

## RETARDED GREEN'S FUNCTION CALCULATION OF MAGNETIC RESONANCE DIPOLAR LINESHAPES FOR ROTATING MOLECULES OR ATOMIC GROUPS IN SOLIDS

M. MARTIN LANDROVE and J.A. MORENO

*Departamento de Física, Escuela de Física y Matemáticas, Facultad de Ciencias Universidad Central de Venezuela,  
Caracas, Venezuela*

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The powerful two-times Green's function formalism is applied to the calculation of the NMR dipolar lineshape corresponding to hindered rotating spin-carrying molecules or atomic groups in solids. The rotation of the molecules is quantum-mechanically considered as one-phonon induced transitions between the hindered rotator levels. The nuclear spin system is assumed to be coupled to the bath of thermal phonons through the phonon-rotation interaction. The retarded Green's functions, pertinent to the lineshape problem, are determined by a second order decoupling of their equations of motion. The lineshape expression is shown to be a weighted superposition of Lorentzians.

### 1. Introduction

The purpose of this paper is to present a formal derivation, in the linear response regime, of the NMR lineshape of a relatively simple spin system interacting with a more complex system acting as a thermal reservoir. In actual lineshape calculations on dipolar solids [1, 2] the spin system is often considered to be isolated from the lattice vibrations accounting for the effect of the thermal bath classically. That is, the source of Magnetic Resonance Absorption lineshape, (the dipole-dipole interaction in the present case) is considered to be a random function of time due to the lattice motion. This procedure, which has shown to be fruitful in the interpretation of measurements at relatively high temperatures (above 70 K), results in an excessive simplification of the lattice dynamics requiring frequently a posteriori corrections [3, 4].

In the present paper we shall consider a system of spin-carrying molecules or atomic group in a solid, subjected to a strong static magnetic field and a small perpendicular hf magnetic field, both of external origin. The spin-carrying molecules are assumed to undergo a hindered rotational motion considered to occur due to the scattering of phonons. In this sense the rotational degrees of freedom are modelled by a Hamiltonian whose potential energy term is taken as the interaction energy of the molecule with all other atoms and molecules in the solid fixed at their equilibrium positions. The existence of collective vibrational modes in the crystal alters this interaction energy and gives rise to an interaction between the rotational degrees of freedom and the lattice vibrations (phonons). For simplicity, we shall consider the effect of the phonon-rotation interaction only to terms linear in the displacements of the atoms and molecules from their equilibrium positions, allowing in this way only for one-phonon processes. In regard to the magnetic interaction involved, the nuclear spins are taken to interact among themselves through magnetic dipolar forces assumed to be of intramolecular character. A general Hamiltonian, including all the above interacting systems, is used to establish a chain of equations obeyed by a two-times retarded Green's function. This function contains all pertinent

information to the NMR lineshape [5]. The chain of equations is then solved by a second order decoupling scheme.

In section 2, we introduce the formalism of Linear Response Theory applied to the calculation of Magnetic Resonance Absorption lines. In this context, we introduce the two-times retarded Green's functions, show its relation to the lineshape and construct its equation of motion. In section 3, the total system Hamiltonian is discussed. Section 4 deals with the establishment and second order decoupling of the chain of equations leading to the Green's function of interest. The last section serves to discuss our results.

## 2. Linear response theory and NMR lineshape

Let us consider an arbitrary spin system interacting with external fields and coupled with another system which is going to work, eventually, as a heat bath. In NMR experiments the main concern is the study of the spin system linear response to the driving field when a periodic perturbation is turned on adiabatically:

$$H_t^1 = -\mathbf{M} \cdot \mathbf{H}(t) = \text{Re}\{H^1 e^{\varepsilon t - i\omega t}\} \quad (\varepsilon \rightarrow 0^+), \quad (1)$$

$$H^1 = -\gamma \hbar H_1 I^- . \quad (2)$$

$\mathbf{H}(t) = H_1 (\mathbf{i} \cos \omega t - \mathbf{j} \sin \omega t) \exp(\varepsilon t)$  is the external r.f. field.  $\gamma$  is the gyromagnetic ratio and  $I^-$  stands for the total nuclear spin ladder operator of the system. As discussed elsewhere [6], the energy absorption under the influence of the perturbation  $H_t^1$  and averaged over a period, is determined by the double time retarded Green's function of the perturbation:

$$\frac{dE}{dt} = -\frac{\omega}{2} \gamma^2 \hbar^2 H_1^2 \text{Im}\langle\langle I^+ | I^- \rangle\rangle_\omega . \quad (3)$$

$\langle\langle A/B \rangle\rangle_\omega$  is the Fourier transform of the double time retarded Green's function defined as

$$\langle\langle A(t)B(t') \rangle\rangle = -\frac{i}{\hbar} \theta(t-t') \langle[A(t), B(t')]\rangle_0, \quad (4)$$

where the bracket  $\langle \dots \rangle_0$  stands for the average over an equilibrium ensemble and  $\theta(t)$  represents the step function.

In most NMR experiments it turns out to be a good approximation for the lineshape to use the following expression:

$$I(\omega) = -\frac{\omega_0}{2} \gamma^2 \hbar^2 H_1^2 \text{Im}\langle\langle I^+ | I^- \rangle\rangle_\omega . \quad (5)$$

The reason for this being that the main contribution of the NMR absorption lines lies in a frequency interval around the Larmor frequency  $\omega_0$  and the other contributions far from  $\omega_0$  are negligible. This fact must be accounted for in expression (5) where the Hamiltonian must be conveniently truncated [1] in such a way that the poles of  $\text{Im}\langle\langle I^+ | I^- \rangle\rangle_\omega$  lie only in the frequency interval of interest, which in most cases is very small compared to  $\omega_0$ .

