

Coherent Cross-Polarization Theory for a Spin- $\frac{1}{2}$ Coupled to a General Object

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Zero-order average-Hamiltonian theory is used to extend the product-operator description of coherent spin-spin cross-polarization to the case of a spin- $\frac{1}{2}$ coupled to a general object, like a molecular rotor or a quantum oscillator. The object, which is not necessarily in a Boltzmann equilibrium state, is assumed to have no interaction with the lattice and no internal relaxation capacity. The Bloch-Wangsness-Redfield (BWR) theory for incoherent processes like spin-lattice relaxation does not apply for such an isolated spin-object pair. Nevertheless spectral density at the Larmor frequency, of key importance in BWR theory, also plays a central role in object-induced spin polarization. Spectral density in our theory is represented by quantum operators J_- and J_+ . If J_- and J_+ do not commute, the spin-object coupling may cause spin polarization in an initially saturated spin system. This represents a coherent mechanism for spin cooling, which in specific cases may lead to enhanced spin polarization above the thermal equilibrium value. A master equation is derived for general spin-object cross-polarization, and applied to the case of a spin pair inside a uniaxial rotor, and a spin coupled to a microelectronic LC circuit. © 2000

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INTRODUCTION

The low equilibrium polarization of nuclear spins in a magnetic field at ambient temperature has challenged numerous investigators to enhance the spin polarization (1–6). A well-known and routinely applied technique in solid-state NMR is cross-polarization (CP), whereby polarization is transferred between different nuclear spin species (1, 7). In general spins not only are coupled to other spins, but also interact with other “objects.” An example of such coupling to a nonspin object is represented by a spin in a spatially inhomogeneous magnetic field. In this case the spin is coupled to the source of the gradient, e.g., a magnetic particle, through the position dependence of the Zeeman interaction. As a result of this coupling

irradiation of the spin can lead to translational motion of the particle, which is the basis of force-detected NMR spectroscopy (8). A spin may also be coupled to the molecule or particle, in which it resides, through the orientation dependence of the chemical shift, the quadrupolar interaction, or the dipolar coupling. In magnetic resonance it is commonly assumed that nonspin objects, like quantum oscillators and molecular rotors, are intimately linked to the surroundings, so that their state is practically unaffected by the interaction with the spin. This leads to incoherent spin-object processes, such as spin-lattice relaxation, which can be described in the theoretical framework of Bloch, Wangsness, and Redfield (9, 10). As opposed to the incoherence assumed in relaxation theories, in this article we study the *coherent* interaction between a spin- $\frac{1}{2}$ coupled to a general object. The object may, e.g., be another spin, a cluster of spins, or a specific lattice mode, which is only weakly coupled to the other lattice modes. As a starting point we treat the spin-object pair as isolated from its surroundings and neglect the possible occurrence of internal object relaxation. Furthermore we do not necessarily assume a Boltzmann state for the object.

The main question we want to answer is whether types of spin-object coupling other than spin-spin coupling can be used to enhance the spin polarization in a way similar to the spin-spin CP technique. From a semiclassical point of view many types of spin-object interactions can be regarded to contribute to the local magnetic field at the spin site. If this contribution has a transverse component and fluctuates in the range of the Larmor frequency, the spin-object coupling can cause transitions between the spin states. The question is whether these transitions lead to saturation or polarization. On the one hand electromagnetic radiation, for instance, equally affects the transition probability between the two spin states in both directions and thus results in saturation. On the other hand, if a spin system is in contact with a thermal bath at temperature T , the spin state populations should reach values given by the Boltzmann equation. Semiclassical relaxation theory, in which the coupling with the lattice is represented by real functions, always leads to a steady state described by an infinite temperature (9, 11). Such arguments, however, neglect the quantum character of the object coupled to the spin. Wang-

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ness and Bloch have presented a theory for incoherent spin–lattice interaction, which takes the quantum character of the lattice into account (9). Their theory is based on the assumptions that the lattice has an infinite heat capacity and a rapid internal relaxation, so that it is always in a Boltzmann state. Below we present a theoretical framework for coherent polarization exchange in an isolated pair of a spin- $\frac{1}{2}$ and a general quantum-mechanical object.

GENERAL THEORY OF CROSS-POLARIZATION

(a) Average Spin–Object Hamiltonian in the Interaction Frame

The Hamiltonian H of a spin- $\frac{1}{2}$ coupled to an object, such as another spin or an oscillator, consists of a spin part H^I , an object part H^O , and an interaction part $H^{I,O}$:

$$H = H^I + H^O + H^{I,O}. \quad [1]$$

In a magnetic field the spin part is given by

$$H^I = -\hbar\omega_{0I}\mathbf{I}_z, \quad [2]$$

where ω_{0I} denotes the Larmor frequency. The unperturbed object Hamiltonian H^O needs no further specification at this stage, except that it is assumed to be time-independent. The term $H^{I,O}$ denotes the coupling between the spin and the object and depends on the specific interaction involved. Since the operators $\mathbf{I}_e = \frac{1}{2}\mathbf{1}$, \mathbf{I}_x , \mathbf{I}_y , and \mathbf{I}_z represent a complete basis of spin- $\frac{1}{2}$ space, the general form of $H^{I,O}$ is

$$H^{I,O} = -\hbar g(\mathbf{O}_x\mathbf{I}_x + \mathbf{O}_y\mathbf{I}_y + \mathbf{O}_z\mathbf{I}_z), \quad [3]$$

where g is a real scalar reflecting the size of the coupling, to be defined more exactly below, and where the “coordinates” \mathbf{O}_x , \mathbf{O}_y , and \mathbf{O}_z are operators in object space. Note that a possible term $\mathbf{O}_e\mathbf{I}_e$ can always be included into the definition of H^O . The principle of energy conservation requires the total spin–object Hamiltonian (Eq. [1]) to be time-independent (Appendix 1). Therefore, if H^I and H^O are assumed to be stationary, $H^{I,O}$ should also be time-independent. Interactions, which are time-dependent from a semiclassical perspective, can generally be translated into a quantum-physical form without explicit time dependence.

The polarization exchange between the spin and the object can be derived from the density operator ρ in the interaction frame,

$$\rho^*(t) = \mathbf{U}(t)\rho^*(0)\mathbf{U}^{-1}(t), \quad [4]$$

whereby the propagator $\mathbf{U}(t)$ should satisfy the Schrödinger equation in the interaction frame

$$\frac{d\mathbf{U}}{dt} = -\frac{i}{\hbar}H^*(t)\mathbf{U}(t) \quad [5]$$

with boundary condition $\mathbf{U}(0) = 1$. $H^*(t)$ is the coupling Hamiltonian in the interaction frame,

$$\begin{aligned} H^*(t) &= e^{i(H^I+H^O)t/\hbar}H^{I,O}e^{-i(H^I+H^O)t/\hbar} \\ &= -\frac{1}{2}\hbar g(\mathbf{I}_+\mathbf{O}_-^*(t)e^{-i\omega_{0I}t} + \mathbf{I}_-\mathbf{O}_+^*(t)e^{i\omega_{0I}t} + 2\mathbf{I}_0\mathbf{O}_0^*(t)), \end{aligned} \quad [6]$$

where $\mathbf{I}_\pm = \mathbf{I}_x \pm i\mathbf{I}_y$, $\mathbf{I}_0 = \mathbf{I}_z$, $\mathbf{O}_\pm^*(t) = \mathbf{T}_0(\mathbf{O}_x \pm i\mathbf{O}_y)\mathbf{T}_0^{-1}$, and $\mathbf{O}_0^*(t) = \mathbf{T}_0\mathbf{O}_z\mathbf{T}_0^{-1}$ with $\mathbf{T}_0 = \exp\{iH^O t/\hbar\}$. We can split the spin–object coupling into a secular part which commutes with the unperturbed Hamiltonian $H^I + H^O$ and a nonsecular part which is purely oscillatory in the interaction frame:

$$H^*(t) = H_{\text{sec}}^{I,O} + e^{i(H^I+H^O)t/\hbar}H_{\text{nonsec}}^{I,O}e^{-i(H^I+H^O)t/\hbar}. \quad [7]$$

Solving the Schrödinger equation is generally complicated by the time dependence of $H^*(t)$. The situation may be compared to the specific case of spin–spin CP, where $H^{I,O}$ is represented by the heteronuclear dipolar coupling Hamiltonian. For spin–spin CP the time-dependent nonsecular part of $H^*(t)$ is commonly neglected. We intend to use a similar effective-Hamiltonian approach for the general spin–object case. Without prior knowledge of the object Hamiltonian H^O and the object operators \mathbf{O}_k we cannot derive an expression for the secular Hamiltonian on the basis of their commutation properties. However, we may do so by using average-Hamiltonian theory (12), in which the system evolves under an effective Hamiltonian given by a series of terms

$$H = H^{(0)} + H^{(1)} + \dots \quad [8a]$$

with the zero-order term

$$\begin{aligned} H^{(0)}(t) &= \frac{1}{t} \int_0^t H^*(t')dt' \\ &= H_{\text{sec}}^{I,O} + \frac{1}{t} \int_0^t e^{i(H^I+H^O)t'/\hbar}H_{\text{nonsec}}^{I,O}e^{-i(H^I+H^O)t'/\hbar}dt' \end{aligned} \quad [8b]$$

and higher-order terms $H^{(n)}(t)$, which in the weak-coupling limit tend to be much smaller, $\|H^{(n)}(t)\| \ll \|H^{(0)}(t)\|$. Since the nonsecular part of $H^*(t)$ consists of purely oscillatory terms, $H^{(0)}(t)$ converges into H_{sec} on the timescale of the slowest oscillation. Depending on the rate of convergence relative to the size of the spin–object interaction we distinguish between

a slow and a fast limit. For both limits it makes sense to use a time-independent effective Hamiltonian of the form

$$H_{\text{eff}} = -\frac{\hbar g}{2} (\mathbf{I}_+ \mathbf{J}_- + \mathbf{I}_- \mathbf{J}_+ + 2\mathbf{I}_0 \mathbf{J}_0). \quad [9]$$

