PHYSICAL REVIEW A **81**, 032111 (2010)

Quasiequilibria in open quantum systems

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(Received 17 August 2009; published 9 March 2010)

In this work, the steady-state or quasiequilibrium resulting from periodically modulating the Liouvillian of an open quantum system, $\widehat{\mathscr{L}}(t)$, is investigated. It is shown that differences between the quasiequilibrium and the instantaneous equilibrium occur due to nonadiabatic contributions from the gauge field connecting the instantaneous eigenstates of $\widehat{\mathscr{L}}(t)$ to a fixed basis. These nonadiabatic contributions are shown to result in an additional rotation and/or depolarization for a single spin-1/2 in a time-dependent magnetic field and to affect the thermal mixing of two coupled spins interacting with a time-dependent magnetic field.

DOI: 10.1103/PhysRevA.81.032111 PACS number(s): 03.65.Yz, 75.10.Jm, 05.30.−d, 76.60.−k

I. INTRODUCTION

Elucidating the quantum dynamics of open systems is important for designing and implementing quantum computing (QC) [1] and quantum information (QI) applications [2,3] and for understanding the foundations of quantum statistical mechanics [4–8]. In particular, since most applications use systems which are initially in thermal equilibrium, understanding thermalization and the nature of the thermal equilibrium for an open quantum system is very important for optimizing QC and QI applications. Both thermalization and thermal equilibrium depend upon the system, environment, and system-environment Hamiltonians, $\widehat{H}_{\text{sys}}$, $\widehat{H}_{\text{env}}$, and $\widehat{H}_{\text{sys-env}}$ respectively, and these Hamiltonians can in principle be controlled in order to guide the thermalization process. For instance, recent work has demonstrated that directly engineering [9] or coherently modulating [10–12] $\widehat{H}_{\text{env}}$ and/or $\widehat{H}_{\text{sys-env}}$ for environments consisting of only a few degrees of freedom can effectively influence the system's dynamics and control the thermalization process [13].

For more complex environments, however, it is in general easier to control the system's dynamics by coherently modulating $\widehat{H}_{\text{sys}}$. By coherently controlling the energies and eigenstates of $\widehat{H}_{\text{sys}}$, the incoherent dynamics and thermalization can also be indirectly controlled since the transition and dephasing rates depend parametrically on the spectrum of $\widehat{H}_{\text{sys}}$. This indirect, parametric modulation of the "incoherent" dynamics can significantly affect the thermalization process and the resulting steady state or quasiequilibrium of the system. In this work, I focus on calculating the quasiequilibria under periodic modulations of $\widehat{H}_{\text{sys}}$ in open quantum systems. A master equation approach is employed where the environmentally induced transition and dephasing rates depend only upon the instantaneous eigenenergies of the system [14]. Theoretical calculations of the quasiequilibrium for a single spin-1/2 and for two coupled spin-1/2s interacting with a time-dependent magnetic field are presented.

II. BASIC THEORY

In this section, the basic equations describing the evolution of an open quantum system undergoing parametric modulation of its Liouvillian are reviewed [15], and a simple framework is presented where the effects of periodic modulations of the Liouvillian on the resulting quasiequilibrium can be explicitly calculated. Consider the equation of motion for an N-state quantum system, $|\widehat{\rho}(t)\rangle\rangle$, where the influence of $\widehat{H}_{\text{sys-env}}$ and $\widehat{H}_{\text{env}}$ on the dynamics of $|\widehat{\rho}(t)\rangle\rangle$ is described by an effective Liouvillian operator, $\widehat{\mathscr{L}}(t)$, acting on the quantum system. In the limit where the modulations are slow compared to the correlation time of the environment, τ_c, the equation of motion can be written in Liouville space as [16,17]

$$\frac{d|\widehat{\rho}(t)\rangle\rangle}{dt} = \widehat{\mathscr{L}}(t)|\widehat{\rho}(t)\rangle\rangle = \widehat{\mathscr{L}}(t)[|\widehat{\rho}(t)\rangle\rangle - |\widehat{\rho}_{\text{eq}}(t)\rangle\rangle]. \quad (1)$$

The form of Eq. (1) makes it explicit that there exists an instantaneous equilibrium state, $|\widehat{\rho}_{\text{eq}}(t)\rangle\rangle$, at each time t. In the following, $|\widehat{\rho}_{\text{eq}}(t)\rangle\rangle$ will be taken to be an instantaneous Boltzmann distribution at a temperature T, $|\widehat{\rho}_{\text{eq}}(t)\rangle\rangle = |Z(t)^{-1}\exp[-\beta\widehat{H}_{\text{sys}}(t)]\rangle\rangle$, with $Z(t) = \text{Tr}\{\exp[-\beta\widehat{H}_{\text{sys}}(t)]\}$ and $\beta = \frac{1}{k_B T}$.

If the instantaneous eigenvalues of $\widehat{\mathscr{L}}(t)$, $\lambda_n(t)$ for $n = 1$ to $n = N^2$, are nondegenerate, then $\widehat{\mathscr{L}}(t)$ can be expanded in a set of instantaneous eigenstates of $\widehat{\mathscr{L}}(t)$, $|\widehat{\Psi}_n^R(t)\rangle\rangle$, and $\langle\langle\widehat{\Psi}_n^L(t)|$, such that $\widehat{\mathscr{L}}(t) = \sum_{n=1}^{N^2}\lambda_n(t)|\widehat{\Psi}_n^R(t)\rangle\rangle\langle\langle\widehat{\Psi}_n^L(t)|$ and $\langle\langle\widehat{\Psi}_n^L(t)|\widehat{\mathscr{L}}(t)|\widehat{\Psi}_k^R(t)\rangle\rangle = \lambda_n(t)\delta_{nk}$ (note that if $\lambda_n(t) = \lambda_j(t)$ for $n \neq j$, $\widehat{\mathscr{L}}(t)$ may not be diagonalizable but can always be written in Jordan form [18]). If $\widehat{\mathscr{L}}(t)$ conserves total probability, the identity operator will be an eigenstate of $\widehat{\mathscr{L}}(t)$ with $\lambda_1(t) = 0$, $\langle\langle\widehat{\Psi}_1^L(t)| \equiv \widehat{1}$, and the corresponding right eigenvector is $|\widehat{\Psi}_1^R(t)\rangle\rangle \equiv |\widehat{\rho}_{\text{eq}}(t)\rangle\rangle$ [Eq. (1)], and $|\widehat{\Psi}_n^R(t)\rangle\rangle$ represent traceless operators for $n \neq 1$, since $\langle\langle\widehat{\Psi}_1^L(t)|\widehat{\Psi}_n^R(t)\rangle\rangle = \delta_{n1}$. Note in the following discussion, only one instantaneous stationary state for $\widehat{\mathscr{L}}(t)$ with $\lambda(t) = 0$ is assumed to exist, and the presence of multiple stationary or decoherence-free subspaces [19] will not be considered. Finally, $\text{Re}[\lambda_{j\neq 1}(t)] < 0$ will be assumed, thereby ensuring that the system will relax to a fixed equilibrium state, $|\widehat{\rho}_{\text{qeq}}(t)\rangle\rangle$, in the absence of time-dependent modulations of $\widehat{\mathscr{L}}(t)$. This assumption will be important when discussing under which conditions $|\widehat{\rho}_{\text{qeq}}(t)\rangle\rangle \approx |\widehat{\rho}_{\text{eq}}(t)\rangle\rangle$ [20].

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Defining the transformation $\widehat{\widehat{W}}(t,0) = \sum_{k=1}^{N^2} |\widehat{\Psi}_k^R(t)\rangle\rangle\langle\langle\widehat{\Psi}_k^L(0)|$ which connects the fixed eigenbasis of $\widehat{\mathscr{L}}(0)$ to the instantaneous eigenbasis of $\widehat{\mathscr{L}}(t)$, the density matrix can be written as $|\widehat{\rho}(t)\rangle\rangle = \sum_{k=1}^{N^2} \rho_k(t)|\widehat{\Psi}_k^R(t)\rangle\rangle = \widehat{\widehat{W}}(t,0)|\widehat{\rho}_0(t)\rangle\rangle$, where $|\widehat{\rho}_0(t)\rangle\rangle = \sum_{k=1}^{N^2} \rho_k(t)|\widehat{\Psi}_k^R(0)\rangle\rangle$. The equation of motion for $|\widehat{\rho}_0(t)\rangle\rangle$ differs from Eq. (1) by the addition of a gauge field,

$$\begin{aligned}\frac{d|\widehat{\rho}_0(t)\rangle\rangle}{dt} &= \left[-\widehat{\widehat{W}}^{-1}(t,0)\frac{d\widehat{\widehat{W}}(t,0)}{dt} + \widehat{\widehat{W}}^{-1}(t,0)\widehat{\mathscr{L}}(t)\widehat{\widehat{W}}(t,0)\right]|\widehat{\rho}_0(t)\rangle\rangle \\ &= \widehat{\mathscr{L}}_{\mathrm{EFF}}(t)|\widehat{\rho}_0(t)\rangle\rangle, \end{aligned} \quad (2)$$

where $\widehat{\mathscr{L}}_{\mathrm{EFF}}(t) = \widehat{\mathscr{L}}_0(t) + \widehat{\mathscr{L}}_{\mathrm{gauge}}(t)$, with

$$\widehat{\mathscr{L}}_0(t) = \widehat{\widehat{W}}^{-1}(t,0)\widehat{\mathscr{L}}(t)\widehat{\widehat{W}}(t,0) = \sum_{k=1}^{N^2} \lambda_k(t)\big|\widehat{\Psi}_k^R(0)\big\rangle\big\rangle\big\langle\big\langle\widehat{\Psi}_k^L(0)\big|$$

