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ON THE INFLUENCE OF NOISE  
ON THE DENSITY  
OF STATES AND ABSORPTION  
IN DISORDERED MOLECULAR SYSTEMS

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## 1. Introduction

The characterization of excitons in molecular system has been one of the important problems of solid state physics since the concept of molecular excitons was introduced by Frenkel because of its wide applications ranging from optical properties of molecular crystals to energy transfer by excitons in molecular units in the primary processes of photosynthesis. Among the basic problems to be considered in this connection is the exciton - phonon interaction influencing both the optical and transport properties of excitons. A fruitful approach developed for an approximate treatment of the exciton - phonon interaction in the last decade was that of replacing this interaction by that with a stochastic field originating in /1/ and being further developed in a number of papers reviewed in /2/. In this approach the molecular vibrations are treated as a heat bath pushing the excitonic system in a stochastic manner.

So far, however, this approach has been restricted to systems periodic in the absence of noise, i.e., the corresponding Hamiltonians are translationally invariant if the interaction of the excitons with the stochastic process is switched off. In this paper we consider the case when the noise is perturbing the excitons in a disordered molecular system, i.e., we have two stochastic sources in the Hamiltonian: a time independent part representing the static disorder and a time dependent one modelling the exciton - phonon interaction.

For the noise we use the Gaussian coloured noise possessing an exponential correlation function. Periodic systems perturbed by the Gaussian coloured noise (or the discrete Poisson noise) were investigated using self - consistent approaches like the dynamical CPA in /3-5/ or by cumulant expansions /6/. In our case the situation is more complicated because of the presence of static disorder besides the noise and we will use a simpler decoupling approach when the noise average is performed which is equivalent to second order perturbation theory for the mass operator. As we will show, however, even this lowest order expression for the mass operator sensitively depends on the form of the wave functions of the unperturbed system and is more complicated if a disordered system is perturbed by the noise (section 2).

As an explicit example for the static disorder we consider

the Lloyd model with a Lorentzian distribution for the random part of the site energies. This model has simple averaging properties as far as only the retarded or advanced Green function is calculated, what is sufficient for the density of states (dos). Furthermore, the Fourier - transform of the exponential correlation function of the noise is also of the Lorentzian form which makes both stochastic perturbations formally similar resulting in a shift of the poles of the Green functions (section 3).

Finally, we consider the influence of both types of disorder on the form of the excitonic absorption spectrum and the relation between the dos and the absorption. As is expected this relation is not direct due to the additional presence of the transition matrix elements in the expression for the dielectric function. We discuss some cases where this relation becomes more direct or indirect, respectively (section 4).

## 2. Model Hamiltonian and Approximation for the Mass Operator

We consider the following Hamiltonian in the site representation

$$\hat{H} = \hat{H}_{exc} + \hat{H}_{int}, \quad (1)$$

where

$$\hat{H}_{exc} = \sum_{n,m} (\epsilon_n d_{nm} + T_{nm}) \hat{a}_n^+ \hat{a}_m \quad (2)$$

and

$$\hat{H}_{int} = \sum_n \Delta_n(t) \hat{a}_n^+ \hat{a}_n. \quad (3)$$

Here  $\hat{a}_n^+$  ( $\hat{a}_n$ ) are exciton creation (annihilation) operators at molecule  $n$  ( $m$ ),  $\epsilon_n$  and  $T_{nm}$  are the exciton site energy and transfer matrix element for the static disordered molecular system, respectively, and  $\Delta_n(t)$  is a stochastic process given at lattice site  $n$  approximating the exciton - phonon interaction. For a discussion of the diagonal approximation of the interaction we refer to /3/. We assume

$$\langle \Delta_n(t) \rangle_N = 0, \quad (4)$$

where  $\langle \dots \rangle_N$  denotes the average over the noise and

$$\langle \Delta_n(t) \Delta_m(t') \rangle_N = d_{nm}^2 \Delta_0^2 e^{-|t-t'|/\tau} \quad (5)$$

Here  $\Delta_0^2$  and  $\tau$  are the mean square and correlation time of the noise, respectively.

We consider the retarded Green function corresponding to the Hamiltonian (1)

$$g(n,t; m,t') = -i\theta(t-t') \langle [\hat{a}_n(t), \hat{a}_m^+(t')] \rangle \quad (6)$$

Here the brackets  $\langle \dots \rangle$  denote the average over the excitonic variables of the density matrix. The function (6) has to be averaged over the realizations of the stochastic processes  $\{\Delta_n(t)\}$ ,  $\langle \dots \rangle_N$ . This average approximates the trace over the phonon variables in a microscopic formulation of the exciton - phonon interaction.