In the slow limit the oscillations in $H^*(t)$ are extremely slow on the timescale of the spin-object interactions, $H^*(t) \approx H^*(0)$. We may then use an effective Hamiltonian H_{eff} equal to $H^*(0)$, and the operators \mathbf{J}_σ ($\sigma = -, 0, +$) in Eq. [9] correspond to the respective \mathbf{O}_σ operators in Eq. [3]. In the fast limit the nonsecular part of $H^*(t)$ averages to zero before significant effects of the spin-object interaction arise. Thus H_{eff} is represented by the remaining secular part H_{sec} . The operators \mathbf{J}_σ follow from the limiting behavior form of the average Hamiltonian $H^{(0)}(t)$. For times t beyond a certain minimum time t_{\min} , say, one order of magnitude larger than the period of the slowest oscillation in $H^*(t)$, $H^{(0)}(t)$ becomes independent of a further increase in t . Replacing t by the fixed t_{\min} in Eq. [8b] we obtain a time-independent expression for the \mathbf{J}_σ operators

$$\mathbf{J}_\sigma = \frac{1}{t_{\min}} \int_0^{t_{\min}} \mathbf{O}_\sigma^*(t') e^{i\sigma\omega_0 t'} dt'. \quad [10]$$

The operators \mathbf{J}_σ may be compared to the spectral density functions in relaxation theory. Between the slow and fast limit there is the intermediate range, in which the frequency of some oscillations in $H^*(t)$ is comparable to the size of the spin-object interaction. Then the effective-Hamiltonian description is invalid, and other approaches based on, e.g., higher-order average-Hamiltonian theory (12) or Floquet theory (13) should be employed. In addition we may encounter combined slow and fast limiting cases, when $H^*(t)$ contains both slow and fast oscillating terms well separated in frequency. In the derivation below we will generally assume the fast limit, and employ the secular Hamiltonian, or, equivalently, the zero-order average Hamiltonian (ZOAH) to calculate the behavior of the spin-object system beyond a certain minimum time t_{\min} associated with the initial transient behavior of $H^{(0)}(t)$ (Eq. [8b]). Some authors have pointed out that there is generally an upper bound to the validity of average-Hamiltonian theory (14, 15), as well. A full explanation thereof is beyond the scope of this article. Assuming the first-order term $H^{(1)}(t)$ to be next in importance, however, we may expect that the zero-order propagator $\exp\{-iH^{(0)}t/\hbar\}$ starts to deviate significantly from the more accurate first-order propagator $\exp\{-i(H^{(0)} + H^{(1)})t/\hbar\}$, when $\|H^{(1)}\|t > \hbar$. This yields a roughly estimated upper bound $t_{\max} = \hbar/\|H^{(1)}\|$ for the validity of a ZOAH approach.

The \mathbf{J}_σ operators correspond to quantum operators such as position, momentum, charge, and current and are generally not dimensionless. They can be made dimensionless by dividing them by the expectation value $J = \sqrt{\langle \mathbf{J}_- \mathbf{J}_+ + \mathbf{J}_+ \mathbf{J}_- + \mathbf{J}_0^2 \rangle}$ at $t = 0$

TABLE 1
Product $\mathbf{I}_a \mathbf{I}_b$ of the Spin- $\frac{1}{2}$ Operators $\mathbf{I}_a, \mathbf{I}_b \in \{2\mathbf{I}_e, 2\mathbf{I}_0, \mathbf{I}_+, \mathbf{I}_-\}$

\mathbf{I}_a	\mathbf{I}_b			
	$2\mathbf{I}_e$	$2\mathbf{I}_0$	\mathbf{I}_+	\mathbf{I}_-
$2\mathbf{I}_e = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$2\mathbf{I}_e$	$2\mathbf{I}_0$	\mathbf{I}_+	\mathbf{I}_-
$2\mathbf{I}_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$2\mathbf{I}_0$	$2\mathbf{I}_e$	\mathbf{I}_+	$-\mathbf{I}_-$
$\mathbf{I}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$	\mathbf{I}_+	$-\mathbf{I}_+$	$\mathbf{0}$	$\mathbf{I}_e + \mathbf{I}_0$
$\mathbf{I}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$	\mathbf{I}_-	\mathbf{I}_-	$\mathbf{I}_e - \mathbf{I}_0$	$\mathbf{0}$

(supposed to be nonzero), and at the same time multiplying g by J . Such normalization has the advantage that g reflects the size of the interaction in frequency units, which is convenient for checking the validity of the secular-Hamiltonian approximation.

Specific commutator properties of the \mathbf{J}_σ operators can be derived from fact that the limiting form H_{sec} of $H^{(0)}$ commutes with $H^0 + H^1$. Insertion of a secular Hamiltonian of the form of Eq. [9] into the vanishing commutator $[H^0 + H^1, H_{\text{sec}}]$ yields

$$\begin{aligned} & [H^0, \mathbf{I}_+ \mathbf{J}_- + \mathbf{I}_- \mathbf{J}_+ + 2\mathbf{I}_0 \mathbf{J}_0] \\ & = -[H^1, \mathbf{I}_+ \mathbf{J}_- + \mathbf{I}_- \mathbf{J}_+ + 2\mathbf{I}_0 \mathbf{J}_0]. \end{aligned} \quad [11]$$

Splitting up the commutator term by term on the left-hand side of the equation, and using Eq. [2] and the spin-operator commutation rules on the right-hand side, we then have

$$\begin{aligned} & \mathbf{I}_+ [H^0, \mathbf{J}_-] + \mathbf{I}_- [H^0, \mathbf{J}_+] + 2\mathbf{I}_0 [H^0, \mathbf{J}_0] \\ & = \hbar\omega_0 \mathbf{I}_+ \mathbf{J}_- - \hbar\omega_0 \mathbf{I}_- \mathbf{J}_+. \end{aligned} \quad [12]$$

From the orthogonal properties of the spin operators (Table 1), it thus follows

$$[H^0, \mathbf{J}_0] = 0 \quad [13a]$$

$$[H^0, \mathbf{J}_\pm] = \mp \hbar\omega_0 \mathbf{J}_\pm. \quad [13b]$$

Even without specifying the object involved, we thus know that the operators \mathbf{J}_\pm act as raising and lowering operators which connect object states with energy separation of $\pm \hbar\omega_0$.

H_{eff} (Eq. [9]) may be divided into $H_{\text{eff,A}} = -(\hbar g/2)(\mathbf{I}_+ \mathbf{J}_- + \mathbf{I}_- \mathbf{J}_+)$, on the one hand, and $H_{\text{eff,B}} = -\hbar g \mathbf{I}_0 \mathbf{J}_0$, on the other. $H_{\text{eff,A}}$ directly affects the spin polarization $\langle \mathbf{I}_0 \rangle$ by causing flip-flop transitions between the two spin states and pairs of object levels separated by $\hbar\omega_0$. By changing the magnetic field B_0 we may match $\hbar\omega_0$ to the separation of specific object levels. Because $H_{\text{eff,B}}$ commutes with \mathbf{I}_0 , it only has a higher-

order polarization effect, which, as shown in Appendix 3, even vanishes completely, when $H_{\text{eff,A}}$ and $H_{\text{eff,B}}$ commute. In typical cases, like the examples discussed in this paper, $H_{\text{eff,B}}$ vanishes, or commutes with $H_{\text{eff,A}}$. For this reason we neglect $H_{\text{eff,B}}$ in the following and assume an effective Hamiltonian of the form of $H_{\text{eff,A}}$.

(b) *Product-Operator Description of Object-Induced Spin (De)polarization*

In the previous section we showed that in the weak-coupling limit the spin–object system between certain time bounds t_{\min} and t_{\max} can be described by the zero-order average Hamiltonian $H^{(0)}$. The density operator can then be solved from an effective Liouville–von Neumann equation:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H^{(0)}, \rho(t)]. \quad [14]$$

Note that, although Eq. [14] cannot be used to calculate $\rho(t)$ for $t < t_{\min}$, we may nevertheless use it for integration from $t = 0$ in order to derive $\rho(t)$ between t_{\min} and t_{\max} . Since the operators $\mathbf{I}_e = \frac{1}{2}\mathbf{1}$, \mathbf{I}_x , \mathbf{I}_y , and \mathbf{I}_z represent a complete basis of spin- $\frac{1}{2}$ space, $\rho(t)$, like any operator in spin–object space, can be expanded as

$$\rho(t) = 2\mathbf{I}_e\mathbf{R}_e(t) + 2\mathbf{I}_0\mathbf{R}_0(t) + \mathbf{I}_+\mathbf{R}_-(t) + \mathbf{I}_-\mathbf{R}_+(t), \quad [15]$$

where $\mathbf{R}_e(t)$, $\mathbf{R}_0(t)$, $\mathbf{R}_+(t)$, and $\mathbf{R}_-(t)$ are time-dependent operators in object space. Equation [15] implicitly defines the object operators $\mathbf{R}_\sigma(t)$ in such a manner that owing to the spin- $\frac{1}{2}$ properties (Table 1) the expectation value of any spin operator \mathbf{I}_σ equals the trace of $\mathbf{R}_\sigma(t)$ in object space:

$$\langle \mathbf{I}_\sigma \rangle_t = \text{Tr}\{\mathbf{R}_\sigma(t)\}. \quad [16]$$