One important fact that follows from eq. (5) is that all the relevant information about the lineshape is contained in the Green's function  $\langle\langle I^+ | I^- \rangle\rangle_\omega$  [5]. In this sense, this expression provides a very convenient way for the calculation of the linear response lineshapes of NMR spectra.

In general the Green's function  $\langle\langle A/B \rangle\rangle_\omega$  obeys the following equation of motion [6]:

$$\hbar\omega\langle\langle A/B \rangle\rangle_\omega = \langle[A, B]\rangle_0 + \langle\langle[A, H]|B \rangle\rangle_\omega, \quad (6)$$

where  $H$  is the total Hamiltonian of the system.

This expression will be used in the calculation of the Green's function  $\langle\langle I^+ | I^- \rangle\rangle_\omega$ . However, it must be noticed that in the right-hand side of eq. (6) higher order Green's functions appear and an infinite chain of coupled equations is generated. Then, the basic problem in this Green's functions formalism is to find a decoupling scheme. This decoupling scheme is usually performed as early as possible in order to keep the mathematical complexity at a manageable level.

### 3. Hamiltonian of the system

In this paper we are interested in the calculation of the NMR absorption lineshape due to the nuclei in symmetric molecules or molecular ionic groups in solids. This includes molecular crystals such as  $\text{CH}_4$ ,  $\text{NH}_4\text{X}$ ,  $\text{CH}_3\text{X}$ , etc. In neglecting internal vibration modes of the molecules, the Hamiltonian of a molecular crystal placed in an external magnetic field is written as

$$H = H_Z + H_R + H_{\text{Ph}} + H_{\text{D-D}} + H_{\text{R-Ph}}, \quad (7)$$

where  $H_Z$  is the nuclear Zeeman Hamiltonian in the external magnetic field.  $H_{\text{Ph}}$  is the phonon Hamiltonian given by

$$H_{\text{Ph}} = \sum_{ks} \varepsilon_{ks} (b_{ks}^+ b_{ks} + 1/2), \quad (8)$$

where  $b_{ks}^+$  and  $b_{ks}$  are phonon creation and annihilation operators,  $s$  denotes the branch and polarization of the phonons and  $k$  its wave vector.  $H_{\text{D-D}}$  represents the intramolecular magnetic dipolar interaction Hamiltonian between the nuclei. We assume that the intermolecular part of this interaction is negligible as in most cases of practical interest. Finally, the terms  $H_R$  and  $H_{\text{R-Ph}}$  represent the molecular rotation Hamiltonian and the rotation-phonon interaction Hamiltonian, respectively. In what follows we discuss the explicit form of these terms. In general, the rotational Hamiltonian for a molecule can be written as [7-9]

$$H_R = \frac{\hat{J}^2}{2I} + V(\Omega, \mathbf{r}_M, \{\mathbf{r}_i\}), \quad (9)$$

where  $\hat{J}$  is the molecular angular momentum operator,  $I$  is the moment of inertia,  $V$  represents the intermolecular interaction potential which depends on the set of Eulerian angles describing the molecular orientation with respect to the lattice axes, the position  $\mathbf{r}_M$  of the pertinent molecule or ionic group in the lattice and on the set  $\{\mathbf{r}_i\}$  of positions of all other molecules and atoms in the lattice. This interaction potential  $V(\Omega, \mathbf{r}_M, \{\mathbf{r}_i\})$  must be at least invariant with respect to the point symmetry group of the molecule or ionic group [8] and it can be expanded as

$$V(\Omega, \mathbf{r}_M, \{\mathbf{r}_i\}) = \sum_{\alpha} C_{\alpha}(\mathbf{r}_M, \{\mathbf{r}_i\}) V_{\alpha}(\Omega), \quad (10)$$

where  $V_{\alpha}(\Omega)$  is some linear combination of Wigner matrices  $D_{KM}^J(\Omega)$  with the appropriate molecular symmetry invariance properties [10]. The molecular positions in the crystal are not fixed but are undergoing displacements around its lattice equilibrium sites due to the presence of the collective vibrational modes, i.e. phonons. Assuming that the displacements are very small we can expand, to first order, the coefficients  $C_{\alpha}$  in Taylor series around the molecular equilibrium positions, obtaining

$$\begin{aligned} V(\Omega, \mathbf{r}_M, \{\mathbf{r}_i\}) = & \sum_{\alpha} C_{\alpha}(\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}) V_{\alpha}(\Omega) + \sum_{\alpha} (\nabla_M C_{\alpha}(\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}) \cdot \mathbf{U}_M) V_{\alpha}(\Omega) \\ & + \sum_{\alpha} \sum_i (\nabla_i C_{\alpha}(\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}) \cdot \mathbf{U}_i) V_{\alpha}(\Omega). \end{aligned} \quad (11)$$

The first term in the right-hand side of eq. (11) must be invariant under the molecular symmetry group at the equilibrium positions  $\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}$  whereas the other two terms must account for the difference in symmetry due to the displaced molecular positions  $\mathbf{r}_{0M} + \mathbf{U}_M, \{\mathbf{r}_{0i} + \mathbf{U}_i\}$  so that the potential is invariant under the actual symmetry group. In this approximation the main interaction term, described in general in [10]:

$$V(\Omega, \mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}) = \sum_{\alpha} C_{\alpha}(\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}) V_{\alpha}(\Omega), \quad (12)$$

is taken to be the main interaction potential in the rotation Hamiltonian:

$$H_R = \frac{\hat{\mathbf{j}}^2}{2I} + V(\Omega, \mathbf{r}_{0M}, \{\mathbf{r}_{0i}\}). \quad (13)$$

On the other hand, the other two terms in eq. (11) are interaction terms that couple the rotational degrees of freedom to the lattice vibrations. These terms take into account only one-phonon processes because the expansion in eq. (11) was carried out only to first order in the displacements. We simplify matters further by assuming that, out of the two terms in the rotation-phonon interaction, the main coupling term is due to the vibration of the molecule or ionic group about its equilibrium position, so that

$$H_{R-Ph} = \sum_{\alpha} \mathbf{C}_{\alpha}^M \cdot \mathbf{U}_M V_{\alpha}(\Omega), \quad (14)$$

where  $\mathbf{C}_{\alpha}^M = \nabla_M C_{\alpha}(\mathbf{r}_{0M}, \{\mathbf{r}_{0i}\})$ .

