Abstract Small spin systems at the interface between analytical studies and experimental application have been intensively studied in recent decades. The spin ring consisting of four spins with uniform antiferromagnetic Heisenberg interaction is an example of a completely integrable system, in the double sense: quantum mechanical and classical. However, this does not automatically imply that the thermodynamic quantities of the classical system can also be calculated explicitly. In this work, we derive analytical expressions for the density of states, the partition function, specific heat, entropy, and susceptibility. These theoretical results are confirmed by numerical tests. This allows us to compare the quantum mechanical quantities for increasing spin quantum numbers $s$ with their classical counterparts in the classical limit $s \to \infty$. As expected, a good agreement is obtained, except for the low temperature region. However, this region shrinks with increasing $s$, so that the classical state variables emerge as envelopes of the quantum mechanical ones.

1 Introduction

Small spin systems have been studied theoretically for two main reasons. In some cases, they can be realized by magnetic molecules and analyzed by measurements, e.g., of magnetization curves, which allows comparison with theoretical predictions [1–5]. Another reason is that some small spin systems can be described analytically and thus can be used to test numerical calculations or theoretical conjectures, either quantum-theoretically [6–11] or classically [8, 9, 12–21]. In the case for the spin square, primarily the second motive applies. However, just recently we got aware of the successful synthesis of $\{\text{Gd}_4 \text{Ga}_4\}$. In this molecule the Gd ions are arranged on the vertices of an almost perfect square and further magnetic investigation are in progress [22].

It is well known that the spin square with constant Heisenberg interaction and arbitrary spin quantum number $s$ is analytically solvable due to the additional conserved quantities of the partial spin sums corresponding to the diagonals. The square belongs to a class of integrable spin systems where the Hamiltonian is a linear combination of squared partial spin sums obtained by an iterative coupling scheme [23]. Other systems of this class are the bow-tie and the octahedron. Nevertheless, the explicit calculation of thermodynamical quantities as, e.g., the specific heat or the susceptibility becomes more and more difficult for large $s$, due to the increasing number of terms, even if one uses computer-algebraic software. An obvious way out would be to consider...
the classical limit \( s \to \infty \), see [24,25]. Here one encounters the difficulty that, while the time evolution of the classical spin square can be derived in an elementary way, see Sect. 2, there is, to our best knowledge, no explicit representation of the mentioned thermodynamic quantities in the literature. The closest thing to this is a series representation for the partition function of a spin ring [26] and an integral representation for the partition function of the square [13]. Following [26] simplified expressions of the partition function of the \( N \)-chain have been derived [27], especially for \( N = 2, 3, 4 \).

To describe observables in isolated integrable quantum systems after equilibration, the generalized Gibbs ensemble (GGE) was introduced more than a decade ago [28,29]. Later, the GGE was also used for classical systems, see for instance [30]. In the present work, however, we restrict ourselves to the traditional Gibbs ensemble, which provides an adequate description for systems exposed to a heat bath.

The paper is organized as follows. After recalling some general definitions and results in Sect. 2 we briefly explain, in Sect. 3, the numerical methods used to evaluate classical thermodynamical functions in our case. Then we calculate a closed analytical expression for the density of states (dos) function of the classical spin square in Sect. 4. This is accomplished by replacing the counting of quantum spin states by integrals in the limit \( s \to \infty \). Consequently, the partition function and the specific heat can be obtained by integrations using computer-algebraic tools, see Sect. 5, analogously for the entropy, see Sect. 6. The results are somewhat complicated, but can still be presented explicitly. Similar integrations lead to the zero field static susceptibility, see Sect. 7. All these expressions will be checked by comparison with numerical calculations using Monte Carlo and Wang-Landau techniques. In addition, we will make comparisons between the classical quantities and the corresponding quantum analogues, for increasing \( s \). This will allow us to visualize the classical limit directly. We will summarize our findings in Sect. 8.

Comparing our results with the above mentioned series representation in [26], we obtain a certain remarkable identity for a series with modified spherical Bessel functions. This and related identities have been moved to the Appendix A.

### 2 General Definitions and Results Concerning Classical Time Evolution

We consider a classical spin system described by four spin vectors \( s_\mu, \mu = 1, \ldots, 4 \), of unit length. The total spin vector will be written as

\[
S := s_1 + s_2 + s_3 + s_4, \tag{1}
\]

with components \( S^{(i)}, i = 1, 2, 3 \), and its length as \( S \). Analogously, we define the partial sums of spins

\[
S_a := s_1 + s_3, \quad S_b := s_2 + s_4. \tag{2}
\]

with lengths \( S_a \) and \( S_b \), resp., such that \( S = S_a + S_b \). The general Heisenberg Hamiltonian will be written as

\[
H = J \left( s_1 \cdot s_2 + s_2 \cdot s_3 + s_3 \cdot s_4 + s_4 \cdot s_1 \right) = \frac{J}{2} (S^2 - S_a^2 - S_b^2), \tag{4}
\]

with a positive coupling coefficient \( J > 0 \) that will be set to 1 in what follows. The possible energies range from \( E = -4 \) to \( E = 4 \), such that the ground state with \( E_{\text{min}} = -4 \) will be the Néel state \( \uparrow \downarrow \uparrow \downarrow \) and the maximal energy \( E = 4 \) is assumed by the FM state \( \uparrow \uparrow \uparrow \uparrow \).

More generally, the partial spin inversion \( s_2 \mapsto -s_2, \ s_4 \mapsto -s_4 \) transforms a state of energy \( E \) into a state of energy \( -E \). This implies that the density of states to be calculated in the next section will be an even function of \( E \) that, according to the above remarks, vanishes outside the interval \([-4, 4]\).

