Quantum Tunneling in Half-Integer Spin Systems

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Motivated by the experimental observations of resonant tunneings in the systems with half-integer spin, such as V_{15} and Mn_{4}, we study the mechanism of adiabatic change of the magnetization in systems with the time-reversal symmetry. Within the time-reversal symmetric models, effects of several types of perturbations are investigated. Although tunneling between the ground states is suppressed in a simple Kramers doublet, we show that the nonadiabatic transition governed by the Landau-Zener-Stückelberg mechanism occurs in many cases due to the additional degeneracy of the ground state. We also found more general cases where LZS mechanism can not be applied directly even the system shows a kind of adiabatic change of the magnetization.

§1. Introduction

Recently the dynamics of nanoscale molecular magnets has attracted much interest. In particular, the magnetization processes in some of molecules show step-wise structures of hysteresis in the sweeping magnetic field. This phenomenon is attributed to the quantum mechanical resonance at level crossing points in discrete energy structure of the small magnets, and is called resonant tunneling. The low-energy magnetic properties of such molecules is usually given by a model of a single large spin. For example, the system of Mn_{12}\textsuperscript{1)} or Fe_{8}\textsuperscript{2,3)} is represented by

$$\mathcal{H}_0 = -D(S_\zeta)^2 - HS_z, \quad S = 10, \quad D > 0.$$ \hspace{1cm} (1.1)

Level-mixing interactions such as

$$\mathcal{H}_1 = C((S_i^+)^4 + (S_i^-)^4) \quad \text{or} \quad \mathcal{H}_1 = E((S_i^x)^2 - (S_i^y)^2).$$ \hspace{1cm} (1.2)

cause hybridization of the degenerate states of different values of the magnetization, and the resonance between the two states takes place, i.e., the resonance tunneling. The hybridization causes an energy gap, i.e., the tunneling gap. In particular, in the case of integer spin S, the hybridization occurs between two-fold degenerate ground states with the total magnetization M = ±S at H = 0. This tunneling phenomena has been studied by a kind of path-integral method\textsuperscript{4)} which has provided various important informations. There the tunneling probability is expressed by a form of path integral representation, e.g.,

$$P = \langle \pi | e^{-\beta\mathcal{H}} | 0 \rangle,$$ \hspace{1cm} (1.3)

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where $H = K_x(S^x)^2 + K_y S^y$, $K_x > K_y > 0$ and $|\pi\rangle$ and $|0\rangle$ denote the states directing $\pm z$ directions (the easy axis), respectively.

However, in this picture of a single large spin model, the tunneling in half-integer spin particle is known to be suppressed due to the interference of the Berry phase $^5)^-^7$. This fact is originated from the time-reversal symmetry and it corresponds to the Kramers theorem that all the energy levels must be at least doubly degenerate in half-integer spin systems. In the context of eq.(1.3), the contributions from the pair of the two paths related by the time-reversal operation cancel with each other and

$$\langle \pi | e^{-\beta H} | 0 \rangle = 0,$$

when $S = \text{half-integer}$, from which one may conclude the absence of the tunneling gap.

Generally, systems have the time-reversal symmetry when the hamiltonian of the system consists of products of even number of spins, e.g., the usual two spin interactions, etc. Therefore, in systems of odd number of spins, the eigenstates must be at least doubly degenerate at $H = 0$, i.e. the Kramers theorem. However, in many half-integer spin systems, e.g. $V_{15}(S = 3/2)^8,^9$ and $\text{Mn}_4(S = 9/2)^10$, temperature independent relaxation phenomena have been found, which suggests the existence of a tunneling splitting in half-integer systems.

In this paper, we consider this tunneling problem in time-reversal symmetric systems. The key point is the fact that the realistic molecule consists of many atoms and many degrees of freedom exist. There the magnetic property can not be simply expressed by a single large spin. We find that the system can show tunneling behavior making use of additional degrees of freedom, even if each level are the Kramers doublet.

