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Abstract. Motivated by a three-dimensional LDA band structure calculation for *trans*-polyacetylene (PA) we construct an effective two-dimensional model for a film of conjugated polymers. In real materials a non-perfect structural order is found. It has its origin in the finite conjugation length of single chain segments, impurities and crystalline defects. We model these effects through a fluctuating contribution to the interchain hopping amplitude. Using a supersymmetric path integral formalism we obtain the averaged one-particle Green function giving the electronic density of states (DOS) and furthermore the current correlation function determining the optical absorption coefficient and DC conductivity. As a consequence of the interchain coupling we find a broad shoulder at the band edge in the DOS and the optical absorption. The main effect of disorder is seen in a broadening of the interband transition peak and an increasing intraband absorption. The anisotropy in the absorption coefficient parallel and perpendicular to the chain direction allows us to fix the interchain coupling strength; the line shape contains information about the effective disorder strength.

1. Introduction

Only a few attempts have been made so far to study the electronic properties of conjugated polymers beyond simple one-dimensional models. On one hand one-dimensional calculations are indeed able to explain many of the experimentally observed features such as the Peierls instability or the occurence of non-linear intragap excitations. On the other hand some phenomena, such as the conductivity, cannot be explained in the framework of strictly one-dimensional systems. An infinitesimally small interchain coupling changes the dimensionality of the system and enables thus a non-vanishing conductivity also in the presence of disorder.

A first step towards a theoretical understanding of the impact of interchain coupling in quasi-one-dimensional real materials has been made studying the model of two coupled chains [1]. Thus elementary processes such as the hopping of charged carriers from one chain to another can be described. However, the nature of the electronic structure and consequently of absorption processes is oversimplified in this way. The coupling of two chains leads to a splitting of the original one-dimensional bands into bonding and antibonding states, which is not observed experimentally. An additional complication in understanding the electronic properties of real conjugated polymers lies in the non-perfect crystallinity of most materials that has to be taken into account as structural disorder.

In the study of optical properties of conjugated polymers no exact solution for a disordered system is known. There are several approaches starting from simple one-dimensional models without disorder [2–4]. Anisotropic optical properties have been calculated so far only for a model of two coupled chains [5] and for the zig-zag geometry

of the polymer backbone [6]. All these calculations show a singularity at the band gap $\omega = 2\Delta$. Disorder and vibronic effects are incorporated through a Gaussian broadening of the absorption structure.

Here we attempt to overcome this shortcoming in studying a simple two-dimensional model of an array of coupled polymer chains. We derive this model from the results of a density functional calculation of the electronic structure of crystalline *trans*-polyacetylene PA [7,8]. We believe, however, that the resulting model for a polymer film is general enough to be applicable to a whole class of conjugated polymers. We allow for a non-perfect structural alignment of the chains through a fluctuating contribution to the interchain hopping amplitude.

Using a supersymmetric path integral representation [9] for the averaged one- and two-particle Green functions we can perform the ensemble average over the random part of our model. In more than one dimension no exact solution to path integrals is available. With the help of a Hubbard–Stratonovich (HS) transformation and a mean field approximation for the auxiliary field we compute the one-particle Green function from which we extract the electronic density of states (DOS), as well as the current correlation function, which yields the optical absorption spectrum and the DC conductivity of the system.

As a result of our calculations we find a shoulder of width $2t_1$ in the DOS at the band edges. This can be explained as a typical two-dimensional effect introduced through the interchain coupling, which removes the band edge singularity found in one-dimensional theories.

In order to fix the parameters of our model appropriately we compare our results with reflectivity measurements of highly conducting PA [10]. The anisotropy of the optical constants α_x and α_y depends sensitively on the transverse bandwith, which is proportional to the strength of the interchain hopping amplitude t_1. The line shape indicates the degree of disorder and can be used to guess the variance D of the fluctuating contributions.

The paper is organized as follows. In section 2 we introduce the model of the polymer film. The averaging over the random contributions to the interchain coupling is performed in section 3 with the help of a supersymmetric path integral technique. We obtain the averaged one-particle Green function determining the electronic DOS as well as the current correlation function giving the optical absorption coefficients of the system. In section 4 we present the numerical results and compare them with experimental data. Problems and shortcomings of our model are discussed in section 5.
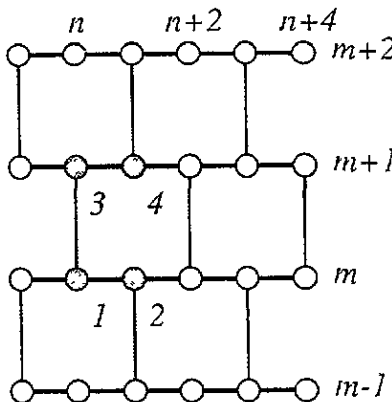

Figure 1. Chain arrangement and corresponding unit cell in the model of the polymer film.

