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Heat Capacity of a Quantum Dimer With General Spin S

Nick Valverde

Senior Undergraduate Student, Department of Physics and Astronomy, Arizona State University, Tempe, Arizona, USA

Abstract. In this paper we look at the thermodynamic properties of a system consisting of a quantum spin dimer for spins $S = 1/2,\ 1,\ 3/2,$ and 2 using a Hamiltonian of the form $H = -J(\vec{S_1} \cdot \vec{S_2})$ where J is the coupling constant between two spins $\vec{S_1}$ and $\vec{S_2}$. We find different and interesting behaviors in the temperature and S dependence of heat capacity depending on whether the coupling is ferromagnetic ($J > 0$) or antiferromagnetic ($J < 0$). Lastly, I try to shed some light on the possible causes for the observed behaviors, although some of the phenomena are not completely understood.

Keywords. Quantum dimer, Heat capacity, Heisenberg Hamiltonian.

1. INTRODUCTION

In localized magnetism one deals with single quantum spins ($\vec{S}$) interacting with each other represented by a spin Hamiltonian. Ground state and excited state properties of spin Hamiltonians have been extensively studied over the past many decades. There are quantum systems in which the basic building blocks are quantum spin clusters, QSC (dimers, trimers, tetramers etc) where the interaction between spins inside one cluster are very strong and the interaction between spins belonging to different clusters are much weaker. For these systems it is better to start with the QSC to understand their properties first and then look at the physics of interacting QSCs.

In this paper I will discuss the thermodynamic properties of a quantum spin dimers (QSD) of spin S (each member of the dimer) for S= $1/2$, 1, $3/2$, and 2. Although in most of the known QSDs the interaction between the spins is antiferromagnetic (AF), I will consider both AF and ferromagnetic cases to see how the difference in the ground state (degeneracy) and the spectral structure show up in the temperature dependence of the heat capacity C. The arrangement of the paper is as follows: first, I will discuss the model and then I will look extensively at the simplest dimer possible, which is the spin half dimer ($S = 1/2$). Following that, with some understanding of the physics of the system, I will then look at ferromagnetic and AF systems with different spin S. Lastly, several relationships arise by studying each system and discussing each behavior along with a possible reason for them.

2. THE MODEL

The system I am interested in consists of two interacting quantum spins $\vec{S_1}$ and $\vec{S_2}$ with same magnitude $S_1 = S_2 = S$. The Hamiltonian is of isotropic Heisenberg form give by

$$H = -J(\vec{S_1} \cdot \vec{S_2}). \tag{1}$$

Where J is the coupling between the two spins. The coupling constant can be thought of as how much the spins "feel" each other. If the two spins are hardly affected by one another, then J can be taken to be small and vice versa. Both signs of J are considered, anti-ferromagnetic when $J < 0$ and ferromagnetic when $J > 0$. In order to obtain the eigenvalue of *H*, it is convenient to write *H* as

$$H = \frac{-J}{2}\Big(S_T^2 - S_1^2 - S_2^2\Big) \tag{2}$$

where $\vec{S_T}$ is the total spin operator $\vec{S_T} = \vec{S_1} + \vec{S_2}$. Since the operators S_T^2, S_1^2, S_2^2 commute with each other, they can be simultaneously diagonalized giving the eigenvalues of *H* in terms of their individual eigenvalues $S_T(S_T+1), S_1(S_1+1),$ and $S_2(S_2+1)$ respectively. For the total spin $\vec{S_T}$ there is a magnetic degeneracy where the projection of the total spin along a particular (arbitrary) direction, the $\hat{z}$-direction perhaps, $S_{T,z}$ takes the value $M = -S_T, -S_T+1, ..., +S_T$, giving a degeneracy factor $g(S_T) = 2S_T + 1$. The corresponding energy is given by

$$E(S_T) = \frac{-J}{2}\Big(S_T(S_T+1) - S_1(S_1+1) - S_2(S_2+1)\Big). \tag{3}$$

Note that these calculations can be easily generalized to the case of two dissimilar spins. Here I consider $S_1 = S_2$

