A QUANTUM-STATISTICAL THEORY OF CROSS RELAXATION

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A system of equations describing cross relaxation in spin systems is derived from the quantum mechanical equation for the density matrix. These equations differ from those derived from qualitative considerations by Bloembergen et al[1] in that they contain additional terms due to a consistent account of the change in the mean dipole-dipole interaction energy during the cross-relaxation process.

SINCE the publication[1] of the first thorough treatment of the phenomenon of cross relaxation, there have appeared many papers on the same subject ([2-4] etc). In all of these papers the theoretical analysis was based on an equation obtained in [1] from qualitative considerations.

Our goal in this paper is the derivation of a more accurate set of equations directly from the general quantum-mechanical equation for the density matrix. For the sake of simplicity we consider a spin system having only two kinds of magnetic moments of almost the same magnitude. However, all conclusions are easily generalized to the case of a large number of different magnetic moments in the spin system or to the case where cross relaxation is associated with transitions between different hyperfine structure levels.

The equation for the density matrix of a spin system consisting of two kinds of magnetic moments under conditions of magnetic resonance has the form (the high-frequency field is assumed adjusted to resonance with the magnetic moments of the first kind)

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}\left[\hat{H} + \hat{F} + \sum_{m=-2}^{2}\hat{H}_{dip}^{m}\right.$$
$$\left. + \frac{\mu_1 H_1}{2I}(\hat{I}^1 e^{i\omega t} + \hat{I}^{-1}e^{-i\omega t}) + G, \rho\right]. \quad (1)$$

Here $\hat{F}$ is the Hamiltonian of the lattice, $\hat{H} = -\mu_1 H_0 \hat{I}_z/I - \mu_2 H_0 \hat{S}_z/S + \bar{H}_{dip}$, $\hat{I}_x$, $\hat{I}_y$, $\hat{I}_z$ and $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$ are the projection operators of the total spin of the particles of the first and second sort, $\hat{I}^{\pm 1} = \hat{I}_x \pm i\hat{I}_y$, $\hat{S}^{\pm 1} = \hat{S}_x \pm i\hat{S}_y$, μ_1, I, and μ_2, S are the magnetic moments and spins of the particles of the first and second sort, respectively, H_0 is the constant magnetic field, ω and H_1 are the frequency and amplitude of the high-frequency field,

$$\hat{G} = \sum_{n=\pm 1}\sum_{\alpha=1}^{2}\hat{F}^{n\alpha}\hat{R}^{n\alpha}$$

is the spin-lattice interaction operator, $\hat{F}^{n\alpha}$ are operators acting only on the spin variables of the particles of sort α and having non-zero matrix elements only for transitions in which $\hat{I}_z$ or $\hat{S}_z$ change by n units, $\hat{R}^{n\alpha}$ are operators acting only on the lattice variables,

$$\bar{H}_{dip} = \hat{H}_{1dip}^0 + \hat{H}_{2dip}^0 + \sum_{i>k}\beta_{ik}\hat{I}_{iz}\hat{S}_{kz}$$

is the part of the dipole-dipole interaction operator that commutes with $\hat{I}_z$ and $\hat{S}_z$ simultaneously, $\hat{H}_{1dip}^0$ and $\hat{H}_{2dip}^0$ are the usual secular parts of the dipole-dipole interaction between particles all of the first or second sort, respectively, $\hat{I}_{ix}$, $\hat{I}_{iy}$, $\hat{I}_{iz}$ and $\hat{S}_{kx}$, $\hat{S}_{ky}$, $\hat{S}_{kz}$ are the projection operators of the individual spins located respectively on the i-th and k-th points of the crystalline lattice and belonging to particles of the first and second sort, respectively.

We can write

$$\hat{H}_{dip}^0 = \hat{H}_{dip}^{0+} + \hat{H}_{dip}^{0-}; \quad \hat{H}_{dip}^{0+} = \sum_{i>k}\alpha_{ik}\hat{I}_i^1\hat{S}_k^{-1},$$
$$\hat{H}_{dip}^{0-} = \sum_{i>k}\alpha_{ik}\hat{I}_i^{-1}\hat{S}_k^1;$$

$\hat{H}_{dip}^0$ being the part of the dipole-dipole interaction operator leading to the cross relaxation effect (we consider here the case in which the magnetic moments of the both particle sorts have the same value; in this case, as is known,[1] the quantity $I_z + S_z$ is conserved during the cross relaxation process). The remaining terms of the type $\hat{H}_{dip}^m$ with m ≠ 0 (the indices m indicate that the operator has matrix elements different from zero only for transitions in which the magnitude of $I_z + S_z$ changes by m units) will lead only to a direct ex-

change of energy between the Zeeman energy and the dipole-dipole interaction energy $\overline{H}_{dip}$.

