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Quasi-Exact Solution of the Optical Jahn-Teller Problem

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The presented method is based on an extension of the Goldberger-Adams theorem and on a systematic application of Wick's theorem. The latter leads to combinatorial problems, which in general are complicated but well-fit to be handled by computers. In the two pure *JT*-cases $E-e$ and $T-t$ the combinatorial problems are simple. In particular in the $E-e$-case (trigonal) the optical response can be written in a concise analytical form. It is shown further that by means of a one-to-one correspondence of the respective combinatorial problems it suffices to calculate the complete sequence of moments in the strong coupling limit to write down expressions for the optical response with arbitrary coupling, which are exact both in the strong and weak coupling limit.

1. Introduction

The interaction of degenerate molecular or lattice vibrations with degenerate levels of localized electronic systems has gained much interest during the 30 years, since Jahn and Teller[1] have stated the static part of the problem. The dynamical problem has not been solved exactly, except for trivial cases, but many approximation methods have been developed. For a good review the articles of Longuet-Higgins[2] and of Sturge[3] may be consulted.

The general characterization of a Jahn-Teller problem is the interaction of a degenerate high-energy system (electronic system, high-frequency oscillator) with a degenerate low-energy system (oscillators). The dynamical situation may be understood as a resonance phenomenon between the effective splitting of the high-energy states and the excitations in the low-energy system.

Because of the large energy differences in the high-energy system it is convential to adopt the adiabatic principle (appropriately modified for the *JT*-problem) and to assume that the electronic wavefunctions $\psi_0^{(a)}(x)$ and $\psi_i^{(b)}(x)$ are independent of the vibrational coordinates q, although the functions $\psi_i^{(b)}(x)$ may be mixed dynamically by the coupling.

1 Jahn, H. A., Teller, E.: Proc. Roy. Soc. (London) Ser. A **161**, 220 (1937).
2 Longuet-Higgins, H. C.: Advan. Spectr. **2**, 429 (1961).
3 Sturge, M. D.: In: Solid state physics (ed. Seitz-Turnbull), vol. 20, p. 91. New York: Academic Press 1967.

The latter assumption corresponds to the Condon approximation in the non-degenerate coupling problem. Since the restrictive effect of these two presuppositions is of no significance for the *JT*-problem, we will accept them throughout this paper. They are incorporated in the formalism, if the electronic Hamiltonian $H_e(x)$ commutes with the interaction Hamiltonian $V(x, q)$,

$$[H_e(x), V(x, q)] = 0. \tag{1}$$

If this is postulated, each electronic state defines an independent subspace of the total Hilbert-space.

For optical transitions only two electronic states are involved. Since, by means of (1) the interaction with the vibrations does not mix in other electronic states, we may use an oscillator description for the electronic two-level system also,

$$H_e(x) = \omega_0 \sum_i a_i^+ a_i. \tag{2}$$

Here the boson operators a_i^+ and a_i describe the degenerate electronic excitation and the de-excitation respectively (i = index of electronic degeneracy), ω_0 is the electronic excitation energy, and a system of units is used for which $\hbar = 1$. For the vibrational Hamiltonian we have

$$H_v(q) = \sum_{kj} \omega_k b_{kj}^+ b_{kj} \tag{3}$$

where b_{kj}^+ and b_{kj} are the oscillator creation and annihilation operators respectively (j = index of vibrational degeneracy). The total *JT*-Hamiltonian is then

$$H(x, q) = H_e(x) + H_v(q) + \kappa V(x, q). \tag{4}$$

According to our assumption that each electronic energy-level characterizes an independent subspace of the total Hilbert-space, the wave-functions of $H(x, q)$ must be of the form[4]

$$\Psi_m^{(a)}(x, q) = \psi_0^{(a)}(x) \Phi_{0m}(q), \quad E_{00}^{(a)} = 0 \tag{5a}$$

for the electronic groundstate a, and

$$\Psi_m^{(b)}(x, q) = \sum_i \psi_i^{(b)}(x) \Phi_{im}^{(b)}(q) \tag{5b}$$

for the excited electronic state b. The *JT*-functions $\Phi(q)$ are solutions of the reduced Schrödinger equations

$$[H_v(q) + \kappa \langle V \rangle_{00}] \Phi_m^{(a)}(q) = \omega_m^{(a)} \Phi_m^{(a)}(q), \tag{6a}$$

4 Wagner, M.: Z. Physik **230**, 460 (1970).

and

$$\sum_k \{(\omega_0 + H_v(q))\,\delta_{ik} + \kappa\,\langle V\rangle_{ik}\}\,\Phi_{km}^{(b)}(q) = \omega_m^{(b)}\,\Phi_{im}^{(b)}(q), \tag{6b}$$

where

$$\langle V\rangle_{00} = \int dx\,\psi_0^{(a)}(x)^*\,V(x,q)\,\psi_0^{(a)}(x), \tag{7a}$$

$$\langle V\rangle_{ik} = \int dx\,\psi_i^{(b)}(x)^*\,V(x,q)\,\psi_k^{(b)}(x). \tag{7b}$$