and

$$\begin{aligned}\widehat{\mathscr{L}}_{\mathrm{gauge}}(t) &= -\widehat{\widehat{W}}^{-1}(t,0)\frac{d\widehat{\widehat{W}}(t,0)}{dt} \\ &= -\sum_{k=1}^{N^2} c_{kk}(t)\big|\widehat{\Psi}_k^R(0)\big\rangle\big\rangle\big\langle\big\langle\widehat{\Psi}_k^L(0)\big| \\ &\quad - \sum_{j<k}^{N^2}\big[c_{kj}(t)\big|\widehat{\Psi}_k^R(0)\big\rangle\big\rangle\big\langle\big\langle\widehat{\Psi}_j^L(0)\big| \\ &\quad + c_{jk}(t)\big|\widehat{\Psi}_j^R(0)\big\rangle\big\rangle\big\langle\big\langle\widehat{\Psi}_k^L(0)\big|\big],\end{aligned}$$

with $c_{kj}(t) = \langle\langle\widehat{\Psi}_k^L(t)|\frac{\partial}{\partial t}\widehat{\Psi}_j^R(t)\rangle\rangle$. From the normalization condition $\langle\langle\widehat{\Psi}_k^L(t)|\widehat{\Psi}_j^R(t)\rangle\rangle = \delta_{jk}$,

$$\left\langle\left\langle \frac{\partial}{\partial t}\widehat{\Psi}_k^L(t)\right|\widehat{\Psi}_j^R(t)\right\rangle\right\rangle + \left\langle\left\langle \widehat{\Psi}_k^L(t)\right|\frac{\partial}{\partial t}\widehat{\Psi}_j^R(t)\right\rangle\right\rangle = 0. \quad (3)$$

From Eq. (2), the $\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)$ term in $\widehat{\mathscr{L}}_{\mathrm{EFF}}(t)$ can result in a quasiequilibrium, $|\widehat{\rho}_{\mathrm{qeq}}(t)\rangle\rangle$, that is different than the instantaneous equilibrium state given in Eq. (1); that is, $|\widehat{\rho}_{\mathrm{qeq}}(t)\rangle\rangle = \lim_{t\gg 1}\widehat{\widehat{W}}(t,0)\widehat{T}\exp[\int_0^t dt'\widehat{\mathscr{L}}_{\mathrm{EFF}}(t')]|\widehat{\rho}_0(0)\rangle\rangle = |\widehat{\Psi}_1^R(t)\rangle\rangle + \sum_{k=2}^{N^2}\overline{c}_{qeq,k}(t)|\widehat{\Psi}_k^R(t)\rangle\rangle \neq |\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle$, where $\widehat{T}$ is the Dyson time-ordering operator. In order to understand how $|\widehat{\rho}_{\mathrm{qeq}}(t)\rangle\rangle$ relates to $|\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle$ and under what conditions $|\widehat{\rho}_{\mathrm{qeq}}(t)\rangle\rangle \approx |\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle$ (adiabatic case), we must first understand how $|\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle = |\widehat{\Psi}_1^R(0)\rangle\rangle$ couples to the other states via $\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)$. While from Eq. (3), $[\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)]_{1k} \equiv \langle\langle\widehat{\Psi}_1^L(0)|\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)|\widehat{\Psi}_k^R(0)\rangle\rangle = c_{1k}(t) = 0$ for $k=1$ to $k=N^2$ [simply a consequence of the conservation of probability and the choice of normalization for $|\widehat{\Psi}_1^R(0)\rangle\rangle$ and $\langle\langle\widehat{\Psi}_1^L(0)|$], in general, $[\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)]_{k1} = c_{k1}(t) \neq 0$ for $k=2$ to $k=N^2$; these matrix elements, which represent the incoherent portion of $\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)$, are responsible for $|\widehat{\rho}_{\mathrm{qeq}}(t)\rangle\rangle \neq |\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle$. I now focus on determining the general conditions for adiabaticity, that is, under what conditions is the quasiequilibrium given by the instantaneous equilibrium state, $|\widehat{\rho}_{\mathrm{qeq}}(t)\rangle\rangle \approx |\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle$. In order to do this, we must consider the "nonidentity" portion of $|\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle$, $|\widehat{\Delta\rho}_{\mathrm{eq}}(t)\rangle\rangle$, where $|\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle = \frac{1}{N}|\widehat{1}\rangle\rangle + |\widehat{\Delta\rho}_{\mathrm{eq}}(t)\rangle\rangle$ and $|\widehat{\Delta\rho}_{\mathrm{eq}}(t)\rangle\rangle = \sum_{n=2}^{N^2}\rho_{\mathrm{eq},n}(t)|\widehat{\Psi}_n^R(t)\rangle\rangle$, where $\rho_{\mathrm{eq},n}(t)$ represents the contribution of $|\widehat{\Psi}_n^R(t)\rangle$ to the instantaneous equilibrium state. With this choice of expansion, $\langle\langle\widehat{\Psi}_n^L(t)|$ for $n=2$ to $n=N^2$ can be written as $\langle\langle\widehat{\Psi}_n^L(t)| = -\rho_{\mathrm{eq},n}(t)\langle\langle\widehat{\Psi}_1^L(t)| + \langle\langle\widetilde{\Psi}_n^L(t)|$ with $\langle\langle\widetilde{\Psi}_n^L(t)|\widehat{\Psi}_k^R(t)\rangle\rangle = \delta_{nk}$. Using this expansion for $|\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle$, we can write the quasiequilibrium as

$$\begin{aligned}|\widehat{\rho}_{\mathrm{qeq}}(t)\rangle\rangle &= |\widehat{\rho}_{\mathrm{eq}}(t)\rangle\rangle + \sum_{n=2}^{N^2}\overline{c}_{\mathrm{qeq},n}(t)\big|\widehat{\Psi}_n^R(t)\big\rangle\big\rangle \\ &= \frac{1}{N}|\widehat{1}\rangle\rangle + \sum_{n=2}^{N^2}[\rho_{\mathrm{eq},n}(t) + \overline{c}_{\mathrm{qeq},n}(t)]\big|\widehat{\Psi}_n^R(t)\big\rangle\big\rangle.\end{aligned} \quad (4)$$

From Eq. (4), a variety of possible conditions for "adiabatic" evolution suggest themselves. On a component-by-component basis, a strict condition for adiabaticity would be that $|\rho_{\mathrm{eq},n}(t)| \gg |\overline{c}_{\mathrm{qeq},n}(t)|$ for $n=2$ to $n=N^2$ for all times t. A less strict, and more useful, adiabaticity condition would be to compare the magnitude of the quasiequilibrium coefficients to the maximum coefficient in the expansion of the instantaneous equilibrium state . In this case, adiabaticity is achieved if $|\overline{c}_{\mathrm{qeq},n}(t)| \ll \chi(t)$ for all n, where $\chi(t) = \max\{|\rho_{\mathrm{eq},2}(t)|, |\rho_{\mathrm{eq},3}(t)|, \ldots, |\rho_{\mathrm{eq},N^2}(t)|\}$. In order to utilize the adiabaticity condition $|\overline{c}_{\mathrm{qeq},n}(t)| \ll \chi(t)$, an expansion of the quasiequilibrium coefficients, $\overline{c}_{\mathrm{qeq},n}(t)$, in terms of $\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)$ must be found. Since the present work focuses on periodic modulation of $\widehat{\mathscr{L}}(t)$, effective Liouvillian theory and Floquet theory [21] can be utilized to understand the effects of $\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)$ on $|\widehat{\rho}_{\mathrm{qeq}}(t)\rangle\rangle$. Defining the following expansions in terms of the modulation frequency, ω_r, $\lambda_k(t) = \sum_n \lambda_k^{(n)}\exp(in\omega_r t)$, and

$$c_{kj}(t)\exp\left\{\sum_{n\neq 0}\frac{[\lambda_j^{(n)} - \lambda_k^{(n)}][\exp(in\omega_r t) - 1]}{in\omega_r}\right\} = \sum_n \widetilde{c}_{kj}^{(n)}\exp(in\omega_r t),$$

the coefficients $\overline{c}_{\mathrm{qeq},k}(t)$ can be calculated in a power series expansion of $\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)$. To second-order in $\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)$, the conditions for adiabaticity are of the form

$$\begin{aligned}|\overline{c}_{\mathrm{qeq},k}(t)| &= \left|\sum_{n_1}\frac{\widetilde{c}_{k1}^{(n_1)}e^{in_1\omega_r t}}{\lambda_k^{(0)} + in_1\omega_r}\right. \\ &\quad \left. + \sum_j\sum_{n1,n2}\frac{\widetilde{c}_{kj}^{(n_2)}\widetilde{c}_{j1}^{(n_1)}e^{i(n_1+n_2)\omega_r t}}{\big[\lambda_k^{(0)} + i(n_1+n_2)\omega_r\big]\big(\lambda_j^{(0)} + in_1\omega_r\big)}\right| \\ &\ll \chi(t)\end{aligned} \quad (5)$$

for all k. The condition $\mathrm{Re}(\lambda_k^{(0)}) < 0$ ensures that no resonant "Rabi-like" oscillations can occur with $\lambda_k^{(0)} = im\omega_r$ where m is an integer. The adiabaticity criteria in Eq. (5) are a consequence of the fact that $|[\widehat{\mathscr{L}}_{\mathrm{gauge}}(t)]_{1k}| = 0$, which ensures that there will exist a $|\widehat{\rho}_{\rm qeq}(t)\rangle\rangle$ with $\lambda_1(t)=0$ for all times t. For the case when the instantaneous equilibrium is close to being a pure state [i.e., $\chi(t)\approx 1$], the adiabaticity condition in Eq. (5) is similar to those found in previous works on adiabatic theorem in open quantum systems [20,22], although the results in Eq. (5) consider the true quasiequilibrium under $\widehat{T}\exp[\int_0^t dt'\widehat{\mathscr{L}}_{\rm eff}(t')]$ in the infinite time limit, $t\to\infty$. In the following work, we will be interested in studying the quasiequilibria when Eq. (5) is not satisfied, that is, when nonadiabatic corrections from $\widehat{\mathscr{L}}_{\rm gauge}(t)$ lead to $|\widehat{\rho}_{\rm qeq}(t)\rangle\rangle = \sum_{k=1}^{N^2}\bar{c}_{{\rm qeq},k}|\widehat{\Psi}_k^R(t)\rangle\rangle \neq |\widehat{\rho}_{\rm eq}(t)\rangle\rangle$.

