Influence of the external pressure on the quantum correlations of molecular magnets

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Abstract – The study of quantum correlations in solid-state systems is a large avenue for research and their detection and manipulation are an actual challenge to overcome. In this context, we show by using first-principles calculations on the prototype material KNaCuSi\(_4\)O\(_{10}\) that the degree of quantum correlations in this spin cluster system can be managed by external hydrostatic pressure. Our results pave the way for research in detection and manipulation of quantum correlations in magnetic systems with promising applications in quantum information science.

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Introduction. – Quantum correlations play an important role in quantum information science as a remarkable resource in quantum information processing \([1–4]\). The existence of pure quantum correlations has been usually inferred by the presence of entanglement. Nevertheless, although quantum entanglement provides a way to find out pure quantum correlations, it does not encompass all quantum correlations of the system \([5–28]\). Nowadays, the notion of quantum correlations has been greatly expanded; and the measure of quantumness of the correlation has been named quantum discord. The study of quantum discord has been attracting considerable attention due to its important role in many quantum information processing even when the entanglement is absent \([4,5,15,16,23]\).

Despite much effort by the scientific community, the characterization of quantum correlations consists in a rather complicated task, theoretically and experimentally speaking \([5,24–30]\), specially in condensed-matter systems; since this difficulty increases with the number of constituents of the system. This fact has stimulated alternative measurements of quantum correlations, allowing a better control of these quantum properties in these systems \([5,15,16,24–29]\).

In the past few years, it was understood that quantum discord can be evaluated through the measurement of some thermodynamic properties of solids, such as magnetic susceptibility \([5,15,16]\), internal energy \([15,16]\), specific heat \([5,15,16]\) and diffractive properties of neutron scattering \([29]\). Recently, it has been shown that quantum discord can also exist at higher temperature, for instance, at thousands of kelvins above room temperature \([5]\), showing that quantum correlations are related to significant macroscopic effects, allowing a better control of quantum correlations in solid-state systems by means of materials engineering \([5]\).

In this context, we show in the present work that the degree of correlation in a spin cluster system can be affected by the structural parameters, by applying external hydrostatic pressure. We performed first-principles calculations to investigate the dependence, under external pressure,
of the magnetic coupling constant of the metal-silicate framework KNaCuSi$_2$O$_{10}$ [31]—a Heisenberg dimer on a $d^9$ electronic configuration; from which we obtain the entropic quantum discord and the entanglement of formation as a function of its magnetic susceptibility. Our results show that it is possible to manipulate the degree of quantum correlation in a magnetic system inducing a structural contraction by applying an external pressure. This leads to a better management of the quantum properties of these systems and paves the way for experimental and theoretical research of quantum correlations via first principles, leading to a better understanding of these quantum properties with promising applications in emerging quantum technologies.

**Pairwise quantum correlations in a prototype material.**—Our prototype material in which we investigate the influence of an external pressure on the quantum correlations via first-principles calculations is the metal-silicate framework KNaCuSi$_2$O$_{10}$ [31]. This compound is synthetic analog to a natural occurring mineral litidionite, a Heisenberg dimer in a $d^9$ electronic configuration and, therefore, an ideal realization of a two-qubit system (spin-(1/2) dimer) ruled by a Heisenberg-Dirac-Van Vleck Hamiltonian $H = -J \vec{S}_1 \cdot \vec{S}_2$ [23,32], where $J$ is the magnetic coupling constant [32]. The magnetic susceptibility of this system satisfies the Bleaney-Bowers equation [32,33]:

$$\chi(T) = \frac{2N(g\mu_B)^2}{k_B T} \frac{1}{3 + e^{-\frac{1}{k_B T}}},$$  

where, $g$ is the Landé factor, $\mu_B$ is the Bohr magneton, $k_B$ is the Boltzmann constant and $N$ is the number of dimers.

The density matrix of the system under consideration has the Gibbs form, $\rho(T) = e^{-\chi(T)/k_B T}/Z$ [5,15,16,32], where $Z = \text{Tr}(e^{-\chi(T)/k_B T})$ is the partition function. It can be written on Bell’s diagonal mixed state in the computational basis \{00,01,10,11\} [15,16]:

$$\rho(T) = \frac{1}{4} \begin{bmatrix} 1 + c(T) & 0 & 0 & 0 \\ 0 & 1 - c(T) & 2c(T) & 0 \\ 0 & 2c(T) & 1 - c(T) & 0 \\ 0 & 0 & 0 & 1 + c(T) \end{bmatrix},$$

where

$$c(T) = \langle \vec{S}_1 \cdot \vec{S}_2 \rangle = -1 + \frac{4}{3 + e^{-2J/k_B T}}$$

is the pairwise correlation function.