Assuming one-atom unit-cell we can write eq. (14) in terms of the phonon creation and annihilation operators:

$$H_{R-Ph} = \sum_{ks} \sum_{\alpha} \frac{\hbar}{(2M\epsilon_{ks})^{1/2}} [(\mathbf{C}_{\alpha}^M \cdot \mathbf{e}_s) e^{ik \cdot \mathbf{r}_{0M}} b_{ks} + (\mathbf{C}_{\alpha}^M \cdot \mathbf{e}_s^*) e^{-ik \cdot \mathbf{r}_{0M}} b_{ks}^+] V_{\alpha}(\Omega), \quad (15)$$

where the  $\mathbf{e}_s$  are the polarization vectors and  $M$  is the mass of the crystal.

The Hamiltonian (7) will be now used in conjunction with eq. (6) to obtain an expression for  $\langle\langle I^+ / I^- \rangle\rangle_{\omega}$ .

#### 4. Calculation of Green's function

It was shown in [11] that a convenient representation basis for the operators occurring in the system Hamiltonian is the set of eigenstates of the Zeeman and rotation Hamiltonians:

$$(H_Z + H_R)|\mu\rangle = (E_\mu^Z + E_\mu^R)|\mu\rangle. \quad (16)$$

The states  $|\mu\rangle$  are linear combinations of products of spin and rotational wave functions [13] so that the label  $\mu$  represents a set of quantum numbers which, in general, can be chosen as  $(Im_I; Jm_J; \Gamma_I \Gamma_J \Gamma_0 t)$  where  $I$  is the total nuclear spin,  $m_I$  its projection on the  $z$  axis,  $J$  the angular momentum and  $m_J$  its projection on the laboratory-frame  $z$  axis. For the most frequently studied hindered rotators of the type  $XY_3$  and  $XY_4$  with molecular point groups  $C_{3V}$  and  $T_d$ , respectively, it is safe to assume that the "feasible" operations of the full molecular symmetry group  $P_N \times S_2$  ( $P_N$  is the symmetric group of  $N$  elements) form a subgroup which is isomorphic to the molecular point group. In this case the  $\Gamma_s$  denotes irreducible representations of the molecular point group.  $\Gamma_I$  is the irreducible representation associated with a particular spin species of total nuclear spin  $I$ .  $\Gamma_J$  is the irreducible representation according to which the rotational wave function transforms and  $\Gamma_0$  must be  $A_1$  or  $A_2$  depending on our choice of the state  $|\mu\rangle$  as a symmetric or antisymmetric state with respect to the exchange of two identical nuclei. Finally, the label  $t$  distinguishes between the distinct states where all other quantum numbers are the same. In most cases  $t$  can be left out since there are no such other states. In what follows and for the sake of simplicity in our notation we will denote these Zeeman-rotation states only by the label  $\mu$ .

In this representation the operators can be written as follows:

$$I^+ = \sum_{\mu\mu'} \langle \mu' | I^+ | \mu \rangle |\mu'\rangle \langle \mu|, \quad (17)$$

$$H_{D-D} = \sum_{\mu\mu'} h_{\mu'\mu} |\mu'\rangle \langle \mu|, \quad h_{\mu'\mu} = \langle \mu' | H_{D-D} | \mu \rangle, \quad (18)$$

$$H_{R-Ph} = \sum_{\substack{\mu\mu' \\ ks}} \{ F_{\mu\mu'}^*(ks) |\mu'\rangle \langle \mu| b_{ks}^+ + F_{\mu\mu'}(ks) |\mu\rangle \langle \mu'| b_{ks} \}, \quad (19)$$

where

$$F_{\mu\mu'}(ks) = \sum_{\alpha} \frac{\langle \mu | V_{\alpha}(\Omega) | \mu' \rangle \hbar}{(2M\epsilon_{ks})^{1/2}} (\mathbf{C}_{\alpha}^M \cdot \mathbf{e}_s) e^{ik \cdot \mathbf{r}_{0M}}. \quad (20)$$

The evaluation of the matrix elements for the different operators involved in the relations (17)–(20) is highly simplified by considering the symmetry properties of the  $|\mu\rangle$  states together with those of the relevant operators. In this sense the application of a convenient form of the Wigner–Eckart theorem to finite groups [13] will be particularly useful.

On the other hand, as Green's function  $\langle\langle I^+ / I^- \rangle\rangle_{\omega}$  is a bilinear form in the spin ladder operators it can be written as [11]

$$\langle\langle I^+ / I^- \rangle\rangle_{\omega} = \sum_{\mu\mu'} \langle \mu' | I^+ | \mu \rangle \langle \langle \mu' | \mu \rangle | I^- \rangle\rangle_{\omega}. \quad (21)$$

In this form Green's function  $\langle\langle I^+ / I^- \rangle\rangle_{\omega}$  is decomposed into a combination of new Green's functions

$\langle\langle|\mu'\rangle\langle\mu||I^-\rangle\rangle_\omega$  that can be considered as its "components" in the given representation. Now the calculation of  $\langle\langle I^+/I^-\rangle\rangle_\omega$  reduces to the evaluation by means of eq. (6) of each one of its components.

