THE PRINCIPLES OF NUCLEAR MAGNETISM

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OXFORD
AT THE CLARENDON PRESS

Oxford University Press, Walton Street, Oxford OX2 6DP

OXFORD LONDON GLASGOW
NEW YORK TORONTO MELBOURNE WELLINGTON
KUALA LUMPUR SINGAPORE JAKARTA HONG KONG TOKYO
DELHI BOMBAY CALCUTTA MADRAS KARACHI
IBADAN NAIROBI DAR ES SALAAM CAPE TOWN

ISBN 0 19 851236 8

First published 1961
Reprinted from corrected sheets of the first edition
1962, 1967, 1970, 1973, 1978

Printed in Great Britain
at the University Press, Oxford
by Vivian Ridler
Printer to the University

and it is apparent that $|A_n/A_{n-1}| \cong [\overline{|\mathscr{H}_1|^2}\tau_c^2]^{\frac{1}{2}}$, which is very small if the correlation time is very short.

To conclude, the equation (33) is valid if $[\overline{|\mathscr{H}_1|^2}\tau_c^2]^{\frac{1}{2}}$ is a very small number.

For the validity of the master equation (35) with constant coefficients a further assumption is required: all differences $\alpha-\beta$ or even combined differences $(\alpha-\alpha')-(\beta-\beta')$ between the energies (on the frequency scale) of the unperturbed Hamiltonian $\hbar\mathscr{H}_0$, unless identically zero, must be large compared with the constant $1/T \cong \overline{|\mathscr{H}_1|^2}\tau_c$ which gives the relative rate of change of σ^*.

D. Quantum mechanical formulation of the problem

The semi-classical treatment where the coupling with the lattice is represented by random functions suffers from several defects, the main one being that, for the spin system, it always leads to a steady state described by an infinite temperature.

It will be shown that a quantum mechanical description of the lattice can be cast in a form very similar to that of the semi-classical description, but will lead for a spin system to a finite temperature equal to that of the lattice.

We start with a time-independent Hamiltonian

$$\hbar\mathscr{H} = \hbar(\mathscr{H}_0+\mathscr{F}+\mathscr{H}_1), \tag{47}$$

where $\hbar\mathscr{H}_0$ and $\hbar\mathscr{F}$ are the unperturbed Hamiltonians of the spin system S and the lattice, respectively, with eigenstates $|\alpha)$ and $|f)$, and $\hbar\mathscr{H}_1$ describes the perturbing coupling between them and contains parameters of both the spin system and the lattice.

$\mathscr{H}_1$ can be expanded as

$$\mathscr{H}_1 = \sum_q F^{(q)}A^{(q)}, \tag{48}$$

where the $F^{(q)}$ and the $A^{(q)}$ are respectively lattice and spin operators.

To pursue the parallel with the previous semi-classical formalism we define

$$\mathscr{H}_1(t) = e^{i\mathscr{F}t}\mathscr{H}_1 e^{-i\mathscr{F}t} = \sum_q F^{(q)}(t)A^{(q)}, \tag{49}$$

with

$$F^{(q)}(t) = e^{i\mathscr{F}t}F^{(q)}e^{-i\mathscr{F}t}$$

and

$$\mathscr{H}_1^*(t) = e^{i\mathscr{H}_0t}\mathscr{H}_1(t)e^{-i\mathscr{H}_0t} = \sum_q F^{(q)}(t)A^{(q)}(t) = \sum_{q,p} F^{(q)}(t)A_p^{(q)}e^{i\omega_p^{(q)}t}. \tag{49'}$$

The similarity in form with the notation of the previous sections is complete.

