

Spin dynamics of quantum and classical Heisenberg dimers

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Abstract

Analytical solutions for the time-dependent autocorrelation function of the classical and quantum mechanical spin dimer with arbitrary spin are presented and compared. For large spin quantum numbers or high temperature the classical and the quantum dimer become more and more similar, yet with the major difference that the quantum autocorrelation function is periodic in time whereas the classical is not.

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1 Introduction and summary

There is a growing interest in the magnetic properties of synthesized molecules [1–4] containing relatively small numbers of paramagnetic ions. With the ability to control the placement of magnetic moments of diverse species within stable molecular structures, one can test basic theories of magnetism and even begin to explore the design of novel systems that offer the prospect of useful applications. Most species of organic-based molecular magnets exhibit very weak intermolecular magnetic interactions, so that measurements performed on a bulk sample actually

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reflect intramolecular interactions only. The magnetic interaction appears to be well described by the Heisenberg model with isotropic, nearest-neighbor exchange. A key quantity is the time- and temperature-dependent correlation function for pairs of magnetic moments, as it serves as the basic ingredient for understanding diverse dynamical phenomena, such as inelastic neutron scattering [5] and spin lattice relaxation [6].

The present study is motivated by a desire to achieve a deeper understanding of spin dynamics in the Heisenberg model, especially concerning the trends that occur in arrays of N interacting moments (individual spins s) for increasing values of both N and s . The classical Heisenberg model turns out to provide accurate quantitative results for static properties, such as magnetic susceptibility, down to thermal energies of the order of the exchange coupling [7,8]. It is quite easy to establish the connection of that model, for static properties, to the corresponding quantum model for arbitrary s . However, considerable care is required to successfully link up with classical Heisenberg spin dynamics starting from quantum Heisenberg spin dynamics.

In this article we present the analytical form of the time-dependent equilibrium autocorrelation function of the quantum mechanical dimer with general spin s . The trends for increasing s are explored in some detail and in particular we compare the quantum results with the exact analytical result recently derived [9,10] for a classical Heisenberg spin dimer. The quantum results for arbitrary s are obtained using Mathematica[®] to evaluate the Clebsch-Gordan coefficients. Results have previously been obtained for $s = \frac{1}{2}$ spin rings of length up to $N = 16$ by complete diagonalization methods [11], and in Ref. [12] some aspects of the high spin limit were discussed.

The present study of the equilibrium autocorrelation function for large values of s is timely given the fact that NMR measurements have very recently been performed [13] on a dimer molecular magnet composed of Fe^{3+} ($s = 5/2$) ions. Heretofore only $s = \frac{1}{2}$ dimers have been available for NMR studies [14–16]. For comparison between theory and experiment it will also be necessary to incorporate molecular and single-ion anisotropy terms in the Hamilton operator. This will be the subject of a forthcoming article.

2 The quantum dimer

The quantum dimer is specified by the Hamilton operator

$$\tilde{H} = \frac{J}{\hbar^2} \vec{\xi}_1 \cdot \vec{\xi}_2 = \frac{J}{2\hbar^2} \left(\vec{\xi}^2 - \vec{\xi}_1^2 - \vec{\xi}_2^2 \right) \quad ; \quad \vec{\xi} = \vec{\xi}_1 + \vec{\xi}_2 , \quad (1)$$

where $J > 0$ describes antiferromagnetic and $J < 0$ ferromagnetic coupling. Throughout this article it is assumed that the spin quantum numbers of both sites of the dimer are identical, $s_1 = s_2 = s$. The eigenstates $|SM\rangle$ of total spin \vec{S}^2

$$\vec{S}^2 |SM\rangle = \hbar^2 S(S+1) |SM\rangle, \quad \vec{S}_z |SM\rangle = \hbar M |SM\rangle \quad (2)$$

are also eigenstates of the Hamilton operator with eigenvalues E_S , which, in the absence of a magnetic field, do not depend on the total magnetic quantum number M

$$\vec{H} |SM\rangle = \frac{J}{2} (S(S+1) - 2s(s+1)) |SM\rangle = E_S |SM\rangle. \quad (3)$$

