Frustrated quantum three-spins coupled with vibration modes:
Quantum chaos in the context of dynamical Jahn-Teller problem

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本研究では、固体物性論の枠組みで量子カオスを考察する。具体的に、2つのd電子系に含まれる縮退 E_g 軌道を持つ電子状態（2準位系）と格子振動モード e_g（2重縮退の2つの振動モード Q_1, Q_2）が結合した動的ヤーン・テラー系を考察する。その量子ハミルトニアンは線形の電子格子相互作用と非調和ポテンシャルで構成される。後者は Henon-Heiles 系と呼ばれるカオスを示す典型的な系と一致する。古典論でこの系がカオスを示すことを数値計算で確かめ、量子系でそのカオスの影響を探る。そして、1) 磁気的 g 因子によってカオスの情報を得ることを提案し、2) さらに、電子遷移スペクトルからもカオスの情報が得られることを示す。最後に、3) 電子状態の役割を量子スピンに置き換えた新しいモデルも導入する。それは、3角格子の格子点に反強磁性を示すスピンを並べ、格子振動と結合する系である。この系のフラストレーションを定量化するカイラリティを採用してカオスの量子系における影響を調べる。本講演では特に 3) の内容について述べた。

The triangular Heisenberg antiferromagnets play an important role in our understanding the resonating valence bond (RVB) state, in which the scalar chirality for 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. We investigate a triangular cluster model of the Heisenberg antiferromagnet in which quantum spins are coupled with lattice vibrations, for the purpose to see magnetic properties of its high-lying states in relation to a typical dynamical Jahn-Teller system. The spin-lattice interaction is introduced by expanding the exchange interaction with respect to deviation of lattice displacements from equilibrium. We shall address the issue: the present model becomes equivalent to that of the well-known vibronic problem for $E_g \otimes e_g$ Jahn-Teller system.

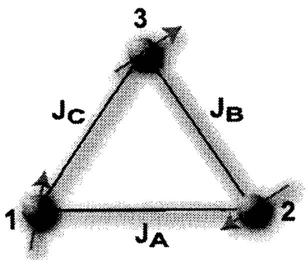

FIG. 1: Triangle with antiferromagnetic spins.

Let us consider the quantum spin system where three spins of spin=1/2 are localized at lattice sites 1,2 and 3 on triangle. The coupling between neighboring spins are expressed by the antiferromagnetic exchange interactions J_A, J_B and J_C as shown in Fig.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 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 arrows denote s_{jz} for site j.

By using these bases, we obtain the Hamiltonian matrix,

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

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 Fig.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 center 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

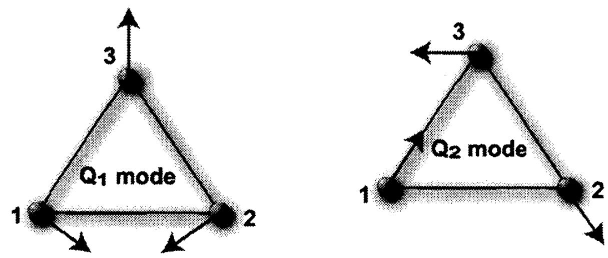

FIG. 2: The normal modes Q_1 and Q_2 in the triangle.

is obtained as a result of the the expansion of J_A, J_B and J_C linearly in the 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.

Concerning the spin system, on the other hand, we introduce the following bases introduced by Nakamura and Bishop for the triangular spin plaquet[5–7]:

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

These bases reflect clockwise and anticlockwise rotations of a spin configuration on the plane of the triangle. The wave numbers $k=0,\pm 2\pi/3$ correspond to phase factors in Bloch's theorem for the system with discrete rotational symmetry. From a viewpoint of the ligand-field theory[8], 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 this new bases, the Hamiltonian matrix (2) can be transformed to

$$\mathcal{H}/\left(-\frac{3}{4}\hbar^2 J\right) = \begin{array}{c} \\ \langle k=0| \\ \langle k=\frac{2\pi}{3}| \\ \langle k=-\frac{2\pi}{3}| \end{array} \begin{array}{c} \begin{array}{ccc} |k=0\rangle & |k=\frac{2\pi}{3}\rangle & |k=-\frac{2\pi}{3}\rangle \end{array} \\ \left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & \alpha(-Q_1-iQ_2) \\ 0 & \alpha(-Q_1+iQ_2) & -1 \end{array}\right) \end{array}. \tag{5}$$