The existence of the tunneling gap causes an avoided level crossing structure of the energy level as a function of the magnetic field $H$

$$\mathcal{H}_Z = -H \sum_i S_i^z,$$

and we expect the adiabatic motion of the magnetization when we sweep the magnetic field. As time-dependent phenomena, the magnetization adiabatically follows the ground state value if the field-sweeping is slow. There the sign of the magnetization changes near $H = 0$, which is the adiabatic motion. If we sweep $H$ fast, then generally the nonadiabatic transition occurs$^{11)^-21}$, and the transition probability of the nonadiabatic transition was given by Landau, Zener and St¨uckelberg$^{11)^-13)$ as

$$p = \exp\left(-\frac{\pi(\Delta E)^2}{2v}\right),$$

where $v$ is the sweeping rate of the field $dH/dt$, and $\Delta E$ is the energy gap at the avoided level crossing structure. This transition rate plays an important role in the resonant tunneling phenomena in nanoscale molecular magnets such as $\text{Mn}_{12}$ and $\text{Fe}_8(3,17)^-^21)$. In the present paper we point out that the various types of avoided level crossing structures are possible in half-integer spin systems which are time-
reversal symmetric at $H = 0$, and also we study properties of adiabatic changes of the magnetization.

§ 2. Effects of magnetization-nonconserving matrix elements

In this paper, we mainly consider the Heisenberg model with odd number of spins as the unperturbed system. In order to change the value of the magnetization, the system must contain some terms which violates the conservation of the magnetization. That is, the hamiltonian must not commute with the total magnetization. We will see that some of such systems have the avoided level crossing structures.

Here we study an antiferromagnetic Heisenberg chain for $H_0$

$$H_0 = \sum_{(ij)} J_{ij} S_i \cdot S_j$$

(2.1)

with various types of perturbations $H_1$ of the form

$$H_1 = \sum_{ij} \alpha_{ij} S^z_i S^z_j.$$ 

(2.2)

First we study a simple case of three spins ($N = 3$), and more complicated cases will be studied later. The states of the pure Heisenberg model ($\alpha_{ij} = 0$) are classified by the total spin $S$, that is, the four states of $S = 3/2$ and two sets of two states of $S = 1/2$ for the present case of $N = 3$. In Fig. 1(a), we show the energy level structure of the system for $\alpha = 0.0$ as a reference. Here we see six lines but the levels crossing at low energy consist of two degenerate states. That is, there are four states of $S = 1/2$. This degeneracy for the $S = 1/2$ states appears due to the rotational symmetry.

When we apply the perturbation (2.2), the total spin is not a good quantum number. However, it gives still good description of the states as far as the perturbation is small. Thus hereafter we also use $S$ to denote the states.

Here we study the following five categories of the perturbation:

| Model | Rotational symmetry | Reflection symmetry |
|-------|---------------------|---------------------|
| I     | $\alpha_{12} = \alpha_{23} = \ldots = \alpha_{N1} = \alpha$ | $\alpha_{ij} = \alpha_{ji}$ |
| II    | $\times$           | $\alpha_{12} = \alpha_{21} = \alpha$, others = 0 |
| III   | $\times$           | $\alpha_{ij} = -\alpha_{ji} = \alpha$ |
| IV    | $\times$           | $\alpha_{12} = -\alpha_{21} = \alpha$, others = 0 |
| V     | $\times$           | $\alpha_{12} \neq \alpha_{21}$, others = 0 |

Table 1 Types of perturbations

2.1. Model I

In Fig. 1(b) we show the energy level structure for Model I with $\alpha = 0.2$. There we find that the hybridization does not occur at lower crossing point while it occurs at higher crossing point. In this model the perturbation is symmetric for both the
rotation and reflection, and does not affect the symmetry of the wavefunctions. Here we have

\[
\mathcal{H}_1 |\frac{3}{2}\rangle = |\frac{3}{2}\rangle \\
\mathcal{H}_1 |\frac{1}{2}\rangle = |\frac{1}{2}\rangle,
\]

