FISICA
Acta Científica Venezolana 38: 322-328, 1987

GREEN'S FUNCTION CALCULATION OF SPIN-LATTICE RELAXATION TIME FOR NUCLEI COUPLED TO MAGNETIC IMPURITIES*

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ABSTRACT

A general method using two times Green's functions together with Linear Response Theory is proposed to calculate the relaxation times in nuclear spin systems. The method is applied to a nuclear spin coupled to a magnetic impurity, which is described by Bloch type equations of motion. the results obtained are in agreement with earlier theories and experimental results.

CALCULO CON FUNCIONES DE GREEN DEL TIEMPO DE RELAJACION SPIN-RED PARA NUCLEOS ACOPLADOS A IMPUREZAS MAGNETICAS

RESUMEN

Se propone un método general basado en las funciones de Green de dos tiempos, junto con la Teoría de Respuesta Lineal, para calcular los tiempos de relajación en sistemas nucleares. El método es aplicado a un sistema de un spin nuclear acoplado a una impureza magnética, la cual se encuentra descrita por ecuaciones del tipo Bloch. Los resultados concuerdan con teorías ya establecidas y resultados experimentales.

INTRODUCTION

The determination of the theorical dependence with temperature of the nuclear relaxation times T_1 and T_2 at very low temperatures, even comparable with the nuclear spin temperature, has been of major in interest among the NMR research groups over the last years (1) (2) (3). Many successful attempts has been done in the range of low temperatures, but its extension to the whole range implies, in many cases, the addition of new assumptions and postulates. The purpose of this work is to give an application of the two times Green's function formalism (4) in the calculation of the spin-lattice relaxation time T_1 for any temperature. The lines of reasoning followed in this work for the derivation of the general relations, within the linear response regime, are the same as those of Deutch and Oppenheim (5), but we explicitly substitute the response function by the more general two times Green's function, to make use of its extremely powerful and general properties.

First, we consider a system, with the Hamiltonian:

$$H = H_Z + H_{SL} + H_L \tag{I.1}$$

subject to a perturbation

$$H_1^t = -\underline{M} \cdot \underline{H}_1^t \tag{I.2}$$

with:

$$\underline{H}_1^t = \theta(-t)\, e^{\varepsilon t}\, \underline{H}_1 \,,\ \varepsilon \to 0^+ \tag{I.3}$$

According to the linear response theory, the magnetization at time t is given by (4):

$$<\underline{M}(t)> = <\underline{M}>_0 - \int_{-\infty}^{+\infty} <<\underline{M}(t)\,;\,\underline{M}(t')>> \cdot \underline{H}_1^{t'}\, dt' \tag{I.4}$$

which can be written:

$$<\delta\underline{M}\,(t)> = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} dt' <<\underline{M}|\underline{M}>>_\omega \cdot \underline{H}_1 e^{-i\omega(t-t')}\theta(-t')\, e^{\varepsilon t'} \tag{I.5}$$

$$\varepsilon \to 0^+$$

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*Recibido 04/03/86
Aceptado 14/07/87

where $<\delta\underline{M}(t)> = <\underline{M}(t)> - <\underline{M}>_0$, and $<<\underline{M}|\underline{M}>>_\omega$ is the Fourier Transform of the Green's function $<<\underline{M}(t)\,;\,\underline{M}(t')>>$.

The integral over t' can be explicity done and we get the following result:

$$<\delta\underline{M}(t)> = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \frac{<<\underline{M}|\underline{M}>>_\omega \cdot \underline{H}_1}{i(\omega - i\varepsilon)}\, e^{-i\omega t},\ \varepsilon \to 0^+ \qquad (I.6)$$

By making the Laplace Tramsform, taking $z = \omega + in$, $n \to 0^+$, we get:

$$<\delta\underline{M}(\omega)> = \lim_{n\to 0^+} <\delta\underline{M}(z)> = \frac{i}{\omega}\left[<<\underline{M}|\underline{M}>>_\omega - <<\underline{M}|\underline{M}>>_0\right]\cdot\underline{H}_1 \qquad (I.7)$$

