Chapter 3

Resonator-induced spin relaxation

1 Trapping of the spin system due to angular momentum conservation

The idea that the transverse field of a mechanical resonator can polarize N spins might at first glance seem surprising or implausible, since we would in general expect a resonant transverse field to rotate a system of spins without polarizing it. Indeed, if we replace the resonator's field with a time-dependent applied transverse field and consider a set of noninteracting spins which evolve under this applied field, the evolution operator is simply a rotation of the spin system. This follows from the fact that at each instant, the system's Hamiltonian is the generator of a rotation operator. When the transverse field is that of a resonator which interacts with the spins, however, the spins can be polarized by the field. For instance, if the spins are initially at a higher temperature than the resonator, then heat transfer between spins and resonator must occur as the spin-resonator system moves toward equilibrium, and the spins become polarized as they are cooled by the resonator.

A spin system coupled to a resonator at zero Kelvins will not necessarily relax to its ground state, however. The Hamiltonian (2.1) commutes with $\mathbf{I}^2$, and spin angular momentum will be conserved during the relaxation if the spin Hamiltonian H_s also commutes with $\mathbf{I}^2$. The ground state of a system of spins has the maximum possible value of $\mathbf{I}^2$, and angular momentum conservation would prohibit most initial spin distributions from relaxing to this state. For example, a distribution of N spins 1/2 contains only one angular momentum manifold with $I = N/2$. The ground state of the spin system is the low-energy state of this manifold. Relaxation under the spin-resonator interaction does not transfer population between angular momentum systems of different I, and if the initial state of the spins has population in any of the angular momentum manifolds with $I < N/2$, then spin-resonator relaxation will not transfer this population to the angular momentum manifold containing the ground state. Rather, the population belonging to a given angular momentum manifold will be transferred to the lowest energy state belonging to that manifold and will remain "trapped" in this state. In particular, if the initial distribution of N spins 1/2 is completely disordered, then all states of all angular momentum manifolds are equally populated, and spin relaxation induced by a resonator at zero Kelvins under the constraint of angular momentum conservation will leave population trapped in the ground state of each manifold, yielding an eventual spin polarization of [15]

$$\begin{aligned} P_{\text{trap}} &= \frac{1}{2^{N-1}N}\sum_{J}^{N/2}\frac{N!\,(2J+1)^2}{(N/2+J+1)!\,(N/2-J)!} \\ &\approx \sqrt{2/N}, \quad N \gg 1. \end{aligned} \tag{3.1}$$

To illustrate this "trapping," we consider an example presented by Dicke [16]. A single spin 1/2 initially in its excited state will eventually relax to the ground state by spontaneous emission, as a result of the coupling between the spin and the resonant modes of the electromagnetic field. If two spins 1/2 are separated from each other by a distance which is small compared to the radiation frequency $|\omega_0|$, however, then the system interacting with the electromagnetic modes contains a singlet and a triplet, and the singlet cannot radiate to the field. If the initial state has one spin 1/2 in the excited state $|-\rangle$ and the other in the state $|+\rangle$, then the singlet and triplet initially have the same population. The triplet decays by spontaneous emission, while the population of the singlet remains trapped. After the triplet has fully decayed, the probability of detecting an excited spin is $1/2$, and only half the population is in the ground state of the two-spin system.

In addition to pointing out that a system coupled to the electromagnetic field can become trapped in a nonradiative state that differs from the ground state, Dicke showed that coherent spontaneous emission, or "super-radiance," can occur in a collection of two-level atoms which share the same coupling to the electromagnetic field. For example, he showed that the largest rate at which a gas of N two-level atoms can radiate by spontaneous emission is [16]

$$I = \frac{N}{2}\left(\frac{N}{2}+1\right) I_0. \tag{3.2}$$

In (3.2), I_0 is the rate of radiation when only one atom is present and in its excited state. A model in which each atom radiates independently would have emission proportional to N, whereas the super-radiance described by equation (3.2) is proportional to N^2. The surprising nature of this result can be understood by expressing it in the language of the spin-resonator system. If a collection of N spins $1/2$ is initially aligned along a transverse axis and then precesses in unison, the transverse dipole moment which drives the resonator is proportional to N, and the spontaneous emission rate is proportional to N^2. However, if the spin system is initially in the eigenstate having $I_z = 0$, $I = N/2$, then the spontaneous emission rate is also proportional to N^2, in spite of the fact that the expected value of the transverse dipole moment is identically zero. A number of theoretical and experimental studies of super-radiance have been performed, and the subject is reviewed in reference [17].

For both trapped states and super-radiant states, correlated motion changes the nature of spontaneous emission dramatically from what would be observed in a system of spins radiating independently. For a system of N spins $1/2$ interacting with a mechanical resonator and simultaneously evolving under the interaction-frame Hamiltonian H_s, the contribution to spin relaxation associated with spin-spin correlations can be highlighted by writing the equations of motion for the Cartesian spin components as

$$\begin{aligned}
\frac{d}{dt}\left\langle I_z \right\rangle &= -i\left\langle [I_z, H_s] \right\rangle - R_h \left\{ \left\langle I_z \right\rangle - \frac{N/2}{2n_{\text{th}}+1} \right\} - R_0 \left\langle N/2 - I_x^2 - I_y^2 \right\rangle , \\
\frac{d}{dt}\left\langle I_x \right\rangle &= -i\left\langle [I_x, H_s] \right\rangle - \frac{1}{2} R_h \left\langle I_x \right\rangle - R_0 \left\langle \frac{1}{2}\left(I_x I_z + I_z I_x \right) \right\rangle , \\
\frac{d}{dt}\left\langle I_y \right\rangle &= -i\left\langle [I_y, H_s] \right\rangle - \frac{1}{2} R_h \left\langle I_y \right\rangle - R_0 \left\langle \frac{1}{2}\left(I_y I_z + I_z I_y \right) \right\rangle .
\end{aligned}$$

In each of these equations, the term proportional to R_0 is zero if the components of distinct spins are uncorrelated. In an ensemble of N spins 1/2 which relax without developing spin-spin correlations, the relaxation induced by the resonator is thus exponential, with a rate constant proportional to R_h. It is correlations of the form $\left\langle I_{x,j} I_{x,k} \right\rangle$, $\left\langle I_{y,j} I_{y,k} \right\rangle$, $\left\langle I_{x,j} I_{z,k} \right\rangle$, and $\left\langle I_{y,j} I_{z,k} \right\rangle$ which are responsible for phenomena such as trapping and super-radiance.

2 Indirect spin-spin interaction

The semiclassical equation introduced in section 5 of chapter 2 can be used to visualize the way in which an indirect spin-spin interaction develops as a result of the spins' coupling to the same resonator. We consider an example in which the classical resonator is at zero Kelvins, with no direct interaction between spins. In the absence of coupling between spins and resonator, the spins simply precess around the static field, while the resonator is motionless. In the coupled system, the resonator quickly achieves a steady-state response to the torque exerted on it by the spins, and energy is donated from spins to resonator by means of this driving torque. The driven mechanical motion creates a resonant transverse field which rotates the spins, thereby changing their energy. As the spins drive the resonator, the oscillating field associated with the mechanical motion causes the energy of the spins to change.

An indirect spin-spin interaction arises because the resonator's field is the sum of its steady-state response to all spins. The field torque associated with the resonator's linear response to spin j acts on spin k, and so the state of spin j affects the field acting on spin k. The torque acting on spin k due to the driving of the resonator by spin j can be interpreted as an indirect torque exerted on spin k by spin j, and the indirect torques which link each pair of spins cause the development of spin-spin correlations during mechanical cooling. In order to quantify the strength of the indirect torques, we consider the state of the spin-resonator system during a time step $\Delta t \gg \tau_h$ which is short compared to the time needed for the spin-resonator interaction to change the spin state. If the initial orientation of semiclassical spin j at $t = 0$ is given by angles ϕ_j and α_j, with ϕ_j the azimuthal angle and α_j the angle between the spin and the z-axis, then the resonator's steady state motion during Δt is

$$\theta\left(t\right) = \frac{dB_x}{d\theta} \gamma \hbar I \frac{\tau_h}{2 I_h \omega_h} \sum_j \sin \alpha_j \sin\left(\omega_h t + \phi_j\right),$$

where we have assumed that all spins experience the same field and have Larmor frequency $\omega_0 = -\omega_h$. (In order to simplify notation in this section, we have dropped the superscript c used to distinguish semiclassical variables from analogous quantum operators.) The transverse field is

$$\frac{dB_x}{d\theta} \theta\left(t\right) = \left(\frac{dB_x}{d\theta}\right)^2 \gamma \hbar I \frac{\tau_h}{2 I_h \omega_h} \sum_j \sin \alpha_j \sin\left(\omega_h t + \phi_j\right), \tag{3.3}$$

and since this field is established quickly and changes negligibly in amplitude during the time step Δt, we can consider the jth term in this sum to be the effective field of spin j experienced by the other spins. The amplitude of this effective field is

$$B_{j,\text{eff}} = \left(\frac{dB_x}{d\theta}\right)^2 \gamma \hbar \frac{\tau_h}{2 I_h \omega_h} \left(I \sin \alpha_j\right).$$

In a reference frame rotating around the z-axis at the Larmor frequency of the spins, the resonant component of this effective field has magnitude $B_{j,\text{eff}}/2$, and the precession frequency of spin k in a resonant field of this magnitude is

$$\gamma B_{j,\text{eff}}/2 = R_0 I_{j,\text{trans}},$$

where

$$I_{j,\mathrm{trans}} \equiv I \sin \alpha_j$$

is the magnitude of the transverse component of spin j. We see that the semiclassical model predicts that spin j indirectly exerts a torque on spin k which in the absence of any other interactions would cause spin k to precess at frequency $R_0 I_{j,\mathrm{trans}}$.

