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## Magnetic-Resonance Relaxation and Saturation of Quadrupole-Interacting Spin System

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A system of equations describing spin-lattice relaxation, saturation, and cross relaxation of a quadrupole-interacting spin system is derived from the Liouville equation by combining the orthogonal-operator-expansion method with energy-level population operators. The theory is applied to quadrupole-perturbed nuclear magnetic resonance where spin-lattice relaxation and saturation coefficients are calculated. There is a difference between the dipolar spin-lattice relaxation rates of systems with equally and unequally spaced energy levels.

### I. INTRODUCTION

Magnetic resonance investigations often deal with nonequally spaced spin energy levels. In addition to interaction with external magnetic fields, the spins are influenced by internal electric and magnetic fields which cause shifted Zeeman levels. An example is levels in a quadrupole-interacting-nuclear-spin system.

This paper is an application of the work of Shimizu<sup>1</sup> on saturation and relaxation in the spin system to a case of unequally spaced energy levels. In contrast to other techniques, his method, known as the method of orthogonal-operator expansion, makes possible the derivation of the rate equations without need for independence of the system variables<sup>2</sup> and without unnecessary suppositions about the density matrix.<sup>3</sup> The new feature in this paper is the formulation of the spin-system rate equations by combining the orthogonal-operator-expansion method with the energy-level population operators. This technique has been applied to the quadrupole-interacting nuclear-spin system which is under the influence of an oscillating magnetic field and a fluctuating local-electric-field-gradient tensor. It is supposed that the oscillating

magnetic field and the fluctuating electric-field-gradient tensor have a weaker effect on the spin system than mutual dipolar spin interactions. Although the method could be applied equally well to the spin system together with the lattice,<sup>1</sup> attention has been restricted here to the spin system only. The lattice is in thermodynamic equilibrium at all times.

In Sec. II the description of general quadrupole-interacting nuclear-spin systems is considered. Instead of using the description with the total angular-momentum operator which is valid in the pure Zeeman case, the population number operators are defined to describe the unequally spaced level system. Then the motion equations for these new variables are derived using Shimizu's technique. In Sec. III the theory is applied to a quadrupole-perturbed nuclear-magnetic-resonance (NMR) case. Taking into account the dipolar spin interaction, the expressions for spin-lattice relaxation and saturation coefficients are derived.

Although some of the results are not completely new and they are the same as those obtained by other methods, this technique makes it possible to obtain the spin motion equations in a very straightforward way. The lack of necessity for certain

assumptions distinguishes this technique from others.

## II. HAMILTONIAN AND KINETIC EQUATIONS

It is generally accepted<sup>4</sup> that after an initial disturbance the energy-level populations relax to thermal equilibrium following rate equations of the form

$$\frac{dp_m}{dt} = \sum_n W_{nm}(p_n - p_m), \quad (1)$$

where  $p_m$  is defined to be the deviation of the  $m$ th population from its equilibrium value and  $W_{nm}$  are transition probabilities. These equations were deduced from qualitative considerations and in principle they provide a correct description of the phenomena in the appointed approximation. The goal of this paper is a more accurate derivation of Eq. (1) directly from the general quantum-mechanical equation for the density matrix of the spin system.

Generally, the Hamiltonian of the spin system and the lattice consists of three parts:

$$\mathcal{H} = \mathcal{H}'_Z + \mathcal{H}'_L + \mathcal{H}^*_{int}. \quad (2)$$

Here  $\mathcal{H}'_L$  is the Hamiltonian of the lattice and  $\mathcal{H}'_Z$  describes the spin interactions with external fields.  $\mathcal{H}^*_{int}$ , which is the Hamiltonian of the interaction between spins and a lattice, may be split into two parts:

$$\mathcal{H}^*_{int} = \mathcal{H}_{int} + \mathcal{H}'_{int}.$$

The first term which describes the spins in the rigid structure is the lattice average of the interaction Hamiltonian

$$\mathcal{H}_{int} = \langle \mathcal{H}^*_{int} \rangle_L \equiv \text{Tr}_L \rho_L \mathcal{H}^*_{int}.$$

Here  $\text{Tr}_L$  indicates a trace over the eigenstates of the lattice Hamiltonian and  $\rho_L$  is equilibrium density matrix for the lattice.  $\mathcal{H}'_{int}$  is the fluctuating term due to spin-lattice coupling and it is responsible for the relaxation of the spin system toward thermal equilibrium with the lattice.