On the other hand, by using eqn. (I.6), the value of $<\delta\underline{M}(t=0)>$ can be found:

$$<\delta\underline{M}(t=0)> = -<<\underline{M}|\underline{M}>>_0 \cdot H_1 \qquad (I.8)$$

so we can write:

$$\underline{H}_1 = -<<\underline{M}|\underline{M}>>_0^{-1} \cdot <\delta\underline{M}(t=0)> \qquad (I.9)$$

and finally:

$$<\delta\underline{M}(\omega)> = \frac{1}{i\omega}\left(<<\underline{M}|\underline{M}>>_\omega <<\underline{M}|\underline{M}>>_0^{-1} - \underset{\sim}{1}\right)\cdot <\delta\underline{M}(t=0)> \qquad (I.10)$$

An analogous procedure can be followed to derive an equivalent equation to (I.10) starting from phenomenological Bloch type equations of motion for the nuclear spin system. We get:

$$\delta M(\omega) = \left(\frac{1}{\underset{\sim}{R} - i\omega\,\underset{\sim}{1}}\right)\cdot \delta\underline{M}(t=0) \qquad (I.11)$$

where $R_{\alpha\alpha} = R'_{\alpha\alpha} + i\,\alpha\omega_0$, ω_0 is the nuclear Larmor Frecuency and $R'00 = 1/T_1$, $R'11 = R'\,{-1}{-1} = 1/T_2$. If we equate egns. (I.10) and (I.11), which can be done under the assumption of a single exponential relaxation process for the nuclear spin system, we get the following result:

$$\frac{1}{R'_{\alpha\alpha} - i(\omega - \alpha\omega_0)} = \frac{1}{i\omega}\left[\left(<<\underline{M}|\underline{M}>>_\omega\right)_{\alpha\beta}\left(<<\underline{M}|\underline{M}>>_0^{-1}\right)_{\beta\alpha} - 1\right] \qquad (I.12)$$

By taking the real part at both sides of egn. (I.12), we get:

$$\frac{R'_{\alpha\alpha}}{R'^{\,2}_{\alpha\alpha} + (\omega - \alpha\omega_0)^2} = \frac{I_m\left[\left(<<\underline{M}|\underline{M}>>_\omega\right)_{\alpha\beta}\left(<<\underline{M}|\underline{M}>>_0^{-1}\right)_{\beta\alpha}\right]}{\omega} \qquad (I.13)$$

Using the symmetry properties of the Green's functions (4) and making the supposition that there is no correlation between different components of nuclear spins, which is consistent with the above assumptions and holds very well in the practice, we get the simpler equations:

$$\frac{R'_{\alpha\alpha}}{R'^{\,2}_{\alpha\alpha} + (\omega - \alpha\omega_0)^2} = \frac{1}{\omega}\frac{I_m\left(<<\underline{M}|\underline{M}>>_\omega\right)_{\alpha-\alpha}}{Re\left(<<\underline{M}|\underline{M}>>_0\right)_{\alpha-\alpha}} \qquad (I.14)$$

This equation is a consequence of Onsager assumption about the equality between the evolution of a physical macroscopical observable and the evolution of the fluctuations associated with it. The purpose of this work is to calculate the T_1 relaxation time for a nuclear spin system in the presence of paramagnetic impurities, so if we take the limit $\omega \to 0$ for the $\alpha = 0$ component in egn. (I.14), we get the following equation for the spin-lattice relaxation time:

$$T_1 = \lim_{\omega\to 0} \frac{1}{\omega}\frac{I_m<<M_0\,|\,M_0>>_\omega}{Re<<M_0\,|\,M_0>>_0} \qquad (I.15)$$

This will be the basic equation to be used in the rest of the work.