\( H \) yields the corresponding Hamiltonian equations of motion, see [19],

\[
\dot{s}_1 = (s_2 + s_4) \times s_1, \quad \dot{s}_2 = (s_1 + s_3) \times s_2, \quad \dot{s}_3 = (s_2 + s_4) \times s_3, \quad \dot{s}_4 = (s_3 + s_1) \times s_4. \tag{6}
\]
These equations of motion admit the conserved quantities \( S_a^2, S_b^2, S^2, M := S^{(3)} \), which satisfy the inequalities
\[
-S \leq M \leq S, \tag{10}
\]
\[
|S_a - S_b| \leq S \leq S_a + S_b. \tag{11}
\]
Moreover, all three components of \( S \) are conserved as it holds for every Heisenberg spin system. The partial spin sums satisfy the equations of motion
\[
\dot{S}_a^{(6)} (s_2 + s_4) \times s_1 + (s_2 + s_4) \times s_3 = S_b \times S_a = S \times S_a, \tag{12}
\]
and, analogously,
\[
\dot{S}_b = S \times S_b. \tag{13}
\]
This means that \( S_a \) and \( S_b \) will rotate about the fixed vector \( S \) with angular velocity \( S \). In a correspondingly rotating frame \( s_1 \) and \( s_3 \) will rotate about \( S_a \) with angular velocity \(-S_a\). This follows from
\[
\dot{s}_1^{(6)} (s_2 + s_4) \times s_1 = S_b \times S_a = (S - S_a) \times s_1, \tag{14}
\]
and, analogously,
\[
\dot{s}_3 = (S - S_a) \times s_3. \tag{15}
\]
In the same manner, \( s_2 \) and \( s_4 \) will rotate about the rotating \( S_b \) with angular velocity \(-S_b\), see Fig. 1.

3 Classical Numerical Methods

For a numerical investigation of the classical properties of the AF spin square we have performed standard Monte-Carlo spin dynamics simulations [31]. One obtains the specific heat from such a simulation by calculating the fluctuations of the energy Eq. (4) according to
\[
c(\beta) = \beta^2 \left( \langle E^2 \rangle - \langle E \rangle^2 \right), \tag{16}
\]
\[\text{cp. (46).}\] Here, \( \langle \ldots \rangle \) denotes sample averaging during a Monte-Carlo simulation at a given inverse temperature \( \beta \). Likewise, one obtains the susceptibility by calculating the fluctuations of the total magnetization \( S \) according to
\[
\chi(\beta) = \frac{\beta}{3} \left( \langle S^2 \rangle - \langle S \rangle^2 \right), \tag{17}
\]
\[\text{cp. (60).}\] For the numerical calculation of the classical density-of-states (dos) function \( D(E) \) we have used the method developed by Wang and Landau [32]. One advantage of this method is that once the density of states is known one can directly calculate thermodynamic quantities for any temperature without the need of performing any further simulations. Hence, by numerical integration of the dos in Eq. (42) we obtain the temperature-dependent partition function \( Z(\beta) \) as well as the inner energy \( U_1(\beta) = \langle E \rangle \) and the 2nd moment \( U_2(\beta) = \langle E^2 \rangle \) by evaluating Eq. (44). Given this, one can directly calculate the temperature-dependent specific heat using Eqs. (16) or (46), resp. and the entropy using Eq. (50). The Wang-Landau method can be extended to calculate the dos as a function of energy and magnetization, see [33–35]. We have implemented this extension to numerically calculate the susceptibility additionally to the Monte-Carlo simulation, see Fig. 10.

4 Density of States

It turns out that the classical density-of-states (dos) function \( D(E) \) can be obtained in closed, even quite simple form. To explain our method of calculating \( D(E) \), it is appropriate to make a brief digression into the quantum theory of the AF spin square.
4.1 Quantum Case

The quantum version of the Eq. (5) can be written as

$$ H \simeq = \frac{1}{2} \left( S^2 - S_{a}^2 - S_{b}^2 \right), $$

(18)

where the Hermitean operators $H$, $S$ etc. are defined on a $(2s + 1)^4$-dimensional Hilbert space $\mathcal{H}$ and $s = 1/2, 1, 3/2, \ldots$ is the individual spin quantum number. A convenient base of $\mathcal{H}$ is given by the product base, the vectors of which being written as $|m_1, m_2, m_3, m_4\rangle$ where $m_i = -s, -s+1, \ldots, s-1, s$ for $i = 1, \ldots, 4$. The $m_i$ are the eigenvalues of individual spin operators $S_i^{(3)}$. 

Fig. 1 Illustration of the time evolution of the spin square consisting of a superposition of different rotations. The partial sum vectors $S_a$ and $S_b$ rotate anti-clockwise around the total conserved spin vector $S$ with angular velocity $\tilde{S}$ (red circle). The individual spin vectors $s_1$ and $s_3$ in turn rotate clockwise around $S_a$ with angular velocity $S_a$ (green circle), analogously $s_2$ and $s_4$ around $S_b$ (blue circle).
The coupling of the two spins of number 1 and 3 gives rise to another basis in the \((2s+1)^2\)-dimensional Hilbert space \(\mathcal{H}_{13}\) denoted by
\[
|S_a, m_a\rangle = \sum_{m_1, m_3} CG (S_a, m_a; s, m_1, s, m_3) |m_1, m_3\rangle,
\]
(19)
where the \(CG(\ldots)\) are the Clebsch-Gordan coefficients, see, e.g., [37], 27.9. This is the common eigenbasis of \(S_a^2\) and \(S_a^{(3)}\) with eigenvalues \(S_a (S_a + 1)\) and \(m_a\), resp. Analogous remarks apply to the coupling of the two spins of number 2 and 4 which yields
\[
|S_b, m_b\rangle = \sum_{m_2, m_4} CG (S_b, m_b; s, m_2, s, m_4) |m_2, m_4\rangle.
\]
(20)
Finally, we consider the coupling \((1, 3), (2, 4) \rightarrow (1, 2, 3, 4)\) which yields a common eigenbasis of \(S^2, S_a^2, S_b^2, S^{(3)}\) with eigenvalues \(S (S + 1), S_a (S_a + 1), S_b (S_b + 1), M\), resp.:
\[
|S, S_a, S_b, M\rangle = \sum_{m_a, m_b} CG (S, M; S_a, m_a, S_b, m_b) |S_a, m_a, S_b, m_b\rangle.
\]
(21)
These states are also eigenstates of the Hamiltonian (18) with eigenvalues
\[
\varepsilon = \frac{1}{2} (S(S + 1) - S_a (S_a + 1) - S_b (S_b + 1)).
\]
(22)
Solving this equation for \(S \geq 0\) yields
\[
S = S_E := \frac{1}{2} \left( \sqrt{8\varepsilon + (2S_a + 1)^2 + (2S_b + 1)^2} - 1 - 1 \right).
\]
(23)
This result can be used to calculate the number \(\mathcal{N}_q(E)\) of eigenstates with an energy \(\varepsilon \leq E\). Note that the Clebsch-Gordan coefficient (20) vanishes if the triangle inequality \(|S_a - S_b| \leq S \leq S_a + S_b\) is violated. For each \(S\) satisfying this inequality and, additionally, \(S \leq S_E\) there are \(2S + 1\) states with the same energy corresponding to different \(M\) in (21). Hence
\[
\mathcal{N}_q(E) = \sum_{S = \min(S_a, S_b + 1)}^{\min(S_E, S_a + S_b)} \sum_{S = |S_a - S_b|} 2S + 1.
\]
(24)
4.2 Classical Case
Now we consider the classical limit \(s \to \infty\). This means: All quantum numbers are scaled according to \(S = S/s, S_a = S_a/s, E = E/(s(s + 1)), \ldots\) etc., all functions are expanded into \(1/s\)-series and only the leading terms independent of \(s\) are kept. The function \(S_E\) according to (23) will hence be replaced by
\[
S_E := \sqrt{2E + S_a^2 + S_b^2}.
\]
(25)
The sums occurring in (24) are replaced by corresponding integrals resulting in the following expression
\[
\mathcal{N}(E) = \int_0^2 dS_a \int_0^2 dS_b \int_{|S_a - S_b|}^{\min(S_E, S_a + S_b)} 2S dS
\]
(26)
for the volume formed of phase space points with energy \(\leq E\).

