Tunneling of a large spin via hyperfine interactions

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We consider a large spin $S$ in the magnetic field parallel to the uniaxial crystal field, interacting with $N \gg 1$ nuclear spins $I_i$ via Hamiltonian $H = -D S^2 - H_z S_z + AS \cdot \sum_{i=1}^{N} I_i$, with $A \ll D$, at temperature $T$. Tunneling splittings and the selection rules for the resonant values of $H_z$ are obtained perturbatively. The quantum coherence exists at $T \ll AS I$ while at $T \gtrsim AS I$ the coherence is destroyed and the relaxation of $S$ is described by a stretched dependence which can be close to $\log t$ under certain conditions. Relevance to Mn$_{12}$ acetate is discussed.

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The effect of nuclear spins on tunneling of a large spin $S$ has been the subject of intensive research in the last decade. The interest to this problem is two-fold: Firstly, nuclear spins are likely to significantly affect tunneling and coherence. Secondly, they represent a non-conventional dissipative environment that cannot be treated by the Caldeira-Leggett method. Models studied to date assume that tunneling of $S$ is induced by those terms in the Hamiltonian, e.g., transverse field or transverse anisotropy, which do not commute with, e.g., a longitudinal anisotropy term. In that case nuclear spins interfere with tunneling by producing a bias field on the spin $S$ and driving it off resonance. The rate of tunneling of $S$ then decreases by a statistical factor that reflects the probability of the environmental spins arranging such that $\sum_{i=1}^{N} I_i = 0$.

In this paper we study a different situation when tunneling is actually induced by the interaction of $S$ with nuclear spins. This situation may be relevant to Mn$_{12}$ acetate, where the crystal-field terms responsible for tunneling are very small. We consider the following Hamiltonian

$$\hat{H} = -DS^2 - H_z S_z + AS \cdot \mathbf{I}_{\text{tot}}, \quad \mathbf{I}_{\text{tot}} = \sum_{i=1}^{N} \mathbf{I}_i, \quad (1)$$

where the electronic spin $S \gg 1$, $\mathbf{I}_{\text{tot}}$ is the sum of $N \gg 1$ nuclear spins with magnitude $I$, and $A \ll D$ is an effective hyperfine constant. As an illustration we will keep in mind the example of Mn$_{12}$ with $S = 10$, $I = 5/2$, $N = 12$, $D = 0.6$ K, and $A = 2$ mK. We shall assume that the nuclear time $T_1$ needed for $I_i$ to flip is larger than the tunneling time for $S$. The Hamiltonian conserves the magnitude $I_{\text{tot}}$ of $\mathbf{I}_{\text{tot}}$, thus dynamically it describes a two-spin problem within each subspace of fixed $I_{\text{tot}}$. On the other hand, for an assembly of Mn$_{12}$ molecules there is a distribution over the values of $I_{\text{tot}}$, and all results should be averaged over this distribution. Contrary to previous approaches to problems with nuclear spins, we shall solve the above-formulated problem rigorously, using the smallness of $A$ in comparison with $D$.

The longitudinal part of the hyperfine interaction, $AS I_{\text{tot},z}$ splits the energy levels of the electronic spin which become

$$\varepsilon_{m,m_I} = -Dm^2 - H_z m + Amm_I, \quad (2)$$

where $m$ and $m_I$ are the projections of $S$ and $I_{\text{tot}}$ on the $z$ axis. The transverse part of the hyperfine interaction, $(A/2)(S^+ I_{\text{tot},-} + S^- I_{\text{tot},+})$, yields only small corrections to the energy levels in the wells in the second order of the perturbation theory which are of order $A^2/D$ and can be neglected. On the other hand, the transverse spin terms may cause transitions between degenerate energy levels on different sides of the barrier.

