MACROSCOPIC EQUATIONS FOR NUCLEAR SPIN
RESONANCE IN DENSITY MATRIX FORMALISM

by

SHRIDHAR DATTATRAYA JOG

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

Physics

We accept this thesis as conforming to the

standard required from candidates for the

degree of MASTER OF SCIENCE

_____

_____

Members of the Department of Physics

THE UNIVERSITY OF BRITISH COLUMBIA

SEPTEMBER 1960

In presenting this thesis in partial fulfilment of
the requirements for an advanced degree at the University
of British Columbia, I agree that the Library shall make
it freely available for reference and study. I further
agree that permission for extensive copying of this thesis
for scholarly purposes may be granted by the Head of my
Department or by his representatives. It is understood
that copying or publication of this thesis for financial
gain shall not be allowed without my written permission.

Department of ___Physics___

The University of British Columbia,
Vancouver 8, Canada.

Date ___Sept 26, 1960___

ABSTRACT

Methods of setting up generalized Bloch equations governing the time dependence of macroscopic magnetization for a system of nuclei of spin I, in given magnetic and electric fields, have been proposed for the degenerate case by Bloom, Hahn and Herzog and by Lurçat, and for the non-degenerate case by Bloom, Robinson and Volkoff. In this thesis an attempt is made to give a unified discussion of these methods by utilizing the density matrix formalism and to demonstrate the interrelationship between them. Relaxation effects are not considered.

The general theory is developed in terms of the density matrix formalism and is applied to the non-degenerate and the degenerate cases. The results are discussed and compared with those of the previous investigators.

TABLE OF CONTENTS

iii

ACKNOWLEDGMENTS

I wish to thank Professor G. M. Volkoff for suggesting the problem and for his constant help in all the phases of development of this work.

I also wish to thank the National Research Council for providing financial assistance throughout the year in the form of a research grant.

CHAPTER I

INTRODUCTION

A nucleus of spin I having a magnetic moment μ and (for $I \geqslant 1$) an electric quadrupole moment eQ has $2I + 1$ energy levels (which in some special cases become degenerate in pairs) when placed in a combination of a non-uniform electric field (characterized by an electric field gradient tensor with or without axial symmetry) and a constant uniform magnetic field H_o. Transitions between such levels usually fall in the radio-frequency region, and can be studied experimentally by subjecting the similarly situated nuclei in a single crystal to a weak oscillating magnetic field (usually linearly polarized along the axis of the coil producing it) of variable radio frequency $\frac{\omega}{2\pi}$, and by observing as a function of ω the resonances in the absorption or the induction signals in some of the by now conventional types of spectrometers. Alternatively, free precession or spin-echo techniques can be utilized.

The observed signal strength in all such experiments is proportional to the time derivative of the component along the axis of a receiver coil of the macroscopic magnetization of the sample. Methods of setting up generalized Bloch equations governing the time dependence of this macroscopic magnetization have been proposed for different cases in which relaxation effects are neglected by Bloom, Hahn and Herzog[1], by Lurçat[4] and by Bloom, Robinson and Volkoff[2]. The object

of the present thesis is to give a unified discussion of
these methods by utilizing the density matrix formalism
(cf., for example, Fano[3]) and to demonstrate the
interrelationship between them.

An assembly of N mutually non-interacting nuclei
of spin I subjected to identical electric and magnetic
fields can be described by a Hermitian density matrix ρ of 2I+1
rows and columns containing $(2I+1)^2$ real parameters. The
expectation value of any operator A is given by

$$\langle A \rangle = Tr\,(A\rho) = \sum_{nn'} A_{nn'}\,\rho_{n'n} \tag{1}$$

Taking A to be the identity operator we have $Tr(\rho) = \sum_n \rho_{nn} = 1$,
leaving $4I\,(I+1)$ independent real parameters to describe the
system. This means that $4I\,(I+1)$ independent physical
quantities are needed to describe completely the macroscopic
behaviour of the system. For such macroscopic quantities it is
in some cases convenient to utilize the three components of
the macroscopic magnetization, the five components of the
electric quadrupole moment density, the seven components of
the magnetic octopole moment density, etc., each set expressed
in tensorial form U_{kq} transforming under co-ordinate rotations
like the spherical harmonics Y_{kq} with k being an integer
running up to 2I, and q running in integral steps from
- k to k. Thus, for nuclei of $I = \frac{1}{2}$ the three components of
the magnetization describe the system completely, for $I = 1$ the
five components of the quadrupole moment density are in general
needed in addition to give a complete description in terms of

eight quantities, while for $I = 3/2$ the seven octopole moment density components are also needed to provide 15 quantities, etc. Equations (1) establish the connection between the density matrix elements and these macroscopic quantities if we take A to be in turn equal to each one of the appropriate $4 I (I+1)$ multipole moment operators.

Since the time dependence of the density matrix when relaxation processes are neglected is governed by the equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} \left[\mathcal{H}_{total} \, \rho - \rho \, \mathcal{H}_{total} \right] \tag{2}$$

where $\mathcal{H}_{total}$ is the total Hamiltonian for a single nucleus acted upon by the given magnetic and electric fields, the time dependence of the $4 I (I+1)$ macroscopic physical quantities describing the system can in this case be expressed in the form of $4 I (I+1)$ simultaneous first order differential equations obtained by combining (1) and (2).

For $I = \frac{1}{2}$ the complete macroscopic behaviour of the system is described by three equations in terms of the three magnetization components M_x, M_y, M_z, or alternatively M_z can be eliminated by introducing the difference n between the fractional populations of the $m = \pm \frac{1}{2}$ states.

Lurçat discusses the special pure quadrupole case with an axially symmetric field gradient and first obtains for nuclei with $I = 1$, $3/2$ and $5/2$ complicated sets of 8, 15 and 35 simultaneous equations respectively. He then shows how under

resonance conditions each of these sets reduces to three approximate equations analogous to the three equations determining the magnetization in the case of $I = \frac{1}{2}$.

Bloom, Hahn and Herzog and also Bloom, Robinson and Volkoff arrive more directly at sets of three approximate equations for nuclei of arbitrary spin I under certain specified conditions.

In this thesis we start with equations (2) for the $4I$ $(I + 1)$ independent parameters of the density matrix corresponding to a fairly general Hamiltonian and examine the method of reducing this system of equations under resonance conditions to three approximate equations which are then compared to the results of the previous investigations.

CHAPTER II

TIME DEPENDENCE OF THE DENSITY MATRIX

The Hamiltonian $\mathcal{H}_{total}$ for a nucleus of spin I interacting with arbitrary static electric and magnetic fields and a weak oscillating magnetic field can be split into two parts $\mathcal{H}_o$ and $\mathcal{H}$ where $\mathcal{H}_o$ does not and $\mathcal{H}$ does depend on the time, so that

$$\mathcal{H}_{total} = \mathcal{H}_o + \mathcal{H} \tag{3}$$

where, for example, (cf. Bloom, Robinson and Volkoff)

$$\mathcal{H}_o = \frac{e Q \phi_{zz}}{4 I (2I-1)} \left[(3 I_z^2 - \vec{I}^2) + (I_x^2 - I_y^2) \eta \right]$$
$$- \gamma \hbar \, \vec{I} \cdot \vec{H}_o \tag{4}$$

and

$$\mathcal{H} = \gamma \hbar \, \vec{I} \cdot \vec{H}(t) \tag{5}$$

In (4) x, y, z are the principal axes of the electric field gradient tensor whose component along the z - axis (usually chosen to be the one of greatest absolute value) is ϕ_{zz} , and whose asymmetry parameter is $\eta = (\phi_{xx} - \phi_{yy})/\phi_{zz}$. The time dependent part of the Hamiltonian (5) is assumed to be due to a weak applied r . f . field $\vec{H}(t)$ of frequency ω which is usually linearly polarized.

