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THE USE OF GREEN FUNCTIONS FOR THE CALCULATION OF DYNAMIC JAHN-TELLER EFFECT IN ELECTRON SPIN RESONANCE SPECTRA

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ABSTRACT

With the use of the Green function techniques at finite temperature the electron spin resonance spectra is calculated in a system that presents a dynamic Jahn-Teller effect . The system is a paramagnetic ion with total spin 1 situated in the site of a vibrating octahedron field. The state of the ion transforms as the T_{1g} of O_h and is coupled to the ε_g and τ_{2g} vibrational modes. The problem is used as an example when a simple linearisation cannot be used to decouple the Green function. The geometric approximation, however, can be used giving appropriate results for the line shape.

INTRODUCTION

The purpose of this work is to apply the Green function method$^{(1)}$ to the dynamic Jahn-Teller effect. Some care must be exerted in the approximation of the Green functions in this particular physical problem.

We shall see how simple linearisation cannot be used in the particular problem worked here, however under the same circumstances the geometric decoupling can be. The physical problem is an ion with spin 1 (transforms as T_{1g} of O_h) in the site of an octahedron which is vibrating (vibrate as $\varepsilon_g \oplus \tau_{2g}$ normal modes on O_h). In Section II the problem is worked out in detail. In Section I we summarize the general Jahn-Teller problem. In the following section we calculate the line shape in terms of the advanced and retarded Green functions at finite temperature and finally we present RPA calculations to decouple the equation of motion in Section IV.

I. THE JAHN-TELLER EFFECT

Jahn and Teller$^{(2)}$ demostrated that for non-linear polyatomic molecules there was at least one deformation of the nuclear positions that conduced to a state with lower energy. As it was pointed our by Van Vleck$^{(3)}$, systems where it is specially important the Jahn-Teller theorem are in ionic crystals.

In the case of the strong manifestation the system can suffer a permanent distortion given to the so called static Jahn-Teller effect. The dynamic effect comes when the relation between the vibrational zero-point of the nuclei and the electronic states are comparable in energy. The static Jahn-Teller can be considered as the strong limit case of the dynamic one$^{(4)}$.

Ham$^{(5)}$ pointed out the fact that the symmetry of the vibronic state must be conserved; the product of the IR associated with the electonic and vibrational state should transform as a IR of the symmetry group of the molecule. Physically this means that the electronic charge distribution should change properly, to preserve the initial total symmetry of the system, according to the motion of the nuclei. Also Ham$^{(6)}$ clarified what one should expect as a Jahn-Teller manifestation, defining the quenching factors. These factors are the quantities by the ones are affected the observables (angular momentum, spin-orbit interaction...) and they depend of the way the corresponding operators transform under the relevant point group, and the kind of problem worked out.

In the theoretical sense, the numerical prediction of the Jahn-Teller effect in different systems has shown a very interesting and difficult problem to solve. The main attempts use the perturbation approach considering a model hamiltonian that should have the relevant physical terms and giving also a reasonable algebraic handling. Several models$^{(7)}$ have been used for a number of limited systems with suitable physical approximations.

Another type of approaches make use of group theoretical techniques, borrowed from nuclear physics, to study the dynamic Jahn-Teller effect for the $T_{1g} \otimes (\varepsilon_g + \tau_{2g})$ coupling in some special cases$^{(8)}$.

Through the years it was of interest to deal with the effects of crystal fields with cubic symmetry considering not only localized vibrational modes. A calculation taking into account the coupling of the ε and τ_{2_g} modes in the continuum was made by Stevens$^{(9)}$. Stevens's proposition was the introduction of the Green function methods to calculate the crystal spectra. Ham et al.$^{(10)}$ showed the calculation of Fe^{2+} in MgO considering spin-orbit interaction and a discrete and continuum spectra of phonons interacting with the ion.

We have pursued the Stevens's suggestion further using the double time Green function theory to calculate the spectral intensity. In the following section we present the physical problem, although it is simple enough, it contains the main futures to calculate the electron spin resonance spectrum. Besides, it has special characteristics which make it very interesting to apply the Green function technique.