In matrix notation,

$$\begin{gathered} \boldsymbol{H}_0^{(b)}(q) \equiv \{(\omega_0 + H_v(q))\,\delta_{ik}\}, \qquad \boldsymbol{V}(q) \equiv \{\langle V\rangle_{ik}\} \\ \vec{\Phi}_m^{(b)}(q) \equiv \{\Phi_{im}^{(b)}(q)\}, \end{gathered} \tag{8}$$

Eq. (6b) may be rewritten in a more concise form,

$$\boldsymbol{H}^{(b)}(q)\,\vec{\Phi}_m^{(b)}(q) = \omega_m^{(b)}\,\vec{\Phi}_m(q) \tag{9}$$

where

$$\boldsymbol{H}^{(b)}(q) = \boldsymbol{H}_0^{(b)}(q) + \kappa\,\boldsymbol{V}(q). \tag{10}$$

As a further consequence of the separation of the total Hilbert-space into independent subspaces the *JT*-functions $\Phi_{im}^{(b)}(q)$ satisfy the closure property[4]

$$\sum_m \Phi_{im}^{(b)}(q')^*\,\Phi_{km}^{(b)}(q) = \delta_{ik}\,\delta(q-q'). \tag{11}$$

2. The Optical Response

Our method is based on an extension of a formalism first developed by Lax[5] and on a subsequent application of Wick's theorem. The solution will be in the form of an optical response which is displayed if an optical transition is made from the non-degenerate initial states $\Psi_n^{(a)}(x,q)$ to the final *JT*-states. The functional form of the optical absorption is given by

$$\sigma(\omega) = K\cdot\omega\cdot I_{ba}(\omega) \tag{12}$$

where

$$\begin{aligned} I_{ba}(\omega) = {} & [\mathrm{Tr}^{(a)}\exp(-H/kT)]^{-1}\sum_n\sum_m e^{-\omega_n^{(a)}/kT} \\ & \cdot\left|\langle\Psi_m^{(b)}(x,q)\,|\,P^{(i)}(x)\,|\,\Psi_n^{(a)}(x,q)\rangle\right|^2\,\delta(\omega_m^{(b)} - \omega_n^{(a)} - \omega). \end{aligned} \tag{13}$$

The constant K contains the static and dynamic dielectric constants and the local electric field[4]; it is of no importance in our context. $P^{(i)}(x)$ is the dipole operator,

$$P^{(i)}(x) = e\,x_i = p(a_i + a_i^+) \tag{14}$$

5 Lax, M.: J. Chem. Phys. **20**, 1752 (1952).

if we assume, without loss of generality, the lightfield to be polarized in x_i-direction. $\omega_m^{(b)}$ and $\omega_n^{(a)}$ are the respective energies of the initial and final states, and again with no loss of generality we may choose $\omega_0^{(a)}=0$. Employing expr. (14) for the dipole operator and the forms (5a, b) for the wavefunctions, the integration over the electronic space is possible, and we arrive at (abr. $I_{ba}(\omega)=p^2 G(\omega)$)

$$G(\omega)=[\mathrm{Tr}^{(a)}\exp(-H/kT)]^{-1}\sum_n\sum_m e^{-\omega_n^{(a)}/kT} \cdot \langle \Phi_n^{(a)}(q)\,|\,\Phi_{im}^{(b)}(q)\rangle\langle\Phi_{im}^{(b)}(q)\,|\,\Phi_n^{(a)}(q)\rangle\,\delta(\omega_m^{(b)}-\omega_n^{(a)}-\omega). \tag{15}$$

The Fourier transformation of this expression is the optical response function; it is given by

$$\tilde{G}(t)=[\mathrm{Tr}^{(a)}\ldots]^{-1}\sum_n\sum_m e^{-\omega_n^{(a)}/kT}\langle\Phi_n^{(a)}\,|\,\Phi_{im}^{(b)}\rangle\langle\Phi_{im}^{(b)}\,|\,\Phi_n^{(a)}\rangle \cdot \exp[-i\,\omega_m^{(b)}\,t+i\,\omega_n^{(a)}\,t] \tag{16}$$

which, in virtue of Eqs. (6a) and (9) can be transcribed into

$$\tilde{G}(t)=[\mathrm{Tr}^{(a)}\ldots]^{-1}\sum_n\sum_m\langle\Phi_n^{(a)}|\sum_k[\exp(-i\,\boldsymbol{H}^{(b)}\,t)]_{ik}|\Phi_{km}^{(b)}\rangle \cdot\langle\Phi_{im}^{(b)}|\exp\left[\left(i\,t-\frac{1}{kT}\right)H^{(a)}\right]|\Phi_n^{(a)}\rangle. \tag{17}$$