When the transverse components of individual spins are distributed randomly in the plane, the indirect torques exerted on a spin k by the remaining spins do not add coherently. Although the sum Z of the resonant effective fields exerted on spin k by the other spins has an expected value of zero, its actual value during the time step Δt will in general have an order of magnitude comparable to the standard deviation of S. Consider a frame rotating around the z-axis with spin k during Δt and having its x-axis aligned with the transverse component of spin k. Assume that spins are initially independent and have identical probability distributions, with the distribution of ϕ_j flat and uncorrelated with α_j. It follows from (3.3) that the root-mean-square value of γZ is

$$\gamma Z = \sqrt{N-1} R_0 \bar{I}_{\mathrm{trans}},$$

where $\bar{I}_{\mathrm{trans}}$ is the root-mean-square value of $I_{j,\mathrm{trans}}$.

If a spin system is completely disordered or has weak Zeeman order at the beginning of Δt, the sum of the indirect torques exerted on spin k by the other spins would cause spin k to precess with a frequency of order $R_0 I \sqrt{N}$. If the spins are all aligned in the transverse plane at the beginning of Δt, the indirect torques on spin k add coherently, and the precession frequency of spin k due to the sum of the indirect torques is of order $R_0 I N$. (In this case, the uniform rotation of $\mathbf{I}$ toward the static applied field would be the mechanical analog of "radiation damping.") We define T_{corr} to be the characteristic evolution time of each spin in the net field exerted on it indirectly by all of the other spins:

$$\begin{aligned} T_{\mathrm{corr}} &\approx 1/\left(R_0 I N\right), \text{ spins aligned along transverse axis,} \\ T_{\mathrm{corr}} &\approx 1/\left(R_0 I \sqrt{N}\right), \text{ disordered system.} \end{aligned} \tag{3.4}$$

We can expect that relaxation associated with these indirect torques will be disrupted if they vary sinusoidally with a period substantially less than T_{corr}. Consider, for instance, an example where two semiclassical spins whose Larmor frequencies differ by $\delta\omega$ are initially aligned along the x-axis. In a frame rotating with spin 1, the indirect torque exerted by spin 2 will initially tend to rotate spin 1 toward B_z, but after a time $t = \pi/\delta\omega$, the two spins will be aligned in opposite directions in the transverse plane, and the indirect torque on spin 1 will tend to rotate it away from B_z. More generally, we can expect that for a system of N spins, a perturbation which reverses the signs of the indirect torques within a time T_{perturb} will partially disrupt the contribution of spin-spin correlations to relaxation if T_{perturb} is of the order of T_{corr} or smaller. If $T_{\mathrm{perturb}} \ll T_{\mathrm{corr}}$, the contribution of the indirect torques should be effectively suppressed.

3 Modification of the relaxation processes by the spin Hamiltonian

Arguments based on the semiclassical model suggest that a resonator at zero Kelvins will induce the spins to relax exponentially to the ground state if the indirect spin-spin torques are modulated sufficiently quickly by terms in the spin Hamiltonian. To move beyond this conjecture and characterize resonator-induced relaxation under a given spin Hamiltonian requires an analysis of the way in which perturbations to the spin Hamiltonian modify the coefficients of the master equation. In order to clarify the nature of the arguments being presented, we frame the discussion in this section in terms of general properties of the master equation. Sections 4 and 5 apply the results of this section to the problems of longitudinal and transverse spin relaxation.

Reference [7] derives a general expression for the master equation which governs a small system S interacting with a large reservoir R. The sets $\{|a\rangle\}$, $\{|\mu\rangle\}$ are respective orthonormal bases of S, R, and would be energy eigenstates in the absence of the coupling between S and R. The eigenfrequency of a state $|a\rangle$ is denoted by ω_a, and the difference of two such eigenfrequencies by

$$\omega_{ab} = \omega_a - \omega_b.$$

For the discussion in sections 3, 4, and 5, it will be convenient to define the interaction frame as one in which the only surviving terms in the Hamiltonian are those which characterize interactions between S and R. Note that this definition differs from the one used for equation (2.24), which was defined so as to eliminate only the terms $\omega_0 I_z$ and $\omega_h \left(a^\dagger a + 1/2\right)$ from the Hamiltonian. The interaction-frame master equation for S can be written as

$$\frac{d}{dt}\rho_{ab}\left(t\right) = \sum_{c,d} \exp\left\{i\left(\omega_{ab} - \omega_{cd}\right)t\right\}\mathcal{R}_{abcd}\,\rho_{cd}\left(t\right), \tag{3.5}$$

where $\mathcal{R}_{abcd}$ is time-independent.

Perturbations in the Hamiltonian H_s of the small system S can affect equation (3.5) by perturbing the constants $\mathcal{R}_{abcd}$ as well as the difference frequencies ω_{ab}. We will find that these two types of changes in the master equation have different effects on spin relaxation. Each coefficient $\mathcal{R}_{abcd}$ can be expressed as a sum of terms of the form

$$M_1 M_2 \int_0^\infty g\left(\tau\right)\exp\left(i\omega_{nm}\tau\right)\,d\tau,$$

where M_1 and M_2 are matrix elements of operators acting on S which contribute to the interaction Hamiltonian, and $g\left(\tau\right)$ is a reservoir correlation function. If the eigenfrequencies $\{\omega_a\}$ are perturbed while the eigenstates $\{|a\rangle\}$ do not change, the matrix elements M_1 and M_2 are unaffected by the perturbation; if, in addition, the perturbation in the frequencies ω_{nm} is small compared to the spectral width of the correlation functions $g\left(\tau\right)$, then $\mathcal{R}_{abcd}$ will be unaffected by the perturbation. Since correlation times of a reservoir are in general extremely short, we will consistently consider the spectral width of $g(\tau)$ to be large compared to any perturbations in ω_{nm}. Under these conditions, perturbing the eigenfrequencies but not the eigenstates leaves $\mathcal{R}_{abcd}$ unmodified in (3.5). By way of contrast, perturbations to H_s which modify the eigenstates can change the values of the matrix elements M_1 and M_2, thereby modifying the coupling constants $\mathcal{R}_{abcd}$ which characterize the physical processes occurring during the correlation time of the reservoir.

The difference $(\omega_{ab} - \omega_{cd})$ in the oscillation frequencies of lab-frame density matrix elements appears in the interaction-frame relaxation equation as an oscillation in the phase of the coupling responsible for transfer from ρ_{cd} to ρ_{ab}. If the frequency difference $|\omega_{ab} - \omega_{cd}| \ll 2\pi\mathcal{R}_{abcd}$ is perturbed to a value much larger than $2\pi\mathcal{R}_{abcd}$, then the transfer from ρ_{cd} to ρ_{ab} characterized by $\mathcal{R}_{abcd}$ will be suppressed. More precisely, the physical processes responsible for such transfer will continue to occur, but the relative phase of lab-frame density matrix elements will vary within a period which is short compared to the characteristic time $1/\mathcal{R}_{abcd}$ required for the transfers to cause a non-negligible change in ρ_{ab}, and the fast phase variation will ensure that the sum of the transfers to ρ_{ab} continually stays near zero. Under these conditions, the coefficient $\mathcal{R}_{abcd}$ will not contribute to the evolution of ρ_{ab}.

