Entanglement temperature in molecular magnets composed of S-spin dimers

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Abstract – In the present work, we investigate the quantum thermal entanglement in molecular magnets composed of dimers of spin S, using an Entanglement Witness built from measurements of magnetic susceptibility. An entanglement temperature, \( T_e \), is then obtained for some values of spin S. From this, it is shown that \( T_e \) is proportional to the intradimer exchange interaction \( J \) and that entanglement appears only for antiferromagnetic coupling. The results are compared to experiments carried on three isostructural materials: KNaMSi\(_4\)O\(_{10}\) (M=Mn, Fe or Cu).

Introduction. – For about a decade it has been realized that quantum entanglement is a valuable resource for quantum information processing, since it allows forms of communication that are classically impossible [1,2]. However, until recently it was believed that the phenomenon could not exist beyond atomic scale, due to the interaction between the system and the environment. Such interaction would lead to decoherence of the quantum state, destroying entanglement.

However, some theoretical works raised the possibility that solid-state systems could also exhibit quantum entanglement at finite temperatures [3,4]. This “thermal entanglement” might be experimentally detected with the help of some observables, or “witnesses”, that are related to thermodynamical quantities, which could be directly measured [5–10]. An Entanglement Witness (EW), by definition, has a negative expectation value for certain types of entangled states [11–14]. The demonstration that quantum entanglement can influence the behavior of thermodynamical properties of solids, such as magnetic susceptibility [8–10,15–18], shows that quantum effects can be related to important macroscopic quantities. These features have established that the study of entanglement in solid-state systems [19] based on the observation of such EWs are helpful tools to quantum information and quantum computation, since many proposals of quantum chips are solid state based [20–25].

The class of materials known as molecular magnets [26] are among those which can exhibit thermal entanglement. In this class of materials, the intermolecular magnetic interactions are extremely weak compared to those within individual molecules. Thus a bulk sample, comprised by a set of non-interacting molecular clusters, is completely described in terms of independent clusters. The small number of coupled spins is very convenient from the point of view of the theoretical description, which can be made through analytical functions on a low dimensional Hilbert space. From a physical point of view, a molecular magnet can combine classical properties found in a macroscopic magnet [26] and quantum properties, such as quantum interference [27] and entanglement [5–9]. Recently, molecular magnets have been pointed out as good systems to be used in high-density information memories and also, due

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to their long coherence times [28], in quantum computing devices [20–25].

In this work, we investigate the quantum entanglement of molecular magnetic materials with \( S \)-spin dimers, that can be theoretically modeled by a Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian. The magnetic susceptibility of these systems can be directly related to an EW. Based on this model, we have obtained, for different spin values, the temperature below which the quantum entanglement exists, or the temperature of entanglement \((T_e)\). The results are experimentally verified using the magnetic susceptibility data, from a previous work (see ref. [29] for details), obtained for three isostructural materials: the first composed of antiferromagnetic Cu-dimers \((S = 1/2)\), the second composed of ferromagnetic Fe-dimers \((S = 2)\), and the third composed of antiferromagnetic Mn-dimers \((S = 5/2)\).

**Magnetic susceptibility of \( S \)-spin dimers.** – The magnetism of two interacting \( S \)-spins, or dimers, has been described quantitatively in the literature by the HDVV Hamiltonian [30]:

\[
\mathcal{H} = -J \mathbf{S}_A \cdot \mathbf{S}_B - g \mu_B \mathbf{B} \cdot (\mathbf{S}_A + \mathbf{S}_B),
\]

where \( J \) is the exchange interaction, \( \mathbf{S}_A \) and \( \mathbf{S}_B \) are the spins of each ion of the dimeric unit, \( g \) is the Landé factor, \( \mu_B \) is the Bohr magneton and \( \mathbf{B} \) is an external magnetic field. When the system is in thermal equilibrium, its thermal state is described by the density operator \( \rho = e^{-\beta \mathcal{H}} / Z \), in which \( Z = \text{tr}(e^{-\beta \mathcal{H}}) \) is the partition function, \( \beta = 1/k_B T \) and \( k_B \) is the Boltzmann constant. With this operator, one can calculate, among other thermodynamical quantities, the magnetic susceptibility, in which, for \( S_A = S_B \) and \( \mathbf{B} \to 0 \), holds as [30]

\[
\chi(T) = \frac{2N(g \mu_B)^2}{k_B T} \mathcal{F}^{(S)}(J, T),
\]

where, for \( S = 5/2 \)

\[
\mathcal{F}^{(5/2)}(J, T) = \frac{x}{J k_B T},
\]

\[
\mathcal{F}(1/2) = \frac{1}{J k_B T}.
\]

\[
\mathcal{F}(3/2) = \frac{1}{3 + e^{-x}},
\]

\[
x = J/k_B T
\]

