

## Easily evaluated expressions for second and fourth moments of resonant absorption spectra for spin systems

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We present an efficient method to generate the second and fourth self-energy and Van Vleck moments for NMR and EPR absorption spectra for systems with bilinear spin Hamiltonians. The results are helpful in obtaining analytic expressions for these moments and are in a form appropriate for evaluation on computers. We include a few examples to illustrate the method, including the nontrivial calculation of the moments of the correlation functions for the electric quadrupole-quadrupole interaction encountered in the study of solid hydrogen compounds. In the present work we restrict our attention to high temperatures.

### I. INTRODUCTION

The calculation of moments of resonant absorption spectra is a tedious task which must be confronted to compare the results of experiment and theory in many applications of spectroscopy. Since its inception, the method of moments has been the principal theoretical tool available for characterizing NMR rigid-lattice absorption spectra. While the moments by themselves can often be misleading, their careful use has been of great value in fields such as NMR and other kinds of magnetic spectroscopy. Also, it has recently been shown that information theory (the method of maximum entropy) is a good technique for obtaining fits to spectra from a limited number of moments. In the report we obtain easily evaluated expressions for the second and fourth moments of Green functions needed in NMR and EPR work. These expressions are valid for systems described by the large class of bilinear spin Hamiltonians.

$$H = \sum_{\substack{\beta, \gamma, i, j \\ i \neq j}} \xi_{\beta\gamma}(ij) A_{\beta}(i) A_{\gamma}(j) . \quad (1)$$

In this and all future equations, greek indices denote irreducible tensor operators<sup>1</sup> [ $A_{\alpha}$  for  $\alpha = (L, M)$ ] and Latin symbols index sites on a lattice. The conventional method for evaluating moments for Green functions is to either evaluate the necessary nested commutators (which can be excruciating for the fourth moment), or to employ diagrammatic representations of the moments using vertices which represent the matrix elements of the Liouville operator in the space dual to the Hilbert space of accessible spin states for a system. Our method is based upon a generalization of the diagrammatic work of Reiter.<sup>2</sup>

Some examples of physical relevance are multipolar spin-spin interactions. We have used the present technique to obtain the full second and fourth moments of the electric quadrupole-quadrupole (EQQ) correlation functions of interest in the study of mixtures of  $J=0$  and  $J=1$  molecules in the solid phases of the hydrogens. In the present paper, we present the general formulas, and give some examples of their use.

### II. METHOD

We consider a general bilinear spin Hamiltonian [Eq. (1)]. For purposes of obtaining information about the resonance properties of such a coupled spin system, it is useful to obtain good approximations to the two-point Green's functions of the type

$$G_{ij}^{\alpha}(t) = \Theta(t) \langle A_{\alpha}(i;t) A_{\alpha}^{\dagger}(j;0) \rangle , \quad (2)$$

where  $\Theta(t)$  is the Heaviside step function, and  $\langle \rangle$  denotes an infinite temperature average on the canonical ensemble. The tensor operators of Eq. (2) are in the Heisenberg representation. We are motivated to study these functions because if

$$G_{ij}^{\alpha}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} G_{ij}^{\alpha}(t) , \quad (3)$$

then the experimentally accessible line shapes are of the form

$$G^{\alpha}(\omega) = \sum_{i,j} G_{ij}^{\alpha}(\omega) . \quad (4)$$

Also, quantities such as the spin-lattice relaxation time  $T_1$  and the transverse relaxation time  $T_2$  in NMR are readily extracted from the  $G^{\alpha}$ .<sup>3</sup> From previous work,<sup>1,4</sup> it is evidently worthwhile to introduce a self-energy function  $\Sigma^{\alpha}$  which is related to the Green's function by the relation

$$G_i^{\alpha}(\omega) = i / [\omega - \Sigma_i^{\alpha}(\omega)] , \quad (5)$$

where  $G$  and  $\Sigma$  are in general, both complex-valued functions of  $\omega$ , and the functions with a single-site index are just the two-site functions summed on one-site index. The reader may be more familiar with the self-energy method in the equivalent, but different looking formalism of "memory functions."<sup>5</sup> It has been shown elsewhere<sup>1</sup> that  $G$  and  $\Sigma$  may be completely characterized by their spectral functions.

$$\Gamma_{ij}^{\alpha}(\omega) = -\text{Im} \Sigma_{ij}^{\alpha}(\omega) , \quad (6)$$

$$A_{ij}^{\alpha}(\omega) = \text{Re} G_{ij}^{\alpha}(\omega) .$$

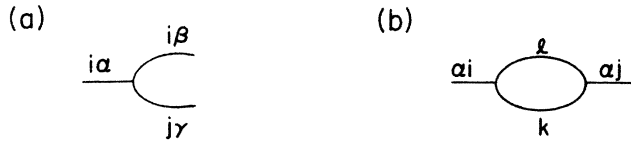


FIG. 1. (a) Basic vertex from which  $M_n$  and  $L_n$  are constructed. (b) Graph from which second moment is obtained.