It should be noted that the operator  $I^+$  in relation (21) has non-zero matrix elements only between states of equal nuclear symmetry, so that the double sum in (21) has to be carried out for Zeeman-rotation states belonging to the same spin species.

The equation of motion for any of the components in (21) is given by

$$\begin{aligned}
& \{\hbar(\omega - \omega_0) - (h_{\mu\mu} - h_{\mu'\mu'})\}\langle\langle|\mu'\rangle\langle\mu||I^-\rangle\rangle_\omega \\
&= \langle\langle|\mu'\rangle\langle\mu||I^-\rangle\rangle_0 + \sum_{\mu_1 \neq \mu} h_{\mu\mu_1} \langle\langle|\mu'\rangle\langle\mu_1||I^-\rangle\rangle_\omega - \sum_{\mu_1 \neq \mu'} h_{\mu_1\mu'} \langle\langle|\mu_1\rangle\langle\mu||I^-\rangle\rangle_\omega \\
&+ \sum_{\mu_1 k s} \{F_{\mu\mu_1}(ks) \langle\langle|\mu'\rangle\langle\mu_1|b_{ks}|I^-\rangle\rangle_\omega - F_{\mu_1\mu'}(ks) \langle\langle|\mu_1\rangle\langle\mu|b_{ks}|I^-\rangle\rangle_\omega\} \\
&+ \sum_{\mu_1 k s} \{F_{\mu\mu_1}^*(ks) \langle\langle|\mu'\rangle\langle\mu_1|b_{ks}^+|I^-\rangle\rangle_\omega - F_{\mu_1\mu'}^*(ks) \langle\langle|\mu_1\rangle\langle\mu|b_{ks}^+|I^-\rangle\rangle_\omega\}. \tag{22}
\end{aligned}$$

The new higher order Green's functions that appear and which contain phonon creation and annihilation operators obey the following equations of motion:

$$\begin{aligned}
& \{\hbar\omega - \Delta E_{\mu_2\mu_1}^{(1)} + \varepsilon_{ks}\}\langle\langle|\mu_1\rangle\langle\mu_2|b_{ks}^+|I^-\rangle\rangle_\omega \\
&= \langle\langle|\mu_1\rangle\langle\mu_2|b_{ks}^+|I^-\rangle\rangle_0 + \sum_{\mu_3 \neq \mu_2} h_{\mu_2\mu_3} \langle\langle|\mu_1\rangle\langle\mu_3|b_{ks}^+|I^-\rangle\rangle_\omega - \sum_{\mu_3 \neq \mu_1} h_{\mu_3\mu_1} \langle\langle|\mu_3\rangle\langle\mu_2|b_{ks}^+|I^-\rangle\rangle_\omega \\
&+ \sum_{\mu_3 k' s'} \{F_{\mu_2\mu_3}(k' s') \langle\langle|\mu_1\rangle\langle\mu_3|b_{ks}^+ b_{k' s'}|I^-\rangle\rangle_\omega - F_{\mu_3\mu_1}(k' s') \langle\langle|\mu_3\rangle\langle\mu_2|b_{ks}^+ b_{k' s'}|I^-\rangle\rangle_\omega\} \\
&+ \sum_{\mu_3 k' s'} \{F_{\mu_3\mu_2}^*(k' s') \langle\langle|\mu_1\rangle\langle\mu_3|b_{ks}^+ b_{k' s'}^+|I^-\rangle\rangle_\omega - F_{\mu_1\mu_3}^*(k' s') \langle\langle|\mu_3\rangle\langle\mu_2|b_{ks}^+ b_{k' s'}^+|I^-\rangle\rangle_\omega\} \\
&- \sum_{\mu_3} F_{\mu_3\mu_1}(ks) \langle\langle|\mu_3\rangle\langle\mu_2||I^-\rangle\rangle_\omega \tag{23}
\end{aligned}$$

and

$$\begin{aligned}
& \{\hbar\omega - \Delta E_{\mu_2\mu_1}^{(1)} - \varepsilon_{ks}\}\langle\langle|\mu_1\rangle\langle\mu_2|b_{ks}|I^-\rangle\rangle_\omega \\
&= \langle\langle|\mu_1\rangle\langle\mu_2|b_{ks}|I^-\rangle\rangle_0 + \sum_{\mu_3 \neq \mu_2} h_{\mu_2\mu_3} \langle\langle|\mu_1\rangle\langle\mu_3|b_{ks}|I^-\rangle\rangle_\omega - \sum_{\mu_3 \neq \mu_1} h_{\mu_3\mu_1} \langle\langle|\mu_3\rangle\langle\mu_2|b_{ks}|I^-\rangle\rangle_\omega \\
&+ \sum_{\mu_3 k' s'} \{F_{\mu_2\mu_3}(k' s') \langle\langle|\mu_1\rangle\langle\mu_3|b_{ks} b_{k' s'}|I^-\rangle\rangle_\omega - F_{\mu_3\mu_1}(k' s') \langle\langle|\mu_3\rangle\langle\mu_2|b_{ks} b_{k' s'}|I^-\rangle\rangle_\omega\} \\
&+ \sum_{\mu_3 k' s'} \{F_{\mu_3\mu_2}^*(k' s') \langle\langle|\mu_1\rangle\langle\mu_3|b_{k' s'}^+ b_{ks}|I^-\rangle\rangle_\omega - F_{\mu_1\mu_3}^*(k' s') \langle\langle|\mu_3\rangle\langle\mu_2|b_{k' s'}^+ b_{ks}|I^-\rangle\rangle_\omega\} \\
&+ \sum_{\mu_3} F_{\mu_3\mu_2}^*(ks) \langle\langle|\mu_1\rangle\langle\mu_3||I^-\rangle\rangle_\omega, \tag{24}
\end{aligned}$$

where

$$\Delta E_{\mu_2\mu_1}^{(1)} = (E_{\mu_2}^Z - E_{\mu_1}^Z) + (E_{\mu_2}^R - E_{\mu_1}^R) + (h_{\mu_2\mu_2} - h_{\mu_1\mu_1}). \quad (25)$$