The eigenvalue problem

$$\mathcal{H}_o \Psi_k = E_k \Psi_k \tag{6}$$

can be solved (numerically if necessary) and leads to $2I + 1$

eigenvalues E_k and time-independent eigenfunctions

$$\Psi_k = \sum_{\ell} u_\ell \, c_{\ell k} \quad , \quad k, \ell = 1, 2, \cdots (2I+1),$$

where the u_ℓ are eigenfunctions of I_z. An example for $I = 5/2$ (Al^{27} in Spodumene) is discussed by Bloom, Robinson and Volkoff.

If we define the transition frequencies $\omega_{jk}/2\pi$ by

$$\omega_{jk} = (E_j - E_k)/\hbar = -\omega_{kj} \tag{7}$$

then in the Ψ_j representation equations (2) - (7) lead to the $(2I+1)^2$ equations

$$\frac{d}{dt} \rho_{jk} = -i\omega_{jk}\rho_{jk} + \frac{i}{\hbar} \mathcal{H}_{jk}(\rho_{jj} - \rho_{kk})$$
$$+ \frac{i}{\hbar} \left(\sum_{\ell \neq j}' \rho_{j\ell} \mathcal{H}_{\ell k} - \sum_{\ell \neq k}' \mathcal{H}_{j\ell} \rho_{\ell k} \right) \tag{8}$$

where

$$\mathcal{H}_{jk} = \gamma \hbar \, \vec{I}_{jk} \cdot \vec{H}(t) \tag{8'}$$

is the matrix element of the time dependent perturbing operator $\mathcal{H}$ of equation (5) between the states Ψ_j and Ψ_k, and $\vec{I}_{jk}$ is the time-independent matrix element of the spin operator $\vec{I}$ between these states which can be explicitly evaluated in terms of the known $c_{\ell k}$ in $\Psi_k = \sum_{\ell} u_\ell c_{\ell k}$.

In the absence of an applied r. f. field $\mathcal{H} = 0$, and equations (8) have the solutions

$$\rho_{jk} = (\rho_{jk})_0 \; e^{-i\omega_{jk} t} \tag{9}$$

where the $(\rho_{jk})_0$ are constants determined by the initial conditions, so that ρ_{jk} oscillate harmonically with the frequencies $\omega_{jk}/2\pi$.

We are interested in investigating the behaviour of the system of nuclei when a weak perturbing magnetic field of frequency $\omega/2\pi$ is applied to the system with ω very close to a particular one of the ω_{jk} characterizing the system, say $\omega_{\lambda s} = \omega_0$. The discussion will differ somewhat depending on whether all the ω_{jk} are different (we shall speak of this as a non-degenerate system), or not (we shall speak of a system having two or more ω_{jk} the same as degenerate even when no energy levels are degenerate). The perturbing effect of the time dependent $\mathcal{H}$ can be conveniently discussed by introducing a transformation to replace the ρ_{jk} by the possibly also time-dependent transformed quantities ρ_{jk}^* related to ρ_{jk} and to some arbitrarily selected constant frequencies $\omega'_{jk}/2\pi$ by

$$\rho_{jk} = \rho_{jk}^* \; e^{-i\omega'_{jk} t} \tag{10}$$

where, as we shall presently see, it will be convenient to choose the arbitrary quantities ω'_{jk} to be either exactly or very nearly equal to the corresponding ω_{jk} characterizing the system. In terms of ρ_{jk}^* equations (8) become

$$\frac{d}{dt} \rho_{jk}^* = i(\omega_{jk}' - \omega_{jk}) \rho_{jk}^* + \frac{i}{\hbar} \mathcal{H}_{jk} (\rho_{jj}^* - \rho_{kk}^*) e^{i\omega_{jk}' t}$$

$$+ \frac{i}{\hbar} \sum_{\ell \neq j}' \rho_{j\ell}^* \mathcal{H}_{\ell k} e^{i(\omega_{jk}' - \omega_{j\ell}')t} \tag{11}$$

$$- \frac{i}{\hbar} \sum_{\ell \neq k}' \mathcal{H}_{j\ell} \rho_{\ell k}^* e^{i(\omega_{jk}' - \omega_{\ell k}')t}$$

The system of $(2I + 1)^2$ simultaneous equations
(8) or (11) gives the exact time dependence of ρ_{jk} or
ρ_{jk}^* for both degenerate and non-degenerate systems
(neglecting all relaxation effects), but is tedious to set
up and to integrate exactly for $I > \frac{1}{2}$. We therefore use an
approximate method of solving systems of differential
equations described by Bogoliubov and Mitropol'skii (as quoted
by Lurçat[5]).

Consider a system of simultaneous differential
equations

$$\frac{d x_k}{dt} = \varepsilon X_k (t, x_1, x_2, \cdots x_n) \qquad k = 1, 2, \cdots n \tag{12}$$

where ε is a small parameter, and X_k are of the form

$$X_k (t, x_1, \cdots x_n) = \sum_{\nu} e^{i\nu t} X_{k\nu} (x_1, \cdots x_n) \tag{13}$$

the $\nu's$ being any fixed frequencies. Then according to
Bogoliubov and Mitropol'skii the solution of (12) is given

to a first approximation by the solution of

$$\frac{dx_k}{dt} = \varepsilon \ \overline{X_k (t, x_1, \cdots x_n)} \qquad (14)$$

where $\overline{X_k}$ denotes the time average of X_k.

We assume $\vec{H}(t)$ in equations (5) and (8) to be a weak time dependent magnetic field involving a single frequency $\omega/_{2\pi}$ in such a way as to make the time average of $\vec{H}(t) e^{i\omega t}$ equal to a small constant vector

$$\overline{\vec{H}(t) e^{i\omega t}} = \vec{V} \qquad (15)$$

and the time average of $\vec{H}(t) e^{i\omega' t}$ equal to zero for any other $\omega' \neq \omega$. For example, for a linearly polarized field we have:

$$\vec{H}(t) = \vec{H_1} \cos \omega t \quad , \quad \vec{V} = \frac{1}{2} \vec{H_1} \qquad (16)$$

Equations (11) where the $\mathcal{H}_{jk}$ are given by (16) can be brought into the form (12), since $|\vec{H}(t)|$ is assumed to be small, and we can choose the arbitrary transformation frequencies ω'_{jk} in equation (10) to make $\omega'_{jk} - \omega_{jk}$ in equations (11) to be either zero or small. In the following we assume that the time average of $e^{i\nu t}$ is 1 if $\nu = 0$, and is zero if ν differs appreciably from zero. To obtain the latter result it is necessary for ν to be large in comparison with the reciprocal of the time over which the time-average is taken.