2. Model

The interchain coupling in three-dimensional PA is mediated via the overlap of the hydrogen orbitals. Since in addition individual chains are tilted against each other this overlap changes from one site to the next if one moves along one fixed chain. Consequently an effective tight-binding description of a two-dimensional array of parallel chains results in a 'bricklayer' structure as depicted in figure 1: only every second cross link is realized. The corresponding Hamiltonian then can be written as

$$H = \sum_m H_m^{SSH} + H_{m,m+1} \tag{1}$$

$$H_m^{SSH} = \sum_n \left(-\left[t_0 - \alpha(u_{m,n+1} - u_{m,n}) \right] \left[c_{m,n+1}^\dagger c_{m,n} + HC \right] + \frac{1}{2} K \left(u_{m,n+1} - u_{m,n} \right)^2 \right) \tag{2}$$

$$H_{m,m+1} = -\sum_n t_{m,n} \left(c_{m,n}^\dagger c_{m+1,n} + HC \right) \tag{3}$$

where an electron can hop along chain m from site n to $n+1$ with amplitude t_0 modified by the lattice distortion $(u_{m,n+1} - u_{m,n})$. α denotes the electron–phonon coupling constant. The interchain hopping $t_{m,n}$ has the structure

$$t_{m,n} = \begin{cases} t_\perp & m+n \text{ odd} \\ 0 & m+n \text{ even.} \end{cases} \tag{4}$$

In the following we shall assume a constant in phase dimerization

$$u_{m,n} = (-1)^n u_0. \tag{5}$$

In order to stress the universal aspects of the polymer film we go over to the long-wavelength (continuum) approximation of the model (1). Corresponding to a unit cell with four atoms we arrive at an anisotropic field theory with four-component spinors Ψ_r for the electronic part of (1) [11]

$$H = \int dx\, dy \int_{-1}^1 dr\, \Psi_r^\dagger h_r \Psi_r + \frac{\Delta^2}{2\lambda} \tag{6}$$

$$h_r = -i\partial_x \sigma_1 - \Delta \sigma_2 - t_\perp M_r \tag{7}$$

with

$$M_r = \begin{pmatrix} 0 & 0 & \exp(i\pi r) & 0 \\ 0 & 0 & 0 & \exp(-i\pi r) \\ \exp(i\pi r) & 0 & 0 & 0 \\ 0 & \exp(-i\pi r) & 0 & 0 \end{pmatrix} \tag{8}$$

due to the structure of the Fermi surface $k_F = (\pm\pi/2a, (\pi/b)r)$, $-1 \leqslant r < 1$ [13]. Hereafter we use dimensionless units $t_0 = \hbar = 2a = 1$. Δ is the constant dimerization

$\Delta = 4\alpha u_0$. The elastic lattice energy in (1) contributes a term $\Delta^2/2\lambda$ with the dimensionless coupling constant λ to the Hamiltonian (6). The non-perfect chain alignment is modelled by site-dependent random contributions $\tilde{t}(R)$, $R = (x, y)$, with Gaussian white noise characteristics in addition to an otherwise constant interchain coupling t_1

$$t_\perp = t_1 + \tilde{t}(R) \qquad \langle \tilde{t}(R) \rangle = 0 \qquad \langle \tilde{t}(R)\tilde{t}(R') \rangle = 2D\,\delta(R - R'). \qquad (9)$$

For later convenience we separate the total Hamiltonian (6) into a deterministic part and a fluctuating part $H = H_0 + \tilde{t}H_1$. The variance $2D$ of the Gaussian distribution is a measure for the disorder strengths; here we are interested in the nearly crystalline limit $D \ll t_1^2$.

