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Quasi-one-dimensional Heisenberg antiferromagnetic model for an organic polymeric chain

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Abstract

Using the exact diagonalization technique, we study the properties of the ground state of a spin-$\frac{1}{2}$ antiferromagnetic Heisenberg model for a zigzag polymer chain with side radicals connected to the even sites. We consider the nearest-neighbour exchange J and the next-nearest-neighbour exchange αJ along the main chain, and J_1 between the even site on the main chain and the radical site. For small α the ground state is ferrimagnetic. For $\alpha > \alpha_{c1}$, the ground state is a spiral phase, which is characterized by a peak of the static structure factor $S(q)$ locating at an incommensurate value q_{max}. For $\alpha > \alpha_{c2}$, the ground state is antiferromagnetic. With increasing J_1, α_{c1} decreases while α_{c2} has a maximum at about $J_1 = 0.5$. For very small J_1 and $\alpha = 0.5$, the spin configuration on the main chain is a product of nearest-neighbour singlets. In the antiferromagnetic phase, if J_1 is large enough the even site and the radical site form a singlet with exchange-decoupling from the odd site while the odd sites approximately form an antiferromagnetic chain.

1. Introduction

Molecule ferromagnetism has attracted a great deal of interest over the past decades since some organic ferromagnets such as *p*-NPNN [1–3], DTDA [4–6], *p*-CDTV [7] and *poly*-BIPO [8] were synthesized. For *poly*-BIPO, a simplified structure was proposed in figure 1 of [8]. The main chain consists of carbon atoms that each have a π-electron and R is a kind of side radical containing an unpaired electron. In the original work in [8], both the π-electron and the radical electron were assumed to be localized, and there exist antiferromagnetic correlations between these electrons. The ground state is a ferrimagnet in which the nearest-neighbour spin correlations are antiferromagnetic. This structure has also been described by the itinerant models such as the Hubbard–Kondo model [9] and the Hubbard model [10, 11]. Both the Hartree–Fock approximation (HFA) [9, 10] and the rigorous results [11] of these models exhibit

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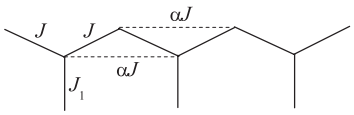

Figure 1. A quasi-one dimensional organic polymer chain. J, αJ and J_1 label the exchange interactions.

ferrimagnetic long-range ordering. However, if the next-nearest-neighbour (NNN) hopping is considered, the ferrimagnetic ground state with high spin is unstable [12]. The HFA result shows that there appear to be two kinds of charge density wave (CDW) and spin density wave (SDW) successively when the NNN hopping increases. The exact diagonalization (ED) and the constrained-path Monte Carlo (CPMC) techniques also show that when the NNN hopping increases the ground state transits from the high-spin state to the low-spin state.

In this paper, we describe this structure as an antiferromagnetic Heisenberg chain with both nearest-neighbour (NN) exchange J and NNN exchange αJ along the main chain, and J_1 between the even site of the main chain and the radical site. We are interested in the influence of the frustration α on the ground state. In some localized spin systems, magnetic frustration suppresses long-range order and stabilizes some exotic states such as the spin liquid resonating valence bond state [13, 14]. For the antiferromagnetic Heisenberg model on the pyrochlore lattice, when the ratio of the two competing exchange couplings is varied, quantum phase transitions occur between spin gapped phases and the antiferromagnetic phases [15]. In the quasi-one-dimensional inorganic spin-Peierls compound $CuGeO_3$, due to the competition between the nearest exchange and the next-nearest exchange, the system exhibits a transition from a gapless phase to a gapped dimerized ground state [16, 17]. The critical NNN exchange was obtained by the ED method [18, 19] and the density matrix renormalization group (DMRG) techniques [20]. If an alternation δ of the NN exchanges is considered, the numerical results by the DMRG method have shown that there is a disorder line in the parameter space separating the antiferromagnetic phase and the spiral phase.

