Relaxation and equilibrium of a spin system coupled to a radiation field

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The paper presents a field-theoretical view of the long-time evolution and equilibrium properties of a large number of mutually coupled spins subject to an external radiation field, and contrasts this view to the usual semiclassical approach. It is shown that the semiclassical approach breaks down at long times because it has no provision for the spins and radiation field to equilibrate to a common temperature. The field-theory view predicts that a macroscopic collection of spins will relax to the temperature of the radiation field much in the same way that a spin system equilibrates with phonons in spin-lattice relaxation. This idea is used to explain the saturation of magnetization observed experimentally after long times in the off-resonance irradiation of a dipole-coupled spin system, a phenomenon not satisfactorily described by conventional average Hamiltonian methods. The saturation rate is calculated and compared to experiment. The theory predicts that a critical field intensity is required for the saturation effects to occur.

I. INTRODUCTION

In their book, *Nuclear Magnetism: Order and Disorder,* Abragam and Goldman[1] discuss a problem they call the "Magnus paradox." It arises for the following reason. On one hand, the existence of a spin temperature[2] in the rotating frame is well established, providing insight into phenomena ranging from cw spin locking[3] to cross polarization.[4] On the other hand, the average Hamiltonian theory[5–7] (AHT) is a powerful and well-known tool for analyzing magnetic-resonance spectra obtained under multiple-pulse and a variety of other forms of irradiation. Yet, combining these two ideas to predict the long-time evolution of spins subject to radio-frequency irradiation in some situations leads to contradictions with experiment. It is the purpose of this paper to address this issue from a field-theoretical view of the radiation field. Comparison of this view to the semiclassical approach will clarify the difficulties described by Abragam and Goldman.[1]

The advent of multiple-pulse spectroscopy,[5–7] and other experiments using complex forms of rf irradiation, brought with it extensions of the spin-temperature hypothesis from the rotating frame to toggling and other interaction frames. The standard semiclassical description of these experiments produces a time dependent, nonconservative spin Hamiltonian, one not suitable for the application of thermodynamic principles. The AHT provides a prescription for finding a time-independent effective Hamiltonian $\bar{H}$, under which the evolution of the system, when observed stroboscopically, mimics the true evolution of the system. The accuracy in the predicted magnetic-resonance spectra confirms that the AHT accurately describes the short-time dynamics of the irradiated spins.

The situation at long times is less clear. Pines and Waugh[8] combine the AHT with spin thermodynamics to determine the dipolar spin temperature of a spin system irradiated by a phase-alternated sequence of resonant pulses and obtain predictions agreeing with experimental values. Similarly, Quiroga *et al.*[9,10] investigate the effect of adiabatic variation of the pulse angle in the Waugh, Huber, and Haeberlen[11] (WHH) pulse sequence on the final dipolar spin temperature and find agreement between the spin-thermodynamics–AHT predictions and experimental results. For other experiments, however, the theory is not so good.

In a series of experiments on pulsed-spin locking in a crystalline sample of CaF_2, Erofeev and co-workers[12–14] find that the experimentally measured magnetization approaches the "equilibrium" value predicted by the spin-thermodynamics–AHT theory at intermediate times, but then decays over longer times. In addition to this experiment, Abragam and Goldman[1] describe a nonpulsed experiment for which the spin-thermodynamics–AHT arguments also lead to incorrect conclusions. They consider a dipole-coupled spin system irradiated by a weak cw field far above resonance. As in the experiment of Erofeev and co-workers,[12–14] the spin system approaches over intermediate times the "equilibrium" state predicted from an apparently straightforward use of the AHT, but then continues to decay over longer times. The paradox exists because one obtains via the Magnus expansion[15] a conservative model of the system; yet it fails to predict the correct equilibrium state.

Previous measures to resolve the "Magnus paradox" have retained the semiclassical perspective. Provotorov and coworkers[16–18] abandoned the AHT. Instead they transform the pulsed-spin-locking Hamiltonian into a toggling frame and use time-dependent perturbation theory to obtain satisfactory agreement with experiment.

I have subsequently shown that the AHT is not fundamentally at fault; it is the transformation that provides Provotorov and co-workers the improved agreement with experiment.[19–21] The AHT can lead to poor results for two reasons[22]. (1) It is becoming clear that the Magnus expansion generally does not converge,[23–25] and (2) spin thermodynamics can be applied to $\bar{H}$ only under certain

restrictions. The principal requirement for both (1) and (2) is that

$$|\lambda_i-\lambda_j|<2\pi/\tau \tag{1.1}$$

for all pairs of eigenvalues λ_i and λ_j of $\bar{H}$, where τ is the period of the semiclassical Hamiltonian.[19–21] The transformation of the pulsed-spin-locking Hamiltonian into the toggling frame goes some way in satisfying condition (1.1), but does not completely satisfy it.

It is relatively easy to understand the difficulty in the semiclassical description at long times. The averaging process of the AHT eliminates oscillating terms from the semiclassical Hamiltonian. For example, in the experiment described by Abragam and Goldman[1] the Hamiltonian is

$$\mathcal{H}(t)=H_{20}^d+\omega_1\cos(\omega t)I_x\ , \tag{1.2}$$

with H_{20}^d the secular dipole interaction. When $\omega\ll H_L$, the local field experienced by the spins, the AHT yields $\bar{H}=H_{20}^d$. Indeed, $\bar{H}$ provides a good description of the short-time dynamics viewed stroboscopically at intervals of $2\pi/\tau$. It might provide a good account of the long-time behavior *if* condition (1.1) were met. But even with $\omega\ll H_L$ there are some pairs of levels in the wings of the dipole line shape that differ in frequency by more than $2\pi/\tau$. Because of these levels, averaging out the oscillating term in Eq. (1.2) produces a serious error. It ignores absorption by the spin system of quanta the size $\hbar\omega$ from the radiation field. Over short times this does not present a significant problem, because the absorption is slow. Over long times it causes heating of the spin system. Some progress can be made in dealing with the errant levels, namely a transformation is used to reduce their energy spacing;[26] however, the process is not entirely satisfactory.

The problems with the semiclassical approach arise because the spins and radiation field are not treated on equal footing. The radiation field is constrained to a classical coherent state, while the spins are described by time-dependent operators. In the present approach, we consider a system of N spins coupled to $\bar{n}$ photons of a single-mode radiation field. The evolution of the coupled oscillator-spin system is studied via the *dressed-state* approach introduced by Cohen-Tannoudji.[27–29] This approach has a number of advantages: it puts the spins and radiation field on equal quantum-mechanical footing, the spin–radiation-field Hamiltonian is conservative, unlike its semiclassical counterpart, and it has provision for the spins and radiation field to evolve to a common equilibrium temperature. We show that relaxation of the spins by the photons is responsible for the saturation observed in the experiments of Abragam and Goldman.[1] Essentially the radiation field plays a role analogous to the lattice in the phenomenon of spin-lattice relaxation.[30]

I apply the dressed-state approach to two situations. One is the near-resonant irradiation of a dipole-coupled spin system in a static magnetic field, i.e., the cw spin-locking experiment.[2,3] The second is the experiment cited by Abragam and Goldman[1] in their discussion of the "Magnus paradox." In both cases the Hamiltonian consists of two quasiconserved components plus small noncommuting terms. For the second example, these are the radiation field and the model Hamiltonian found by applying the AHT to Eq. (1.2), namely H_{20}^d. Over intermediate times these components evolve to states characterized by separate temperatures. Over long times the oscillator and dipole energies evolve to a common temperature. I demonstrate that when the applied field surpasses a critical value, the final temperature is very high; it is essentially the temperature of the radiation field. Thus, equilibration of the spins with the radiation field, for which there is no provision within the semiclassical framework, explains the saturation of the dipole order observed in this experiment. Below the critical applied field, the system evolves to a much colder equilibrium temperature nearly equal to the quasistationary value, and the system is predicted not to saturate.

The small noncommuting terms, e.g., the counterrotating terms of the rotating-frame Hamiltonian, provide a weak thermal link that leads to the equilibrium between the spins and radiation field. The Provotorov theory of saturation[31] is used to find the rate at which the subsystems approach equilibrium. The value obtained here agrees with that of Abragam and Goldman.

In Sec. II, I introduce the Hamiltonian for a spin system in a quantized radiation field and decompose it into a sum of quasiconserved terms and a noncommuting term. Section III describes the quasistationary state of the irradiated spin system that develops at intermediate times while Sec. IV considers the eventual equilibrium that develops between the spins and the radiation field. Section V compares the present results to predictions obtained within the semiclassical description. Section VI describes the dynamics of the approach to equilibrium.

II. SPINS DRESSED BY A RADIATION FIELD

A. Hamiltonian

This paper considers the long-term effects of a nearly resonant radiation field on the evolution of the spins in a spin-locking experiment and the long-term effects of off-resonance irradiation of an initially-dipole-ordered state. These two examples differ primarily in the initial state of the spins and in the values of certain parameters of the Hamiltonian. Both involve a system of N mutually interacting spins coupled to $\bar{n}$ single-mode photons, which for the sake of definiteness we place in a cavity of volume V. The starting point for describing how spins interact with a radiation field is the Hamiltonian[28,32]

$$\mathcal{H}=\omega a^\dagger a+\omega_0 I_z+H^d+\lambda\mathbf{I}\cdot(\hat{\epsilon}a+\hat{\epsilon}^* a^\dagger)\ . \tag{2.1}$$

The first term represents the energy of a radiation field having frequency ω, omitting the zero-point contribution. Here $a^\dagger$ and a are, respectively, the photon creation and annihilation operators. The second and third terms are the Zeeman and dipolar energies of the spin system, where $H^d\equiv\sum_m H_{2m}^d$ in general contains both secular ($m=0$) and nonsecular ($m\neq 0$) contributions. The fourth term in Eq. (2.1) describes the coupling between the spins and a single mode of the radiation field with po-

larization $\hat{\epsilon}$. In the case of near-resonant-spin locking, $\omega \simeq \omega_0$ in Eq. (2.1). For the example of Abragam and Goldman,[1] $\omega_0=0$, and the nonsecular terms are omitted.

