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Optical absorption, magnetic circular dichroism, and reduction factors in the Jahn-Teller system $E\otimes\epsilon$: Exact solution with the continued-fraction formalism

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We consider the Jahn-Teller system $E\otimes\epsilon$ consisting of an orbital doublet coupled with a two-dimensional phonon. We attack the problem within the continued-fraction formalism, and we provide exact solutions for the optical absorption, the magnetic circular dichroism, and the reduction factors of the electronic orbital angular momentum. The elegant solutions provided by the continued-fraction formalism allow us to study the system in any range of coupling, where other methods in the literature would be inadequate. In particular, Slonczewsky resonances are clearly established in the strong-coupling case.

I. INTRODUCTION

The Jahn-Teller effect in localized systems has been the subject of many investigations in recent years (see, for instance, the comprehensive book of Perlin and Wagner[1] and references quoted therein). In general, a vibronic system includes a huge number of electronic-vibrational states, and several approaches have been developed in the literature to treat such large numbers of degrees of freedom. Among them, the continued fraction approach is having an increasing interest as a very flexible tool to treat the problem.[2]

The $E\otimes\epsilon$ vibronic system is of particular importance for its prototype character. The system includes any orbital non-Kramers doublets belonging to the doubly degenerate irreducible representation both of the cubic, tetrahedral point groups as well as the point groups having nonvanishing angular momentum (D_{6h}, D_6, C_{6h}, C_{6v}, C_6 D_{3d}, D_{3h}, D_3, C_{3i}, C_{3v}, C_{3h}, C_3) interacting with a two-dimensional mode of ϵ symmetry.

The purpose of this paper is to examine the $E\otimes\epsilon$ Jahn-Teller system by systematically applying the powerful tool of iterative procedures.[3,4] In the literature there are only some preliminary attempts in this direction,[5-7] especially for what concerns the optical properties. The main result of this work is to provide a continued-fraction solution not only for the optical absorption, but also for the angular momentum reduction values and for the magnetic circular dichroism, because we can construct a continued fraction whose coefficients are analytic. We can thus calculate, without restrictions, all the physical quantities of interest.

In Sec. II we briefly outline some relevant concepts of the adiabatic principle, in order to make our paper reasonably self-contained and to show explicitly why and where to apply the continued-fraction procedure. As a specific example we consider the system of E symmetry interacting with a two-dimensional vibration of ϵ symmetry. In Sec. III, we consider the $E\otimes\epsilon$ Jahn-Teller system adopting the continued-fraction procedure. We give the explicit continued-fraction expression of all relevant physical quantities, including magnetic field effects, for any values of the coupling constants. We then calculate for a number of situations the absorption spectrum, the magnetic circular dichroism, and the Slonczewsky oscillations. Section IV contains the conclusions.

II. OUTLINE OF THE ADIABATIC APPROXIMATION AND STANDARD TREATMENT OF THE JAHN-TELLER $E\otimes\epsilon$ MODEL

In this section we briefly discuss the adiabatic approximation and the traditional treatment of the Jahn-Teller $E\otimes\epsilon$ model by means of the coupled differential equation formulation; this summary is done in order to allow a useful comparison with the continued-fraction method, which is exploited in the next section.

The Hamiltonian of a general polyatomic system (molecules, clusters, or crystals) constitutes a formidable problem whose solution goes through the adiabatic approximation,[8] completely discussed, for instance, in Ref. 9; a very detailed analysis of the concepts and the procedures is also provided in Ref. 10, with attention to the approximations, and consequent terminologies, usually adopted. Here we only remind the leading role of the two basic approaches known as the "moving-basis approach," and the "fixed-basis approach"; in the former the vibronic system is expressed in terms of the electronic wave functions depending parametrically on the nuclear coordinates, while in the latter the basis wave functions are eigenfunctions of the Hamiltonian with the nuclei fixed in a given configuration, usually a high symmetry one.

Both the approaches lead to a system of coupled differential equations, completely equivalent from a formal point of view, because a unitary transformation can be found to pass from a basis to another. However, the moving-basis approach is particularly useful in the situations where the electronic wave functions are smooth functions of the nuclear coordinates, otherwise their first and second derivatives, with respect to the nuclear coordinates, may introduce strong "effective" potentials in the differential equations. Near the connection of two (or more) surface potential sheets, it can be convenient to use the alternative fixed-basis approach; this avoids the explicit appearance of derivatives of the wave function with respect to nuclear coordinates and instead a well-behaved potential function matrix element couple the different degenerate (or quasidegenerate) electronic states.