II. THE EPR PROBLEM

Let us consider a paramagnetic ion with spin 1 which is situated at the site of an octahedron in a lattice which is vibrating$^{(9)}$. Our hamiltonian will consist of an uncoupled part H_o formed by the interaction of the spin with the static lattice plus the phonons of the lattice, and the interaction between the ion and the crystal field H_{int}, that is

$$H = H_o + H_{int}$$

$$H_o = -h\omega_o S_z + \sum_k h\omega_k \alpha_k + \alpha_k$$

$$H_{int} = \Sigma\,(\alpha_k \;\; \overset{+}{\alpha}_k)\; S \cdot T_k \cdot S$$

where we suppose that the magnetic field of the static lattice is directed along the Z axis, ω_o being the magnetic resonance frequency, the α_k and $\overset{+}{\alpha}_k$ are the annihilation and creation operators associated to the - k'th mode with frequency ω_k. $S \cdot T_k \cdot S$ gives the proper spin interaction with the crystal field being invariant under the symmetry operations of the cubic group. The ion is in a three-fold degenerate state that transforms according to the T_{1g} IR of the cubic group. The interaction will contain only the ε_g and τ_{2_g} modes if we consider the motion of nearest neighbours. We can write for $S \cdot T_k \cdot S$

$$\sum_{k} (\alpha_k+\alpha_k^+) \{A_k(3S_z^2-2) + B_k(S_+S_z+S_zS_+) + \bar{B}_k(S-S_z+S_zS_-) - C_kS_+^2+\bar{C}_kS_-^2\} \quad (1)$$

The sets $\{A_k, C_k + \bar{C}_k\}$ and $\{B_k + \bar{B}_k, i(B_k-\bar{B}_k), i(C_k-\bar{C}_k)\}$,transforms as the ε_g and τ_{2g} irreducible representations of O_h respectively.

This kind of EPR problem presents a dynamic Jahn-Teller effect. In the following section we show how to calculate the spectral intensity.

III. SPECTRAL INTENSITY

It is very well known that if we are interested in processes that imply an absorption in the transition associated with the operator A, the spectral intensity$^{(1,9)}$ can be written as the sum of the transition probability times a lorentzian line of infinitesimal width for each transition.

$$I(\omega) = \frac{1}{Z_o} \ell im \sum_{n,m} (e^{-\beta E_n} - e^{-\beta E_m}) \mid <m|A|n> \frac{2\varepsilon}{(E+E_n-E_m)^2-\varepsilon^2} \quad (2)$$

Z_o is the partition function associated to the canonical ensamble and $\beta = 1/KT$. I(E) can be rewritten as

$$\frac{i}{Z_o} \ell im \Sigma (e^{-\beta E_n} - e^{-\beta E_m}) \mid <m|A|n>|^2 \left(\frac{1}{E+E_n-E_m+i\varepsilon} - \frac{1}{E+E_n-E_m-i\varepsilon}\right) \quad (3)$$

which can be written in terms of the double time Green functions at finite temperature defined as$^{(1)}$

$$<<A;B>> = \frac{1}{2\pi Z_o} \Sigma (e^{-\beta E_n} - e^{-\beta E_m}) \frac{<n|A|m><m|B|n>}{E+E_n-E_m}$$

If we are interested in the electron spin transition, then

$$I(\omega) = -2\pi i \lim_{\varepsilon\to 0} \{ <<S_x;S_x>>_{\omega+i\varepsilon} - <<S_x;S_x>>_{\omega-i\varepsilon} \} \quad (4)$$

that means we are taking the difference between the Fourier transforms of the retarded and advanced Green functions.

To obtain the line shape we only need to evaluate the Green functions $<<S_x;S_x>>_\omega$ under a suitable approximation. We show in the next section some RPA calculations.