At this point it is convenient to discuss first the non-degenerate case (all ω_{jk} different), and then to return to the degenerate case when two or more of the ω_{jk} coincide.

CHAPTER III

NON - DEGENERATE CASE

In this chapter first we shall treat the non-degenerate case (all $\omega_{jk}'s$ different) on the basis of the theory developed in Chapter II. We shall then compare the results with those of Bloom, Robinson and Volkoff, who also have considered the non-degenerate case.

If ω is very close to some one particular $\omega_{rs} = \omega_o > o$, then we can choose all the $\omega_{jk}' = \omega_{jk}$ except for ω_{rs}' , which is chosen equal to ω , rather than to $\omega_{rs} = \omega_0$ in order to avoid ambiguity in evaluating the average value of $e^{i(\omega_{rs}' - \omega)t}$. Equations (11) then become on taking the time averages of the right hand sides:

for non-diagonal terms $(j \neq k)$

$$\frac{d}{dt}\left(\rho_{jk}^*\right) = 0 \qquad \text{unless } j = r \text{ and } k = s \text{ simultaneously}$$

$$\frac{d}{dt}\left(\rho_{rs}^*\right) = i(\omega-\omega_o)\left(\rho_{rs}^*\right)_o + i\gamma\left(\rho_{rr}^* - \rho_{ss}^*\right)_o \vec{I}_{rs}\cdot\overrightarrow{\vec{H}(t)e^{i\omega t}}$$

$$(17_a)$$

for diagonal terms $(j = k)$

$$\frac{d}{dt}\left(\rho_{jj}^*\right) = 0 \qquad \text{unless } j = r \text{ or } j = s$$

$$\frac{d}{dt}\left(\rho_{rr}^*\right) = -\frac{d}{dt}\left(\rho_{ss}^*\right) = i\gamma\left[\left(\rho_{rs}^*\right)_o \vec{I}_{sr}\cdot\overrightarrow{\vec{H}(t)e^{-i\omega t}} - \left(\rho_{sr}^*\right)_o \vec{I}_{rs}\cdot\overrightarrow{\vec{H}(t)e^{i\omega t}}\right]$$

$$(17_b)$$

where $\left(\rho_{ij}^{*}\right)_{o}$ denotes the leading time-independent term in the expansion of ρ_{ij}^{*} in powers of $|\vec{V}|$ and $(\omega - \omega_o)$.

These equations are in the form of equations (14) with the right hand sides completely independent of the time. To the first approximation the solutions of these equations are the same as the solutions of any other set of equations whose right hand sides reduce to (17) on being averaged with respect to time. In particular equations (17) may be replaced by a similar set with the subscript zero left off the ρ_{ij}^{*} and the time averaging left off $\vec{H}(t)\, e^{\mp i\omega t}$, and it is convenient to carry out this replacement.

Transforming back to the original density matrix elements with the aid of equations (10) we then obtain: for non-diagonal terms $(j \neq k)$

$$\frac{d}{dt}\rho_{jk} = -i\,\omega_{jk}\rho_{jk} \qquad \text{unless } j = r \text{ and } k = s \text{ simultaneously}$$

$$\frac{d}{dt}\rho_{rs} = -i\,\omega_o\,\rho_{rs} + i\gamma\,(\rho_{rr} - \rho_{ss})\,\vec{I}_{rs}\cdot\vec{H}(t) \qquad (18_a)$$

for diagonal terms $(j = k)$

$$\frac{d}{dt}\rho_{jj} = 0 \qquad \text{unless } j = r \quad \text{or} \quad j = s$$

$$(18_b)$$

$$\frac{d}{dt}(\rho_{rr}) = -\frac{d}{dt}(\rho_{ss}) = i\gamma\left(\rho_{rs}\,\vec{I}_{sr}\cdot\vec{H}(t) - \rho_{sr}\,\vec{I}_{rs}\cdot\vec{H}(t)\right)$$

Although no relaxation mechanisms have been incorporated into the above formalism such mechanisms do in fact exist in an actual system, and the initial state before the radio-frequency field is applied will be one of thermal equilibrium which is described by:

$$\left(\rho_{jk}\right)_{th} = 0 \quad , \quad \left(\rho_{jk}^{*}\right)_{th} = 0 \quad , \quad j \neq k$$

$$\left(\rho_{jj}^{*}\right)_{th} = \left(\rho_{jj}\right)_{th} = const. = \frac{e^{-E_j/kT}}{\sum_j e^{-E_j/kT}} \tag{19}$$

The expectation value of any operator A for a system in thermal equilibrium is thus given by

$$\langle A \rangle_{th} = \sum_n A_{nn}\left(\rho_{nn}\right)_{th} \tag{20}$$

Equations (17) (or (18)) together with the initial conditions (19) imply that to our degree of approximation all the ρ_{jk} (and consequently all the ρ_{jk}^{*}), $j \neq k$, remain zero except $\rho_{\lambda s}$, and all the $\rho_{jj} (= \rho_{jj}^{*})$ remain constant in time except $\rho_{\lambda\lambda}$ and ρ_{ss} whose sum remains constant but whose difference varies. If we denote this difference by

$$n = \rho_{\lambda\lambda} - \rho_{ss} = \rho_{\lambda\lambda}^{*} - \rho_{ss}^{*} = n^{*} \tag{21}$$

the time varying properties of the system which determine the deviation of $\langle A \rangle$ from $\langle A \rangle_{th}$ will be given by

(cf. modified equation (17))

$$\frac{d}{dt}\left(\rho_{rs}^{*}\right) = i\left(\omega - \omega_0\right)\rho_{rs}^{*} + i\gamma n^{*}\ \vec{I}_{rs}\cdot\vec{H}(t)\ e^{i\omega t}$$

$$\frac{d n^{*}}{dt} = 2i\gamma\left(\rho_{rs}^{*}\ \vec{I}_{sr}\cdot\vec{H}(t)\ e^{-i\omega t} - \rho_{sr}^{*}\ \vec{I}_{rs}\cdot\vec{H}(t)\ e^{i\omega t}\right)$$

(22)

or equivalently by (cf. equation (18))

$$\frac{d}{dt}\left(\rho_{rs}\right) = -i\,\omega_0\,\rho_{rs} + i\gamma n\ \vec{I}_{rs}\cdot\vec{H}(t)$$

$$\frac{dn}{dt} = 2i\gamma\left(\rho_{rs}\ \vec{I}_{sr}\cdot\vec{H}(t) - \rho_{sr}\ \vec{I}_{rs}\cdot\vec{H}(t)\right)$$

(23)

We note that (22) or (23) each represents a set of three equations since ρ_{rs} and ρ_{rs}^{*} are complex. Thus if we write

$$\rho_{rs} = X + i\,Y$$

(24)

where X and Y are real parameters, then we can rewrite equations (23) explicitly in terms of the three real parameters X , Y and n:

$$\frac{dX}{dt} = \omega_0 Y - n\gamma\ Im\left(\vec{I}_{rs}\cdot\vec{H}(t)\right)$$

$$\frac{dY}{dt} = -\omega_0 X + n\gamma\ Re\left(\vec{I}_{rs}\cdot\vec{H}(t)\right)$$

(25)

$$\frac{dn}{dt} = 4\gamma\left[X\ Im\left(\vec{I}_{rs}\cdot\vec{H}(t)\right) - Y\ Re\left(\vec{I}_{rs}\cdot\vec{H}(t)\right)\right]$$