Although the dos is symmetric w. r. t. \(E\) we will consider both cases \(E > 0\) and \(E < 0\) separately in order to simplify the presentation of the analogous calculations for the susceptibility, see Sect. 7.1.
Fig. 2 The region in \((S_a, S_b, S)\)-space for the integration (26). The dark yellow polyhedron represents the triangle inequality (11) and the light red surface is the graph of \(S = SE(S_a, S_b)\) for the example \(E = 1\). This graph intersects the boundary of the polyhedron at the blue curve which is projected onto the \(S_a - S_b\)-plane and yields the hyperbola \(S_a S_b = E\) according to (27). The domain of integration (26) will hence be the intersection of the polyhedron with the region below the surface \(S = SE\).

4.2.1 \(E > 0\):

To simplify the evaluation of the minimum in the upper integral limit in (26) we will divide the \(S_a - S_b\)-square into two regions according to whether \(S_a + S_b \leq SE\) or not. Note that

\[
S_a + S_b \leq SE \Leftrightarrow (S_a + S_b)^2 \leq S_{E}^2 = 2E + S_a^2 + S_b^2 \Leftrightarrow S_a S_b \leq E.
\]

Hence the \(S_a - S_b\)-square is divided into two regions separated by a hyperbola, see Fig. 2.

Next, we will perform the integration (26) step by step. The integral over \(S\) has two different forms, depending on whether \(S_a + S_b \leq SE\) or not. In the first case we obtain

\[
I_1 = \int_{|S_a - S_b|}^{S_a + S_b} S \, dS = 2S_a S_b,
\]

(28)

where we have omitted the overall factor 2 that can be absorbed by the normalization constant. The second case yields

\[
I_2 = \int_{|S_a - S_b|}^{SE} S \, dS = E + S_a S_b.
\]

(29)

The following integrations over \(S_a\) and \(S_b\) can be split into three parts corresponding to the regions \(A\), \(B\) and \(C\), see Fig. 3, left panel. For the contribution from \(A\) we obtain

\[
I_A \overset{(28)} = \int_0^{E/2} dS_a \left( \int_0^2 dS_b(2S_a S_b) \right) = \frac{E^2}{2}.
\]

(30)
Fig. 3 The region in the \((S_a, S_b)\)-plane for the integration (26) divided by the hyperbola \(S_a S_b = |E|\). Left panel: \(E > 0\). The integral (26) assumes different forms in the three regions \(A\), \(B\) and \(C\). Right panel: \(E < 0\). The integral (26) is only non-zero in the region \(A\).

The region \(B\) contributes the integral

\[
I_B = \int_{E/2}^{2} dS_a \left( \int_{0}^{E/S_a} dS_b \left( 2 S_a S_b \right) \right) = E^2 \log \left( \frac{4}{E} \right).
\]  
(31)

In the region \(C\) the upper bound of \(S\) will be \(S_E\) and hence the corresponding integral reads

\[
I_C = \int_{E/2}^{2} dS_a \left( \int_{E/S_a}^{2} dS_b \left( E + S_a S_b \right) \right) = 4 + 4E - \frac{5E^2}{4} - \frac{3}{2} E^2 \log \left( \frac{4}{E} \right).
\]  
(32)

The sum of (30), (31) and (32) can be simplified to

\[
\mathcal{N}(E) = I_A + I_B + I_C = C \left( \frac{-3E^2}{4} - \frac{1}{2} E^2 \log \left( \frac{4}{E} \right) + 4E + 4 \right),
\]  
(33)

where the normalization constant \(C\) is preliminarily left open. The derivative of \(\mathcal{N}(E)\) gives the dos:

\[
D(E) = \frac{\partial \mathcal{N}(E)}{\partial E} = C \left( 4 - E \left( 1 + \log \left( \frac{4}{E} \right) \right) \right), \quad \text{for} \ 0 \leq E \leq 4.
\]  
(34)

4.2.2 \(E < 0\) :

For \(E < 0\) we have

\[
S_E = \sqrt{2E + S_a^2 + S_b^2} < \sqrt{S_a^2 + S_b^2} \leq S_a + S_b,
\]  
(35)

and hence the upper integral limit in (26) will always be \(S_E\). However, it may happen that the lower integral limit in (26) is above \(S_E\), in which case the integral (26) vanishes. This occurs iff

\[
S_E \leq |S_a - S_b| \Leftrightarrow 2E + S_a^2 + S_b^2 \leq S_a^2 - 2S_a S_b + S_b^2 \Leftrightarrow S_a S_b \leq -E = |E|,
\]  
(36)

that is, iff \((S_a, S_b)\) lies outside the region \(A\), see Fig. 3, right panel. Therefore the only contribution to (26) will be given by

\[
\mathcal{N}(E) = \int_{-E/2}^{2} dS_a \left( \int_{-E/S_a}^{2} dS_b \left( E + S_a S_b \right) \right) = \frac{3E^2}{4} - \frac{1}{2} E^2 \log \left( \frac{-E}{4} \right) + 4E + 4.
\]  
(37)
Fig. 4 Comparison of the analytical density of states (dos) function \( D(E) \) according to (39) (blue curve) with the numerical result (red points) obtained by Wang-Landau sampling [32].

