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Solitary waves on finite-size antiferromagnetic quantum Heisenberg spin rings

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Abstract

Motivated by the successful synthesis of several molecular quantum spin rings we are investigating whether such systems can host magnetic solitary waves. The small size of these spin systems forbids the application of a classical or continuum limit. We therefore investigate whether the time-dependent Schrödinger equation itself permits solitary waves. Example solutions are obtained via complete diagonalization of the underlying Heisenberg Hamiltonian.

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1. Introduction

Magnetic solitons are detected in many magnetic systems due to their special influence on magnetic observables [1,2,3,4,5]. From a theoretical point of view magnetic solitons are solutions of non-linear differential equations, e. g. of the cubic Schrödinger equation [6,7,8], which result from classical approximations of the respective quantum spin problem. The cubic Schrödinger equation for instance is obtained if the spins are replaced by a classical spin density [6].

Due to the success of coordination chemistry one can nowadays realize finite size quantum spin rings in the form of magnetic ring molecules. Such wheels – Fe₆, Fe₁₀, and Cr₈ rings as the most prominent examples – are almost perfect Heisenberg spin rings with a single isotropic antiferromagnetic exchange parameter and weak uniaxial anisotropy [9,10,11,12].

The aim of the present article is to discuss whether solitary waves can exist on such spin rings and if they do, how they look like. The finite size and the resulting discreteness of the energy spectrum forbid any classical or continuum limit. We therefore investigate, whether the ordinary *linear* time-dependent Schrödinger equa-

tion allows for solitary waves. Solitary excitations in quantum spin chains of Ising or sine-Gordon type have already been discussed [7]. Nevertheless, such soliton solutions are approximate in the sense that a kind of Holstein-Primakov series expansion is applied, and the results are accurate only for anisotropies large compared to the spin-spin coupling [7]. This article deals with antiferromagnetic Heisenberg chains without anisotropy, where such derivations cannot be applied. Starting from the time-dependent Schrödinger equation therefore automatically addresses the questions how soliton solutions might be approached starting from a full quantum treatment – a question that to the best of our knowledge is not yet answered [13].

In order to apply the concept of solitons or solitary waves to the linear Schrödinger equation some redefinitions are necessary. The first redefinition concerns the term soliton itself. It is mostly used for domain-wall like solitons which are of topological character. It is also applied to localized deviations of the magnetization or energy distribution (envelope solitons), here one distinguishes between bright and dark solitons. We will generalize this class of objects and speak only of solitary waves in the following. We call a state $|\Psi_s\rangle$ solitary wave if there exists a time τ for which the time evolution equals (up to a global phase) the shift by one site on the spin ring. This means that solitary waves

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travel with permanent shape. The property that two solitons scatter into soliton states cannot be used as a definition in the context of the Schrödinger equation since it is trivially fulfilled for a linear differential equation.

A nontrivial question concerns useful observables in order to visualize solitary waves $|\Psi_s\rangle$. The expectation value of the local operator $\underline{s}_z(i)$, which reflects a local magnetization is used classically and meaningful also as a quantum mechanical expectation value. Then nontrivial, i. e. non-constant magnetization distributions $\langle \Psi_s | \underline{s}_z(i) | \Psi_s \rangle$ arise only for those solitary waves which possess components with a common total magnetic quantum number M , because matrix elements of $\underline{s}_z(i)$ between states of different total magnetic quantum number vanish. The energy density which in classical calculations is also used to picture solitons, could quantum mechanically be defined as $\underline{g}(i) \cdot \underline{s}(i+1)$ starting from a Heisenberg Hamiltonian, compare Eq. (1). It turns out that this observable is not so useful since it is featureless in most cases because the off-diagonal elements for energy eigenstates belonging to different total spin S are zero.

The article is organized as follows. In Sec. 2 we shortly introduce the Heisenberg model and the used notation, while in Sec. 3 solitary waves are defined. We will then discuss the construction and stability of (approximate) solitary waves in Sec. 4. A number of example spin systems will be investigated in Sec. 5. The article closes with conclusions in Sec. 6.

