Dynamic spin correlations near neutral-ionic phase transitions

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Abstract

Near the neutral-ionic phase transition in the one-dimensional extended Hubbard model with alternating potentials at half filling, the effects of alternating transfer integrals and a staggered magnetic field on the local spin excitation spectrum are studied by using the finite-temperature density-matrix renormalization-group method. In the neutral phase, the alternation increases the ionicity and lowers the spin excitation energies toward the ionic phase, while the staggered magnetic field does not modify the spectrum up to a critical field above which the system becomes ionic.

Key words: Neutral-ionic phase transition; dimerization; finite-temperature DMRG

The mixed-stack organic charge-transfer complex, TTF-CA (TTF=tetrathiafulvalene, CA=chloranil), has been known to show a discontinuous structural transition, on lowering temperature or on increasing pressure, from the regular neutral phase to the dimerized ionic phase [1]. Under high pressure, dimerization is melted in the ionic phase near the boundary [2]. Its pressure-temperature phase diagram is explained by crystallization of charge-transfer excitations with a solid-liquid-gas phase diagram. In fact, the equilibrium line can be described by the Clapeyron equation [2].

Theoretically, the dimerization is often assumed to be caused by alternating transfer integrals (spin-Peierls mechanism) [3], but a modification of the long-range Coulomb interaction strength may be more crucial [4]. Here we treat the infinitely long, quantum system at a finite temperature T by the finite-T density-matrix renormalization-group (DMRG) method. It is already pointed out that charge-transfer fluctuations are important in determining the relative stability of the neutral and ionic phases [5] and that the free energy is nonlinearly gained by alternating transfer integrals near the phase boundary [6]. Local spin excitation spectra calculated here would help clarify the nature of the neutral-ionic phase transition.

The model we use here is written as

$$\begin{aligned} H = &-\sum_{j\sigma}[t+(-1)^j(\delta/2)](c^\dagger_{j\sigma}c_{j+1\sigma}+c^\dagger_{j+1\sigma}c_{j\sigma}) \\ &-\sum_{j\sigma}(-1)^j(h/2)\mathrm{sgn}(\sigma)n_{j\sigma}+\frac{\Delta}{2}\sum_j(-1)^j n_j \\ &+U\sum_j n_{j\uparrow}n_{j\downarrow}+V\sum_j n_j n_{j+1} \ , \end{aligned} \quad (1)$$

where $c^\dagger_{j\sigma}$ creates an electron with spin σ at site j, $n_{j\sigma}=c^\dagger_{j\sigma}c_{j\sigma}$, and $n_j=\sum_\sigma n_{j\sigma}$. The nearest-neighbor transfer integral is denoted by t, the site-energy difference between the donor and acceptor molecules by Δ, the on-site repulsion strength by U, the nearest-neighbor repulsion strength by V, the degree of dimerization in the transfer integrals by δ, and the staggered magnetic field by h. The donor sites have odd j, while the acceptor sites have even j. In the finite-T DMRG procedure, m=30 states are kept. The quantum transfer matrix is decomposed with the Trotter number, M=36. The present data are thus more precise than in [6]. We use the temperature T=0.1 and the repulsion strengths, U=7.5 and V=3.5, with the energy unit t=1.0 that corresponds to about 0.2eV for TTF-CA. The electronic phase at δ=h=0 is ionic for $\Delta \leq 0.61$ and neutral for $\Delta \geq 0.62$ with present m and M.

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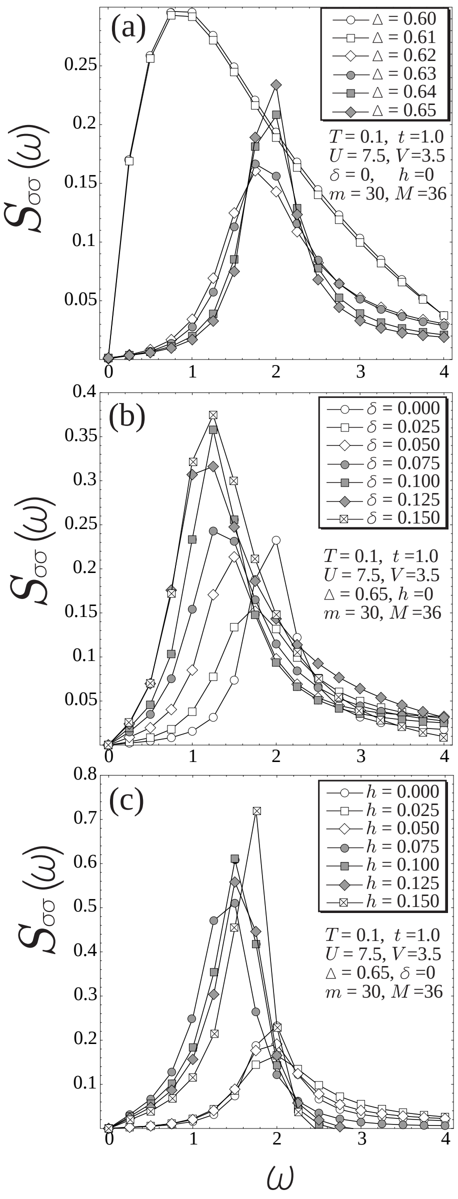

Fig. 1. Dynamic structure factor for the local spin density, (a) with varying Δ for δ=h=0, (b) with varying δ for Δ=0.65 and h=0, and (c) with varying h for Δ=0.65 and δ=0.

The dynamic spin structure factor is defined in [6] and obtained by analytic continuation of the imaginary-time-dependent spin correlation function. For δ=h=0 [Fig. 1(a)], in the ionic phase with smaller Δ, it is a paramagnetic Mott insulator, so that the spin excitations are gapless and dominate the spectrum at low energies. Meanwhile, in the neutral phase with larger Δ, it is a nonmagnetic band insulator with a large spin gap, so that the low-energy spectral weight is strongly suppressed. Here the transition is discontinuous, but a larger t or T can make it continuous [5].

With increasing dimerization δ, the ionicity generally increases in the neutral phase because δ enhances the delocalization of electrons from the donor to acceptor sites. In the ionic phase, however, the ionicity slightly decreases because the bonding tendency competes with the single occupation favored by the strong on-site repulsion. In the present case [Fig. 1(b)], the system is in the neutral phase for δ=0, while the ionicity quickly increases around δ=0.025-0.05 accompanied with the decreasing spin gap. The spectral weight is accordingly shifted to low energies. At $\delta \geq$0.75, the system is roughly in the ionic phase. Although the spin gap remains finite, it is much smaller in the ionic phase than in the neutral phase.

Though both the h term and the δ term produce a spin gap in the ionic phase, their effects are quite different, as seen in Figs. 1(b) and 1(c). The neutral phase is almost independent of the field h up to a critical field h_c, $\mid h \mid < h_c$, due to the finite spin gap. It is because the h effect appears only through thermally activated excitations. For $\mid h \mid > h_c$, the system becomes ionic. Then, the system is affected by the field h in the same way as in the ionic phase.

Here, the quantum spin fluctuations are shown to behave quite differently in the neutral and ionic phases. This is because the spin-Peierls mechanism is effective in determining the relative stability. On the other hand, if the long-range Coulomb interaction is dominant in determining the relative stability, the spin excitation spectrum may not so dramatically be changed at the transition. For instance, if thermal fluctuations are dominant in addition, the free-energy gain through different magnitudes of the spin gap would be so small that the spectrum would look very similar. Therefore, the nature of the neutral-ionic phase transition could be clarified when spin excitation spectra are experimentally measured near the transition.

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