As calculated in ref. [5], it is possible to write the pairwise correlation function of the Heisenberg dimer as a function of its magnetic susceptibility, eq. (1), at finite temperature,

$$c(T) = \frac{2k_B T}{N(g\mu_B)^2} \chi(T) - 1.$$  

Hence, with $c(T)$, one can easily obtain the quantum correlations of KNaCuSi$_2$O$_{10}$, as a function of their magnetic susceptibility [15,16,28].

The total amount of correlation in the system which is identified by the mutual information $I(\rho_A : \rho_B) = S(\rho_A) - S(\rho_A) - S(\rho_B)$ can be split into the quantum part $Q$ and the classical ones $C(\rho_{AB})$, where $S(\rho_{AB}) = -\text{Tr}[\rho_{AB} \log \rho_{AB}]$ is the von Neumann entropy [5,17,18,23–25,28,29,34–38]. The amount of genuinely quantum correlations, called quantum discord can be defined as the difference between the total and the classical correlation, $Q(\rho_{AB}) = I(\rho_A : \rho_B) - C(\rho_{AB})$. This difference is due to the quantum effects on the correlation between the subsystems $A$ and $B$. Thus, the entropic quantum discord depends on the magnetic susceptibility of the compound as

$$Q(T) = \frac{1}{4} \left[ [2 - 3\alpha T \chi(T)] \log_2 [2 - 3\alpha T \chi(T)] + 3\alpha T \chi(T) \log_2 [\alpha T \chi(T)] \right] - \frac{1}{2} \left[ [1 + |\alpha T \chi(T) - 1|] \log_2 [1 + |\alpha T \chi(T) - 1|] + [1 - |\alpha T \chi(T) - 1|] \log_2 [1 - |\alpha T \chi(T) - 1|] \right],$$

where $\alpha = 2k_B/N(g\mu_B)^2$ [5].

Furthermore, in order to quantify the amount of entanglement in this spin system and make a comparison with the measurements of quantum discord, we adopt the measurement of entanglement of formation defined by [39,40]

$$E = -\Lambda_+ \log_2 (\Lambda_+) - \Lambda_- \log_2 (\Lambda_-),$$

where

$$\Lambda_{\pm} = \frac{1 \pm \sqrt{1 - C^2}}{2}$$

and $C$ is the concurrence [1,39,40] that is written as a function of the magnetic susceptibility as [5,15,16]

$$C = \begin{cases} -\frac{1}{2} \left[ 2 + 3\frac{2k_B T}{N(g\mu_B)^2} \chi(T) \right], & T < T_t, \\ 0, & T \geq T_t, \end{cases}$$

where

$$T_t \approx 0.91 |J|/k_B$$

is the threshold temperature, the maximum temperature below which there is entanglement in the system [41,42].

**First-principles calculations.**—We performed first-principles calculations to investigate the dependence of the magnetic coupling constant of the metal-silicate framework KNaCuSi$_2$O$_{10}$ [31] under external pressure in order to evaluate this influence on the quantum correlations obtained as a function of the magnetic susceptibility of this compound.

**Technical details.**—We approached this problem by using the density functional [43] theory (DFT) in the generalized gradient approximation (GGA) with
the Perdew-Burke-Ernzerhof parametrization for the exchange-correlation functional [44]. The Kohn-Sham equations were solved by using the plane-wave pseudopotential method as implemented in the Quantum ESPRESSO software [45]. The plane-wave energy cutoff was 47.5 Ha for the wave function and 237.5 Ha for the charge density. The crystal structure was optimized at each volume of the unit cell. During the ionic relaxation, all positions were relaxed until Hellmann-Feynman forces were less than 0.05 Ha/bohr and the total energy converged below to 5 \times 10^{-6} Ha for the charge density. The k-point sampling of the Brillouin zone was done with an 5 \times 5 \times 5 grid following the Monkhorst-Pack scheme [46] and with a Marzari-Vanderbilt smearing width of 5 \cdot 10^{-4} Ha [47]. The crystal structure was optimized with respect to the Brillouin zone integration. The equation of state (EoS) of the KNaCuSi_4O_{10} compound was obtained by fitting the total energy as a function of volume to the third-order Birch-Murnaghan equation [48]:

\[
E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left(\frac{V_0}{V}\right)^{\frac{3}{2}} - 1 \right\}^3 B_0' + \left\{ \left(\frac{V_0}{V}\right)^{\frac{3}{2}} - 1 \right\}^2 \left\{ 6 - 4 \left(\frac{V_0}{V}\right)^{\frac{3}{2}} \right\},
\]

where \(V_0\), \(B_0\) and \(B_0'\) are the equilibrium volume, the bulk modulus at ambient pressure and its pressure derivative, respectively. The values found for these parameters were the following: \(V_0 = 3271\) bohr\(^3\), \(B_0 = 54.1\) GPa and \(B_0' = 3.3\). Figure 1 shows the structural optimization curve, i.e., the results for the total energy vs. the volume of the unit cell obtained for DFT calculations and fitted by the third-order Birch-Murnaghan equation of state (eq. (10)).

For a Heisenberg spin-(1/2) dimer there are two eigenvalues of the energy, one being \(E_T\) the triplet state and the other \(E_S\) being the singlet state of the dimeric unit. Hence, its magnetic coupling constant \(J\) is the difference between these two states \(J = E_S - E_T\). On the other hand, the Hohenberg-Kohn theorem asserts that the total energy of a system is a functional of the charge density. Thus, we have used this theorem along with the Kohn-Sham scheme to calculate the total energy for each spin alignment for several volumes and fitted them by using the above equation of state. Based on such procedure it is possible to write the total energy as a function of pressure and we can therefore calculate the other physical quantities from first principles accordingly.

**Results.** The external pressure applied on a molecular magnetic system induces a structural contraction that reduces its lattice parameters leading to strengthening or weakening of the magnetic coupling of the system, due to its strong dependence with the structural properties of the sample material. For the prototype material KNaCuSi_4O_{10} its magnetic coupling constant \(J\) increases and becomes positive, i.e., the system changes from an antiparallel alignment \((J < 0)\) to a parallel alignment \((J > 0)\) due to the application of an external pressure, as can be seen in fig. 2(a). Hence, we obtain the threshold
temperature \((T_t)\), eq. (9), using the magnetic coupling constant. Figure 2(b) shows the dependence of \(T_t\) in the prototype compound under pressure. As can be seen, the change in the magnetic alignment leads to the decrease of \(T_t\) down to the disappearance of the entanglement (see fig. 2(b)), when the system achieves a parallel alignment. This means that the degree of entanglement in a magnetic system can be controlled by significant macroscopic effects when applying external pressure.

On the other hand, in order to evaluate the influence of external pressure on the quantum correlations, we calculate the magnetic susceptibilities (eq. (1)) from each magnetic coupling constant presented in fig. 2(a). Using eqs. (5), (6), it is possible to evaluate the quantum correlations as a function of these susceptibilities. We obtain the quantum correlation curves measured by this thermodynamic property for each magnetic configuration of the system. Thus, we establish a relationship between the quantum properties with significant macroscopic effects.

In sequence, fig. 3(a) and (b) shows the entropic quantum discord (eq. (5)) and entanglement of formation (eq. (6)) curves as a function of the temperature and pressure, respectively. Note that the degree of quantum correlations in the system decreases by increasing the external pressure as a consequence of the changes of the magnetic coupling constant as shown in fig. 2(a). Also remarkable is the management of the ground state in the system by reducing the temperature and controlling the external pressure; it achieves this state when the entropic discord (fig. 3(a)) and entanglement (fig. 3(b)) reach the maximum value of unity. As pointed out before, the system changes from the entangled ground state to a separable one due to the changes of the magnetic configuration of the system induced by the external pressure. It is reflected in the quantum correlations when entanglement goes to zero (see fig. 3(b)), i.e., the system reaches the threshold temperature \(T = T_t\), eq. (9). Hence, this fact yields a minimization on the quantum discord in the system (see fig. 3(a)). However, it remains significantly different from zero even in separable states when the entanglement is absent as can be seen in fig. 3(a). In this way, we can control the quantum correlations of this molecular magnet by means of macroscopic properties such as temperature and pressure.

