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Thermodynamics for many-body systems evolving under a periodic time-dependent Hamiltonian: Application to pulsed magnetic resonance

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A discussion is presented on the use of statistical thermodynamics to describe the long-time behavior of a many-body Hamiltonian that also depends periodically on time. Floquet's theorem is applied to the dynamics of the system in order to exploit the time symmetry. This approach produces an effective Hamiltonian that propagates the system over one time cycle. This is taken as the fundamental *constant of the motion* for the system and forms the basis for the thermodynamic description. Under suitable conditions, the resulting formulas for the equilibrium values of observables have a strong analogy to the usual thermodynamic expressions for time independent systems. These ideas are applied to describe the equilibrium magnetization for multiply pulsed spin systems, in particular to the Ostroff-Waugh and Waugh-Huber-Haeberlen pulse sequences. For these systems a quasistationary state develops after a few times T_2. This is followed by a slow decay to an equilibrium state. The dynamics of the decay is discussed in terms of an application of the Provotorov theory of saturation to the effective Hamiltonian.

I. INTRODUCTION

When posed with the problem of understanding the equilibrium properties of a many-body system, the methods of statistical mechanics provide a powerful set of tools with which to study the system. If time-varying external forces also act on the system, then these methods no longer apply for they depend on the Hamiltonian being conservative. On the other hand, the direct solution of the dynamics of the system is hampered by the multitude of internal interactions between particles. This raises the following question: It is possible to adapt the laws of statistical thermodynamics to a physical system when the Hamiltonian depends explicitly on time? The purpose of this paper is to address this question in the particular case in which the time dependence is periodic. The discussion is focused on a class of problems of interest in pulsed magnetic resonance. However, the ideas developed here are applicable to a wider class of physical systems that consist of many interacting particles subject to periodic time-varying forces.

Pulsed magnetic resonance is a technique that has been developed in an effort to obtain high-resolution NMR spectra of solid samples.[1–4] An appropriate choice of pulse sequence enables the experimenter to selectively suppress one, or more, internal spin interactions, thereby eliminating the contribution of that interaction to the magnetic resonance spectrum. Because interactions, such as the dipolar coupling, significantly broaden spectral features, and thereby obliterate desired information, their suppression provides a significant advantage.

The theory developed to explain the time evolution of a spin system that is driven by multiple-pulse irradiation and to interpret the resultant spectra is the average Hamiltonian theory (AHT).[1,5,6] Although it has been widely successful for describing the response of the spins at short times, questions have been raised about the validity of the AHT for describing the long-time behavior of the spin system and the equilibrium magnetization. These questions arise from studies on the relaxation of the transverse magnetization in samples of CaF_2 that are subject to the generalized Ostroff-Waugh pulse sequence,[7,8]

$$90°_y\text{-}\tau\text{-}\phi_x\text{-}2\tau\text{-}\phi_x\text{-}2\tau\text{-}\phi_x\text{-}\cdots ,$$

which is a pulsed analog of spin locking. The results of experiments performed by Erofeev *et al.*[9–11] and by Rhim *et al.*,[12] and the calculations of Provotorov and coworkers,[13–15] find the relaxation time and equilibrium magnetization of the ^{19}F nuclei to vary with ϕ_x and the detuning Δ in a way that apparently contradicts the predictions of the AHT. The endeavor to reconcile the apparent failure of the AHT in the long-time regime with its success for short-time predictions brings us to the question of applying thermodynamics to periodic, time-dependent systems. The starting point that I take to address this question is Floquet's theorem,[16] and the generalized version of the AHT derived from it.[17]

A critical point in analyzing the evolution of the spin system subject to a pulse sequence is to correctly combine the AHT with the methods of spin thermodynamics.[18] To elucidate the nature of this problem, let us first examine the basis of thermodynamic description of the spins. Because of the strong dipolar coupling, the spins in a solid can be considered to be an ensemble of interacting particles, and therefore be described by a temperature. The hypothesis is made that the equilibrium density matrix can be written, in the high-temperature approximation, as

$$\rho_{eq}=1-\beta_{eq}\mathscr{H} , \tag{1.1}$$

where $\beta_{eq}=1/k_BT$ is the inverse temperature of the spins at equilibrium. Let us assume that the magnetization is initially prepared parallel to the x axis, so that $\rho_i=1-\beta_i\omega_0 I_x$. In the case that the Hamiltonian is time independent, the conservation of energy requires that

$$\frac{\beta_{eq}}{\beta_i}=\omega_0\frac{\mathrm{Tr}I_x\mathscr{H}}{\mathrm{Tr}\mathscr{H}^2}\ , \tag{1.2}$$

whence the equilibrium magnetization is determined from

$$\frac{M_{eq}}{M_i}=\frac{(\mathrm{Tr}I_x\mathscr{H})^2}{\mathrm{Tr}\mathscr{H}^2\mathrm{Tr}I_x^2}\ . \tag{1.3}$$

The foregoing idea has been applied successfully to a wide variety of magnetic resonance phenomena.[18] However, in its present form it is not appropriate for use with the multiple-pulse experiments. The reason is that the Hamiltonian in this case is nonconservative and therefore the calculation of β_{eq} by Eq. (1.2) is not valid. The way to overcome this limitation was first proposed by Redfield[19] in connection with the analysis of cw spin locking. He considered the problem in the rotating frame, in which the time-dependent Hamiltonian could be approximated by a conservative one, and the spin thermodynamics applied to the latter. Couched in terms of the average Hamiltonian theory, the original time-dependent Hamiltonian is transformed into an appropriate interaction frame. This frame is one in which the dominant portion of the Hamiltonian does not appear explicitly, so that the AHT can be applied and convergent results obtained. The result is that the evolution of the spin system is given by

$$\rho(n\tau)=e^{-i\bar{H}n\tau}\rho(0)e^{i\bar{H}n\tau}\ , \tag{1.4}$$

with the observation times limited to multiples of the cycle time, $n\tau$. The interesting point to note is that upon stroboscopic observation,[20] the spin system appears to evolve under a time-independent effective Hamiltonian $\bar{H}$.

This raises some intriguing questions. How is it that one can effectively convert a time-dependent, nonconservative system into a conservative one? Is the spin system under multiple-pulse irradiation really identical to a time-independent system described by the effective Hamiltonian? These questions are considered in some detail in Sec. II, where it is demonstrated that $\bar{H}$ is not unique. This leads to the proposition that the evolution of the spin system in the intervals between cycle times serves to distinguish the time-dependent system from a truly time-independent one evolving under $\bar{H}$. The Floquet theory is applied to the solution of the Schrödinger equation and a correction to M_{eq}, as given by Eq. (1.3), is found in Sec. II. The results are applied to the Ostroff-Waugh[7] and the Waugh-Huber-Haeberlen[5] (WHH) pulse sequences in Sec. III.

Although the thermodynamic approach is extremely useful for the calculation of the equilibrium properties of a system, it is incapable of providing any information about the rate of approach to the equilibrium state. However, this dynamical information can also be obtained from the Floquet solution for the evolution operator.

In the following I consider the stroboscopic[20] evolution of the spins according to Eq. (1.4). It is often the case that the first-order term in $\bar{H}$, the average Hamiltonian, is the sum of two commuting observables. Each of these is a quasi-invariant of the motion. In thermodynamic terms, these form independent heat baths, each with a separate temperature.[18] As an example, the Zeeman bath and the dipolar bath evolve quasi-independently in the pulsed spin-locking experiment.

In such a situation, a spin system that is initially polarized transverse to the Zeeman field arrives after a time of approximately T_2 at a quasistationary state characterized by two spin temperatures. The term *quasistationary state* is used here because the corrections to the average Hamiltonian that complete $\bar{H}$ do not commute with the quasi-invariant observables; instead, the only constant of the motion is $\bar{H}$ itself. Therefore, there will ensue, on a longer-time scale, the mixing of the two heat baths to an equilibrium state described by a single temperature.

The calculation of the relaxation rate to the final equilibrium state is accomplished by applying a version of the Provotorov saturation theory[21] to the effective Hamiltonian calculated by the AHT. The method is described in Sec. IV and applied to the Ostroff-Waugh pulse sequence.

II. THEORETICAL DESCRIPTION OF THE EQUILIBRIUM MAGNETIZATION

A. Floquet theory

In order to elucidate the derivation of the equilibrium magnetization in a pulsed-magnetic-resonance experiment, I first present a brief review of the Floquet solution for the evolution operator.[17] A collection of spins, driven by a multiple-pulse sequence, is one example of a system characterized by a Hamiltonian periodic in time. Such a system has the property that the evolution operator at time $t+n\tau$ is related to the evolution operator at time t by a linear transformation,

$$\mathscr{P}_{n\tau}:\ U(t)\rightarrow U(t+n\tau)\ . \tag{2.1}$$

The $\mathscr{P}_{n\tau}$ obey the group properties, and $\mathscr{P}_\tau$ is termed the cycle propagator.

This transformation preserves the norm of the state vectors, so that the cycle propagator must be unitary. Therefore, we write

$$U(t+\tau)=U(t)e^{-i\bar{H}\tau}\ , \tag{2.2}$$

where $\bar{H}$ is a time-independent Hermitian operator, the effective Hamiltonian. As a result of this property, the evolution operator can be written in the form[22,23]

$$U(t)=P(t)e^{-i\bar{H}t}\ , \tag{2.3}$$

where $P(t)$ is a periodic operator with the initial condition that $P(0)=U(0)=1$. In the limit that the system is observed stroboscopically, $P(n\tau)=1$, and the evolution of the spins is described by Eq. (1.4), i.e., the average Hamiltonian result is obtained.

Perturbation solutions for $P(t)$ and $\bar{H}$ are obtained by invoking the expansions

$$P(t)=\sum_n \lambda^n P_n(t) \tag{2.4}$$

and

$$\bar{H}=\sum_n \lambda^n \bar{H}^{(n)}\ , \tag{2.5}$$

substituting these into Eq. (2.3), and substituting the result into the time-dependent Schrödinger equation. Using

the factor λ to keep track of the various orders of terms in the expansion, the following recursion relation are obtained:

$$P_n(t)=-i\int_0^t\left[\mathscr{H}(t')P_{n-1}(t')-\sum_{k=1}^{n-1}P_k(t')\bar{H}^{(n-k)}-\bar{H}^{(n)}\right]dt' \tag{2.6}$$

and

$$\bar{H}^{(n)}=(1/\tau)\int_0^\tau\left[\mathscr{H}(t')P_{n-1}(t')-\sum_{k=1}^{n-1}P_k(t')\bar{H}^{(n-k)}\right]dt' . \tag{2.7}$$

Because $P_0(t)=1$, the lowest-order term in the series for $\bar{H}$, i.e., $n=1$, is the average of $\mathscr{H}(t)$ over one period; thus, $\bar{H}^{(1)}$ is termed the *average* Hamiltonian.[24] The higher-order terms in Eq. (2.7) are equal to those obtained via the usual derivation[1,6] of the AHT by use of the Magnus expansion.[25,26]

These series can be shown to converge in the mathematical sense. However, an important practical question is at which term can they be *truncated*? There is no definitive answer. An example, given in Ref. 17, would indicate that $|\lambda_i-\lambda_j|<2\pi/\tau$, for all eigenvalues λ_i and λ_j of $\bar{H}$, is a sufficient condition in order to truncate the series for $\bar{H}$ after the first few terms. This is not strictly possible in the case of the dipole Hamiltonian, but it is certainly desirable to make τ sufficiently small to ensure that this inequality is met everywhere except at the wings of the dipole line shape.