Associated with the radiation field is a magnetic field[28]

$$\mathbf{H}_1=\mu(\hat{\epsilon}ae^{ikr}+\hat{\epsilon}^* a^\dagger e^{-ikr}) , \tag{2.2}$$

where

$$\mu=\left[\frac{\hbar\omega\mu_0}{2V}\right]^{1/2} . \tag{2.3}$$

For radio-frequency fields the wavelength of the radiation is sufficiently large compared to atomic dimensions to permit the approximation $e^{ikr}\simeq 1$. The constant μ essentially represents the magnetic field due to a photon. From the interaction of the magnetic moment of a spin with the magnetic field of the radiation, given by $\gamma\mathbf{H}_1\cdot\mathbf{I}$ we deduce that

$$\lambda=\gamma\mu , \tag{2.4}$$

where γ is the gyromagnetic ratio of the spins.

Before embarking on an analysis of the dynamics and equilibrium properties of a system described by the Hamiltonian of Eq. (2.1), it is instructive to compare it with the corresponding semiclassical Hamiltonian,

$$\mathcal{H}(t)=\omega_0 I_z+H^d+\omega_1\cos(\omega t+\phi)\,\hat{\epsilon}\cdot\mathbf{I} . \tag{2.5}$$

In particular, it is from this Hamiltonian, possibly including modifications of the third term to account for the modulation used to produce various pulse sequences, that the methods of spin thermodynamics in the rotating frame begin. One derives the semiclassical version from the fully quantum-mechanical Hamiltonian in a straightforward manner, first by a unitary transformation of Eq. (2.1) via $V(t)=e^{i\omega a^\dagger at}$ into an interaction representation with respect to the radiation field and second by taking the expectation value in a coherent state[33] of the radiation field. The choice of coherent state,

$$|\alpha\rangle=e^{-|\alpha|^2/2}\sum_k \frac{\alpha^k}{(k!)^{1/2}}|k\rangle , \tag{2.6}$$

where $|k\rangle$ are harmonic-oscillator eigenstates, is made because it is uniquely this state that corresponds to a classical stable electromagnetic wave.[32] Two important properties of these states are (i) $a|\alpha\rangle=\alpha|\alpha\rangle$, implying that coherent states are eigenstates of the annihilation operator, and (ii) $\langle\alpha|a^\dagger a|\alpha\rangle=|\alpha|^2=\bar{n}$, the average number of photons in the state.

Taking the expectation value over the oscillator operators and setting $\langle\alpha|a|\alpha\rangle=\bar{n}^{1/2}e^{-i\phi}$ yields a Hamiltonian,

$$\mathcal{H}(t)=\omega_0 I_z+H^d+\lambda\bar{n}^{1/2}(\hat{\epsilon}e^{-i(\omega t+\phi)}+\hat{\epsilon}^* e^{i(\omega t+\phi)})\cdot\mathbf{I} \tag{2.7}$$

that depends only on spin operators, but one that is also time dependent. Comparison of the Hamiltonians given by Eqs. (2.5) and (2.7) reveals that the intensity of the classical radio-frequency field is related to the coupling parameter by

$$\omega_1=2\lambda\bar{n}^{1/2} . \tag{2.8}$$

A complete discussion of the quantized radiation field, its interaction with matter, and the derivation of the appropriate Hamiltonians is available in the text by Loudon.[32]

B. Quasiconstants of the motion

We turn next to examine the combined Hamiltonian for the spin system and radiation field. For simplicity we choose the polarization to lie along the x axis. In a basis of states $|m_1\cdots m_N,n\rangle$, where m_i are the magnetic quantum numbers of the spins, the Hamiltonian of Eq. (2.1) has the form illustrated by Fig. 1. The kth diagonal block represents the energy of the spin system plus the energy of k photons. The off-diagonal blocks couple diagonal blocks differing by one photon in addition to mixing states within a given block.

When the coupling between the spins and the radiation field is weak, the off-diagonal blocks and the nonsecular dipole interaction

$$V=\lambda I_x(a^\dagger+a)+\sum_{m(\neq 0)} H^d_{2m} , \tag{2.9}$$

act as a perturbation on the unperturbed Hamiltonian,

$$\mathcal{H}_0=\omega a^\dagger a+\omega_0 I_z+H^d_{20} , \tag{2.10}$$

which has the energy-level diagram shown schematically in Fig. 2(a). In general, the unperturbed Hamiltonian supports three constants of the motion, the energy of the oscillator associated with the single-mode radiation field, the Zeeman energy, and the secular component of the dipole energy. Under the unperturbed Hamiltonian, the radiation field remains in its initial state over intermediate times, while the spins evolve to a quasistationary state characterized by independent temperatures for the Zee-

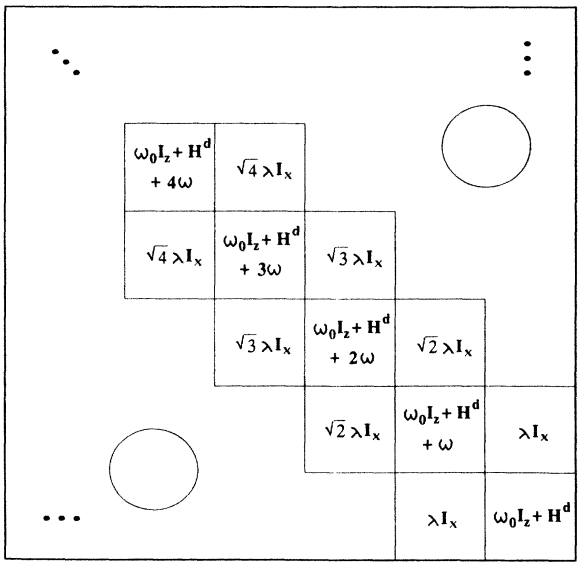

FIG. 1. Matrix representation of the coupled spin-radiation Hamiltonian in a basis of simultaneous eigenstates of I_z and $a^\dagger a$.

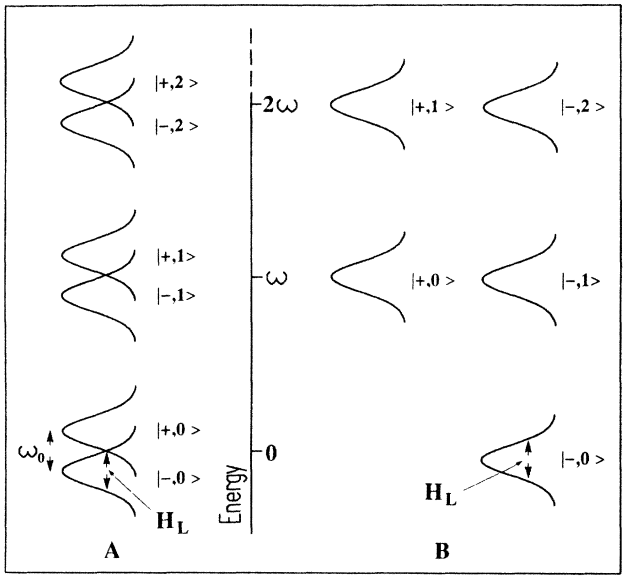

FIG. 2. (a) Simplified energy-level diagram of the spin-radiation Hamiltonian for $\omega_0 \ll H_L \ll \omega$. The corresponding eigenstates are labeled with + and − denoting the Zeeman state and $n=0,1,2$ denoting the number of photons. The Gaussian-shaped curves represent the broadening of the levels into a continuum by the many-body dipole interaction. (b) Simplified energy-level diagram of the spin-radiation Hamiltonian in the resonant case with $\omega=\omega_0$.

man and dipole thermodynamic reservoirs. Over long times the perturbation V mixes these reservoirs to a common temperature.

A special case occurs if $\omega \simeq \omega_0$. The energy levels of $\mathcal{H}_0$ in this situation are shown in Fig. 2(b). Note that because $\omega \simeq \omega_0$ it is the group of states $|M-k,n+k\rangle$, with $M=\sum_i m_i$ and $k=1,2,\ldots$, and not the states of a given diagonal block, that are nearly degenerate and are therefore most strongly coupled by the perturbation. It therefore becomes necessary to block diagonalize the Hamiltonian given by Eq. (2.1) in such a way that off-diagonal blocks do not couple nearly degenerate states of the unperturbed Hamiltonian. A group of nearly degenerate levels has an unperturbed energy approximately given by

$$\mathcal{H}|M-k,n+k\rangle=(M+n)\omega|M-k,n+k\rangle .$$

This suggests that $\sum_i m_i+n$ is an "almost good" quantum number and that the energy,

$$\mathcal{H}_A=\omega(a^\dagger a+I_z) , \tag{2.11}$$

is approximately conserved for the irradiated spin system. A second approximate constant of the motion that commutes with $\mathcal{H}_A$ is easily found; namely,

$$\mathcal{H}_B=\Delta I_z+H^d_{20}+(\lambda/2)(I_+a+I_-a^\dagger) . \tag{2.12}$$

Note the similarity of $\mathcal{H}_B$ to the usual truncated Hamiltonian in the rotating frame;[3,7] taking the expectation value of Eq. (2.12) in a coherent state $|\alpha\rangle$ produces the exact expression. Upon defining the remaining terms as

$$V'=(\lambda/2)(I_+a^\dagger+I_-a)+\sum_{m(\neq 0)} H^d_{2m} , \tag{2.13}$$

we have the alternate decomposition of the Hamiltonian

$$\mathcal{H}=\mathcal{H}_A+\mathcal{H}_B+V' . \tag{2.14}$$

When the coupling between the spins and the radiation field is moderately weak, the above procedure enables us to decompose the Hamiltonian into two quasiconserved energies plus a small noncommuting term. $\mathcal{H}_A$ represents the total number of quanta at frequency ω, that is, the energy of n photons plus the net energy of M spins aligned with a Zeeman field of $H_0=\omega/\gamma$. $\mathcal{H}_B$ represents the energy of the spins in an effective Zeeman field determined by the detuning of the radiation from the Larmor frequency and the component of the coupling between spins and radiation field that conserves the total number of quanta at frequency ω. It also contains the secular component of the dipole interaction between spins. The noncommuting term contains, in the language of the rotating-wave approximation, the counter-rotating component of the applied alternating magnetic field along with the nonsecular parts of the dipole interaction.