Reference [7] derives formulas which are helpful in interpreting the processes associated with the various coupling constants $\mathcal{R}_{abcd}$. If $c \neq a$, for instance, then $\mathcal{R}_{aacc}$ can be expressed as

$$\mathcal{R}_{aacc} = \frac{2\pi}{\hbar} \sum_{\mu} p_{\mu} \sum_{\nu} |\langle \nu, a \,|V|\, \mu, c\rangle|^2 \, \delta\left(E_{\mu} + E_c - E_{\nu} - E_a\right). \tag{3.6}$$

Here δ is the Dirac delta function, E_i is an energy eigenvalue for the system or reservoir, V is the interaction Hamiltonian coupling the system to the reservoir, p_{μ} is the thermal population of state μ, and μ, ν range over the orthonormal basis of R. This equation is interpreted to mean that $\mathcal{R}_{aacc}$ gives the summed probability per unit time that a state from the continuum $\{|\mu, c\rangle\}$ makes the transition to the continuum $\{|\nu, a\rangle\}$, where a and c are fixed, while μ, ν range over the orthonormal basis of R. This interpretation is highlighted by the use of the notation

$$\Gamma_{c\to a} \equiv \mathcal{R}_{aacc}.$$

Reference [7] also shows that the relaxation of coherences ρ_{ab} is governed by the constants

$$\begin{aligned}
\Gamma_{ab} &= \Gamma_{ab}^{\text{nonad}} + \Gamma_{ab}^{\text{ad}}, \\
\Gamma_{ab}^{\text{nonad}} &= \frac{1}{2}\left(\sum_{n\neq a}\Gamma_{a\to n} + \sum_{n\neq b}\Gamma_{b\to n}\right), \\
\Gamma_{ab}^{\text{ad}} &= \frac{2\pi}{\hbar}\sum_{\mu} p_{\mu}\sum_{\nu}\delta\left(E_{\mu}-E_{\nu}\right) \qquad (3.7) \\
&\times \frac{1}{2}\left(\left|\langle \nu, a\left|V\right|\mu, a\rangle\right|^2 + \left|\langle \nu, b\left|V\right|\mu, b\rangle\right|^2 - 2\,\mathrm{Re}\,\langle \mu, a\left|V\right|\nu, a\rangle\langle \nu, b\left|V\right|\mu, b\rangle\right).
\end{aligned}$$

The constant $\Gamma_{ab}^{\text{nonad}}$ is interpreted as giving the rate at which transitions away from $|a\rangle$ and $|b\rangle$ disrupt the coherence between these states and cause "nonadiabatic" relaxation, while the "adiabatic" constant Γ_{ab}^{ad} characterizes damping of a coherence due to interactions in which the system A does not change state. When A represents a spin system, we would expect $\Gamma_{ab}^{\text{nonad}}$ and Γ_{ab}^{ad} to be associated with "lifetime broadening" and "secular broadening," respectively. (Lifetime broadening is transverse spin relaxation caused by spin transitions which shorten the lifetime of a coherence, while secular broadening is caused by fluctuations in B_z which modulate the precession frequency of the spins.) Consistent with this interpretation is the fact that $\Gamma_{ab}^{\text{ad}} = 0$ if fluctuations in B_z are excluded from the model of the spin-resonator system by the use of the Jaynes-Cummings Hamiltonian (2.11) as the interaction Hamiltonian. This can be seen by noting first that

$$\begin{aligned}
\left\langle \nu, b\left|I_{+}a^{\dagger}\right|\mu, b\right\rangle &= 0, \\
\left\langle \nu, b\left|I_{-}a\right|\mu, b\right\rangle &= 0,
\end{aligned}$$

for any eigenstate $|b\rangle$ of a secular spin Hamiltonian, since I_+ and I_- do not couple states within a given eigenspace of I_z. It follows that

$$\langle \nu, b\,|V|\,\mu, b\rangle = 0 \tag{3.8}$$

for each energy eigenstate $|b\rangle$, which implies $\Gamma_{ab}^{\mathrm{ad}} = 0$. In discussing the relaxation of coherences due to spin-resonator interactions, we will therefore consider only nonadiabatic relaxation, and we will simplify notation by dropping the label "nonadab."

An interpretation of the coupling constants $\mathcal{R}_{abcd}$, with $a \neq c$, $b \neq d$, will be helpful in our analysis of spin relaxation. Reference [7] derives the formula

$$\begin{aligned}\mathcal{R}_{abcd} = \frac{2\pi}{\hbar} \sum_{\mu} p_{\mu} \sum_{\nu} &\langle \mu, d\,|V|\,\nu, b\rangle \langle \nu, a\,|V|\,\mu, c\rangle \\ &\times \delta\left(E_{\mu} + E_{c} - E_{\nu} - E_{a}\right).\end{aligned} \tag{3.9}$$

In suggesting an interpretation for (3.9), we note first that it is not a formula for a transition amplitude, so we cannot immediately associate the product $\langle \mu, d\,|V|\,\nu, b\rangle \langle \nu, a\,|V|\,\mu, c\rangle$ with a process in which a transition from $|\mu, c\rangle$ to $|\nu, a\rangle$ is followed by a transition from $|\nu, b\rangle$ to $|\mu, d\rangle$. If it were correct to interpret in this way the matrix elements which characterize relaxation processes, then the product

$$|\langle \nu, a\,|V|\,\mu, c\rangle|^2 = \langle \mu, c\,|V|\,\nu, a\rangle \langle \nu, a\,|V|\,\mu, c\rangle$$

appearing in (3.6) should be associated with a process in which a transition from $|\mu, c\rangle$ to $|\nu, a\rangle$ is followed by a transition from $|\nu, a\rangle$ back to $|\mu, c\rangle$; since we associate $\mathcal{R}_{aacc}$ with one-way transfer from $|\mu, c\rangle$ to $|\nu, a\rangle$, this interpretation would be problematic. We can obtain an unproblematic interpretation of (3.9) by first recalling that the equation of motion for a density matrix ρ can be written as

$$\frac{d}{dt}\rho(t) = (-iH)\,\rho(t) + \rho(t)\,(iH). \tag{3.10}$$

The factor $(-iH)$ in the product $(-iH)\,\rho(t)$ is obtained from the evolution operator

e^{-iHt} responsible for evolving the kets forward in time, while the factor (iH) in the product $\rho(t)(iH)$ is associated with the evolution of the bras. If we use first-order perturbation theory to study the motion of ρ, we can interpret the results in terms of two sets of processes: those in which the kets evolve while the bras are unchanged, and those in which the bras evolve while the kets are unchanged. Similarly, evolution of ρ, as calculated using second-order perturbation theory, can be interpreted in terms of four types of processes, each associated with one of the terms in the double commutator

$$i^2\left[\left[\rho, H(t_1)\right], H(t_2)\right] = -\rho H(t_1) H(t_2) + H(t_1)\rho H(t_2) + H(t_2)\rho H(t_1) - H(t_2) H(t_1)\rho. \tag{3.11}$$

For instance, the term $\rho H(t_1) H(t_2)$ is associated with processes in which bras are evolved in two consecutive steps, while $H(t_1)\rho H(t_2)$ is associated with processes in which the kets evolve during the first step and the bras during the second.

Note as well that the transfers of probability amplitude associated with $H(t_1)$ and $H(t_2)$ each involve a phase change of magnitude 90°. This can be seen by examining (3.10), in which the respective factors of $-i$ and i yield phase changes of opposite sign for the transfers associated with evolution of the kets and the bras. The factor $(-iH)\rho\,dt$, for example, represents a change to ρ in which the term added to a given element ρ_{jk} is

$$-i\sum_{|n\rangle}\langle j\left|H\right|n\rangle\,\rho_{nk}.$$

This can be interpreted to mean that the interaction characterized by the matrix element $\langle j\left|H\right|n\rangle$ causes a transfer to occur from ρ_{nk} to ρ_{jk}, while the factor $-i$ yields a phase change of -90°. Note that for processes in which a bra evolves during one step and a ket evolves during the other, the phase changes occurring during the two steps will cancel. If kets are evolved twice or bras are evolved twice, however, the phase change associated with the process will be 180°. In particular, probability amplitude which is transferred by such processes will change sign.

The physical process associated with a product M_1M_2 of matrix elements can be interpreted by determining whether bras or kets were evolving during the two consecutive stages of motion. We find that the coefficient $\mathcal{R}_{abcd}$ given by (3.9) depends on processes in which the ket $|c\rangle$ makes a transition to $|a\rangle$ during one stage of motion, while the bra $\langle d|$ makes a transition to $\langle b|$ during the other. Although the distinction between bras and kets is helpful in making sense of formulas such as (3.9), we can simplify language and notation by neglecting to distinguish between bras and kets in discussing physical processes; for instance, we will consider (3.9) to characterize processes in which $|c\rangle \rightarrow |a\rangle$ and $|d\rangle \rightarrow |b\rangle$ without a change of phase. This simplification is motivated by the idea that we can consider these processes to be occurring within an ensemble of systems, with each system represented by a linear combination of kets. The appearance of bras in our formalism can be considered an artifact of the choice to represent the ensemble by a matrix rather than a collection of state functions.

In analyzing spin relaxation due to spin-resonator interactions, we will find that coefficients such as $\mathcal{R}_{abad}$, with $b \neq d$, play an important role. The arguments given in reference [7] can be extended to yield formulas for these coefficients and obtain an interpretation of the processes characterized by them. When V represents the spin-resonator interaction Hamiltonian, we find that $\mathcal{R}_{abad}$ characterizes processes in which probability amplitude is transferred first from $|d\rangle$ to $|m\rangle$ and then from $|m\rangle$ to $|b\rangle$, with $m \neq b, d$, and the matrix elements associated with these processes are

$$M_{abad} = \langle d, \mu| V |m, \nu\rangle \langle m, \nu| V |b, \mu\rangle . \tag{3.12}$$

During the two steps, the transferred probability amplitude changes phase by $180\,^{\circ}$. In the general case, $\mathcal{R}_{abad}$ also depends on matrix elements of the form $\langle a, \mu| V |a, \nu\rangle \langle d, \nu| V |b, \mu\rangle$, but it follows from (3.8) that these products are zero for the Jaynes-Cummings Hamiltonian.