To derive an approximate equation for the function (6) averaged over the noises, we pass to the  $\lambda$ -representation where the Hamiltonian (2) is diagonal. This representation is realized on the eigenfunctions  $\mathcal{S}_\lambda(n)$  of  $H_{\text{exo}}$  satisfying

$$\sum_m (\epsilon_n \delta_{nm} + T_{nm}) \mathcal{S}_\lambda(m) = \epsilon_\lambda \mathcal{S}_\lambda(n) \quad (7)$$

where  $\epsilon_\lambda$  are the corresponding eigenvalues. In a disordered system the explicit form of the system  $\{\mathcal{S}_\lambda(n)\}$  is usually unknown. However, the basis  $\{\mathcal{S}_\lambda(n)\}$  is useful for considering general properties as well approximations, as is the case in the electronic problem /7/.

Averaging the iterated Dyson equation for the Green function (6) and using (4) we get in the  $\lambda$ -representation

$$\begin{aligned} \langle g(\lambda, t; \lambda', t') \rangle_N &= d_{\lambda\lambda'}^2 G(\lambda; t-t') + \\ &+ \sum_{\nu, \sigma} \int d\tau \int d\tau' G(\lambda; t-\tau) \langle h_{\lambda\nu}(\tau) G(\nu; \tau-\tau') h_{\nu\sigma}(\tau') g(\sigma, \tau'; \lambda', t') \rangle_N \end{aligned} \quad (8)$$

Here  $G(\lambda, t)$  is the Green function of the system without noise corresponding to  $H_{\text{ex}}$  and  $h_{\lambda\nu}(t)$  are the transformed noise functions

$$h_{\lambda\nu}(t) = \sum_n \mathcal{S}_\lambda^*(n) \Delta_n(t) \mathcal{S}_\nu(n) \quad (9)$$

In (8) we choose the decoupling corresponding to second order perturbation theory for the mass operator ( $M \sim \Delta_0^2$ )

$$\begin{aligned} \langle h_{\lambda\nu}(\tau) h_{\nu\sigma}(\tau') g(\sigma, \tau'; \lambda', t') \rangle_N &\approx \\ \langle h_{\lambda\nu}(\tau) h_{\nu\sigma}(\tau') \rangle_N \langle g(\sigma, \tau'; \lambda', t') \rangle_N \end{aligned} \quad (10)$$

Passing to the Fourier representation

$$\langle g(\lambda, t; \lambda', t') \rangle_N = \int d\omega g(\lambda, \lambda'; \omega) e^{-i\omega(t-t')}$$

(we include the  $\langle \dots \rangle_N$  operation into the definition of  $g(\lambda, \lambda'; \omega)$ , for a stationary process the average depends on  $t - t'$ ) we get

$$g(\lambda, \lambda'; \omega) = d_{\lambda\lambda'}^2 G(\lambda; \omega) + \sum_{\sigma} G(\lambda; \omega) M_{\lambda\sigma}(\omega) g(\sigma, \lambda'; \omega) \quad (11)$$

where the mass operator  $M_{\lambda\sigma}(\omega)$  is given by

$$M_{\lambda\sigma}(\omega) = (2\pi)^2 \int d\omega' \sum_{\mu} G(\mu, \omega-\omega') K_{\lambda\mu\sigma}(\omega') \quad (12)$$

Here  $K_{\lambda\mu\sigma}(\omega)$  is the Fourier transform of

$$K_{\lambda\mu\sigma}(t-t') \equiv \langle h_{\lambda\mu}(t) h_{\mu\sigma}(t') \rangle_N \quad (13)$$

With

$$G(\lambda; \omega) = \frac{1}{2\pi} \frac{1}{\omega^+ - \epsilon_\lambda} \quad (14)$$

(we use units where  $\hbar = 1$ ) and eqs. (5), (9), (13) in (12) we find the following explicit form of  $M_{\lambda\sigma}(\omega)$

$$M_{\lambda\sigma}(\omega) = (2\pi\Delta_0)^2 \sum_n \mathcal{S}_\lambda^*(n) \mathcal{S}_\sigma(n) \sum_{\mu} |\mathcal{S}_\mu(\omega)|^2 G(\mu; \omega + i\epsilon) \quad (15)$$

It is instructive to consider the limiting case when the system in the absence of the noise is periodic. Then  $\epsilon_n$  and  $T_{nm}$  in (7) correspond to a molecular crystal and we have

$$\lambda \rightarrow \bar{k}, \quad \mathcal{S}_\lambda(\bar{n}) \rightarrow \frac{1}{\sqrt{N}} e^{i\bar{k}\bar{n}}, \quad \epsilon_\lambda \rightarrow \epsilon_{\bar{k}},$$

$\bar{k}$ ,  $\epsilon_{\bar{k}}$  and  $N$  being the exciton wave vector, dispersion relation and number of lattice sites, respectively. Then, we get from (15) a diagonal mass operator

$$M_{\bar{k}\bar{k}}(\omega) = \delta_{\bar{k}\bar{k}} m(\omega), \quad (16)$$

where

$$m(\omega) = 2\pi \Delta_0^2 \frac{1}{N} \sum_{\bar{k}} \frac{1}{\omega + \frac{i}{\tau} - \epsilon_{\bar{k}}} = (2\pi \Delta_0)^2 G(\omega + \frac{i}{\tau}). \quad (17)$$