The analysis of the long-time behavior of a spin system in a resonant quantized radiation field is based on the decomposition of the Hamiltonian given by Eq. (2.14). The analysis of spins in a nonresonant field is based on the decomposition of the Hamiltonian given by Eq. (2.10). In order to take advantage of the forms (2.10) and (2.14), we require that the noncommuting terms represent a perturbation. Hence we limit the ensuing discussion to the interaction of spins with a moderately weak radio-frequency field.

III. QUASISTATIONARY STATE

A. Resonant radiation

If the noncommuting term V' is small, a collection of spins irradiated near its Larmor frequency evolves during short- and intermediate-time intervals under the unperturbed Hamiltonian $\mathcal{H}_A+\mathcal{H}_B$ which supports two approximate constants of the motion. As a consequence, the irradiated spins evolve to a quasistationary state that consists of two independent thermodynamic baths. In this section we explore the temperatures of the baths and the characteristics of the quasistationary state.

The analysis of the quasistationary state follows the standard principles of statistical mechanics.[3] Problems encountered in applications of spin thermodynamics to nonconservative semiclassical Hamiltonians do not arise in the present theory because the radiation field is explicitly included in the Hamiltonian. The treatment here differs somewhat from the usual applications of spin thermodynamics because of the need to include the harmonic oscillator degree of freedom in the thermodynamic description.

For the remainder of this section we ignore the effects that arise from the noncommuting terms in V'. Under the spin-temperature hypothesis, the system evolves to a quasistationary state (a true equilibrium state only if $V'=0$)

$$\rho_{qs}=Z^{-1}\exp(-\beta_A\mathcal{H}_A)\exp(-\beta_B\mathcal{H}_B)\ , \tag{3.1}$$

characterized by two inverse temperatures β_A and β_B. In the high-temperature approximation this expression simplifies to the form

$$\rho_{qs}=Z^{-1}\exp(-\beta_A\omega a^\dagger a)(1-\beta_A\omega I_z-\beta_B\mathcal{H}_B)\ . \tag{3.2}$$

Within this approximation the partition function is $Z=(1-e^{-\beta_A\omega})^{-1}\mathrm{Tr}\mathbf{1}$, where for N spins $\frac{1}{2}$, $\mathrm{Tr}\mathbf{1}=2^N$. The conservation of energy for each thermodynamic bath,

$$\langle\mathcal{H}_A\rangle=\mathrm{Tr}(\mathcal{H}_A\rho_i)=\mathrm{Tr}(\mathcal{H}_A\rho_{qs}) \tag{3.3}$$

and

$$\langle\mathcal{H}_B\rangle=\mathrm{Tr}(\mathcal{H}_B\rho_i)=\mathrm{Tr}(\mathcal{H}_B\rho_{qs})\ , \tag{3.4}$$

where ρ_i is the initial density matrix for the system, produces two equations from which to determine the two inverse temperatures needed to complete the description of the quasistationary state.

It remains to define the initial state of the spins and radiation field. We assume that the spins interact initially with a classical electromagnetic wave and therefore choose a coherent state $|\alpha\rangle$ as the initial state of the radiation field. The spin-locking experiments[3,7] typically begin with a 90° pulse applied to a sample of spins in a large static field and at equilibrium with a lattice at inverse temperature β_i; therefore

$$\rho_i=(\mathrm{Tr}\mathbf{1})^{-1}(1-\beta_i\omega_0 I_x)\,|\alpha\rangle\langle\alpha| \tag{3.5}$$

is the initial density matrix for the combined spin-radiation system.

The energy of the Zeeman-radiation reservoir in the initial state is

$$\mathrm{Tr}(\mathcal{H}_A\rho_i)=\omega\,|\alpha|^2=\bar{n}\omega\ , \tag{3.6}$$

whereas in the quasistationary state it is

$$\mathrm{Tr}(\mathcal{H}_A\rho_{qs})=\omega(e^{\beta_A\omega}-1)^{-1}-\beta_A\omega^2N/4-\beta_B\omega\Delta N/4\ . \tag{3.7}$$

Equating (3.6) and (3.7), and expanding the exponential function to first order, yields a quadratic equation

$$(\beta_A\omega)^2N/4+(\beta_A\omega)(\bar{n}+\beta_B\Delta N/4+\tfrac{1}{2})-1=0 \tag{3.8}$$

for the inverse temperature β_A. This equation has one relatively large negative root and one positive root lying close to zero. Because of the oscillator degree of freedom, only positive temperatures are physically meaningful. Using Newton's method to approximate the positive root, with an initial guess of zero, gives

$$\beta_A\omega\simeq(\bar{n}+\beta_B\Delta N/4+\tfrac{1}{2})^{-1}\ . \tag{3.9}$$

Even in a weak radio-frequency field the temperature is dominated by the photon number; for example, Eqs. (2.4) and (2.8) show that a 1-Gauss field at 100 krad/s has 4×10^{20} photons in a volume of 1 cm^3. An exception occurs if the detuning is large and the initial spin temperature is cold that serves to raise the quasistationary temperature when the radiation is above the Larmor frequency and lower it when the field is below resonance.

In order to determine the temperature of the dipole-effective field bath, we equate its energy in the initial state,

$$\mathrm{Tr}(\mathcal{H}_B\rho_i)=-\beta_i\omega_0\lambda\bar{n}^{1/2}\cos(\phi)N/4\ , \tag{3.10}$$

to the energy

$$\mathrm{Tr}(\mathcal{H}_B\rho_{qs})=-[\beta_B(\Delta^2+H_L^2)+\beta_A\omega\Delta+\beta_B\lambda^2/(\beta_A\omega)]N/4 \tag{3.11}$$

that it has in the quasistationary state. Here $H_L\equiv[\mathrm{Tr}(H_{20}^d)^2/\mathrm{Tr}(I_z^2)]^{1/2}$ represents the local field produced by the spins. After inserting the value for $\beta_A\omega$ given by Eq. (3.9) into Eq. (3.11), we obtain the quadratic equation

$$(\beta_B\lambda)^2\Delta N/4+\beta_B(\Delta^2+H_L^2+\bar{n}\lambda^2)-\beta_i\omega_0\lambda\bar{n}^{1/2}\cos(\phi)=0 \tag{3.12}$$

for the inverse temperature β_B. This has a continued-fraction solution given by

$$\beta_B=\frac{\beta_i\omega_0\lambda\bar{n}^{1/2}\cos(\phi)}{\Delta^2+H_L^2+\lambda^2\bar{n}+\lambda^2\beta_B\Delta N/4}\ . \tag{3.13}$$

The first-order solution, obtained by setting $\beta_B=0$ on the right-hand side of Eq. (3.13), is identical to the standard result found by applying spin thermodynamics in the rotating frame and agrees with the experimental facts.[3,7]

One could argue against this line of reasoning by pointing out that the Zeeman-radiation energy may continue to evolve coherently over the same time period that the dipole-effective field energy reaches quasiequilibrium. If this is the case, the density matrix of Eq. (3.1) is not valid because the Zeeman-radiation energy could not yet be characterized by a temperature. In fact, it would have nonzero off-diagonal elements unlike ρ_{qs}. However, this does not alter the conclusions regarding the dipole-effective field reservoir. Because the two energies evolve independently under $\mathcal{H}_0$, the quasistationary temperature β_B depends only on how the energy is partitioned, on average, between the Zeeman-radiation and dipole-effective field reservoirs in the initial state. In turn, this depends only on the expectation value, i.e., diagonal elements, of the Zeeman-radiation energy. Since the diagonal matrix elements of ρ_{qs} are constructed to conserve the Zeeman-radiation energy, the analysis produces in Eq. (3.13) the correct result.

In summary we find that near-resonant radio-frequency irradiation of a spin system strongly couples the radiation field and Zeeman energies and causes them to evolve as a single unit to a quasistationary state having a very high temperature. It is the large number of photons required to generate even a weak alternating magnetic field that is the cause of the elevated temperature. Evolving quasi-independently from this bath is the coupled spin system in an effective field determined by the intensity and detuning of the applied field. The energy of this thermodynamic bath is identical to the energy of the spin system

in the rotating frame. It reaches a quasistationary temperature much lower than the Zeeman-radiation bath. In fact, the temperature is lower than the initial value because the major portion of the static magnetic field ω_0 couples strongly to the radiation field, and therefore the spin system evolves under $\mathcal{H}_B$ in a relatively weak effective magnetic field.

B. Nonresonant radiation

In the second example we consider the evolution of spin system, initially prepared in a dipole-ordered state,

$$\rho_i=(\mathrm{Tr}1)^{-1}(1-\beta_i H_{20}^d)\,|\,\alpha\rangle\langle\alpha\,|\ , \tag{3.14}$$

under irradiation by a radio-frequency field far above resonance. As in the previous example the initial state of the radiation field is taken to be a coherent state. The appropriate Hamiltonian, including the radiation field and a small static magnetic field, is given by Eq. (2.1) with $\omega_0 \ll \omega$ and with $\hat{\epsilon}$ lying along the x axis. In the actual experimental situation, the off-resonant irradiation is carried out in the rotating frame, and therefore the nonsecular terms of the dipole interaction are absent.[34] Accordingly they are omitted from the analysis.

