The Line Shape of Optical and Electron Spin Resonance Absorption under the Influence of Exciton Motion

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The line shape of optical and electron spin resonance absorption under the influence of the coupled coherent and incoherent exciton motion is calculated analytically. The exciton motion is described by a stochastic Hamiltonian comprising both its coherent and its incoherent part. The coherent motion is represented by the transition matrix element and the incoherent one by the strengths of local and non-local fluctuations. Starting from this Hamiltonian, equations of motion of two-time correlation functions for two arbitrary operators are derived. Using these equations, the line shape of optical absorption of crystals containing two inequivalent molecules per unit cell is calculated. Furtheron an exact analytical expression for the ESR line shape of two differently oriented molecules is derived and discussed in detail as a function of the parameters of the model. From this exact expression for the line shape approximations for several limiting cases are obtained. A comparison between the exact and the approximate expressions is given.

1. Introduction

Since some years the motion of excitons in molecular crystals is again the subject of a lot of experimental and theoretical investigations. In order to describe this energy transport, two different models have been proposed, namely that of coherent and that of incoherent motion. In the coherent case[1] the exciton is assumed to move through the crystal like a Bloch wave, which is eventually scattered by phonons. In the incoherent case[2, 3] it is assumed that the phase of the exciton is destroyed by molecular and lattice vibrations in a short time interval compared to the time the exciton stays at a molecule. In this case the motion of the exciton is due to a hopping process which is described mathematically by a master equation or, in the limiting case of a continuum description, by a diffusion equation.

Some years ago Haken and Strobl[4, 5] have developed a stochastic model for the description of energy transfer by excitons which includes both the coherent and the incoherent cases. The coherent motion is described by the transition matrix element between the molecules including the Coulomb and the exchange interaction integral. The influence of the phonons is taken into account by local and non-local fluctuations expressing fluctuations of the energy and of the transition matrix elements, respectively.

For this stochastic model a density matrix equation has been derived by different methods[4–6]. Once the solution of the density matrix is obtained, one has the full information about the system under consideration. Especially one may calculate all correlation functions using a theorem of Haken and Weidlich[7]. Unfortunately it is not very easy to get the general solution of the density matrix equation. In fact it has been solved analytically or by computer calculation only for special cases[8–10]. For the comparison with experimental results, however, often only two-time correlation functions are needed. Thus the line shapes of optical and ESR absorption are obtained from the two-time correlation functions of the electric and magnetic dipol moment operators, respectively. Therefore it is more straightforward, to derive equations of motion for these correlation functions directly. A further motivation for this procedure is the hope that these equations may be solved more easily than the density matrix equation.

Starting from an Hamiltonian, which is a generalization of that of the model of Haken and Strobl, the equations of motion for the two-time correlation functions of two arbitrary operators are given in the next section. Using these equations, in § 3 the line shape of optical absorption for crystals with two differently oriented molecules per unit cell is derived and discussed as a function of the parameters of the model. In § 4 we calculate the influence of the coupled coherent and incoherent exciton motion on the ESR absorption line and obtain an exact analytic expression for the line shape. The dependence of this expression on the parameters of the system, i. e. on the exchange interaction integral and on the

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strengths of the local and non-local fluctuations is discussed. Finally by expanding the exact expression for several limiting cases, we obtain approximate formulas, which describe well the line shapes in these situations.

2. The Equations of Motion for the Correlation Functions

2.1. The Hamiltonian

The Hamiltonian of the systems we wish to consider consists of two parts

$$H = H_0 + H_1(t)\,, \tag{2.1}$$

with

$$H_1(t) = \sum_{\lambda,\lambda'} h_{\lambda\lambda'}(t)\, A_{\lambda\lambda'}\,. \tag{2.2}$$

H_0 is a time independent operator describing the coherent part of the motion. Explicit expressions for H_0 are given in sections 3 and 4 when investigating optical and spin resonance absorption. This coherent motion is disturbed by the phonons, and their influence is taken into account by the stochastic operator $H_1(t)$ of (2.2). $A_{\lambda\lambda'}$ are quantum mechanical operators and $h_{\lambda\lambda'}(t)$ fluctuating classical functions. functions. We assume $h_{\lambda\lambda'}(t)$ to be a Gaussian Markov process with disappearing mean value[4, 5]. This means that the fluctuations are generated by many independent vibrations with broad frequency spectrum. The indices λ and λ' describe a complete set of functions, e. g. Wannier or molecular functions. In the Heisenberg picture we have for the equation of motion of an operator O

$$\dot{O} = \frac{i}{\hbar}\,[H, O] \tag{2.3}$$

with the solution

$$O(t) = \left(T \exp\left\{\frac{1}{i\hbar}\int_t^0 H(\tau)\,\mathrm{d}\tau\right\}\right) \cdot O(0)\left(\tilde{T} \exp\left\{-\frac{1}{i\hbar}\int_t^0 H(\tau)\,\mathrm{d}\tau\right\}\right), \quad t<0\,, \tag{2.4}$$

$$O(t) = \left(\tilde{T} \exp\left\{-\frac{1}{i\hbar}\int_0^t H(\tau)\,\mathrm{d}\tau\right\}\right) \cdot O(0)\left(T \exp\left\{\frac{1}{i\hbar}\int_0^t H(\tau)\,\mathrm{d}\tau\right\}\right), \quad t>0\,. \tag{2.5}$$

T and $\tilde{T}$ are time ordering operators, ordering later times more to the left and more to the right, respectively.

2.2 The equations of motion for the correlation functions

The two-time correlation function of two operators O_1 and O_2 for $t>0$ is defined by

$$\langle\langle O_1(t)\,O_2(0)\rangle\rangle = \mathrm{Tr}\left\{\varrho(0)\left\langle\left(\tilde{T}\exp\left\{-\frac{1}{i\hbar}\int_0^t H(\tau)\,\mathrm{d}\tau\right\}\right) O_1\left(T\exp\frac{1}{i\hbar}\int_0^t H(\tau)\,\mathrm{d}\tau\right\}\right)\right\rangle O_2\right\}. \tag{2.6}$$

In this expression Tr means trace operation using a complete set of functions, $\varrho(0)$ is the density operator at time $t=0$, and the brackets $\langle\ldots\rangle$ on the right side stand for the statistical average. Differentiating with respect to time we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle O_1(t)\,O_2(0)\rangle\rangle = \mathrm{Tr}\left\{\varrho(0)\left\langle\left(\tilde{T}\exp\left\{-\frac{1}{i\hbar}\int_0^t H(\tau)\,\mathrm{d}\tau\right\}\right)\right.\right. \cdot\left(-\frac{1}{i\hbar}H(t)\,O_1 + \frac{1}{i\hbar}O_1\,H(t)\right)\left.\left.\left(T\exp\left\{\frac{1}{i\hbar}\int_0^t H(\tau)\,\mathrm{d}\tau\right\}\right)\right\rangle O_2\right\}. \tag{2.7}$$

This expression may be rewritten after introducing an arbitrary function $a(t)$ and forming the variational derivate with respect to $a(t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle O_1(t)O_2(0)\rangle\rangle=\mathrm{Tr}\left\{\varrho(0)\,2\frac{\delta}{\delta\,\alpha(t)}\left\langle\!\!\left\langle\left(\tilde{T}\exp\left\{-\frac{1}{i\hbar}\int_0^t\alpha(\tau)H(\tau)\,\mathrm{d}\tau\right\}\right)O_1\right.\right.\right.$$
$$\left.\left.\left.\cdot\left(T\exp\left\{\frac{1}{i\hbar}\int_0^t\alpha(\tau)H(\tau)\,\mathrm{d}\tau\right\}\right)\right\rangle\!\!\right\rangle O_2\right\}\Bigg|_{\alpha(t)=1}. \tag{2.8}$$

The evaluation of the angular bracket is given in the appendix. From there we have the following equations of motion for the correlation functions:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle O_1(t)O_2(0)\rangle\rangle=\frac{i}{\hbar}\langle\langle[H_0,O_1]_t\,O_2(0)\rangle\rangle$$
$$-\frac{s}{4}\sum_{\{\lambda\}}\Lambda(\{\lambda\})\,\langle\langle\{(A_{\lambda''\lambda'''}A_{\lambda\lambda'}O_1)_t+(A_{\lambda\lambda'}A_{\lambda''\lambda'''}O_1)_t+(O_1A_{\lambda\lambda'}A_{\lambda''\lambda'''})_t$$
$$+(O_1A_{\lambda''\lambda'''}A_{\lambda\lambda'})_t-2(A_{\lambda\lambda'}O_1A_{\lambda''\lambda'''})_t-2(A_{\lambda''\lambda'''}O_1A_{\lambda\lambda'})_t\}\,O_2(0)\rangle\rangle, \tag{2.9}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle O_1(0)O_2(t)\rangle\rangle=\frac{i}{\hbar}\langle\langle O_1(0)\,[H_0,O_2]_t\rangle\rangle$$
$$-\frac{s}{4}\sum_{\{\lambda\}}\Lambda(\{\lambda\})\langle\langle O_1(0)\;\{(A_{\lambda''\lambda'''}A_{\lambda\lambda'}O_2)_t+(A_{\lambda\lambda'}A_{\lambda''\lambda'''}O_2)_t+(O_2A_{\lambda\lambda'}A_{\lambda''\lambda'''})_t$$
$$+(O_2A_{\lambda''\lambda'''}A_{\lambda\lambda'})_t-2(A_{\lambda\lambda'}O_2A_{\lambda''\lambda'''})_t-2(A_{\lambda''\lambda'''}O_2A_{\lambda\lambda'})_t\}\rangle\rangle. \tag{2.10}$$

