Dynamical Jahn-Teller Systems: Internal Energy Resonance Structures of Isolated Jahn-Teller Molecules (*E-b* and *T-t* System)

E. Sigmund and S. Brühl
Institut für Theoretische Physik, Universität Stuttgart

Z. Naturforsch. **36a**, 685–693 (1981); received May 12, 1981

The internal energetic transfer processes of an $E-b$ and $T-t$ Jahn-Teller system are considered. The first system allows an exact description, whereas in the case of the second one approximations must be introduced in the region of intermediate electron-phonon coupling strengths. The occupation probabilities of the states of the uncoupled systems change with time by virtue of the electron-phonon interaction. The energies are directly related to these occupation probabilities. The resonant nature of the $T-t$ system is reflected in the internal dynamics of the latter.

1. Introduction

Recently new experimental techniques for short-time measurements have become available. Thus, in combination with laser spectroscopy, it is possible to study fast processes in molecular systems or at defects in crystals.

An important class of such problems is the interplay between localized electronic states and phonons [1–4]. E.g. we may think of an experiment in which such a physical system is affected by a short laser pulse which excites a specific polarization direction, characterized by an electronic operator a_i^+. Via the interaction between the different subsystems the polarization will change in time, since there is no eigenstate of the form $|a_i^+\rangle \cdot f_i^{(n)}(Q)$, where $f_i^{(n)}(Q)$ is the n-th harmonic oscillator wavefunction of the symmetry coordinate Q. After some time there will be admixtures of the form $|a_j^+\rangle \cdot f_j^{(m)}(Q)$ with $j \neq i$, which can be measured via the polarization given by a_j^+. These effects may be observed in experiments in which the emitted light is studied a short time after the excitation of the system by the laser pulse.

In the present paper we study non-adiabatically coupled electron-phonon systems. Because of the resonant nature of the interaction we may expect new effects [5]. Specific examples of such systems are the Jahn-Teller cases [6], in which degenerate electronic states interact with the vibrational modes of the surrounding crystal. In the following we will discuss the internal dynamics of the $E-b$ and $T-t$ Jahn-Teller problems.

In the $T-t$ case the usual adiabatic decoupling procedures between the subsystems are no longer applicable, and therefore several other methods have been introduced [7–9]. We will base our calculations on an operator method which has been derived and discussed in an earlier paper [10]. It has been successfully applied to the internal dynamics of an $E-e$ Jahn-Teller system [11].

In this article the method is applied to $E-b$ and $T-t$ electron-phonon interactions. In both cases the time evolution of the occupation of the eigenstates pertaining to the electronic and vibrational subsystems is calculated. The derived results elucidate the short-time energy exchange processes in the subsystems.

2. A Short Review of the Method

In earlier work the method has already been demonstrated [10, 11]. Hence we will only give a short review. We consider a system, e.g. an impurity center or a molecule, which is totally isolated from all its surroundings. Under the influence of the interaction between different subsystems the time evolution of an arbitrary state is given by the U-matrix formalism:

$$\Psi(t) = U(t, t_0)\, \Psi(t_0)\,, \tag{1}$$

where the U-matrix is defined by

$$U(t, t_0) = T_t \exp\left\{ -i \int_{t_0}^{t} H_I(t')\, \mathrm{d}t' \right\}. \tag{2}$$

T_t is the Dyson chronological operator and $H_I(t)$ is the coupling term between the different subsystems in interaction representation. In [11] it is shown that the time-ordered exponential operator can be

---

Reprint requests to Dr. E. Sigmund, Institut für Theoretische Physik III, Universität Stuttgart, Pfaffenwaldring 57, D-7000 Stuttgart 80.

0340-4811 / 81 / 0700-0685 $ 01.00/0. — Please order a reprint rather than making your own copy.

expressed in the form

$$T_t \exp\left\{-i\int_{t_0}^{t} H_I(t')\,\mathrm{d}t'\right\} = \exp\left\{-i\int_{t_0}^{t} H_I(t')\,\mathrm{d}t'\right\} \tag{3}$$

$$\cdot \exp\left\{-\tfrac{1}{2}\int_{t_0}^{t}\left[\int_{t_0}^{t'} H_I(t''), H_I(t')\right]\mathrm{d}t' - \frac{i}{3}\int_{t_0}^{t}\left[\int_{t_0}^{t'} H_I(t'')\,\mathrm{d}t'', \left[\int_{t_0}^{t'} H_I(t'')\,\mathrm{d}t'', H_I(t')\right]\right]\mathrm{d}t' + \ldots - \ldots\right\}.$$

The commutator series expansion in the second exponential function leads to approximations of different quality. The first neglected commutator is a measure for the validity of the approximation.