A. Quasiequilibrium for a single spin-1/2

For an explicit example of the preceding theory, consider the quintessential spin-1/2 particle in the presence of a time-dependent magnetic field, $\vec{B}(t)=|\vec{B}(t)|(\cos[\theta(t)]\widehat{z}+\sin[\theta(t)]\{\cos[\phi(t)]\widehat{x}+\sin[\phi(t)]\widehat{y}\})$, where $\theta(t)$ and $\phi(t)$ give the instantaneous orientation of the magnetic field, and $|\vec{B}(t)|$ is the instantaneous magnitude of the applied field. In this case, the time-dependent eigenstates of $\frac{\widehat{H}_{\rm sys}(t)}{\hbar}=-\gamma\vec{B}(t)\cdot\vec{S}$ are

$$\begin{aligned}|\pm(t)\rangle &= \exp[-i\phi(t)\widehat{S}_Z]\exp[-i\theta(t)\widehat{S}_Y]|\pm\rangle\\ &= \widehat{U}(t)|\pm\rangle,\end{aligned} \tag{6}$$

where $\widehat{\mathbf{S}}=\frac{1}{2}\widehat{\sigma}$, $\widehat{\sigma}$ are the Pauli spin matrices, and $\widehat{S}_Z|\pm\rangle=\pm\frac{1}{2}|\pm\rangle$. The instantaneous eigenenergies of $\widehat{H}_{\rm sys}(t)$ are $E_\pm(t)=\mp\frac{\hbar\omega(t)}{2}$ with $\hbar\omega(t)=\gamma|\vec{B}(t)|$ and γ denoting the spin's gyromagnetic ratio. $\widehat{H}_{\rm sys}(t)$ can be written in the time-dependent eigenbasis as $\widehat{H}_{\rm sys}(t)=\widehat{U}(t)\widehat{H}_0(t)\widehat{U}^{-1}(t)$ with

$$\begin{aligned}\widehat{H}_0(t) &= E_+(t)|+(0)\rangle\langle+(0)|+E_-(t)|-(0)\rangle\langle-(0)|\\ &\equiv E_+(t)|\widehat{+,+,0}\rangle\rangle+E_-(t)|\widehat{-,-,0}\rangle\rangle,\end{aligned}$$

where the notation $|\widehat{a,b,t}\rangle\rangle\equiv|a(t)\rangle\langle b(t)|$ is used. With regards to relaxation, the only processes that will be considered are the dephasing of the coherence between the simultaneous eigenstates (i.e., T_2 relaxation) and population transfer between $|+(t)\rangle$ and $|-(t)\rangle$ (i.e., T_1 relaxation). If $|E_+(t)-E_-(t)|=|\hbar\omega(t)|\gg|\widehat{H}_{\text{sys-env}}|$, then one can utilize the "secular" approximation and consider the relaxation of coherences and populations separately [23]. For the processes under consideration, $\widehat{\mathscr{L}}(t)$ can be written in the basis of $\{|\widehat{+,+,t}\rangle\rangle,|\widehat{-,-,t}\rangle\rangle,|\widehat{+,-,t}\rangle\rangle,|\widehat{-,+,t}\rangle\rangle\}$ as

$$\widehat{\mathscr{L}}(t)=\begin{pmatrix}-\mathscr{W}_{+-}(t) & \mathscr{W}_{-+}(t) & 0 & 0\\ \mathscr{W}_{+-}(t) & -\mathscr{W}_{-+}(t) & 0 & 0\\ 0 & 0 & i|\omega(t)|-\frac{1}{T_2(t)} & 0\\ 0 & 0 & 0 & -i|\omega(t)|-\frac{1}{T_2(t)}\end{pmatrix}, \tag{7}$$

where $\mathscr{W}_{\pm\mp}(t)=\frac{1\mp P_{\rm eq}(t)}{2T_1(t)}$ are the time-dependent transition rates, $P_{\rm eq}(t)=\tanh[\frac{\hbar|\omega(t)|}{2k_BT}]$ is equal to the instantaneous equilibrium polarization for a given magnitude of the magnetic field, and $T_1(t)$ and $T_2(t)$ are the instantaneous longitudinal and transverse relaxation times, respectively. The time-dependent eigenvalues of $\widehat{\mathscr{L}}(t)$ are

$$\begin{aligned}\lambda_1(t)&=0,\\ \lambda_2(t)&=-[\mathscr{W}_{+-}(t)+\mathscr{W}_{-+}(t)]=-\frac{1}{T_1(t)},\\ \lambda_3(t)&=i|\omega(t)|-\frac{1}{T_2(t)},\end{aligned}$$

and

$$\lambda_4(t)=-i|\omega(t)|-\frac{1}{T_2(t)}.$$

The corresponding right eigenvectors are

$$\begin{aligned}|\widehat{\Psi}_1^R(t)\rangle\rangle &= T_1(t)[\mathscr{W}_{-+}(t)|\widehat{+,+,t}\rangle\rangle+\mathscr{W}_{+-}(t)|\widehat{-,-,t}\rangle\rangle]\\ &= |\widehat{\rho}_{\rm eq}(t)\rangle\rangle,\\ |\widehat{\Psi}_2^R(t)\rangle\rangle &= |\widehat{+,+,t}\rangle\rangle-|\widehat{-,-,t}\rangle\rangle,\\ |\widehat{\Psi}_3^R(t)\rangle\rangle &= |\widehat{+,-,t}\rangle\rangle,\end{aligned}$$

and

$$|\widehat{\Psi}_4^R(t)\rangle\rangle = |\widehat{-,+,t}\rangle\rangle,$$

and the left eigenvectors are

$$\begin{aligned}\langle\langle\widehat{\Psi}_1^L(t)| &= \langle\langle\widehat{+,+,t}|+\langle\langle\widehat{-,-,t}|\equiv\widehat{1},\\ \langle\langle\widehat{\Psi}_2^L(t)| &= T_1(t)[\mathscr{W}_{+-}(t)\langle\langle\widehat{+,+,t}|-\mathscr{W}_{-+}(t)\langle\langle\widehat{-,-,t}|],\\ \langle\langle\widehat{\Psi}_3^L(t)| &= \langle\langle\widehat{+,-,t}|,\end{aligned}$$

and

$$\langle\langle\widehat{\Psi}_4^R(t)| = \langle\langle\widehat{-,+,t}|.$$

As in Eq. (4), $|\rho_{\rm eq}(t)\rangle\rangle=\frac{1}{2}|\widehat{1}\rangle\rangle+\frac{P_{\rm eq}(t)}{2}|\widehat{\Psi}_2^R(t)\rangle\rangle$ and $\langle\langle\widehat{\Psi}_2^L(t)|=-\frac{P_{\rm eq}(t)}{2}\langle\langle\widehat{1}|+\langle\langle\widehat{+,+,t}|-\langle\langle\widehat{-,-,t}|$, so that $\chi(t)=\frac{P_{\rm eq}(t)}{2}$.

As described previously, we can write $\widehat{\mathscr{L}}(t)$ in a fixed basis, $\{|\widehat{\Psi}_1^R(0)\rangle\rangle,|\widehat{\Psi}_2^R(0)\rangle\rangle,|\widehat{\Psi}_3^R(0)\rangle\rangle,|\widehat{\Psi}_4^R(0)\rangle\rangle\}$ as $\widehat{\mathscr{L}}_{\rm EFF}(t)=\widehat{\mathscr{L}}_{\rm gauge}(t)+\widehat{\mathscr{L}}_0(t)$, where $\widehat{\widehat{\mathscr{L}}}_0(t)=\sum_{k=1}^4\lambda_k(t)|\widehat{\Psi}_k^R(0)\rangle\rangle\langle\langle\widehat{\Psi}_k^L(0)|$ and

$$\widehat{\mathscr{L}}_{\rm gauge}(t) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ -\frac{1}{2}\frac{dP_{\rm eq}(t)}{dt} & 0 & -G_{-+}(t) & G_{+-}(t) \\ -P_{\rm eq}(t)G_{+-}(t) & -2G_{+-}(t) & G_{++}(t)-G_{--}(t) & 0 \\ P_{\rm eq}(t)G_{-+}(t) & 2G_{-+}(t) & 0 & G_{--}(t)-G_{++}(t) \end{pmatrix}, \tag{8}$$

where

$$G_{ab}(t) = \left\langle a\left|\frac{{\rm d}\widehat{U}^\dagger(t)}{{\rm d}t}\widehat{U}(t)\right|b\right\rangle = \langle a|i\dot{\theta}(t)\widehat{S}_Y + i\dot{\phi}(t)\{\cos[\theta(t)]\widehat{S}_Z - \sin[\theta(t)]\widehat{S}_X\}|b\rangle.$$

Both $T_1(t)$ and $T_2(t)$ are assumed to depend only upon the instantaneous energy difference, $\hbar\omega(t)$. Possible modifications of the environment's coupling with the spin system due to changing field direction [24] and any non-Markovian effects of the environment are not considered. It should be noted that for a two-state system, the normalization of the right and left eigenstates of $\widehat{\mathscr{L}}(t)$ can always be chosen such that the only terms in $\widehat{\mathscr{L}}_{\rm gauge}(t)$ that survive in the adiabatic limit are simply the geometric phases for the coherences [25] in Eq. (8). For an N-state system with $N \geqslant 3$, however, it is possible for $\langle\langle\widehat{\Psi}_k(0)|\widehat{\Psi}_k(t)\rangle\rangle\exp[\int_0^t\langle\langle\widehat{\Psi}_k(t')|\frac{d|\widehat{\Psi}_k(t')}{dt'}\rangle\rangle dt'] \neq 1$.