Further, consideration will be limited to nuclear spins in solids. Hence the main contributions to the interaction between spins and a lattice are the spin interaction with the local electric field gradient and the mutual dipolar spin-spin interaction:

$$\mathcal{H}^*_{int} = \mathcal{H}^*_D + \mathcal{H}^*_B. \quad (3)$$

This means that also the spin-lattice coupling describes the spin interaction with the electric-field-gradient fluctuations and the interaction with the local magnetic field fluctuations,

$$\mathcal{H}'_{int} = \mathcal{H}'_D + \mathcal{H}'_B. \quad (4)$$

In NMR experiment the spins are subjected to a high stationary magnetic field and a small oscillating magnetic field (rf field). Hence the Zeeman

part of the Hamiltonian consists of

$$\mathcal{H}'_Z = \mathcal{H}'_Z + \mathcal{H}'_{rf}(t).$$

All considerations here are restricted to rf fields which affect the spin system to the same degree as the spin lattice coupling  $\mathcal{H}'_{int}$ , but to a smaller degree than the mutual spin-spin interaction  $\mathcal{H}'_D$ .

$\mathcal{H}'_Z$  and  $\mathcal{H}'_D$  are the sum of the single-spin Hamiltonians  $h_{Zi}$  and  $h_{Di}$ , and can be replaced by the sum over single-spin energy levels

$$\mathcal{H}'_Z + \mathcal{H}'_D = \sum_{k=1}^n E_k \mathcal{N}_k. \quad (5)$$

Here  $E_k$  is energy of the  $k$ th single-spin energy level.  $\mathcal{N}_k$  is the spin-level-population operator<sup>5</sup> which defines the number of the spins in the  $k$ th level. Further, we assume that the eigenvalues of the population operators are good quantum numbers. It is satisfied if the differences between several pairs of the energy levels are larger than the energy-level broadening due to the dipolar spin-spin interaction.

Finally, the system Hamiltonian might be written

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}(t), \quad (6)$$

where the main term is

$$\mathcal{H}_0 = \sum_{k=1}^n E_k \mathcal{N}_k + \mathcal{H}^{(s)}_D + \mathcal{H}'_L \quad (6a)$$

and the perturbation is

$$\mathcal{V}(t) = \mathcal{H}^{(n)}_D + \mathcal{H}'_{int} + \mathcal{H}'_{rf}(t). \quad (6b)$$

$\mathcal{H}^{(s)}_D$  is the secular part of dipolar interaction which commutes with the  $\sum_{k=1}^n E_k \mathcal{N}_k$ . The large differences between the several energy-level pairs enables us to consider the nonsecular part  $\mathcal{H}^{(n)}_D$  as a small perturbation.

We consider here the energy-level population and the changes of averaged value of the dipolar energy  $\langle \mathcal{H}^{(s)}_D \rangle$ , but we assume that the lattice remains in the thermodynamic equilibrium at all times. In order to obtain motion equations for the spin variables, the following operators are chosen:

$$O_k = \begin{cases} \mathcal{N}_k, & k = 1, 2, \dots, n \\ \mathcal{H}^{(s)}_D, & k = n + 1. \end{cases} \quad (7)$$