II. Hamiltonian.

Let us suppose a general interaction Hamiltonian between the electrons and the nuclei of the form:

$$H_{se} = \sum_{i,j\,;\,m,n} J^{mn}_{i\,j}\, S^n_j\, I^m_i \qquad (II.1)$$

where m, n, denote the components of spin (both nuclear and electronic) and i, j, denote the position of nuclear and electronic spin respectively. It is worthwhile to note that (II.1), although it is directly applicable to a system with localized electronic spins, it can be equally well be used to describe the interaction in a system with nonlocalized spins, i.e. a metal, using the well known Fermi contact type interaction.

The total Hamiltonian for the system is then:

$$H = H_S + H_{se} + H_e \qquad \text{(II. 2)}$$

and in order to simplify matters further we will suppose just one localized electronic spin, which means a very dilute paramagnetic system:

$$H_{se} = \sum_{i;\,m,n} J_i^{mn} S^n I_i^m \qquad \text{(II. 3)}$$

and H_S , H_e and respectively

$$H_S = -\gamma \hbar H_0 \sum_i I_i^0 \qquad \text{(II. 4)}$$

$$H_e = g\mu_B \; H_0 \, S^0 + H'_e \qquad \text{(II. 5)}$$

with the following properties:

$$[H_s , H_e] = 0 \qquad \text{(II. 6)}$$

$$\left(J_i^{mn}\right)^* = \left(J_i^{-m-n}\right) \qquad \text{(II. 7)}$$

In egn. (II.5) we have introduced H_e as the Hamiltonian that will take into account the interactions, apart from Zeeman energy, acting on the spin S. The explicit form of this Hamiltonian will not be of interest in this work and we will consider its action on the operator S, only through a phenomenological point of view. We will return to this assumption explicitly later in this work.

III. Equation of Motion for the Green's Function $<<I_i^0|I_j^0>>_\omega^{(\pm)}$.

As it is usual in this kind of formalism, we have to set the equation of motion for the original Green's function $<<I_i^0 \mid I_j^0>>_\omega^{(\pm)}$, together with the equations for the generated Green's functions and try to solve the whole system by making certain decoupling assumptions. It is also convenient to calculate this equations for conmutator and anticonmutator Green's functions in order to search which kind of decoupling scheme is more efficient. We will show in the next section the use of the anticonmutator Green's function to calculate the relaxation time T_1 . The original equation is:

$$\hbar\omega <<I_i^0 \mid I_j^0>>_\omega^{(\pm)} = <\left[I_i^0, I_j^0\right]_{(\pm)}>_o + \sum_{m,n} m J_i^{mn} <<S^n I_i^m \mid I_j^0>>_\omega^{(\pm)} \qquad \text{(III.1)}$$

and the equations for the generated Green's functions are:

$$\begin{aligned}\hbar(\omega - m\omega_0) <<S^n I_i^m \mid I_j^0>>_\omega^{(\pm)} &= <\left[S^n I_i^m, I_j^0\right]_{(\pm)}>_o + \\ &+ i\hbar <<\dot{S}^n I_i^m \mid I_j^0>>_\omega^{(\pm)} + \\ &+ \sum_{m_1 n_1} J_i^{m_1 n_1} <<S^n S^{n_1} \left[I_i^m, I_i^{m_1}\right] \mid I_j^0>>_\omega^{(\pm)} + \\ &+ \sum_{k;m_1,n_1} J_k^{m_1 n_1} <<\left[S^n, S^{n_1}\right] I_k^{m_1} I_i^m \mid I_j^0>>_\omega^{(\pm)}\end{aligned} \qquad \text{(III.2)}$$

where we have used the relation:

$$\dot{S}^n = \frac{1}{i\hbar}\left[S^n, H\right] \qquad \text{(III. 3)}$$

In order to decouple this set of equations, we propose the following decoupling scheme:

$$<<S^n S^{n_1} I_i^{\pm} \mid I_j^0>>_\omega^{(\pm)} \simeq <S^{n_1}>_0 <<S^n I_i^{\pm} \mid I_j^0>>_\omega^{(\pm)} \qquad \text{(III. 4)}$$

if there is no correlation between S^{n_1} and S^n,

$$<<S^n S^{n_1} I_i^0 \mid I_j^0>>_\omega^{(\pm)} \simeq <S^n S^{n_1}>_0 <<I_i^0 \mid I_j^0>>_\omega^{(\pm)} \qquad \text{(III. 5)}$$

$$<<I_k^0 S^n I_i^{\pm} \mid I_j^0>>_\omega^{(\pm)} \simeq <I_k^0>_0 <<S^n I_i^{\pm} \mid I_j^0>>_\omega^{(\pm)} \qquad \text{(III. 6)}$$

$$<<I_k^{\pm\dagger} S^n I_i^{\pm} \mid I_j^0>>_\omega^{(\pm)} \simeq <S^n>_0 \delta_{ik} <<I_i^{\pm\dagger} I_i^{\pm} \mid I_j^0>>_\omega^{(\pm)} \qquad \text{(III. 7)}$$

and

$$i\hbar\langle\langle \dot{S}^n I_i^{\pm}|I_j^0\rangle\rangle_\omega^{(\pm)} = i\hbar\langle\langle \underset{\sim}{\dot{S}}^n I_i^{\pm}|I_j^0\rangle\rangle_\omega^{(\pm)} - ng\mu_B H_0\langle\langle S^n I_i^{\pm}|I_j^0\rangle\rangle_\omega^{(\pm)} \approx$$

$$\approx \frac{-i\hbar}{\tau_{en}}\langle\langle \delta S^n I_i^{\pm}|I_j^0\rangle\rangle_\omega^{(\pm)} - n\hbar\omega_e\langle\langle S^n I_i^{\pm}|I_j^0\rangle\rangle_\omega^{(\pm)} \qquad \text{(III. 8)}$$

where we have defined:

$$i\hbar\underset{\sim}{\dot{S}}^n = \left[S^n, H'_e\right] \qquad \text{(III. 9)}$$

and we have made the assumption that the evolution of the electronic system is given by Bloch type equations of motion, i.e.:

$$\dot{S}^n = in\omega_e S^n - \frac{\delta S^n}{\tau_{en}} \qquad \text{(III.10)}$$

with $\delta S^n = S^n - \langle S^n\rangle_0$ and τ_{en} corresponds to the nth component relaxation time.

By means of this decoupling scheme the resulting equations for the generated Green's functions are:

$$\left\{\hbar(\omega-m\omega_0)+n\hbar\omega_e+\frac{i\hbar}{\tau_{en}}+mJ_i^{00}\langle S^0\rangle_0+n\sum_k J_k^{00}\langle I_k^0\rangle_0\right\}\langle\langle S^n I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} =$$

$$= 2mJ_i^{-m-n}\langle S^n S^{-n}\rangle_0\langle\langle I_i^0|I_j^0\rangle\rangle_\omega^{(\pm)} + 2nJ_i^{-m-n}\langle S^0\rangle_0\langle\langle I_i^{-m}I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} +$$

$$+ n\left\{2\sum_k J_k^{0-n}\langle S^0\rangle_0\langle I_k^0\rangle_0 - J_i^{0-n}\langle S^n S^{-n}\rangle_0\right\}\langle\langle I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} \qquad \text{(III.11)}$$

and

$$\left\{\hbar(\omega-m\omega_0)+\frac{i\hbar}{\tau_{eo}}\right\}\langle\langle S^0 I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} = 2mJ_i^{-m0}\langle S^{0\,2}\rangle_0\langle\langle I_i^0|I_j^0\rangle\rangle_\omega^{(\pm)} +$$

$$+\left\{\frac{i\hbar\langle S^0\rangle_0}{\tau_{eo}} - mJ_i^{00}\langle S^{0\,2}\rangle_0\right\}\langle\langle I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} +$$

$$+\sum_k J_k^{0+}\langle I_k^0\rangle_0\langle\langle S^+ I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} - \sum_k J_k^{0-}\langle I_k^0\rangle_0\langle\langle S^- I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} \qquad \text{(III.12)}$$

for m, n, equal to +-1.