Transforming Eq. (1) to the interaction representation

$$\rho = \exp\left[-\frac{i}{\hbar}(\hat{H}+\hat{F})t\right]\rho'\exp\left[\frac{i}{\hbar}(\hat{H}+\hat{F})t\right], \quad (2)$$

we obtain

$$\frac{\partial\rho'}{\partial t} = -\frac{i}{\hbar}[\hat{V}(t), \rho'], \quad (3)$$

where

$$\hat{V}(t) = \sum_{m=-2}^{2} \hat{H}_{dip}^{m}(t) + \hat{I}(t) + \hat{G}(t),$$

$$\hat{I}(t) = \frac{\mu_1 H_1}{2I}(\hat{I}^{+1}(t)\exp(i\omega t) + \hat{I}^{-1}(t)\exp(-i\omega t)),$$

$$\hat{I}^{\pm1}(t) = \exp\left(\frac{i\hat{H}t}{\hbar}\right)\hat{I}^{\pm1}\exp\left(\frac{-i\hat{H}t}{\hbar}\right),$$

$$\hat{H}_{dip}^{m}(t) = \exp\left(\frac{i\hat{H}t}{\hbar}\right)\hat{H}_{dip}^{m}\exp\left(-\frac{i\hat{H}t}{\hbar}\right),$$

$$\hat{G}(t) = \sum_{n=\pm1}\sum_{\alpha=1}^{2}\hat{F}^{n\alpha}(t)\hat{R}^{n\alpha}(t),$$

$$\hat{F}^{n\alpha}(t) = \exp\left(\frac{i\hat{H}t}{\hbar}\right)\hat{F}^{n\alpha}\exp\left(-\frac{i\hat{H}t}{\hbar}\right),$$

$$\hat{R}^{n\alpha}(t) = \exp\left(\frac{i\hat{F}t}{\hbar}\right)\hat{R}^{n\alpha}\exp\left(-\frac{i\hat{F}t}{\hbar}\right). \quad (4)$$

To derive the kinetic equation we shall introduce the projection operator $\hat{P}$,[5] which extracts from the density matrix that part which is diagonal in the representation in which the pairwise commuting operators $\hat{I}_z$, $\hat{S}_z$, $\overline{H}_{dip}$ are simultaneously diagonal (henceforth we shall have only this representation in mind).

Multiplying Eq. (3) on the left by the operators $\hat{P}$ and $(1-\hat{P})$, we have

$$\frac{\partial\rho_1}{\partial t} = -\frac{i}{\hbar}\hat{P}[\hat{V}(t), \rho_2],$$

$$\frac{\partial\rho_2}{\partial t} = -\frac{i}{\hbar}[\hat{V}(t), \rho_1] - \frac{i}{\hbar}(1-\hat{P})[\hat{V}(t), \rho_2]. \quad (5)$$

Here $\rho_1 = \hat{P}\rho'$ and $\rho_2 = (1-\hat{P})\rho'$.

In Eq. (5) we have left out a term $\hat{P}[\hat{V}(t), \rho_1]$, since from the definitions (4) it follows directly that the diagonal matrix elements of the operator $[\hat{V}(t), \rho_1]$ are zero. For the same reason we omit the operator $1-\hat{P}$ before the first term of the right-hand member of Eq. (5).