For a system in which the Hamiltonian commutes with the \( z \) spin component, \([\mathcal{H}, \mathbf{S}_z] = 0\), the average magnetic susceptibility of \( N \)-spins in a complete separable state, \( \chi(T) \), measured along the three orthogonal axes, satisfies the relation [16,31]

\[
\chi(T) = \chi_x + \chi_y + \chi_z \geq \frac{(g \mu_B)^2 N S}{3 k_B T}.
\]

The EW is given by [16]

\[
\mathcal{E}(N) = \frac{3 k_B T \chi(T)}{(g \mu_B)^2 N S} - 1.
\]

Systems presenting \( \mathcal{E}(N) < 0 \) are in an entangled state. Such an EW has been used in recent works to detect entanglement in molecular magnets [5–8]. In ref. [6], the magnetic susceptibility is compared to a correlation function (see fig. 1 of ref. [6]) measured by neutron diffraction. The correlation function shows entanglement in the same range of temperature as the magnetic susceptibility, supporting the use of the magnetic susceptibility as an Entanglement Witness.

From eq. (6), together with eq. (2), one can identify the maximum temperature below which there is entanglement between the spins of the dimers, for different spin values. This temperature can be obtained from the inequality shown in eq. (7), i.e., dimers with \( S \)-spin are in an entangled state if the inequality below is satisfied:

\[
\mathcal{F}^{(S)}(J, T) < \frac{S}{3}.
\]

Considering that \( x_c = J/k_B T_e \) and eq. (3), one can obtain the temperature of entanglement. For example, for \( S = 1/2 \),

\[
\mathcal{F}^{(1/2)}(J, T) < \frac{1}{6}
\]

and then

\[
T_e^{(1/2)} = -0.91 \frac{J}{k_B}.
\]

Following this method, it is straightforward to obtain the temperature of entanglement for the different spins. The temperatures of entanglement and the respective ground states are summarized in table 1 for spins ranging from 1/2 to 5/2. In the limit \( T \to 0 \), the Entanglement Witness tends to \(-1\), as shown in fig. 1. This happens because the ground states, shown in table 1, violate maximally the entanglement condition in eq. (6). A similar calculation for entanglement temperature can be found in ref. [32], but for other spin-(1/2) systems.

This result shows that the temperature below which the entanglement emerges, or the temperature of entanglement, is directly connected to the exchange interaction between the \( S \)-spins of the dimer. Furthermore, as the exchange interaction \( J \) is strictly connected to the structure of the material, one can affirm that entanglement...
Table 1: Theoretical determination of the temperatures of entanglement $T_e$ for $S$-spin dimers. The ground states of the antiferromagnetic interacting dimers, written on the basis $|m_{SA}, m_{SB}\rangle$, are entangled states as shown by the red solid symbol in fig. 1. These ground states were numerically calculated and the eigenvalues, with their respective eigenvectors, were determined. The case $S = 2$ is included here for completeness. In the actual experiment the coupling is ferromagnetic for this spin value (see text).

| Temperature of entanglement | Ground state $\langle m_{SA}, m_{SB} \rangle$ |
|-----------------------------|--------------------------------------------|
| $T_e^{(1/2)} = -0.91 \frac{J}{k_B}$ | $\frac{1}{\sqrt{2}} \left( |\frac{1}{2}, -\frac{1}{2} \rangle - |\frac{1}{2}, \frac{1}{2} \rangle \right)$ |
| $T_e^{(1)} = -1.30 \frac{J}{k_B}$ | $\frac{1}{\sqrt{3}} \left( |1, -1 \rangle - |0, 0 \rangle + |1, 1 \rangle \right)$ |
| $T_e^{(3/2)} = -1.74 \frac{J}{k_B}$ | $\frac{1}{2} \left( |\frac{3}{2}, -\frac{3}{2} \rangle - |\frac{3}{2}, \frac{3}{2} \rangle + |\frac{1}{2}, \frac{1}{2} \rangle - |\frac{1}{2}, -\frac{1}{2} \rangle \right)$ |
| $T_e^{(2)} = -2.21 \frac{J}{k_B}$ | $\frac{1}{\sqrt{5}} \left( -|2, -2 \rangle + |1, -1 \rangle - |0, 0 \rangle + |1, 1 \rangle - |2, 2 \rangle \right)$ |
| $T_e^{(5/2)} = -2.69 \frac{J}{k_B}$ | $\frac{1}{\sqrt{6}} \left( -|\frac{5}{2}, -\frac{5}{2} \rangle + |\frac{3}{2}, -\frac{3}{2} \rangle - |\frac{3}{2}, \frac{3}{2} \rangle - |\frac{1}{2}, \frac{1}{2} \rangle + |\frac{1}{2}, -\frac{1}{2} \rangle \right)$ |

Fig. 1: (Colour on-line) Numerical calculation of the EW, eq. (6), for ferromagnetic (upper figure) and antiferromagnetic (lower figure) dimers. For the antiferromagnetic dimers, the temperature of entanglement appears when $EW = 0$. The entanglement in these systems exists because its ground states are entangled. The red solid symbol shows that $EW = -1$ for all the ground states in table 1. On the other hand, for the ferromagnetic dimers the EW never goes below zero.