Within the same approximations the equation of motion for $\langle\langle I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)}$ with m = +-1 can be written:

$$\left\{\hbar(\omega-m_0)+mJ_i^{00}\langle S^0\rangle_0\right\}\langle\langle I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} = 2mJ_i^{-m0}\langle S^0\rangle_0\langle\langle I_i^0|I_j^0\rangle\rangle_\omega^{(\pm)} \qquad \text{(III.13)}$$

and by means of the identity:

$$I_i^{-m}I_i^m = I\,(I+1) - (I_i^0)^2 - m\,I_i^0 \qquad \text{(III.14)}$$

for m = +-1,we can write the Green's function $\langle\langle I_i^{-m}I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)}$ as:

$$\langle\langle I_i^{-m}I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} = -\langle\langle (I_j^0)^2|I_j^0\rangle\rangle_\omega^{(\pm)} - m\langle\langle I_j^0|I_j^0\rangle\rangle_\omega^{(\pm)} \qquad \text{(III.15)}$$

Substituting egns. (III.13) and (III.15) in (III.11) and (III.12) and discarding terms of order J and superior, we find:

$$\langle\langle S^n I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} =$$

$$= \frac{2mJ_i^{-m-n}\left\{\langle S^0 S^{-n}\rangle_0 - n\langle S^0\rangle_0\right\}\langle\langle I_i^0|I_j^0\rangle\rangle_\omega^{(\pm)} - 2nJ_i^{-m-n}\langle S^0\rangle_0\langle\langle I_i^{0\,2}|I_j^0\rangle\rangle_\omega^{(\pm)}}{\hbar(\omega-m\omega_0)+n\hbar\omega_e+\frac{i\hbar}{\tau_{e+}}+mJ_i^{00}\langle S^0\rangle_0+n\sum_k J_k^{00}\langle I_k^0\rangle_0} \qquad \text{(III.16)}$$

$$\langle\langle S^0 I_i^m|I_j^0\rangle\rangle_\omega^{(\pm)} =$$

$$=2mJ_i^{-m0}\left[\frac{\langle S^{0\,2}\rangle_0}{\hbar(\omega-m\omega_0)+\frac{i\hbar}{\tau_{eo}}} + \frac{\frac{i\hbar}{\tau_{eo}}\langle S^0\rangle_0^2}{\left(\hbar(\omega-m\omega_0)+\frac{i\hbar}{\tau_{eo}}\right)\left(\hbar(\omega-m\omega_0)+mJ_i^{00}\langle S^0\rangle_0\right)}\right]$$

$$\langle\langle I_i^0|I_j^0\rangle\rangle_\omega^{(\pm)} \qquad \text{(III.17)}$$

If we make the definitions:

$$\hbar\underset{\sim}{\omega}{}^{i}_{0} = \hbar\omega_{0} - J^{00}_{i}\langle S^{0}\rangle_{0}$$

$$\hbar\underset{\sim}{\omega}{}_{e} = \hbar\omega_{e} + \sum_{k} J^{00}_{k}\langle I^{0}_{k}\rangle_{0} \tag{III.18}$$

which corresponds to the nuclear (electronic) effective energies corrected by the mean local interaction with the electron (nucleus) respectively, we finally get, after subtitution in egn. (III.1):

$$\left\{\hbar\omega - W_{i}(\omega)\right\}\langle\langle I^{0}_{i} | I^{0}_{j}\rangle\rangle_{\omega}^{(\pm)} = \langle\left[I^{0}_{i}, I^{0}_{j}\right]_{(\pm)}\rangle_{\omega} + F_{i}(\omega)\langle\langle (I^{0}_{j})^{2} | I^{0}_{j}\rangle\rangle_{\omega}^{(\pm)} \tag{III.19}$$