An analogous system of equations has been considered previously.[6] A derivation completely analogous to that presented in [6] gives the following kinetic equation:

$$\frac{\partial\rho_1}{\partial t} = -\frac{\pi}{2}\left(\frac{\mu_1 H_1}{I\hbar}\right)^2 \hat{P}'[(\hat{I}^1)_{-\Delta_1}[(\hat{I}^{-1})_{\Delta_1}, \rho_1]]$$

$$-\frac{2\pi}{\hbar^2}\hat{P}'[(\hat{H}_{dip}^{0+})_{-\Delta_{12}}[(\hat{H}_{dip}^{0-})_{\Delta_{12}}, \rho_1]]$$

$$-\frac{2\pi}{\hbar^2}\sum_{\alpha=1}^{2}\hat{P}'[(\hat{H}_{dip}^{1\alpha})_{-\omega_{\alpha0}}[(\hat{H}_{dip}^{-1\alpha})_{\omega_{\alpha0}}, \rho_1]]$$

$$-\frac{2\pi}{\hbar^2}\sum_{\alpha=1}^{2}\int_{-\infty}^{+\infty}d\omega\hat{P}'[(\hat{F}^{1\alpha})_{-\omega}$$

$$\times (\hat{R}^{1\alpha})_{-\omega_{\alpha0}+\omega}[(\hat{F}^{-1\alpha})_{\omega}(\hat{R}^{-1\alpha})_{\omega_{\alpha0}-\omega}, \rho_1]]. \quad (6)$$

[The operator $\hat{P}'\delta(0) = \hat{P}$, just as in [6].] Here

$$\omega_{10} = \frac{\mu_1 H_0}{I\hbar}, \quad \omega_{20} = \frac{\mu_2 H_0}{S\hbar}, \quad \Delta_{1,2} = \omega - \omega_{10,20}, \quad \Delta_{12} = \omega_{10} - \omega_{20}.$$

The operators $(\hat{A})_{\omega}$ are defined in the following way:

$$(\hat{A})_{\omega} = \frac{1}{2\pi}\int_{-\infty}^{+\infty}dt\exp\left(\frac{i(\overline{H}_{dip}+\hat{F})t}{\hbar}\right)\hat{A}\exp\left(-\frac{i(\overline{H}_{dip}+\hat{F})t}{\hbar}\right)e^{i\omega t}. \quad (7)$$

We note that according to this definition the operators $(\hat{A})_{\omega}$ have non-zero matrix elements only for transitions involving a change of $\hbar\omega$ in the energy $\overline{H}_{dip} + \hat{F}$.

To each term on the right hand side of Eq. (6) there correspond transitions of a definite type between the levels of the spin system. The first term, for example, describes transitions under the influence of the high-frequency field (this term has been considered in detail in a previous paper [6]).

The transitions associated with cross relaxation are described by the second term. During each such transition I_z is changed by ± 1 with a simultaneous change in S_z of ∓ 1. The accompanying change in Zeeman energy $\hbar\Delta_{12}$ is compensated by a corresponding change in the dipole-dipole interaction energy $\overline{H}_{dip}$, as can be easily seen from the structure of this term.

The third term is obviously connected with the direct conversion of Zeeman energy into dipole-dipole interaction energy. In this term the operators $\hat{H}_{dip}^{\pm1\alpha}$ have non-zero matrix elements only for transitions involving a change in the z component of the total spin of particles of sort α by ± 1. In this term of Eq. (6) terms of the type $\hat{H}_{dip}^{m}$ with $m = \pm 2$ are also omitted, since these are not important in the case $\omega_{10,20} \gg \mu H_{loc}/\hbar$. ($H_{loc} = \mu/d^3$, where d is the shortest distance between magnetic moments.)

Finally, the last term in the right hand member of the equation describes the transitions in the spin system that occur because of the spin-lattice

interaction. The integration over ω in this term reflects the possibility of an exchange of energy between the spin system and the lattice with direct transfer of small quantities of energy $\sim \mu H_{loc}$ to the dipole-dipole interaction energy $\overline{H}_{dip}$.

It is to be noted that an inaccuracy in the derivation of Eq. (6) arises on account of discarding a term proportional to ρ_2 from the right hand side of Eq. (5). As can be seen from Eq. (5) this inaccuracy will not be large for the condition $\rho_2 \ll \rho_1$. We shall now determine the conditions for which this inequality holds. To this end, we integrate Eq. (5) with respect to the time [in the case considered $\rho_2(0) = 0$]:

$$\rho_2(t) = -\frac{i}{\hbar}\int_0^t dt' \, [\hat{I}(t'), \, \rho_1(t')] - \frac{i}{\hbar}\int_0^t dt' \, [\hat{H}_{dip}^0(t'), \, \rho_1(t')]$$