The moments of these functions are given by

$$\begin{aligned} L_n^a(ij) &= \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^{n-2} \Gamma_{ij}^a(\omega), \quad n \geq 2, \\ M_n^a(ij) &= \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^n A_{ij}^a(\omega), \quad n \geq 0. \end{aligned} \quad (7)$$

General considerations from analytic function theory imply that knowledge of  $\Gamma(A)$  completely specifies  $\Sigma(G)$ . Reiter and others have shown<sup>1,2</sup> that the moments  $M_n$  and  $L_n$  are expressible as a sum of graphs constructed from vertices of the type illustrated in Fig. 1(a). It has been shown that the second moment can be represented as the sum of all topologically distinct<sup>2</sup> graphs of the type indicated in Fig. 1(b), where the internal-site indices must be summed over. Note that we did not explicitly attach operator indices to the internal lines: In applying Reiter's method, it is necessary to write down and evaluate each graph form [Fig. 1(b)] producing each graph with distinct operator labels separately.

While explicitly writing out all internal operator lines is practical for some simple Hamiltonians, this becomes quite laborious for complicated interactions, even for the second moment, if the structure of the graphs is not strongly constrained. To illustrate this point, consider the EQQ Hamiltonian. In this case, 30 distinct graphs must be considered for the second moment for each Green's



FIG. 2. (a) Corresponds to first term of Eq. (8); (b) corresponds to second term of Eq. (8).

function. There are very many more graphs for the fourth moment. A simple way to alleviate this proliferation of diagrams is to take a different point of view. It is possible to construct the moments by writing out all possible internal-site lines explicitly, and summing only on operator indices for the internal lines. The second moment can then be expressed as

$$\begin{aligned} M_2^a(ij) = L_2^a(ij) &= \delta_{ij} \sum_{k,\beta,\gamma} \Omega_{a\beta\gamma}(ik) \Omega_{a\beta\gamma}^*(ik) \\ &+ \sum_{\beta,\gamma} \Omega_{a\gamma\beta}(ij) \Omega_{a\beta\gamma}^*(ij). \end{aligned} \quad (8)$$

In this and future equations, an asterisk denotes complex conjugate. The first term of Eq. (8) corresponds to Fig. 2(a), the second to Fig. 2(b). While this approach is completely equivalent to Reiter's method, it enables us to obtain such general representations for moments as in Eq. (8). For the fourth moment we use the same method, but the number of graphs involved is too great to reproduce here. We will just observe that the self-energy moment  $L_4^a(i,j)$  is made up of graphs of the variety depicted in Fig. 3. We show examples of the bubble diagrams [Fig. 3(a)] and vertex corrections [Fig. 3(b)]. There are 8 distinct bubbles and 16 vertex corrections for the fourth moment. Adding up all of these contributions, we obtain the following formidable looking expression for the fourth self-energy moment