In (2.9) and (2.10) we have $s=-1$ for $t<0$ and $s=+1$ for $t>0$. The lower index t at the brackets means that their contents have to be understood as Heisenberg operators. The function $\Lambda(\{\lambda\})$ is defined by the correlation function of the stochastic process $h_{\lambda\lambda'}(t)$ in the following way:

$$\langle h_{\lambda\lambda'}(t_1)h_{\lambda''\lambda'''}(t_2)\rangle=\delta(t_1-t_2)\hbar^2\Lambda(\lambda,\lambda',\lambda'',\lambda''')=\delta(t_1-t_2)\hbar^2\Lambda(\{\lambda\}). \tag{2.11}$$

2.3 Application to Frenkel-excitons

In order to apply the above equations to Frenkel-excitons, we have to write

$$A_{\lambda\lambda'}=b_\lambda^+\,b_{\lambda'}, \tag{2.12}$$

where b_λ^+, b_λ are creation and annihilation operators, respectively, for excitons at site λ. λ stands for two variables n and j, where n numerates the unit cells of the crystal and j the molecules within the unit cells. Using such a localized basis, the diagonal elements $h_{\lambda\lambda}(t)$ of the stochastic process describe fluctuations of the energy of the exciton when sitting at site λ, and the non-diagonal elements $h_{\lambda\lambda'}(t)$ express fluctuations of the transition matrix element. In this case for the function $\Lambda(\{\lambda\})$ we write[5]

$$\Lambda(\{\lambda\})=\frac{2}{\hbar}\gamma_{|\lambda-\lambda'|}\{\delta_{\lambda\lambda''}\,\delta_{\lambda'\lambda'''}$$
$$+\delta_{\lambda\lambda'''}\,\delta_{\lambda'\lambda''}-\delta_{\lambda\lambda'}\,\delta_{\lambda\lambda''}\,\delta_{\lambda'\lambda'''}\} \tag{2.13}$$

with $\gamma_{|\lambda-\lambda'|}=\gamma_{|n-n'|,\,|j-j'|}$ and $\delta_{\lambda\lambda'}=\delta_{nn'}\,\delta_{jj'}$. From (2.11) and (2.13) we see that in this model energy fluctuations $[h_{\lambda\lambda}(t)]$ at different molecules and fluctuations of the transition matrix elements $[h_{\lambda\lambda'}(t)]$ between different pairs of molecules are not correlated. The strength of the energy fluctuations, i. e. the local fluctuations, is described by γ_0, that of the transition matrix elements, i. e. of the non-local fluctuations, by $\gamma_{|\lambda-\lambda'|}$, $\lambda\neq\lambda'$.

Confining to the subspace of Hilbert-space containing the state without any excitation and all states with only a single excitation, we may write

$$A_{\lambda\lambda'}A_{\lambda''\lambda'''}=b_\lambda^+\,b_{\lambda'}\,b_{\lambda''}^+b_{\lambda'''}=\delta_{\lambda'\lambda''}\,b_\lambda^+\,b_{\lambda'''}. \tag{2.14}$$

With this rule the equations of motion for the correlation functions read:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle O_1(t)O_2\rangle\rangle=\frac{i}{\hbar}\langle\langle[H_0,O_1]_t\,O_2(0)\rangle\rangle-\frac{s}{\hbar}\{\sum_{\lambda,\lambda'}\gamma_{|\lambda-\lambda'|}\langle\langle(b_\lambda^+\,b_\lambda\,O_1)_t\,O_2\rangle\rangle$$
$$+\sum_{\lambda,\lambda'}\gamma_{|\lambda-\lambda'|}\langle\langle(O_1\,b_\lambda^+\,b_\lambda)_t\,O_2\rangle\rangle-2\sum_{\lambda,\lambda'}\gamma_{|\lambda-\lambda'|}\langle\langle(b_\lambda^+b_{\lambda'}\,O_1\,b_\lambda^+\,b_{\lambda'})_t\,O_2\rangle\rangle \tag{2.15}$$
$$-2\sum_{\lambda,\lambda'}\gamma_{|\lambda-\lambda'|}\langle\langle(b_\lambda^+\,b_{\lambda'}\,O_1\,b_{\lambda'}^+\,b_\lambda)_t\,O_2\rangle\rangle+2\sum_{\lambda}\gamma_0\langle\langle(b_\lambda^+\,b_\lambda\,O_1\,b_\lambda^+\,b_\lambda)_t\,O_2\rangle\rangle\},$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle O_1 O_2(t)\rangle\rangle = \frac{i}{\hbar}\langle\langle O_1[H_0, O_2]_t\rangle\rangle - \frac{s}{\hbar}\{\sum_{\lambda,\lambda'}\gamma_{|\lambda-\lambda'|}\langle\langle O_1(b_\lambda^+ b_\lambda O_2)_t\rangle\rangle$$
$$+\sum_{\lambda,\lambda'}\gamma_{|\lambda-\lambda'|}\langle\langle O_1(O_2 b_\lambda^+ b_\lambda)_t\rangle\rangle - 2\sum_{\lambda,\lambda'}\gamma_{|\lambda-\lambda'|}\langle\langle O_1(b_\lambda^+ b_{\lambda'} O_2 b_\lambda^+ b_{\lambda'})_t\rangle\rangle$$
$$-2\sum_{\lambda,\lambda'}\gamma_{|\lambda-\lambda'|}\langle\langle O_1(b_\lambda^+ b_{\lambda'} O_2 b_{\lambda'}^+ b_\lambda)_t\rangle\rangle + 2\sum_{\lambda}\gamma_0\langle\langle O_1(b_\lambda^+ b_\lambda O_2 b_\lambda^+ b_\lambda)_t\rangle\rangle\}. \qquad (2.16)$$

Usually on the right side of these equations new correlation functions appear, for which also equations of motion must be written down thus leading to a hierarchy of equations, and one is very happy, if the system is closed after a limited number of steps.

3. Optical Absorption in Molecular Crystals

3.1 The operator H_0

We wish to consider optical absorption in crystals, whose unit cells contain two differently oriented molecules of the same kind. Examples are anthracene or naphtalene crystals. In our model we assume that each molecule has two energy levels, which are important for the process of optical absorption, a ground level ($\varphi_{\lambda 0} = \varphi_{nj0}$) and an excited level ($\varphi_{\lambda 1} = \varphi_{nj1}$). The distance between the two levels be ε. The Hamiltonian H_0 of this system is given by

$$H_0 = \sum_{\lambda} \varepsilon\, b_\lambda^+ b_\lambda + \sum_{\lambda,\lambda'} H_{\lambda-\lambda'}\, b_\lambda^+ b_{\lambda'} \qquad (3.1)$$

$$= \sum_{n,j} \varepsilon\, b_{nj}^+ b_{nj} + \sum_{\substack{n,n'\\ j,j'}} H_{n-n',j-j'}\, b_{nj}^+ b_{n'j'} \,. \qquad (3.2)$$

$H_{n-n',j-j'}$ describes the (coherent) interaction between molecules at different sites ($H_{0,0} = 0$), n runs over all unit cells of the crystal, and j ($j = 1, 2$) numerates the two molecules in the unit cell. The ground state of the crystal will be denoted by $|0\rangle$, and the state of the crystal with an exciton present at site (n, j) by $|n, j\rangle = b_{nj}^+|0\rangle$.

3.2 The expression for the line shape

Applying a time dependent electric field

$$\mathbf{E}(\boldsymbol{x}, t) = 2\,\mathbf{E}\cos(\boldsymbol{k}\cdot\boldsymbol{x} - \omega t)\,, \qquad (3.3)$$

our system described by $H = H_0 + H_1(t)$ is disturbed. The Hamiltonian of the perturbation is given by

$$H_s = -\sum_{n,j} e\,\boldsymbol{x}_{nj}\cdot\mathbf{E}(\boldsymbol{x}_{nj}, t)\,. \qquad (3.4)$$

$\boldsymbol{x}_{n,j}$ is the position vector of the j-th molecule in the n-th unit cell. Using Kubo's formalism [11], we obtain for the fourier transform of the α, α'-component of the dielectric susceptibility tensor

$$\chi''_{\alpha\alpha'}(\omega) = \frac{N}{2\hbar}\sum_{j,j'}\mu^*_{j\alpha}\mu_{j'\alpha'}$$
$$\cdot\left\{\int_{-\infty}^{\infty}\mathrm{d}\tau\exp\{-i\,\omega\,\tau\}[\langle\langle b_{\boldsymbol{k}j}(0)\,b^+_{\boldsymbol{k}j'}(\tau)\rangle\rangle \qquad (3.5)\right.$$
$$\left. -\langle\langle b_{-\boldsymbol{k},j}(\tau)\,b^+_{-\boldsymbol{k},j}(0)\rangle\rangle]\right\}.$$

N is the number of unit cells in the region defined by periodic boundary conditions and

$$\mu_{j\alpha} = (\varphi_{nj1}|x_\alpha|\varphi_{nj0})\,. \qquad (3.6)$$

$$b_{\boldsymbol{k},j} = \frac{1}{\sqrt{N}}\sum_n \exp\{-i\,\boldsymbol{k}\,\boldsymbol{x}_n\}\,b_{n,j}\,. \qquad (3.7)$$

$\boldsymbol{k}$ is the wave-vector of the light field and $\boldsymbol{x}_n$ the position vector of the n-th unit cell. In writing (3.5) we have assumed that before applying the perturbation H_s the crystal was in the ground state and therefore $\varrho(0) = |0\rangle\langle 0|$, and furtheron used the fact that the Hamiltonian H of the unperturbed system conserves the number of excitons.