Because we wish to calculate the spin polarization $\langle \mathbf{I}_0 \rangle_t$, our aim is to derive $\mathbf{R}_0(t)$ as a function of time. Substituting Eq. [15] and $H^{(0)} = -(\hbar g/2)(\mathbf{I}_+\mathbf{J}_- + \mathbf{I}_-\mathbf{J}_+)$ into Eq. [14], and taking the product properties of the spin operators (Table 1) and their orthogonality into account, we find

$$\mathbf{R}_e^{(1)}(t) = \frac{ig}{4} ([\mathbf{J}_+, \mathbf{R}_-(t)] + [\mathbf{J}_-, \mathbf{R}_+(t)]) \quad [17a]$$

$$\mathbf{R}_0^{(1)}(t) = \frac{ig}{4} (-\{\mathbf{J}_+, \mathbf{R}_-(t)\} + \{\mathbf{J}_-, \mathbf{R}_+(t)\}) \quad [17b]$$

$$\mathbf{R}_+^{(1)}(t) = \frac{ig}{2} ([\mathbf{J}_+, \mathbf{R}_e(t)] + \{\mathbf{J}_+, \mathbf{R}_0(t)\}) \quad [17c]$$

$$\mathbf{R}_-^{(1)}(t) = \frac{ig}{2} ([\mathbf{J}_-, \mathbf{R}_e(t)] - \{\mathbf{J}_-, \mathbf{R}_0(t)\}) \quad [17d]$$

with $\mathbf{R}_\sigma^{(1)} = d\mathbf{R}_\sigma/dt$ and curly braces denoting an anticommutator $\{A, B\} = AB + BA$. Equation [17] shows how $\mathbf{R}_e(t)$, $\mathbf{R}_0(t)$, $\mathbf{R}_+(t)$, and $\mathbf{R}_-(t)$ are coupled. Being most interested in the spin polarization $\langle \mathbf{I}_0 \rangle_t = \text{Tr}\{\mathbf{R}_0(t)\}$, we may obtain a new set of equations with less coupled variables by differentiating Eqs. [17a] and [17b] once more, and replacing the resulting first-order derivatives on the right-hand side by use of Eqs. [17c] and [17d]. Adding and subtracting the two resulting second-order differential equations yield

$$\mathbf{R}_\Sigma^{(2)}(t) = -\frac{g^2}{4} (\mathbf{J}_-\mathbf{J}_+\mathbf{R}_\Sigma(t) - 2\mathbf{J}_-\mathbf{R}_\Delta(t)\mathbf{J}_+ + \mathbf{R}_\Sigma(t)\mathbf{J}_-\mathbf{J}_+) \quad [18a]$$

$$\mathbf{R}_\Delta^{(2)}(t) = -\frac{g^2}{4} (\mathbf{J}_+\mathbf{J}_-\mathbf{R}_\Delta(t) - 2\mathbf{J}_+\mathbf{R}_\Sigma(t)\mathbf{J}_- + \mathbf{R}_\Delta(t)\mathbf{J}_+\mathbf{J}_-), \quad [18b]$$

respectively, with $\mathbf{R}_\Sigma(t) = \{\mathbf{R}_e(t) + \mathbf{R}_0(t)\}/2$ and $\mathbf{R}_\Delta(t) = \{\mathbf{R}_e(t) - \mathbf{R}_0(t)\}/2$, and $\mathbf{R}_\Sigma^{(2)}(t)$ and $\mathbf{R}_\Delta^{(2)}(t)$ the respective second-order time derivatives. Although simpler, Eq. [18] is still difficult to solve, because \mathbf{J}_+ and \mathbf{J}_- do not generally commute with $\mathbf{R}_\Sigma(t)$ and $\mathbf{R}_\Delta(t)$. Fortunately, we do not need to know the exact solution $\{\mathbf{R}_\Sigma(t), \mathbf{R}_\Delta(t)\}$ in full detail to calculate $\langle \mathbf{I}_0 \rangle_t = \text{Tr}\{\mathbf{R}_0(t)\}$. By subtracting Eqs. [18a] and [18b] and taking the trace we obtain

$$\frac{d^2\text{Tr}\{\mathbf{R}_0(t)\}}{dt^2} = -g^2\text{Tr}\{\mathbf{J}_-\mathbf{J}_+\mathbf{R}_\Sigma(t) - \mathbf{J}_+\mathbf{J}_-\mathbf{R}_\Delta(t)\}, \quad [19]$$

where we used the property that the trace of an operator product stays invariant under cyclic permutation, $\text{Tr}\{\mathbf{ABC}\} = \text{Tr}\{\mathbf{BCA}\} = \text{Tr}\{\mathbf{CAB}\}$. Differentiating Eq. [19] twice with respect to time followed by substitution of Eqs. [18a] and [18b] and cyclic permutation of the operators within the trace one finds for the even-order derivatives

$$\frac{d^{2k}\text{Tr}\{\mathbf{R}_0(t)\}}{dt^{2k}} = (ig)^{2k} \text{Tr}\{(\mathbf{J}_-\mathbf{J}_+)^k\mathbf{R}_\Sigma(t) - (\mathbf{J}_+\mathbf{J}_-)^k\mathbf{R}_\Delta(t)\}. \quad [20]$$

The uneven-order derivatives may be obtained by differentiating one step further,

$$\frac{d^{2k+1}\text{Tr}\{\mathbf{R}_0(t)\}}{dt^{2k+1}} = (Ig)^{2k} \text{Tr}\{(\mathbf{J}_-\mathbf{J}_+)^k\mathbf{R}_\Sigma^{(1)}(t) - (\mathbf{J}_+\mathbf{J}_-)^k\mathbf{R}_\Delta^{(1)}(t)\}. \quad [21]$$

If, by assumption, there is no spin coherence at $t = 0$, $\langle \mathbf{I}_\pm \rangle_0 = 0$, then the initial density operator has the form $\rho^*(0) = 2\mathbf{I}_e \mathbf{R}_e(0) + 2\mathbf{I}_o \mathbf{R}_o(0)$, and the uneven-order derivatives at $t = 0$, $\mathbf{R}_0^{(2n+1)}(0)$, vanish. Substituting the even-order derivatives into a Taylor expansion of $\langle \mathbf{I}_0 \rangle_t = \text{Tr}\{\mathbf{R}_0(t)\}$ then yields the difference between two cosine series:

$$\begin{aligned} \text{Tr}\{\mathbf{R}_0(t)\} &= \text{Tr}\{\cos(gt\sqrt{\mathbf{J}_-\mathbf{J}_+})\mathbf{R}_\Sigma(0) \\ &\quad - \cos(gt\sqrt{\mathbf{J}_+\mathbf{J}_-})\mathbf{R}_\Delta(0)\}. \end{aligned} \quad [22]$$

$\mathbf{R}_{\Sigma,\Delta}(0)$ in Eq. [22] may be resubstituted by $\{\mathbf{R}_e(0) \pm \mathbf{R}_o(0)\}/2$. The operators $\cos(gt\sqrt{\mathbf{J}_-\mathbf{J}_+})$ and $\cos(gt\sqrt{\mathbf{J}_+\mathbf{J}_-})$ have pure object character. Now, for any pure object operator \mathbf{Q} it follows from the general form of the spin-object density operator (Eq. [15]) and the orthogonality of the spin- $\frac{1}{2}$ operators (Table 1) that $\text{Tr}\{\mathbf{Q}\mathbf{R}_e(0)\}$ and $\text{Tr}\{\mathbf{Q}\mathbf{R}_o(0)\}$ respectively correspond to the expectation values $\langle \mathbf{I}_e \mathbf{Q} \rangle_0 = \frac{1}{2} \langle \mathbf{Q} \rangle_0$ and $\langle \mathbf{I}_o \mathbf{Q} \rangle_0$ at $t = 0$.

To evaluate such an expectation value $\langle \mathbf{I}_o \mathbf{Q} \rangle_0$ further, we assume that the initial density operator $\rho^*(0)$ is the product $\rho_o \rho_i$ of an object operator ρ_o and a spin operator ρ_i . In the weak-coupling limit this is approximately the case, when before $t = 0$ the spin and the object are in thermal equilibrium, $\rho^*(0) = \exp\{-\beta(H^1 + H^o + H^{1o})\} \approx \exp\{-\beta H^1\} \exp\{-\beta H^o\}$. For such $\rho^*(0) = \rho_o \rho_i$ the expectation value $\langle \mathbf{I}_o \mathbf{Q} \rangle_0$ equals the product of the separate expectation values $\langle \mathbf{I}_o \rangle_0 \langle \mathbf{Q} \rangle_0$. Note that this represents an incoherent state of the spin-object system at $t = 0$ only. At $t = 0$ we perturb the system, e.g., invert the spin polarization, and the coherent effect of the spin-object interaction may well be that $\rho^*(t)$ can no longer be factorized into an object and a spin part. Consequently the equality $\langle \mathbf{I}_o \mathbf{Q} \rangle_t = \langle \mathbf{I}_o \rangle_t \langle \mathbf{Q} \rangle_t$ does not generally hold for $t > 0$. This is a marked difference from incoherent relaxation theories, in which $\langle \mathbf{O} \rangle_t$ typically represents some lattice variable behaving independently from the spin. Making the substitutions in Eq. [22]

$$\text{Tr}\{\mathbf{R}_0(t)\} = \langle \mathbf{I}_0 \rangle_t \quad [23a]$$

$$\begin{aligned} \text{Tr}\{\cos(gt\sqrt{\mathbf{J}_-\mathbf{J}_+})\mathbf{R}_\Sigma(0)\} \\ = \langle \cos(gt\sqrt{\mathbf{J}_-\mathbf{J}_+}) \rangle_0 (\langle \mathbf{I}_e \rangle_0 + \langle \mathbf{I}_o \rangle_0) / 2 \end{aligned} \quad [23b]$$

