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A Non-Linear Canonical Transformation for the Dynamical Jahn-Teller Problem in Cubic Symmetry (Optical Resonance Effect)

By

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One of the two fundamental dynamical Jahn-Teller problems in point-symmetry surrounding, the T–t problem, is handled by means of a non-linear canonical transformation. The latter is established by analogy to the doubly degenerate problem, where the corresponding tranformation is shown to be quasi-exact. Combinatorial as well as series expansion methods are presented. Pronounced resonance effects are found for the zero, one, and higher phonon lines. This reflects the fact that the effective splitting of the degeneracy in the high energy system may be of the same order of magnitude as the elementary excitation in the low energy one.

Eines der beiden fundamentalen dynamischen Jahn-Teller-Probleme in Punkt-Symmetrie-Umgebung, das sogenannte T–t-Problem, wird mit Hilfe einer nichtlinearen kanonischen Transformation behandelt. Zur Aufstellung der letzteren wird die Analogie zum zweifach entarteten Problem benutzt, wo gezeigt werden kann, daß die entsprechende Transformation quasi-exakt ist. Es werden sowohl kombinatorische als auch Reihenentwicklungsmethoden dargelegt. Ausgeprägte Resonanzeffekte ergeben sich für die Null-, Ein-, und Mehr-Phononen-Llinien. Dies reflektiert die Tatsache, daß die effektive Aufspaltung der Entartung im hochenergetischen System von derselben Größenordnung sein kann wie die Elementaranregung im niederenergetischen.

1. Introduction

After the formulation of the Jahn-Teller (J. T.) theorem on the configurational stability of molecules [1] ("static J. T. effect", "J.T. distortion"), it has been only recently that there has been a growing interest for the fundamental problem of the coupling between degenerate high- and low-energy systems ("dynamical J.T. effect"). For a good review we refer to the articles of Longuet-Higgins [2], Sturge [3], and Ham [4].

In this study we discuss one of the two fundamental pure J.T. situations which may appear in a point-symmetry configuration. It consists of a threefold degenerate "fast" system (excitonic high-frequency oscillator) which interacts with a threefold degenerate "slow" system (low-frequency oscillator). We call this the T–t system. For more details about the characterization of this system we refer to two preceding papers of one of us (M. W.) [5, 6]. Since the corresponding non-degenerate coupling problem can be completely diagonalized by a non-linear canonical transformation [6], and since in the case of the coupled twofold degeneracies (J.T. case E–e) a quasi-exact non-linear canonical trans-

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formation can also be found, as shown in a preceding paper [7], we are confident to have some success with a similar transformation for the triply degenerate coupling case. This will be the aim of the present investigation.

We define our system by the Hamiltonian [5, 6] ($\hbar = 1$)

$$H(x, X) = H_e(x) + H_v(X) + \varkappa V(x, X) , \tag{1.1}$$

where the Hamiltonian for the fast (two-level) system is given by

$$H_e = \omega_0 \sum_{i=1}^{3} a_i^+ a_i , \tag{1.2}$$

and for the slow system by

$$H_v = \omega_1 \sum_{j=1}^{3} b_j^+ b_j . \tag{1.3}$$

The interaction operator is of the form [5, 6]

$$V = \sum_{k=1}^{3} (a_k^+ a_{k+1} + a_k a_{k+1}^+) (b_{k+2} + b_{k+2}^+) , \tag{1.4}$$

where we have omitted all terms with $a_i^+ a_i^+$, $a_i a_i$ (double creation and annihilation). The form of the interaction follows from group-theoretical argumentation in a cubic system [5, 6]. The total Hamiltonian is chosen in a form of utmost simplicity, which however still incorporates the "dynamical resonance effect", which is expected to appear between the effective splitting of the excited electronic state and the elementary excitation in the low-frequency system. We continually assume

$$\omega_0 \gg \omega_1, \varkappa$$

which allows us the kind of "Condon approximation" incorporated in the choice of the Hamiltonian (1.1). From this we have an electronic subspace of the total Hilbert space, the eigenstates of which are fixed in their analytic form, and only originally degenerate states can be mixed via the interaction. The total J.T. wave functions for the excited electronic state "b" read

$$\Psi_m^{(b)}(x, X) = \sum_{i=1}^{3} \psi_i^{(b)}(x) \, \Phi_{i\,m}^{(b)}(X) , \tag{1.5a}$$