1. Case I: Quasiequilibrium for a rotating magnetic field

First consider the case of a magnetic field rotating about a cone of angle θ with respect to the $\widehat{z}$ axis at a frequency of ω_r, $\gamma\vec{B}(t) = \hbar\omega\{\cos(\theta)\widehat{z} + \sin(\theta)[\cos(\omega_r t)\widehat{x} + \sin(\omega_r t)\widehat{y}]\}$. In this case, $\dot{\theta}(t) = 0$, $\dot{\phi}(t) = \omega_r$, and $|\gamma\vec{B}(t)| =$ constant, which gives

$$\widehat{\mathscr{L}}_{\rm gauge}(t) = i\frac{\omega_r\sin(\theta)}{2}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ P_{\rm eq} & 2 & 2\cot(\theta) & 0 \\ -P_{\rm eq} & -2 & 0 & -2\cot(\theta) \end{pmatrix}. \tag{9}$$

In the adiabatic limit, if $\frac{\omega_r\sin(\theta)P_{\rm eq}}{|\frac{1}{T_2}\pm i\omega|} \ll \frac{P_{\rm eq}}{2}$ in Eq. (5), the quasiequilibrium spin polarization will follow and point along the instantaneous direction of the $\vec{B}(t)$. For $\omega_r \geqslant |\frac{1}{T_2}\pm i\omega|$, deviations from adiabaticity will occur, and the spin polarization will no longer be aligned with the applied magnetic field.

For arbitrary ω_r and for time-independent T_1 and T_2, $|\widehat{\rho}_{\rm qeq}(t)\rangle\rangle$ is given by

$$\begin{aligned} |\widehat{\rho}_{\rm qeq}(t)\rangle\rangle &= |\widehat{\Psi}_1^R(t)\rangle\rangle - T_1\omega_r\sin(\theta)\zeta\frac{P_{\rm eq}}{2}|\widehat{\Psi}_2^R(t)\rangle\rangle \\ &\quad - i\zeta\frac{P_{\rm eq}}{2}[|\widehat{\Psi}_3^R(t)\rangle\rangle - |\widehat{\Psi}_4^R(t)\rangle\rangle] \\ &\quad + [\omega+\omega_r\cos(\theta)]T_2\zeta\frac{P_{\rm eq}}{2}[|\widehat{\Psi}_3^R(t)\rangle\rangle + |\widehat{\Psi}_4^R(t)\rangle\rangle] \\ &= \frac{1}{2}|\widehat{1}\rangle\rangle + P_{\rm eq}\{[1 - T_1\omega_r\sin(\theta)\zeta]|\widehat{S}_{Z'}(t)\rangle\rangle \\ &\quad + [\omega+\omega_r\cos(\theta)]T_2\zeta|\widehat{S}_{X'}(t)\rangle\rangle + \zeta|\widehat{S}_{Y'}(t)\rangle\rangle\}, \end{aligned} \tag{10}$$

where

$$\zeta = \frac{T_2\omega_r\sin(\theta)}{1+[\omega+\omega_r\cos(\theta)]^2T_2^2 + T_1T_2\omega_r^2\sin^2(\theta)}$$

and $|\widehat{S}_{j'}(t)\rangle\rangle = \frac{1}{2}\widehat{U}(t)\widehat{\sigma}_j\widehat{U}^\dagger(t)$ is jth spin operator that is quantized along the instantaneous field direction, $\frac{\vec{B}(t)}{|\vec{B}(t)|}$. In this case, $|\widehat{\rho}_{\rm qeq}(t)\rangle\rangle$ represents a spin polarization vector that follows, but is slightly rotated away from, the applied magnetic field when $\omega_r T_2\sin(\theta) \gg 1$. For the case where the applied field is rotating in the x-y plane ($\theta = \pi/2$), the magnetization generates a component perpendicular to the plane of rotation. The tilting of the magnetization due to rotation of the applied field has been previously observed in electron paramagnetic resonance experiments [26] and recently in nuclear magnetic resonance using a SQUID magnetometer [27]. The results from Eq. (10) will remain valid as long as $\omega_r\tau_c \ll 1$, where τ_c is the environment's correlation time.

2. Case II: Quasiequilibrium for a magnetic field whose magnitude is periodically modulated

Next, consider the case where the direction of the magnetic field is fixed, but the magnitude of the magnetic field varies periodically in time between ω and $\delta\omega$, $\omega(t) = \frac{\omega+\delta\omega}{2} + \cos(\omega_r t)\frac{\omega-\delta\omega}{2}$. From Eq. (8), the coherences and populations are completely decoupled, and the only nonzero matrix element of $\widehat{\mathscr{L}}_{\rm gauge}(t)$ arises from the time-dependence of the instantaneous equilibrium polarization, $P_{\rm eq}(t) = \tanh[\frac{\hbar\omega(t)}{2k_BT}] = \sum_{m=-\infty}^{\infty}P_{\rm eq}^{(m)}\exp(im\omega_r t)$. In this case, $\widehat{\mathscr{L}}_{\rm gauge}(t) = -\frac{1}{2}\frac{dP_{\rm eq}(t)}{dt}|\widehat{\Psi}_2^R(0)\rangle\rangle\langle\langle\widehat{\Psi}_1^L(0)| = -\frac{i\omega_r}{2}[\sum_m mP_{\rm eq}^{(m)}\exp(im\omega_r t)]|\widehat{\Psi}_2^R(0)\rangle\rangle\langle\langle\widehat{\Psi}_1^L(0)|$. From Eq. (5), when $\frac{\omega_r T_1}{2}|\sum_m\frac{mP_{\rm eq}^{(m)}e^{im\omega_r t}}{1+im\omega_r T_1}| \ll \frac{P_{\rm eq}(t)}{2}$, $\widehat{\mathscr{L}}_{\rm gauge}(t)$ can be neglected, and the quasiequilibrium is given by the instantaneous equilibrium state, $|\widehat{\Psi}_1^R(t)\rangle\rangle = \frac{1}{2}|\widehat{1}\rangle\rangle + P_{\rm eq}(t)|\widehat{S}_Z\rangle\rangle$, where the polarization is given by the instantaneous equilibrium polarization, $P_{\rm eq}(t)$.

For arbitrary ω_r, $|\widehat{\rho}_{\rm qeq}(t)\rangle\rangle$ is given by (assuming T_1 is time-independent)

$$\begin{aligned} |\widehat{\rho}_{\rm qeq}(t)\rangle\rangle &= |\widehat{\Psi}_1^R(t)\rangle\rangle - \frac{1}{2}\left[\int_0^{t\gg1}dt'\frac{dP_{\rm eq}(t')}{dt'}f(t,t')\right]|\widehat{\Psi}_2^R(t)\rangle\rangle \\ &\approx \frac{1}{2}|\widehat{1}\rangle\rangle + \frac{1}{2}P_{\rm eff}(t)[|\widehat{+,+},(0)\rangle\rangle - |\widehat{-,-},(0)\rangle\rangle], \\ P_{\rm eff}(t) &= P_{\rm eq}^{(0)} + \sum_{m\neq0}P_{\rm eq}^{(m)}\exp(im\omega_r t)\left(1 - \frac{im\omega_r T_1}{im\omega_r T_1+1}\right), \end{aligned} \tag{11}$$

where $f(t,t') = \exp[-\int_{t'}^t\frac{dt''}{T_1(t'')}]$. The effective polarization, $P_{\rm eff}(t)$, oscillates about $P_{\rm eq}^{(0)}$ with a frequency of ω_r but with a slight phase lag that can be approximated by $\phi_{lag} = \operatorname{atan}(\omega_r T_1)$. For $\omega_r T_1 \gg 1$, $\frac{im\omega_r T_1}{1+im\omega_r T_1} \approx 1$, and the sum in Eq. (11) vanishes. In this case, $P_{\rm eff}(t)$ is effectively time-independent and is given by the time-averaged polarization, $P_{\rm eq}^{(0)}$. For $\omega_r T_1 \ll 1$, the evolution is adiabatic, and $P_{\rm eff}(t) \approx P_{\rm eq}(t)$. We see from Eq. (11) that the effect of the $\widehat{\mathscr{L}}_{\rm gauge}(t)$ term is to cause $P_{\rm eff}(t) \to P_{\rm eq}^{(0)} \neq P_{\rm eq}(t)$ for $\omega_r \gg \frac{2\pi}{T_1}$. Without the gauge term, $P_{\rm eff}(t) = P_{\rm eq}(t)$ for all ω_r; that is, without the gauge term, the spin's polarization would instantaneously relax to or follow $P_{\rm eq}(t)$ as previously mentioned. Remember that the gauge term can be neglected if $\frac{\omega_r T_1}{2}|\sum_m \frac{mP_{\rm eq}^{(m)}e^{im\omega_r t}}{1+im\omega_r T_1}| \ll \frac{P_{\rm eq}(t)}{2}$ [Eq. (5)], so neglect of the gauge term is equivalent to taking $\frac{1}{T_1}$ to be very large, which is another way of saying that the system relaxes quickly to the instantaneous equilibrium state. A similar result is found in the case of a driven damped oscillator.