$$\begin{aligned} \text{Tr}\{\cos(gt\sqrt{\mathbf{J}_+\mathbf{J}_-})\mathbf{R}_\Delta(0)\} \\ = \langle \cos(gt\sqrt{\mathbf{J}_+\mathbf{J}_-}) \rangle_0 (\langle \mathbf{I}_e \rangle_0 - \langle \mathbf{I}_o \rangle_0) / 2 \end{aligned} \quad [23c]$$

with $\langle \mathbf{I}_e \rangle = \frac{1}{2}$, we find that the spin polarization may be decomposed into two terms,

$$\langle \mathbf{I}_0 \rangle_t = \langle \mathbf{I}_0 \rangle_t^{\text{pol}} + \langle \mathbf{I}_0 \rangle_t^{\text{depol}}, \quad [24a]$$

with

$$\langle \mathbf{I}_0 \rangle_t^{\text{pol}} = \frac{1}{4} \langle \cos(gt\sqrt{\mathbf{J}_-\mathbf{J}_+}) - \cos(gt\sqrt{\mathbf{J}_+\mathbf{J}_-}) \rangle_0 \quad [24b]$$

$$\langle \mathbf{I}_0 \rangle_t^{\text{depol}} = \frac{1}{2} \langle \cos(gt\sqrt{\mathbf{J}_-\mathbf{J}_+}) + \cos(gt\sqrt{\mathbf{J}_+\mathbf{J}_-}) \rangle_0 \langle \mathbf{I}_0 \rangle_0. \quad [24c]$$

The suffix 0 means that the expectation values of the time-dependent cosine operators and the spin operators are to be evaluated with respect to the density operator $\rho^*(0)$ at $t = 0$. The polarization term $\langle \mathbf{I}_0 \rangle_t^{\text{pol}}$ is the spin polarization component induced by the object in the case of an initially saturated spin system. The depolarization term $\langle \mathbf{I}_0 \rangle_t^{\text{depol}}$ shows what happens to the initial spin polarization under the influence of the object. $\langle \mathbf{I}_0 \rangle_t^{\text{pol}}$ is nonzero only if \mathbf{J}_+ and \mathbf{J}_- do not commute. Object-induced spin polarization thus requires the object to have significant quantum character. In the classical limit \mathbf{J}_+ and \mathbf{J}_- become identical to their expectation values $\langle \mathbf{J}_\pm \rangle = j_\pm$. Then $\langle \mathbf{I}_0 \rangle_t^{\text{pol}}$ vanishes, and $\langle \mathbf{I}_0 \rangle_t^{\text{depol}}$ equals $\cos(gt\sqrt{j_+j_-})$. Due to the normalization $J = \sqrt{\langle \mathbf{J}_-\mathbf{J}_+ + \mathbf{J}_+\mathbf{J}_- \rangle} = 1$, this further reduces to $\cos(gt/\sqrt{2})$. As noticed above, \mathbf{J}_- and \mathbf{J}_+ are raising and lowering operators, which connect object states separated in energy by $\hbar\omega_o$. If we assume a nondegenerate set of object energy levels, the matrix representation of $\mathbf{J}_+\mathbf{J}_-$ and $\mathbf{J}_-\mathbf{J}_+$ with respect to the object states is diagonal. Evaluating the expectation values of the cosine operators in Eq. [24] then involves the diagonal elements of the initial object density matrix only. Any off-diagonal elements, reflecting coherences between nondegenerate object states, are irrelevant for the object-induced spin polarization. Moreover, not all diagonal elements necessarily play a role. Careful analysis shows that only the diagonal elements associated with the object states separated by $\hbar\omega_o$ and coupled by the spin-object interaction determine the spin-object polarization process.

(c) Object in a Boltzmann State

We now specify Eq. [24] for the case of an object initially in thermal equilibrium with its surroundings. This will generally be the state of an object left alone sufficiently long before establishing the coupling with the spin at $t = 0$. The expectation value of $\cos(gt\sqrt{\mathbf{J}_-\mathbf{J}_+})$ with respect to a Boltzmann operator, $\rho_o = N \exp(-\beta H^o)$ with $N = 1/\text{Tr}\{\exp(-\beta H^o)\}$ and $\beta = 1/kT$, may be derived from the cosine Taylor series

$$\langle \cos(gt\sqrt{\mathbf{J}_-\mathbf{J}_+}) \rangle_0 = 1 + N \sum_{k=1}^{\infty} \frac{(igt)^{2k}}{2k!} \text{Tr}\{(\mathbf{J}_-\mathbf{J}_+)^k e^{-\beta H^o}\}. \quad [25]$$

Changing the product order of the operators within the trace and multiplying from the right with $\mathbf{1} = \exp(\beta H^o) \exp(-\beta H^o)$, we obtain for the separate terms

$$\text{Tr}\{(\mathbf{J}_-\mathbf{J}_+)^k e^{-\beta H^o}\} = \text{Tr}\{(\mathbf{J}_+\mathbf{J}_-)^{k-1} \mathbf{J}_+ e^{-\beta H^o} \mathbf{J}_- e^{\beta H^o} e^{-\beta H^o}\} \quad [26]$$

in which we recognize the imaginary rotation

$$e^{-\beta H^0} \mathbf{J}_- e^{\beta H^0} = \mathbf{J}_- e^{-\beta \hbar \omega_{01}} \quad [27]$$

as follows from the commutation property $[H^0, \mathbf{J}_-] = \hbar \omega_{01} \mathbf{J}_-$. Substitution of Eq. [27] into Eq. [26] yields

$$\text{Tr}\{(\mathbf{J}_- \mathbf{J}_+)^k e^{-\beta H^0}\} = \text{Tr}\{(\mathbf{J}_+ \mathbf{J}_-)^k e^{-\beta H^0}\} e^{-\beta \hbar \omega_{01}}. \quad [28]$$

Reinserting this into Eq. [25], we obtain

$$\begin{aligned} \langle \cos(gt \sqrt{\mathbf{J}_- \mathbf{J}_+}) \rangle_0 &= 1 - e^{-\beta \hbar \omega_{01}} \\ &+ e^{-\beta \hbar \omega_{01}} \langle \cos(gt \sqrt{\mathbf{J}_+ \mathbf{J}_-}) \rangle_0 \end{aligned} \quad [29]$$

which may be substituted into Eqs. [24b] and [24c], yielding

$$\langle \mathbf{I}_0 \rangle_t^{\text{pol}} = \frac{1}{4} (1 - e^{-\beta \hbar \omega_{01}}) \langle 1 - \cos(gt \sqrt{\mathbf{J}_+ \mathbf{J}_-}) \rangle_0 \quad [30a]$$

$$\begin{aligned} \langle \mathbf{I}_0 \rangle_t^{\text{depol}} &= \frac{1}{2} \langle 1 - e^{-\beta \hbar \omega_{01}} + (1 + e^{-\beta \hbar \omega_{01}}) \\ &\times \cos(gt \sqrt{\mathbf{J}_+ \mathbf{J}_-}) \rangle_0 \langle \mathbf{I}_0 \rangle_0. \end{aligned} \quad [30b]$$

To interpret Eq. [30] let us introduce the following parameters,

$$\langle \mathbf{I}_0 \rangle^T = \frac{1}{2} \frac{1 - e^{-\beta \hbar \omega_{01}}}{1 + e^{-\beta \hbar \omega_{01}}} \quad [31a]$$

$$N_\beta = \frac{1 + e^{-\beta \hbar \omega_{01}}}{2} \quad [31b]$$

with $\langle \mathbf{I}_0 \rangle^T$ the equilibrium spin polarization at the initial object temperature T , and N_β a temperature-dependent number inversely proportional to the occupation of the lowest spin state. Its value ranges from $\frac{1}{2}$ at 0 K to 1 in the high-temperature limit. With these parameters substituted into Eq. [30], the equation for the total spin polarization (Eq. [24a]) assumes a more familiar form,

$$\begin{aligned} \langle \mathbf{I}_0 \rangle_t &= N_\beta \langle \mathbf{I}_0 \rangle^T + (1 - N_\beta) \langle \mathbf{I}_0 \rangle_0 \\ &+ N_\beta (\langle \mathbf{I}_0 \rangle_0 - \langle \mathbf{I}_0 \rangle^T) f(gt) \end{aligned} \quad [32a]$$

with

$$f(gt) = \langle \cos(gt \sqrt{\mathbf{J}_+ \mathbf{J}_-}) \rangle_0. \quad [32b]$$

Thus, if the spin and object temperature are the same at $t = 0$, the polarization flow from the object to the spin balances the flow in the opposite direction, and the spin polarization stays constant. This is similar to what one would expect for incoherent processes on the basis of thermodynamics. Indeed, there is a close similarity in the high-temperature limit, when $N_\beta \approx$

1, between Eq. [32a] and the corresponding equation for exponential spin-lattice relaxation:

$$\langle \mathbf{I}_0 \rangle_t = \langle \mathbf{I}_0 \rangle^T + (\langle \mathbf{I}_0 \rangle_0 - \langle \mathbf{I}_0 \rangle^T) \exp(-t/T_1). \quad [32c]$$

Apparently, in coherent spin-object processes the function $f(gt)$ has the role which the exponential decay has in spin-lattice relaxation. In Appendix 3 we show that $f(gt)$ is generally multiperiodic with values between -1 and 1 depending on the number and occupation of the object eigenstates involved in the spin-object cross-polarization. For multilevel systems one may typically expect a damped oscillatory decay of $f(gt)$ toward some final stationary value.