4 Longitudinal relaxation

In this section, we analyze in greater detail the processes which cause spin population to be trapped away from the ground state during resonator-induced spin polarization, as well as the mechanisms by which such trapping could be disrupted by the presence of additional terms in the spin Hamiltonian.

4.1 Noninteracting spins

We first consider a system of N noninteracting spins 1/2 which have identical Larmor frequencies. The eigenstates $\{|a\rangle\}$ can be chosen as product states. Longitudinal relaxation can occur due to direct couplings $\mathcal{R}_{aacc}$ between populations, and it can also occur when two populations are coupled to the same coherence: simultaneous transfer from ρ_{aa} to ρ_{bd} and from ρ_{bd} to ρ_{cc} yields indirect transfer from ρ_{aa} to ρ_{cc}. Appendix E presents a proof that if these indirect transfers are eliminated, then $\langle I_z\rangle$ relaxes exponentially to thermal equilibrium with rate constant R_h, regardless of initial conditions. The proof depends on a selection rule, namely, the fact that the matrix element $\langle \nu, a\,|V|\,\mu, c\rangle$ will be nonzero only if eigenstates $|a\rangle$, $|c\rangle$ differ by exactly one spin flip. When the matrix element is nonzero, then the transfer between populations which it characterizes can be calculated as if the other spins were absent.

4.1.1 Two spins

While the single-spin flips associated with direct coupling between populations do not introduce spin-spin correlations, such correlations can be introduced as the result of couplings between populations and coherences. Consider, for example, a system of two noninteracting spins with basis set

$$|1\rangle \equiv |{+}{+}\rangle \tag{3.13}$$

$$|2\rangle \equiv |{+}{-}\rangle \tag{3.14}$$

$$|3\rangle \equiv |{-}{+}\rangle \tag{3.15}$$

$$|4\rangle \equiv |{-}{-}\rangle\,. \tag{3.16}$$

Writing out explicit expressions [7] for the coefficients of the master equation governing this system shows that for each state i, the coefficients $\mathcal{R}_{ii23}$, $\mathcal{R}_{23ii}$, $\mathcal{R}_{ii32}$, and $\mathcal{R}_{32ii}$, which couple coherences to populations, have the same order of magnitude as coefficients which couple populations directly, and since $\omega_{23} = \omega_{32} = \omega_{ii} = 0$, the time-dependent exponential terms appearing in (3.5) do not modulate into the coupling between the population ρ_{ii} and the coherences ρ_{23} and ρ_{32}. Note that $\mathcal{R}_{23ii}$ and $\mathcal{R}_{32ii}$ in particular are responsible for converting populations into coherent superpositions of product states and can therefore introduce spin-spin correlations into the system.

For $i = 2, 3$, these coefficients tend to introduce a negative correlation between states 2 and 3. For instance, it follows from the last paragraph of section 3 that $\mathcal{R}_{2322}$ is associated with processes in which probability amplitude is first transferred from $|2\rangle$ to $|m\rangle$ and then from $|m\rangle$ to $|3\rangle$, where $m = 1$ or $m = 4$, with the probability amplitude changing sign during the two transfers. The change in sign during transfer of probability amplitude from $|2\rangle$ to $|3\rangle$ introduces a negative correlation between the two states. More formally, we can say that since

$$\mathcal{R}_{2322} = -R_0\,(n_{\mathrm{th}} + 1/2)$$

is negative, it tends to introduce a negative correlation between states 2 and 3. Similar processes are associated with the coefficients $\mathcal{R}_{23ii}$ and $\mathcal{R}_{32ii}$, for $i = 2, 3$, and these coefficients have the same value.

In the case where an initially disordered sample relaxes to a trapped state due to its interaction with a resonator at zero Kelvins, we can view these processes as continually renewing the probability amplitude of the coherent superposition $(|+-\rangle - |-+\rangle)/\sqrt{2}$, thereby preventing it from decaying due to the single-spin flips which occur as population is transferred between product-state populations. An alternative point of view would be that the transfers which occur between populations and the coherences ρ_{23} and ρ_{32} constitute an indirect coupling between product-state populations which depletes the ground state and renews the populations of states 2 and 3. For instance, $\mathcal{R}_{1123}$ and $\mathcal{R}_{1132}$ are associated with processes in which both $|2\rangle$ and $|3\rangle$ make a transition to the ground state. Because of the negative correlation which is maintained between states 2 and 3, the product of the probability amplitudes simultaneously transferred from $|2\rangle$ to $|1\rangle$ and from $|3\rangle$ to $|1\rangle$ tends to be negative, which decreases the population of the ground state. The population which disappears from the ground state as a result of its coupling to the coherences ρ_{23} and ρ_{32} is simultaneously added to the populations of states 2 and 3 because of their coupling to the same coherences.

Note that this simple analysis of spin trapping has not taken into account all couplings between coherences and populations. However, the coefficients which take $\rho_{11} \rightarrow \rho_{23}$, $\rho_{11} \rightarrow \rho_{32}$, $\rho_{23} \rightarrow \rho_{44}$, and $\rho_{32} \rightarrow \rho_{44}$ are insignificant at $0\,\mathrm{K}$, since they depend on transitions in which the resonator donates a quantum to the spins. (Indeed, the coupling constants associated with these transfers are proportional to n_{th}.) In addition, transfers from ρ_{44} to ρ_{23} and ρ_{32}, although relevant in the early stages of spin-trapped relaxation, are negligible in later stages, since the population of $|--\rangle$ is entirely depleted by the single-spin flips that couple it to the populations of $|+-\rangle$ and $|-+\rangle$. In the product-state basis, spin trapping can be interpreted in terms of the processes which contribute to $\mathcal{R}_{ii23}$, $\mathcal{R}_{23ii}$, $\mathcal{R}_{ii32}$, and $\mathcal{R}_{32ii}$.

Spin trapping can be suppressed by a perturbation H_1 to the spin Hamiltonian H_s that changes the eigenfrequencies but not the eigenstates. The fastest transfers between the ground state and the coherences ρ_{23}, ρ_{32} are governed by the rate constant

$R_0\left(n_{\mathrm{th}}+1\right)$, and if the lab-frame coherences oscillate in phase with a frequency

$$\left|\omega_{23}\right| \gg 2\pi R_0\left(n_{\mathrm{th}}+1\right),$$

then the couplings between populations and coherences will not contribute to the relaxation of the populations. Under these conditions, the spin-spin flips will cause the longitudinal relaxation to proceed exponentially with rate constant R_h.

4.1.2 N spins

A similar result holds for an initially disordered system of N spins. The matrix elements of the interaction Hamiltonian V allow for two types of processes which can create spin-spin correlations by transferring the populations of product states into coherent superpositions of states. If $a \neq b, c$, then transfer from ρ_{aa} to coherence ρ_{bc} can occur by a process involving the two transitions $|a\rangle \rightarrow |b\rangle$ and $|a\rangle \rightarrow |c\rangle$. The selection rule obtained from (3.9) is

$$\langle a,\mu|\, V\, |b,\nu\rangle\, \langle c,\nu|\, V\, |a,\mu\rangle \neq 0, \tag{3.17}$$

where μ and ν label states of the reservoir. This rule requires that $|b\rangle$ and $|c\rangle$ each differ from $|a\rangle$ by exactly one spin flip, and the transitions $|a\rangle \rightarrow |b\rangle$ and $|a\rangle \rightarrow |c\rangle$ both involve spin flips in the same direction, since both transitions have the reservoir moving from $|\mu\rangle$ to $|\nu\rangle$. We can conclude that ρ_{bc} is a zero-quantum coherence between states which differ by two spin flips in opposite directions. A second type of process which can create spin-spin correlations occurs when $a = b$ or $a = c$. Without loss of generality, we suppose that $a = b$, $a \neq c$. The processes contributing to the development of spin-spin correlations involve transfer from $|a\rangle \rightarrow |m\rangle$ and then from $|m\rangle \rightarrow |c\rangle$ during the correlation time of the reservoir, and (3.12) implies that these processes are allowed if

$$\langle a,\mu|\, V\, |m,\nu\rangle\, \langle m,\nu|\, V\, |c,\mu\rangle \neq 0. \tag{3.18}$$

Rule (3.18) implies that the two transitions $|a\rangle \rightarrow |m\rangle$ and $|m\rangle \rightarrow |c\rangle$ involve a spin flip in opposite directions, since the first is accompanied by the reservoir transition $|\mu\rangle \rightarrow |\nu\rangle$ and the second by the transition $|\nu\rangle \rightarrow |\mu\rangle$, and since the interaction Hamiltonian V only couples product states which differ by a single spin flip. For this case as well, ρ_{bc} is a zero-quantum coherence between states differing by a "flip-flop."