To simplify the following considerations we assume the state Φ_ν, which is an eigenstate of the uncoupled system, to be excited at an initial time t_0 via an external source, e.g. an electromagnetic field (laser). The probability that, at a later time t, a distinct state Φ_μ of the system is excited, is given by

$$\begin{aligned} P_{\mu\nu}(t) &= |\langle \Phi_\mu | \Psi_\nu(t)\rangle|^2 \\ &= |\langle \Phi_\mu | U(t, t_0) | \Phi_\nu\rangle|^2 . \end{aligned} \tag{4}$$

This probability is directly related to the energy of the undisturbed eigenstates $\{\Phi_\mu\}$ by

$$E_\mu^{(0)}(t) = P_{\mu\mu}(t)\langle \Phi_\mu | H | \Phi_\mu\rangle . \tag{5}$$

Expression (5) represents one diagonal element of the total energy $\langle \Psi(t)|H|\Psi(t)\rangle = \text{const.}$, if the function $\Psi(t)$ is projected onto the basis of the undisturbed eigenstates $\{\Phi_\mu\}$.

3. Two Coupled Excitonic Oscillators (*E* – *b* Problem)

The first model to be discussed is a system of two oscillators which have the same energy and which are coupled via a vibrational mode. This system is called an $E-b$ Jahn-Teller system [6] (a doubly degenerate electronic level interacts with a nondegenerate vibrational mode). Its Hamiltonian reads ($\hbar = 1$)

$$H = H_0 + H_I , \tag{6a}$$

$$H_0 = \Omega(a_1^+ a_1 + a_2^+ a_2) + \omega b^+ b , \tag{6b}$$

$$H_I = \varkappa(a_1^+ a_1 - a_2^+ a_2)(b^+ + b) . \tag{6c}$$

The quantity $a_1^+ a_1 + a_2^+ a_2 = 1$ is a constant of motion (closure relation).

a_i^+, $a_i (i = 1, 2)$ and b^+, b are the electronic and vibrational creation and annihilation operators, Ω and ω are the respective energies. $\varkappa$ is the coupling parameter.

Since the second and all higher commutators of the series expansion (3) vanish we can write down an exact and simple expression for the time evolution operator $U(t, 0)$:

$$\begin{aligned} U(t,0) = {} & \exp\left\{-i\left(\frac{\varkappa}{\omega}\right)^2(\omega t - \sin\omega t)\right\} \\ & \cdot \exp\left\{-\frac{\varkappa}{\omega}(a_1^+ a_1 - a_2^+ a_2)\right. \\ & \left.\cdot [b^+(e^{i\omega t} - 1) + b(1 - e^{-i\omega t})]\right\} . \end{aligned} \tag{7}$$

At the initial time $t = 0$ we assume only the state $a_1^+|0\rangle$ to be excited. Then at a later time t the occupation probability $P_n^{(i)}(t)$ of an arbitrary state $a_i^+|n\rangle (i = 1, 2)$ with $|n\rangle = (n!)^{-1/2}(b^+)^n|0\rangle$ is given by ($\lambda = \varkappa/\omega$)

$$\begin{aligned} P_{2n}^{(1)}(t) = {} & \frac{2^{2n}}{(2n)!}[\lambda^{2n}(\mathrm{d}/\mathrm{d}\lambda^2)^n \\ & \cdot \exp\{\lambda^2(\cos\omega t - 1)\}]^2 , \end{aligned} \tag{8a}$$

$$\begin{aligned} P_{2n+1}^{(1)}(t) = {} & \frac{2^{2n+1}}{(2n+1)!} \\ & \cdot (1 - \cos\omega t)[\lambda^{2n+1}(\mathrm{d}/\mathrm{d}\lambda^2)^n \\ & \cdot \exp\{\lambda^2(\cos\omega t - 1)\}]^2 , \end{aligned} \tag{8b}$$

$$P_n^{(2)}(t) = 0 . \tag{8c}$$

These results are periodic in time ($T = 2\pi/\omega$), because damping effects are neglected. In Figs. 1a–c the occupation probabilities $P_0^{(1)}$, $P_1^{(1)}$ and $P_2^{(1)}$ are drawn for different coupling parameters.

With increasing coupling strength the occupation probability $P_0^{(1)}$ of the initially excited state $a_1^+|0\rangle$ decreases in the middle of the periodicity interval.

For small coupling values only a few low lying excited states are occupied (vid. Figure 1a). For higher coupling values, however, the occupation probability is transferred to higher energetic states. Thus the maximum values of $P_1^{(1)}$ and $P_2^{(1)}$ are shifted to the boundaries of the periodicity interval, whereas for $t = \pi/\omega$ they show a minimum (vid. Figs. 1b and 1c).

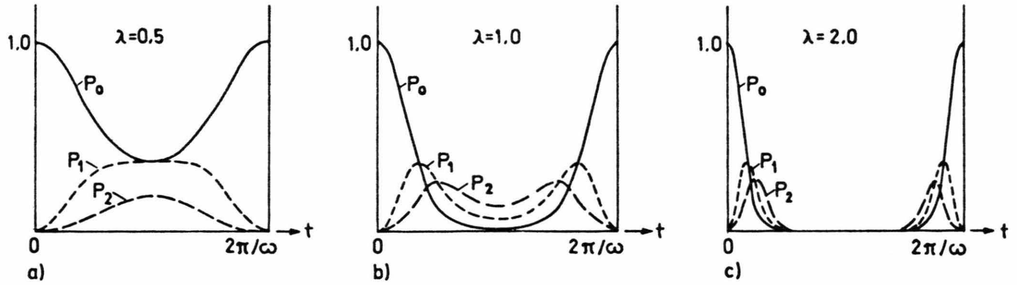

Fig. 1a—c. Amplitude of the occupation probabilities $P_0^{(1)}$, $P_1^{(1)}$ and $P_2^{(1)}$ in dependence of time t for various coupling parameters ($E-b$ system, see text).

