

ADVANCES IN MAGNETIC RESONANCE

Formal Theory of Spin–Lattice Relaxation

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I. INTRODUCTION

Spin–lattice relaxation is the irreversible evolution of a spin system toward thermal equilibrium with the orbital degrees of freedom of the medium in which the spins are embedded, called the lattice. This encompasses all spin variables amenable to observation: longitudinal or transverse magnetizations, spin–spin energy or multiple-quantum coherences. It is only when the evolution is due to static spin–spin interactions that we will speak of spin–spin relaxation. Although it attracted attention even before the existence of resonance, for electronic spin systems (1) it is mostly with the development of resonance methods that spin–lattice relaxation proved to be a central concept, both as a fundamental topic in thermodynamics and as a tool of prime importance for investigating the dynamical and structural properties of condensed matter. This is particularly so in NMR. The basic understanding and the elaboration of the main formalisms of nuclear spin–lattice relaxation were developed from 1948 to about 1960, in parallel with those of electronic spins. The basic references are Bloembergen, Purcell, and Pound (BPP) (2), Wangsness and Bloch (3), and Bloch (4), Solomon (5), Abragam (6), Redfield (7), Bloch (8), and Tomita (9).

These works were described in detail by Abragam (6) and Slichter (10). Many developments have and continue to take place on various extensions and specific applications of spin–lattice relaxation. A good introduction, with references, can be found in the “Relaxation” articles of the *Encyclopedia of Nuclear Magnetic Resonance* (11).

The purpose of this article is somewhat different. It is to present *ab initio* a compact, clear, and complete description of a general formalism of spin–lattice relaxation theory, with two objectives: provide the reader with a well-defined procedure for performing relaxation calculations of practical usefulness, together with a full and convincing justification of its derivation. As a corollary, its purpose is not to give credit nor to analyze in detail the various relaxation mechanisms, except when needed for pedagogy, nor to provide an extensive bibliography. Although of general applicability, the formalism will

concern, by priority, systems where it is a good approximation to treat the lattice classically and the spin–lattice coupling as a random perturbation of the spin system: molecules in solution or insulating solids where the nuclei are relaxed by paramagnetic impurities. Nothing specific will be said on systems where a quantum description of the lattice is mandatory: metals, semiconductors, superconductors, quantum solids, quadrupole relaxation, etc., for which satisfactory full treatments can be found in the literature. Nor will we give any qualitative description of relaxation, which is assumed to be known by the reader. Such an introduction can be found, e.g., in Ref. (12), Ch. 9.

The article is organized as follows. In Section II, we use a classical description of the lattice, and we derive the master equation for the density matrix and for the expectation value of an observable, for a spin system subjected to a random perturbation. The treatment is made in turn for a static Hamiltonian and a time-dependent one, limited to off-resonance RF irradiation. An account for the finite temperature of the lattice is made phenomenologically. This part follows closely the procedure of Ref. (13). It departs in several respects from earlier treatments; in particular it does not use the adiabatic approximation, which makes it possible to treat on the same footing heteronuclear and nearly identical homonuclear spins. In Section III, the lattice is treated quantum-mechanically, so as to take rigorously into account its finite temperature. For a static spin Hamiltonian, the treatment is inspired from the description by Abragam (6) of the Wangsness–Bloch approach (3, 4, 8). The case when the spin Hamiltonian is time-dependent is treated in several steps: RF irradiation with an effective field in the rotating frame successively much smaller than and comparable with the static field, and the general case of a time-dependent spin Hamiltonian. This part does not quite follow the approaches of Bloch (8) or Redfield (7).

Although an effort has been made toward clarity and simplicity, some calculations are per force somewhat lengthy and complicated. The last two sections contain such calculations, and their study is not mandatory in a first reading. They are indicated by an asterisk.

II. CLASSICAL DESCRIPTION OF THE LATTICE

A. Static Spin Hamiltonian

1. Derivation of the Master Equation

We consider a nuclear spin system whose Hamiltonian consists of a main, time-independent Hamiltonian \mathcal{H}_0 , plus a spin-lattice coupling term $\mathcal{H}_1(t)$ of vanishing average value:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t). \quad [1]$$

We assume in a first step that \mathcal{H}_0 has only discrete levels, i.e., it is a Zeeman interaction in a liquid, so that the dipolar interactions average out.

We call σ the spin density matrix. Its evolution is given by the Liouville–von Neumann equation:

$$\frac{d\sigma}{dt} = -i[\mathcal{H}, \sigma]. \quad [2]$$

We begin by removing the static Hamiltonian \mathcal{H}_0 , so as to single out the effect of the perturbation $\mathcal{H}_1(t)$. This is done by the use of an interaction representation which, for a purely Zeeman interaction, corresponds to the well-known passage to the rotating frame. We replace all operators Q in the laboratory frame by the operators

$$Q \rightarrow \tilde{Q}(t) = \exp(i\mathcal{H}_0 t) Q \exp(-i\mathcal{H}_0 t). \quad [3]$$

The evolution of the density matrix in this representation is given by

$$\begin{aligned} \frac{d}{dt} \tilde{\sigma} &= \frac{d}{dt} \{ \exp(i\mathcal{H}_0 t) \sigma \exp(-i\mathcal{H}_0 t) \} \\ &= i\mathcal{H}_0 \tilde{\sigma} + \exp(i\mathcal{H}_0 t) \frac{d\sigma}{dt} \exp(-i\mathcal{H}_0 t) - i\tilde{\sigma} \mathcal{H}_0, \end{aligned} \quad [4]$$

that is, according to Eqs. [1] and [2],

$$\frac{d}{dt} \tilde{\sigma} = i[\mathcal{H}_0, \tilde{\sigma}] - i \exp(i\mathcal{H}_0 t) [(\mathcal{H}_0 + \mathcal{H}_1), \sigma] \exp(-i\mathcal{H}_0 t). \quad [5]$$

When U and U^\dagger are hermitian conjugate unitary operators (i.e., $UU^\dagger = 1$), we have in full generality

$$U[A, B]U^\dagger = [UAU^\dagger, UBU^\dagger], \quad [6]$$

so that the last term on the right-hand side of Eq. [5] is equal to

$$\exp(i\mathcal{H}_0 t) [(\mathcal{H}_0 + \mathcal{H}_1), \sigma] \exp(-i\mathcal{H}_0 t) = [(\mathcal{H}_0 + \tilde{\mathcal{H}}_1(t)), \tilde{\sigma}]. \quad [7]$$

Equation [5] then yields

$$\frac{d}{dt} \tilde{\sigma} = -i[\tilde{\mathcal{H}}_1(t), \tilde{\sigma}]. \quad [8]$$

The Hamiltonian $\tilde{\mathcal{H}}_1(t)$ has a double time dependence: that due to its random character and that due to the passage to the interaction representation.

By formal integration of Eq. [8], we obtain

$$\tilde{\sigma}(t) = \tilde{\sigma}(0) - i \int_0^t [\tilde{\mathcal{H}}_1(t'), \tilde{\sigma}(t')] dt', \quad [9]$$

a form which is inserted into the right-hand side of Eq. [8]. We obtain

$$\frac{d\tilde{\sigma}}{dt} = -i[\tilde{\mathcal{H}}_1(t), \tilde{\sigma}(0)] - \int_0^t [\tilde{\mathcal{H}}_1(t), [\tilde{\mathcal{H}}_1(t'), \tilde{\sigma}(t')]] dt'. \quad [10]$$

This expression is rigorous. For physical reasons, we subject it to two modifications.

1. We take an ensemble average of all terms. The reason is that remote parts of a large system relax independently of each other. Each of them experiences a random coupling with a different evolution history, leading to a different local density matrix $\tilde{\sigma}$. These parts are simulated by different members of a Gibbs ensemble. All have identical initial $\tilde{\sigma}(0)$ and, since $\mathcal{H}_1(t)$ has a vanishing average, the first term on the right-hand side of Eq. [10] vanishes.

2. In the remaining term on the right-hand side of Eq. [10], we replace $\tilde{\sigma}(t)$ by

$$\tilde{\sigma}(t) \rightarrow \tilde{\sigma}(t) - \tilde{\sigma}_{\text{eq}},$$

where $\tilde{\sigma}_{\text{eq}}$ is the thermal equilibrium form of the density matrix for the Hamiltonian \mathcal{H}_0 . This is the phenomenological account for the finite lattice temperature, which will be justified in Section III.

We obtain in place of Eq. [10]

$$\frac{d}{dt} \bar{\tilde{\sigma}}(t) = - \int_0^t \overline{[\tilde{\mathcal{H}}_1(t), [\tilde{\mathcal{H}}_1(t'), (\tilde{\sigma}(t') - \tilde{\sigma}_{\text{eq}})]]} dt', \quad [11]$$

where the ensemble average is noted by an overbar.

In the next step, we expand the spin-lattice Hamiltonian in the form

$$\mathcal{H}_1(t) = \sum_{\alpha} V_{\alpha} F_{\alpha}(t) = \sum_{\alpha} V_{\alpha}^{\dagger} F_{\alpha}^{*}(t), \quad [12]$$

where the V_{α} are spin operators and the $F_{\alpha}(t)$ are random functions of time. The equality of the two forms is a consequence

of the fact that \mathcal{H}_1 , being a Hamiltonian, is hermitian:

$$\mathcal{H}_1(t) = \mathcal{H}_1^\dagger(t).$$

The decomposition [12] is made in such a way that

$$[\mathcal{H}_0, V_\alpha] = \omega_\alpha V_\alpha, \quad [13]$$

whence

$$\tilde{V}_\alpha(t) = \exp(i\mathcal{H}_0 t) V_\alpha \exp(-i\mathcal{H}_0 t) = \exp(i\omega_\alpha t) V_\alpha. \quad [14]$$

Such a decomposition is always possible. As an example, let us choose

$$V_\alpha = |i\rangle\langle i|\mathcal{H}_1|j\rangle\langle j|, \quad [15]$$

where $|i\rangle$ and $|j\rangle$ are eigenkets of \mathcal{H}_0 . Then

$$\omega_\alpha = \langle i|\mathcal{H}_0|i\rangle - \langle j|\mathcal{H}_0|j\rangle. \quad [16]$$

The operator V_α defined by Eq. [15] has only one nonvanishing matrix element. In usual problems, the operators V_α have several nonvanishing matrix elements, and there are several possible choices for the V_α .

We can write Eq. [11] under the form

$$\begin{aligned} & \frac{d}{dt} \tilde{\sigma}(t) \\ &= - \sum_{\alpha, \beta} \int_0^t \overline{[\tilde{V}_\alpha(t), [\tilde{V}_\beta^\dagger(t'), (\tilde{\sigma}(t') - \tilde{\sigma}_{\text{eq}})]] F_\alpha(t) F_\beta^*(t')} dt'. \end{aligned} \quad [17]$$

Because of the different density matrices $\tilde{\sigma}(t')$ in different members of the Gibbs ensemble experiencing different time evolutions of the random functions $F_\alpha(t)$, $F_\beta^*(t')$, it is essential to use a joint average over the spin part (i.e., $\tilde{\sigma}(t')$), and the lattice part (i.e., $(F_\alpha(t)F_\beta^*(t'))$) under the integral of Eq. [17]. This last equation is nearly as rigorous as Eq. [10], but in full generality it is well nigh insoluble. There is an exception, the case when the evolution of $\mathcal{H}_1(t)$ corresponds merely to a variation of resonance frequency of the spins: modulation of the chemical shift or of the indirect interaction by chemical exchange or molecular reorientations. In this case, the perturbations $\mathcal{H}_1(t)$ at different times commute with each other as well as with the Hamiltonian \mathcal{H}_0 . The theory appropriate to this case is specific and it will not be treated here (see, e.g., Refs. (13–15)).

For the general case when the random perturbations at different times do not commute, a clean theory of relaxation is possible only in the limit when the fluctuation of the random perturbation is fast compared with the evolution through relaxation of the physical variables under study. More specifically, let τ_c be the time scale for the fluctuation of the random functions $F(t)$: it is the time scale $t - t' = \tau_c$ over which a typical product $F_\alpha(t)F_\beta^*(t')$ decays by a substantial amount (a better definition

of the correlation time τ_c will be given later). We *assume* that the quantity $\langle Q \rangle$ we are interested in has a slow evolution on the time scale τ_c , and we choose $t \gg \tau_c$ in Eq. [17]. The expectation value $\langle Q \rangle$ depends on given matrix elements of $\tilde{\sigma}(t)$, and although other physical variables may have a much faster evolution than $\langle Q \rangle$, we state for the moment that the evolution of $\tilde{\sigma}(t)$ is slow on the time scale τ_c . This will soon be justified. We first derive the evolution equation for $\langle Q \rangle(t)$ under the assumption that it is slow, compared with τ_c^{-1} , and then we determine *a posteriori* which are the conditions for the result to be consistent with this assumption.

The shortness of τ_c compared to the time scale of evolution of $\tilde{\sigma}$ and the choice of $t \gg \tau_c$ have three main consequences, as we show next.

The first consequence is that we may replace $\tilde{\sigma}(t')$ by $\tilde{\sigma}(t)$ on the right-hand side of Eq. [17], since only values of t' differing from t by only a few times τ_c contribute to the integral. The second consequence is that, since each member of the Gibbs ensemble has experienced its random perturbation for many times τ_c , the effect of the difference in their random evolutions averages out, so that the various $\tilde{\sigma}(t)$ are equal, and we may replace $\tilde{\sigma}(t)$ by $\tilde{\sigma}(t)$. As a consequence, there is a decoupling between the average over the spin part and that over the lattice part. Equation [17] is then replaced by

$$\begin{aligned} \frac{d}{dt} \tilde{\sigma}(t) = & - \sum_{\alpha, \beta} \int_0^t [V_\alpha(t), [V_\beta^\dagger(t'), (\tilde{\sigma}(t) \\ & - \tilde{\sigma}_{\text{eq}})]] \overline{F_\alpha(t) F_\beta^*(t')} dt'. \end{aligned} \quad [18]$$

We limit ourselves to stationary random functions, a realistic assumption in most practical cases, that is such that

$$\overline{F_\alpha(t) F_\beta^*(t')} = G_{\alpha\beta}(|t - t'|). \quad [19]$$

Equation [18] is the master equation for the evolution of the density matrix $\tilde{\sigma}(t)$ in the interaction representation. We use it to write down the master equation for $\sigma(t)$ in the initial Schrödinger representation. By inverting Eq. [3], we have

$$\sigma(t) = \exp(-i\mathcal{H}_0 t) \tilde{\sigma}(t) \exp(i\mathcal{H}_0 t), \quad [20]$$

whence, by differentiating both sides,

$$\frac{d}{dt} \sigma(t) = -i[\mathcal{H}_0, \sigma(t)] + \exp(-i\mathcal{H}_0 t) \frac{d\tilde{\sigma}}{dt} \exp(i\mathcal{H}_0 t). \quad [21]$$

From the expression [18] for $d\tilde{\sigma}/dt$, together with the property [6] and the definition [19], we obtain

$$\begin{aligned} \frac{d}{dt} \sigma(t) = & -i[\mathcal{H}_0, \sigma(t)] - \sum_{\alpha, \beta} \int_0^t [V_\alpha, [\tilde{V}_\beta^\dagger(t' - t), \\ & (\sigma(t) - \sigma_{\text{eq}})]] G_{\alpha\beta}(t - t') dt'. \end{aligned} \quad [22]$$

The term under the integral depends on t' only through $t - t' = \tau$, which extends from 0 to t . The third consequence of having $t \gg \tau_c$ is that we can extend the integral to infinity. From Eq. [14], we have

$$\tilde{V}_\beta^\dagger(t' - t) = \exp[-i\omega_\beta(t' - t)]V_\beta^\dagger = \exp(i\omega_\beta\tau)V_\beta^\dagger, \quad [23]$$

and we obtain finally

$$\begin{aligned} \frac{d}{dt}\sigma(t) = & -i[\mathcal{H}_0, \sigma(t)] - \sum_{\alpha,\beta} [V_\alpha, [\tilde{V}_\beta^\dagger, (\sigma(t) \\ & - \sigma_{\text{eq}})]]J_{\alpha\beta}(\omega_\beta), \end{aligned} \quad [24]$$

where $J_{\alpha\beta}(\omega)$, called a spectral density, is defined by

$$J_{\alpha\beta}(\omega) = \int_0^\infty G_{\alpha\beta}(\tau) \exp(i\omega\tau) d\tau. \quad [25]$$

Being Fourier transforms over positive time only, the spectral densities are complex. It can be shown quite generally that their real part corresponds to relaxation proper, whereas their imaginary part produces a shift of the resonance frequencies, known as the dynamical shift. We do not consider these shifts in the present article. A comprehensive analysis can be found in (16) and references therein.

2. Evolution of Expectation Values: Cross-Relaxation

We are not so much interested in the evolution of the density matrix itself as in that of measurable spin variables. Let Q be the operator corresponding to such a variable. We have

$$\langle Q \rangle = \text{Tr}\{Q\sigma\} \quad [26]$$

and

$$\frac{d}{dt}\langle Q \rangle = \text{Tr}\left\{Q \frac{d\sigma}{dt}\right\}. \quad [27]$$

We use the following general property:

$$\text{Tr}\{A[B, C]\} = \text{Tr}\{[A, B]C\}. \quad [28]$$

Applied twice in succession to Eq. [27], with $d\sigma/dt$ given by Eq. [24], this yields

$$\begin{aligned} \frac{d}{dt}\langle Q \rangle = & \langle -i[Q, \mathcal{H}_0] \rangle(t) - \sum_{\alpha,\beta} J_{\alpha\beta}(\omega_\beta) \{ \langle [[Q, V_\alpha], V_\beta^\dagger] \rangle(t) \\ & - \langle [[Q, V_\alpha], V_\beta^\dagger] \rangle_{\text{eq}} \}. \end{aligned} \quad [29]$$

This is an equation relating expectation values, and there is no need to make assumptions as to the form of $\sigma(t)$. It is the master equation for expectation values in the Schrödinger representation, that is in the laboratory frame.

The double commutators $[[Q, V_\alpha], V_\beta^\dagger]$ will often yield operators differing from Q . Some of them may not correspond to observable physical variables. However, since the observable quantity Q depends on them, it is necessary to calculate their evolution as well. The process must be repeated until reaching a closed system of operators Q_j with coupled relaxation evolutions. Some among them may correspond to independently measurable quantities. One then speaks of cross-relaxation proper, although there is no fundamental difference between the two cases as regards the formal calculations.

Let us consider such a closed set, chosen in such a way that we have

$$[Q_i, \mathcal{H}_0] = -\Omega_i Q_i. \quad [30]$$

Equation [29] then yields a system of coupled equations of the form

$$\frac{d}{dt}\langle Q_i \rangle(t) = i\Omega_i \langle Q_i \rangle(t) - \sum_j \lambda_{ij} \{ \langle Q_j \rangle(t) - \langle Q_j \rangle_{\text{eq}} \}, \quad [31]$$

whose solution is straightforward.