Because, in the absence of frustration, the quasi-one-dimensional model in figure 1 has a ferrimagnetic ground state, its phase diagram with frustration will be different from that of the one-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnetic chain. Our calculation by ED shows that as the frustration α increases to a critical value α_{c1}, there is a transition from the ferrimagnetic (FI) phase to a spiral (SP) phase. As α increases continuously to another critical value α_{c2}, the SP phase transits to the antiferrimagnetic (AF) phase. These two critical points depend on the NN exchange J_1 between the site on the main chain and the radical site. In small-J_1 and large-J_1 limits, the SP phase disappears. In small-J_1 limit and when $\alpha = 0.5$, the spin structure of the main chain can be described as a product of NN singlets, which is a characteristic of the 1D spin-$\frac{1}{2}$ Heisenberg antiferromagnetic chain [21]. However, for $\alpha < 0.5$ and $\alpha > 0.5$ the ground state is FI and AF respectively because the spin correlations between the radical sites can be ferromagnetic or antiferromagnetic.

In quasi-one-dimensional systems, lattice dimerization may be important to the physical properties. In the case of $CuGeO_3$ and *poly*-BIPO, the dimerization has been considered in previous works. Our calculations show that the dimerization does not have a qualitative influence on the phase diagram since it does not change the translation symmetry in the present model. In this paper, we will neglect the alternation of the NN exchanges.

The organization of the paper is as follows. In section 2 the details of the model and technique are given. In section 3 the phase diagram and the properties of the ground-state phases are studied.

2. Model and computational method

We consider the quasi-one-dimensional spin-$\frac{1}{2}$ antiferromagnetic Heisenberg chain in figure 1. The Hamiltonian can be written as follows:

$$H = J\Big(\sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \alpha \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+2}\Big) + J_1 \sum_{i\,(\mathrm{even})} \mathbf{S}_i \cdot \mathbf{T}_{i/2}, \tag{1}$$

where $\mathbf{S}_i$ denotes the spin operator at the ith site on the main chain, and $\mathbf{T}_i$ is the spin operator at the ith radical site, which connects to the $2i$th site on the main chain. J is the NN exchange and αJ is the NNN exchange along the main chain. J_1 is the NN exchange between the site on the main chain and the radical site. In the following discussion, we take J as the energy unit. The parameters J, α and J_1 are positive.

We use the Lanczos algorithm to diagonalize the Hamiltonian in a subspace with a given z component S_z of the total spin $\mathbf{S}$ of the system [22]. In order to determine the quantum number S of the total spin of the ground state, we calculate the mean value of the operator $\mathbf{S}^2$ in the ground state with $S_z = 0$. Since $\langle \mathbf{S}^2 \rangle = S(S+1)$, we can deduce the value of S. The ground-state phases are characterized through the spin structure factor $S(q)$:

$$S(q) = \frac{1}{N} \sum_{l,m} \mathrm{e}^{\mathrm{i}q(l-m)} \langle \mathbf{P}_l \cdot \mathbf{P}_m \rangle, \tag{2}$$

here $\mathbf{P}_l = \mathbf{S}_{2l-1} + \mathbf{S}_{2l} + \mathbf{T}_l$ is the total spin operator in the lth unit cell. N is the number of sites in the system. Although the ED can only deal with a small system, for the quasi-one-dimensional inorganic spin-Peierls compound $CuGeO_3$ the critical NNN exchange was obtained by this method [18, 19]. For other one-dimensional interacting system such as the periodic Anderson model and the Kondo lattice [23, 24], the magnetic correlation and phase diagram have been determined accurately on the basis of the precise treatments of the finite-size effects observed in the ED data.