The derivative of \( N(E) \) gives the dos:

\[
D(E) = \frac{\partial N(E)}{\partial E} = C \left( 4 + E \left( 1 + \log \left( -\frac{E}{4} \right) \right) \right), \quad \text{for } -4 \leq E \leq 0.
\]

This agrees with (34) if \( E \) is replaced by \(-E\), thereby again confirming the symmetry of the dos.

### 4.2.3 \(-4 \leq E \leq 4\):

Extending \( D(E) \) to all values of \( E \) and calculating the normalization constant as \( C = \frac{1}{8} \) finally gives the result

\[
D(E) = \begin{cases} 
\frac{1}{8} \left( 4 - |E| \left( 1 + \log \left( \frac{4}{|E|} \right) \right) \right) & -4 \leq E \leq 4, \\
0 & \text{else},
\end{cases}
\]

see Fig. 4.

For later purposes we expand the dos at \( E = E_{\text{min}} = -4 \) into a power series in the variable \( \epsilon = E - E_{\text{min}} = E + 4 \):

\[
D(E) = D(-4 + \epsilon) = \sum_{n=2}^{\infty} \frac{2^{-2n-1}}{(n-1)n} \epsilon^n
\]

\[
= \frac{\epsilon^2}{64} + \frac{\epsilon^3}{768} + \frac{\epsilon^4}{6144} + \frac{\epsilon^5}{40960} + \frac{\epsilon^6}{245760} + \frac{\epsilon^7}{1376256}
\]

\[
+ \frac{\epsilon^8}{7340032} + \frac{\epsilon^9}{37748736} + \frac{\epsilon^{10}}{188743680} + O(\epsilon^{11})
\]

### 5 Specific Heat

#### 5.1 Classical Case

For the calculation of the specific heat we do not have to resort to the phase space, but can use the density-of-states function \( D(\epsilon) \) modulated by the Boltzmann factor \( e^{-\beta \epsilon} \), where \( \beta = 1/T \) denotes the (dimensionless) inverse temperature, as usual. Then the partition function can be expressed as

\[
Z(\beta) = \int_{-4}^{4} D(\epsilon) e^{-\beta \epsilon} \, d\epsilon.
\]
For the spin square the inner energy assumes the form

$$Z(\beta) = \frac{1}{4\beta^2} (\text{Chi}(4\beta) - \log(4\beta) - \gamma),$$  

(43)

where \(\text{Chi}(z)\) denotes the hyperbolic cosine integral, see [36], 6. 2. 16., and \(\gamma\) the Euler-Mascheroni constant.

The inner energy is obtained as the first moment \(U_1(\beta)\) where the \(n\)-th moment is defined by

$$U_n(\beta) = \frac{1}{Z(\beta)} \int_{-\infty}^{\infty} e^{\varepsilon n} D(\varepsilon) e^{-\beta \varepsilon} d\varepsilon.$$  

(44)

For the spin square the inner energy assumes the form

$$U_1(\beta) = \frac{1}{\beta} \left( 2 + \frac{2 \sinh^2(2\beta)}{\log(\beta) - \text{Chi}(4\beta) + \gamma + \log(2)} \right).$$  

(45)

After a short calculation the specific heat \(c(T) := \frac{\beta}{\beta^2} U_1(1/T)\) can be written in the well-known form as

$$c(\beta) = \beta^2 \left( U_2 (\beta) - U_1^2 (\beta) \right),$$  

(46)

where \(U_2(\beta)\) denotes the second moment according to the general definition (44). The explicit form reads

$$c(\beta) = \frac{1}{(\log(\beta) - \text{Chi}(4\beta) + \gamma + \log(4))} \times \frac{2 \sinh^2(2\beta)}{(\log(\beta) - \text{Chi}(4\beta) + \gamma + \log(4)) (6 \log(\beta) - 4\beta \sinh(4\beta) + 5 \cosh(4\beta) - 6\text{Chi}(4\beta) + 6\gamma - 5 + 12 \log(2))}.$$  

(47)

Using the series expansion (40) of the dos we can easily derive a low temperature expansion of \(c(T)\) of the form

$$c(T) \sim 3 + \frac{T}{2} + \frac{9T^2}{16} + \frac{13T^3}{16} + \frac{355T^4}{256} + \frac{1383T^5}{512} + \frac{24129T^6}{4096} + \frac{29093T^7}{2048} + \frac{2460087T^8}{65536} - \frac{2182975T^9}{131072} - \frac{7263267T^{10}}{1048576} + O\left(T^{11}\right).$$  

(48)

The low temperature limit \(\lim_{T \to 0} c(T) = \alpha + 1 = 3\) is due to the lowest non-vanishing power of \(\alpha = 2\) in the expansion (40). It can also be derived by the following elementary argument: The number of degrees of freedom of the spin square is \(2 \times 4 = 8\) and the Néel ground state is collinear and can be freely rotated in spin space. This reduces the number of quadratic modes for excitations close to the ground state to \(8 - 2 = 6\). Each quadratic mode contributes \(\frac{1}{2}\) to the specific heat at \(T = 0\) which confirms the above result of \(\lim_{T \to 0} c(T) = 3\).

The high temperature limit of \(c(T)\) is obtained by a Taylor expansion of (47) in the variable \(\beta = 1/T:\)

$$c(T) \sim 4 \frac{1}{3} \frac{1}{T^2} + \frac{8}{45} \frac{1}{T^4} - \frac{16}{63} \frac{1}{T^6} + \frac{6304}{91125} \frac{1}{T^8} + \frac{64}{66825} \frac{1}{T^{10}} + O\left(\frac{1}{T^{12}}\right) \quad \text{for } T \to \infty.$$  

(49)

Hence \(c(T)\) decays for \(T \to \infty\) with the leading power of \(\frac{4}{3T^2}\). Moreover, it has a global maximum at \(T_m = 0.371046\) with height \(c_m = c(T_m) = 3.27751\), see Fig. 5.
Specific heat $c(T)$ as a function of temperature $T$. We show the analytical result (47) (blue curve), the low-temperature expansion (48) (black, dotted curve), the leading power $\frac{4}{3T}$ of the high temperature limit according to (49) (dashed, yellow curve) as well as the numerical results using Monte-Carlo simulation (red points) and Wang-Landau calculation (cyan points). Note the low temperature limit $c(T=0) = 3$ as well as the global maximum at $T_m = 0.371046$ with height $c_m = c(T_m) = 3.27751$ (thin red lines).