2. Heisenberg model

The Hamilton operator of the Heisenberg model with antiferromagnetic, isotropic nearest neighbor interaction between spins of equal spin quantum number s is given by

$$\underline{H} \equiv 2 \sum_{i=1}^N \underline{g}(i) \cdot \underline{g}(i+1), \quad N+1 \equiv 1. \quad (1)$$

\underline{H} is invariant under cyclic shifts generated by the shift operator \underline{T} . \underline{T} is defined by its action on the product basis $|\mathbf{m}\rangle$

$$\underline{T} |m_1, \dots, m_N\rangle \equiv |m_N, m_1, \dots, m_{N-1}\rangle, \quad (2)$$

where the product basis is constructed from single-particle eigenstates of all $\underline{s}_z(i)$

$$\underline{s}_z(i) |m_1, \dots, m_N\rangle = m_i |m_1, \dots, m_N\rangle. \quad (3)$$

The shift quantum number $k = 0, \dots, N-1$ modulo N labels the eigenvalues of \underline{T} which are the N -th roots of unity

$$z = \exp \left\{ -i \frac{2\pi k}{N} \right\}. \quad (4)$$

k is related to the “crystal momentum” via $p = 2\pi k/N$.

Altogether \underline{H} , \underline{T} , the square \underline{S}^2 , and the z -component \underline{S}_z of the total spin are four commuting operators.

3. Solitary waves

We call a state $|\Psi_s\rangle$ solitary wave if there exists a time τ for which the time evolution equals (up to a global phase) the shift by one site on the spin ring either to the left or to the right, i. e.

$$\underline{U}(\tau) |\Psi_s\rangle = e^{-i\Phi_0} \underline{T}^{\pm 1} |\Psi_s\rangle. \quad (5)$$

Decomposing $|\Psi_s\rangle$ into simultaneous eigenstates $|\Psi_\nu\rangle$ of \underline{H} and \underline{T} ,

$$|\Psi_s\rangle = \sum_{\nu \in I_s} c_\nu |\Psi_\nu\rangle, \quad (6)$$

yields the following relation

$$\sum_{\nu \in I_s} e^{-i \frac{E_\nu \tau}{\hbar}} c_\nu |\Psi_\nu\rangle = e^{-i\Phi_0} \sum_{\mu \in I_s} e^{\mp i \frac{2\pi k \mu}{N}} c_\mu |\Psi_\mu\rangle. \quad (7)$$

The set I_s contains the indices of those eigenstates which contribute to the solitary wave. Therefore,

$$\frac{E_\mu \tau}{\hbar} = \pm \frac{2\pi k \mu}{N} + 2\pi m_\mu + \Phi_0 \quad \forall \mu \in I_s \quad (8)$$

with $m_\mu \in \mathbb{Z}$.

Equation (8) means nothing else than that solitary waves are formed from such simultaneous eigenstates $|\Psi_\nu\rangle$ of \underline{H} and \underline{T} which fulfill a (generalized) linear dispersion relation.

Since our definition (8) is rather general it comprises several solutions. Some of them are rather trivial waves whereas others indeed do possess soliton character:

- Single eigenstates $|\Psi_\nu\rangle$ of the Hamiltonian fulfill the definition, but they are of course stationary and they possess a constant magnetization distribution. One would not call these states solitary waves or solitons.
- Superpositions of two eigenstates $|\Psi_\mu\rangle$ and $|\Psi_\nu\rangle$ with different shift quantum numbers k_μ and k_ν are also solutions of definition (8) since two points are always on a line in the E - k -plane. It is clear that such a state cannot be well localized because of the very limited number of momentum components. Nevertheless, these states move around the spin ring with permanent shape.

An example of such solitary waves are superpositions consisting of ground state and first excited state which have already been investigated under a

different focus [14]. The characteristic time τ to move by one site is related to the frequency of the coherent spin quantum dynamics discussed for these special superpositions [14,15].

- The existence of more than two eigenstates with linear dispersion relation cannot be proven for Heisenberg models in contrast to the Ising model [7]. In fact it is very likely that such a combination does not exist at all for a small system. Therefore, superpositions of three or more eigenstates will – hopefully only slightly – deviate from the linear dispersion relation and therefore describe (slowly) decaying solitary waves. This will be explained in detail below.
- The character of the solitary waves assembled according to definition (8) can be different. As section 5 will show some of them are localized magnetization distributions (envelope solitons) which could be denoted as bright or dark solitary waves others are of topological nature as for example in the case of superpositions of the ground state and the first excited state on an odd membered spin ring. Nevertheless, the distinction is not sharp. As shown in Ref. [16] envelope solitons can be of topological nature when looked at from a different perspective.

4. Construction and stability of solitary waves

When constructing solitary waves we focus on two principles:

- Energetically low-lying solitons can be formed by superimposing the ground state with low-lying excited states. For this purpose it is advantageous that for antiferromagnetic rings the lowest energy eigenvalues depend on momentum approximately via a sine function. Therefore, for large systems, where the sine function can be approximated by its argument, an almost linear dependence between k_μ and E_μ is expected.
- General solitons can be formed by superimposing states with arbitrary pairs (k_μ, E_μ) as long as they fulfill (8). For this purpose two states are selected which define a straight line in $E - k$ -space. Then a search algorithm is used to find other states whose energy and momentum quantum numbers constitute a point on (or in close vicinity) of the line. The search extends not only to the first Brillouin zone, but also to higher zones.