B. Quasiequilibrium for a two-spin system

Consider the case of two coupled, spin-1/2s, I and S, where the single-spin energies of either the S spin or both the S and the I spins are periodically modulated in time. In this case, the Hamiltonian for the IS system is given by $\widehat{H}_{\rm sys} = -\hbar\omega_S(t)\widehat{S}_Z - \hbar\omega_I(t)\widehat{I}_Z + \hbar\omega_{Z,IS}\widehat{S}_Z\widehat{I}_Z + \hbar\omega_{T,IS}(\widehat{S}_X\widehat{I}_X + \widehat{S}_Y\widehat{I}_Y)$, where the coupling has been taken to be symmetric with respect to X and Y directions. In the following discussion, I will consider the case where $\omega_S \gg \omega_I$, which, for example, could represent a system where S is an electron spin and I is a nuclear spin.

The relaxation contribution to the Liouvillian is given by

$$\begin{aligned}\widehat{\mathscr{L}}_{\rm relax} = &-\frac{1}{T_2^S(t)}\big[\big|\widehat{\Psi}_3^R(0)\big\rangle\!\big\rangle\big\langle\!\big\langle\widehat{\Psi}_3^L(0)\big| + \big|\widehat{\Psi}_4^R(0)\big\rangle\!\big\rangle\big\langle\!\big\langle\widehat{\Psi}_4^L(0)\big|\big] \otimes \widehat{1}_I\\ &-\frac{1}{T_2^I(t)}\widehat{1}_S \otimes (|\widehat{+,-,t}\rangle\rangle\langle\langle\widehat{+,-,t}| + |\widehat{-,+,t}\rangle\rangle\\ &\times \langle\langle\widehat{-,+,t}|) - \frac{1}{T_1^S(t)}\big|\widehat{\Psi}_2^R(0)\big\rangle\!\big\rangle\big\langle\!\big\langle\widehat{\Psi}_2^L(0)\big| \otimes \widehat{1}_I\\ &+\widehat{1}_S \otimes \mathscr{W}_{+-}^I(t)(|\widehat{-,-,t}\rangle\rangle\langle\langle\widehat{+,+,t}|\\ &-|\widehat{+,+,t}\rangle\rangle\langle\langle\widehat{+,+,t}|) + \widehat{1}_S \otimes \mathscr{W}_{-+}^I(t)(|\widehat{+,+,t}\rangle\rangle\\ &\times \langle\langle\widehat{-,-,t}| - |\widehat{-,-,t}\rangle\rangle\langle\langle\widehat{-,-,t}|),\end{aligned} \tag{12}$$

where $\mathscr{W}_{\pm\mp}^I(t) = \frac{1\mp P_{{\rm eq},I}(t)}{2T_1^I(t)}$, $T_1^{S(I)}(t)$, and $T_2^{S(I)}(t)$ are the $S(I)$ spin longitudinal and transverse relaxation times respectively, $P_{{\rm eq},I}(t) = \tanh[\frac{\hbar\omega_I(t)}{2k_BT}]$, and $\widehat{1}_S$ and $\widehat{1}_I$ are the identity Liouvillian superoperators [28] in the S and I spaces, respectively. In the absence of coupling between the I and the S spins and for fixed ω_I and ω_S, the equilibrium for the combined system is $|\widehat{\rho}_{{\rm eq},IS}\rangle\rangle = |\widehat{\rho}_{{\rm eq},S}\rangle\rangle|\widehat{\rho}_{{\rm eq},I}\rangle\rangle$, where $|\widehat{\rho}_{{\rm eq},S(I)}\rangle\rangle = \frac{1}{2}|\widehat{1}\rangle\rangle + P_{{\rm eq},S(I)}|\widehat{S(I)}_Z\rangle\rangle$.

Consider the case where the IS coupling is nonzero but is much weaker than the individual spin energies; that is, $\omega_S \gg \omega_I \gg |\omega_{Z(T),IS}|$. If the relaxation rates of the S spin are assumed to be much larger than those for the I spin, that is, $T_1^S, T_2^S \ll T_1^I, T_2^I$, then the equilibrium of the combined system can be approximated by $|\widehat{\rho}_{{\rm eq},IS}\rangle\rangle \approx |\widehat{\rho}_{{\rm eq},S}\rangle\rangle|\widehat{\rho}_{{\rm eq}',I}\rangle\rangle$ where $|\widehat{\rho}_{{\rm eq},S}\rangle\rangle + \frac{1}{2}|\widehat{1}\rangle\rangle + P_{{\rm eq},S}|\widehat{S}_Z\rangle\rangle$. $P_{{\rm eq},S}$ is relatively unchanged by the coupling to the I spin. However, $|\widehat{\rho}_{{\rm eq}',I}\rangle\rangle \equiv \frac{1}{2}|\widehat{1}\rangle\rangle + P_{{\rm eq}',I}|\widehat{I}_Z\rangle\rangle$, where $P_{{\rm eq}',I}$ is the equilibrium I spin polarization that, under the preceding assumptions, is given to second order in $\omega_{T,IS}$ as

$$P_{{\rm eq}',I} = \frac{T_1^{IS}P_{{\rm eq},I} + T_1^I P_{{\rm eq},S}}{T_1^{IS} + T_1^I}. \tag{13}$$

In Eq. (13), $\frac{1}{T_1^{IS}} = \frac{\omega_{T,IS}^2 T_2^{IS}}{2\{1+[T_2^{IS}(\omega_S-\omega_I)]^2\}}$ and $T_2^{IS} = \frac{T_2^I T_2^S}{T_2^I+T_2^S}$. The time scale in which the I spin relaxes to $|\widehat{\rho}_{{\rm eq}',I}\rangle\rangle$ is given by $T_1^I + T_1^{IS}$. When $T_1^{IS} \ll T_1^I$, $P_{{\rm eq}',I} \to P_{{\rm eq},S} \gg P_{{\rm eq},I}$. Note that the polarization transfer between the I and the S spins is more efficient when $|T_2^{IS}(\omega_S - \omega_I)| \ll 1$ and when $|\omega_{T,IS}T_2^{IS}| \gg 1$ since T_1^{IS} is small under these conditions. Note also that $P_{{\rm eq}',I}$ is maximal when $T_2^{IS} = \frac{1}{\omega_S-\omega_I}$; having a short relaxation time T_2^{IS} can actually help increase $P_{{\rm eq}',I}$ since this reduces the importance of the energy mismatch, $\hbar|\omega_S - \omega_I|$.

C. Quasiequilibrum I spin polarization under periodic modulations of ω_S

Consider the case when the S spin's energy, $\hbar\omega_S(t)$, is periodically modulated in time between the values $\hbar\omega_S$ and $\hbar\delta\omega_S$, $\omega_S(t) = \cos(\omega_r t)\frac{\omega_S-\delta\omega_S}{2} + \overline{\omega}_S$, where $\overline{\omega}_S = \frac{\omega_S+\delta\omega_S}{2}$. In this case, the effects of $\widehat{\mathscr{L}}_{\rm gauge}(t)$ upon the resulting quasiequilibrium I spin polarization, $P_{{\rm qeq},I}$, must be considered. Since only the S spin's energy is time-dependent, $\widehat{\mathscr{L}}_{\rm gauge}(t) = -\frac{1}{2}\frac{dP_{{\rm eq},S}(t)}{dt}|\widehat{\Psi}_2^R(0)\rangle\rangle\langle\langle\widehat{\Psi}_1^L(0)| \otimes \widehat{1}_I$. In terms of the quasiequilibrium I spin polarization, $\widehat{\mathscr{L}}_{\rm gauge}(t)$ will affect $P_{{\rm qeq},I}$ by affecting the available S spin polarization that can be transferred to the I spin. As discussed in Case II, for modulation frequencies such that $\omega_r T_1^S \gg 1$, the available S spin polarization is time dependent and is given by $P_{{\rm eq},S}^{(0)}$, the time-averaged S spin polarization. For $\omega_r T_1^S \ll 1$, the S spin polarization is given by the instantaneous S spin polarization, $P_{{\rm eq},S}(t)$. As discussed later in this article, the time dependence and size of the S spin polarization dramatically affects the resulting $P_{{\rm qeq},I}$.