5.2 Quantum Case

Using the results of Sect. 4.1 it is a straightforward task to calculate the eigenvalues $\varepsilon_n = \varepsilon_{S_x, S_y, S_z, M}$, see (22), together with their multiplicity $d_n$. In general, further degeneracies occur, additional to the degeneracy w. r. t. $M$, which reduce the number of different eigenvalues. For the largest chosen value of the individual quantum number $s = 30$ we thus obtain 6103 different eigenvalues with multiplicities $d_n$ that sum up to the dimension of the Hilbert space of $(2s + 1)^4 = 13,845,841$. Therefore, in this case, the partition function $Z = \sum_n d_n \exp(-\beta \varepsilon_n)$ has 6103 terms and the specific heat $c(\beta)$ has about four times as many terms, that can, nevertheless, be handled in reasonable computing times by a computer-algebraic software like MATHEMATICA® [38].

We will plot $c(T)$ for the quantum numbers $s = 1/2, 5, 30$ as well as for the classical limit $s \to \infty$ calculated in the previous section. For the sake of comparison we have chosen the scaled temperature $\frac{T}{(2s + 1)}$ as the independent variable, see Fig. 6. For a finite quantum spin system and $T \to 0$, $c(T)$ always converges in a flat-foot fashion to 0. This can be clearly seen in Fig. 6 for $s = 1/2$ but not for $s = 5$ or $s = 30$ due to numerical instabilities. However, Fig. 6 also illustrates how this fact can be reconciled with $\lim_{T \to 0} c(T) = 3$ in the classical case: Besides the global maximum, the specific heat for the quantum systems at low temperatures and increasing $s$ forms a shoulder and the classical $c(T)$ is the envelope of these shoulders for $s \to \infty$.

6 Entropy

6.1 Classical Case

The entropy $S(\beta)$ can be generally defined by

$$S(\beta) := \beta U_1(\beta) + \log Z(\beta).$$

Inserting the above results for $U_1$, see (45), and $Z$, see (43), we obtain

$$S(\beta) = 2 + \log \left( -\frac{\log(4\beta) - \text{Chi}(4\beta) + \gamma}{4\beta^2} \right) + \frac{2 \sinh^2(2\beta)}{\log(\beta) - \text{Chi}(4\beta) + \gamma + \log(4)}. \tag{51}$$

For $T \to 0$ the entropy diverges logarithmically. In order to determine the asymptotic form of $S(T)$ for $T \to 0$ we first consider

$$\text{Chi}(x) \sim \frac{1}{2} \exp(x) \left( \frac{1}{x} + \frac{1!}{x^2} + \frac{2!}{x^3} + \frac{3!}{x^4} + \ldots \right) \text{ for } x \to \infty, \tag{52}$$
Fig. 6 Specific heat $c$ as a function of scaled temperature $\frac{T}{s(s+1)}$. We show the classical result (47) (blue curve), as well as the quantum results for $s = 1/2, 5, 30$ (magenta, green, red curves).

Fig. 7 Reduced classical entropy $S(T) - 3 \log T$ as a function of temperature $T$. We show the analytical result (51) (blue curve), the numerical Monte-Carlo calculations (red points) and the low-temperature expansion (55) (yellow, dashed curve).

which can be derived from [36], 6.5.4., 6.2.20., 6.12.3., and 6.12.4.. Using $Z(\beta) \sim \frac{1}{4\beta^2} \text{Chi}(4\beta)$ for $\beta \to \infty$ we thus obtain

$$\log Z \sim \frac{4}{T} + 3 \log T - 5 \log 2 + \frac{T}{4} + \ldots \text{ for } T \to 0. \quad (53)$$

Together with

$$\beta U_1 \sim -\frac{4}{T} + 3 + \frac{T}{4} + \ldots \text{ for } T \to 0 \quad (54)$$

we thus obtain for $T \to 0$

$$S(T) \sim 3 \log T + (3 - 5 \log(2)) + \frac{T}{2} + \frac{9T^2}{32} + \frac{13T^3}{48} + \frac{355T^4}{1024} + \frac{1383T^5}{2560} + \ldots \quad (55)$$

Hence it is meaningful not to plot $S(T)$ but the reduced entropy $S(T) - 3 \log T$, see Fig. 7.
Fig. 8 Plot of the entropy $S$ as a function of scaled temperature $\frac{T}{s(s+1)}$. We show the classical entropy $S_{cl}$ according to (51) (blue curve) and the quantum entropies $S_{qu}$ for $s = 1/2, 5, 30$ (magenta, green, red curves), where the zero-point of $S_{qu}$ has been chosen as explained in the text. The low temperature limits $S_{qu}(T \to 0) = -4 \log(2s + 1)$ are indicated by small colored dots.

6.2 Quantum Case

The calculation of the entropy $S_{qu} = \beta U_1 + \log(Z)$ in the quantum case is largely analogous to the calculation of the specific heat explained in Sect. 5.2. However, there occurs an additional problem. In the high-temperature limit $\beta \to 0$ we have

$$S_{qu} \to \lim_{\beta \to 0} \log Z = \lim_{\beta \to 0} \log \text{Tr} \exp(-\beta H) = \log \text{Tr} \mathbb{I} = \log \text{dim},$$

where $\text{dim} = (2s + 1)^4$ is the dimension of the Hilbert space. This means that the high temperature limit depends on $s$. In contrast, the high temperature limit of the classical entropy vanishes: $S_{cl} \to \lim_{\beta \to 0} \log Z = \log Z(0) = \log 1 = 0$. Therefore, approximate agreement of $S_{qu}$ and $S_{cl}$ for large temperatures can only be achieved by an $s$-dependent shift of the zero-point of entropy. We decide to shift the quantum entropy and replace $\log Z$ by $\log \text{dim}^{\text{eff}}$ in the definition of $S_{qu}$, following a common practice, see e.g., [24], (3.1). This has the consequence that the low temperature limit of $S_{qu}(T)$ no longer vanishes, as it would follow for a non-degenerate ground state, but will be shifted to $S_{qu}(T \to 0) = -\log \text{dim}$. This is in accordance with the logarithmic divergence of the classical entropy to $-\infty$, see Sect. 6.1 and Fig. 8.