It is clear that in a finite system the linear dispersion relation (8) might only be fulfilled approximately which leads to decaying solitary waves. That the time evolution must be recurrent in a Hilbert space of finite dimension is only of principle interest since the recurrence time would be very long.

A good measure of the stability of a solitary wave is the overlap of the time-evolved state and the shifted

one. For perfect stability these two states coincide. Let's assume that the wave travels in the same direction as the shift operator acts, then we define the stability measure as

$$\eta(\tau) = \langle \Psi_s | \tilde{T}^{-1} \tilde{U}(\tau) | \Psi_s \rangle . \quad (9)$$

$\eta(\tau)$ is a complex number, and for dispersionless movement it's absolute value equals one. Decomposing the approximate solitary wave $|\Psi_s\rangle$ into simultaneous eigenstates $|\Psi_\nu\rangle$ of \tilde{H} and \tilde{T} yields

$$\begin{aligned} \eta(\tau) &= \sum_{\nu \in I_s} |c_\nu|^2 e^{-\frac{i\tau}{\hbar} \{E_\nu - \frac{2\pi\hbar k\nu}{N\tau}\}} \\ &= \sum_{\nu \in I_s} |c_\nu|^2 e^{-i\frac{\delta_\nu\tau}{\hbar}} , \end{aligned} \quad (10)$$

where δ_ν is the energy mismatch of energy level ν . In order to consider a motion across n sites the exponent has to be multiplied by n .

As a simple example we want to consider an approximate solitary wave which consists of three eigenstates as for instance in the example of Fig. 4. The first two levels define the linear dependence, and the third level deviates by δ_3 from that dependence. Then, taking the normalization condition into account, the overlap turns out to be

$$\eta(\tau) = 1 - |c_3|^2 + |c_3|^2 e^{-i\frac{\delta_3\tau}{\hbar}} . \quad (11)$$

Thus we face a decaying overlap which later oscillates back to one. For the specific example of Fig. 4 we can estimate how much time this will take. The characteristic time τ is given by

$$\frac{\hbar}{\tau} = \frac{\Delta E}{\Delta k} \frac{N}{2\pi} , \quad (12)$$

which is approximately 3 in the given units, compare Fig. 1. The energy mismatch is of the order of 10^{-2} . In order to have a deviation of the exponential in (11) of 1 % from unity the argument has to grow up to 0.1, which means that the solitary wave has to move across about 30 sites. Or in other words, the approximate three state solitary wave of Fig. 4 has to circumvent the spin ring three times in order to produce a deviation of the overlap with the original state of about one percent. This means that such approximate solitary waves are rather stable. Nevertheless, with increasing energy mismatch the situation will be worse.

5. Special solutions for spin rings

In this section we discuss some typical examples for magnetic solitary waves on finite spin rings. We have

chosen examples which are as large as numerically possible, i.e. $N = 11, 12, 14$ and $s = 1/2$, because a too small size yields only a very limited number of eigenstates with different shift (i.e. momentum) quantum numbers that can be superimposed to form the solitary wave. Then, the solitary waves obviously cannot be of such perfect shape and localization as known from continuous models. Nevertheless, our general ideas are applicable as well to systems with spin quantum numbers $s > 1/2$, which in future investigations might be accessible by means of Density Matrix Renormalization Group (DMRG) techniques [17].

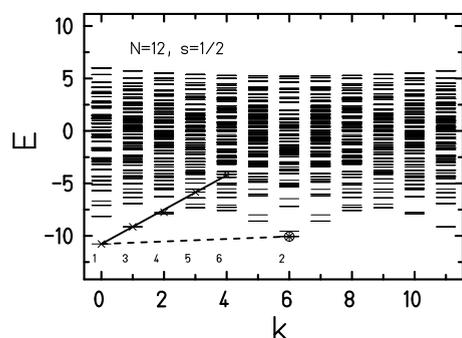


Fig. 1. Energy spectrum of an antiferromagnetic spin ring with $N = 12$ and $s = 1/2$: The solid as well as the dashed line connect states which are superimposed to form a solitary wave. The numbers label these states.