If T_1^S and T_2^S are taken to be time-independent, the quasiequilibrium density matrix for the IS system can be approximated as $|\widehat{\rho}_{{\rm qeq},IS}(t)\rangle\rangle \approx |\widehat{\rho}_{{\rm qeq},S}(t)\rangle\rangle|\widehat{\rho}_{{\rm qeq},I}\rangle\rangle$, where $|\widehat{\rho}_{{\rm qeq},S}(t)\rangle\rangle = \frac{1}{2}|\widehat{1}\rangle\rangle + P_{\rm eff}(t)|\widehat{S}_Z\rangle\rangle$, $P_{\rm eff}(t)$ is given in Eq. (11), and $|\widehat{\rho}_{{\rm qeq},I}\rangle\rangle = \frac{1}{2}|\widehat{1}\rangle\rangle + P_{{\rm qeq},I}|\widehat{I}_Z\rangle\rangle$. $P_{{\rm qeq},I}$ can be approximated to second order in $\omega_{T,IS}$ using Floquet theory [29,30] as

$$P_{{\rm qeq},I} = \frac{T_1^{IS,0}P_{{\rm eq},I} + T_1^I P_{{\rm eq},S}^{(0)} + T_1^I\sum_{m\neq 0}P_{{\rm eq},S}^{(m)}\frac{T_1^{IS,0}}{T_1^{IS,m}}\left(1 - \frac{\eta im\omega_r T_1^S}{1+im\omega_r T_1^S}\right)}{T_1^I + T_1^{IS,0}}, \tag{14}$$

where

$$\frac{1}{T_1^{IS,0}} = \frac{\omega_{T,IS}^2 T_2^{IS}}{2} \sum_{k=-\infty}^{\infty} \frac{[J_k(\zeta)]^2}{1+\left[T_2^{IS}(\Delta\omega_{IS}-k\omega_r)\right]^2}$$

$$\frac{1}{T_1^{IS,m}} = \frac{\omega_{T,IS}^2 T_2^{IS}}{4} \sum_{k=-\infty}^{\infty} \left[\frac{J_k(\zeta)J_{k-m}(\zeta)}{1+iT_2^{IS}(\Delta\omega_{IS}+k\omega_r)} + \frac{(-1)^m J_k(\zeta)J_{k-m}(\zeta)}{1-iT_2^{IS}(\Delta\omega_{IS}-k\omega_r)}\right], \quad (15)$$

$\zeta = \frac{\omega_S-\delta\omega_S}{2\omega_r}$, $\Delta\omega_{IS} = \overline{\omega}_S - \omega_I$, $J_n(\zeta)$ is a Bessel function of order n, and $P_{\text{eq},S}(t) = \tanh(\frac{\hbar\omega_S(t)}{2k_BT}) = \sum_n P_{\text{eq},S}^{(n)} \exp(in\omega_r t)$. In Eq. (14), η simply labels those terms in $P_{\text{qeq},I}$ that arise from the noncommutivity of the S spin's relaxation rates, $\mathscr{W}_{\pm,\mp}^S(t)$, that is, from the gauge term $-\frac{1}{2}\frac{dP_{\text{eq},S}(t)}{dt}|\widehat{\Psi}_2^R(0)\rangle\rangle\langle\langle\widehat{\Psi}_1^L(0)|$ in Eq. (8); η is set to $\eta = 1$ in the full calculations of $P_{\text{qeq},I}$. The "cross-relaxation times" that are responsible for polarization transfer between the S and I spins, $T_1^{IS,n}$ in Eq. (15), depend upon ω_r, and for $n \neq 0$, $T_1^{IS,n}$ can be negative and result in a decrease in $P_{\text{qeq},I}$. Calculations of $P_{\text{qeq},I}$ using Eq. (14) are valid for $\omega_r > \frac{1}{T_1^I + T_1^{IS,0}}$, where the quasiequilibrium I polarization saturates to a steady-state value given by $P_{\text{qeq},I}$. For $\omega_r \ll \frac{1}{T_1^I+T_1^{IS,0}}$, the quasiequilibrium spin polarization will not saturate to a fixed value and will become periodic. In this case, the I spin relaxes to $P_{\text{qeq},I}(t) = P_{\text{eq}',I}[\omega_S(t)]$, where $P_{\text{eq}',I}[\omega_S(t)]$ from Eq. (13) is evaluated at the instantaneous S spin energy, $\hbar\omega_S(t)$.

Using Eq. (14), $P_{\text{qeq},I}$ is plotted as a function of the modulation frequency, ω_r, in Fig. 1(A) (the exact parameters are given in the figure caption). It should be noted that over the range of ω_r shown in Fig. 1, $P_{\text{qeq},I}$ calculated using Eq. (14) is to within 0.1% of calculations of $P_{\text{qeq},I}$ using the numerically calculated propagator, $\widehat{T}\exp[\int_0^t \widehat{\mathscr{L}}(t')dt']$. In Fig. 1(A), $P_{\text{qeq},I}$ exhibits maxima at $\Delta\omega_{IS} = n\omega_r$, where n is an integer. With the parameters used in Fig. 1(A), $\Delta\omega_{IS} = 49.67\omega_I$, and no additional peaks in $P_{\text{qeq},I}$ are observed for $\omega_r > 49.67\omega_I$. For $\omega_r > 49.67\omega_I$, $P_{\text{qeq},I} = P_{\text{eq}',I} = 0.0067$, where $\overline{\omega}_S$ was used in evaluating $P_{\text{eq}',I}$ in Eq. (13). For $\omega_r > \frac{2\pi}{T_1^S}$, the S spin polarization is given by $P_{\text{eff},S} = P_{\text{eq},S}^{(0)} = 0.2412$ [see Eq. (11)]. Thus $P_{\text{qeq},I} \leqslant P_{\text{eff},S} = 0.2412$; in Fig. 1(A), the maximum $P_{\text{qeq},I}$ occurs at $\omega_r = \Delta\omega_{IS}$ with $P_{\text{qeq},I} = 0.2394$, which is close to $P_{\text{eff},S}$.

In order to understand the effects of the gauge term $[-\frac{dP_{\text{eq},S}(t)}{2dt}|\widehat{\Psi}_2^R(0)\rangle\rangle\langle\langle\widehat{\Psi}_1^L(0)|$ in Eq. (8)] upon the I spin's quasiequilibrium polarization, calculations of $P_{\text{qeq},I}$ with ($\eta = 1$, solid blue line) and without ($\eta = 0$, dotted red line) the gauge term are shown in Figs. 1(B) and 1(C). As can be seen from Fig. 1(B), $P_{\text{qeq},I}$ does not significantly increase from $P_{\text{eq}',I}$ in Eq. (13) in the absence of the gauge term ($\eta = 0$, dotted red line), indicating that the gauge term has an important effect on $P_{\text{qeq},I}$ for $\omega_r > 2\pi \times 10^{-2}\frac{1}{T_1^S} \approx \frac{1}{16T_1^S}$ with the parameters used in the calculation. This can be understood by examining Eq. (14); the conditions under which the gauge term can be neglected occur when $|m\omega_r T_1^S| \ll 1$, where m is a nonzero integer related to the Fourier expansion of $P_{\text{eq},S}(t) = \tanh[\frac{\hbar\omega_S(t)}{2k_BT}] = \sum_m P_{\text{eq},S}^{(m)}\exp(im\omega_r t)$. As expected

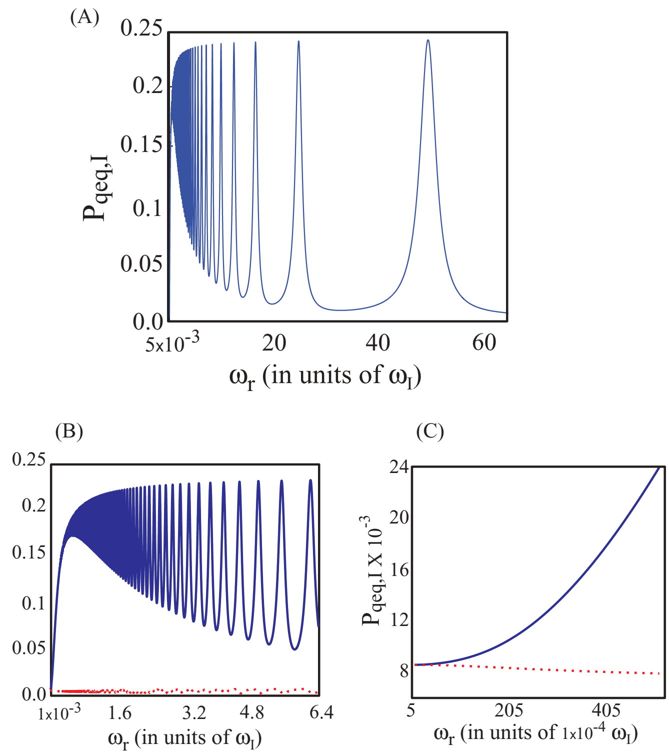

FIG. 1. (Color online) The calculated quasiequilibrium I spin polarization, $P_{\text{qeq},I}$ in Eq. (14), in an IS spin system undergoing periodic modulation of the S spin's energy, $\hbar\omega_S(t)$, as a function of the modulation frequency, ω_r. In all simulations, $\omega_S(t) = \frac{\omega_S+\delta\omega_S}{2} + \cos(\omega_r t)\frac{\omega_S-\delta\omega_S}{2}$, $\frac{\hbar\omega_S}{k_BT} = 1$, $\frac{\delta\omega_S}{\omega_S} = \frac{1}{75}$, $\frac{\omega_I}{\omega_S} = \frac{1}{100}$, $\omega_{T,IS} = \omega_{Z,IS} = 0.03\omega_I$, $T_1^S = T_2^S = \frac{2\pi}{\omega_I}$, and $T_1^I = T_2^I = 2\pi\frac{4\times10^4}{\omega_I}$. In (A), peaks in $P_{\text{qeq},I}$ are observed at modulation frequencies that satisfy the resonance condition $n\omega_r = \overline{\omega}_S - \omega_I$ for integer n, where $\overline{\omega}_S = \frac{\omega_S+\delta\omega}{2} = 50.67\omega_I$ for the preceding parameters. In (B) and (C), $P_{\text{qeq},I}$ calculated using Eq. (14) with ($\eta = 1$, solid blue curve) and without ($\eta = 0$, dotted red curve) the gauge term $-\frac{1}{2}\frac{dP_{\text{eq},S}(t)}{dt}|\widehat{\Psi}_2^R(0)\rangle\rangle\langle\langle\widehat{\Psi}_1^L(0)|$, included in the calculation. As can be seen, the gauge term has a significant impact on the resulting $P_{\text{qeq},I}$ for $\omega_r \geqslant \frac{1}{16T_1}$ since $P_{\text{eff},S}(t) = P_{\text{eq},S}^{(0)} = 0.2412$. This ensures that there is substantial S spin polarization throughout the modulation period, thereby enabling the I spin to develop a substantial spin polarization at the resonance conditions, $n\omega_r = \Delta\omega_{IS}$. For $\omega_r \ll \frac{1}{T_1^S}$, $P_{\text{eff},S}(t) \approx P_{\text{eq},S}(t)$, so there is little S spin polarization available for transfer to the I spin at times $t_{\min,n} = \frac{\pi}{\omega_r}(2n+1)$ where polarization transfer is most efficient.

from Eq. (14), if $|m\omega_r T_1^S| \ll 1$, the gauge term's contribution to $P_{\text{qeq},I}$ can be safely neglected, which for the simulation in Fig. 1(C) corresponds to $\omega_r \leqslant \frac{1}{16T_1^S}$.