It has to be noticed that only terms presenting poles in the neighborhood of the Larmor frequency  $\omega_0$  need to be kept in the last three equations. On the other hand, in order to decouple the chain of equations, we will make the following approximation for the higher order two-phonon Green's functions appearing in eqs. (23) and (24):

$$\langle\langle |\mu_3\rangle\langle\mu_2| b_{k_s}^+ b_{k'_s}^+ | I^- \rangle\rangle_\omega = \langle\langle |\mu_3\rangle\langle\mu_2| b_{k_s} b_{k'_s} | I^- \rangle\rangle_\omega = 0, \quad (26)$$

$$\langle\langle |\mu_1\rangle\langle\mu_2| b_{k'_s}^+ b_{k_s} | I^- \rangle\rangle_\omega = \langle n(\mathbf{k}s) \rangle_0 \delta_{\mathbf{k}\mathbf{k}'} \delta_{ss'} \langle\langle |\mu_1\rangle\langle\mu_2| I^- \rangle\rangle_\omega. \quad (27)$$

Here  $\langle n(\mathbf{k}s) \rangle_0 = \langle b_{k_s}^+ b_{k_s} \rangle_0 = \bar{n}(\mathbf{k}s)$  is the Bose-Einstein distribution formula.

The approximation in eq. (26) is justified because as explained in section 3 we take into account in our rotation-phonon interaction only one-phonon processes so that terms involving the creation or annihilation of two phonons must be dropped out. On the other hand, the phonon operators appearing in Green's function in eq. (27) denote phonon scattering processes and our approximation consists in considering only the elastic part of this scattering together with the assumption that the operator for the number of phonons in the state  $\mathbf{k}s$ ,  $\bar{n}_{\mathbf{k}s}$  is uncorrelated with the operator  $I^-$ . These approximations effectively decouple the chain of equations for the "component" Green's function obtaining

$$\langle\langle |\mu'\rangle\langle\mu| I^- \rangle\rangle_\omega = \langle [|\mu'\rangle\langle\mu|, I^-] \rangle_0 / \{ \hbar\omega - \Delta E_{\mu\mu'}^{(1)} - M_{\mu\mu'}(\omega) \}. \quad (28)$$

We introduce in eq. (28) the function  $M_{\mu\mu'}(\omega)$  which by analogy with the quantum theory of fields can be called the mass operator. This function,  $M_{\mu\mu'}(\omega)$ , accounts for the effects of the phonon interaction over the Zeeman-rotational levels, and for calculational purposes it is generally assumed to be a "small quantity" [12].

The explicit form of the mass operator is

$$\begin{aligned} M_{\mu\mu'}(\omega) = & \sum_{\mu_1 \mathbf{k}s} \left\{ \frac{|F_{\mu'\mu_1}(\mathbf{k}s)|^2 (\bar{n}(\mathbf{k}s) + 1)}{\Delta_{\mu\mu_1}^+} + \frac{|F_{\mu_1\mu}(\mathbf{k}s)|^2 \bar{n}(\mathbf{k}s)}{\Delta_{\mu_1\mu'}^+} \right\} \\ & - \sum_{\mathbf{k}s} \left\{ \frac{2 \operatorname{Re}(F_{\mu\mu}^*(\mathbf{k}s) F_{\mu'\mu'}(\mathbf{k}s)) \bar{n}(\mathbf{k}s) + F_{\mu\mu}^*(\mathbf{k}s) F_{\mu'\mu'}(\mathbf{k}s)}{\Delta_{\mu\mu'}^+} \right\} \\ & + \sum_{\mu_1 \mathbf{k}s} \left\{ \frac{|F_{\mu\mu_1}(\mathbf{k}s)|^2 (\bar{n}(\mathbf{k}s) + 1)}{\Delta_{\mu_1\mu'}^-} + \frac{|F_{\mu_1\mu'}(\mathbf{k}s)|^2 \bar{n}(\mathbf{k}s)}{\Delta_{\mu\mu_1}^-} \right\} \\ & - \sum_{\mathbf{k}s} \left\{ \frac{2 \operatorname{Re}(F_{\mu\mu}^*(\mathbf{k}s) F_{\mu'\mu'}(\mathbf{k}s)) \bar{n}(\mathbf{k}s) + F_{\mu'\mu'}(\mathbf{k}s) F_{\mu\mu}^*(\mathbf{k}s)}{\Delta_{\mu\mu'}^-} \right\} \end{aligned} \quad (29)$$

with  $\Delta_{\mu_2\mu_1}^\pm = \hbar\omega - \Delta E_{\mu_2\mu_1}^{(1)} \pm \varepsilon_{\mathbf{k}s}$ .