The deviation of the expectation value of any operator $<A>$ given by (1) from its thermal equilibrium value $<A>_{th}$ given by (20) is equal to

$$<A> - <A>_{th} = \rho_{\lambda s} A_{s\lambda} + \rho_{s\lambda} A_{\lambda s}$$

$$+ \left[\rho_{\lambda\lambda} - (\rho_{\lambda\lambda})_{th}\right] A_{\lambda\lambda} + \left[\rho_{ss} - (\rho_{ss})_{th}\right] A_{ss}$$

$$= (X + iY)\overline{A}_{\lambda s} + (X - iY)A_{\lambda s}$$

$$+ \tfrac{1}{2}\left[(\rho_{\lambda\lambda} - \rho_{ss}) - (\rho_{\lambda\lambda} - \rho_{ss})_{th}\right](A_{\lambda\lambda} - A_{ss})$$

$$+ \tfrac{1}{2}\left[(\rho_{\lambda\lambda} + \rho_{ss}) - (\rho_{\lambda\lambda} + \rho_{ss})_{th}\right](A_{\lambda\lambda} + A_{ss})$$

$$= 2X \, Re(A_{\lambda s}) + 2Y \, Im(A_{\lambda s})$$

$$+ \tfrac{1}{2}\left(A_{\lambda\lambda} - A_{ss}\right)(n - n_{th}) \qquad (26)$$

Thus the time dependence of all the $4I(I + 1)$ macroscopic physical quantities describing the system is expressed in terms of the three variables X, Y, n which can in turn be expressed in terms of, for example, the three components of the macroscopic magnetization.

To relate these results to those of Bloom, Robinson and Volkoff we consider their Hamiltonian for which

$$(I_x)_{\lambda s} \equiv P \quad , \quad (I_y)_{\lambda s} \equiv iS \quad , \quad (I_z)_{\lambda s} \equiv T \qquad (27)$$

with P, S, T real. Then we have

$$\langle I_x \rangle - \langle I_x \rangle_{th} = 2 X P + \tfrac{1}{2} \left[(I_x)_{\lambda\lambda} - (I_x)_{ss} \right] (n - n_{th})$$

$$\langle I_y \rangle - \langle I_y \rangle_{th} = 2 Y S + \tfrac{1}{2} \left[(I_y)_{\lambda\lambda} - (I_y)_{ss} \right] (n - n_{th}) \qquad (28)$$

If we introduce the variables

$$\overline{I}_x \equiv \langle I_x \rangle - \langle I_x \rangle_{th} \quad , \quad \overline{I}_y \equiv \langle I_y \rangle - \langle I_y \rangle_{th} \qquad (29)$$

and neglecting the terms containing the diagonal matrix elements in (28) substitute

$$X = \overline{I}_x / 2 P \quad , \quad Y = \overline{I}_y / 2 S$$

and (27) into (25) we obtain equations [13] of Bloom, Robinson and Volkoff[2].

CHAPTER IV

DEGENERATE CASE

In the degenerate case where two or more transition frequencies may be equal a correspondingly greater number of matrix elements ρ_{jk} may vary in time (not just 4 as in the non-degenerate case). The general formulation becomes too complicated, and hence we discuss below some special cases.

We will first outline the method developed by Lurçat for the degenerate case in general. Then we shall investigate by the method of previous chapters the special cases treated by him, and shall compare and discuss the results.

1. Lurçat's Method

We shall outline in this section Lurçat's method in general.

The Schrödinger's time dependent equation for a physical quantity A can be written in the form

$$\frac{d\langle A \rangle}{dt} = \frac{i}{\hbar} \langle [\mathcal{H}, A] \rangle \qquad (30)$$

For a nucleus of spin I, placed in an electric field gradient of axial symmetry $(\eta = 0)$ and in a magnetic field $\overrightarrow{H}$, the Hamiltonian is

$$\mathcal{H}_{total} = \hbar \Omega_o \left[I_3^2 - \frac{1}{3} I(I+1) \right] - \frac{1}{2} \gamma \hbar \left(H^+ I^- + H^- I^+ + 2 H_3 I_3 \right)$$

$$\hbar \Omega_o = \frac{3 e q Q}{4 I (2I-1)} = \frac{q \alpha}{2} \qquad (31)$$

$$H^{\pm} = H_x \pm i H_y \quad , \quad I^{\pm} = I_x \pm i I_y$$

where $q = \frac{\partial^2 \phi}{\partial 3^2}$ is the value of the electric field gradient.

Let $Y_{k\mu}$ be tensor operators defined by the commutation relations

$$\left[I^{\pm}, Y_{k\mu} \right] = \sqrt{k(k+1) - \mu(\mu \pm 1)} \; Y_{k, \mu \pm 1}$$

$$\left[I_3, Y_{k\mu} \right] = \mu \, Y_{k\mu} \qquad (32)$$

with the normalization condition

$$Y_{kk} = (-1)^k (I^+)^k \qquad (33)$$

As a result of these definitions we get

$$Y_{10} = \sqrt{2} \; I_3 \quad , \quad Y_{1, \pm 1} = \mp I^{\pm}$$

$$\alpha Y_{20} = \sqrt{\frac{3}{2}} \; \alpha \left[2 I_3^2 - \frac{2}{3} I(I+1) \right] = \sqrt{\frac{3}{2}} \; D_{33}$$

$$\alpha Y_{2, \pm 1} = \mp \alpha \left(I_3 I^{\pm} + I^{\pm} I_3 \right) = \mp \left(D_{x3} \pm i D_{y3} \right)$$

$$\alpha \, Y_{2,\pm 2} \;=\; \alpha \, (I^{\pm})^2 \;=\; \tfrac{1}{2} \, (D_{xx} - D_{yy}) \pm i \, D_{xy}$$

$$\alpha \;=\; \frac{3\,e\,Q}{2\,I\,(2I-1)} \tag{34}$$

where D_{ik} are the components of the quadrupole moment operators. Taking the average values of $Y_{k\mu}$ we get the following formulae for the components of the macroscopic magnetization $\vec{M}$ and of the macroscopic quadrupole moment tensor $\widetilde{Q}$:

$$N\,\gamma\,\hbar \, \langle Y_{10} \rangle \;=\; \sqrt{2} \; M_3$$

$$N\,\gamma\,\hbar \, \langle Y_{1,\pm 1} \rangle \;=\; \mp \, (M_x \pm i\,M_y)$$

$$N\,\alpha \, \langle Y_{20} \rangle \;=\; \sqrt{\tfrac{3}{2}} \; Q_{33} \tag{35}$$

$$N\,\alpha \, \langle Y_{2,\pm 1} \rangle \;=\; \mp \, (Q_{x3} \pm i\,Q_{y3})$$

$$N\,\alpha \, \langle Y_{2,\pm 2} \rangle \;=\; \tfrac{1}{2} \, (Q_{xx} - Q_{yy}) \pm i\,Q_{xy}$$

with similar expressions for $Y_{3\mu}$ etc., in terms of octopole and higher moments.