where

$$W_{i}(\omega) = 2{\sum_{m}}'\left\{{\sum_{n}}'|J^{mn}_{i}|^{2}\left\{S(S+1) - \langle S^{02}\rangle_{0}\right\}\left[\frac{1}{\hbar(\omega - m\underset{\sim}{\omega}{}^{i}_{0} + n\underset{\sim}{\omega}{}_{e}) + \frac{i\hbar}{\tau_{en}}}\right] + \right.$$

$$\left. + |J^{m0}_{i}|^{2}\left[\frac{\langle S^{02}\rangle_{0}}{\hbar(\omega - m\omega_{0}) + \frac{i\hbar}{\tau_{e}}} + \frac{\frac{ih}{\tau_{eo}}\langle S^{0}\rangle^{2}_{0}}{\left(\hbar(\omega - m\omega_{0}) + \frac{i\hbar}{\tau_{eo}}\right)\hbar\left(\omega - m\underset{\sim}{\omega}{}^{i}_{0}\right)}\right]\right\} \tag{III.20}$$

where the prime indicate that the sums are done over the values +-1 and use of the property (II.7) has been done.
Also:

$$F_{i}(\omega) = 2\sum_{m}\sum_{n} mn\, |J^{mn}_{i}|^{2}\langle S^{0}\rangle_{0}\frac{1}{\hbar(\omega - m\underset{\sim}{\omega}{}^{i}_{0} + n\underset{\sim}{\omega}{}_{e}) + \frac{i\hbar}{\tau_{en}}} \tag{III.21}$$

IV. Determination of the Nuclear Relaxation Time T_1.

As discused in Section I in order to calculate T_1 , we must first evaluate the real and imaginary parts of the conmutator. Green's function $\langle\langle I^{0}_{i} | I^{0}_{i}\rangle\rangle_{\omega}^{(-)}$ in the limit of $\omega \to 0$. It results easier to evaluate the imaginary part of the corresponding anticonmutator Green's function (6) (7) and then to use the following general relation (4):

$$I_{m}\langle\langle I^{0}_{i} | I^{0}_{i}\rangle\rangle_{\omega}^{(-)} = \tanh\frac{\beta\hbar\omega}{2}\, I_{m}\langle\langle I^{0}_{i} | I^{0}_{i}\rangle\rangle_{\omega}^{(+)} \tag{IV.1}$$

The real part can be evaluated through the Kramers-Kronig relations (4) and in the limit $kT \gg \hbar\underset{\sim}{\omega}{}^{i}_{0}$, it is simply:

$$\mathrm{Re}\,\langle\langle I^{0}_{i} | I^{0}_{i}\rangle\rangle_{\omega}^{(-)} = -\beta\langle I^{0}_{i} | I^{0}_{i}\rangle_{0} \tag{IV.2}$$

The solution of the equation (III.19) for the anticonmutator Green's function can be written as:

$$\langle\langle I^{0}_{i} | I^{0}_{i}\rangle\rangle_{\omega}^{(+)} \simeq \frac{2\langle I^{0}_{i} | I^{0}_{i}\rangle_{0}}{\hbar\omega - W_{i}(\omega)} \tag{IV.3}$$

where $W_1(\omega) = A_i(\omega) - iB_i(\omega)$, with

$$A_{i}(\omega) = \mathrm{Re}\,W_{i}(\omega) =$$

$$= 2\sum_{m}\left\{\sum_{n}|J^{mn}_{i}|^{2}\left\{S(S+1) - \langle S^{02}\rangle_{0}\right\}\frac{\hbar(\omega - m\underset{\sim}{\omega}{}^{i}_{0} + n\underset{\sim}{\omega}{}_{e})}{\hbar^{2}(\omega - m\underset{\sim}{\omega}{}^{i}_{0} + n\underset{\sim}{\omega}{}_{e})^{2} + \frac{\hbar^{2}}{\tau^{2}_{en}}} + \right.$$

