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LETTER TO THE EDITOR

Frustrated quantum-spin system on a triangle coupled with e_g lattice vibrations: correspondence to Longuet-Higgins *et al*'s Jahn–Teller model

Hisatsugu Yamasaki[1,3], **Yuhei Natsume**[2], **Akira Terai**[1] **and Katsuhiro Nakamura**[1]

[1] Department of Applied Physics, Osaka City University, Osaka 558-8585, Japan
[2] Graduate School of Science and Technology, Chiba University, Chiba 263-8522, Japan

E-mail: hisa@a-phys.eng.osaka-cu.ac.jp

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Abstract

We investigate the frustrated quantum three-spin model $(\mathbf{S_1}, \mathbf{S_2}, \mathbf{S_3})$ of spin $= 1/2$ on a triangle, in which spins are coupled with lattice-vibrational modes through the antiferromagnetic exchange interaction depending on distances between spin sites. The present model corresponds to the dynamic Jahn–Teller system $E_g \otimes e_g$ proposed by Longuet-Higgins *et al* (1958 *Proc. R. Soc.* A **244** 1). This correspondence is revealed by using the transformation to Nakamura–Bishop's bases used in *Phys. Rev. Lett.* **54** 861 (1985). Furthermore, we elucidate the relationship between a chiral order parameter $\hat{\chi} = \mathbf{S_1} \cdot (\mathbf{S_2} \times \mathbf{S_3})$ in the spin system and the electronic orbital angular momentum $\hat{\ell}_z$ in $E_g \otimes e_g$ vibronic model: the regular oscillatory behaviour of the expectation value $\langle\hat{\chi}\rangle$ with increasing energy can be found as in the case of $\langle\hat{\ell}_z\rangle$ for vibronic structures. The increase of the additional anharmonicity(chaoticity) is found to yield a rapidly decaying irregular oscillation of $\langle\hat{\chi}\rangle$.

(Some figures in this article are in colour only in the electronic version)

Triangular Heisenberg antiferromagnets play an important role in our understanding of the resonating valence bond (RVB) state, in which the scalar chirality for the three spins $\mathbf{S_1} \cdot (\mathbf{S_2} \times \mathbf{S_3})$ is expected to have a nonzero expectation value [1–4]. This subject has been a focus of recent experimental activities [5–7], since it was expected that frustrated $s = 1/2$ triangular antiferromagnets might be realized in $NaTiO_2$ and $LiNiO_2$ [8].

[3] Author to whom any correspondence should be addressed.

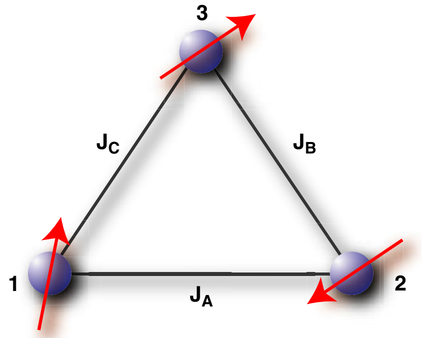

Figure 1. Triangle with antiferromagnetic spins.

In this letter, we investigate a triangular cluster model of the Heisenberg antiferromagnet in which quantum spins are coupled with lattice vibrations, for the purpose of seeing the magnetic properties of its high-lying states in relation to a typical dynamical Jahn–Teller system. In short, the spin–lattice interaction is introduced by expanding the exchange interaction with respect to deviation of lattice displacements from equilibrium. We shall address the following issue: with the use of a unitary transformation for this spin system, the present model becomes equivalent to that of the well-known vibronic problem for the $E_g \otimes e_g$ Jahn–Teller system [9].