3. Method

The one-particle properties of the system are governed by the disorder averaged retarded Green function $\mathcal{G}(E) = \langle G^R(E) \rangle$. We are especially interested in the ensemble averaged DOS, which is determined through the relation

$$n(E) = -(1/\pi)\,\mathrm{Im}\,\mathrm{Tr}\,\mathcal{G}(E). \qquad (10)$$

We use a supersymmetric path integral formalism following Efetov [9] in which $\mathcal{G}(E)$ can be written as

$$\mathcal{G}_{rr'\alpha\alpha}(E) = i \int D\Phi^\dagger D\Phi \; \chi_{r\alpha}\bar{\chi}_{r'\alpha} \exp\left[i\Phi^\dagger(E - h^0)\Phi - D\left(\Phi^\dagger M \Phi\right)^2\right] \qquad (11)$$

with short-hand notation

$$i\Phi^\dagger(E - h^0)\Phi - D\left(\Phi^\dagger M \Phi\right)^2 = i \int dx\,dy \int dr\, \Phi_r^\dagger(E - h_r^0)\Phi_r$$

$$- \int dx\,dy\, D\left(\int dr\, \Phi_r^\dagger M_r \Phi_r\right)^2 \qquad (12)$$

and eight-component supervectors $\Phi_r = (\chi_{r\alpha}, s_{r\alpha})$, $\alpha = 1, \dots, 4$ with commuting and anticommuting variables $\chi_{r\alpha}$ and $s_{r\alpha}$. Now first the quartic interaction part in (6) is decoupled via an HS transformation with a single real auxiliary field q using

$$\exp(-A^2) = \int dq\, \exp(-\pi q^2 \pm iq A) \qquad (13)$$

$$\mathcal{G}_{rr'\alpha\alpha}(E) = i \int Dq \int D\Phi^\dagger D\Phi \; \chi_{r\alpha}\bar{\chi}_{r'\alpha} \exp\left[i\Phi^\dagger\left(E - h^0 + \frac{q}{\tau M}\right)\Phi - \pi q^2\right]. \qquad (14)$$

In contrast to strictly one-dimensional models where the path integral can be evaluated exactly with the help of a transfer matrix technique in two dimensions we are restricted to

approximations for the solution of the functional integral. In the integral over the auxiliary field q the main contributions are given by slowly varying paths, thus we are looking for a mean field solution $\bar{q}$ that does not depend on coordinates. A comparison with different calculations [9, 12] reveals that this is justified in the limit of small disorder $D \ll t_1$ where the terms omitted by this procedure can be treated as perturbations.

In a next step we can integrate out the superfields $\Phi^\dagger$ and Φ using [9]

$$\int D\Phi^\dagger D\Phi \, \chi_{r\alpha} \bar{\chi}_{r'\beta} \exp(-\bar{\chi} A \chi) = \left(A^{-1}\right)_{r\alpha, r'\beta} \tag{15}$$

and express the effective Hamiltonian in (7) in momentum representation. We then finally arrive at

$$\mathcal{G}(E) = \text{Tr} \int_{-\infty}^{\infty} dq \, \exp(-\pi q^2) \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \int_{-\pi/b}^{\pi/b} \frac{dk_y}{2\pi} \, g_{k_x k_y}(q) \tag{16}$$

$$g_{k_x k_y}(q) = \begin{bmatrix} -E & -k_x + i\Delta & t_\perp \exp(i\pi r) & 0 \\ -k_x - i\Delta & -E & 0 & t_\perp \exp(-i\pi r) \\ t_\perp \exp(i\pi r) & 0 & -E & -k_x + i\Delta \\ 0 & t_\perp \exp(-i\pi r) & -k_x - i\Delta & -E \end{bmatrix}^{-1} . \tag{17}$$

Due to the continuum approximation the integration in k_x ranges from $-\infty$ to $+\infty$, whereas in the y direction due to the additional expansion parameter r the wave vector k_y has the correct periodicity $-\pi/b \leqslant k_y < \pi/b$. With the help of the auxiliary field the transverse coupling $t_\perp$ is written as

$$t_\perp = t_1 + q/\tau. \tag{18}$$

Further, we use the fact that in momentum representation the expansion parameter πr differs from k_y only by a multiple integer of 2π.

In order to obtain the averaged optical absorption spectrum we have to compute the two-particle Green function $G^{(2)}(r_1, r_2)$. The optical absorption $\alpha(\omega)$ follows from the frequency-dependent conductivity $\sigma(k, \omega)$ in the limit $k \to 0$. The conductivity can be computed from the retarded current correlation function $\Pi^R(k, \omega)$:

$$\sigma(k, \omega) = \text{Re} \, \frac{i}{\omega} \, \Pi^R(k, \omega) \qquad \alpha(\omega) = \lim_{k \to 0} \sigma(k, \omega). \tag{19}$$