(2.3)

where $|\frac{3}{2}\rangle$, and $|\frac{1}{2}\rangle$ denote the Hilbert space of the wave functions with $S = \frac{3}{2}$ and $\frac{1}{2}$, respectively. In particular, in the space of $S = \frac{1}{2}$ the symmetric operation $\mathcal{H}_1$ does not have matrix elements

\[
\mathcal{H}_1 |\frac{1}{2}\rangle = 0.
\]

(2.4)

Therefore the degenerate crossing structure of $S = \frac{1}{2}$ states in Fig.1(a) is preserved. On the other hand, in the space of $S = \frac{3}{2}$, $\mathcal{H}_1$ has matrix elements between $M = \frac{3}{2}$ and $\frac{1}{2}$, and between $M = -\frac{3}{2}$ and $-\frac{1}{2}$, where $M$ is the $z$ component of the magnetization. The absence of matrix elements between $M = \frac{1}{2}$ and $-\frac{1}{2}$ is due to an peculiar interference of operations of this type of $\mathcal{H}_1$ (see Appendix).

Thus, avoided level crossing structures are formed only between the states $M = \frac{3}{2}$ and $\frac{1}{2}$ and between $M = -\frac{3}{2}$ and $-\frac{1}{2}$.

Thus if we consider the antiferromagnetic model of the type of Model I, the adiabatic transition can not occur between the $M = \frac{1}{2}$ and $-\frac{1}{2}$ states as we expected from the single spin model.

In the present paper we will not mention for the ferromagnetic model in detail. However, it should be noted that the property of the ferromagnetic case is simply obtained by reversing the energy axis. In the present model, adiabatic transitions occur between $M = -\frac{3}{2}$ and $-\frac{1}{2}$, and $M = \frac{1}{2}$ and $\frac{3}{2}$.

2.2. Model II

Model II of $\alpha = 0.2$ shows a similar structure to that in Fig. 1(b) as shown in Fig. 2(a). However due to the lack of the rotational symmetry, it shows more
complicated structure as shown in Fig. 2(b), where we use $\alpha = 0.8$ to emphasize the crossing structure. This model has the reflection symmetry with respect to the exchange $R_{12}$ of the sites 1 and 2. Thus the states are classified as

$$R_{12}|+\rangle = +|+\rangle$$
$$R_{12}|−\rangle = −|−\rangle,$$

where $|+\rangle$ and $|−\rangle$ denote the symmetric and antisymmetric states with respect to the exchange $R_{12}$. The four states in $S = 1/2$ are separated into sets of $|+\rangle$ and $|−\rangle$. The antisymmetric states $|−\rangle$ do not contain all up state or all down state, and are kept in strict $S = 1/2$ space. Thus they are not affected by $H_1$ and degenerate at $H = 0$. These two states of $|+\rangle$ in $S = 1/2$ contain a little components of the all up and down state and no more are in $S = 1/2$ space strictly. However the two states of $|+\rangle$ also must degenerate at $H = 0$ because of the time-reversal symmetry. In this model, the adiabatic transition can not occur between the $M = 1/2$ and $−1/2$ states when the field crosses zero similarly to the previous model. The state of $S = 3/2$ also forms complicated avoided structure.

In Fig. 3(a), we show the magnetization of the states of four low energies as functions of the field for the case of $\alpha = 0.8$. The bold solid line, bold dotted-line, dashed-line and thin solid line denote the magnetization of the levels 1, 2, 3 and 4, respectively. When the levels cross the order of the lines changes. Therefore the types of lines change discontinuously. However, the adiabatic motion of magnetization is given by smooth continuation of a level. The adiabatic magnetization starting with the ground state at $H = −5$ is shown by big circles. It shows a strange field dependence. That is, around $H ≃ 2$ the magnetization has a peak, where the coefficient of the all up state becomes large.

When we sweep the field,

$$H(t) = −H_0 + vt,$$
the evolution of the state is expressed by

$$|\Psi(t)\rangle = \exp \left(-i\hbar \int_{t}^{t+\Delta t} \mathcal{H}(s) ds \right) |\Psi(t)\rangle, \quad \mathcal{H}(t) = \mathcal{H} - H(t) \sum_{i} S_{z}^{i}, \quad (2.7)$$

where \( \exp \) means the time ordered exponential. In Fig. 3(b), the magnetization process with sweeping field with velocity \( v = 0.02, 0.2 \) and 2.0, are shown. In the case of \( v = 0.02 \) the magnetization in the time dependent process reproduces well the adiabatic one.