B. Nonuniqueness of $\bar{H}$

One important property of a conservative system is the following: A state of the system is an eigenstate of the Hamiltonian if and only if it does not change as a function of time, except to be multiplied by a complex scalar of magnitude unity. The same statement is not true for the stroboscopic evolution of a system under the effective Hamiltonian. To understand the reason for this, consider the evolution of a linear combination of two eigenstates of $\bar{H}$,

$$a_1|\phi_1(n\tau)\rangle+a_2|\phi_2(n\tau)\rangle=e^{-i\omega_1 n\tau}[a_1|\phi_1(0)\rangle+a_2e^{-i(\omega_2-\omega_1)n\tau}|\phi_2(0)\rangle], \tag{2.8}$$

where ω_1 and ω_2 are the energies of the eigenstates $|\phi_1\rangle$ and $|\phi_2\rangle$, respectively. If $\omega_2-\omega_1=k2\pi/\tau$ for some integer k, the linear combination appears to evolve with the same property that ordinarily is reserved for eigenstates; yet the linear combination is not an eigenstate of $\bar{H}$. The consequence of this is that the eigenvalues of $\bar{H}$ are only determined modulo $2\pi/\tau$, that is, if an operator N commutes with $\bar{H}$ and has eigenvalues that are integer multiples of $2\pi/\tau$, then $\bar{H}+N$ is equivalent to $\bar{H}$, because both satisfy Eq. (2.2).

There are two implications to be drawn from the degeneracy modulo $2\pi/\tau$ of the eigenvalues of $\bar{H}$. The first is that in the perturbation series $\bar{H}=\bar{H}^{(1)}+\bar{H}^{(2)}+\cdots$, we can consider the terms of second and higher order to mix, not only those eigenstates of $\bar{H}^{(1)}$ that have the same energy, but also those that differ by $k2\pi/\tau$, for integer k. The latter non-energy-conserving transitions result from the fact that the system is really time dependent. The influence of these transitions in the decay of the equilibrium magnetization is further discussed below. Note that the range of eigenvalues of $\bar{H}$ and the existence of eigenvalues that differ by $k2\pi/\tau$ are intimately related to the convergence of the series expansion for $\bar{H}$.

The second implication is that the evolution of the spin system between stroboscopic observation points should be accounted for in calculating quantities such as $M_{\rm eq}$. While $\bar{H}$ may not be unique, it does dictate the operator $P(t)$ required to complete the propagator of Eq. (2.3). The choice of a particular combination rests with the question of the rapid convergence of the series expansions.

C. Equilibrium properties from time averages

The purpose of this section is to derive the expression for the equilibrium magnetization of a system of spins subject to periodic, time-dependent external forces. The explicit time dependence of the Hamiltonian precludes the direct application of the ensemble average to calculate equilibrium properties. One approach to surmount this problem is to approximate the time-dependent system by a system that evolves under the time-independent effective Hamiltonian. The disadvantage of this procedure is that one is then confronted by the question of the uniqueness of $\bar{H}$, as described above. In order to arrive at an equilibrium value that is independent of the choice for $\bar{H}$, the alternative tack is taken to calculate the equilibrium magnetization from the time average of $M(t)$. This is based on the following idea.

A macroscopic collection of spins in a solid sample obeys the mixing property;[27] that is, if a nonequilibrium population of spin states is introduced locally, so that only a small portion of the sample is affected, spin diffusion assures that, after a time, the nonequilibrium state will spread uniformly throughout the sample. A dynamical system that obeys the mixing property is ergodic.[27] In the case of a conservative Hamiltonian governing the spin system, this guarantees the equality between the time average of the magnetization (taken along the x axis),

$$M_{\rm eq}^x=\lim_{T\to\infty}(1/T)\int_0^T{\rm Tr}I_x\rho(t)dt , \tag{2.9}$$

and the ensemble average given by Eq. (1.3).

Let us explore the extension of the time-average approach for calculating equilibrium properties to a periodic, time-dependent Hamiltonian. For the sake of clarity, I concentrate on the x magnetization, although a different observable could easily be substituted. The initial density matrix is assumed to have the form

$$\rho(0)=1-\beta_i Q \tag{2.10}$$

in the high-temperature approximation. Here, Q is a

traceless Hermitian operator and β_i is the initial inverse temperature of the spins. Calculation of the x magnetization using the Floquet form for the evolution operator leads to an equilibrium value of

$$M_{\rm eq}^x = \lim_{T\to\infty} (1/T)\int_0^T \mathrm{Tr}[I_x P(t) e^{-i\bar{H}t}\rho(0)e^{-i\bar{H}t}P^\dagger(t)]dt \ . \tag{2.11}$$

By interchanging the order of $P^\dagger(t)$ and the remainder of the expression in the trace, we can consider the magnetization to arise from the product of two terms: the quantity $\xi(t)\equiv e^{-i\bar{H}t}\rho(0)e^{i\bar{H}t}$, in which the spin system appears to evolve under a conservative Hamiltonian $\bar{H}$, and the time-dependent observable $P^\dagger(t)I_xP(t)$.

The limit, as $T\to\infty$, of the integral in Eq. (2.11), is nonzero only if the integrand has a constant component. This, in turn, depends on the Fourier spectra of the operators $P^\dagger(t)I_xP(t)$ and $\xi(t)$. Because $P(t)$ has a periodicity of τ, we can write

$$P^\dagger(t)I_xP(t)=\sum_k B_k e^{ik2\pi t/\tau} \ , \tag{2.12}$$

whereby the spectrum is discrete. In order that a particular frequency component, B_k, contribute to the time average, the operator $\xi(k)$ must include a component that oscillates with frequency $-k2\pi/\tau$. The application of the spectral theorem to $\bar{H}$ provides the expansion

$$\xi(t)=\int\int d\lambda\, d\lambda' e^{-i(\lambda-\lambda')t}|\lambda\rangle\langle\lambda|\rho(0)|\lambda'\rangle\langle\lambda'| \ , \tag{2.13}$$

from which it is apparent that the range of frequencies is dictated by the differences between the eigenvalues of $\bar{H}$, and the line shape is determined by the matrix elements of $\rho(0)$ (equivalently, Q) in the basis of the eigenstates of $\bar{H}$. Combining the term in Eq. (2.12) proportional to $e^{ik2\pi t/\tau}$ with the counter-rotating component in Eq. (2.13) yields the equilibrium magnetization,

$$M_{\rm eq}^x=\sum_k{}' \int d\lambda\langle\lambda-k2\pi/\tau|B_k|\lambda\rangle\langle\lambda|\rho(0)|\lambda-k2\pi/\tau\rangle. \tag{2.14}$$

The prime indicates that the sum over k includes only those terms for which $\lambda-k2\pi/\tau$ is an eigenvalue of $\bar{H}$. Those terms with $k\neq 0$ represent the contribution from transitions between states with different energies.

The use of this formula requires knowledge of the eigenstates of $\bar{H}$. This is readily obtained for systems in which a small groups of spins interact strongly among themselves but weakly with the rest of the sample. In that case the matrix operators that describe the interactions within the group are of a manageable size and can be diagonalized. However, in more general circumstances, where strong interactions between many spins are involved, the above expression is not very convenient.

Expression (2.14) for the equilibrium magnetization can be transformed into a more appealing form under the assumption that only the $k=0$ term contributes significantly to the sum, i.e., only the constant components of $P^\dagger(t)I_xP(t)$ and $\xi(t)$ are important. This assumption is valid under the following circumstance: $|\lambda_i-\lambda_j|<2\pi/\tau$ for all eigenvalue pairs of $\bar{H}$. If this is the case, then the spectrum of $\xi(t)$ lies entirely between the frequencies $-\pi/\tau$ and π/τ, whereby $\lambda-k2\pi/\tau$ is an eigenvalue of $\bar{H}$ only for $k=0$. Equation (2.14) reduces, under these conditions, to

$$M_{\rm eq}^x=\int d\lambda\langle\lambda|[P^\dagger I_xP]_{\rm av}|\lambda\rangle\langle\lambda|\rho(0)|\lambda\rangle \ , \tag{2.15}$$

where B_0 has been replaced by the average over one cycle of $P(t)^\dagger I_xP$. Each of the operators $[P^\dagger I_xP]_{\rm av}$ and $\rho(0)$ can be written as the sum of the two terms: one operator that commutes with $\bar{H}$ and is diagonal in the $|\lambda\rangle$ basis, and a second that is completely off diagonal. Clearly, the diagonal part of $\rho(0)$ is the equilibrium density matrix.

Consider for a moment a conservative system, i.e., one with $P(t)=1$. If the energy is the only constant of the motion, two important properties hold true: First, any operator that commutes with the Hamiltonian must be expressible as a function of it, and second, the system is ergodic.[27] In the case of a time-dependent, periodic Hamiltonian, $\bar{H}$ plays the role of the constant of the motion, although it does so only at intervals of τ. Nevertheless, we use the first property to write the diagonal portion of the initial density matrix as

$$\mathrm{diag}[\rho(0)]=\rho_{\rm eq}=f(\bar{H})=\sum_\lambda f(\lambda)|\lambda\rangle\langle\lambda| \ . \tag{2.16}$$

If there were a second constant of the motion, $\rho_{\rm eq}$ should be expanded in a basis of simultaneous eigenfunctions of the two constants of the motion, and therefore would be a function of both operators.

The second property enables us to use the laws of statistical mechanics to determine the function $f(\lambda)$. This is accomplished by maximizing the entropy of the system,

$$S=-k_B\mathrm{Tr}[\rho_{\rm eq}\ln(\rho_{\rm eq})] \ ,$$

subject to the constraints that the density matrix is normalized, i.e., $\int d\lambda f(\lambda)=1$, and subject to the energy constraint $\langle E_i\rangle=\mathrm{Tr}\bar{H}\rho_{\rm eq}$. The result is

$$f(\lambda)=\frac{1}{Z}e^{-\beta_{\rm eq}\lambda}\cong 1-\beta_i\frac{\mathrm{Tr}\bar{H}Q}{\mathrm{Tr}\bar{H}^2}\lambda \ , \tag{2.17}$$

where Z is the partition function, the high-temperature approximation is invoked to expand the exponential, and the equilibrium temperature is written in terms of the initial temperature from energy conservation. Equation (2.17) is substituted into Eq. (2.16) to find $\rho_{\rm eq}$, which, in turn, is used to replace the diagonal part of $\rho(0)$ in Eq. (2.15) to give

$$M_{\rm eq}^x=\int d\lambda\langle\lambda|[P^\dagger I_xP]_{\rm av}|\lambda\rangle\left[1-\beta_i\frac{\mathrm{Tr}\bar{H}Q}{\mathrm{Tr}\bar{H}^2}\lambda\right] .$$

This is easily rearranged into the desired form,

$$M_{\rm eq}^x=-\beta_i\frac{(\mathrm{Tr}\bar{H}Q)(\mathrm{Tr}[P^\dagger I_xP]_{\rm av}\bar{H})}{\mathrm{Tr}\bar{H}^2} \ , \tag{2.18}$$

and in many of the applications made below, it is normalized by dividing by $M_i=-\beta_i\mathrm{Tr}I_xQ$, when the latter is not equal to zero.