To understand how the description of the spin-lattice coupling leads to a finite temperature for the spin system, consider for simplicity the case where the expansion (48) contains a single term $\mathscr{H}_1 = FA$ which induces in the spin system S a probability per unit time $W_{\alpha\beta}$ of passing from a state $|\beta)$ to a state $|\alpha)$, which differ in energy by $\omega_{\alpha\beta} = \alpha - \beta$. We consider first the more detailed transition $|\beta,f) \to |\alpha,f')$ of the combined system spins plus lattice:

$$W_{\alpha f',\beta f} = \int_0^t (\beta,f \mid \mathscr{H}_1 \mid \alpha,f')(\alpha,f' \mid \mathscr{H}_1 \mid \beta,f)e^{-i[\alpha-\beta+f'-f](t-t')}\,dt' + \text{c.c.}, \quad (50)$$

which can be made very similar in appearance to formula (2) by using

$$\mathscr{H}_1(t) = e^{i\mathscr{F}t}\mathscr{H}_1\,e^{-i\mathscr{F}t} = Ae^{i\mathscr{F}t}Fe^{-i\mathscr{F}t} = AF(t),$$

$$W_{\alpha f',\beta f} = \int_0^t (\beta,f \mid \mathscr{H}_1(t) \mid \alpha,f')(\alpha,f' \mid \mathscr{H}_1(t-\tau) \mid \beta,f)e^{-i\omega_{\alpha\beta}\tau}\,d\tau + \text{c.c.}$$

$$= |(\alpha \mid A \mid \beta)|^2 \int_0^t (f \mid F(t) \mid f')(f' \mid F(t-\tau) \mid f)e^{-i\omega_{\alpha\beta}\tau}\,d\tau + \text{c.c.} \quad (51)$$

The total probability $W_{\alpha\beta} = \sum_{f,f'} P(f)W_{\alpha f',\beta f}$, where $P(f) = ae^{-\hbar f/kT}$ is the probability of finding a lattice at a temperature T, in any initial state $|f)$, is given by

$$W_{\alpha\beta} = |(\alpha \mid A \mid \beta)|^2 \int_{-\infty}^{\infty} e^{-i\omega_{\alpha\beta}\tau} \sum_{f,f'} P(f)(f \mid F(t) \mid f')(f' \mid F(t-\tau) \mid f)\,d\tau. \quad (52)$$

The discrete summation over the index f should actually, because of the continuous spectrum of the lattice, be replaced by an appropriate integration $\int \eta(f)\,df$, where $\eta(f)$ is the density of lattice states. We will continue to write symbolically $\sum_f$ for simplicity. The expression

$$\sum_{f,f'} P(f)(f \mid F(t) \mid f')(f' \mid F(t-\tau) \mid f)$$

which from the definition of $F(t)$ is clearly independent of t, can be written

$$g(\tau) = \text{tr}_f\,\{F(t)\mathscr{P}(\mathscr{F})F(t+\tau)\}, \quad (53)$$

where $\mathscr{P}(\mathscr{F})$ is the statistical operator

$$\mathscr{P}(\mathscr{F}) = ae^{-\hbar\mathscr{F}/kT} = \exp\left(\frac{-\hbar\mathscr{F}}{kT}\right)\Big/\text{tr}_f\left\{\exp\left(\frac{-\hbar\mathscr{F}}{kT}\right)\right\}. \quad (54)$$

$g(\tau)$ is the quantum mechanical analogue of the classical correlation function $g(\tau)$ of a classical random function $F(t)$, defined previously as $g(\tau) = \overline{F(t).F(t+\tau)}$, where the bar represented an ensemble average over the probability distribution of the random function. Defining

$$J(\omega) = \int_{-\infty}^{\infty} g(\tau)e^{-i\omega\tau}\,d\tau, \quad (55)$$

