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ELEMENTARY DERIVATION OF SPIN-RELAXATION PARAMETERS

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ABSTRACT

This paper presents an elementary derivation of formulas for the spin-relaxation parameters. The derivation is based on the solution of the equation of motion for time correlation functions of the magnetization. The use of the assumption of regression of fluctuations allows the determination of non linear integral equations for the relaxation parameters. The method leads to the conclussion that the information obtained through Magnetic Resonance experiments is totally contained in two time Green's functions of the magnetization components.

DEDUCCION ELEMENTAL DE LOS PARAMETROS DE RELAJACION DE SPIN

RESUMEN

En este trabajo se presenta una deducción elemental de las fórmulas para los parámetros de relajación de spin. La deducción está basada en la solución para la ecuación de movimiento de las funciones de correlación temporales de la magnetización. El uso de la suposición de regresión de las fluctuaciones permite establecer ecuaciones integrales no-lineales para los parámetros de relajación. El método conduce a la conclusión de que la información obtenible a través de experimentos de Resonancia Magnética está totalmente contenida en las funciones de Green de dos tiempos de las componentes de la magnetización.

I. INTRODUCTION

The purpose of this paper is to present an elementary derivation of the expressions for the spin-relaxation parameters indicating at the same time a very convenient method for their calculation. This derivation has already been done many times by means of a variety of formalisms with diverse degrees of complexity.[1-3, 5, 9, 10] In contrast we give in this article an alternate derivation which can be characterized by its compactness and mathematical simplicity. Our approach is based on a method proposed by Tserkovnikov[6] for the calculation of two-times Green's functions together with Onsager's basic postulate of regression of fluctuations. With this procedure we arrive at a self consistent expression for the relaxation parameters from which the well known formulas can be derived in the lowest order of approximation. A further advantage of our approach lies in its close relationship with the powerfull two times Green's function formalism[10] which can be readily applied in the calculation of particular relaxation problems.

The organization of this paper is as follows: In section II we introduce the symmetrized time correlation functions for the magnetization components and derive their equation of motion. In this context we define the form of the total system Hamiltonian and introduce a shorthand notation for the different commutators involved. At the end of the section a formal solution for the equation of motion is presented. In section III Onsager's basic postulate is recalled and expressions for the spin-relaxation parameters are identified from the formal solution obtained. In section IV we show that the common formulas for the spin-relaxation rates in the laboratory frame are the lowest order approximation of the derived expression. Finally in section V we briefly show how the Green's function formalism can be used in the calculation of the spin-relaxation parameters.

II. CORRELATION FUNCTIONS AND THEIR EQUATIONS OF MOTION

Let us consider the symmetrized quantum mechanical time correlation functions of the components of the systems magnetization with vanishing ensemble average

$$\{\Delta M^\alpha(t)\,\Delta M^\beta\} = $$
$$= 1/2(<\Delta M^\alpha(t)\,\Delta M^\beta>_0 + <\Delta M^\beta \Delta M^\alpha(t)>_0) \quad \text{(II.1)}$$

where $M^\alpha(t)$ is the Heisenberg representation of the operator M^α, $\Delta M^\alpha(t) = M^\alpha(t) - <M^\alpha>_0$ represents the deviation of the α-component of the magnetization from thermal equilibrium at arbitrary times and

$$<\ldots>_0 = Z^{-1}\ \mathrm{Tr}\,(\exp(-\beta H)\ldots) \quad \text{(II.2)}$$

where Z is the partition function, $\beta = (k_B T)^{-1}$ and H is the Hamiltonian of the total system.