IV. DECOUPLING OF THE GREEN FUNCTIONS

The Fourier transform of the Green function (causal, retarded or advanced) obeys the equation of motion(1)

$$E <<A_i;B_i>>_E \;=\; <[A_i,B_i]> \;+\; <<[A_i,H];\, B_i>>_E \qquad (5)$$

A decoupling that conserves the first two energy moments which leads to RPA is the so called geometric approximation (GA)(11,12). Defining the matrix notation

$$G \;\equiv\; \{<<A_i;B_j>>_E\} \qquad (6a)$$

$$M \;\equiv\; \{<[A_i;B_j]>\} \qquad (6b)$$

$$N \;\equiv\; \{<[[A_i,H],\, B_j]>\} \qquad (6c)$$

for the one particle Green function, zero and first order moments respectively, the GA looks like

$$G \simeq \; M\,[EM-N]^{-1}M \qquad (7)$$

According to the eq. (4) the set of operators which we are interested in, are the three spin components S_x, S_y and S_z of the central ion. The Green function matrix has dimension 3 x 3.

Conventional linearisation(13) consists in finding a matrix K such that

$$[A_i,H] \;=\; \sum_j K_{ij}A_j \qquad (8)$$

which gives, for the approximate Green function

$$G = M \ \{EI - K\}^{-1} \tag{9}$$

One can derive from the GA the same result by two-term expansion of eq. (7) and assuming that M^{-1} exists$^{(12)}$.

In the present case the matrix M has the form

$$i \begin{pmatrix} 0 & \langle S_z\rangle & -\langle S_y\rangle \\ -\langle S_z\rangle & 0 & \langle S_x\rangle \\ \langle S_y\rangle & -\langle S_x\rangle & 0 \end{pmatrix} \tag{10}$$

If we are consistent with the RPA, the thermal averages must be calculated through second order in the coupling coefficients.

It is found that the elements $\langle S_x\rangle$ and $\langle S_y\rangle$ are zero at this degree of accuracy and the matrix M has no inverse implying that the linearisation involved in eq. (8) and (9) is not feasible$^{(14)}$.

Fortunately the derivation of eq. (7) by inner-projection techniques$^{(12)}$ does not depend of the non-singularity of the zero matrix moment. Provided the first matrix moment N is non-singular, the decoupling makes sense, as we shall illustrate.

It can be found, making a two-term expansion in eq. (7), what approximation is implied for the higher order Green function (this is valid even if M^{-1} does not exist):

$$E\,G = E\langle\langle A;B\rangle\rangle_E = M + N\,\{EM-N\}^{-1}\,M$$

and comparing with eq. (5) we get

$$\langle\langle [A,H]\,;\,B\rangle\rangle_E \simeq N\{EM-N\}^{-1}\,M$$

which is not proportional to G if M^{-1} does not exist.

To calculate the line shape of the preceding section, we only need the (1,1) element of the Green function matrix, which in terms of M_{ij} and N_{ij} is

$$\langle\langle S_x;S_x\rangle\rangle_{\omega} = \frac{M_{12}\,R_{22}\,M_{21}}{|\omega M-N|} \tag{11}$$

where $R = \{R_{ij}\} = \omega M - N$

After a lengthy process to evaluate the commutators and relevant integrals, the needed matrix elements of N are

$$N_{11} = N_{22} = -\{\hbar\omega_o \langle S_z\rangle + \Sigma \, |3A_k^2 \langle(\alpha_k+\overset{+}{\alpha_k})S_z^2\rangle + 5|B_k|^2 \langle(\alpha_k+\overset{+}{\alpha_k})(S_+S_z+S_zS_+)\rangle$$

$$+ \frac{3}{2} \; A_k^2 \; \frac{16}{\omega_k} + 2|C_k|^2 \langle(\alpha_k+\overset{+}{\alpha_k})S_+^2\rangle\}$$

$$N_{12} = N_{21} = 3 \, \Sigma \; 3|B_k|^2 \langle(\alpha_k+\overset{+}{\alpha_k}) \; (S_+S_z+S_zS_+)\rangle$$

$$N_{13} = N_{23} = N_{31} = N_{32} = 0$$

$$N_{33} = -2 \, \Sigma \, | \; |B_k|^2 \langle(\alpha_k+\overset{+}{\alpha_k}) \; (S_+S_z+S_+S_z)\rangle + 2|C_k| \; \langle(\alpha_k+\overset{+}{\alpha_k}) \; S_+^2\rangle| \qquad (12)$$

where the needed expectation values are summarized in the appendix. From eq. (11) the Green function takes the form

$$\langle\langle S_x;S_x\rangle\rangle_\omega = \frac{N_{11}|M_{12}|^2}{\omega^2|M_{12}|^2 \underset{-}{\oplus} N_{11}^2+N_{12}^2} = \frac{\langle S_z\rangle^2 \; N_{11}}{\langle S_z\rangle^2\omega^2-N_{11}^2+N_{12}^2} \qquad (13)$$