Let us consider the quantum spin system where three spins of spin $= 1/2$ are localized at lattice sites 1, 2 and 3 on a triangle. The couplings between neighbouring spins are expressed by the antiferromagnetic exchange interactions J_A, J_B and J_C as shown in figure 1. The corresponding Heisenberg Hamiltonian is

$$\mathcal{H} = J_A \mathbf{S_1} \cdot \mathbf{S_2} + J_B \mathbf{S_2} \cdot \mathbf{S_3} + J_C \mathbf{S_3} \cdot \mathbf{S_1}. \tag{1}$$

We concentrate our attention on the spin state where the z component of the total spin satisfies $s_{1z} + s_{2z} + s_{3z} = 1/2$. Therefore, these bases are expressed explicitly as $|\downarrow\uparrow\uparrow\rangle, |\uparrow\downarrow\uparrow\rangle, |\uparrow\uparrow\downarrow\rangle$, where the arrows denote s_{jz} for site j. By using these bases, we obtain the Hamiltonian matrix,

$$\mathcal{H} \Big/ \left(-\frac{\hbar^2}{4}\right) = \begin{array}{c} \\ \langle\downarrow\uparrow\uparrow| \\ \langle\uparrow\downarrow\uparrow| \\ \langle\uparrow\uparrow\downarrow| \end{array} \begin{array}{c} \begin{array}{ccc} \quad|\downarrow\uparrow\uparrow\rangle\quad & \quad|\uparrow\downarrow\uparrow\rangle\quad & \quad|\uparrow\uparrow\downarrow\rangle\quad \end{array} \\ \begin{pmatrix} -J_A + J_B - J_C & 2J_A & 2J_C \\ 2J_A & -J_A - J_B + J_C & 2J_B \\ 2J_C & 2J_B & J_A - J_B - J_C \end{pmatrix} \end{array}. \tag{2}$$

Next we introduce the interaction between the spins and lattice vibrations, noting the dependence of J_A, J_B and J_C on distances between spin sites. As for the lattice vibration, we employ the normal modes for the triangle; the normal e_g modes, Q_1 and Q_2 which are degenerate are given in figure 2. The remaining a_{1g} mode (the breathing mode) has a much higher strain energy and is ignored hereafter. (There are other global degrees of freedom related to translation of the centre of mass and to rotation around the axis perpendicular to the triangular plane. They however have nothing to do with lattice vibrations and are also ignored.) Then the spin–lattice interaction is obtained as a result of the expansion of J_A, J_B and J_C linear in e_g modes as follows:

$$\begin{aligned} J_A &= J \cdot \left[1 + \frac{\alpha}{2}(Q_1 - \sqrt{3}Q_2)\right] \\ J_B &= J \cdot [1 - \alpha Q_1] \\ J_C &= J \cdot \left[1 + \frac{\alpha}{2}(Q_1 + \sqrt{3}Q_2)\right], \end{aligned} \tag{3}$$

where α is the coupling constant.

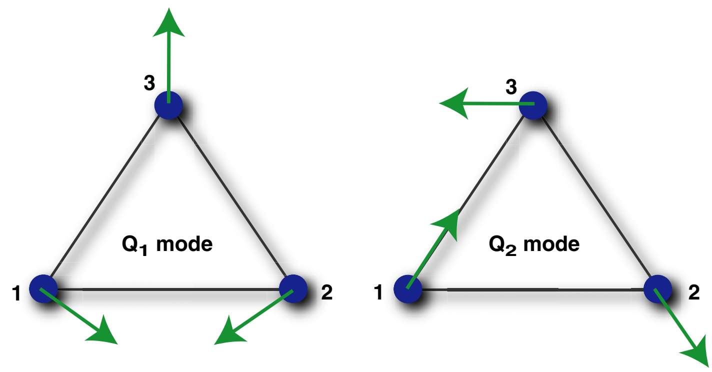

Figure 2. Normal modes Q_1 and Q_2 in the triangle.