Thus the partition function in the canonical ensemble reads

$$\begin{aligned} Z &= \text{tr} \{ e^{-\beta \vec{H}} \} = \sum_{S,M} \langle SM | e^{-\beta \vec{H}} | SM \rangle \\ &= e^{\beta J s(s+1)} \sum_{S=0}^{2s} (2S+1) e^{-\frac{\beta J}{2} S(S+1)} \end{aligned} \quad (4)$$

and, considering that the Hamilton operator (1) is isotropic, one obtains for the unnormalized autocorrelation function

$$\begin{aligned} \langle \langle \vec{s}_1(t) \cdot \vec{s}_1(0) \rangle \rangle &= \frac{3}{Z} \sum_{S,M} \langle SM | \vec{s}_{1z}(t) \cdot \vec{s}_{1z}(0) e^{-\beta \vec{H}} | SM \rangle \\ &= \frac{3}{Z} \sum_{S,M,S',M'} e^{\frac{i\hbar}{\hbar}(E_S - E_{S'})} e^{-\beta E_S} |\langle SM | \vec{s}_{1z} | S' M' \rangle|^2. \end{aligned} \quad (5)$$

The last expressions simplifies when we take into account that only matrix elements with $M = M'$ and a difference in total spin not larger than one contribute [17], i.e.

$$\langle SM | \vec{s}_{1z} | S' M' \rangle = 0 \quad \text{if} \quad |S - S'| > 1 \quad \text{or} \quad M \neq M'. \quad (6)$$

The resulting expression is shown in Eq. (A.1) in the appendix. Note that the angular frequency spectrum of the spin dimer is given by integer multiples of J/\hbar , which in turn means that the autocorrelation function is periodic in time and that the recurrence time τ only depends on the coupling J but not on the spin quantum number s

$$\omega \in \left\{ \frac{J}{\hbar} S \right\}, \quad S = 0, \dots, 2s \quad \Rightarrow \quad \tau = \frac{2\pi \hbar}{J}. \quad (7)$$