4. The $T-t$ Jahn-Teller Case

In this section we calculate the occupation dynamics of the $T-t$ Jahn-Teller system. In contrary to the $E-b$ case discussed in the previous section, we now expect resonances caused by the nonadiabatic interaction terms. Similar to the $E-e$ problem they will manifest themselves in the internal energy exchange processes. The Hamiltonian reads [6]

$$H = H_0 + H_I\,, \tag{9a}$$

$$H_0 = \Omega \sum_{i=1}^{3} a_i^+ a_i + \omega \sum_{j=1}^{3} b_j^+ b_j\,, \tag{9b}$$

$$H_I = \varkappa \sum_{i=1}^{3} (a_i^+ a_{i+1} + a_{i+1}^+ a_i)(b_{i+2}^+ + b_{i+2})\,, \tag{9c}$$

where the operators are defined in the same way as in (6a—c). Applying the results for the time evolution operator $U(t, 0)$ onto the $T-t$ problem, one gets

$$-i\int_0^t H_I(t')\,\mathrm{d}t' = -\frac{\varkappa}{\omega}\sum_{i=1}^{3}(a_i^+ a_{i+1} + a_{i+1}^+ a_i)\{b_{i+2}^+(e^{i\omega t} - 1) + b_{i+2}(1 - e^{-i\omega t})\} \tag{10a}$$

$$-i\left[\int_0^t H_I(t')\,\mathrm{d}t', H_I(t)\right] = \frac{\varkappa^2}{\omega}(1 - \cos\omega t)\left\{4 - \sum_{i=1}^{3}(a_i^+ a_{i-1} - a_{i-1}^+ a_i)(b_i^+ b_{i-1} - b_{i-1}^+ b_i)\right\}. \tag{10b}$$

From Ref. [11] it is evident that the commutator (10b) is zero in the very extreme coupling cases. This would mean that the character of the operator factor in (10b) will not play any role in the very extreme coupling cases. But naturally, the validity region can be extended if the properties of this operator are taken into account. In the following however, we will neglect this commutator. Nevertheless, this leads to good results also in the region of intermediate coupling strengths as shown in [11].

Then the time development operator $U(t, 0)$ gets the simple form

$$U(t, t_0) = \exp\left\{-i\int_{t_0}^{t} H_I(t')\,\mathrm{d}t'\right\}. \tag{11}$$

α) *Occupation Probability of the State* $a_1^+|0\rangle$

In the same way as before we assume the electronic state $a_1^+|0\rangle$ to be excited at time $t_0 = 0$. At a later time t the occupation probability is given by

$$\begin{aligned} P_0^{T-t}(t) &= |\langle 0|\, a_1 U(t, 0)\, a_1^+ \,|0\rangle|^2 \\ &= \left|\sum_{n=0}^{\infty}\frac{1}{(2n)!}\left\{\left(\frac{\varkappa}{\omega}\right)^{2n}(-1 + \cos\omega t)^n \cdot \sum_{x_1, x_2, x_3}^{n}\frac{(2x_1)!\,(2x_2)!\,(2x_3)!}{x_1!\,x_2!\,x_3!}Z_{\text{tot}}^{\text{e}}(x_1, x_2, x_3)\right\}\right|^2. \end{aligned} \tag{12}$$

The integrations in the electronic subsystem lead to the summations over x_1, x_2 and x_3. The function $Z_{\text{tot}}^{\text{e}}(x_1, x_2, x_3)$ is the result of a sequence of combinational calculations which are given in [12]. The explicit results are reported in Appendix A. Introducing the expressions for the moments of the optical absorption line shape in the strong coupling limit (see [12] and Appencix A) one gets

$$P_0^{T-t}(t) = \left| \sum_{n=0}^{\infty} \frac{1}{(2n)!} \left(\frac{-1+\cos\omega t}{\omega^2} \right)^n M_{2n} \right|^2 . \quad (13)$$

As seen in Figs. 2a–d, the probability of the state $a_1^+ |0\rangle$ oscillates with a periodicity of $T = 2\pi/\omega$. For small values of λ the occupation probability decreases only little in the middle of the periodicity interval.

Already for $\lambda = 0.9$ a pronounced difference occurs, compared to the behaviour of the $E-b$ case: The occupation probability reaches a maximum value at $t = T/2$. For $\lambda > 1.1$ the typical antiresonance structure which is a characteristic feature of the $T-t$ problem has developed (vid. Figs. 2c and 2d).

β) *Occupation Probabilities of Arbitrary States*

In this section we consider the time dependent occupation probabilities of states which are unoccupied at the beginning time $t_0 = 0$. These states are of the form $|a_i^+ m_1 m_2 m_3\rangle$ with $i = 1, 2, 3$ and m_1, m_2, m_3 arbitrary. The matrix elements which are to be calculated read

$$\langle m_1 m_2 m_3 | a_i U(t,0) a_1^+ |0\rangle , \quad (14)$$

where $U(t,0)$ is the U-matrix (11). In Appendix B the calculations and the final results are given. Since the expressions are rather lengthy and complicated we will not write them down here.