A physical picture that helps to explain the results in Fig. 1 is as follows: in the absence of any modulations to the S spin's energy, $\hbar\omega_S$, the ratio of the I spin's equilibrium polarization with and without coupling to the S spin, $\frac{P_{\text{eq}',I}}{P_{\text{eq},I}}$, is generally on the order of one, indicating that there is little enhancement of the I spin's polarization (for parameters used in Fig. 1, $\frac{P_{\text{eq}',I}}{P_{\text{eq},I}} = 1.168$). This is due to the fact that the energy mismatch, $\hbar|\omega_S - \omega_I|$, for the "flip-flop" transitions that are responsible for polarization transfer between the S

and the I spins, $|\pm\rangle_S|\mp\rangle_I \leftrightarrow |\mp\rangle_S|\pm\rangle_I$, is much larger than the coupling generating these transitions; that is, $|\omega_S - \omega_I| \gg |\omega_{T,IS}|$. However, when the S spin's energy is periodically modulated between ω_S and $\delta\omega_S \ll \omega_S$ with a time averaged value of $\overline{\omega}_S$, the periodic modulation can provide the "flip-flop" transitions with additional energy in integer multiples of the modulation frequency, $\pm n\hbar\omega_r$, to make up for the energy deficit during the "flip-flop" transitions. Therefore, at the resonance conditions $\overline{\omega}_S - \omega_I = \Delta\omega_{IS} = n\omega_r$ for integer n, efficient polarization transfer between the S and the I spin occurs. The peaks in $P_{\text{qeq},I}$ observed in Fig. 1 correspond to values of ω_r satisfying the preceding resonance conditions. For those resonance conditions that occur when $\omega_r > \frac{2\pi}{T_1^S}$, the maximum I spin polarization possible is given by the time-averaged S spin polarization, $P_{\text{eff},S} = P^{(0)}_{\text{eq},S} = 0.2412$. When $\omega_r > \Delta\omega_{IS}$, no additional resonance conditions exist, and the I spin polarization is given by $P_{\text{qeq},I} = P_{\text{eq}',I}(\overline{\omega}_S) = 0.0067$, where $P_{\text{eq}',I}$ in Eq. (13) is evaluated using the time-averaged S frequency, $\overline{\omega}_S$.

While the resonance condition, $\Delta\omega_{IS} = n\omega_r$, explains the appearance of the peaks in $P_{\text{qeq},I}$ observed in Fig. 1, it does not explain the decrease in $P_{\text{qeq},I}$ for $\omega_r < \frac{2\pi}{T_1^S}$. This decrease can be understood by examining the dynamics of polarization transfer during a modulation period of $\omega_S(t)$. As previously stated, polarization transfer is most efficient when $\hbar|\omega_S(t) - \omega_I| \ll \hbar\omega_{T,IS}$. While $\omega_S(t)$ is periodically modulated between ω_S and $\delta\omega_S$, the most efficient polarization transfer therefore occurs when $|\omega_S(t) - \omega_I|$ achieves its lowest value, $|\delta\omega_S - \omega_I|$, which occurs at times $t_{\text{min},n} = (2n+1)\frac{\pi}{\omega_r}$. At these times, the I spin polarization can increase up to the S spin polarization at time $t_{\text{min},n}$, $P_{\text{eff},S}(t_{\text{min},n})$. For $\omega_r > \frac{2\pi}{T_1^S}$, the S spin's polarization is simply given by $P_{\text{eff},S} = P^{(0)}_{\text{eq},S} \approx 0.2412$ independent of ω_r and time t; thus, the I spin can build up a polarization close to $P^{(0)}_{\text{eq},S}$ over a time scale of $\frac{1}{T^{(0)}_{1,IS}} + \frac{1}{T_1^I}$. However, for $\omega_r \ll \frac{1}{T_1^S}$, $P_{\text{eff},S}(t) \approx P_{\text{eq},S}(t)$, so at the times $t_{\text{min},n}$ when the polarization transfer is most efficient, $P_{\text{eff},S}(t_n) \approx \tanh(\frac{\hbar\delta\omega_S}{2k_BT}) = 6.67 \times 10^{-3}$, and so there is very little polarization available to be transferred to the I spin even at the resonance conditions, $\Delta\omega_{IS} = n\omega_r$. This explains the importance of the gauge term on developing substantial I spin polarization that is clearly illustrated in Figs. 1(B) and 1(C). In the absence of the gauge term, $P_{\text{eff},S}(t) \approx P_{\text{eq},S}(t)$ for all ω_r, so that at times $t_{\text{min},n}$, there is little S spin polarization available for transfer to the I spin. With the gauge term, $P_{\text{eff},S} \to P^{(0)}_{\text{eq},S} = 0.2412$ for $\omega_r \gg \frac{2\pi}{T_1^S}$, which ensures that there is substantial S spin polarization transfer from the S spin to the I spin at the resonance conditions, $\Delta\omega_{IS} = n\omega_r$.

It should be noted that for actual spin systems, it would be experimentally difficult to modulate the S spin's energy and relaxation rates while keeping the I spin's energy fixed. However, this situation can be experimentally realized in many nonspin, effective two-state systems. For example, recent experiments [31] in closed lateral double quantum dots have demonstrated that the energy splitting between the singlet and one of the triplet states can be periodically modulated using time-dependent gate voltages while the energy of the nuclear spins in the quantum dot remain fixed. Such systems could be used to illustrate the theory presented in this section, although in these systems, the effective S spin (the singlet and a triplet state) is coupled to many I spins. In fact, it was shown that the nuclear spin polarization increased when the modulation frequency between singlet and triplet states was equal to a multiple of ω_I [31]. Since the electronic state is periodically shuttled between the singlet and triplet states (analogous to the S spin being periodically "shuttled" between spin up and spin down), $\overline{\omega}_S = 0$ so that the theory presented previously would predict efficient polarization transfer at one of the experimentally observed resonance conditions, $\omega_r = \omega_I$. However, there are two important caveats before one applies the theory presented in this work to those experiments. First of all, the theory presented here was for a single IS spin system, whereas in the double quantum dot system, there are on the order of 10^6–10^7 nuclei [32]. In fact, experimentally observed resonance conditions at multiples of the I spin Larmour frequency, $\omega_r = n\omega_I$, could possibly be related to transitions where n I spins flip. The second caveat is that in the preceding theory, $\delta\omega$ was assumed to be greater than $|\widehat{H}_{\text{sys-env}}|$ so that the evolution of coherences and populations could be treated separately. If $|\omega_S(t)| \leqslant |\widehat{H}_{\text{sys-env}}|$, then this secular approximation could not be used, and a more detailed theory would be needed. Extensions of the theory to larger spin systems and a more accurate characterization of the breakdown of the secular approximation are left for future study.

D. Periodic modulations of both ω_S and ω_I

For the case of actual spin systems, it is easier experimentally to modulate both ω_S and ω_I and their relaxation rates by using a time-dependent magnetic field that affects both spins such that $\omega_S(t) = \overline{\omega}_S + \frac{\omega_S - \delta\omega_S}{2}\cos(\omega_r t)$ and $\omega_I(t) = \overline{\omega}_I + \frac{\omega_I - \delta\omega_I}{2}\cos(\omega_r t)$, where $\frac{\delta\omega_I}{\overline{\omega}_I} = \frac{\delta\omega_S}{\overline{\omega}_S}$. In this case, using similar arguments as above, efficient polarization transfer can occur when an integer multiple of the modulation frequency equals the time-averaged frequency difference between the I and the S spins, $n\omega_r \approx |\overline{\omega}_S - \overline{\omega}_I|$. To verify this, a calculation of $P_{\text{qeq},I}$ as a function of ω_r, was performed using the numerically calculated propagator, $\widehat{T}\exp[\int_0^t dt' \widehat{\mathscr{L}}(t')]$. The result is shown in Fig. 2(A) (solid, blue curve), where, for comparison, $P_{\text{qeq},I}$ generated from periodic modulations of $\omega_S(t)$ alone [Fig. 1(A)] is also shown (dotted red curve). The differences between modulating both ω_I and ω_S versus modulating only ω_S are slight and mainly due to the difference in resonance conditions, $n\omega_r = \overline{\omega}_S - \overline{\omega}_I$ versus $n\omega_r = \overline{\omega}_S - \omega_I$, which can be seen in the slight shift in the peaks of $P_{\text{qeq},I}$ for the solid blue curve (both ω_S and ω_I) and the dotted red curve (ω_S only) in Fig. 2(A). Since the I spin's relaxation rates, $\mathscr{W}^I_{\pm,\mp}(t)$, are now time dependent, there will also be an additional gauge term proportional to $\frac{dP_{\text{eq},I}(t)}{dt}$, which will simply result in $P_{\text{qeq},I}$ being equal to $P_{\text{eq}',I}$ away from the resonance conditions, $n\omega_r = |\overline{\omega}_S - \overline{\omega}_I|$, where $P_{\text{eq}',I}$ in Eq. (13) is evaluated using the time-averaged I and S spin polarizations.