3. Results and discussion

We use the Lanczos algorithm to determine the quantum number S of the total spin of the system with $N = 12$, 18 and 24 sites. We use the open boundary condition to lift the twofold degeneracy, which is also observed in the 1D spin-$\frac{1}{2}$ chain with first- and second-neighbour antiferromagnetic exchange [21]. As the frustration α is small, the ground state is ferrimagnetic and has the spin $S = \frac{1}{2}$ per unit cell. As α increases to a critical value α_{c1}, the system has spin $S = 0$. In order to exhibit the properties of the ground-state phases, in figure 2 we show the spin structure factor $S(q)$ for $J_1 = 1$ and different α and lattice size N. For small α, $S(q)$ has a peak at $q_{\max} = 0$, which indicates a ferrimagnetic (FI) state. As $\alpha > \alpha_{c1}$ (e.g. $\alpha = 0.42$), the total spin is zero and the peak of $S(q)$ locates at incommensurate value of q. This characteristic indicates a spiral (SP) phase which is observed in the 1D spin-$\frac{1}{2}$ antiferromagnetic Heisenberg system with dimerization and frustration [20]. The spiral-like phase is also found in the 1D Kondo and Hund lattice [25]. As the frustration α is enhanced continuously to another critical value α_{c2}, the antiferromagnetic (AF) phase is clearly identified with a peak of $S(q)$ at $q_{\max} = \pi$ and the total spin is still zero. Figures 2(a)–(c) show that the behaviour of the spin structure factor $S(q)$ is very similar for three lattice sizes although a size dependence of $S(q)$ exists.

In figure 3 we present the phase diagram for systems with different lattice size N. The lines with open circles separate the FI phase from the SP phase while the lines with filled circles correspond to the transition points from the SP phase to the AF phase. In the whole parameter space, the first critical point α_{c1} has a very small finite-size effect. For the second critical point α_{c2}, the finite-size effect is large near $J_1 = 0.5$ and is small far from $J_1 = 0.5$.

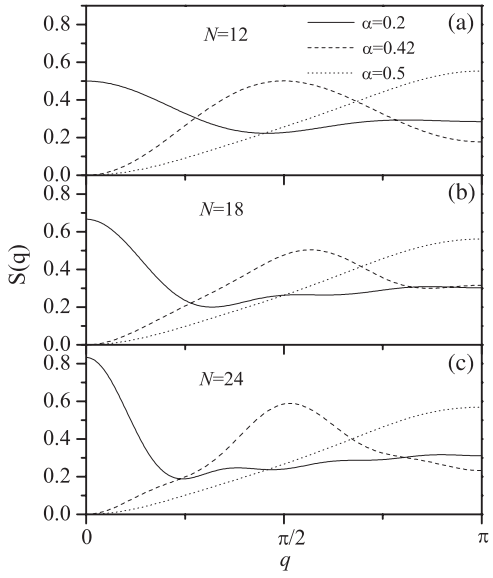

Figure 2. Spin structure factor $S(q)$ for $J_1 = 1$ and different α and lattice size N.

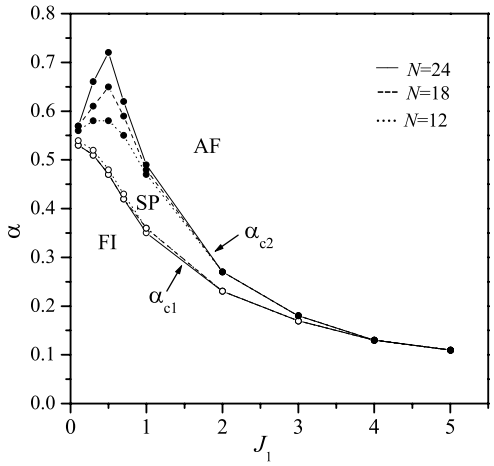

Figure 3. Phase diagram for systems with different lattice size N. The lines with open circles separate the FI phase from the SP phase while the lines with filled circles separate the SP phase from the AF phase.

The critical frustrations α_{c1} and α_{c2} depend on the exchange J_1 between the even site on the main chain and the radical site. As J_1 is enhanced, α_{c1} decreases while the second critical point α_{c2} increases for $J_1 < 0.5$ and decreases for $J_1 > 0.5$. In the small-J_1 or large-J_1 limit, the SP phase does not exist. We will give further discussion of this later.