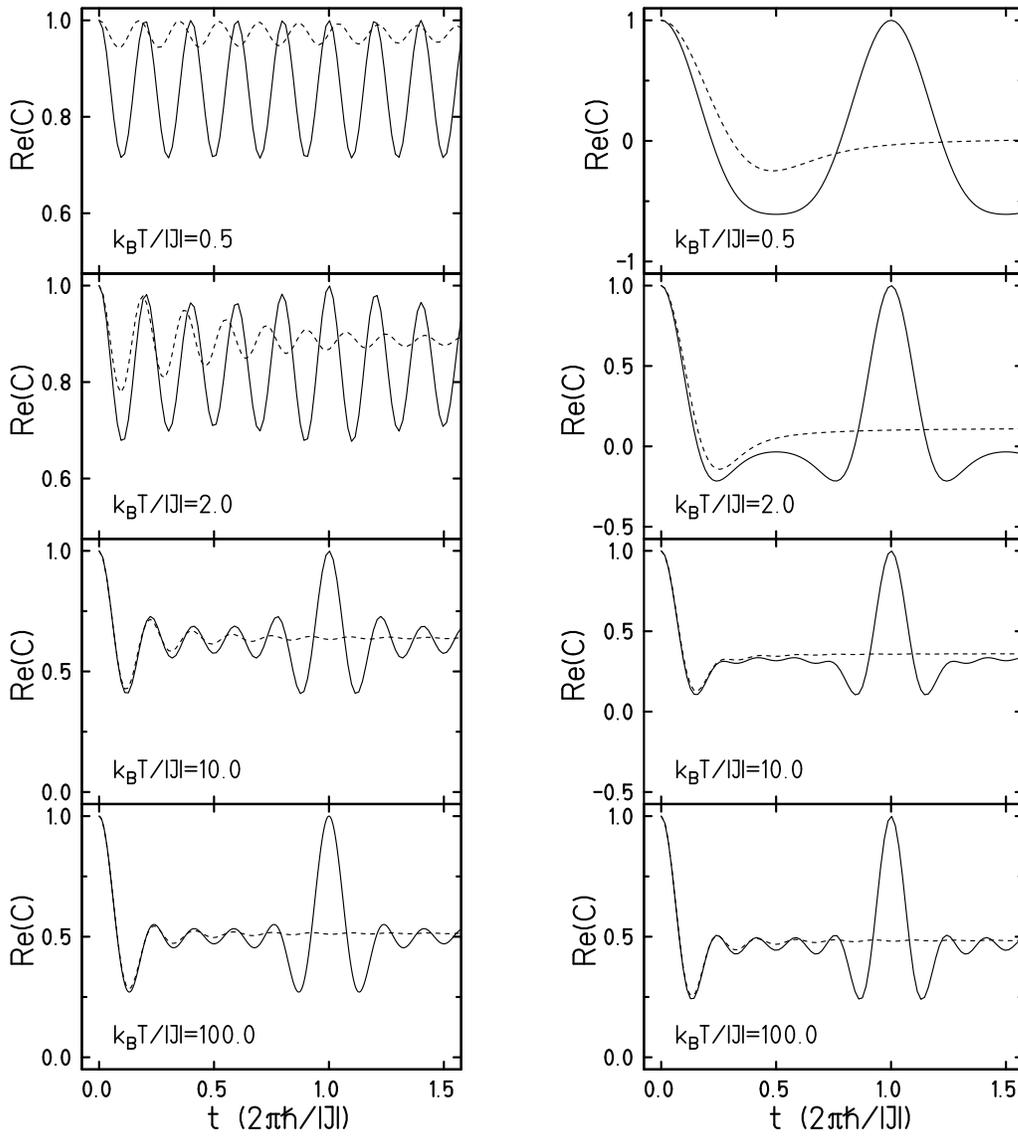


Fig. 1. Normalized autocorrelation function $\text{Re}(C(t))$, see Eq. (A.2), for a spin- $\frac{5}{2}$ -dimer for four different temperatures (solid lines). The left panels display our results for the ferromagnetic dimer, the right panels the antiferromagnetic case [20]. The dashed lines show the classical result; for details see the next section.

This is of course true for all Hamilton operators that can be written like the term on the r.h.s. of Eq. (1), namely for the spin trimer and the spin tetrahedron.

Figure 1 shows the autocorrelation function normalized to unity at $t = 0$ for a spin- $\frac{5}{2}$ -dimer, a system that has been synthesised (Fe dimer) and that is currently under investigation [13]. The analytical expression for this autocorrelation function is given in Eq. (A.2) in the appendix. One clearly sees that the autocorrelation function, which is a superposition of five harmonic oscillations and a constant, is dominated at low temperatures by the highest frequency in the ferromagnetic case

and by the lowest frequency in the antiferromagnetic case. At higher temperatures other frequencies also contribute. One also notices that, independent of temperature, the autocorrelation function returns to its initial value after $\tau = \frac{2\pi\hbar}{J}$.

3 Comparison to the classical dimer

In order to compare the results of the quantum dimer for different spin quantum numbers s with each other and with the classical dimer it is useful to introduce normalized spin operators

$$\vec{\xi}_n = \frac{\vec{\tilde{s}}_n}{\sqrt{\hbar^2 s(s+1)}}, \quad n = 1, 2, \quad (8)$$

which depend on s . Note, that

$$[\xi_{nx}, \xi_{ny}] = \frac{i}{\sqrt{s(s+1)}} \xi_{nz}, \quad (9)$$

and hence these become commuting operators for $s \rightarrow \infty$. Eq. (8) suggests that we define a classical Hamilton function H_c