The development of resonator-induced spin-spin correlations in an initially disordered system depends on transfer from product-state populations to zero-quantum "flip-flop" coherences. If the periods of such coherences are short compared to the time required for this transfer, the cumulative effect of the transfers will be negligible, and no coherences will be excited. In this case, we can consider the populations to be coupled only to populations, which yields a problem for which the longitudinal relaxation proceeds exponentially with rate constant R_h. Note that as the number N of spins is increased, the number of processes which contribute to coefficients such as $\mathcal{R}_{acaa}$ increases, since many states $|m\rangle$ become accessible to $|a\rangle$ as intermediates in the transition to $|c\rangle$. In addition, the rate at which coherent superpositions of product states are renewed by these processes in general depends on the instantaneous value of many elements in the density matrix, as well as on the value of many coupling constants. It is therefore not immediately obvious how large the frequencies of the "flip-flop" zero-quantum coherences must be in order to suppress the cumulative effect of the processes responsible for spin-trapping.

We can obtain a rough estimate of the time T_{trap} required for the resonator to induce spin-spin correlations in an initially disordered system. For large N, equation (3.1) implies that

$$\langle I_z \rangle_{\text{trap}} \approx \sqrt{\frac{N}{2}} \tag{3.19}$$

is the final value of $\langle I_z \rangle$ when the resonator at zero Kelvins. Substituting (3.19) into the relaxation equation for $\langle I_z \rangle$ and setting the derivative equal to zero yields

$$0 \approx -R_0 \langle I_z \rangle_{\text{trap}} + R_0 \left\langle I_x^2 + I_y^2 \right\rangle_{\text{trap}},$$

from which it follows that

$$\left\langle I_x^2 + I_y^2 \right\rangle_{\text{trap}} \approx \sqrt{\frac{N}{2}}.$$

Our estimate of the time T_{trap} depends on the claim that $\left\langle I_x^2 + I_y^2 \right\rangle$ decreases monotonically from $N/2$ to $\sqrt{N/2}$ as spin-spin correlations develop. In supporting this claim, we use a basis of angular momentum eigenstates $|I, M\rangle$, where M denotes the eigenvalue for the operator I_z. The states $|I, M\rangle$ are also eigenstates of the operator $I_x^2 + I_y^2$:

$$\begin{aligned} \left(I_x^2 + I_y^2\right) |I, M\rangle &= \left(I_- I_+ + I_z\right) |I, M\rangle \\ &= \left\{ I\left(I+1\right) - M^2 \right\} |I, M\rangle . \end{aligned}$$

Note that within each angular momentum manifold, the value of $\left\langle I_x^2 + I_y^2 \right\rangle$ varies as $-M^2$. A completely disordered system has equal population in each state $|I, M\rangle$, and resonator-induced relaxation eventually moves the entire population to the state with $M = I$. It is clear that once the bulk of the population of a given angular momentum manifold has been transferred to states with positive M, continued spontaneous emission from the spins to the resonator's mode will decrease $\left\langle I_x^2 + I_y^2 \right\rangle$, since emission from a state with positive M increases the value of M. For several values of I between $I = 2$ and $I = 100$, we have used the formulas for the spontaneous emission rate of states $|I, M\rangle$ [16] to simulate the mechanical cooling of a single angular momentum system in which all states $|I, M\rangle$ initially have equal population. In these simulations, $\left\langle I_x^2 + I_y^2 \right\rangle$ decreased monotonically throughout the cooling process. It is reasonable to conclude that monotonic decrease of $\left\langle I_x^2 + I_y^2 \right\rangle$ would occur for any value of $\dot{I}$, which implies that $\left\langle I_x^2 + I_y^2 \right\rangle$ decreases monotonically in a disordered spin system.

This conclusion allows us to obtain a lower bound on the time required for resonator-induced spin-spin correlations to develop. We rewrite the longitudinal relaxation equation as

$$\frac{d}{dt} \langle I_z \rangle \approx -R_0 \left(\langle I_z \rangle - \left\langle I_x^2 + I_y^2 \right\rangle \right), \tag{3.20}$$

and note that $\langle I_z \rangle$ increases exponentially toward the instantaneous value of $\left\langle I_x^2 + I_y^2 \right\rangle$. If $\left\langle I_x^2 + I_y^2 \right\rangle$ were constant during the spin-trapped cooling, the polarization would evolve exponentially, with a rate constant independent of N. When $\left\langle I_x^2 + I_y^2 \right\rangle$ decreases from $N/2$ down to $\sqrt{2/N}$, however, the derivative of $\langle I_z \rangle$ is decreased by the presence of resonator-induced spin-spin correlations. We might guess that $\langle I_z \rangle$ initially follows the relaxation curve predicted for a system in which such correlations are suppressed, but then flattens out as $\langle I_z \rangle$ takes on a value of order $\langle I_z \rangle_{\text{trap}}$. (Note that if $\langle I_z \rangle_{\text{trap}}$ is significantly smaller than the thermal value of $\langle I_z \rangle$, then the resulting curve can be interpreted as fast, coherent relaxation to the trapped state, since $\langle I_z \rangle$ relaxes to $\langle I_z \rangle_{\text{trap}}$ much faster than a function decaying exponentially toward $\langle I_z \rangle_{\text{trap}}$ with rate constant R_h.) Since it follows from (3.20) that the magnitude of $d \langle I_z \rangle / dt$ decreases with time, a lower bound T_{trap} on the time required for this coherent relaxation to occur can be obtained using the initial value of the derivative:

$$
\begin{aligned}
T_{\text{trap}} &= \left(\langle I_z \rangle_{\text{trap}} \right) / \frac{d \langle I_z \rangle}{dt} (0) \\
&= \frac{1}{R_0 \sqrt{N/2}}.
\end{aligned}
\tag{3.21}
$$

Simulations of spin-trapped cooling presented in section 2.1 of chapter 6 suggest that for an initially disordered sample, T_{trap} is a good estimate of the time required for $\langle I_z \rangle$ to relax from zero to a value which differs from $\langle I_z \rangle_{\text{trap}}$ by a factor of order unity. Note as well that since we are considering spins 1/2, (3.21) is consistent with the estimate (3.4) obtained from the semiclassical model.

For an initially disordered system of noninteracting spins which all experience the same field, we can also consider T_{trap} to be a lower bound on the time required for the resonator-induced spin-spin correlations to develop fully. This follows from the fact that $\left\langle I_x^2 + I_y^2 \right\rangle$ depends strongly on M, since transitions between states of different M causes changes in both $\langle I_z \rangle$ and $\left\langle I_x^2 + I_y^2 \right\rangle$. We can conclude that if all "flip-flop" zero-quantum coherences oscillate within a period of time $\lesssim T_{\text{trap}}$, then spin trapping of an initially disordered sample will be partially disrupted, since the relative phase of the populations and these coherences will vary on the time scale needed for transfers between coherences and populations to induce spin-spin correlations. If the periods of these coherences are much less than T_{trap}, then spin trapping should be effectively suppressed.

4.2 Dipole-dipole coupled spins

4.2.1 Two spins

We turn our attention to the longitudinal relaxation of a system of spins coupled by the secular dipolar Hamiltonian H_D, beginning with a system of two spins. If no chemical shifts are present, then the eigenstates of the system are given by the set $B \equiv \{|p\rangle, |q\rangle, |r\rangle, |s\rangle\}$, where

$$|p\rangle \equiv |{+}{+}\rangle, \tag{3.22}$$

$$|q\rangle \equiv \left(|{+}{-}\rangle + |{-}{+}\rangle\right)/\sqrt{2}, \tag{3.23}$$

$$|r\rangle \equiv |{-}{-}\rangle, \tag{3.24}$$

$$|s\rangle \equiv \left(|{+}{-}\rangle - |{-}{+}\rangle\right)/\sqrt{2}. \tag{3.25}$$

When the master equation is projected onto this basis set, we find that there is no coupling between populations and coherences, and the population ρ_{ss} does not relax at all. These results, which can be obtained by considering the matrix elements of the interaction Hamiltonian V, do not depend on the exact eigenfrequencies of the system. Indeed, if the eigenfrequencies are perturbed, then the longitudinal relaxation will be unaffected, since transfer between populations is unaffected by such perturbations. In particular, longitudinal relaxation does not depend on the strength of the dipolar coupling.