where i labels the degeneracy of the fast system and m the quantum number of the slow system. For the electronic ground state "a" we have

$$\Psi_n^{(a)}(x, X) = \psi_0^{(a)}(x) \, \Phi_n^{(a)}(X) . \tag{1.5b}$$

The orthonormality and closure relations of the wavefunctions of the slow system read [5]

$$\sum_i \langle \Phi_{i\,m}^{(b)}(X) | \Phi_{i\,m'}^{(b)}(X) \rangle = \delta_{m\,m'} , \tag{1.6a}$$

$$\sum_m | \Phi_{i\,m}^{(b)}(X) \rangle \langle \Phi_{i'\,m}^{(b)}(X') | = \delta_{i\,i'} \, \delta\,(X - X') . \tag{1.6b}$$

We describe the dynamical behaviour of our system by its response to an electromagnetic stimulans from outside. This response is given as the optical absorption cross-section [8]

$$\sigma(\omega) = K \, \omega \, I_{b\,a}(\omega) , \tag{1.7}$$

where

$$I_{\mathrm{ba}}(\omega) = \left[\mathrm{Tr}^{(\mathrm{a})} \exp\left(-\frac{H}{k_{\mathrm{B}}T}\right)\right]^{-1} \times$$
$$\times \sum_n \sum_m \exp\left(-\frac{\omega_n^{(\mathrm{a})}}{k_{\mathrm{B}}T}\right) |\langle \Psi_m^{(\mathrm{b})}(x, X)|\ P(x)\ |\Psi_n^{(\mathrm{a})}(x, X)\rangle|^2 \times$$
$$\times\ \delta\,(\omega_m^{(\mathrm{b})} - \omega_n^{(\mathrm{a})} - \omega) \tag{1.8a}$$

and K is a constant containing the static and dynamic dielectric constants and the local electric field. In our context K is of no relevance. The external light field is assumed to be coupled to the electronic system only, whence we choose the following form for the dipole operator (polarization in x_1-direction):

$$P(x) = e\,x_1 = p\,(a_1 + a_1^+)\ . \tag{1.9}$$

$\omega_n^{(\mathrm{a})}$ and $\omega_m^{(\mathrm{b})}$ are the energies of the initial and final states, respectively. We may put $\omega_0^{(\mathrm{a})} = 0$.

Limiting ourselves to $T = 0$ we arrive at

$$\underset{T\to 0}{I_{\mathrm{ba}}(\omega)} = p^2\,G_0(\omega)\ , \tag{1.8b}$$

where

$$G_0(\omega) = \sum_m |\langle \Psi_m^{(\mathrm{b})}|\ (a_1 + a_1^+)\ |\Psi_0^{(\mathrm{a})}\rangle|^2\ \delta\,(\omega - \omega_m^{(\mathrm{b})})\ . \tag{1.10}$$

2. Non-Linear Canonical Transformation

We perform the unitary transformation

$$\tilde{H} = H + [H, S] + \frac{1}{2!}\,[[H, S], S] + \cdots\ , \tag{2.1}$$
$$\tilde{\Psi} = \mathrm{e}^{-S}\,\Psi\ ,$$

where S is anti-Hermitian, $S^+ = -S$, and in close analogy with the non-degenerate [6] and the E–e cases [9] we choose $\big(\lambda = (\varkappa/\omega_1)\,\eta(\varkappa)\big)$

$$S = \lambda \sum_{l=1}^{3} (a_l^+\,a_{l+1} + a_{l+1}^+\,a_l)\,(b_{l+2} - b_{l+2}^+)\ , \tag{2.2}$$

where a cyclic notation has been used, $l + 3 \equiv l$. The transformed Hamiltonian has the form

$$\tilde{H} = [\omega_0 - 2\,\varkappa\,(\lambda - \eta(\varkappa))] \sum_{i=1}^{3} a_i^+\,a_i + \omega_1 \sum_{j=1}^{3} b_j^+\,b_j + H_{\mathrm{nd}}\ , \tag{2.3}$$

where $\eta(\varkappa)$ very nearly is a constant, $\eta \sim \mathrm{O}(\lambda^2)$ for $\lambda \to 0$. From the E–e case we know that the remaining non-diagonal term H_{nd} is of order λ^2 for $\lambda \to 0$, and equally $H_{\mathrm{nd}} \to 0$ for $\lambda \gg 1$ [7]. By analogy we tacitly assume here also that H_{nd} does not play any decisive role. Hence we will neglect it in the following. The transformed J.T. wave functions then are given by

$$|\tilde{f}\rangle = \psi_i^{(\mathrm{b})}\,\Phi_{m_1 m_2 m_3} = a_i^+ \prod_{j=1}^{3} \frac{(b_j^+)^{m_j}}{\sqrt{m_j!}}\,|0\rangle; \qquad i = 1, 2, 3\ . \tag{2.4}$$

