The Ferric Wheel Revisited

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We reinvestigate the low temperature magnetic properties of the ferric wheel, a 10 spin (S = 5/2) iron(III) complex. The energy levels for a Heisenberg antiferromagnet with ten $S = 5/2$ spins are calculated exactly and found to be in excellent agreement with the observed low-temperature experimental data. By comparing the low-temperature magnetic susceptibility data with the exact energy levels, a coupling constant of 9.7 cm^{-1} is determined.

1. Introduction

The "ferric wheel" was synthesized by Taft et al.[1] in 1990. The central part of the molecule is a ring consisting of 10 ferric ions linked by 20 bridging methoxide and 10 bridging chloroacetate ligands. It has ideal D_{5d} symmetry, and the iron atoms lie in an approximately coplanar arrangement. It is a highly symmetric one-dimensional ring of magnetic ions. These features render it an ideal molecule for the study of magnetism in one-dimensional systems and for the comparison of the magnetic properties of large clusters with those of linear chains.

In this note, we first briefly review the experimental and theoretical investigations of Taft et al.[1] We then calculate the exact energy levels for the 10-membered Heisenberg antiferromagnet with $S = 5/2$ and compare to the experimental data. We now find essentially perfect agreement between the low- and high-temperature data with a coupling constant of 9.7 cm^{-1}. In addition, the small deviation between theory and experiment at very low temperature can be ascribed to a low concentration impurity.

2. The Ferric Wheel

The magnetic properties of the ferric wheel were investigated by Taft et al.[1] It was found that the molar magnetic susceptibility, measured at 3 kG, exhibits a temperature dependence typical of antiferromagnetic exchange coupling, reaching a maximum at around 65 K. Below this temperature it decreases rapidly to zero, and above this temperature it decreases toward zero, but more slowly. A small bump, whose nature is not very well understood, is observed below about 5 K.

The Heisenberg Hamiltonian for a system of N magnetic atoms in the presence of an external magnetic field can be written as

$$H = -\sum_{i=1}^{N}\sum_{j=1}^{N} J_{ij}\,\mathbf{S}_i\cdot\mathbf{S}_j - g\mu_B\sum_{i=1}^{N}\mathbf{H}\cdot\mathbf{S}_i$$

The first term in this expression represents the interaction of the magnetic atoms (with spin **S** among themselves), while the second term represents the interaction of the magnetic moments with the applied field. Nearest-neighbor coupling is assumed.

In 1963 Fisher[2] used a classical treatment, in which spin quantization is absent, to study the properties of this Hamiltonian (for an open chain) and found analytical solutions for the thermodynamic properties of the system, such as specific heat, free energy, magnetic susceptibility, etc, as a function of N and S.

Ring closure was taken into account in 1966 by Joyce[3] who imposed cyclic boundary conditions. He obtained a closed form expression for the classical partition function and the magnetic susceptibility of a ring of interacting magnetic atoms with nearest-neighbor interactions.

Numerous quantum mechanical calculations have been made for this Hamiltonian, mostly for $S = 1/2$ spin chains.[4] Calculations for larger S became more interesting after Haldane's conjecture[5] regarding the presence of an energy gap (as the number of spins gets large) for even S systems. In recent years, there have been a number of calculations for $S = 1$ and $S = 3/2$ chains using a variety of methods.[6] In this paper, we will be concerned with the energy levels of the $N = 10$, $S = 5/2$ chain in particular.

To fit the experimental temperature dependence of the magnetic susceptibility of the ferric wheel, Taft et al.[1] first used the classical treatment of the Heisenberg Hamiltonian. A coupling constant J of approximately 10 cm^{-1} with $g = 2.0$ was obtained. This treatment satisfactorily reproduces the temperature dependence down to 50 K; however, the magnetic susceptibility deviates considerably at lower temperatures. In particular, the classical molar susceptibility does not approach zero as the temperature approaches zero because spin quantization is absent. In general, the classical treatment only works well for small J/kT.

Taft et al.[1] also attempted to diagonalize the quantum mechanical Hamiltonian for the 10 member $S = 5/2$ ring. The molecule can have spin states with integer values that range from 0 to 25, and has a total number of $6^{10} = 60{,}466{,}176$ magnetic spin states. Even using point group symmetry and irreducible tensor operators to calculate the energy levels, only rings of up to 8 spin 5/2 were able to be treated. These authors observed that the reduced susceptibility versus reduced temperature of the 4-, 6-, and 8-member rings appeared to converge rapidly and thus concluded that the calculated magnetic susceptibility curve for the 8-member ring could be extrapolated

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to obtain the corresponding magnetic susceptibility curve for the 10-member ring with small error.