Employing now the closure property (11) the expression simplifies to

$$\tilde{G}(t)=[\mathrm{Tr}^{(a)}\ldots]^{-1}\sum_n\langle\Phi_n^{(a)}|\,[\exp(-i\,\boldsymbol{H}^{(b)}\,t)]_{ii} \cdot\exp\left[\left(i\,t-\frac{1}{kT}\right)H^{(a)}\right]|\Phi_n^{(a)}\rangle \tag{17a}$$

and by means of Eqs. (8) and (10):

$$\tilde{G}(t)=e^{-i\,\omega_0\,t}[\mathrm{Tr}^{(a)}\ldots]^{-1}\sum_n\langle\Phi_n^{(a)}|\,[\exp(-i(H_v\boldsymbol{I}+\kappa\,\boldsymbol{V})\,t)]_{ii} \cdot\exp\left[\left(i\,t-\frac{1}{kT}\right)H^{(a)}\right]|\Phi_n^{(a)}\rangle \tag{18}$$

where $\boldsymbol{I}$ is the unity matrix. The further aim of our study will be the evaluation of the optical response function, as given by (18). If this is achieved, the absorption function $G(\omega)$ can be found as the Fourier transform of $\tilde{G}(t)$,

$$\tilde{G}(\omega)=\frac{1}{2\pi}\int\tilde{G}(t)\,e^{+i\,\omega\,t}\,d\,t. \tag{19}$$

3. Application of an Operator Calculus

At this stage we employ a theorem first introduced by Goldberger and Adams[6]. It reads

$$\exp[-i(H_0+W)t]=e^{-iH_0t}P\exp\left[-i\int_0^t W_I(t')\,dt'\right] \tag{20}$$

where P is the Dyson chronological operator, and where

$$W_I(t)=e^{iH_0t}We^{-iH_0t}. \tag{21}$$

The theorem (20) is wellknown also in the theory of the $U(t, t')$-operator in quantum field theory. For our purpose we need an extension to matrix operators. Now, if H_0 and V are taken to be matrix operators, (vid. Eq. (8)), $H_0\to\boldsymbol{H}_0\equiv H_0\boldsymbol{I}\equiv H_0\delta_{ik}$, $W\to\boldsymbol{W}\equiv W_{ik}$, where $\boldsymbol{H}_0$ is a diagonal matrix, one finds the theorem

$$\exp[-i(\boldsymbol{H}_0+\boldsymbol{W})t]=e^{-iH_0t}P\exp\left[-i\int_0^t \boldsymbol{W}_I(t')\,dt'\right] \tag{22}$$

where

$$(\boldsymbol{W}_I)_{ik}=e^{iH_0t}W_{ik}e^{-iH_0t}. \tag{23}$$

The derivation of the theorem (22) can be achieved, if one repeats step by step the Goldberger-Adams[6]-derivation of (20) for the matrix operators $\boldsymbol{H}_0$ and $\boldsymbol{W}$. This procedure is straightforward and does not lead to any difficulties, provided $\boldsymbol{H}_0$ is a diagonal matrix. Therefore it is not necessary to write down this derivation here. If we apply the theorem (22) in the expression for the response function (18) we arrive at

$$\begin{aligned}\tilde{G}(t)=e^{-i\omega_0t}[\mathrm{Tr}^{(a)}\ldots]^{-1}\sum_n\langle\Phi_n^{(a)}|\,e^{-iH_vt}\left[P\exp\left(-i\kappa\int_0^t V_I(t')\,dt'\right)\right]_{ii}\\ \cdot\exp\left[\left(it-\frac{1}{kT}\right)H^{(a)}\right]|\Phi_n^{(a)}\rangle.\end{aligned} \tag{24}$$

4. Application of Wick's Theorem

In all *JT*-cases and also in the non-degenerate coupling case the choice of vibrational coordinates and the choice of the energy can be made in such a way, that for the ground state one has without loss of generality $\langle V\rangle_{00}=0$, i.e. $H^{(a)}(q)\equiv H_v(q)$. Then by means of (6a) the optical response function (24) reduces to

$$\begin{aligned}\tilde{G}(t)=e^{-i\omega_0t}(1-\lambda)^r\sum_{m_1,\ldots,m_r}\lambda^{m_1+\cdots+m_r}\\ \cdot\langle m_1,\ldots,m_r|\,P\exp\left[-i\kappa\int_0^t V_I(t')\,dt'\right]_{ii}|m_1,\ldots,m_r\rangle\end{aligned} \tag{25}$$