A case often encountered is that when the difference in the oscillation frequencies ($\Omega_i - \Omega_j$) of two operators Q_i and Q_j is much larger than their cross-relaxation rate λ_{ij} . It then results, from the general theory of linear differential equations, that the effect of cross-relaxation on the evolution of either $\langle Q_i \rangle$ or $\langle Q_j \rangle$ is negligible: it yields a relative contribution of the order of

$$\lambda_{ij}/|\Omega_i - \Omega_j| \ll 1.$$

For such couples of operators, one may then discard the cross-relaxation terms from Eqs. [31]. This corresponds to the so-called adiabatic approximation.

3. Evolution in the Interaction Representation

One is often led to calculate an expectation value in the interaction representation. Since most of the time it corresponds to a rotating frame, we note it with the subscript r ,

$$\langle Q \rangle_r(t) = \text{Tr}\{Q\tilde{\sigma}(t)\}, \quad [32]$$

and

$$\frac{d}{dt}\langle Q \rangle_r(t) = \text{Tr}\left\{Q \frac{d}{dt}\tilde{\sigma}\right\}. \quad [33]$$

On the other hand, by inserting the condition [13] into Eq. [18], we have

$$\begin{aligned} \frac{d}{dt}\tilde{\sigma}(t) = & - \sum_{\alpha,\beta} \int_0^t \exp\{i\omega_\alpha t\} \exp\{-i\omega_\beta(t - \tau)\} G_{\alpha\beta}(\tau) d\tau \\ & \times [V_\alpha, [V_\beta^\dagger, (\tilde{\sigma}(t) - \tilde{\sigma}_{\text{eq}})]]. \end{aligned} \quad [34]$$

We extend the integral over τ to infinity and use the definition [25], whence, from Eq. [33],

$$\begin{aligned} \frac{d}{dt} \langle Q \rangle_r(t) &= - \sum_{\alpha, \beta} \exp[i(\omega_\alpha - \omega_\beta)t] J_{\alpha\beta}(\omega_\beta) \\ &\times \{ \langle [[Q, V_\alpha], V_\beta^\dagger] \rangle_r(t) - \langle [[Q, V_\alpha], V_\beta^\dagger] \rangle_{r \text{ eq}} \}. \end{aligned} \quad [35]$$

This derivative is a sum of smoothly varying terms, when $\omega_\alpha = \omega_\beta$, and of oscillatory terms. When the oscillatory frequencies $\omega_\alpha - \omega_\beta$ are large compared with the average decay rate of $\langle Q \rangle_r(t)$, their contributions are fast oscillations of small amplitude, and they can be ignored. This was the first formulation of the adiabatic approximation. When on the other hand the oscillations are not fast, the present treatment is ill adapted to quantifying their effect. By contrast, this is easily done by calculating the derivatives of expectation values in the Schrödinger representation, that is in the laboratory frame, as done in Section IIA2. This is in fact the main advantage of using the laboratory frame picture.

The simplest way of establishing the connection between both formulations is as follows. Let us consider the same set of operators Q_i as in Section IIA2. We have

$$\begin{aligned} \langle Q_i \rangle_r(t) &= \text{Tr}\{Q_i \tilde{\sigma}(t)\} \\ &= \text{Tr}\{Q_i \exp(i\mathcal{H}_0 t) \sigma(t) \exp(-i\mathcal{H}_0 t)\} \\ &= \text{Tr}\{\exp(-i\mathcal{H}_0 t) Q_i \exp(i\mathcal{H}_0 t) \sigma(t)\}, \end{aligned} \quad [36]$$

or else, according to Eq. [30],

$$\langle Q_i \rangle_r(t) = \exp(-i\Omega_i t) \langle Q_i \rangle(t). \quad [37]$$

If we have $\langle Q_j \rangle_{\text{eq}} = 0$, Eq. [31] then yields

$$\frac{d}{dt} \langle Q_i \rangle_r(t) = - \sum_j \exp[-i(\Omega_i - \Omega_j)t] \lambda_{ij} \langle Q_j \rangle_r(t). \quad [38]$$

We see the origin of the oscillatory terms in Eq. [35]: they correspond to cross-relaxation between operators having different resonance frequencies in the steady spin Hamiltonian \mathcal{H}_0 .

4. Intermediate Representation

There are cases when it is convenient to use a representation intermediate between the Schrödinger and the interaction representations. This will be illustrated for a system of homonuclear spins I and S in a liquid, whose resonance frequencies ω_I and ω_S are close, as a result of different chemical shifts. Let us consider the contribution to their relaxation from the random modulation of their dipolar interaction (6). It involves spectral densities at

the frequencies ω_I , ω_S , $\omega_I + \omega_S$, and $\omega_I - \omega_S$. We write

$$\begin{cases} \omega_I = \omega_0 + \delta \\ \omega_S = \omega_0 - \delta \end{cases} \quad [39]$$

with $\delta \ll \omega_0$.

We assume that the correlation functions $G(t)$ are exponential with a single correlation time τ_c :

$$G(t) = G(0) \exp(-t/\tau_c). \quad [40]$$

It is only with correlation functions of this form that the correlation time τ_c has a well-defined meaning. The spectral densities (real part) are Lorentzian:

$$J(\omega) = G(0) \frac{\tau_c}{1 + \omega^2 \tau_c^2}. \quad [41]$$

We have then

$$\begin{aligned} J(\omega_I) &= G(0) \frac{\tau_c}{1 + \omega_0^2 \tau_c^2 (1 + \delta/\omega_0)^2} \\ &\simeq G(0) \frac{\tau_c}{1 + \omega_0^2 \tau_c^2}. \end{aligned} \quad [42]$$

Likewise,

$$\begin{aligned} J(\omega_S) &= G(0) \frac{\tau_c}{1 + \omega_0^2 \tau_c^2 (1 - \delta/\omega_0)^2} \\ &\simeq G(0) \frac{\tau_c}{1 + \omega_0^2 \tau_c^2}, \end{aligned} \quad [43]$$

$$J(\omega_I - \omega_S) = G(0) \frac{\tau_c}{1 + 4\delta^2 \tau_c^2}. \quad [44]$$

We assume that $\delta \tau_c \ll 1$, so that

$$J(\omega_I - \omega_S) \simeq J(0), \quad [45]$$

a situation very common for homonuclear spins in liquids.

As a consequence of Eqs. [42]–[45], the relaxation is the same as if both spins had resonance frequencies equal to ω_0 .

Instead of using the full interaction representation, defined by the operator

$$U = \exp[i(\omega_I I_z + \omega_S S_z)t], \quad [46]$$

we could have used a frame rotating at frequency ω_0 for both spins, defined by the operator

$$U' = \exp[i\omega_0(I_z + S_z)t]. \quad [47]$$

If we write

$$\tilde{Q}' = U' Q U'^{\dagger} \quad [48]$$

in this representation, we have

$$\frac{d}{dt}\tilde{\sigma}'(t) = -i[\delta(I_z - S_z), \tilde{\sigma}'(t)] - i[\tilde{\mathcal{H}}'_1(t), \tilde{\sigma}'(t)]. \quad [49]$$

The second term is processed as in Section IIA1, and it yields the correct result.

If on the other hand the condition $\delta\tau_c \ll 1$ is not fulfilled, one must use the full interaction representation, which leads to Eq. [34] for $d\tilde{\sigma}/dt$. Then it is permissible to limit oneself to the intermediate representation, defined by

$$\sigma_{\text{int}}(t) = \exp[-i\delta(I_z - S_z)t]\tilde{\sigma}(t)\exp[i\delta(I_z - S_z)t]. \quad [50]$$

The evolution equation in this representation is

$$\begin{aligned} \frac{d}{dt}\sigma_{\text{int}}(t) &= -i[\delta(I_z - S_z), \sigma_{\text{int}}(t)] + \exp[-i\delta(I_z - S_z)t] \\ &\times \frac{d}{dt}\tilde{\sigma}(t)\exp[i\delta(I_z - S_z)t]. \end{aligned} \quad [51]$$

If we use the approximations [42] and [43], the only oscillating terms are with frequencies ω_0 and $2\omega_0$. Since in all resonance experiments the frequency ω_0 is much larger than all relaxation rates, we can discard the oscillating terms as a result of the adiabatic approximation. Equation [51] describes correctly transverse cross-relaxation between spins I and S in the presence of a differential precession.

The intermediate representation is also useful in other cases: indirect interactions or RF irradiation, as seen in Section IIB.

5. Conditions of Validity of the Theory

As seen above, the theory assumes that the relaxation times under consideration are much longer than the correlation time τ_c . We consider as an example transverse and longitudinal relaxations in a liquid, due to dipolar couplings (see, e.g., Ref. (6)). We call $(\Delta\omega)^2$ the average square of the dipolar interactions and ω_0 the Larmor frequency.

Transverse relaxation can be produced by the longitudinal components of the dipolar field, for which $\omega_\beta = 0$. Then we have as an order of magnitude

$$\frac{1}{T_2} \sim (\Delta\omega)^2\tau_c. \quad [52]$$

The condition of validity of the theory is for that case

$$\tau_c/T_2 \ll 1, \quad [53]$$

that is,

$$|\Delta\omega|\tau_c \ll 1. \quad [54]$$

Longitudinal relaxation involves only transverse dipolar

fields, with $\omega_\beta = \omega_0$ or $2\omega_0$. We have then

$$\frac{1}{T_1} \sim \frac{(\Delta\omega)^2\tau_c}{1 + \omega_0^2\tau_c^2}. \quad [55]$$

The requirement becomes in that case

$$\frac{\tau_c}{T_1} \sim \frac{(\Delta\omega\tau_c)^2}{1 + \omega_0^2\tau_c^2} \ll 1. \quad [56]$$

It is fulfilled either by condition [54] or by the usually less stringent condition,

$$\frac{\Delta\omega}{\omega_0} \ll 1, \quad [57]$$

in the limit when $\omega_0\tau_c \gg 1$.

6. Extension to Solids

In NMR, a solid is characterized by the existence of static spin-spin interactions, usually much smaller than interactions giving rise to discrete levels: Zeeman or quadrupolar or a combination of both. The spin-spin interactions, mostly dipolar, limited to their secular part, produce a quasi-continuous broadening of the otherwise discrete levels. The decay of the transverse magnetization is then governed by the spin-spin interactions and is nonexponential. Spin-lattice relaxation in that case concerns other variables such as the longitudinal magnetization or the quadrupole alignment or the dipolar energy.

We take as an example a Hamiltonian \mathcal{H}_0 consisting of Zeeman and secular dipolar interactions, of the form

$$\mathcal{H}_0 = Z + \mathcal{H}'_D. \quad [58]$$

The random perturbation can still be written under the form [12], but with the V_α chosen so as to have

$$[Z, V_\alpha] = \omega_\alpha V_\alpha \quad [59]$$

in place of [13].

Since the terms Z and \mathcal{H}'_D are commuting, we have from Eq. [3]

$$\begin{aligned} \tilde{V}_\alpha(t) &= \exp(i\mathcal{H}_0 t)V_\alpha \exp(-i\mathcal{H}_0 t) \\ &= \exp(i\mathcal{H}'_D t)\exp(iZt)V_\alpha \exp(-iZt)\exp(-i\mathcal{H}'_D t) \\ &= \exp(i\omega_\alpha t)V_\alpha(t), \end{aligned} \quad [60]$$

where $V_\alpha(t)$ is defined by

$$V_\alpha(t) = \exp(i\mathcal{H}'_D t)V_\alpha \exp(-i\mathcal{H}'_D t). \quad [61]$$

When calculating the evolution of a variable $\langle Q_i \rangle$, we have by analogy with Eqs. [25] and [28] to calculate integrals of the

form

$$\int_0^\infty \langle [[Q_i, V_\alpha], V_\beta^\dagger(-\tau)](t) \exp(i\omega_\beta \tau) G_{\alpha\beta}(\tau) d\tau.$$

For an exponential correlation function of the form [40], the integral is of the form

$$\mathcal{I} = \int_0^\infty K(\tau; t) \exp[(i\omega_\beta - 1/\tau_c)\tau] d\tau \quad [62]$$

The variation of K with τ is due to the dipolar interactions and is therefore complicated. However, the integral [62] has a simple solution if the decay of K is slow on the time scale $|i\omega_\beta - 1/\tau_c|^{-1}$: it is the same as if the dipolar term \mathcal{H}'_D were absent, that is,

$$\mathcal{I} \simeq K(0; t) \frac{\tau_c}{1 - i\omega_\beta \tau_c}. \quad [63]$$

The reason lies in a general characteristics of functions whose decay is due to dipolar interactions, namely that their Fourier transforms have fast decaying wings, approximately like a Gaussian function. The justification goes as follows. Let the Fourier transforms (over positive time) of $K(\tau; t)$ and $G(\tau)$ be $\mathcal{K}(\omega)$ and

$$\mathcal{G}(\omega) = \frac{1}{1/\tau_c - i\omega}. \quad [64]$$

The Fourier transform \mathcal{I} of the product $K(\tau; t)G(\tau)$ (Eq. [62]) is equal to the convolution of their Fourier transforms:

$$\begin{aligned} \mathcal{I}(\omega_\beta) &\propto \int_{-\infty}^{+\infty} \mathcal{K}(\omega) \mathcal{G}(\omega_\beta - \omega) d\omega \\ &= \int_{-\infty}^{+\infty} \mathcal{K}(\omega) / [1/\tau_c - i(\omega_\beta - \omega)] d\omega \\ &= \frac{1}{1/\tau_c - i\omega_\beta} \int_{-\infty}^{+\infty} \frac{\mathcal{K}(\omega) d\omega}{1 + i\omega/[1/\tau_c - i\omega_\beta]}. \end{aligned} \quad [65]$$

It is equivalent to say that $K(\tau; t)$ evolves slowly over the time scale $|1/\tau_c - i\omega_\beta|^{-1}$, or to say that the width of $\mathcal{K}(\omega)$ is small compared with $|1/\tau_c - i\omega_\beta|$. As a consequence, only those values of ω for which

$$|\omega| \ll |1/\tau_c - i\omega_\beta|$$

contribute to the integral. For these values, the denominator does not differ significantly from unity and the integral is approximately equal to

$$\int_{-\infty}^{+\infty} \mathcal{K}(\omega) d\omega \propto K(0; t), \quad [66]$$

which justifies statement [63].

Under these conditions, the calculation of relaxation in a solid is exactly the same as in a liquid.

7. Synthesis and Discussion

The derivation leading to the master equation [29] follows a well-defined succession of steps, which we first recapitulate.

1. Start with the Liouville–von Neumann equation [2] for the evolution of the density matrix.

2. Go over to an interaction representation so as to single out the effect of the random spin–lattice coupling.

3. Perform a formal integration of σ and reinject into the evolution equation, so as to have a two-time product of random functions.

4. Take an ensemble average jointly over spin and lattice variables.

5. Replace $\tilde{\sigma}$ by $\tilde{\sigma} - \tilde{\sigma}_{\text{eq}}$, in a phenomenological treatment of the finite lattice temperature.

6. Expand the spin–lattice coupling into a sum of products of spin operators by random lattice functions.

7. Choose the time t much longer than the correlation time τ_c of the random functions. This has three consequences:

- We can replace $\tilde{\sigma}(t')$ by $\tilde{\sigma}(t)$;
- The average of the products spin \times lattice decouples into the products of the averages spin \times lattice. The latter are correlation functions of random lattice functions;
- We can extend the integration limit to infinity, which introduces well-defined spectral densities.

8. Go back to the Schrödinger representation and write the evolution equations for the expectation value of variables. They have the following characteristics:

- The derivative of an expectation value is a sum of two terms: the contribution of the static spin Hamiltonian and that of spin–lattice relaxation;
- It depends on expectation values, not on the detailed form of the density matrix;
- The relaxation part contains no oscillatory terms;
- Cross-relaxation shows up without ambiguity.

This procedure avoids, explicitly or implicitly, a number of traps encountered when performing relaxation calculations. We come back briefly on some of them.

(a) Use of an interaction representation that does not remove all of \mathcal{H}_0 . It is a representation defined by

$$Q \rightarrow \tilde{Q}' = \exp(i\mathcal{H}t) Q \exp(-i\mathcal{H}t)$$

with $\mathcal{H} \neq \mathcal{H}_0$.

The evolution of the density matrix in this representation is

$$\frac{d}{dt} \tilde{\sigma}'(t) - i[(\tilde{\mathcal{H}}'_0 - \mathcal{H} + \tilde{\mathcal{H}}'_1(t)), \tilde{\sigma}'(t)], \quad [67]$$

i.e., it involves a nonrandom term ($\tilde{\mathcal{H}}'_0 - \mathcal{H}$) in addition to the random one. This procedure does not allow a clean derivation of a master equation where the effect of relaxation is properly accounted for, because the time dependence of $\tilde{V}_\beta^\dagger(-\tau)$ is not correct and leads to spectral densities with the wrong frequency. However, we have seen in Section IIA4 that it may nevertheless yield the correct result when the extra frequency corresponding to the residual Hamiltonian is much smaller than the inverse correlation time. In case of doubt, it is safer to go first to the full interaction representation and then go back to an intermediate representation if it is more convenient than the laboratory frame. Among more serious wrongdoings is the fact of treating the effect of the residual term ($\tilde{\mathcal{H}}'_0 - \mathcal{H}$) perturbatively, or even worse, to use a term \mathcal{H} which does not commute with \mathcal{H}_0 , so that ($\tilde{\mathcal{H}}'_0 - \mathcal{H}$) is time dependent.

(b) Make the premature assumption that the average over spin and lattice variables is the product of the independent averages.

As an example, let us consider the derivative of $\langle Q \rangle_r(t)$ in the interaction representation. According to Eq. [17], it involves terms of the form

$$\exp[i(\omega_\alpha - \omega_\beta)t] \int_0^t \text{Tr}\{[[Q, V_\alpha], V_\beta^\dagger] \tilde{\sigma}(t')\} \\ \times \exp[i\omega_\beta(t - t')] G(t - t') dt'.$$

The integral is of the form

$$\mathcal{I}(t) = \int_0^t C(t') D(t - t') dt'. \quad [68]$$

It is easily solved by the Laplace transform method. Let $\mathcal{I}(\mathcal{Z})$, $\mathcal{C}(\mathcal{Z})$, and $\mathcal{D}(\mathcal{Z})$, the Laplace transforms of $I(t)$, $C(t)$, and $D(t)$, respectively, i.e., for instance,

$$\mathcal{I}(\mathcal{Z}) = \int_0^\infty I(t) \exp(-\mathcal{Z}t) dt. \quad [69]$$

It is a well-known property of Laplace transforms that to Eq. [68] there corresponds

$$\mathcal{I}(\mathcal{Z}) = \mathcal{C}(\mathcal{Z}) \mathcal{D}(\mathcal{Z}), \quad [70]$$

which would mean that $\langle Q \rangle_r(t)$ could be calculated rigorously at any time t , and even in the case when the relaxation rates are not small compared with τ_c^{-1} . This conclusion is totally erroneous, as results from the formal treatment detailed above. This provides a proof *ad absurdum* of the necessity of using a joint average over spins and lattice at short times.