$$H_c = J_c \vec{e}_1 \cdot \vec{e}_2, \quad J_c = J s(s+1), \quad (10)$$

where \vec{e}_1 and \vec{e}_2 are unit vectors (c-numbers). We expect that the thermal properties of this classical Heisenberg system will coincide with those of the quantum Heisenberg dimer if $s \gg 1$ except for very low temperatures. This is because the spectrum of eigenvalues of ξ_{nz} is confined within $(-1, 1)$ and becomes dense for $s \rightarrow \infty$ and thus coincides with the continuous range of e_{nz} .

Similarly, if we substitute Eq. (8) in the quantum equations of motion for $\vec{\tilde{s}}_1$ and $\vec{\tilde{s}}_2$, we have

$$\dot{\vec{\xi}}_1 = -\Omega \vec{\xi}_1 \times \vec{\xi}_2, \quad \dot{\vec{\xi}}_2 = +\Omega \vec{\xi}_1 \times \vec{\xi}_2 \quad (11)$$

where

$$\Omega = \frac{J \sqrt{s(s+1)}}{\hbar} = \frac{J_c}{\hbar \sqrt{s(s+1)}}. \quad (12)$$

This suggests that we prescribe the following equations of motion for the classical unit vectors \vec{e}_1 and \vec{e}_2 ,

$$\dot{\vec{e}}_1 = -\Omega \vec{e}_1 \times \vec{e}_2 \quad , \quad \dot{\vec{e}}_2 = +\Omega \vec{e}_1 \times \vec{e}_2 . \quad (13)$$

We emphasize that in these equations Ω is given by Eq. (12). It is expected that the autocorrelation function derived using (13) and the canonical ensemble average based on H_c will coincide in the large s limit with the normalized autocorrelation derived from Eq. (A.1). This expectation is in fact confirmed as discussed below.

Using the fact that the total spin is a constant of motion the classical partition function can be derived as [18,19]

$$\begin{aligned} Z_c &= \frac{1}{2} \int_0^2 dS S \exp \left\{ -\frac{\beta J_c}{2} (S^2 - 2) \right\} \\ &= \frac{1}{2 J_c} \int_{-J_c}^{J_c} dE \exp \{-\beta E\} = \frac{\sinh(\beta J_c)}{\beta J_c} . \end{aligned} \quad (14)$$

Note that the classical density of states turns out to be a constant in the energy interval $[-J_c, J_c]$. This coincides nicely with the quantum density of states which can be obtained by counting the discrete eigenvalues per unit energy interval and normalizing the density so that its integral gives 1. One can show, starting from Eq. (4), that the quantity $Z/(4s(s+1))$ is in close numerical agreement with Z_c for temperatures $k_B T > 0.2 J s(s+1)$. This serves to clearly define the classical regime for the thermal properties of the dimer.

For the classical autocorrelation function one finds that [9,10]

$$\begin{aligned} C_c(t) &= \frac{1}{2} \left[1 - \coth(\beta J_c) + \frac{1}{\beta J_c} \right] + \frac{\beta J_c}{1 - \exp(-2\beta J_c)} \\ &\quad \times \int_0^2 dS S \left(1 - \frac{S^2}{4} \right) \exp \left(-\frac{\beta J_c S^2}{2} \right) \cos(S \Omega t) , \end{aligned} \quad (15)$$

which can be integrated using error functions of complex arguments, see Ref. [20]. In contrast to the quantum autocorrelation function (5), the classical quantity is real. The reason is that $\vec{\xi}_1(t) \cdot \vec{\xi}_1(0)$ is not a hermitian operator for $t \neq 0$. If one would like to construct a hermitian operator, $\frac{1}{2} \left(\vec{\xi}_1(t) \cdot \vec{\xi}_1(0) + \vec{\xi}_1(0) \cdot \vec{\xi}_1(t) \right)$ would be appropriate. This coincides with the real part of our definition Eqs. (5) and (A.1). It is also interesting to note that the imaginary part of $\langle \langle \vec{\xi}_1(t) \cdot \vec{\xi}_1(0) \rangle \rangle$ does indeed vanish in the high temperature limit.