3.3 The equations of motion for the correlation functions

In order to get the line shape of optical absorption, we have to calculate the correlation functions $\langle\langle b_{\boldsymbol{k},j}(0)\,b^+_{\boldsymbol{k},j'}(\tau)\rangle\rangle$ and $\langle\langle b_{-\boldsymbol{k},j}(\tau)\,b^+_{-\boldsymbol{k},j'}(0)\rangle\rangle$, i. e. we have to put $O_1 = b_{\pm\boldsymbol{k}j}$ and $O_2 = b^+_{\pm\boldsymbol{k}j}$ in Eqs. (2.15) and (2.16). Because O_1 and O_2 contain only annihilation and creation operators, respectively, and on account of the limitation of the Hilbert space to states with at most a single excitation, the expressions $\langle\langle(b_\lambda^+ b_\lambda O_1 b_\lambda^+ b_\lambda)_t O_2\rangle\rangle$ etc. vanish. Furtheron, for the equation of motion of $\langle\langle O_1(t) O_2\rangle\rangle$ we get no contribution from $\langle\langle(b_\lambda^+ b_\lambda O_1)_t O_2\rangle\rangle$ and in the equation of $\langle\langle O_1 O_2(t)\rangle\rangle$ the term $\langle\langle O_1(O_2 b_\lambda^+ b_\lambda)_t\rangle\rangle$ vanishes. Calculating the commutators and using (2.14), we arrive at

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle b_{-\boldsymbol{k},j}(t)\,b^{+}_{-\boldsymbol{k},j'}\rangle\rangle=\frac{i}{\hbar}\Big\{-\varepsilon\langle\langle b_{-\boldsymbol{k},j}(t)\,b^{+}_{-\boldsymbol{k},j'}(0)\rangle\rangle-\sum_{i=1}^{2}\tilde{H}_{\boldsymbol{k},j-i}\langle\langle b_{-\boldsymbol{k},i}(t)\,b^{+}_{-\boldsymbol{k},j'}\rangle\rangle\Big\}-\frac{s}{\hbar}\,\Gamma\langle\langle b_{-\boldsymbol{k},j}(t)\,b^{+}_{-\boldsymbol{k},j'}\rangle\rangle\,, \tag{3.8}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\langle b_{\boldsymbol{k},j}\,b^{+}_{\boldsymbol{k},j'}(t)\rangle\rangle=\frac{i}{\hbar}\Big\{\varepsilon\langle\langle b_{\boldsymbol{k},j}\,b^{+}_{\boldsymbol{k},j'}(t)\rangle\rangle+\sum_{i=1}^{2}\tilde{H}_{\boldsymbol{k},i-j}\langle\langle b_{\boldsymbol{k},j}\,b^{+}_{\boldsymbol{k},i}(t)\rangle\rangle\Big\}-\frac{s}{\hbar}\,\Gamma\langle\langle b_{\boldsymbol{k},j}\,b^{+}_{\boldsymbol{k},j'}(t)\rangle\rangle\,. \tag{3.9}$$

j and j' assume the values 1 and 2, $s=-1$ for $t<0$ and $s=+1$ for $t>0$. Furtheron we have

$$\tilde{H}_{\boldsymbol{k},t}=\sum_{m}H_{m,t}\exp\{i\,\boldsymbol{k}\,\boldsymbol{x}_m\}\,, \tag{3.10}$$

$$\Gamma=\sum_{m,t}\gamma_{|m|,|t|}\,. \tag{3.11}$$

With the initial condition $\varrho(0)=|0\rangle\langle 0|$, which means that for $t=0$ no molecule is excited, we get as initial conditions for the correlation functions

$$\langle\langle b_{\boldsymbol{k},j}\,b^{+}_{\boldsymbol{k},j'}\rangle\rangle=\langle\langle b_{-\boldsymbol{k},j}\,b^{+}_{-\boldsymbol{k},j'}\rangle\rangle=\delta_{jj'}\,. \tag{3.12}$$

3.4 *Solution of the equations of motion. Line shape of optical absorption*

The solution of the system of differential Eqs. (3.8) and (3.9) with the initial condition (3.12) is given by

$$\langle\langle b_{-\boldsymbol{k},1}(t)\,b^{+}_{-\boldsymbol{k},1}\rangle\rangle=\langle\langle b_{-\boldsymbol{k},2}(t)\,b^{+}_{-\boldsymbol{k},2}\rangle\rangle=\tfrac{1}{2}K_1\,, \tag{3.13}$$

$$\langle\langle b_{\boldsymbol{k},1}\,b^{+}_{\boldsymbol{k},1}(t)\rangle\rangle=\langle\langle b_{\boldsymbol{k},2}\,b^{+}_{\boldsymbol{k},2}(t)\rangle\rangle=\tfrac{1}{2}K_1{}^{*}\,, \tag{3.14}$$

$$\langle\langle b_{-\boldsymbol{k},2}(t)\,b^{+}_{-\boldsymbol{k},1}\rangle\rangle=\frac{1}{2}\,\frac{\tilde{H}_{\boldsymbol{k},1}}{|\tilde{H}_{\boldsymbol{k},1}|}\,K_2\,,\quad \langle\langle b_{\boldsymbol{k},1}\,b^{+}_{\boldsymbol{k},2}(t)\rangle\rangle=\frac{1}{2}\,\frac{\tilde{H}_{\boldsymbol{k},-1}}{|\tilde{H}_{\boldsymbol{k},1}|}\,K_2{}^{*}\,, \tag{3.15}$$

$$\langle\langle b_{-\boldsymbol{k},1}(t)\,b^{+}_{-\boldsymbol{k},2}\rangle\rangle=\frac{1}{2}\,\frac{\tilde{H}_{\boldsymbol{k},-1}}{|\tilde{H}_{\boldsymbol{k},1}|}\,K_2\,,\quad \langle\langle b_{\boldsymbol{k},2}\,b^{+}_{\boldsymbol{k},1}(t)\rangle\rangle=\frac{1}{2}\,\frac{\tilde{H}_{\boldsymbol{k},1}}{|\tilde{H}_{\boldsymbol{k},1}|}\,K_2{}^{*}\,. \tag{3.16}$$

K_1 and K_2 are given by

$$K_1=\exp\Big\{\frac{1}{\hbar}\,[-i(\varepsilon+\tilde{H}_{\boldsymbol{k},0}-|\tilde{H}_{\boldsymbol{k},1}|)-s\Gamma]t\Big\}+\exp\Big\{\frac{1}{\hbar}\,[-i(\varepsilon+\tilde{H}_{\boldsymbol{k},0}+|\tilde{H}_{\boldsymbol{k},1}|)-s\Gamma]t\Big\}\,, \tag{3.17}$$

$$K_2=-\exp\Big\{\frac{1}{\hbar}\,[-i(\varepsilon+\tilde{H}_{\boldsymbol{k},0}-|\tilde{H}_{\boldsymbol{k},1}|)-s\Gamma]t\Big\}+\exp\Big\{\frac{1}{\hbar}\,[-i(\varepsilon+\tilde{H}_{\boldsymbol{k},0}+|\tilde{H}_{\boldsymbol{k},1}|)-s\Gamma]t\Big\}\,. \tag{3.18}$$

Using these expressions we have for the line shape of optical absorption

$$\begin{aligned}\chi''_{\alpha\alpha'}=&\frac{N}{2|\tilde{H}_{\boldsymbol{k},1}|}\Big(\sqrt{\tilde{H}_{\boldsymbol{k},-1}}\,\mu^{*}_{1\alpha}+\sqrt{\tilde{H}_{\boldsymbol{k},1}}\,\mu^{*}_{2\alpha}\Big)\Big(\sqrt{\tilde{H}_{\boldsymbol{k},1}}\,\mu_{1\alpha'}+\sqrt{\tilde{H}_{\boldsymbol{k},-1}}\,\mu_{2\alpha'}\Big)\\&\cdot\left\{\frac{\Gamma}{[\tilde{\omega}-(\varepsilon+\tilde{H}_{\boldsymbol{k},0}+|\tilde{H}_{\boldsymbol{k},1}|)]^2+\Gamma^2}-\frac{\Gamma}{[\tilde{\omega}+(\varepsilon+\tilde{H}_{\boldsymbol{k},0}+|\tilde{H}_{\boldsymbol{k},1}|)]^2+\Gamma^2}\right\}\\&+\frac{N}{2|\tilde{H}_{\boldsymbol{k},1}|}\Big(\sqrt{\tilde{H}_{\boldsymbol{k},-1}}\,\mu^{*}_{1\alpha}-\sqrt{\tilde{H}_{\boldsymbol{k},1}}\,\mu^{*}_{2\alpha}\Big)\Big(\sqrt{\tilde{H}_{\boldsymbol{k},1}}\,\mu_{1\alpha'}-\sqrt{\tilde{H}_{\boldsymbol{k},-1}}\,\mu_{2\alpha'}\Big)\\&\cdot\left\{\frac{\Gamma}{[\tilde{\omega}-(\varepsilon+\tilde{H}_{\boldsymbol{k},0}-|\tilde{H}_{\boldsymbol{k},1})]^2+\Gamma^2}-\frac{\Gamma}{[\tilde{\omega}+(\varepsilon+\tilde{H}_{\boldsymbol{k},0}-\tilde{H}_{\boldsymbol{k},1}|)]^2+\Gamma^2}\right\}.\end{aligned} \tag{3.19}$$

For the discussion of this expression we assume that the dipol moments at the two sites in the unit cell have the same amount and are arranged symmetrically with respect to the z-axis, as shown in Figure 1. Furtheron, we assume the matrix elements to be real. With these assumptions we have

$$\mu_1+\mu_2=\mu_1{}^{*}+\mu_2{}^{*}=2\,\mu_z\,\boldsymbol{e}_z\,,\qquad \mu_1-\mu_2=\mu_1{}^{*}-\mu_2{}^{*}=-2\,\mu_x\,\boldsymbol{e}_x\,. \tag{3.20, 3.21}$$

The only non-vanishing components of the tensor of the dielectric susceptibility are given by

$$\chi''_{xx}=2\,\mu_x{}^2\left\{\frac{\Gamma}{[\tilde{\omega}-(\varepsilon+\tilde{H}_{\boldsymbol{k},0}-|\tilde{H}_{\boldsymbol{k},1}|)]^2+\Gamma^2}-\frac{\Gamma}{[\tilde{\omega}+(\varepsilon+\tilde{H}_{\boldsymbol{k},0}-|\tilde{H}_{\boldsymbol{k},1}|)]^2+\Gamma^2}\right\}, \tag{3.22}$$

$$\chi''_{zz} = 2\,\mu_z^2 \left\{ \frac{\Gamma}{[\tilde{\omega} - (\varepsilon + \tilde{H}_{\boldsymbol{k},0} + |\tilde{H}_{\boldsymbol{k},1}|)]^2 + \Gamma^2} - \frac{\Gamma}{[\tilde{\omega} + (\varepsilon + \tilde{H}_{\boldsymbol{k},0} + |\tilde{H}_{\boldsymbol{k},1}|)]^2 + \Gamma^2} \right\}. \tag{3.23}$$