(c) Make guesses about the form of the density matrix in the course of relaxation.

We have seen in Section IIA2 that the derivative of $\langle Q \rangle$ depends on terms of the form

$$\text{Tr}\{Q[V_\alpha, [V_\beta^\dagger, \sigma(t)]]\},$$

which, through repeated use of property [28], is equal to

$$\text{Tr}\{Q[V_\alpha, [V_\beta^\dagger, \sigma(t)]]\} = \text{Tr}\{[[Q, V_\alpha], V_\beta^\dagger] \sigma(t)\} \\ = \langle [[Q, V_\alpha], V_\beta^\dagger] \rangle(t). \quad [71]$$

By using [28] only once, it is found that this trace is also equal to

$$\text{Tr}\{Q[V_\alpha, [V_\beta^\dagger, \sigma(t)]]\} = \text{Tr}\{[Q, V_\alpha][V_\beta^\dagger, \sigma(t)]\}, \quad [72]$$

i.e., the trace of a product of single commutators. The latter are (slightly) simpler to calculate than double commutators, which seems to be an advantage. However, Eq. [72] is *not* equal to the expectation value of an operator, and in order to calculate it, it is necessary to guess what the form of $\sigma(t)$ is. This is usually done by performing a partial decomposition of $\sigma(t)$ into a set of orthogonal operators, limited to those expected to be relevant. We write then

$$\sigma(t) = \sum_i \xi_i Q_i + P, \quad [73]$$

with

$$\text{Tr}(Q_i Q_j) = \text{Tr}(Q_i P) = 0. \quad [74]$$

Only the operators Q_i are supposed to intervene in relaxation and are explicitated. The remaining term P is supposed not to play any role.

The coefficients ξ_i are obtained from

$$\langle Q_i \rangle = \text{Tr}\{\sigma(t) Q_i\} = \xi_i \text{Tr}(Q_i^2). \quad [75]$$

The right-hand side of Eq. [72] then reads

$$\text{Tr}\{[Q, V_\alpha][V_\beta^\dagger, \sigma(t)]\} = \sum_i \xi_i \text{Tr}\{[Q, V_\alpha][V_\beta^\dagger, Q_i]\}. \quad [76]$$

This procedure is all right *provided* that the choice of the Q_i is a good one. Some of its triumphs in the past have been:

- to miss cross-relaxation (5, 17),
- to miss cross-correlation effects between dipolar interactions of adjacent spin pairs (18) or between dipolar and anisotropic nuclear shielding interactions (19),
- to miss the fact that, for spins larger than 1/2, the relaxation of linear spin components may depend on higher powers of the spin operators (13).

The advantage of calculating the double commutators in Eq. [29] is that the operators on which the variation of $\langle Q_i \rangle$ depends show up naturally. There is no need to make “intelligent” guesses.

B. Time-Dependent Spin Hamiltonian: Off-Resonance RF Irradiation

The case of an arbitrary time-dependent spin Hamiltonian is complicated. It will be discussed at the end of Section III. We limit ourselves to the practically only case of interest: that of a system in a static magnetic field subjected to an irradiation with a much smaller periodic field of frequency ω in the vicinity of the Larmor frequency ω_0 corresponding to the static field. Any component of the RF field parallel to the dc field can be ignored, since its effect is negligible. Irradiation is usually made with a linearly polarized RF field, which can be decomposed into a sum of circularly polarized fields rotating in opposite directions, that is with opposite frequencies $+\omega$ and $-\omega$. The only effective one is that rotating at the frequency close to ω_0 , say $+\omega$, and we discard the other one. The spin Hamiltonian is then a Zeeman interaction with a static part plus a much smaller normal part rotating at frequency ω :

$$\begin{aligned}\mathcal{H}_0 &= \omega_0 I_z + \omega_1 (I_x \cos \omega t + I_y \sin \omega t) \\ &= \omega_0 I_z + \omega_1 \exp(-i\omega I_z t) I_x \exp(i\omega I_z t) \\ &= \exp(-i\omega I_z t) (\omega_0 I_z + \omega_1 I_x) \exp(i\omega I_z t),\end{aligned}\quad [77]$$

to which we add the spin–lattice coupling $\mathcal{H}_1(t)$. The first step of the formal treatment, passage to an interaction representation which singles out the effect of the spin–lattice coupling, is performed by two successive unitary transformations, as follows.

(i) Each operator is replaced by

$$Q \rightarrow \tilde{Q}(t) = \exp(i\omega I_z t) Q \exp(-i\omega I_z t),\quad [78]$$

which corresponds to the passage to a frame rotating at frequency ω around the direction $0z$ of the static field.

Through the same treatment as from Eq. [4] to Eq. [8], the evolution of the density matrix in this representation is given by

$$\frac{d}{dt} \tilde{\sigma}(t) = -i[(\tilde{\mathcal{H}}_0 - \omega I_z + \tilde{\mathcal{H}}_1(t)), \tilde{\sigma}(t)].\quad [79]$$

The new spin Hamiltonian is

$$\begin{aligned}\mathcal{H}_{\text{eff}} &= \tilde{\mathcal{H}}_0 - \omega I_z = (\omega_0 - \omega) I_z + \omega_1 I_x \\ &= \Delta I_z + \omega_1 I_x = \Omega I_z,\end{aligned}\quad [80]$$

where Δ is equal to the resonance offset. The effective Hamiltonian in this rotating frame is a Zeeman interaction with a static field oriented along an axis $0Z$ in the $0xz$ plane at an angle Θ from the direction $0z$ of the static field, with

$$\tan \Theta = \frac{\omega_1}{\Delta}.\quad [81]$$

The corresponding Larmor frequency is

$$\Omega = (\Delta^2 + \omega_1^2)^{1/2}.\quad [82]$$

We consider the case when Ω is much larger than the relaxation rates, or the spin–spin resonance width in solids.

As regards the spin–lattice coupling, we write it in a form adapted to the specific nature of the spin Hamiltonian:

$$\mathcal{H}_1(t) = \sum_m V_m F_m(t),\quad [83]$$

with

$$[I_z, V_m] = m V_m,\quad [84]$$

whence, according to Eq. [78],

$$\tilde{\mathcal{H}}_1(t) = \sum_m \exp(im\omega t) V_m F_m(t).\quad [85]$$

(ii) We go over to a doubly rotating frame by the transformation

$$\tilde{Q}(t) \rightarrow \tilde{\tilde{Q}}(t) = \exp(i\Omega I_z t) \tilde{Q} \exp(-i\Omega I_z t),\quad [86]$$

in which representation the evolution of the density matrix is given by

$$\frac{d}{dt} \tilde{\tilde{\sigma}}(t) = -i[\tilde{\tilde{\mathcal{H}}}_1(t), \tilde{\tilde{\sigma}}(t)].\quad [87]$$

In order to write $\tilde{\tilde{\mathcal{H}}}_1(t)$, we express the operators V_m in a form adapted to the tilted axes pertaining to the doubly rotating frame,

$$V_m = \sum_p \lambda_m^p V'_p,\quad [88]$$

with

$$[I_z, V'_p] = p V'_p.\quad [89]$$

We then obtain from Eqs. [85] and [86]

$$\tilde{\tilde{\mathcal{H}}}_1(t) = \sum_{m,p} F_m(t) \lambda_m^p V'_p \exp[i(m\omega + p\Omega)t].\quad [90]$$

To proceed, we solve Eq. [87] exactly as in Section IIA2, for the case of a static spin Hamiltonian, and then we go back to the first rotating frame. This is a convenient intermediate representation, in which the effective Zeeman interaction is static. Possible periodic terms as a function of t will have frequencies equal to multiples of ω , and they may safely be discarded. The evolution equation for $\langle Q \rangle_r(t)$ is of a form slightly more complicated than Eq. [35], but otherwise very similar:

$$\begin{aligned}\frac{d}{dt} \langle Q \rangle_r(t) &= \langle -i\Omega [Q, I_z] \rangle(t) - \sum_{m,p,q} \lambda_m^p \lambda_m^{q*} J_{m,m}(m\omega + q\Omega) \\ &\quad \times \{ \langle [[Q, V'_p], V_q^{\dagger}] \rangle_r(t) - \langle [[Q, V'_p], V_q^{\dagger}] \rangle_{\text{req}} \}.\end{aligned}\quad [91]$$

The only question is about which $\tilde{\sigma}_{\text{eq}}$ has to be used in order to account for the finite lattice temperature. This is discussed at length in Section III. The answer is that it is not the same for all terms in the decomposition of the spin–lattice coupling $\mathcal{H}_1(t)$. In the case under study, where the effective frequency Ω in the rotating frame is much smaller than the RF frequency ω , the answer, intuitively correct, is the following:

- For the terms V_m which do not commute with I_z , it is the same as in the absence of RF irradiation,

$$\sigma_{\text{eq}} = 1 - \beta_L \omega_0 I_z, \quad [92]$$

where β_L is the inverse lattice temperature.

- For all other terms, it is equal to unity and yields no contribution. Furthermore, for $m \neq 0$, we have approximately

$$J_{m,m}(m\omega + p\Omega) \simeq J_{m,m}(m\omega), \quad [93]$$

a result similar to [42] and [43]. Combining these results, the relaxation due to the terms of \mathcal{H}_1 with $m \neq 0$ is exactly the same as in the absence of RF irradiation, and that due to the other ones is toward zero.

For actual calculations, it is also possible to express the V'_p as a function of the V_m . We give below two examples of relaxation under RF irradiation. They are intended to illustrate the formalism for actual physical cases. The complexity of the formulas should not conceal the formal simplicity of the calculations.

1. Local Nuclear Relaxation by a Fixed Paramagnetic Center

In insulating solids, the nuclear relaxation of spins 1/2 is due to the random modulation of their dipolar coupling with fixed paramagnetic impurities at low concentration. The modulation is that of the expectation value of the electronic spin components under the effect either of their own spin–lattice relaxation or through flip–flop processes among electronic spins. The corresponding correlation time is in general not short compared with the nuclear Larmor period,

$$\omega_0 \tau_c \gtrsim 1. \quad [94]$$

Since the electronic Larmor frequency ω_e is about 3 orders of magnitude larger than ω_0 , we have

$$\omega_e \tau_c \gg 1. \quad [95]$$

We have then for the spectral densities

$$J(\omega_e) \ll J(\omega_0) \lesssim J(\Omega) \lesssim J(0) \quad [96]$$

and the contribution to relaxation of the transverse electron spin components, proportional to $J(\omega_e)$, is negligible compared with

that of the longitudinal one, with terms proportional to $J(\omega_0)$, $J(\Omega)$, and $J(0)$.

The only effective time-dependent dipolar interaction between an electronic spin S and a nuclear spin I at fixed positions is equal to

$$\mathcal{H}_1(t) = S_z(t)\{AI_z + BI_+ + B^*I_-\}. \quad [97]$$

We assume the lattice temperature high enough for the equilibrium value $\langle S_z \rangle_{\text{eq}}$ to be negligibly small, with

$$\begin{cases} A = \frac{\gamma_I \gamma_S \hbar}{r^3} (1 - 3 \cos^2 \theta) \\ B = -\frac{\gamma_I \gamma_S \hbar}{r^3} \times \frac{3}{2} \cos \theta \sin \theta \exp(-i\varphi), \end{cases} \quad [98]$$

where r is their mutual distance, and θ and φ are the polar angles of \mathbf{r} in a frame where $0z$ is along the static part of the field (see, e.g., Ref. (6)).

In the first reference frame, this coupling is

$$\tilde{\mathcal{H}}_1(t) = S_z(t)\{AI_z + B \exp(i\omega t)I_+ + B^* \exp(-i\omega t)I_-\}. \quad [99]$$

As stated above, the contribution of the terms in I_{\pm} is calculated as in the absence of irradiation, that is according to Eq. [35] and [92]. The result is

$$\frac{d}{dt} \langle I_z \rangle_B = -\frac{S(S+1)}{3} \cdot 4BB^* J(\omega) (\langle I_z \rangle - I_0), \quad [100]$$

where I_0 is equal to $\langle I_z \rangle_{\text{eq}}$ for σ_{eq} of the form [92]. Here, the normalization of $J(\omega)$ corresponds to $G(0) = 1$ in Eq. [40].

$$\frac{d}{dt} \langle I_{\pm} \rangle_B = -\frac{S(S+1)}{3} \cdot 2BB^* J(\omega) \langle I_{\pm} \rangle, \quad [101]$$

which can be written

$$\frac{d}{dt} \langle I_{x,y} \rangle_B = -\frac{S(S+1)}{3} \cdot 2BB^* J(\omega) \langle I_{x,y} \rangle. \quad [102]$$

This contribution to relaxation along the axes $OXYZ$ of the tilted frame is obtained from the relations

$$\begin{cases} I_z = cI_Z - sI_X \\ I_x = sI_Z + cI_X \\ I_y = I_Y \end{cases} \quad [103]$$

$$\begin{cases} I_Z = cI_z + sI_x \\ I_X = -sI_z + cI_x \\ I_Y = I_y, \end{cases} \quad [104]$$

with $c = \cos \Theta$ and $s = \sin \Theta$. We have

$$\begin{aligned} \frac{d}{dt} \langle I_z \rangle_B &= c \frac{d}{dt} \langle I_z \rangle + s \frac{d}{dt} \langle I_x \rangle \\ &= -\frac{S(S+1)}{3} \cdot 2BB^* J(\omega) \{2c \langle I_z \rangle - 2c I_0 + s \langle I_x \rangle\} \\ &= -\frac{S(S+1)}{3} \cdot 2BB^* J(\omega) \\ &\quad \times \{2c^2 + s^2 \langle I_z \rangle - cs \langle I_x \rangle - 2c I_0\}, \end{aligned} \quad [105]$$

and likewise,

$$\begin{aligned} \frac{d}{dt} \langle I_x \rangle_B &= -s \frac{d}{dt} \langle I_z \rangle + c \frac{d}{dt} \langle I_x \rangle \\ &= -\frac{S(S+1)}{3} \cdot 2BB^* J(\omega) \{-2s \langle I_z \rangle + 2s I_0 + c \langle I_x \rangle\} \\ &= -\frac{S(S+1)}{3} \cdot 2BB^* J(\omega) \{(2s^2 + c^2) \langle I_x \rangle \\ &\quad - cs \langle I_z \rangle + 2s I_0\} \end{aligned} \quad [106]$$

$$\frac{d}{dt} \langle I_y \rangle_B = -\frac{S(S+1)}{3} \cdot 2BB^* J(\omega) \langle I_y \rangle. \quad [107]$$

For calculating the contribution of the term in I_z , we write the first Eq. [103] under the form

$$I_z = c I_Z - \frac{s}{2} (I'_+ + I'_-). \quad [108]$$

We have in the doubly rotating frame

$$\tilde{I}_z = c I_Z - \frac{s}{2} [I'_+ \exp(i\Omega t) + I'_- \exp(-i\Omega t)]. \quad [109]$$

Since $I_z = \tilde{I}_z$, the calculation of relaxation in the first rotating frame is similar to that in the laboratory frame with a static spin Hamiltonian (Eq. [29]), but with $\langle Q \rangle_{\text{eq}} = 0$. We obtain after a trivial calculation

$$\begin{aligned} \frac{d}{dt} \langle I_Z \rangle_A &= -\frac{S(S+1)}{3} A^2 \left[s^2 J(\Omega) \langle I_Z \rangle \right. \\ &\quad \left. - \frac{1}{2} cs J(0) (\langle I'_+ \rangle + \langle I'_- \rangle) \right] \\ &= -\frac{S(S+1)}{3} A^2 [s^2 J(\Omega) \langle I_Z \rangle - cs J(0) \langle I_x \rangle] \end{aligned} \quad [110]$$

$$\begin{aligned} \frac{d}{dt} \langle I'_+ \rangle_A &= -\frac{S(S+1)}{3} A^2 \left[c^2 J(0) \langle I'_+ \rangle + \frac{1}{2} s^2 J(\Omega) (\langle I'_+ \rangle \right. \\ &\quad \left. - \langle I'_- \rangle) + cs J(\Omega) \langle I_Z \rangle \right], \end{aligned} \quad [111]$$

or else, by separating the real and imaginary parts,

$$\frac{d}{dt} \langle I_x \rangle_A = -\frac{S(S+1)}{3} A^2 [c^2 J(0) \langle I_x \rangle + cs J(\Omega) \langle I_Z \rangle] \quad [112]$$

$$\frac{d}{dt} \langle I_y \rangle_A = -\frac{S(S+1)}{3} A^2 [c^2 J(0) + s^2 J(\Omega)] \langle I_y \rangle. \quad [113]$$

We add both contributions to relaxation, as well as the evolution under the effective spin Hamiltonian [80], and we obtain finally

$$\begin{aligned} \frac{d}{dt} \langle I_Z \rangle &= -\frac{S(S+1)}{3} \{ [s^2 A^2 J(\Omega) \\ &\quad + 2BB^* (2c^2 + s^2) J(\omega)] \langle I_Z \rangle - cs [A^2 J(0) \\ &\quad + 2BB^* J(\omega)] \langle I_x \rangle - 4c BB^* J(\omega) I_0 \} \end{aligned} \quad [114]$$

$$\begin{aligned} \frac{d}{dt} \langle I_x \rangle &= -\Omega \langle I_x \rangle - \frac{S(S+1)}{3} \{ [c^2 A^2 J(0) \\ &\quad + 2BB^* (2s^2 + c^2) J(\omega)] \langle I_x \rangle \\ &\quad + cs [A^2 J(\Omega) - 2BB^* J(\omega)] \langle I_Z \rangle \\ &\quad + 4s BB^* J(\omega) I_0 \} \end{aligned} \quad [115]$$

$$\begin{aligned} \frac{d}{dt} \langle I_y \rangle &= \Omega \langle I_y \rangle - \frac{S(S+1)}{3} [c^2 A^2 J(0) + s^2 A^2 J(\Omega) \\ &\quad + 2BB^* J(\omega)] \langle I_y \rangle. \end{aligned} \quad [116]$$

Since we assume that the effective frequency Ω is much larger than the relaxation rates, we can neglect the cross-relaxation between $\langle I_x \rangle$ and $\langle I_z \rangle$.

Let us calculate within this approximation the expectation values of the various spin components in the steady state.