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can be “engineered” by adjusting this quantity. In fig. 1, one can see numerical calculations for the Entanglement Witnesses of different spin values. The results show that only the entangled state of antiferromagnetic interacting dimers can be detected. This can be understood considering the ground state of the dimers. For antiferromagnetic interacting dimers, the ground state is an entangled state, thus maximally violating the criterion presented in eq. (6).

On the other hand, for ferromagnetic interacting dimers, the ground state corresponds to a mixture of entangled and non-entangled states and its respective EW do not indicate (or detect) entanglement. However, other Entanglement Witnesses are capable of detecting entanglement in ferromagnetic states, as discussed in ref. [32]. For that, other types of experiments are needed.

Experimental verification of the temperatures of entanglement. – In order to experimentally verify our theoretical prediction for the temperature of entanglement, we have used the data obtained from the magnetic-susceptibility measurements of three isostuctural transition metal silicates with formula KNaMSi$_8$O$_{16}$ ($M=Mn$, Fe or Cu) [29]. For copper ($S=1/2$) and manganese ($S=5/2$) the interaction within the dimers is antiferromagnetic and for iron ($S=2$) a ferromagnetic interaction holds [29]. These materials cover our theoretical results, since they are dimers with different $S$ values, different $J$ amplitudes and signals.

In fig. 2 it is shown the experimental determination of the EW for the three compounds. As predicted in table 2, only for antiferromagnetic interacting systems the entanglement appears and the estimative of the temperature of entanglement $T_e$ agrees with those obtained experimentally.

Conclusions. – In summary, we have shown a method to estimate the temperature of entanglement in low dimensional magnetic materials composed of $S$-spin dimers, for
Table 2: Comparison between the theoretical and experimental temperatures of entanglement $T_e$. It can be seen that one can only find a physical temperature if the interaction among the dimers is antiferromagnetic. Although the results are not exactly the same, one can have an estimate of the order of magnitude of the temperature of entanglement $T_e$ for different $S$-spin dimers.

|       | $J$ (K) | $T_e^{\text{theo}}$ (K) | $T_e^{\text{exp}}$ (K) | Magnetic order       |
|-------|---------|------------------------|-------------------------|----------------------|
| Cu ($S = 1/2$) | -2.86   | 2.60                   | 2.43(7)                 | antiferromagnetic     |
| Fe ($S = 2$)    | 7.6     | -16.8                  | 8.91(9)                 | ferromagnetic         |
| Mn ($S = 5/2$)  | -3.83   | 10.30                  |                         | antiferromagnetic     |

[Fig. 2: (Colour on-line) Entanglement Witnesses for the three transition metal oxides. For the manganese and the copper compounds (antiferromagnetic interacting systems), the EW goes below zero, showing the existence of entanglement among the spins. For the iron compound, the EW never goes below zero. Inset: detail around $T_e$. The orders of magnitude correspond to the ones theoretically obtained (see table 2).]

different spin values. We have found that $T_e \propto J$ and, therefore, the stronger the exchange interaction the higher the entanglement temperature. The results were experimentally verified using the magnetic susceptibility data from ref. [29] obtained for three isostructural materials, KNaMSi$_4$O$_9$ (M=Mn, Fe or Cu). The experiments reported in ref. [29] intended only to characterize the basic magnetic properties of these materials. From these data and the Entanglement Witness given in eq. (6), the existence of entangled states was determined, which proves that the theoretical model is in good agreement with the experimental results. These results also allow affirming that this EW can only detect entanglement in antiferromagnetic interacting dimers. This happens because the ground state of ferromagnetic interacting dimer is a mixture of entangled and non-entangled states and this EW cannot distinguish them. On the other hand, the ground state of an antiferromagnetic interacting dimer is an entangled state. The theoretical prediction was experimentally verified using three isostructural materials, which can be theoretically modeled by a HDVV Hamiltonian. As one possible direction for further studies, we suggest the investigation of entanglement upon the increasing of the spin values. It is important to mention that systems containing relatively large spins can accurately be treated as classical Heisenberg spin systems [33].

The study of classical and quantum spin clusters state and dynamics [34–36] can be very interesting for the architecture of novel materials for quantum information processing. Besides, these studies allow the investigation of the role of the temperature in a crossover between the quantum and classical descriptions of magnetic systems.

