Abstract

The coupling between doubly degenerate electronic states and doubly degenerate vibrations is analysed for an octahedral system on the basis of the introduction of an anharmonic Morse potential for the vibronic part. The vibrations are described by anharmonic coherent states and their linear coupling with the electronic states is considered. The matrix elements of the vibronic interaction are built and the energy levels corresponding to the interaction Hamiltonian are derived.

1 Introduction

The case of an octahedrally coordinated metal-ion presenting a doubly degenerate (non-Kramers) electronic state of symmetry $E$ interacting with a doubly degenerate vibrational state of symmetry $\varepsilon$ constitutes one of the most studied Jahn-Teller system [1-9]. In a cluster model [10], the Hamiltonian $H$ of the system reads

$$H = H_e + H_v + H_{JT}. \quad (1)$$

In Eq. (1), $H_e$ stands for the Hamiltonian of the electronic part, $H_v$ represents the vibrational Hamiltonian and $H_{JT}$ is the Jahn-Teller interaction. To fix the notations, we briefly review the different contributions to $H$ in the usual case of harmonic vibrations.
The electronic Hamiltonian $H_e$ is well-known. For transition metal-ions, it is convenient to work in the strong-field coupling scheme. We denote as $|\theta\rangle$ and $|\varepsilon\rangle$ the uncoupled electronic wavefunctions corresponding to $H_e$ and transforming according to the two-dimensional irreducible representation $E$ (or $E_g$) of the octahedral (or complete octahedral) point group $O$ (or $O_h$).

We consider vibrations for the doubly degenerate modes with normal co-ordinates $Q_1$ and $Q_2$ sharing a common frequency $\omega$. Let $P_1$ and $P_2$ be the generalized momenta associated to $Q_1$ and $Q_2$, respectively. Both sets \{Q_1, Q_2\} and \{P_1, P_2\} transform as basis functions for the irreducible representation $E$ of the group $O$. The vibrational Hamiltonian $H_v$ is

$$H_v = \frac{1}{2m}(P_1^2 + P_2^2) + \frac{m\omega^2}{2}(Q_1^2 + Q_2^2),$$

(2)

where $m$ is the effective mass for the two-dimensional harmonic oscillator in the plane $(Q_1, Q_2)$. The operator $H_v$ can be expressed as

$$H_v = \hbar \omega (a_1^\dagger a_1 + a_2^\dagger a_2 + 1)$$

in terms of $\hbar \omega$ and of the creation operators $a_k^\dagger$ and the annihilation operators $a_k$ associated to the couples $(Q_k, P_k)$ with $k = 1, 2$.

The coupling between the harmonic vibrations of the ligands and the electronic functions localized around the metal-cation can be described by means of the linear Jahn-Teller Hamiltonian

$$H_{JT} = \sqrt{2m\omega^2E_{JT}}(Q_1D_\theta + Q_2D_\varepsilon).$$

(3)

In Eq. (3), $D_\theta$ and $D_\varepsilon$ are normalized operators in the electronic space with the well-known representation [11,12]

$$D_\theta = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad D_\varepsilon = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

and $E_{JT}$ is the Jahn-Teller energy. The energy $E_{JT}$ is connected to the vibronic coupling constant $K$ by the relationships

$$K = \sqrt{\hbar \omega E_{JT}}.$$

The interaction Hamiltonian $H_{JT}$ can thus be rewritten as

$$H_{JT} = K[(a_1^\dagger + a_1)D_\theta + (a_2^\dagger + a_2)D_\varepsilon].$$
in terms of $K$ and of the operators $a_k^\dagger$ and $a_k$ with $k = 1, 2$. A simple consideration of the interaction Hamiltonian $H_{JT}$ shows that the mode $Q_1$ splits the two-fold degeneracy of the electronic partners $|\theta\rangle$ and $|\varepsilon\rangle$ while the mode $Q_2$ mode mixes $|\theta\rangle$ and $|\varepsilon\rangle$.

In order to obtain analytic expressions for quantities of physical interest, as for example the energies of the levels or the Ham factor, it is necessary to use wavefunctions for the part $H_e + H_v$ of the Hamiltonian (1). Such wavefunctions are products of electronic wavefunctions (of type $|\theta\rangle$ or $|\varepsilon\rangle$) with wavefunctions that describe the vibration of the ligands. For the latter wavefunctions, we can use coherent states arising from an harmonic oscillator with a linear potential that changes the equilibrium point but not the frequency.