For a system in which one of the two spins has a chemical shift, the longitudinal relaxation depends strongly on the relative magnitude of the chemical shift and the dipolar coupling. If H_D is much larger than the chemical shift Hamiltonian H_{shift}, then the spin eigenstates are approximately those of the set B, and the longitudinal relaxation is only weakly affected by the presence of the chemical shift. If $H_{\text{shift}} \gg$

H_D, then the eigenstates are perturbed product states, and the longitudinal relaxation will proceed exponentially with rate constant R_h, provided that $|\omega_{23}|$ is sufficiently large to disrupt transfer between coherences and populations, where

$$\begin{aligned} |2\rangle &\equiv |{+}{-}\rangle \, , \\ |3\rangle &\equiv |{-}{+}\rangle \, , \end{aligned}$$

as in (3.13) through (3.16). If $n_{\text{th}} \ll 1$, as in the case of the example resonator presented in table 5.3, then the condition

$$|\omega_{23}| \gg 2\pi R_0 \tag{3.26}$$

is sufficient to guarantee that the contribution of spin-spin correlations to longitudinal relaxation is suppressed, regardless of initial conditions. This follows from the fact that the terms coupling populations to coherences between $|2\rangle$ and $|3\rangle$ have magnitude $\lesssim R_0$ when $n_{\text{th}} \ll 1$. In the limit where $H_{\text{shift}} \gg H_D$, we can consider H_D to be a perturbation of H_{shift} and use first-order perturbation theory to find ω_2 and ω_3. From

$$\begin{aligned} H_{\text{shift}} &= \omega_{\text{shift}} I_{z,1}, \\ H_D &= \omega_{dd} \left(3 I_{z,1} I_{z,2} - \mathbf{I}_1 \cdot \mathbf{I}_2 \right) , \end{aligned}$$

we obtain

$$\omega_1 \approx \omega_0 + \frac{1}{2} \left(\omega_{\text{shift}} + \omega_{dd} \right) , \tag{3.27a}$$

$$\omega_2 \approx \frac{1}{2} \left(\omega_{\text{shift}} - \omega_{dd} \right) , \tag{3.27b}$$

$$\omega_3 \approx \frac{1}{2} \left(-\omega_{\text{shift}} - \omega_{dd} \right) , \tag{3.27c}$$

$$\omega_4 \approx -\omega_0 + \frac{1}{2} \left(-\omega_{\text{shift}} + \omega_{dd} \right) , \tag{3.27d}$$

which allows us to express (3.26) as

$$|\omega_{\text{shift}}| \gg 2\pi R_0.$$

An alternative way of understanding the ineffectiveness of a small chemical-shift difference in modifying the relaxation of the dipole-coupled system is to transform H_{shift} into the rotating frame in which the fast evolution due to the secular dipolar coupling is absent. In this rotating frame, the time-independent component of H_{shift} is proportional to I_z, and therefore has no effect on relaxation. Using the language of the semiclassical model introduced in the first section, we can say that the component of H_{shift} which survives averaging due to oscillations induced by the dipolar coupling does not modulate the indirect spin-spin torques responsible for coherent relaxation.

4.2.2 Three spins

We now consider a system of three spins which are coupled by the secular dipolar Hamiltonian

$$\begin{aligned} H_D = {} & \omega_{12}\left(3I_{z,1}I_{z,2} - \mathbf{I}_1 \cdot \mathbf{I}_2\right) + \omega_{13}\left(3I_{z,1}I_{z,3} - \mathbf{I}_1 \cdot \mathbf{I}_3\right) \\ & + \omega_{23}\left(3I_{z,2}I_{z,3} - \mathbf{I}_2 \cdot \mathbf{I}_3\right). \end{aligned}$$

The rules for addition of angular momenta allow a collection of three spins 1/2 to be represented as a single angular momentum $I = 3/2$ and two angular momenta $I = 1/2$. For our purposes, it is convenient to define one of the $I = 1/2$ angular momentum systems to be

$$|1/2,+\rangle = \{(\omega_{13}-\omega_{23})\,|++-\rangle + (\omega_{23}-\omega_{12})\,|+-+\rangle + (\omega_{12}-\omega_{13})\,|-++\rangle\}\,\frac{1}{C}, \tag{3.28}$$

$$|1/2,-\rangle = \{(\omega_{13}-\omega_{23})\,|--+\rangle + (\omega_{23}-\omega_{12})\,|-+-\rangle + (\omega_{12}-\omega_{13})\,|+--\rangle\}\,\frac{-1}{C}, \tag{3.29}$$

$$C \equiv (\omega_{12}-\omega_{13})^2 + (\omega_{12}-\omega_{23})^2 + (\omega_{13}-\omega_{23})^2 .$$

The states of this angular momentum system are also eigenstates of H_D:

$$H_D\,|1/2,+\rangle = H_D\,|1/2,-\rangle = 0.$$

Population which begins in one of these states can only move between the two states during the mechanical cooling, since the matrix elements of the spin-resonator interaction Hamiltonian V ensure that the population of any angular momentum system is not coupled to the population of any other spin eigenstate or to any coherences between eigenstates. For an initially disordered system cooled by a resonator at 0 K, one-fourth of the population will eventually be trapped in the nondecaying state $|1/2,+\rangle$. As in the case of two spins, additional terms in the spin Hamiltonian can only be effective in suppressing this spin trapping if they significantly perturb the spin eigenstates. Since H_D does not in general commute with the Hamiltonian which shifts the Larmor frequencies of distinct spins by different amounts, chemical shifts of magnitude comparable to the dipolar coupling would modify the eigenstates sufficiently to break the selection rule responsible for trapping the population away from the ground state.

In order to determine whether the population of the remaining $I = 1/2$ manifold will quickly reach the ground state during spin-resonator relaxation, we considered ten example systems having randomly generated coupling constants ω_{ij}. For five of these examples, the value of each $\omega_{ij}/2\pi$ was a uniformly distributed random number between 1 kHz and 2 kHz, and for the remaining five examples, $\omega_{ij}/2\pi$ was uniformly

$(\omega_{12}, \omega_{13}, \omega_{23})/2\pi$	p
$(1476, 352, 1843)$ Hz	0.85
$(1871, 1834, 811)$ Hz	0.92
$(1787, 116, 821)$ Hz	0.78
$(1626, 20, 706)$ Hz	0.76
$(406, 397, 278)$ Hz	0.98

Table 3.1: Mixing of angular momentum systems.

distributed between 0 Hz and 2 kHz. In the cases where $1\,\text{kHz} \leq \omega_{ij}/2\pi \leq 2\,\text{kHz}$, each spin eigenstate had at least 95% of its population in a single angular momentum manifold. In these systems, H_D induces only weak mixing of the angular momentum manifolds, and we would expect that the population would first relax quickly to the low-energy state of each manifold, and would then relax slowly as population is transferred from one of $I = 1/2$ manifolds to the $I = 3/2$ manifold. Simulations of relaxation in a three-spin system confirmed this conjecture, and section 2.2 of chapter 6 presents similar simulations for four-spin systems. After the population of each angular momentum system (or "manifold") has reached the low-energy state of the manifold, the rate of longitudinal relaxation depends on the efficiency with which H_D couples manifolds.

Choosing $0\,\text{Hz} \leq \omega_{ij}/2\pi \leq 2\,\text{kHz}$ generally gave more effective mixing of the two angular momentum manifolds. We found that for a given set of values ω_{ij}, the mixing of the two angular momentum systems could be characterized by just one probability p. Calculation of the eigenstates for these systems shows that for each eigenstate $|a\rangle$ which includes contributions from both manifolds, the probability of detecting angular momentum I_a is p, where I_a is the angular momentum of the manifold making the dominant contribution to $|a\rangle$, and p is independent of $|a\rangle$. Table 3.1 shows that mixing was most effective when the values of ω_{ij} were well separated.

4.2.3 N spins

For larger systems, we note first that since H_D commutes with I_z, it can only couple states having the same value of I_z. We thus consider two limiting cases. When resonator-induced relaxation within a manifold is fast compared to the rate at which

H_D transfers population between manifolds, then the population of a manifold will quickly decay to the low-energy state of that manifold and then slowly be transferred to unpopulated states having the same value of I_z but belonging to manifolds of higher angular momentum. In the opposite limit, H_D will quickly equalize the population of all states which have the same value of I_z. Resonator-induced transfers of population to low-energy states within a manifold immediately results in compensating transfers that equalize the populations of all states within a given eigenspace of I_z. Section 2.2 of chapter 6 presents simulations of longitudinal relaxation for this regime.

Note that if the spin system were temporarily moved out of the large applied field, the nonsecular part of the dipolar Hamiltonian would be "turned on," and we could expect a spin temperature to be established, so that the system could be viewed as an ensemble of independent spins. If the secular dipolar Hamiltonian is found to couple angular momentum systems too weakly for efficient cooling, moving the spin-resonator system adiabatically in and out of the high field might speed up the relaxation. When the spins have been moved out of the high field, a low spin temperature would correspond to a strong dipole order. Moving the system adiabatically back into the high field would convert the dipolar order of the thermal spin system to Zeeman order, and interactions with the resonator could then cool the system for a period of time until the ground states of the angular momentum systems have accumulated excess population and the cooling has slowed. The changes in the field at the spins would need to be slow enough that the entropy of the spin system would not change as the field varies. If the spin temperature could be repeatedly re-established on a time scale short compared to the time needed for resonator-induced spin-spin correlations to develop, then the spins could be considered independent during the relaxation. In the limiting case where the time needed to re-establish the spin temperature is negligible, longitudinal relaxation would proceed exponentially with a time constant $1/R_h$.