Using this procedure, an interaction constant J of 9.6 cm^{-1} with $g = 2.0$ was obtained. Although this treatment worked well for the higher temperature susceptibility, it was unable to reproduce the bump observed at 5 K. Other models employed, such as Hamiltonians with next nearest-neighbor interactions or with alternating exchange constants, were also unable to account for the bump. Taft[1] suggested that it might be caused by an impurity, possibly a diiron(III) complex.

Magnetization measurements by Taft et al.[1] conducted at 4.2 and 0.6 K in applied fields of up to 20 T indicate that, at 4.2 K, the magnetization increases smoothly with no sign of saturation, but at 0.6 K, the magnetization increases in a stepwise fashion. The magnetization data at 0.6 K show that from zero to 4 T, the magnetization is very small, which is consistent with an $S = 0$ state. However, as the applied magnetic field is increased further, the magnetization rapidly increases to about 2 μ_B, corresponding to an $S = 1$ state. At 9.2 T, the magnetization increases to 4 μ_B in agreement with an $S = 2$ state. Increasing the applied field even further produces net magnetizations that are consistent with spin states with total spin $S = 3$ and 4. In another experiment reported by Gatteschi et al.,[7] where the highest magnetic field achievable under the experimental set up was 42 T, spin states with total spin $S = 1, 2, 3, ..., 9$ were observed.

The different magnetic behaviors can be accounted for if one examines the lowest lying energy states of the ferric wheel. The stepwise increase in the magnetization observed at 0.6 K is a direct consequence of Zeeman splitting of the energy levels with the applied magnetic field, H. The interaction energy of the system with the applied field is given by $H_{int} = g\mu_B \mathbf{H}M$, where $\mu_B = \hbar e/2m_e c$ is the *Bohr magneton*, and M is the magnetic spin quantum number. Therefore, the crossover of higher spin multiplets at higher applied fields is responsible for the stepwise increase in the magnetization as the decrease in energy leads to new ground states.

At 0.6 K and zero applied field, the state $|S = 0, M = 0\rangle$ is the ground state and the only state thermally populated. As the applied field is increased, a magnetic subcomponent of the first excited state with nonzero spin, the $|1, -1\rangle$ state, decreases in energy by $-g\mu_B H$ and it becomes the ground state at approximately 4.6 T. The $|0,0\rangle$ and $|1, -1\rangle$ have the same energy when the following relation is satisfied:

$$\mathbf{H}_{0,1} = \frac{E(1) - E(0)}{g\mu_B} \tag{1}$$

In general, the crossover transition between the S and $S + 1$ states occurs when the expression

$$\mathbf{H}_{S,S+1} = \frac{E(S+1) - E(S)}{g\mu_B} \tag{2}$$

is satisfied. The expected saturation magnetization value for the new ground state $|1,-1\rangle$ is 2 $g\mu_B$. This is in agreement with the observed magnetization at this applied field. As the applied field increases, the state $|2, -2\rangle$ decreases in energy at a faster rate than the $|1,-1\rangle$ state, $-2g\mu_B$ vs $-g\mu_B$; it eventually crosses the $|1,-1\rangle$ state and becomes the new ground state. The expected saturation value for the magnetization of the $|2, -2\rangle$ state is $4\mu_B$, which again agrees with the observed magnetization. The subcomponents of higher $|S, -S\rangle$ spin states are affected in a similar manner. The stepwise increase in the magnetization is not observed at 4.2 K because at this temperature several of the excited spin states are populated and they contribute to the observed magnetization.

TABLE 1: Exact Energy Results for a Closed-Chain System with 4 Spin 5/2 Particles

$N = 4$	matrix dim = 20		
level	energy	$S(S+1)$	S
ground state	−30.0000000000	0.0	0.0
first excited state	−29.0000000000	2.0	1.0.
second excited state	−27.0000000000	6.0	2.0
third excited state[a]	−24.0000000000	2.0	1.0
fourth excited state[a]	−24.0000000000	2.0	1.0
fifth excited state[a]	−24.0000000000	12.0	3.0

[a] State is degenerate.