It is pertinent, at this point, to indicate some interesting

features concerning the above derivation. The result is quite similar to the ensemble average of Eq. (1.3); simply the operator I_x is replaced by $[P^\dagger I_x P]_{\rm av}$, the average taken over one cycle, in the numerator. This similarity underlines the importance of the effective Hamiltonian, which is responsible for the evolution of the system by one cycle time, in determining the equilibrium properties of the spin system. On the other hand, the appearance of the operator $P(t)$ signifies that the behavior of the spins during the entire cycle must be accounted for in order to correctly predict $M^x_{\rm eq}$.

The solution for $M^x_{\rm eq}$ given by Eq. (2.18) is valid only under the condition that the spectrum of $\bar{H}$ lies in the frequency interval $(-\pi/\tau, \pi/\tau)$. Recall (Sec. II A) that the same condition applies to the truncation of the series expansion for $\bar{H}$. Therefore, in the case in which we wish to use the perturbation solutions for the Floquet form of the propagator, the condition that allows the series to be truncated also allows us to use the result of Eq. (2.18) to calculate the equilibrium magnetization. Of course, for the dipolar interaction the wings of the line shape extend beyond $\pm\pi/\tau$, so that (2.18) is approximate.

Upon substitution of the series expansions for $\bar{H}$ and $P(t)$ into Eq. (2.18), the expression

$$M^x_{\rm eq}=-\beta_i\frac{{\rm Tr}Q(\bar{H}^{(1)}+\cdots)\{{\rm Tr}I_x(\bar{H}^{(1)}+\cdots)+{\rm Tr}[I_x,\bar{P}_1](\bar{H}^{(1)}+\cdots)+\cdots\}}{{\rm Tr}(\bar{H}^{(1)}+\cdots)^2} \tag{2.19}$$

is obtained. The first term in the curly brackets is the result obtained by Redfield,[19] who applied spin thermodynamics to the truncated Hamiltonian in the rotating frame. The second term represents a correction that arises from considering the entire dynamical history of the spins and not merely the stroboscopic observation points. In other words, the oscillating behavior of the magnetization vector about its average trajectory contributes to the equilibrium value.

III. APPLICATION TO PULSED NMR

The preceding ideas are applied, in this section, to evaluating the equilibrium magnetization for the spin-locking experiment and the WHH pulse sequence. The choice of interaction frame used in the analysis depends on the size of the pulse flip angle; hence the discussion is divided accordingly.

A. Pulsed spin locking for small θ

The Hamiltonian for the pulsed spin-locking experiment, in the rotating frame, is

$$\mathcal{H}(t)=-\omega(t)I_x+\Delta I_z+H^d_{20}\ , \tag{3.1}$$

where Δ is the detuning from the Larmor frequency, H^d_{20} is the secular part of the dipole interaction (the $m=0$ spherical tensor component), and

$$\omega(t)=\theta\sum_{k=1}^{\infty}\delta(t-(2k-1)\tau) \tag{3.2}$$

represents the pulse sequence. The pulses are polarized in the x direction with a flip angle of θ and a period of 2τ.

For the choice of $\theta<1$ the rotating frame is appropriate for applying the perturbation solution for $\bar{H}$ and $P(t)$. The conclusion of a straightforward calculation, using the recursion relation (2.7), is that

$$\begin{aligned}
&\bar{H}^{(1)}=\Delta I_z-(\theta/2\tau)I_x+H^d_{20}\ ,\\
&\bar{H}^{(2)}=0\ ,\\
&\bar{H}^{(3)}=-(\theta\tau/12)([[I_x,H^d_{20}],H^d_{20}]-2i\Delta[I_y,H^d_{20}]+\Delta^2 I_x)\\
&\qquad\qquad -(\theta^2/12)([[H^d_{20},I_x],I_x]+\Delta I_z)
\end{aligned} \tag{3.3}$$

are the three lowest-order terms for $\bar{H}$. These terms progress as powers of θ and $(H^d_{20}+\Delta)\tau$, so that both should be less than 1 in order to truncate the series and retain an accurate result.

The expansion for $P(t)$ has terms

$$\begin{aligned}
&P_1(t)=-i\int_0^t[\theta/2\tau-\omega(t')]dt' I_x\equiv-i\chi(t)I_x\\
&\text{and}\\
&P_2(t)=\int_0^t\chi(t')[\omega(t')-\theta/2\tau]dt' I_x^2\\
&\qquad\qquad+\int_0^t\chi(t')dt'[I_x,H^d_{20}+\Delta I_z]\ ,
\end{aligned} \tag{3.4}$$

in addition to the leading term $P_0(t)=1$. The expansion is carried out to second order because the first-order correction in Eq. (2.19) is ${\rm Tr}[I_x,P_1]\bar{H}=0$. The second-order contribution to the terms in curly brackets of Eq. (2.19) (not shown explicitly) is

$${\rm Tr}(\bar{P}_2^\dagger I_x+I_x\bar{P}_2+[P_1^\dagger I_x P_1]_{\rm av})\bar{H}^{(1)}=(\theta\tau/12)(\Delta^2+3\bar{H}_L^2)\ , \tag{3.5}$$

where the local field is defined by

$$H_L=[{\rm Tr}(H^d_{20})^2/{\rm Tr}I_x^2]^{1/2}\ . \tag{3.6}$$

This correction term is combined with the leading term, the equilibrium magnetization obtained for a system evolving under the time-independent Hamiltonian $\bar{H}$, to give

$$\frac{M^x_{\rm eq}}{M^x_i}=\frac{\left[\frac{\theta}{2\tau}\right]^2\left[1+\frac{\tau^2}{2}H_L^2+\frac{\tau^2}{6}\Delta^2\right]^2-\frac{\theta^2}{24}\left[1+\frac{\tau^2}{2}H_L^2+\frac{\tau^2}{6}\Delta^2\right](\Delta^2+3H_L^2)}{\left[\frac{\theta}{2\tau}\right]^2+\left[1-\frac{\theta^2}{4}\right]H_L^2+\left[1-\frac{\theta^2}{12}\right]\Delta^2}\ . \tag{3.7}$$

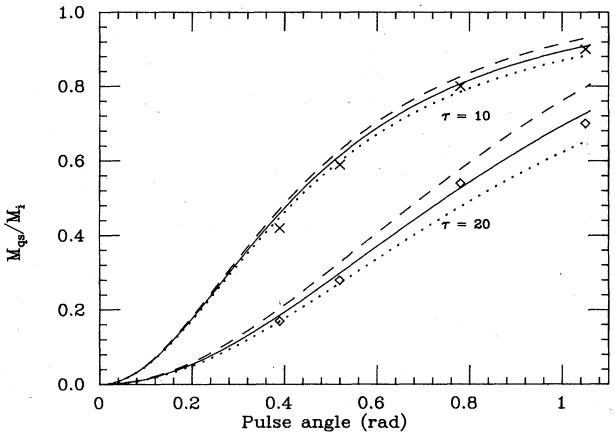

FIG. 1. Quasistationary magnetization vs pulse angle θ for various τ (in μsec). The solid curve is from Eq. (3.7). The dashed curve shows this result minus the contribution due to $P(t)$. The dotted curve is obtained using Eq. (37) of Ref. 14 and the data points are from Ref. 9. The value of $H_L = 22\,000$ rad/sec is the same as used in Ref. 9.

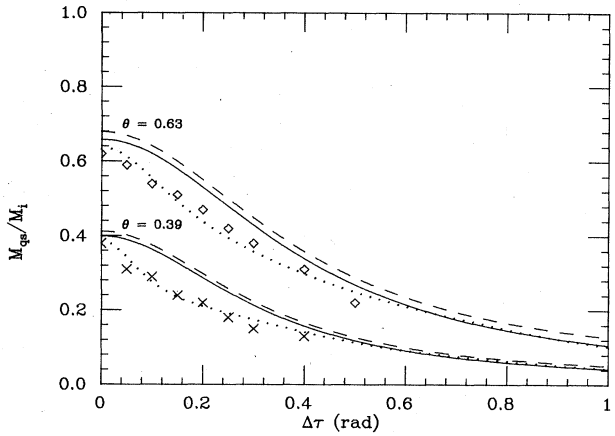

FIG. 2. Quasistationary magnetization vs detuning Δ for various values of θ (in rad). The solid line is from Eq. (3.7). The dashed curve is the same result minus the contribution due to $P(t)$. The dotted curve is obtained from Eq. (10) of Ref. 10, as are the data. $\tau = 10$ μsec and $H_L = 25\,000$ rad/sec, as in Ref. 10.

The values predicted for M_{eq}^x/M_i^x as a function of θ, with $\Delta = 0$, are compared to the data of Erofeev *et al.*,[9] and the calculation of Ivanov *et al.*[14] in Fig. 1. The dashed curve indicates the results obtained in the present framework when only the stroboscopic evolution under $\bar{H}$ is considered, while the solid curve includes the correction term of Eq. (3.5). Figure 2 shows the analogous comparison for M_{eq}^x/M_i^x versus the detuning from line center.

B. cw spin locking

It is instructive to compare the above results to the better known example of cw spin locking. In this case, spins that are initially polarized along the x axis of the rotating frame are irradiated by a continuous, near-resonant, rf field. The Hamiltonian in the rotating frame is

$$\mathcal{H} = \Delta I_z - \omega_1 I_x - (\omega_1/\sqrt{2})(e^{i2\omega t} I_{-1} - e^{-i2\omega t} I_1) + \sum_m (-1)^m R^d_{2,-m} e^{-im\omega t} T_{2m} \quad (3.8)$$

prior to truncation. The last term is the full dipole Hamiltonian, with the spherical tensor components T_{2m} containing the spin terms, and the R_{2m} components containing the information about the internuclear vector. The latter are typically written[1]

$$R^d_{2m} = \frac{-\sqrt{6}\gamma^2\hbar}{r^3}(4\pi/5)^{1/2} Y_{2m}(\theta,\phi) \quad (3.9)$$

in terms of the gyromagnetic ratio, the internuclear distance, and the spherical harmonics.

The first-order term in the effective Hamiltonian series is

$$\bar{H}^{(1)} = \Delta I_z - \omega_1 I_x + R^d_{20} T_{20} , \quad (3.10)$$

the usual truncated Hamiltonian. In order to complete the analogy to the pulsed spin-locking experiment, and to apply Eq. (2.19) for M_{eq}^x, let us also consider

$$\bar{P}_1 = -\sum_{m\neq 0} \frac{(-1)^m}{m\omega} R^d_{2,-m} T_{2m} + \frac{i\omega_1}{2\omega} I_y . \quad (3.11)$$

Including both quantities in the calculation for M_{eq}^x yields

$$\frac{M_{eq}^x}{M_i^x} = \frac{\omega_1^2 + \Delta\omega_1^2/2\omega - (\sqrt{3}\omega_1/\omega) R^d_{20}(R^d_{21} - R^d_{2,-1})[\mathrm{Tr}(T_{20})]^2/\mathrm{Tr} I_x^2}{\Delta^2 + \omega_1^2 + H_L^2} . \quad (3.12)$$

The latter two terms in the numerator arise from $\bar{P}_1$ in Eq. (2.19). Both of these provide a negligible contribution to the magnetization under normal conditions because ω, the Larmor frequency, is orders of magnitude larger than the resonance offset or the local fields (contained in the R_{2m}). Thus they can be omitted and the well-known formula for the equilibrium magnetization under spin locking is obtained.[18]

The results for the pulsed ($\theta < 1$) and cw spin-locking calculations are very similar if we make the identification $\omega_1 \leftrightarrow \theta/2\tau$. The major difference is the greater dependence of M_{eq}^x/M_i^x, in Eq. (3.7), on the higher-order corrections to $\bar{H}$ and $P(t)$. In the case of pulsed spin locking this is manifested by the terms $\tau^2 H_L^2$, $\tau^2\Delta^2$, θ^2, etc., the analogs of which are omitted in Eq. (3.12). The omission is justified in one case and not the other because $H_L\tau \gg H_L/\omega$, where these are the approximate ratios of successive terms in the perturbation series for the pulsed and cw cases, respectively.