This wave function later will be denoted by $|a_i^+\ m_1\ m_2\ m_3\rangle$. For the absorption function (see. equation (1.10)) we then arrive at

$$G_0(\omega) = \left\{ \sum_{i=1}^{3} \sum_{m=0}^{\infty} \sum_{(m_1, m_2, m_3 = 0)}^{(m = m_1 + m_2 + m_3)} |\langle \tilde{f}| \, e^{-S} \, a_1^+ \, e^{+S} \, |0\rangle|^2 \right\} \times$$
$$\times \, \delta \left(\omega - \omega_0 + 2 \varkappa (\lambda - \eta) - \omega_1 (m_1 + m_2 + m_3) \right) . \quad (2.5)$$

In this approximation we expect equidistant lines as in the non-J.T. case. The delta functions are at the positions $\omega_m = \omega_0 - 2\varkappa(\lambda - \eta) + \omega_1 m$ with $m = 0, 1, 2, \ldots$. From (2.5) it is seen that in our further procedure we have to concentrate on the calculation of the matrix elements $\langle \tilde{f}| \, e^{-S} \, a_1^+ \, e^{+S} \, |0\rangle$. In calculating these exactly we use two equivalent approaches. The first one is outlined in Section 3: After applying e^{+S} onto the vacuum state, we expand e^{-S} in a power series in S. By introducing complete orthonormal systems the problem is reduced to the calculation of three combinatorial problems and the matrix elements $\langle m| \, (b_i - b_i^+)^\nu \, |0\rangle$. No analytically closed form, however, is found for these combinatorial problems.

We avoid the difficulties of solving these combinatorial problems in our second approach. By means of a recurrence formula (cf. Section 4) we find an exact expression for a_1^+, which is suitable to calculate the zero-, one-, etc. phonon lines.

3. First Approach in Calculating the Transformed Optical Absorption Function

After expanding e^{-S} in (2.5) in a power series in S and introducing the closure relation for the wave functions of the fast system we arrive at

$$G_0(\omega) = \sum_{i=1}^{3} \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \sum_{m_3=0}^{\infty} \Bigg| \sum_{p=0}^{\infty} \frac{(-1)^p}{p!} \sum_{j_1=1}^{3} \sum_{j_2=1}^{3} \cdots \sum_{j_{p-1}=1}^{3} \times$$
$$\times \, \langle \Phi_{m_1 m_2 m_3}| \underbrace{S_{1 j_1} S_{j_1 j_2} S_{j_2 j_3} \ldots S_{j_{p-1} 1} \, |\Phi_0\rangle}_{p\text{-factors}} \Bigg|^2 \delta(\ldots) , \quad (3.1)$$

where the elements of the matrix S_{ik} are

$$S = \{\langle a_k^+| \, S \, |a_l^+\rangle\} = (\lambda) \begin{pmatrix} 0 & b_3 - b_3^+ & b_2 - b_2^+ \\ b_3 - b_3^+ & 0 & b_1 - b_1^+ \\ b_2 - b_2^+ & b_1 - b_1^+ & 0 \end{pmatrix} . \quad (3.2)$$

A single term in (3.1) has p factors S_{kl} and is characterized by the set (ν_1, ν_2, ν_3). Its form is

$$(\lambda)^{\nu_1 + \nu_2 + \nu_3} \langle m_1| \, B_1^{\nu_1} \, |0\rangle \langle m_2| \, B_2^{\nu_2} \, |0\rangle \langle m_3| \, B_3^{\nu_3} \, |0\rangle , \quad (3.3)$$

where

$$B_i = b_i - b_i^+ ; \qquad i = 1, 2, 3 . \quad (3.4)$$

B_i occurs ν_i-times and

$$\nu_1 + \nu_2 + \nu_3 = p . \quad (3.5)$$

The total number $Z_i(\nu_1, \nu_2, \nu_3)$ of existing terms belonging to a certain set (ν_1, ν_2, ν_3) is described by three combinatorial problems (for $i = 1, 2, 3$). We obtain