In the context of this work we shall define the total system Hamiltonian as

$$H = H_S + H_{SL} + H_L \quad \text{(II.3)}$$

where H_S, H_{SL}, H_L are respectively the spin-system, spin-lattice interaction and lattice Hamiltonians. This allows us to write the equations of motion for the magnetization components.

$$i\hbar \frac{dM^\alpha(t)}{dt} = [M^\alpha(t), H] = T^\alpha M^\alpha(t) + J^\alpha(t) \quad \text{(II.4)}$$

In this equation we have defined

$$[M^\alpha, H_S] = T^\alpha M^\alpha \text{ and } [M^\alpha, H_{SL}] = J^\alpha \quad \text{(II.5)}$$

The term T^α describes motion in the external field but without interaction between the spins. The interaction between the spins is accounted for by J^α which represents the flux operator corresponding to the α-component of magnetization.

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Based on these definitions we can now establish, in accordance with,[6] the equation of motion for the correlation function (I.1):

$$i\hbar \frac{d}{dt}\{\Delta M^\alpha(t), \Delta M^\beta\} = (T^\alpha + \Gamma^{\alpha\beta}(t))\cdot\{\Delta M^\alpha(t), \Delta M^\beta\} \tag{II.6}$$

where $\Gamma^{\alpha\beta}(t)$ is the term which includes higher correlation functions and has the form

$$\Gamma^{\alpha\beta} = \frac{\{J^\alpha(t), \Delta M^\beta\}}{\{\Delta M^\alpha(t), \Delta M^\beta\}} \tag{II.7}$$

Using the following identity

$$\Gamma^{\alpha\beta}(t) = \Gamma^{\alpha\beta}(0) - \int_0^t dt' \frac{d}{dt'}\Gamma^{\alpha\beta}(t-t') \tag{II.8}$$

equation (II.6) can be rewritten as

$$\frac{d}{dt}\{\Delta M^\alpha(t), \Delta M^\beta\} = -(i\Omega_{\alpha\beta}/\hbar + R^{\alpha\beta}(t))\cdot\{\Delta M^\alpha(t), \Delta M^\beta\} \tag{II.9}$$

where

$$\Omega_{\alpha\beta} = T^\alpha + \Gamma^{\alpha\beta}(0) = T^\alpha + \frac{\{J^\alpha, \Delta M^\beta\}}{\{\Delta M^\alpha, \Delta M^\beta\}} \tag{II.10}$$

and

$$R^{\alpha\beta}(t) = \frac{1}{\hbar^2}\int_0^t dt \left[\frac{\{J^\alpha(t), J^\beta(t')\}}{\{\Delta M^\alpha(t), \Delta M^\beta(t')\}} - \frac{\{J^\alpha(t), \Delta M^\beta(t')\}\cdot\{\Delta M^\alpha(t), J^\beta(t')\}}{\{\Delta M^\alpha(t), \Delta M^\beta(t')\}^2}\right] \tag{II.11}$$

The decay rate of the correlation function is determined by the real part of $R^{\alpha\beta}(t)$. Whereas the imaginary part is responsible for the oscilatory behavior. It is to be noted that these dynamic parameters are explicitly proportional, through the flux operators of the magnetization components involved, to the square of the spin-lattice interaction Hamiltonian.

III. ONSANGER'S POSTULATE AND THE SPIN-RELAXATION RATES

The correlation function in equation (I.1) describes the behaviour in time of the spontaneous fluctuations from thermal equilibrium of the magnetization components of the system. This may be compared with the average time-dependence of the macroscopic magnetization when the system is initially not in equilibrium. The comparison is based on Onsager's postulate of regression of fluctuations which assumes that macroscopic evolution laws are obeyed, on the average, by the decay of spontaneous fluctuations from thermal equilibrium. This postulate enables one to identify the spin-relaxation rate with the real part of $R^{\alpha\beta}(t)$ and its imaginary part with the dynamic frequency shift.