C. Pulsed spin locking for large θ

If either of the conditions $\theta \geq 1$ or $\Delta\tau \geq 1$ hold, then the rapid convergence of the perturbation series for $\bar{H}$ and

$P(t)$ in the rotating frame cannot be guaranteed. A better reference frame is one in which the terms $\Delta I_z - \omega(t) I_x$ do not explicitly appear in the Hamiltonian of Eq. (3.1). Such a frame is suggested by considering the combined effect of the resonance offset and the pulse sequence on the spin system over one cycle.

Ignoring for the moment the dipole interaction, the state of the system at time $t = 2\tau$ is dictated by the operator

$$U_0(2\tau) = e^{-i\Delta I_z \tau} e^{i\theta I_x} e^{-i\Delta I_z \tau} , \tag{3.13}$$

which represents a rotation of the state vector by $\Delta\tau$ about the z axis, $-\theta$ about the x axis, and another $\Delta\tau$ about the z axis of rotating frame. These can be combined into a single rotation by an effective angle $\omega_e 2\tau$ about an effective axis $\hat{n}$:

$$U_0(2\tau) = e^{-i\omega_e \hat{n}\cdot\vec{I}} . \tag{3.14}$$

Here, $\vec{I} = (I_x, I_y, I_z)$ is the vector of spin angular momentum operators. Equating the two forms for $U_0(2\tau)$ yields the following relations:

$$\cos(\omega_e \tau) = \cos(\Delta\tau)\cos(\theta/2) \tag{3.15}$$

and

$$n_1 = \frac{-\sin(\theta/2)}{\sin(\omega_e \tau)}, \quad n_2 = 0, \quad n_3 = \frac{\cos(\theta/2)\sin(\Delta\tau)}{\sin(\omega_e \tau)} \tag{3.16}$$

for the effective frequency and the orientation of the effective axis. This is essentially the same result as that obtained by Ivanov *et al.*[14]

In the present application the objective is to transform the Hamiltonian for the spin-locking pulse sequence into an interaction frame that accounts for the combined action of the resonance offset and the rf pulses as indicated by Eq. (3.13). This transformation produces an interaction-frame Hamiltonian that, in general, is not periodic. There are, however, special cases for which periodicity is retained, namely when

$$\omega_e = n\pi/m\tau . \tag{3.17}$$

This condition states that n complete *rotations* are made in m cycles of 2τ each. The cycle time in the interaction frame is therefore $\tau_I = m\,2\tau$. Provotorov and coworkers[14,15] call Eq. (3.17) the *resonance* condition.

Substitution of condition (3.17) into Eq. (3.15) provides the relationship that must hold between the detuning and the pulse angle for the interaction-frame Hamiltonian to be periodic. This relationship is illustrated in Fig. 3. There are two special cases. When $m = 1$, θ must be a multiple of 2π, so that this case is trivial. For $m = 2$, two pulses are required for one complete rotation whereby either $\Delta\tau = \pi/2$ and θ can be any angle, or $\theta = \pi$ and $\Delta\tau$ can be any resonance offset. The general behavior shown in Fig. 3 holds for $m \geq 3$. Because the difficulty in analysis increases with an increase in m, the case $m = 3$ is studied in detail below.

It is a straightforward but lengthy process to find the

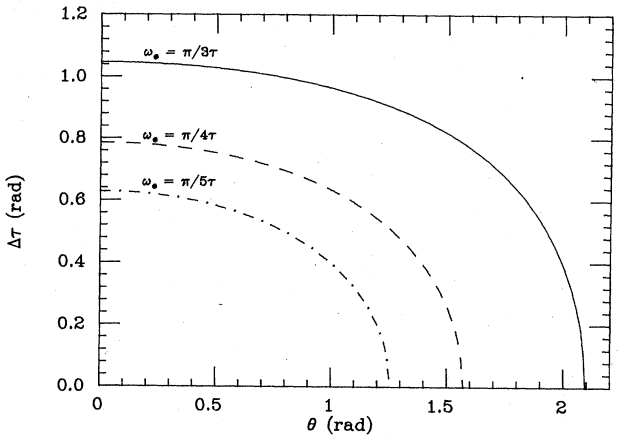

FIG. 3. *Resonance curves* in which three, four, and five periods of 2τ are required to complete one rotation around the effective axis.

time-dependent interaction-frame Hamiltonian and then to apply the recursion relations to determine the effective Hamiltonian. Therefore it will only be outlined here. The transformation to the interaction frame is performed separately for the time interval $(0,\tau)$, insertion of the pulse, the time interval $(\tau,3\tau)$, insertion of the next pulse, etc. In each region, the transformation operator $U_0(t)$ is a product of rotations by $\Delta\tau$ about the z axis and by $-\theta$ about the x axis of the rotating frame. The average Hamiltonian is obtained by piecewise integration of the interaction-representation Hamiltonian. Finally, the interaction frame is tilted by α about the y axis, with

$$\tan\alpha = -\frac{\tan(\theta/2)}{\sin(\Delta\tau)} , \tag{3.18}$$

in order to align the effective axis of rotation $\hat{n}$ with the z axis.

The result of the above calculation is an average Hamiltonian,

$$\tilde{\bar{H}}^{(1)} = \left[\frac{1+2\cos\theta}{3}\right]^{1/2} \delta I_z + (\cos\theta) H^d_{20} , \tag{3.19}$$

that is diagonal in the tilted frame. Tildes are used here to distinguish operators in the tilted interaction frame from those in the rotating frame. The factor

$$\delta = \Delta - \Delta_R \tag{3.20}$$

is the deviation of the detuning from the *resonance condition* dictated by Eq. (3.15) and by $\omega_e = \pi/6\tau$. In addition, trigonometric functions of $\Delta\tau$ that would ordinarily appear in Eq. (3.19) have been eliminated in favor of the variable θ by substitution of the *resonance condition.* It is worthwhile to note that $\tilde{\bar{H}}^{(1)}$ can be interpreted as the projection of the Hamiltonian of Eq. (3.1) onto the effective axis of rotation.

In order to apply the analysis of Sec. II C to the present problem, the first-order correction to $\tilde{P}(t)$ is needed. Averaged over a cycle time of 6τ, the result

$$\tilde{\bar{P}}_1 = (i\,2\tau/3)\delta\sin(\theta/2) I_y - (\sqrt{2}\tau/3)\sin(\theta/2)(1+2\cos\theta)^{1/2}(H^d_{21} + H^d_{2,-1}) - (\sqrt{2}\tau/3)\sin^2(\theta/2)(H^d_{22} - H^d_{2,-2}) \tag{3.21}$$

is obtained, written in terms of the pulse angle θ.

We now desire to use $\tilde{\bar{H}}^{(1)}$ and $\tilde{\bar{P}}_1$ to determine the ratio M_{eq}^x/M_i^x using the method described in Sec. II C. Note, however, that in contradiction to the assumption that $\tilde{\bar{H}}^{(1)}$ is the only *constant of the motion,* the operator I_z also commutes with $\tilde{\bar{H}}^{(1)}$. This implies that a quasistationary state,

$$\tilde{\rho}_{qs}=1-\beta_{qs}\delta I_z-\alpha_{qs}H_{20}\ , \tag{3.22}$$

characterized by two temperatures, is arrived at after a few times T_2. The initial and quasistationary Zeeman energies are equated, whereupon

$$\beta_{qs}=(\beta_i\omega_0/\delta)\sin\alpha\ , \tag{3.23a}$$

while the fact that the initial dipolar energy is zero implies that

$$\alpha_{qs}=0\ . \tag{3.23b}$$

The quasistationary density matrix is substituted for the diagonal part of $\rho(0)$ in Eq. (2.15), which, upon evaluation, reveals that

$$\frac{M_{qs}}{M_i}=\tfrac{4}{3}\sin^2(\theta/2)+\tfrac{4}{9}\tau\delta\sin^2(\theta/2)(1+2\cos\theta)^{1/2} \tag{3.24}$$

is the ratio of the quasistationary magnetization to initial magnetization. The first term arises from the effective Hamiltonian, while the second term accounts for the evolution of the system within each cycle. An asymmetry in terms of the deviation of the detuning from resonance is introduced by the latter. This disappears as θ approaches $2\pi/3$, for reasonable values of δ, ensuring that the ratio M_{qs}/M_i does not exceed unity.

The qualification, *quasi,* is made above because the quasistationary state does not persist; rather it decays slowly to a new equilibrium state. The reason is simple. $\tilde{\bar{H}}^{(1)}$ is not the effective Hamiltonian, only an approximation to it. The second- and higher-order corrections to $\tilde{\bar{H}}^{(1)}$ preclude the existence of two separate *constants of motion.* In the context at hand, although I_z commutes with $\tilde{\bar{H}}^{(1)}$, it is unlikely to do so with $\tilde{\bar{H}}^{(2)}$. The consequence is that the two heat baths, Zeeman and dipolar in the case of $\tilde{\bar{H}}^{(1)}$, will be mixed under the action of the second-order corrections, and therefore equilibrate to a new state described by a single temperature.

The equilibrium magnetization can be calculated from Eq. (2.19) by substituting the sum $\tilde{\bar{H}}^{(1)}+\tilde{\bar{H}}^{(2)}$ for $\tilde{\bar{H}}^{(1)}$ in that formula. The application of the recursion relation (2.7) provides a simple form for $\tilde{\bar{H}}^{(2)}$ in terms of $\tilde{\bar{P}}_1$ and $\tilde{\bar{H}}^{(1)}$, namely

$$\tilde{\bar{H}}^{(2)}=-\tfrac{1}{2}[\tilde{\bar{P}}_1,3\tilde{\bar{H}}^{(1)}-e^{i\alpha I_y}(\delta I_z+H_{20}^d)e^{-i\alpha I_y}]\ , \tag{3.25}$$

as cast in the tilted frame. The diagonal part of $\tilde{\rho}(0)$ is now proportional solely to $\tilde{\bar{H}}^{(1)}+\tilde{\bar{H}}^{(2)}$, and, accordingly, the remainder of the analysis of Sec. II C is apposite. The value for the equilibrium magnetization, referenced to the initial value, which emerges is written as ($\tilde{I}_x=\cos\alpha I_x+\sin\alpha I_z$) is the x component of the angular momentum operator written in the tilted frame)

$$\frac{M_{eq}^x}{M_i^x}=\frac{\mathrm{Tr}\tilde{I}_x\tilde{\bar{H}}(\mathrm{Tr}\tilde{I}_x\tilde{\bar{H}}+\mathrm{Tr}[\tilde{I}_x,\tilde{\bar{P}}_1]\tilde{\bar{H}})}{\mathrm{Tr}\tilde{\bar{H}}^2\mathrm{Tr}\tilde{I}_x^2}\ , \tag{3.26}$$

with

$$\mathrm{Tr}\tilde{I}_x(\tilde{\bar{H}}^{(1)}+\tilde{\bar{H}}^{(2)})=-\tfrac{2}{3}\sin(\theta/2)(1+2\cos\theta)^{1/2}\delta+(2\tau/3)\sin(\theta/2)\cos\theta[\delta^2+3(\cos\theta)H_L^2]\ , \tag{3.27}$$

$$\mathrm{Tr}[\tilde{I}_x,\tilde{\bar{P}}_1](\tilde{\bar{H}}^{(1)}+\tilde{\bar{H}}^{(2)})=\frac{-2\tau}{9}\sin(\theta/2)(1+2\cos\theta)[\delta^2+3(\cos\theta)H_L^2]$$
$$-\frac{4\tau^2}{9}(\sin^3(\theta/2)(1+2\cos\theta)^{1/2}[\delta^3+3(1+2\cos\theta)\delta H_L^2]\ , \tag{3.28}$$

and

$$\mathrm{Tr}(\tilde{\bar{H}}^{(1)}+\tilde{\bar{H}}^{(2)})^2=\frac{\delta^2}{3}[(1+2\cos\theta)^{1/2}+\tfrac{2}{3}\tau\delta\sin^2(\theta/2)]^2+\tfrac{4}{27}\tau^2\delta^4\sin^2(\theta/2)(1+2\cos\theta)$$
$$+[\cos\theta+\tfrac{4}{3}\tau\delta\sin^2(\theta/2)(1+2\cos\theta)^{1/2}]^2H_L^2$$
$$+\tfrac{4}{3}\tau\delta\sin^2(\theta/2)\cos\theta[(1+2\cos\theta)^{1/2}+\tfrac{2}{3}\tau\delta\sin^2(\theta/2)]H_L^2+\tfrac{4}{9}\tau^2\delta^2\sin^2(\theta/2)(7\cos^2\theta+8\cos\theta+3)H_L^2$$
$$+\tfrac{2}{27}\tau^2H_L^4\sin^2(\theta/2)(62\cos^3\theta+42\cos^2\theta+27\cos\theta+31)\ . \tag{3.29}$$