By definition, the mass operator is a complex function of the real variable  $\omega$  and it can be decomposed into its real and imaginary parts using the symbolic identity:

$$\frac{1}{\omega - \omega' \pm i\varepsilon} = \text{P} \frac{1}{\omega - \omega'} \mp i\pi\delta(\omega - \omega'), \quad (30)$$

to rewrite

$$M_{\mu\mu'}(\omega \pm i\varepsilon) = A_{\mu'\mu}(\omega) \mp i\pi B_{\mu'\mu}(\omega) \quad (\varepsilon \rightarrow 0^+). \quad (31)$$

In this last equation

$$\begin{aligned} A_{\mu'\mu}(\omega) = & \text{P} \sum_{\mu_1 ks} \left\{ \frac{|F_{\mu'\mu_1}(ks)|^2(\bar{n}(ks) + 1)}{\Delta_{\mu\mu_1}^+} + \frac{|F_{\mu_1\mu}(ks)|^2\bar{n}(ks)}{\Delta_{\mu_1\mu'}^+} \right\} \\ & + \text{P} \sum_{\mu_1 ks} \left\{ \frac{|F_{\mu\mu_1}(ks)|^2(\bar{n}(ks) + 1)}{\Delta_{\mu_1\mu'}^-} + \frac{|F_{\mu_1\mu'}(ks)|^2\bar{n}(ks)}{\Delta_{\mu\mu_1}^-} \right\} \\ & - \text{P} \sum_{ks} \text{Re}(F_{\mu\mu}^*(ks)F_{\mu'\mu'}(ks)) \left\{ \frac{1}{\Delta_{\mu\mu'}^+} + \frac{1}{\Delta_{\mu\mu'}^-} \right\} (2\bar{n}(ks) + 1) \\ & + \pi \sum_{ks} \text{Im}(F_{\mu\mu}^*(ks)F_{\mu'\mu'}(ks)) \{ \delta(\Delta_{\mu\mu'}^+) + \delta(\Delta_{\mu\mu'}^-) \} \end{aligned} \quad (32)$$

and

$$\begin{aligned} B_{\mu'\mu}(\omega) = & \sum_{\mu_1 ks} \{ |F_{\mu'\mu_1}(ks)|^2(\bar{n}(ks) + 1)\delta(\Delta_{\mu\mu_1}^+) + |F_{\mu_1\mu}(ks)|^2\bar{n}(ks)\delta(\Delta_{\mu_1\mu'}^+) \} \\ & + \sum_{\mu_1 ks} \{ |F_{\mu\mu_1}(ks)|^2(\bar{n}(ks) + 1)\delta(\Delta_{\mu_1\mu'}^-) + |F_{\mu_1\mu'}(ks)|^2\bar{n}(ks)\delta(\Delta_{\mu\mu_1}^-) \} \\ & - \sum_{ks} \text{Re}(F_{\mu\mu}^*(ks)F_{\mu'\mu'}(ks)) \{ \delta(\Delta_{\mu\mu'}^+) + \delta(\Delta_{\mu\mu'}^-) \} (2\bar{n}(ks) + 1) \\ & + \frac{1}{\pi} \text{P} \sum_{ks} \text{Im}(F_{\mu\mu}^*(ks)F_{\mu'\mu'}(ks)) \left\{ \frac{1}{\Delta_{\mu\mu'}^+} + \frac{1}{\Delta_{\mu\mu'}^-} \right\}. \end{aligned} \quad (33)$$

(P indicates that the principal value of the corresponding integral must be taken.)

These newly defined functions  $A_{\mu'\mu}(\omega)$  and  $B_{\mu'\mu}(\omega)$  are real functions of the variable  $\omega$  whereas  $A_{\mu'\mu}(\omega)$  determines phonon-induced corrections for the energies at which the magnetic resonance transitions occurs, the imaginary part of the mass operator  $B_{\mu'\mu}(\omega)$  includes dissipative effects due to the redistribution of energy among the phonon degrees of freedom in the system. That is there is some dissipation of the energy absorbed at resonance.

An expression for the lineshape can now be obtained if we substitute relations (28)–(33) in expression (21) and make use of the expansion [11]

$$\begin{aligned} \langle [|\mu'\rangle\langle\mu|, I^-]_0 \rangle &= \sum_{\mu_1} \{ \langle \mu | I^- | \mu_1 \rangle \langle \mu' | \mu_1 \rangle_0 - \langle \mu_1 | I^- | \mu' \rangle \langle \mu_1 | \mu \rangle_0 \} \\ &= \langle \mu | I^- | \mu' \rangle \{ \langle \mu' | \mu' \rangle_0 - \langle \mu | \mu \rangle_0 \}. \end{aligned} \quad (34)$$

In the last equation we have made use of the fact that [11]

$$\langle |\mu_1\rangle\langle\mu_2| \rangle_0 = \delta_{\mu_1\mu_2} \exp(-\beta E_{\mu_1}^{(1)}) / \sum_{\mu} \exp(-\beta E_{\mu}^{(1)}), \quad (35)$$

where  $E_{\mu}^{(1)} = E_{\mu}^Z + E_{\mu}^R + h_{\mu\mu}$  is the Zeeman-rotation energy corrected up to first order in the spin–spin dipolar interaction.



In this way we finally obtain for the lineshape the expression:

$$\begin{aligned} \text{Im}\langle\langle I^+ | I^- \rangle\rangle_\omega = & - \sum_{\substack{\mu\mu' \\ \Gamma_I}} |\langle\mu'|I^+|\mu\rangle|^2 \{ \langle|\mu'\rangle\langle\mu'|\rangle_0 - \langle|\mu\rangle\langle\mu|\rangle_0 \} \\ & \times [\pi B_{\mu'\mu}(\omega)] / [\{\hbar\omega - \Delta E_{\mu\mu'}^{(1)} - A_{\mu'\mu}(\omega)\}^2 + \pi^2 B_{\mu'\mu}^2(\omega)]. \end{aligned} \quad (36)$$

In this equation the sum has to be carried out for states  $\mu, \mu'$  of the same nuclear symmetry. This condition is indicated through the index of the relevant irreducible representation  $\Gamma_I$ . It is clear that the final spectrum is a superposition of Lorentzian functions corresponding to different spin-species weighted according to their transition probabilities. Its temperature dependence comes from the thermal distribution function for the Zeeman-rotation levels (35) and from the phonon distribution formulas appearing in the expressions for  $A_{\mu'\mu}(\omega)$  and  $B_{\mu'\mu}(\omega)$ .