$$-\frac{i}{\hbar}\int_0^t dt' \sum_{m=\pm 1, \pm 2} [\hat{H}_{dip}^m(t'), \, \rho_1(t')]$$

$$-\frac{i}{\hbar}\int_0^t dt' \, [G(t'), \, \rho_1(t')]. \tag{8}$$

Direct calculation yields the following evaluations of the terms in the right-hand member of this equation:

$$S_1 \sim \frac{H_1}{H_{loc}}\rho_1, \quad S_2 \sim \frac{\mu H_{loc}}{\hbar \Delta_{12}}\rho_1, \quad S_3 = \frac{\mu H_{loc}}{\hbar \omega_{\alpha 0}}\rho_1,$$

$$S_4 = \frac{\hbar}{\mu H_{loc}T_1}\rho_1. \tag{9}$$

As an example we show how the first term is calculated. Using the commutation properties of the operators I_z, S_z, and $\overline{H}_{dip}$ and the integral

$$\hat{I}^{\pm 1}(t) = \int_{-\infty}^{+\infty} d\omega \hat{I}_\omega^{\pm 1} e^{i\omega t}, \tag{10}$$

we obtain, in accordance with (10),

$$S_1 \approx \frac{\mu_1 H_1}{I\hbar}\int_0^t dt' \int_{-\infty}^{+\infty} d\omega \, \{[\hat{I}^1_{-\omega}, \, \rho_1(t')]\exp[i(\omega_{10}-\omega)t']$$

$$+ [\hat{I}_\omega^{-1}, \, \rho_1(t')]\exp[-i(\omega_{10}-\omega)t']\}. \tag{11}$$

Noting further, that $\rho_1(t')$ changes little in time $\sim \hbar/\mu H_{loc}$, and the average value of the difference $\omega - \omega_{10} \sim \mu_1 H_{loc}/I\hbar$, we obtain, after averaging over time, the estimate given above.

The other terms in the right-hand side of Eq. (8) are evaluated in a similar way. The frequencies Δ_{12} and $\omega_{\alpha 0}$ appear in these evaluations because of the presence in the exponentials of definitions (4) of the Zeeman energy $-\hbar\omega_{10}\hat{I}_z - \hbar\omega_{\alpha 0}\hat{S}_z$, which commutes with the operator $\overline{H}_{dip}$. [In the calculation it is also essential that under conditions of cross relaxation $\Delta_{12} \gg \mu H_{loc}/\hbar$.[1]] Thus, it follows from Eqs. (8) and (9) that when the fol-

lowing inequalities are simultaneously fulfilled

$$\frac{H_1}{H_{loc}} \ll 1, \quad \frac{\mu H_{loc}}{\hbar \Delta_{12}} \ll 1, \quad \frac{\mu H_{loc}}{\hbar \omega_{\alpha 0}} \ll 1, \quad \frac{\hbar}{\mu H_{loc}T_1} \ll 1 \tag{12}$$

the condition $\rho_2 \ll \rho_1$ introduced earlier is indeed valid.

It is to be noted that this circumstance not only justifies the assumptions made earlier, but also allows the determination of the general form of the solution to Eq. (6). In fact, within the accuracy of the small quantities in (12), we can now consider the density matrix of the spin system to be diagonal. In addition, because of the homogeneity of our macroscopic system, this density matrix should obviously have the property:[6]

$$\rho_1(t) = \rho_1^1(t)\rho_1^2(t). \tag{13}$$

Here $\rho_1^1(t)$ and $\rho_1^2(t)$ are the density matrices of any two parts of the spin system resulting from its division into two arbitrary macroscopic parts. But a density matrix having the two aforementioned properties has the form[7]

$$\rho_1(t) = C\exp[\alpha(t)\hat{I}_z + \beta(t)\hat{S}_z + \gamma(t)\overline{H}_{dip} - \hat{F}/kT_0]. \tag{14}$$

(The lattice temperature T_0 is assumed not to change, because of the high heat capacity of the lattice.)

Physically, a solution of this form means that, correct to the quantities in (12), the system considered is in a state of thermodynamic equilibrium at every moment of time. The quantity C is defined from the normalization condition $Sp \, \rho_1(t) = 1$:

$$C = (2I+1)^{-N_1}(2S+1)^{-N_2}[Sp\exp(-\hat{F}/kT_0)]^{-1} \tag{15}$$

(in the case considered $\hbar\omega_{\alpha 0}/kT_0 \ll 1$.) Here N_1 and N_2 are the numbers of particles of the first and second sort in the sample.