From Eq.(5) we find that the $k=0$ manifold is completely separated from other manifolds, i.e., $\mathcal{H}=\mathcal{H}_{k=0}\otimes\mathcal{H}_{k=\pm 2\pi/3}$. $\mathcal{H}_{k=0}$ and $\mathcal{H}_{\pm 2\pi/3}$ correspond to A and E_g representation, 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:

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

we obtain

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

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

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

Thus, we would like to emphasize that the present system for quantum spins on the triangle coupled with doubly-degenerate vibrational e_g modes is equivalent to $E_g\otimes e_g$ 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 the kinetic energy ($(P_1^2 + P_2^2)/2$) and $\mathcal{H}_{JT}$ of (8), the p-th eigenstate of the $\ell = 1/2$ manifold, $\Psi_{p,1/2}$ is given by

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

where the $\psi_{n,m}$'s 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 $\phi_\pm = d_u \pm i d_v$. The expansion (9) was found by rewriting $\mathcal{H}_{JT}$ in (8) into a suitable form with the use of $\phi_\pm$[9]. 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 wave function 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

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

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[10], and has received a renewed attention recently in the context of nonlinear dynamics[9].

Now let's 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 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 $k = \pm 2\pi/3$ states (4) are

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

(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 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 p-th eigenstate is given by

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

This means that the behavior 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 the energy(see Fig.3(a)), just as in the case of $\langle \hat{\ell}_z \rangle_p$ in the dynamical Jahn-Teller system[10]. This is a consequence of the integrable system which includes no anharmonic term. If chiral order parameter of one triangular lattice is observed, we can propose 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 Toda-lattice potential[11]

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

where x is the deviation of inter-particle 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 kind of deviations for three segments of the regular triangle. In the limit $d << 1$ under the constraint cd = constant, we obtain the following expansion in x:

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

Suppressing a high-frequency a_{1g} mode and noting the symmetry of the e_g modes in Fig.2, the bilinear term in (16) leads to the 2-d 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 behavior. Then, in the fully quantized system $\langle \chi \rangle$ has the largest

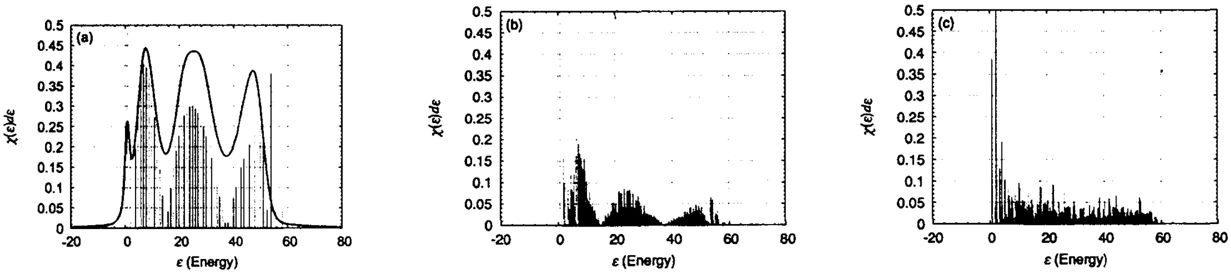

FIG. 3: Energy(ε) dependence of partially-averaged chirality $\chi(\varepsilon)d\varepsilon(=\sum'_p|\sum_{n=1}^{\infty}(-1)^n a_{n,p}^2|d\varepsilon)$ with $d\varepsilon = 0.25$ in unit of Ξ_χ. Figures 3(a), 3(b) and 3(c) correspond to $\gamma = 0, 0.2, 1.50$, respectively.(γ is strength of the trigonal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

value at low energies and shows a rapidly decaying irregular oscillation with respect to energy by increasing the anharmonicity(chaoticity)γ(see Figs.3(b) and 3(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, quntum 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 Fig.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 to play 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 $E_g \otimes e_g$ 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.

This talk is based on the joint work with Y.Natsume, A.Terai and K.Nakamura[13]

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