6 Goldberger, M. L., Adams II, E. N.: J. Chem. Phys. 20, 240 (1952).

where

$$|m_1, \ldots, m_r\rangle = (m_1!)^{-\frac{1}{2}} \ldots (m_r!)^{-\frac{1}{2}} (b_1^+)^{m_1} \ldots (b_r^+)^{m_r} \Phi_0^{(a)}, \tag{26}$$

$$V_I(t') = e^{i H_v t} V(q) e^{-i H_v t}. \tag{27}$$

For simplicity we have assumed that there is only one set of degenerate oscillators with frequency ω_1, r being the degree of degeneracy, $j = 1, \ldots, r$. The problem is nontrivial only, if the electronic degeneracy is also assumed to be r. For one set of degenerate oscillators we have

$$\mathrm{Tr}^{(a)} \exp(-H_v/kT) = (1-\lambda)^{-r}, \quad \lambda = \exp(-\omega_1/kT).$$

Performing the series expansion of the exponential operator in (25), a typical term in the optical response function reads

$$\begin{aligned} &\frac{(-i\kappa)^{2\mu}}{(2\mu)!} \sum_{m_1, \ldots, m_r} \lambda^{m_1 + \cdots + m_r} \\ &\qquad \cdot \langle m_1, \ldots, m_r | P[V_I(t_1) \ldots V_I(t_{2\mu})]_{ii} | m_1, \ldots, m_r \rangle. \end{aligned} \tag{29}$$

In the nontrivial *JT*-cases the elements $(V_I(t))_{ij}$ of the matrix operator are $\pm(b_j(t) + b_j^+(t))$, $j = 1, \ldots, r$, where

$$b_j(t) = e^{i H_v t} b_j e^{-i H_v t}.$$

For this reason only even terms appear in the series expansion of the operator exponential of Eq. (25), as already accounted for in (29). Now, it has to be emphasized that the time-ordering operator in Eq. (29) acts onto the products of matrix operators $V_I(t_\nu)$, which is not identical with the time-ordering of the products of elements. E.g. for

$$t_2 > t_1 > t_3 > \cdots > t_{2\mu}$$

we would have

$$[P V_I(t_1) \ldots V_I(t_{2\mu})]_{ii} = \sum_{j_1 j_2 \ldots} V(t_2)_{ij_1} V_{j_1 j_2}(t_1) \ldots$$

whereas

$$P \sum_{j_1 j_2} V(t_1)_{ij_1} V_{j_1 j_2}(t_2) \ldots = \sum_{j_1 j_2 \ldots} V(t_2)_{j_1 j_2} V_{ij_1}(t_1) \ldots .$$

However, in order to end up with a closed solution one is forced to neglect this difference and to make the approximation

$$[P V_I(t_1) \ldots V_I(t_{2\mu})]_{ii} \approx \sum_{j_1 j_2 \ldots} P V_{ij_1}(t_1) V_{j_1 j_2}(t_2) \ldots V_{j_{(2\mu-1)} i}(t_{2\mu}). \tag{30}$$

It is not known, whether the neglected terms can be collected in a systematic way. They are not negligible in the intermediate coupling region.

Nevertheless, it can be shown, that the result based on the approximation (30) is exact both in the weak ($\kappa \ll \omega$) and strong ($\kappa \gg \omega$) coupling limit. This can be seen, if one compares the moments of the absorption band, as calculated by adopting Eq. (30), with the exact moments [7].

By means of Eq. (30) and the commutation relation

$$[(b_j(t)+b_j^+(t)),\, b_{j'}(t')+b_{j'}^+(t')]=0 \qquad \text{for } j \neq j' \tag{31}$$

any P-product of the sequence of products in (29) factorizes into a product of P-products, where each single one contains only the operators $(b_j(t)+b_j^+(t))$ of the same j. Let $2\mu_j$ be the number of $(b_j+b_j^+)$-factors in one of these P-products,

$$\mu_1+\cdots+\mu_r=\mu \tag{32}$$

and further let ν_j be the number of $(b_j+b_j^+)$-factors with sign $(-)$, and ν_j' the respective number with sign $(+)$. Then we have

$$\begin{aligned}\langle m_1, \ldots, m_r | P[V_I(t_1) \ldots V_I(t_{2\mu})] | m_1, \ldots, m_r\rangle \\ = \sum_{\mu_1,\ldots,\mu_r}^{(\mu_1+\cdots+\mu_r=\mu)} \prod_{j=1}^{r} \langle m_j | P[(b_j(t_1^{(j)})+b_j^+(t_1^{(j)})) \\ \ldots (b_j(t_{2\mu_j}^{(j)})+b_j^+(t_{2\mu_j}^{(j)}))] | m_j\rangle \\ \cdot \sum_{\nu_1=0}^{2\mu_1} \cdots \sum_{\nu_r=0}^{2\mu_r} (-1)^{\nu_1+\cdots+\nu_r} Z(\mu_1, \ldots, \mu_r | \nu_1, \ldots, \nu_r)\end{aligned} \tag{33}$$

where $Z(\mu_1, \ldots, \mu_r | \nu_1, \ldots, \nu_r)$ is the number of all allowed combinations of the elements of V_I in expr. (29), for which the factors $(b_j+b_j^+)$ appear $2\mu_j$-times and the factors (-1) appear $(\nu_1+\cdots+\nu_r)$-times. This number is the solution of a combinatorial problem, which is specific to each type of JT-situations. We shall return to this problem in the next section.