$$\left. + |J^{m0}_{i}|^{2}\left[\frac{\hbar\langle S^{02}\rangle_{0}(\omega - m\omega_{0})}{\hbar^{2}(\omega - m\omega_{0})^{2} + \frac{\hbar^{2}}{\tau^{2}_{eo}}} + \frac{\frac{\hbar^{2}}{\tau^{2}_{eo}}\langle S^{0}\rangle^{2}_{0}}{\left(\hbar^{2}(\omega - m\omega_{0})^{2} + \frac{\hbar^{2}}{\tau^{2}_{eo}}\right)\hbar\left(\omega - m\underset{\sim}{\omega}{}^{i}_{0}\right)}\right]\right\} \tag{IV.4}$$

and:

$$B_{i}(\omega) = -\mathrm{Im}\,W_{i}(\omega) =$$

$$= 2\sum_{m}\left\{\sum_{n}|J^{mn}_{i}|^{2}\left\{S(S+1) - \langle S^{02}\rangle_{0}\right\}\left[\frac{\frac{i\hbar}{\tau_{en}}}{\hbar^{2}(\omega - m\underset{\sim}{\omega}{}^{i}_{0} + n\underset{\sim}{\omega}{}_{e})^{2} + \frac{\hbar^{2}}{\tau^{2}_{en}}}\right] + \right.$$

$$\left. + \frac{|J^{m0}_{i}|^{2}}{\hbar^{2}(\omega - m\omega_{0})^{2} + \frac{\hbar^{2}}{\tau^{2}_{eo}}}\left[\frac{\hbar}{\tau_{eo}}\langle S^{02}\rangle_{0} - \frac{\hbar}{\tau_{eo}}\frac{(\omega - m\omega_{0})}{(\omega - m\underset{\sim}{\omega}{}^{i}_{0})}\langle S^{0}\rangle^{2}_{0}\right]\right\} \tag{IV.5}$$

with the property that $A_i(0) = 0$, $B_i(0) \neq 0$. By using (IV.1), the imaginary part of $<<I_i^0 \mid I_i^0>>_\omega^{(-)}$ is:

$$I_m <<I_i^0 \mid I_i^0>>_\omega^{(-)} = -2<<I_i^0 \mid I_i^0>>_0 \tanh \frac{\beta\hbar\omega}{2} \frac{B_i(\omega)}{\left(\hbar\omega - A_i(\omega)\right)^2 + B_i^2(\omega)} \tag{IV.6}$$

and

$$T_1^i = \lim_{\omega\to O} \frac{1}{\omega} \frac{I_m <<I_i^0 \mid I_i^0>>_\omega^{(-)}}{R_e <<I_1^0 \mid I_i^0>>_\omega^{(-)}} = \frac{\hbar}{B_i(O)} \tag{IV.7}$$

or more explicitly, the spin-lattice relaxation rate is:

$$\begin{aligned}(T_1^i)^{-1} = {} & \frac{4\,|J_i^{++}|^2}{\hbar^2} \left\{S(S+1) - <S^{02}>_0\right\} \frac{T_{2e}}{1+T_{2e}^2 (\underset{\sim}{\omega}_e - \underset{\sim}{\omega}_0^i)^2} + \\ & + \frac{4\,|J_i^{+0}|^2}{\hbar^2} \left\{<S^{02}>_0 - \frac{\omega_0}{\underset{\sim}{\omega}_0^i} <S^0>_0^2\right\} \frac{T_{1e}}{1+T_{1e}^2\,\omega_0^2} + \\ & + \frac{4\,|J_i^{+-}|^2}{\hbar^2} \left\{S(S+1) - <S^{02}>_0\right\} \frac{T_{2e}}{1+T_{2e}^2 (\underset{\sim}{\omega}_e + \underset{\sim}{\omega}_0^i)^2}\end{aligned} \tag{IV.8}$$

where we have made use of the fact that $\tau_{e+} = \tau_{e-} = T_{2e}$ and $\tau_{e0} = T_{1e}$.