These expressions have also been derived by Haken and Schwarzer [5a, b]. Thus from our model we obtain an absorption line polarized parallel to the x-axis with its maximum at $\varepsilon + \tilde{H}_{\boldsymbol{k},0} - |\tilde{H}_{\boldsymbol{k},1}|$ and a second absorption line polarized parallel to the z-axis with its maximum at $\varepsilon + \tilde{H}_{\boldsymbol{k},0} + |\tilde{H}_{\boldsymbol{k},1}|$. As compared to the distance of the energy levels of the isolated molecules, the lines are displaced by $\tilde{H}_{\boldsymbol{k},0} - |\tilde{H}_{\boldsymbol{k},1}|$ and by $\tilde{H}_{\boldsymbol{k},0} + |\tilde{H}_{\boldsymbol{k},1}|$. Thus the distance between the lines, the Davydov-splitting, is given by $2|\tilde{H}_{\boldsymbol{k},1}|$. The line width of the Lorentzian lines is determined by Γ which, according to (3.11), is the sum of all fluctuation parameters. In our model we have assumed that the fluctuations are caused by the phonons. Therefore their strengths should increase width increasing temperature leading to a broadening of the absorption line.

Considering instead of a crystal a two-molecule system [6], the parameters in (3.22) and (3.23) assume the following values:

$$\Gamma = \gamma_0 + \gamma_1; \quad \tilde{H}_{k,0} = 0; \quad \tilde{H}_{k,1} = J.$$

Here J is the interaction between the molecules.

4. ESR Line Shape for Two-Molecule Systems*

4.1 The operator H_0

We wish to investigate the ESR line shape of a system of two differently oriented molecules sitting at sites 1 and 2, respectively. Such systems are realized in anthracene and naphtalene crystals. In earlier papers [12, 13] the motion of a spin carrying excitation in such a two-molecule system was assumed to occur via a hopping process. This kind of motion has been taken into account in our Hamiltonian by $H_1(t)$. In addition, however, we consider also the coherent contribution of the motion which, in the case of triplet excitons, is described by the exchange interaction integral J. Because of the different orientations of the molecules, the exciton sees different magnetic fields when sitting at molecule 1 and 2, respectively. Thus for this system H_0 is given by

$$H_0 = J(b_1^+ b_2 + b_2^+ b_1) + A\, b_1^+ b_1 \sigma_z + B\, b_2^+ b_2 \sigma_z. \tag{4.1}$$

b_i^+ and b_i are creation and annihilation operators for excitons. A and B describe the contributions of the local magnetic fields at the two sites to the Hamiltonian. For simplicity, instead of a triplet system with spin $S = 1$, we consider a system with spin $S = \frac{1}{2}$. The Hilbert space of our system therefore consists of all states $|n, \sigma\rangle$, where n indicates whether the exciton is sitting at molecule 1 or at molecule 2, $\sigma = +1$ if the spin is aligned in $+z$-direction and $\sigma = -1$ if the spin points in $-z$-direction.

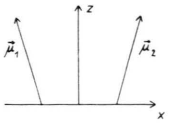

Fig. 1. Orientation of the dipole moments for the two inequivalent molecules in the unit cell.

4.2 The expression for the line shape

In the Hamiltonian H_0 a static magnetic field pointing in z-direction is taken into account. Applying still a time dependent magnetic field, say in the x-direction,

$$H_x(t) = 2\,H_1 \cos \omega t, \tag{4.2}$$

the system represented by $H_0 + H_1(t)$ is disturbed. The perturbation Hamiltonian is given by

$$H_s(t) = -2\,\mathrm{H}_1 \cos(\omega t) M_x, \tag{4.3}$$

where M_x is the x-component of the magnetic moment operator.

Using again Kubo's theory, the imaginary part of the magnetic susceptibility is given by

$$\chi''(\omega) = \frac{1}{2\hbar} \int_{-\infty}^{\infty} \mathrm{d}\tau \exp\{-i\,\omega\,\tau\} \{\langle\langle \sigma_x(0)\sigma_x(\tau)\rangle\rangle - \langle\langle \sigma_x(\tau)\sigma_x(0)\rangle\rangle\}. \tag{4.4}$$

The σ_x's are Pauli-operators. Assuming that before applying the perturbation the spin is aligned in $-z$-direction, we have for the density operator at initial time

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* Part of this section has been done during the authors stay at the Institut für Theoretische Physik der Universität Stuttgart.

$$\varrho(0) = \mathrm{d}(|1,-1\rangle\langle 1,-1| + |2,-1\rangle\langle 2,-1|) \tag{4.5}$$

($d = \frac{1}{2}$ on account of normalization). Using this form of the density operator and separating for $\tau < 0$ and $\tau > 0$ we have from (4.4)

$$\begin{aligned}\chi''(\omega) = \frac{1}{2\hbar}\Bigg(& \int_{-\infty}^{0} \mathrm{d}\tau \exp\{-i\,\omega\,\tau\}\ \langle\langle \sigma^-(0)\,\sigma^+(\tau)\rangle\rangle - \int_{-\infty}^{0} \mathrm{d}\tau \exp\{-i\,\omega\,\tau\}\ \langle\langle \sigma^-(\tau)\,\sigma^+(0)\rangle\rangle \\ & + \int_{0}^{\infty} \mathrm{d}\tau \exp\{-i\,\omega\,\tau\}\ \langle\langle \sigma^-(0)\,\sigma^+(\tau)\rangle\rangle - \int_{0}^{\infty} \mathrm{d}\tau \exp\{-i\,\omega\,\tau\}\ \langle\langle \sigma^-(\tau)\,\sigma^+(0)\rangle\rangle \Bigg).\end{aligned} \tag{4.6}$$

(4.6) is rewritten as

$$\chi''(\omega) = \frac{1}{2\hbar}(\tilde{G}_1(\tilde{\omega},-1,-1) - \tilde{G}_1(\tilde{\omega},-1,1) + \tilde{G}_1(\tilde{\omega},1,-1) - \tilde{G}_1(\tilde{\omega},1,1), \tag{4.7}$$

where $\tilde{\omega} = \hbar\,\omega$ and the $\tilde{G}_1(\tilde{\omega}, s, p)$'s are defined by Eqs. (4.11) and (4.12).

4.3 Equations for the correlation functions

Writing the equation of motion (2.15) for one of the four correlation functions of Eq. (4.6), we see that we arrive at further correlation functions, for which we have to set up equations of motion, too. In order to get a complete set of equations, for each correlation function of (4.6) we have to consider a set of nine equations. To make the way of writing as concise as possible, we introduce the following notation:

$$\begin{array}{ll}
G_1(t,s,p=1) = \langle\langle \sigma^-(t)\,\sigma^+\rangle\rangle\ ; & G_1(t,s,p=-1) = \langle\langle \sigma^-\,\sigma^+(t)\rangle\rangle \\
G_2(t,s,p=1) = \langle\langle (b_1^+\,b_1\,\sigma^-)_t\,\sigma^+\rangle\rangle\ ; & G_2(t,s,p=-1) = \langle\langle \sigma^-(b_1^+\,b_1\,\sigma^+)_t\rangle\rangle \\
G_3(t,s,p=1) = \langle\langle (b_2^+\,b_2\,\sigma^-)_t\,\sigma^+\rangle\rangle\ ; & G_3(t,s,p=-1) = \langle\langle \sigma^-(b_2^+\,b_2\,\sigma^+)_t\rangle\rangle \\
G_4(t,s,p=1) = \langle\langle (b_1^+\,b_2\,\sigma^-)_t\,\sigma^+\rangle\rangle\ ; & G_4(t,s,p=-1) = \langle\langle \sigma^-(b_1^+\,b_2\,\sigma^+)_t\rangle\rangle \\
G_5(t,s,p=1) = \langle\langle (b_2^+\,b_1\,\sigma^-)_t\,\sigma^+\rangle\rangle\ ; & G_5(t,s,p=-1) = \langle\langle \sigma^-(b_2^+\,b_1\,\sigma^+)_t\rangle\rangle \\
G_6(t,s,p=1) = \langle\langle (b_1^+\,b_2\,\sigma^-\,\sigma_z)_t\,\sigma^+\rangle\rangle\ ; & G_6(t,s,p=-1) = \langle\langle \sigma^-(b_1^+\,b_2\,\sigma^+\,\sigma_z)_t\rangle\rangle \\
G_7(t,s,p=1) = \langle\langle (b_2^+\,b_1\,\sigma^-\,\sigma_z)_t\,\sigma^+\rangle\rangle\ ; & G_7(t,s,p=-1) = \langle\langle \sigma^-(b_2^+\,b_1\,\sigma^+\,\sigma_z)_t\rangle\rangle \\
G_8(t,s,p=1) = \langle\langle (b_1^+\,b_1\,\sigma^-\,\sigma_z)_t\,\sigma^+\rangle\rangle\ ; & G_8(t,s,p=-1) = \langle\langle \sigma^-(b_1^+\,b_1\,\sigma^+\,\sigma_z)_t\rangle\rangle \\
G_9(t,s,p=1) = \langle\langle (b_2^+\,b_2\,\sigma^-\,\sigma_z)_t\,\sigma^+\rangle\rangle\ ; & G_9(t,s,p=-1) = \langle\langle \sigma^-(b_2^+\,b_2\,\sigma^+\,\sigma_z)_t\rangle\rangle
\end{array} \tag{4.8}$$

where $s = -1$ for $t < 0$ and $s = +1$ for $t > 0$.