Making use of the properties of tensor operators it can be shown that

$$\left[I_3^2, Y_{k\mu} \right] = I_3 \left[I_3, Y_{k\mu} \right] + \left[I_3, Y_{k\mu} \right] I_3$$

$$= \mu \left[I_3 Y_{k\mu} + Y_{k\mu} I_3 \right]$$

$$= \frac{\mu (2I+k+1)(2I-k+1)}{2k+1} \sqrt{\frac{k(k+\mu)(k-\mu)}{2(2k-1)}} \; Y_{k-1,\mu} \qquad (36)$$

$$+ \sqrt{\frac{2(k+1+\mu)(k+1-\mu)}{(k+1)(2k+1)}} \; Y_{k+1,\mu}$$

Substituting (31) in (30) and making use of equation (36) we get

$$\frac{d \langle Y_{k\mu} \rangle}{dt} = i\mathcal{R}_0 \mu \; \frac{(2I+k+1)(2I-k+1)}{2k+1} \sqrt{\frac{k(k+\mu)(k-\mu)}{2(2k-1)}} \langle Y_{k-1,\mu} \rangle$$

$$+ i\mathcal{R}_0 \mu \sqrt{\frac{2(k+1+\mu)(k+1-\mu)}{(k+1)(2k+1)}} \langle Y_{k+1,\mu} \rangle$$

$$- \frac{1}{2} i\gamma \sqrt{(k+1+\mu)(k-\mu)} \; H^- \langle Y_{k,\mu+1} \rangle$$

$$- \frac{1}{2} i\gamma \sqrt{(k-\mu+1)(k+\mu)} \; H^+ \langle Y_{k,\mu-1} \rangle$$

$$- i\gamma H_3 \mu \langle Y_{k,\mu} \rangle. \qquad (37)$$

We note at this point that this equation is an exact equation where all the energy levels are taken into account, and holds for integral as well as for half-integral values of spin. Using equations (37) and (35) Lurçat then obtains for the special cases $I = 1$, 3/2 and 5/2 equations giving the time

dependence of the macroscopic physical quantities $\vec{M}$, $\widetilde{Q}$ etc.

In order to see the basic equivalence of Lurçat's method with the one presented in this thesis we recall that the mean value of any operator can be expressed in terms of the density matrix (cf. equation (1)). Thus the mean values of the operators $Y_{k\mu}$ and also those of M_x, M_y, M_z, Q_{xx}, Q_{xy} etc., can be written down in terms of the density matrix ρ. To get the variation in time of the macroscopic physical quantities $\vec{M}$, $\widetilde{Q}$ etc., one may utilize the time dependence of $\langle Y_{k\mu} \rangle$, as Lurçat has done, or one may use the time dependence of the density matrix directly, as is done in the present thesis.

2. Case of spin I = 1:

We shall first state the results of Lurçat for this case and then shall show how the same equations can be obtained by the method of previous chapters.

Using equations (37) and definitions (35) Lurçat obtains the following equations for the time dependence of the components of the macroscopic physical quantities $\vec{M}$, $\widetilde{Q}$:

$$\frac{d M_x}{dt} = -\omega_0 \frac{\gamma \hbar}{\alpha} Q_{yz}$$

$$\frac{d}{dt}\left(\frac{\gamma \hbar}{\alpha} Q_{yz}\right) = \omega_0 M_x + \gamma H_x \left(\frac{\gamma \hbar}{\alpha}(Q_{zz}-Q_{yy})\right)$$

$$\frac{d}{dt}\left(\frac{\gamma \hbar}{\alpha}(Q_{zz}-Q_{yy})\right) = -4\gamma H_x \frac{\gamma \hbar}{\alpha} Q_{yz}$$

I

$$\frac{d\,Q_{xx}}{dt} = 0 \qquad\qquad\qquad\qquad \text{II}$$

$$\left.\begin{aligned}
\frac{dM_y}{dt} &= \omega_0\,\frac{\gamma\hbar}{\alpha}\,Q_{x3} + \gamma H_x M_3 \\[2mm]
\frac{dM_3}{dt} &= -\gamma H_x M_y \\[2mm]
\frac{d}{dt}\left(\frac{\gamma\hbar}{\alpha}\,Q_{x3}\right) &= -\omega_0 M_y - \gamma H_x\left(\frac{\gamma\hbar}{\alpha}\,Q_{xy}\right) \\[2mm]
\frac{d}{dt}\left(\frac{\gamma\hbar}{\alpha}\,Q_{xy}\right) &= \gamma H_x\left(\frac{\gamma\hbar}{\alpha}\,Q_{x3}\right)
\end{aligned}\right\} \quad \text{III}$$

$$(38)$$

Note that the eight equations break up into three subsystems I, II and III, that is variables in one subsystem do not occur in any other subsystem. If initially the system is in thermal equilibrium, then the initial conditions are

$$Q_{xx}(0) = Q_{yy}(0) = -\tfrac{1}{2}\,Q_{33}(0)$$

$$Q_{ik}(0) = 0 \quad (i \neq k), \quad M_i(0) = 0 \qquad (39)$$

Consequently the quantities appearing in equations (38 II) are constant and in (38 III) are zero initially and remain zero at any later time. Thus we are left with only three useful equations, namely (38 I). It is convenient to introduce the transformation

$$M_x = M_x^* \cos \omega t - \frac{\gamma \hbar}{\alpha} Q_{\gamma \delta}^* \sin \omega t$$

$$\frac{\gamma \hbar}{\alpha} Q_{\gamma \delta} = M_x^* \sin \omega t + \frac{\gamma \hbar}{\alpha} Q_{\gamma \delta}^* \cos \omega t \qquad (40)$$

$$Q_{\delta\delta} = Q_{\delta\delta}^* \quad , \quad Q_{\gamma\gamma} = Q_{\gamma\gamma}^*$$

Lurçat considers the case where there is no static magnetic field and where the time varying magnetic field is

$$H_x = H_1 \cos \omega t \quad , \quad H_y = 0 \quad , \quad H_\delta = 0$$

Applying transformation (40) to (38 I) and neglecting terms in $\sin 2\omega t$ and $\cos 2\omega t$ the transformed equations are:

$$\frac{dM_x^*}{dt} + (\omega_0 - \omega) \frac{\gamma \hbar}{\alpha} Q_{\gamma \delta}^* = 0$$

$$\frac{d}{dt}\left(\frac{\gamma \hbar}{\alpha} Q_{\gamma \delta}^*\right) - (\omega_0 - \omega) M_x^* + 4 \frac{\gamma H_1}{2} \frac{\gamma \hbar}{\alpha} \frac{Q_{\gamma\gamma}^* - Q_{\delta\delta}^*}{4} = 0 \qquad (41)$$

$$\frac{d}{dt}\left(\frac{\gamma \hbar}{\alpha} \frac{Q_{\gamma\gamma}^* - Q_{\delta\delta}^*}{4}\right) - \frac{\gamma H_1}{2} \frac{\gamma \hbar}{\alpha} Q_{\gamma \delta}^* = 0$$

where ω_0 is the resonance frequency.