Over intermediate times we ignore the effects of the perturbation V and consider the quasistationary state established under the unperturbed Hamiltonian given by Eq. (2.10). Although there are three constants of the motion under $\mathcal{H}_0$, characterizing this state is simpler than in the resonant case. The initial coherent state of the radiation field commutes with all except the oscillator energy component of $\mathcal{H}_0$. In particular it evolves independently from the spin system. Under $\mathcal{H}_0$, the expectation value of the magnetic field associated with the coherent state,

$$\begin{aligned}\langle\omega_1(t)\rangle&=\mathrm{Tr}[\lambda I_x(a^\dagger+a)e^{-i\omega a^\dagger at}\,|\,\alpha\rangle\langle\alpha\,|\,e^{i\omega a^\dagger at}]\\&=2\lambda\bar{n}^{1/2}\cos(\omega t+\phi)\ ,\end{aligned} \tag{3.15}$$

has the time evolution of a free classical electromagnetic wave.

Under $\mathcal{H}_0$, the spins evolve independently from the radiation field because the spin operators commute with $\omega a^\dagger a$. In accordance with the principles of spin thermodynamics,[3] they evolve to a quasistationary state,

$$\rho_{\mathrm{qs}}=Z^{-1}(1-\beta_C\Delta I_z-\beta_B H_{20}^d)\ , \tag{3.16}$$

which consists of independent Zeeman and dipolar thermodynamic baths. The quasistationary temperatures can be deduced by inspection. As the initial-dipolar state commutes with $\mathcal{H}_0$, the dipolar temperature remains constant at $\beta_B=\beta_i$. The Zeeman energy also commutes with $\mathcal{H}_0$; however, because the energy of the Zeeman bath initially equals zero, $\beta_C=0$ also. This situation differs from the near-resonant case considered above. In that case, the radiation field couples with the Zeeman energy on a short-time scale, leaving the spins to evolve quasi-independently in a small static transverse magnetic field. The order parameter defined by

$$\eta=\mathrm{Tr}(H_{20}^d\rho_{\mathrm{qs}})/\mathrm{Tr}(H_{20}^d\rho_i) \tag{3.17}$$

equals unity for the quasistationary state. This behavior is observed in experiments over intermediate times; however η decays at long times.[1] The reason for the decay is the subject of the next section.

IV. EQUILIBRIUM STATE

A casual inspection of the noncommuting perturbation V or V' gives the impression that it has only a minor effect on the evolution of the spin-radiation system. When the coupling λ between spins and radiation field is small, the perturbation introduces only small shifts to the energy levels of $\mathcal{H}_0$. If care has been taken that the perturbation does not connect nearly degenerate states then it only mixes small amounts of the other basis vectors into a given eigenstate of $\mathcal{H}_0$. The latter effect, though small, is important. The admixture of other states into a given eigenstate means that the state no longer is a simultaneous eigenstate of the individually conserved energies under $\mathcal{H}_0$. In turn, this implies that the quasistationary state, with its multiple-bath structure, is not appropriate as the equilibrium state; rather the equilibrium state

$$\rho_{\mathrm{eq}}=Z^{-1}\exp(-\beta_{\mathrm{eq}}\mathcal{H}) \tag{4.1}$$

is characterized by a single common temperature. Physically the perturbation V or V' provides a thermal link that mixes the Zeeman, dipolar, and radiation thermodynamic baths to a common temperature. Because the coupling constant λ is small, the mixing process takes a long time (the dynamics are investigated in Sec. VI). It is this fact that gives significance to the concept of the quasistationary state. Given sufficient time, however, the system will decay to the equilibrium state indicated by Eq. (4.1)

The analysis of the equilibrium state proceeds essentially in the same manner for resonant and nonresonant irradiation; only the values of ω_0 and the initial state differ in the two examples. We begin by making a perturbation expansion of the density matrix following the procedure of Feynman.[35] The expansion is based on the property that the density matrix satisfies the differential equation

$$\frac{d\rho(\beta)}{d\beta}=-\mathcal{H}\rho(\beta) \tag{4.2}$$

with respect to the inverse temperature. For the purpose of this section, we write

$$\mathcal{H}=\mathcal{H}_0+V \tag{4.3}$$

with $\mathcal{H}_0$ and V given by Eqs. (2.10) and (2.9), respectively. Transformation of the density matrix into an "interaction frame" via

$$\rho(\beta)=e^{-\beta\mathcal{H}_0}\tilde{\rho}(\beta) \tag{4.4}$$

yields an equation

$$\frac{d\tilde{\rho}(\beta)}{d\beta}=-e^{\beta\mathcal{H}_0}Ve^{-\beta\mathcal{H}_0}\tilde{\rho}(\beta) \tag{4.5}$$

which is amenable to an approximate solution. The mutual commutativity of the three terms comprising $\mathcal{H}_0$ per-

mits us to factor

$$e^{-\beta\mathcal{H}_0}=e^{-\beta H^d_{20}}e^{-\beta\omega_0 I_z}e^{-\beta\omega a^\dagger a}\ .$$

Two of the transformations are easily accomplished by taking advantage of

$$e^{\beta\omega_0 I_z}I_x e^{-\beta\omega_0 I_z}=I_x\cosh(\beta\omega_0)+iI_y\sinh(\beta\omega_0)\ ,$$

$$e^{\beta\omega a^\dagger a}a e^{-\beta\omega a^\dagger a}=e^{-\beta\omega}a\ ,$$

etc. Thus, Eq. (4.5) becomes

$$\frac{d\tilde{\rho}(\beta)}{d\beta}=-\left\{\lambda[\tilde{I}_x\cosh(\beta\omega_0)+i\tilde{I}_y\sinh(\beta\omega_0)]\times(e^{-\beta\omega}a+e^{\beta\omega}a^\dagger)+\sum_{m(\neq 0)}e^{\beta\omega_0 m}\tilde{H}^d_{2m}\right\}\tilde{\rho}(\beta)\ , \tag{4.6}$$

with

$$\tilde{I}_x\equiv e^{\beta H^d_{20}}I_x e^{-\beta H^d_{20}}$$

and similarly for $\tilde{I}_y$ and $\tilde{H}^d_{2m}$.

At this point we invoke the high-temperature limit to approximate the hypertrigonometric and exponential functions in Eq. (4.6) and solve the equation in a Piccard series. The series converges rapidly for small β and produces

$$\tilde{\rho}(\beta)\simeq 1-\beta\left[\lambda I_x(a+a^\dagger)+\sum_{m(\neq 0)}H^d_{2m}\right]\ . \tag{4.7}$$

Therefore the perturbation expansion for the equilibrium density matrix is

$$\rho_{\rm eq}=Z^{-1}e^{-\beta_{\rm eq}\mathcal{H}_0}\left[1-\beta_{\rm eq}\left[\lambda I_x(a+a^\dagger)+\sum_{m(\neq 0)}H^d_{2m}\right]\right]\simeq Z^{-1}e^{-\beta_{\rm eq}\omega a^\dagger a}\{1-\beta_{\rm eq}[\omega_0 I_z+\lambda I_x(a+a^\dagger)+H^d]\}\ . \tag{4.8}$$

The conservation of energy provides a means for determining the temperature needed to complete the description of the equilibrium state.

A. Resonant radiation

The initial state of the cw spin-locking example is given by Eq. (3.5). Its energy is

$$\mathrm{Tr}(\mathcal{H}\rho_i)=\bar{n}\omega-\beta_i\omega_0\lambda\bar{n}^{1/2}\cos(\phi)N/2\ , \tag{4.9}$$

whereas the energy of the equilibrium state is

$$\mathrm{Tr}(\mathcal{H}\rho_{\rm eq})=\omega(e^{\beta_{\rm eq}\omega}-1)^{-1}-\beta_{\rm eq}(\omega_0^2+H_D^2)N/4-\lambda^2 N/(2\omega)\ , \tag{4.10}$$

with $H_D\equiv[\mathrm{Tr}(H^d)^2/\mathrm{Tr}(I_z^2)]^{1/2}$. The conservation of energy yields the quadratic equation,

$$\beta_{\rm eq}^2(\omega_0^2+H_D^2)N/4+\beta_{\rm eq}[\bar{n}\omega-\beta_i\omega_0\lambda\bar{n}^{1/2}\cos(\phi)N/2+\lambda^2 N/(2\omega)]-1=0\ , \tag{4.11}$$

for the equilibrium inverse temperature. The solution of Eq. (4.11) depends on the relative size of the initial energy of the radiation field versus the initial energy of the spin system.

In the limit of large photon number, for which

$$\bar{n}^{1/2}/N>\beta_i\omega_0\lambda\cos(\phi)/(2\omega)\ , \tag{4.12}$$

Eq. (4.11) has two real roots; one is negative, but relatively large in absolute value while the other is positive and lies close to zero. The negative root is physically untenable. The use of Newton's method, with an initial guess of $\beta_{\rm eq}=0$, to determine the positive root leads to the first-order approximation of

$$\beta_{\rm eq}\simeq[\bar{n}\omega-\beta_i\omega_0\lambda\bar{n}^{1/2}\cos(\phi)N/2]^{-1}\ , \tag{4.13}$$

for the equilibrium inverse temperature. The large photon number limit holds under normal experimental conditions. In a typical high-field NMR, for example a 1-cm^3 sample containing $\simeq 5\times 10^{22}$ fluorine spins in a 100-MHz static field at room temperature and irradiated on resonance, condition (4.12) requires that $\bar{n}>1.1\times 10^9$ photons. Equivalently, this requires that the applied alternating magnetic field exceed $\omega_1/\gamma>1.4\times 10^{-4}$ G; thus, the large photon limit is obtained with a small field indeed. In a very low intensity radiation field, for which the initial spin energy exceeds the radiation energy and condition (4.12) does not hold, Eq. (4.11) has a relatively large positive root and a negative root lying close to zero. The physically acceptable solution is

$$\beta_{\rm eq}\simeq\frac{\beta_i\omega_0 2\lambda\bar{n}^{1/2}\cos(\phi)-4\bar{n}\omega/N}{\omega_0^2+H_D^2}\ . \tag{4.14}$$

A plot of the ratio of the equilibrium inverse temperature to the quasistationary value for the dipole-effective field, β_B versus photon number in Fig. 3 illustrates the predicted transition from low to large photon number. I have chosen a static magnetic field of $\omega_0=100$ krad/s and a low initial spin temperature of $\beta_i^{-1}=0.1$ K (however, one satisfying the high-temperature approximation) for this example. The small static field is chosen because, as shown in Sec. VI, it takes much too long for the system to reach the equilibrium state for a typical high-field magnet. Reducing the static field decreases the relaxation time, however, it also drastically reduces the critical value of $\bar{n}$ separating high and low photon number limits, a problem that is rectified by choosing a low initial spin temperature.