With the aid of (4.8) we obtain from (2.15) and (2.16)

$$\begin{aligned}
\dot{G}_1 &= -p\,\frac{i}{\hbar}\,[2\,A\,G_2 + 2\,B\,G_3]\,, \\
\dot{G}_2 &= \frac{i}{\hbar}\,[J(G_5 - G_4) - 2\,p\,A\,G_2] - s\,\frac{2}{\hbar}\,\gamma_1[G_2 - G_3]\,, \\
\dot{G}_3 &= \frac{i}{\hbar}\,[J(G_4 - G_5) - 2\,p\,B\,G_3] - s\,\frac{2}{\hbar}\,\gamma_1[G_3 - G_2]\,, \\
\dot{G}_4 &= \frac{i}{\hbar}\,[J(G_3 - G_2) + (A - B)\,G_6 - 2\,p\,A\,G_4] - s\,\frac{2}{\hbar}\,[\Gamma\,G_4 - \gamma_1\,G_5]\,, \\
\dot{G}_5 &= \frac{i}{\hbar}\,[J(G_2 - G_3) - (A - B)\,G_7 - 2\,p\,B\,G_5 - s\,\frac{2}{\hbar}\,[\Gamma\,G_5 - \gamma_1\,G_4]\,, \\
\dot{G}_6 &= \frac{i}{\hbar}\,[J(G_9 - G_8) + (A - B)\,G_4 - 2\,p\,A\,G_6] - s\,\frac{2}{\hbar}\,[\Gamma\,G_6 - \gamma_1\,G_7]\,, \\
\dot{G}_7 &= \frac{i}{\hbar}\,[J(G_8 - G_9) - (A - B)\,G_5 - 2\,p\,B\,G_7] - s\,\frac{2}{\hbar}\,[\Gamma\,G_7 - \gamma_1\,G_6]\,,
\end{aligned}$$

$$\dot{G}_8 = \frac{i}{\hbar}\,[J(G_7 - G_6) - 2\,p\,A\,G_8] - s\,\frac{2}{\hbar}\,\gamma_1[G_8 - G_9]\,,$$

$$\dot{G}_9 = \frac{i}{\hbar}\,[J(G_6 - G_7) - 2\,p\,B\,G_9] - s\,\frac{2}{\hbar}\,\gamma_1[G_9 - G_8]$$

with $G_j = G_j)t, s, p)$.

To get the initial conditions for this set of differential equations, we remember that according to (4.5)

$$\varrho(0) = \mathrm{d}(|1,-1\rangle\langle 1,-1| + |2,-1\rangle\langle 2,-1|)$$

and thus

$$\begin{aligned} G_1(0,s,p) &= 2\,\mathrm{d}\,, \\ G_2(0,s,p) &= G_3(0,s,p) = \mathrm{d}\,, \\ G_4(0,s,p) &= G_5(0,s,p) = G_6(,0\,s,p) \\ &= G_7(0,s,p) = 0\,, \\ G_8(0,s,p) &= G_9(0,s,p) = p\,\mathrm{d}\,. \end{aligned}$$

Now we could calculate the correlation functions $G_1(t,s,p)$, from which we get the line shape by performing a Fourier transformation according to (4.6). However, the calculation is simplified considerably by doing the integral transformation first.

Introducing the transform $\mathcal{F}G_j(t,s,p) = \tilde{G}_j(\omega,s,p)$ of $G_j(t,s,p)$ by

$$\mathcal{F}\,G_j(t,-1,p) = \int_{-\infty}^{0} \mathrm{d}\tau \exp\{-i\,\omega\,\tau\}\,G_j(\tau,-1,p)$$

$$= \tilde{G}_j(\omega,-1,p)\,, \quad t<0 \qquad (4.11)$$

$$\mathcal{F}G_j(t,1,p) = \int_{0}^{\infty} \mathrm{d}\tau \exp\{-i\,\omega\,\tau\}\,G_j(\tau,1,p)$$

$$= \tilde{G}_j(\omega,1,p)\,, \quad t>0 \qquad (4.12)$$

we get

$$\mathcal{F}\,\dot{G}_j(t,s,p) = -s\,G_j(0,s,p) + i\,\omega\,\tilde{G}_j(\omega,s,p)\,. \qquad (4.13)$$

With the aid of (4.11), (4.12) and (4.13) and with the notation $\hbar\,\omega = \tilde{\omega}$, $\hbar\,d = \tilde{d}$ the system of differential equations is simplified to the following system of algebraic equations:

$$\begin{aligned}
&i\,\tilde{\omega}\,\tilde{G}_1 + i\,2\,p\,A\,\tilde{G}_2 + i\,2\,p\,B\,\tilde{G}_3 &&= 2\,s\,\tilde{d}\,,\\
&(i\,\tilde{\omega} + i\,2\,p\,A + 2\,s\,\gamma_1)\,\tilde{G}_2 - 2\,s\,\gamma_1\,\tilde{G}_3 + i\,J\,\tilde{G}_4 - i\,J\,\tilde{G}_5 &&= s\,\tilde{d}\,,\\
&-2\,s\,\gamma_1\,\tilde{G}_2 + (i\,\tilde{\omega} + i\,2\,p\,B + 2\,s\,\gamma_1)\,\tilde{G}_3 - i\,J\,\tilde{G}_4 + i\,J\,\tilde{G}_5 &&= s\,\tilde{d}\,,\\
&i\,J\,\tilde{G}_2 - i\,J\,\tilde{G}_3 + (i\,\tilde{\omega} + i\,2\,p\,A + 2\,s\,\Gamma)\,\tilde{G}_4 - 2\,s\,\gamma_1\,\tilde{G}_5 - i(A-B)\,\tilde{G}_6 &&= 0\,,\\
&-i\,J\,\tilde{G}_2 + i\,J\,\tilde{G}_3 - 2\,s\,\gamma_1\,\tilde{G}_4 + (i\,\tilde{\omega} + i\,2\,p\,B + 2\,s\,\Gamma)\,\tilde{G}_5 + i(A-B)\,\tilde{G}_7 &&= 0\,,\\
&-i(A-B)\,\tilde{G}_4 + (i\,\tilde{\omega} + i\,2\,p\,A + 2\,s\,\Gamma)\,\tilde{G}_6 - 2\,s\,\gamma_1\,\tilde{G}_7 + i\,J\,\tilde{G}_8 - i\,J\,\tilde{G}_9 &&= 0\,,\\
&i(A-B)\,\tilde{G}_5 - 2\,s\,\gamma_1\,\tilde{G}_6 + (i\,\tilde{\omega} + i\,2\,p\,B + 2\,s\,\Gamma)\,\tilde{G}_7 - i\,J\,\tilde{G}_8 + i\,J\,\tilde{G}_9 &&= 0\,,\\
&i\,J\,\tilde{G}_6 - i\,J\,\tilde{G}_7 + (i\,\tilde{\omega} + i\,2\,p\,A + 2\,s\,\gamma_1)\,\tilde{G}_8 - 2\,s\,\gamma_1\,\tilde{G}_9 &&= s\,p\,d\,,\\
&-i\,J\,\tilde{G}_6 + i\,J\,\tilde{G}_7 - 2\,s\,\gamma_1\,\tilde{G}_8 + (i\,\tilde{\omega} + i\,2\,p\,B + 2\,s\,\gamma_1)\,\tilde{G}_9 &&= s\,p\,d\,,\\
& &&\tilde{G}_j = \tilde{G}_j(\tilde{\omega},s,p)\,.
\end{aligned} \qquad (4.14)$$

4.4 Solution of (4.14) and evaluation of the line shape

For the calculation of the line shape we have to know $\tilde{G}_1(\omega,s,p)$ only. From (4.14) we obtain

$$\tilde{G}_1(\tilde{\omega},s,p) = 2\,s\,\tilde{d}\,\frac{D_1(\tilde{\omega},s,p)}{D(\tilde{\omega},s,p)}\,. \qquad (4.15)$$

According to (4.7) the line shape becomes

$$\chi''(\tilde{\omega}) = \frac{1}{2\,\hbar}\sum_{s,p} -p\,\tilde{G}_1(\tilde{\omega},s,p)$$

$$= -\frac{1}{2}\sum_{s,p} s\,p\,\frac{D_1(\tilde{\omega},s,p)}{D(\omega,s,p)} \qquad (4.16)$$

where we have used $d = \frac{1}{2}$.

The quantities $D_1(\tilde{\omega},s,p)$ and $D(\tilde{\omega},s,p)$ are given by

$$D_1 = (P_1\,P_2 + P_3)\,(P_4\,P_2 + P_5) + 2\,(A-B)^4\,(P_5 - 2\,P_1\,P_4)\,, \qquad (4.17)$$

$$D = (P_1\,P_2 + P_3)^2 - 4\,(A-B)^4\,P_1^2 \qquad (4.18)$$

with

$$P_1 = (i\,\tilde{\omega} + i\,2\,p\,A)\,(i\,\tilde{\omega} + i\,2\,p\,B) + 4\,s\,\gamma_1\,(i\,\tilde{\omega} + i\,p\,(A+B))\,,$$

$$P_2 = 4\,s\,\gamma_1[i\,\tilde{\omega} + i\,p(A+B) + 2\,s\,\gamma_0] + (i\,\tilde{\omega} + i\,2\,p\,A + 2\,s\,\gamma_0)\,(i\,\tilde{\omega} + i\,2\,p\,B + 2\,s\,\gamma_0) + (A-B)^2\,, \qquad (4.19)$$

$$P_3 = 4\,J^2[i\,\tilde{\omega} + i\,p(A+B) + 2\,s\,\gamma_0]\,[i\,\tilde{\omega} + i\,p(A+B)]\,,$$
$$P_4 = i\,\tilde{\omega} + i\,p(A+B) + 4\,s\,\gamma_1\,,$$
$$P_5 = 4\,J^2[i\,\tilde{\omega} + i\,p(A+B) + 2\,s\,\gamma_0]\,.$$

The Eq. (4.16) for the ESR line shape contains the parameters of our model, namely A and B, which describe the strengths of the effective magnetic fields at the sites of the two inequivalent molecules, the exchange interaction integral J stemming from the coherent interaction between the molecules, and the quantities γ_0 and γ_1 representing the strengths of the local and non-local fluctuations, respectively. In the model we have assumed that the fluctuations are due to the phonons, and therefore γ_0 and γ_1 should depend on temperature, whereas the other quantities should be constant for a given system. In the following we wish to discuss especially the dependence of the ESR line shape on the fluctuation parameters γ_0 and γ_1.