The assumption of a Gaussian form for the dipole line shape allows the substitution $M_4=27H_L^4$ to be made in the above trace. Although the formula for the equilibrium magnetization is not a simple one, it is immediately apparent that it differs considerably from the quasistationary magnetization. The difference is most noticeable for $\delta=0$, at which

$$M_{qs}^x/M_i^x=\tfrac{4}{3}\sin^2(\theta/2)\ ,$$

in contrast to $M_{eq}^x/M_i^x\cong 0$. It is a direct consequence of

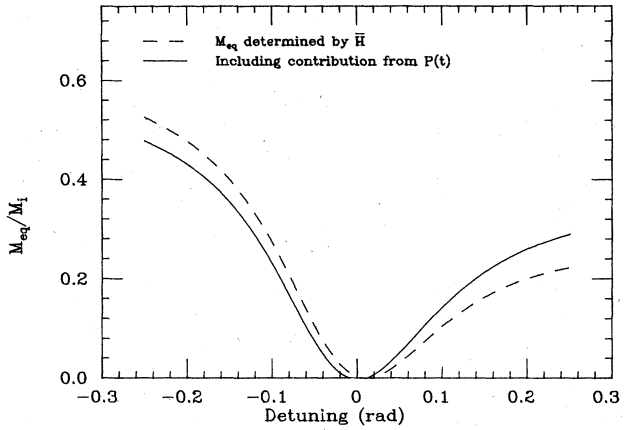

FIG. 4. Equilibrium magnetization vs detuning δ from the *resonance* condition. The difference between the predictions from the full vs stroboscopic evolution of the spin system is shown. (Parameters: $\theta=1.3$ rad, $H_L=25\,000$ rad/sec, and $\tau=10$ μsec.)

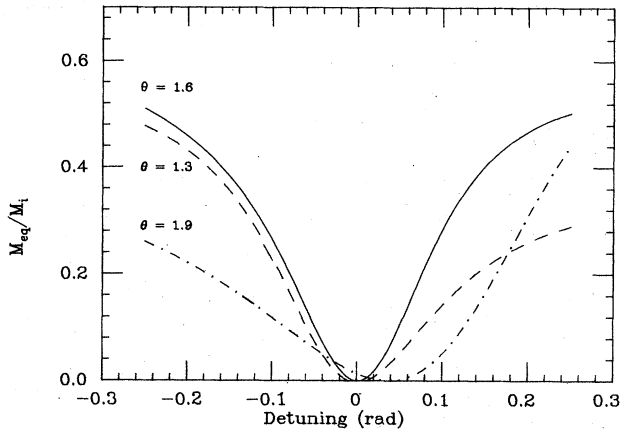

FIG. 6. Equilibrium magnetization vs the detuning δ from the *resonance* condition for various values of θ. These are determined from the Eq. (3.26). (Parameters: $H_L=25\,000$ rad/sec and $\tau=10$ μsec.)

$\tilde{\tilde{H}}^{(2)}$ mixing the Zeeman and dipolar heat baths to a common temperature. Including higher-order corrections such as $\tilde{\tilde{H}}^{(3)}$, in the calculation, will change this outcome only quantitatively and slightly, the major qualitative change being affected by $\tilde{\tilde{H}}^{(2)}$.

The results of the above calculation are perhaps best illustrated pictorially. In Fig. 4, M^x_{eq}/M^x_i is plotted as a function of δ, the deviation from *resonance,* in order to indicate the role of the second term in the parentheses of Eq. (3.26). Without this term the magnetization is that of a spin system evolving under the time-independent effective Hamiltonian: the result that the average Hamiltonian theory would predict. By incorporating this term, the entire history of the spin system is considered in determining M^x_{eq}. The same comparison is made in Fig. 5 for M^x_{eq}/M^x_i versus θ with Δ fixed. This plot is actually made by determining the value of Δ_R that corresponds to each value of θ and the inserting $\delta=\Delta-\Delta_R$ into Eq. (3.26).

Figure 6 shows how the shapes of the *resonance* curves for M^x_{eq}/M^x_i versus δ vary with the pulse angle. Note that the *resonance* is narrowest for $\theta=\pi/2$. At this value, the dipole interaction is absent from $\tilde{\tilde{H}}^{(1)}$ and enters the calculation only in second order. Similar changes in the curves for M^x_{eq}/M^x_i versus θ as Δ is varied are depicted in Fig. 7.

It is of interest to compare the results obtained herein to the experimental data of Erofeev *et al.*,[10] and to the quite different, theoretical approach of Provotorov and co-workers.[13–15] In particular, this is of some importance because of the claims made by the latter authors that the average Hamiltonian theory is incapable of predicting the equilibrium magnetization for the pulsed spin systems. Contrary to this, Figs. 8 and 9 show very good agreement

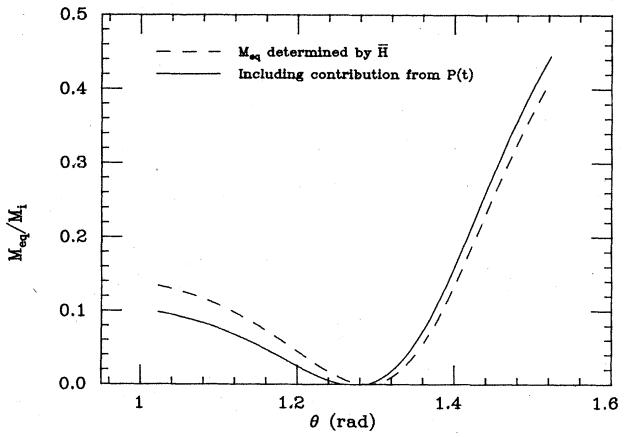

FIG. 5. Equilibrium magnetization vs θ, as the latter is varied in the vicinity of a *resonance* point. The difference between the predictions from the full vs stroboscopic evolution of the spin system is shown. (Parameters: $\Delta\tau=0.9$ rad, $H_L=25\,000$ rad/sec, and $\tau=6.6$ μsec.)

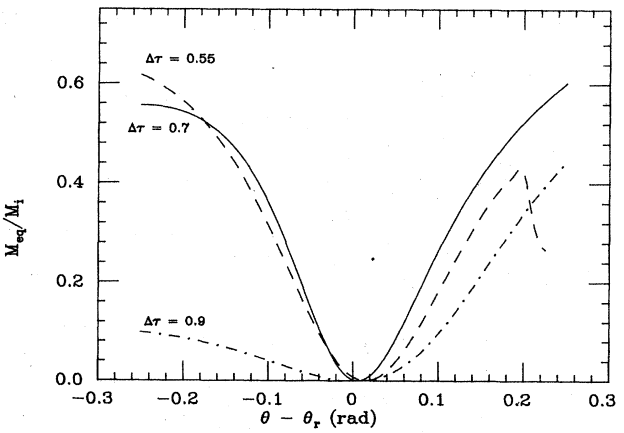

FIG. 7. Equilibrium magnetization vs the deviation of θ from *resonance* for various values of $\Delta\tau$. The curves are deduced from Eq. (3.26) by determining the δ required to bring θ into *resonance.* (Parameters: $H_L=25\,000$ rad/sec and $\tau=6.6$ μsec.)

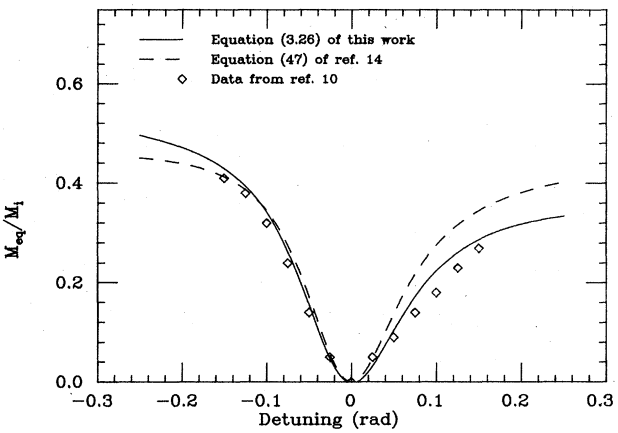

FIG. 8. Comparison of theory to experiment (Ref. 28) for the equilibrium magnetization vs the detuning δ when θ is held constant. (Parameters: $\theta=1.25$ rad, $H_L=25\,000$ rad/sec, and $\tau=6.6\,\mu$sec.)

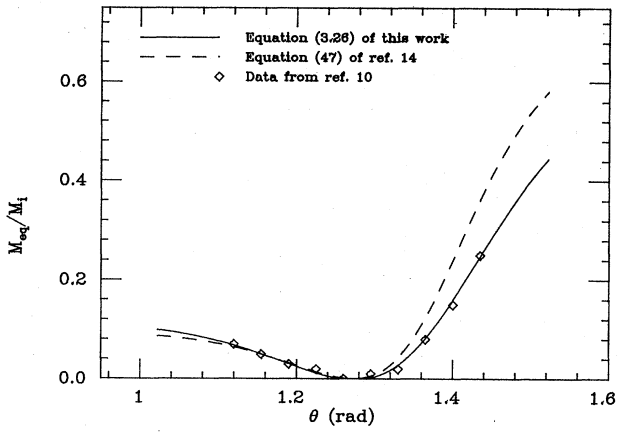

FIG. 9. Comparison of theory to experiment (Ref. 28) for the equilibrium magnetization vs θ with $\Delta\tau$ held constant. (Parameters: $\Delta\tau=0.9$ rad, $H_L=25\,000$ rad/sec, and $\tau=6.6\,\mu$sec.)

between the predictions of the present Floquet-theory approach to spin thermodynamics and the experimental data. As a consequence of the close relationship between the Floquet theory and the AHT, we may conclude that the latter is valid, not only for its short-time predictions, but also for establishing the equilibrium properties of the spin system. The theory is successful in this instance because of the choice of interaction frame. Clearly, the series solution for the effective Hamiltonian does not converge rapidly in the rotating frame [cf. Eq. (3.3)]. However, by removing the pulse and detuning operators from the Hamiltonian, the transformation to the interaction frame improves the convergence properties of the series for $\tilde{\bar{H}}$.