we obtain
$$W_{\alpha\beta} = |(\alpha \mid A \mid \beta)|^2 J(\omega_{\alpha\beta}), \tag{56}$$
which is formally identical with formula (24′). There is, however, an important difference because now
$$J(-\omega) = \exp(\hbar\omega/kT)J(\omega),$$
and according to (56) a lattice induced transition where the lattice gains the energy $\hbar\omega$ is more probable than the opposite one by a factor $\exp(\hbar\omega/kT)$. This is seen from the definitions (53) and (55) of $J(\omega)$:
$$\begin{aligned} J(\omega) &= a \int_{-\infty}^{\infty} \sum_{f,f'} |(f \mid F \mid f')|^2 e^{-\hbar f/kT} e^{i(f-f'-\omega)\tau}\, d\tau \\ &= 2\pi a \sum_f |(f \mid F \mid f-\omega)|^2 e^{-\hbar f/kT}, \\ J(-\omega) &= 2\pi a \sum_f |(f \mid F \mid f+\omega)|^2 e^{-\hbar f/kT}, \end{aligned} \tag{57}$$
or, since the summation over f is actually a continuous integration from $-\infty$ to $+\infty$, replacing $f+\omega$ by f we get
$$J(-\omega) = 2\pi a \sum_f |(f-\omega \mid F \mid f)|^2 e^{-\hbar(f-\omega)/kT} = e^{\hbar\omega/kT} J(\omega). \tag{58}$$
We now pass on to the more general problem of deriving a master equation describing the motion of the spin system S, analogous to the equations (34), (35), or (42) of this chapter. A density matrix ρ now describes the behaviour of the combined quantum mechanical system: spins+lattice. Its transform in the interaction representation
$$\rho^* = e^{i(\mathscr{H}_0+\mathscr{F})t} \rho e^{-i(\mathscr{H}_0+\mathscr{F})t}$$
obeys the equation
$$\frac{i\, d\rho^*}{dt} = -[\mathscr{H}_1^*(t), \rho^*], \tag{59}$$
where $\mathscr{H}_1^*(t)$ is defined by equation (49′). A forward integration of (59) leads to an equation similar in form to equation (32):
$$\frac{d\rho^*}{dt} = -i[\mathscr{H}_1^*(t), \rho^*(0)] - \int_0^t d\tau\, [\mathscr{H}_1^*(t), [\mathscr{H}_1^*(t-\tau), \rho^*(0)]] + \text{higher-order terms}. \tag{60}$$
Since all the observations are performed on the spin system, all the relevant information is contained in the reduced density matrix
$$\sigma^* = \mathrm{tr}_f\{\rho^*\}$$
with matrix elements $(\alpha \mid \sigma^* \mid \alpha') = \sum_f (f\alpha \mid \rho^* \mid f\alpha')$. We make the fundamental assumption that the lattice, because of its very large heat capacity, remains in thermal equilibrium so that $\rho^*(t) = \mathscr{P}(\mathscr{F})\sigma^*(t)$, where $\mathscr{P}(\mathscr{F})$ is the statistical operator (54).

In order to obtain an equation for the rate of change of the spin density matrix σ^*, we perform on both sides of (60) the operation trace with respect to the lattice parameters f.

Assume first that the temperature of the lattice is infinite so that the statistical operator $\mathscr{P}(\mathscr{F})$ is proportional to the unit operator and $\rho^*(0) = a\sigma^*(0)$.

$$a = [\mathrm{tr}_f\{\exp(-\hbar\mathscr{F}/kT)\}]^{-1}$$

becomes in that case $1/L$, where L is the number (astronomically large) of degrees of freedom of the lattice. We shall represent by a bar the operation $a\,\mathrm{tr}_f\{\ \ \}$. In that case we get

$$\frac{d\sigma^*}{dt} = -i\overline{[\mathscr{H}_1^*(t), \sigma^*(0)]} - \int_0^t d\tau\, \overline{[\mathscr{H}_1^*(t), [\mathscr{H}_1^*(t-\tau), \sigma^*(0)]]}. \quad (61)$$

This equation is formally identical to the equation (32), and using the expansion (49) for $\mathscr{H}_1(t)$ a master equation of exactly the same form as equations (40) and (42) can be obtained for σ^*.

The only change is that correlation functions of classical random functions $F^{(q)}(t)$ are replaced by correlation functions of operators $F^{(q)}$, defined by

$$g_{qq'}(\tau) = \overline{F^{(q)}(t)F^{(-q')}(t+\tau)} = \frac{1}{L}\sum_{f,f'} (f \mid F^{(q)} \mid f')(f' \mid F^{(-q')} \mid f) e^{i(f'-f)\tau}, \quad (62)$$

a special case of the definition (53) given for a finite temperature of the lattice. The conditions of validity of the master equation, relative to the shortness of the correlation time, are formulated in the same way as in Section II C (g).