As Fig. 3 demonstrates, the quasistationary inverse temperature of the dipole-effective field bath increases with the intensity of the radiation field (proportional to $\bar{n}^{1/2}$) in accordance with the predictions spin thermodynamics applied in the rotating frame and in agreement with experimental measurements. Eventually, however, the dipole-effective field bath heats up due to coupling with the Zeeman-radiation bath. For very low-intensity radiation fields, the heating is relatively ineffective, i.e., $\beta_{\rm eq}/\beta_B$ is slightly less than unity and is primarily due to coupling of energy to the Zeeman part of the Zeeman-radiation bath. In the vicinity of the critical photon number, corresponding to $\omega_1/\gamma\simeq 6\times 10^{-5}$ G in Fig. 3,

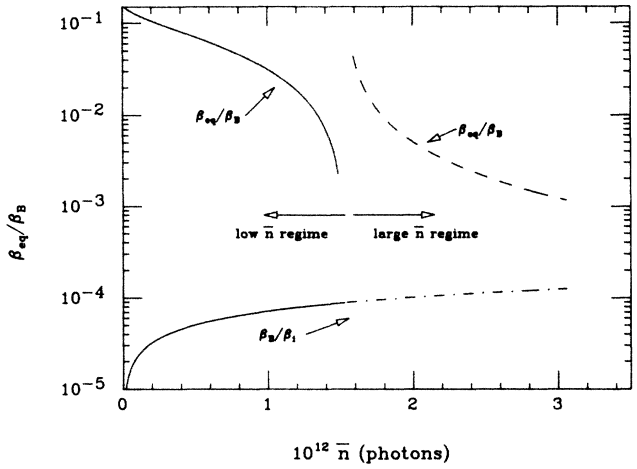

FIG. 3. The ratio of the equilibrium to quasistationary spin temperature as a function of photon number in the critical region that separates large and low photon number regimes. These curves apply to resonant irradiation of a spin system in a large static field initially prepared by a 90° pulse. The two curves marked β_{eq}/β_B illustrate the two branches obtained from the approximate solution for the positive root of the quadratic equation for β_{eq}. The exact solution varies continuously between these branches. Shown for comparison is the ratio of the quasistationary spin temperature to its initial value. For the purpose of illustration $\omega_0=100$ krad/s, $\Delta=0$, $H_L=30$ krad/s, $(\beta_i)^{-1}=0.1$ K, and $\lambda=6.5\times10^{-7}$ rad/s.

β_{eq} decreases rapidly with applied field. Above the critical photon number, at a more typical field of $\omega_1/\gamma\simeq1$ G, the photon energy dominates the expression for the expression for the equilibrium temperature. The conclusion is that given sufficient time, the spin system irradiated under typical magnetic-resonance conditions is heated from the quasistationary temperature to the much higher temperature of the radiation field. A consequence of the heating is a decay of observables such as the magnetization of the spins.

B. Nonresonant radiation

We now consider the fate, at long times, of a dipole-coupled spin system initially prepared in a dipole ordered state and evolving under irradiation by a low-intensity alternating magnetic field far above resonance. Besides the difference in initial state, this example differs from the previous one in that the static magnetic field, if existent, is weak; $\omega_0\ll\omega$. It has, however, many features in common with the previous example; for instance, the analysis proceeds in essentially the same manner.

The initial density matrix for the dipole-ordered spin-radiation system is given by Eq. (3.14). The energy of this state is

$$\mathrm{Tr}(\mathcal{H}\rho_i)=\bar{n}\omega-\beta_i H_L^2 N/4\ , \tag{4.15}$$

as compared to the energy of the equilibrium state given by Eq. (4.10) with H_D replaced by H_L. Equating initial and equilibrium energies yields

$$\beta_{eq}^2(\omega_0^2+H_L^2)N/4 +\beta_{eq}[\bar{n}\omega-\beta_i H_L^2 N/4+\lambda^2 N/(2\omega)]-1=0\ , \tag{4.16}$$

an equation very similar to the corresponding equation for resonant irradiation in high field. This equation, too, has different solutions depending upon the relative values of the initial energy in the radiation field versus the dipolar bath. In the limit of large photon number, for which

$$\bar{n}/N>\beta_i H_L^2/(4\omega)\ , \tag{4.17}$$

the acceptable root for the equilibrium inverse temperature is approximately

$$\beta_{eq}\simeq(\bar{n}\omega-\beta_i H_L^2 N/4)^{-1}\ . \tag{4.18}$$

As Fig. 4 shows, the large photon number limit is achieved for $\bar{n}>8.5\times10^{15}$ photons, that is for an applied field of $\omega_1/\gamma>0.005$ G, in the case that the local field is $H_L=30$ krad/s and $\beta_i^{-1}=0.1$ K. With higher initial spin temperatures the critical field is even lower. When the intensity of the applied radiation field does not satisfy Eq. (4.17), the two roots of Eq. (4.16) change sign and the physically acceptable solution for the equilibrium inverse temperature in the low photon number regime is approximately given by

$$\beta_{eq}\simeq\frac{\beta_i H_L^2-4\bar{n}\omega/N}{\omega_0^2+H_L^2}\ . \tag{4.19}$$

The transition between low and high photon number regimes is very sharp, as evident from Fig. 4. Below a critical intensity of the radiation field, the spin system

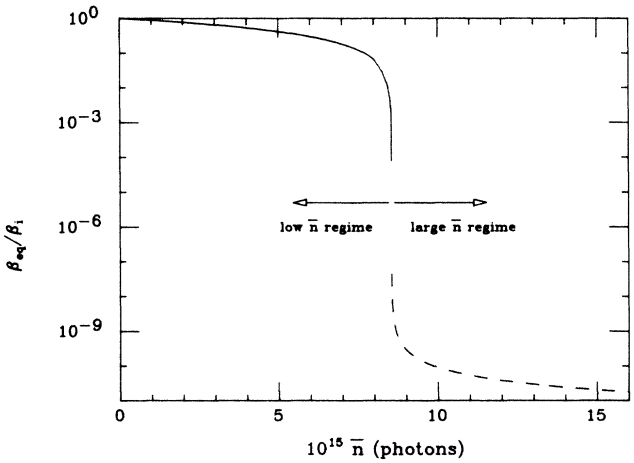

FIG. 4. The ratio of the equilibrium to initial (=quasistationary) spin temperature as a function of photon number in the critical region that separates large and low photon number regimes. These curves apply to weak irradiation far above resonance of an initially-dipole-ordered spin system. The solid and dashed curves illustrate the two branches obtained from the approximate solution for the positive root of the quadratic equation for β_{eq}. The exact solution varies continuously between these branches. For the purpose of illustration $\omega_0=0$, $\omega=100$ krad/s, $H_L=30$ krad/s, $(\beta_i)^{-1}=0.1$ K, and $\lambda=6.5\times10^{-7}$ rad/s.

remains essentially at its quasistationary temperature (equal in this case to the initial temperature). Above the critical applied field, at intensities typically employed in experiments, the spin system evolves from a quasistationary state at low temperature to an equilibration state with a considerably higher temperature. At this temperature, the dipolar order parameter $\eta=\beta_{eq}/\beta_i$ has decayed from a quasistationary value of one to nearly zero. The equilibration of the spins with the radiation field to the temperature of the latter provides an explanation for the saturation, discussed by Abragam and Goldman,[1] for the weakly irradiated, dipole ordered state.

V. COMPARISON TO SEMICLASSICAL RESULTS

The two examples considered in this paper are well-known problems in magnetic resonance. The preparation of a spin system by a 90° pulse into an initial state with magnetization transverse to a strong static field, followed by irradiation of spins near their Larmor frequency by an alternating field polarized in the direction of the magnetization is known as spin locking. The standard derivation of the relationship between the magnetization that remains at long times and the intensity of the irradiating field is via spin thermodynamics applied in the rotating frame.[2,3,7]

The spin-locking problem is described in the laboratory frame by the semiclassical Hamiltonian given by Eq. (2.5). The absorption of energy by the near resonance of the perturbation prohibits the direct application of spin-thermodynamic principles. However, in a frame rotating about the z axis of the laboratory frame at the Larmor frequency the Hamiltonian becomes

$$\mathcal{H}_I(t)=\Delta I_z+H_{20}^d+\frac{\omega_1}{2}[1+\cos(2\omega t)]I_x - \frac{\omega_1}{2}\sin(2\omega t)I_y+\sum_{m(\neq 0)} e^{im\omega t}H_{2m}^d , \quad (5.1)$$

and the oscillations of the time-dependent terms lie far above resonance.

In calculating the evolution of the density in the rotating frame one takes advantage of the periodic time dependence of $\mathcal{H}_I(t)$ and Floquet's theorem[36,37] to write

$$\rho_I(n\tau)=\exp(-i\bar{H}n\tau)\rho_I(0)\exp(i\bar{H}n\tau) \quad (5.2)$$

after n periods of τ. The Magnus expansion[15] provides a convenient means to determine the effective Hamiltonian $\bar{H}$. The great advantage of Eq. (5.2) is that is provides a conservative model for the stroboscopic evolution of the spin system.