As pointed out by Lurçat these equations become formally identical with equations [23] of Bloom, Hahn and Herzog[1], except for a factor of 2 in the coefficient of H_1 in the second equation, if one makes the following

transformation:

Bloom, Hahn and Herzog		Lurçat
u	$\longleftrightarrow$	$\frac{1}{2} M_x^*$
v	$\longleftrightarrow$	$\frac{1}{2} \frac{r\hbar}{\alpha} Q_{y3}^*$
M_3	$\longleftrightarrow$	$\frac{1}{2} \frac{r\hbar}{\alpha} \frac{Q_{yy}^* - Q_{33}^*}{4}$

Of course the discrepancy of the factor of 2 is not surprising. There is no reason to expect the two sets to be identical (even formally) since the Bloom, Hahn and Herzog equations hold only for half integral spins where it was possible to consider only half of the total number of nuclei corresponding to $+m$ states. This can not be done for the present case of spin $I = 1$, since the $m = 0$ state can not be classified as belonging to $+m$ state or to $-m$ state.

However, if we start with the complete system of nuclei as in chapter II and then follow a procedure similar to the one followed in chapter III (non-degenerate case), then we are led exactly to the Lurçat's equations, as is shown below.

For the degenerate case $\left(\eta = 0, \vec{H}_0 = 0 \right)$ two of the three energy levels, say 1 and 2, will coincide so that

$$\omega_{12} = 0 \quad , \quad \omega_{23} = \omega_{13} = \omega_0 \qquad (42)$$

Let the frequency ω of the applied r.f. field be close

to the transition frequency $\omega_{23} = \omega_{13} = \omega_0$. We choose the arbitrary transformation frequencies ω'_{13} and ω'_{23} to satisfy $\omega'_{13} = \omega'_{23} = \omega$. Then equations (11) lead, with the approximation discussed in the previous chapters, to the following equations for the transformed matrix elements ρ^*_{jk}, $j,k = 1,2,3$:

$$\frac{d}{dt}\rho^*_{13} = i(\omega - \omega_{13})\rho^*_{13} + \frac{i\gamma}{2}(\rho^*_{11} - \rho^*_{33})\vec{I}_{13}\cdot\vec{H}_1$$
$$+ \frac{i\gamma}{2}\rho^*_{12}\vec{I}_{23}\cdot\vec{H}_1 \quad\text{—(i)}$$

$$\frac{d}{dt}\rho^*_{23} = i(\omega - \omega_{23})\rho^*_{23} + \frac{i\gamma}{2}(\rho^*_{22} - \rho^*_{33})\vec{I}_{23}\cdot\vec{H}_1$$
$$+ \frac{i\gamma}{2}\rho^*_{21}\vec{I}_{13}\cdot\vec{H}_1 \quad\text{—(ii)}$$

$$\frac{d}{dt}\rho^*_{12} = \frac{i\gamma}{2}\rho^*_{13}\vec{I}_{32}\cdot\vec{H}_1 - \frac{i\gamma}{2}\rho^*_{32}\vec{I}_{13}\cdot\vec{H}_1 \quad\text{—(iii)}$$

$$\frac{d}{dt}\rho^*_{11} = \frac{i\gamma}{2}\rho^*_{13}\vec{I}_{31}\cdot\vec{H}_1 - \frac{i\gamma}{2}\rho^*_{31}\vec{I}_{13}\cdot\vec{H}_1 \quad\text{—(iv)}$$

$$\frac{d}{dt}\rho^*_{22} = \frac{i\gamma}{2}\rho^*_{23}\vec{I}_{32}\cdot\vec{H}_1 - \frac{i\gamma}{2}\rho^*_{32}\vec{I}_{23}\cdot\vec{H}_1 \quad\text{—(v)}$$

$$(43)$$

Note that the equations involve eight independent real parameters (ρ^*_{13}, ρ^*_{23}, ρ^*_{12}, being complex, give six and ρ^*_{11}, ρ^*_{22}, being real, give two).

In the special case discussed by Lurçat

($H_x(t) = H_1 \cos \omega t$, $H_y = H_3 = 0$) we get $\vec{I}_{\lambda s} \cdot \vec{H}_1 =$ $I_{x,\lambda s} H_1$. $I_{x,\lambda s}$ is equal to $1/\sqrt{2}$ for all non-vanishing matrix elements of I_x which are in fact the ones that appear in (43). It is now possible to choose a complete set of 8 linearly independent parameters (which are combinations of the matrix elements ρ_{jk}) such that only three parameters are time dependent. The corresponding equations for these parameters are then enough to describe the behaviour of the system.

Thus we define

$$\rho_{13}^* + \rho_{23}^* \equiv Q^* \equiv X^* + i Y^* \tag{44}$$

$$\rho_{11}^* + \rho_{22}^* - 2\rho_{33}^* + \rho_{12}^* + \rho_{21}^* \equiv Z^*$$

where X, Y, Z are real parameters. Moreover let $(cf. (42))$ $\omega_{23} = \omega_{13} = \omega_0$ for convenience of notation. Then the equations for Q^* (obtained by adding (i) and (ii) of (43)) and Z^* (obtained from (iii), (iv), (v) of (43)) are :

$$\frac{d}{dt}(Q^*) = i(\omega - \omega_0) Q^* + \frac{i}{\sqrt{2}} \frac{\gamma H_1}{2} Z^*$$

$$\frac{d}{dt}(Z^*) = \frac{d}{dt} 3(\rho_{11}^* + \rho_{22}^*) + \frac{d}{dt}(\rho_{12}^* + \rho_{21}^*)$$

$$= 4 \frac{d}{dt}(\rho_{11}^* + \rho_{22}^*) \quad , \quad since \quad \frac{d}{dt}(\rho_{11}^* + \rho_{22}^*) = \frac{d}{dt}(\rho_{12}^* + \rho_{21}^*)$$

$$(cf \; (iii) \; and \; (iv) \; of \; (43))$$

$$= 4 \frac{i\gamma}{2} (Q^* - \bar{Q}^*) \frac{1}{\sqrt{2}} H_1$$

Or writing in terms of X^*, Y^*, Z^* these equations give:

$$\frac{dX^*}{dt} = -(\omega - \omega_0) Y^*$$

$$\frac{dY^*}{dt} = (\omega - \omega_0) X^* + \frac{1}{\sqrt{2}} \frac{\gamma H_1}{2} Z^* \tag{45}$$

$$\frac{dZ^*}{dt} = -4 \cdot \frac{1}{\sqrt{2}} \frac{\gamma H_1}{2} \cdot 2 Y^*$$

Applying equations (1) and (35) to the present case of $I = 1$, a straightforward calculation leads to the following expressions for the components of the macroscopic physical quantities $\vec{M}$, $\widetilde{Q}$ in terms of the density matrix:

$$M_x = \frac{N\gamma\hbar}{\sqrt{2}} \left(\rho_{13} + \rho_{31} + \rho_{32} + \rho_{23} \right)$$

$$M_y = \frac{N\gamma\hbar}{\sqrt{2}} i \left(\rho_{13} + \rho_{32} - \rho_{31} - \rho_{23} \right)$$

$$M_3 = N\gamma\hbar \left(\rho_{11} - \rho_{22} \right)$$

$$Q_{xy} = iN\alpha \left(\rho_{12} - \rho_{21} \right) \tag{46}$$

$$Q_{yz} = \frac{iN\alpha}{\sqrt{2}} \left(\rho_{13} + \rho_{23} - \rho_{31} - \rho_{32} \right)$$

$$Q_{3x} = \frac{N\alpha}{\sqrt{2}} \left(\rho_{13} + \rho_{31} - \rho_{32} - \rho_{23} \right)$$

$$Q_{xx} - Q_{yy} = \frac{N\alpha}{\sqrt{2}} \cdot \frac{1}{2} \left(\rho_{12} + \rho_{21} \right)$$

$$Q_{33} - Q_{yy} = N\alpha \left(\rho_{11} + \rho_{22} - 2\rho_{33} + \rho_{12} + \rho_{21} \right); \quad Q_{xx} + Q_{yy} + Q_{33} = 0$$