Figure 1 shows a typical spectrum for an antiferromagnetically coupled Heisenberg ring. The ground state of such a ring is a singlet with $k = 0$ for the special case of $N = 12$. The first excited state is a triplet with $k = 6$, compare the theorems of Lieb, Schultz, and Mattis [18,19,20] for quantum numbers of ring systems with an even number of sites and Ref. [21] for quantum numbers of ring systems with an odd number of sites.

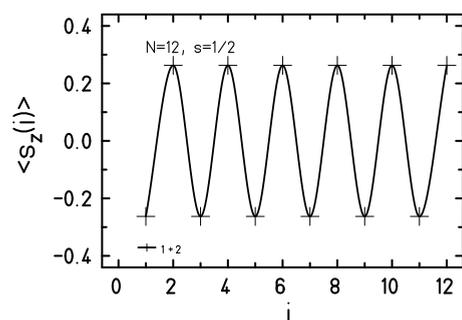


Fig. 2. Solitary wave for $N = 12$ and $s = 1/2$ consisting of ground state and first excited state with $M = 0$ (crosses). The curve is drawn as a guide for the eye. In the course of time such a wave moves around the spin ring without dispersion. The local magnetization distribution is the quantum expression of the classical Néel state.

Two basic types of low-energy solitary waves can be formed. The first one is a superposition of the ground state and the triplet state with $M = 0$ (dashed line in Fig. 1). If added up the result is a sinusoidal magnetization function – sometimes also called spin-density wave – which is depicted in Fig. 2. A subtraction leads to an inverted local magnetization. In the course of time these distributions just move along the spin ring without dispersion. This dynamics is equivalent to an oscillation of the local magnetization, which was intensely discussed under the aspect of tunneling of the Néel vector [14,22,15].

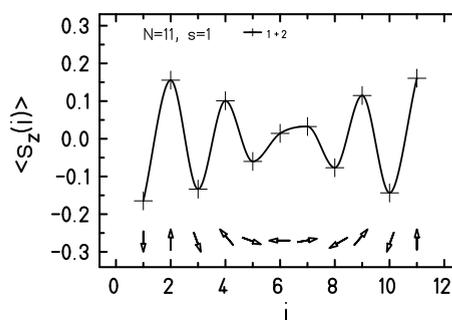


Fig. 3. Solitary wave for $N = 11$ and $s = 1$ consisting of ground state ($k = 0$) and first excited state ($k = 5$) with $M = 0$ (crosses). The curve is drawn as a guide for the eye. The local magnetization distribution is the quantum expression of a topological solitary wave, where the Néel up-down sequence is broken and continued with a displacement of one site. This state propagates without dispersion.

Although these states look rather unspectacular the same procedure applied to rings of an odd number of spins leads to topological solitary waves. The reason is that due to the periodic boundary condition the antiferromagnetic order is frustrated in such cases. Figure 3 shows the case of eleven spins with $s = 1$. Here the ground state has $S = 0$ and $k = 0$ and the first excited one, which is sixfold degenerate, has $S = 1$ and $k = 5$ as well as $k = 6$. The superposition which is depicted in Fig. 3 consists of the non-degenerate ground state and the ($M = 0, k = 5$)-component of the first excited state. One realizes that this state describes a displacement of the classical Néel order by one site. As sketched by the arrows the Néel order starts at the l.h.s. as a sequence where up spins are located at even sites and down spins at odd sites. This sequence is separated by a “domain wall region” from the sequence at the r.h.s. where up spins are located at odd sites and down spins at even sites. Such a behavior of the local magnetization can equally well be pictured as a Möbius strip, compare Ref. [23], although the system discussed in that reference does not possess translational symmetry.

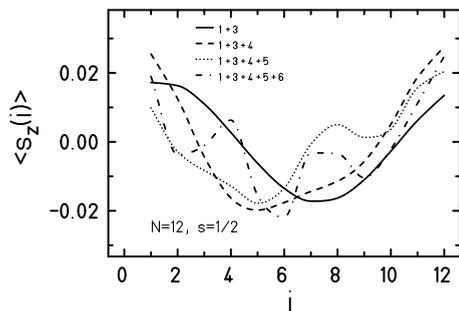


Fig. 4. Several solitary waves depending on contributing eigenstates of \tilde{H} and \tilde{T} with $M = 0$. All states contribute with the same weight in this presentation. All states with more than two components disperse slowly according to (12). We estimate that the overlap with the initial state decreases by about 1 % after two cycles around the ring.