The semi-classical treatment of relaxation is thus formally equivalent to the quantum mechanical one for the limiting case of infinite lattice temperatures.

The case of a finite lattice temperature is more complex, for then the lattice operators $F^{(q)}$ and $\mathscr{P}(\mathscr{F})$ do not commute and it is necessary to expand the double commutator on the right-hand side of (60) into four different terms and consider each of them separately. This situation has been studied in great detail (**2**, **3**), and has been shown to lead again to a linear master equation for σ^* which is, however, more complex than (33) or (42). Furthermore, generalized correlation functions of the forms (53) occur in it, with spectral densities $J(\omega)$ having the property

$$J(-\omega) = \exp(\hbar\omega/kT)J(\omega), \quad (63)$$

with, as a consequence, a steady state solution of the form

$$\sigma_0^* = \sigma_0 = \exp(-\hbar\mathscr{H}_0/kT)/\mathrm{tr}\{\exp(-\hbar\mathscr{H}_0/kT)\}.$$

For simplicity we shall first demonstrate this on the assumption (actually seldom realized in practice) that the lattice temperature is sufficiently high to allow a linear expansion of $\exp(-\hbar\mathscr{F}/kT)$ into $1-(\hbar\mathscr{F}/kT)$ and that the state of the spin system described by the density matrix $\sigma^*(t)$ is never very remote from one of equal populations of all spin energy levels. Then

$$\rho^*(t) = \sigma^*(t)\mathscr{P}(\mathscr{F}) \cong a\left\{\sigma^*(t)-\frac{1}{A}\frac{\hbar\mathscr{F}}{kT}\right\}, \tag{64}$$

where A is the number of degrees of freedom of the spin system.

As a consequence, on the right-hand side of the master equation for σ^* there appears an extra term

$$\int\limits_0^\infty \overline{\left[\mathscr{H}_1^*(t), \left[\mathscr{H}_1^*(t-\tau), \frac{\hbar\mathscr{F}}{kT}\frac{1}{A}\right]\right]}\, d\tau \tag{65}$$

or, neglecting small imaginary terms,

$$\frac{1}{2}\int\limits_{-\infty}^\infty \overline{\left[\mathscr{H}_1^*(t), \left[\mathscr{H}_1^*(t-\tau), \frac{\hbar\mathscr{F}}{kT}\frac{1}{A}\right]\right]}\, d\tau.$$

It is easily verified that

$$\int\limits_{-\infty}^\infty [\mathscr{H}_1^*(t-\tau), \mathscr{H}_0+\mathscr{F}]\, d\tau = i\int\limits_{-\infty}^\infty \frac{d}{d\tau}[\mathscr{H}_1^*(t-\tau)]\, d\tau = 0,$$

a consequence of the conservation of total energy $\mathscr{F}+\mathscr{H}_0$. It is permissible to replace $\mathscr{F}$ in (65) by $-\mathscr{H}_0$ and, since a unit operator commutes with everything, to rewrite it as

$$\int\limits_0^\infty \overline{\left[\mathscr{H}_1^*(t), \left[\mathscr{H}_1^*(t-\tau), \left(1-\frac{\hbar\mathscr{H}_0}{kT}\frac{1}{A}\right)\right]\right]}\, d\tau,$$

thus obtaining for the master equation

$$\frac{d\sigma^*}{dt} = -\int\limits_0^\infty \overline{[\mathscr{H}_1^*(t), [\mathscr{H}_1^*(t-\tau), \sigma^*-\sigma_0]]}\, d\tau. \tag{66}$$

The empirical rule whereby in the relaxation equation obtained by the semi-classical method σ^* should be replaced by $\sigma^*-\sigma_0$ is thus justified.