In this section we will investigate further the P-products of the last expression; by writing them in the context in which they actually appear in the response function (25), one is confronted with the integration problem

$$\begin{aligned}I_{2\mu_j}^{(m_j)}(t) = \int_0^t dt_1 \ldots \int_0^t dt_{2\mu_j} P\langle m_j | (b_j(t_1)+b_j^+(t_1)) \\ \ldots (b_j(t_{2\mu_j})+b_j^+(t_{2\mu_j})) | m_j\rangle.\end{aligned} \tag{34}$$

This integral can be calculated by a systematic application of Wick's theorem, which also leads to certain combinatorial problems; their

7 The result (58) for the optical response in the system $E-e$ has been published previously by the author in a short note in Phys. Letters **29** A, 472 (1969). Rosenfeld, Yu. B., Tsukerblat, B. S., Vekhter, B. G., have kindly informed the author that they have calculated the moments of (58) up to the 6th one and compared them with the exact moments. They coincide exactly up to the 4th one, and for the weak and strong coupling limit there is coincidence for all moments.

solution turns out to be wellknown. This calculation has been given in another paper of the author (see Ref.[4], Appendix B). There it is found[4]

$$I_{2\mu_j}^{(m_j)}(t)=(2\mu_j)!\sum_{\nu=0}^{\mu_j}\frac{1}{\nu![(\mu_j-\nu)!]^2} \cdot C(t)^\nu D(t)^{\mu_j-\nu} m_j(m_j-1)\ldots\big(m_j-(\mu_j-\nu-1)\big) \tag{35}$$

where:

$$C(t)=\frac{1}{\omega_1^2}\left[-i\,\omega_1 t+1-e^{-i\omega_1 t}\right], \tag{36}$$

$$D(t)=\frac{2}{\omega_1^2}\left[1-\cos\omega_1 t\right]. \tag{37}$$

Employing expr. (35) in (25), the summation over m_j can be performed,

$$(1-\lambda)\sum_{m_j}\lambda^{m_j} m_j(m_j-1)\ldots\big(m_j-(\sigma-1)\big)=\left(\frac{\lambda}{1-\lambda}\right)^\sigma\cdot\sigma!. \tag{38}$$

Hence we have

$$\begin{aligned}(1-\lambda)\sum_{m_j}\lambda^{m_j} I_{2\mu_j}^{(m_j)}(t)&=(2\mu_j)!\sum_{\nu=0}^{\mu_j}\frac{1}{\nu!(\mu_j-\nu)!}C^\nu\left(\frac{\lambda}{1-\lambda}D\right)^{\mu_j-\nu}\\ &=\frac{(2\mu_j)!}{\mu_j!}\left[C+\frac{\lambda}{1-\lambda}D\right]^{\mu_j}.\end{aligned} \tag{39}$$

Inserting this via (33) into Eq. (25) the optical response function takes form

$$\tilde{G}(t)=e^{-i\omega_0 t}\sum_{\mu=0}^{\infty}\frac{1}{(2\mu)!}u(t)^{2\mu}\underbrace{\sum_{\mu_1,\ldots,\mu_r}^{(\mu_1+\cdots+\mu_r=\mu)}\frac{(2\mu_1)!\ldots(2\mu_r)!}{\mu_1!\ldots\mu_r!}\cdot\sum_{\nu_1=0}^{2\mu_1}\cdots\sum_{\nu_r=0}^{2\mu_r}(-1)^{\nu_1+\cdots+\nu_r}Z(\mu_1,\ldots,\mu_r\,|\,\nu_1,\ldots,\nu_r)}_{\text{combinatorial problem}} \tag{40}$$

where the abbreviation

$$u(t)=-\frac{i\kappa}{\omega_1}\left[-i\,\omega_1 t+\frac{1+\lambda}{1-\lambda}-\frac{1}{1-\lambda}e^{-i\omega_1 t}-\frac{\lambda}{1-\lambda}e^{i\omega_1 t}\right]^{\frac{1}{2}}, \tag{41}$$

has been used. Introducing the further abbreviation

$$\zeta(\mu)=\sum_{\mu_1,\ldots,\mu_r}^{(\mu_1+\cdots+\mu_r=\mu)}\frac{(2\mu_1)!\ldots(2\mu_r)!}{\mu_1!\ldots\mu_r!}\cdot\sum_{\nu_1=0}^{2\mu_1}\cdots\sum_{\nu_r=0}^{2\mu_r}(-1)^{\nu_1+\cdots+\nu_r}Z(\mu_1,\ldots,\mu_r\,|\,\nu_1,\ldots,\nu_r) \tag{42}$$

we may write

$$\tilde{G}(t) = e^{-i\omega_0 t} \sum_{\mu=0}^{\infty} \frac{\zeta(\mu)}{(2\mu)!} u(t)^{2\mu}. \tag{40a}$$