Each of the component Lorentzians corresponds to a resonant transition in the Zeeman-rotation system. Their occurrence in the frequency domain depends on the energy difference for the corresponding levels and on the real part of the mass operator. The width of the Lorentzian depends on the imaginary part of the mass operator. On the other hand, the contribution of each of these Lorentzians to the total lineshape will be mainly determined – if the transition is allowed – by the thermal distribution of the involved Zeeman-rotation levels.

## 5. Discussion

The physical content of eqs. (32), (33) and (36) will be much more accessible after we introduce into the theory simplifications concerning the strength of the phonon-rotation interaction and the particular phonon branch involved.

The first simplification is to consider that the damping may be assumed to be very small, then the component Lorentzians in eq. (36), corresponding to the transition  $\mu \rightarrow \mu'$ , have a steep maximum at some value  $\omega = \tilde{\omega}_{\mu'\mu}$ . Expanding  $A_{\mu'\mu}(\omega)$  in power series in  $\omega$  near  $\tilde{\omega}_{\mu'\mu}$  and taking into account that  $B_{\mu'\mu}(\omega)$  is a slowly varying function of  $\omega$ , we can write for the Lorentzians

$$\begin{aligned} & [\pi B_{\mu'\mu}(\omega)] / [\{\hbar\omega - \Delta E_{\mu\mu'}^{(1)} - A_{\mu'\mu}(\omega)\}^2 + \pi^2 B_{\mu'\mu}^2(\omega)] \\ & = \pi \left[ 1 - \frac{1}{\hbar} \left( \frac{dA_{\mu'\mu}(\omega)}{d\omega} \right)_{\omega=\tilde{\omega}_{\mu'\mu}} \right]^{-1} \tilde{B}_{\mu'\mu} [\{\hbar\omega - \hbar\tilde{\omega}_{\mu'\mu}\}^2 + \pi^2 \tilde{B}_{\mu'\mu}^2]^{-1} \end{aligned} \quad (37)$$

where

$$\tilde{B}_{\mu'\mu} = B_{\mu'\mu}(\tilde{\omega}_{\mu'\mu}) \left[ 1 - \frac{1}{\hbar} \left( \frac{dA_{\mu'\mu}}{d\omega} \right)_{\omega=\tilde{\omega}_{\mu'\mu}} \right]^{-1}. \quad (38)$$

In the above derivation it has been assumed that

$$\frac{1}{\hbar} \left( \frac{dA_{\mu'\mu}}{d\omega} \right)_{\omega=\tilde{\omega}_{\mu'\mu}} \ll 1. \quad (39)$$

On the other hand,  $\tilde{\omega}_{\mu'\mu}$  is determined from the transcendental equation

$$\hbar\tilde{\omega}_{\mu'\mu} - \Delta E_{\mu\mu'}^{(1)} - A_{\mu'\mu}(\tilde{\omega}_{\mu'\mu}) = 0. \quad (40)$$

This last equation determines the occurrence, in the frequency domain, of the Lorentzian line corresponding to the transition  $\mu \rightarrow \mu'$ . It is clear that the temperature dependence of the line position is determined by the real part of the mass operator, whereas the damping or dissipative effects are included in the terms  $\tilde{B}_{\mu'\mu}$ .

In order to calculate these two functions we make a second simplification by assuming that the phonons involved correspond to the acoustic branch. This allows us to approximate the sums over  $\mathbf{k}$ s in (32) and (33) with integrals, taking the Debye expression as density of phonon states:

$$\rho(\omega) = \frac{9N\hbar}{k_B T_D} \left[ \frac{\hbar\omega(\mathbf{k})}{k_B T_D} \right]^2 \quad (41)$$

here  $T_D$  is the Debye temperature of the solid.

With the latter consideration and defining

$$f_{\mu\mu'} = \sum_{\alpha} \frac{\langle \mu | V_{\alpha}(\Omega) | \mu' \rangle \hbar}{(2M)^{1/2}} (\mathbf{C}_{\alpha}^M \cdot \mathbf{e}_s), \quad (42)$$

so that

$$F_{\mu\mu'}(\mathbf{k}s) \equiv f_{\mu\mu'} \frac{e^{i\mathbf{k} \cdot \mathbf{r}_{0M}}}{(\hbar\omega(\mathbf{k}))^{1/2}}.$$

The consideration of the rotational symmetry properties in the evaluation of the matrix elements for the operators  $V_{\alpha}(\Omega)$ , occurring in  $f_{\mu\mu'}$ , allows the simplification of equations (32) and (33). Recalling that the spin-independent operators  $V_{\alpha}(\Omega)$  are invariant with respect to the operations of the molecular symmetry group it can be concluded that the states they connect must belong to the same  $I, m_I$  manifold. The complete evaluation of the matrix element  $\langle \mu | V_{\alpha}(\Omega) | \mu' \rangle$  can be easily carried out by the application of the Wigner-Eckart theorem [13]. In any case, we can write

$$A_{\mu'\mu}(\omega) = \frac{9N\hbar}{(k_B T_D)^2} \left\{ \sum_{\substack{\mu_1 \\ \Gamma_I}} |f_{\mu'\mu_1}|^2 \Gamma_{+}^{\mu\mu_1} + \sum_{\substack{\mu_1 \\ \Gamma_I}} |f_{\mu\mu_1}|^2 \Gamma^{\mu_1\mu'} - |f_{\mu\mu}^*| |f_{\mu'\mu'}| J_{\mu\mu'} \right\}, \quad (43)$$

$$B_{\mu'\mu}(\omega) = \frac{9N\hbar}{(k_B T_D)^2} \left\{ \sum_{\substack{\mu_1 \neq \mu' \\ \Gamma_I}} |f_{\mu'\mu_1}|^2 \frac{\alpha_{\mu\mu_1}}{\exp(\beta' \alpha_{\mu\mu_1}) - 1} + \sum_{\substack{\mu_1 \neq \mu \\ \Gamma_I}} |f_{\mu\mu_1}|^2 \frac{\alpha_{\mu_1\mu'}}{1 - \exp(-\beta' \alpha_{\mu_1\mu'})} \right\}. \quad (44)$$