The components Π_{ii}, $i = x, y$ along the x and y directions have the spectral representations

$$\Pi_{xx}^R(k, \omega) = \sum_n \left(\frac{|\langle 0|j_x(-k)|n\rangle|^2}{\omega - E_n + E_0 + i0} - \frac{|\langle 0|j_x(k)|n\rangle|^2}{\omega + E_n - E_0 + i0} \right) \tag{20}$$

and the off-diagonal elements Π_{xy} are zero. From the current operator of the discrete model (1)

$$j_x(R) = e\left(c_{n+1,m}^\dagger c_{n,m} - c_{n,m}^\dagger c_{n+1,m}\right) \tag{21}$$

$R = (na, mb)$, j_x is found to be

$$j_x(R) = 2e \sum_r \Psi_r^\dagger \tau_1 \Psi_r \qquad \tau_1 = \sigma_1 \otimes \mathbf{1}. \tag{22}$$

In a similar way from (1) and (4) the y component of the current correlation function

$$j_y(R) = \sum_n et_\perp \left(c_{n,m+1}^\dagger c_{n,m} - c_{n,m}^\dagger c_{n,m+1} \right) \tag{23}$$

can be translated to the form

$$j_y(R) = e \frac{b}{a} t_\perp \sum_r \left\{ [\exp(i\pi r)] (\Psi_{1r}^\dagger \Psi_{3r} + \Psi_{4r}^\dagger \Psi_{2r}) - \text{HC} \right\}. \tag{24}$$

Note that in the quotient j_y/j_x a constant factor $t_\perp/t_0$ occurs. Consequently the anisotropy in the optical absorption depends quadratically on this factor.

Computing the disorder averaged conductivity $\langle \sigma_{ii} \rangle$ we use the fact that the current operators j_x and j_y are local in the coordinates. Therefore the components $\Pi_{ii\alpha\beta}$ can be expressed with the help of the components of the two-particle Green function $G_{\alpha\beta\gamma\delta}^{(2)}$

$$\Pi_{xx\alpha\beta}(r_1, r_2) = \langle 0 | \Psi_\alpha^\dagger(r_1) \tau_1 \Psi_\alpha(r_1) \Psi_\beta^\dagger(r_2) \tau_1 \Psi_\beta(r_2) | 0 \rangle = \left[\tau_1 G^{(2)}(r_1, r_2) \right]_{\alpha\beta} \tag{25}$$

$$\tau_1 \Psi_\alpha = \Psi_{\alpha'} \qquad \tau_1 \Psi_\beta = \Psi_{\beta'}.$$

To simplify the notation the additional index r has been omitted. In an analogous way we find for the transversal polarization propagator

$$\Pi_{yy\alpha\beta}(r_1, r_2) = \sum_r \left[M_r G_{rr}^{(2)}(r_1, r_2) \right]_{\alpha\beta}. \tag{26}$$

With the supersymmetric representation of the two-particle Green function from [9] we perform the average over the fluctuating contributions. Using an HS decoupling as introduced in equation (12) we obtain

$$\langle \Pi_{xx\alpha\beta}(r_1, r_2, E, \omega) \rangle = -\int Dq \, D\Phi^{\dagger(1)} D\Phi^{(1)} D\Phi^{\dagger(2)} D\Phi^{(2)} \, \chi_{\alpha'}^{(1)} \bar\chi_\beta^{(1)} \chi_{\beta'}^{(2)} \bar\chi_\alpha^{(2)} \exp(-\pi q^2)$$

$$\times \exp \left\{ i \int dx \, dy \left[-\Phi^{(1)\dagger} \left(E - i0 - \omega - h_0 - \frac{q}{\tau M} \right) \Phi^{(1)} \right. \right.$$

$$\left. \left. + \Phi^{(2)\dagger} \left(E + i0 - h_0 - \frac{q}{\tau M} \right) \Phi^{(2)} \right] \right\}. \tag{27}$$

After a Fourier transform we perform the limit $k \to 0$ and arrive at

$$\langle \Pi(0, \omega) \rangle = -\int \frac{dk_x}{2\pi} \frac{dk_y}{2\pi} dE \, dq \, \exp(-\pi q^2)$$

$$\times \left[G_{\alpha'\beta}^R(k_x, k_y, E) \, G_{\alpha\beta'}^A(-k_x, -k_y, E - \omega) \right]_{t_\perp = t_1 + q/\tau}. \tag{28}$$