Here  $G(\omega)$  is the diagonal element of the Green function of the crystal in site representation. Eq. (17) gives the first order term of a continued fraction representation of the self-energy of the dynamical CPA /3/. In this case  $m(\omega)$  is independent of  $\bar{k}$  (or  $\bar{n}$  in site representation) of the state perturbed by the noise. A diagonal mass operator multiplied by a state independent factor as in (16) results also for a weakly disordered system. To derive this property we represent the  $\mu$ -sum in eq. (14) by  $G(n,n; \omega + \frac{i}{\tau})$ , i.e.,

$$M_{\lambda\delta}(\omega) = (2\pi \Delta_0)^2 \sum_n \mathcal{S}_\lambda^*(n) \mathcal{S}_\delta(n) G(n,n; \omega + \frac{i}{\tau}). \quad (18)$$

If the system is weakly disordered in the sense that the local density of states  $\rho(n; \omega) \sim \text{Im} G(n,n; \omega)$  is approximately independent of the site  $n$ , the  $n$  dependence of the diagonal elements becomes negligible,  $G(n,n; \omega + \frac{i}{\tau}) = G(0,0; \omega + \frac{i}{\tau}) \equiv G(\omega + \frac{i}{\tau})$ . Then, (18) reduces to

$$M_{\lambda\delta}(\omega) = \delta_{\lambda\delta} (2\pi \Delta_0)^2 G(\omega + \frac{i}{\tau}) \quad (19)$$

$\lambda$  and  $\delta$  now being eigenstates of the "weakly disordered" Hamiltonian  $H_{exc}$ .

In the general case of arbitrary disorder it is, however, impossible to reduce (15) to a form with a state independent site

energy (which is the usual assumption for improving (16) along the line of the self-consistent CPA procedure /3,4,6/). In this case the system of functions  $\{\mathcal{S}_\lambda(n)\}$  can display the transition from localized to extended states and a rather complicated behaviour of

$M_{\lambda\delta}$  can be expected. Without explicitly solving the localization problem we consider a simple case by putting localization "by hands" into (15). To this end we assume that the localized states are roughly of the minimal possible extent of order of the spacings between the molecules. Then, a nonvanishing overlap results if

$$\sum_n \mathcal{S}_\lambda^*(n) \mathcal{S}_\delta(n) |\mathcal{S}_\mu(n)|^2 \approx \delta_{\lambda\delta} \delta_{\mu\lambda} \quad (20)$$

and (15) reduces to

$$M_{\lambda\delta}(\omega) = \delta_{\lambda\delta} 2\pi \Delta_0^2 \frac{1}{\omega + \frac{i}{\tau} - \epsilon_\lambda}. \quad (21)$$

In this case  $M_{\lambda\delta}(\omega)$  is diagonal, but contrary to (19) it depends explicitly on the state  $\lambda$  through  $\epsilon_\lambda$ , i.e., the self-energy describing the noise action becomes state dependent. Furthermore (21) is the first term of a continued fraction representation of the Anderson/Kubo theory for the lineshape of a localized electron the energy of which fluctuates obeying the Gaussian-Markoff process (compare the derivation of formula (3.25) of ref. /3/). This example demonstrates the importance of the behaviour of the wave functions in (15) in determining the form of  $M_{\lambda\delta}$ . There is, however, a special case in which the behaviour of the system  $\{\mathcal{S}_\lambda(n)\}$  does not matter at all. This is the white noise limit,  $\tau \rightarrow 0$ ,  $\Delta_0^2 \rightarrow \infty$  and

$$\Gamma \equiv \Delta_0^2 \tau = \text{const.} \quad (22)$$

when, as is well known /8-10/, the decoupling (10) and hence (15) become exact. In this limit  $\Delta_0^2 G(\mu; \omega + \frac{i}{\tau}) \rightarrow -2\pi i \Gamma$  and one gets from (15)

$$M_{\lambda\delta}^{WN}(\omega) = -2\pi i \delta_{\lambda\delta} \Gamma \quad (23)$$

i.e., the mass operator is diagonal, imaginary and constant. The Green function is given by

$$g^{WN}(\alpha, \alpha'; \omega) = \frac{\delta \alpha'}{2\pi} \frac{1}{\omega + i\Gamma - \varepsilon \alpha} \quad (24)$$

Eq. (23) includes the result for a periodic system perturbed by white noise /10/ as a special case and generalizes it to that of an arbitrary system of eigenfunctions  $\{\mathcal{S}_\lambda(n)\}$  corresponding to a disordered Hamiltonian  $H_{exc}$  (2). This result shows that the white noise is not selective to the kind of system which is perturbed: For an ordered as well as a disordered system the mass operator reduces to the diagonal constant imaginary form. Hence,  $\tau > 0$ , i.e., "coloured" noise is required to establish the difference between different forms of eigenfunctions in the spectrum.