They can be defined in such a way to be mutually orthogonal

$$\text{Tr } O_k O_{k'}^\dagger = C_k \delta_{kk'}$$

and commutable

$$[O_k, O_{k'}] = 0.$$

Having orthogonal operators, a method where the density matrix is expanded into a sum over orthogonal operators can be used. Derivation similar to that in Ref. 1 gives, from the Liouville equation, a system of integro-differential equations for

averaged values

$$\frac{d}{dt} \langle O_k(t) \rangle = - \sum_{k'=1}^{n+1} \int_0^t dt' \langle O_k | \hat{v}(t) e^{i\mathcal{H}_0(t-t')} \hat{v}(t') | O_{k'} \rangle$$

$$\times \frac{\langle O_{k'}(t) \rangle}{\langle O_{k'} | O_{k'} \rangle} - \int_0^t dt' \langle O_k | \hat{v}(t) e^{i\mathcal{H}_0 t} (1-P) \hat{v}(t') (1-P) | \rho \rangle$$

$$(k=1, 2, \dots, n+1). \quad (8)$$

The notation is identical to that in Ref. 1.  $P$  is the projection operator into the space of the orthogonal operators and  $\rho$  is the equilibrium density matrix taken as

$$\rho = e^{-\beta \mathcal{H}_0} / \text{Tr} e^{-\beta \mathcal{H}_0}.$$

Equation (8) is simplified if the effect of the dipolar interaction is taken into account. Because of this interaction, the kernels under integrals decay to zero in the time  $T_2$ . If we consider only times longer than  $T_2$  the equations become

$$\frac{d}{dt} \langle O_k(t) \rangle = - \sum_{k'=1}^{n+1} G(O_k, O_{k'}) \langle O_{k'}(t) \rangle - G_0(O_k, \rho), \quad (9)$$

with

$$G(O_k, O_{k'}) = \int_0^\infty dt' \text{Tr} e^{i\mathcal{H}_0 t'} \times [O_k, v(t')] e^{-i\mathcal{H}_0 t'} [v(0), O_{k'}].$$

It can be shown that  $G_0(O_k, \rho)$  is independent of the rf perturbation and cross relaxation in the high-temperature approximation. From the Hamiltonian (6) it follows that  $G(O_k, O_{k'})$  is the sum of the spin-lattice relaxation  $T_{1kk'}^{-1}$ , the cross relaxation  $\tau_{kk'}^{-1}$ , and the saturation coefficient  $W_{kk'}$ . These coefficients can be collected into matrices  $\{T^{-1}\}$ ,  $\{\tau\}$ , and  $\{W\}$ . If a generalized vector

$$\vec{R} = [\langle O_1(t) \rangle, \langle O_2(t) \rangle, \dots, \langle O_{n+1}(t) \rangle]$$

is also defined, Eq. (9) becomes

$$\frac{d}{dt} \vec{R} = - \{W\} \vec{R} - \{\tau^{-1}\} \vec{R} + \{T^{-1}\} (\vec{R}_0 - \vec{R}). \quad (10)$$

Here  $G_0(O_k, \rho)$  is written as the  $k$ th component of the generalized vector  $\{T^{-1}\} \vec{R}_0$ , where  $\vec{R}_0$  is equilibrium value of the  $\vec{R}$  when the saturation and cross relaxation is absent.

Insofar as the cross relaxation is not taken into account, Eq. (10) looks like the well-known Bloembergen, Purcell, and Pound (BPP) equation,<sup>6</sup> if the population difference of two levels stands here instead of the vector  $\vec{R}$ . But in our case the  $\vec{R}$  is a generalized vector whose components are the populations of the levels  $\langle \mathcal{N}_k(t) \rangle$  and averaged dipolar energy  $\langle \mathcal{H}_D^{(s)}(t) \rangle$ .

Calculation of the matrices in Eq. (10) demands exact knowledge of the spin and lattice Hamiltonians. The spin Hamiltonian is usually known but

the lattice is assumed to be in thermodynamic equilibrium. The factor  $\text{Tr}_L e^{i\mathcal{H}_L t} \mathcal{L} e^{-i\mathcal{H}_L t} \mathcal{L}$  which appears, might be replaced by the thermodynamic average  $\langle \mathcal{L}(t), \mathcal{L}(0) \rangle_L$ . Here  $\mathcal{L}$  includes only lattice operators and  $\text{Tr}_L$  indicates a trace over lattice eigenstates.