$$\tilde{G}_0(\omega) = \sum_{i=1}^{3} \sum_{m_1, m_2, m_3 = 0}^{\infty} \Bigg| \sum_{p=0}^{\infty} \frac{(-1)^p}{p!} (\lambda)^p \sum_{\nu_1 + \nu_2 + \nu_3 = 0}^{\nu_1, \nu_2, \nu_3 = p} Z_i(\nu_1, \nu_2, \nu_3) \times$$
$$\times \, \langle m_1| \, B_1^{\nu_1} \, |0\rangle \langle m_2| \, B_2^{\nu_2} \, |0\rangle \langle m_3| \, B_3^{\nu_3} \, |0\rangle \Bigg|^2 \delta(\ldots) . \quad (3.6)$$

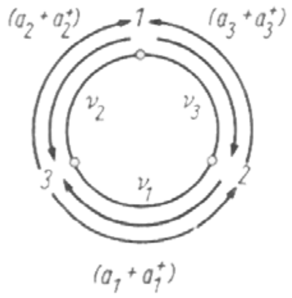

Fig. 1. Illustration for the combinatorial problem of the Jahn-Teller system T–t (explanation see text)

By introducing Z_i in the expression of the optical absorption function the $(p-1)$ sums over j are reduced to only three sums over ν_i the latter ones are actually only two independent sums because of (3.5).

To solve the combinatorial problems it is convenient to express them as a circle (Fig. 1) (see [5]). $Z_i(\nu_1, \nu_2, \nu_3)$ is equal to the number of paths starting in point i $(i = 1, 2, 3)$ and ending in point 1 and intersecting section 1 ν_1-times, section 2 ν_2-times, section 3 ν_3-times.

In particular for $i = 1$ we write $Z_1(\nu_1, \nu_2, \nu_3) \equiv X(\nu_1, \nu_2, \nu_3)$, where X is obtained by means of the recurrence formula

$$X(\nu_1, \nu_2, \nu_3) = \sum_{i=0}^{2i \leq \nu_1} [X(\nu_1 - 2i, \nu_2, \nu_3 - 2) + X(\nu_1 - 2i, \nu_2 - 2, \nu_3)] + \\ + 2 \sum_{i=0}^{2i \leq (\nu_1 - 1)} X(\nu_1 - 1 - 2i, \nu_2 - 1, \nu_3 - 1) \tag{3.7}$$

with the boundary condition

$$X(0, 0, 0) = 1 . \tag{3.8}$$

(For the derivation of this formula see [5].) Similarly for $i = 2$, writing $Z_2(\nu_1, \nu_2, \nu_3) \equiv P(\nu_1, \nu_2, \nu_3)$, we have the recurrence formula (see [5])

$$P(\nu_1, \nu_2, \nu_3) = P(\nu_1, \nu_2 - 2, \nu_3) + Q(\nu_1 - 1, \nu_2 - 1, \nu_3) + \\ + Q(\nu_1, \nu_2, \nu_3 - 1) , \tag{3.9}$$

where $Q(\nu_1, \nu_2, \nu_3)$ is the number of closed paths starting and ending in point 2. For Q follows a recurrence formula which has a similar structure as (3.7). The boundary conditions are now

$$P(0, 0, 1) = P(1, 1, 0) = 1, \qquad Q(0, 0, 0) = 1 . \tag{3.10}$$

For the case $i = 3$, writing $Z_3(\nu_1, \nu_2, \nu_3) \equiv U(\nu_1, \nu_2, \nu_3)$, we have

$$U(\nu_1, \nu_2, \nu_3) = U(\nu_1, \nu_2, \nu_3 - 2) + W(\nu_1 - 1, \nu_2, \nu_3 - 1) + \\ + W(\nu_1, \nu_2 - 1, \nu_3) \tag{3.11}$$

and the boundary conditions

$$U(0, 1, 0) = U(1, 0, 1) = 1 , \qquad W(0, 0, 0) = 1 , \tag{3.12}$$

and similarly to X and Q the values for $W(\nu_1, \nu_2, \nu_3)$ are obtained from a recurrence formula which denotes the number of closed paths starting and ending in point 3.