$\zeta(\mu)$ represents the solution of the combinatorial problem which is specific for each JT-case. Before investigating these it is interesting to note a connection of $\zeta(\mu)$ to the moments of the absorption band in the strong coupling limit. For the normalized absorption function $G(\omega)$ the moments are defined by

$$M_m = \int_{-\infty}^{+\infty} G(\omega)\,(\omega-\omega_0)^m\, d\omega. \tag{43}$$

Now by means of the Fourier representation of $G(\omega)$ we may write

$$\begin{aligned}\tilde{G}(t) &= \int_{-\infty}^{+\infty} G(\omega)\, e^{-i\omega_0 t}\, d\omega \\ &= e^{-i\omega_0 t} \int_{-\infty}^{+\infty} G(\omega) \sum_{m=0}^{\infty} \frac{1}{m!} (\omega-\omega_0)^m (-i\,t)^m\, d\omega\end{aligned} \tag{44}$$

or, in view of Eq. (43):

$$\tilde{G}(t) = e^{-i\omega_0 t} \sum_{m=0}^{\infty} \frac{1}{m!} M_m (-i\,t)^m. \tag{45}$$

Hence, we may calculate M_m directly from $\tilde{G}(t)$:

$$M_m = \left(i \frac{d}{dt}\right)^m [e^{i\omega_0 t}\, \tilde{G}(t)]_{t=0}. \tag{46}$$

Now, expanding $\tilde{G}(t)$ in a power-series in t, in each μ-term of (40a) only the lowest t-power must be considered for the calculation of the moments (strong coupling limit). From (41) we have

$$u(t)^2 = -\frac{1}{2}\left(\frac{1+\lambda}{1-\lambda}\right) \kappa^2 t^2 + O(t^3), \tag{47}$$

whence, by means of (46) the moments of (40a) in the strong coupling limit are given by

$$M_{2m} = \left(\frac{1+\lambda}{1-\lambda}\, \frac{\kappa^2}{2}\right)^m \zeta(m), \qquad M_{2m+1} = 0 \tag{48}$$

i.e. the solution of the combinatorial problem, $\zeta(m)$, is proportional to the even moments M_{2m}. This, in reversion, yields the possibility of expressing the response function (for arbitrary coupling strength) by the moments of the strong coupling limit,

$$\tilde{G}(t) = e^{-i\omega_0 t} \sum_{\mu=0}^{\infty} \frac{M_\mu(0)}{(2\mu)!} \left(\frac{2}{\kappa^2}\right)^\mu u(t)^{2\mu} \tag{49}$$

where $M_\mu(0)$ are the strong-coupling moments for $T=0$. This gives the moment-calculations a new significance (vid. Ref.[4]). To conclude this section, it should be noted that the form (40) for the optical response also applies to the non-degenerate coupling case (nondegenerate electronic excition, single oscillator) characterized by the Hamiltonian

$$H^{(A)}(x, q)=\omega_0 a^+ a+\omega_1 b^+ b+\kappa a^+ a(b+b^+). \tag{50}$$

In this case we have $Z(\mu|0)\equiv 1$ and therefore $\zeta^{(A)}(\mu)=(2\mu)!/\mu!$, from which we arrive at

$$\tilde{G}^{(A)}(t)=e^{-i\omega_0 t}\sum_{\mu=0}^{\infty}\frac{1}{\mu!}u^{2\mu}=e^{-i\omega_0 t+u^2}. \tag{51}$$

This is a wellknown result and yields δ-functions for $G^{(A)}(\omega)$ at the positions $\omega_n=\omega_0-(k^2/\omega_1)+\omega_1 n, n=0, \pm 1, \ldots$. It has been derived first by Lax[5] in an approximative manner.

5. Combinatorial Problems for *JT*-Systems

Among the multitude of *JT*-situations which appear, if orbital degeneracy only is considered in the electronic system, there are two fundamental nontrivial types[4]. The first is present in trigonal symmetries and involves a coupling of a doubly degenerate electronic level with doubly degenerate vibrational modes (system $E-e$)*. The second is found in cubic symmetries, where a triply degenerate electronic level may interact with triply degenerate modes (system $T-t$). For further details another paper of the author may be consulted[4].