### III. QUADRUPOLE PERTURBED NUCLEAR MAGNETIC RESONANCE

Consider the case when the electric quadrupole interaction is strong compared to the magnetic dipole interaction between nuclei, but weak compared to interaction of the nuclei with the applied high magnetic field. Using the formalism of Sec. II, the motion equations for averaged values of the level populations and dipolar energy can be derived.

Since the electric quadrupole interaction is weak compared to the Zeeman interaction, we retain only that part of the quadrupole Hamiltonian  $\mathcal{H}_Q^{(0)}$  which commutes with the Zeeman Hamiltonian  $\mathcal{H}_Z$ . Further, we take into account only the secular part of the dipolar Hamiltonian which commutes with  $\mathcal{H}_Z + \mathcal{H}_Q^{(0)}$ . The nonsecular part is neglected since there is no overlap between the lines. The Hamiltonian reduces to

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}(t), \quad (11)$$

where the main part is

$$\mathcal{H}_0 = \mathcal{H}_Z + \mathcal{H}_Q^{(0)} + \mathcal{H}_D^{(s)} + \mathcal{H}_L = \sum_{m=-s}^{m=s} E_m \mathcal{N}_m + \mathcal{H}_D^{(s)} + \mathcal{H}_L \quad (11a)$$

and the perturbation is

$$\mathcal{V}(t) = \mathcal{H}'_{\text{int}} + \mathcal{H}'_{\text{rf}}(t). \quad (11b)$$

$E_m$  is the single-spin energy  $E_m = -m\omega_0 + \langle m | \mathcal{H}_Q^{(0)} | m \rangle$  and  $\mathcal{N}_m$  is the sum of the single-spin population operators  $\mathcal{N}_{mi}$ ,

$$\mathcal{N}_m = \sum_{i=1}^N \mathcal{N}_{mi} - (N - \sqrt{N}) / (2s + 1). \quad (12)$$

( $N$  is the total number of nuclei and  $s$  is the spin.)  $\mathcal{N}_{mi}$  has the property

$$\mathcal{N}_{mi} | m' \rangle_i = \delta_{mm'} | m' \rangle_i.$$

Besides  $\mathcal{N}_m$  we define the operators  $\mathcal{N}_m^+$  and  $\mathcal{N}_m^-$  which are the sum of the single-spin operators  $\mathcal{N}_{mi}^+$  and  $\mathcal{N}_{mi}^-$  with the properties

$$\mathcal{N}_{mi}^\pm | m' \rangle_i = \delta_{mm'} | m' \pm 1 \rangle_i.$$

Total spin components  $J_Z$  and  $J^\pm$  can be expressed as

$$J_Z = \sum_{m=-s}^{m=s} m \mathcal{N}_m$$

and

$$J^\pm = \sum_{m=-s}^{m=s} A_m^\pm \mathcal{N}_m^\pm, \quad (13)$$

where

$$A_m^\pm = [s(s+1) - m(m \pm 1)]^{1/2}.$$

The operators  $\mathfrak{N}_m$  and  $\mathfrak{N}_m^\pm$  ( $m = -s, -s+1, \dots, +s$ ) are mutually orthogonal

$$\begin{aligned} \text{Tr} \mathfrak{N}_m \mathfrak{N}_{m'} &= \delta_{mm'} N(2s+1)^{N-1}, \\ \text{Tr} \mathfrak{N}_m \mathfrak{N}_{m'}^\pm &= 0. \end{aligned} \quad (14)$$

Other useful relations which also will enable us to derive coefficients in the motion equations are

$$\begin{aligned} \text{Tr} \mathfrak{N}_m^+ \mathfrak{N}_{m'}^- &= \delta_{mm'} N(2s+1)^{N-1}, \\ \text{Tr} \mathfrak{N}_m &= \sqrt{N} (2s+1)^{N-1}. \end{aligned}$$

In Secs. III A and III B the spin-lattice relaxation and the saturation matrices will be calculated using the formalism just derived.