Equation [114] yields

$$\langle I_Z \rangle_{\text{ss}} = I_0 \frac{c}{c^2 + K s^2}, \quad [117]$$

with

$$K = \frac{1}{2} + \frac{A^2 J(\Omega)}{4BB^* J(\omega)}. \quad [118]$$

Equation [116] yields

$$\begin{aligned} \langle I_x \rangle_{\text{ss}} &= \frac{S(S+1)}{3\Omega} [c^2 A^2 J(0) + s^2 A^2 J(\Omega) \\ &\quad + 2BB^* J(\omega)] \langle I_y \rangle_{\text{ss}}, \end{aligned} \quad [119]$$

that is,

$$\langle I_x \rangle_{\text{ss}} \ll \langle I_y \rangle_{\text{ss}}. \quad [120]$$

Therefore, we neglect $\langle I_x \rangle_{\text{ss}}$ in Eq. [115] and we replace $\langle I_Z \rangle_{\text{ss}}$ by the value [117]. We obtain

$$\begin{aligned} \langle I_y \rangle_{\text{ss}} &= -\frac{S(S+1)}{3\Omega} \left\{ \frac{c^2 s [A^2 J(\Omega) - 2BB^* J(\omega)]}{c^2 + K s^2} \right. \\ &\quad \left. + 4s BB^* J(\omega) \right\} I_0, \end{aligned} \quad [121]$$

that is,

$$\langle I_Y \rangle_{ss} \ll \langle I_Z \rangle_{ss}, \quad [122]$$

except for $c \ll 1$, where it can be checked that all components are vanishingly small.

The physically evident result is that in a large effective field the steady-state spin orientation is locked along this effective field.

Remark. In the case when $\Omega\tau_c \ll 1$, that is $J(\Omega) \simeq J(0)$, the relaxation is the same as in the absence of RF irradiation. The corresponding equations are

$$\begin{cases} \frac{d}{dt} \langle I_z \rangle_{\text{rel}} = -\frac{1}{T_1} (\langle I_z \rangle - I_0) \\ \frac{d}{dt} \langle I_x \rangle_{\text{rel}} = -\frac{1}{T_2} \langle I_x \rangle, \end{cases} \quad [123]$$

whence, according to Eqs. [103] and [104],

$$\frac{d}{dt} \langle I_Z \rangle = -\left(\frac{c^2}{T_1} + \frac{s^2}{T_2} \right) \left(\langle I_Z \rangle - \frac{c}{c^2 + (T_1/T_2)s^2} I_0 \right). \quad [124]$$

The result turns out to be exactly the same as Eq. [114], except for $J(0)$ in place of $J(\Omega)$. The indiscriminate replacement of $J(0)$ by $J(\Omega)$ under RF irradiation would, however, yield erroneous results, since from Eqs. [115] and [116] the derivatives of $\langle I_X \rangle$ and $\langle I_Y \rangle$ depend on both spectral densities. It is only through the complete calculation given above that one can obtain the right answer.

2. Dipolar Relaxation of a Homonuclear Spin Pair in a Liquid

We consider two homonuclear spins I and S of resonance frequencies given by Eq. [39]:

$$\begin{cases} \omega_I = \omega_0 + \delta \\ \omega_S = \omega_0 - \delta. \end{cases} \quad [125]$$

They are subjected to RF excitation at an offset Δ from ω_0 ($\Delta = \omega_0 - \omega$), and their relaxation is due to the modulation of their dipolar interaction by Brownian rotation at constant distance, with a correlation time τ_c . The spin-lattice coupling is of the form (6, 12)

$$\mathcal{H}_1(t) = A(t)I_z S_z + B(t)(I_+ S_- + I_- S_+) + C(t)(I_+ S_z + I_z S_+) + \text{c.c.} + E(t)I_+ S_+ + \text{c.c.} \quad [126]$$

The notation for the orbital parts corresponds to the Van Vleck notation (see, e.g., Ref. (6), Ch. IV). They are related to nor-

malized functions F_m through

$$\begin{cases} A = -\frac{\gamma^2 \hbar}{r_3} \times \sqrt{\frac{2}{3}} F_0 \\ B = \frac{\gamma^2 \hbar}{r_3} \times \frac{1}{2\sqrt{6}} F_0 = -\frac{1}{4} A \\ C = \frac{\gamma^2 \hbar}{r_3} \times \frac{1}{2} F_1^* \\ E = -\frac{\gamma^2 \hbar}{r_3} \times \frac{1}{2} F_2^*. \end{cases} \quad [127]$$

The F_m , of vanishing average value, obey the following relations:

$$\overline{F_m F_{m'}} = \frac{6}{5} \delta_{m,m'}. \quad [128]$$

They are themselves proportional to second-order spherical harmonics of the polar angles of \mathbf{r}_{IS} (see, e.g., (12), (13), (20)).

Since we content ourselves with a formal treatment, the alphabet notation is simpler to use and there is no need to detail its specific form. As above, we assume that

$$J(\omega \pm \Omega) \simeq J(\omega).$$

Furthermore, we assume δ large enough to allow the separate observation of the spins I and S , but much smaller than the mean effective frequency Ω in the rotating frame (Eq. [82] as well as the correlations rate τ_c^{-1}).

The effective Hamiltonian in the rotating frame (first interaction representation) is

$$\tilde{\mathcal{H}}(t) = \Omega(I_Z + S_Z) + \delta(I_z - S_z) + \tilde{\mathcal{H}}_1(t), \quad [129]$$

where I and S have parallel axes Z , defined by Eq. [81]. Since $\delta \ll \Omega$, we can project I_z and S_z onto I_Z and S_Z . The effective spin Hamiltonian in this representation is then

$$\mathcal{H}_{\text{eff}} = (\Omega + \delta c)I_Z + (\Omega - \delta c)S_Z. \quad [130]$$

As for the spin-lattice coupling $\tilde{\mathcal{H}}_1$, it is

$$\begin{aligned} \tilde{\mathcal{H}}_1(t) = & A(t)I_z S_z + B(t)(I_+ S_- + I_- S_+) + C(t) \exp(i\omega t) \\ & \times (I_+ S_z + I_z S_+) + \text{c.c.} + E(t) \exp(i2\omega t) I_+ S_+ + \text{c.c.} \end{aligned} \quad [131]$$

In complete analogy with the preceding section, the relaxation due to terms C and E of Eq. [126] is the same as in the absence of irradiation. Through the use of Eq. [35], one finds (see, e.g., (6), (10), and (12)),

$$\begin{aligned} \frac{d}{dt} \langle I_z \rangle_{C,E} = & -CC^* J(\omega) \{ \langle I_z \rangle - I_0 \} - 2EE^* J(2\omega) \\ & \times \{ \langle I_z \rangle + \langle S_z \rangle - 2I_0 \} \end{aligned} \quad [132]$$

$$\begin{aligned} \frac{d}{dt} \langle I_{x,y} \rangle_{C,E} = & -CC^* J(\omega) \left\{ \frac{3}{2} \langle I_{x,y} \rangle + \langle S_{x,y} \rangle \right\} \\ & - EE^* J(2\omega) \langle I_{x,y} \rangle \end{aligned} \quad [133]$$

and similar expressions for the spin S , by interchanging the letters I and S .

We can use Eqs. [103] and [104], and similar ones for the spins S , to express the corresponding relaxation rates along the axes $OXYZ$. We write explicitly the evolution along OZ only. Through a straightforward calculation, we obtain the following results

$$\begin{aligned} \frac{d}{dt}\langle I_Z \rangle_{C,E} = & - \left\{ \left(c^2 + \frac{3}{2}s^2 \right) CC^* J(\omega) \right. \\ & + (2c^2 + s^2) EE^* J(2\omega) \left. \right\} \langle I_Z \rangle \\ & - \{ s^2 CC^* J(\omega) + 2c^2 EE^* J(2\omega) \} \langle S_Z \rangle \\ & + \{ c CC^* J(\omega) + 4s EE^* J(2\omega) \} I_0. \quad [134] \end{aligned}$$

We have discarded the cross-relaxation terms between $\langle I_Z \rangle$ and $\langle I_X \rangle$.

The evolution equations for the S spin components are obtain by permutation.

Let us now consider the contribution from the terms in A and B in Eq. [126]. We rewrite them as

$$\begin{aligned} \mathcal{H}_{1,AB} = \tilde{\mathcal{H}}_{1,AB} = & A(t) \left\{ (cI_Z - sI_X)(cS_Z - sS_X) \right. \\ & \left. - \frac{1}{2} [(sI_Z + cI_X)(sS_Z + cS_X) + I_Y S_Y] \right\}, \quad [135] \end{aligned}$$

or else, by using the operators I'_\pm and S'_\pm ,

$$\begin{aligned} \tilde{\mathcal{H}}_{1,AB}(t) = & A(t) \left\{ \frac{1}{2}(3c^2 - 1) \left[I_Z S_Z - \frac{1}{4}(I'_+ S'_- + I'_- S'_+) \right] \right. \\ & - \frac{3}{4} cs (I_Z S'_+ + S_Z I'_+ + I_Z S'_- + S_Z I'_-) \\ & \left. + \frac{3}{8} s^2 (I'_+ S'_+ + I'_- S'_-) \right\}. \quad [136] \end{aligned}$$

We neglect δc in Eq. [130] for going to the doubly rotating frame, and we obtain

$$\begin{aligned} \tilde{\tilde{\mathcal{H}}}_1(t) = & A(t) \left\{ \frac{1}{2}(3c^2 - 1) \left[I_Z S_Z - \frac{1}{4}(I'_+ S'_- + I'_- S'_+) \right] - \frac{3}{4} \right. \\ & \times cs [\exp(i\Omega t)(I_Z S'_+ + S_Z I'_+) \\ & + \exp(-i\Omega t)(I_Z S'_- + S_Z I'_-)] \\ & \left. + \frac{3}{8} s^2 [\exp(2i\Omega t)I'_+ S'_+ + \exp(-2i\Omega t)I'_- S'_-] \right\} \quad [137] \end{aligned}$$

We proceed as in Section IIB1 and we find after a straightforward calculation of the same structure as Eq. [29] with

$$\langle Q \rangle_{\text{eq}} = 0,$$

$$\begin{aligned} \frac{d}{dt}\langle I_Z \rangle_{A,B} = & -A^2 \left\{ \left[\frac{1}{32}(3c^2 - 1)^2 J(0) \right. \right. \\ & \left. \left. + \frac{9}{16} c^2 s^2 J(\Omega) + \frac{9}{32} s^4 J(2\Omega) \right] \langle I_Z \rangle \right. \\ & \left. - \left[\frac{1}{32}(3c^2 - 1)^2 J(0) - \frac{9}{32} s^4 J(2\Omega) \right] \langle S_Z \rangle \right\}, \quad [138] \end{aligned}$$

and a similar expression for the derivative of $\langle S_Z \rangle_{A,B}$. We can add these contributions to those of C , E (Eq. [134]). The equations of evolution of $\langle I_{X,Y} \rangle$ and $\langle S_{X,Y} \rangle$ turn out to be much more complicated.

C. Alternative Approaches to Relaxation

We cite only two of them, which are particularly known and of wide use. They concern essentially the case when the spin Hamiltonian is time-independent.

1. Relaxation Matrix of the Density Matrix

This approach consists of writing differential equations for the various matrix elements of the density matrix as a function of other matrix elements. In the preceding formalism, it amounts to choosing for the Q_i the projections $|\beta\rangle\langle\alpha|$, where $|\alpha\rangle$ and $|\beta\rangle$ are basis kets of the spin Hilbert space, most of the time eigenkets of the static spin Hamiltonian \mathcal{H}_0 . Their expectation values are

$$\begin{aligned} \langle |\beta\rangle\langle\alpha| \rangle &= \text{Tr}(|\beta\rangle\langle\alpha|\sigma) = \langle \beta|\beta\rangle\langle\alpha|\alpha\rangle\langle\alpha|\sigma|\beta\rangle \\ &= \langle \alpha|\sigma|\beta\rangle = \sigma_{\alpha\beta}. \quad [139] \end{aligned}$$

The differential system is of the form

$$\frac{d}{dt}\sigma_{\alpha\beta} \Big|_{\text{rel}} = \sum_{\alpha\delta} R_{\alpha\beta,\gamma\delta} \sigma_{\gamma\delta}. \quad [140]$$

The matrix $R_{\alpha\beta,\gamma\delta}$ is called the relaxation matrix. Each of its indexes corresponds to the labels of two kets of the Hilbert space. If n is the number of dimensions of the Hilbert space, the number of elements of σ is n^2 and that of the matrix R is n^4 , although many of them may vanish. Equation [140] is general, rigorous, and compact. As such, it is often very convenient for stating general relaxation properties of the system under study.

By contrast, the expectation values $\langle Q_i \rangle$ used in Section IIA2 correspond to linear combinations of such matrix elements of σ . All calculations involve a number of such combinations much smaller than n^2 . It has sometimes been argued that the determination of the time evolution of all matrix elements of σ provides a much better (in fact complete) description of relaxation. Let us consider, as an example, the modest case of five spins $1/2$

linked by relaxation. The number of states in the Hilbert space is $n = 2^5 = 32$, the number of matrix elements is $n^2 = 2^{10} = 1024$, and the number of elements of R is $2^{20} = 1,048,576$. A collection of 1024 evolution curves, furthermore dependent on the initial conditions, does *not* represent an information, but the burial of any information. However, this conclusion must be somewhat moderated. First, the interdependent elements of σ will usually be grouped into separate sets of dimension much smaller than n^2 . Second, in systems with not too many dimensions, it may turn out to be convenient to solve the system [140] by computer and then to perform the physically relevant combinations. Third, for systems with few dimensions, the solution of the system [140] may be simpler and faster than by any other method.

However, in most cases the use of Eq. [29], where the Q_i are observable physical quantities, saves both time and effort.

2. The Memory Function Approach

An excellent and comprehensive description of this method can be found in Ref. (21). We give but a simplified hint at its principle.

Let us write the evolution of a function $G(t)$ under the form

$$\frac{d}{dt}G(t) = - \int_0^t K(t, t')G(t') dt'. \quad [141]$$

The function $K(t, t')$ is called the memory function of $G(t)$. Equation [141] can be used for its definition. However, when $G(t)$ describes the evolution of some property of a system acted upon by a random interaction $f(t)$, the memory function can be physically interpreted in terms of the correlation function associated to $\bar{f}(t)f^*(t')$ (22). It often happens that this correlation function depends only on $(t - t')$. Then, this is also the case of the function K , and Eq. [141] becomes

$$\frac{d}{dt}G(t) = - \int_0^t K(t - t')G(t') dt'. \quad [142]$$

This last equation can be generalized to the case of different functions $G_i(t)$ whose evolutions are coupled. We then get

$$\frac{d}{dt}G_i(t) = - \sum_j \int_0^t K_{ij}(t - t')G_j(t') dt'. \quad [143]$$

As a next step, we consider a system involving a large number of time-dependent functions. It may be possible, by an appropriate choice, to select a set p of “functions of interest” and to write, for this set, an equation of the form [143] plus, on each right-hand side, an extra function $H_i(t)$ which, through physical arguments, is small and evolves on a much faster time scale than $G_i(t)$. Its effect is then negligible and it can be discarded.

In relaxation problems, these functions are the expectation values of physical quantities Q_i of interest (or rather the departure of these expectation values from thermal equilibrium).

The system [143] then reads

$$\frac{d}{dt}\langle Q_i \rangle(t) = - \sum_j \int_0^t K_{ij}(t - t')\langle Q_j \rangle(t') dt'. \quad [144]$$

The next physical argument is that the decay of the memory functions K_{ij} is much faster than that of the expectation values $\langle Q_j \rangle$. In that case, we may choose t long enough, replace $\langle Q_j \rangle(t')$ by $\langle Q_j \rangle(t)$, and extend the integral to infinity. We obtain

$$\frac{d}{dt}\langle Q_i \rangle = - \sum_j \lambda_{ij}\langle Q_j \rangle, \quad [145]$$

with

$$\lambda_{ij} = \int_0^\infty K_{ij}(\tau) d\tau. \quad [146]$$

Equation [145] describes the evolution due to the sole relaxation. If the contribution from the static spin Hamiltonian is added, we obtain a system identical with Eq. [31].

This method is sound, elegant, and efficient. Particularly seducing is the fact that Eq. [144] is *rigorous* (provided that the functions $H_i(t)$ have indeed a negligible effect). One is then tempted to assume that Eqs. [145] and [146] are also rigorous, that is that all memory functions do indeed quickly decay to zero.

This will be true *provided* that the choice of the variables of interest Q_j is correct. There lies the main danger of this method: the choice of the Q_j is made a priori through physical intuition. If this intuition fails, that is if the set Q_j is incomplete, the results will be wrong although the system [144] is correct. By taking a definite example, it can be shown that when the set of Q_j is incomplete, not all of the restricted set of memory functions decay fast enough to allow the passage from Eqs. [144] to [145]. Although this method and that of Section IIA look very similar, there is a fundamental difference between them. In the passage from Eqs. [29] to [31], the various variables $\langle Q_j \rangle$ on which the decay of $\langle Q_i \rangle$ depends are not *guessed*: they are *deduced* from the calculation of the double commutators on the right-hand side of Eq. [29]. There is no need to exert one's physical intuition.

As a last remark, one must use a joint ensemble average over the two functions under the integral in Eq. [144]. The argument is the same as that in Section IIA1. It is only at large t that it is decoupled into the product of the averages of K_{ij} and $\langle Q_j \rangle$. If this is neglected, one might use Eq. [144] to describe relaxation at arbitrarily short times, in a way similar to that criticized in Section IIA7 (Eqs. [68]–[70]).

To sum up, the memory function method is excellent when used with care.

III. QUANTUM DESCRIPTION OF THE LATTICE

We consider now the system under study from the purely quantum mechanical point of view. It depends on both spin variables and lattice variables. Its Hamiltonian is of the form

$$\mathcal{H} = \mathcal{H}_I + \mathcal{H}_{I\mathcal{F}} + \mathcal{F}. \quad [147]$$

Here \mathcal{H}_I is the spin Hamiltonian, which depends only on spin variables, \mathcal{F} is the lattice Hamiltonian, which depends only on lattice (orbital) variables, and $\mathcal{H}_{I\mathcal{F}}$ is the spin–lattice coupling, which depends on both types of variables and commutes with neither \mathcal{H}_I nor \mathcal{F} .

The density matrix describing the state of the whole system, including both spin and lattice variables, is called ρ . Its evolution equation is of the same form as Eq. [2],

$$\frac{d}{dt}\rho = -i[\mathcal{H}, \rho]. \quad [148]$$

It acts on a Hilbert space which is the tensorial product of a spin and of a lattice Hilbert space. What this means is that we can choose in it basis kets with a double index: $|i, f\rangle$ referring to spin variables i and lattice variables f .

In the absence of spin–lattice coupling, the main Hamiltonian,

$$\mathcal{H}_0 = \mathcal{H}_I + \mathcal{F}, \quad [149]$$

would consist of two commuting operators whose expectation values would remain constant in time. It would then be possible to write the density matrix ρ in the form of a product,

$$\rho = \sigma \mathcal{P}, \quad [150]$$

where σ and \mathcal{P} depend only on spin and lattice variables, respectively. The role of the term $\mathcal{H}_{I\mathcal{F}}$ is to couple \mathcal{H}_I and \mathcal{F} and to induce a mutual evolution with possible exchange of energy. This is what spin–lattice relaxation consists of.

The theory is made for systems subjected to the following conditions.