### 3. Lloyd model for $H_{exc}$

Now we specify the disorder parameters in  $\hat{H}_{exc}$  by using the Lloyd model /11/. In this model the site energy  $\varepsilon_n$  in (2) has a random part  $\delta \varepsilon_n$ ,  $\varepsilon_n = \varepsilon_0 + \delta \varepsilon_n$  with a Lorentzian distribution

$$P(\delta \varepsilon_n) = \frac{1}{\pi} \frac{\gamma}{(\delta \varepsilon_n)^2 + \gamma} \quad (25)$$

The  $\delta \varepsilon_n$  at different lattice sites are uncorrelated and  $T_{nm}$  is translationally invariant. Rewriting (11) and (15) in the site representation we get for  $g(n, n'; \omega)$  the equation

$$g(n, n'; \omega) = G(n, n'; \omega) + (\pi \Delta_0)^2 \sum_m G(n, m; \omega) G(m, m; \omega + \frac{i}{\tau}) g(m, n'; \omega) \quad (26)$$

or after iteration

$$g(n, n'; \omega) = G(n, n'; \omega) + (\pi \Delta_0)^2 \sum_m G(n, m; \omega) G(m, m; \omega + \frac{i}{\tau}) \cdot G(m, n'; \omega) + (\pi \Delta_0)^4 \sum_{m, l} G(n, m; \omega) G(m, m; \omega + \frac{i}{\tau}) G(m, l; \omega) G(l, l; \omega + \frac{i}{\tau}) G(l, n'; \omega) + \dots \quad (27)$$

Eq. (27) has to be averaged over the static disorder with the distribution  $P(\delta \varepsilon_n)$  for different lattice sites. We denote this average by  $\langle \dots \rangle_D$ . Averaging (27) we use the following properties of the Lloyd model (see, e.g., /12/):

- 1) the average of the product of an arbitrary number of matrix elements of Green's functions factorizes, if all the functions are of one type (retarded or advanced), i.e.,

$$\langle G(n, m; \omega) G(m, m; \omega + \frac{i}{\tau}) \dots G(l, n'; \omega) \rangle_D = \langle G(n, m; \omega) \rangle_D \langle G(m, m; \omega + \frac{i}{\tau}) \rangle_D \dots \langle G(l, n'; \omega) \rangle_D \quad (28)$$

and ii)

$$\langle G(n, m; \omega) \rangle_D = G^0(n, m; \omega + i\gamma) \quad (29)$$

where the Green function  $G^0$  corresponds to  $H_{exc}$  (2) with  $\varepsilon_n$  replaced by  $\varepsilon_0$ .

With (28), (29) one gets from (27)

$$\begin{aligned} \langle g(n, n'; \omega) \rangle_D &= G^0(n, n'; \omega + i\gamma) + (\pi \Delta_0)^2 \sum_m G^0(n, m; \omega + i\gamma) \cdot \\ &\cdot G^0(m, m; \omega + i(\gamma + \frac{1}{\tau})) G^0(m, n'; \omega + i\gamma) + (\pi \Delta_0)^4 \sum_{m, l} G^0(n, m; \omega + i\gamma) \cdot \\ &\cdot G^0(m, m; \omega + i(\gamma + \frac{1}{\tau})) G^0(m, l; \omega + i\gamma) G^0(l, l; \omega + i(\gamma + \frac{1}{\tau})) G^0(l, n'; \omega + i\gamma) \end{aligned} \quad (30)$$

The adding of the static disorder parameter  $\gamma$  to the noise parameter  $\frac{1}{\tau}$  in the diagonal matrix elements of the Green functions  $G(m, m; \omega + i(\gamma + \frac{1}{\tau}))$  is the consequence of the similar properties of (5) and (25): the Fourier transform of (5) is of the Lorentzian form as the distribution (25) and the corresponding integrals in energy representation result in a shift of the poles. Passing to the Fourier transform

$$\langle g(\bar{n}, \bar{n}'; \omega) \rangle_D = \frac{1}{N} \sum_{\bar{k}} e^{i\bar{k}(\bar{n} - \bar{n}')} g(\bar{k}; \omega) \quad (31)$$

and using

$$G^o(\bar{k}; \omega) = \frac{1}{2\pi} \frac{1}{\omega + i\gamma - \varepsilon_{\bar{k}}} \quad (32)$$

one obtains from (30)

$$G(\bar{k}; \omega) = \frac{1}{2\pi} \left\{ \omega + i\gamma - \varepsilon_{\bar{k}} - \frac{\Delta_o^2}{N} \sum_{\bar{q}} \frac{1}{\omega + i(\gamma + \gamma_{\bar{q}}) - \varepsilon_{\bar{q}}} \right\}^{-1} \quad (33)$$