SPECIFIC EXAMPLES

(a) I Spin Coupled to an S Spin

To check the consistency of the general CP equation (Eq. [24]) with secular Hamiltonian theory for spin-spin CP we consider the case where the object is another spin S. In the basic spin-spin CP experiment resonant, linearly polarized RF fields are simultaneously applied to both spins I and S. As a simple example, also treated in the paper by Hartmann and Hahn (7), we consider a heteronuclear pair of spin- $\frac{1}{2}$ I and S with scalar coupling $J_z S_z$ only. We assume perfect Hartmann-Hahn matching and neglect off-resonance effects. The secular Hamiltonian in the tilted interaction frame is (7)

$$H_{\text{sec}} = -\frac{\hbar J}{4} (\mathbf{I}_+ \mathbf{S}_- + \mathbf{I}_- \mathbf{S}_+). \quad [33]$$

Comparing Eq. [33] with Eq. [9], we see that the spin operators \mathbf{S}_\pm in the first equation correspond to \mathbf{J}_\pm . The normalization condition is also fulfilled, because $\mathbf{S}_- \mathbf{S}_+ + \mathbf{S}_+ \mathbf{S}_- = 2\mathbf{S}_z = 1$ (Table 1). We characterize the initial spin-locked state of the S spin by a spin temperature T , and replace $\langle \mathbf{I}_0 \rangle^T$ in Eq. [32a] by the initial S spin polarization $\langle \mathbf{S}_0 \rangle_0$. The calculation of $f(gt)$ in Eq. [32b] is facilitated by the simple matrix representation of the operator $\mathbf{J}_+ \mathbf{J}_- = \mathbf{S}_+ \mathbf{S}_-$:

$$\mathbf{S}_+ \mathbf{S}_- = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad [34]$$

(Table 1). The cosine operator in Eq. [32b] may thus be rewritten as

$$\cos(\frac{1}{2} Jt \sqrt{\mathbf{S}_+ \mathbf{S}_-}) = 1 + \mathbf{S}_+ \mathbf{S}_- \cos(\frac{1}{2} Jt) - \mathbf{S}_+ \mathbf{S}_-. \quad [35]$$

Using $\langle \mathbf{S}_+ \mathbf{S}_- \rangle_0 = (\exp(-\beta \hbar \omega_{01}) + 1)^{-1} = (2N_\beta)^{-1}$ and some goniometrics we then obtain from Eq. [32a]

$$\langle \mathbf{I}_0 \rangle_t = \langle \mathbf{S}_0 \rangle_0 \cos^2(\tfrac{1}{4}Jt) + \langle \mathbf{I}_0 \rangle_0 \sin^2(\tfrac{1}{4}Jt) \quad [36]$$

which is fully consistent with spin–spin CP theory (7).

(b) *Spin- $\frac{1}{2}$ Pair Coupled to Rotational Motion*

As a second example we discuss the case of a coupled spin pair inside a uniaxial rotor. The coupling between the rotor and the spin pair results from the orientation dependence of the dipolar interaction. In magic-angle-spinning (MAS) experiments rotational resonance occurs between coupled nuclei whose Larmor-frequency difference equals the rotation rate or multiples thereof (16). Because the Zeeman splitting of the two spins are not exactly equal, it may seem that energy is not conserved in such process. To restore the energy balance energy must be borrowed from, or lent to, the MAS rotor. The offset of the Hartmann–Hahn condition for dinuclear CP in MAS experiments by a multiple of the spinning rate as compared to the stationary condition (17) is caused by a comparable mechanism. These rotor-induced effects on spin pairs are usually described in a semiclassical way by treating the rotor as a macroscopic object. The purpose of the discussion below is to present these effects as a specific case of spin–object cross-polarization between a fictitious spin- $\frac{1}{2}$ and a quantum rotor.

For a spin pair I and S inside a uniaxial rotor it is convenient to specify the orientation of the dipolar tensor by the Euler angles $\Omega = (\alpha, \beta, \gamma)$ in a coordinate system fixed to the rotor and the Euler angles $\Omega'' = (\zeta, \theta, \phi)$ of this rotor-fixed frame in the laboratory frame. Truncating the dipolar Hamiltonian after the secular and the flip-flop term we may express the dependence of the dipolar interaction on the rotation angle ϕ as (12)

$$H^D(t) = \hbar \omega_D \sum_{k=-2}^2 c_k \exp(ik\phi) \mathbf{T}_{20}, \quad [37a]$$

where $\omega_D = \hbar \mu_0 \gamma_I \gamma_S / 4\pi r^3$; c_k are specific complex factors depending on α, β , and θ ($|c_k| < 1$); and

$$\mathbf{T}_{20} = \mathbf{I}_0 \mathbf{S}_0 - \frac{1}{4} (\mathbf{I}_+ \mathbf{S}_- + \mathbf{I}_- \mathbf{S}_+). \quad [37b]$$

Upon transformation into the so-called doubly rotating frame (spin-pair interaction frame) the operator \mathbf{T}_{20} becomes time-dependent,

$$\mathbf{T}_{20}^*(t) = \mathbf{I}_0 \mathbf{S}_0 - \frac{1}{4} (\mathbf{I}_+^{23} e^{-i\omega_{23}t} + \mathbf{I}_-^{23} e^{i\omega_{23}t}), \quad [38]$$

with $\mathbf{I}_\pm^{23} = \mathbf{I}_\pm \mathbf{S}_\mp$ fictitious spin- $\frac{1}{2}$ operators (18) and $\omega_{23} = \omega_{0I} - \omega_{0S}$ the Larmor-frequency difference. Because $\mathbf{I}_0 \mathbf{S}_0$ commutes with \mathbf{I}_\pm^{23} , \mathbf{I}_0 , and \mathbf{S}_0 , it has no effect on the longitudinal polarization of the two spins $\langle \mathbf{I}_0 \rangle$ and $\langle \mathbf{S}_0 \rangle$, and may be neglected (Appendix 2).

Quantum mechanically the factors $\exp(ik\phi)$ in Eq. [37a] act as raising and lowering operators

$$\mathbf{R}_k = e^{ik\phi} = \sum_{n=0}^{\infty} |n+k\rangle \langle n| \quad [39]$$

on the eigenstates $|n\rangle = \exp(in\phi)$ of the unperturbed uniaxial-rotor Hamiltonian,

$$H^{\text{rot}} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \quad [40]$$

with I the moment of inertia of the rotor. The corresponding energy levels of the free uniaxial rotor are $E_n = \hbar B n^2$, with B the rotational constant $\hbar/2I$. For simplicity we do not take rotor driving and friction into account, so that the discussion strictly applies to free rotors with negligible friction at the timescale of the dipolar interaction. A driving force may have been employed to prepare the rotor in a specific initial state, but it should be switched off at $t = 0$. Upon transformation into the rotor–spin-pair interaction frame the operators $\mathbf{R}_k = e^{ik\phi}$ in H^D (Eq. [37a]) become

$$\begin{aligned} \mathbf{R}_k^*(t) &= e^{iH^{\text{rot}}t/\hbar} e^{ik\phi} e^{-iH^{\text{rot}}t/\hbar} \\ &= \sum_{n=0}^{\infty} e^{iB(2kn+k^2)t} |n+k\rangle \langle n|. \end{aligned} \quad [41]$$

Combining Eqs. [38] and [41] we may derive the zero-order average Hamiltonian $H^{(0)}$ for rotor–spin-pair cross-polarization. When ω_{23} matches the separation between two specific rotor levels E_p and E_q ($q - p = 1, 2$), $H^{(0)}$ converges toward

$$H^{(0)} = -\frac{1}{4} \hbar \omega_D \{ c_{q-p} |q\rangle \langle p| \mathbf{I}_+^{23} + c_{p-q} |p\rangle \langle q| \mathbf{I}_-^{23} \}, \quad [42]$$

where we left out the $\mathbf{I}_0 \mathbf{S}_0$ term, and assumed $\omega_{0I} > \omega_{0S}$. There can maximally be a single pair of rotor levels which satisfies the matching condition $\omega_{23} = E_q - E_p$. Equation [42] represents a Hamiltonian of the type as in Eq. [9], and \mathbf{J}_+ , \mathbf{J}_- , and g in Eq. [9] can respectively be identified as $|p\rangle \langle q|$, $|q\rangle \langle p|$, and $\frac{1}{2} \omega_D c_{pq}$ with $c_{pq} = \sqrt{c_{p-q} c_{q-p}}$. Calculating the expectation values of the corresponding cosine operators in Eq. [24] is easy due to the simple matrix representation of $\mathbf{J}_+ \mathbf{J}_-$ and $\mathbf{J}_- \mathbf{J}_+$ with only a single nonvanishing diagonal element $(\mathbf{J}_+ \mathbf{J}_-)_{pp} = 1$ and $(\mathbf{J}_- \mathbf{J}_+)_{qq} = 1$. For example, for $\mathbf{J}_- \mathbf{J}_+ = |q\rangle \langle q|$ we obtain, similarly to Eq. [35],

$$\cos(\tfrac{1}{2} \omega_D c_{pq} t \sqrt{|q\rangle \langle q|}) = 1 + |q\rangle \langle q| \cos(\tfrac{1}{2} \omega_D c_{pq} t) - |q\rangle \langle q| \quad [43]$$

and an analogous equation for $|p\rangle\langle p|$. Inserting Eq. [43] and its analogue for $|p\rangle$ into Eq. [24] yields

$$\langle \mathbf{I}_0^{23} \rangle_t^{\text{pol}} = \frac{1}{2} \{1 - \cos(\frac{1}{2} \omega_D c_{pq} t)\} \langle \mathbf{P}_{pq} \rangle_0 \quad [44a]$$

$$\langle \mathbf{I}_0^{23} \rangle_t^{\text{depol}} = \{1 - \langle \mathbf{O}_{pq} \rangle_0 + \langle \mathbf{O}_{pq} \rangle_0 \cos(\frac{1}{2} \omega_D c_{pq} t)\} \langle \mathbf{I}_0^{23} \rangle_0 \quad [44b]$$

with the rotor operators \mathbf{O}_{pq} and \mathbf{P}_{pq} defined as

$$\mathbf{O}_{pq} = \frac{1}{2} (|q\rangle\langle q| + |p\rangle\langle p|) \quad [45a]$$

$$\mathbf{P}_{pq} = \frac{1}{2} (|q\rangle\langle q| - |p\rangle\langle p|). \quad [45b]$$