The use of the coherent states in the Jahn-Teller effect goes back to the idea that the coupling between local vibrations and electronic orbitals involves an operator linear in the normal modes in a first approximation [13,14]. In this direction, the study of the Jahn-Teller effect using Glauber coherent states as well as some applications to particular systems are well-known [15-19]. The Glauber coherent states can be written as

$$|G(\rho)\rangle = \exp\left(-\frac{1}{2}|\rho|^2\right) \exp(\rho a^\dagger)|00\rangle,$$

where $|00\rangle$ is the usual ground state for the two-dimensional harmonic oscillator with vanishing occupation numbers $n_1$ and $n_2$. In Eq. (4), we use the vectors $\rho = (\rho_1, \rho_2)$ and $a^\dagger = (a_1^\dagger, a_2^\dagger)$. In view of

$$a_k|G(\rho)\rangle = \rho_k|G(\rho)\rangle,$$

the Glauber coherent state $|G(\rho)\rangle$ is an eigenstate of the annihilation operator $a_k$ with the complex eigenvalue $\rho_k$ ($k = 1, 2$).

In orbital doublet systems, the potential energy surface, in the linear coupling approximation, has a continuous set of minimas which are commonly described as forming a "Mexican hat". In actual (i.e., physical) $E \otimes \varepsilon$ systems, isolated minimas arise either from an ion - lattice interaction term which is quadratic in the displacements of the normal coordinates or from vibrations which are anharmonic in such coordinates. Both terms warp the potential energy surface so that three minimas are formed as a result of one of these terms acting either separately or together with the others. For these
reasons the surface that represents the adiabatic potential warps and, along the bottom of the trough of the hat, three wells occur, alternating regularly with three humps known as "tricorns" [8]. Öpik and Pryce [2] and O'Brien [6] took into account the quadratic terms of vibronic coupling in the Jahn-Teller Hamiltonian and established the influence of these terms on the energy levels of the system.

In general, the replacement of the harmonic oscillator potential by the anharmonic Morse potential [20,21] turns out to be an efficient way for describing anharmonicity of the vibrations. On the other hand, the anharmonic coherent states for the Morse potential have been recently investigated with great details [22]. Therefore, it is the aim of the present paper to consider a deviation from the harmonic approximation in the nuclear motions, i.e., to explicitly introduce the vibronic anharmonicity by using the Morse potential. More precisely, we study in this work the case of an octahedral Jahn-Teller system for which the doubly degenerate electronic states are coupled with the doubly degenerate vibrational states taken as the anharmonic coherent states for a two-dimensional Morse potential.

2 Morse anharmonic vibrations

The Hamiltonian $H$ of the $E \otimes \varepsilon$ octahedral Jahn-Teller system has the same form as in (1) but the contribution $H_v$ represents now the vibrational Hamiltonian for a two-dimensional Morse oscillator. We thus replace the Hamiltonian (2) by the double Morse oscillator Hamiltonian:

$$H_v = \sum_{k=1}^{2} H_{vk}$$

with

$$H_{vk} = \frac{p_k^2}{2m} + V_0(e^{-2\alpha x_k} - 2e^{-\alpha x_k}),$$

where $m$ is as before the effective mass for the oscillator, $\alpha$ (with $\alpha > 0$) the anharmonic constant and $V_0$ a positive constant. Furthermore, $x_k$ is the displacement from the equilibrium position for the $k$-th dimension and $p_k$ the associated momentum ($k = 1, 2$). (The new conjugated variables $x_k$ and $p_k$ correspond to the variables $Q_k$ and $P_k$ of Section 1, respectively.) We also
use the reduced parameter
\[ \nu = \sqrt{\frac{8mV_0}{\alpha^2 \hbar^2}}. \]

The eigenvalues \( E_0(n_k) \) of the operator \( H_{v_k} \) are given by
\[ E_0(n_k) = -\hbar \Omega \left( n_k - \frac{\nu - 1}{2} \right)^2, \]
where
\[ \hbar \Omega = \frac{4V_0}{\nu^2} \]
and
\[ n_k = 0, 1, \ldots, N \]
with
\[ N = \left\lfloor \frac{\nu - 1}{2} \right\rfloor. \]
(As usual, \( \lfloor r \rfloor \) denotes the entire part of the real number \( r \).)