One final point deserves to be made. The equilibrium state predicted above is also not expected to last indefinitely, even in the absence of spin-lattice relations. It will decay, on a time scale longer than the one for M^x_{qs}, because of the coupling between levels of $\tilde{\bar{H}}$ that differ by $n\,2\pi/\tau$ in frequency. This was omitted in the transition from Eq. (2.14) to Eq. (2.15) and would not be present if the spectrum of $\tilde{\bar{H}}$ were contained entirely in the interval $(-\pi/\tau, \pi/\tau)$. The rate is expected to be quite slow, however, for $\tau H_L < 1$ and to decrease as τH_L is made similar.

D. WHH PULSE SEQUENCE

The analysis rendered for the pulsed spin-locking experiment can also be applied to the WHH pulse sequence[5,6,29] with similar consequences. The truncated Hamiltonian in the rotating frame is

$$\mathcal{H}(t)=\Delta I_z+H^d_{20}+\Psi(t)\ , \tag{3.30}$$

where $\Psi(t)$ represents the pulse sequence. In the case that neither the pulse angle nor the detuning are small quantities, the equation of motion is preferably solved in an interaction frame that evolves under their combined action. The evolution of this frame over one cycle of 6τ,

$$U_0(6\tau)=e^{-i\Delta I_z\tau}e^{-i\theta I_y}e^{-i\Delta I_z\tau}e^{i\theta I_x}e^{-i\Delta I_z 2\tau}e^{-i\theta I_x}e^{-i\Delta I_z\tau}e^{i\theta I_y}e^{-i\Delta I_z\tau}\ , \tag{3.31}$$

is the product of rotations by $\Delta\tau$ about the z axis, and $\pm\theta$ about the x and y axes, of the rotating frame. This is equivalent to a rotation

$$U_0(6\tau)=e^{-i\omega_e 6\tau\hat{n}\cdot\vec{I}} \tag{3.32}$$

of angle $\omega_e 6\tau$ about an effective axis, $\hat{n}$. Equating the two forms of $U_0(6\tau)$ leads to the following relations between ω_e and $\hat{n}$ on one hand, and θ and Δ on the other:

$$\cos^4(\theta/2)\cos^3(\Delta\tau)+[\tfrac{1}{4}-\cos^4(\theta/2)]\cos(\Delta\tau)-\tfrac{1}{4}\cos(3\omega_e\tau)=0 \tag{3.33}$$

and

$$n_1=\frac{\sin\theta\sin(2\Delta\tau)\cos^2(\theta/2)}{\sin(3\omega_e\tau)},\quad n_2=\frac{\sin\theta\sin(\Delta\tau)}{\sin(3\omega_e\tau)},\quad n_3=\frac{\sin(3\Delta\tau)\cos^4(\theta/2)+\sin(\Delta\tau)\sin^4(\theta/2)}{\sin(3\omega_e\tau)}\ . \tag{3.34}$$

As before, the transformation to an interaction frame under $U_0(t)$ does not necessarily produce a periodic Hamiltonian. The special cases for which it does are when

$$\omega_e=m\pi/n\,3\tau\ , \tag{3.35}$$

where m rotations are produced in n cycles each of duration 6τ. The case of one rotation in a single cycle is trivial because θ must be a multiple of π.

The more fascinating cases, with periods of 12τ, 18τ, and 24τ, produce the intriguing *resonance* curves pictured

in Fig. 10. These portray an equation, cubic in $\cos(\Delta\tau)$, that makes a transition from having three real roots, for θ smaller than a critical value, to only a single real root for θ larger than this value. For $n=3$, $\theta_c \cong 0.87$ rad, while for $n=4$, $\theta_c \cong 0.61$ rad. It is pertinent to point out that the *resonance* condition is not attained for $\Delta\tau \cong 0$, thus excluding the important case of the on-resonance WHH experiment with 90° pulses. The latter is a special case for which Eq. (3.33) is satisfied when $\omega_e = 0$, i.e., no net rotation is effected.

The transformation to the interaction frame and subsequent evolution of the effective Hamiltonian is encumbered by the large number of pulses per period. Fortunately, the form of $\tilde{\tilde{H}}^{(1)}$ can be deduced more simply by noting that it is of necessity invariant to rotations about the effective axis, and therefore must be a linear combination of operators that are diagonal in the frame tilted by

$$T = e^{i\alpha I_y} e^{i\beta I_z} \tag{3.36}$$

with respect to the interaction frame. The Euler angles α and β are related to the orientation of $\hat{n}$ through $\cos\alpha = n_3$, $\sin\beta\sin\alpha = n_2$, and $\cos\beta\sin\alpha = n_1$. In this frame, $\tilde{\tilde{H}}^{(1)} = a\delta I_z + bH_{20}$. The proportionality factors a and b are determined by finding the average component of $\mathcal{H}_I(t)$, along I_z and H^d_{20}, over the five time intervals $(0,\tau)$, $(\tau,2\tau)$, $(2\tau,4\tau)$, etc. The result is

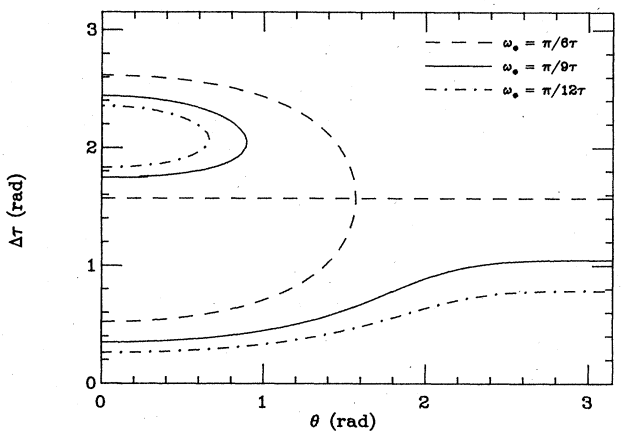

FIG. 10. *Resonance curves* for the WHH pulse sequence in which two, three, and four periods of 6τ are required to complete one rotation around the effective axis.

$$\tilde{\tilde{H}}^{(1)} = \tfrac{1}{3}\left[n_3\delta I_z + \tfrac{1}{2}(3n_3^2-1)H^d_{20} + \sum_{L,m} d^L_{m0}(\theta) d^L_{0m}(\alpha)\cos(m\Delta\tau)\cos(m\beta) A_{L0} \right.$$
$$\left. + \sum_{L,m,m'} d^L_{m0}(-\theta) d^L_{m'm}(\theta) d^L_{0m'}(\alpha)\cos[(m+m')\Delta\tau] C_m A_{L0} \right], \tag{3.37}$$

where the $d^L_{mm'}$ are the Wigner matrix elements, $A_{10} = \delta I_z$, $A_{20} = H^d_{20}$, and $C_m = i^m\cos(m'\beta)$ for even m, and $C_m = i^{m+1}\sin(m'\beta)$ for odd m. Here, L ranges from 1 to 2, and m and m' range from $-L$ to L.

Under $\tilde{\tilde{H}}^{(1)}$ the dipole and Zeeman energies are separately conserved. After a time T_2 the system will arrive at a quasistationary state characterized by separate temperatures for these baths. The quasistationary magnetization is the square of the component of the initial magnetization lying along the $\hat{n}$ axis,

$$\frac{M^x_{qs}}{M^x_i} = n_1^2 . \tag{3.38}$$

The higher-order corrections to $\tilde{\tilde{H}}^{(1)}$ will mix the two reservoirs, in a time long compared to T_2, to an equilibrium state described by a single spin temperature. An accurate determination of the equilibrium state requires explicit knowledge of $\tilde{\tilde{H}}^{(2)}$ and $\tilde{\tilde{P}}_1$ (cf. Sec. II C). This being an arduous task, a simpler approach is taken in which the corrections to $\tilde{\tilde{H}}^{(1)}$ are implicitly used to establish a common temperature, but Eq. (2.19) is applied solely to $\tilde{\tilde{H}}^{(1)}$. In this way,

$$\frac{M^x_{eq}}{M^x_i} = \frac{a^2\delta^2 n_1^2}{a^2\delta^2 + b^2 H_L^2} \tag{3.39}$$

is obtained, with a and b determined from Eq. (3.37), and δ the deviation from *resonance*.

A graphical view of the equilibrium magnetization, in the neighborhood of a variety of *resonance* points, is presented in Fig. 11. The symmetry of these curves, about $\delta = 0$, occurs because $\tilde{\tilde{H}}^{(2)}$ and $\tilde{\tilde{P}}_1$, which are the sources of the asymmetry in the analogous plots of Sec. III C,

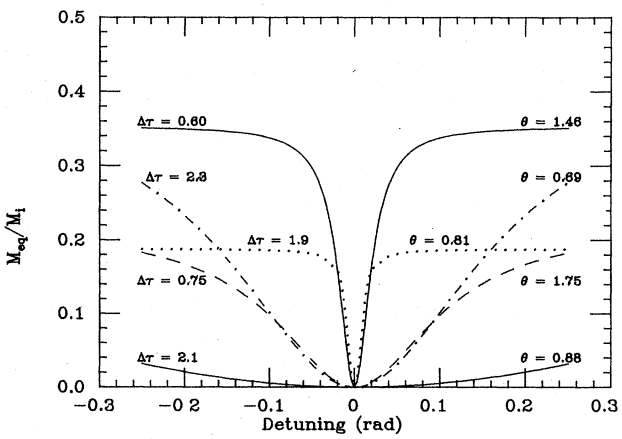

FIG. 11. Equilibrium magnetization vs the detuning δ from the *resonance* condition for various combinations of θ and $\Delta\tau$. The curves are obtained from Eq. (3.39). (Parameters: $H_L = 25\,000$ rad/sec and $\tau = 10$ μsec.)

have been omitted from the calculation of M^x_{eq}. The prediction of a decrease of the equilibrium magnetization to zero, at the special values of θ and Δ that obey Eq. (3.33), however, remains. The variation in the widths of the curves is also interesting to note. Very narrow *resonances* are found for $\theta=\pi/4$ and for θ slightly smaller than $\pi/2$. In the region of large $\Delta\tau$, this resonance broadens considerably, with a simultaneous decrease in M^x_{eq}, as the detuning is raised to $\Delta\tau=2.1$ rad. Then M^x_{eq} increases substantially for $\Delta\tau=2.3$ rad. In contrast, note that this large variation is not found in M^x_{qs}.

IV. THE DYNAMICS

Up to this point, the primary concern has been to understand the quasiequilibrium and equilibrium states that characterize a spin system driven by multiple-pulse irradiation. An important question that deserves attention is at what rate does the quasiequilibrium state decay? It is the purpose of this section to address this question.

A. Overview

The time development of the pulsed spins can be divided into three characteristic regions. The first is the short-time regime, during which the spins evolve effectively under the action of $\overline{H}^{(1)}$. This time period features a wide spectrum of oscillations of the magnetization that occur because the precession rate of each spin is determined by the local field surrounding it, in addition to the deviation from *resonance*. These oscillations arise from the component of the magnetization vector initially perpendicular to the effective axis. There is, in addition, a constant contribution to the magnetization that arises from the parallel component of the initial magnetization. After a time of approximately T_2, the transverse component decays to zero and a quasistationary state is reached. The time required is determined by H_L and θ. It depends only indirectly on the interval between pulses, in the sense that if τ is too large, $\overline{H}^{(1)}$ does not represent the effective Hamiltonian even for short times.