Substituting in the line shape formula eq. (4)

$$I(\omega) = 2\pi i \; \lim_{\varepsilon\to 0} \; N_{11} \left| \frac{1}{(\omega+i\varepsilon)^2-\gamma^2} - \frac{1}{(\omega-i\varepsilon)^2-\gamma^2} \right|$$

$$= 2\pi^2 \; N_{11} \; \delta(\omega^2-\gamma^2) \qquad (14)$$

where $\gamma^2 = (N_{11}^2-N_{12}^2)|\langle S_z\rangle^2$ and the resonance energy is found at

$$\omega = \pm \gamma \qquad (15)$$

The results in eqs. (2.15) are what we expect as the physical manifestation of our problem. Ham$^{(15)}$ pointed out that no splitting can be obtained from an interaction such as the one considered in eq. (1). The effect is just to quench and shift the resultant energy spectra exactly as we found out.

V. DISCUSSION

The use of Green function theory gives in a relative simple way the energy spectra for the dynamic Jahn-Teller effect in an electron spin resonance experiment.

No splitting was obtained in agreement with Ham's discussión. It is important though to evaluate the propagator at a higher level of approximation, i.e., by including more operators in the projection basis. In the process of doing so one should take account of the full symmetry of the problem. Symmetry violations may occur in a linearisation --- scheme(9). They do not occur if one used the full hamiltonian superoperator in generating matrices like (6c). The choice of operators in the projection basis can be motivated by physical considerations, e.g., dominating modes, rather than by moment generation. The general form of the Green function matrix is given by:

$$<<A;A^{+}>>_{E} = (A|h)\ (h|E\hat{1}-\hat{H}|h)^{-1}\ (h|A)$$

which are matrices of the type given by eqs. (6) and (7) but with a larger set of operators involved. This technique has been successful for systematising atomic and molecular Green's fuction calculations(16).

APPENDIX

The integrals involved in the calculation of the N matrix are calculated up to first order in perturbation theory.

The thermal averages, using the eigenfuctions of H_o as basis, can be written as

$$<A> = -\frac{1}{2\pi i z_o} \oint e^{-\beta H}\ \mathrm{Tr}|RA|\ dz$$

where R, the resolvent, can be expanded as

$$R = (H-z)^{-1} = (H_o-z)^{-1} - (H_o-z)^{-1} H_{int} (H_o-z)^{-1} + \ldots$$

where H_o, H_{int} are the non-interacting hamiltonian and potential interaction respectively, z_o is the partition function azzociated to the canonical ensamble.

All the needed expectation values were calculated up to first order giving the following results:

$$<(\alpha_k+\alpha_k^+)S_z^2> \;=\; \frac{2}{\hbar\omega_k}\;(e^{\beta\hbar\omega_0}+e^{-\beta\hbar\omega_0})/(1+e^{\beta\hbar\omega_0}+e^{-\beta\hbar\omega_0})$$

$$<(\alpha_k+\alpha_k^+)(S_+S_z+S_zS_+)> \;=\; 2\,F(\hbar\omega_0)\;(1+e^{\beta\hbar\omega_0})$$

$$<(\alpha_k+\alpha_k^+)(S_+^2)> \;=\; 4\,F\,(2\hbar\omega_0)\;e^{\beta\hbar\omega_0}$$

$$F(b) \;=\; \frac{1}{b^2-\hbar^2\omega_k^2}\;\left[b(1-e^{-\beta b})(2<n_k>_o+1)-\hbar\omega_k(1+e^{-\beta b})\right]\;/(1+e^{\beta\hbar\omega_0}+e^{-\beta\hbar\omega_0})$$

$$<n_k>_o \;=\; \frac{1}{e^{\beta\hbar\omega_k}-1} \;=\; <\alpha_k^+\;\alpha_k>_o$$

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