$$\begin{aligned} L_4^a(ij) &= [(\alpha\beta\gamma ij)(\beta\delta\epsilon ik)(\zeta\delta\epsilon ik)^*(\alpha\zeta\gamma ij)^* + (\alpha\gamma\beta ij)(\beta\delta\epsilon jk)(\zeta\delta\epsilon jk)^*(\alpha\gamma\zeta ij)^* \\ &+ (\alpha\gamma\beta ij)(\beta\epsilon\delta jk)(\zeta\delta\epsilon jk)^*(\alpha\gamma\zeta ik)^* + (\alpha\beta\gamma ij)(\gamma\delta\zeta jk)(\epsilon\beta\delta ij)^*(\alpha\epsilon\zeta ik)^* \\ &+ (\alpha\gamma\beta ij)(\gamma\delta\zeta ik)(\epsilon\delta\beta ij)^*(\alpha\epsilon\zeta ik)^* + (\alpha\gamma\beta ij)(\gamma\zeta\delta ik)(\epsilon\beta\delta jk)^*(\alpha\zeta\epsilon ji)^* \\ &+ (\alpha\beta\gamma ij)(\gamma\zeta\delta jk)(\epsilon\beta\delta ik)^*(\alpha\epsilon\zeta ij)^* + (\alpha\gamma\beta ij)(\gamma\zeta\delta ik)(\epsilon\delta\beta jk)^*(\alpha\zeta\epsilon ki)^*] \delta_{ij} \\ &+ (\alpha\gamma\beta ij)(\beta\delta\epsilon jk)(\zeta\delta\epsilon jk)^*(\alpha\zeta\gamma ij)^* + (\alpha\beta\gamma ij)(\beta\delta\epsilon ik)(\zeta\delta\epsilon ik)^*(\alpha\gamma\zeta ij)^* \\ &+ (\alpha\gamma\beta ik)(\beta\epsilon\delta jk)(\zeta\delta\epsilon jk)^*(\alpha\zeta\gamma ij)^* + (\alpha\beta\gamma ij)(\beta\delta\epsilon ik)(\zeta\epsilon\delta ik)^*(\alpha\gamma\zeta jk)^* \\ &+ (\alpha\beta\gamma ik)(\beta\delta\epsilon ij)(\zeta\epsilon\delta ij)^*(\alpha\zeta\gamma jk)^* + (\alpha\beta\gamma ik)(\gamma\delta\zeta jk)(\epsilon\delta\beta ik)^*(\alpha\zeta\epsilon kj)^* \\ &+ (\alpha\beta\gamma ik)(\gamma\zeta\delta jk)(\epsilon\delta\beta ij)^*(\alpha\epsilon\zeta jk)^* + (\alpha\gamma\beta ik)(\gamma\delta\zeta ij)(\epsilon\beta\delta ik)^*(\alpha\zeta\epsilon kj)^* \\ &+ (\alpha\beta\gamma ik)(\gamma\delta\zeta kj)(\epsilon\beta\delta ik)^*(\alpha\zeta\epsilon ij)^* + (\alpha\beta\gamma ij)(\gamma\zeta\delta kj)(\epsilon\delta\beta ik)^*(\alpha\zeta\epsilon kj)^* \\ &+ (\alpha\gamma\beta ij)(\gamma\zeta\delta ik)(\epsilon\beta\delta jk)^*(\alpha\epsilon\zeta ij)^* + (\alpha\beta\gamma ij)(\gamma\zeta\delta jk)(\epsilon\beta\delta ik)^*(\alpha\zeta\epsilon ij)^* \\ &+ (\alpha\gamma\beta ik)(\gamma\zeta\delta ij)(\epsilon\delta\beta jk)^*(\alpha\epsilon\zeta ij)^* + (\alpha\gamma\beta ik)(\gamma\delta\zeta ij)(\epsilon\delta\beta ik)^*(\alpha\zeta\epsilon ij)^* \\ &+ (\alpha\beta\gamma ij)(\gamma\delta\zeta jk)(\epsilon\delta\beta ij)^*(\alpha\epsilon\zeta jk)^* + (\alpha\gamma\beta ij)(\gamma\delta\zeta ik)(\epsilon\beta\delta ij)^*(\alpha\epsilon\zeta jk)^*, \end{aligned} \quad (9)$$

where for brevity  $(\alpha\beta\gamma ij) \equiv \Omega_{a\beta\gamma}(ij)$ , and sums are implicit on  $\beta, \gamma, \delta, \epsilon, \zeta, k$ , and  $j$  in the diagonal part. The Van Vleck fourth moment is

$$M_4^a(ij) = L_4^a(ij) + \sum_{\delta,k} M_2^{a\delta}(ik) M_2^{a\delta}(kj), \quad \text{for } M_2^{a\delta}(ij) = \delta_{ij} \sum_{\beta,\gamma,k} (\alpha\beta\gamma ik)(\delta\beta\gamma ik)^* + \sum_{\beta,\gamma} (\alpha\gamma\beta ij)(\delta\beta\gamma ij)^*.$$

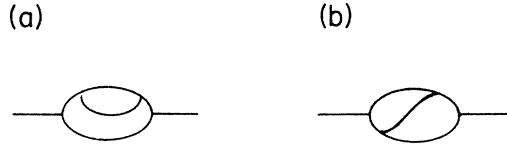


FIG. 3. Schematic representations of graphs contributing to the fourth moments. (a) Bubble diagram; (b) vertex correction.