Concerning the spin system, on the other hand, we introduce the wavenumber bases exploited by Nakamura and Bishop for the triangular spin plaquet [10–12]:

$$\begin{aligned} |k=0\rangle &= \frac{1}{\sqrt{3}}\left(|{\downarrow\uparrow\uparrow}\rangle + |{\uparrow\downarrow\uparrow}\rangle + |{\uparrow\uparrow\downarrow}\rangle\right) \\ \left|k=\frac{2\pi}{3}\right\rangle &= \frac{1}{\sqrt{3}}\left(|{\downarrow\uparrow\uparrow}\rangle + \mathrm{e}^{\frac{2\pi}{3}\mathrm{i}}|{\uparrow\downarrow\uparrow}\rangle + \mathrm{e}^{-\frac{2\pi}{3}\mathrm{i}}|{\uparrow\uparrow\downarrow}\rangle\right) \\ \left|k=-\frac{2\pi}{3}\right\rangle &= \frac{1}{\sqrt{3}}\left(|{\downarrow\uparrow\uparrow}\rangle + \mathrm{e}^{-\frac{2\pi}{3}\mathrm{i}}|{\uparrow\downarrow\uparrow}\rangle + \mathrm{e}^{\frac{2\pi}{3}\mathrm{i}}|{\uparrow\uparrow\downarrow}\rangle\right). \end{aligned} \tag{4}$$

These bases reflect clockwise and anticlockwise rotations of a spin configuration on the plane of the triangle. The wavenumbers $k = 0, \pm 2\pi/3$ correspond to phase factors in Bloch's theorem for the system with discrete rotational symmetry. From a viewpoint of the ligand–field theory [13], the construction of the bases (4) from $|{\downarrow\uparrow\uparrow}\rangle$, $|{\uparrow\downarrow\uparrow}\rangle$ and $|{\uparrow\uparrow\downarrow}\rangle$ is regarded as a formation of E_g and A representations in D_{3d} symmetry from the triply-degenerate T_{2g} ones in O_h symmetry. By using these new bases, the Hamiltonian matrix (2) can be transformed to

$$\mathcal{H}\big/\left(-\tfrac{3}{4}\hbar^2 J\right) = \begin{array}{c} \\ \langle k=0| \\ \langle k=\frac{2\pi}{3}| \\ \langle k=-\frac{2\pi}{3}| \end{array} \begin{array}{c} \begin{array}{ccc} |k=0\rangle & |k=\frac{2\pi}{3}\rangle & |k=-\frac{2\pi}{3}\rangle \end{array} \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & \alpha(-Q_1 - \mathrm{i}Q_2) \\ 0 & \alpha(-Q_1 + \mathrm{i}Q_2) & -1 \end{pmatrix} \end{array}. \tag{5}$$

From equation (5) we find that the $k = 0$ manifold is completely separated from other manifolds, i.e., $\mathcal{H} = \mathcal{H}_{k=0} \oplus \mathcal{H}_{k=\pm 2\pi/3}$. $\mathcal{H}_{k=0}$ and $\mathcal{H}_{\pm 2\pi/3}$ correspond to the A and E_g representations, respectively. The interaction Hamiltonian $\mathcal{H}_{k=\pm 2\pi/3}$ can result in a pair of adiabatic energy surfaces, which together with the harmonic term $(\propto Q_1^2 + Q_2^2)$, forms the Mexican hat potential. In fact, by applying the unitary transformation

$$U = -\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & \mathrm{i} \\ -1 & \mathrm{i} \end{pmatrix}, \tag{6}$$

we obtain

$$\begin{aligned} \tilde{H}_{k=\pm 2\pi/3} &= U^{-1}\mathcal{H}_{k=\pm 2\pi/3}U \\ &= \frac{3}{4}\hbar^2 J\mathbf{I} - \frac{3\alpha}{4}\hbar^2 J\begin{pmatrix} Q_1 & +Q_2 \\ +Q_2 & -Q_1 \end{pmatrix}. \end{aligned} \tag{7}$$

This expression just accords with the electron–lattice interaction part of the vibronic Hamiltonian for the Jahn–Teller system $E_g \otimes e_g$,

$$\mathcal{H}_{\mathrm{JT}} = \tfrac{1}{2}\omega^2(Q_1^2 + Q_2^2) + \alpha'\begin{pmatrix} Q_1 & +Q_2 \\ +Q_2 & -Q_1 \end{pmatrix}. \tag{8}$$

Thus, we would like to emphasize that the present system for quantum spins on the triangle coupled with doubly-degenerate vibrational $\mathrm{e_g}$ modes is equivalent to the $\mathrm{E_g} \otimes \mathrm{e_g}$ vibronic system intensively investigated in the context of the dynamical Jahn–Teller problem.