In contrast to the problem of spin tunneling in the transverse field, here the projection of the total spin of the system $S + I_{\text{tot}}$ on the $z$ axis is conserved. The value of the bias field $H_z$ for which resonant transitions occur, is defined by the conservation laws

$$\varepsilon_{m,m_I} = \varepsilon_{m',m'_I}, \quad m + m_I = m' + m'_I \quad (3)$$

and can be parametrized by the two quantum numbers $k, k_I$

$$H_z(k, k_I) = Dk + Ak_I, \quad (4)$$

where $k$ and $k_I$ satisfy

$$m' = -m - k, \quad m_I = m' + k_I$$

$$m'_I = m - m' + m_I = m + k_I. \quad (5)$$

Here, by definition, $m < 0$ (see Fig. 1 of Ref. 19 for an illustration of electronic resonances). Whereas the
number \( k \) is integer and labels the main electronic resonance, the number \( k_I \) may be integer or half integer and describes its hyperfine splitting. For the zero-field resonance, \( k = k_I = 0 \), the projection of the total spin of the system on the \( z \) axis is zero for both initial and final states. This only takes place, however, if both \( S \) and \( I_{\text{tot}} \) are integer or half integer. If one of them is integer and another half integer, there is no resonance at zero field.

For a fixed value of \( I_{\text{tot}} \), the possible values of \( k_I \) are defined by the conditions \(-I_{\text{tot}} \leq m_I, m'_I \leq I_{\text{tot}} \) and satisfy

\[
-I_{\text{tot}} - m = -I_{\text{tot}} + m' + k \leq k_I \leq I_{\text{tot}} - m'.
\]

One can see that close to the top of the barrier, where \( m \) and \( m' \) are close to each other, the number of values of \( k_I \) is slightly less then \( 2I_{\text{tot}} + 1 \). Since \( I_{\text{tot}} \leq NI \), the maximal number of these resonances is about \( 2NI + 1 \). On the contrary, for the unbiased ground-state resonance \((m = -S, m' = S)\) there are only \( 2(I_{\text{tot}} - S) + 1 \) values of \( k_I \). For systems with \( NI < S \), there are no resonant transitions between ground-state levels.

Let us consider now the tunneling splitting \( \Delta \varepsilon \) between the resonant levels. Since the hyperfine constant \( A \) is much smaller than the anisotropy \( D \), it can be calculated with the help of the high-order perturbation theory.

One has

\[
\Delta \varepsilon_{m,m';m,m'} = 2(m, m')|\hat{H}|m + 1, m - 1\]

\[
\times \frac{1}{\varepsilon_{m+1,m-1} - \varepsilon_{m,m}} \langle m + 1, m - 1|\hat{H}|m + 2, m - 2\rangle
\]

\[
\ldots \frac{1}{\varepsilon_{m'-1,m'+1} - \varepsilon_{m,m}} \langle m' - 1, m' + 1|\hat{H}|m', m'\rangle.
\]

Performing products in this formula, one obtains at the final result

\[
\Delta \varepsilon_{m,m';m,m'} = \frac{2(D + A)}{[(m' - m - 1)!!^2]^2} \left( \frac{A}{2(D + A)} \right)^{m'-m}
\]

\[
\times \sqrt{\frac{(S + m')!(S - m')!(I_{\text{tot}} - m')!(I_{\text{tot}} + m)!}{(S - m')!(S + m)! (I_{\text{tot}} + m')!(I_{\text{tot}} - m)!}}.
\]

The part of this expression depending on the state of the nuclear subsystem,

\[
f_{\text{nuc}}(I_{\text{tot}}, k_I) = \sqrt{\frac{(I_{\text{tot}} - m - k_I)!(I_{\text{tot}} + m' + k_I)!(I_{\text{tot}} + m + k)}{(I_{\text{tot}} + m + k)!(I_{\text{tot}} - m' - k_I)!}},
\]

has its maximum at \( k_I \) in the middle of its interval, \( k_I = -(m + m')/2 = k/2 \) [see Eq. (8)], and the minimal value at the borders of this interval, \( k_I = -I_{\text{tot}} - m \) and \( k_I = I_{\text{tot}} - m' \). If the number of allowed values of \( k_I \) is much greater than one, \( f_{\text{nuc}} \) approaches a Gaussian (see Fig. 1).