The expectation values of \mathbf{O}_{pq} and \mathbf{P}_{pq} reflect the average occupation and the polarization of the pair of rotor states $|p\rangle$ and $|q\rangle$. In this respect \mathbf{O}_{pq} and \mathbf{P}_{pq} may be compared to the spin- $\frac{1}{2}$ operators \mathbf{I}_e and \mathbf{I}_o . Equation [44] describes an oscillatory polarization transfer back and forth between the rotor and the spin pair. In the specific case when $|p\rangle$ and $|q\rangle$ are the only occupied rotor states, $\langle \mathbf{O}_{pq} \rangle$ equals $\frac{1}{2}$, and the polarization exchange is similar to spin-spin cross-polarization (Eq. [36]). In general, however, other rotor states are occupied, as well, which reduces the amplitude of the oscillatory polarization exchange. If $|p\rangle$ and $|q\rangle$ are not occupied at all, there is neither a polarization transfer from the rotor to the spin, nor vice versa. The zero-quantum polarization $\langle \mathbf{I}_0^{23} \rangle$ then stays constant.

Equation [44] describes the development of zero-quantum polarization under a zero-order average Hamiltonian $H^{(0)}$ described by Eq. [42]. However, an important criterion for the validity of the ZOAH approach is the timescale on which $H^{(0)}$ approaches its limiting form. In this respect we made a distinction between a fast and a slow limit depending on the rate of convergence relative to the size of the spin-object coupling (Eq. [9]). In the fast limit a ZOAH approach can be used, and in the slow limit we may treat the Hamiltonian in the interaction frame as stationary. To determine when the fast limit applies for rotor-spin-pair cross-polarization, and when the slow limit applies, let us, e.g., consider the case in which specific neighboring rotor levels (E_p , E_{p+1}) differ by the required amount $\hbar\omega_{23}$. Then, the separation of adjacent pairs (E_{p-1} , E_p) and (E_{p+1} , E_{p+2}) equals $\hbar(\omega_{23} - \hbar/I)$ and $\hbar(\omega_{23} + \hbar/I)$, respectively. This determines the timescale, $t_{\text{min}} \approx I/\hbar$, on which the average Hamiltonian converges into its limiting form. Thus, only a microscopic or molecular rotor can satisfy the fast limit condition $\hbar/I \gg \omega_D |c_{p-q}|$, if one assumes the latter to be in the order of 10^2 Hz or larger. For macroscopic rotors, like MAS rotors, the convergence tends to be extremely slow, $\hbar/I \ll \omega_D |c_{p-q}|$, and the slow limit applies.

In the microscopic regime the average Hamiltonian quickly converges into the limiting form described by Eq. [42], which leads to the above-derived polarization exchange according to Eq. [44]. A macroscopic rotor spinning at a rate ω_r is characterized by a narrow probability distribution over eigenstates $|n\rangle$

with large quantum numbers $n \approx I\omega_r/\hbar$ and energy levels almost equally interspaced by $\hbar B(2n+1) \approx \hbar\omega_r$. Hereby we neglect energy differences in the order of $\hbar B$ with respect to $\hbar\omega_r$. Within the subspace S of occupied rotor states the raising and lowering rotor operators $\mathbf{R}_k^*(t)$ are approximately given by (Eq. [41])

$$\mathbf{R}_k^*(t) \approx e^{ik\omega_r t} \sum_{|n\rangle \in S} |n+k\rangle\langle n| \approx e^{ik\omega_r t} e^{ik\phi}, \quad [46]$$

whereby we assume the properties of $e^{ik\phi}$ outside subspace S to be negligible for the behavior of the macroscopic rotor. This time-dependent behavior of the rotor raising and lowering operators may be compared to the operators in the theory by Boender *et al.* (19). Insertion of Eq. [46] into Eq. [44] for $\omega^{23} = k\omega_r$ yields a periodic Hamiltonian with frequency ω_r . Omitting the uninteresting $\mathbf{I}_0 \mathbf{S}_0$ term we obtain, e.g., for $k = 1$ the average Hamiltonian

$$H^{(0)} = -\frac{1}{4} \omega_D \{c_+ e^{i\phi} \mathbf{I}_+^{23} + c_{-1} e^{-i\phi} \mathbf{I}_-^{23}\}. \quad [47]$$

When the size of the dipolar interaction is small compared to the frequency of the rotor, $\omega_D \ll \omega_r$, the zero-order average Hamiltonian can be used to calculate the spin polarization. Strictly this represents a case of a combined fast and slow limit, because, on the one hand, we neglect the Hamiltonian terms oscillating with frequency $\omega_r \gg \omega_D$, and, the other hand, we treat the remaining terms oscillating with frequencies $\sim \hbar/I \ll \omega_D$ as stationary. For intermediate MAS rates ($\omega_r \approx \omega_D$), or “submacroscopic” rotors ($\hbar/I \approx \omega_D$), the evolution of the system can no longer be described with an effective Hamiltonian of the form of Eq. [47], and a more refined method, for instance, based on Floquet theory must be used (13). Comparing Eq. [47] with Eq. [9] one sees that the operators $e^{\pm i\phi}$ for spin-rotor coupling correspond to the operators \mathbf{J}_{\mp} for the general spin-object case. Thus we may insert $\mathbf{J}_{\mp} = e^{\pm i\phi}$ into Eq. [24] to derive the polarization $\langle \mathbf{I}_0^{23} \rangle$ as a function of time. Because the operators $e^{i\phi}$ and $e^{-i\phi}$ commute, the polarization term $\langle \mathbf{I}_0^{23} \rangle_t^{\text{pol}}$ vanishes and only initial depolarization occurs:

$$\langle \mathbf{I}_0^{23} \rangle_t^{\text{depol}} = \cos(\frac{1}{2} \omega_D c_{pq} t) \langle \mathbf{I}_0^{23} \rangle_0. \quad [48]$$

Since $\mathbf{I}_0^{14} = \mathbf{I}_0 + \mathbf{S}_0$ commutes with \bar{H}^D (Eq. [47]), the total spin polarization $\langle \mathbf{I}_0^{14} \rangle = \langle \mathbf{I}_0 \rangle + \langle \mathbf{S}_0 \rangle$ is conserved. Combined with the oscillatory character of $\langle \mathbf{I}_0^{23} \rangle = \langle \mathbf{I}_0 \rangle - \langle \mathbf{S}_0 \rangle$ this results in a periodic polarization exchange between spins I and S, whereby the rotor supplies or absorbs the required energy. Because spinning rates of macroscopic rotors typically are in the range 10^3 – 10^5 Hz, rotary resonance will usually be a homonuclear process between like spins. Molecules may rotate much faster and thereby cause rotary resonance within a heteronuclear pair of dipolarly coupled spins. For such cases the

two-level description may be valid and equations like Eqs. [44a] and [44b] can be used to calculate the polarization exchange.

(c) *Spin- $\frac{1}{2}$ Coupled to a Harmonic Oscillator*

We now turn to the case of a one-dimensional oscillator coupled to a spin- $\frac{1}{2}$ in a strong magnetic field. As for *mechanical* oscillation this may, e.g., be a spin mounted on an oscillating device in a magnetic field gradient. One may further think of a spin in a molecule coupled to torsional vibrations through the anisotropic chemical shift or dipolar interaction with other spins in the molecule. The oscillator may also be of an *electronic* nature. For example, an *LC* circuit can be coupled to a spin through the magnetic field raised by the coil. A familiar example is the detection circuit of a NMR probe. Tuned to the spins inside the detection coil, the circuit and the spins can exchange heat. In principle, this could lead to an enhanced spin polarization in cryogenic NMR probe heads, in which the electronic parts are cooled to liquid helium temperature. However, the heat exchange between a spin- $\frac{1}{2}$ and such macroscopic circuit would be slow, as compared to the longitudinal spin relaxation. The question addressed in this section is whether specific microscopic electronic devices presently available through microelectronic technology can be used to cool the spins at the timescale of seconds, at least in theory. In principle, the spin-oscillator system may be regarded as a special case of Feynman's theory for a general system coupled to a harmonic oscillator (20). Shirley's discussion of an atom interacting with a quantized field (as a physical interpretation of Floquet theory) is also related (21). The purpose of discussing the spin-oscillator case below is simply to illustrate the application of the above-derived general equations (Eqs. [24] and [32]) to some specific nonfamiliar case in NMR spectroscopy.

The unperturbed Hamiltonian of a one-dimensional harmonic oscillator is (22)

$$H^{OS} = \frac{1}{2} \hbar \omega_{OS} (\mathbf{A}_+ \mathbf{A}_- + \mathbf{A}_- \mathbf{A}_+), \quad [49]$$

with \mathbf{A}_+ and \mathbf{A}_- the raising and lowering operators, respectively, acting on the oscillator eigenstates $|n\rangle$ with energy $E_n = (n + \frac{1}{2})\hbar\omega_{OS}$. For example, for an electronic circuit consisting of an inductor L coil and a capacitor C with resonance frequency $\omega_{os} = 1/\sqrt{LC}$ the operators \mathbf{A}_\pm are related to the capacitor charge \mathbf{q} and the coil current \mathbf{i} as (23)

$$\mathbf{A}_\pm = \sqrt{\frac{\frac{1}{2}L}{\hbar\omega_{OS}}} (\omega_{OS}\mathbf{q} \mp i\mathbf{i}) \quad [50]$$

(with the voltage operator \mathbf{u} in the paper referred to replaced by the charge operator $\mathbf{q} = C\mathbf{u}$ in ours).

