Comparison between the methods of Glauber states and Lanczos applied to the Jahn-Teller effect in ZnSe:Fe^{2+}

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Vibronic levels in the strong-coupling limit are not easy to obtain since vibrational and electronic components are extremely mixed. Usual methods based on extrapolations from the adiabatic limit fail. In the present paper we want to compare the Lanczos method and the Glauber states method applied to a case were the strong-coupling limit is approached. The application considers parameters valid suited to the system ZnSe:Fe^2 for a more realistic interpretation. Stability of the solutions is found and discussed. Advantages and disadvantages of both methods are also discussed.

Keywords: Absorption spectra; magnetic impurities; Jahn-Telller effect; Jahn-Teller energy; Lanczos and Glauber states

Los niveles vibrónicos en el límite de acoplamiento Jahn-teller fuerte no son fáciles de obtener debido a que las componentes vibracionales y electrónicas están extremadamente mezcladas. Los métodos usuales, basados en extrapolaciones desde el límite adiabático fracasan. En el artículo presente queremos comparar los métodos de Lanczos y de Glauber, aplicados a un caso en el que se aproxima el límite de acoplamiento fuerte. La aplicación considera los parámetros válidos para el sistema ZnSe:Fe^{2+} para una interpretación más realista. La estabilidad de las soluciones se encuentra y se discute. Las ventajas y desventajas de ambos metodos son tambien discutidas.

Descriptores: Espectro de absorción; impurezas magnéticas; efecto Jahn-Teller; energía de Jahn-Teller; estados de Lanczos y Glauber

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1. Introduction and theory

Outer orbitals of crystalline atoms are more exposed to coupling with vibrations of the surrounding atoms in what is usually called vibronic coupling or Jahn-Teller effect [1, 2]. Since these are end states for absorption transitions, we expect strong corrections to the absorptions spectra due to the intermediate or strong Jahn-Teller coupling. We compare here for the first time two mathematical methods to attempt calculations for such coupling intensities: the Lanczos method and the Glauber method. Both of them have been presented elsewhere so here we mention them giving the appropriate references for the interested reader.

The total Hamiltonian is

$$H = H_e + H_v + H_{JT} \tag{1}$$

where H_e is the electronic Hamiltonian, it includes atomic parameters ($\lambda\ S \cdot L$) and crystal field parameter ($10\ |Dq|$). H_v is the vibrational Hamiltonian associated to modes Q_i, of generalized momenta P_i, frequency ω_i and effective mass μ_i and it can be written either as

$$H_v = \sum_i \frac{\mu_i \omega_i^2}{2} Q_i^2 + \sum_i \frac{1}{2\mu_i} P_i^2 , \tag{2}$$

or, in second quantized notation,

$$H_v = \sum_i \hbar\omega_i \left(a_i^\dagger a_i + \frac{1}{2} \right). \tag{3}$$

The vibrational modes are those that possess the symmetry of the coupling modes. Their energies $\hbar\omega_i$ are known from the corresponding lattice dynamics. Small variations around these values are allowed to compensate for local symmetry breakings or frequency shifts due to presence of impurity atoms.

H_{JT} is the coupling Jahn-Teller or vibronic Hamiltonian. It is formed by a scalar product of a vector in the vibrational space $\mathbf{Q} = (\mathrm{Q}_1, \mathrm{Q}_2, \ldots, \mathrm{Q}_i, \ldots)$ and a vector in the electronic coordinates $\mathbf{D} = (\mathrm{D}_1, \mathrm{D}_2, \ldots, \mathrm{D}_i, \ldots)$. The coupling constant can be expressed as the square root of the product of the vibrational quantum $\hbar\omega_i$ and the so-called Jahn-Teller

energy for that mode E_{JTi}. In terms of second quatization notation we can write,

$$H_{JT} = \sum_i \sqrt{E_{JTi}\,\hbar\omega_i}\,(a_i^\dagger + a_i)D_i\ . \qquad (4)$$

The aim here is to find the vibronic energies and vibronic wave functions for an electronic system interacting with the vibrations of its surroundings. The different functions in the original electronic multiplet mix with vibrations of appropriate symmetry including an arbitrarily large number of vibrational quanta for the normal modes. So the basis of functions need to be increased until stability of the solutions is reached. This we do independently and separately by the two methods outlined below.