TABLE 2: Exact Energy Results for a Closed-Chain System with 6 Spin 5/2 Particles

$N = 6$	matrix dim = 229		
level	energy	$S(S+1)$	S
ground state	−43.9347105280	0.0	0.0
first excited state	−43.2430219026	2.0	1.0
second excited state	−41.8602667289	6.0	2.0
third Ex St	−39.7877720086	12.0	3.0

Taft et al.,[1] using an approximate procedure based on the assumption that the Lande interval rule is obeyed in the lowest states of the system (which they had found in quantum calculations of the 6 spin and 8 spin systems) and the experimental 0.6 K magnetization data (up to 50 T), found a coupling constant J of approximately 9.4 cm^{-1}, in reasonably good agreement with that found from the magnetic susceptibility data.

Because of (a) the possible impurity contribution to the magnetic susceptibility, (b) the small discrepancy between the value of J found from the high T data and the low-T energy level crossover data, and (c) the fact that the previous authors had been unable to calculate the exact eigenvalues of the system, we decided to calculate the energy levels of the 10 spin complex exactly and compare to the low T experimental data.

3. Exact Solutions

Using the translational symmetry of the system,[8] we were able to calculate exactly the lowest energy levels for a system of up to 10 spin 5/2 particles. These calculations were performed on a Sun-ultra machine with 2, 200 MHz processors and 0.5 megabytes of RAM. Arnoldi's procedure was used in order to diagonalize the Hamitonian matrices. The code for these programs was written in C. A more detailed description of the method and the results will be published elsewhere, along with results for a number of different spin chain systems.[9]

3.1. Results. In this section we present the energies and the angular momenta for the lowest few eigenstates of different sized spin 5/2 closed chains (setting $J = 1$ for convenience). Tables 1−4 give the energy levels of the lowest eigenstates of the $N = 4$, 6, 8, and 10 rings with spin 5/2 particles.

The spin angular momenta for the 10 particle system for the ground state, first excited state, second excited state, and third excited state are equal to 0, 1, 2, and 3, respectively, in agreement with Taft's experimental results. Also, if we define ϵ_i to be the energy difference between the ith excited state and the ground state, we find that the following relationship is satisfied:

$$\epsilon_i = \frac{S_i(S_i + 1)}{2} \times E_1 \tag{3}$$

TABLE 3: Exact Energy Results for a Closed-Chain System with 8 Spin 5/2 Particles

$N = 8$	matrix dim = 4535		
level	energy[a]	$S(S+1)$	S
ground state	−58.1104953669	0.0	0.0
first excited state	−57.5738959986	2.0	1.0
second excited state	−56.5021132916	6.0	2.0
third excited state	−54.8978551674	12.0	3.0

[a] Energies were calculated using the translational−symmetry groups procedure.

TABLE 4: Exact Energy Results for a Closed-Chain System with 10 Spin 5/2 Particles

$N = 10$	matrix dim = 111366		
level	energy[a]	$S(S+1)$	S
ground state	−72.3737430372	0.0	0.0
first excited state	−71.9316502917	2.0	1.0
second excited state	−71.0494041866	6.0	2.0
third excited state	−69.7305711647	12.0	3.0

[a] Energies were calculated using the translational∼symmetry groups procedure.

where E_1 is equal to 0.4421, or the energy difference between the first excited state and the ground state (see Table 4). Equation 3 indicates that the lowest spin states obey the Lande interval rule, in agreement with Taft's conjecture.

3.2. Comparison to Low-Temperature Experiments. We could use the theoretical expression for the magnetic susceptibility to fit the experimental data for the magnetic susceptibility gathered by Taft over the entire temperature range, and in this way determine the coupling constant J for the ferric wheel. However, it is more direct to use the magnetic fields at which the steps in the susceptibility occur. We use the fact that the crossover between the first excited state and the ground state was observed to occur when the applied magnetic field was equal to 4.6 T, and that the crossover transition between the second excited state and the first excited state occurred when the applied magnetic field was equal to 9.2 T. Using eq 2 we obtain a coupling constant equal to 9.727 cm^{-1} when the data for the 4.6 T crossover transition is used, and equal to 9.748 cm^{-1} when the data for the 9.2 T crossover transition is used. The average of these two values is 9.74 cm^{-1}, which we take as the coupling constant for the ferric wheel. This value is in excellent agreement with Taft's previous estimate based on the high T susceptibility data (9.6 cm^{-1}), and corrects the value determined using their approximate calculation based on the crossover data (9.4 cm^{-1}).