The eigenfunction \( \psi_{n_k} : \mathbb{R}_+ \to \mathbb{R} \) of \( H_{v_k} \) corresponding to the level \( E_0(n_k) \) is given by [20]
\[ \psi_{n_k}(y_k) = c_{n_k} y_k^{s_k} e^{-\frac{\nu - 1}{2} y_k} F(-n_k, 2s_k + 1, y_k), \quad (5) \]
in terms of the new variable
\[ y_k = \nu e^{-\alpha x_k}. \]

In Eq. (3), the function \( F \) is the confluent hypergeometric function, the parameter \( s_k \) reads
\[ s_k = \frac{\nu - 1}{2} - n_k, \]
and the factor
\[ c_{n_k} = \frac{1}{\Gamma(\nu - 2n_k) \sqrt{\frac{\Gamma(\nu - n_k)}{n_k!}}} \]
is a normalization constant. Finally, we shall use the Dirac notation
\[ |n_1, n_2\rangle = \psi_{n_1}(y_1)\psi_{n_2}(y_2) \]
for the vibrational eigenstates of the two-dimensional Morse oscillator. In
this notation, the relationships
\[ \langle n_1, n_2 | n'_1, n'_2 \rangle = \delta(n'_1, n_1)\delta(n'_2, n_2). \]
expresses the orthonormalization of the states \(|n_1, n_2\rangle\) on the Hilbert space \(L^2(\mathbb{R}^2_+, dx_1dx_2)\).

3 The anharmonic coherent states

In some previous works [22], we have discussed the rôle played by a creation
operator \(b_+\), an annihilation operator \(b_-\) and an energy operator \(b_0\) for de-
scribing the dynamical algebra of the one-dimensional Morse oscillator. The
results of Ref. [22] can be extended to a two-dimensional isotropic Morse
oscillator by introducing creation operators \(b_{+k}\), annihilation operators \(b_{-k}\)
and energy operators \(b_{0k}\) (with \(k = 1, 2\)) that parallel the operators \(b_+\), \(b_-\)
and \(b_0\), respectively. The operators \(b_{\pm k}\) and \(b_{0k}\) are defined by the differential
forms
\[ b_{\pm k} = (2s_k \mp 1) \frac{\partial}{\partial y_k} \pm \frac{s_k(2s_k + 1)}{y_k} \mp \frac{\nu}{2}, \quad (6) \]
\[ b_{0k} = -y_k \frac{\partial^2}{\partial y_k^2} - \frac{\partial}{\partial y_k} + \frac{s_k^2}{y_k} + \frac{y_k}{2} - s_k + \frac{\nu}{2} - 1, \quad (7) \]
with \(k = 1, 2\). They obey the commutation relations
\[ [b_{+k}, b_{-l}] = 2b_{0k}\delta(k, l), \quad [b_{\pm k}, b_{0l}] = \pm b_{\pm k}\delta(k, l), \]
where \(k\) and \(l = 1, 2\). Therefore, the set \(\{b_{\pm k}, b_{0k} : k = 1, 2\}\) generates the
Lie algebra of the group \(\text{SU}(1, 1) \otimes \text{SU}(1, 1)\). The action of this set on the
space \(L^2(\mathbb{R}^2_+, dx_1dx_2)\) is defined through
\[ b_{+1}|n_1, n_2\rangle = \sqrt{(n_1 + 1)(\nu - n_1 - 1)}|n_1 + 1, n_2\rangle, \]
\[ b_{+2}|n_1, n_2\rangle = \sqrt{(n_2 + 1)(\nu - n_2 - 1)}|n_1, n_2 + 1\rangle, \]
\[ b_{-1}|n_1, n_2\rangle = -\sqrt{n_1(\nu - n_1)}|n_1 - 1, n_2\rangle, \]
\[ b_{-2}|n_1, n_2\rangle = -\sqrt{n_2(\nu - n_2)}|n_1, n_2 - 1\rangle, \]
\[ b_{0k}|n_1, n_2\rangle = \left(\frac{\nu - 1}{2} - n_k\right)|n_1, n_2\rangle, \quad k = 1, 2. \]