In Figs. 3a–d the time dependent occupation number of the one-phonon state is drawn for different coupling parameters. It shows a similar resonant behaviour as that of the zero-phonon line, except that it is unoccupied at the time $t = 2\pi n/\omega\,(n = 0, 1, \ldots)$.

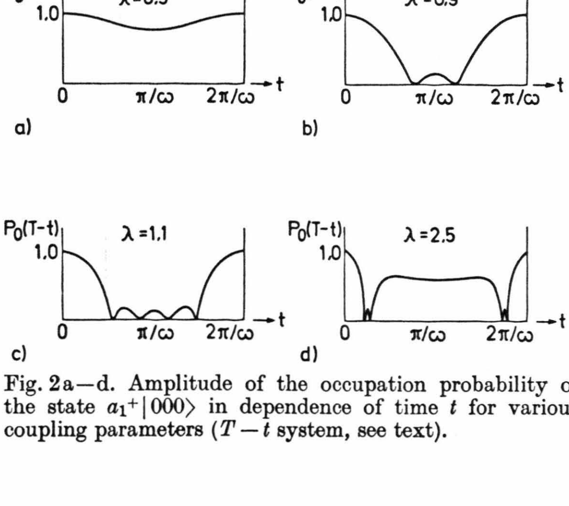

Fig. 2a–d. Amplitude of the occupation probability of the state $a_1^+|000\rangle$ in dependence of time t for various coupling parameters ($T-t$ system, see text).

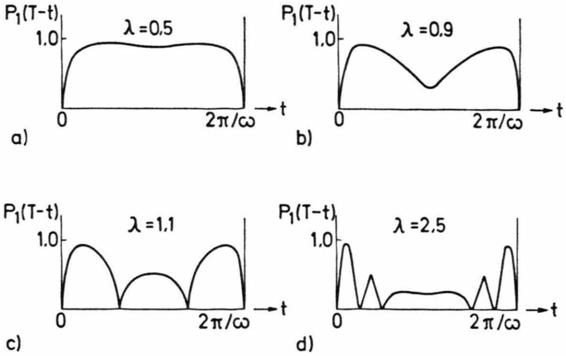

Fig. 3a–d. Amplitude of the occupation probability of the state $a_3^+|100\rangle$ in dependence of time t for various coupling parameters ($T-t$ system, see text).

5. Summary and Discussion

We have studied the internal dynamics of an $E-b$ and a $T-t$ Jahn-Teller system. In both cases it has been assumed that the system is totally separated from all its surroundings so that no damping effects can occur.

Via an external source the system is excited into an eigenstate $a_1^+ |0\rangle \cdot f^{(n)}(Q)$ of the uncoupled system H_0, which, however, is no eigenstate of the total system. Since the interaction does not commute with H_0, the time evolution of this state leads to transitions into other states $a_i^+ |0\rangle f^{(m)}(Q)$. By means of this we can calculate the time dependent occupation probability of each of these states.

In the $E-b$ case our method is exact, and the occupation probabilities are simple functions of time (Figs. 1a–c). The results are more complicated for the $T-t$ problem. Here the occupation probabilities show additional structures depending on the specific electron-phonon interaction, which enables a resonant energy transfer between the subsystems. They are also more structured than the results for the $E-e$ problem [11, 13]. A somewhat similar distinction is already evident in the optical absorption, where the $T-t$ spectrum shows 3 maxima and the $E-e$ only 2.

Concerning experiments some facts should be mentioned:

a) The model system we have considered does not exist in nature in such pure form. There are a number of competitive processes (spatial energy transport processes), which make it difficult to observe the effect discussed in this article. These processes, however, can be eliminated, if one chooses a crystal with a dilute concentration of point defects which are strongly localized (molecular internal oscillations).

b) In the case of the $T-t$ system the optical emission from different electronic states is of different polarization. Therefore the time dependence of the occupation probabilities can be measured by studying the change of the intensity of the emitted light in different polarization directions.

c) The calculations have shown that the time of the periodicity T is proportional to the inverse of the phonon frequency ω. Furtheron, the resonance effects are more pronounced for stronger electron-phonon coupling. Thus, for experimental verification, one should search for systems where the phonon frequency is very low and where the electron-phonon coupling is strong. The latter is often fulfilled in realistic Jahn-Teller systems, whereas the former requirement is more difficult to be realized.