![Fig. 3. (a) Adiabatic magnetization process of the Model II with \( \alpha = 0.8 \), (b) Magnetization process with sweeping field \( v = 0.02, 0.2 \) and 2.0, shown by the solid line, dotted-line and thin solid line, respectively.](image)

Here, it should be noted that the magnetization process shows a non-monotonic dependence on the field, which violates the thermodynamical stability. That is, the Zeeman energy (1.5) decreases when the field increases. Namely, if we increase the magnetic field the magnetic field receives some energy but not gives the energy as in the normal cases. This thermodynamically unstable behavior comes from the fact that this adiabatic state is no more the ground state. In the ground state the Zeeman energy must increase monotonically with \( H \). In the present case, the ground state for \( H < 0 \) adiabatically becomes an excited state after the crossing point due to the crossing. It would be interesting to find phenomenon corresponding to the present observation and to make use this peculiar behavior of the magnetization.

2.3. Model III

In Fig. 4(a), we show the energy level structure for Model III with \( \alpha = 0.2 \). Using a similar argument for Model I,

$$\mathcal{H}_1 |3/2\rangle = 0, \quad (2.8)$$

and thus we find that the structure of \( S = 3/2 \) states is preserved. On the other hand, \( \mathcal{H}_1 \) can change the magnetization in the space of \( S = 1/2 \). Here the states of \( S = 1/2 \) with different magnetizations \( M = \pm 1/2 \) are hybridized and form two sets of avoided
Fig. 4. (a) Energy structure and (b) ground state magnetization, of the Model III of $N = 3$ with $\alpha = 0.2$

level crossing structure. The magnetization process of the ground state is shown in Fig. 4(b). They are completely degenerate due to the rotational symmetry. The adiabatic transition between the different sets of avoided cross structure is prohibited. Let us take a ground state $|a\rangle$ at $H = -H_0$ in one set of avoided cross structure as an initial state. We have another ground state $|b\rangle$ in the other set which is orthogonal to $|a\rangle$. The orthogonality does not change by the sweeping operation because of the symmetry. For example if we begin with a state whose eigenvalue is $e^{4i\pi/3}$ for one third rotation, the state with the eigenvalue $e^{8i\pi/3}$ is not mixed at all. Thus we can consider the time evolution for both states separately. In each branch, the nonadiabatic transition probability is exactly given by the equation (1.6), and thus the total change of the magnetization for any combination is given by the LZS formula.

2.4. Model IV

In Fig. 5(a), we show the energy level structure for Model IV with $\alpha = 0.2$. There we find a similar structure to that of Model III. However, because of the lack of the symmetry, the four levels of low energies are no more degenerate and if we look the state carefully they have different field dependences (see the inset). In order to emphasize the structure, the energy structure of $\alpha = 0.8$ is also shown in Fig. 5(b). Although this model has no geometrical symmetry, the model has a peculiar symmetry due to the special interference in the triangle lattice. That is, the all up state $|+++\rangle$ can not reach to the all down state $|--\rangle$. Thus the states is classified into the following two categories

$$|A\rangle = a|++\rangle + b|+\rangle_o + c|-\rangle_e,$$
$$|B\rangle = a'|--\rangle + b'|-\rangle_o + c'|+\rangle_e,$$

(2.9)

where $|+\rangle_o$ is a symmetric state of $M = 1/2$ with respect to the exchange of the sites 1 and 2, and $|-\rangle_o$ is the antisymmetric state of $M = -1/2$, and so on. In the inset of 5(a), the open circles denote the level of $|A\rangle$ and the closed circles $|B\rangle$. 