The general equations corresponding to the different approach can be specified to our case of interest, i.e., a double degenerate electronic system of symmetry E interacting with a vibrational mode of symmetry ϵ, a problem considered under one or another of its several and interesting aspects by a number of authors.[7,11–18] The standard treatment with coupled differential equations, leads through a quite laborious procedure, to the well-known results provided in Ref. 12. Looking back to these results and noticing how relatively complicated the procedure was to obtain them, our inkling was that a much simpler road should be available to arrive at them. It is evident that it is important to find it, both for its intrinsic interest and for the possibility of appropriate generalization (for instance, the inclusion of magnetic field effects).

III. CONTINUED FRACTION SOLUTION OF THE $E\otimes\epsilon$ SYSTEM

Lead by some formal similarities with recent treatments[2] of Jahn-Teller systems, we decided to study the Hamiltonian of the $E\otimes\epsilon$ system directly, with the recursion method. For this purpose we use the fixed-basis approach. Let us indicate with ψ_1,ψ_2 the degenerate electronic states of symmetry E for the nuclei fixed in the symmetry position. We consider a linear coupling with a vibrational mode of symmetry ϵ, and we take the energy of the electronic states as the reference energy. By expanding the Hamiltonian up to the second order in the normal symmetrized coordinates Q_1 and Q_2, we obtain

$$H=-\frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial Q_1^2}+\frac{\partial^2}{\partial Q_2^2}\right]+V_E\begin{vmatrix}-Q_1 & Q_2\\ Q_2 & Q_1\end{vmatrix} +\tfrac{1}{2}M\omega_\epsilon^2(Q_1^2+Q_2^2)\ . \tag{1}$$

In Eq. (1) V_E is the linear coupling constant, ω_ϵ is the angular frequency of the ϵ mode, and the operators that are not written explicitly in matrix form, are intended to be multiplied by the identity 2×2 unit matrix.

It is convenient to introduce the phonon creation and annihilation operators a_1, $a_1^\dagger$ and a_2, $a_2^\dagger$ for the two partner modes of symmetry ϵ; the corresponding states can be labeled by the occupation numbers 1 and m, respectively. The basis functions chosen are thus the direct product of the two degenerate electronic functions $|\psi_1\rangle$, $|\psi_2\rangle$ and of the vibrational functions $|lm\rangle$. In such a basis, the total Hamiltonian (1), which is the sum of the electronic and of the vibrational parts (H_e+H_L) and of the coupling part (H_{e-L}), can be written as

$$H=H_e+H_L+H_{e-L} \tag{2a}$$

with

$$H_e+H_L=\hbar\omega_\epsilon\sum_{\substack{i=1,2\\ l,m=0,\infty}}|\psi_i;lm\rangle(l+m+1)\langle\psi_i;lm| \tag{2b}$$

and

$$\begin{aligned}H_{e-L}=k_E\hbar\omega_\epsilon\sum_{l,m=0,\infty}[&-|\psi_1;lm\rangle\langle\psi_1;lm|(a_1+a_1^\dagger)+|\psi_2;lm\rangle\langle\psi_2;lm|(a_1+a_1^\dagger)\\ &+|\psi_1;lm\rangle\langle\psi_2;lm|(a_2+a_2^\dagger)+|\psi_2;lm\rangle\langle\psi_1;lm|(a_2+a_2^\dagger)]\ ,\end{aligned} \tag{2c}$$

here $\hbar\omega_\epsilon$ is the energy of the mode ϵ and k_E is an adimensional coupling constant related to V_E in the form

$$\frac{V_E}{(2M\hbar)^{1/2}\omega_\epsilon^{3/2}}\equiv k_E\ .$$

It is now straightforward to apply the general concepts[3] and methodology of the recursion method.[2,19,20] Starting from an appropriate initial state we can generate a hierarchical chain of states according to the standard three terms recursion relations, which we can briefly summarize as follows. Let $|f_0\rangle$, $|f_1\rangle$, $\cdots$ $|f_n\rangle$ indicate the first $n+1$ normalized functions of the recursion hierarchy and a_n,b_n the corresponding parameters; let $|F_{n+1}\rangle$ be the (unnormalized) function defined as