The calculation of the matrix elements $\langle m_i| (b_i - b_i^+)^{\nu_i} |0\rangle$ is carried out by an extension of a method used in a previous paper (see [5] and [9]). The result is

$$\langle m| (b - b^+)^{m+2\mu} |0\rangle = (-1)^{m+\mu} \frac{(m + 2\mu)!}{\mu!\, m!} \sqrt{m!} \left(\frac{1}{2}\right)^{\mu}, \tag{3.13}$$

all matrix elements for $\nu \neq m + 2\mu$ being zero.

Hence the normalized optical absorption function ($T = 0$) reads

$$G_0(\omega) = \sum_{i=1}^{3} \sum_{m_1, m_2, m_3 = 0}^{\infty} \left| \sum_{p=0}^{\infty} \frac{1}{p!} \left(\frac{\varkappa}{\omega_1}\right)^p \frac{\sqrt{m_1!\, m_2!\, m_3!}}{m_1!\, m_2!\, m_3!} \times \right.$$
$$\times \sum_{\mu_1, \mu_2, \mu_3 = 0}^{\text{cond. } I^*} \left(-\frac{1}{2}\right)^{\mu_1+\mu_2+\mu_3} \frac{(m_1 + 2\mu_1)!\, (m_2 + 2\mu_2)!\, (m_3 + 2\mu_3)!}{\mu_1!\, \mu_2!\, \mu_3!} \times$$
$$\left. \times Z_i (m_1 + 2\mu_1, m_2 + 2\mu_2, m_3 + 2\mu_3) \right|^2 \delta\left(\omega - \omega_0 + 2\varkappa(\lambda - \eta) - \omega_1 m\right). \tag{3.14}$$

where the condition I^* is given by

$$\mu_1 + \mu_2 + \mu_3 = \frac{1}{2} (p - m_1 - m_2 - m_3) \geqq 0$$

and even. From this we obtain the zero-phonon line as a specialization. Since in this case $m_1 = m_2 = m_3 = 0$, we obtain

$$Z_1 (2\mu_1, 2\mu_2, 2\mu_3) \neq 0, \quad Z_2 (2\mu_1, 2\mu_2, 2\mu_3) = Z_3 (2\mu_1, 2\mu_2, 2\mu_3) = 0$$

for $\mu_i = 0, 1, 2, \ldots$ ($i = 1, 2, 3$), and for the strength of the zero-phonon line:

$$A_0 = \left| \sum_{p=0}^{\infty} \frac{(-1)^p}{(2p)!} (\lambda)^{2p} M_{2p} \right|^2, \tag{3.15}$$

where

$$M_{2p} = \sum_{\mu_1, \mu_2, \mu_3 = 0}^{p = \mu_1 + \mu_2 + \mu_3} (2\mu_1 - 1)!!\, (2\mu_2 - 1)!!\, (2\mu_3 - 1)!!\, Z_1(2\mu_1, 2\mu_2, 2\mu_3) \tag{3.16}$$

and

$$\frac{(2\mu)!}{\mu!\, 2^\mu} = (2\mu - 1)!!; \qquad (-1)!! = 1\,. \tag{3.17}$$

The quantity M_{2p} has been tabulated up to $p = 6$ (see [5]) and is proportional to the $(2p)$-th moment in the strong coupling limit.

4. Calculation of the Transformed Dipole Operator by Means of a Recurrence Formula

The alternative approach in calculating the matrix element $\langle f| \tilde{a}_1^+ |0\rangle$ is to express the dipole part $\tilde{a}_1^+ = e^{-S} a_1^+ e^{+S}$ in a closed formula. We expand

$$\tilde{a}_1^+ = a_1^+ + [a_1^+, S] + \frac{1}{2} [[a_1^+, S] S], + \cdots =$$
$$= \sum_{n=0}^{\infty} \frac{S^{(n)}\{a_1^+\}}{n!} = \exp S\{a_1^+\}, \tag{4.1}$$

where $S^{(n)}\{a_1^+\}$ is the n-th commutator,

$$S^{(n)}\{a_1^+\} = \Big[[[\ldots [a_1^+, S], S], \ldots], S\Big]_n, \tag{4.2}$$

and $\exp S\{a_1^+\}$ is only a shorthand notation of the preceding series. Employing the abbreviations

$$\beta = \lambda\, B_1\,, \quad \gamma = \lambda\, B_2\,, \quad \delta = \lambda\, B_3\,, \tag{4.3}$$

where $B_i = (b_i - b_i^+)$, we find the following general structure for the n-th commutator:

$$S^{(n)}\{a_1^+\} = a_1^+\,\beta_n + a_2^+\,\gamma_n + a_3^+\,\delta_n\,, \tag{4.4}$$

where the coefficients $\beta_n, \gamma_n, \delta_n$ can be calculated by means of the recurrence formula

$$\left.\begin{aligned} \beta_{n+1} &= -(\gamma\,\gamma_n + \delta\,\delta_n)\,,\\ \gamma_{n+1} &= -(\gamma\,\beta_n + \beta\,\delta_n)\,,\\ \delta_{n+1} &= -(\delta\,\beta_n + \beta\,\gamma_n) \end{aligned}\right| \tag{4.5}$$

with the boundary condition

$$\beta_0 = 1\,, \qquad \gamma_0 = \delta_0 = 0\,. \tag{4.6}$$

Although the recurrence formula is cyclic, we obtain a non-cyclic application because of the boundary condition (4.6). Employing the abbreviations

$$\Pi = \beta\,\delta\,\gamma\,, \quad (\Sigma) = \beta^2 + \gamma^2 + \delta^2\,, \quad S = \gamma^2 + \delta^2\,, \tag{4.7}$$

we can calculate now the coefficients step by step and find the general expressions

$$\begin{aligned} &\beta_0 = 1 \qquad \text{for} \qquad n = 0\,,\\ &\beta_{2n} = \sum_{l=0}^{3l\leq n} (2\,\Pi)^{2l}\,(\Sigma)^{n-3l-1} \left\{\binom{n-l-1}{2l-1}(\Sigma) + S\binom{n-l-1}{2l}\right\}, \end{aligned} \tag{4.8a}$$

$$\begin{aligned} &\gamma_0 = 0 \qquad \text{for} \qquad n = 0\,,\\ &\gamma_{2n} = \beta\,\delta \sum_{l=0}^{3l\leq(n-1)} (2\,\Pi)^{2l}\,(\Sigma)^{n-3l-2} \left\{\binom{n-l-1}{2l}(\Sigma) + 2\,\gamma_1^2\binom{n-l-1}{2l+1}\right\}, \end{aligned} \tag{4.8b}$$

$$\begin{aligned} &\beta_1 = 0 \qquad \text{for} \qquad n = 0\,,\\ &\beta_{2n-1} = -2\,\Pi \sum_{l=0}^{3l\leq(n-1)} (2\,\Pi)^{2l}\,(\Sigma)^{n-3l-2} \left\{\binom{n-l-1}{2l}(\Sigma) + S\binom{n-l-1}{2l+1}\right\}, \end{aligned} \tag{4.8c}$$

$$\begin{aligned} &\gamma_1 = -\gamma \qquad \text{for} \qquad n = 0\,,\\ &\gamma_{2n-1} = -\gamma \sum_{l=0}^{3l\leq n} (2\,\Pi)^{2l}\,(\Sigma)^{n-3l-2} \left\{\binom{n-l}{2l}(\Sigma)^2 + 2\,\beta_1^2\,\delta_1^2\binom{n-l-1}{2l+1}\right\}, \end{aligned} \tag{4.8d}$$

where the expressions for δ_{2n} and δ_{2n+1} are identical to (4.8b) and (4.8c), when we exchange, respectively, δ and γ.

In (4.8) we have used the usual boundary conditions for the binominal coefficients:

$$\binom{0}{k} = \delta_{0k}\,, \quad \binom{n}{0} = 1 \quad \text{for} \quad n = 0, \pm 1, \pm 2, \ldots\,. \tag{4.9}$$

From (4.1) we thus have

$$\tilde{a}_1^+ = \sum_{n=0}^{\infty} \left(\frac{S^{2n}\{a_1^+\}}{(2n)!} + \frac{S^{2n+1}\{a_1^+\}}{(2n+1)!} \right) = \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} \times$$
$$\times \{a_1^+ [(2n+1)\beta_{2n} + \beta_{2n+1}] + a_2^+ [(2n+1)\gamma_{2n} + \gamma_{2n+1}] +$$
$$+ a_3^+ [(2n+1)\delta_{2n} + \delta_{2n+1}]\} . \qquad (4.10)$$