The operators \( b_{\pm k} \) and \( b_{0k} \) given by (6) and (7) are \( s_k \)-dependent, i.e., energy-dependent. It is hence necessary to introduce new generators of the Lie group \( SU(1, 1) \otimes SU(1, 1) \) which do not depend on \( s_k \) and which have an action on the states \( |n_1, n_2\rangle \) similar to the one of \( b_{\pm k} \) and \( b_{0k} \). This may be achieved with the aid of two auxiliary variables \( \xi_k \) of a phase type \((\xi_k \in [0, 2\pi])\) for \( k = 1, 2 \). To be precise, let us define the operators

\[
a_{\pm k} = e^{\mp i\xi_k} \left\{ \frac{2}{i} \frac{\partial}{\partial y_k} \pm 1 \right\} \frac{\partial}{\partial y_k} \pm \frac{1}{y_k} \left[ \frac{1}{i} \frac{\partial}{\partial \xi_k} \left( \frac{2}{i} \frac{\partial}{\partial \xi_k} \mp 1 \right) \right] \mp \frac{\nu}{2} \}
\]

and

\[
a_{0k} = \frac{1}{i} \frac{\partial}{\partial \xi_k},
\]

with \( k = 1, 2 \). The commutators of the operators \( a_{+k}, a_{-k} \) and \( a_{0k} \) are

\[
[a_{+k}, a_{-l}] = 2a_{0k}\delta(k, l), \quad [a_{\pm k}, a_{0l}] = \pm a_{\pm k}\delta(k, l),
\]

with \( k \) and \( l = 1, 2 \). In addition, we have

\[
[a_{0k}, e^{\pm i\xi_l}] = \pm e^{\pm i\xi_k}\delta(k, l),
\]

with \( k \) and \( l = 1, 2 \).

As a result of our transformation from the \( b \)'s to the \( a \)'s, it appears that the wave-function \( \psi_{n_k} \) belongs to a ray defined via

\[
\Phi_{n_k}(y_k, \xi_k) = e^{i\xi_k\psi_{n_k}(y_k)}.
\]

The function \( \Phi_{n_k} \) is of course an eigenfunction of \( H_v \) with the eigenvalue \( E_0(n_k) \) and the action of the operators \( a_{\pm k} \) and \( a_{0k} \) on \( \Phi_{n_k} \) is

\[
a_{+l}\Phi_{n_k}(y_k, \xi_k) = \sqrt{(n_k + 1)(\nu - n_k - 1)}\Phi_{n_k+1}(y_k, \xi_k)\delta(k, l), \]

\[
a_{-l}\Phi_{n_k}(y_k, \xi_k) = -\sqrt{n_k(\nu - n_k)}\Phi_{n_k-1}(y_k, \xi_k)\delta(k, l), \]

\[
a_{0l}\Phi_{n_k}(y_k, \xi_k) = s_k\Phi_{n_k}(y_k, \xi_k)\delta(k, l),
\]

where \( k \) and \( l = 1, 2 \). We close this section with a remarkable result: The vibrational Hamiltonian \( H_v \) can be written as

\[
H_v = -\hbar\Omega(a_{01}^2 + a_{02}^2)
\]

in terms of the energy operators \( a_{01} \) and \( a_{02} \).
The Jahn-Teller interaction

The Jahn-Teller interaction Hamiltonian \( H_{JT} \) for the studied system has the form

\[
H_{JT} = \kappa \hbar \Omega (\mu^+ \mu^{\dagger})^E (x_1 + x_2),
\]

where \( \mu^+ \) and \( \mu \) represent the creation and annihilation operators for the doubly degenerate electronic states of the system (the label \( E \) indicates that the operator acts on the electronic states) and \( \kappa \) is the strength of the Jahn-Teller coupling (\( \kappa \) corresponds to \( K \) in units of \( \hbar \Omega \)).