$$|F_{n+1}\rangle=H|f_n\rangle-a_n|f_n\rangle-b_n|f_{n-1}\rangle\ . \tag{3}$$

The next pairs of parameters b_{n+1} and a_{n+1} is given by the normalization of the state $|F_{n+1}\rangle$ and by the expectation value of the Hamiltonian on it, namely,

$$b_{n+1}^2=\langle F_{n+1}|F_{n+1}\rangle,\quad a_{n+1}=\frac{\langle F_{n+1}|H|F_{n+1}\rangle}{\langle F_{n+1}|F_{n+1}\rangle}\ . \tag{4}$$

After normalization, the steps reported above can be repeated and further functions of the hierarchy can be obtained.

The above procedure is now applied to our vibronic model $E\otimes\epsilon$, described by the Hamiltonian (2). In general, we may write the expansion

$$|F_n\rangle=\sum_{\substack{i=1,2\\ l,m=0,\infty}}c_{i,lm}^{(n)}|\psi_i;lm\rangle\ . \tag{5}$$

By means of Eqs. (2), (3), and (4) the explicit recursion relations for the coefficients $c_{i,lm}^{(n)}$ can be easily obtained, and the parameters a_n and b_n determined. If we choose as an initial state of the hierarchy $|f_0\rangle = |\psi_1;00\rangle$ (corresponding to the total angular momentum $j=\frac{1}{2}$), we obtain for the coefficients a_n and b_n^2 of the recursion the useful analytic expression

$$\begin{aligned} a_n &= (n+1)\hbar\omega_E, \quad n=0,1,\ldots, \\ b_n^2 &= 2I\left[\frac{n+1}{2}\right](k_E\hbar\omega_\epsilon)^2, \quad n=1,2,\ldots, \end{aligned} \tag{6}$$

where $I(\cdots)$ indicates the integer part of $(\cdots)$. We define the Huang-Rhys factor S in the usual form $S=k_E^2$ or equivalently $S\hbar\omega_\epsilon = E_{\mathrm{JT}}$ (the Jahn-Teller energy) and we can write a close expression for the Green's function:

$$G_{00}(E)=\cfrac{1}{E-\hbar\omega_\epsilon-\cfrac{2S(\hbar\omega_\epsilon)^2}{E-2\hbar\omega_\epsilon-\cfrac{2S(\hbar\omega_\epsilon)^2}{E-3\hbar\omega_\epsilon-\cfrac{4s(\hbar\omega_\epsilon)^2}{E-4\hbar\omega_\epsilon\ddots}}}} \tag{7}$$

The poles of the continued fraction of Eq. (7) give the eigenvalues of the vibronic system and their residua give the projected density of states, which is proportional to the absorption spectrum. The eigenvalues can be determined with any wished accuracy considering a sufficient number of steps of the continued fraction (7) (typically from a few tens to a few thousands, depending on the coupling k_E increasing from $k_E \le 1$ to $k_E \approx 30$). To have the residua in the poles we notice that $1/G_{00}(E)$ is a linear function of E in a small interval around the pole (in the limit of E tending to the eigenvalue) and the angular coefficients is the inverse of the residuum in the pole. It is thus straightforward to calculate any property related to the projected density of states.

We begin to discuss the optical properties of the $E\otimes\epsilon$ vibronic system and the dipole-allowed transition between a nondegenerate ground state (called A for brevity) and the double degenerate E states ($A\rightarrow E$ transition). For increasing values of S, the absorption shape exhibits two peaks of different height and width, separated by almost $2\sqrt{S}\,\hbar\omega_\epsilon$, as predicted by the distribution probability of a two-dimensional harmonic oscillator in the ground state. This behavior has been found experimentally in several systems: for example, in the optical absorption spectra of Fe^{2+} and Ti^{3+} in AgCl and AgBr,[21–23] of Fe^{2+} in CdCl and CdBr (Ref. 24) taken at different temperatures. Increasing the temperature, the separation between the peaks is increased and also the height of the second peak, similarly to what expected increasing the effective value of S.