Introducing the dos of the periodic system

$$\rho^o(\omega) = \frac{1}{N} \sum_{\bar{k}} \delta(\omega - \varepsilon_{\bar{k}}) \quad (34)$$

one finds with  $\rho(\omega) = -2\text{Im} \int p G(\omega)$  from (33)

$$\rho(\omega) = -\frac{1}{\pi} \text{Im} \int d\omega' \rho^o(\omega') \left\{ \omega - \omega' + i\gamma - \Delta_o^2 \int d\omega'' \frac{\rho^o(\omega'')}{\omega + i(\gamma + \gamma_{\bar{q}}) - \omega''} \right\}^{-1} \quad (35)$$

For  $\Delta_o^2 = 0$  (35) reduces to the dos of the Lloyd model

$$\rho_L(\omega) = \int d\omega' \rho^o(\omega') \frac{1}{\pi} \frac{\gamma}{(\omega - \omega')^2 + \gamma^2} \quad (36)$$

From (35) several limiting cases can be considered. Here we are mainly interested in the influence of the static disorder where  $\gamma$  should not be negligible compared to the other parameters. In the opposite case of small  $\gamma$  the situation effectively reduces to that considered in /3/

1) small bandwidth of the periodic system:  $\rho^o(\omega) = \delta(\omega - \omega_o)$ .  
In this case the bandwidth given by  $\rho^o(\omega)$  is small compared to  $\gamma$  (the effective bandwidth). Then (35) reduces to

$$\rho(\omega) = \frac{1}{\pi} \frac{\gamma(\omega - \omega_o)^2 + \gamma(\gamma + \gamma_{\bar{q}})^2 + \Delta_o^2(\gamma + \gamma_{\bar{q}})}{[(\omega - \omega_o)^2 - \gamma(\gamma + \gamma_{\bar{q}}) - \Delta_o^2]^2 + [(2\gamma + \gamma_{\bar{q}})(\omega - \omega_o)]^2} \quad (37)$$

For the Gaussian process as an approximation of the exciton phonon interaction, the integral in the denominator of (35) should be a

small correction. In this case it is convenient to represent the phonon influence in (37) in the following form

$$\rho(\omega) = \frac{1}{\pi} \frac{\gamma + (\gamma + \gamma_{\bar{q}}) \xi(\omega)}{(\omega - \omega_o)^2 [1 - \xi(\omega)]^2 + \gamma^2 [1 + \frac{1 + \gamma_{\bar{q}}}{\gamma} \xi(\omega)]^2} \quad (38)$$

where

$$\xi(\omega) = \frac{\Delta_o^2}{(\omega - \omega_o)^2 + (\gamma + \gamma_{\bar{q}})^2} \quad (39)$$

is a correction function resulting in an additional broadening of the Lorentzian.

The Dyson equation (26) can also be used to consider the dichotomic process /4/ jumping between  $+\Delta_o$  and  $-\Delta_o$ , and possessing as the Gaussian an exponential correlation function. For the dichotomic process we can find the disorder influence specified by  $\gamma$  on the transition between bimodal and monomodal shape of the dos and compare this transition with that occurring in a periodic system perturbed by dichotomic noise. For the critical value of the noise amplitude  $\Delta_{oc}$  dividing bimodal ( $\Delta_o > \Delta_{oc}$ ) from monomodal ( $\Delta_o < \Delta_{oc}$ ) shape in the dos, one obtains from (37)

$$\Delta_{oc}(\gamma) = \frac{(\gamma + \gamma_{\bar{q}})^{3/2}}{(3\gamma + 2/\varepsilon)^{1/2}} \quad (40)$$

One easily verifies  $\Delta_{oc}(\gamma) - \Delta_{oc}(\gamma=0) > 0$ , i.e., in the presence of static disorder the critical value for the "bifurcation" from monomodal to bimodal shape of the dos shifts to higher energies.

ii) white noise limit

Taking the corresponding limit in the  $\omega''$  integral in (35) and using  $\int d\omega' \rho^o(\omega') = 1$  one finds

$$\rho_L^{WN}(\omega) = \int d\omega' \rho^o(\omega') \frac{1}{\pi} \frac{\gamma + \Gamma}{(\omega - \omega')^2 + (\gamma + \Gamma)^2} \quad (41)$$

where  $\Gamma$  is given by (22). In (41) the static disorder and noise parameters add in a convolution of a Lorentzian with the dos of the periodic system. We note that (41) is an exact expression, because the mass operator in (15) becomes exact in the white noise limit.

#### iii) Fast motion limit

In this limit  $\gamma \rightarrow 0$ ,  $\Delta_0^2 = \text{const.}$  and (35) reduces to (36), i.e., the noise is ineffective and the dos tends to the unperturbed expression of the Lloyd model (motional narrowing).

### 4. Absorption

A consequence of the static and temporal disorder in the Hamiltonian (1) is the broadening of the optical absorption spectrum. Generally the form of the spectrum is determined by the combined action of the Green function and the transition matrix elements into the excitonic states. In the case of periodic systems these matrix elements are singular in k-representation resulting in the k-selection rule/13/ (for simplicity we neglect the photon wave vector). In disordered systems there is a breaking of this selection rule, as was intensively discussed for electronic systems, see, e.g., /7/. Here we examine this point closer for the case of excitonic systems. We consider two types of approximations: complete breaking of selection rules (4.1) and energetic fluctuations in the transition matrix elements of the molecules (4.2). We conclude that the latter case corresponds to a weak breaking of selection rules.