For a given resonance \((k, k_I)\) the splitting depends, apart from the initial and final electronic states, \( m \) and \( m' \), also on the value of \( I_{\text{tot}} \). Inverting Eq. (9), one obtains the range of possible values of \( I_{\text{tot}} \) for a given resonance

\[
\text{max}\{m' + k_I, -m - k_I, (m' - m)/2\} \leq I_{\text{tot}} \leq NI.
\]

The nuclear quantum number \( k_I \) itself changes in the range \(-NI - m \leq k_I \leq NI - m' \), as follows from Eq. (9) if one replaces \( I_{\text{tot}} \) by its maximal value \( NI \). According to Eq. (8), one has \( m_I = -NI \) on the left border and \( m_I = NI \) on the right border of this interval. For these border values of \( k_I \), there is obviously only one possible value \( I_{\text{tot}} = NI \) satisfying Eq. (9). On the other hand, for \( k_I = k/2 \) the number of values of \( I_{\text{tot}} \) attains its maximal value of about \( NI - m' - k/2 \). In addition, each value of \( I_{\text{tot}} \) can be built up of individual nuclear spins in a number of different ways, if \( I_{\text{tot}} < NI \). The latter shows that the hyperfine resonances near the center of the splitted electronic resonance, \( k_I = k/2 \), are much stronger than those for \( k_I \) away from the center. It is, however, difficult to parametrize the strength of these hyperfine lines since the resonance dynamics is rather complicated, as will be seen shortly.

The dependence of the level splitting on \( I_{\text{tot}} \) for a given hyperfine resonance results in the decoherence of tunneling. If electronic spins are prepared in the state \( m \), then only molecules with \( m_I \) satisfying the resonance condition of Eq. (7) will take part in the process. Among those with a given \( m_I \), there are molecules with different possible values of \( I_{\text{tot}} \), which will show oscillations between the degenerate states with different frequencies. If in the initial state nuclear spins are in equilibrium, the probability of finding the electronic spin in the initial state \( m \) depends on time according to

\[
p_m(t) = 1 - \frac{e^{-Amm_I/T}}{Z_I} \sum_{I_{\text{tot}}} N(I_{\text{tot}})[1 - \cos(\Delta \varepsilon t)],
\]

where \( Z_I = \sinh\{(1 + 1/(2I))\xi / \sinh(\xi / 2I)\} \) with \( \xi = AmI/T \) is the partition function of an individual nuclear spin, \( I_{\text{tot}} \) satisfies Eq. (11), \( \Delta \varepsilon = \Delta \varepsilon_{m,m';m,m'}(I_{\text{tot}}) \) is given by Eq. (8), and \( N(I_{\text{tot}}) \) is the number of ways to combine \( I_{\text{tot}} \). For temperatures larger than the characteristic nuclear temperature, \( \xi \ll 1 \), the statistical factor...
in front of the sum simplifies to \((2I + 1)^{-N}\). Under typical conditions, only a small part of the molecules have a given value of \(m_I\) and thus take part in the resonant tunneling, thus the dynamical term in Eq. (11) is much smaller than one. This is a mechanism of tunneling reduction due to nuclear spins pointed out in Refs. 2 and 3. The rest of molecules which do not have the required value of \(m_I\) for a given resonance are “frozen in”, and they should wait for a longer time \(T_1\) required for the nuclear spins to relax. The study of the latter is beyond the scope of this paper.

The number of realizations \(N(I_{\text{tot}})\) in Eq. (11) can be computed recurrently. If the total spin of a system of \(N\) nuclei is \(I_{\text{tot}}\), the total spin of its subsystem of \(N - 1\) nuclei \(I_{\text{tot}}'\) assume the values \(|I_{\text{tot}} - I| \leq I_{\text{tot}}' \leq \min\{I_{\text{tot}} + I, (N - 1)I\}\). Thus for the number of realizations \(N(I_{\text{tot}}, N)\) one can write:

\[
N(I_{\text{tot}}, N) = \sum_{I_{\text{tot}}'} N(I_{\text{tot}}', N - 1). \tag{12}
\]

The initial condition for this recurrence relation is \(N(I_{\text{tot}}', 2) = 1\) for \(0 \leq I_{\text{tot}}' \leq 2I\). The quantity \(N(I_{\text{tot}})\) obeys the normalization condition

\[
\sum_{I_{\text{tot}}=\text{fun}(N)}^{NI} (2I + 1)N(I_{\text{tot}}) = (2I + 1)^N. \tag{13}
\]