For very large values of S, other peaks appear, due to a nonadiabatic mixing of different vibronic states (Slonczewski resonances between vibrational levels of the two adiabatic surface sheets).[24–27] Habitz and Schwarz calculate these resonance energies near the branching points by the quasiclassical quantization rule:

$$\int_0^{\rho_t}\sqrt{2M[E-W_2(\rho)]}\,d\rho = n\pi\hbar, \quad n=1,2,\ldots . \tag{8}$$

Here ρ_t is one of the turning points $[\rho_t = \rho_0(-1+\sqrt{1+E/E_{\mathrm{JT}}})]$; ρ_0 is the coordinate ρ at the

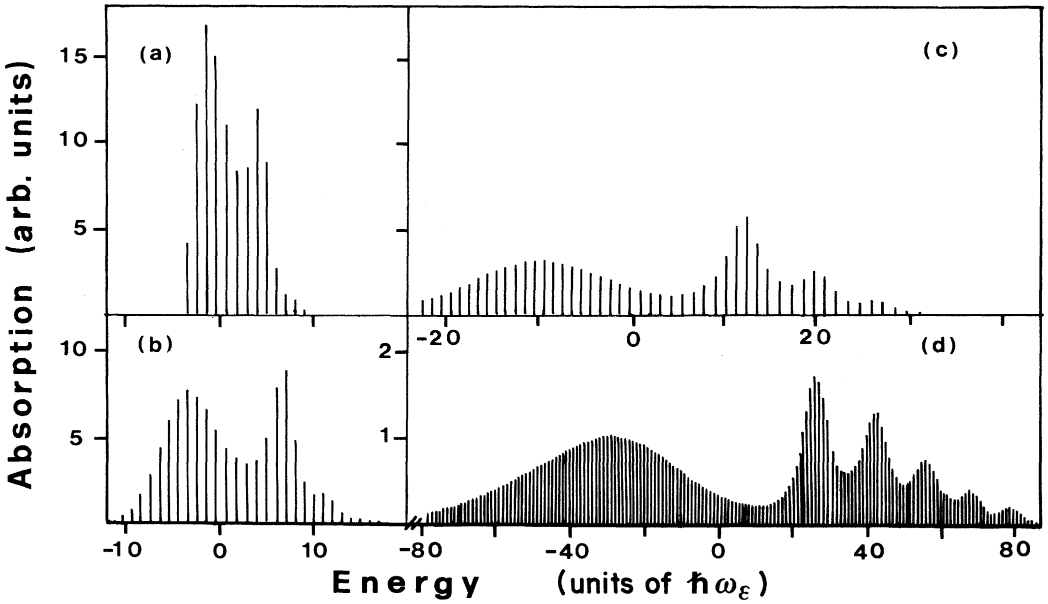

FIG. 1. Calculated absorption, in arbitrary units, of the transition $A\rightarrow E$ for a vibronic $E\otimes\epsilon$ system. (a) $S=4$; (b) $S=16$; (c) $S=100$; (d) $S=900$. The energy is in units of $\hbar\omega_\epsilon$.

minimum of the potential sheet; W_2 is the upper branch of the potential sheet. This calculation gives $E_n=(\frac{3}{2}n\pi\hbar\omega_\epsilon)^{2/3}E_{\mathrm{JT}}^{1/3}$. It is easily verified that the differences between the peaks (for $E_n>0$) found by our exact calculations with continued fractions, confirm the qualitative results of the quasiclassical model.

In Fig. 1 we show the typical palisades for the absorption spectrum obtained with $S=4$ (case a), $S=16$ (case b), $S=100$ (case c), $S=900$ (case d). Technically, the spectra (a) and (b) can be obtained either diagonalizing the tridiagonal matrix of suitable dimensions or by direct calculations of the Green's function $G_{00}(E)$. The spectra (c) and (d) have been obtained from $G_{00}(E)$ with a large number of recursions ($\sim 10\,000$).