E. Case where $T_1^S(t)$ and $T_2^S(t)$ are time dependent

In the previous discussion, the relaxation times T_1^S and T_2^S were taken to be time independent even though the S spin energy difference was time dependent. In general, however, both T_1^S and T_2^S will depend upon $\omega_S(t)$. Although the

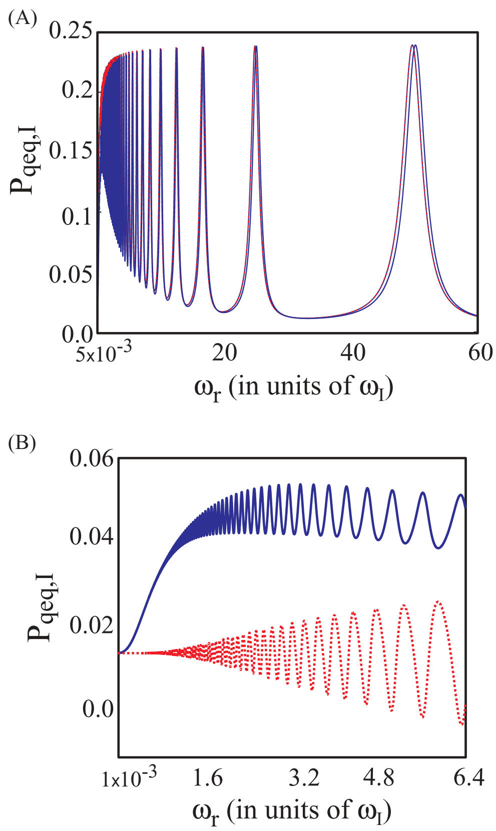

FIG. 2. (Color online) (A) A plot of the resulting quasiequilibrium I spin polarization, $P_{\text{qeq},I}$ (solid blue curve), in a coupled IS spin system where both the I and the S spin's energies are periodically modulated in time, versus the modulation frequency, ω_r, where $\omega_{S(I)}(t) = \overline{\omega}_{S(I)} + \frac{\omega_{S(I)}-\delta\omega_{S(I)}}{2}\cos(\omega_r t)$. The results are similar to those found in Fig. 1(A), where only the S spin's energy was periodically modulated [$P_{\text{qeq},I}$ for that case is also shown in Fig. 2(A) for reference (dotted red curve)]. The major difference between the two cases is that maxima in $P_{\text{qeq},I}$ occur at $n\omega_r = \overline{\omega}_S - \overline{\omega}_I$ (solid blue curve) when both ω_I and ω_S are modulated, as opposed to occurring at $n\omega_r = \overline{\omega}_S - \omega_I$ (dotted red curve), when only ω_S is modulated. $P_{\text{qeq},I}$ for the case where both ω_I and ω_S are periodically modulated was determined by using the numerically calculated propagator, $\widehat{T}\exp[\int_0^t dt'\widehat{\mathscr{L}}(t')]$. The same parameters as in Fig. 1 were used in addition to $\frac{\delta\omega_I}{\omega_I} = \frac{\delta\omega_S}{\omega_S} = \frac{1}{75}$. In (B), $P_{\text{qeq},I}$ is calculated using the numerically calculated propagator with (solid blue curve) and without (dotted red curve) the gauge term for periodic modulations of $\omega_S(t)$ and where the relaxation times of the S spin were modeled as arising from the S spin coupling to a collection of harmonic oscillators with frequency uniformly distributed between ω_S and $\delta\omega_S$, $T_1^S(t) = T_2^S(t) = \frac{2\pi}{\omega_I}\coth[\frac{\hbar\omega_S(0)}{2k_BT}]\tanh[\frac{\hbar\omega_S(t)}{2k_BT}]$. For the preceding time dependence, $P_{\text{qeq},I} \leqslant \max[P_{\text{eff},S}(t)] = 0.0575$.

time dependence of $T_1^S(t)$ and $T_2^S(t)$ does not enter into the gauge term for the single and two-spin cases, $\widehat{\mathscr{L}}_{\text{gauge}}(t)$, the time-dependence of the relaxation times will affect the spin dynamics of the S spin and the resulting $P_{\text{qeq},I}$ for the two-spin case. As an example, consider the case where T_1^S and T_2^S result from the coupling of the S spin to a collection of harmonic oscillators with frequency uniformly distributed between ω_S and $\delta\omega_S$. In this case [33], $T_2^S(t)$ and $T_1^S(t)$ can be taken as $T_1^S(t) = T_2^S(t) = \lambda^{-2}\tanh[\frac{\hbar\omega_S(t)}{2k_BT}]$, where λ is related to the frequency-independent coupling constant between the oscillators and the S spin. Furthermore, it is also assumed that there are no "memory effects" in the oscillators so that $T_1^S(t)$ and $T_2^S(t)$ depend only upon the instantaneous S spin energy, $\hbar\omega_S(t)$.

In Fig. 2(B), calculations of $P_{\text{qeq},I}$ obtained from the numerically calculated propagator $\widehat{T}\exp[\int_0^t dt'\widehat{\mathscr{L}}(t')]$ with $T_1^S(t) = T_2^S(t) = \frac{2\pi}{\omega_I}\coth[\frac{\hbar\omega_S(0)}{2k_BT}]\tanh[\frac{\hbar\omega_S(t)}{2k_BT}]$ used in $\widehat{\mathscr{L}}_{\text{relax}}$ [Eq. (12)] are shown with (solid blue curve) and without (dotted red curve) the gauge term. The parameters used in the simulation are given in the figure caption. The time dependence of $T_1^S(t)$ and $T_2^S(t)$ does have a significant effect on $P_{\text{qeq},I}$, as can be seen by comparing Fig. 1(B) to Fig. 2(B). The resonance conditions again occur at $n\omega_r = \Delta\omega_{IS}$, although the maximum $P_{\text{qeq},I}$ is less than that observed in Fig. 1. This is due to the time dependence of $T_1^S(t)$; at times $t_{\min,n} = \frac{\pi}{\omega_r}(2n+1)$, $T_1^S(t_{\min,n}) = 0.0144T_1^S(0)$; that is, the relaxation rate has increased by a factor of 70 relative to the unmodulated relaxation rate. For $\omega_r \gg \frac{2\pi}{T_1^{S(0)}} \approx \frac{2\pi}{8\omega_I}$ [where $T_1^{S(0)}$ is the time average of T_1^S], $P_{\text{eff},S}(t) \approx 0.0575 < P_{\text{eq},S}^{(0)}$; the time-dependence of $T_1^S(t)$ results in a smaller average S spin polarization. For $\omega_r > \frac{2\pi}{8\omega_I}$, $P_{\text{qeq},I} \leqslant 0.0575$. Thus, the smaller $P_{\text{qeq},I}$ observed in Fig. 2(B) is a result of the smaller $P_{\text{eff},S}$. As in Fig. 1, the gauge term has a significant effect on $P_{\text{qeq},I}$, although, in this case, the time dependence of $T_1^S(t)$ and $T_2^S(t)$ results in larger $P_{\text{qeq},I}$ in the absence of the gauge term compared the to results shown in Fig. 1. This is due to the fact that a smaller T_2^S can help lessen the impact of energy mismatch, $\hbar|\omega_S - \omega_I|$ and increase the efficacy of polarization transfer between the S and the I spins.

III. CONCLUSIONS

In summary, I have shown that periodically modulating the Hamiltonian and thereby indirectly modulating the incoherent dynamics in an open quantum system can result in a quasiequilibrium state, $|\widehat{\rho}_{\text{qeq}}(t)\rangle\rangle$, that significantly differs from the instantaneous equilibrium state when the modulations are nonadiabatic. For a spin-1/2 system, modulations of the Hamiltonian resulted in a small rotation of the magnetization for the case of a rotating magnetic field. For an amplitude modulated magnetic field, the gauge term resulted in the polarization decreasing to its time-averaged polarization as opposed to being given by the instantaneous polarization, $P_{\text{eq},S}(t) = \tanh[\frac{\hbar\omega_S(t)}{2k_BT}]$. For the case of a two-spin system where the instantaneous equilibrium polarization of one of the spins was modulated in time, the nonadiabatic corrections from $\widehat{\mathscr{L}}_{\text{gauge}}(t)$ had a significant effect on the quasiequilibrium polarization of the unmodulated spin (Figs. 1 and 2). The $\widehat{\mathscr{L}}_{\text{gauge}}(t)$ term prevents the effective polarization on the S spin from following the instantaneous polarization, $P_{\text{eff},S}(t) \neq P_{\text{eq},S}(t)$. This results in increased I polarization at the resonance conditions, $n\omega_r = \overline{\omega}_S - \omega_I$ (if only the S spin's frequency is modulated) or at $n\omega_r = \overline{\omega}_S - \overline{\omega}_I$ (if both the I and the S spins' frequencies are modulated), where $\overline{\omega}_{S(I)}$ is the time-averaged frequency of the $S(I)$ spin.

The results in this work should have applications in a variety of condensed-matter systems, such as for increasing nuclear spin polarization in quantum dots [31] and for designing algorithmic cooling procedures [34], and chemical systems [35,36] where the chemical rate constants could be experimentally controlled by temperature or pressure modulations [37]. Extensions of this work to polarization transfer in larger numbers of spins and to cases where both the energy levels and the eigenstates are modulated in time are currently under way.

ACKNOWLEDGMENTS

The author thanks Dr. J. Y. Vaishnav for comments on the manuscript and acknowledges support from the Camille and Henry Dreyfus Foundation and the University of Miami.

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