5. Zero-Phonon Line ($T = 0$)

In order to calculate the zero-phonon line we use (4.10) and (2.5) for $m_1 = m_2 = m_3 = m = 0$. After integrating over the electronic coordinates we arrive at

$$A_0 = \left| \sum_{n=0}^{\infty} \frac{1}{(2n)!} \langle 0| \beta_{2n} |0\rangle \right|^2 , \qquad (5.1)$$

where we have used the fact that the matrix elements $\langle 0| (b_i - b_i^+)^\nu |0\rangle$ are non-zero only for the specification given in (3.13). By symmetry argumentation

$$\langle 0| S |0\rangle = \frac{2}{3} \langle 0| (\Sigma) |0\rangle \qquad (5.2)$$

and using (4.8a),

$$A_0 = \left| 1 + \sum_{n=1}^{\infty} \frac{1}{3(2n-1)!} \sum_{l=0}^{3l \leq n} 2^{2l} \frac{1}{(n-l)} \binom{n-l}{2l} \langle 0| (\Pi)^{2l} (\Sigma)^{n-3l} |0\rangle \right|^2 . \qquad (5.3)$$

Inserting (4.7) and employing (3.13) for $m = 0$ we obtain after some elementary transcriptions

$$\langle 0| (\Pi)^{2l} (\Sigma)^{n-3l} |0\rangle = \left[-\frac{(\lambda)^2}{2} \right]^n I_1^{(0)} . \qquad (5.4)$$

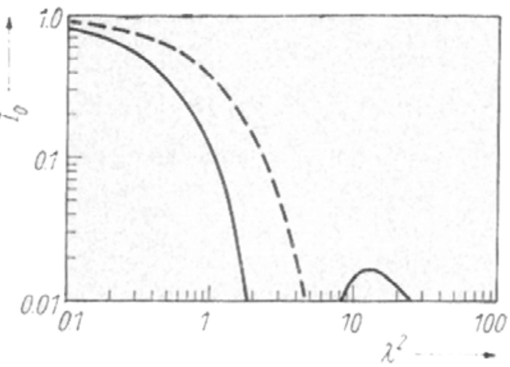

Fig. 2

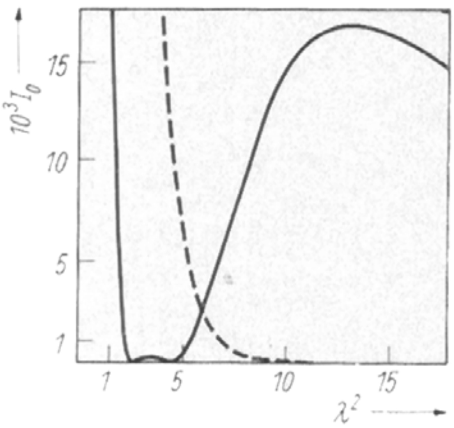

Fig. 3

Fig. 2. Intensity $I_0(\lambda^2)$ of the zero-phonon absorption for the T–t J.T. case. λ is a measure for the coupling strength. For comparison the non-J.T. result is given also (dashed line)

Fig. 3. Intensity $I_0(\lambda^2)$ of the zero-phonon absorption for the T–t J.T. case. λ is a measure for the coupling strength. For comparison the non-J.T. result is given also (dashed line). (Enlarged picture in a linear measure)

where

$$I_1^{(0)} = \sum_{\nu=0}^{n-3l} \binom{n-3l}{\nu} \frac{[2(n-2l-\nu)]!}{(n-2l-\nu)!} I_2^{(0)} ; \tag{5.5}$$

$$I_2^{(0)} = \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} \frac{[2(l+\nu-\mu)]!\,[2(l+\mu)]!}{(l+\nu-\mu)!\,(l+\mu)!} . \tag{5.6}$$

With the help of combinatorial identities [10] we are able to perform the summations over μ and ν in (5.5) and (5.6) and finally arrive at the following expression for the zero-phonon line:

$$A_0 = \left| 1 + \frac{2}{3} \sum_{n=1}^{\infty} \frac{(2n+1)}{(n-1)!} \left[-\frac{(\lambda)^2}{2} \right]^n \sum_{l=0}^{3l \leq n} \frac{4^l\,[(2l)!]^2\,(3l)!\,(n-l-1)!}{(l!)^3\,(6l+1)!\,(n-3l)!} \right|^2 . \tag{5.7}$$

In Fig. 2 and 3 the strength of the zero-phonon line is plotted against $(\lambda)^2$. The line has the two minima for $(\lambda)^2 \approx 2.769$ and ≈ 4.423 and two maxima for $(\lambda)^2 \approx 3.48$ and ≈ 13.15. For very small and large values of $(\lambda)^2$ the strength approaches the behaviour of the non-J.T. case. The minimal points are explained as quantum-mechanical resonance points of the dynamic J.T. system, which occur when the energy splitting of the degenerate high-frequency levels is in the same order as the energy excitations of the low-frequency oscillators.