7 Susceptibility

7.1 Classical Case

If we apply a magnetic field $B$ in 3-direction, the Hamiltonian (4) is modified by an additional Zeeman term to

$$H_B = H - S^{(3)}B.$$

The resulting magnetization $M(B)$ is given by the expectation value of $S^{(3)}$ using the modified partition function. Due to the isotropy of the Hamiltonian (4) the magnetization will vanish at $B = 0$ and hence the first generally non-vanishing term of the Taylor expansion of $M(B)$ at $B = 0$ will be given by the "zero field susceptibility"

$$\chi(\beta) = \frac{dM}{dB} \bigg|_{B=0}.$$
After a short calculation one obtains the well-known expression

$$\chi(\beta) = \frac{\beta}{Z_0} \int \left( S(3) \right)^2 \exp(-\beta H) \, dV =: \beta \langle (S(3))^2 \rangle. \quad (59)$$

Again using isotropy of $H$ we have $\langle (S(1))^2 \rangle = \langle (S(2))^2 \rangle = \langle (S(3))^2 \rangle$ and thus

$$\chi(\beta) = \frac{\beta}{3} \langle S^2 \rangle = \frac{\beta}{3Z(\beta)} \int_{-4}^{4} \tilde{D}(E) \exp(-\beta E) \, dE, \quad (60)$$

where

$$\tilde{D}(E) = \frac{\partial}{\partial E} \frac{1}{8} \int_{0}^{2} dS_a \int_{0}^{2} dS_b \int_{|S_a - S_b|}^{\text{Min}(S_E, S_a + S_b)} S^3 \, dS, \quad (61)$$

analogously to (26). The factor $\frac{1}{8}$ has been introduced in (61) according to the normalization constant determined in (39). Analogously to Sect. 4.2 we consider a case distinction according to the sign of $E$.

7.1.1 $E > 0$:

To simplify the evaluation of the minimum in the upper integral limit in (61) we will divide the $S_a - S_b$-square into two regions according to whether $S_a + S_b \leq S_E$ or not, separated by the hyperbola $S_a S_b = E$, see Fig. 2. The integral over $S$ has two different forms, depending on whether $S_a + S_b \leq S_E$ or not. In the first case we obtain

$$J_1 = \int_{|S_a - S_b|}^{S_a+S_b} S^3 \, dS = 2S_a S_b \left( S_a^2 + S_b^2 \right). \quad (62)$$

The second case yields

$$J_2 = \int_{|S_a - S_b|}^{S_E} S^3 \, dS = (S_a S_b + E) \left( -S_a S_b + S_a^2 + S_b^2 + E \right). \quad (63)$$

The following integrations over $S_a$ and $S_b$ can be split into three parts corresponding to the regions A, B and C, see Fig. 3, left panel. For the contribution from A we obtain

$$J_A \overset{(62)}{=} \int_{0}^{E/2} dS_a \left( \int_{0}^{2} dS_b \, J_1 \right) = E^2 + \frac{E^4}{16}. \quad (64)$$

The region B contributes the integral

$$J_B \overset{(62)}{=} \int_{E/2}^{2} dS_a \left( \int_{0}^{E/S_a} dS_b \, J_1 \right) = 3E^2 - \frac{3E^4}{16}. \quad (65)$$

In the region C the upper bound of $S$ will be $S_E$ and hence the corresponding integral reads

$$J_C \overset{(63)}{=} \int_{E/2}^{2} dS_a \left( \int_{E/S_a}^{2} dS_b \, J_2 \right) = \frac{7E^4}{48} + \frac{2}{3} E^3 \log(E) - \frac{4}{9} E^3 (2 + \log(8)) - 2E^2 + \frac{32E}{3} + \frac{80}{9}. \quad (66)$$
The sum of (64), (65) and (66) can be simplified to
\[ \tilde{N}(E) = J_A + J_B + J_C = \frac{E^4}{48} + \frac{2}{3}E^3 \log(E) - \frac{4}{9}E^3(2 + \log(8)) + 2E^2 + \frac{32e}{3} + \frac{80}{9}. \] (67)

The derivative of \( \tilde{N}(E) \) gives the function
\[ \tilde{D}(E) = \frac{1}{8} \frac{d\tilde{N}(E)}{dE} = \frac{1}{8} \left( \frac{E^3}{12} + 2E^2 \log(E) - E^2(2 + \log(16)) + 4E + \frac{32}{3} \right), \text{ for } 0 \leq E \leq 4. \] (68)

7.1.2 \( E < 0 \):
Analogously to Sect. 4.2 the only contribution to (61) will be given by
\[ \tilde{N}(E) \text{ (63)} \int_{-E/2}^{2} dS_a \left( \int_{-E/S_a}^{2} dS_b J_2 \right) = -\frac{E^4}{48} - \frac{2}{3}E^3 \log(-E) + \frac{4}{9}E^3(2 + \log(8)) + 6E^2 + \frac{32E}{3} + \frac{80}{9}. \] (69)

The derivative of \( \tilde{N}(E) \) gives the function
\[ \tilde{D}(E) = \frac{1}{8} \frac{d\tilde{N}(E)}{dE} = -\frac{1}{8} \left( \frac{E^3}{12} - 2E^2 \log(-E) + E^2(2 + \log(16)) + 12E + \frac{32}{3} \right), \text{ for } -4 \leq E \leq 0. \] (70)

7.1.3 \(-4 \leq E \leq 4\):
Extending \( \tilde{D}(E) \) to all values of \( E \) finally gives the result
\[ \tilde{D}(E) = \begin{cases} \frac{1}{8} \left( -\frac{E^3}{12} - 2E^2 \log(-E) + E^2(2 + \log(16)) + 12E + \frac{32}{3} \right) & -4 \leq E \leq 0, \\ \frac{1}{8} \left( \frac{E^3}{12} + 2E^2 \log(E) - E^2(2 + \log(16)) + 4E + \frac{32}{3} \right) & 0 \leq E \leq 4, \\ 0 & \text{else.} \end{cases} \] (71)