At this point the reader may wonder what advantage has been obtained considering the ungainly Eq. (9). In fact, these equations are useful for two reasons: (1) In the form of Eqs. (8) and (9), it is very easy to code the moments and extract numerical results for computer simulations of the dynamics of spin systems. This can be done once and for all with the expressions above. The only analytical work required is the evaluation of the vertices  $\Omega$ , which we discuss below. (2) The forms Eqs. (8) and (9) also can facilitate the calculation of analytic expressions for the self-energy and Van Vleck moments. For example, in the solid molecular hydrogens, the dominant interaction between  $J=1$  molecules is the rather complicated anisotropic EQQ interaction. Application of the present method makes the evaluation of the moments quite straightforward: one just has to calculate the vertices (these are already in the literature),<sup>6-8</sup> and we find that the diagonal part of our Van Vleck moments match those of Harris<sup>6</sup> and Hama, Inuzuka, and Nakamura.<sup>8</sup>

### III. APPLICATIONS AND EXAMPLES

In this section, we consider two examples of the method which illustrate the general approach. We first derive a simple equation that the vertices  $\Omega_{\alpha\beta\gamma}$  satisfy which will be useful in the implementation of the method. To obtain the vertices for a spin Hamiltonian [Eq. (1)], we note that in frequency space

$$\omega A_\alpha(i) = \sum_{\beta,\gamma,j} \Omega_{\alpha\beta\gamma}(ij) A_\beta(i) A_\gamma(j) ,$$

form the Heisenberg equation of motion for  $A_\alpha(i)$ . For the common case  $\xi_{\alpha\beta} = \xi_{\beta\alpha}$ , we see that

$$\sum_{\beta,\gamma,j} \Omega_{\alpha\beta\gamma}(ij) A_\gamma(j) A_\beta(i) = 2 \sum_{\beta,\gamma,j} \xi_{\beta\gamma}(ij) [A_\alpha(i), A_\beta(i)] A_\gamma(j) . \quad (10)$$

So to find the vertices, we merely evaluate the *single* commutator in Eq. (10), and make the obvious identifications to specify  $\Omega$ . To make things clearer, we consider a few examples. The first is intended to show the reader how the method is used in a very simple case—one so simple, in fact, that there is little advantage over the conventional method. The full power of the technique is demonstrated in example 2.

#### A. Example 1: Heisenberg paramagnet for spin $\frac{1}{2}$ .

The Hamiltonian reads

$$\mathcal{H} = \sum_{\substack{i,j \\ i \neq j}} J_{ij} \mathbf{I}(i) \cdot \mathbf{I}(j) .$$

This is easily put into the form of Eq. (1). Since only multipolar operators with  $L=1$  appear, we abbreviate  $\alpha = (1, M)$  by  $\alpha = M$  and

$$\xi_{\beta\gamma} = J_{ij} (\delta_{\beta 0} \delta_{\gamma 0} - \delta_{\beta 1} \delta_{-\gamma 1} - \delta_{-\beta 1} \delta_{\gamma 1}) / 4 . \quad (11)$$

To obtain the second and fourth moments of  $\Gamma^\alpha(i, j)$  or  $A^\alpha(i, j)$ , we need the vertices  $\Omega$ . These are readily obtained from Eqs. (10) and (11) and the spin- $\frac{1}{2}$  angular momentum commutation relations which are compactly expressed by

$$\begin{aligned} \frac{1}{2} [A_\alpha, A_\beta] &= -\delta_{\alpha 1} (\delta_{\beta 0} A_1 + \delta_{\beta -1} A_0) \\ &+ \delta_{\alpha -1} (\delta_{\beta 0} A_{-1} + \delta_{\beta 1} A_0) \\ &+ \delta_{\alpha 0} (\delta_{\beta 1} A_1 - \delta_{\beta -1} A_{-1}) . \end{aligned}$$

It is clear by inspection of the three aforementioned equations that the vertices are given by

$$\Omega_{\alpha\beta\gamma}(ij) = J_{ij} (\alpha \delta_{\beta 0} - \delta_{\beta 1} + \delta_{-\beta 1}) \delta_{\gamma, \alpha - \beta} .$$

Using the general formula [Eq. (8)] we see that

$$M_2^{(0)}(ij) = 2 \left( \delta_{ij} \sum_k J_{ik}^2 - J_{ij}^2 \right) .$$

This is identical to the result of Ref. 2 when  $\alpha=0$ . The fourth moment is evaluated in a completely analogous fashion. While the expression is unwieldy, it is simple to code, or one could simply calculate the vertices and code the Eqs. (8) and (9) once and for all.