### A. Spin-Lattice Relaxation Rates

The spin-lattice relaxation times of the nuclei with spin  $s > \frac{1}{2}$  in crystals of sufficiently high purity is due to the interaction of the nuclear electric quadrupole with the thermal fluctuations in the local electric field gradient (EFG). In the remaining derivation only quadrupole interactions are taken into account.

$$\mathfrak{H}'_{\text{int}} = \mathfrak{H}'_Q = \sum_{\alpha=-2}^{\alpha=2} \sum_{j=1}^N W_j^{(-\alpha)} Q^{(\alpha)}, \quad (15)$$

where  $W_j^{(-\alpha)}$  is a fluctuating EFG tensor and  $Q^{(\alpha)}$  is a tensor of the nuclear quadrupole moment as defined in Ref. 7. Using relation (9), the spin-lattice relaxation matrix of the spin system defined by the Hamiltonian (11) has the form

$$\{T_1^{-1}\} = \begin{pmatrix} T_{1s}^{-1} & T_{1s(s-1)} & \dots & T_{1s(-s)} & 0 \\ T_{1(s-1)s}^{-1} & T_{1(s-1)(s-1)}^{-1} & \dots & T_{1(s-1)(-s)}^{-1} & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ T_{1(-s)s}^{-1} & T_{1(-s)(s-1)}^{-1} & \dots & T_{1(-s)(-s)}^{-1} & 0 \\ 0 & 0 & \dots & 0 & T_{1D}^{-1} \end{pmatrix}, \quad (16)$$

where the matrix components are as follows:

$$\begin{aligned} T_{1mm'}^{-1} &= \frac{1}{\text{Tr} \mathfrak{N}_m^2} \int_0^\infty dt \text{Tr} e^{i\mathfrak{H}_0 t} [\mathfrak{N}_m, \mathfrak{H}'_Q] e^{-i\mathfrak{H}_0 t} [\mathfrak{H}'_Q \mathfrak{N}_{m'}] \\ &= I_{2m} (\delta_{m,m'} - \delta_{m,m'+2}) + I_{2(2m+2)} (\delta_{m,m'} - \delta_{m,m'-2}) \\ &\quad + I_{1m} (\delta_{m,m'} - \delta_{m,m'+1}) + I_{1(m+1)} (\delta_{m,m'} - \delta_{m,m'-1}). \end{aligned} \quad (16a)$$

Here is

$$\begin{aligned} I_{1m} &= (3/2N) \bar{Q}^2 (2m+1)^2 (A_m^-)^2 \mathcal{G}^{(1)}(\omega_{m-1}^m), \\ I_{2m} &= (3/2N) \bar{Q}^2 (A_m^- A_{m-1}^-)^2 \mathcal{G}^{(2)}(\omega_{m-2}^m), \end{aligned}$$

and

$$g^{(\alpha)}(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} \sum_{j=1}^N \langle W_j^{(-\alpha)}(t), W_j^{(\alpha)}(0) \rangle_L dt,$$

with

$$\bar{Q} = eQ/2\hbar s(2s-1), \quad \omega_m^m = (E_m - E_{m'}) \hbar^{-1}.$$

In the above calculation the role of the dipolar interaction is neglected and the thermodynamic average over the lattice coordinates is taken. Matrix components which describe relaxation between  $\langle \mathfrak{N}_m(t) \rangle$  and  $\langle \mathfrak{H}'_D^{(s)}(t) \rangle$  are zero,<sup>5</sup> and spin-lattice relaxation of the dipolar energy is

$$T_{1D}^{-1} = (1/\text{Tr} \mathfrak{H}'_D^{(s)2}) \int_0^\infty dt \text{Tr} e^{i\mathfrak{H}_0 t} [\mathfrak{H}'_D^{(s)}, \mathfrak{H}'_Q]$$