In this respect we must recall that the spin-relaxation behaviour is generally assumed to be exponential, that is the observation time t is considered to be much longer than the correlation time τ of the microscopic events causing relaxation. In order to account for this assumption we must construct an asymptotic representation of the function $R^{\alpha\beta}$ as $t \to \infty$; in this way the resulting expression is time-independent. Accounting for this consideration the formal solution to equation (II.9) can be written as

$$\{\Delta M^\alpha(t), \Delta M^\beta\} = \{\Delta M^\alpha, \Delta M^\beta\}\ \exp(-(i\Omega_{\alpha\beta}/\hbar + R^{\alpha\beta})t) \tag{III.1}$$

Substituting this last expression in (II.11) we obtain in the long time approximation

$$R^{\alpha\beta} = \frac{1}{\hbar^2}\int_0^\infty dt' \left[\frac{\{J^\alpha(t'), J^\beta\}}{\{\Delta M^\alpha, \Delta M^\beta\}}\exp((i\Omega_{\alpha\beta}/\hbar + R^{\alpha\beta})t') - \frac{\{J^\alpha(t'), \Delta M^\beta\}\cdot\{\Delta M^\alpha(t'), J^\beta\}}{\{\Delta M^\alpha, \Delta M^\beta\}^2}\exp(2(i\Omega_{\alpha\beta}/\hbar + R^{\alpha\beta}t'))\right] \tag{III.2}$$

This expression shows that $R^{\alpha\beta}$ satisfies a nonlinear integral equation whose kernel can be expressed in terms of higher order correlation functions, for which equations of motion similar to (II.6) can also be written. In any case equation (III.2) can be used to establish the following very convenient expressions for the determination of the spin-relaxation rates and the dynamic frequency shift

$$1/T_{1+\alpha} = \mathrm{Re}\{R^{\alpha-\alpha}\} \qquad \alpha = 0, \pm 1 \tag{III.3}$$

$$\Delta\omega = \mathrm{Im}\{R^{\alpha-\alpha}\} \qquad \alpha = \pm 1 \tag{III.4}$$

It is worth noting that in the derivation of expressions (III.2) – (III.4) we did not use any perturbation theory approximation. This means that this equations hold for arbitrary relation between τ and T_1, T_2, i.e., they hold for both weak and strong collision regimes. Nevertheless, it is important to emphasize that these equations describe exponential damping of the spin time correlation function only for the asymptotic limit $t \to \infty$ ($t \gg T_1, T_2, \tau$). This agreess with the conclusions that follow from the general theory of magnetic relaxation[1] and the theory of irreversible processes.[11] In the general case, when t is arbitrary, the spin-relaxation is not exponential, in accordance with (II.11).

IV. LABORATORY FRAME SPIN-RELAXATION RATES

In this section let us consider the particular case of spin-relaxation in the laboratory frame. In this situation the spin Hamiltonian is the Zeeman Hamiltonian ($H_s = H_z$) and by virtue of the cylindrical symmetry of the problem it is convenient to use a representation where the magnetization components are denoted as M^α ($\alpha = 0, \pm 1$) with the 0-direction determined by the external magnetic field. It must also be noted that in all applications of interest, the equilibrium average of H_{SL} vanishes, i.e.

$$< H_{SL} >_0 = 0 \tag{IV.1}$$

This has the consequence that terms linear in H_{SL} vanish when averaged over the ensemble. Accordingly, the second terms in the right hand side of both equations (II.10) and (III.2) vanish. Now accounting in the lowest order for the time evolution of the correlation function,

that is approximating the term $(i\Omega_{\alpha\beta}/\hbar + R^{\alpha\beta})$ in the exponent of (III.2) by $iT^{\alpha}/\hbar$ we obtain from (III.3) the following relations for the laboratory frame spin-relaxation times

$$\frac{1}{T_1} = \mathrm{Re}\{R^{00}\} = \mathrm{Re}\left[\frac{1}{\hbar^2}\int_0^{\infty} dt' \frac{\{J^0(t'), J^0\}}{\{\Delta M^0, \Delta M^0\}}\right] \quad \text{(IV.2)}$$

$$\frac{1}{T_2} = \mathrm{Re}\{R^{1-1}\} = \mathrm{Re}\left[\frac{1}{\hbar^2}\int_0^{\infty} dt' \frac{\{J^1(t'), J^{-1}\}}{\{\Delta M^1, \Delta M^{-1}\}} - \right.$$

$$\left. - \exp(i\omega_0 t')\right] \quad \text{(IV.3)}$$

where we have used that $T^{\alpha} = \alpha\hbar\omega_0$ with ω_0 denoting the Larmor frequency.