This proof is clearly inadequate in most situations since the very broad and unnecessary requirement $\exp(-\hbar\mathscr{F}/kT) \cong 1-(\hbar\mathscr{F}/kT)$ leads through (62) to expressions for the correlation function, and thus to values for the relaxation times, that are temperature-independent. Actually the much less stringent assumption

$$\left|\frac{\hbar\mathscr{H}_0}{kT}\right| \ll 1, \qquad \left|\sigma^* - \frac{1}{A}\right| \ll 1$$

need only be made. Starting from

$$\frac{d\sigma^*}{dt} = -\mathrm{tr}_f\left\{\int\limits_0^t [\mathscr{H}_1^*(t), [\mathscr{H}_1^*(t-\tau), \rho^*]]\, d\tau\right\}$$

$$\cong -\mathrm{tr}_f\left\{\tfrac{1}{2}\int\limits_{-\infty}^{\infty} [\mathscr{H}_1^*(t), [\mathscr{H}_1^*(t'), \sigma^*\mathscr{P}(\mathscr{F})]]\, dt'\right\}, \tag{66'}$$

where $\mathscr{P}(\mathscr{F}) = ae^{-\beta\mathscr{F}}$ and $\beta = \hbar/kT$, (66′) can be rewritten as

$$-\mathrm{tr}_f\left\{\tfrac{1}{2}\int\limits_{-\infty}^{\infty} [\mathscr{H}_1^*(t), [\mathscr{H}_1^*(t'), \sigma^*]]\, dt'\,.\,\mathscr{P}(\mathscr{F}) - \right.$$

$$\left. -\tfrac{1}{2}\int\limits_{-\infty}^{\infty} [\mathscr{H}_1^*(t'), \mathscr{P}(\mathscr{F})]\, dt'\,.\,\sigma^*\mathscr{H}_1^*(t) + \tfrac{1}{2}\mathscr{H}_1^*(t)\sigma^* \int\limits_{-\infty}^{\infty} [\mathscr{H}_1^*(t'), \mathscr{P}(\mathscr{F})]\, dt'\right\}. \tag{66''}$$

Consider the matrix element

$$\left(\alpha f\left|\int\limits_{-\infty}^{\infty} [\mathscr{H}_1^*(t'), \mathscr{P}(\mathscr{F})]\, dt'\right|\alpha' f'\right)$$

$$= \int\limits_{-\infty}^{\infty} e^{i(f+\alpha-f'-\alpha')t'}\, dt'(\alpha f\,|\,\mathscr{H}_1\,|\,\alpha' f')a(e^{-\beta f'} - e^{-\beta f})$$

$$= 2\pi a\delta(f+\alpha-f'-\alpha')(\alpha f\,|\,\mathscr{H}_1\,|\,\alpha' f')(e^{-\beta f'} - e^{-\beta f}). \tag{66'''}$$

Since

$$\beta(f-f') = \beta(\alpha'-\alpha) \ll 1,$$

(66‴) can be rewritten as

$$\int\limits_{-\infty}^{\infty} e^{i(f+\alpha-f'-\alpha')t'}\, dt'(\alpha f\,|\,\mathscr{H}_1\,|\,\alpha' f')ae^{-\beta f'}(1 - e^{-\beta(\alpha'-\alpha)})$$

$$\cong \int\limits_{-\infty}^{\infty} e^{i(f+\alpha-f'-\alpha')t'}\, dt'(\alpha f\,|\,\mathscr{H}_1\,|\,\alpha' f')ae^{-\beta f'}\beta(\alpha'-\alpha)$$

$$\cong \int\limits_{-\infty}^{\infty} (\alpha f\,|\,[\mathscr{H}_1^*(t'), \beta\mathscr{H}_0]\mathscr{P}(\mathscr{F})\,|\,\alpha' f')\, dt'$$

$$\cong \int\limits_{-\infty}^{\infty} (\alpha f\,|\,\mathscr{P}(\mathscr{F})[\mathscr{H}_1^*(t'), \beta\mathscr{H}_0]\,|\,\alpha' f')\, dt'.$$