In order to get some insight into the order of magnitude of the parameters A and B, we consider the ESR measurements of Haarer and Wolf [14] at anthracene crystals. In these crystals the spectral positions of the maxima of the ESR lines of the molecules at the two inequivalent sites in the unit cell depend on the orientation of the external magnetic field and, in our model, are given by $2\,A$ and $2\,B$, respectively. For that orientation of the external field with the largest distance of the two maxima, i.e where $2\,A - 2\,B$ is largest, we have $A = 0.595\ \mathrm{cm}^{-1}$ and $B = 0.63\ \mathrm{cm}^{-1}$. The exchange interaction integral J may be obtained from the Davydov-splitting of the optical absorption [15, 16]. For anthracene crystals we have $J = 2.1\ \mathrm{cm}^{-1}$. Using still measurements of the diffusion constant [15] or of the ESR line width, γ_1 is derived [17] as $\gamma_1 = 0.1\ \mathrm{cm}^{-1}$. The same order of magnitude of the parameters is valid also for excitations moving between pairs of inequivalent molecules in naphtalene crystals [18]. Line shapes using these parameter values are given in Figs. 2 to 4. in 1.4 dibromo-naphtalene [19], however, the exchange interaction integral between inequivalent molecules is less than $0.05\ \mathrm{cm}^{-1}$ and thus much smaller than the value for anthracene crystals. Therefore in Figs. 5 and 6 we shall also consider ESR line shapes for a smaller value of J.

In Figs. 2 a and 2 b we have represented the line shapes according to Eq. (4.16) for $A = 0.595\ \mathrm{cm}^{-1}$, $B = 0.63\ \mathrm{cm}^{-1}$, $J = 2.1\ \mathrm{cm}^{-1}$, $\gamma_1 = 0\ \mathrm{cm}^{-1}$ and several values of γ_0. Note that in Figs. 2 a and 2 b the scale at both axes is different and that the line shape for $\gamma_0 = 10\ \mathrm{cm}^{-1}$ is contained both in Fig. 2 a and Figure 2 b. The figures show that for small values of γ_0 we have a single line at $\tilde{\omega} = A + B = 1.225\ \mathrm{cm}^{-1}$, which broadenes with increasing γ_0. For large values of γ_0 we have two lines which narrow at $2\,A = 1.19\ \mathrm{cm}^{-1}$ and at $2\,B = 2.26\ \mathrm{cm}^{-1}$, when γ_0 increases. The transition from the single line at small values of γ_0 to the two lines at large γ_0 has nothing to do with the transition from coherent to incoherent exciton motion. This transition occurs when $\gamma_0 > 2\,J$ [4, 5, 18], whereas the transition from a single line to two lines happens apparently when

$$J^2/\gamma_0 < |A - B|\,.$$

In Fig. 3 the parameters A, B and J are the same as in Figs. 2 a and 2 b, but now $\gamma_0 = 100\ \mathrm{cm}^{-1}$ and the line shapes are given for several values of γ_1. The line for $\gamma_1 = 0$ is also represented in Figure 2 b. We see that the ESR line narrows when γ_1 increases. This is still more obvious when we consider Fig. 4, which represents the line shapes for the same values of A, B and J, but now $\gamma_0 = 1000\ \mathrm{cm}^{-}$. The curve for $\gamma_1 = 0$ is also contained in Fig. 2 b, showing two lines at $2\,A$ and $2\,B$ approximately. With increasing γ_1, these lines broaden until for $2\,\gamma_1 > |A - B|$ we find a single line at $\tilde{\omega} = A + B$, which narrows with increasing γ_1.

In Figs. 5 and 6 the line shapes are given for the same values of A and B as in the previous figures, but now the exchange interaction integral J is assumed to be $0.2\ \mathrm{cm}^{-1}$ and thus much smaller than the value of J used in Figs. 2 to 4. Figure 5 shows the line shapes for $\gamma_1 = 0.001\ \mathrm{cm}^{-1}$ and several values of γ_0. The transition from a single line to the two lines occurs at much smaller values of γ_0 than in Fig. 2 a, but the condition $J^2/\gamma_0 < |A - B|$ is also fulfilled. Figure 6 finally gives the line shapes for $\gamma_0 = 100\ \mathrm{cm}^{-1}$, whereas γ_1 assumes several between $\gamma_1 = 0.001\ \mathrm{cm}^{-1}$ and $\gamma_1 = 0.039\ \mathrm{cm}^{-1}$. We observe the transition from two lines for small values of γ_1 to a single line when $2\,\gamma_1 > |A - B|$.

4.5 *Approximate expressions for the line shapes*

In Figs. 2 to 5 we have seen that in limiting cases we have either a single narrow ESR line at $\tilde{\omega} = A + B$ or two lines at $\tilde{\omega} = 2\,A$ and at $\tilde{\omega} = 2\,B$ with small line widths. Therefore it seems useful, espepially with respect to the comparison with experimental

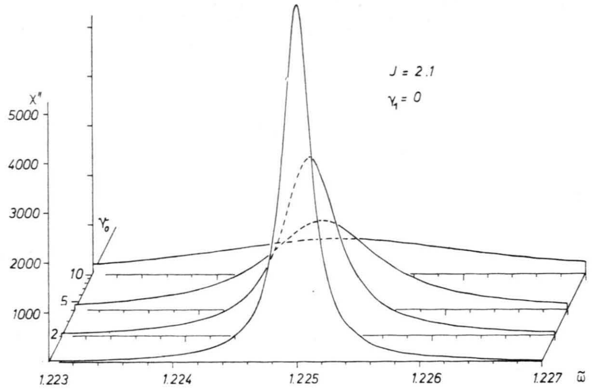

Fig. 2 a. ESR line shapes according to (4.16) for $A=0.595$, $B=0.63$, $J=2.1$, $\gamma_1=0$, and several values of γ_0 (units of $A, B, J, \gamma_0, \gamma_1$, and $\tilde{\omega}$ in cm^{-1}).

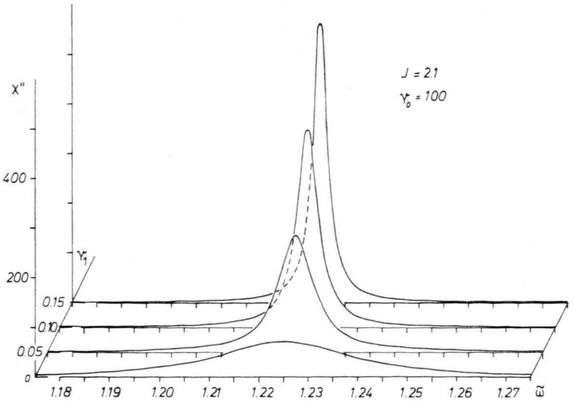

Fig. 3. ESR line shapes according to (4.16) for $A=0.595$, $B=0.63$, $J=2.1$, $\gamma_0=100$, and several values of γ_1 (units of $A, B, J, \gamma_0, \gamma_1$, and $\tilde{\omega}$ in cm^{-1}).

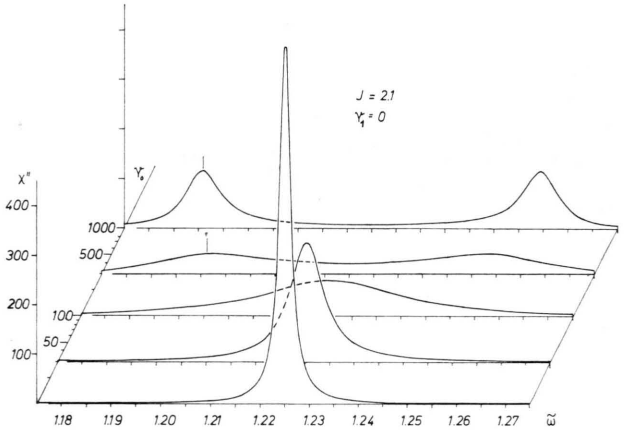

Fig. 2 b. ESR line shapes according to (4.16) for $A=0.595$, $B=0.63$, $J=2.1$, $\gamma_1=0$, and several values of γ_0 (units of $A, B, J, \gamma_0, \gamma_1$, and $\tilde{\omega}$ in cm^{-1}).

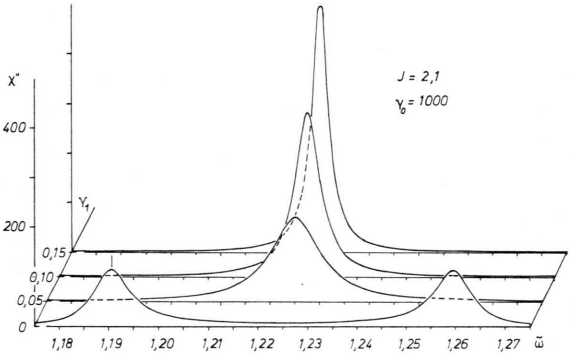

Fig. 4. ESR line shapes according to (4.16) for $A=0.595$, $B=0.63$, $J=2.1$, $\gamma_0=1000$ and several values of γ_1 (units of $A, B, J, \gamma_0, \gamma_1$, and $\tilde{\omega}$ in cm^{-1}).