In order to visualize the behaviour of spin configuration in the SP phase, we show in figure 4 the spin structure factor $S(q)$ for $J_1 = 0.5$ and different α and lattice size $N = 24$. At the first critical point $\alpha_{c1} = 0.47$, $S(q)$ peaks at about $q_{max} = 0.3\pi$, while near the second critical point $\alpha_{c2} = 0.72$, q_{max} continuously approaches π. For points close to α_{c2}, $S(q)$ has a very broad peak near $q = \pi$ and we cannot identify the maximum exactly. Since q_{max} is

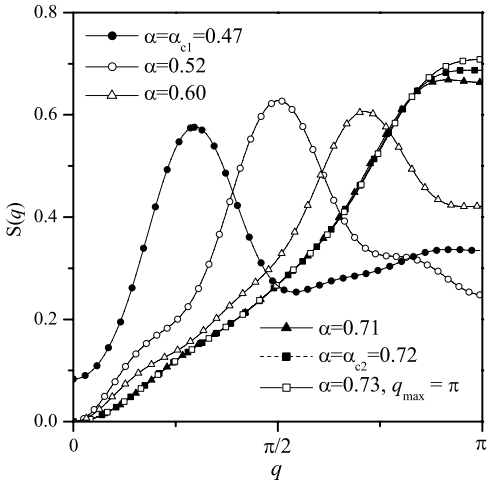

Figure 4. Spin structure factor $S(q)$ for $J_1 = 0.5$, $N = 24$ and different α.

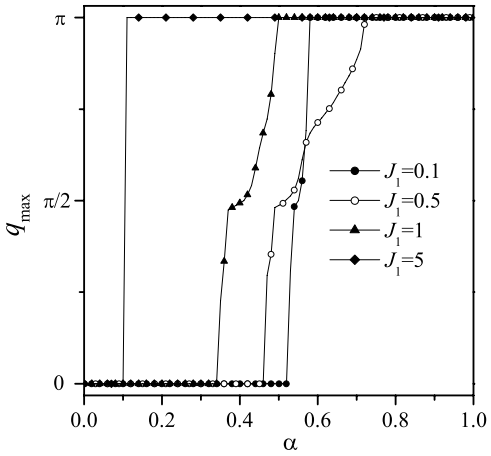

Figure 5. The location $q_{\max}$ of the peak of $S(q)$ as a function of the frustration α for different J_1.

incommensurate and cannot be determined exactly near α_{c2}, $q_{\max}$ will vary with lattice size and the finite-size effect is larger near α_{c2} than near α_{c1}. One can find this feature in figure 3. Figure 5 shows the location $q_{\max}$ of the peak of $S(q)$ as a function of the frustration α for different J_1.

In the Hubbard model, the finite-size effect decreases with increasing the on-site Coulomb repulsion U because U is the short-range interaction [26]. Hence, we believe that the larger the correlation length is, the stronger the finite-size effect becomes. Figure 6 shows the spin–spin correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_8 \rangle$ between the middle site and the ith site for $N = 24$ and $\alpha = \alpha_{c2}$. One can find that at the second critical point α_{c2} the spin–spin correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_8 \rangle$ for $i \leqslant 6$ has a larger size for $J_1 = 0.5$. This means that the correlation decreases with distance more slowly for $J_1 = 0.5$ than for $J_1 = 0.1$ and 1.0. Therefore, the finite-size effect is larger at $J_1 = 0.5$ than that far from $J_1 = 0.5$ because the correlation length is larger for $J_1 = 0.5$.

In the 1D spin-$\frac{1}{2}$ chain with first- and second-neighbour antiferromagnetic exchange, at the special frustration $\alpha = 0.5$, the exactly solvable ground state is a product of nearest-

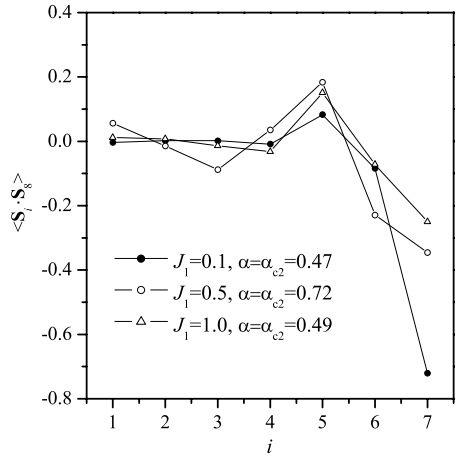

Figure 6. Spin–spin correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_8 \rangle$ between the middle site and the ith site for the lattice size $N = 24$.