The leading term in the Magnus expansion is the *average Hamiltonian*

$$\bar{H}^{(1)}=\frac{1}{\tau}\int_0^\tau \mathcal{H}_I(t)dt=\Delta I_z+H_{20}^d+\frac{\omega_1}{2}I_x , \quad (5.3)$$

also known as the truncated Hamiltonian.[5-7] We postulate that the density matrix in Eq. (5.2) evolves to the equilibrium state

$$\rho_{eq}=1-\beta_{eq}\bar{H} . \quad (5.4)$$

A comparison of the energy of the initial state $\rho_i=1-\beta_i\omega_0 I_x$ to the energy of the equilibrium state yields the expression

$$\beta_{eq}=\frac{1}{2}\frac{\beta_i\omega_0\omega_1}{\Delta^2+H_L^2+\omega_1^2/4} \quad (5.5)$$

for the equilibrium inverse temperature. Spin locking takes its name from the fact that if $\omega_1 \gg H_L$, the equilibrium magnetization approximately equals the initial value. Except for couching the derivation of Eq. (5.5) in the language of Haeberlen and Waugh[5] of the average Hamiltonian theory, this is essentially the procedure employed by Redfield.[2]

The interesting feature of the "equilibrium" temperature calculated in the rotating frame is that it is identical to the first-order expression for the *quasistationary* temperature of the dipole-effective field bath given by Eq. (3.13) (with $\phi=0$). The semiclassical calculation does not predict the decay of this state because it depends only on quantum-mechanical expectation values of the oscillator degree of freedom and therefore there is no Zeeman-radiation bath with which the spin system can equilibrate. Because the Magnus expansion does not converge when Eq (1.1) is not satisfied,[23-25] in this case when $m\omega$ does not lie above all resonances of the spin system, the AHT also introduces the following error.[22] The averaging process eliminates in Eq. (5.1) terms oscillating at $m\omega$, terms that are responsible for absorption of energy by the few levels in the dipolar line shape that are separated by $m\hbar\omega$. It is this absorption, albeit very weak, that leads at long times to the equilibrium between the Zeeman-radiation bath and the dipole-coupled spins.

Predicting the equilibrium temperature in the experiment described by Abragam and Goldman via the semiclassical approach follows the procedure used above. The Hamiltonian, assuming zero static field, is simply $\mathcal{H}(t)=H_{20}^d+\omega_1\cos(\omega t)I_x$. Further transformation to an interaction frame is not necessary because of the assumption that $\omega \gg H_L$. Application of the average Hamiltonian theory yields an effective Hamiltonian $\bar{H}^{(1)}=H_{20}^d$ to first order. From an initial state $\rho_i=1-\beta_i H_{20}^d$ and assuming an equilibrium state $\rho_{eq}=1-\beta_{eq}\bar{H}^{(1)}$, we conclude that the equilibrium temperature is $\beta_{eq}=\beta_i$.

This reproduces the result obtained in Sec. III for the quasistationary temperature of the dipole bath but not its equilibrium temperature. Again the reasons are that the semiclassical description has no provision for an equilibrium between the spins and the radiation field and that the AHT ignores absorption at frequency ω.

VI. RELAXATION DYNAMICS

The conclusion that a spin system coupled to a radiation field eventually reaches equilibrium with the radiation field naturally raises the question of how long it takes the system to reach equilibrium. The spin system typically evolves to the quasistationary state in a time approximately a few time constants T_2 in duration. The evolution of the system over this time scale conserves in-

dividually the energies $\mathcal{H}_A$ and $\mathcal{H}_B$ that comprise the unperturbed Hamiltonian $\mathcal{H}_0=\mathcal{H}_A+\mathcal{H}_B$. During the time T_2 the off-diagonal elements of the initial density matrix associated with the spin degrees of freedom decay to zero; thus, we can characterize the thermodynamic bath containing the energy of the spins $\mathcal{H}_B$ with a quasistationary temperature β_B. As discussed in Sec. III, the off-diagonal elements of the initial density matrix corresponding to the radiation field may not decay to zero on the same time scale of T_2; however, we can assign the diagonal component a temperature β_A. In effect, we assume that the evolution of the spin-radiation field over intermediate times is described by a density matrix of the form[38]

$$\rho_{qs}(t)=Z^{-1}\exp[-\beta_A(t)\mathcal{H}_A]\exp[-\beta_B(t)\mathcal{H}_B]+\rho_{od}(t)$$
$$\simeq Z^{-1}\exp[-\beta_A(t)\omega a^\dagger a][1-\beta_A(t)(\mathcal{H}_A-\omega a^\dagger a)-\beta_B(t)\mathcal{H}_B]+\rho_{od}(t)\ , \tag{6.1}$$

where $\rho_{od}(t)$ represents the off-diagonal elements of the density matrix that persist beyond a time period of a few T_2.

The time dependence of the quasistationary temperatures reflects the fact that the quasistationary state continues to evolve under the full Hamiltonian

$$\mathcal{H}=\mathcal{H}_0+V\ . \tag{6.2}$$

The relatively small size of the perturbation V (or V'), implies that it does not contribute rapid oscillations to the time dependence of $\rho_{qs}(t)$. Nor does it significantly alter the energy of either $\mathcal{H}_A$ or $\mathcal{H}_B$. Instead, its main function is as a thermal link between the two thermodynamics baths. It allows the exchange of energy between $\mathcal{H}_A$ and $\mathcal{H}_B$, whereby the quasistationary temperatures evolve slowly to a common equilibrium value $\beta_A(\infty)=\beta_B(\infty)=\beta_{eq}$, and the off-diagonal elements of the density matrix decay to $\rho_{od}(\infty)=0$. The purpose of this section is to examine the rate at which β_A and β_B approach their equilibrium values.

One can determine the rate of approach to equilibrium by a variety of methods. A simple procedure would be to estimate a transition rate for the exchange of energy between $\mathcal{H}_A$ and $\mathcal{H}_B$ from the Fermi Golden rule. A more sophisticated procedure would employ the memory-function technique of Deninghaus and Mehring[39] to describe the evolution of the quasistationary temperatures. I employ a method of intermediate sophistication that is related to the Provotorov theory of saturation.[31] The text by Goldman[3] gives a lucid discussion on the use of the Provotorov theory with the spin-temperature hypothesis. The theory is based on a second-order perturbation solution for the evolution of the density matrix. It is appropriate in the present circumstances because of the weak nature of the coupling introduced by the perturbation V.

In the spirit of the perturbation treatment, we write the evolution of the density matrix

$$\rho(t)=e^{-i(\mathcal{H}_0+V)t}\rho(0)e^{i(\mathcal{H}_0+v)t} \tag{6.3}$$

in the approximate form

$$\rho(t)=e^{-i\mathcal{H}_0t}\left[\rho(0)-i\int_0^t dt'[V(t'),\rho(0)]-\int_0^t dt'\int_0^{t'}dt''[V(t'),[V(t''),\rho(0)]]+\cdots\right]e^{i\mathcal{H}_0t}\ , \tag{6.4}$$

with the definition

$$V(t')=e^{i\mathcal{H}_0t'}Ve^{-i\mathcal{H}_0t'}\ .$$

We will monitor the evolution of the quasistationary temperature by the change in time of the average energy associated with $\mathcal{H}_A$,

$$\langle\mathcal{H}_A(t)\rangle=\mathrm{Tr}[\mathcal{H}_A\rho_{qs}(t)]\ , \tag{6.5}$$

and similarly for $\mathcal{H}_B$. Because $\mathcal{H}_A$ and $\mathcal{H}_B$ commute with $\mathcal{H}_0$, only the term in parenthesis on the right side of Eq. (6.4) contributes to the time dependence of $\langle\mathcal{H}_A(t)\rangle$; thus

$$\langle\mathcal{H}_A(t)\rangle\simeq\mathrm{Tr}[\mathcal{H}_A\rho_{qs}(0)]-i\int_0^t dt'\,\mathrm{Tr}\{\mathcal{H}_A[V(t'),\rho_{qs}(0)]\}-\int_0^t dt'\int_0^{t'}dt''\,\mathrm{Tr}\{\mathcal{H}_A[V(t'),[V(t''),\rho_{qs}(0)]]\}\ . \tag{6.6}$$

The diagonal portion of ρ_{qs} also commutes with $\mathcal{H}_0$ implying that its contribution to the first-order term in Eq. (6.6) is zero; thus, we must go to second order to determine the evolution of $\beta_A(t)$ and $\beta_B(t)$. As is typical of perturbation theories, the first-order contribution from the off-diagonal portion of the density matrix is comparable in size to the second-order contribution from the diagonal portion. We will examine the first-order contribution of ρ_{od} to the evolution of $\langle\mathcal{H}_A(t)\rangle$ below; but we omit ρ_{od} from the second-order term.