Avoided crossing structure is formed in each category. Thus there are no mixing between different sets of the avoided crossing structure. Because of the Kramers theorem, they cross at $H = 0$ and recover the degeneracy. For any combination of the initial populations of the two sets, the nonadiabatic transition probability in each set is given by (1-6), and the change of the total magnetization follows the LZS mechanism. In this model, if we sweep the field in a wide range, e.g., from $-4$ to $4$, the magnetization adiabatically changes from $M = -3/2$ to $M = 1/2$, but not to $3/2$. This asymmetry of the adiabatic change is one of the characteristics of the present model.

Up to the model IV, the system has some symmetry with respect to the exchange of spin 1 and 2. Now we try to remove this symmetry. Now we put only $\alpha S_1^z S_2^z$, but there we found essentially the same structure to that of Model IV. We found that there is still some symmetry which causes the decoupling of the space into $2+2$. Even if we add a term $\beta S_2^y S_3^z$ in order to reduce possible symmetry, we find that there still exists two sets of states. These separations are due to rather special interference on the triangle structure.

2.5. Model V

Finally we put $\alpha_{12} = 0.2$ and $\alpha_{21} = -1.0$. In Fig. 6, we show the energy level structure for this case, which is similar to the previous one. But in this model we found that there is no separation into $2+2$ subspaces any more. The overlaps of the ground state at $H = -0.3$ ($\langle G(H = -0.3) \rangle$) and the eigenstates at $H$ ($\langle \phi_k(H) \rangle$) at $H$ of four lowest eigenvalues are measured by the quantity

$$x(k) = |\langle G(H = -0.3) | \phi_k(H) \rangle|^2, \quad k = 1, \cdots, 4,$$

(2.10)
as shown in Figs. 7. In Fig. 7(a), we show the overlaps in a case of $\alpha_{12} = 0.2$ and $\alpha_{21} = 0$ where the separation into $2+2$ occurs, and in Fig. 7(b) the present case ($\alpha_{12} = 0.2$ and $\alpha_{21} = -1.0$). Here, the data for $k = 1, \cdots, 4$ are shown by bold-solid, bold-dotted, dashed and thin-solid lines, respectively. While the set of states of $k = 1$ and $3$ and that of $k = 2$ and $4$ do not mix at all in Fig. 7(a), all the four states have some overlap with the state $|G(H = -0.3)\rangle$ in Fig. 7(b). The bold line in Fig. 7(b) shows very small but nonzero values at $H > 0$. The wave functions consist of all the states

$$|\Psi(t)\rangle = a|+++\rangle + b|+e\rangle + c|--\rangle + a'|---\rangle + b'|--\rangle + c'|+e\rangle.$$  
(2.11)

Thus, the simple LZS transition mechanism does not work in this model. Dynamical property of this model will be studied in the next section.

2.6. Summary

Here we study the simple case of $N = 3$, but we can learn general properties for higher spins. That is, although the time-reversal symmetry prohibits the tunneling between the Kramers doublets at $H = 0$, it does not mean the absence of the adiabatic change of magnetization when the field swept at $H = 0$. If the system has additional degree of freedom and more than two states are degenerate, e.g. 4-fold degeneracy, at $H = 0$ in the unperturbed system $\mathcal{H}_0$, the avoided level crossing structure is formed with respect to the field as in the cases of Model III, IV, and V.
If the system has additional symmetries, then the avoided level crossing structures are classified by the symmetry and they are independent each other, where the LZS transition mechanism works as in the two-level system. On the other hand, in the absence of additional symmetry, the degenerate states forms an irreducible space except $H = 0$. There the simple LZS transition mechanism does not work. In the next section we study the magnetization change under the sweeping field in the latter case.

§3. Quasi-Landau-Zener-Stückelberg Transition

Fig. 8. (a) Magnetization process in the sweeping speed $v = 0.04$, 0.08, 0.12, and 0.4 from the top to the bottom. $\alpha_{12} = 0.02$, $\alpha_{21} = -0.1$ (b) The overlaps with the $k$-th adiabatic state $p_k(H)$ for $k=1,2,3$ and 4 by the bold solid, bold dotted, dashed and solid lines, respectively. $\alpha_{12} = 0.02$, $\alpha_{21} = -0.1$, $v = 0.04$.