1. The coupling $\mathcal{H}_{I\mathcal{F}}$ is small enough that it is still meaningful to speak of separate spin and lattice energy levels.
2. The density matrix ρ can still be written in the form [150].
3. The lattice part is in a statistical equilibrium state characterized by a temperature, i.e., it is of the form

$$\mathcal{P} = \exp(-\beta_L \mathcal{F}) / \text{Tr}\{\exp(-\beta_L \mathcal{F})\}, \quad [151]$$

where

$$\beta_L = \hbar / kT_L \quad [152]$$

is called the lattice inverse temperature.

4. The lattice is an “infinite thermostat,” in the sense that its temperature is not altered by energy exchanges with the spin system: form [151] for \mathcal{P} does not vary with time.

The development of the theory, very similar to that of Section IIA2, is made in succession for different cases.

A. Static Spin Hamiltonian

The Hamiltonian \mathcal{H}_I does not depend on time.

In the absence of $\mathcal{H}_{I\mathcal{F}}$, the unitary operator of evolution of the system would be

$$U(t) = \exp(-i\mathcal{H}_0 t) = \exp[-i(\mathcal{H}_I + \mathcal{F})t]. \quad [153]$$

In order to single out the effect of $\mathcal{H}_{I\mathcal{F}}$, we go over to an interaction representation defined by the operator

$$U^\dagger(t) = \exp[i(\mathcal{H}_I + \mathcal{F})t], \quad [154]$$

a generalization to spin and lattice of the passage to the rotating frame, whence we get, in place of Eq. [8],

$$\frac{d}{dt}\tilde{\rho} = -i[\tilde{\mathcal{H}}_{I\mathcal{F}}(t), \tilde{\rho}]. \quad [155]$$

The following steps are:

- (1) Through formal integration, we obtain an equation similar to [10]:

$$\frac{d}{dt}\tilde{\rho} = -i[\tilde{\mathcal{H}}_{I\mathcal{F}}, \tilde{\rho}(0)] - \int_0^t [\tilde{\mathcal{H}}_{I\mathcal{F}}(t), [\tilde{\mathcal{H}}_{I\mathcal{F}}(t'), \tilde{\rho}(t')]] dt'. \quad [156]$$

- (2) We take an ensemble average, whose meaning in the present case will be given later. This allows us to drop the first term on the right-hand side.

(3) The system is assumed to have two widely different time scales: the evolution time for $\tilde{\rho}(t)$, or more precisely that for the evolution of the expectation value of an observable, and a much shorter correlation time τ_c , whose meaning will be precised later. We choose the time t much longer than τ_c . This has the same three consequences as in Section IIA1. The first two are that we have a decoupling between spin and lattice ensemble averages and that we may replace $\tilde{\rho}(t')$ by $\tilde{\rho}(t)$ on the right-hand side of Eq. [156].

- (4) We go back to the Schrödinger representation, which yields

$$\frac{d}{dt}\rho(t) = -i[\mathcal{H}_0, \rho(t)] - \int_0^t [\mathcal{H}_{I\mathcal{F}}, [\tilde{\mathcal{H}}_{I\mathcal{F}}(-\tau), \rho(t)]] d\tau. \quad [157]$$

We use now the third consequence of having chosen $t \gg \tau_c$, namely we extend the integral to infinity.

With the new notation,

$$\hat{\mathcal{H}}_{I\mathcal{F}}(\tau) = \tilde{\mathcal{H}}_{I\mathcal{F}}(-\tau) = \exp(-i\mathcal{H}_0\tau)\mathcal{H}_{I\mathcal{F}}\exp(i\mathcal{H}_0\tau), \quad [158]$$

we obtain

$$\frac{d}{dt}\rho(t) = -i[\mathcal{H}_0, \rho] - \int_0^\infty [\mathcal{H}_{I\mathcal{F}}, [\hat{\mathcal{H}}_{I\mathcal{F}}(\tau), \rho(t)]] d\tau. \quad [159]$$

(5) We expand $\rho(t)$ according to Eq. [150]. As for $\mathcal{H}_{I\mathcal{F}}$, we write it in the form of an expansion similar to that of Eq. [12],

$$\mathcal{H}_{I\mathcal{F}} = \sum_\alpha V_\alpha F_\alpha = \sum_\alpha V_\alpha^\dagger F_\alpha^\dagger, \quad [160]$$

where the V_α are spin operators and the F_α are time-independent lattice operators which take the place of the random functions used in Section II. The V_α are chosen so as to obey the relations

$$[\mathcal{H}_I, V_\alpha] = \omega_\alpha V_\alpha. \quad [161]$$

Equation [159] becomes

$$\begin{aligned} \frac{d}{dt}\rho(t) = & -i[\mathcal{H}_0, \rho] - \sum_{\alpha,\beta} \int_0^\infty [V_\alpha F_\alpha, [\hat{V}_\beta^\dagger(\tau) \\ & \times \hat{F}_\beta^\dagger(\tau), \sigma\mathcal{P}]] d\tau. \end{aligned} \quad [162]$$

Since V_β^\dagger and F_β^\dagger depend only on spin and lattice variables, respectively, and owing to the form [149] of \mathcal{H}_0 , we have

$$\hat{V}_\beta^\dagger(\tau) = \exp(-i\mathcal{H}_I\tau)V_\beta^\dagger\exp(i\mathcal{H}_I\tau) = \exp(i\omega_\beta\tau)V_\beta^\dagger \quad [163]$$

$$\hat{F}_\beta^\dagger(\tau) = \exp(-i\mathcal{F}\tau)F_\beta^\dagger\exp(i\mathcal{F}\tau). \quad [164]$$

(6) We will use Eq. [162] to calculate the evolution of the expectation values of spin variables, i.e., of operators Q depending only on the spins, that is

$$\langle Q \rangle = \text{Tr}\{Q\rho\} = \text{Tr}\{Q\sigma\mathcal{P}\}. \quad [165]$$

If one uses reduced traces, the trace of a product of commuting operators (such as $Q\sigma$ and \mathcal{P}) is equal to the product of their traces (see, e.g., Ref. (12), Ch. 4).

Equation [165] is then

$$\langle Q \rangle = \text{Tr}_I\{Q\sigma\} \times \text{Tr}_\mathcal{F}\{\mathcal{P}\} = \text{Tr}\{Q\sigma\}. \quad [166]$$

In the first term on the right, the traces are on spin variables and lattice variables, respectively. According to Eq. [151], we have

$$\text{Tr}_\mathcal{F}\{\mathcal{P}\} = 1, \quad [167]$$

whence the second term.

This provides an unambiguous definition of the spin density matrix σ , consistently used in Section II:

$$\sigma = \text{Tr}_\mathcal{F}\rho. \quad [168]$$

We use this definition in Eq. [162]. The first term on the right-hand side yields

$$\begin{aligned} -i\text{Tr}_\mathcal{F}\{[\mathcal{H}_0, \rho]\} &= -i\text{Tr}_\mathcal{F}\{\mathcal{H}_I + \mathcal{F}, \sigma\mathcal{P}\} \\ &= -i\text{Tr}_\mathcal{F}\{[\mathcal{H}_I, \sigma]\mathcal{P} + \sigma[\mathcal{F}, \mathcal{P}]\}. \end{aligned} \quad [169]$$

We use Eq. [167] together with the property that the trace of a commutator vanishes, and we obtain

$$-i\text{Tr}_\mathcal{F}\{[\mathcal{H}_0, \rho]\} = -i[\mathcal{H}_I, \sigma], \quad [170]$$

which is identical with the first term on the right-hand side of Eq. [24].

(7) We have to take the trace over lattice variables of the second term on the right-hand side of Eq. [162]. The double commutator under the sign sum is over products of two operators: a spin one and a lattice one. We recall the general formulas for commutators of products,

$$[AB, C] = A[B, C] + [A, C]B, \quad [171]$$

whence

$$[C, AB] = -[AB, C] = A[C, B] + [C, A]B. \quad [172]$$

For the commutator of two products, we obtain

$$\begin{aligned} [AB, CD] &= A[B, CD] + [A, CD]B \\ &= AC[B, D] + A[B, C]D \\ &\quad + C[A, D]B + [A, C]DB. \end{aligned} \quad [173]$$

We consider a typical term under the integral on the right-hand side of Eq. [162], for which we use provisionally the following simplified notation:

$$\begin{cases} V_\alpha \rightarrow V \\ F_\alpha \rightarrow F \\ \hat{V}_\beta^\dagger(\tau) \rightarrow \hat{V} \\ \hat{F}_\beta^\dagger(\tau) \rightarrow \hat{F}, \end{cases} \quad [174]$$

and we write schematically, for the evolution of the spin density matrix σ ,

$$\frac{d}{dt}\sigma(t) = -i[\mathcal{H}_I, \sigma(t)] - \text{Tr}_\mathcal{F} \int_0^\infty [VF, [\hat{V}\hat{F}, \sigma\mathcal{P}]] d\tau. \quad [175]$$

According to rule [173], the first commutator is equal to

$$\begin{aligned}
[\hat{V}\hat{F}, \sigma\mathcal{P}] &= \hat{V}\sigma[\hat{F}, \mathcal{P}] & (a) \\
&+ \hat{V}[\hat{F}, \sigma]\mathcal{P} & (b) \\
&+ \sigma[\hat{V}, \mathcal{P}]\hat{F} & (c) \\
&+ [\hat{V}, \sigma]\mathcal{P}\hat{F} & (d).
\end{aligned} \tag{176}$$

The terms (b) and (c) contain the commutator of a spin operator by a lattice operator. These operators commute, since they depend on different variables, and these terms vanish. We are left with

$$[\hat{V}\hat{F}, \sigma\mathcal{P}] = \hat{V}\sigma[\hat{F}, \mathcal{P}] + [\hat{V}, \sigma]\mathcal{P}\hat{F}. \tag{177}$$

Now we write its commutator with VF and take the trace with respect to lattice variables. We obtain

$$\begin{aligned}
\text{Tr}_{\mathcal{F}}\{[VF, [\hat{V}\hat{F}, \sigma\mathcal{P}]]\} &= \text{Tr}_{\mathcal{F}}\{[VF, (\hat{V}\sigma[\hat{F}, \mathcal{P}] + [V, \sigma]\mathcal{P}\hat{F})]\} \\
&= \text{Tr}_{\mathcal{F}}\{V\hat{V}\sigma[F, [\hat{F}, \mathcal{P}]]\} & (a) \\
&+ [V, \hat{V}\sigma][\hat{F}, \mathcal{P}]F & (b) \\
&+ V[\hat{V}, \sigma][F, \mathcal{P}\hat{F}] & (c) \\
&+ [V, [\hat{V}, \sigma]]\mathcal{P}\hat{F}F. & (d)
\end{aligned} \tag{178}$$

The terms (a) and (c) vanish: they involve the trace over \mathcal{F} of a commutator of lattice operators. Reporting the remaining terms into Eq. [175] yields

$$\begin{aligned}
\frac{d}{dt}\sigma(t) &= -i[\mathcal{H}_I, \sigma] - \int_0^\infty [V, [\hat{V}, \sigma]]\text{Tr}_{\mathcal{F}}(\mathcal{P}\hat{F}F) d\tau \\
&+ \int_0^\infty [V, \hat{V}\sigma]\text{Tr}_{\mathcal{F}}([\mathcal{P}, \hat{F}]F) d\tau.
\end{aligned} \tag{179}$$

Let us compare the second term on the right-hand side with the corresponding term in Eq. [22] (with the same simplified notation for a typical term). They look very much alike, except for two differences:

The correlation function of random functions $\overline{F\hat{F}(\tau)}$ is replaced by the trace $\text{Tr}_{\mathcal{F}}[\mathcal{P}\hat{F}(\tau)F]$. The latter must therefore be considered a quantum correlation function. It is this one whose decay time τ_c is assumed very short compared to that of spin quantities of interest. Its variation with temperature originates from that of \mathcal{P} (Eq. [151]).

The term in σ_{eq} added by hand in the classical lattice model is absent. If the ‘‘ansatz’’ used in Section II is indeed correct, this term must correspond to the third term on the right-hand side of Eq. [179]. This is what we must analyze next, in three successive steps.

(8) In order that they have comparable lattice parts (correlation functions), we must arrange the trace over \mathcal{F} of the third term on the right to be of the same form as that of the second

term, that is

$$\text{Tr}_{\mathcal{F}}(\mathcal{P}\hat{F}F).$$

We do this by writing explicitly the trace in a basis of eigenkets of the lattice Hamiltonian \mathcal{F} . We bypass completely the difficulty of defining a reduced trace in a Hilbert space whose dimensions form a continuous set, as is the case for the lattice. We use formally a complete trace over numerable basis kets. This will not influence the final result.

We write then

$$\begin{aligned}
\text{Tr}([\mathcal{P}, \hat{F}]F) &= \sum_{ff'} (\langle f|\mathcal{P}|f\rangle\langle f|\hat{F}|f'\rangle\langle f'|F|f\rangle \\
&\quad - \langle f|\hat{F}|f'\rangle\langle f'|\mathcal{P}|f\rangle\langle f'|F|f\rangle) \\
&= \sum_{f,f'} (\langle f|\mathcal{P}|f\rangle\langle f|\hat{F}|f'\rangle\langle f'|F|f\rangle) \\
&\quad \times \left(1 - \frac{\langle f'|\mathcal{P}|f'\rangle}{\langle f|\mathcal{P}|f\rangle}\right).
\end{aligned} \tag{180}$$

With the notation

$$\begin{aligned}
\langle f|\mathcal{F}|f\rangle &= \omega_f \\
\langle f'|\mathcal{F}|f'\rangle &= \omega_{f'}
\end{aligned} \tag{181}$$

we have, according to Eq. [151],

$$\frac{\langle f'|\mathcal{P}|f'\rangle}{\langle f|\mathcal{P}|f\rangle} = \exp\{\beta_L(\omega_f - \omega_{f'})\}. \tag{182}$$

(9) The third term on the right-hand side of Eq. [179] involves an integral over τ . The two terms depending on τ are \hat{V} and \hat{F} . The variation of \hat{V} (i.e., $\hat{V}_\beta^\dagger(\tau)$ in full notation) is given by Eq. [163]. Let us consider the matrix element,

$$\langle f|\hat{F}|f'\rangle = \langle f|\hat{F}_\beta^\dagger(\tau)|f'\rangle.$$

According to Eq. [164] it is equal to

$$\langle f|\hat{F}|f'\rangle = \exp\{-i(\omega_f - \omega_{f'})\tau\}\langle f|F_\beta^\dagger|f'\rangle. \tag{183}$$

The integral over τ is then

$$\mathcal{J} = \int_0^\infty \exp\{i(\omega_\beta - \omega_f + \omega_{f'})\tau\} d\tau. \tag{184}$$

Its real part, the only one we consider, is proportional to

$$\mathcal{J} \propto \delta(\omega_\beta - \omega_f + \omega_{f'}). \tag{185}$$

As a consequence we may replace ratio [182] by

$$\exp\{\beta_L(\omega_f - \omega_{f'})\} \rightarrow \exp\{\beta_L\omega_\beta\}. \tag{186}$$

without altering the value of this third term. That is, we may use in place of Eq. [180]

$$\begin{aligned} & \text{Tr}([\mathcal{P}, \hat{F}]F) \\ & \rightarrow [1 - \exp(\beta_L \omega_\beta)] \sum_{f, f'} (\langle f | \mathcal{P} | f \rangle \langle f | \hat{F} | f' \rangle \langle f' | F | f \rangle) \\ & = [1 - \exp(\beta_L \omega_\beta)] \text{Tr}(\mathcal{P} \hat{F} F). \end{aligned} \quad [187]$$

Let us insert this result into Eq. [179], reverse the connection [174], and go back to Eq. [162]. We obtain

$$\begin{aligned} \frac{d}{dt} \sigma(t) & = -i[\mathcal{H}_I, \sigma] - \sum_{\alpha, \beta} J_{\alpha\beta}(\omega_\beta) \{ [V_\alpha, [V_\beta^\dagger, \alpha]] \\ & - [V_\alpha, V_\beta^\dagger \sigma] (1 - \exp(\beta_L \omega_\beta)) \}. \end{aligned} \quad [188]$$

We can multiply all terms by a spin operator Q and take the traces, following property [28], We obtain

$$\begin{aligned} \frac{d}{dt} \langle Q \rangle(t) & = \langle -i[Q, \mathcal{H}_I] \rangle(t) - \sum_{\alpha, \beta} J_{\alpha\beta}(\omega_\beta) \{ \langle [[Q, V_\alpha], V_\beta^\dagger] \rangle(t) \\ & - \langle [Q, V_\alpha] V_\beta^\dagger \rangle(t) (1 - \exp(\beta_L \omega_\beta)) \}. \end{aligned} \quad [189]$$

Equation [188] is the master equation for the density matrix and Eq. [189] is the master equation for expectation value. Both are compact and of direct usefulness. However, they are puzzling in two respects. First, it is not immediately clear toward which value spin-lattice relaxation makes the quantity (Q) evolve. Second, it seems we have not kept our promise: Equations [188] and [189] have little resemblance to Eqs. [24] and [29], obtained by the phenomenological replacement of $\sigma(t)$ by $\sigma(t) - \sigma_{\text{eq}}$. This is done next.

(10) Let us consider a specific matrix element of $\hat{V}_\beta^\dagger(\tau)$,

$$\begin{aligned} \langle i | \hat{V}_\beta^\dagger(\tau) | j \rangle & = \langle i | \exp(-i\mathcal{H}_I \tau) V_\beta^\dagger \exp(i\mathcal{H}_I \tau) | j \rangle \\ & = \exp\{-i(\omega_i - \omega_j)\tau\} \langle i | V_\beta^\dagger | j \rangle, \end{aligned} \quad [190]$$

where ω_i and ω_j are the eigenvalues:

$$\begin{cases} \langle i | \mathcal{H}_I | i \rangle = \omega_i \\ \langle j | \mathcal{H}_I | j \rangle = \omega_j. \end{cases} \quad [191]$$

By comparison with Eq. [163] we have

$$\omega_\beta = \omega_j - \omega_i, \quad [192]$$

which can be inserted into the last term on the right-hand side of Eq. [188].