The second basic type of low-energy solitary waves is built of states along the solid line in Fig. 1. Adding up two to five components with the same amplitude yields the magnetization distributions shown in Fig. 4. These solitary waves are similar to two domain walls on a larger ring system which separate a spin-up region from a spin-down region (Two domain walls are needed because the ring has an even number of sites.). For a small system such as the investigated one the size of the two domain walls is similar to the size of the whole system. The solitary waves in Fig. 4 with more than two components are not stable because they fulfill the linear dispersion relation (8) only approximately, compare Sec. 4.

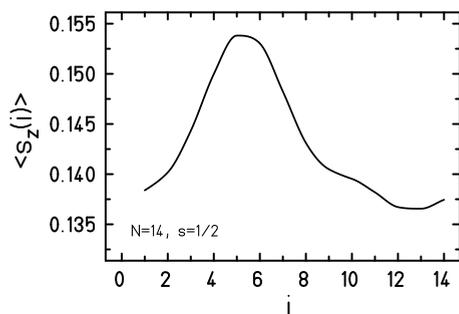


Fig. 5. Solitary wave built of six components for $N = 14$, $s = 1/2$, and $M = 2$ [24]. The deviation of the energy levels from a strict linear behavior is less than 10^{-4} , which means that this state disperses very slowly, i.e., it can perform many cycles around the ring without noticeable deviation from the initial shape.

The above discussed low-energy solitary waves have a magnetic quantum number $M = 0$ and are accessible in low-temperature experiments. Of course, solitary waves can be constructed also for larger magnetic quantum numbers M although it might not be easy to

excite or detect them. Figure 5 presents an example of a rather well localized solitary wave in a subspace with non-zero magnetic quantum number [24].

6. Conclusions

Summarizing, we have presented a framework to discuss solutions of the time-dependent Schrödinger equation which are of permanent shape, i.e. travel without dispersion. Besides solutions which have a close affinity to solitary waves our rather general definition (8) also comprises solutions which are simpler waves, which nevertheless propagate without dispersion. In general one can say, that due to the two reasons that the investigated systems are small and that the Heisenberg Hamiltonian (1) does not possess any anisotropy the observed solitary waves are rather broad.

The special case of a superposition of the ground state and the first excited state of a spin ring should be well observable at low temperatures for instance by Nuclear Magnetic Resonance (NMR). For rings with an even number of sites this is currently aimed at [14,15]. Rings with an odd number of sites are difficult to produce due to steric arrangement problems of the extended ligands. First attempts resulted in rings where one paramagnetic ion is different from the others [23]. The prospects of interesting features due to frustration nevertheless fuel future efforts to synthesize odd rings.

Another important aspect is the role of anisotropic terms in the Hamiltonian. Such terms are relevant for the magnetic properties of several magnetic molecules, e.g. for ferric wheels comprising six iron ions of spin $s = 5/2$ [25,26,22]. Easy axis anisotropy would for instance amplify the magnetization oscillations, which arise when ground state and first excited state are superimposed. Figure 6 shows in its bottom panel such oscillations again, this time for a hexanuclear iron ring. One notices that the local magnetization reaches at most an amplitude of 1.6 due to strong quantum fluctuations in the Heisenberg model. Increasing easy axis anisotropy would result in more Ising-like behavior with increased local magnetizations. It will be the subject of further studies how that in general would influence solitary waves, but it is already clear that under such conditions solitary waves would be more localized [27].

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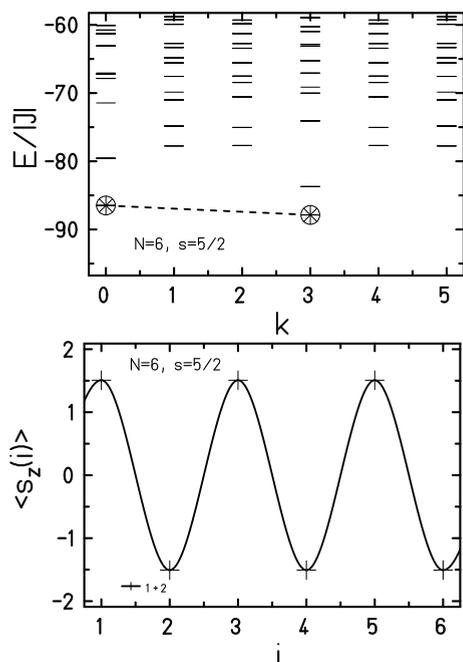


Fig. 6. Top panel: Low-lying energy spectrum of an antiferromagnetic spin ring with $N = 6$ and $s = 5/2$: The dashed line connects the ground state and the first excited state. Bottom panel: Solitary wave for $N = 6$ and $s = 5/2$ consisting of ground state ($k = 3$) and first excited state ($k = 0$) with $M = 0$ (crosses). The curve is drawn as a guide for the eye.

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