel) and the optimized atomic configuration (right) for the (undoped) polyaminotriazole obtained by the GGA-DFT. The solid (dotted) lines represent bands with $\pi$ ($\sigma$) character.

FIG. 3. The band structure of the doped system with an optimized structure obtained with the GGA-SDFT. The solid (dotted) lines represent the bands with $\pi$ ($\sigma$) character.

FIG. 4. Band structure for the doped system optimized by allowing the Peierls distortion in the GGA-DFT (left panel), and that for the antiferromagnetic state obtained with the GGA-SDFT (right).

FIG. 5. The energy band dispersion of the tight-binding model with $\epsilon_0 = -1.43$ eV, $\epsilon_1 = -0.5$ eV, $t_{CN} = t_{CC} = t_f = 2.5$ eV, and $t_{NN} = 3.0$ eV. To facilitate comparison with Fig. 2, we have folded the band to have a two-ring unit cell.

FIG. 6. Bloch wave functions on the flat $\pi$-electron bands in polyaminotriazole obtained with the GGA-DFT (top panels) are compared with the corresponding ones in the tight-binding model (bottom panels). Left/right panels correspond to two eigenstates on the flat band at $\Gamma$. White/black regions (or circles) represent the sign of the wavefunction, while the size of the circles the amplitude.

FIG. 7. Phase diagram for the Hubbard model on a lattice depicted in Fig. 5 against $U$ and $\epsilon_1$ for various values of $t_{NN}$ for $t_0 = 2.5$ eV. The inset shows the relation between $\epsilon_1$ and $\epsilon_0$ to realize the flat band.