Therefore, the structural contraction on the system, achieved by increasing the external pressure, lead to a change in the magnetic configuration of the system, as can be seen in fig. 2. As a consequence, the quantum correlations (fig. 3) are drastically affected, since these quantum properties are directly related to the magnetic behaviour of the system (eqs. (5), (6)). Thus, it is possible to manage the degree of quantum correlation in a magnetic system by the control of external pressure and temperature. Furthermore, this external pressure can be achieved experimentally reducing the lattice parameter of the system by chemical substitution or hydrostatically, for example. This fact opens a large avenue for research in experimental detection and manipulation of quantum correlations. It allows a better understanding of the quantum properties of molecular magnets by the management of significant macroscopic properties, leading to promising applications in quantum information science such as the development of novel candidate platforms for quantum information processing by means of materials engineering.

Conclusions. – In summary, we performed first-principles calculations to investigate the dependence under hydrostatic pressure, of the quantum correlations of the prototype material \(\text{KNaCuSi}_4\text{O}_{10}\), which is a Heisenberg dimer in a \(d^9\) electronic configuration and, consequently, an ideal realization of a two-qubit system (spin-(1/2) dimer). We show that an external pressure induces a structural contraction on the prototype material, leading to a change of its magnetic alignment. This changes yields a minimization on the degree of the quantum correlations in the system; showing that quantum correlations are related to significant macroscopic effects. Also remarkable is the possibility to handle the ground state by controlling
the temperature and pressure. Our results allow a better management of the quantum properties in magnetic systems and pave the way for experimental and theoretical research of quantum correlations in these systems via first principles, leading to a better understanding of their quantum properties with promising applications in the emerging quantum technologies.