We want to write the operator \( H_{JT} \) in terms of the operators \( a_{\pm k} \) and \( a_{0k} \). For this purpose, we start from the relations

\[
\frac{\partial}{\partial y_k} = -\frac{1}{2} \sum_{m=0}^{\infty} (2a_{0k})^m \left\{ e^{+i\xi_k}a_{+k} - (-1)^m e^{-i\xi_k}a_{-k} + \frac{\nu}{2} \left[ 1 + (-1)^m \right] \right\}
\]

and

\[
\frac{1}{y_k} = -\sum_{m=0}^{\infty} (2a_{0k})^{m-1} \left\{ e^{+i\xi_k}a_{+k} + (-1)^m e^{-i\xi_k}a_{-k} + \frac{\nu}{2} \left[ 1 - (-1)^m \right] \right\}.
\]

The coordinate

\[
x_k = \frac{1}{\alpha} (\ln \nu - \ln y_k)
\]

can be expanded in the form of a series

\[
x_k = \frac{\ln \nu}{\alpha} - \frac{1}{\alpha} \sum_{n=1}^{\infty} \frac{1}{n} \left( 1 - \frac{1}{y_k} \right)^n
\]

or more precisely

\[
x_k = \frac{1}{\alpha} \left\{ \ln \nu - \sum_{n=1}^{\infty} \frac{1}{n} \left[ 1 + \nu \sum_{m=0}^{\infty} (2a_{0k})^{2m} \right] \right. \\
+ \left. \sum_{m=0}^{\infty} (2a_{0k})^{m-1} \left[ e^{+i\xi_k}a_{+k} + (-1)^m e^{-i\xi_k}a_{-k} \right] \right\}.
\]

As a result, the Hamiltonian \( H_{JT} \) can be expressed as

\[
H_{JT} = \frac{1}{\alpha} \kappa \hbar \Omega (\mu^+ \mu^{\dagger})^{(E)} \left\{ 2 \ln \nu - \sum_{k=1}^{2} \sum_{n=1}^{\infty} \frac{1}{n} \left[ 1 + \nu \sum_{m=0}^{\infty} (2a_{0k})^{2m} \right] \right. \\
+ \left. \sum_{m=0}^{\infty} \left[ e^{+i\xi_k}a_{+k} + (-1)^m e^{-i\xi_k}a_{-k} \right] \right\}.
\]
\[ + \sum_{m=0}^{\infty} (2a_{0k})^{m-1} [e^{i\xi k} a_{+k} + (-1)^m e^{-i\xi k} a_{-k}]^m \] \right\}.

The latter development in powers of the operators \(a_{\pm k}\) and \(a_{0k}\) (with \(k = 1,2\)) is of central importance for the treatment of the vibronic interaction.

Following the approach in Ref. [14], the wavefunctions of the electron-phonon system will be written as the overlap

\[ |\beta_{nz}\rangle = \int_{0}^{2\pi} d\varphi |\beta\rangle e^{iz\varphi} e^{ika} (a_+ - \kappa)^n \Phi_0(y_1, \xi_1) \Phi_0(y_2, \xi_2), \]

where \(\beta\) refers to the lower branch (\(\beta = l\)) or to the upper branch (\(\beta = u\)) for which we have

\[ |l\rangle = \cos \frac{\varphi}{2} |\theta\rangle - \sin \frac{\varphi}{2} |\varepsilon\rangle, \]

\[ |u\rangle = \sin \frac{\varphi}{2} |\theta\rangle + \cos \frac{\varphi}{2} |\varepsilon\rangle, \]

and where the creation operator \(a_+\) is defined by

\[ a_+ = a_1 \cos \varphi + a_2 \sin \varphi. \]

The phase factor \(\varphi\) in Eqs. (10-13) is an arbitrary angle and the parameter \(z\) in Eq. (10) characterizes the type of vibronic coupling. For example, the case \(z = \frac{1}{2}\) corresponds to the states accessible by electric dipole radiation from the zero-phonon ground state.

The states \(|\beta_{nz}\rangle\) can be rewritten in a new form by expanding the right hand-side of (10). This leads to

\[ |\beta_{nz}\rangle = \sum_{p=0}^{\infty} \sum_{q=0}^{n} \int_{0}^{2\pi} d\varphi |\beta\rangle e^{iz\varphi} C_q^n a_+^{n+p-q} |00\rangle \]

\[ = \sum_{p=0}^{\infty} \sum_{q=0}^{n} (-1)^q \frac{p^q L_{n+p}^{n-p} \kappa^{n-p} \kappa^n \Phi_{\beta}^n}{p!} |\beta_{n,c}\rangle, \]

where \(C_q^n\) is a binomial coefficient, \(|\beta_{pz}\rangle_0\) stands for \(|\beta_{pz}\rangle\) with \(\kappa = 0\), and \(L_n^{n-p}\) is a generalized Laguerre polynomial [23]. Thus, the states \(|\beta_{n0}\rangle\) correspond to the case of a vanishing coupling and \(|\beta_{n\frac{1}{2}}\rangle\) to the case of a weak interaction.
coupling. The states (10) are eigenstates of the operators $b_{+k}$ (with $k = 1, 2$) and of the Hamiltonian (8). Therefore, they are appropriate for obtaining the energy due to the Jahn-Teller interaction.