Now we demonstrate the time dependent process with sweeping field where $H$ is swept from $-H_0$ to $H_0$.

$$|\Psi(t_f)\rangle = \exp \left( i \int_{t_i}^{t_f} \mathcal{H}(s) ds \right) |G(H = -H_0)\rangle,$$

where $|G(H)\rangle$ is the ground state for $H$, and $H(t_1) = -H_0$ and $H(t_f) = H_0$. In Fig. 8(a) we show the magnetization for the case of $\alpha_{12} = 0.02$ and $\alpha_{21} = -0.1$ (Model V). Here we take small values of $\alpha$'s in order to facilitate the observation of the nonadiabatic transition. The speed $v$ of the field-sweep is 0.02, 0.04, 0.08, and 0.2 from the top to the bottom, respectively. As we saw in the previous section, the simple LZS mechanism can not be applied for this model because all the four low energy states contribute to this transition. However we find similar $v$-dependence of the magnetization change to that in the LZS mechanism. In order to study the detail of the transition we investigate the population of the $k$-th eigenstate at the field $H$ by

$$p_k(H) = |\langle \Psi(t) | \phi_k(H) \rangle|^2, \quad H = H(t).$$
In Fig. 8(b), the change of the populations are shown, where we find the ground state at large negative field is scattered to all the four states and they change with the field. This is a characteristic feature of the present model in contrast with the other cases: e.g., in the case of $\alpha_{21} = 0$, where the four states are separated into two sets and the ground state at high negative field is scattered only to the second and forth states.

![Fig. 9. Nonadiabatic transition probabilities in the Model V with $\alpha_{12} = -\alpha_{21}/5 = 0.03, 0.02,$ and 0.01, from the top to the bottom. The solid curves represents the value estimated by the LZS formula (1.6).](image)

However, if we sum up the populations of the first two states,

$$p_0 = |\langle \Psi(t_f)|\phi_1(H)\rangle|^2 + |\langle \Psi(t_f)|\phi_2(H)\rangle|^2,$$

the sum almost satisfies the dependence of LZS transition probability (1.6) as shown in Fig. 9 where

$$p_0 = 1 - p.$$

Here we use the energy gap at $H = 0$ as $\Delta E$. The data for the system of $\alpha_{12} = -\alpha_{21}/5 = 0.03, 0.02,$ and 0.01 are shown by circle, square, and triangular, respectively. The lines denote the corresponding dependences due to the relation (1.6).

This is a problem of nonadiabatic transition of four levels. But the mechanism of the present model seems to belong to a different type from that of the bow-tie model. The present transition may be attributed to some multiple crossings, and then have some relation with the Brundoiber and Elser hypothesis. The mechanism of this quasi-LZS behavior of the sum of the population would be an interesting problem in the future.

From a viewpoint of the present study, the resonant tunneling from $-1/2$ to $1/2$ at $H = 0$ in molecular magnets with half-inter spin such as $V_{15}$ does not contradict with general theory of the symmetry. Here it would be interesting to point out the following fact. If the field is swept slowly from a large negative value where the magnetization is $-3/2$, the magnetization change adiabatically as $-3/2 \rightarrow -1/2 \rightarrow 1/2$, Steam.
but not to $3/2$ as shown in Fig. 10(a), although the ground state magnetization process is, of course, symmetric (Fig. 10(b)). We found this behavior exactly in the Model IV. However, in the present model the wave functions contain both components of $|++\rangle$ and $|--\rangle$. Therefore this asymmetry of the adiabatic magnetization seems to occur widely in model on the triangle. If the system essentially consists of three spins, this asymmetric adiabatic process would be observed in a slow sweeping field at low temperatures. However, if other spins strongly contribute to the interaction, the states of $3/2$ could be also degenerate. In such cases also the transition from $1/2$ to $3/2$ would be allowed. It would be an interesting problem to study the magnetization change of $V_{15}$ in a slowly sweeping field, i.e., adiabatic change of the field. This enables us to determine whether only three spins in the middle of the molecule mainly contribute to the interaction, or the whole 15 spins contribute. We hope that some experimental study on this problem will be done, although the thermal effects would easily smear out the pure quantum selection rule.