Note that had the exact eigenvalues of the 8-membered ring beeen used instead of those of the 10-membered ring, a value of $J = 8.0$ cm^{-1} would have been calculated when fitting the crossover transition data, in sharp disagreement with the value found from the high-temperature data. Hence the 8 spin system eigenvalues cannot be used to study the low-temperature properties of the ferric wheel. With the correct eigenvalues, the agreement between the high and low-temperature data is excellent.

3.3. Magnetic Susceptibility. The magnetic susceptibility for the system can be easily calculated once the energy levels and the corresponding spin angular momenta have been determined. The expression for the molar magnetic susceptibility is

$$\chi N_A = \left(\frac{3.752}{3\ \mathrm{T}}\right)\mu_{\mathrm{eff}}^2 \tag{4}$$

TABLE 5: Comparison between Low-Temperature Experimental Magnetic Susceptibility for the Ferric Wheel and Its Theoretical Magnetic Susceptibility[a]

temp (K)	exp χ (emu/mol)	theor χ (emu/mol)
2.50	0.142	0.833×10^{-1}
3.00	0.148	0.989×10^{-1}
3.50	0.151	0.109
4.00	0.153	0.117
4.50	0.155	0.122
5.00	0.156	0.127

[a] Taft et al. experimental data.

TABLE 6: Comparison between Low-Temperature Experimental and Theoretical μ_{eff}^2 for the Ferric Wheel[a]

temp (K)	exp μ_{eff}^2	theor μ_{eff}^2	impurity μ_{eff}^2
1.69	2.49	5.73×10^{-1}	1.91
1.86	2.83	7.82×10^{-1}	2.05
2.09	3.25	1.09	2.16
2.30	3.62	1.38	2.23
2.57	4.04	1.77	2.28
2.87	4.50	2.19	2.31
3.12	4.86	2.54	2.32
3.66	5.62	3.28	2.34
3.97	6.04	3.70	2.34
4.28	6.45	4.11	2.34
4.69	6.99	4.66	2.33
4.90	7.27	4.94	2.33
5.90	8.56	6.25	2.32

[a] Taft et al. experimental data. The impurity μ_{eff}^2 was calculated as the difference between the experimental and the theoretical data.

where μ_{eff}^2 is defined as

$$\mu_{\mathrm{eff}}^2 = \frac{g^2 \sum_i S_i(S_i+1)(2S_i+1)\mathrm{e}^{-E_{i0}/kT}}{\sum_i (2S_i+1)\mathrm{e}^{-E_{i0}/kT}} \tag{5}$$

and $(\mu_B^2 N_A/k)$ has been replaced by its its numerical value of 3.752.

We compute the values of μ_{eff}^2 at low temperatures using the lowest eigenvalues of the 10-spin ring and compare those to Taft's values in Tables 5 and 6. Note that the theoretical values are smaller than the experimental values. This is consistent with Taft's suggestion that at low temperatures an impurity contributes to the observed experimental magnetic susceptibility and is therefore responsible for the bump observed at about 5 K. If we assume that it is a diiron(III) complex as suggested by Taft, then the relative mole fraction of this complex compared to the ferric wheel is 0.033. Since the value of μ_{eff}^2 for the impurity contribution saturates by 3 K, the coupling constant J for this dimer is quite small, about 0.1 cm^{-1}.

4. Conclusion

We have calculated the magnetic eigenstates of a 10-spin Heisenberg antiferromagnetically coupled ring that represents the ferric wheel. The agreement between experiment and theory is now essentially exact.

Comparison with Taft's data shows that (a) the ferric wheel is a Heisenberg antiferromagnet with a coupling constant J equal to 9.7 cm^{-1} from both low-temperature and high-temperature data, (b) an impurity seems to contribute to the magnetic susceptibility at very low temperatures, (c) Taft's quantum treatment of the ferric wheel utilizing the energy levels of the

8-member antiferromagnetic ring is a reasonably good model for the magnetic susceptibility; however, a more quantitative fit requires the eigenvalues of the 10-spin system.

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