#### 4.1. Complete breaking of selection rules/ Approximation

$$|\bar{p}_\lambda|^2 = \text{const.} / |\bar{a}_\lambda|^2 = \text{const.}$$

Representing the dielectric function by the exciton Green function we find for the imaginary part in  $\lambda$ -representation

$$\begin{aligned} \epsilon_{2,\alpha\beta}(\omega) = & -\text{Im} \left( \frac{e}{m\omega} \right)^2 \frac{2\pi}{V} \sum_{\lambda, \lambda'} \left\{ p_{\alpha\lambda} p_{\beta\lambda'} g(\lambda, \lambda'; \omega) + \right. \\ & \left. + p_{\alpha\lambda} p_{\beta\lambda'}^* g(\lambda, \lambda'; -\omega) \right\}. \end{aligned} \quad (42)$$

Here  $p_{\alpha\lambda}$  are the matrix elements corresponding to the excitation of excitons in  $\lambda$  states

$$p_{\alpha\lambda} = \sum_n \mathcal{S}_\lambda(n) p_\alpha(n), \quad (43)$$

where  $\mathcal{S}_\lambda(n)$  are the eigenfunctions of  $H_{\text{exc}}$  (7) and

$$p_\alpha(n) = \langle f_n | \hat{p}_\alpha | 0_n \rangle \quad (44)$$

is the standard momentum transition matrix element of excitation of the nth molecule from its ground (0) into the excited state (f). For a molecular crystal  $\lambda \rightarrow \bar{k}$ ,  $\mathcal{S}_\lambda(n) \rightarrow \frac{1}{\sqrt{N}} e^{ikn}$  and  $p_{\alpha\bar{k}}$  becomes singular,  $p_{\alpha\bar{k}} \sim \delta_{\bar{k},0}$  resulting in the k selection rule. For a disordered system the simplest situation is that of "maximal" disorder where the  $\lambda$ -dependence in  $p_{\alpha\lambda}$  is smooth enough to be neglected at all. We consider the special cases:

#### 1) No noise

Neglecting the second non resonant Green function in the r.h.s. of (42) one obtains

$$\epsilon_2(\omega) = \frac{1}{d} |\bar{p}|^2 \left( \frac{e}{m\omega} \right)^2 \frac{2\pi}{V} \sum_\lambda (-\text{Im} G(\lambda; \omega)), \quad (45)$$

i.e., with (14) the absorption is proportional to the excitonic dos

$$\epsilon_2(\omega) \sim \rho(\omega) = \frac{1}{V} \sum_\lambda \delta(\omega - \epsilon_\lambda). \quad (46)$$

In (45) we substituted  $|p_\alpha|^2$  by  $\frac{1}{d} |\bar{p}|^2$  (d is the dimension of the system) assuming an isotropic system. The parallel approximation neglecting the  $\lambda$  dependence of the transition matrix elements for disordered electron systems results in a convolution of the dos functions for the initial and final states /7/. The "contraction" into one dos function for exciton systems is a result of the structure of the exciton operators being composed of two electron operators. An expression analogous to (45) results for  $\lambda$  independent dipole transition matrix elements. Using the relation  $\frac{e}{m} p_{\alpha\lambda} = i \epsilon_\lambda d_{\alpha\lambda}$ , where  $d_{\alpha\lambda}$  are the dipole moments for

transition into  $\lambda$  states and the approximation  $|d_{\alpha\lambda}|^2 \approx |d_{\alpha}|^2$ , one obtains (45) with  $|\bar{p}|^2$  replaced by  $|\bar{d}|^2$  and without the  $\omega^2$  dependence in the denominator.

ii) White noise limit

Independent of the type of static disorder the Green function is diagonal in the  $\lambda$  representation and given by (24). One obtains

$$\varepsilon_2(\omega) = \left(\frac{e}{m\omega}\right)^2 \frac{1}{d} |\bar{p}|^2 \int d\omega' \frac{1}{\mathfrak{I}} \frac{\Gamma}{(\omega-\omega')^2 + \Gamma^2} \rho(\omega') \quad (47)$$

where the unperturbed dos  $\rho(\omega)$  is given by (46).

iii) Coloured noise, strong localization

For the approximate mass operator (21) the Green function is

$$g(\lambda, \lambda'; \omega) = \frac{d_{\lambda\lambda'}}{2\pi} \frac{1}{\omega - \varepsilon_{\lambda} - \Delta_0^2 \frac{1}{\omega + \frac{1}{\varepsilon} - \varepsilon_{\lambda}}} \quad (48)$$

and obtains

$$\varepsilon_2(\omega) = \left(\frac{e}{m\omega}\right)^2 \frac{1}{d} |\bar{p}|^2 \int d\omega' \rho(\omega') \frac{1}{\mathfrak{I}} \frac{\Gamma}{(\omega-\omega')^2 [1 - (\varepsilon\Delta_0)^2 + \varepsilon^2(\omega-\omega')^2] + (\varepsilon\Delta_0)^2} \quad (49)$$

For  $\varepsilon$  small the quantities  $(\varepsilon\Delta_0)^2$  and  $\varepsilon^2(\omega-\omega')^2$  are corrections to the white noise limit (47).