The Lanczos recursion method is based on a progressive appropriate building of orthonormal states, starting from a trial seed state and basic properties of the system. In its traditional form the numerical calculations suffer the finite precision arithmetic of computers; instabilities in the recursion coefficients can occur and the higher excited states are bad convergent [3]. In this situation the modified Lanczos technique, allows us to obtain whatever excited state with the desired precision [4].

The method of Glauber states makes use of a basis constructed in the supposedly distorted system after a strong Jahn-Teller energy has split the electronic multiplet leading to a less degenerate electronic ground state [5]. Then a diagonalization is performed for lower values of the vibronic coupling. Full use of the point symmetry group T_d is done to improve convergence and to label wave functions [6, 7].

An unexpected irregular optical spectrum, with more lines than expected, is one of the signatures of a Jahn-Teller effect. To explain this phenomenon vibronic wave functions and vibronic energies must be found. Energy intervals lead to frequencies of the possible lines present in the spectra; wave functions allow calculating the transition probabilities corresponding to all possible lines.

To better understand how the methods work we apply them to the infrared absorption spectra of Fe^{2+} in compounds with zinc-blende structure such as ZnSe. Iron enters as a substitutional impurity for Zn in these crystals. The local symmetry corresponds to point group T_d. Crystalline field splits the ^{5}D atomic multiplet into levels ^5E and $^5T_2$ in order of increasing energy [8–10]. The separation varies with the host crystal but is nearly one quarter of an eV. A useful energy-level scheme is given in Ref. 10.

Absorption spectra show the transitions that originate in the lower ^5E multiplet and end at the excited $^5T_2$ multiplet. At very low temperatures only absorptions from the true ground state to states allowed by the selection rules are possible. We consider here only those levels that are involved in electric-dipole transitions corresponding to operators of symmetry T_2.

2. Results ans discussion

For Fe^{2+} we use the free-ion value of the spin-orbit constant $\lambda = -100$ cm^{-1}. The value of the crystal field parameter $10|Dq|$ is 2944 cm^{-1} for ZnSe. The energy of the coupling phonon used here is 65 cm^{-1}. This phonon corresponds to points TA1(K) of the Brillouin zone [11, 12].

Such modes are doubly degenerate with components Q_θ and Q_ϵ. The excited states correspond to states with different occupation numbers for these vibrational modes, n_θ and n_ϵ respectively. The notation for such state will be (n_θ, n_ϵ). In the Lanczos method, the vibrational states considered to construct the Lanczos chain are those going from (0,0) to (M, M), including all intermediate combinations, where M is an integer number that defines the basis on which calculations will be performed with Lanczos. On the other hand, in the method of Glauber states we considered vibrational states between (0,0) and $(n_\theta, N - n_\theta)$, with n_θ taking all values between 0, and N, where N is an integer number that defines the basis in the method of Glauber. So M and N are unrelated numbers. This difference is due to the independent calculations done previously by the groups in Italy and Chile but is not important for the agreement found below.

What really matters to compare results from the two methods is that the number of vibronic functions used by them is approximately the same at a given stage of the calculations. Here we refer to one the triple degenerate vibronic functions of symmetry T_2 mixed with phonons of different occupation numbers. It turns out that $f_L(M)$, the number of vibronic functions in the Lanczos method with M defined as in previous paragraph, is given by [4]:

$$f_L(M) = 4(M+1)^2\ . \qquad (5)$$

On the other hand, $f_G(N)$, the number of vibronic functions in the Glauber method with N defined as above, is [13]:

$$f_G(N) = (N+1)(N+2)\ . \qquad (6)$$

Then, in the limit of high vibrational quantum numbers, we have that the number of functions considered in the two methods is approximately the same, if

$$N \approx 2M\ . \qquad (7)$$

That is to say, $f_L(M) \approx f_G(2M)$. This point is better illustrated by the 4 columns on the left-hand side of Table I.