In can be appreciated that these results, to lowest order in the integral equation (III.2), are coincident with those obtained by other more sofisticated formalisms when those theories are carried out to second order in the spin-lattice interaction.[1-3, 5, 9, 10]

V. CONCLUSION

We have shown above how, in those cases where Onsager's postulate applies that is in spin systems that are not driven too far away from equilibrium, the well known expressions for the spin-relaxation parameters can be readily obtained. Since these expressions are given in terms of higher order correlation functions, the problem of calculating these relaxation parameters for a particular case, is by no means an easy task. Nevertheless, our derivation suggests that a convenient procedure for the determination of the relaxation parameters could be the application of the two-time Green's function formalism.[8, 10] In fact the Green's function defined as

$$\ll \Delta M^{\alpha}(t); \Delta M^{\beta} \gg = (i\hbar)^{-1}\Theta(t)\{\Delta M^{\alpha}(t), \Delta M^{\beta}\} \quad \text{(V.1)}$$

is found to have the same dynamic parameters as the correlation function (II.1).[6]

In the Green's function method one must consider an infinite system of coupled equations for these functions. The technique of terminating such chains consists in expanding the higher order Green functions and then ignoring the irreducible parts.[7, 8] In the Fourier representation, the approximate solutions can be shown to have the form

$$\ll \Delta M^{\alpha}/\Delta M^{\beta} \gg_{\omega} = -(2\pi i)^{-1}\frac{\sigma}{\hbar\omega - T^{\alpha} - M^{\alpha\beta}(\omega)} \quad \text{(V.2)}$$

where

$$\sigma = -(2\hbar i)\ [\Delta M^{\alpha}, \Delta M^{\beta}]^{t} \quad \text{(V.3)}$$

and $M^{\alpha\beta}(\omega)$ is called, by analogy with the quantum theory of fields, the mass operator.

The oscilatory frequency and decay rate of the correlation function (I.1) are determined by the poles of the Green's function (V.2):

$$\hbar q = T^{\alpha} + M^{\alpha\beta}(\omega) \quad \text{(V.4)}$$

Since in most cases the mass operator is considered to be a "small correlation" the solutions seeked for equation (V.4) are of the form $\omega = \omega + iR^{\alpha\beta}$. Assuming that

$$M^{\alpha\beta}(\omega \pm iR^{\alpha\beta}) = M^{\alpha\beta'}(\omega, R^{\alpha\beta}) \mp iM^{\alpha\beta''}(\omega, R^{\alpha\beta}) \quad \text{(V.5)}$$

where $M^{\alpha\beta'}$, $M^{\alpha\beta''}$ are real functions, we obtain the following system of equations for the determination of the frequency shift and relaxation rate

$$\Delta\omega = (1/\hbar)\, M^{\alpha\beta'}(\omega, R^{\alpha\beta}) \quad \text{(V.6)}$$

$$R^{\alpha\beta} = -(1/\hbar)\, M^{\alpha\beta''}(\omega, R^{\alpha\beta}) \quad \text{(V.7)}$$

At this point we must recall that since we are in general interested in the exponential pole approximation, equations (V.6) – (V.7) are to be considered in their low frequency limit. Taking this last consideration into account it can be easily seen that these equations are formally equivalent to equations (III.3) and (III.4) so that the problems in the determination of the spin-relaxation parameters are reduced to the calculation of the Green's function (V.1) by an appropriate approximation scheme.[7, 8]

In conclusion, these results together with those in reference[4] lead us to recognize the important point that all the relevant information regarding the Magnetic Resonance lineshape and relaxation of a spin system is contained in Green's functions of the type (V.1). This fact highly recommends the application of the powerful two-time Green's function technique, of considerable use in other areas of condensed matter physics, to the problems of magnetic resonance spectroscopy.

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