Given the energy spectrum and degeneracy, it is straight forward to carry out the statistical mechanics of the system at a finite temperature T using the Canonical partition function

$$Z = \sum_{S_T} g(S_T) e^{-E(S_T)/kT} \tag{4}$$

where *k* is the Boltzmann constant. Once the partition function is found the thermodynamic identities

$$F = -kT\ln(Z)\,,\; S = -\frac{\partial F}{\partial T}\,,\; C = T\frac{\partial S}{\partial T} \tag{5}$$

can be used to find the specific heat *C* after first finding the Helmholtz free energy *F* and entropy *S*.

3. PHYSICS OF S = 1/2

The spin half dimer is a well documented case and can be found in many textbooks[1]. Therefore, reviewing the physics of the spin half dimer will aid in our understanding of higher spin dimer

[1] Schroeder, Daniel V. An Introduction to Thermal Physics. San Francisco, CA: Addison Wesley, 2000. Print.

cases. Fig. 1 gives the T dependence of the heat capacity (in units of k) obtained for a spin half dimer ($S = 1/2$). From Fig. 1 we can see that changing the nature of the coupling between the spins (equivalently, the sign of J) has a profound effect on the system. The most apparent difference is in the height of the peaks between the ferromagnetic case ($J > 0$) and the AF case ($J < 0$). The peak itself is dubbed the Schottky anomaly and the temperature this occurs at will be called T^*. This difference is due to the differences in the degeneracies of the ground and excited states between the two cases, although the total number of states are the same. For the spin half dimer, there are two configurations: the singlet ($S_T = 0$) with $g_n = 1$ and the triplet ($S_T = 1$) with $g_n = 3$. For the ferromagnetic case the ground state is the triplet, making the first excited state the singlet and the reverse situation occurs for the AF case. Thus, for positive J, when energy is added to the system the spins only have one energy state to transition to. However, in the AF case there are three options. This difference in the accessible excited states is what causes this dramatic difference in the Schottky anomaly.

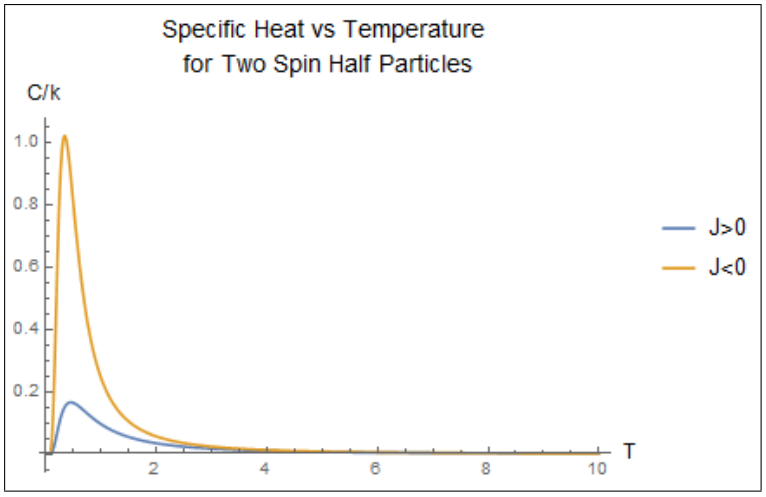


Figure 1. Heat capacity (in units of k) as a function of the temperature T for a spin 1/2 dimer for both ferromagnetic ($J > 0$) and anti-ferromagnetic ($J < 0$) coupling between the spins.