Inserting this result into (60) and performing the integral gives, after some simplifications,
\[ \chi(\beta) = \frac{4\beta(2\beta + 2\gamma - 1 + \log(16)) + 8\beta \log(\beta) - 4\beta \sinh(4\beta) + (4\beta + 1) \cosh(4\beta) - 8\beta \text{Chi}(4\beta) - 1}{6\beta(\log(\beta) - \text{Chi}(4\beta) + \gamma + \log(4))}, \] (72)

see Fig. 10. A Taylor expansion of (72) at \( \beta = 0 \) yields the high temperature limit
\[ \chi(T) \sim \frac{4}{3T} - \frac{8}{9} \frac{1}{T^2} + \frac{8}{27} \frac{1}{T^3} - \frac{16}{405} \frac{1}{T^4} - \frac{16}{405} \frac{1}{T^5} + \frac{32}{945} \frac{1}{T^6} - \frac{416}{127575} \frac{1}{T^7} - \frac{12608}{1913625} \frac{1}{T^8} + \frac{1856}{637875} \frac{1}{T^9} - \frac{128}{1804275} \frac{1}{T^{10}} + O \left( \frac{1}{T^{11}} \right). \] (73)

For \( T \to 0 \) the susceptibility is of the form \( \frac{0}{0} \) since the total spin of the Néel ground state vanishes. A closer inspection of (72) shows that \( \lim_{T \to 0} \chi(T) = 2/3 \), see Fig. 10.

It will be instructive to sketch another derivation of this result. To this end we consider Cartesian coordinates \((x_{\mu}, y_{\mu}), \mu = 1, 2, 3, 4 \) in the tangent planes at \( s_{\mu} \) for a Néel ground state \( \uparrow \downarrow \uparrow \downarrow \) and calculate the Hessian \( K \) of the Hamiltonian \( H \) w. r. t. these coordinates. \( K \) has the eigenvalues 2, 2, 1, 1, 1, 1, 0, 0 corresponding to six quadratic modes and two zero modes describing rotations of the ground state. The eigenvectors characterizing these modes give rise to an alternative set of “normal” coordinates \( \xi_i \), \( i = 1, \ldots, 8 \). The total energy \( H \) as
Thermodynamics of the Spin

Fig. 9 Plot of two modes of excitation from the Néel ground state $↑↓↑↓$. The first mode (left panel) leads to finite total spin square $S^2$ (red double arrow), whereas the total spin square $S^2$ of the second mode (right panel) vanishes in quadratic order. There are two modes of the first kind (the one shown and its rotation by 90°) and four modes of the second kind (resulting from interchanging the pairs (1,3) and (2,4) and rotations by 90°).

well as the square of the total spin $S^2$ of a superposition of excitations can be expanded into a Taylor series in the $\xi_i$, namely

$$H = -4 + 2(\xi_1^2 + \xi_2^2) + \sum_{j=3}^{6} \xi_j^2 + O(\xi^3),$$

$$S^2 = 4(\xi_1^2 + \xi_2^2) + O(\xi^3).$$

This means that only the first two quadratic modes contribute to $S^2$ and hence to the susceptibility $\chi(T = 0)$, see Fig. 9. We will calculate the contribution of the first mode:

$$\langle S^2 \rangle = \int_0^\infty 4\xi_1^2 \exp(-\beta(-4 + 2\xi_1^2)) \, d\xi_1 / \int_0^\infty \exp(-\beta(-4 + 2\xi_1^2)) \, d\xi_1$$

$$= \frac{1}{\beta}.$$

In view of $\chi = \langle S^2 \rangle / S^2$ the first mode contributes 1/3 to the susceptibility; and analogously for the second mode which explains $\lim_{T \to 0} \chi(T) = 2/3$.

7.2 Quantum Case

Also the calculation of the susceptibility $\chi_{qu}$ in the quantum case is largely analogous to the procedure for the specific heat and for the entropy. The difference is that we have to calculate not only the different energy eigenvalues $\varepsilon_n$ and their degeneracies $d_n$ but have also to resolve for different total spin quantum numbers resulting in a number of triples $(d_m, \varepsilon_m, S_m)$. For $s = 20$ there are already 20, 239 such triples and corresponding numbers of terms for $\chi_{qu}$. Hence we restrict ourselves to $s = 20$ as the maximal spin quantum number.

Since the spin square has a unique ground state with $S = 0$ the susceptibility $\chi_{qu}(T)$ converges to 0, even in a flat-footed fashion. This can be seen for $s = 1/2, 1, 5/2, 5$ in Fig. 11. The classical susceptibility $\chi_{cl}(T)$ again appears as the envelope of all $\chi_{qu}$, plotted versus scaled temperature $T / (S + T)$, with the aforementioned finite limit $\chi_{cl}(T \to 0) = 2/3$, see Fig. 11.
8 Summary and Outlook

We have derived closed-form expressions for certain thermodynamic quantities of the classical AF spin square, viz. density of states, partition function, specific heat, entropy, and susceptibility. The partition function of the square has already been given in [13] albeit in terms of definite integrals, which could not be computed explicitly. Our results were numerically verified by Monte Carlo simulations and/or Wang-Landau calculations. The quantum version of the thermodynamic functions was also calculated analytically using known identities for the coupling of four spins, but these are too intricate to be stated explicitly. For practical reasons, we have limited these calculations to quantum numbers of $s \leq 20$ for susceptibility and to $s \leq 30$ for the other cases.

With analytical results for thermodynamic functions in both cases, quantum and classical, a comparison with the classical limit $s \to \infty$ is obvious. This comparison not only shows the consistency between the two classes of results, but also illustrates the precise way to understand the classical limit. The first point to pay attention to is the correct scaling of the temperature in the form $T/(s+1)$, which follows the scaling of the energy.
Another point is the behavior for $T \to 0$. Quantum mechanically, the specific heat and susceptibility approach 0 flatly, while the classical counterparts take positive values. This apparent contradiction can be resolved by observing that the "quantum flat feet" are increasingly compressed with respect to the scaled temperature, yielding the classical quantities as their envelopes, see Figs. 6 and 11.