Appendix A

The integrations in the electronic subsystems can be solved using combinatorial techniques. This is done in Ref. [8] for matrix-elements of the form

$$\left\langle 0 \left| a_j \left[\sum_{i=1}^{3} (a_i^+ a_{i+1} + a_{i+1}^+ a_i) \right]^n a_j^+ \right| 0 \right\rangle = Z_{\text{tot}}^n . \tag{A.1}$$

There, the result is given by $(x_1 + x_2 + x_3 = n)$

$$\begin{aligned} & Z_{\text{tot}}^{\text{e}}(x_1, x_2, x_3) \\ &= \sum_{\eta=0}^{K} \binom{x_1 + x_3}{x_3 + \eta} \binom{x_2 + x_3 - 1}{x_3 + \eta - 1} \binom{2 x_3 + 2\eta}{2 x_3} \\ &= Z_{\text{tot}}^{2n} \end{aligned} \tag{A.2a}$$

for $x_1, x_2, x_3 =$ even, and

$$\begin{aligned} & Z_{\text{tot}}^{2}(x_1, x_2, x_3) \\ &= \sum_{\eta=0}^{K} \binom{x_1 + x_3 + 1}{x_3 + \eta + 1} \binom{x_2 + x_3}{x_3 + \eta} \binom{2 x_3 + 2\eta + 2}{2 x_3 + 1} \\ &= Z_{\text{tot}}^{2n+1} \end{aligned} \tag{A.2b}$$

for $x_1, x_2, x_3 =$ odd. K is given by

$$K = \begin{cases} x_1 & \text{for } x_1 < x_2 , \\ x_2 & \text{for } x_1 > x_2 . \end{cases}$$

x_i is the number of how often the operator $a_i^+ a_{i+1} + a_{i+1}^+ a_i$ with $i = 1, 2, 3$ appears in single sequence of Expression (A.1). It is easy to verify that either the combinations $x_1, x_2, x_3 =$ even or $x_1, x_2, x_3 =$ odd can exist for matrix elements of the form

$$\left\langle 0 \left| a_j \left[\sum_{i=1}^{3} (a_i^+ a_{i+1} + a_{i+1}^+ a_i) \right]^n a_k^+ \right| 0 \right\rangle , \quad j \neq k . \tag{A.3}$$

We are able to derive a recurrence formula. Without loss generality we set $j = 1$ and $k = 2$. For $j = 1$ and $k = 3$ the results are the same. We characterize the partial sum of these matrix elements of (A.3) which belong to a given set y_1, y_2, y_3 by

$$\langle a_1^+ \,|\, y_1, y_2, y_3 \,|\, a_2^+ \rangle . \tag{A.4}$$

Now the y_i instead of the x_i count the number of appearances of the different electronic operators in this partial sum. Then (A.4) has the recurrence relation

$$\langle a_1^+ \,|\, y_1, y_2, y_3 \,|\, a_2^+ \rangle = \langle a_1^+ \,|\, y_1 - 1, y_2, y_3 \,|\, a_1^+ \rangle + \langle a_1^+ \,|\, y_1, y_2 - 1, y_3 \,|\, a_3^+ \rangle \tag{A.5}$$

and similarily

$$\langle a_1^+ \,|\, y_1, y_2 - 1, y_3 \,|\, a_2^+ \rangle = \langle a_1^+ \,|\, y_1, y_2 - 1, y_3 - 1 \,|\, a_1^+ \rangle + \langle a_1^+ \,|\, y_1, y_2 - 2, y_3 \,|\, a_2^+ \rangle . \tag{A.6}$$

Combining both equations one gets

$$\langle a_1^+ \,|\, y_1, y_2, y_3 \,|\, a_2^+ \rangle = \sum_{j=0} \langle a_1^+ \,|\, y_1 - 1, y_2 - 2j, y_3 \,|\, a_1^+ \rangle + \sum_{k=0} \langle a_1^+ \,|\, y_1, y_2 - 2k - 1, y_3 - 1 \,|\, a_1^+ \rangle \tag{A.7}$$

by means of which one is brought back to diagonal matrix elements. There are two different possible combinations:

α) $y_1 = \text{even} = 2 z_1 ; \quad y_2 = \text{odd} = 2 z_2 + 1 ; \quad y_3 = \text{odd} = 2 z_3 + 1 .$

Inserting Eq. (A.2a–b) in (A.7) one gets

$$\begin{aligned} Z_{\text{tot}}^{(\alpha)}(y_1, y_2, y_3) &\equiv \langle a_1^+ \,|\, 2 z_1, 2 z_2 + 1, 2 z_3 + 1 \,|\, a_2^+ \rangle \\ &= \sum_{j=0}^{z_2} Z_{\text{tot}}^{0}(z_1 - 1, z_2 - j, z_3) + \sum_{j=0}^{z_2} Z_{\text{tot}}^{\text{e}}(z_1, z_2 - j, z_3) . \end{aligned} \tag{A.8}$$

In Table 1 values of $Z_{\text{tot}}^{(\alpha)}(y_1, y_2, y_3)$ are given.

β) $y_1 = \text{odd} = 2z_1 + 1$; $y_2 = \text{even} = 2z_2$; $y_3 = \text{even} = 2z_3$.