In Fig. 2 the dashed curves display the classical autocorrelation function obtained from (15) together with the quantum result (solid lines) for three different spin

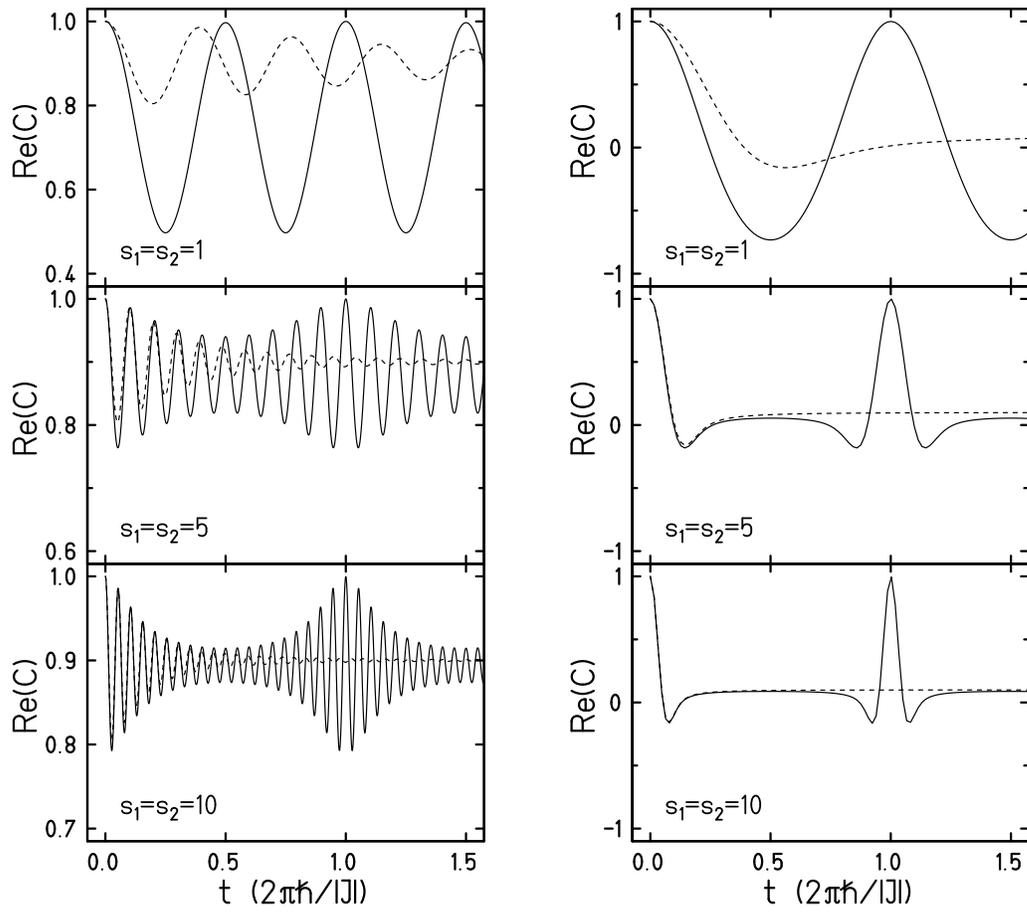


Fig. 2. Normalized autocorrelation function for three different spins at the temperature $k_B T / (J s(s+1)) = 0.2$. The left panels displays the ferromagnetic dimer, the right panels the antiferromagnetic one. The solid lines show the quantum result, the dashed lines the classical.