Before proceeding to the argument on the chiral order parameter of the spin system, we shall recall the definition of the electronic orbital angular momentum in the dynamical Jahn–Teller system. For the quantal Hamiltonian consisting of kinetic energy $((P_1^2 + P_2^2)/2)$ and $\mathcal{H}_{\mathrm{JT}}$ of (8), the pth eigenstate of the $\ell = 1/2$ manifold, $\Psi_{p,1/2}$, is given by

$$\Psi_{p,1/2} = a_{1,p}\psi_{1,0}\phi_+ + a_{2,p}\psi_{2,1}\phi_- + a_{3,p}\psi_{3,0}\phi_+ + a_{4,p}\psi_{4,1}\phi_- + \cdots \tag{9}$$

where the $\psi_{n,m}$ are the eigenfunctions of the isotropic two-dimensional harmonic oscillator (n and m are radial and azimuthal quantum numbers, respectively), and ϕ_+ and ϕ_- are degenerate electronic states $\phi_\pm = d_u \pm \mathrm{i}d_v$. The expansion (9) was found by rewriting $\mathcal{H}_{\mathrm{JT}}$ in (8) into a suitable form with the use of $\phi_\pm$ [14]. In the context of the spin–lattice system under consideration, the block matrix $\mathcal{H}_{k=\pm 2\pi/3}$ in (5) already takes such a suitable form with the use of Nakamura–Bishop's bases $|k = \pm 2\pi/3\rangle$, and the whole wavefunction takes the same form as (9).

In the vibronic state $\Psi_{p,1/2}$ in the dynamical Jahn–Teller system, the expectation value of the electronic orbital angular momentum $\hat{\ell}_z$ is given as

$$\begin{aligned} \langle \hat{\ell}_z \rangle_p &= \langle \Psi_{p,1/2} | \hat{\ell}_z | \Psi_{p,1/2} \rangle \\ &= \sum_{n=1}^{\infty} |a_{n,p}|^2 (-1)^{n-1} \Xi_\ell \qquad (p = 1, 2, \ldots). \end{aligned} \tag{10}$$

Here, Ξ_ℓ is the expectation value of $\hat{\ell}_z$ in the electronic states ϕ_+ and ϕ_-:

$$\Xi_\ell = \langle \phi_+ | \hat{\ell}_z | \phi_+ \rangle = -\langle \phi_- | \hat{\ell}_z | \phi_- \rangle. \tag{11}$$

The emergence of an outstanding regular oscillation of $\langle \hat{\ell}_z \rangle_p$ as a function of energy (p) was pointed out three decades ago [15], and has received renewed attention recently in the context of nonlinear dynamics [14].

Now let us come back to the argument of the characteristic operator for the frustrated quantum spin system. With use of the bases (4), we evaluate the expectation values for the chiral order parameter

$$\hat{\chi} = \mathbf{S_1} \cdot (\mathbf{S_2} \times \mathbf{S_3}) \tag{12}$$

which characterizes the degree of frustration of the triangular antiferromagnet [4]. The expectation values of $\hat{\chi}$ in each of the $k = \pm 2\pi/3$ states (4) are

$$\begin{aligned} \left\langle k = \frac{2\pi}{3} \middle| \hat{\chi} \middle| k = \frac{2\pi}{3} \right\rangle &= -\frac{\sqrt{3}}{4} \equiv -\Xi_\chi \\ \left\langle k = -\frac{2\pi}{3} \middle| \hat{\chi} \middle| k = -\frac{2\pi}{3} \right\rangle &= \frac{\sqrt{3}}{4} \equiv \Xi_\chi. \end{aligned} \tag{13}$$