Using (44) and (46) we get

$$X^* = \frac{1}{2} \sqrt{2} \cdot \frac{M_x^*}{N \gamma \hbar}$$

$$Y^* = -\frac{1}{2} \cdot \sqrt{2} \cdot \frac{Q_{Y3}^*}{N \alpha} \tag{47}$$

$$Z^* = \frac{Q_{33}^* - Q_{YY}^*}{N \alpha}$$

Substituting (47) in (45) we finally get

$$\frac{dM_x^*}{dt} + (\omega_0 - \omega) \frac{\gamma \hbar}{\alpha} Q_{Y3}^* = 0$$

$$\frac{d}{dt}\left(\frac{\gamma \hbar}{\alpha} Q_{Y3}^*\right) - (\omega_0 - \omega) M_x^* - 4 \frac{\gamma H_1}{2} \frac{\gamma \hbar}{\alpha} \frac{Q_{YY}^* - Q_{33}^*}{4} = 0 \tag{48}$$

$$\frac{d}{dt}\left(\frac{\gamma \hbar}{\alpha} \frac{(Q_{YY}^* - Q_{33}^*)}{4}\right) + \frac{\gamma H_1}{2}\left(\frac{\gamma \hbar}{\alpha} Q_{Y3}^*\right) = 0$$

These are exactly the equations (41) which are obtained by Lurçat. The apparent difference in the signs of the terms involving H_1 is due to the fact that whereas we take the time-dependent Hamiltonian $\mathcal{H}$ to be $+ \gamma \hbar \ \vec{I} \cdot \vec{H}(t)$ (cf. equation (5)), Lurçat takes it to be $- \gamma \hbar \ \vec{I} \cdot \vec{H}(t)$.

We have thus illustrated, for the case of spin
I = 1, the complete equivalence of our treatment with that
of Lurçat.

3. The case of spin I = 3/2 :

We now consider the case of I = 3/2 as an example
of half integral spins. Lurçat obtains for this case the
following equations

$$\frac{dM_x^*}{dt} + (\omega_0 - \omega)\left(\frac{1}{2} \frac{\gamma \hbar}{\alpha} Q_{\gamma z}^*\right) = 0$$

$$\frac{d}{dt}\left(\frac{1}{2} \frac{\gamma \hbar}{\alpha} Q_{\gamma z}^*\right) - (\omega_0 - \omega) M_x^* + 3 \frac{\gamma H_1}{2}\left(-\frac{1}{4} \frac{\gamma \hbar}{\alpha} Q_{zz}^*\right) = 0 \qquad (49)$$

$$\frac{d}{dt}\left(-\frac{1}{4} \frac{\gamma \hbar}{\alpha} Q_{zz}^*\right) - \frac{\gamma H_1}{2}\left(\frac{1}{2} \frac{\gamma \hbar}{\alpha} Q_{\gamma z}^*\right) = 0$$

where ω_0 is the resonance frequency and ω the frequency
of r. f. field.

We shall assume with Lurçat that the electric field
gradient is axially symmetric $(\eta = 0)$ and that the static
magnetic field $H_o = 0$. Let 1, 2, 3, and 4 be the four

$(m = -3/2)$ 4 ─────────────────── 1 $(m = 3/2)$

$(m = -1/2)$ 3 ─────────────── 2 $(m = 1/2)$

states corresponding to m = 3/2 , $\frac{1}{2}$, $-\frac{1}{2}$ and -3/2
respectively. Then

$$\omega_{14} = \omega_{23} = 0$$

$$\omega_{12} = \omega_{43} = \omega_{42} = \omega_{13} = \omega_0 \text{ , say .}$$

(50)

Then equations (11) lead, with the approximation discussed in previous chapters, to the following equations for the transformed matrix elements ρ_{jk} , $j, k = 1, 2, 3, 4$.

$$\left. \begin{aligned} \frac{d}{dt}\left(\rho_{12}^*\right) &= i(\omega - \omega_0)\rho_{12}^* + \frac{i\gamma}{2}\left(\rho_{11}^* - \rho_{22}^*\right)\vec{I}_{12}\cdot\vec{H}_1 \\[2mm] \frac{d}{dt}\left(\rho_{11}^*\right) &= -\frac{d}{dt}\left(\rho_{22}^*\right) = \frac{i\gamma}{2}\left(\rho_{12}^*\,\vec{I}_{21}\cdot\vec{H}_1 - \rho_{21}^*\,\vec{I}_{12}\cdot\vec{H}_1\right) \end{aligned} \right\} \quad I$$

$$\left. \begin{aligned} \frac{d}{dt}\left(\rho_{43}^*\right) &= i(\omega - \omega_0)\rho_{43}^* + \frac{i\gamma}{2}\left(\rho_{44}^* - \rho_{33}^*\right)\vec{I}_{43}\cdot\vec{H}_1 \\[2mm] \frac{d}{dt}\left(\rho_{33}^*\right) &= -\frac{d}{dt}\left(\rho_{44}^*\right) = \frac{i\gamma}{2}\left(\rho_{34}^*\,\vec{I}_{43}\cdot\vec{H}_1 - \rho_{43}^*\,\vec{I}_{34}\cdot\vec{H}_1\right) \end{aligned} \right\} \quad II$$

(51)

$$\left. \begin{aligned} \frac{d}{dt}\left(\rho_{13}^*\right) &= i(\omega - \omega_0)\rho_{13}^* + \frac{i\gamma}{2}\left(\rho_{14}^*\,\vec{I}_{43}\cdot\vec{H}_1 - \rho_{23}^*\,\vec{I}_{12}\cdot\vec{H}_1\right) \\[2mm] \frac{d}{dt}\left(\rho_{24}^*\right) &= -i(\omega - \omega_0)\rho_{24}^* + \frac{i\gamma}{2}\left(\rho_{23}^*\,\vec{I}_{34}\cdot\vec{H}_1 - \rho_{14}^*\,\vec{I}_{21}\cdot\vec{H}_1\right) \\[2mm] \frac{d}{dt}\left(\rho_{14}^*\right) &= \frac{i\gamma}{2}\left(\rho_{13}^*\,\vec{I}_{34}\cdot\vec{H}_1 - \rho_{24}^*\,\vec{I}_{12}\cdot\vec{H}_1\right) \\[2mm] \frac{d}{dt}\left(\rho_{23}^*\right) &= \frac{i\gamma}{2}\left(\rho_{24}^*\,\vec{I}_{43}\cdot\vec{H}_1 - \rho_{13}^*\,\vec{I}_{21}\cdot\vec{H}_1\right) \end{aligned} \right\} \quad III$$

Note that (51) is made up of three separate subsets I , II and III (that is, variables appearing in one subset do not occur in another subset).