The commutativity of $\rho_d(t)$, the diagonal part of the density matrix, and $\mathcal{H}_A$ and $\mathcal{H}_0$ enables a straightforward evaluation of one integral of the second-order term. This result combined with the first-order contribution from ρ_{od} yields

$$\langle \mathcal{H}_A(t)\rangle - \langle \mathcal{H}_A(0)\rangle = -\int_0^t dt'(t-t')\mathrm{Tr}\{\mathcal{H}_A[V(t'),[V,\rho_d(0)]]\} - i\int_0^t dt'\,\mathrm{Tr}\{\mathcal{H}_A[V(t'),\rho_{\mathrm{od}}(0)]\}\ . \tag{6.7}$$

A similar equation holds for $\langle \mathcal{H}_B(t)\rangle$. Our concern here is with the evolution of $\langle \mathcal{H}_A(t)\rangle$ over time periods $t \gg T_2$, but with t sufficiently short that the quasistationary temperatures do not vary significantly. Because of the many-body nature of the dipolar coupling between spins, coherence in $V(t)$ is rapidly lost, and the contribution to the integrals in Eq. (6.7) from $t \gg T_2$ is negligible. This permits us to replace the upper limits of integration with $t \to \infty$ and to replace $\rho_{\mathrm{qs}}(0)$ by $\rho_{\mathrm{qs}}(t)$. It also allows us to approximate $t-t' \simeq t$. The average rate of change in $\langle \mathcal{H}_A(t)\rangle$ over a time t long compared to T_2 is found by dividing Eq. (6.7) by t; thus,

$$\frac{d}{dt}\langle \mathcal{H}_A(t)\rangle \simeq -\int_0^\infty dt'\,\mathrm{Tr}\{[\mathcal{H}_A,V(t')][V,\rho_d]\} - i/t\int_0^\infty dt'\,\mathrm{Tr}\{\mathcal{H}_A[V(t'),\rho_{\mathrm{od}}]\}\ , \tag{6.8}$$

represents the approximate equation of motion for the quasiconserved energy $\mathcal{H}_A$. Because of the $1/t$ factor, the second term of Eq. (6.8) generally makes a negligible contribution to the evolution of the quasistationary energy. However, in light of the fact that the radiation field may contribute off-diagonal elements to the density matrix that persist over times longer than T_2 we will consider separately the contribution of the second term in the application of Eq. (6.8) to the examples below.

A. Nonresonant radiation

The quasistationary state of an initially-dipole-ordered spin system irradiated far above resonance is somewhat of a special case because it is the same as the initial state. That is, the dipole-ordered spins remain in that state under $\mathcal{H}_0$ and the radiation field, initially in a coherent state, evolves as a coherent state under $\mathcal{H}_0$. Nonetheless, it is useful to assume that the spin-radiation system evolves to equilibrium via a quasistationary state of the form (6.1) that has separate temperatures to describe the spin and radiation energies and includes an off-diagonal component.[38] It is the rate at which this state approaches equilibrium that we address here.

The expression for the rate of change in the energy $\mathcal{H}_A$ leads to an equation of motion for the corresponding inverse temperature upon substitution of the density matrix (6.1) into Eq. (6.8). Before proceeding, let us examine the first-order contribution to Eq. (6.8) that arises from ρ_{od}. Starting from the initial density matrix of Eq. (3.15), the density matrix to first order is

$$\rho(t) = e^{-i\mathcal{H}_0 t}\left[\rho_i - i\int_0^t dt'[V(t'),(1-\beta_i H_{20}^d)\,|\,\alpha\rangle\langle\alpha\,|\,](\mathrm{Tr}\mathbf{1})^{-1}\right]e^{i\mathcal{H}_0 t}\ .$$

The first-order contribution to $\langle \mathcal{H}_A(t)\rangle$, including both diagonal and off-diagonal matrix elements of $\rho(t)$, is

$$i\beta_i\int_0^t dt'\,\mathrm{Tr}_s(I_x H_{20}^d)\langle\alpha\,|\,[\omega a^\dagger a,(e^{-i\omega t'}a + e^{i\omega t'}a^\dagger)]\,|\,\alpha\rangle(\mathrm{Tr}\mathbf{1})^{-1} = 0\ ,$$

which equals zero because the trace over spin operators is $\mathrm{Tr}_s(I_x H_{20}^d)=0$. Thus, in spite of the existence of off-diagonal elements in the quasistationary density matrix, they do not affect the evolution of $\langle \mathcal{H}_A(t)\rangle$ to first order.

Proceeding with the substitution of Eq. (6.1) into (6.8), after some algebra and taking the trace with respect to the oscillator states, leads to

$$\frac{d}{dt}(1/\beta_A) = 2i\lambda^2\beta_B/\beta_A\int_0^\infty dt'\,\mathrm{Tr}([H_{20}^d,\tilde{I}_x(t')]I_x)\sin(\omega t')(\mathrm{Tr}\mathbf{1})^{-1} + 2\omega\lambda^2\int_0^\infty dt'\,\mathrm{Tr}[\tilde{I}_x(t')I_x]\cos(\omega t')(\mathrm{Tr}\mathbf{1})^{-1}\ , \tag{6.9}$$

where the remaining trace is over the spin variables and where $\tilde{I}_x(t)$ is defined by

$$\tilde{I}_x(t) \equiv \exp(iH_{20}^d t)I_x\exp(-iH_{20}^d t)\ .$$

By rewriting $[H_{20}^d,\tilde{I}_x(t')] = -id/dt'\,\tilde{I}_x(t')$ and integrating the first term by parts, Eq. (6.9) simplifies to

$$\begin{aligned}\frac{d}{dt}(1/\beta_A) &= -2(\beta_B/\beta_A - 1)\omega\lambda^2\int_0^\infty dt'\,\mathrm{Tr}[\tilde{I}_x(t')I_x]\cos(\omega t')(\mathrm{Tr}\mathbf{1})^{-1} \\ &= -2\pi(\beta_B/\beta_A - 1)\omega\lambda^2 g(\omega)N/4\ ,\end{aligned} \tag{6.10}$$

where $g(\omega)$ is the absorption line shape of the dipole spectrum. This provides a differential equation from which to determine the evolution of β_A. However, it depends on a second independent variable, namely the spin temperature β_B. It is possible to obtain a second differential equation from the evolution of $\langle \mathcal{H}_B(t)\rangle$ and thereby have two equations for the two unknown temperatures. A simpler procedure is to use the conservation of total energy

$$\langle \mathcal{H}_A(t)\rangle + \langle \mathcal{H}_B(t)\rangle \simeq E_{\mathrm{tot}} = \bar{n}\omega - \beta_i H_L^2 N/4\ , \tag{6.11}$$

ignoring the small contribution from V, to obtain a relationship,

$$\beta_B(t)=[1/\beta_A(t)-E_{\rm tot}]4/(NH_L^2)\ , \tag{6.12}$$

between the two quasistationary temperatures. This relation allows us to rewrite Eq. (6.10) entirely in terms of the spin temperature β_B, which is of more immediate interest than β_A; thus,

$$\frac{d}{dt}\beta_B=-2\pi[\beta_B^2+\beta_B E_{\rm tot}4/(NH_L^2) -4/(NH_L^2)]\omega\lambda^2 g(\omega)N/4\ . \tag{6.13}$$

The quadratic factor in β_B is the same as Eq. (4.16), which is used to determine the equilibrium spin temperature; therefore, one root is simply $\beta_{\rm eq}$. The negative root, abbreviated by A, is approximately $-E_{\rm tot}4/(NH_L^2)\equiv -A$ in the large photon number limit and $1/E_{\rm tot}\equiv -A$ in the low photon number limit. Factoring the quadratic term enables a straightforward integration of Eq. (6.13) and yields

$$\frac{\beta_B(t)-\beta_{\rm eq}}{\beta_B(t)+A}=\frac{\beta_B(0)-\beta_{\rm eq}}{\beta_B(0)+A} \times\exp[-2\pi\omega\lambda^2 g(\omega)(\beta_{\rm eq}+A)tN/4] \tag{6.14}$$

for the evolution of the quasistationary spin temperature.

Equation (6.14) predicts a nonexponential decay of the quasistationary spin temperature to its equilibrium value. A similar expression holds for the time dependence of $\beta_A(t)$. The decay is decidedly nonexponential in the low photon number regime for which A is small compared to $\beta_B(t)$. However, in the large photon number limit, when condition (4.17) holds, $A\gg\beta_B(t)$ and the quasistationary temperature decays exponentially to the equilibrium value with a rate constant

$$k\simeq\pi\omega^2\omega_1^2 g(\omega)/(2H_L^2)\ . \tag{6.15}$$

Here, Eq. (2.8) has been used to express the coupling parameter λ in terms of the classical field intensity ω_1. This is precisely the expression that Abragam and Goldman[1] report for the rate of saturation of the dipole-ordered system by a weak rf field. Their point is to give an example of a spin system for which use of the Magnus expansion to find a model Hamiltonian compatible with spin thermodynamics predicts an equilibrium state that contradicts experimental observations. The experiments show that the equilibrium state predicted via the model Hamiltonian is reached after a time T_2, but that the system saturates over long times. The present theory predicts that the spin-radiation system reaches a quasistationary state after a time T_2, which is identical with the state predicted as "equilibrium" via the Magnus expansion within the semiclassical treatment of the radiation field. An explanation for the saturation of the system is that the dipolar spin reservoir slowly equilibrates with the radiation field, an eventuality that is not provided for within a semiclassical framework.

In order to gain an idea of the time required for the spins to equilibrate with the radiation field, let us determine the time constant for the example given in Sec. IV B. Consider a 1-cm^3 sample of fluorine spins prepared in a dipole-ordered state with $\beta_i=0.1\ {\rm K}^{-1}$ and interacting with a local field of $H_L=30$ krad/s. The dipolar line shape is assumed to be Gaussian with a standard deviation of $\sqrt{3}H_L$ and the system is irradiated by an rf field having $\omega=100$ krad/s. In the large photon number limit, for example, with $\bar{n}=10^{17}$ photons or equivalently with an applied field of $\omega_1/\gamma=0.016$ G, the spins relax to the temperature of the radiation field with a time constant of $k^{-1}\simeq 300$ ms. If the spin system is prepared with a low initial temperature, then the transition from low to high photon number occurs at a relatively large value of $\bar{n}$; i.e., at a relatively large applied field ω_1. If the lattice is also at this initial temperature, so that the spin-lattice relaxation time is long, then it should be feasible to measure the relaxation of the quasistationary state to the quite different equilibrium state predicted in the low photon number regime. Using the analog to Eq. (6.15) appropriate in the low photon number regime and assuming $\bar{n}=5\times 10^{15}$, the predicted time constant is $\simeq 8$ s for the spin system to relax to equilibrium in this regime.