Let us consider a microscopic NMR detection coil close to

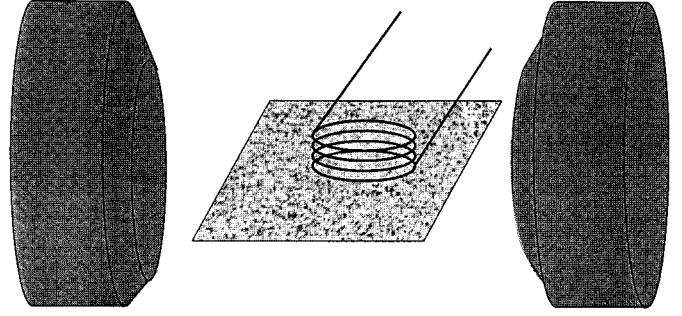


FIG. 1. Sketch of the microelectronic NMR imaging setup discussed in the body of text as a potential application of oscillator-spin cross-polarization.

a material surface with the coil axis perpendicular to the surface and the external magnetic field (Fig. 1). Combined with a capacitor the coil forms a resonant circuit, which is tuned to the Larmor frequency of the spins to be observed. The coupling between the oscillator and a spin located on the coil axis is caused by the magnetic field B_1 produced by the coil, which, in turn, is proportional to the current i in the oscillator. This gives rise to a spin-oscillator coupling Hamiltonian of the form

$$H^{1,OS} = -\hbar G \mathbf{i} \mathbf{I}_x, \quad [51]$$

where $G = \gamma_1 dB_1/di$ is determined by parameters like the shape and diameter of the coil, and the distance of the spin from the coil center. After substituting the operators \mathbf{I}_\pm and \mathbf{A}_\pm into Eq. [51] we use the commutator properties $[H^1, \mathbf{I}_\pm] = \mp \hbar \omega_{0l} \mathbf{I}_\pm$ and $[H^{OS}, \mathbf{A}_\pm] = \pm \hbar \omega_{OS} \mathbf{A}_\pm$ to transform $H^{1,OS}$ into the spin-oscillator interaction frame. If the oscillator frequency matches the spin Larmor frequency, $\omega_{OS} = \omega_{0l}$, we obtain a monoperoic Hamiltonian $H^*(t)$ with frequency $2\omega_{0l}$ and time-independent part H_{sec} :

$$H_{sec} = -\frac{i}{4} \hbar G \sqrt{\frac{\hbar \omega_{OS}}{\frac{1}{2}L}} (\mathbf{A}_+ \mathbf{I}_+ - \mathbf{A}_- \mathbf{I}_-). \quad [52]$$

Comparison with Eq. [9] combined with the normalization $\sqrt{\langle \mathbf{J}_- \mathbf{J}_+ + \mathbf{J}_+ \mathbf{J}_- \rangle} = 1$ and the requirement of a real-valued g shows that \mathbf{J}_\pm corresponds to $\mp i \sqrt{\hbar \omega_{OS}/2\langle H^{OS} \rangle} \mathbf{A}_\mp$ and g to $G i_0 / (2 \rightarrow \sqrt{2})$ with $i_0 = \sqrt{2\langle H^{OS} \rangle} / L$. In the macroscopic limit i_0 corresponds to the current amplitude, as follows from the classical equation for the oscillator energy $E = \frac{1}{2} L i_0^2$, and $g = G i_0 / \sqrt{2}$ to the effective size of the spin-oscillator coupling (rad/s). Since the nonsecular terms of $H^*(t)$ oscillate with frequency $2\omega_{0l}$, the validity of the zero-order Hamiltonian approach requires $g \ll 2\omega_{0l}$.

To calculate the effect of an oscillator in a Boltzmann state on the spin polarization we replace $\mathbf{J}_+ \mathbf{J}_-$ in Eq. [32b] by $(\frac{1}{2} \hbar \omega_{OS} / \langle H^{OS} \rangle) \mathbf{A}_- \mathbf{A}_+$. This, in turn, may be rewritten by use of Eq. [49] and the commutator $[\mathbf{A}_-, \mathbf{A}_+] = \mathbf{1}$ as $(H^{OS} + \frac{1}{2} \hbar \omega_{OS} \mathbf{1}) / 2 \langle H^{OS} \rangle$. In the high-temperature limit, $\hbar \omega_{OS} \ll \langle H^{OS} \rangle$

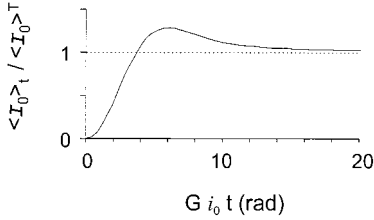


FIG. 2. Relative polarization of a spin- $\frac{1}{2}$ coupled to a harmonic oscillator as a function of contact time, when there is no spin polarization at $t = 0$ and the oscillator starts from a thermal-equilibrium state characterized by a temperature T .

$= kT$, the operator $\frac{1}{2}\hbar\omega_{\text{OS}}\mathbf{1}$ can be neglected with respect to H^{OS} . Setting $\langle \mathbf{I}_0 \rangle_0 = 0$ in Eq. [32] yields for the oscillator-induced polarization $\langle \mathbf{I}_0 \rangle_t^{\text{pol}}$ of an initially saturated spin

$$\begin{aligned} \langle \mathbf{I}_0 \rangle_t^{\text{pol}} &= N_\beta \langle \mathbf{I}_0 \rangle^T - N_\beta \langle \mathbf{I}_0 \rangle^T f(gt) \\ &\approx \langle \mathbf{I}_0 \rangle^T \left\langle 1 - \cos\left(\frac{gt}{\sqrt{2}\langle H^{\text{OS}} \rangle} \sqrt{H^{\text{OS}}}\right) \right\rangle_0, \end{aligned} \quad [53]$$

where we used the high-temperature approximation $N_\beta = \{\exp(-\beta\hbar\omega_{\text{OS}}) + 1\}/2 \approx 1$. This can be expanded as

$$\langle \mathbf{I}_0 \rangle_t^{\text{pol}} = -\langle \mathbf{I}_0 \rangle^T \sum_{n=1}^{\infty} \frac{(igt/\sqrt{2})^{2n}}{2n! \langle H^{\text{OS}} \rangle^n} \langle (H^{\text{OS}})^n \rangle_0. \quad [54]$$

For $\hbar\omega_{\text{OS}} \ll kT$, the expectation values $\langle (H^{\text{OS}})^n \rangle_0 = \text{Tr}\{(H^{\text{OS}})^n \exp(-\beta H^{\text{OS}})\} / \text{Tr}\{\exp(-\beta H^{\text{OS}})\}$ can be approximately calculated from continuous integrals, yielding

$$\begin{aligned} \langle (H^{\text{OS}})^n \rangle_0 &= \langle H^{\text{OS}} \rangle_0^n \int_0^\infty x^n e^{-x} dx \\ &= 2 \langle H^{\text{OS}} \rangle_0^n \int_0^\infty y^{2n} e^{-y^2} y dy \end{aligned} \quad [55]$$

with x and y as convenient integration variables related by $x = y^2$. Resubstituting this into Eq. [54], we obtain

$$\langle \mathbf{I}_0 \rangle_t^{\text{pol}} = \langle \mathbf{I}_0 \rangle^T \left\langle 1 - 2 \int_0^\infty \cos(gty/\sqrt{2}) e^{-y^2} y dy \right\rangle_0. \quad [56]$$

Thus $\langle \mathbf{I}_0 \rangle_t^{\text{pol}}$ can be calculated as the cosine Fourier transform of $y \exp(-y^2)$ (Fig. 2). Starting from 0 at $t = 0$, it has a maximum of 130% at $Gi_0 t = 6$ (determined graphically) and finally approaches the end level, where the spin temperature equals the initial oscillator temperature. This behavior may be

compared to incoherent spin-lattice relaxation. As for achieving the highest possible polarization enhancement there are two opposite effects of the initial oscillator temperature on spin polarization. On the one hand, one should cool down the oscillator to a temperature as low as possible for the highest final polarization level. On the other hand, cooling down the oscillator also reduces its thermal-current amplitude i_0 , and thereby the polarization transfer rate $g/\sqrt{2} = \frac{1}{2}Gi_0$. In practice there will always be some spin-lattice relaxation, which will counteract spin cooling below the lattice temperature. Because the oscillator energy in thermal equilibrium at a given temperature T equals $\frac{1}{2}Li_0^2 = kT$, decreasing the coil inductance L speeds up the polarization process.

As an example, let us discuss the possible use of a microscopic NMR probe to enhance the polarization of ^{31}P nuclei at the surface of specific materials (Fig. 1). As the detection coil we take the microscopic pickup loop of a fully integrated magnetometer recently developed by Kirtley *et al.* (24). The pickup loop is an octagon $10 \mu\text{m}$ across with a $1.2\text{-}\mu\text{m}$ line-width. Integrated with a $20\text{-}\mu\text{m}$ -long section of coplanar lead structure the system has an inductance $L \approx 100 \text{ pH}$. We add a capacitance $C = 10 \text{ nF}$ to change the loop system into an electronic oscillator with resonance frequency $\omega_0/2\pi = (2\pi\sqrt{LC})^{-1} = 159 \text{ MHz}$. This corresponds to the Larmor frequency of ^{31}P nuclei in a magnetic field of 9.3 T. In thermal equilibrium the energy stored in our 159-MHz oscillator is $\frac{1}{2}Li_0^2 = kT$. For example, at 10 K the amplitude i_0 of the thermal current thus equals $1.7 \mu\text{A}$.

