

# ELEMENTARY DERIVATION OF THE $n$ th MOMENT OF MAGNETIC RESONANCE ABSORPTION LINES FROM SUM RULES FOR TWO TIME RETARDED GREEN'S FUNCTIONS †

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This paper presents an elementary derivation for the  $n$ th moment of magnetic resonance linear response lineshape using sum rules for two time retarded Green's functions. The results can be particularized to the high-temperature regime where van Vleck's well-known relations are obtained.

## 1. Introduction

The purpose of this paper is to present a general derivation of the moments of magnetic resonance absorption lines in systems where the assumptions of linear response theory (LRT) apply. That is, our discussion shall be limited to cases where, as in most experiments, saturation effects can be neglected. It is our purpose to demonstrate that the moments can readily be calculated theoretically, using the sum rules of two time retarded Green's functions [1].

In section 2 we introduce the formalism of (LRT) applied to the calculation of magnetic resonance absorption lines. In this context, we introduce the two time retarded Green's functions and their relation to the lineshape and expressions for the moments of the lines are derived. The main advantage of the present formalism is that it allows to obtain in a straightforward manner general expressions for moments of arbitrary order which hold at all temperatures. In section 3 the general  $n$ th moment relations are particularized in the high temperature limit together with the "rigid lattice" assumption, so as to obtain the well-known van Vleck's formulas [2] of common use in magnetic resonance.

## 2. The linear response formalism

We shall summarize briefly some of the results of the linear response theory which are appropriate to our discussion. Let  $H$  be the total system Hamiltonian defined as

$$H = H_Z + H_S + H_B, \quad (1)$$

where  $H_Z, H_S, H_B$  are respectively the Zeeman, spin interaction and lattice Hamiltonians. We shall consider the response of this system to the adiabatic turning on of a periodic perturbation:

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$$H_t^1 = -M \cdot H(t) = \text{Re} [H^1 \exp(et - i\omega t)], \quad e \rightarrow 0^+, \quad H^1 = -M \cdot H, \quad (2)$$

where  $H(t)$  is the external magnetic rf field with  $H$  as its time independent part.  $M$  represents the operator of the total magnetic moment of the system. As discussed elsewhere [1] the energy absorption in the system, under the influence of the perturbation  $H_t^1$  and averaged over a period, is determined by the two time retarded Green's function of the perturbation:

$$dE/dt = -\frac{1}{2}\omega \text{Im} \langle\langle H^1 * |H^1 \rangle\rangle_\omega. \quad (3)$$

Here  $\langle\langle A | B \rangle\rangle_\omega$  is the Fourier transform of the two time Green's function defined as:

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

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

In many of the experiments where the moment formalism is applied the main contribution of the magnetic resonance absorption line lay in a frequency interval around the Larmor frequency  $\omega_0$ , and other contributions at frequencies far from  $\omega_0$  are negligible. For this reason the measurements are carried out in this limited range of frequencies. This fact must be accounted for in expression (3) where the Hamiltonian  $H$  must be conveniently truncated [2,3] in such a way that the poles of  $\text{Im} \langle\langle H^1 * |H^1 \rangle\rangle_\omega$  lay only in the frequency interval of interest. Because in most cases this frequency interval is very small compared to  $\omega_0$ , it is a very good approximation to write for the lineshape

$$I(\omega) = -\frac{1}{2}\omega_0 \text{Im} \langle\langle H^1 * |H^1 \rangle\rangle_\omega. \quad (5)$$

This expression provides a very convenient way for the calculation of the linear response lineshape of magnetic resonance spectra.

One important fact that follows from eq. (5) is that all the relevant information about the lineshape is contained in the Green's function  $\langle\langle H^1 * |H^1 \rangle\rangle_\omega$ . In this sense we can make use of the well-known sum rules for the retarded two time Green's functions [1] to derive general relations for the moments of magnetic resonance absorption line. In our case the sum rules of interest are:

$$\begin{aligned} \int_{-\infty}^{\infty} \langle\langle H^1 * |H^1 \rangle\rangle_\omega d\omega &= (\pi/i\hbar)\langle[H^1*(0), H^1(0)]\rangle_0 \\ &\times \int_{-\infty}^{\infty} \left[ \langle\langle H^1 * |H^1 \rangle\rangle_\omega - \frac{1}{\hbar\omega} \left( \langle[H^1*, H^1]\rangle_0 + \sum_{k=1}^n \langle[H^1*, d^k H^1/dt^k]\rangle_0 \frac{1}{(i\omega)^k} \right) \right] \omega^{n+1} d\omega \\ &= -(\pi/\hbar i^n)\langle[H^1*, d^{n+1}H^1/dt^{n+1}]\rangle_0. \end{aligned} \quad (6)$$