In these equations we have defined

$$\Gamma_{\pm}^{\mu_1\mu_2} = \text{P} \int_{-1}^{+1} dx \frac{x}{(1 - e^{-\beta'x})(\alpha_{\mu_1\mu_2} \pm x)},$$

$$J_{\mu\mu'} = \text{P} \int_{-1}^1 dx \frac{\alpha_{\mu\mu'} x}{(\alpha_{\mu\mu'}^2 - x^2)} \text{cth} \left( \frac{\beta' x}{2} \right) \quad (45)$$

and

$$\alpha_{\mu\mu'} = \frac{\hbar\omega - \Delta E_{\mu\mu'}^{(1)}}{k_B T_D}; \quad \beta' = \frac{T_D}{T}. \quad (46)$$

It should be noted that in the above derivation use has been made of the fact that  $|\alpha_{\mu\mu'}| \ll 1$  for those states connected by  $I^+$ .

We are thus led to a self-consistent set of nonlinear equations for the functions  $A_{\mu'\mu}(\tilde{\omega}_{\mu'\mu})$ ,  $\tilde{B}_{\mu'\mu}$  and  $\text{Im}\langle\langle I^+ | I^- \rangle\rangle_\omega$  very characteristic for approximations of the kind of interpolation decoupling methods for the chains of equations for Green's functions.

At the lowest temperatures the coupling of the spin system to the phonon bath becomes negligible. In this limit we can replace expression (37), for very small values of the damping  $\tilde{B}_{\mu'\mu}$ , by a  $\delta$ -function

$$\left[ 1 - \frac{1}{\hbar} \left( \frac{dA_{\mu'\mu}(\omega)}{d\omega} \right)_{\omega=\tilde{\omega}_{\mu'\mu}} \right]^{-1} \delta(\hbar\omega - \hbar\tilde{\omega}_{\mu'\mu}). \quad (47)$$

In this case, sometimes referred to as the not-interrupted coherent tunneling limit [4], the dipolar spectrum is simply a superposition of  $\delta$ -functions at the tunneling frequency  $\tilde{\omega}_{\mu'\mu}$ . As the temperature is raised, the coherent tunneling of the hindered rotator is interrupted by the interaction with the lattice phonons and each  $\delta$ -line broadens attaining the Lorentzian form given by eq. (37). It is noteworthy that the broadening of each of the Lorentzian components continues, beyond the latter transition, when the temperature is raised. This is easily seen from relation (44), for the damping  $B_{\mu'\mu}(\omega)$ , since this function increases with temperature. A final remark can be made concerning the experimentally observed narrowing of the dipolar spectrum as the temperature is raised. Our expression (36) together with (37) is not suitable for the unambiguous calculation of the absorption lineshape second moment, since in such a case we have a superposition of Lorentzian lines. However, since the width of the individual lines, given by  $\pi\tilde{B}_{\mu'\mu}$ , will have a negligible effect on the total linewidth, the second moment of the spectrum will be mainly determined by the frequency separation between the component lines together with their relative intensities. That is, the temperature variation of  $\tilde{\omega}_{\mu'\mu}$  and of the weighting factors in (36) will be determinant for the temperature behaviour of the second moment. With these considerations in mind, we can use the  $\delta$ -line limit (47) together with relation (36) in order to evaluate the second moment, and after dropping small terms

$$\begin{aligned} (\overline{\Delta\omega})^2 = & \left( \sum_{\substack{\mu\mu' \\ \Gamma_I}} |\langle \mu' | I^+ | \mu \rangle|^2 \{ \langle \mu' | \mu' \rangle_0 - \langle \mu | \mu \rangle_0 \} \tilde{\omega}_{\mu'\mu}^2 \right) \left( \sum_{\substack{\mu\mu' \\ \Gamma_I}} |\langle \mu' | I^+ | \mu \rangle|^2 \{ \langle \mu' | \mu' \rangle_0 - \langle \mu | \mu \rangle_0 \} \right)^{-1} \\ & - \left[ \left( \sum_{\substack{\mu\mu' \\ \Gamma_I}} |\langle \mu' | I^+ | \mu \rangle|^2 \{ \langle \mu' | \mu' \rangle_0 - \langle \mu | \mu \rangle_0 \} \tilde{\omega}_{\mu'\mu} \right) \left( \sum_{\substack{\mu\mu' \\ \Gamma_I}} |\langle \mu' | I^+ | \mu \rangle|^2 \{ \langle \mu' | \mu' \rangle_0 - \langle \mu | \mu \rangle_0 \} \right)^{-1} \right]^2. \end{aligned} \quad (48)$$

The first term in the right-hand side of (48) constitutes the most important contribution and determines the temperature dependence of the second moment. This is because the second term gives the square of the average frequency for the dipolar lineshape which can be safely assumed to be  $\omega_0^2$ .

A similar expression, for a hindered two-spin rotor, was calculated in a previous paper [11]. In that case, we indeed demonstrated that this expression accounts for a line-narrowing as the temperature is

raised. Nevertheless, it must be noted that the theoretical decrease of the second moment took place in a wide temperature interval in contrast to the observed abrupt narrowing of the dipolar spectrum.

In forthcoming papers, the present formalism, will be applied to the calculation of the low-temperature dipolar lineshape for hindered rotating atomic groups of the type  $\text{NH}_4\text{X}$  and  $\text{CH}_3\text{X}$  in solids.

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