The calculation of the absorption spectrum for whatever value of S is not the only goal achieved by the recursion techniques. It is also possible to evaluate the effect of an external field, for example, a magnetic field applied along the trigonal axis of a trigonal-symmetry compound. The doubly degenerate vibronic levels are split by the applied magnetic field H_a into two Zeeman sublevels. It is straightforward to introduce the Zeeman term $H_z=\mu H_a L_z$ in the total Hamiltonian (2) of the system and to construct the recursion coefficients. On the basis functions ψ_1 and ψ_2, previously defined, the Hamiltonian H_z takes the form

$$H_z=\mu H_a\begin{vmatrix} 0 & -i \\ i & 0 \end{vmatrix} . \tag{9}$$

It is convenient to choose as the initial state of the recursion

$$|f_0\rangle=(|\psi_1;00\rangle+i|\psi_2;00\rangle)/\sqrt{2}\ .$$

Without any approximation, we obtain the following coefficients of the recursion:

$$\begin{aligned} a_n&=(n+1)\hbar\omega_\epsilon+(-1)^n\mu H_a, \quad n=0,1,\cdots ,\\ b_n^2&=2I\left[\frac{n+1}{2}\right](k_E\hbar\omega_\epsilon)^2, \quad n=1,2,\cdots . \end{aligned} \tag{10}$$

The calculation of the continued fraction

$$G_{00}(E)=\cfrac{1}{E-\hbar\omega_\epsilon-\mu H_a-\cfrac{2S(\hbar\omega_\epsilon)^2}{E-2\hbar\omega_\epsilon+\mu H_a-\cfrac{2S(\hbar\omega_\epsilon)^2}{E-3\hbar\omega_\epsilon-\mu H_a-\cfrac{4S(\hbar\omega_\epsilon)^2}{\ddots}}}} \tag{11}$$

gives, for any vibronic coupling and Zeeman term, the eigenvalues and the intensity of the absorption $I_+(\omega)$ for the right-hand circularly polarized light. Changing the polarization [the initial state of the chain is now $|f_0\rangle=1/\sqrt{2}(|\psi_1;00\rangle-i|\psi_2 00\rangle)$] the coefficients a_n and b_n^2 are as follows:

$$\begin{aligned} a_n&=(n+1)\hbar\omega_\epsilon+(-1)^{n+1}\mu H_a, \quad n=0,1,\cdots ,\\ b_n^2&=2I\left[\frac{n+1}{2}\right](k_E\hbar\omega_\epsilon)^2, \quad n=1,2,\cdots . \end{aligned} \tag{12}$$

We can calculate the magnetic circular dichroism (MCD) I_+-I_- (neglecting the small-energy difference introduced by the magnetic field). In Fig. 2 we show the MCD calculated for $S=4$ and $S=16$. We observe an oscillatory behavior of the MCD, quenched by the vibronic coupling. We can also calculate the reduction factor γ_p (see Fig. 3) for the electronic orbital angular momentum in the p vibronic level, defined as the ratio of the effective g value in the presence and in the absence of the Jahn-Teller coupling. In our case γ_p is given by the ratio

$$\gamma_p=(E_{+p}^{\mathrm{JT}}-E_{-p}^{\mathrm{JT}})/(-1)^p2\mu H_a\ . \tag{13}$$

$E_{\pm p}^{\mathrm{JT}}$ are the eigenvalues in the presence of the vibronic coupling and the magnetic field. The reduction factors can now be easily calculated for any coupling S. It is shown to be oscillating and quenched by the vibronic coupling, as previously observed in Ref. 28 for small S.

As a final remark we notice that we have considered the Hamiltonian H, defined by Eqs. (2), in connection with seed states with $j=\frac{1}{2}$. We can derive the general form of the coefficients a_n and b_n^2 of the recursion, whatever the total angular momentum of the initial state. Properly choosing the initial state we easily obtain

$$\begin{aligned} a_n&=(j+\tfrac{1}{2}+n)\hbar\omega_\epsilon, \quad n=0,1,\cdots ,\\ b_{2n-1}^2&=2(j-\tfrac{1}{2}+n)(k_E\hbar\omega_\epsilon)^2, \\ &\qquad\qquad n=1,2,\cdots ,\\ b_{2n}^2&=2n(k_E\hbar\omega_\epsilon)^2\ . \end{aligned} \tag{14}$$

In the case of $j=\frac{1}{2}$ we obtain back the expression (6) of the recursion parameters.