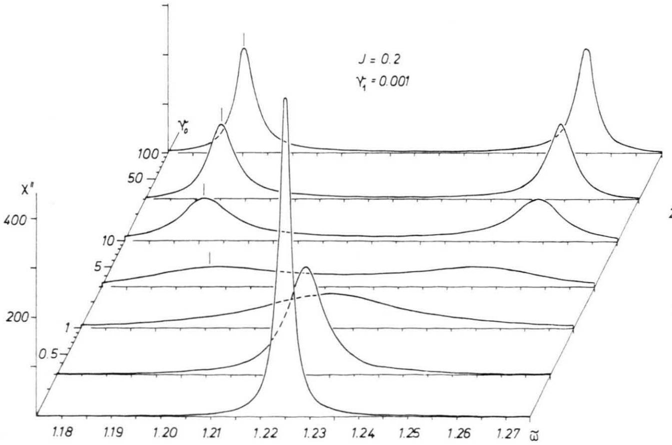

Fig. 5. ESR line shapes according to (4.16) for $A=0.595$, $B=0.63$, $J=0.2$, $\gamma_1=0.001$, and several values of γ_0 (units of $A, B, J, \gamma_0, \gamma_1$, and $\tilde{\omega}$ in cm^{-1}).

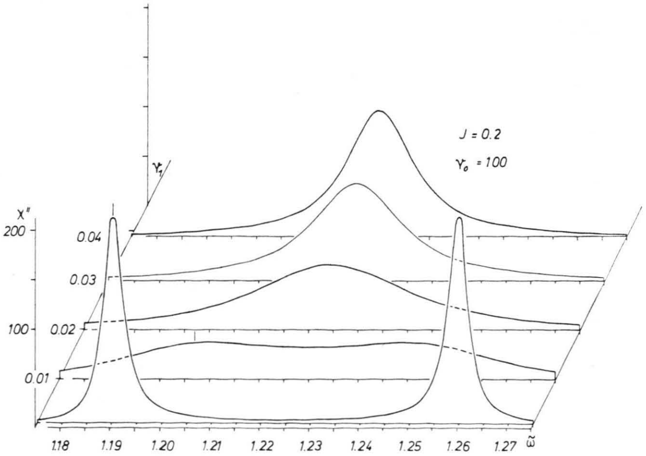

Fig. 6. ESR line shapes according to (4.16) for $A=0.595$, $B=0.63$, $J=0.2$, $\gamma_0=100$, and several values of γ_1 (units of $A, B, J, \gamma_0, \gamma_1$, and $\tilde{\omega}$ in cm^{-1}).

results, to get approximate analytical expressions for the line shapes in these limiting situations, starting from the exact expression (4.16).

4.5.1 Expansion at $\tilde{\omega} = A + B$ for $\gamma_0 < 2J$ (coherent exciton motion)

The line shape is given by

$$\chi''(\varepsilon) \sim \Gamma / (\varepsilon^2 + \Gamma^2) \tag{4.20}$$

with

$$\varepsilon = \tilde{\omega} - (A + B) \tag{4.21}$$

and

$$\Gamma = (A - B)^2 / (J^2/\gamma_0) \,. \tag{4.22}$$

Thus the maximum of the ESR line is at $\tilde{\omega} = A + B$, i. e. in the middle between the two lines that one would expect from the isolated molecules at sites 1 and 2, respectively, and the line width is given by Γ. The parameter γ_0, describing the local fluctuations, increases with increasing temperature; therefore, at low temperature, where $\gamma_0 < 2J$ is fulfilled, we expect a broadening of the absorption line when temperature is rised.

The comparison with the curves for $\gamma_0 = 1$, 2 and 4 in Fig. 2 a shows that the approximation is very good. The deviation of the approximation from the exact curve is less than 0.02% in the range from $\varepsilon = 0$ to $\pm\varepsilon_h$, where $\varepsilon = 0$ and $\pm\varepsilon_h$ are the ε-values at maximum and at half maximum, respectively. But the approximation is also very good for the curves with $\gamma_0 = 10\,\text{cm}^{-1}$ and $\gamma_0 = 30\,\text{cm}^{-1}$ of Fig. 2 b; the deviations between $\varepsilon = 0$ and $\pm\varepsilon_h$ are less than 0.2% and 2%, respectively. This indicates that for the ESR line shape it is not important whether the exciton motion is coherent or incoherent, i. e. whether $\gamma_0 < 2J$ or $\gamma_0 > 2J$. What is of importance in this context is the magnitude of J^2/γ_0 compared to $|A - B|$.

4.5.2 Expansion at $\tilde{\omega} = A + B$ for $\gamma_0 \gg J$ (incoherent exciton motion) and $2\gamma_1, J^2/\gamma_0 \gg |A - B|$

For the line shape we have the expression (4.20), where ε is given by (4.21) and

$$\Gamma = (A - B)^2 / 2(2\gamma_1 + J^2/\gamma_0) \,. \tag{4.23}$$

Again the maximum of the ESR line is at $\tilde{\omega} = A + B$. The temperature dependence of the line width Γ is now determined by γ_0 and by γ_1, where γ_1 describes the strength of the non-local fluctuations. If $2\gamma_1$ increases more rapidly than J^2/γ_0 decreases when temperature is rised, the ESR line narrows. In the opposite case we obtain a broadening of the absorption line.

Comparing (4.22) and (4.23), we see that (4.22) is a special case of (4.23) obtained for $2\gamma_1 \ll J^2/\gamma_0$, which may be realized for low enough temperatures. But we see once more that for the ESR line shape the magnitude of $(2\gamma_1 + J^2/\gamma_0)$ compared to $|A - B|$ is the decisive quantity. At this place it may be remarked that, in the case of incoherent exciton motion, $(2\gamma_1 + J^2/\gamma_0)$ was derived[20] to be proportional to the diffusion constant of exciton transport.

The comparison with the exact line shapes shows that the deviation between $\varepsilon = 0$ and ε_h even for the relatively broad lines with $J = 2.1$, $\gamma_0 = 100$, $\gamma_1 = 0.05$ of Fig. 3 and $J = 2.1$, $\gamma_0 = 1000$, $\gamma_1 = 0.05$ of Fig. 4 is less than 2% and 4%, respectively. The deviation in the same range of ε as above from the curve with $J = 0.2$, $\gamma_0 = 0.3$, $\gamma_1 = 0.001$ of Fig. 5 and from the curve with $J = 0.2$, $\gamma_0 = 100$, $\gamma_1 = 0.03$ of Fig. 6 is less than 2% and 11%, respectively.

4.5.3 Expansion at $\tilde{\omega} = A + B$ for very large γ_0 (limiting case of the hopping model for the exciton motion)

Expansion to second order in ε gives for the line shape of ESR

$$\chi''(\varepsilon) \sim \frac{4\gamma_1}{(A - B)^2} \cdot \left\{ 1 - \varepsilon^2 \left[16 \frac{\gamma_1^2}{(A - B)^4} - \frac{2}{(A - B)^2} \right] \right\}. \tag{4.24}$$

Now we consider two cases:

$$\gamma_1 \gg |A - B|: \quad \chi''(\varepsilon) \sim \frac{4\gamma_1}{(A - B)^2} \left\{ 1 - \varepsilon^2\, 16 \frac{\gamma_1^2}{(A - B)^2} \right\} \tag{4.25}$$

$$\text{or} \quad \chi''(\varepsilon) \sim \frac{\Gamma}{\varepsilon^2 + \Gamma^2}, \quad \Gamma = \frac{(A - B)^2}{4\gamma_1}, \tag{4.26}$$

$$\gamma_1 \ll |A - B|: \quad \chi''(\varepsilon) \sim \frac{4\gamma_1}{(A - B)^4} \{ (A - B)^2 + 2\varepsilon^2 \} \,. \tag{4.27}$$

In the first case of rapid incoherent motion ($2\gamma_1$ is the hopping rate in the limiting case of the hopping model[18]) we have a line at $\tilde{\omega} = (A + B)$ with line width Γ given by (4.26), whereas in the second case we find a minimum at $\tilde{\omega} = A + B$.

4.5.4 Expansion at $\tilde{\omega}=2A$ for $\gamma_0 \gg 2J$ (incoherent exciton motion) and $2\gamma_1, J^2/\gamma_0 \ll |A-B|$

Expanding for $\varepsilon=\tilde{\omega}-2A$ to second order, we arrive at

$$\chi''(\varepsilon) \sim \frac{1}{2(2\gamma_1+J^2/\gamma_0)^3}\left\{(2\gamma_1+J^2/\gamma_0)^2 - \left[\varepsilon+\frac{(2\gamma_1+J^2/\gamma_0)^2}{(A-B)^2}\right]^2\right\}, \tag{4.28}$$

which may also be written as

$$\chi''(\varepsilon) \sim \frac{1}{2}\,\frac{\Gamma}{(\varepsilon-\bar{\varepsilon})^2+\Gamma^2} \tag{4.29}$$

with

$$\bar{\varepsilon} = -\frac{(2\gamma_1+J^2/\gamma_0)^2}{(A-B)}, \tag{4.30}$$

$$\Gamma = 2\gamma_1+J^2/\gamma_0 . \tag{4.31}$$

Equations (4.29) and (4.30) show that the maximum of the absorption line is displaced from $2A$ towards $A+B$. The line width is given by Equation (4.31). Analoguous expressions are obtained by expanding at $\tilde{\omega}=2B$. In these cases we have a broadening of the line and an increase in the shift, if $2\gamma_1$ is growing more rapidly than J^2/γ_0 is decreasing with increasing temperature.

The positions of the maxima of the ESR lines as calculated according to Eq. (4.30) is shown in the figures by small vertical strokes and demonstrates that the relative deviation is small and for none of the represented lines larger than 0.3%.

In the following we still wish to compare the exact values of $\chi''(\varepsilon)$ with those calculated according to (4.29). For the line shape with $J=2.1$, $\gamma_0=1000$, $\gamma_1=0$ in Fig. 4 the deviation is at $\varepsilon=\bar{\varepsilon}$: 2%, at $\varepsilon=\bar{\varepsilon}-\varepsilon_h$: 5% and at $\varepsilon=\bar{\varepsilon}+\varepsilon_h$: 15%. This unsymmetry comes in, because the line shape according to the approximation formula is symmetric with respect to $\bar{\varepsilon}$, whereas in the exact line shape the influence of the absorption line at $\tilde{\omega}=2B$ is larger on the right side of $\varepsilon=\bar{\varepsilon}$ than on the left side.