With respect to entropy, another apparent contradiction occurs: The quantum entropy at $T = 0$ should vanish due to a non-degenerate ground state, while the classical entropy diverges logarithmically to $-\infty$. As explained in detail in Sect. 6 the classical limit of the quantum entropy for medium and large $T$ can only be reached if the high temperature limits are properly adjusted. Here we have made the obvious choice of redefining the quantum partition function by $Z_{\text{qu}} = \text{Tr} \left( \exp(-\beta H)/\text{dim} \right)$, which resolves the aforementioned contradiction in the low temperature region.

The comparison of our results with the series representation of the partition function in [26] has led to certain identities, see the appendix A. For the spin triangle, it appears that the result of [26] needs to be modified, a discovery that requires further investigation. Another future task would be to extend the present results to other similarly integrable spin systems, e. g., the bow-tie or the octahedron.

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Declarations

Competing interests The authors declare no competing interests.

Appendix A: Comparison to Other Results

Using transfer matrix methods, a series representation of the partition function of the AF Heisenberg $N$-ring has been derived [26] that reads

$$Z_N(\beta) = \sum_{\ell=0}^{\infty} (2\ell + 1) \left( \frac{\pi}{2\beta} I_{\ell + \frac{1}{2}}(\beta) \right)^N. \quad \text{(A1)}$$
This series can be re-written using the definition of the modified spherical Bessel function \( i_\ell(z) := \sqrt{\frac{\pi}{2z}} I_{\ell + \frac{1}{2}}(z) \), see [36], 10.47.7. For \( N = 2, 3, 4 \) there exist independent expressions for \( Z_N(\beta) \). Let us start with \( N = 2 \). According to [8], Eq. (14) and setting \( J_c = 2 \), we have

\[
Z_2(\beta) = \frac{\sinh(2\beta)}{2\beta}.
\]  
(A2)

This result also follows from [13], Eq. (37), in the limit of vanishing magnetic field and leads to the identity

\[
\sum_{\ell=0}^{\infty} (2\ell + 1) I_{\ell + \frac{1}{2}}(\beta)^2 = \frac{\sinh(2\beta)}{\pi}.
\]  
(A3)

The latter identity can also be obtained by multiplying the recurrence relation

\[
2\ell + 1 \beta \frac{d}{d\beta} i_\ell(\beta) = i_{\ell-1}(\beta) - i_{\ell+1}(\beta),
\]  
(A4)

see [39], Eq. (37), with \( i_\ell(\beta) \) and summing over \( \ell = 0, \ldots, \infty \).

Curiously, the analog procedure does not work for \( N = 3 \). We adopt the explicit form of \( Z_3 \) from [13], Eq. (23), up to the factor \( \frac{3}{4\pi} \),

\[
Z_3(\beta) = e^{3\beta/2} \frac{\sqrt{\pi}}{4^{3/2}} \left( \frac{\sqrt{\beta}}{2} \right)^3 \left( 3 \text{erf} \left( \frac{\sqrt{\beta}}{2} \right) - \text{erf} \left( 3\frac{\sqrt{\beta}}{2} \right) \right).
\]  
(A5)

This equation has been independently checked using the methods of this paper. But (A5) differs numerically from (A1) for \( N = 3 \). Instead we found the following identity

\[
Z_3(\beta) = -\sum_{\ell=0}^{\infty} (2\ell + 1) \left( \frac{\pi}{2\beta} I_{\ell + \frac{1}{2}}(-\beta) \right)^3,
\]  
(A6)

which agrees with (A5) as verified by Fig. 12. When evaluating the modified spherical Bessel function for negative real arguments we have to consider that this function has a cut on the negative real axis, cp. [36], §10.25. In (A6) we have used the convention, also adopted by MATHEMATICA® [38], that \( i_\ell(z) \) will be an odd function for even \( \ell \) and an even function for odd \( \ell \).

Now we pass to \( N = 4 \). In order to evaluate

\[
Z_4(\beta) = \sum_{\ell=0}^{\infty} (2\ell + 1) \left( \frac{\pi}{2\beta} \right)^2 I_{\ell + \frac{1}{2}}(\beta)^4 = \sum_{\ell=0}^{\infty} (2\ell + 1) i_\ell(\beta)^4,
\]  
(A7)

which is (A1) for \( N = 4 \), we consider the equation

\[
2\beta^2 \frac{d}{d\beta} i_\ell(\beta) + \frac{\beta}{2} i_\ell(\beta) = i_{\ell-1}(\beta) + i_{\ell+1}(\beta),
\]  
(A8)

see [36] 10.51.4. Following a similar procedure as in [39] this equation will be multiplied with (A4) and further with \( i_\ell(\beta)^2 \). The result is summed over \( \ell = 0, \ldots, \infty \) and can be written as

\[
\frac{1}{\beta^2} \frac{d}{d\beta} Z_4(\beta) + \frac{1}{\beta^2} Z_4(\beta) = \sum_{\ell=0}^{\infty} i_\ell(\beta)^2 (i_{\ell-1}(\beta)^2 - i_{\ell+1}(\beta)^2) = i_{-1}(\beta)^2 i_0(\beta)^2 = \frac{\sinh^2 2\beta}{4\beta^2}.
\]  
(A9)

This differential equation with initial condition \( Z_4(0) = 1 \) has the solution

\[
Z_4(\beta) = \frac{1}{\pi^2} (\text{Chi}(4\beta) - \log(4\beta) - \gamma),
\]  
(A10)

where \( \gamma \) is the Euler-Mascheroni constant. This result coincides with the partition function of the square \( Z(\beta) \) calculated above, see (43).
For the sake of completeness we add the analogous identity for $N = 1$ which follows from [37], 10.2.26, and $\theta = 0$, but has no physical interpretation in terms of partition functions for spin systems:

$$
\sum_{\ell=0}^{\infty} (2\ell + 1) I_{\ell+\frac{1}{2}}(\beta) = \sqrt{\frac{2\beta}{\pi}} \exp \beta. \tag{A11}
$$

This identity can also be derived by summing (A4) over $\ell = 0, \ldots, \infty$.

All identities mentioned here have been numerically tested.

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