We can thus replace $\int_{-\infty}^{\infty}[\mathscr{H}_1^*(t'),\mathscr{P}(\mathscr{F})]\,dt'$ in (66″) by means of

$$\int_{-\infty}^{\infty}[\mathscr{H}_1^*(t'),\beta\mathscr{H}_0]\mathscr{P}(\mathscr{F})\,dt' \simeq -A\int_{-\infty}^{\infty}[\mathscr{H}_1^*(t'),\sigma_0]\mathscr{P}(\mathscr{F})\,dt',$$

where
$$\sigma_0 \simeq \frac{1}{A}\{1-\beta\mathscr{H}_0\} \simeq e^{-\beta\mathscr{H}_0}/\mathrm{tr}\{e^{-\beta\mathscr{H}_0}\}.$$

(66″) can thus be rewritten as

$$-\mathrm{tr}_f\Big\{\tfrac{1}{2}\int_{-\infty}^{\infty}[\mathscr{H}_1^*(t),[\mathscr{H}_1^*(t'),\sigma^*]]\,dt'\mathscr{P}(\mathscr{F})+ \\ +\tfrac{1}{2}\int_{-\infty}^{\infty}[\mathscr{H}_1^*(t'),\sigma_0]A\sigma^*\mathscr{H}_1^*(t)\mathscr{P}(\mathscr{F})\,dt'- \\ -\tfrac{1}{2}\int_{-\infty}^{\infty}\mathscr{H}_1^*(t)\sigma^*A[\mathscr{H}_1^*(t'),\sigma_0]\,dt'\,\mathscr{P}(\mathscr{F})\Big\}.$$

In the last two terms we replace $A\sigma^*$ by unity within the approximation $|\sigma^*-1/A| \ll 1$, whence (66″) becomes

$$-\mathrm{tr}_f\Big\{\tfrac{1}{2}\int_{-\infty}^{\infty}[\mathscr{H}_1^*(t),[\mathscr{H}_1^*(t'),\sigma^*-\sigma_0]]\mathscr{P}(\mathscr{F})\,dt'\Big\}.$$

The definition (62) of the correlation function should be replaced by the following:

$$\begin{aligned} g_{qq'}(\tau) &= \overline{F^{(q)}(t)F^{(-q')}(t+\tau)} \\ &= \mathrm{tr}_f\{e^{i\mathscr{F}t}F^{(q)}e^{-i\mathscr{F}t}e^{i\mathscr{F}(t+\tau)}F^{(-q')}e^{-i\mathscr{F}(t+\tau)}\mathscr{P}(\mathscr{F})\} \\ &= \frac{1}{\mathrm{tr}_f\{e^{-\hbar\mathscr{F}/kT}\}}\sum_{f,f'}(f\,|\,F^{(q)}\,|f')(f'\,|\,F^{(-q')}\,|f)e^{-i(f-f')\tau}e^{-\hbar f/kT}, \end{aligned}$$

where the dependence on the lattice temperature is apparent.

E. Relaxation by dipolar coupling

The dipole-dipole interaction between two spins I and S can be written

$$\hbar\mathscr{H}_1 = \sum_q F^{(q)}A^{(q)}, \tag{67}$$

where the $F^{(q)}$ are random functions of the relative positions of two spins and the $A^{(q)}$ are operators acting on the spin variables with the convention $F^{(q)} = F^{(-q)*}$; $A^{(q)} = A^{(-q)\dagger}$.

$$F^{(1)} = \frac{\sin\theta\cos\theta\,e^{-i\varphi}}{r^3}, \qquad F^{(2)} = \frac{\sin^2\theta\,e^{-2i\varphi}}{r^3}, \qquad F^{(0)} = \frac{1-3\cos^2\theta}{r^3}, \tag{68}$$

$$\begin{aligned} A^{(0)} &= \alpha\{-\tfrac{2}{3}I_zS_z+\tfrac{1}{6}(I_+S_-+I_-S_+)\}, \\ A^{(1)} &= \alpha\{I_zS_++I_+S_z\}, \\ A^{(2)} &= \tfrac{1}{2}\alpha I_+S_+, \qquad \alpha = -\tfrac{3}{2}\gamma_I\gamma_S\hbar. \end{aligned} \tag{69}$$