$$\begin{aligned} \times e^{-i\mathfrak{H}_0 t} [\mathfrak{H}'_Q, \mathfrak{H}'_D^{(s)}] &= \frac{3}{2} \bar{Q}^2 \sum_m [(2m-1)^2 (A_m^-)^2 \\ &\times \int_{-\infty}^{\infty} \omega^2 \mathcal{G}^{(1)}(\omega + \omega_{m-1}^m) G_\omega^{(1m)} d\omega \\ &+ (A_m^- A_{m-1}^-)^2 \int_{-\infty}^{\infty} \omega^2 \mathcal{G}^{(2)}(\omega + \omega_{m-2}^m) G_\omega^{(2m)} d\omega], \end{aligned} \quad (16b)$$

with

$$G_\omega^{(1m)} = (1/\text{Tr} \mathfrak{H}'_D^{(s)2}) \int_{-\infty}^{\infty} e^{-i\omega t} \text{Tr} e^{i\mathfrak{H}_0 t} \mathfrak{N}_{m-1}^+ e^{-i\mathfrak{H}_0 t} \mathfrak{N}_m^- dt$$

and

$$\begin{aligned} G_\omega^{(2m)} &= (1/\text{Tr} \mathfrak{H}'_D^{(s)2}) \int_{-\infty}^{\infty} e^{-i\omega t} \text{Tr} e^{i\mathfrak{H}_0 t} \mathfrak{N}_{m-1}^+ \mathfrak{N}_{m-2}^+ \\ &\quad \times e^{-i\mathfrak{H}_0 t} \mathfrak{N}_{m-1}^- \mathfrak{N}_m^- dt. \end{aligned}$$

A new situation arises when the static quadrupole interaction  $\mathfrak{H}'_Q^{(0)}$  in the Hamiltonian (11) is zero or smaller than the dipolar interaction. The eigenvalues of the population operators are no longer good quantum numbers and the  $z$  component of the total angular momentum describes the spin system. The Hamiltonian is written as follows:

$$\mathfrak{H} = -\omega_0 J_z + \mathfrak{H}'_D^{(0)} + \mathfrak{H}'_Z + \mathfrak{H}'_{\text{rf}}(t) + \mathfrak{H}'_Q. \quad (17)$$

Here the secular part of the dipolar interaction  $\mathfrak{H}'_D^{(0)}$ , which commutes with  $J_z$ , differs from the secular part of the dipolar interaction in expression (11a),  $\mathfrak{H}'_D^{(s)}$ . The nonsecular part of the dipolar

interaction is neglected again. Defining orthogonal and commutable operators  $J_Z$  and  $\mathcal{H}_D^{(0)}$ , the kinetic coefficients can be derived in the same way as before. The spin-lattice relaxation matrix has only two diagonal components  $T_1^{-1}$  and  $T_D^{-1}$ :

$$T_1^{-1} = K \mathcal{J}^{(1)}(\omega_0) + 4K \mathcal{J}^{(2)}(2\omega_0),$$

with

$$K = (3/10N) \bar{Q}^2 (2s + 3)$$

and

$$T_{1D}^{-1} = \int_{-\infty}^{\infty} d\omega \omega^2 \left[ \frac{1}{2} \mathcal{J}^{(0)}(\omega) G_{\omega}^{(0)} + \sum_{\alpha=1}^2 \mathcal{J}^{(\alpha)}(\alpha\omega_0 + \omega) G_{\omega}^{(\alpha)} \right],$$

with

$$G_{\omega}^{(\alpha)} = (1/\text{Tr} \mathcal{H}_D^{(0)2}) \int_{-\infty}^{\infty} dt e^{-i\omega t} \text{Tr} e^{i\mathcal{H}_D^{(0)} t} Q^{(\alpha)} \times e^{-i\mathcal{H}_D^{(0)} t} Q^{(-\alpha)}.$$

In contrast to the dipolar spin-lattice relaxation rate of the spin system with unequally spaced energy levels, here we have the term  $\mathcal{J}^{(0)}(\omega)$  which describes the spin interaction with the very slow lattice motions. With a suitable choice of crystal orientation in the magnetic field, it is possible to measure the dipolar spin-lattice relaxation rates for the equidistant and nonequidistant case separately in the same sample. And by analyzing this data the information about slow and fast lattice motion can be separated.