§4. Higher Spin Cases

So far we studied magnetic properties the crossings which are mainly consists of $S = 1/2$ states. Here let us study the cases of higher spins. As an example, we study a system of five spins shown in Fig. 11, where the bold line denotes $J$, and the thin line denotes $J'$. The perturbation (2.2) is set between the sites 1 and 2 only with $\alpha_{12} = \alpha$. 

Fig. 10. (a) Adiabatic magnetization process ($v = 0.002$) and (b) Magnetization process of the ground state, of Model V for $\alpha_{12} = 0.02$ and $\alpha_{21} = -0.1$.
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If we set $J = J' = 1$ and $\alpha = 0$, the ground state at $H = 0$ is given by 4-fold degenerate $S = 1/2$ states, and the energy structure is similar to Fig. 1(a). If we put $\alpha = 0.2$, the energy structure is similar to Fig. 5(a), and we find two sets of independent avoided level crossing structure again. Thus, it is expected that the LZS transition works in a wide range of systems when the ground state is in $S = 1/2$.

In order to have the ground state with a higher spin in antiferromagnetically interacting system, we set $J = 1, J' = 0.2$. For $\alpha = 0$, the ground state at $H = 0$ is given by 4-fold degenerate $S = 3/2$ states. The energy structures for $\alpha = 0$ and 0.2 are given in Fig. 12(a) and (b), respectively. The zoom-up around $H = 0$ is shown in Fig. 13(a), where we find a complicated structure.

![Fig. 12. (a) Energy structure of the pure Heisenberg model and (b) of the Model V with $\alpha = 0.2$.](image)

The overlaps among all the four states are nonzero. In Fig. 13(b) the overlap functions are shown as in the same manner as eq.(2.10), where the solid line, bold dotted-line, dotted-line, dashed-line, dot-dashed line, and dot-dot-dashed line denote $x(k), k = 1, \cdots, 6$, respectively. Here we do not expect simple LZS transition.

Although we will report elsewhere detail properties of this non-LZS type adiabatic transition of high spin states, we show the adiabatic magnetization processes of the present model in Fig. 14(a). If we sweep the field from a large negative value, the adiabatic magnetization is given by the bold solid line for $H < 0$. This bold solid line jumps at $H = 0$. But the ground state for $H < 0$ adiabatically continues to the second level, and the adiabatic magnetization is given by the bold dotted-line. The second level forms an avoided level crossing with the third level near $H = 0.02$. If the nonadiabatic transition occurs at this point, the magnetization is given by the dashed-line instead of the bold dotted-line after this point. Thus we expect that if $v << 1$ then the magnetization curve is given by the bold dotted-line, and if $v >> 1$ then by the dashed-line. If the field is swept with a finite speed, the magnetization is located between the bold dotted-line and the dashed-line depending on the speed.
In Fig. 14(b), the magnetization change with sweeping velocity $v = 0.0002$ is shown, which is indeed between the dotted-line and the dashed-line.

Here we adopt a peculiar example for higher spin case. The property of the crossing would depend on the types of perturbation. It should be also noted here that so far we study only isotropic model for $\mathcal{H}_0$. However, when we study high spin cases, the uniaxial anisotropy (1·1) plays an important role, too. Thus, we expect a variety of types of adiabatic transition of the magnetization in high spin cases, which will be reported elsewhere.
§5. Summary

We have studied the resonant tunneling phenomena in half-integer spin systems with the time-reversal symmetry. If the system has only single degree of freedom, the time-reversal symmetry prohibits the adiabatic change of the magnetization as has been pointed out. However, if the system consists of many spins and there exist another degree of freedom, various types of adiabatic change of the magnetization occurs.

In the present paper, we found degenerate (or quasi-degenerate) avoided level crossing structures in Model III (or IV, V), where the Landau-Zener-Stückelberg mechanics works. Appearance of avoided cross structures in half-integer spin systems does not contradict with the Kramers theorem in all cases because the states belonging to different avoided level crossing structures degenerate at $H = 0$.