B. Resonant radiation

Having determined the rate at which the quasistationary state approaches equilibrium with the radiation field in the case of off-resonant irradiation, we turn our attention to the relaxation process when the spin system is in a large static magnetic field and is irradiated near the Larmor frequency. As above, we assume that the spin-radiation system evolves to equilibrium via a quasistationary state of the form (6.1). The analysis of the relaxation dynamics proceeds along the same lines as in the previous section; except that it is more difficult to calculate $V(t)$ owing to the more complex nature of $\mathcal{H}_B$ in the resonant situation. For this reason, the following discussion is limited to weak applied fields $\omega_1\ll H_L$ for which it is justified to retain only the leading term of

$$\exp(i\mathcal{H}_B t)V\exp(-i\mathcal{H}_B t)\ .$$

The analysis is further complicated by the fact that the nonsecular components of the dipole interaction contribute to the relaxation. In the discussion below we concentrate on the effect that the counter rotating terms of the radiation field have on the relaxation dynamics and do not include the contribution from the nonsecular dipole interaction.

Insertion of the quasistationary density matrix into Eq. (6.8), after performing the unitary transformations required to determine $V(t')$, taking the trace with respect to the operators of the radiation field, and integrating by parts, leads to

$$\frac{d}{dt}(1/\beta_A-\beta_A\omega^2 N/4-\beta_B\Delta\omega N/4)=-4(\beta_B/\beta_A-1)\omega\lambda^2\int_0^\infty dt'\,{\rm Tr}[\tilde{I}_x(t')I_x]\cos[(2\omega+\Delta)t'](\mathrm{Tr}\mathbf{1})^{-1}\ .$$

The conservation of total energy, neglecting the small contribution from V', provides the relation

$$\beta_A(t) \simeq [\beta_B(t)(\Delta\omega+\Delta^2+H_L^2)N/4+E_{\rm tot}]^{-1} \quad (6.16)$$

between the two quasistationary temperatures, where

$$E_{\rm tot}=\bar{n}\omega-\beta_i\omega_0\lambda\bar{n}^{1/2}\cos(\phi)N/2 \ .$$

After rewriting the above expression in terms of β_B, we find that

$$\frac{d}{dt}\beta_B=-\pi(\beta_B^2+\beta_B E_{\rm tot}/Q-1/Q)\omega\lambda^2 g(2\omega+\Delta)N \quad (6.17)$$

provides the equation of motion for the quasistationary temperatures of the dipole-effective field bath, where $Q\equiv(\Delta\omega+\Delta^2+H_L^2)N/4$ and where

$$g(\omega)\equiv(\pi)^{-1}\int_0^\infty dt'\,{\rm Tr}[\tilde{I}_x(t')I_x]\cos(\omega t')({\rm Tr}I_x^2)^{-1}$$

represents the dipolar absorption line shape. The quadratic term in Eq. (6.17) can be factored to $(\beta_B-\beta_{\rm eq})(\beta_B+A)$, with $A\equiv E_{\rm tot}/Q$ in the large-$\bar{n}$ limit and $A\equiv -1/E_{\rm tot}$ in the low-$\bar{n}$ limit. A straightforward integration of Eq. (6.17) shows that the quasistationary temperature evolves to equilibrium via

$$\frac{\beta_B(t)-\beta_{\rm eq}}{\beta_B(t)+A}=\frac{\beta_B(0)-\beta_{\rm eq}}{\beta_B(0)+A}\times\exp[-\pi\omega\lambda^2 g(2\omega+\Delta)N(\beta_{\rm eq}+A)t] \ . \quad (6.18)$$

The evolution of the spin-radiation system to equilibrium in the case of near-resonant irradiation is similar to relaxation behavior of the dipole-coupled spin system irradiated far above resonance. In the low photon number regime, the relaxation follows a nonexponential decay. In the large-$\bar{n}$ regime, the relaxation is approximately exponential in nature and has a rate constant of

$$k\simeq\pi\omega^2\omega_1^2 g(2\omega+\Delta)/(\Delta\omega+\Delta^2+H_L^2) \ . \quad (6.19)$$

The principal difference between the near-resonant versus off-resonant irradiation is the dependence of the rate constant on the dipolar line shape at a frequency $2\omega+\Delta$ from the center of the absorption line in the former case as compared to a frequency of ω when the rf field is far above resonance. Because the line shape function decreases rapidly with increasing frequency, the fact that k is proportional to $g(2\omega+\Delta)$ under resonant irradiation as opposed to $g(\omega)$ in the nonresonant case implies that the relaxation to equilibrium at a given ω takes much longer under resonant than nonresonant irradiation.

The dependence of the rate constant for the decay to equilibrium on $g(2\omega+\Delta)$ accounts for the success of the standard methods of spin thermodynamics. As pointed out in Secs. III and V, the "equilibrium" state is in reality a quasistationary state of the combined spin-radiation system. Given the high Larmor frequency of a typical high-field magnetic-resonance spectrometer (e.g., 100 MHz), the value of the line shape function at frequency $2\omega+\Delta$ is infinitesimal and hence the time constant for relaxation of the quasistationary state to equilibrium is nearly infinite.

VII. CONCLUSION

The current understanding of the long-term behavior of a spin system subject to an external time-dependent perturbation derives principally from the extension of spin thermodynamics to rotating, toggling, or other interaction frames. The standard procedure used to predict equilibrium properties involves finding a suitable interaction frame and identifying a time-independent model Hamiltonian under which the evolution of the spin system mimics "sufficiently" closely the evolution under the true Hamiltonian. Invariably errors are made in finding the model. For example, the counter-rotating terms are omitted from the truncated Hamiltonian in the rotating-wave approximation. Well-known, if often minor, consequences of the counter-rotating term are the Bloch-Siegert shift[40] and the absorptions at odd subharmonics of the Larmor frequency.[23,41] In this paper we find a new effect of the counter-rotating terms; they can lead at long times to the spins equilibrating to the temperatures of the radiation field and accordingly to a saturation of the observed order parameters of the system.

The semiclassical description of the radiation field suffers from the deficiency that it has no provision for the spins and radiation field to reach equilibrium. Furthermore it is very difficult to satisfy the requirement that all the eigenvalues of the model Hamiltonian found via the AHT fall into an interval of length $2\pi/\tau$ which is necessary for convergence of the Magnus expansion and the validity of applying spin thermodynamics to the model. One error that not satisfying this requirement introduces is to average out terms in the semiclassical Hamiltonian that lead to absorption at frequencies $n2\pi/\tau$ by the spin system. This error has only minor consequences over short times, hence the success of the AHT in analyzing pulsed NMR spectra. Over long times, this error ignores heating of the spins by the radiation field and leads to more serious errors.

An examination of the full spin-radiation Hamiltonian, for a weak rf field, shows it to consist of two (or more) quasiconserved energies plus a small noncommuting term. The exact decomposition of the Hamiltonian depends on whether or not the frequency of the rf field is resonant with the spins. If it is not, then the Zeeman, dipole, and radiation energies are each quasiconserved. The equivalent semiclassical treatment includes only the first two. If the radiation is resonant, then the Zeeman (minus the resonance offset) and radiation energies couple strongly to form one quasiconserved component, the Zeeman-radiation term. The energy of the spins, interacting among themselves and with a transverse effective field, is also conserved. The analogous semiclassical treatment includes only the second of these—namely the energy of the spins in the rotating frame. The conclusion is that the equilibrium state within the semiclassical framework corresponds to a quasistationary state of the full spin-radiation system. The semiclassical

predictions, therefore, are valid only as long as the quasistationary state persists.

The small noncommuting (counter-rotating) terms provide a weak thermal link between the quasi-independent thermodynamic reservoirs corresponding to the spins and radiation field. To determine the equilibrium state, one needs only know that this link exists. The properties of this state depend on the relative temperatures of the quasistationary reservoirs. Even for weak intensity rf irradiation, the spins interact with a very large number of photons—a sufficiently large number that the temperature of the radiation field, or Zeeman-radiation field, is very much higher than the spin temperature. Thus, the thermal link provided by the counter-rotating terms causes a substantial heating of the spins and, accordingly, saturation of observables such as magnetization or dipole order. As the intensity of the field is reduced, there is a critical photon number at which a sharp transition appears in the final temperature of the spin-radiation system. Below the critical photon number, the energy in the radiation, or Zeeman-radiation, reservoir is too small to heat the spin system, which remains comparatively close to its quasistationary temperature.

From the above analysis we draw the conclusion that in the experiment described by Abragam and Goldman relaxation of the spin system by the radiation field is responsible for saturation of the dipolar order by low-intensity, off-resonant rf irradiation. Both the description of the quasistationary state and the rate at which the system relaxes to equilibrium agree with the known features of this experiment. Furthermore, with a low initial lattice temperature used to provide a large initial dipole order and to increase the time of spin-lattice relaxation, it should be feasible to observe the transition in equilibrium temperature from high to low photon number regime.

Though the analysis of this paper concentrates on the interactions of a spin system with a single-mode radiation field, the extension to arbitrary time-dependent fields, e.g., multiple-pulse sequences, is straightforward. One mode of the radiation field is introduced for each Fourier component of the time-dependent perturbation. The details will be presented elsewhere, however, the general conclusions remains the same. At long times the spin system will equilibrate with the radiation field, and this is difficult to incorporate into the semiclassical description of the irradiated spins.

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frame produces the Schrödinger-representation-like Hamiltonian $\mathcal{H}=H_{20}^{d}+\omega_1\cos(\omega t)I_x$ in the rotating frame. The discussion in this paper applies to both Hamiltonians. Note that whereas the full dipole interaction appears in the laboratory frame, only the secular component appears in the rotating frame.

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