Combining again Eqs. (A.2) and (A.7) we get a second recurrence formula:

$$Z_{\text{tot}}^{(\beta)}(y_1, y_2, y_3) \equiv \langle a_1^+ \,|\, 2z_1 + 1, 2z_2, 2z_3 \,|\, a_3^+ \rangle = \sum_{j=0}^{z_2} Z_{\text{tot}}^{\text{e}}(z_1, z_2 - j, z_3) + \sum_{j=1}^{z_2} Z_{\text{tot}}^{0}(z_1, z_2 - j, z_3 - 1). \tag{A.9}$$

In Table 2 values of $Z_{\text{tot}}^{(\beta)}(y_1, y_2, y_3)$ are given. With the result of Ref. [12] and the two recurrence formulae (A.8–9) we are able to calculate all matrix elements of the electronic three level system. It is easy to test the validity of relations (A.8–9) by means of a single unitary transformation. This is done in Appendix C.

In Appendix D we have given a table with values of $Z_{\text{tot}}^{\text{e}}(x_1, x_2, x_3)$ and $Z_{\text{tot}}^{0}(x_1, x_2, x_3)$. With this table we can derive the results of Table 1 and 2.

In Ref. [12] the moments of the optical absorption spectrum in the strong coupling limit are calculated. They read (temperature $T = 0$)

$$M_{2m} = \varkappa^{2m}\, 2^{-m} \sum_{x_1 x_2 x_3}^{m} \frac{(2x_1)!\,(2x_2)!\,(2x_3)!}{x_1!\,x_2!\,x_3!} \cdot Z_{\text{tot}}^{\text{e}}(x_1, x_2, x_3) \tag{A.10}$$

and

$$M_{2m+1} = 0. \tag{A.11}$$

Table 1. Values of the electronic matrix element $(i \neq j)$ $\langle a_i{}^+ | 2y_1, 2y_2 + 1, 2y_3 + 1 | a_j{}^+ \rangle = Z_{\text{tot}}^{(\alpha)}(y_1, y_2, y_3)$ for some different parameters y_1, y_2, y_3. Explanation see text.

$n = 2m + 2 = z_1 + 2z_2 + 1 + 2z_3 + 1$	z_1	z_2	z_3	$Z_{\text{tot}}^{(\alpha)}(y_1\, y_2\, y_3)$	$n = 2m + 2 = 2z_1 + 2z_2 + 1 + 2z_3 + 1$	z_1	z_2	z_3	$Z_{\text{tot}}^{(\alpha)}(y_1\, y_2\, y_3)$
2	0	0	0	1	8	3	0	0	7
4	1	0	0	3		0	3	0	1
	0	1	0	1		0	0	3	1
	0	0	1	1		2	1	0	15
6	2	0	0	5		2	0	1	15
	0	2	0	1		1	2	0	9
	0	0	2	1		1	0	2	9
	1	1	0	6		0	2	1	3
	1	0	1	6		0	1	2	3
	0	1	1	2		1	1	1	22

Table 2. Values of the electronic matrix element $(i \neq j)$ $\langle a_i^+ | 2y_1 + 1, 2y_2, 2y_3 | a_j^+ \rangle = Z_{\text{tot}}^{(\beta)}(y_1, y_2, y_3)$ for some different parameters y_1, y_2, y_3. Explanation see text.

$n = 2m + 1 = z_1 + 1 + 2z_2 + 2z_3$	z_1	z_2	z_3	$Z_{\text{tot}}^{(\beta)}(y_1, y_2, y_3)$	$n = 2m + 1 = 2z_1 + 1 + 2z_2 + 2z_3$	z_1	z_2	z_3	$Z_{\text{tot}}^{(\beta)}(y_1, y_2, y_3)$
1	0	0	0	1	7	3	0	0	1
3	1	0	1	1		0	3	0	1
	0	1	0	1		0	0	3	1
	0	0	1	1		2	1	0	3
5	2	0	0	1		2	0	1	3
	0	2	0	1		1	2	0	3
	0	0	2	1		1	0	2	3
	1	1	0	2		0	2	1	7
	1	0	1	2		0	1	2	7
	0	1	1	4		1	1	1	14

Appendix B

With the result of Appendix A we can calculate the occupation probabilities of arbitrary states. Furtheron, we use the relations

$$\langle 2m|(c_1 b + c_2 b^+)^{2n}|0\rangle = c_1^{n-m} c_2^{n+m} \frac{(2n)!}{(n-m)!} \frac{1}{\sqrt{(2m)!}} \left(\frac{1}{2}\right)^{n-m}, \tag{B.1}$$

$$\langle 2m+1|(c_1 b + c_2 b^+)^{2n+1}|0\rangle = c_1^{n-m} c_2^{n+m+1} \frac{(2n+1)!}{(n-m)!} \frac{1}{\sqrt{(2m+1)!}} \left(\frac{1}{2}\right)^{n-m}. \tag{B.2}$$