5 Transverse relaxation of freely-precessing spins

For sufficiently large N, we expect "radiation damping" to rotate the magnetization away from the transverse axis and toward the longitudinal axes, causing the transverse magnetization to decay more quickly than it would if only a single spin were present. As Abragam points out, this process is reversible and is not properly considered a form of relaxation [12]. However, the resonator could also induce fast, irreversible transverse relaxation. We can see this by considering a two-spin system with the basis of eigenstates given by equations (3.13) through (3.16), which we restate here for convenience:

$$|1\rangle \equiv |{+}{+}\rangle\,,$$

$$|2\rangle \equiv |{+}{-}\rangle\,,$$

$$|3\rangle \equiv |{-}{+}\rangle\,,$$

$$|4\rangle \equiv |{-}{-}\rangle\,.$$

The rotating-frame evolution equation for a coherence ρ_{ab} is

$$\frac{d}{dt}\rho_{ab}\left(t\right) = \sum_{c,d} \exp\left\{i\left(\omega_{ab}-\omega_{cd}\right)t\right\}\mathcal{R}_{abcd}\,\rho_{cd}\left(t\right),$$

and the cumulative effect on ρ_{ab} of the physical processes characterized by the coupling $\mathcal{R}_{abcd}$ will be negligible if

$$\left|\omega_{ab}-\omega_{cd}\right| \gg 2\pi\mathcal{R}_{abcd},$$

due to fast variation in the phase of lab-frame coherences. Assume for the sake of simplicity that frequency differences $\left|\omega_{12}-\omega_{cd}\right|$ suppress couplings between ρ_{12} and other terms of the density matrix so that the relaxation of ρ_{12} is governed by the single constant

$$\begin{aligned}\Gamma_{12} &= \frac{1}{2}\left(\sum_{n\neq 1}\Gamma_{1\to n} + \sum_{n\neq 2}\Gamma_{2\to n}\right)\\ &= \frac{1}{2}\left(\Gamma_{1\to 2} + \Gamma_{1\to 3} + \Gamma_{2\to 1} + \Gamma_{2\to 4}\right)\\ &= \frac{R_0}{2}\left\{n_{\text{th}} + n_{\text{th}} + (n_{\text{th}} + 1) + n_{\text{th}}\right\}\\ &= \frac{R_0}{2}\left(4n_{\text{th}} + 1\right).\end{aligned}$$

The damping constant Γ_{12} includes contributions from four transitions; by way of contrast, note that for a single spin, the damping constant for a coherence between the states $|+\rangle$, $|-\rangle$ includes contributions from only two transitions, $|+\rangle \to |-\rangle$ and $|-\rangle \to |+\rangle$, and has magnitude $(R_0/2)\,(2n_{\text{th}} + 1)$. At temperatures for which n_{th} is of order unity or larger, the two-spin single-quantum coherence will decay much more quickly than the single-spin coherence.

The reasoning used in this example can be extended to suggest that the damping constant for a single-quantum coherence between product states will increase in magnitude as N is increased. An increase in the damping constants for single-quantum coherences does not always imply that the rate of transverse relaxation increases, however. Consider, for instance, a system of two spins for which the spin Hamiltonian is

$$H = \omega_0 I_z + \omega_{\text{shift}} I_{z,1},$$

with

$$|\omega_{\text{shift}}| \gg 2\pi R_0\,(n_{\text{th}} + 1)\,.$$

The coherences in the set $Z_2 = \{\rho_{12}, \rho_{34}\}$ have the same frequency, since they both involve a flip of spin 2; similarly, the coherences $Z_1 = \{\rho_{13}, \rho_{24}\}$ both involve a flip of spin 1. Physical processes which cause transfer from a coherence in Z_1 to one in Z_2 have no cumulative effect on the relaxation of Z_2 coherences, since the phase difference between a Z_1 coherence and a Z_2 coherence cycles quickly during the time required for the transfer to accumulate. The coupling between the two coherences of

Z_1 is significant, however, and the relaxation equations for ρ_{12} and ρ_{34} can be written as

$$\frac{d}{dt}\rho_{12} = -R_0\left(n_{\text{th}} + \frac{1}{2}\right)\rho_{12} + \left\{-R_0 n_{\text{th}}\rho_{12} + R_0\left(n_{\text{th}} + 1\right)\rho_{34}\right\},$$
$$\frac{d}{dt}\rho_{34} = -R_0\left(n_{\text{th}} + \frac{1}{2}\right)\rho_{34} + \left\{R_0 n_{\text{th}}\rho_{12} - R_0\left(n_{\text{th}} + 1\right)\rho_{34}\right\}.$$

Note that the first term on the right side of each equation tends to yield exponential relaxation with rate constant $R_0\left(n_{\text{th}} + \frac{1}{2}\right)$, while the second is responsible for reversible transfer between ρ_{12} and ρ_{34}. Adding together these two equations yields

$$\frac{d}{dt}\left(\rho_{12} + \rho_{34}\right) = -R_0\left(n_{\text{th}} + \frac{1}{2}\right)\left(\rho_{12} + \rho_{34}\right).$$

The other coherences which contribute to $\langle I_x \rangle$ can similarly be paired to form sums which decay exponentially, and we find that

$$\frac{d}{dt}\langle I_x \rangle = -R_0\left(n_{\text{th}} + \frac{1}{2}\right)\langle I_x \rangle. \tag{3.30}$$

This result can be generalized to N spins. If the product states are eigenstates of the spin Hamiltonian, then each single-quantum coherence involves a flip of just one spin. Group the single-quantum coherences into sets Z_k, where the coherences in set Z_k are between states which differ by a flip of spin k. If the eigenfrequencies of the product states are such that all couplings between coherences within a set Z_k are preserved, while all couplings responsible for transfer between a Z_k coherence and another coherence are suppressed by frequency differences, then equation (3.30) holds. A simple spin Hamiltonian which meets these conditions is

$$H = \omega_0 I_z + \sum_{i=1}^{n} \omega_i I_{z,i}, \tag{3.31}$$

provided the spacing between Larmor frequencies of distinct spins is sufficiently large.

These conditions can be stated more transparently in terms of the physical processes responsible for transfer between coherences. Consider first a single-quantum coherence ρ_{ab} in Z_k. The matrix elements of the Jaynes-Cummings Hamiltonian allow transfer from ρ_{ab} to other coherences by two types of processes: 1) Processes associated with two transitions, $|a\rangle \rightarrow |c\rangle$ and $|b\rangle \rightarrow |d\rangle$, with both transitions involving a flip of spin j in the same direction, for some $j \neq k$, and 2) Processes such as $|a\rangle \rightarrow |m\rangle \rightarrow |c\rangle$, in which one transition has spin i flipping up and the other has spin $j \neq i$ flipping down. The first type of process couples a coherence ρ_{ab} in Z_k to other coherences in Z_k, while the second type couples ρ_{ab} to coherences in Z_j, for $j \neq k$, as well as to triple-quantum coherences. If the eigenfrequencies are such that the couplings associated with the first type of process are preserved, while those associated with the second type of process are suppressed, then (3.30) holds. This result is derived in Appendix F.

Section 2.2 of chapter 6 presents simulations which show that "turning on" the dipolar coupling can increase the rate of resonator-induced transverse relaxation in a four-spin system. A similar result can be obtained analytically for a system of two spins, as we now show. First, note that if all couplings allowed by the matrix elements of the interaction Hamiltonian V contribute to spin relaxation, the transverse relaxation is not governed by a single exponential. This can be illustrated by using the spin Hamiltonian

$$H = \omega_0 I_z,$$

and the basis set B:

$$\begin{aligned}
|p\rangle &\equiv |{+}{+}\rangle , \\
|q\rangle &\equiv \left(|{+}{-}\rangle + |{-}{+}\rangle\right)/\sqrt{2}, \\
|r\rangle &\equiv |{-}{-}\rangle , \\
|s\rangle &\equiv \left(|{+}{-}\rangle - |{-}{+}\rangle\right)/\sqrt{2}.
\end{aligned}$$

We have

$$\langle I_x\rangle = \frac{1}{\sqrt{2}}\left(\rho_{pq} + \rho_{qr} + \rho_{qp} + \rho_{rq}\right).$$

The coefficients of the master equation can be found by calculating the matrix elements of V, and for a resonator at zero Kelvins, we find that

$$\begin{aligned}\langle I_x\rangle(t) &= \frac{1}{\sqrt{2}}\left\{\rho_{pq}(0)+\rho_{qp}(0)\right\}\exp\left(-R_0t\right) \\ &+ \frac{1}{\sqrt{2}}\left\{\rho_{qr}(0)+\rho_{rq}(0)\right\}\left\{2\exp\left(-R_0t\right)-\exp\left(-2R_0t\right)\right\}.\end{aligned} \tag{3.32}$$

For this system, curves for transverse relaxation are sums of exponentials having rate constants R_0 and $2R_0$, rather than a single exponential with rate constant $R_0/2$, as would be expected for lifetime broadening.