The problem of the spin-lattice relaxation of the

quadrupole-interacting spin system has been studied before,<sup>4,8</sup> but the consideration have been restricted to systems with a fixed spin. Expression (16a) makes it possible to calculate the spin-level population relaxation for systems with any spin. Beside it, the results in expression (16b) together with expression (17a) throw a new light on the spin-lattice relaxation of the dipolar energy in systems with equally and unequally spaced energy levels.

## B. Saturation

The oscillating magnetic field, perpendicular to the high stationary magnetic field, can produce effects of a different kind. The case when the probabilities of transition induced by the rf field are comparable with those induced by the spin-lattice coupling is of concern, but are weaker than those caused by the dipolar spin-spin interaction. This situation is known as partial saturation.

The spin interaction with the oscillating magnetic field perpendicular to the high magnetic field is described as follows:

$$\mathcal{H}_{\text{rf}}(t) = \frac{1}{2} \mu_N H_1 [J^+ e^{i\omega t} + J^- e^{-i\omega t}]. \quad (19)$$

Using Eq. (9), the saturation matrix of the spin system with unequally spaced energy levels, as defined by the Hamiltonian (11) is

$$\{W\} = \begin{pmatrix} W_{ss} & W_{s(s-1)} & \cdots & W_{s(-s)} & W_{sD} \frac{\text{Tr} \mathcal{H}_D^{(s)2}}{\text{Tr} \mathcal{H}_m^2} \\ W_{(s-1)s} & W_{(s-1)(s-1)} & \cdots & W_{(s-1)(-s)} & W_{(s-1)D} \frac{\text{Tr} \mathcal{H}_D^{(s)2}}{\text{Tr} \mathcal{H}_m^2} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ W_{(-s)s} & W_{(-s)(s-1)} & \cdots & W_{(-s)(-s)} & W_{(-s)D} \frac{\text{Tr} \mathcal{H}_D^{(s)2}}{\text{Tr} \mathcal{H}_m^2} \\ W_{sD} & W_{(s-1)D} & \cdots & W_{(-s)D} & W_D \end{pmatrix}. \quad (20)$$

The matrix components can be derived in a similar manner to the spin-lattice relaxation case. The rf field influence to the level population is

$$\begin{aligned} W_{mm'} &= \frac{1}{\text{Tr} \mathcal{H}_m^2} \int_0^{\infty} dt \text{Tr} e^{i\mathcal{H}_0 t} [\mathcal{H}_m, \mathcal{H}_{\text{rf}}(t)] \\ &\quad \times e^{-i\mathcal{H}_0 t} [\mathcal{H}_{\text{rf}}(0), \mathcal{H}_m] \\ &= \left( \frac{\mu_N H_1}{2} \right)^2 \frac{\text{Tr} \mathcal{H}_D^{(s)2}}{\text{Tr} \mathcal{H}_m^2} [(A_m^+)^2 G_{\Delta_{m-1}^{(1m)}} (\delta_{mm'} - \delta_{m, m'-1}) \\ &\quad + (A_m^+)^2 G_{\Delta_{m+1}^{(1m)}} (\delta_{m, m'} - \delta_{m, m'+1})], \end{aligned} \quad (20a)$$

with

$$\Delta_m^m = \omega - (E_m - E_{m'}) \hbar^{-1}.$$

The mixing between the level population energy and the dipolar energy is defined by

$$\begin{aligned} W_{m,D} &= \frac{1}{\text{Tr} \mathcal{H}_D^{(s)2}} \int_0^{\infty} dt \text{Tr} e^{i\mathcal{H}_0 t} [\mathcal{H}_m, \mathcal{H}_{\text{rf}}(t)] \\ &\quad \times e^{-i\mathcal{H}_0 t} [\mathcal{H}_{\text{rf}}(0), \mathcal{H}_D^{(s)}] \\ &= \left( \frac{\mu_N H_1}{2} \right)^2 [(A_m^+)^2 \Delta_m^{m+1} G_{\Delta_{m+1}^{(1m)}} - (A_m^-)^2 \Delta_{m-1}^m G_{\Delta_{m-1}^{(1m)}}], \end{aligned} \quad (20b)$$