In the second region, the Zeeman and dipolar heat baths have separately equilibrated to distinct temperatures. When viewed from the *toggling* frame, the magnetization has a small periodic variation due to $P(t)$, and decays slowly. The transformation back to the rotating frame accentuates the periodicity of $2\pi/\omega_e$ observed in the magnetization.

The Zeeman and dipole energies are individually conserved only to an approximation. Under the action of $\overline{H}^{(2)}$, the reservoirs are mixed and equilibrate to a common temperature—hence the decay of M^x_{qs}. A qualitative explanation of this is provided with the aid of Fig. 12. Pictured are the energy levels of $\overline{H}^{(1)}$ versus the density of states. Without the dipole interaction, there are two levels separated by δ. The effect of the dipolar coupling is

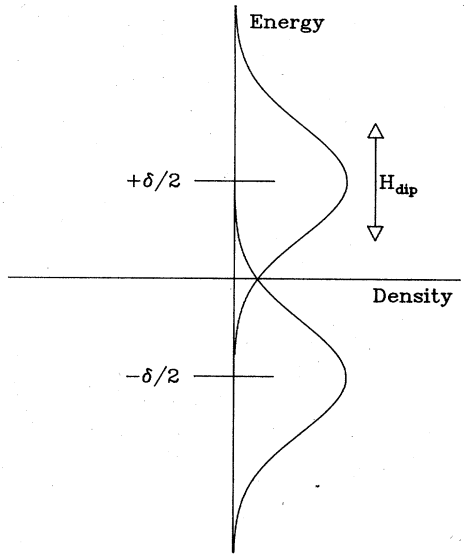

FIG. 12. Energy-level diagram for the average Hamiltonian of the spin-locking pulse sequence [Eq. (3.19)]. Pictured is the energy vs the density of states. H_{dip} is the dipolar contribution to $\overline{H}^{(1)}$.

a broadening of the levels due to the influence of the local fields. In the region that the levels overlap, $\overline{H}^{(2)}$ can introduce energy-conserving transitions between the Zeeman levels. This causes a transfer of energy between the Zeeman and dipolar reservoirs.

The influence of the various physical parameters on the decay rate can be understood from Fig. 12. The overlap between the broadened levels becomes larger as $\delta\rightarrow 0$, which increases the decay rate. Similarly, the overlap grows as H_L is increased, whereupon the decay rate is predicted to rise. The dependence on θ is complicated by the fact that this parameter enters into the splitting of the Zeeman levels, the broadening caused by the dipolar interaction, and the size of the coupling term, $\overline{H}^{(2)}$. When $\delta=0$, the overlap is independent of θ, but $\overline{H}^{(2)}$ becomes larger as θ is increased, making the decay rate faster.

The equilibrium state comprises the third region of the time development. If the interaction frame is such that there are no eigenvalues of $\overline{H}$ satisfying $|\lambda_i-\lambda_j|\geq 2\pi/\tau$, then the equilibrium is a *true* one and it will persist. If there are eigenvalues separated in frequency by $2\pi/\tau$, or multiples of this value, non-energy-conserving transitions can take place between these levels, and a new final state will slowly evolve. The rate of this decay depends not on the overlap of levels broadened by the dipole interaction and separated by δ as above, but on the overlap of levels separated by $2\pi/\tau$. This overlap is proportional to the intensity of the ordinary dipole line shape at the frequency $2\pi/\tau$. Being much smaller than the intensity at δ, the decay rate is much slower than for the quasistationary state.

B. Combining the Provotrov theory (Ref. 21) with the average Hamiltonian

The analysis of the decay of the quasistationary state begins by writing the cycle propagator in the form

$$e^{-i(\overline{H}^{(1)}+\overline{H}^{(2)})t}=e^{-i\overline{H}^{(1)}t}\exp_D\left[-i\int_0^t dt' e^{i\overline{H}^{(1)}t'}\overline{H}^{(2)}e^{-i\overline{H}^{(1)}t'}\right], \tag{4.1}$$

which is amenable to a perturbation treatment under the condition that $\overline{H}^{(2)}$ is smaller than $\overline{H}^{(1)}$. The time-ordered exponential (denoted by the subscript D) is approximated by a series representation, so that

$$\rho(t)=e^{-i\overline{H}^{(1)}t}\left[\rho_0-i\int_0^t dt'[\overline{H}^{(2)}(t'),\rho_0]-\int_0^t dt'\int_0^{t'}dt''[\overline{H}^{(2)}(t'),[\overline{H}^{(2)}(t''),\rho_0]]+\cdots\right]e^{i\overline{H}^{(1)}t} \tag{4.2}$$

gives the time evolution of the density matrix. Note that only the propagation under the effective Hamiltonian is considered. The operator $P(t)$, which completes the full evolution operator, causes a periodic modulation of the density matrix; however, it does not contribute to the overall decay. The decay of the modulation envelope can be determined by considering the stroboscopic evolution of the system under $\overline{H}$.

The remainder of the analysis follows the exposition given by Goldman.[18] The expectation value of any observable, A, evolves according to

$$\langle A(t)\rangle=\mathrm{Tr}A\rho(t)\ . \tag{4.3}$$

Let us consider the evolution of those operators that commute with the average Hamiltonian. Because the point is to follow the evolution of the quasistationary state,

$$\rho_0=1-\beta_{\rm qs}f(\theta)\delta I_z-\alpha_{\rm qs}g(\theta)H_{20}^d \tag{4.4}$$

is chosen for the initial density matrix. The functions of θ account for the dependence of the Zeeman and dipolar energies in $\overline{H}^{(1)}$ on the pulse angle. ρ_0 is substituted into Eq. (4.2) and the trace with A is taken. The first-order term,

$$-i\,\mathrm{Tr}A\,e^{-i\overline{H}^{(1)}t}\int_0^t dt'[e^{i\overline{H}^{(1)}t'}\overline{H}^{(2)}e^{-i\overline{H}^{(1)}t'},\rho_0]e^{i\overline{H}^{(1)}t}=-i\,\mathrm{Tr}A\,[\overline{H}^{(2)},\rho_0]t=0\ , \tag{4.5}$$

vanishes, because both A and ρ_0 commute with $\overline{H}^{(1)}$. The second-order term remains, and

$$\mathrm{Tr}A\rho(t)=\mathrm{Tr}A\rho_0-\mathrm{Tr}A\int_0^t dt'\int_0^{t'}dt''[\overline{H}^{(2)}(t'-t''),[\overline{H}^{(2)},\rho_0]] \tag{4.6}$$

is obtained after some rearrangement of terms. A substitution of $t'-t''$ as one of the variables of integration allows one integral to be evaluated easily, with the result

$$\mathrm{Tr}A[\rho(t)-\rho_0]=-\mathrm{Tr}A\int_0^t dt'(t-t')[\overline{H}^{(2)}(t'),[\overline{H}^{(2)},\rho_0]]\ . \tag{4.7}$$

The intent here is to understand the decay of the quasistationary magnetization. This occurs over times long compared to T_2. At these long times, the off-diagonal matrix elements of $\overline{H}^{(2)}(t)$ have decayed to nearly zero, so that little error is introduced by extending the upper integration limit from $t\to\infty$. Similarly, for large t, $t-t'\cong t$ for those t' that contribute significantly to the integral. Combining the two approximations and dividing by t yields

$$\frac{d}{dt}\mathrm{Tr}A\rho(t)=-\int_0^\infty dt'\mathrm{Tr}[A,\overline{H}^{(2)}(t')][\overline{H}^{(2)},\rho_0] \tag{4.8}$$

for the rate of change in the expectation value of A.

The rate of change in the temperatures is now deduced by specific choices for A. Substitution of $A=I_z$, and the density matrix of Eq. (4.4) into Eq. (4.8), produces two terms: one proportional to $\beta_{\rm qs}-\alpha_{\rm qs}$ and the other proportional to $\alpha_{\rm qs}$. The latter can be easily integrated, and produces a contribution of

$$\frac{g(\theta)}{f(\theta)}\int_0^\infty dt'\mathrm{Tr}[I_z,\overline{H}^{(2)}(t')][\overline{H}^{(2)},\overline{H}^{(1)}]=\frac{g(\theta)}{f(\theta)}\mathrm{Tr}[I_z,\overline{H}^{(2)}][\overline{H}^{(2)}(\infty)-\overline{H}^{(2)}(0)]=0 \tag{4.9}$$

to the rate of change in $\beta_{\rm qs}$. The trace with $\overline{H}^{(2)}(\infty)$ equals zero, because the off-diagonal elements of $\overline{H}^{(2)}$ decay to zero for long times and the commutator is completely off diagonal. The term proportional to $\beta_{\rm qs}-\alpha_{\rm qs}$ provides the main result,

$$\frac{d\beta_{\rm qs}}{dt}=\frac{-(\beta_{\rm qs}-\alpha_{\rm qs})}{\mathrm{Tr}I_z^2}\int_0^\infty dt'\mathrm{Tr}[I_z,\overline{H}^{(2)}(t')][\overline{H}^{(2)},I_z]\ . \tag{4.10}$$

A similar solution for $d\alpha_{\rm qs}/dt$ can be determined by choosing $A=H_{20}^d$ and following the same reasoning as used here. It is simpler, though, to recognize that the conservation of energy requires that

$$\frac{d\beta_{\rm qs}}{dt}f^2(\theta)\delta^2+\frac{d\alpha_{\rm qs}}{dt}g^2(\theta)H_L^2\cong 0\ . \tag{4.11}$$

The relation is approximate because the total energy is not solely determined by $\overline{H}^{(1)}$, but also includes a small contribution from $\overline{H}^{(2)}$.

Equations (4.10) and (4.11) are the basic relations that govern the equilibration of the dipole and Zeeman reservoirs to a common temperature. The solution of Eq. (4.10) is a decaying exponential function for $\beta_{\rm qs}$ that has a rate constant of $1+f^2(\theta)\delta^2/g^2(\theta)H_L^2$ times the integral on the right-hand side of the equation. The important contribution to this rate constant is the strength of the coupling produced by $\overline{H}^{(2)}$.

C. Application to pulsed spin locking

Let us consider the relaxation of the quasistationary magnetization at *resonance,* i.e., with $\delta=0$. Define

$$G(t)=\mathrm{Tr}[I_z, e^{i(\cos\theta)H_{20}^d t}\tilde{\bar{H}}^{(2)}e^{-i(\cos\theta)H_{20}^d t}][\tilde{\bar{H}}^{(2)},I_z] \tag{4.12}$$

to be the integrand in Eq. (4.10). Because the time dependence arises solely from the action of the dipole interaction, $G(t)$ is a simply decaying function of time. It is assumed to have a Gaussian form,

$$G(t)/G(0)=e^{-\sigma t^2/2}, \tag{4.13}$$

where the parameter

$$\sigma=-\frac{\mathrm{Tr}[I_z,[(\cos\theta)H_{20}^d,[(\cos\theta)H_{20}^d,\tilde{\bar{H}}^{(2)}]]][\tilde{\bar{H}}^{(2)},I_z]}{\mathrm{Tr}[I_z,\tilde{\bar{H}}^{(2)}]^2} \tag{4.14}$$

is deduced from the expansion of $G(t)/G(0)$ in a power series to second order in t. The decay parameter is

$$\sigma=15(\cos^2\theta)H_L^2 \tag{4.15}$$

after the traces are evaluated. The rate constant is determined by integrating $G(t)$ from 0 to ∞. From Eq. (4.13), the result

$$R=G(0)\frac{1}{2}\left[\frac{2\pi}{\sigma}\right]^{1/2} \tag{4.16}$$

is easily found.