#### 4.2. Fluctuations of the excitation energies of the molecules

To take into account spatial fluctuations in the transition matrix elements explicitly we pass to the  $n$  representation

$$\varepsilon_{2,\alpha\alpha}(\omega) = -\text{Im} \left(\frac{e}{m\omega}\right)^2 \frac{2\pi}{V} \left\langle \sum_{n,n'} \left\{ p_{\alpha n}^* p_{\alpha n'} g(n,n'; \omega) + p_{\alpha n} p_{\alpha n'}^* g^*(n,n'; -\omega) \right\} \right\rangle_D \quad (50)$$

For a periodic system with one molecule in the unit cell we would have  $p_{\alpha n} = p_{\alpha}$  and (50) reduces to

$$\varepsilon_{2,\alpha\alpha}(\omega) = |p_{\alpha}|^2 n \left(\frac{e}{m\omega}\right)^2 (-2\pi \text{Im} g(k=0; \omega)) \quad (51)$$

i.e., in this case the shape of the absorption band is given by the imaginary part of the noise broadened  $k=0$  Green function,  $n=N/V$  is the concentration of molecules. For a disordered system the relation

$$\frac{e}{m} p_{\alpha n} = i \varepsilon_n d_{\alpha n} \quad (52)$$

implies that  $p_{\alpha n}$  contains the fluctuating excitation energies of the molecules,  $\varepsilon_n = \varepsilon_0 + \delta\varepsilon_n$ . Now we consider the influence of such fluctuations on the spectral dependences. Inserting (52) into (50) and assuming  $n$  independent dipole moments<sup>1)</sup>,  $d_{\alpha n} = d_{\alpha}$ , we get

$$\varepsilon_{2,\alpha\alpha}(\omega) = \frac{|d_{\alpha}|^2}{\omega^2} \frac{(-2\pi)}{V} \text{Im} \left\langle \sum_{n,n'} (\varepsilon_0 + \delta\varepsilon_n) (\varepsilon_0 + \delta\varepsilon_{n'}) g(n,n'; \omega) \right\rangle_D \quad (53)$$

(here  $\Sigma$  is left as a tensor including possible anisotropies). To perform the average over the static disorder in (53) we use the Lloyd model.

i) No noise

The averages in (53) are easily calculated using the Lorentz distribution

$$\langle \delta\varepsilon_n G(n,n'; \omega) \rangle_D = (-i\chi) \langle G(n,n'; \omega) \rangle_D \quad (54)$$

$$\langle \delta\varepsilon_n \delta\varepsilon_{n'} G(n,n'; \omega) \rangle_D \Big|_{n \neq n'} = -\chi^2 \langle G(n,n'; \omega) \rangle_D \quad (55)$$

$$\langle \delta\varepsilon_n^2 G(n,n'; \omega) \rangle_D = -\chi^2 \langle G(n,n'; \omega) \rangle_D - \frac{i\chi}{2\pi} \quad (56)$$

In the last average (56) a diverging real contribution (due to the slow convergence of the Lorentzian distribution) was omitted because it drops out when the imaginary part is taken in (53). Using

<sup>1)</sup>By an expansion possible fluctuations in  $d_{\alpha n}$  due to  $\delta\varepsilon_n$  are easily included. For terms up to the second order in  $\delta\varepsilon_n$  this changes however only the prefactor in (57) leaving the same spectral dependence.



(54) - (56) in (53) and passing to the Fourier transforms with (29), (31), one obtains

$$\varepsilon_{2,\alpha\alpha}(\omega) = n \frac{|d_{\alpha}|^2}{\omega^2} (-2\pi) \left\{ (\varepsilon_0^2 - \gamma^2) \text{Im} G^0(k=0, \omega) - 2\varepsilon_0 \gamma \text{Re} G^0(k=0, \omega) - \frac{\gamma}{2\pi} \right\}. \quad (57)$$

With the explicit form of  $G^0(k=0, \omega)$  given by (32) one finds from (57)

$$\varepsilon_{2,\alpha\alpha}(\omega) = n |d_{\alpha}|^2 \frac{(\omega + \varepsilon_0 - \varepsilon_{k=0})^2}{\omega^2} \cdot \frac{\gamma}{(\omega - \varepsilon_{k=0})^2 + \gamma^2}, \quad (58)$$

i.e., the absorption is a Lorentzian centered at  $\varepsilon_{k=0}$ , modified by the prefactor introducing an asymmetry into the shape of the absorption band. This asymmetry due to the mixing of the real and imaginary parts in (57) is, however, small in the optical region ( $\omega \gg \varepsilon_0 - \varepsilon_{k=0}$ ). We note an important difference to the analogous case 1) of 4.1: In (45) the absorption is proportional to the dos, i.e., the linewidth is proportional to the full bandwidth, whereas in (58) the disorder parameter  $\gamma$  contributes to the width only.

