Thermodynamics of spin systems in periodic magnetic fields

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During the evolution of the spin system in multiple-pulse experiments, multiple-spin resonances change the structure of quasiequilibrium states. These changes are responsible for the divergence of power-series expansions of the effective Hamiltonians.

1. The dynamics of spins which are coupled by a dipole-dipole interaction and which are acted upon by a rapidly oscillating periodic field can be studied by means of a time-independent effective Hamiltonian.[1-3] An averaging of the dipole-dipole interaction by an external field for this Hamiltonian leads to a power series in the parameter $\epsilon = t_c \omega_{\rm loc}$, where t_c is the field period, and $\omega_{\rm loc} \sim \|\hat{\mathscr{H}}_d\|$ ($\hat{\mathscr{H}}_d$ is the Hamiltonian of the dipole-dipole interaction). When the thermodynamic methods of Ref. 4 are applied to a system with average dipole-dipole interactions, the results agree well with experimental data[5-7] obtained for times $t \sim T_2$ ($T_2 \sim \omega_{\rm loc}^{-1}$). At $T_{1\rho} \gg t \gg T_2$ ($T_{1\rho}$ is the spin-lattice relaxation time in a rotating coordinate system, $T_{1\rho} \gg T_2$, however, there are substantial discrepancies between the theory based on a time-dependent effective Hamiltonian[1] and experimental data.[6] A theory for relaxation processes with $T_{1\rho} \gg t \gg T_2$ is extremely important for studying slow molecular motions in solids.[8]

In the present letter we show that the reason for the discrepancies between theory and experiment is that at $t \gg T_2$ the power-series expansion of the effective Hamiltonian, which has been used successfully at $t \sim T_2$, becomes divergent. The divergence results from multiple-spin resonant processes,[9] which are important at $T_{1\rho} \gg t \gg T_2$. We also show that the most important of these processes forms a new quasiequilibrium state of the system at $t \gg T_2$, and we describe a method for constructing effective Hamiltonians for describing the spin dynamics for $T_{1\rho} \gg t \gg T_2$.

2. To analyze the convergence of the power-series expansions of effective Hamiltonians we consider the example of a problem which can be solved exactly: a spin ($s = 1/2$) in a static magnetic field and also a circularly polarized alternating magnetic field. In this case the density matrix $\rho(t)$ obeys the equation

$$i\frac{d\rho(t)}{dt} = \left[\omega_0 \hat{S}_z + \frac{\omega_1}{2}\left(e^{-i\omega t}\hat{S}^{1} + e^{i\omega t}\hat{S}^{-1}\right), \rho(t)\right], \tag{1}$$

where $\hat{S}_\alpha$ ($\alpha = x, y, z$) are the Pauli matrices, $S^{\pm 1} = \hat{S}_x \pm i\hat{S}_y$, ω is the frequency of the alternating field, and ω_0 and ω_1 are the amplitudes of the static and alternating magnetic fields (expressed in frequency units).

In this very simple problem it is possible not only to derive a power-series expansion of the time-dependent effective Hamiltonian in the parameter $\lambda = 1/\omega$ (a Magnus expansion[10]) but also to find its sum $\bar{\hat{\mathscr{H}}}(\lambda)$ defined by

$$\bar{\hat{\mathcal{H}}}(\lambda) = \left\{1 - \frac{1}{\sqrt{1-[2\omega_0\lambda - (\omega_0^2+\omega_1^2)\lambda^2]}}\right\}\left[(\omega_0 - {}^1/_\lambda)\hat{S}_z + \omega_1\hat{S}_x\right]. \tag{2}$$

To resolve the question of the convergence of the resulting series, we analytically continue $\bar{\hat{\mathscr{H}}}(\lambda)$ into the plane of the complex variable λ. This continuation is possible in the interior of the circle $|\lambda| < 1/\sqrt{\omega_0^2+\omega_1^2}$. On the circle $|\lambda| = 1/\sqrt{\omega_0^2+\omega_1^2}$ there are two singularities (branch points) in $\bar{\hat{\mathscr{H}}}(\lambda)\,[\lambda_{1,2} = (\omega_0 \pm i\omega_1)/(\omega_0^2+\omega_1^2)]$. It thus follows[11] that the convergence radius of the Magnus expansion is $1/\sqrt{\omega_0^2+\omega_1^2}$. It has been asserted[12] erroneously that this expansion converges for all λ. Under the customary condition $\omega_1 \ll \omega_0$, the Magnus expansion converges at $\omega > \omega_0$, i.e., when the frequency of the alternating field exceeds the resonant frequency of the system; it diverges in the opposite case.