IV. CONCLUSIONS

We have examined systematically the $E\otimes\epsilon$ vibronic system in connection with the continued fraction formalism, whose flexibility provides an elegant solution of all the physical properties of interest. We can obtain an ana-

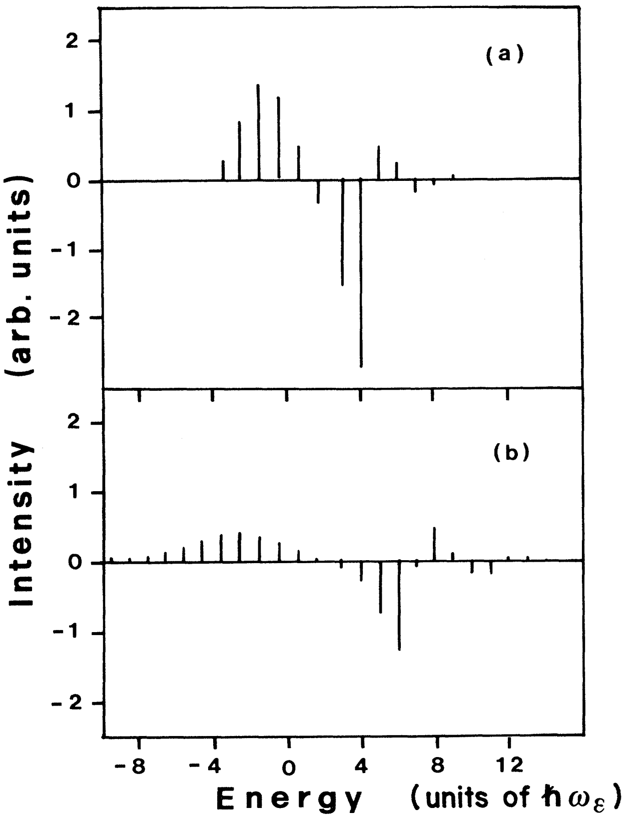

FIG. 2. Magnetic circular dichroism, in arbitrary units, of the transition $A \rightarrow E$ for a vibronic $E \otimes \epsilon$ system. (a) $S=4$; (b) $S=16$. The energy is in units of $\hbar\omega_\epsilon$.

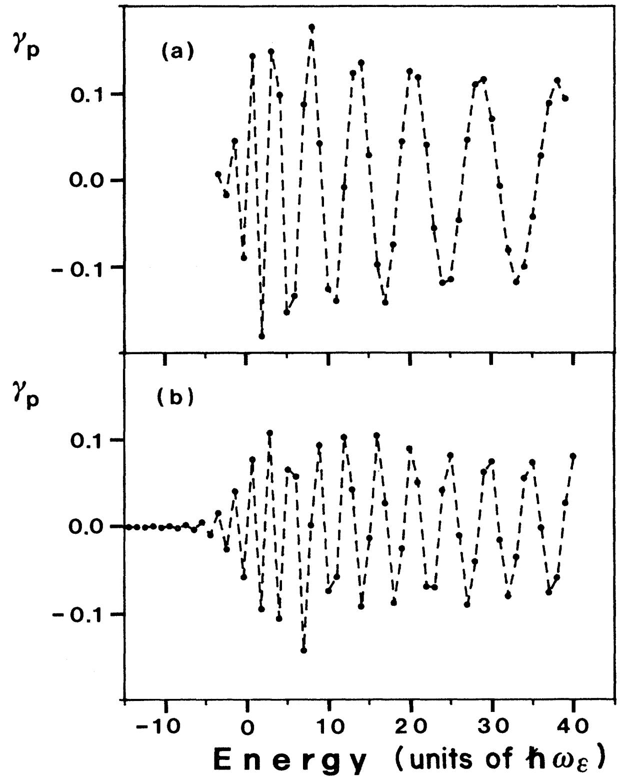

FIG. 3. Reduced orbital angular momentum γ_p of the vibronic levels with $j=\frac{1}{2}$, (a) $S=4$; (b) $S=16$. The energy is in units of $\hbar\omega_\epsilon$.

lytic expression for the coefficients of the continued fraction, also in the presence of an external magnetic field. The vibronic system spectrum can be calculated accurately for any strength of the electron-phonon coupling parameter. This study of the absorption spectrum, of the magnetic dichroism, and of the reduction factors in the prototype $E \otimes \epsilon$ vibronic system, besides its intrinsic interest, should foster a more widespread use of the continued-fraction apparatus in the study of coupled electron-boson systems.

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