To find the energy levels of the system with vibronic interactions, we calculate the matrix elements of the Hamiltonian $H_{JT}$ with respect to the states (10) and use standard perturbation theory. For this purpose, we use the notation $|n\rangle^0 = |\beta nz\rangle$ for the state vectors in the zero-th order approximation and consider the Jahn-Teller interaction as a perturbation of the system described by $H_e + H_v$. The wavefunctions of the Hamiltonian (8), in the first-order approximation of perturbation theory, have the expression

$$|n\rangle^1 = |n\rangle^0 - \sum_{m=0, m\neq n}^N \frac{1}{E_0(m) - E_0(n)} |m\rangle^0 \langle m|H_{JT}|n\rangle^0 |m\rangle^0.$$  

As a result, the first-order energy of the system is

$$E = E_0 + E_{JT},$$

where

$$E_0 = \langle n|H_e + H_v|n\rangle^0$$

is the energy without the Jahn-Teller interaction and

$$E_{JT} = \langle n|H_{JT}|n\rangle^0$$

is the energy of the Jahn-Teller interaction. The calculation of the wavefunctions and the energy corrections using the coherent states (10) is difficult because the expressions for the matrix elements of $H_{JT}$ are very complicated. Moreover, the utilization of the operator $\exp(i\kappa a_+)$ instead of the unitary operator $\exp(i(\kappa a_+ - \kappa^* a))$, where $a$ is the adjoint of $a_+$, in building the coherent states is rigorous only for the case of the harmonic oscillator corresponding to the ordinary Weyl-Heisenberg algebra. For this reason, we calculate the matrix elements $E_{JT}$ by using the Jahn-Teller Hamiltonian (4). It can be proved that the matrix elements corresponding to the last term of Eq. (4) vanish. As a final result, we obtain

$$E_{JT} = \frac{1}{\alpha \kappa \hbar \Omega} \sum_{p,q=0}^N (-1)^p \frac{n!^2 \kappa^{p+q-2n}}{plq!} L_p^{n-p} L_q^{n-q} (\kappa^2) L_p^{n-q} (\kappa^2)$$

$$10$$
\[ \langle \beta | (\mu^+ \mu)^{(E)} | \beta \rangle \left\{ 2 \ln \nu - \sum_{k=1}^{2} \sum_{l=0}^{\infty} \frac{1}{l} \left[ 1 + \nu \sum_{m=0}^{\infty} (\nu - 1 - 2p)^{2m} \right]^l \right\}, \]

where \( N \) is such that \( N + 1 \) is the total number of states for the one-dimensional Morse oscillator.

5 Conclusions

We studied the vibronic coupling between doubly degenerate vibrations and doubly degenerate electronic states of an octahedral system. In order to describe the vibrations of the system, we used a new type of anharmonic coherent states. We described the dynamical system by introducing two auxiliary variables \( \xi_k \) (with \( k = 1, 2 \)) of extra-phase type and new eigenfunctions of the Hamiltonian for the anharmonic vibrations. The eigenfunctions of the Hamiltonian of the system in absence of the vibronic interaction were builted using the overlap of electronic states and these new anharmonic coherent states. In the first-order approximation of perturbation theory, the energies due to the Jahn-Teller interaction were calculated. The results show that the anharmonic effects on the Jahn-Teller interaction can be expressed in a rigorous form and are contained in the constants \( s_k (k = 1, 2) \). The work reported in this paper constitutes the most general algebraic analysis of the Jahn-Teller interaction for \( E \otimes \varepsilon \) octahedral systems with anharmonic vibrations.

Acknowledgements

The authors are grateful to Prof. E. Duval (Université Claude Bernard Lyon 1) for interesting comments. Two of the authors (N.M. A. and Gh.E. D.) wish to acknowledge the Institut de Physique Nucléaire de Lyon for the kind hospitality extended to them in the final stage of this paper and the CNCSIS (Romania) for financial support under the grant 12625/1(1998).

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