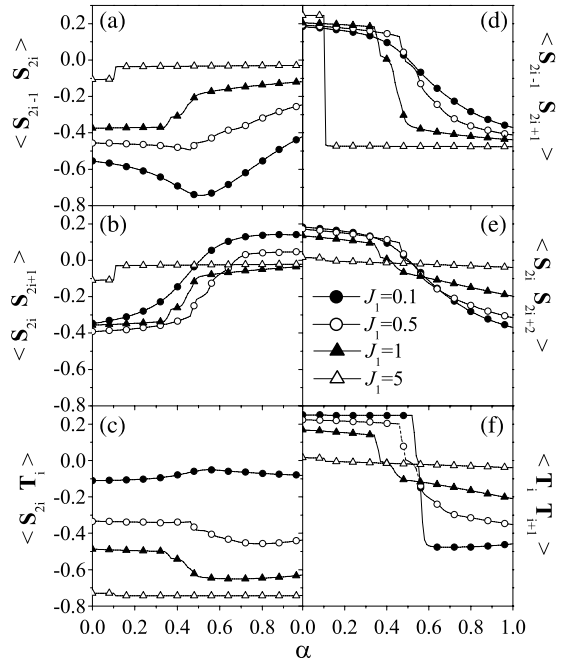

Figure 7. The local spin–spin correlations as a function of α for different J_1.

neighbour singlets and is twofold degenerate [21]. In the present model, a similar spin structure is also found in the small-J_1 limit. In figure 7, we show the local spin–spin correlations as a function of α for different J_1. Under the open boundary condition, the spin–spin correlations are averaged over the full system. For small J_1 (e.g. $J_1 = 0.1$) and small α, there is a strong NN antiferromagnetic correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+1} \rangle$ (figures 7(a) and (b)) along the main chain while the antiferromagnetic correlation $\langle \mathbf{S}_{2i} \cdot \mathbf{T}_i \rangle$ between the even site on the main chain and the radical site is weak. In the FI phase, these two kinds of antiferromagnetic correlation mediate the NNN

ferromagnetic correlations (figures 7(d) and (e)) along the main chain and the ferromagnetic correlation between the radical sites (figure 7(f)). For $J_1 = 0.1$, as α increases to about 0.5 the NN correlation $\langle \mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i} \rangle$ in figure 7(a) reaches the saturation value -0.75 of a spin singlet. However, the NN correlation $\langle \mathbf{S}_{2i} \cdot \mathbf{S}_{2i+1} \rangle$ in figure 7(b) nearly vanishes. Meanwhile, the NNN correlations $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+2} \rangle$ (figures 7(d) and (e)) approach zero. This behaviour indicates that the spin configuration on the main chain is a product of the NN singlets, which is similar to the 1D spin-$\frac{1}{2}$ chain with NN and NNN antiferromagnetic exchanges [21]. However, the twofold degeneracy is lifted because of the open boundary condition. Because the antiferromagnetic correlation $\langle \mathbf{S}_{2i} \cdot \mathbf{T}_i \rangle$ still exists, the correlation $\langle \mathbf{T}_i \cdot \mathbf{T}_{i+1} \rangle$ between two radical sites can be ferromagnetic (e.g. 0.25) or antiferromagnetic (e.g. -0.5) near $\alpha = 0.5$. As a result, for $\alpha < 0.5$ and $\alpha > 0.5$, the ground state is ferrimagnetic and antiferromagnetic, respectively. In figure 7, because $J_1 = 0.1$ approaches but is not exactly zero, the SP phase still exists in a narrow regime $0.57 > \alpha > 0.53$. For $J_1 = 0$, the SP phase will disappear.

As the exchange J_1 increases, the antiferromagnetic correlation $\langle \mathbf{S}_{2i} \cdot \mathbf{T}_i \rangle$ is enhanced while the NN correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+1} \rangle$ decreases. The transition between the FI phase and the SP phase results from the competition between the frustration α and this NN correlation. Therefore, the smaller the NN correlation is, the smaller the critical α_{c1}. As a result, with increasing J_1 the critical α_{c1} decreases, as shown in figure 3.