If additional terms in the spin Hamiltonian perturb the difference frequencies ω_{pq} and ω_{qr} so as to yield a sufficiently large frequency difference $|\omega_{pq}-\omega_{qr}|$, the physical processes previously responsible for the reversible transfer between ρ_{pq} and ρ_{qr} will instead produce irreversible loss of order. Transfers away from a given coherence decrease the magnitude of that coherence without increasing the magnitude of any other coherences, due to fast variation in the relative phase of coherences. A single-quantum coherence ρ_{ab} will then decay at a rate determined by the damping constant Γ_{ab}, which may be calculated by evaluating the transition probabilities for all allowed transitions $|a\rangle\rightarrow|m\rangle$ and $|b\rangle\rightarrow|n\rangle$. If the two spins are coupled by a sufficiently strong dipolar Hamiltonian, we have

$$\begin{aligned}\langle I_x\rangle(t) &= \frac{1}{\sqrt{2}}\left\{\rho_{pq}(0)+\rho_{qp}(0)\right\}\exp\left\{-R_0t\right\} \\ &+ \frac{1}{\sqrt{2}}\left\{\rho_{qr}(0)+\rho_{rq}(0)\right\}\exp\left\{-2R_0t\right\}.\end{aligned} \tag{3.33}$$

"Turning on" the dipolar coupling increases the rate of transverse relaxation by changing the interaction-frame equation for $\langle I_x\rangle(t)$ from (3.32) to (3.33). If all spins are initially aligned with the x-axis, for instance, then the initial values of the coherences ρ_{pq}, ρ_{qr}, ρ_{qp}, ρ_{rq} are equal, and the contribution $\left\{\rho_{qr}(t)+\rho_{rq}(t)\right\}$ to $\langle I_x\rangle(t)$ decays more quickly when the dipolar coupling is present.

Resonator-induced transverse relaxation faster than that expected for a single spin can be distinguished from radiation damping. Since radiation damping rotates the sample dipole, it causes growth in $\langle I_z \rangle$ that is simultaneous with the decay of the transverse dipole. However, fast transverse relaxation may occur even under conditions which guarantee that longitudinal relaxation will proceed exponentially with rate constant R_h. If the frequencies of "flip-flop" zero-quantum coherences between product states differ sufficiently from zero, the contribution of spin-spin correlations to longitudinal relaxation will be suppressed, regardless of the initial conditions. If, in addition, degeneracies among the frequencies of single-quantum coherences are sufficiently perturbed, the rate of transverse relaxation will be determined by the damping constants Γ_{ab}, which tend to increase in magnitude as the number of spins is increased.

A two-spin system having weak dipolar coupling and a large chemical shift offset between the spins would satisfy these conditions. When the chemical shift offset is much larger than the dipolar coupling, the energy eigenstates are weakly perturbed product states, and the resonator will induce exponential longitudinal relaxation with rate constant R_h if the offset is large enough to suppress the couplings between product-state populations and zero-quantum coherences. When a weak dipolar coupling is also present, the rate of transverse relaxation can be characterized using (3.27a) through (3.27d) to estimate the frequencies of single quantum coherences. We have

$$\begin{aligned}
\omega_{12} &\approx \omega_0 + \omega_{dd}, \\
\omega_{13} &\approx \omega_0 + \omega_{\text{shift}} + \omega_{dd}, \\
\omega_{24} &\approx \omega_0 + \omega_{\text{shift}} - \omega_{dd}, \\
\omega_{34} &\approx \omega_0 - \omega_{dd},
\end{aligned}$$

where the eigenfunctions are weakly perturbed from those given in (3.13) through (3.16). If

$$|\omega_{dd}| \gg \pi R_0,$$

then all transfer between single-quantum coherences will be suppressed due to the fast variation in the relative phase between each pair of coherences, and the damping constants for single-quantum coherences will determine the rate of transverse relaxation. We find that

$$\begin{aligned}\langle I_x\rangle = &\frac{1}{2}\left(\rho_{12}+\rho_{21}+\rho_{13}+\rho_{31}\right)\exp\left\{-\frac{1}{2}R_0 t\right\} \\ &+\frac{1}{2}\left(\rho_{42}+\rho_{24}+\rho_{43}+\rho_{34}\right)\exp\left\{-\frac{3}{2}R_0 t\right\}.\end{aligned} \tag{3.34}$$

Section 2.2 of chapter 6 presents a simulation of a four-spin system for which the chemical-shift offset between spins is large compared to the dipolar coupling. Although the large spacing of the chemical shifts yields longitudinal relaxation with time constant $1/R_h$, as discussed in section 4, the presence of the dipolar coupling accelerates the transverse relaxation induced by the resonator. The transverse dipole decays in a fraction of the time required for transverse relaxation of a single-spin sample.

6 Transverse relaxation during spin-locking

Resonator-induced longitudinal relaxation between transients is potentially useful as a substitute for spin-lattice relaxation, but fast transverse relaxation induced by the resonator is generally undesirable, since it would tend to shorten the lifetime of the signal. In this section, we show that spin-locking can in principle be used to limit resonator-induced transverse relaxation to exponential relaxation with rate constant

$$T_{1\rho}^{-1} = R_h/2. \tag{3.35}$$

We begin from the reduced master equation (2.17) for the spin system:

$$\begin{aligned}\frac{d}{dt}\rho_s &= -i\left[H_s,\rho_s\right] - \frac{1}{2}R_0\left(n_{\mathrm{th}}+1\right)\left[I_-I_+,\rho_s\right]_+ + R_0\left(n_{\mathrm{th}}+1\right)I_+\rho_sI_- \\ &\quad - \frac{1}{2}R_0n_{\mathrm{th}}\left[I_+I_-,\rho_s\right]_+ + R_0n_{\mathrm{th}}I_-\rho_sI_+, \\ H_s &= H^{\mathrm{int}}_{\mathrm{secular}} + \omega_1I_y,\end{aligned} \tag{3.36}$$

where $H^{\mathrm{int}}_{\mathrm{secular}}$ is the secular internal Hamiltonian, and ω_1I_y is the Hamiltonian for the spin-locking field. We switch to a reference frame in which the fast motion associated with ω_1I_y has been eliminated. (We shall refer to this frame as the "toggling frame.") The density matrix in the toggling frame can be written as

$$\begin{aligned}\rho_s' &= U_1^{-1}\left(t\right)\rho_sU_1\left(t\right), \\ U_1\left(t\right) &= \exp\left(-i\omega_1I_yt\right),\end{aligned}$$

and it follows from (3.36) that the time derivative of ρ_s' is

$$\begin{aligned}\frac{d}{dt}\rho_s' &= -i\left[H^{\mathrm{int}}_{\mathrm{toggling}},\rho_s'\right] \\ &\quad - \frac{1}{2}R_0\left(n_{\mathrm{th}}+1\right)\left[I_-'I_+',\rho_s'\right]_+ + R_0\left(n_{\mathrm{th}}+1\right)I_+'\rho_s'I_-' \\ &\quad - \frac{1}{2}R_0n_{\mathrm{th}}\left[I_+'I_-',\rho_s'\right]_+ + R_0n_{\mathrm{th}}I_-'\rho_s'I_+',\end{aligned} \tag{3.37}$$

where

$$\begin{aligned}H^{\mathrm{int}}_{\mathrm{toggling}} &= U_1^{-1}\left(t\right)H^{\mathrm{int}}_{\mathrm{secular}}U_1\left(t\right), \\ I_+' &= U_1^{-1}\left(t\right)I_+U_1\left(t\right), \\ I_-' &= U_1^{-1}\left(t\right)I_-U_1\left(t\right).\end{aligned}$$

From (3.37) we obtain the equation of motion for $\langle I_y \rangle$ in the toggling frame:

$$\begin{aligned}\frac{d}{dt}\langle I_y\rangle &= -i\left\langle\left[I_y\,, H^{\mathrm{int}}_{\mathrm{toggling}}\right]\right\rangle \\ &\quad -\frac{1}{2}R_0\left(n_{\mathrm{th}}+1\right)\left\langle\left[I_y, I'_- I'_+\right]_+\right\rangle + R_0\left(n_{\mathrm{th}}+1\right)\left\langle I'_- I_y I'_+\right\rangle \\ &\quad -\frac{1}{2}R_0 n_{\mathrm{th}}\left\langle\left[I_y, I'_+ I'_-\right]_+\right\rangle + R_0 n_{\mathrm{th}}\left\langle I'_+ I_y I'_-\right\rangle .\end{aligned} \tag{3.38}$$

Equation (3.38) can be written as

$$\frac{d}{dt}\langle I_y\rangle = -\frac{1}{2}R_h\langle I_y\rangle - i\left\langle\left[I_y\,, H^{\mathrm{int}}_{\mathrm{toggling}}\right]\right\rangle + \langle L_{\mathrm{osc}} I_y\rangle\,, \tag{3.39}$$

where L_{osc} is a superoperator which averages to zero during a time period of length $2\pi/\omega_1$. For sufficiently large ω_1, only the first term on the right side of (3.39) makes a nonnegligible contribution to the evolution, since the time average of the remaining terms is zero. The fact that the commutator on the right side of (3.39) averages to zero can be established by noting that $H^{\mathrm{int}}_{\mathrm{toggling}}$ is obtained by performing a rotation of $H^{\mathrm{int}}_{\mathrm{secular}}$ around the y-axis in spin space, and the time average of $H^{\mathrm{int}}_{\mathrm{toggling}}$ is invariant under infinitesimal rotations around the same axis. Spin-locking can therefore be used to limit the rate of resonator-induced transverse relaxation, provided ω_1 is large enough to average the internal Hamiltonian and the relaxation superoperator in the toggling frame. Section 2.2 of chapter 6 presents a simulation of an artificial four-spin system for which spin-locking yields transverse relaxation closely approximating an exponential curve with rate constant $R_h/2$.