We can further understand this difference if we look at the following formula which relates specific heat to internal energy U,

$$C = \frac{\partial U}{\partial T}. \tag{6}$$

From (6), specific heat can be interpreted as the ability for a system to either absorb or release energy as the external temperature changes. Thus, the AF system is more readily able to absorb/release energy than the ferromagnetic system, which again, is due to the difference in the accessibility of excited states. Lastly, it is worthwhile to mention the low ($T << T^*$) and high temperature

($T >> T^*$) behaviors of C/k for both the cases. Looking at the figure we can discern that both cases approach zero exponentially. For the low T case, the reason is that there is not enough thermal energy for particles to make a jump to an excited state (cross gap in energy spectrum). In the high T case, there is plenty of thermal energy to allow the system to make transitions to the excited state. Each state has nearly equal probability of being occupied and thus, adding thermal energy to the system does not change the state of the system appreciably.

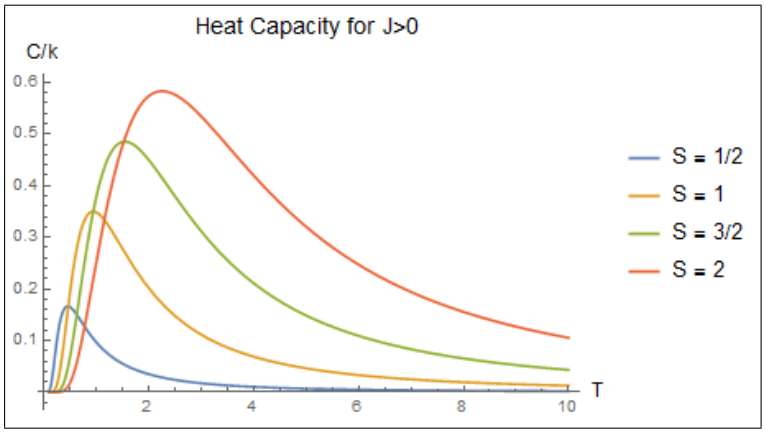


Figure 2. Heat capacity (in units of k) for ferromagnetically coupled dimers with $S = 1/2,\ 1,\ 3/2,$ and 2.

3.1 *Ferromagnetic Case (*$\mathbf{J > 0}$*)*

I will now discuss the specific heat trends for a ferromagnetic system with spin half, one, three-half, and two dimers. The specific heat curves for each case are presented in Fig. 2 where we see several interesting trends.

First, there is the increasing peak height. Looking back at equation (6) this behavior is consistent with our understanding of both the number and availability of states. As spin increases, the number of states consequently goes up. Thus, increasing spin increases the number of states the system can occupy, which makes the ability of the system to absorb energy greater. Second, peak temperature T^* of the Schottky anomaly also shifts to higher temperatures. Again, we can reason this behavior by thinking about the energy of the lowest excited states as measured from the ground state and the number of states. Since this energy difference increases with S and there are more excited states for higher spin, the system will need more thermal energy to populate these states, hence, a higher peak temperature T^*.

The ferromagnetic case presents orderly trends that make intuitive sense. Increasing the spin increases the number of states which increases the maximum heat capacity and the energy needed for C_{max} to be reached. The AF case, as we will see below, is more complex.

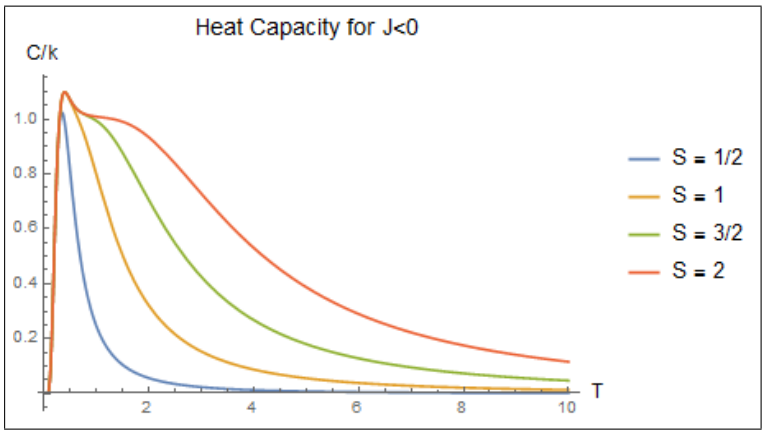


Figure 3. Heat capacity (in units of k) for AF coupled dimers with $S = 1/2,\ 1,\ 3/2,$ and 2.