and the changes of the dipolar energy owing to the rf field are determined by

$$W_D = \frac{1}{\text{Tr } \mathcal{H}_D^{(s)2}} \int_0^\infty dt \text{Tr} e^{i\mathcal{H}_0 t} [\mathcal{H}_D^{(s)}, \mathcal{H}_{\text{rf}}(t)] \\ \times e^{-i\mathcal{H}_0 t} [\mathcal{H}_{\text{rf}}(0), \mathcal{H}_D^{(s)}] \\ = \left( \frac{\mu_N H_1}{2} \right)^2 \sum_{m=-s}^s (\Delta_{m-1}^m A_m^-)^2 G_{\Delta_{m-1}}^{(1m)}. \quad (20c)$$

Here  $G_{\Delta}^{(1m)}$  was defined in expression (16b).

The saturation matrix elements are similar to those which have been obtained in Provotorov's paper<sup>9</sup> but here the operators  $\mathcal{H}_m^+$  and  $\mathcal{H}_m^-$  are used instead of the total spin operators.

#### IV. CONCLUSION

The above derivation is limited to a weak quad-

rupole interactions and enables one to obtain the kinetic equations for the system of any spin. In addition, the formalism can be applied to any kind of quadrupole-interacting spin system with the appropriately defined energy-level population operators and with a suitable choice of the secular part of the dipolar energy. For instance, in the case of a pure quadrupole-interacting spin system, with the axially symmetric EFG tensor, the level population operators are the sum of the above defined

$$\mathcal{H}_k = \mathcal{H}_m + \mathcal{H}_{-m}.$$

The secular part of the dipolar interaction is defined to be that part of the  $\mathcal{H}_D$ , which commutes with  $\mathcal{H}_k$ . The coefficients in the kinetic equations are, then, the combination of the coefficients in the expressions (16) and (20).

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## Electrical Resistivity of $\alpha$ -Cerium\*

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Electrical-resistivity measurements have been made between 1.5 and 300 °K on  $\alpha$ -cerium cooled while at pressures of 10 or 18 kbar. Two types of behavior were found: Cerium quenched from 300 to 77 °K showed the presence of a magnetic impurity, possibly clusters of  $\beta$ -cerium; and cerium which was slowly cooled from room temperature showed no evidence of magnetic behavior. Whereas the "magnetically impure" sample showed a strong  $\rho \propto T^2$  dependence at low temperatures, the slowly cooled sample had  $\rho \propto T^5$ . It is suggested that the magnetic impurity present in previous studies may have prevented the observation of superconductivity in  $\alpha$ -cerium.

### I. INTRODUCTION

The use of high-pressure techniques has allowed a number of researchers to stabilize the  $\alpha$  phase of cerium ("the collapsed fcc structure") to liquid-helium temperatures.<sup>1-3</sup> In the technique generally used a sample is loaded in a pressure clamp to about 10 kbar at room temperature, quenched into liquid nitrogen, and then measurements may be made. In fact, if the pressure is released with the clamp under liquid nitrogen, samples may be retained in the  $\alpha$  phase at zero pressure and

data at zero pressure may be obtained even below 4 °K. Recent property measurements have included magnetic susceptibility<sup>2,3</sup> and specific heat.<sup>1</sup> One result of these studies has been a picture of  $\alpha$ -cerium with a valence around 3.7, having 0.3 4*f* electrons per atom in a high density of states, virtual level, 0.02 eV wide.<sup>4</sup> This model fits in well with the estimation of exchange enhancements to the Pauli susceptibility of about 5-10. The effect of pressure is to slightly decrease the *f*-level contribution. This model is based on the promotion of ~0.6 4*f* electrons into