We introduce the thermal equilibrium spin density matrix with respect to the spin Hamiltonian \mathcal{H}_I ,

$$\sigma_{\text{eq}} = \exp(-\beta_L \mathcal{H}_I) / \text{Tr}\{\exp(-\beta_L \mathcal{H}_I)\}, \quad [193]$$

and we have, according to Eq. [191],

$$\begin{aligned} 1 - \exp(\beta_L \omega_\beta) & = 1 - \exp[\beta_L(\omega_j - \omega_i)] = 1 - \frac{\langle i | \sigma_{\text{eq}} | i \rangle}{\langle j | \sigma_{\text{eq}} | j \rangle} \\ & = [\langle j | \sigma_{\text{eq}} | j \rangle - \langle i | \sigma_{\text{eq}} | i \rangle] \times \frac{1}{\langle j | \sigma_{\text{eq}} | j \rangle}. \end{aligned} \quad [194]$$

According to this last form, the term in $\langle i | V_\beta^\dagger | j \rangle$, in the last term on the right-hand side of Eq. [188], can be written

$$\langle i | V_\beta^\dagger | j \rangle \times (1 - \exp(\beta_L \omega_\beta)) = \langle i | [V_\beta^\dagger, \sigma_{\text{eq}}] | j \rangle \times \frac{1}{\langle j | \sigma_{\text{eq}} | j \rangle}, \quad [195]$$

from which Eq. [188] becomes

$$\begin{aligned} \frac{d}{dt} \sigma(t) & = -i[\mathcal{H}_I, \sigma] - \sum_{\alpha, \beta} J_{\alpha\beta}(\omega_\beta) \{ [V_\alpha, [V_\beta^\dagger, \sigma]] \\ & - [V_\alpha, [V_\beta^\dagger, \sigma_{\text{eq}}] \sigma_{\text{eq}}^{-1} \sigma] \}. \end{aligned} \quad [196]$$

This last form is still not very palatable and it would not be very easy to use for actual calculations.

The situation undergoes a qualitative change when going to the limit of high temperature. It corresponds to the situation where for all frequencies ω_β , one has

$$\beta_L \omega_\beta \ll 1, \quad [197]$$

so that only terms linear in β_L need be retained (the effect of the average dipolar field (23, 24) is a subject in itself, which is outside the scope of the present article). At high temperature the density matrices σ_{eq} and σ are very close to the unit operator, with a departure of the first order in β_L . The commutator $[V_\beta^\dagger, \sigma_{\text{eq}}]$ contains such a term, because the part proportional to the unit operator yields a vanishing contribution. Therefore, in order to stick to the linear approximation, we need replace $\sigma_{\text{eq}}^{-1} \sigma$ by unity on the right-hand side of Eq. [196].

As another way to obtain the same result, we have at high temperature

$$\begin{aligned} 1 - \exp \beta_L(\omega_j - \omega_i) & \simeq -\beta_L(\omega_j - \omega_i) \\ & = (1 - \beta_L \omega_j) - (1 - \beta_L \omega_i) \\ & = \langle j | \sigma_{\text{eq}} | j \rangle - \langle i | \sigma_{\text{eq}} | i \rangle, \end{aligned} \quad [198]$$

whence

$$\langle i | V_\beta^\dagger | j \rangle \sigma \rightarrow \langle i | [V_\beta^\dagger, \sigma_{\text{eq}}] | j \rangle \sigma \simeq \langle i | [V_\beta^\dagger, \sigma_{\text{eq}}] | j \rangle \quad [199]$$

to the first order in β_L .

As a consequence of discarding $\sigma_{\text{eq}}^{-1}\sigma$ in Eq. [196], we obtain in place of Eq. [188]

$$\frac{d}{dt}\sigma(t) = -i[\mathcal{H}_I, \sigma(t)] - \sum_{\alpha,\beta} J_{\alpha\beta}(\omega_\beta)[V_\alpha, [V_\beta^\dagger, (\sigma(t) - \sigma_{\text{eq}})]], \quad [200]$$

which is identical to Eq. [24] (with \mathcal{H}_I for the static spin Hamiltonian instead of \mathcal{H}_0).

The net result of the present treatment, borrowed from Refs. (3, 4), is that the replacement

$$\sigma(t) \rightarrow \sigma(t) - \sigma_{\text{eq}}$$

is no longer phenomenological: it is proved.

It should be emphatically stressed that Eq. [200] is valid only in the high-temperature domain. The equations valid at all temperatures are Eqs. [188] and [189]. At high temperature Eq. [189] becomes

$$\begin{aligned} \frac{d}{dt}\langle Q \rangle(t) &= \langle -i[Q, \mathcal{H}_I] \rangle(t) - \sum_{\alpha,\beta} J_{\alpha\beta}(\omega_\beta) \{ \langle [Q, V_\alpha], V_\beta^\dagger \rangle(t) \\ &+ \beta_L \omega_\beta \text{Tr}([Q, V_\alpha] V_\beta^\dagger) \}. \end{aligned} \quad [201]$$

The trace is equal to

$$\text{Tr}(Q[V_\alpha, V_\beta^\dagger]). \quad [202]$$

For given terms $V_\alpha, V_\beta^\dagger$, their commutator tells immediately which operators Q evolve toward a nonzero equilibrium value.

Remark I—On ensemble averages. We have stressed the importance of taking an ensemble average for the evolution of σ , which has two consequences: the impossibility of studying the density matrix at times comparable with the correlation time τ_c and the simplicity brought about by choosing a time t intermediate between τ_c and the characteristic evolution time of physical observables. An argument was given for this procedure in the classical treatment of the lattice. What is the corresponding argument when the lattice is treated quantum-mechanically?

The answer is the following. Since we are ultimately interested in the evolution of the spin density matrix σ , it is unnecessary to start from Eq. [148]. We may first go to an interaction representation with respect to lattice only, that is perform the connection

$$Q \rightarrow Q'(t) = \exp(i\langle \mathcal{F}t \rangle) Q \exp(-i\mathcal{F}t), \quad [203]$$

whence

$$\frac{d}{dt}\sigma'(t) = -i\text{Tr}_{\mathcal{F}}[(\mathcal{H}_I + \mathcal{H}_{I\mathcal{F}}(t)), \sigma'(t)] \quad [204]$$

with

$$\mathcal{H}_{I\mathcal{F}}(t) = \exp(i\mathcal{F}t)\mathcal{H}_{I\mathcal{F}}\exp(-i\mathcal{F}t). \quad [205]$$

The beginning of the relaxation evolution is when, starting from spin and lattice thermal equilibrium, the spin part of the system is disturbed out of equilibrium by a spin excitation. The following evolution under relaxation of the spin observables does not depend on the exact instant of time when the spin excitation is performed. That is, Eq. [205] can be replaced by

$$\mathcal{H}_{I\mathcal{F}}(t; T) = \exp[i\mathcal{F}(t + T)]\mathcal{H}_{I\mathcal{F}}\exp[-i\mathcal{F}(t + T)]. \quad [206]$$

The relaxation evolution must be independent of T , and we may use in place of [206] an average over T . This corresponds to choosing a Gibbs ensemble of systems with all possible values of T . This ensures that the first term on the right-hand side of Eq. [156] does indeed vanish.

Remark II. It is a general fact that the evolution of a quantum system, let it be one of its kets or its density matrix, is described by a unitary operator. This is definitely not the case for the relaxation contribution to the evolution of σ (e.g., Eq. [200]). The reason is that σ is not the density matrix of the whole system: it is merely its projection on the spin variables. It is natural that a projection, that is a fraction of the total density matrix, should not behave in the same way as the full density matrix.

In Section II, we have described the density matrix of the whole system, subjected to both steady (time independent or varying in a regular fashion) and random interactions. There, the nonunitary evolution of the density matrix originated from the fact that we truncated it: we did not consider its fast, random fluctuations because it did not give rise to observable phenomena. This truncation is the rule in statistical dynamics and thermodynamics. It is at the origin of the transition from microscopic reversibility to macroscopic irreversibility.

Remark III—On spectral densities. In the general expression [189], it often happens that most, if not all, contributions to the relaxation evolution of $\langle Q \rangle(t)$ originate from terms with $\alpha = \beta$. The corresponding spectral density $J_{\beta\beta}(\omega_\beta)$ is, according to Eqs. [179], [181], [183], [184], and [185], of the form

$$\begin{aligned} J_{\beta\beta}(\omega_\beta) &= \text{Re} \sum_{f,f'} \int_0^\infty \exp(i\omega_\beta\tau) d\tau \langle f | \mathcal{P} | f \rangle \\ &\quad \times \langle f | \hat{F}_\beta^\dagger(\tau) | f' \rangle \langle f' | F_\beta | f \rangle \\ &= \text{Re} \sum_{f,f'} \int_0^\infty \exp[i(\omega_\beta - \omega_f + \omega_{f'})\tau] d\tau \\ &\quad \times \langle f | \mathcal{P} | f \rangle \langle f | F_\beta^\dagger | f' \rangle \langle f' | F_\beta | f \rangle \\ &= \pi \text{Re} \sum_{f,f'} \langle f | \mathcal{P} | f \rangle \langle f | F_\beta^\dagger | f' \rangle \langle f' | F_\beta | f \rangle \\ &\quad \times \delta(\omega_\beta - \omega_f + \omega_{f'}). \end{aligned} \quad [207]$$

In addition to the terms of the form $[Q, V_\beta]\hat{V}_\beta^\dagger(\tau)$... just described, let us consider, in the sum [189], those in $[Q, V_\beta^\dagger]\hat{V}_\beta(\tau)$... for which

$$\hat{V}_\beta(\tau) = \exp(-i\omega_\beta\tau)V_\beta. \quad [208]$$

The corresponding spectral density, named for convenience, $J_{\beta\beta}^\dagger(-\omega_\beta)$, is equal to

$$J_{\beta\beta}^\dagger(-\omega_\beta) = \text{Re} \int_0^\infty \exp(-i\omega_\beta\tau) \text{Tr}\{\mathcal{P}\hat{F}_\beta(\tau)F_\beta^\dagger\} d\tau. \quad [209]$$

Since we have

$$\langle f'|\hat{F}_\beta(\tau)|f\rangle = \langle f|\hat{F}_\beta^\dagger(\tau)|f'\rangle^*, \quad [210]$$

we obtain in place of Eq. [207]

$$\begin{aligned} J_{\beta\beta}^\dagger(-\omega_\beta) &= \text{Re} \sum_{f,f'} \int_0^\infty \exp[-i(\omega_\beta - \omega_f + \omega_{f'})\tau] d\tau \\ &\quad \times \langle f'|\mathcal{P}|f'\rangle \langle f'|F_\beta|f\rangle \langle f|F_\beta^\dagger|f'\rangle \\ &= \pi \text{Re} \sum_{f,f'} \langle f'|\mathcal{P}|f'\rangle \langle f|F_\beta^\dagger|f'\rangle \\ &\quad \times \langle f'|F_\beta|f\rangle \delta(\omega_\beta - \omega_f + \omega_{f'}). \end{aligned} \quad [211]$$

By comparison with Eqs. [182] and [207], we obtain

$$J_{\beta\beta}^\dagger(-\omega_\beta) = \exp(\beta_L\omega_\beta)J_{\beta\beta}(\omega_\beta). \quad [212]$$

In the high-temperature limit, these spectral densities multiply terms linear in inverse temperature β_L (term between curly brackets on the right-hand side of Eq. [201]). In that case, one may forget the exponential in Eq. [212] and use

$$J_{\beta\beta}^\dagger(-\omega_\beta) \simeq J_{\beta\beta}(\omega_\beta), \quad [213]$$

in accordance with the classical treatment of Section IIA.

1. Illustration: Relaxation Transition between Two Quantum Levels

We single out in a system two discrete levels of kets $|a\rangle$ and $|b\rangle$, with an energy separation $\hbar\omega$, and we analyze the relaxation-driven transition probabilities between them.

The simplest way is to describe these two levels by a fictitious spin $I = 1/2$. The up and down level populations correspond to the following expectation values:

$$\begin{cases} P_u = \langle \frac{1}{2} + I_z \rangle \\ P_d = \langle \frac{1}{2} - I_z \rangle. \end{cases} \quad [214]$$

The spin-lattice coupling must have matrix elements between $|a\rangle$ and $|b\rangle$. It can be written in all generality

$$\mathcal{H}_{IF} = I_+F + I_-F^\dagger. \quad [215]$$

Through the use of the general Eq. [189], we have

$$\begin{aligned} \frac{d}{dt}\langle I_z \rangle &= -J(\omega)\{[[I_z, I_+], I_-](t) - \langle [I_z, I_+]I_- \rangle(t) \\ &\quad \times [1 - \exp(\beta_L\omega)]\} - J^\dagger(-\omega)\{[[I_z, I_-], I_+](t) \\ &\quad - \langle [I_z, I_-]I_+ \rangle(t)[1 - \exp(-\beta_L\omega)]\} \\ &= -J(\omega)\{[[I_z, I_+], I_-](t) - \langle [I_z, I_+]I_- \rangle(t) \\ &\quad \times [1 - \exp(\beta_L\omega)] + \exp(\beta_L\omega)\langle [[I_z, I_-], I_+](t) \\ &\quad - \langle [I_z, I_-]I_+ \rangle(t)[\exp(\beta_L\omega) - 1]\}, \end{aligned} \quad [216]$$

where we have used Eq. [212]. Both double commutators are equal to

$$[[I_z, I_+], I_-] = [[I_z, I_-], I_+] = 2I_z, \quad [217]$$

whereas the other terms are

$$\begin{cases} [I_z, I_+]I_- = I_+I_- = \frac{1}{2} + I_z \\ [I_z, I_-]I_+ = -I_-I_+ = -\frac{1}{2} + I_z. \end{cases} \quad [218]$$

When reported into Eq. [216], they yield

$$\begin{aligned} \frac{d}{dt}\langle I_z \rangle &= -J(\omega)\{2[\exp(\beta_L\omega) + 1]\langle I_z \rangle + \exp(\beta_L\omega) - 1\} \\ &= -J(\omega)2[\exp(\beta_L\omega) + 1]\left\{\langle I_z \rangle + \frac{1}{2} \tanh\left(\frac{1}{2}\beta_L\omega\right)\right\}. \end{aligned} \quad [219]$$

According to Eq. [214], we obtain after a little algebra

$$\begin{aligned} \frac{d}{dt}P_u &= -\frac{d}{dt}P_d = -2J(\omega)\{\exp(\beta_L\omega)P_u - P_d\} \\ &= -2J^\dagger(-\omega)\{P_u - \exp(-\beta_L\omega)P_d\} \\ &= -\{W_{u\rightarrow d}P_u - W_{d\rightarrow u}P_d\}. \end{aligned} \quad [220]$$

This yields

$$\begin{pmatrix} P_u \\ P_d \end{pmatrix}_{\text{eq}} = \frac{W_{d\rightarrow u}}{W_{u\rightarrow d}} = \exp(-\beta_L\omega), \quad [221]$$

which is consistent with the general results of statistical mechanics.

It can be checked that for obtaining result [221] it is imperative to use expectation values for the term $[Q, V_\alpha]V_\beta^\dagger$, in Eq. [189].

However, at high temperature, this expectation value is replaced by the trace (Eq. [201]). Let us see what it yields.

With the help of Eqs. [217] and [218], Eq. [201] yields

$$\begin{aligned} \frac{d}{dt}\langle I_z \rangle &= -J(\omega)\{4\langle I_z \rangle(t) + \beta_L\omega\} \\ &= -4J(\omega)\left\{\langle I_z \rangle + \frac{1}{4}\beta_L\omega\right\}. \end{aligned} \quad [222]$$

The same result is obtained from Eq. [219] expanded to the first order in $\beta_L\omega$.

B. Time-Dependent Spin Hamiltonian

1. Off-Resonance Irradiation

We analyze the same problem as in Section IIB 1-1: the relaxation of a nuclear spin subjected to off-resonance irradiation at a frequency ω in the vicinity of its Larmor frequency ω_0 . The spin Hamiltonian \mathcal{H}_I is the same as in Eq. [77], and the spin–lattice coupling is of the same form as in Eq. [160]. The development is a combination of those of Sections IIB and III. We indicate its main steps very succinctly.

Following the formalism at the beginning of Section III, we use an interaction representation where the evolution of the density matrix depends only on the spin–lattice coupling. The corresponding unitary operator is

$$U^\dagger(t) = U_{I_2}^\dagger(t)U_{I_1}^\dagger(t)U_{\mathcal{F}}^\dagger(t), \quad [223]$$

with

$$U_{\mathcal{F}}^\dagger(t) = \exp(i\mathcal{F}t), \quad [224]$$

$$U_{I_1}^\dagger(t) = \exp(i\omega I_z t), \quad [225]$$

$$U_{I_2}^\dagger(t) = \exp(i\Omega I_Z t), \quad [226]$$

where the orientation of the axis 0Z and the effective frequency Ω are given by Eqs. [81] and [82], respectively. As above, we assume that $\Omega \ll \omega$. We use the following notations.

For a spin operator,

$$U_{I_1}^\dagger(t)Q U_{I_1}(t) = \tilde{Q}(t) \quad [227]$$

$$U_{I_2}^\dagger(t)\tilde{Q}(t)U_{I_2}(t) = \tilde{\tilde{Q}}(t). \quad [228]$$

For a lattice operator,

$$U_{\mathcal{F}}^\dagger(t)F U_{\mathcal{F}}(t) = \tilde{F}(t) = \tilde{\tilde{F}}(t) = \hat{F}(-t). \quad [229]$$

Starting from the Liouville–von Neumann equation,

$$\frac{d}{dt}\rho = -i[\mathcal{H}, \rho],$$

we obtain

$$\frac{d}{dt}\tilde{\rho} = -i[\tilde{\mathcal{H}}_{I\mathcal{F}}, \tilde{\rho}], \quad [230]$$

of the same form as Eq. [155], which we transform to a form analogous to Eq. [156]:

$$\frac{d}{dt}\tilde{\rho} = -i[\tilde{\mathcal{H}}_{I\mathcal{F}}, \tilde{\rho}(0)] - \int_0^t [\tilde{\mathcal{H}}_{I\mathcal{F}}(t), [\tilde{\mathcal{H}}_{I\mathcal{F}}(t'), \tilde{\rho}(t')]] dt'. \quad [231]$$

The next steps are:

We take an ensemble average, for which the first term on the right-hand side vanishes.

We use form [160] for $\mathcal{H}_{I\mathcal{F}}$ and form [150] for ρ , with \mathcal{P} given by Eq. [151].

We go back to the Schrödinger representation for the lattice variables and to an intermediate representation (first rotating frame) for the spin variables. The corresponding unitary operator is

$$U_{\mathcal{F}}(t)U_{I_2}(t).$$

We choose t much longer than the correlation time τ_c , as a consequence of which we may replace $\tilde{\sigma}(t')$ by $\tilde{\sigma}(t)$ and we extend all integrals to infinity.