After rather lengthy calculations we get the following results ($\mu_1 + \mu_2 + \mu_3 = n$)

$$|\langle(2m_1)(2m_2)(2m_3)a_1^+|U(t,0)|a_1^+ 0\rangle|^2 = \frac{2^{2m}}{(2m_1)!(2m_2)!(2m_3)!} \cdot \left| \sum_{n=0}^{\infty} \frac{X(t)^{2n}}{(2n)!} \left(-\frac{1}{2}\right)^n \sum_{\mu_1\mu_2\mu_3} \frac{(2\mu_1)!(2\mu_2)!(2\mu_3)!}{(\mu_1-m_1)!(\mu_2-m_2)!(\mu_3-\mathrm{m}_3)!} Z_{\mathrm{tot}}^{\mathrm{e}}(\mu_1,\mu_2,\mu_3) \right|^2, \tag{B.3}$$

$$|\langle(2m_1+1)(2m_2+1)(2m_3+1)a_1^+|U(t_1 0)|a_1^+ 0\rangle|^2 = \frac{2^{2m}}{(2m_1+1)!(2m_2+1)!(2m_3+1)!} \cdot \left| \sum_{n=0}^{\infty} \frac{X(t)^{2n+3}}{(2n+3)!} \left(-\frac{1}{2}\right)^n \sum_{\mu_1\mu_2\mu_3} \frac{(2\mu_1+1)!(2\mu_2+1)!(2\mu_3+1)!}{(\mu_1-m_1)!(\mu_2-m_2)!(\mu_3-m_3)!} Z_{\mathrm{tot}}^{0}(\mu_1,\mu_2,\mu_3) \right|^2. \tag{B.4}$$

$$|\langle(2m_1)(2m_2+1)(2m_3+1)a_2^+|U(t,0)|a_1^+ 0\rangle|^2 = \frac{2^{2m+1}}{(2m_1)!(2m_2+1)!(2m_3+1)!} \cdot \left| \sum_{n=0}^{\infty} \frac{X(t)^{2n+2}}{(2n+2)!} \left(-\frac{1}{2}\right)^n \sum_{\mu_1\mu_2\mu_3} \frac{(2\mu_1)!(2\mu_2+1)!(2\mu_3+1)!}{(\mu_1-m_1)!(\mu_2-m_2)!(\mu_3-m_3)!} Z_{\mathrm{tot}}^{(\alpha)}(\mu_1,\mu_2,\mu_3) \right|^2, \tag{B.5}$$

$$|\langle(2m_1+1)(2m_2)(2m_3)a_3^+|U(t,0)|a_1^+ 0\rangle|^2 = \frac{2^{2m+1}}{(2m_1+1)!(2m_2)!(2m_3)!} \cdot \left| \sum_{n=0}^{\infty} \frac{X(t)^{2n+1}}{(2n+1)!} \left(-\frac{1}{2}\right)^n \sum_{\mu_1\mu_2\mu_3} \frac{(2\mu_1+1)!(2\mu_2)!(2\mu_3)!}{(\mu_1-m_1)!(\mu_2-m_2)!(\mu_3-m_3)!} Z_{\mathrm{tot}}^{(\beta)}(\mu_1,\mu_2,\mu_3) \right|^2, \tag{B.6}$$

where

$$X(t) = \frac{\varkappa}{\omega} \sqrt{2 - 2\cos\omega t}. \tag{B.7}$$

Appendix C

Test of the Recurrence Formula

In an analogous way as in Ref. [12] one can prove our recurrence formulae (A8, A9). Therefore we apply a purely electronic transformation onto our system. Its exponent is given by

$$S = \left\{ \sum_{i=1}^{3} (a_i^+ a_{i+1} + a_{i+1}^+ a_i) \right\} B. \tag{C.1}$$

B is an imaginary coefficient, and so the transformation is unitary. In the following we treat the matrix element of the transformed operator $\tilde{a}_1^+ = e^{-s} a_1^+ e^s$ between the states $|a_2^+ 0\rangle$ and $|0\rangle$. With $e^{+s}|0\rangle = |0\rangle$ we get

$$\langle a_2^+|\tilde{a}_1^+|0\rangle = \langle a_2^+|e^{-S}|a_1^+\rangle. \tag{C.2}$$

α) First we expand the right hand side of Eq. (C.2) and get

$$\langle a_2^+|e^{-S}|a_1^+\rangle = \sum_{n=0}^{\infty} \frac{B^n}{n!} \left\langle a_2^+ \left| \left\{ \sum_{i=1}^{3} (a_i^+ a_{i+1} + a_{i+1}^+ a_i) \right\}^n \right| a_1^+ \right\rangle \tag{C.3}$$

and with our previous results

$$\langle a_2^+ \,|\, e^{-S} \,|\, a_1^+ \rangle = \sum_{m=0}^{\infty} \left\{ \frac{B^{2m+2}}{(2m+2)!} \sum_{y_1, y_2, y_3} Z_{\text{tot}}^{(\alpha)}(y_1, y_2, y_3) + \frac{B^{2m+1}}{(2m+1)!} \sum_{y_1, y_2, y_3} Z_{\text{tot}}^{(\beta)}(y_1, y_2, y_3) \right\}, \tag{C.4}$$

where $y_1 + y_2 + y_3 = m$.