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REFERENCES

[1] Nielsen M. A. and Chuang I. L., *Quantum Computation and Quantum Information* (Cambridge University Press, Cambridge) 2000.
[2] Horodecki R., Horodecki P., Horodecki M. and Horodecki K., *Rev. Mod. Phys.*, 81 (2009) 865.
[3] Arnesen M. C., Bose S. and Vedral V., *Phys. Rev. Lett.*, 87 (2001) 017901.
[4] Anders J., Kaszlikowski D., Lukesci C., Oshihama T. and Vedral V., *New J. Phys.*, 8 (2006) 140.
[5] Vértesi T. and Bene E., *Phys. Rev. B*, 73 (2006) 134404.
[6] Brukner C., Vedral V. and Zeilinger A., *Phys. Rev. A*, 73 (2006) 012110.
[7] Rappoport T. G., Ghvelder L., Fernandes J. C., Guimarães R. B. and Continentino M. A., *Phys. Rev. B*, 75 (2007) 054422.
[8] Souza A. M., Reis M. S., Soares-Pinto D. O., Oliveira I. S. and Sarthour R. S., *Phys. Rev. B*, 77 (2008) 104402.
[9] Souza A. M., Soares-Pinto D. O., Sarthour R. S., Oliveira I. S., Reis M. S., Brandão P. and dos Santos A. M., *Phys. Rev. B*, 79 (2009) 054408.
[10] Lima Sharma A. L. and Gomes A. M., *EPL*, 84 (2008) 60003.
[11] Horodecki M., Horodecki P. and Horodecki R., *Phys. Lett. A*, 223 (1996) 1.
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[12] Bruss D., J. Math. Phys., 43 (2002) 4237.
[13] Mintert F., Carvalho A. R. R., Kuš M. and Buchleitner A., Phys. Rep., 415 (2005) 207.
[14] Plenio M. B. and Virmani S., Quantum Inf. Comput., 7 (2007) 1.
[15] Ghosh S., Rosenbaum T. F., Aeppli G. and Copper-Smith S. N., Nature, 425 (2003) 48.
[16] Wiesniak M., Vedral V. and Brukner C., New J. Phys., 7 (2005) 258.
[17] DeChiara G., Brukner C., Fazio R., Palma G. M. and Vedral V., New J. Phys., 8 (2006) 95.
[18] Souza A. M. C. and Almeida F. A. G., Phys. Rev. A, 79 (2009) 052337.
[19] Amico L., Fazio R., Osterloh A. and Vedral V., Rev. Mod. Phys., 80 (2008) 517.
[20] Leuenberger M. N. and Loss D., Nature, 410 (2001) 789.
[21] Wernsdorfer W., Alliga-Alcalde N., Hendrickson D. N. and Christoug G., Nature, 416 (2002) 406.
[22] Troiani F., Ghirri A., Affronte M., Carretta S., Santini P., Amoretti G., Piligkos S., Timco G. and Wippeny R. E., Phys. Rev. Lett., 94 (2005) 207208.
[23] Troiani F., Affron M., Carretta S., Santini P. and Amoretti G., Phys. Rev. Lett., 94 (2005) 190501.
[24] Affronte M., Troiani F., Ghirri A., Candini A., Evangelisti M., Corradini V., Carretta S., Santini P., Amoretti G., Tuna F., Timco G. and Winpeny R. E. P., J. Phys. D, 40 (2007) 2999.
[25] Lehmann J., Gaita-Ario A., Coronado E. and Loss D., Nat. Nanotechnol., 2 (2007) 312.
[26] Bogani L. and Wernsdorfer W., Nat. Mater., 7 (2008) 179.
[27] Ramsey C. M., del Barco E., Hill S., Shah S. J., Beedle C. C. and Hendrickson D. N., Nat. Phys., 4 (2008) 277.
[28] Ardavan A., Rival O., Morton J. J. L., Blundell S. J., Tyryshkin A. M., Timco G. A. and Winpeny R. E. P., Phys. Rev. Lett., 98 (2007) 057201.
[29] Brandão P., Rocha J., Reis M. S., dos Santos A. M. and Jin R., J. Solid State Chem., 182 (2009) 253.
[30] Kahn O., Molecular Magnetism (Wiley-VCH, New York) 1993.
[31] Tóth G., Phys. Rev. A, 69 (2004) 052327.
[32] Tóth G., Knapp C., Gühne O. and Briegel H. J., Phys. Rev. A, 79 (2009) 042334.
[33] Ciftja O., Luban M., Auslender M. and Luscombe J. H., Phys. Rev. B, 60 (1999) 10122.
[34] Ciftja O., Physica A, 286 (2000) 541.
[35] Mentrup D., Schmidt H. J., Schmack J. and Luban M., Physica A, 278 (2000) 214.
[36] Ciftja O., Nanoscale Res. Lett., 2 (2007) 168.