#### ii) Coloured noise

In this case we have to use the expansion (27) in (53) and to calculate averages over products of Greens functions times  $\delta\varepsilon_n$  factors. For Lorentzian disorder (25) one easily verifies the following modifications of the equations (28), (29)

$$\begin{aligned} & \langle \delta\varepsilon_{n_1} G(n_1, n'_1; \omega_1) G(n_2, n'_2; \omega_2) \dots G(n_k, n'_k; \omega_k) \rangle_D = \\ & = -i\gamma G^0(n_1, n'_1; \omega_1 + i\gamma) G^0(n_2, n'_2; \omega_2 + i\gamma) \dots G(n_k, n'_k; \omega_k + i\gamma) \quad (59) \\ \text{and} \\ & \langle \delta\varepsilon_{n_1} \delta\varepsilon_{n_2} G(n_1, n'_1; \omega_1) G(n_2, n'_2; \omega_2) \dots G(n_k, n'_k; \omega_k) \rangle_D = \\ & = -\gamma^2 G^0(n_1, n'_1; \omega_1 + i\gamma) G^0(n_2, n'_2; \omega_2 + i\gamma) \dots G(n_k, n'_k; \omega_k + i\gamma), \quad (60) \end{aligned}$$

where all the Green functions are of one type. Using (59) and (60) one finds that eqs. (54) - (56) remain valid with  $G(n, n'; \omega)$  replaced by  $G_{\gamma}(n, n'; \omega)$ , i.e.,

$$\varepsilon_{2,\alpha\alpha}(\omega) = n \frac{|d_{\alpha}|^2}{\omega^2} (-2\pi) \left[ (\varepsilon_0^2 - \gamma^2) \text{Im} G_{\gamma}(k=0; \omega) - 2\varepsilon_0 \gamma \text{Re} G_{\gamma}(k=0; \omega) - \frac{\gamma}{2\pi} \right]. \quad (61)$$

In (61) as in (57) a mixing of the real and imaginary parts of the Green function occurs.

#### iii) White noise limit

This is the simplest case to compare the influence of the noise on the optical spectrum with that in 4.1, formula (47). Using for

$G_{\gamma}(k=0, \omega)$  the white noise limit of (33) in (61) one obtains

$$\varepsilon_{2,\alpha\alpha}(\omega) = n |d_{\alpha}|^2 \frac{1}{\omega^2} \left[ \frac{\gamma}{\gamma + \Gamma} (\omega - \varepsilon_{k=0} + \varepsilon_0)^2 + \frac{\Gamma}{\gamma + \Gamma} \varepsilon_0^2 + \gamma \Gamma \right] \cdot \frac{\gamma + \Gamma}{(\omega - \varepsilon_{k=0})^2 + (\gamma + \Gamma)^2}. \quad (62)$$

Comparing (62) with (47) we find that in (47) the absorption is proportional to the full noise broadened dos, i.e., includes the bandwidth of the periodic system, whereas in (62) the static and temporal disorder parameters  $\gamma$  and  $\Gamma$  contribute to the bandwidth only. Furthermore in (45) and (47) the absorption peak is centered in the middle of the exciton band, whereas in eqs. (58) and (62) the center is approximately at  $\varepsilon_{k=0}$ . Clearly the latter situation is closer to the periodic case where a noise broadened peak at  $\varepsilon_{k=0}$  follows from (51). Hence the fluctuations of the excitation energies but constant dipole moments corresponds in a certain sense to a weak breaking of selection rules as contrasted to the complete breaking.

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К влиянию шума на плотность состояний и поглощение  
в неупорядоченных молекулярных системах

Рассматривается неупорядоченная экситонная система, в которой экситон-фононное взаимодействие аппроксимируется случайным гаусс-марковским шумовым процессом. Исследуется структура массового оператора для произвольного экситонного гамильтониана в зависимости от параметров случайного процесса. Явные вычисления плотности состояний и коэффициента поглощения производятся для случая статического беспорядка с лоренцевым распределением. Рассматривается влияние нарушения правила отбора по квазиимпульсу на вид частотной зависимости коэффициента поглощения.

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On the Influence of Noise on the Density of States  
and Absorption in Disordered Molecular Systems

A disordered excitonic system perturbed by Gauss - Markov noise approximating the exciton-phonon interaction is considered. The structure of the mass operator in case of an arbitrary exciton Hamiltonian is investigated in dependence on the parameters of the noise process. Explicit calculations for the density of states and the absorption coefficient are performed for Lorentzian static disorder. The influence of the breaking of the momentum selection rule on the frequency dependence of the absorption coefficient is considered.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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