(The value $\langle k = 0 | \hat{\chi} | k = 0 \rangle = 0$ is now irrelevant since $|k = 0\rangle$ is coupled only with the higher frequency $\mathrm{a_{1g}}$ mode.) Thus, the states $|k = \pm\frac{2\pi}{3}\rangle$ and chiral order parameter $\hat{\chi}$ in the spin–lattice system correspond to states $|\phi_\pm\rangle$ and $\hat{\ell}_z$ in the dynamical Jahn–Teller system, respectively. Taking the eigenstates similar to (9), the value $\langle \hat{\chi} \rangle_p$ in the pth eigenstate is given by

$$\langle \hat{\chi} \rangle_p = \sum_{n=1}^{\infty} |a_{n,p}|^2 (-1)^n \Xi_\chi. \tag{14}$$

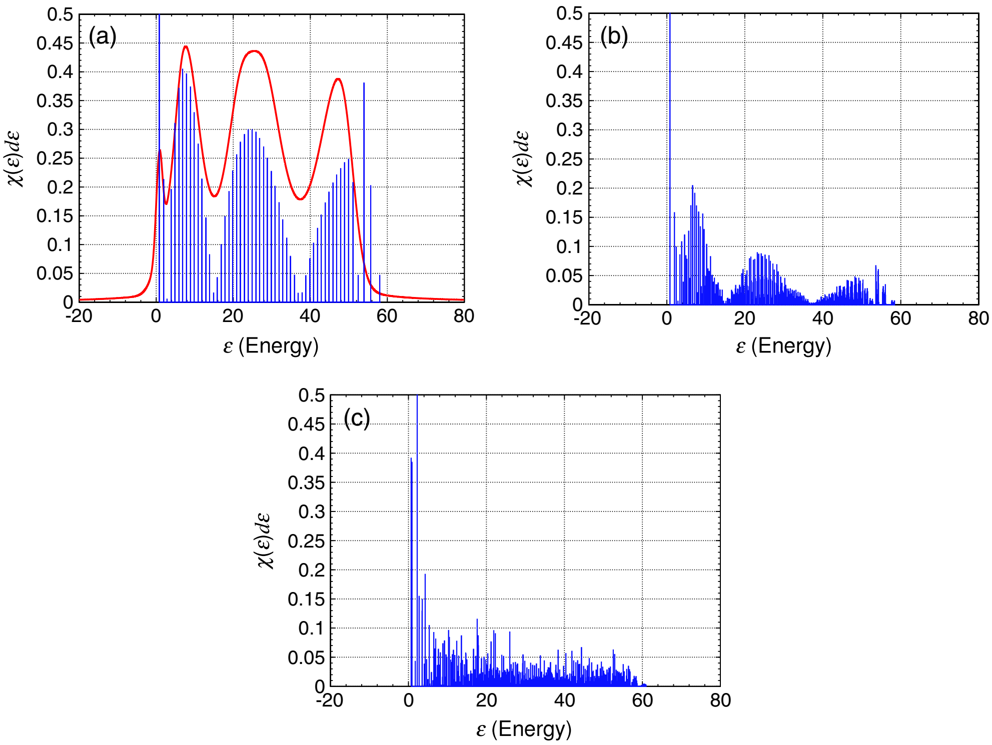

Figure 3. Energy (ε) dependence of partially-averaged chirality $\chi(\varepsilon)\,\mathrm{d}\varepsilon$ $(=\sum_p' |\sum_{n=1}^{\infty}(-1)^n a_{n,p}^2|\,\mathrm{d}\varepsilon)$ with $\mathrm{d}\varepsilon = 0.25$ in units of Ξ_χ. (a)–(c) correspond to $\gamma = 0, 0.2, 1.50$, respectively. (γ is the strength of the trigonal field, i.e., the anharmonicity defined below equation (17).) $\alpha = 0.50$ and the unit of energy is $\hbar\omega$. The envelope function in (a) is constructed by Gaussian coarse-graining of each peak.