Calculating with the aid of the kinetic equation (6) the time derivatives

$$\frac{\partial I_z(t)}{\partial t} = Sp\,\hat{I}_z\frac{\partial\rho_1}{\partial t}, \quad \frac{\partial S_z(t)}{\partial t} = Sp\,\hat{S}_z\frac{\partial\rho_1}{\partial t},$$

$$\frac{\partial H_{dip}(t)}{\partial t} = Sp\,\overline{H}_{dip}\frac{\partial\rho_1}{\partial t},$$

we obtain the following simple system of equations (this calculation is completely analogous to that carried out in [6]):

$$\frac{\partial\alpha}{\partial t} = -f(\Delta_1)(\alpha - \gamma\hbar\Delta_1) - \frac{1}{T_{12}}(\alpha - \beta - \gamma\hbar\Delta_{12})$$

$$-\frac{1}{T_{s1}}(\alpha - \gamma\hbar\omega_{10}) + \frac{\alpha_0 - \alpha}{T_1'},$$

$$\frac{\partial\beta}{\partial t} = \frac{\delta}{T_{12}}(\alpha - \beta - \gamma\hbar\Delta_{12}) - \frac{\delta}{T_{s2}}(\beta - \gamma\hbar\omega_{20}) + \delta\frac{\beta_0 - \beta}{T_1^2},$$

$$\frac{\partial\gamma}{\partial t} = \hbar\Delta_1\varepsilon f(\Delta_1)(\alpha - \gamma\hbar\Delta_1) + \frac{\hbar\Delta_{12}\varepsilon}{T_{12}}(\alpha - \beta - \gamma\hbar\Delta_{12})$$

$$+\frac{\varepsilon\hbar\omega_{10}}{T_{s1}}(\alpha - \gamma\hbar\omega_{10}) + \frac{\varepsilon}{\delta}\frac{\hbar\omega_{20}}{T_{s2}}(\beta - \gamma\hbar\omega_{20}) + \frac{\gamma_0 - \gamma}{T_1''}. \tag{16}$$

Here

$$f(\Delta_1) = \frac{\pi}{2}\left(\frac{\mu_1 H_1}{I\hbar}\right)^2 \frac{\mathrm{Sp}\,\hat{P}'(\hat{I}^1)_{-\Delta_1}(\hat{I}^{-1})_{\Delta_1}}{\mathrm{Sp}\,\hat{I}_z^2},$$

$$\frac{1}{T_{12}} = \frac{2\pi}{\hbar^2}\frac{\mathrm{Sp}\,\hat{P}'(\hat{H}_{dip}^{0+})_{-\Delta_{12}}(\hat{H}_{dip}^{0-})_{\Delta_{12}}}{\mathrm{Sp}\,\hat{I}_z^2},$$

$$\frac{1}{T_{s\alpha}} = \frac{2\pi}{\hbar^2}\mathrm{Sp}\,\hat{P}'(\hat{H}_{dip}^{+1\alpha})_{-\omega_{\alpha 0}}(\hat{H}_{dip}^{-1\alpha})_{\omega_{\alpha 0}},$$

$$\delta = \mathrm{Sp}\,\hat{I}_z^2/\mathrm{Sp}\,\hat{S}_z^2, \quad \varepsilon = \mathrm{Sp}\,\hat{I}_z^2/\mathrm{Sp}\,\overline{H}_{dip}^2,$$

$$\frac{1}{T_1^\alpha} = \frac{2\pi}{\hbar^2}\int_{-\infty}^{+\infty} d\omega\,\mathrm{Sp}\,\hat{P}'\,(\hat{F}^{1\alpha})_{-\omega}(\hat{F}^{-1\alpha})_{\omega}$$

$$\times \mathrm{Sp}\exp(-\hat{F}/kT_0)\,(\hat{R}^{1\alpha})_{\omega_{\alpha 0}-\omega}(\hat{R}^{-1\alpha})_{-\omega_{\alpha 0}+\omega}$$