The simple LZS mechanism of the nonadiabatic transition does not work in some cases where more than two levels are involved in a nonadiabatic transition (Model V). However an interesting sum rule seems to hold, namely when we add the transition probabilities to the two neighboring states, the LZS formula gives an accurate fit to the numerically obtained data. This issue deserves further studies as a possible extension of the LZS theory.

We would like to point out that the adiabatic magnetization does not necessarily coincide with the magnetization of the ground state even the adiabatic change of the sign of the magnetization occurs at $H = 0$. When we sweep the field from a large negative value where the magnetization is $-S$, we could not find any case where the magnetization reaches to $S$ when the field becomes a large positive value. Although the naive extension of (1.4) does not hold when we sweep the field, i.e.,

$$\langle -S | \exp \left( -i \int_0^t (\mathcal{H} - H(s) \sum_i S_i^z) ds \right) | S \rangle \neq 0,$$

where the $H(0) = -H_0 < 0$ and $H(t) = H_0$, the present observation may suggest that the above matrix elements is zero in the limit $H_0 \to \infty$. This problem will be studied in more general cases.

As we saw in Model I and II, if the system has some symmetry and there are only two state in the same symmetry, the levels simply cross at $H = 0$ due to the time-reversal symmetry. Even in such case the adiabatic change of the state can provide nontrivial behavior at $H \neq 0$ as we saw in Model II. The thermodynamical unstable state would cause interesting phenomena when the system is coupled with the dissipative environments.

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Appendix A

Special interference on the triangle lattice

Let us consider $H_1$ of Model I

$$H_1 = \alpha \left( S^x_1 S^z_2 + S^x_1 S^z_3 + S^x_2 S^z_3 + S^x_3 S^z_1 + S^x_1 S^z_3 \right). \quad (A.1)$$

If we consider the total spin operators

$$S^x_{\text{tot}} = S^x_1 + S^x_2 + S^x_3, \quad S^y_{\text{tot}} = S^y_1 + S^y_2 + S^y_3, \quad S^z_{\text{tot}} = S^z_1 + S^z_2 + S^z_3, \quad (A.2)$$

$H_1$ is expressed as

$$H_1 = \frac{\alpha}{2} \left( S^x_{\text{tot}} S^z_{\text{tot}} + S^z_{\text{tot}} S^x_{\text{tot}} \right) = \alpha \left( S^x_{\text{tot}} S^z_{\text{tot}} + \frac{i}{2} S^y_{\text{tot}} \right). \quad (A.3)$$

If we apply $H_1$ to the all-up state $|+ + +\rangle$, we have

$$H_1 |+ + +\rangle = \alpha \left( S^x_{\text{tot}} \times \frac{3}{2} + \frac{i}{2} S^y_{\text{tot}} \right) | + + +\rangle$$

$$= \alpha \left( \frac{3}{4} S^-_{\text{tot}} - \frac{1}{4} S^+_{\text{tot}} \right) | + + +\rangle$$

$$= \frac{\alpha}{2} S^+_{\text{tot}} | + + +\rangle. \quad (A.4)$$

This is a symmetric state in $M = 1/2$. If we apply $H_1$ further, we have

$$H_1^2 | + + +\rangle = \frac{\alpha^2}{2} \left( S^x_{\text{tot}} \times \frac{1}{2} + \frac{i}{2} S^y_{\text{tot}} \right) S^-_{\text{tot}} | + + +\rangle$$

$$= \frac{\alpha^2}{2} \left( \frac{1}{4} S^+_{\text{tot}} + \frac{i}{2} S^y_{\text{tot}} \right) S^-_{\text{tot}} | + + +\rangle$$

$$= \frac{\alpha^2}{4} S^{-}_{\text{tot}} | + + +\rangle \propto | + + +\rangle. \quad (A.5)$$

Thus, the space of $M = -1/2$ cannot be reached from $| + + +\rangle$ by $H_1$.

The present argument is directly extended to general $N$ spin system with interactions between all spin pairs. There we find that $H_1$ in (A.3) has no matrix element between the states of $M = \pm 1/2$. Thus the system of the type of Model I can not adiabatically change the sign of the magnetization.

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