In Figs. 1 and 2 we present the lowest vibronic energy levels associated to the excited multiplet $^5T_2$ of ZnSe:Fe^{2+} calculated by the methods of Lanczos and Glauber respectively. In the former M is the independent variable; for the latter N is the independent variable. Other parameters take the same values for both calculations. The computer codes were prepared completely independent of each other long before this comparison was attempted.

TABLE I. Three leading energy differences calculated by both methods: Lanczos (L) and Glauber (G). Parameters correspond to ZnSe:Fe^{2+}: E_{JT}= 220 cm^{-1}; $\lambda = -100$ cm^{-1}; $\hbar\omega = 65$ cm^{-1}; $10|Dq| = 2944$ cm^{-1}. First and second columns apply to the Lanczos method giving the vibrational quantum number and the total number of vibronic functions, respectively. Third and fourth columns do the same for the Glauber method. In the following columns the leading three energy differences are reported for each method. Lanczos method converge very quickly once the spurious levels are identified and removed. In terms of states, both methods require over 500 wave functions to give stable results that agree up to 4 significant digits. Notice that $M \approx N/2$ as discussed in Eq. 5, so the pace of both methods is not the same leaving every second row blank for the Lanczos method.

M	$f_L(M)$	N	$f_G(N)$	$\lvert E_1 - E_0\rvert$		$\lvert E_2 - E_0\rvert$		$\lvert E_3 - E_0\rvert$	
				L	G	L	G	L	G
5	144	10	132	25.37	30.15	60.85	71.45	73.39	83.66
		11	156		27.93		66.03		79.05
6	196	12	182	24.57	26.35	57.50	62.27	72.14	76.04
		13	210		25.35		59.53		72.10
7	256	14	240	24.25	24.79	55.91	57.56	71.53	72.88
		15	272		24.44		56.41		72.10
8	324	16	306	24.14	24.26	55.25	55.69	71.26	71.64
		17	342		24.17		55.28		71.37
9	400	18	380	24.10	24.12	55.00	55.08	71.14	71.23
		19	420		24.10		54.97		71.15
10	484	20	462	24.09	24.09	54.92	54.92	71.10	71.12
		21	510		24.09		54.88		71.09
11	576	22	552	24.09	24.09	54.89	54.88	71.09	71.09
		23	600		24.09		54.88		71.09
12	676	24	650	24.09	24.09	44.88	54.88	71.09	71.09

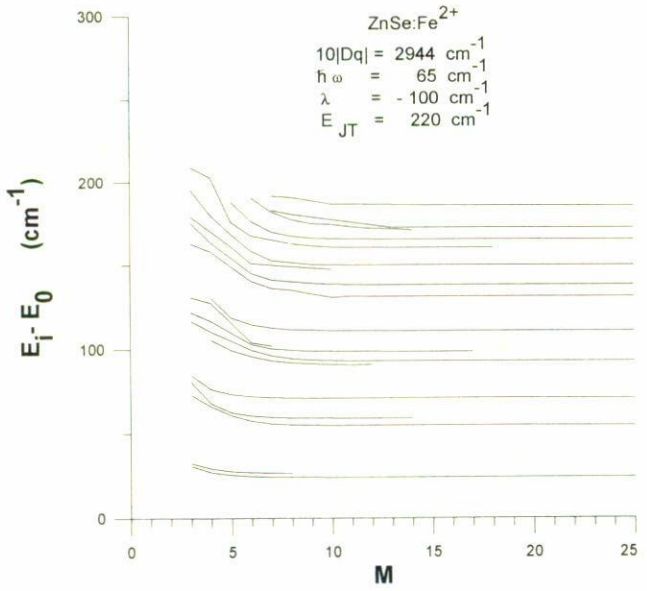

FIGURE 1. Energy differences for the lowest vibronic energy levels according to the method of Lanczos as function of M, the maximal number of phonons of each component. Convergence is quickly achieved; spurious levels vanish when they lead to extremely weak transitions.