β) Second we use the final and closed form of the transformed operator (see Ref. [12]):

$$\tilde{a}_1^+ = \tfrac{1}{3}(a_1^+ + a_2^+ + a_3^+)\, e^{2B} + \tfrac{1}{3}(2\, a_1^+ - a_2^+ - a_3^+)\, e^{-B}. \tag{C.5}$$

Then the left hand side of Eq. (C.2) is given by

$$\langle a_2^+ \,|\, \tilde{a}_1^+ \,|\, 0 \rangle = \frac{1}{3}\, e^{2B} - \frac{1}{3}\, e^{-B} = \frac{1}{3} \sum_{m=0}^{\infty} \frac{B^m}{m!} \{2^m - (-1)^m\}. \tag{C.6}$$

Comparing Eqs. (C.4) and (C.6) we get the relations

$$\sum_{y_1, y_2, y_3}^{m} Z_{\text{tot}}^{(\alpha)}(y_1, y_2, y_3) = \tfrac{1}{3}\{2^{2m+2} - 1\} \tag{C.7a}$$

and

$$\sum_{y_1, y_2, y_3}^{m} Z_{\text{tot}}^{(\beta)}(y_1, y_2, y_3) = \tfrac{1}{3}\{2^{2m+1} + 1\}. \tag{C.7b}$$

In Table 3 we have written down some values of $\frac{1}{3}\{2^{2m+2} - 1\}$ and $\frac{1}{3}\{2^{2m+1} + 1\}$ for different m's.

Table 3. Result of the summarized forms of the recurrence formulae for some values $m = y_1 + y_2 + y_3$. Explanation see text.

$n = 2m + 1$	$\frac{1}{3}\{2^{2m+1} + 1\}$	$n = 2m + 2$	$\frac{1}{3}\{2^{2m+2} - 1\}$
1	1	2	1
3	3	4	5
5	11	6	21
7	43	8	85

If we sum up the values of $Z_{\text{tot}}^{(\alpha)}(y_1; y_2; y_3)$ and $Z_{\text{tot}}^{(\beta)}(y_1; y_2; y_3)$ for each different n in tables 1 and 2 we get the result of Table 3.

Appendix D

Values for $Z_{\text{tot}}^{\text{e}}(x_1, x_2, x_3)$ and $Z_{\text{tot}}^{0}(x_1, x_2, x_3)$.

In Table 4 we have written down values for $Z_{\text{tot}}^{\text{e}}(x_1\, x_2\, x_3)$ and $Z_{\text{tot}}^{0}(x_1\, x_2\, x_3)$. With these results and with Eqs. (A.8) and (A.9) we can construct the Tables 1 and 2. The values for $Z_{\text{tot}}^{\text{e}}(x_1\, x_2\, x_3)$ are already given in [12].

Acknowledgement

The authors are indebted to Prof. Dr. M. Wagner for stimulating remarks and for critical reading of the manuscript.

x_1	x_2	x_3	$n = 2x_1 + 2x_2 + 2x_3$	$Z_{\text{tot}}^{\text{e}}(x_1, x_2, x_3)$	$n = 2x_1 + 2x_2 + 2x_3 + 3$	$Z_{\text{tot}}^{\text{o}}(x_1, x_2, x_3)$
0	0	0	0	1	3	2
1	0	0	2	1	5	4
0	1	0		0		2
0	0	1		1		4
2	0	0	4	1	7	6
0	2	0		0		2
0	0	2		1		6
1	1	0		1		8
1	0	1		2		12
0	1	1		1		8
3	0	0	6	1	9	8
0	3	0		0		2
0	0	3		1		8
2	1	0		2		18
2	0	1		3		24
1	2	0		1		12
1	0	2		3		24
0	2	1		1		12
0	1	2		2		18
1	1	1		8		44

Table 4. Values of the combinatorial results $Z_{\text{tot}}^{\text{e}}(x_1, x_2, x_3)$ and $Z_{\text{tot}}^{\text{o}}(x_1, x_2, x_3)$ for some parameters x_1, x_2, x_3. Explanation see text and Ref. [12].

[1] M. Bixon and J. Jortner, J. Chem. Phys. **48**, 715 (1968).
[2] A. P. Renner, W. Siebrand, and M. Zgierski, J. Chem. Phys. **69**, 5496 (1978).
[3] M. S. De Giambiagi, M. De Giambiagi, and R. Ferreira, Chem. Phys. Lett. **52**, 80 (1977).
[4] R. Reisfeld and Y. Kalisky, Chem. Phys. Lett. **50**, 199 (1977).
[5] M. Wagner, Z. Physik **230**, 460 (1970).
[6] See e.g. R. Englman, The Jahn-Teller Effect in Molecules and Crystals, John Wiley, New York 1972; — M. D. Sturge, The Jahn-Teller Effect in Solids, Solid State Physics, Vol. 20, Academic Press, New York 1967.
[7] B. G. Vekhter, Yu. E. Perlin, V. Z. Polinger, Yu. B. Rosenfeld, and B. S. Tsukerblat, Crystal Lattice Defects **3**, 61 (1972); **3**, 69 (1972).
[8] M. Wagner, Z. Physik, **244**, 275 (1961).
[9] M. Wagner, Z. Physik **256**, 291 (1972).
[10] E. Sigmund and M. Wagner, phys. stat. sol. (b) **76**, 325 (1976).
[11] E. Sigmund, Z. Physik **B26**, 239 (1977).
[12] E. Sigmund, Z. Naturforsch. **31a**, 904 (1976).
[13] S. Muramatsu, private communication.