This means that the behaviour of $\langle\hat{\chi}\rangle_p$ can be revealed by applying the analysis of $\langle\hat{\ell}_z\rangle_p$ in (10). In fact, the expectation value $\langle\hat{\chi}\rangle_p$ in (14) shows regular oscillation with increasing energy (see figure 3(a)), just as in the case of $\langle\hat{\ell}_z\rangle_p$ in the dynamical Jahn–Teller system [15]. This is a consequence of the integrable system which includes no anharmonic term. If a chiral order parameter of one triangular lattice is observed, we can propose the chiral order parameter as a new precursor of quantum chaos.

Finally we note a role of the anharmonic term involved in the triangular three-particle system. Let us introduce the Toda-lattice potential [16]

$$U(x) = \frac{c}{d}\mathrm{e}^{-\mathrm{d}x} + cx - \frac{c}{d}, \tag{15}$$

where x is the deviation of the interparticle distance from the equilibrium lattice constant. c and d are constant with the condition $cd > 0$. The total lattice potential is a sum of $U(x)$ with x the three kinds of deviation for the three segments of the regular triangle. In the limit $d \ll 1$ under the constraint $cd =$ constant, we obtain the following expansion in x:

$$\begin{aligned} U(x) &= \frac{c}{d}\left(1 - dx + \frac{d^2}{2!}x^2 - \frac{d^3}{3!}x^3 + \cdots\right) + cx - \frac{c}{d} \\ &= \frac{cd}{2}x^2 - \frac{cd^2}{6}x^3 + \cdots. \end{aligned} \tag{16}$$

Suppressing a high-frequency a_{1g} mode and noting the symmetry of the e_g modes in figure 2, the bilinear term in (16) leads to the 2d harmonic oscillator potential. On the other hand, the cubic term in (16) leads to the trigonal(anharmonic) potential

$$V_A = V_A(Q_1, Q_2) = -\frac{\gamma}{3}(Q_1^3 - 3Q_1Q_2^2) \tag{17}$$

with $\gamma = cd^2/2$ in terms of normal e_g modes Q_1 and Q_2. Equation (17) is just the Hénon–Heiles potential [17] and the resultant semiclassical dynamics (quantal spin + classical lattice vibrations) can show a chaotic behaviour. Then, in the fully quantized system $\langle\chi\rangle$ has the largest value at low energies and shows a rapidly decaying irregular oscillation with respect to energy by increasing the anharmonicity(chaoticity) γ (see figures 3(b) and (c)).

In real triangular antiferromagnets like $NaTiO_2$ or $LiNiO_2$, the ground-state degeneracy due to the intrinsic frustration is serious. To remove such degeneracy, quantum spins are expected to be coupled with lattice vibrations. These extended lattices should correspond to the cooperative Jahn–Teller system where individual Jahn–Teller clusters are mutually correlated. As shown in figure 3, in the case of coupling with lattice-vibrational modes a chiral order parameter for a three-spins cluster takes the largest value in low energies. Therefore this novel order parameter will keep playing a vital role in quantifying the ground-state frustration in extended triangular lattices coupled with harmonic or anharmonic phonons.

In conclusion the frustrated quantum spin system on a triangle coupled with lattice vibrations is equivalent to an $E_g \otimes e_g$ Jahn–Teller system. The chiral order parameter $\hat{\chi}$ should signify a quantum chaos (or quantum regularity) induced by the interaction between quantum spins and anharmonic (or harmonic) lattice vibrations, and the energy dependence of $\langle\hat{\chi}\rangle$ that quantifies the spin frustration shows the transition from regular to irregular oscillations by increasing anharmonicity. We hope the present work will stimulate further experimental activities on the chiral order in frustrated triangular antiferromagnets.

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