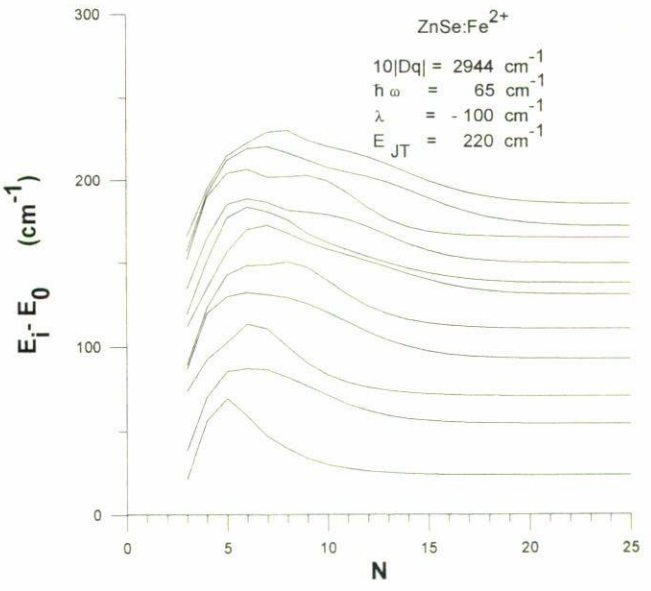

FIGURE 2. Energy differences for the lowest vibronic energy levels according to the method of Glauber as function of N, the maximal number of phonons adding both components. Convergence is achieved smoothly without spurious levels.

The asymptotic values given by both methods coincide extremely well as M and N are large enough. This is encouraging in the sense that they are different from the mathematical point of view. Such difference is notorious when results for low values of M and N are compared. This allows us to say that both methods converge to stable results when a large basis is constructed.

The Lanczos method shows rapid convergence to stable values as follows from Fig. 1. However, some spurious levels of negligible intensity are carried on all the way to vary large values of M where they eventually stop playing any significant role.

On the other hand, Fig. 2 shows the convergence of the Glauber method where no spurious levels are to be found. This method shows an initial slow convergence to the final values that the method of Lanczos.

To examine these results we present in Table I the numerical results for the three lowest energy differences (involving four energy levels) calculated by both methods. In the case of the Lanczos method we report M and $f_L(M)$. Similarly, we report N and $f_G(N)$ establishing the closest approximation as provided by Eq. (7). Lanczos method show stability for $M > 11$ while Glauber method is stable for $N > 22$. However, in terms of number of wave functions involved in the calculations there is no important difference between both methods as they require over 500 states in order to lead to stable solutions. The numerical agreement of both methods within four significant figures is evident.

3. Conclusions

The combination of both methods is a strong tool since it is possible to obtain good initial results with the method of Lanczos, provided spurious levels are eliminated by comparison with results of the Glauber method. For high values of M and N both methods check each other, providing good basis for stability analysis.

There is a remarkable agreement reached by both methods for large values of M and N connected by Eq. (7). This shows that the independent numerical solutions obtained here are the best possible results for the Hamiltonian defined above. If this is not enough to explain an experimental result, this cannot be blamed to the numerical method, or the algorithm or the computer used.

Having established this agreement next step is to attempt a quantitative explanation of the optical spectra of Fe^{2+} in ZnSe, ZnS and other related compounds, including the calculated intensities of electric dipole transitions. This is at the moment beyond the scope of the present article. However, initial comparison between intensities calculated by both methods (not presented here) show also excellent agreement.

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