#### B. Example 2: Electric quadrupole-quadrupole Hamiltonian.

A nontrivial example of this method is the calculation of the second and fourth moments for the EQQ Hamiltonian. As we briefly indicated in the text, the site-diagonal part of the Green's function  $G^\alpha$  are required for a theoretical treatment of longitudinal relaxation in  $H_2$ . In this case there are five independent functions. Harris<sup>6</sup> and Myles and Ebner<sup>7</sup> have calculated the vertices  $\Omega$ . They find that only two types are nonvanishing:  $\Omega_{1l, 2m, 2n}(i, j)$  and  $\Omega_{2l, 1m, 2n}(i, j)$ . Equation (2) gives the diagonal second moment

$$M_2^\xi(ii) = \sum_{l,\beta,\gamma} |\Omega_{\alpha\beta\gamma}(il)|^2 ,$$

which matches Ref. 6. The fourth moment is particularly tedious to calculate directly from the spin algebra commutation relations. However, it is quite straightforward using the current method. Since most of the vertices are zero, only a few of the terms of Eq. (9) contribute to the diagonal part of  $G^\alpha$ . We find that

$$\begin{aligned}
M_4^{(1,m)}(ii) = & \Omega_{1m,2\mu,2\nu}(ij) \Omega_{2\nu,1\lambda,2\chi}(jk) \Omega_{2\eta,1\lambda,2\chi}^*(jk) \Omega_{1m,2\mu,2\eta}^*(ij) + \Omega_{1m,2\mu,2\nu}(ij) \Omega_{2\mu,1\lambda,2\chi}(ik) \Omega_{2\eta,1\lambda,2\chi}^*(ik) \Omega_{1m,2\eta,2\nu}^*(ij) \\
& + \Omega_{1m,2\mu,2\nu}(ij) \Omega_{2\mu,1\lambda,2\chi}(ik) \Omega_{2\eta,1\lambda,2\nu}^*(ij) \Omega_{1m,2\eta,2\chi}^*(ik) + \Omega_{1m,2\nu,2\mu}(ij) \Omega_{1\lambda,2\eta,2\chi}(ij) \Omega_{1\lambda,2\mu,2\nu}^*(ij) \Omega_{1m,2\chi,2\eta}^*(ij) \\
& + \Omega_{1m,2\mu,2\nu}(ij) \Omega_{1\lambda,2\eta,2\chi}(ik) \Omega_{1\lambda,2\mu,2\nu}^*(ij) \Omega_{1m,2\eta,2\chi}^*(ik)
\end{aligned}$$

and

$$\begin{aligned}
M_4^{2,m}(ii) = & \Omega_{2m,1\lambda,2\mu}(ik) \Omega_{1\lambda,2\nu,2\chi}(ij) \Omega_{1\psi,2\nu,2\chi}^*(ij) \Omega_{2m,1\psi,2\mu}^*(ik) + \Omega_{2m,1\lambda,2\mu}(ij) \Omega_{1\lambda,2\nu,2\chi}(ik) \Omega_{1\psi,2\nu,2\mu}^*(ij) \Omega_{2m,1\psi,2\chi}^*(ik) \\
& + \Omega_{2m,1\lambda,2\mu}(ij) \Omega_{2\mu,1\psi,2\chi}(jk) \Omega_{2\nu,1\psi,2\chi}^*(jk) \Omega_{2m,1\lambda,2\nu}^*(ij) + \Omega_{2m,1\lambda,2\mu}(ij) \Omega_{2\nu,1\psi,2\chi}(ik) \Omega_{2\nu,1\lambda,2\mu}^*(ij) \Omega_{2m,1\psi,2\chi}^*(ik),
\end{aligned}$$

where sums are implicit on all indices other than  $i$  and  $m$ , and  $-2 \leq \mu, \nu, \chi, \eta \leq 2$ ,  $-1 \leq \lambda, \psi \leq 1$ , and  $j \neq k$  except for the last term in each of the previous equations, where  $j$  and  $k$  can be identical. Note that these expressions are readily rewritten in analytical forms involving the function  $F_{mn}(i, j)$  of Ref. 7. Further, it is simple to code these expressions in the form of the vertices to obtain moments for a given configuration of impurities: This is useful for calculating  $T_1$  for random mixtures of ortho- and para- $H_2$ , for example.<sup>6-9</sup>

#### IV. CONCLUSIONS

We have obtained general expressions for the first two nontrivial moments of resonant absorption spectra which

should be of interest for magnetic resonance work. The method we have developed yields expressions convenient for practical use with a minimum of detailed commutator algebra. We should also remark that this analysis is not limited to spin systems: Similar equations must hold for more general bilinear Hamiltonians.

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