quantum numbers. In order to compare the different correlation functions all spectra have been mapped on the same energy interval $[-J_c, J_c]$. Thus the different figures show the autocorrelation functions for the same position of the mean excitation energy in the spectrum, i.e. the same

$$\frac{k_B T}{J s(s+1)} = \frac{k_B T}{J_c} = 0.2 . \quad (16)$$

Based on our earlier remark concerning the close numerical agreement of the classical and quantum partition functions when $k_B T > 0.2 J_c$, we anticipate similar agreement for the autocorrelation function in this temperature range. This is confirmed on inspecting the various panels of Fig. 2, which demonstrate nicely that the quantum autocorrelation function approaches the classical result with increasing s . The most prominent difference between these results is that the classical autocorrelation function does not return to its initial value but approaches a unique non-zero

limit, whereas the quantum autocorrelation function is recurrent with a recurrence time independent of spin and temperature. This is due to the fact that the classical system has a continuous spectrum of excitations in the angular frequency interval $[0, 2\Omega]$ whereas the quantum system possesses a discrete spectrum of excitations which are all integer multiples of the lowest one.

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A The quantum dimer

Using the matrix properties (6) the unnormalized autocorrelation function (5) can be simplified to

$$\begin{aligned}
\langle\langle \vec{\xi}_1(t) \cdot \vec{\xi}_1(0) \rangle\rangle &= \frac{3}{Z} e^{\beta J s(s+1)} \tag{A.1} \\
&\times \left\{ \sum_{S,M} e^{-\frac{\beta J}{2} S(S+1)} |\langle S M | \xi_{1z} | S M \rangle|^2 \right. \\
&+ \sum_{S=1}^{2s} \sum_{M=-S+1}^{M=S-1} |\langle S M | \xi_{1z} | S-1 M \rangle|^2 \\
&\times \left(\cos \left[\frac{t J}{\hbar} S \right] \left[e^{-\frac{\beta J}{2} S(S+1)} + e^{-\frac{\beta J}{2} S(S-1)} \right] \right. \\
&\quad \left. \left. + i \sin \left[\frac{t J}{\hbar} S \right] \left[e^{-\frac{\beta J}{2} S(S+1)} - e^{-\frac{\beta J}{2} S(S-1)} \right] \right) \right\}.
\end{aligned}$$

Taking as an example the case $s = 5/2$ yields

$$C(t) = \frac{\langle\langle \vec{s}_1(t) \cdot \vec{s}_1(0) \rangle\rangle}{\langle\langle \vec{s}_1(0) \cdot \vec{s}_1(0) \rangle\rangle} = \quad (\text{A.2})$$

$$\left[\begin{aligned} &330 + 180 e^{5J\beta} + 84 e^{9J\beta} + 30 e^{12J\beta} + 6 e^{14J\beta} \\ &+ 35 e^{J\left(\frac{it}{\hbar} + 14\beta\right)} + 35 e^{J\left(-\frac{it}{\hbar} + 15\beta\right)} + 64 e^{2J\left(\frac{it}{\hbar} + 6\beta\right)} + 64 e^{2J\left(-\frac{it}{\hbar} + 7\beta\right)} \\ &+ 81 e^{3J\left(\frac{it}{\hbar} + 3\beta\right)} + 81 e^{3J\left(-\frac{it}{\hbar} + 4\beta\right)} + 80 e^{J\left(\frac{4it}{\hbar} + 5\beta\right)} + 80 e^{J\left(-\frac{4it}{\hbar} + 9\beta\right)} \\ &+ 55 e^{\frac{5iJt}{\hbar}} + 55 e^{5J\left(-\frac{it}{\hbar} + \beta\right)} \end{aligned} \right]$$

$$\left/ \left[35 \left(11 + 9 e^{5J\beta} + 7 e^{9J\beta} + 5 e^{12J\beta} + 3 e^{14J\beta} + e^{15J\beta} \right) \right] \right.$$

Autocorrelation functions for other spin quantum numbers can be evaluated using a Mathematica[®] 3.0 script, that the reader is encouraged to download from our web site [20].

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