From the expression of  $I(\omega)$  in eq. (5) one can write these sum rules as:

$$\begin{aligned} A &= \int_{-\infty}^{\infty} I(\omega) d\omega = \frac{1}{2}\pi(\omega_0/\hbar)\langle[H^1*, H^1]\rangle_0, \\ \langle\omega^n\rangle &= \int_{-\infty}^{\infty} \omega^n I(\omega) d\omega = -\frac{1}{2}\pi(\omega_0/\hbar^{n+1})\langle[[H, H^1*], [H, \dots, [H, H^1] \dots]]\rangle_0. \end{aligned} \quad (7)$$

Substitution of eq. (7) in the definition for the  $n$ th moment of an absorption line [3], given by:

$$\langle\Delta\omega^n\rangle = \left( \int_{-\infty}^{\infty} (\omega - \langle\omega\rangle)^n I(\omega) d\omega \right) \left( \int_{-\infty}^{\infty} I(\omega) d\omega \right)^{-1} \quad (8)$$

leads to the desired results.

It is noteworthy to point out that the relations (7) are very general expressions for the moments and they are not limited to any particular temperature regime.

### 3. High-temperature limit

It can be said without any doubt that van Vleck's celebrated relations for the second and fourth moment of an absorption line, constitute two of the most used formulas in the interpretation of magnetic resonance spectra. Although the above derived expressions are more general than van Vleck's, we can obtain them by taking the appropriate high-temperature limit in eqs. (7).

This means that we work under the assumption that the involved temperatures are always high enough to allow a linear expansion of the equilibrium density matrix, which we obtain from (7):

$$A = -\frac{1}{2}\pi(\omega_0/\hbar)(\beta/\text{tr}\{I\}) \text{tr}\{[H^{1*}, H^1]H\},$$

$$\langle\omega^n\rangle = \frac{1}{2}\pi(\omega_0/\hbar^{n+1})(\beta/\text{tr}\{I\}) \text{tr}\{[[H, H^{1*}], [H, \dots, [H, H^1] \dots]]H\}, \quad (9)$$

where  $\beta = 1/k_B T$  and  $I$  is the identity operator.

To proceed further in the simplification of the traces in (9) we must assume that the temperature is low enough so that the lattice remains essentially in its ground state. This assumption is usually called rigid lattice condition and it allows to treat the system Hamiltonian,  $H$ , as an effective spin Hamiltonian where the lattice operators are evaluated in the ground state, leaving only a spin dependent part. With this assumption we can evaluate the traces in a representation where the effective spin Hamiltonian is diagonal and recalling the remark made at the beginning, so as to consider only spin transitions between states that fulfill the condition  $(E_n - E_{n'}) \approx \hbar\omega_0$ , it is straightforward to obtain:

$$A = \frac{1}{2}\pi(\omega_0^2\beta/\text{tr}\{I\}) \text{tr}\{H^{1*}H^1\}, \quad \langle\omega^n\rangle = \frac{1}{2}\pi(\omega_0^2\beta/\text{tr}\{I\})(1/\hbar^n)\text{tr}\{[H, H^{1*}][\overset{n-2}{[H, \dots, [H, H^1] \dots]}], H\}. \quad (10)$$

From these relations we can readily obtain van Vleck's formula for the first two even moments:

$$M_2 = \langle\omega^2\rangle/A = \hbar^{-2}\text{tr}\{[H, H^{1*}][H^1, H]\}/\text{tr}\{H^{1*}H^1\}, \quad (11)$$

$$M_4 = \langle\omega^4\rangle/A = \hbar^{-4}\text{tr}\{[H, H^{1*}][[H, [H, H^1]], H]\}/\text{tr}\{H^{1*}H^1\}. \quad (11)$$

### 4. Conclusion

The derivations given above represent a simple example of the application of the powerful double time Green's function formalism in the calculation of quantities of interest in magnetic resonance. The important point is that all the relevant information to the linear response lineshape in a magnetic resonance experiment is included in a Green's function of the type  $\langle\langle I^+ | I^- \rangle\rangle_\omega$ . This allows the determination in a straightforward manner of expressions for the  $n$ th moment of an absorption line by means of sum rules for the Green's functions. The general expressions so obtained can be readily reduced to the van Vleck's relations in the high-temperature rigid lattice regime. It is interesting to note that in spite of the fact that the Green's function formalism has proven to be an outstanding tool in other fields of theoretical physics, it is very seldom used in magnetic resonance theory.

### References

- [1] D.N. Zubarev, Nonequilibrium statistical thermodynamics (Consultants Bureau, New York, 1976).
- [2] J.H. van Vleck, Phys. Rev. 74 (1948) 1168.
- [3] A. Abragam, The principle of nuclear magnetism (Oxford Univ. Press, London, 1961).