Our method can be applied to both cases and also to a mixture of each of the fundamental nontrivial interactions with trivial parts. But in these complicated systems the resulting combinatorial problems are rather awkward and the optical response cannot be given in a condensed closed form. Therefore we will restrict our further consideration to the two pure cases. For these the Hamiltonians read[4]

$$\begin{aligned} H^{(E)}(x, q)=&\omega_0\sum_{i=1}^{2} a_i^+ a_i+\omega_1\sum_{j=1}^{2} b_j^+ b_j \\ &+\kappa[(a_1^+ a_1-a_2^+ a_2)(b_1+b_1^+)+(a_1^+ a_2+a_2^+ a_1)(b_2+b_2^+)], \end{aligned} \tag{52}$$

(system $E-e$)

* It should be noted that the $E-e$ *JT*-case may also arise in cubic-symmetry, but we describe it to trigonal systems, because this is the lowest symmetry where it is found.

and

$$H^{(T)}(x, q)=\omega_0\sum_{i=1}^{3} a_i^+ a_i+\omega_1\sum_{j=1}^{3} b_j^+ b_j \tag{53}$$
$$+\kappa\sum_{k=1}^{3}(a_k^+ a_{k+1}+a_k a_{k+1}^+)(b_{k+2}+b_{k+2}^+), \qquad \text{(system } T-t).$$

Let us first consider the system $E-e$. In this case the interaction matrix operator V_I is of the form

$$V_I(t)=\begin{pmatrix}(b_1(t)+b_1^+(t)), & (b_2(t)+b_2^+(t))\\ (b_2(t)+b_2^+(t)), & -(b_1(t)+b_1^+(t))\end{pmatrix}. \tag{54}$$

Hence, for the calculation of the optical response (40) one has to evaluate expressions of the form (29), where $r=2$. The multitude of different combinations of the elements of $V_I(t)$ in expr. (29) may be depicted as diagrams, the elements of which are given in Fig. 1.

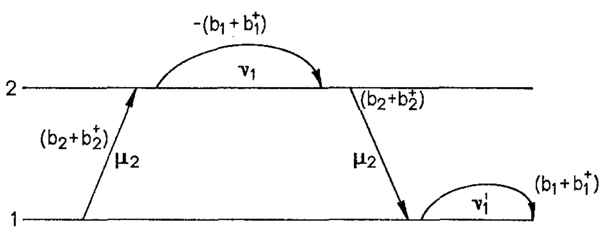

Fig. 1. Combinatorial problem for the *JT*-case $E-e$

The sum of all allowed combinations of the elements of V_I in expr. (29) consists now of all closed diagrams starting and ending on line 1 of Fig. 1, if we choose the incoming light to be polarized in x_1-direction (i.e. $i=1$ in expr. (29)). In each allowed diagram the elements $(V_I)_{12}=(b_2+b_2^+)$ and $(V_I)_{21}=(b_2+b_2^+)$ appear equally often, and in agreement with the preceding section this number will be denoted by μ_2. Accordingly, the multiplicity of $(V_I)_{22}=-(b_1+b_1^+)$ and $(V_I)_{11}=+(b_1+b_1^+)$ are denoted by ν_1 and ν_1' respectively, and we must have $\nu_1+\nu_1'=2\mu_1$. The evaluation of the number $Z(\mu_1, \mu_2 \,|\, \nu_1, 0)$ of allowed paths leads to a combinatorial problem which has been solved in another paper of the author[4]. The result is

$$Z(\mu_1, \mu_2 \,|\, \nu_1, 0)=\binom{\mu_2+\nu_1'}{\nu_1'}\binom{\mu_2+\nu_1-1}{\nu_1} \tag{55}$$

which has to be inserted in Eq. (40) and leaves a summation problem, which again can be performed[4]:

$$\sum_{\nu_1}^{2\mu_1}(-1)^{\nu_1}\binom{\mu_2+2\mu_1-\nu_1}{2\mu_1-\nu_1}\binom{\mu_2+\nu_1-1}{\nu_1}=\binom{\mu_1+\mu_2}{\mu_1}. \tag{56}$$

Inserting this in (42) we have for $\zeta(\mu)$ (vid. Ref.[4]):

$$\zeta^{(E)}(\mu)=\sum_{\mu_1=0}^{\mu}\frac{(2\mu_1)!\,(2\mu-2\mu_1)!}{\mu_1!\,(\mu-\mu_1)!}\binom{\mu}{\mu_1}=2^{2\mu}\mu! \tag{57}$$

Hence the optical response (40) resp. (40a) is simplified to

$$\begin{aligned} G^{(E)}(t)&=e^{-i\omega_0 t}\sum_{\mu=0}^{\infty}\frac{\mu!}{(2\mu)!}(2u(t))^{2\mu}.\\ &=e^{-i\omega_0 t}\{\pi^{\frac{1}{2}}u(t)\,e^{u^2}\mathrm{Erf}(u)+1\}\end{aligned} \tag{58}$$

where $u(t)$ is given by def. (41) and $\mathrm{Erf}(u)$ is the error function[8],

$$\mathrm{Erf}(u)=2\pi^{-\frac{1}{2}}e^{-u^2}\sum_{\nu=0}^{\infty}\frac{2^{\nu}u^{2\nu+1}}{(2\nu+1)!!}. \tag{59}$$