The coupling between the oscillator and a spin in the surface is represented by the magnetic field produced by the coil. According to classical electromagnetic theory (25), the magnetic field along the coil axis caused by a current i is

$$B_1 = \mu_0 \frac{r^2}{(r^2 + d^2)^{3/2}} i, \quad [57]$$

where r denotes the radius of the coil, d denotes the distance from the coil center, and the finite wire thickness of the loop is neglected. For a loop-surface distance equal to the loop radius the coupling gradient $G = \gamma_1 dB_1/di = \gamma_1 \mu_0 / r\sqrt{8}$. With $r = 5 \mu\text{m}$, $i_0 = 1.7 \mu\text{A}$ at 10 K, and $\gamma_1 = 10.8 \times 10^7 \text{ rad/Ts}$ for, e.g., ^{31}P , the polarization transfer rate $g/\sqrt{2} = \frac{1}{2}Gi_0$ thus equals $2\pi \times 1.3 \text{ rad/s}$. This value is much smaller than the Larmor frequency, which justifies the use of only the stationary part of $H^*(t)$ (Eq. [52]) over a large time interval. Thus, when the electronic oscillator at 10 K is brought into contact with a saturated ^{31}P nucleus at a distance of $5 \mu\text{m}$, the spin will cool down to this temperature in a few seconds. Theoretically there is even a transient polarization overshoot corresponding to a spin temperature of 7.8 K at $t = 0.7 \text{ s}$. This polarization maximum equals the room temperature ^{31}P polarization at a hypothetical field of ca. 360 T.

CONCLUSION

Using a zero-order average-Hamiltonian approach we have given a product-operator description of the effect which a general object has on the polarization of the spin to which it is coupled. The spectral density operators \mathbf{J}_- and \mathbf{J}_+ reflecting the fluctuations of the coupling Hamiltonian in the interaction frame at the Larmor or nutation frequency play a key role in the polarization transfer. An increase of the spin polarization may only occur if \mathbf{J}_- and \mathbf{J}_+ do not commute. Object-induced “spin cooling” is therefore a typical quantum effect. The more pronounced the quantum character of the object, the higher the resulting spin polarization or the faster the polarization process. In the classical limit \mathbf{J}_- and \mathbf{J}_+ reduce to their respective expectation values, which yields (initial) depolarization. Spin-object cross-polarization critically depends on the occupation of the object levels concerned. Generalizing the outcome for the example of a molecular rotor coupled to a spin pair, we conclude that pairs of object levels, even those with the required energy separation $\hbar\omega_0$ and connected by the spin-object interaction, do not contribute to spin polarization or depolarization unless they are occupied. This may be compared with BWR theory, which states that spin-lattice relaxation requires spectral density at the Larmor frequency. Spin cooling requires the object-level pairs to be polarized, i.e., unequally populated. The general CP theory presented in this article is derived for an isolated pair of a spin and an object without internal and external relaxation. It would therefore be of interest as a zero-order description of spin-lattice relaxation mechanisms, in which the primary coupling of the spin with a specific lattice mode, although weak compared to the Zeeman interaction, would still be stronger than the internal mechanisms trying to restore the lattice equilibrium. Of course such lattice is not a true lattice according to the usual definition, and the mode coupled relatively strongly to the spin may as well be classified as a separate object.

APPENDIX 1

Energy Conservation and the Time Dependence of the Hamiltonian

Let us consider the complete spin-object Hamiltonian $H(t)$ (Eq. [1]) with possible time dependence. We want to prove that as a consequence of the principle of energy conservation, $dH/dt = 0$. Energy conservation in an isolated system requires the expectation value of the Hamiltonian $H(t)$ to be constant:

$$\frac{d\langle H \rangle}{dt} = \text{Tr} \left\{ \rho(t) \frac{dH}{dt} \right\} + \text{Tr} \left\{ H(t) \frac{d\rho}{dt} \right\} = 0. \quad [\text{A1}]$$

The derivative of the density operator is given by the Liouville-von Neumann equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H(t), \rho(t)]. \quad [\text{A2}]$$

Insertion into Eq. [A1] yields

$$\begin{aligned} \text{Tr} \left\{ \rho(t) \frac{dH}{dt} \right\} - \frac{i}{\hbar} \text{Tr} \{ H^2(t) \rho(t) \} \\ + \frac{i}{\hbar} \text{Tr} \{ H(t) \rho(t) H(t) \} = 0. \end{aligned} \quad [\text{A3}]$$

The trace of an operator product is invariant under a cyclic permutation $\text{Tr}\{\mathbf{ABC}\} = \text{Tr}\{\mathbf{CAB}\}$. It thus follows that the last two terms on the right-hand side of Eq. [A3] cancel each other. Consequently we have

$$\left\langle \frac{dH}{dt} \right\rangle = \text{Tr} \left\{ \rho(t) \frac{dH}{dt} \right\} = 0. \quad [\text{A4}]$$

Equation [A4] only proves that the expectation value $\langle dH/dt \rangle$ vanishes, not the operator dH/dt itself. However, the principle of energy conservation is valid irrespective of the state of the spin-object system, and thus for all possible density operators $\rho(t)$. This can only be satisfied if dH/dt itself equals zero. Consequently energy conservation requires H to be time independent.

APPENDIX 2

Influence of the $\mathbf{I}_0\mathbf{J}_0$ Term in $H^{(0)}$ on Spin Polarization $\langle \mathbf{I}_0 \rangle$

As mentioned above H_{eff} (Eq. [9]) consists of two parts, $H_{\text{eff,A}}$ and $H_{\text{eff,B}}$. $H_{\text{eff,B}}$ commutes with \mathbf{I}_0 and therefore tends to have a smaller effect on the spin polarization $\langle \mathbf{I}_0 \rangle$ than $H_{\text{eff,A}}$. The effect by $H_{\text{eff,B}}$ even vanishes completely, when it commutes with $H_{\text{eff,A}}$, as shown in the following. If $[H_{\text{eff,A}}, H_{\text{eff,B}}] = 0$, we may write the average-Hamiltonian propagator as

$$\mathbf{U}(t) = e^{-iH_{\text{eff,A}}t/\hbar} e^{-iH_{\text{eff,B}}t/\hbar}. \quad [\text{A5}]$$

Thus, it follows for the spin polarization $\langle \mathbf{I}_0 \rangle$

$$\begin{aligned} \langle \mathbf{I}_0 \rangle_t &= \text{Tr} \{ \mathbf{I}_0 \mathbf{U}(t) \rho(0) \mathbf{U}^{-1}(t) \} \\ &= \text{Tr} \{ e^{iH_{\text{eff,B}}t/\hbar} \mathbf{I}_0 e^{-iH_{\text{eff,B}}t/\hbar} e^{-iH_{\text{eff,A}}t/\hbar} \rho(0) e^{iH_{\text{eff,A}}t/\hbar} \}, \end{aligned} \quad [\text{A6}]$$

where we used the property that the trace of a product of two operators stays the same when their order is changed, $\text{Tr}\{\mathbf{AB}\} = \text{Tr}\{\mathbf{BA}\}$. Since \mathbf{I}_0 commutes with $H_{\text{eff,B}}$, it is invariant under the rotation

$$e^{iH_{\text{eff,B}}t/\hbar} \mathbf{I}_0 e^{-iH_{\text{eff,B}}t/\hbar} = \mathbf{I}_0. \quad [\text{A7}]$$

Substitution of Eq. [A7] into [A6] then yields

$$\langle \mathbf{I}_0 \rangle_t = \text{Tr} \{ \mathbf{I}_0 e^{-iH_{\text{eff},A}t/\hbar} \rho(0) e^{-iH_{\text{eff},A}t/\hbar} \}. \quad [\text{A8}]$$

There is thus no effect of $H_{\text{eff},B}$ on the spin polarization $\langle \mathbf{I}_0 \rangle$.

APPENDIX 3

The Time-Dependent Expectation Value $\langle \cos(gt\sqrt{\mathbf{J}_+\mathbf{J}_-}) \rangle_0$

Below we derive some general properties of the function $f(gt) = \langle \cos(gt\sqrt{\mathbf{J}_+\mathbf{J}_-}) \rangle_0$ (Eq. [32b]). As mentioned below Eq. [24], if, by assumption, the set of object energy levels is nondegenerate, the matrix representation of $\mathbf{J}_+\mathbf{J}_-$ and $\mathbf{J}_-\mathbf{J}_+$ with respect to the object states $|n\rangle$ is diagonal. Consequently we may evaluate $f(gt)$ from the trace with respect to the initial object density matrix ρ_0 as

$$f(gt) = \sum_n \cos(gc_n t) \rho_n \quad [\text{A9}]$$

with c_n and ρ_n the diagonal elements $\langle n | \mathbf{J}_+\mathbf{J}_- | n \rangle$ and $\langle n | \rho_0 | n \rangle$, respectively. The general behavior predicted by Eq. [A9] is multiperiodic, whereby the terms with c_n equal to 0 contribute to stationary part of $f(gt)$, and the other terms are oscillatory. The trace of ρ_0 equals 1, so that $f(gt)$ equals 1 at $t = 0$. Since the diagonal elements of a density matrix are always positive or zero, $\rho_n > 0$, the individual oscillatory terms in Eq. [A9] initially decay, causing an initial decrease of $f(gt)$ sufficiently close to $t = 0$. The value of $f(gt)$ can never be smaller than -1 . Beat patterns may arise owing to interference between the different oscillatory terms. In principle, a full echo $f(gt) = 1$ occurs at times when all oscillatory terms have the same phase $2k\pi$ with, in general, a different integer k for every term. However, the more complex the relation between the frequencies, the longer the times between such echoes. In practice, for complex multilevel systems one would expect a damped oscillatory decay of $f(gt)$ toward its final stationary value.

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