For \(NI \gg 1\), the quantity \((2I + 1)N(I_{\text{tot}})/(2I + 1)^N\) is the high-temperature distribution function of the magnitude of \(I_{\text{tot}}\) and it is well approximated by \(4\pi I_{\text{tot}}^2 F(I_{\text{tot}})\), where \(F(I_{\text{tot}})\) is a normalized Gaussian function with respect to the three components of \(I_{\text{tot}}\). Thus one has the asymptotic form for \(NI \gg 1\)

\[
P(I_{\text{tot}}) = \frac{N(I_{\text{tot}})}{(2I + 1)^N} \approx \frac{2\pi I_{\text{tot}}^2}{2\pi \sigma_I} \exp\left(-\frac{I_{\text{tot}}^2}{2\sigma_I^2}\right). \tag{14}
\]

where \(\sigma_I = (N/3)I(I + 1)\). It has a maximum at \(I_{\text{tot}} = \sqrt{\sigma}\) which is about 6 for \(MN_2\) \((I = 5/2, N = 12)\). Fig. 2 shows an agreement between the exactly computed \(P(I_{\text{tot}})\) and its Gaussian approximation for \(I = 5/2\) and \(N = 12\). This agreement improves for higher values of \(NI\).

Due to the summation over \(I_{\text{tot}}\) in Eq. (13) and the dependence of the splitting \(\Delta \varepsilon\) on \(I_{\text{tot}}\), the coherence of tunneling is destroyed. On the other hand, tunneling oscillations are damped due to the finite linewidth of the electronic levels \(\gamma_m\). In the overdamped case \(\gamma_m \gg \Delta \varepsilon\), the relaxation of the initially prepared state \(m\) to the matching state \(m'\) \(\xi \equiv AmI/T \ll 1\) is described by a sum of exponentials (cf. Ref. 9)

\[
p_m(t) = 1 - \sum_{I_{\text{tot}}} P(I_{\text{tot}}) \frac{1}{2}[1 - \exp(-\Gamma_{m,m',k_I,I_{\text{tot}}} t)], \tag{15}
\]