V. Discussion.

The results in the last section in egn. (IV.8) include all the contributions to the spin-lattice relaxation rate, each one related to a different term of the interaction Hamiltonian (II.3). The temperature and field dependence for this relaxation rate is given essentially through the mean values accompanying each one of the terms of (IV.8), besides the temperature dependence already present in T_{1e} and T_{2e}. At sufficiently high temperatures and low field, conditions under a small electronic spin polarization is present, and due to the smallness of $\underset{\sim}{\omega}_0^i$ in comparison to $\underset{\sim}{\omega}_e$, only the second term of (IV.8) has to be considered (unless the coupling constant J_i^{+0} is zero). The simplified expression for the spin-lattice relaxation rate can be written as:

$$(T_1^i)^{-1} = \frac{4\,|J_i^{+0}|^2}{\hbar^2} \left\{<S^{02}>_0 - <S^0>_0^2\right\} \frac{T_{1e}}{1+T_{1e}^2\,\omega_0^2} \tag{V.1}$$

where we have made the approximation $\underset{\sim}{\omega}_0^i \approx \omega_0$.

At low temperatures, we get a reduction of the spin-lattice relaxation rate due to the development of a strong electronic spin polarization, and for the case of spin 1/2, we obtain that (V.1) vanishes in high field. In such a case the first and third terms of (IV.8) represents the only contribution to the relaxation rate, which is indeed very small. Finally, we note that the discussed behaviour of (IV.8) has been confirmed experimentally (8).

VI. Conclusions.

We have developed a general method to calculate the spin-lattice and spin-spin rrelaxation times for nuclear spins based in the general formalism of Linear Response Theory and two times Green's functions. The results obtained in the case of a nuclear spin system coupled to a paramagnetic localized impurity corresponds completely to previous results (1) and experiments (8). The versatility of this method suggests its application to a wide range of systems at temperatures even comparable with the nuclear spin temperature.

REFERENCES

1. **Abragan**, A. and **Goldman**, M. *Nuclear Magnetism: Order and Disorder*. Clarendon Press, Oxford, 1.982.
2. **Shibata**, F. and **Hamano**, Y. "Theory of Spin Relaxation in Metals. Relaxation Time Maximum atLow Temperatures." *J. Phys. Soc. Japan* 52: 1410-14-19, 1.983.
3. **Buishvili**, L. L. and **Fokina**, N.P "Theory of Saturation of Magnetic Resonance in Solids at Low Temperatures." *Sov. Phys. Solid State* 25: 215-218, 1.983.
4. **Zubarev**, D.N. "Non equilibrium Statistical Theomodynamics." Consultants Bureau, New York, 1.974, Cap. 3.
5. **Deutch**, J.M., **Oppenheim**, I. "Time Correlation Functions in Nuclear Magnetic Relaxation." *Advances in Magnetic Resonance*. 3: 43-78, 1.968.
6. **Fernández**, J.F. and **Gersch**, H.A. "Note on the Zero-

frequency Pole in Green's Functions." *Proc. Phys. Soc.* 91: 505-506, 1.967.

7. **Ramos**, J.G. and **Gomes**, A.A. "Remarks on the Retarded, Advanced and Thermodynamic Green's Functions." *Il Nuovo Cimento* 3A:441-455, 1.971.
8. **Gunter**, T.E. and **Jeffries**, C.D. "Proton Spin-Lattice Relaxation in $(Nd, La)_2 Mg_3 (NO_3)_{12}. 24H_2O$ in High Fields and Low Temperatures." *Phys. Rev.* 159: 290-295, 1.967.