We obtain an equation whose terms have a form similar to Eq. [179],

$$\begin{aligned} \frac{d}{dt}\tilde{\sigma}(t) &= -i[\tilde{\mathcal{H}}_{\text{eff}}, \tilde{\sigma}] - \int_0^\infty [\tilde{V}(t), [\hat{V}(t, \tau), \tilde{\sigma}(t)]] \\ &\quad \times \text{Tr}_{\mathcal{F}}(\mathcal{P}\hat{F}(\tau)F) d\tau + \int_0^\infty [\tilde{V}(t), \hat{V}(t, \tau)\tilde{\sigma}(t)] \\ &\quad \times \text{Tr}_{\mathcal{F}}([\mathcal{P}, \hat{F}]F) d\tau, \end{aligned} \quad [232]$$

where \mathcal{H}_{eff} is given by Eq. [80], and

$$\begin{aligned} \hat{V}(t, \tau) &= U_{I_2}(\tau)U_{I_1}^\dagger(t-\tau)V_\beta^\dagger U_{I_1}(t-\tau)U_{I_2}^\dagger(\tau) \\ &= U_{I_2}(\tau)U_{I_1}(\tau)U_{I_1}^\dagger(t)V_\beta^\dagger U_{I_1}(t)U_{I_1}^\dagger(\tau)U_{I_2}^\dagger(\tau), \end{aligned} \quad [233]$$

that is, according to Eqs. [225] and [227],

$$\begin{aligned} \hat{V}(t, \tau) &= \exp(-i\Omega I_Z \tau) \exp(-i\omega I_z \tau) \exp(i\omega I_z t) V_\beta^\dagger \\ &\quad \times \exp(-i\omega I_z t) \exp(i\omega I_z \tau) \exp(i\Omega I_Z \tau). \end{aligned} \quad [234]$$

We use the formulations [83], [84], [88], and [89] for $\mathcal{H}_{I\mathcal{F}}$, and

we obtain, as a general expression for Eq. [232],

$$\begin{aligned} \frac{d}{dt}\tilde{\sigma}(t) &= -i[\mathcal{H}_{\text{eff}}, \tilde{\sigma}(t)] - \sum_{m,p,q} \lambda_m^p \lambda_m^{q*} \\ &\times \int_0^\infty d\tau \exp[i(m\omega + q\Omega)\tau] \\ &\times \{[V'_p, [V_q^\dagger, \tilde{\sigma}(t)]] \text{Tr}_{\mathcal{F}}(\mathcal{P} \hat{F}_m^\dagger(\tau) F_m) \\ &- [V'_p, V_q^\dagger \tilde{\sigma}(t)] \text{Tr}_{\mathcal{F}}([\mathcal{P}, \hat{F}_m^\dagger(\tau)] F_m)\}. \end{aligned} \quad [235]$$

The integral involving the first trace over \mathcal{F} , in the second term on the right-hand side, yields the quantum spectral density $J_{m,m}(m\omega + q\Omega)$. That of the third term is analyzed exactly as in Section IIIA. It yields, in complete analogy with Eqs. [187],

$$\begin{aligned} &\int_0^\infty \exp[i(m\omega + q\Omega)\tau] \text{Tr}_{\mathcal{F}}([\mathcal{P}, \hat{F}_m^\dagger(\tau)] F_m) d\tau \\ &= J_{m,m}(m\omega + q\Omega) [1 - \exp(\beta_L(m\omega + q\Omega))]. \end{aligned} \quad [236]$$

We then obtain an expression similar to Eqs. [188] and [189],

$$\begin{aligned} \frac{d}{dt}\tilde{\sigma}(t) &= -i[\mathcal{H}_{\text{eff}}, \tilde{\sigma}] - \sum_{m,p,q} \lambda_m^p \lambda_m^{q*} J_{m,m}(m\omega + q\Omega) \\ &\times \{[V'_p, [V_q^\dagger, \tilde{\sigma}(t)]] - [V'_p, V_q^\dagger \tilde{\sigma}(t)] \\ &\times [1 - \exp(\beta_L(m\omega + q\Omega))]\} \end{aligned} \quad [237]$$

$$\begin{aligned} \frac{d}{dt}\langle Q \rangle_r(t) &= \langle -i[Q, \mathcal{H}_{\text{eff}}](t) - \sum_{m,p,q} \lambda_m^p \lambda_m^{q*} J_{m,m}(m\omega + q\Omega) \\ &\times \{([Q, V'_p], V_q^\dagger)(t) - \langle [Q, V'_p] V_q^\dagger \rangle(t) \\ &\times [1 - \exp(\beta_L(m\omega + q\Omega))]\}. \end{aligned} \quad [238]$$

In the high-temperature approximation, they reduce to

$$\begin{aligned} \frac{d}{dt}\tilde{\sigma}(t) &= -i[\mathcal{H}_{\text{eff}}, \tilde{\sigma}] - \sum_{m,p,q} \lambda_m^p \lambda_m^{q*} J_{m,m}(m\omega + q\Omega) \\ &\times \{[V'_p, [V_q^\dagger, \tilde{\sigma}(t)]] + [V'_p, V_q^\dagger] \beta_L(m\omega + q\Omega)\} \end{aligned} \quad [239]$$

$$\begin{aligned} \langle Q \rangle_r(t) &= \langle -i[Q, \tilde{\mathcal{H}}_{\text{eff}}](t) - \sum_{m,p,q} \lambda_m^p \lambda_m^{q*} J_{m,m}(m\omega + q\Omega) \\ &\times \{([Q, V'_p], V_q^\dagger)(t) \\ &+ \text{Tr}(Q[V'_p, V_q^\dagger]) \beta_L(m\omega + q\Omega)\}. \end{aligned} \quad [240]$$

These equations are well defined and solve entirely the problem. However, one might try to express Eq. [239] under a form similar to Eq. [200]. There is a fundamental difference between the present case and that of a static spin Hamiltonian analyzed in Section IIB. There, the time evolution of all operators $\hat{V}_\beta^\dagger(\tau)$ is due to the static spin Hamiltonian \mathcal{H}_I (Eq. [163]) and the form

of σ_{eq} is then given by Eq. [193]. When the spin Hamiltonian is time dependent, the various operators $\hat{V}_q^\dagger(t, \tau)$ will have a dependence on τ produced by several operators (Eq. [234]), and the relative dependence on these will not be the same for different operators V_q^\dagger . In order to obtain an expression resembling Eq. [200], one must therefore *invent* a fictitious Hamiltonian $\mathcal{H}_I(m, q)$, tailored so as to yield

$$\hat{V}_q^\dagger(\tau) = \exp[-i\mathcal{H}_I(m, q)\tau] V_q^\dagger \exp[i\mathcal{H}_I(m, q)\tau]. \quad [241]$$

Following the same treatment as from Eqs. [190] to [199], we are led to express Eq. [239] under the form

$$\begin{aligned} \frac{d}{dt}\tilde{\sigma}(t) &= -i[\tilde{\mathcal{H}}_{\text{eff}}, \tilde{\sigma}(t)] - \sum_{m,p,q} \lambda_m^p \lambda_m^{q*} J_{m,m}(m\omega + q\Omega) \\ &\times [V'_p, [V_q^\dagger, (\tilde{\sigma}(t) - \sigma_0(m, q))]], \end{aligned} \quad [242]$$

with

$$\sigma_0(m, q) = 1 - \beta_L \mathcal{H}_I(m, q). \quad [243]$$

Different terms V_q^\dagger require *a priori* different pseudo-Hamiltonians $\mathcal{H}_I(m, q)$, to which there corresponds different “equilibrium” density matrices.

There is still another point. In the absence of a static spin Hamiltonian, there is no “natural” choice of spin components of \mathcal{H}_I . Instead of using V'_p, V'_q , one might as well have expressed them as a function of the initial V_m . Using the latter would lead to “equilibrium,” density matrices $\sigma_0(m)$ different from the $\sigma_0(m, q)$. Then, there is no single limit for the evolution of σ (or $\tilde{\sigma}$) under the effect of relaxation. This of course should make no difference for the steady-state limit of observable physical quantities. Under these conditions, there is little interest in sticking to form [242]: Equations [237]–[240] are just as good and simpler. The various points raised above are illustrated in Section IIIB3.*.

2. Nuclear Relaxation by a Paramagnetic Center: Simplified Treatment

We are now in a position to justify the phenomenological treatment given in Section IIB1, and to its approximations. The conditions correspond to high temperature and effective frequency Ω much smaller than the Larmor frequency ω_0 . We limit ourselves to a short qualitative discussion.

Let us first consider the terms in B, B^* of Eq. [97]. Through the unitary transformation [234], they yield a dependence on τ of the form

$$\exp[i(m\omega + q\Omega)\tau],$$

with $m = \pm 1$ and $q = 0, \pm 1$.

For the relaxation part of $\tilde{\sigma}(t)$ (Eq. [242]), they yield spectral densities,

$$J(m\omega + q\Omega) \simeq J(m\omega), \quad [244]$$

as a result of the smallness of Ω , as noted in Section IIB1-1. These terms also give rise to “equilibrium” density matrices,

$$\sigma_0(m, q) = 1 - \beta_L(m\omega + q\Omega)I_Z \simeq 1 - \beta_L(m\omega)I_Z, \quad [245]$$

for the same reason.

Since we may neglect Ω in both the J and the σ_0 , the result will be the same as if the system had been subjected to a static spin Hamiltonian:

$$\omega I_Z \simeq \omega_0 I_Z. \quad [246]$$

In that case, there is no point in using operators I_z, I'_\pm for the terms in B, B^* . Their effect can be calculated with I_\pm , as in Section IIB1.

As for the terms in AI'_\pm , they give rise to terms in $\exp(\pm i\Omega\tau)$, as inferred from Eq. [109]. The corresponding matrices σ_0 will be of the form

$$\sigma_0 = 1 \pm \beta_L \Omega I_Z, \quad [247]$$

and they correspond to steady-state limits negligibly small compared with those arising from the $\sigma_0(m, q)$ of Eq. [245].

These brief comments are sufficient to justify the approximations made in Section IIB1. The same approximations apply to any practical situation involving off-resonance irradiation.

3. *Nuclear Relaxation by a Paramagnetic Center: Complete Discussion

We consider the same system as above, we still keep the high-temperature approximation, but we lift the preceding constraint on the relative magnitudes of Ω and ω_0 . We consider explicitly the case of a rotating field. With a linearly polarized field which is not small compared to the static field part, one cannot discard one of its rotating components, and the problem becomes seriously complicated. Although of limited usefulness in existing experimental situations, the present discussion is included with the purpose of clarifying through a specific example the main points raised in Section IIIB1.

Let us come back to the spin–lattice coupling [97]. In Section IIB1, the electronic spin component $S_z(t)$ was considered a random variable of vanishing average value. In this section, we must use it as a static operator, whose evolution is produced by the lattice. In the present approach, the “lattice” \mathcal{F} consists of the sum of the electronic Zeeman interaction, the orbital interactions (for instance the phonons), and the coupling of the electronic spin with the latter. Thanks to its orbital part, its spectrum is quasi-continuous. The spin–lattice coupling can

still be written under the form [97], but with

$$S_z(t) = \exp(i\mathcal{F}t)S_z \exp(-i\mathcal{F}t).$$

It would have been possible to make a different separation: use as \mathcal{H}_I the Zeeman interactions of the spins I and S plus the $I-S$ dipolar coupling, as \mathcal{F} the orbital interactions, and as $\mathcal{H}_{I\mathcal{F}}$ the coupling between the electronic spin and the orbital degrees of freedom. For actual relaxation calculations at low temperature, the latter choice might prove more convenient. Of course, both choices should yield the same result for the relaxation of the spin I . This comparison will not be analyzed here.

The calculation will be made successively with spin operators in $\mathcal{H}_{I\mathcal{F}}$ adapted to the axes $OXYZ$ of the tilted frame and adapted to the axes $Oxyz$ of the first rotating frame.

Axes OXYZ. We start from the spin–lattice coupling $\tilde{\mathcal{H}}_{I\mathcal{F}}(t)$ in the first rotating frame (Eq. [99]). With the help of Eq. [103] we write the spin operators in terms of I_Z and $I'_\pm = I_X \pm iI_Y$. We obtain

$$\begin{aligned} \tilde{\mathcal{H}}_{I\mathcal{F}}(t) = S_z(t) & \left\{ A \left[cI_Z - \frac{s}{2}(I'_+ + I'_-) \right] + B \exp(i\omega t) \right. \\ & \times \left[sI_Z + \frac{1+c}{2}I'_+ - \frac{1-c}{2}I'_- \right] + B^* \exp(-i\omega t) \\ & \left. \times \left[sI_Z + \frac{1+c}{2}I'_- - \frac{1-c}{2}I'_+ \right] \right\}. \quad [248] \end{aligned}$$

From Eq. [234], we obtain for $\hat{\mathcal{H}}_{I\mathcal{F}}(t, \tau)$

$$\begin{aligned} \hat{\mathcal{H}}_{I\mathcal{F}}(t, \tau) & = S_z(t) \left\{ A \left[cI_Z - \frac{s}{2} \exp(-i\Omega\tau)I'_+ - \frac{s}{2} \exp(i\Omega\tau)I'_- \right] \right. \\ & + B \exp(i\omega t) \left[\exp(-i\omega\tau)sI_Z + \frac{1+c}{2} \right. \\ & \times \exp(-i(\omega + \Omega)\tau)I'_+ - \frac{1-c}{2} \exp(-i(\omega - \Omega)\tau)I'_- \left. \right] \\ & + B^* \exp(-i\omega t) \left[\exp(i\omega\tau)sI_Z + \frac{1+c}{2} \exp(i(\omega + \Omega)\tau)I'_- \right. \\ & \left. \left. - \frac{1-c}{2} \exp(i(\omega - \Omega)\tau)I'_+ \right] \right\}. \quad [249] \end{aligned}$$

We can use these expressions in Eq. [239], where we discard terms oscillating at $m\omega$. As a consequence, terms V'_p from Eq. [248] are coupled with terms V'_q from Eq. [249] so as to yield products A^2 or BB^* . The result is then of the form

$$\frac{d}{dt} \tilde{\sigma}(t) = -i\Omega[I_Z, \tilde{\sigma}(t)] - A^2\lambda - BB^*\mu. \quad [250]$$

We do not detail the corresponding lengthy calculation. We look

instead at the characteristics of the form [242]. We note that we can write Eq. [249] under the form

$$\begin{aligned} \hat{\mathcal{H}}_{IF}(t, \tau) = S_z(t) & \left\{ A \exp(-i\Omega I_Z \tau) \left[c I_Z - \frac{s}{2}(I'_+ + I'_-) \right] \right. \\ & \times \exp(i\Omega I_Z \tau) + [B \exp(i\omega(t - \tau)) \\ & + B^* \exp(-i\omega(t - \tau))] s I_Z + B \exp(i\omega t) \frac{1+c}{2} \\ & \times \exp(-i(\omega + \Omega) I_Z \tau) I'_+ \exp(i(\omega + \Omega) I_Z \tau) + \text{h.c.} \\ & - B \exp(i\omega t) \frac{1-c}{2} \exp(i(\omega - \Omega) I_Z \tau) I'_- \\ & \left. \times \exp(-i(\omega - \Omega) I_Z \tau) + \text{h.c.} \right\}. \end{aligned} \quad [251]$$

By comparison with Eqs. [241]–[243], these terms yield contributions to $d\tilde{\sigma}/dt$ of the following forms:

the part in I'_\pm of first term on the right-hand side of Eq. [251]:

$$-A^2 J(\Omega) [\dots, [\dots, (\tilde{\sigma}(t) - \sigma_0(\Omega))]],$$

The third term and its Hermitian conjugate:

$$-BB^* \left(\frac{1+c}{2} \right)^2 J(\omega + \Omega) [\dots, [\dots, (\tilde{\sigma}(t) - \sigma_0(\omega + \Omega))]],$$

The fifth term and its Hermitian conjugate:

$$-BB^* \left(\frac{1-c}{2} \right)^2 J(\omega - \Omega) [\dots, [\dots, (\tilde{\sigma}(t) - \sigma_0(-\omega + \Omega))]],$$

with the notation

$$\sigma_0(\omega) = 1 - \beta_L \omega I_Z, \quad [252]$$

which illustrates the fact that different terms of the spin–lattice coupling lead to different limits σ_0 .

The second term needs special attention. The part $\exp(-i\omega\tau)I_Z$ can be written

$$\exp(-i\omega\tau)I_Z = \exp(-i\omega\tau) \times \frac{1}{2} [(I_Z + iI_Y) + (I_Z - iI_Y)] \quad [253]$$

or else

$$\begin{aligned} \exp(-i\omega\tau)I_Z = \frac{1}{2} & \{ \exp(i\omega\tau I_X)(I_Z + iI_Y) \exp(-i\omega\tau I_X) \\ & + \exp(-i\omega\tau I_X)(I_Z - iI_Y) \exp(i\omega\tau I_X) \}. \end{aligned} \quad [254]$$

Its contribution to $d\tilde{\sigma}/dt$ is then of the form

$$\begin{aligned} \mathcal{C}_1 \propto -\frac{s}{2} J(\omega) & \{ [B^* \dots, [B(I_Z + iI_Y), (\tilde{\sigma}(t) - \beta_L \omega I_X)]] \\ & + [B \dots, [B^*(I_Z - iI_Y), (\tilde{\sigma}(t) + \beta_L \omega I_X)]] \}, \end{aligned} \quad [255]$$

whereas the part $\exp(+i\omega\tau)I_Z$ can be written

$$\begin{aligned} \exp(i\omega\tau)I_Z = \frac{1}{2} & \{ \exp(-i\omega\tau I_X)(I_Z + iI_Y) \exp(i\omega\tau I_X) \\ & + \exp(i\omega\tau I_X)(I_Z - iI_Y) \exp(-i\omega\tau I_X) \}. \end{aligned} \quad [256]$$

Its contribution to $d\tilde{\sigma}/dt$ is of the form

$$\begin{aligned} \mathcal{C}_2 \propto -\frac{s}{2} J(\omega) & \{ [B \dots, [B^*(I_Z + iI_Y), (\tilde{\sigma}(t) + \beta_L \omega I_X)]] \\ & + [B \dots, [B^*(I_Z - iI_Y), (\tilde{\sigma}(t) - \beta_L \omega I_X)]] \}. \end{aligned} \quad [257]$$

One might think at first sight that the terms in σ_0 would cancel out in the sum $\mathcal{C}_1 + \mathcal{C}_2$. This is not so because the first terms in the double commutator originate from $\tilde{\mathcal{H}}_{IF}(t)$, and those proportional to B are not the same as those proportional to B^* .