where \(I_{\text{tot}}\) satisfies Eq. (14).
ation due to nuclear spins can become observable at
In the case of Mn
work function to Eq. (9) to obtain
exponentials with a faster rate and smaller amplitude
(larger \( I_{\text{tot}} \)) and slower rate and larger amplitude
(slower \( I_{\text{tot}} \)). To illustrate this fact we have plotted in Fig. 3 the
relaxation function
\[
R(\tilde{t}) = \frac{\sum_{I_{\text{tot}}} P(I_{\text{tot}}) \exp[-f^2_{\text{nucl}}(I_{\text{tot}}, k)]}{\sum_{I_{\text{tot}}} P(I_{\text{tot}})},
\]
where \( f_{\text{nucl}} \) is given by Eq. (3) and \( \tilde{t} \) is the scaled time
including all factors which do not depend on \( I_{\text{tot}} \) and \( k \).
One can see that for the chosen values of the parameters,
the relaxation function \( R(\tilde{t}) \) is stretched for about 14
decades, whereas a single exponential practically decays
within two decades in time. To analytically clarify the
large-time behavior of \( R(\tilde{t}) \) one can apply the Stirling
formula to Eq. (3) to obtain
\[
f^2_{\text{nucl}} \cong (e I_{\text{tot}})^{2(m'-m)} \left[ 1 - \left( \frac{m'+k}{I_{\text{tot}}} \right)^2 \right]^{m'+k} \left[ 1 - \left( \frac{m+k}{I_{\text{tot}}} \right)^2 \right]^{m+k}.
\]
(19)
Here the second factor is only weakly dependent on \( I_{\text{tot}} \).
For large \( m' - m \), the dominant dependence on \( I_{\text{tot}} \) is
given by the first factor. Substituting Eq. (3) into Eq. (3),
replacing the sum by an integral and introducing
\( I_{\text{tot}} = I_{\text{tot}} \tilde{t}^{2(m'-m)} \) as a new integration variable, one
obtains from Eqs. (3) and (18) the large-time behavior
\[
R(\tilde{t}) \propto \tilde{t}^{-\frac{1}{(m'-m)}}.
\]
Since \( m' - m \) can be large, e.g., about ten, the exponent
can be rather small. Therefore Eq. (20) can be approximated by :
\[
R(\tilde{t}) \propto \left( \frac{1}{m'-m} \right) \ln \tilde{t},
\]
(21)
which shows that the relaxation, although being a power
law, may be well approximated by a logarithmic time
dependence. We remind the reader that \( m' - m \) is always
positive.
For temperatures much lower than the nuclear tem-
perature, i.e., for \( \xi = A m I / T \gg 1 \), the coherence is
restored, since the nuclear spins fall in the lowest-energy
state \( m_1 = I_{\text{tot}} = NI \), and there is only one term in Eq. (3).
This term corresponds to \( m' = S - m \), \( m' = S - k \),
and \( m'_1 = NI - 2S + k \), i.e., \( k_1 = NI - S + k \)
(see Fig. 3). Consequently, the low-temperature reso-
nances are characterized by only one number:
\[
H_z(k) = A(NI - S) + (D + A)k.
\]
(22)
In the case of Mn_{12} the corresponding quantum relax-
ation due to nuclear spins can become observable at
\( k > 13 \), as is illustrated by Table 1 that lists tunneling
splittings for \( 10 < k < 19 \). Note that for large
values of \( k \), tunneling due to hyperfine interactions in
Mn_{12} should dominate over the effect of other small non-
diagonal terms unaccounted for in Eq. (3).
In fact, the simplest model used in this paper cannot
be quantitatively accurate for Mn_{12} since each molecule
of Mn_{12} contains eight Mn atoms with the spin value 2
and four Mn atoms with the spin 3/2. The latter couple
ferromagnetically within each group, and the two groups
couple ferrimagnetically with each other to build the
total spin \( S = 10 \) (see the details in the recent Ref. [2]).
The hyperfine Hamiltonian of a Mn_{12} molecule contains
two
hyperfine constants \( A \) and \( A' \) for each type of Mn atoms.
Thus nuclear spins are splitted into two groups which be-
have dynamically as two effective “giant” nuclear spins, if
the nuclear relaxation is neglected. The resulting three-
spin model (one electronic and two nuclear spins) is more
complicated than the simplified two-spin model consid-
ered above, although tunneling splittings between different
resonant states can be obtained by the same method,
cf. Eq. (3). The resonant values of the bias field \( H_z \) are

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
\textbf{k} & \textbf{\( \Delta z \), K} \\
\hline
10 & 2.273148E-18 \\
11 & 4.679795E-16 \\
12 & 8.019877E-14 \\
13 & 1.126574E-11 \\
14 & 1.268525E-09 \\
15 & 1.107789E-07 \\
16 & 7.129369E-06 \\
17 & 3.102200E-04 \\
18 & 7.706470E-03 \\
19 & 6.928205E-02 \\
\hline
\end{tabular}
\caption{Table I. Tunneling splittings due to the nuclear spins for
the zero-temperature resonances \( m = -S \), \( m' = S - k \) for the
Mn_{12} set of parameters.}
\end{table}
parametrized by four quantum numbers instead of two in Eq. (4) and hence there are much more hyperfine lines for each electronic resonance. We do not try to work out this more realistic model here since the calculations should be rather cumbersome and the accurate values of $A$ and $A'$ are unknown. This, however, does not affect our qualitative conclusions derived from a simplified model.

In conclusion, we have studied tunneling and relaxation of a large spin, induced by the hyperfine interactions. This model can be relevant to Mn$_{12}$ acetate in the absence of the transverse field. Our main findings are these. There must be two distinct temperature regimes, above and below the hyperfine temperature, $T_{hf} = ASI$, which for Mn$_{12}$ is about 50 mK. At $T \gtrsim T_{hf}$ the magnetic relaxation is stretched and close to logarithmic due to the contribution of a large number of nuclear states. At $T \ll T_{hf}$ only one nuclear state contributes to the magnetic relaxation at each resonant field, and the coherence of tunneling is restored.

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