3.2 *AF CASE (*$\mathbf{J < 0}$*)*

Now I would like to discuss the different dimer cases for an AF system. T dependence of C/k is shown in Fig. 3.

Clearly the AF system is not as simple as the ferromagnetic system. The trends clearly presented in Fig. 2 are absent in this case. There is a particular trend that warrants further investigation. As the spin of the system is increased there is a double hump feature that begins to become more prominent. It is not until $S = 3/2$ that the double hump is clearly visible. The exact reason for this behavior is still not completely understood. But, it is speculated that this double peak feature occurs due to the competition of energy scales in the system. Thus, there is a superposition of energy spectra interfering with each other to produce the net thermal response. The energy spectrum of the AF dimer is given by Fig. 4. It is also worth noting that, again, the heat capacity for the AF system is greater than the ferromagnetic system for each corresponding S value.

4. TRENDS FOR INCREASING S

Previously, we discussed some of the trends presented in the plots of each respective dimer system. It is beneficial to make a plot of these trends and see if we can deduce the behavior as spin is increased to infinity ($S \to \infty$). The two trends examined were how the peak temperature (T^*) and the maximum heat capacity (C_{max}) change with increasing spin. Figure 5 is a graph of these trends.

Since both curves are plotted as $1/S$ moving from right to left is equivalent to starting from zero spin and proceeding to infinite spin. Fig. 5a shows how T^* varies as we increase spin. The trend

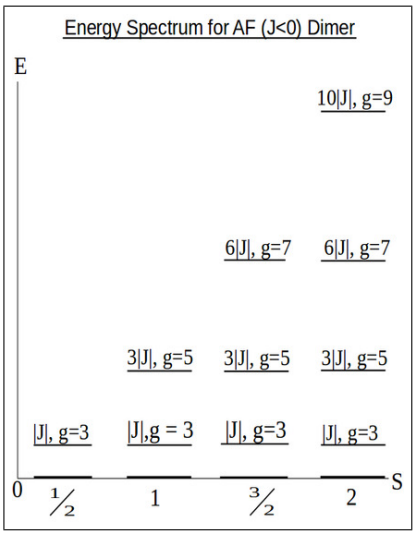


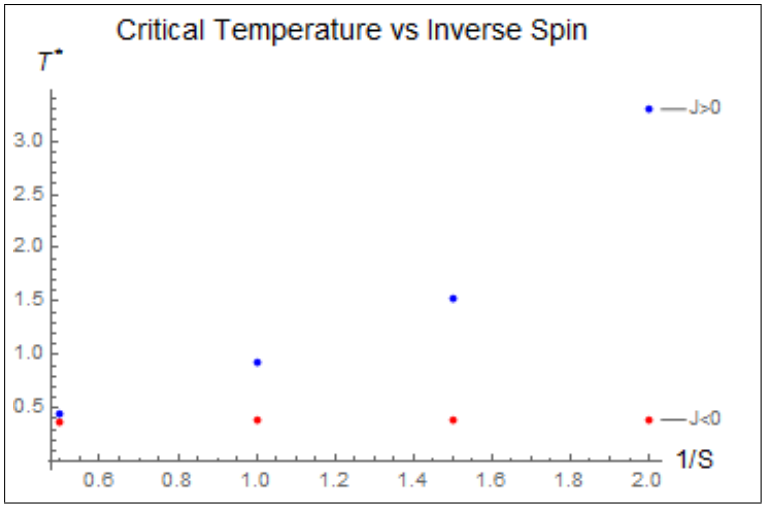
Figure 4. The energy spectrum for the AF dimer for $S = 1/2,\ 1,\ 3/2,$ and 2. Note that the ground state energies have been shifted for each dimer by a constant amount so that the ground stater energies begin at the same value $E = 0$.This constant shift does not affect the thermodynamic properties.