$$\times \{\mathrm{Sp}\,\hat{I}_z^2\,\mathrm{Sp}\exp(-\hat{F}/kT_0)\}^{-1},$$

$$\frac{1}{T_1''} = 2\pi\sum_{\alpha=1}^2\int_{-\infty}^{+\infty} d\omega\omega^2\,\mathrm{Sp}\,\hat{P}'(\hat{F}^{1\alpha})_{-\omega}\,(\hat{F}^{-1\alpha})_{\omega}\,\mathrm{Sp}\exp(-\hat{F}/kT_0)$$

$$\times (\hat{R}^{1\alpha})_{\omega_{\alpha 0}-\omega}(\hat{R}^{-1\alpha})_{-\omega_{\alpha 0}+\omega}\{\mathrm{Sp}\,\overline{H}_{dip}^2\,\mathrm{Sp}\exp(-\hat{F}/kT_0)\}^{-1};$$

$$(17)$$

α_0, β_0, and γ_0 are the equilibrium values of α, β, and γ.

This system of equations differs from the system of equations in [1] in the additional terms containing $\gamma(t)$. These terms describe the physically completely obvious change in the average dipole-dipole interaction energy in saturation processes and cross relaxation and the influence of this change on processes occurring in the spin system.

Equations (16) and (8) allow the easy determination of all the physical characteristics of the spin system (see the analogous calculation in [6]). Since the expressions obtained are so unwieldy, we shall not write out the solution to the system (16). We remark only that the values of α_{st} and β_{st} (the steady state values of α and β) calculated from Eqs. (16) for strong deviations from the equilibrium values α_0 and β_0 differ substantially from the magnitudes of α_{st} and β_{st} calculated from the equations of the aforementioned work.[1]

Essentially different results are also obtained for the relaxation times. As an illustration, let us consider the relaxation processes occurring in the spin system after switching off the high-frequency field. In case $T_{12} \ll T_1^\alpha$, T_1'' the short relaxation time, as can be easily seen from Eqs. (16), will equal $\tau = T_{12}/(1 + \delta + \epsilon\Delta_{12}^2\hbar^2)$, and not $T_{12}/(1 + \delta)$, as is obtained from the system of equations in [1]. In the derivation of these expressions terms proportional to $1/T_{s\alpha}$ were omitted in (16), since in the case $\Delta_{12} \ll \omega_{\alpha 0}$, they are significantly less than terms proportional to $1/T_{12}$.[1]

In conclusion we remark that the conditions (12) in fact determine the accuracy of Eq. (8) only. Actually, since only the squares of the moduli of the non-diagonal matrix elements enter into Eq. (6), the accuracy of this equation is limited by the inequalities

$$\left(\frac{H_1}{H_{loc}}\right)^2 \ll 1, \quad \left(\frac{\mu H_{loc}}{\hbar\Delta_{12}}\right)^2 \ll 1, \quad \left(\frac{\mu H_{loc}}{\hbar\omega_{\alpha 0}}\right)^2 \ll 1. \quad (18)$$

Concerning the form of the solution (14) for $\rho_1(t)$ in the derivation of (16), its validity will be determined by the conditions

$$T_{12} \ll \hbar/\mu H_{loc}, \quad \hbar/\mu H_1 \gg \hbar/\mu H_{loc}. \quad (19)$$

These conditions express the physically obvious requirement that processes associated with the creation of order in the spin system (coherent precession under the influence of a high frequency field and cross relaxation), should proceed sufficiently slowly compared to processes that destroy order (we recall that the time for destroying order in a spin system is of the order $\hbar/\mu H_{loc}$[6]).

Thus the inequalities (18) and (19) determine the conditions of applicability of the fundamental system (16).

We have considered the simplest case of cross relaxation, characterized by the participation of but two spins in each separate elementary act of cross relaxation. In certain cases processes can be observed in which a larger number of spins participate simultaneously.[1,3] In the case when the cross relaxation process occurs with a simultaneous change in I_z by m and in S_z by n units, the term describing the cross relaxation will have the form (when the condition $\hbar\omega_{\alpha 0}/kT_0 \ll 1$ is fulfilled)

$$\frac{1}{T_{12}}(m\alpha - n\beta - \gamma\hbar\Delta_{12}'),$$

where $\hbar\Delta_{12}'$ is the change in the Zeeman energy in the given multi-spin process. However, the determination of the coefficient $1/T_{12}$ in this case will be a much more difficult task.

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