For the absorption line with $J=0.2$, $\gamma_1=0.001$ and $\gamma_0=100$ the fault at $\varepsilon=\bar{\varepsilon}$ is less than 2%, at $\varepsilon=\bar{\varepsilon}-\varepsilon_h$ less than 6% and at $\varepsilon=\bar{\varepsilon}+\varepsilon_h$ less than 8%. The deviation for the curve with the same values of J and γ_1 and with $\gamma_0=10$ is less than 3% at $\varepsilon=\bar{\varepsilon}$, less than 5% at $\varepsilon=\bar{\varepsilon}-\varepsilon_h$ and less than 13% for $\varepsilon=\bar{\varepsilon}+\varepsilon_h$.

Appendix

In order to obtain the equations of motion for the correlation functions (2.9) and (2.10), we have to evaluate the angular bracket of (2.8). We introduce a new ordering operator

$$\mathcal{T} = \hat{T}\,\tilde{T}^{(1)}\,T^{(3)}, \tag{A.1}$$

which allows to simplify the notation. $\hat{T}$ is an ordering operator ordering operators with higher upper index (1), (2) and (3) to the right. $\tilde{T}^{(1)}$ is ordering operators operating at later times to the left, and $T^{(3)}$ orders operators operating at later times to the right. Using (A.1) we may write

$$\left\langle\left(\tilde{T}\exp\left\{-\frac{1}{i\hbar}\int_0^t \alpha(\tau)H(\tau)\,\mathrm{d}\tau\right\}\right)O_1 \cdot\left(T\exp\left\{\frac{1}{i\hbar}\int_0^t \alpha(\tau)H(\tau)\,\mathrm{d}\tau\right\}\right)\right\rangle \tag{A.2}$$

$$= \mathcal{T}\left\langle \exp\left\{-\frac{1}{i\hbar}\int_0^t \alpha(\tau)\,\big(H^{(1)}(\tau)-H^{(3)}(\tau)\big)\,\mathrm{d}\imath\right\} O_1{}^{(2)}\right\rangle$$

$$= \mathcal{T}\exp\left\{-\frac{1}{i\hbar}\int_0^t \alpha(\tau)\,\big(H_0{}^{(1)}(\tau)-H_0{}^{(3)}(\tau)\big)\,\mathrm{d}\tau\right\} \cdot\left\langle\exp\left\{\frac{i}{\hbar}\int_0^t \alpha(\tau)\,\big(H_1{}^{(1)}(\tau)-H_1{}^{(3)}(\tau)\big)\,\mathrm{d}\tau\right\}\right\rangle O_1{}^{(2)} \tag{A.3}$$

$$= \mathcal{T}\exp\left\{-\frac{1}{i\hbar}\int_0^t \alpha(\tau)\,\big(H_0{}^{(1)}(\tau)-H_0{}^{(3)}(\tau)\big)\,\mathrm{d}\tau\right\} \cdot\exp\left\{-\frac{1}{2}\int_0^t \mathrm{d}t_1\int_0^t \mathrm{d}t_2\,\alpha(t_1)\,\alpha(t_2)\,k_2(t_1,t_2)\right\} O_1{}^{(2)} . \tag{A.4}$$

In going from (A.2) to (A.3) we have used the form (2.1) of the Hamiltonian. The transiton from (A.3) to (A.4) is done easily by remembering that the angular bracket in (A.3) is the characteristic functional of the Gaussian Markov process

$$[H_1{}^{(1)}(\tau)-H_1{}^{(3)}(\tau)] .$$

The correlation function $k_2(t_1,t_2)$ is defined by

$$k_2(t_1, t_2) = \frac{1}{\hbar^2} \langle (H_1{}^{(1)}(t_1) - H_1{}^{(3)}(t_1))(H_1{}^{(1)}(t_2) - H_1{}^{(3)}(t_2)) \rangle . \tag{A.5}$$

Using (2.2) (A.5) may be written as

$$k_2(t_1, t_2) = \frac{1}{\hbar^2} \sum_{\substack{\lambda, \lambda' \\ \lambda'', \lambda'''}} \langle h_{\lambda\lambda'}(t_1)\, h_{\lambda''\lambda'''}(t_2) \rangle (A^{(1)}_{\lambda\lambda' t_1} - A^{(3)}_{\lambda\lambda' t_1})(A^{(1)}_{\lambda''\lambda''' t_2} - A^{(3)}_{\lambda''\lambda''' t_2}) . \tag{A.6}$$

Using the Markovian property, we may write

$$\langle h_{\lambda\lambda'}(t_1)\, h_{\lambda''\lambda'''}(t_2) \rangle = \delta(t_1 - t_2) \hbar^2 \Lambda\ (\lambda, \lambda', \lambda'', \lambda''') \tag{A.7}$$

$$= \delta(t_1 - t_2) \hbar^2 \Lambda(\{\lambda\}) . \tag{A.8}$$

Executing the variational derivative with respect to $\alpha(t)$, we have from (A.4)

$$2 \frac{\delta}{\delta \alpha(t)} \left\langle \left(\tilde{T} \exp\left\{ -\frac{1}{i\hbar} \int_0^t \alpha(\tau) H(\tau)\, \mathrm{d}\tau \right\} \right) O_1 \left(T \exp\left\{ \frac{1}{i\hbar} \int_0^t \alpha(\tau) H(\tau)\, \mathrm{d}\tau \right\} \right) \right\rangle \Bigg|_{\alpha(\tau) = 1} \tag{A.9}$$

$$= \mathcal{T} \exp\left\{ -\frac{1}{i\hbar} \int_0^t (H_0{}^{(1)}(\tau) - H_0{}^{(3)}(\tau))\, \mathrm{d}\tau \right\} \cdot \exp\left\{ -\frac{1}{2} \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, k_2(t_1, t_2) \right\} \left[-\frac{1}{i\hbar} (H_0{}^{(1)} - H_0{}^{(3)}) \right] O_1{}^{(2)}$$

$$+ \mathcal{T} \exp\left\{ -\frac{1}{i\hbar} \int_0^t (H_0{}^{(1)}(\tau) - H_0{}^{(3)}(\tau))\, \mathrm{d}\tau \right\} \cdot \exp\left\{ -\frac{1}{2} \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, k_2(t_1, t_2) \right\} \tag{A.10}$$

$$\cdot \left\{ -\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, k_2(t_1, t_2)\, \delta(t - t_2) - \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, k_2(t_1, t_2)\ \delta(t_1 - t) \right\} O_1{}^{(2)} .$$

Integrating the δ-functions in the last line and inserting (A.6), we obtain from (A.10)

$$\frac{i}{\hbar} \langle [H_0, O_1]_t \rangle - \mathcal{T} \exp\left\{ -\frac{1}{i\hbar} \int_0^t (H_0{}^{(1)}(\tau) - H_0{}^{(3)}(\tau))\, \mathrm{d}\tau \right\} \cdot \exp\left\{ -\frac{1}{2} \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, k_2(t_1, t_2) \right\}$$

$$\cdot \frac{1}{2} \left\{ \int_0^t \mathrm{d}t_2\, \delta(t - t_2) \sum_{\{\lambda\}} \Lambda(\{\lambda\}) [A^{(1)}_{t\lambda\lambda'} A^{(1)}_{t_2\lambda''\lambda'''} - A^{(1)}_{t\lambda\lambda'} A^{(3)}_{t_2\lambda''\lambda'''} - A^{(3)}_{t\lambda\lambda'} A^{(1)}_{t_2\lambda''\lambda'''} + A^{(3)}_{t\lambda\lambda'} \mathrm{A}^{(3)}_{t_2\lambda''\lambda'''}] \right. \tag{A.11}$$

$$\left. + \int_0^t \mathrm{d}t_1\, \delta(t - t_1) \sum_{\{\lambda\}} \Lambda\ (\{\lambda\}) [A^{(1)}_{t_1\lambda\lambda'} A^{(1)}_{t\lambda''\lambda'''} - A^{(1)}_{t_1\lambda\lambda'} A^{(3)}_{t\lambda''\lambda'''} - A^{(3)}_{t_1\lambda\lambda'} A^{(1)}_{t\lambda''\lambda'''} + A^{(3)}_{t_1\lambda\lambda'} A^{(3)}_{t\lambda''\lambda'''}] \right\} O_1{}^{(2)} .$$

Applying the ordering operators and integrating once more, (A.11) becomes

$$\frac{i}{\hbar} \langle [H_0, O_1]_t \rangle - \left\langle \left(\tilde{T} \exp\left\{ -\frac{1}{i\hbar} \int_0^t H(\tau)\, \mathrm{d}\tau \right\} \right) \right.$$

$$\cdot \frac{1}{4} \sum_{\{\lambda\}} \Lambda(\{\lambda\}) [A_{\lambda''\lambda'''} A_{\lambda\lambda'} O_1 + A_{\lambda\lambda'} A_{\lambda''\lambda'''} O_1 + O_1 A_{\lambda\lambda'} A_{\lambda''\lambda'''} \tag{A.12}$$

$$\left. + O_1 A_{\lambda''\lambda'''} A_{\lambda\lambda'} - 2 A_{\lambda\lambda'} O_1 A_{\lambda''\lambda'''} - 2 A_{\lambda''\lambda'''} O_1 A_{\lambda\lambda'}] \left(T \exp\left\{ -\frac{1}{i\hbar} \int_0^t H(\tau)\, \mathrm{d}\tau \right\} \right) \right\rangle .$$

Inserting (A.12) into (2.8), we get finally (2.9). The derivation of the equations of motion of the correlation functions for negative times and for $\langle \langle O_1(0)\, O_2(t) \rangle \rangle$ is done in the same way.

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