One may also remark that, say, $\exp(-i\omega\tau)I_Z$ could be written at variance with Eq. [254], as follows,

$$\begin{aligned} \exp(-i\omega\tau)I_Z & \\ = \frac{1}{2} & \{ \exp(-i\omega\tau I_Y)(I_Z + iI_X) \exp(i\omega\tau I_Y) \\ & + \exp(i\omega\tau I_Y)(I_Z - iI_X) \exp(-i\omega\tau I_Y) \}, \end{aligned} \quad [258]$$

and a similar expression for $\exp(i\omega\tau)I_Z$. All these forms are correct and they must yield the same result for the evolution of a physical quantity $\langle Q \rangle$. It turns out to be much more convenient to use the formal Eq. [240]. If in the trace on its right-hand side the operator V_q^\dagger is I_Z , the only operators Q and V_p' for which the trace does not vanish are I'_+ and I'_- , in any order. Let us choose $Q = I'_+$ and $V_p' = I'_-$. The contribution of these terms to the relaxation limit of $\langle I'_+ \rangle$ is proportional to

$$\begin{aligned} -s J(\omega) B B^* \text{Tr}[(I'_+, I'_-) I_Z] & \left\{ \left(\frac{1+c}{2} \times -\beta_L \omega \right) \right. \\ & \left. - \left(\frac{1-c}{2} \times \beta_L \omega \right) \right\} = +\frac{s}{2} J(\omega) B B^* \times \beta_L \omega. \end{aligned} \quad [259]$$

We consider now explicitly the evolution equation for $\langle I_Z \rangle$. Its calculation is trivial and we will give only its result. We introduce the (arbitrary) expectation value,

$$I_0 = \text{Tr}[I_Z \sigma_0(\omega_0)] = -\beta_L \omega_0 \text{Tr}(I_Z^2), \quad [260]$$

and we obtain, ignoring cross-relaxation,

$$\begin{aligned} \frac{d}{dt}\langle I_Z \rangle(t) = & -\frac{1}{3}S(S+1) \left\{ A^2 s^2 J(\Omega) \left(\langle I_Z \rangle(t) - \frac{\Omega}{\omega_0} I_0 \right) \right. \\ & + BB^*(1+c^2)J(\omega+\Omega) \left(\langle I_Z \rangle(t) - \frac{\omega+\Omega}{\omega_0} I_0 \right) \\ & \left. + BB^*(1-c^2)J(\omega-\Omega) \left(\langle I_Z \rangle(t) + \frac{\omega-\Omega}{\omega_0} I_0 \right) \right\}. \end{aligned} \quad [261]$$

In the case treated above, when $\Omega \ll \omega_0$, that is also $\omega \simeq \omega_0$, we obtain a result identical to Eq. [114], where the term in $\langle I_X \rangle$ is ignored.

Axes Oxyz. We keep for $\tilde{\mathcal{H}}_{IF}(t)$ the form [99]. For $\mathcal{H}_{IF}(t; \tau)$ we start from Eq. [249] and express the operators I_Z, I'_\pm in terms of I_z, I_\pm . We have, from Eq. [104],

$$\begin{cases} I_Z = cI_z + \frac{s}{2}(I_+ + I_-) \\ I'_+ = -sI_z + \frac{1+c}{2}I_+ - \frac{1-c}{2}I_- \\ I'_- = -sI_z - \frac{1-c}{2}I_+ + \frac{1+c}{2}I_- \end{cases} \quad [262]$$

We insert these expressions into Eq. [249] and we obtain

$$\begin{aligned} & \tilde{\mathcal{H}}_{IF}(t, \tau) \\ & = S_z(t) \times \left\{ A \left[(c^2 + s^2 \cos \Omega \tau) I_z + \left[\frac{cs}{2} - \frac{s}{4}(1+c) \right] \right. \right. \\ & \quad \times \exp(-i\Omega \tau) + \left. \left. \frac{s}{4}(1-c) \exp(i\Omega \tau) \right] I_+ \right. \\ & \quad + \left[\frac{cs}{2} + \frac{s}{4}(1-c) \exp(-i\Omega \tau) \right. \\ & \quad \left. \left. - \frac{s}{4}(1+c) \exp(i\Omega \tau) \right] I_- \right\} + B \exp(i\omega t) \\ & \quad \times \left[\left[sc \exp(-i\omega \tau) - \frac{s}{2}(1+c) \exp(-i(\omega+\Omega)\tau) \right. \right. \\ & \quad + \left. \left. \frac{s}{2}(1-c) \exp(-i(\omega-\Omega)\tau) \right] I_z + \left[\frac{s^2}{2} \exp(-i\omega \tau) \right. \right. \\ & \quad + \left. \left. \left(\frac{1+c}{2} \right)^2 \exp(-i(\omega+\Omega)\tau) + \left(\frac{1-c}{2} \right)^2 \right. \right. \\ & \quad \times \exp(-i(\omega-\Omega)\tau) \left. \right] I_+ + \left[\frac{s^2}{2} \exp(-i\omega \tau) - \frac{1-c^2}{4} \right. \\ & \quad \times \exp(-i(\omega+\Omega)\tau) - \left. \left. \frac{1-c^2}{4} \exp(-i(\omega-\Omega)\tau) \right] I_- \right. \\ & \quad \left. + B^* \exp(-i\omega t) \left[\left[sc \exp(i\omega \tau) \right. \right. \right. \end{aligned}$$

$$\begin{aligned} & \left. - \frac{s}{2}(1+c) \exp(i(\omega+\Omega)\tau) \right. \\ & \left. + \frac{s}{2}(1-c) \exp(i(\omega-\Omega)\tau) \right] I_z \\ & \quad + \left[\frac{s^2}{2} \exp(i\omega \tau) + \left(\frac{1+c}{2} \right)^2 \right. \\ & \quad \times \exp(i(\omega+\Omega)\tau) + \left. \left(\frac{1-c}{2} \right)^2 \exp(i(\omega-\Omega)\tau) \right] I_- \\ & \quad + \left[\frac{s^2}{2} \exp(i\omega \tau) - \frac{1-c^2}{4} \exp(i(\omega+\Omega)\tau) \right. \\ & \quad \left. - \frac{1-c^2}{4} \exp(i(\omega-\Omega)\tau) \right] I_+ \left. \right\}. \end{aligned} \quad [263]$$

We have written *in extenso* this formidable expression (for the simplest possible system), but we use it only for a qualitative discussion.

By simple inspection of the functions of τ , it is immediately evident that if we use for the derivative of $\tilde{\sigma}$ a form similar to Eq. [242], the terms σ_0 corresponding to Eq. [243] will not all be equal and furthermore they will be very different from those arising in the preceding section.

There are several lessons to be learned from this analysis, as to the contrast between a time-independent and a time-dependent spin Hamiltonian. As regards the latter,

(1) There are no privileged axes adapted to the development of the spin-lattice coupling. The best choice is that which makes the calculation easiest. In the general case analyzed in this section, there is a definite preferences for the axes OXYZ. In the limit when the approximations made in Section IIIB2 are valid, it even turned out that the most convenient was to use different axes for treating the terms in A and those in B, B*.

(2) The density matrix $\tilde{\sigma}(t)$ does not evolve toward a single limit: there are different σ_0 for the different spin terms of the spin-lattice coupling, which depend furthermore on the choice of its expansion. This deprives that kind of presentation of the relaxation equations from much of its “enlightening” interest.

(3) The pedestrian use of the direct expression [237] (or its equivalent Eq. [238]) is both devoid of ambiguity, in general much simpler than Eq. [242], and furthermore valid at all temperatures, whereas Eq. [242] is valid only at high temperature.

These conclusion will show up even more clearly in the next section.

4. *The General Problem of a Time-Dependent Spin Hamiltonian

This section is included for completeness. It refers to a physical situation which does not seem relevant to experimental investigation at present. However, it might be used for problems not involving spins, but whose formulation could be made so as to

formally mimic a spin problem. Furthermore, its very generality provides an overview of the problem of relaxation.

We consider a spin system whose spin Hamiltonian undergoes an arbitrary time variation. The canonical example is that of a Zeeman interaction with a field varying both in orientation and in magnitude. All we request is that its spectrum at all times consists of discrete and energy-split levels. In the case when part of the spectrum is quasi-continuous, as in solids with dipolar interactions, the width of this part should be small compared to the large splittings, so as to allow the kind of treatment used in Section IIA6.

The initial development repeats that of the beginning of Section III. We begin with the Liouville–von Neumann equation [148], where the Hamiltonian \mathcal{H}_0 (Eq. [149]) is the sum of a fixed lattice part and a time-dependent spin part $\mathcal{H}_I(t)$. The interaction representation in which the evolution of the density matrix $\tilde{\rho}$ depends only on the spin–lattice coupling is defined by the replacement of all operators Q by

$$Q \rightarrow \tilde{Q}(t) = U^\dagger(t)QU(t), \quad [264]$$

with

$$\begin{cases} \frac{d}{dt}U(t) = -i(\mathcal{H}_I(t) + \mathcal{F})U(t) \\ \frac{d}{dt}U^\dagger(t) = iU^\dagger(t)(\mathcal{H}_I(t) + \mathcal{F}). \end{cases} \quad [265]$$

We have indeed

$$\begin{aligned} \frac{d}{dt}\tilde{\rho}(t) &= \left(\frac{d}{dt}U^\dagger(t)\right)\rho(t)U(t) + U^\dagger(t)\left(\frac{d}{dt}\rho(t)\right)U(t) \\ &\quad + U^\dagger(t)\rho(t)\left(\frac{d}{dt}U(t)\right) \\ &= iU^\dagger(\mathcal{H}_I + \mathcal{F})\rho U - iU^\dagger[(\mathcal{H}_I + \mathcal{F} + \mathcal{H}_{I\mathcal{F}}), \rho]U \\ &\quad - iU^\dagger\rho(\mathcal{H}_I + \mathcal{F})U \\ &= -iU^\dagger[(\mathcal{H}_I + \mathcal{F} + \mathcal{H}_{I\mathcal{F}} - \mathcal{H}_I - \mathcal{F}), \rho]U \\ &= -i[\tilde{\mathcal{H}}_{I\mathcal{F}}(t), \tilde{\rho}(t)]. \end{aligned} \quad [266]$$

Through formal integration and ensemble average, we obtain an equation similar to [156], without the first term on the right-hand side:

$$\frac{d}{dt}\tilde{\rho}(t) = -\int_0^t [\tilde{\mathcal{H}}_{I\mathcal{F}}(t), [\tilde{\mathcal{H}}_{I\mathcal{F}}(t-\tau), \tilde{\rho}(t-\tau)]] d\tau. \quad [267]$$

We choose the time t much longer than the lattice correlation time, which makes it possible to replace $\tilde{\rho}(t-\tau)$ by $\tilde{\rho}(t)$; we go back to the Schrödinger representations and extend the integral to infinity, in accordance with the procedure of IIA1 and IIIA,

IIIB1, and IIIB2. We obtain the by now familiar expression

$$\begin{aligned} \frac{d}{dt}\rho(t) &= -i[\mathcal{H}_0, \rho(t)] \\ &\quad - \int_0^\infty [\mathcal{H}_{I\mathcal{F}}, [\hat{\mathcal{H}}_{I\mathcal{F}}(t; \tau), \rho(t)]] d\tau, \end{aligned} \quad [268]$$

where

$$\begin{aligned} \hat{\mathcal{H}}_{I\mathcal{F}}(t; \tau) &= U(t)\tilde{\mathcal{H}}_{I\mathcal{F}}(t-\tau)U^\dagger(t) \\ &= U(t)U^\dagger(t-\tau)\mathcal{H}_{I\mathcal{F}}U(t-\tau)U^\dagger(t). \end{aligned} \quad [269]$$

For a general time-dependent Hamiltonian \mathcal{H}_I , the expression of U and U^\dagger is not so simple as in the preceding sections. We have, however, in full generality,

$$U(t) = U(t; t-\tau)U(t-\tau), \quad [270]$$

where $U(t; t-\tau)$ is still defined by Eq. [265] with the initial condition

$$U(t-\tau; t-\tau) = 1, \quad [271]$$

that is

$$U(t; t-\tau) = T \exp\left(-i \int_{t-\tau}^t \mathcal{H}_0(t') dt'\right), \quad [272]$$

where T is the Dyson chronological operator.

Another general property is that

$$U(t-\tau)U^\dagger(t-\tau) = 1, \quad [273]$$

whence, according to Eq. [269],

$$\hat{\mathcal{H}}_{I\mathcal{F}}(t; \tau) = U(t; t-\tau)\mathcal{H}_{I\mathcal{F}}U^\dagger(t; t-\tau). \quad [274]$$

Next, we expand $\mathcal{H}_{I\mathcal{F}}$ under the same form as [160]. However, the various spin operators V_α can no longer have a definite relationship with the time-dependent spin Hamiltonian $\mathcal{H}_I(t)$. They have to be chosen with reference to the physical quantities one wants to observe.

Since $\mathcal{H}_0 = \mathcal{H}_I + \mathcal{F}$ is a sum of two commuting operators, Eq. [272] can be written

$$U(t; t-\tau) = U_I(t; t-\tau)U_{\mathcal{F}}(\tau), \quad [275]$$

with

$$U_I(t; t-\tau) = T \exp\left(-i \int_{t-\tau}^t \mathcal{H}_I(t') dt'\right) \quad [276]$$

$$U_{\mathcal{F}}(\tau) = \exp(-i\mathcal{F}\tau), \quad [277]$$

and Eq. [274] becomes

$$\begin{aligned}\hat{\mathcal{H}}_{I\mathcal{F}}(t; \tau) &= \sum_{\alpha} \hat{V}_{\alpha}(t; \tau) \hat{F}_{\alpha}(\tau) \\ &= \sum_{\alpha} [U_I(t; t - \tau) V_{\alpha} U_I^{\dagger}(t; t - \tau)] \\ &\quad \times [U_{\mathcal{F}}(\tau) F_{\alpha} U_{\mathcal{F}}^{\dagger}(\tau)].\end{aligned}\quad [278]$$

We use Eqs. [150] and [168] and we obtain for the spin density matrix an expression of the same form as Eq. [179],

$$\begin{aligned}\frac{d}{dt}\sigma(t) &= -i[\mathcal{H}_I(t), \sigma(t)] \\ &\quad - \int_0^{\infty} \sum_{\alpha, \beta} \{ [V_{\alpha}, [\hat{V}_{\beta}^{\dagger}(t; \tau), \sigma(t)]] \\ &\quad \times \text{Tr}_{\mathcal{F}}(\mathcal{P} \hat{F}_{\beta}^{\dagger}(\tau) F_{\alpha}) - [V_{\alpha}, \hat{V}_{\beta}^{\dagger}(t; \tau) \sigma(t)] \\ &\quad \times \text{Tr}_{\mathcal{F}}([\mathcal{P}, \hat{F}_{\beta}^{\dagger}(\tau)] F_{\alpha}) d\tau \}.\end{aligned}\quad [279]$$

Since in the present case the evolution of $\hat{V}_{\beta}^{\dagger}(t; \tau)$ is more complicated than Eq. [163], we cannot directly jump to Eqs. [188] and [189]. We do the following.

We consider a complete set of spin operators V_{α} , all of which may not be present in $\mathcal{H}_{I\mathcal{F}}$. We may then write

$$\hat{V}_{\beta}^{\dagger}(t; \tau) = \sum_{\delta} f_{\beta}^{\delta}(t; \tau) V_{\delta}^{\dagger}, \quad [280]$$

which is no more than an expansion of $\hat{V}_{\beta}^{\dagger}$ over the complete set.

Next, we Fourier-analyze the functions f with respect to τ :

$$f_{\beta}^{\delta}(t; \tau) = \int_{-\infty}^{+\infty} \lambda_{\beta}^{\delta}(t; \omega) \exp(i\omega\tau) d\omega. \quad [281]$$

In complete analogy with the passage from Eq. [179] to Eq. [188] we obtain

$$\begin{aligned}\frac{d}{dt}\sigma(t) &= -i[\mathcal{H}_I(t), \sigma(t)] - \sum_{\alpha, \beta, \delta} \int_{-\infty}^{+\infty} \lambda_{\beta}^{\delta}(t; \omega) J_{\alpha\beta}(\omega) d\omega \\ &\quad \times \{ [V_{\alpha}, [V_{\delta}^{\dagger}, \sigma(t)]] - [V_{\alpha}, V_{\delta}^{\dagger} \sigma(t)] (1 - \exp(\beta_L \omega)) \}.\end{aligned}\quad [282]$$

The expectation value of an operator Q evolves according to

$$\begin{aligned}\frac{d}{dt}\langle Q \rangle(t) &= \langle -i[Q, \mathcal{H}_I(t)] \rangle(t) - \sum_{\alpha, \beta, \delta} \int_{-\infty}^{+\infty} \lambda_{\beta}^{\delta}(t; \omega) J_{\alpha\beta}(\omega) d\omega \\ &\quad \times \{ \langle [[Q, V_{\alpha}], V_{\delta}^{\dagger}] \rangle(t) \\ &\quad - \langle [Q, V_{\alpha}] V_{\delta}^{\dagger} \rangle(t) (1 - \exp(\beta_L \omega)) \}.\end{aligned}\quad [283]$$

It is also possible, through a simple algebraic manipulation, to write

$$\begin{aligned}\frac{d}{dt}\langle Q \rangle(t) &= \langle -i[Q, \mathcal{H}_I(t)] \rangle(t) - \sum_{\alpha, \beta, \delta} \int_{-\infty}^{+\infty} \frac{1}{2} \lambda_{\beta}^{\delta}(t; \omega) J_{\alpha\beta}(\omega) \\ &\quad \times (\exp(\beta_L \omega) + 1) d\omega \left\{ \langle [[Q, V_{\alpha}], V_{\delta}^{\dagger}] \rangle(t) + \tanh\left(\frac{\beta_L \omega}{2}\right) \right. \\ &\quad \left. \times \langle [[Q, V_{\alpha}], V_{\delta}^{\dagger}(t)] \rangle(t) \right\},\end{aligned}\quad [284]$$

where the symbol $\{ \dots \}$ has the usual meaning of an anti-commutator:

$$\{A, B\} = AB + BA. \quad [285]$$

In the high-temperature limit, it is possible, through the same procedure as for Eqs. [241]–[243], to replace in Eq. [282] $\sigma(t)$ by $\sigma(t) - \sigma_0$, but there would be a continuous distribution of matrices σ_0 , and this would be even less informative than in the case of a rotating field.

There is one exception, when the spin Hamiltonian $\mathcal{H}_I(t)$ varies very little on the time scale τ_c . Equation [278] would then read

$$\begin{aligned}\hat{\mathcal{H}}_{I\mathcal{F}}(t; \tau) &\simeq \sum_{\alpha} [\exp(-i\mathcal{H}_I(t)\tau) V_{\alpha} \exp(i\mathcal{H}_I(t)\tau)] \\ &\quad \times [\exp(-i\mathcal{F}\tau) F_{\alpha} \exp(i\mathcal{F}\tau)],\end{aligned}\quad [286]$$

and Eq. [279] could be written under the form

$$\begin{aligned}\frac{d}{dt}\sigma(t) &\simeq -i[\mathcal{H}_I(t), \sigma(t)] - \text{Tr}_{\mathcal{F}} \int_0^{\infty} [\mathcal{H}_{I\mathcal{F}}, \\ &\quad [\hat{\mathcal{H}}_{I\mathcal{F}}(t; \tau), (\sigma(t) - \sigma_{\text{eq}}(t))] d\tau,\end{aligned}\quad [287]$$

where

$$\sigma_{\text{eq}}(t) = 1 - \beta_L \mathcal{H}_I(t). \quad [288]$$

This corresponds to a relaxation of the density matrix toward its instantaneous equilibrium value. It happens only in a very special case.

In the general case, Eq. [283] or [284] provides a complete solution of the relaxation problem, valid whatever the variation of the spin Hamiltonian and whatever the lattice temperature. For a given spin Hamiltonian $\mathcal{H}_I(t)$, they can be solved by computer provided that a model is available for the spectral densities.

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