We now turn to the *JT*-case $T-t$. Here the interaction matrix operator V_I follows from the Hamiltonian (53) and is of the form

$$V_I(t)=\begin{pmatrix} 0, & (b_3+b_3^+), & (b_2+b_2^+)\\ (b_3+b_3^+), & 0, & (b_1+b_1^+)\\ (b_2+b_2^+), & (b_1+b_1^+), & 0\end{pmatrix}. \tag{60}$$

Here the multitude of different combinations of the elements of $V_I(t)$ in expr. (29) may be depicted as diagrams, the elements of which are given in Fig. 2.

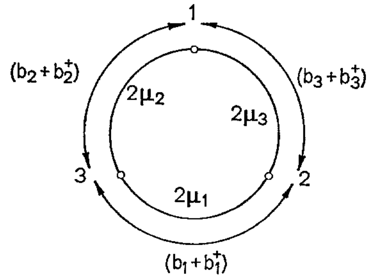

Fig. 2. Combinatorial problem for the *JT*-case $T-t$

8 E.g. see Ryshik, I. M., Gradstein, I. S.: VEB Tables. Berlin: Deutscher Verlag der Wissenschaften 1963.

The number $Z(\mu_1, \mu_2, \mu_3 | 0, 0, 0)$ is now the number of closed paths starting and ending in point 1 of Fig. 2, which interesect regions $\widehat{12}, \widehat{23}, \widehat{31}$ respectively $2\mu_3$-, $2\mu_1$- and $2\mu_2$-times. This combinatorial problem has not been solved for arbitrary $\mu(=\mu_1+\mu_2+\mu_3)$-values. Up to $\mu=5$ the numbers $Z(\mu_1, \mu_2, \mu_3 | 0, 0, 0\rangle$ have been tabulated in Ref.[4]. The number $\zeta(\mu)$ is now given by

$$\zeta^{(T)}(\mu) = \sum_{\mu_1, \mu_2, \mu_3}^{(\mu_1+\mu_2+\mu_3=\mu)} \frac{(2\mu_1)!\,(2\mu_2)!\,(2\mu_3)!}{\mu_1!\,\mu_2!\,\mu_3!} Z(\mu_1, \mu_2, \mu_3 | 0, 0, 0). \quad (61)$$

It has been tabulated up to $\mu=12$ in Ref.[4]. Since the combinatorial problem of Fig. 2 is very clear cut, it is evident that $\zeta(\mu)$ may be easily calculated by computers up to arbitrary μ-numbers, i.e. the absorption function may be calculated via Eq. (40a) to an arbitrary degree of accuracy. A similar statement also holds for more complicated *JT*-systems, e.g. for mixed *JT*-cases, or for systems with more then one set of degenerate oscillators, if the presented method is applied to them.

6. Summary and Discussion

A method has been developed, which allows the calculation of the optical Jahn-Teller problem both in the weak and strong coupling limit. The method is based on an extension of a theorem first given by Goldberger and Adams[6] and on a systematic application of Wick's theorem. The latter leads to combinatorial problems, which in general are rather complicated, but in any case are easy to handle by computers. In the two pure *JT*-cases $E-e$ and $T-t$ the combinatorial problems are clear-cut and simple. In particular in the $E-e$-case a closed solution of the combinatorial problem can be given and the optical response can be written in a concise analytical form.

It is shown further on that the combinatorial problems appearing in the presented operator method have a one to one correspondence with those in the strong coupling limit of the method of moments for the optical *JT*-problem, presented in another paper of the author[4]. This correspondence is of importance, because it has the consequence that the knowledge of the complete set of moments in the strong coupling limit is sufficient to write down the quasi-exact expression for the optical response. In view of this a calculation of the moments gains an extended meaning.

The presented method may also be employed to discuss the quality of approximative methods for the dynamical *JT*-problems, e.g. semi-classical methods[9], etc. But the above investigation, although being

9 Toyozawa, Y., Inoue, M.: J. Phys. Soc. Japan **21**, 1663 (1966).

interesting in itself, has also some significance in a more general sense. It is one of the few examples, where a nonlinear coupling of two systems can be handled almost exactly. It may well be of value for the discussion of nonlinear transport problems. It also appears suggestive, to use the method as a guide for finding a nonlinear canonical transformation, which would simplify the calculation considerably. To illustrate this, let us here return very briefly to the non-*JT*-case as characterized by the Hamiltonian (50). In this case the transformation $H' = e^{-S} H e^{S}$, $\psi' = e^{-S} \psi'$ where

$$S = \frac{\kappa}{\omega_1} (b - b^+) a^+ a ,$$

decouples the two systems completely. For the *JT*-case one may think of a similar transformation, but this is left to future study.

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