6. One-Phonon Line

The calculation of the one-phonon line is done in a similar fashion as the one outlined in Section 5. The only non-vanishing matrix elements are now

$$L_1 = \langle 001 | \gamma_{2n+1} | 0 \rangle \neq 0 \tag{6.1}$$

and

$$K_1 = \langle 010 | \delta_{2n+1} | 0 \rangle \neq 0 . \tag{6.2}$$

K_1 differs from L_1 only in so far as δ and γ are exchanged. Therefore $L_1 = K_1$. And for the one-phonon line we find

$$A_1 = 2 \left| \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \langle 001 | \gamma_{2n+1} | 0 \rangle \right|^2 = 2\lambda^2 \left| 1 + \sum_{n=1}^{\infty} \frac{4(2n+3)}{n!} \left[-\frac{\lambda^2}{2} \right]^n \times \right.$$
$$\times \sum_{l=0}^{3l \leq n} 4^l \frac{[(2l+1)!]^3\,(3l+2)!}{(l!)^3\,(6l+4)!} \left\{ \binom{n-l}{2l} \frac{1}{(2l+1)^2} + \right.$$
$$\left. \left. + \binom{n-l-1}{2l+1} \frac{2}{(6l+5)\,(6l+7)} \right\} \right|^2 . \tag{6.3}$$

Fig. 4 shows the strength of the one-phonon line in dependence of (λ^2). Resonance points occur for $(\lambda^2) \approx 3.48$ and ≈ 13.15. For the three maxima we find the values $(\lambda^2) \approx 0.56$, ≈ 5.72, and ≈ 21.2.

7. Summary and Concluding Remarks

In this paper we have treated the T–t J.T. system by means of a non-linear canonical transformation. To gain deeper insight in the optical absorption spectrum we particularly have investigated the variation of the zero-phonon

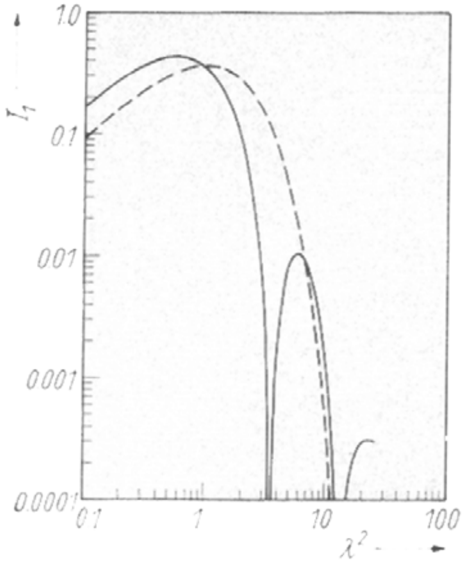

Fig. 4. Intensity $I_1(\lambda^2)$ of the one-phonon line for the T–t J.T. case. λ is a measure for the coupling strength. For comparison the non-J.T. result is given also (dashed line)

and one-phonon line. In order to calculate the matrix elements $\langle f|\, e^{-S}\, a_1^+\, e^{+S}\, |0\rangle$ two approaches were taken.

In the first approach (Section 3) we have been able to express the occurring combinatorial problems only as recurrence formulae, whence no analytically closed expression for the optical absorption function has been reached. For the zero-phonon line, however, we have obtained a one-to-one relationship with the corresponding combinatorial problems of the method of moments (cf. [5]). This enables us to calculate the zero-phonon line in the entire coupling range merely by means of the complete set of moments in the limit of strong coupling.

As shown in Section 4 we do not encounter the combinatorial problems of Section 3 when we expand the total dipole part $e^{-S}\, a_1^+\, e^{+S}$ into a power series. In this case the calculation of the zero-, one-, etc. phonon lines yields expressions whose structures are simpler than the corresponding results of our first approach.

We have found that the phonon lines show a *resonance structure*. This is a consequence of the dynamic J.T. effect and originates from the circumstance that the effective energy splitting of the degenerate high-frequency level is of the same order of magnitude as the energy excitation of the low-frequency oscillator. It is curious to notice that the one-phonon line seems to have minimal points for those λ-values where the zero-phonon line has maxima.

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