In the FI phase, the NN antiferromagnetic correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+1} \rangle$ plays an important role in mediating the ferromagnetic correlation $\langle \mathbf{T}_i \cdot \mathbf{T}_{i+1} \rangle$. This means that with increasing J_1, $\langle \mathbf{T}_i \cdot \mathbf{T}_{i+1} \rangle$ is weakened because $\langle \mathbf{S}_i \cdot \mathbf{S}_{i+1} \rangle$ decreases. For large enough J_1 (e.g. $J_1 = 5$), $\langle \mathbf{T}_i \cdot \mathbf{T}_{i+1} \rangle$ nearly vanishes while $\langle \mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i+1} \rangle$ reaches the saturation value 0.25 of a ferromagnetic correlation. In this case, the ferromagnetism is mainly contributed by the ferromagnetic correlation between the odd sites along the main chain.

In the AF phase, as the exchange J_1 increases a similar behaviour is observed. But there are some quantitative differences. In the AF phase, for large J_1 the correlations in figures 7(a), (b), (e) and (f) almost vanish while the antiferromagnetic correlation $\langle \mathbf{S}_{2i} \cdot \mathbf{T}_i \rangle$ in figure 7(c) reaches the saturation value -0.75 of a spin singlet. The NNN antiferromagnetic correlation $\langle \mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i+1} \rangle$ has a large strength -0.467, which approaches the value -0.443 of the NN spin correlation of an infinite Heisenberg antiferromagnetic chain [27]. This feature shows that in the AF phase if J_1 is large enough the even site on the main chain and the connected radical site nearly forms a singlet with exchange-decoupling from the odd site while the odd sites approximately form an antiferromagnetic chain.

It is interesting to compare the present results with those from the itinerant models. In the Hubbard–Kondo model for this polymer [12], the HFA result shows that as the NNN hopping increases to a critical value ρ_{c1}, the ferromagnetic ground state with high spin is unstable while there appears a phase with incommensurate CDW and SDW along the chain. As the NNN hopping increases continuously to another critical value ρ_{c2}, the ground state exhibits a commensurate CDW and SDW with a period of two sites. It is known that in the limit of large on-site repulsion U, the Hubbard model at half-filling maps to the Heisenberg model. We find that even for small U, the phases predicted by two models have some similarity. Comparing the present results with those in [12], one finds that the SP phase and the AF phase in this paper correspond to the incommensurate phase and commensurate phase in [12]. In the Peierls-extended Hubbard model in [12], both the NNN hopping terms along the chain and between the chain and the radical site are considered. The results by the ED and the CPMC techniques also show that when the NNN hopping increases the ground state transits from the high-spin state to the low-spin state.

In summary, we have studied the ground-state phase diagram of a spin-$\frac{1}{2}$ antiferromagnetic Heisenberg model for a zigzag polymer with side radicals. We take into account the NN

exchange J and the NNN exchange αJ along the main chain, and J_1 between the site of the main chain and the radical site. The numerical results from ED show that for small α the ground state is the FI phase. As α increases to a critical value α_{c1}, the ground state is the SP phase, which is characterized by the peak of the static structure factor $S(q)$ locating at an incommensurate value q_{max}. As α is enhanced to another critical value α_{c2}, there is a transition from the SP phase to the AF phase. These two critical values of α depend on the exchange J_1. With increasing J_1, α_{c1} decreases while α_{c2} has a maximum at about $J_1 = 0.5$. For very small J_1 or large enough J_1, the SP phase does not exist. For very small J_1 (e.g. $J_1 = 0.1$), at $\alpha = 0.5$ the spin configuration on the main chain is a product of nearest-neighbour singlets. In the AF phase, for large enough J_1 the even site on the main chain and the connected radical site forms a singlet with exchange-decoupling from the odd site while the odd sites approximately form an antiferromagnetic chain.

Acknowledgments

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