Inserting σ and the trace that defines $G(0)$ into this expression reveals that

$$R=\frac{2}{3}\left[\frac{2\pi}{15}\right]^{1/2}\frac{\sin^2(\theta/2)(10\cos^3\theta-7\cos^2\theta+6)}{\cos\theta}H_L^3\tau^2 \tag{4.17}$$

determines the rate at which the quasistationary magnetization decays under the condition of *resonance*.

A graph of the relaxation time $1/R$ as a function of θ is featured in Fig. 13 (solid curve). The relaxation time goes to zero at $\theta=\pi/2$ because of the singularity in formula (4.17) at that point. This is on account of the dipolar contribution to $\bar{H}^{(1)}$ vanishing for $\theta=\pi/2$. A reasonable, albeit *ad hoc*, solution is to correct σ by combining the diagonal portion of $\tilde{\bar{H}}^{(2)}$ with $\tilde{\bar{H}}^{(1)}$ in Eqs. (4.12) and (4.14). Thus,

$$\sigma\cong 15[(\cos^2\theta)H_L^2 + \tfrac{4}{27}\sin^4(\theta/2)(34\cos^2\theta+46\cos\theta+19)H_L^4\tau^2] \tag{4.18}$$

can be substituted into Eq. (4.16). The overall effect of this correction is rather small, as can be seen from the figure (dotted curve); however, it does remedy the problem at $\theta=\pi/2$.

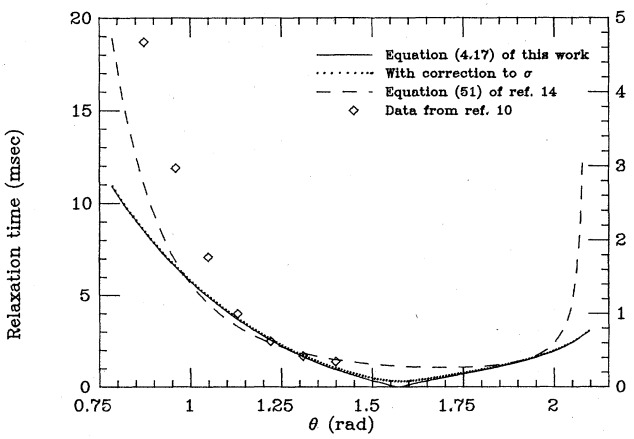

FIG. 13. Relaxation time for the quasistationary magnetization vs the pulsed angle θ. $\Delta\tau$ is also varied to ensure that the *resonance* condition is met for all θ. The left-hand scale is for the data, whereas the right-hand scale is for the solid and dotted curves. The dashed curve was scaled to the data in Ref. 14. (Parameters: $H_L=25\,000$ rad/sec and $\tau=6.6\,\mu$sec.)

The present results are also compared to experiment[10] and to the theoretical predictions of Provotorov and coworkers[14] in Fig. 13. The qualitative features are all in agreement: the decay time is longest at small θ, it decreases to a minimum at $\theta=\pi/2$, and then increases again as $\theta\to 2\pi/3$. Quantitative comparisons, however, are more difficult to make. One reason is that the calculations of Ref. 14 are scaled to fit the data. Separate vertical scales are therefore used for plotting Eq. (4.17) versus the experimental data to achieve the same effect here. Secondly, the rate constant is sensitive to errors in H_L. In Ref. 10 a value of 1.0 G for H_L instead of the predicted 0.86 G was blamed on misalignment of the crystal in the magnetic field. This translates to an uncertainty of nearly a factor of 2 in the relaxation time.

A more important point of concern is the following: Within the theoretical framework of the present study, the pulse angle θ is *not* a free parameter in Eq. (4.17). It must satisfy the auxiliary constraint imposed by the *resonance* condition, Eq. (3.15). In an experiment, therefore, as θ is varied, the detuning Δ must be simultaneously altered to ensure compliance with this condition. This is not to say that it is not worthwhile to study the change in decay rate when only θ is varied, just that in the present framework this would imply a concurrent change in δ, the deviation from *resonance*. The effect is to make the variation of $1/R$ with θ steeper than predicted by Eq. (4.17), and closer to the experimental values. These questions could be further illuminated by additional experiments.

V. CONCLUSION

The emphasis of this paper has been the use of the Floquet theory for solving the time-dependent Schrödinger equation in the presence of periodic time-dependent interactions. The advantage yielded by this approach over other methods of perturbation theory is due to its explicit use of the time symmetry of the Hamiltonian. As a consequence, the effective Hamiltonian emerges as a constant of the motion, where this term is applied here in a broader sense than usual. The effective Hamiltonian, in fact, has many of the properties ordinarily attributed to conservative Hamiltonians. One important feature is that it forms the basis of a thermodynamic description of the equilibrium state for a spin system subject to periodic external torques.

Starting with the equation of motion for the density matrix, the assumption that the effective Hamiltonian is

ergodic is used to deduce the statistical thermodynamic formula for the equilibrium properties of the system, e.g., the magnetization. Under the condition that the eigenvalues of $\overline{H}$ lie entirely in the interval $|\lambda_i-\lambda_j|<2\pi/\tau$, an expression for the equilibrium magnetization is obtained that is similar to Redfield's[19] application of spin thermodynamics in the rotating frame. The results herein both strengthen the validity of the latter approach and present a correction to it. Terms that account for the full evolution of the spins, as opposed to evolution solely under the effective Hamiltonian, comprise the correction. Thus a time-dependent system, with an effective Hamiltonian $\overline{H}$, is inherently different from a conservative system with the same Hamiltonian $\overline{H}$. As the period approaches zero, the difference disappears. When the condition $|\lambda_i-\lambda_j|<2\pi/\tau$ is not met, non-energy-conserving transitions (between levels of $\overline{H}$) are possible and no analogous conservative system can be found.

The analysis of the pulsed spin-locking experiment via the Floquet method predicts values of the quasistationary and equilibrium magnetizations in quite good agreement with experiment. Two cases exist, depending on the size of the pulse angle and the detuning. When these are small, the rotating frame is appropriate for analysis. The effect of the pulses on the equilibrium magnetization is predominantly determined by the average intensity of the rf field. The dependence on the pulse spacing becomes more complicated when second-order corrections to $\overline{H}^{(1)}$ are considered. These depend on $H_L\tau$, and these are not necessarily insignificant.

For large θ or Δ, the principle motion of the spins is a toggling-like precession about the effective axis defined by the pulses and detuning. When the problem is transformed to that frame, an average Hamiltonian is found that permits two constants of the motion. This leads to a quasistationary state with distinct temperatures for the Zeeman and dipolar baths. Under the influence of the second-order correction to $\overline{H}^{(1)}$, the reservoirs mix to a common temperature.

The rate for equilibration of the temperatures depends on the size of the Zeeman and dipolar terms in $\overline{H}^{(1)}$ and on the strength of the coupling introduced by $\overline{H}^{(2)}$. An adaptation of the Provotorov theory[21] to the average Hamiltonian provides a route by which to calculate the rate constant.

These results establish the average Hamiltonian theory, and the more general version based on the Floquet theory, as appropriate for long-time predictions of the behavior of a spin system, in addition to their short-time applications in NMR spectroscopy.

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[1]Detailed reviews are given in U. Haeberlen, *High Resolution NMR in Solids* (Academic, New York, 1976); M. Mehring, *High Resolution NMR Spectroscopy in Solids* (Springer, Berlin, 1983).

[2]P. Mansfield and D. Ware, Phys. Lett. **22**, 133 (1966).

[3]J. S. Waugh and L. M. Huber, J. Chem. Phys. **47**, 1862 (1967).

[4]D. P. Barum and W. K. Rhim, J. Chem. Phys. **77**, 944 (1979).

[5]J. S. Waugh, L. M. Huber, and U. Haeberlen, Phys. Rev. Lett. **20**, 180 (1968).

[6]U. Haeberlen and J. S. Waugh, Phys. Rev. **175**, 453 (1968).

[7]E. D. Ostroff and J. S. Waugh, Phys. Rev. Lett. **16**, 1097 (1966).

[8]D. Suwelack and J. S. Waugh, Phys. Rev. B **22**, 5110 (1980).

[9]L. N. Erofeev and B. A. Shumm, Zk. Eksp. Teor. Fiz. Pis'ma Red. **27**, 161 (1978) [JETP Lett. **3**, 149 (1978)].

[10]L. N. Erofeev, B. A. Shumm, and G. B. Manelis, Zh. Eksp. Teor. Fiz. **75**, 1837 (1978) [Sov. Phys.—JETP **48**, 925 (1979)].

[11]B. A. Shumm and L. N. Erofeev, Fiz. Tverd. Tela (Leningrad) **22**, 213 (1969) [Sov. Phys.—Solid State **22**, 123 (1980)].

[12]W. K. Rhim, D. P. Barum, and D. D. Elleman, Phys. Rev. Lett. **37**, 1764 (1976).

[13]Yu. N. Ivanov, B. N. Provotorov, and E. B. Fel'dman, Zh. Eksp. Teor. Fiz. Pis'ma Red. **27**, 164 (1978) [JETP Lett. **3**, 153 (1978)].

[14]Yu. N. Ivanov, B. N. Provotorov, and E. B. Fel'dman, Zh. Eksp. Teor. Fiz. **75**, 1847 (1978) [Sov. Phys.—JETP **48**, 930 (1979)].

[15]B. N. Provotorov and E. B. Fel'dman, Zh. Eksp. Teor. Fiz. **79**, 2206 (1980) [Sov. Phys.—JETP **52**, 1116 (1980)].

[16]M. G. Floquet, Ann. Ec. Norm. Suppl. **12**, 47 (1883).

[17]M. M. Maricq, Phys. Rev. B **25**, 6622 (1982).

[18]M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Oxford University Press, Oxford, 1970).

[19]A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

[20]A. Askar, Phys. Rev. A **10**, 2395 (1974).

[21]B. N. Provotorov, Zh. Eksp. Teor. Fiz. **41**, 1582 (1961) [Sov. Phys.—JETP **14**, 1126 (1962)].

[22]J. H. Shirley, Phys. Rev. **138**, B979 (1965).

[23]V. I. Arnold, *Ordinary Differential Equations* (MIT Press, Cambridge, Massachusetts, 1978).

[24]In the Floquet formalism, the lowest order term in $\overline{H}$ naturally acquires the label $\overline{H}^{(1)}$, as opposed to $\overline{H}^{(0)}$ as in the AHT (also see Ref. 17).

[25]W. Magnus, Commun. Pure Appl. Math. **7**, 649 (1954).

[26]P. Pechukas and J. C. Light, J. Chem. Phys. **44**, 3897 (1966).

[27]V. I. Arnold and A. Avez, *Ergodic Problems of Classical Mechanics* (Benjamin, New York, 1968), p. 20. For quantum-mechanical ergodic problems, see P. J. M. Bongaarts and Th. J. Siskens, Physica (Utrecht) **71**, 529 (1978).

[28]The data of Ref. 19 give M^x_{eq}/M^x_{qs}. These were scaled by M^x_{qs}/M^x_i [Eq. (3.24)] for the plots presented here.

[29]U. Haberlen, J. D. Ellet, Jr., and J. S. Waugh, J. Chem. Phys. **55**, 53 (1971).