for the ferromagnetic system makes intuitive sense. Previously we saw this same trend for for the heat capacity curves. Increasing the spin, increases the available energy levels and, therefore, the system takes more energy to populate the states. However, the AF system has a different behavior. It increases slightly before staying constant. It is unclear why this behavior occurs and the trend is also limited, of course, by the number of data points chosen. Nonetheless I speculate that once again we are seeing some kind of competition between the number of spin configuration's degeneracy as it unfolds with increasing energy. This competition makes it difficult for the system to absorb energy based on the decreasing T^* and C_{max} values.

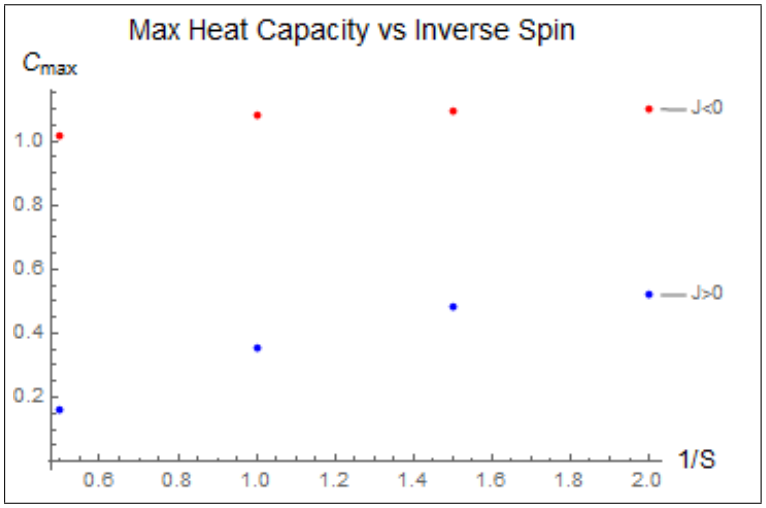
Fig. 5b reveals the trend for C_{max} as spin is increased. The ferromagnetic system again follows the simple intuition. The maximum heat capacity increases as we increase spin. The AF case, in addition to having an overall higher C_{max}, has a slower decrease. The decrease is subtle enough that the trend almost looks constant as in the T^* case. The physical reasoning for this behavior is not well understood and warrants further thinking to develop a deeper understanding.

5. CONCLUSION

We have seen a profound difference in the thermal response as measured through the T dependence of the heat capacity between the ferromagnetic and AF spin dimers. The trends presented for the



(a) T^* behavior for increasing spin.



(b) C_{max} behavior for increasing spin.

Figure 5. The S-dependence of the temperature T^* at which the heat capacity is maximum, for the ferromagnetic ($J > 0$) and AF ($J < 0$) cases.

ferromagnetic case make reasonable physical sense. However, the AF system shows unusual trends consisting of the double peak structure, and the behavior T^* and C_{max} for increasing spin. It is speculated that these behaviors are due to competition of energy levels and spin configurations (degeneracies). But, it is still unknown and warrants further study.

In passing I would like to remark that as technology continues to develop magnetic systems and the underlying physics explaining them will become ever more important. For example, there is now a new field of study dealing with using spins to transmit information. Similar to the way the charge degrees of freedom of electrons are used in electronics, electronic spins will now be used in spintronics. In a magnetic system there is a plethora of interacting spins. But, one can take a simple approximation and consider a dimer in this system and use that to develop the theory further. Thus, understanding these spin configurations and their effects, is not only an intellectual curiosity but also very applicable to today's and possibly the future's technologies.

6. ACKNOWLEDGMENTS

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