Initially when the system is in thermal equilibrium we have seen (cf. equations (19)) that the off-diagonal density matrix elements are zero. From (51 III) we then see that all the density matrix elements appearing therein remain zero at any later time and play no part in the change of the system in time. Moreover equations (51 I) and (51 II) are formally identical. (Replacing indices 1 and 2 everywhere in (51 I) by indices 4 and 3 respectively we get equation (51 II)). That is to say, the nuclei in the states 1 and 2 behave in exactly the same way as would the nuclei in the states 4 and 3 and therefore it is sufficient to consider only half of the total number of nuclei, namely those belonging to the $+m$ states. As a matter of fact Bloom, Hahn and Herzog use this concept right at the start of their development of the theory for the half-integral spins; equations (51 I), if written down explicitly in the parameters $Re(\rho_{12}^{*})$, $Im(\rho_{12}^{*})$ and $n (= \rho_{11}^{*} - \rho_{22}^{*})$ become identical formally with equation [23] of Bloom, Hahn and Herzog[2].

(We choose for this purpose the r. f. field to be linearly polarized in the x-y plane, which is equivalent to two opposite circularly polarized r. f. fields. One of the two components gets eliminated in the process of approximation.

Bloom, Hahn and Herzog take circularly polarized r. f. so that no approximation is necessary in this respect in their transformation.)

We have thus demonstrated that out of the sixteen equations (51) only three are useful, namely equations (51 I) which govern the behaviour of the system of nuclei.

We shall now show, as in the previous section, that if suitable linear combinations of ρ_{jk} are chosen, then equations (51) lead to the three equations (49) of Lurçat. Thus let

$$\rho_{12}^{*} + \rho_{43}^{*} \equiv Q^{*} \equiv X^{*} + i Y^{*}$$

$$\rho_{11}^{*} - \rho_{22}^{*} + \rho_{44}^{*} - \rho_{33}^{*} \equiv Z^{*} \tag{52}$$

where X^{*}, Y^{*} and Z^{*} are real parameters. For Lurçat's case which we are discussing, we have

$$\vec{H}(t) = H_{x} = H_{1} \cos \omega t , \quad H_{y} = H_{3} = 0 .$$

Equations (51 I) and (52 II) lead to the following equations for Q^{*} and Z^{*} :

$$\frac{d Q^{*}}{d t} = i (\omega - \omega_{0}) Q^{*} + i \frac{\gamma H_{1}}{2} \frac{\sqrt{3}}{2} Z^{*}$$

$$\frac{d Z^{*}}{d t} = 2 \frac{\sqrt{3}}{2} i \frac{\gamma H_{1}}{2} (Q^{*} - \bar{Q}^{*})$$

Or equivalently, in terms of X^{*}, Y^{*} and Z^{*} we can write

$$\frac{dX^*}{dt} = -(\omega - \omega_o)\, Y^*$$

$$\frac{dY^*}{dt} = (\omega - \omega_o)\, X^* + \frac{\sqrt{3}}{2}\, \frac{\gamma H_1}{2}\, Z^* \qquad (53)$$

$$\frac{dZ^*}{dt} = -2\sqrt{3}\, \frac{\gamma H_1}{2}\, Y^*$$

As in the case of spin $I = 1$, a straightforward calculation leads to the following expressions for M_x, Q_{yz} and Q_{zz} (the parameters appearing in (49)) in terms of the density matrix ρ :

$$M_x = \frac{\sqrt{3}}{2}\, N\gamma\hbar \left(\rho_{21} + \rho_{12} + \rho_{43} + \rho_{34}\right) + N\gamma\hbar \left(\rho_{32} + \rho_{23}\right)$$

$$\tfrac{1}{2} Q_{yz} = i\, \frac{\sqrt{3}}{2}\, N\alpha \left(-\rho_{21} + \rho_{12} + \rho_{43} - \rho_{34}\right) \qquad (54)$$

$$Q_{zz} = 2 N\alpha \left(\rho_{11} - \rho_{22} - \rho_{33} + \rho_{44}\right)$$

Using (52) and (54) and recalling that ρ_{23} and ρ_{32} always remain zero (cf. equation 51 III and the initial conditions) we get

$$X^* = \frac{1}{\sqrt{3}}\, \frac{M_x^*}{N\gamma\hbar}$$

$$Y^* = -\frac{1}{\sqrt{3}}\, \frac{1}{N\alpha} \left(\tfrac{1}{2} Q_{yz}^*\right) \qquad (55)$$

$$Z^* = \frac{1}{2 N\alpha}\, Q_{zz}^*$$

Substituting (55) in (53) leads finally to the equations :

$$\frac{dM_x^*}{dt} + (\omega_o - \omega)\left(\frac{1}{2}\frac{\gamma\hbar}{\alpha}Q_{yz}^*\right) = 0$$

$$\frac{d}{dt}\left(\frac{1}{2}\frac{\gamma\hbar}{\alpha}Q_{yz}^*\right) - (\omega_o - \omega)M_x^* - 3\frac{\gamma H_1}{2}\left(-\frac{1}{4}\frac{\gamma\hbar}{\alpha}Q_{zz}^*\right) = 0 \qquad (56)$$

$$\frac{d}{dt}\left(-\frac{1}{4}\frac{\gamma\hbar}{\alpha}Q_{zz}^*\right) + \frac{\gamma H_1}{2}\left(\frac{1}{2}\frac{\gamma\hbar}{\alpha}Q_{yz}^*\right) = 0$$

Equations (56) are identical with (49) which are Lurçat's equations. (The apparent difference in the signs of the terms involving H_1 is due to the same reason as that explained in the previous section, namely that whereas we have taken the time dependent Hamiltonian $\mathcal{H}$ to be $+\gamma\hbar\,\vec{I}\cdot\vec{H}(t)$ (cf. equation (5)), Lurçat takes it to be $-\gamma\hbar\,\vec{I}\cdot\vec{H}(t)$.

In this section we have thus demonstrated once again the equivalence of Lurçat's method with the one presented in this thesis. The treatment also brings out the interrelationship between the theories of Lurçat and of Bloom, Hahn, Herzog.

4. The case of higher spins:

The cases for higher values of spin will be naturally more complicated and shall not be discussed here in detail, because the essential features of the general case are contained in the formalism of the previous two sections, as applied to the two special cases of spin $I = 1$ and $3/2$.

For half integral spins, as illustrated for $I = 3/2$, one need consider those nuclei that belong to the $+m$ - states

and then the case reduces essentially to the non-degenerate case, since degeneracy occurs in pairs of $\pm m$ states.

For integral spin the transitions involving the $m = 0$ state can be treated in the same way as the $I = 1$ case was treated. Transitions not involving $m = 0$ state can be treated like the half-integral case in the sense that the transitions $+ m_1 \longrightarrow + m_2$ and the transitions $- m_1 \longrightarrow - m_2$ can be treated separately.

REFERENCES

(1) Bloom M., Hahn E. L., and Herzog B.,
Phys. Rev., 97, 1699 (1955)

(2) Bloom M., Robinson L. B., and Volkoff G. M.,
Can. J. Phys., 36, 1286 (1958)

(3) Fano U., Rev. Mod. Phys., 29, 74 (1957)

(4) Lurçat F., J. de Phys. et Rad., 19, 713 (1958)

(5) Lurçat F., J. de Phys. et Rad., 19, 745 (1958)