3. It is possible in principle to derive power-series expansions of effective Hamiltonians with a far larger convergence radius. To find such expansions, we switch to a representation of the interaction in terms of the field term $\omega_0\hat{S}_z$ in (1). In this representation the alternating field oscillates at a frequency $\Delta\omega = \omega_0 - \omega$, and the power-series expansion of the effective Hamiltonian in the parameter $\lambda' = 1/\Delta\omega$ determined by the method of Ref. 1 converges if $|\lambda'| < 1/\omega_1$. The convergence radius of the series found here is therefore substantially greater than that found in Sec. 2, because of the condition $1/\omega_1 \gg 1/\sqrt{\omega_0^2+\omega_1^2}$ $(\omega_1 \ll \omega_0)$.

4. Let us apply these arguments to the dynamics of a system of spins which are coupled by a dipole-dipole interaction and which are acted upon by a series of pulses $90^0_y - \tau - (\phi_x - 2\tau)^N$, where ϕ_x is an rf pulse which rotates the spins through an angle ϕ around the x axis, and 2τ is the spacing between pulses. After a time $t \sim T_2$, a quasiequilibrium[9,4] is established in the system with a density matrix ρ which can be written in the high-temperature approximation as follows:

$$\rho = \frac{1}{Z}(1 - \beta\hat{\mathcal{H}}), \qquad Z = \mathrm{Sp}(1)\,, \tag{3}$$

where β is the reciprocal spin temperature, and the Hamiltonian $\hat{\mathscr{H}}$ for $\phi/2\tau \sim \omega_{\rm loc}$ is given within terms $\sim \epsilon\omega_{\rm loc}$ by

$$\hat{\mathcal{H}} = \frac{\varphi}{2\tau}\hat{S}_x - \frac{1}{2}\hat{\mathcal{H}}_{dx} + \frac{\sin\varphi}{\varphi}(\hat{\mathcal{H}}_d^2 + \hat{\mathcal{H}}_d^{-2}). \tag{4}$$

Here $\hat{\mathscr{H}}_{dx}$ is the secular part of the dipole-dipole interaction (secular with respect to the x axis of the rotating coordinate system), and $\hat{\mathscr{H}}_d^{\pm 2}$ is the nonsecular part. The quasiequilibrium magnetization at $t \sim T_2$ calculated from (3) and (4) agrees with experimental data. It follows from (3) and (4) that at $T_{1\rho} \gg t \gg T_2$ the magnetization of the system is finite. The experiments of Ref. 6, in contrast, show that at $T_{1\rho} \gg t \gg T_2$ the magnetization falls slowly to zero.

To simplify the further analysis we set $\phi \approx 2\pi/n$ (n is an even number that satisfies

$|\phi - 2\pi/n| \lesssim \epsilon$; in practice, its value is in the range $4 \leqslant n \leqslant 8$). In this case a governing role in the heating of the system at $t \gg T_2$ is played by an n-spin resonant absorption of energy of the external fields, accompanied by the simultaneous flipping of n spins.[9] The amplitude of the perturbation responsible for this process is[9] $\sim \epsilon^{n/2}\omega_{\text{loc}}$, so that at $t \sim T_2$ the effect of the n-spin resonance on the dynamics of the system can be ignored. In this case expression (4) is a good approximation of the effective Hamiltonian.

This resonance cannot, however, be ignored up to the time $t \sim W^{-1} \gg T_2$ ($W \sim \epsilon^n \omega_{\text{loc}} \exp\{-(2\pi - n\phi)^2/6\epsilon^2\}$ is the probability for the process[2]). It is not possible to incorporate the resonant process by refining (4) through the calculation of higher-order terms because of the divergence of the resulting expansion.

We now use the arguments of Sec. 3. We transform to a coordinate system which is rotating at a frequency $\pi/n\tau$ around the x axis, and in this system we average the dipole-dipole interaction by a series of rf pulses by the method of Ref. 1. The average Hamiltonian $\hat{\mathcal{H}}$ then becomes

$$\hat{\mathcal{H}} = \left(\frac{\varphi}{2\tau} - \frac{\pi}{n\tau}\right)\hat{S}_x - \frac{1}{2}\hat{\mathcal{H}}'_{dx} + \hat{R}^n + \hat{R}^{-n}, \tag{5}$$

where the secular part of the dipole-dipole interaction, $\hat{\mathcal{H}}'_{dx}$, differs from $\hat{\mathcal{H}}_{dx}$ by terms $\sim \epsilon\omega_{\text{loc}}$, and $\hat{R}^{\pm n}$ represents the nonsecular terms of the dipole-dipole interaction, which cause transitions involving a flipping of n spins.

By the time $t \sim W^{-1}$, quasiequilibrium (3) is established in the spin system, and the Hamiltonian $\hat{\mathcal{H}}$ is now given by (5). The corresponding quasiequilibrium magnetization is $\sim |2\pi - n\phi|/n\phi$ of its value at $t \sim T_2$.

The slow decay of the magnetization observed[6] at $T_{1\rho} \gg t \gg T_2$ can thus be attributed to a change in quasiequilibrium (3). At $t \sim T_2$, this quasiequilibrium is determined by Hamiltonian (4), while at $t \sim W^{-1}$ it is determined by Hamiltonian (5).

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