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REFERENCES

[1] Nielsen M. A. and Chuang I. L., *Quantum Computation and Quantum Information* (Cambridge University Press) 2010.
[2] Vedral V., *Introduction to Quantum Information Science* (Oxford University Press) 2006.
[3] Horodecki R., Horodecki P., Horodecki M. and Horodecki K., *Rev. Mod. Phys.*, 81 (2009) 865.
[4] Tufarelli T., Girolami D., Vasile R., Bose S. and Adesso G., *Phys. Rev. A*, 86 (2012) 052326.
[5] Cruz C., Soares-Pinto D. O., Brandao P., dos Santos A. M. and Reis M. S., *EPL*, 113 (2016) 40004.
[6] Man Z.-X., Xia Y.-J. and Franco R. L., *Sci. Rep.*, 5 (2015) 13843.
[7] Aaronson B., Franco R. L. and Adesso G., *Phys. Rev. A*, 88 (2013) 012120.
[8] Franco R. L., Bellomo B., Maniscalco S. and Compagno G., *Int. J. Mod. Phys. B*, 27 (2013) 1345053.
[9] Bellomo B., Franco R. L. and Compagno G., *Phys. Rev. A*, 86 (2012) 012312.
[10] Franco R. L., Bellomo B., Andersson E. and Compagno G., *Phys. Rev. A*, 85 (2012) 032318.
[11] Aaronson B., Franco R. L., Compagno G. and Adesso G., *New J. Phys.*, 15 (2013) 093022.
[12] Silva I. A., Souza A. M., Bromley T. R., Cianciaruso M., Marx R., Sarthour R. S., Oliveira I. S., Franco R. L., Glaser S. J., Soares-Pinto D. O. *et al., Phys. Rev. Lett.*, 117 (2016) 160402.
[13] Xu J.-S., Sun K., Li C.-F., Xu X.-Y., Guo G.-C., Andersson E., Franco R. L. and Compagno G., *Nat. Commun.*, 4 (2013) 2851.
[14] Bromley T. R., Cianciaruso M., Franco R. L. and Adesso G., *J. Phys. A: Math. Theor.*, 47 (2014) 405302.
[15] Yurischchev M. A., *Phys. Rev. B*, 84 (2011) 024418.
[16] Aldoshin S., Feldman E. and Yurischchev M., *Low Temp. Phys.*, 40 (2014) 3.
[17] Henderson L. and Vedral V., *J. Phys. A: Math. Gen.*, 34 (2001) 6899.
[18] Vedral V., *Phys. Rev. Lett.*, 90 (2003) 050401.
[19] Dakic B., Vedral V. and BrukNER C., *Phys. Rev. Lett.*, 105 (2010) 190502.
[20] Modi K., Paterek T., Son W., Vedral V. and Williamson M., *Phys. Rev. Lett.*, 104 (2010) 080501.
[21] Modi K., Brodutch A., Cable H., Paterek T. and Vedral V., *Rev. Mod. Phys.*, 84 (2012) 1655.
[22] Gu M., Chrzanski H. M., Assad S. M., Syulm T., Modi K., Ralph T. C., Vedral V. and Lam P. K., *Nat. Phys.*, 8 (2012) 671.
[23] Sarandy M., *Phys. Rev. A*, 80 (2009) 022108.
[24] Nakano T., Piani M. and Adesso G., *Phys. Rev. A*, 88 (2013) 012117.
[25] Girolami D. and Adesso G., *Phys. Rev. A*, 83 (2011) 052108.
[26] Girolami D., Tufarelli T. and Adesso G., *Phys. Rev. Lett.*, 110 (2013) 240402.
[27] Girolami D., Souza A. M., Giovannetti V., Tufarelli T., Filgueiras J. G., Sarthour R. S., Soares-Pinto D. O., Oliveira I. S. and Adesso G., *Phys. Rev. Lett.*, 112 (2014) 210401.
[28] Luo S., *Phys. Rev. A*, 77 (2008) 042303.
[29] Liu B.-Q., Wu L.-A., Zeng G.-M., Song J.-M., Luo W., Lei Y., Sun G.-A., Chen B. and Peng S.-M., *Phys. Lett. A*, 378 (2014) 3441.
[30] Huang Y., *New J. Phys.*, 16 (2014) 033027.
[31] Brandao P., Rocha J., Reis M. S., Dos Santos A. and Jin R., *J. Solid State Chem.*, 182 (2009) 253.
[32] Reis M., *Fundamentals of Magnetism* (Elsevier) 2013.
[33] Bleaney B. and Bowers K., *Anomalous Paramagnetism of Copper Acetate* (The Royal Society) 1952, pp. 451–465.
[34] Oliveira H. and Zurek W. H., *Phys. Rev. Lett.*, 88 (2001) 017901.
[35] Ma Z., Chen Z., Fanchini F. F. and Fei S.-M., *Sci. Rep.*, 5 (2015) 10262.
[36] Paula F., de Oliveira T. R. and Sarandy M., *Phys. Rev. A*, 87 (2013) 064101.
[37] Montvalegre J., Paula F., Sagui A. and Sarandy M., *Phys. Rev. A*, 87 (2013) 042115.
[38] Datta A., Shaj A. and Caves C. M., *Phys. Rev. Lett.*, 100 (2008) 050502.
[39] Wootters W. K., *Phys. Rev. Lett.*, 80 (1998) 2245.
[40] Hill S. and Wootters W. K., *Phys. Rev. Lett.*, 78 (1997) 5022.
[41] Soares-Pinto D., Souza A., Sarthour R., Oliveira I., Reis M., Brandao P., Rocha J. and dos Santos A., *EPL*, 87 (2009) 40008.
[42] Reis M. S., Soriano S., dos Santos A. M., Sales B. C., Soares-Pinto D. and Brandao P., *EPL*, 100 (2012) 50001.
[43] Hohenberg P. and Kohn W., *Phys. Rev.*, 136 (1964) B864.
[44] Perdew J. P., Burke K. and Ernzerhof M., *Phys. Rev. Lett.*, 77 (1996) 3865.
[45] Giannozzi P., Baroni S., Bonini N., Calandra M., Car R., Cavazzoni C., Ceresoli D., Chiarotti G. L., Cococcioni M., Dabo I., De Vita A., Fabris S., Fratesi A., Gebauer R., Gerstmann S., Gougoussis C., Kokalj A., Lazzeri M.,LI M., Lupton M., Mauri F., Mazzarello E., Paolucci S., Pasquarello A., Paulatto L., Sbraccia A., Scandolo S., Seitsonen A. P., Smogunov A., Umari P., Vanderbilt D., *J. Phys.: Condens. Matter*, 21 (2009) 395502.
[46] Monkhorst H. J. and Pack J. D., *Phys. Rev. B*, 13 (1976) 5188.
[47] Marzari N., Vanderbilt D., De Vita A. and Payne M., *Phys. Rev. Lett.*, 82 (1999) 3296.
[48] Birch F., *Phys. Rev.*, 71 (1947) 809.