The Green functions in equation (28) are evaluated using the spectral representation

$$G_{\alpha\beta}^{R/A}(k, E) = \sum_{ij} \frac{\phi_{i\alpha}(k)\phi_{j\beta}^*(k)}{E - \omega_{ij}(k) \pm i0} \tag{29}$$

$$h\phi_i = \epsilon_i\phi_i \qquad \omega_{ij}(k) = \epsilon_i(k) - \epsilon_j(k). \tag{30}$$

We are interested in the imaginary part, so one of the integrations can be done analytically using

$$1/(\omega + i0) = 1/\omega + i\pi\delta(\omega). \tag{31}$$

The remaining integrals will be evaluated numerically. The optical matrix elements that we have defined in (26) are given through off-diagonal elements of $\Pi(0, \omega)$ and can be summed up easily. In a final step in equation (19) we have to perform the trace $\Pi_{il} = \text{Tr}\,\Pi_{il\alpha\beta}$.

4. Results and discussion

Figure 2 shows the influence of the interchain coupling t_1 and the disorder D on the DOS defined in equation (10). The energies $\Delta \pm t_1$ are indicated by vertical chain lines. Due to the electron–hole symmetry of our model we have $n(E) = -n(E)$. We show only the positive energy range; the origin of the energy scale lies in midgap. The effects of disorder and dimensionality can clearly be discerned. Due to the interchain coupling the electronic DOS shows typical two-dimensional features. In contrast to strictly one-dimensional models where a square root singularity at the band edge $E = \Delta$ is found the van Hove singularity is shifted upwards to $E = \Delta + t_1$. Between the new band edge at $E = \Delta - t_1$ and the singularity at $E = \Delta + t_1$ a shoulder of width $2t_1$ comes up which can be taken as a measure for the interchain coupling strength. With increasing disorder D this structure becomes smeared out and a band tail indicating new states below $E = \Delta - t_1$ can be seen. We infer from earlier one-dimensional calculations [14, 17] that these states are strongly localized with a typical extension of $L \simeq 1/\Delta$ in our dimensionless units $2a = 1$.

The anisotropic optical absorption as a function of frequency ω is shown in figure 3 for fixed disorder strength D. To fix the parameters t_1 and D appropriately we have to reproduce the anisotropy $\eta = \alpha_x/\alpha_y$ of the interchain absorption maximum near $\omega = 2\Delta$ to the experimental value $\eta = 26$ found in [10]. Due to the quadratic dependence of the current correlation function Π_{yy} on t_1 the possible values for the interchain coupling t_1 are restricted quite sensitively.

In figure 3 we have shown the absorption curves corresponding to $t_1 = 0.03, 0.04$ and 0.05. With the interchain coupling strength $t_1 = 0.045$ the desired anisotropy can be reproduced fairly well, in accordance with the result predicted by the band structure calculations [7]. The anisotropy is nearly independent of the disorder strength of the model. In order to estimate the strength of the random contributions D we use the fact that in the crystalline limit $D \rightarrow 0$ the perpendicular absorption α_y is sharply peaked at the interband absorption energy 2Δ, whereas the structure is blurred with increasing disorder strength. To reproduce qualitatively the smooth shape of the absorption α_y seen in experiments we have to choose quite large disorder parameters $D \simeq 0.015$–0.02. At first sight these values
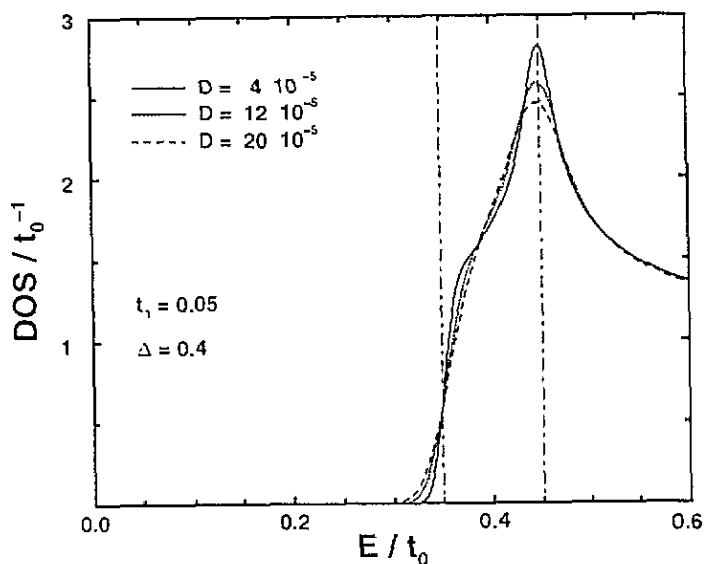
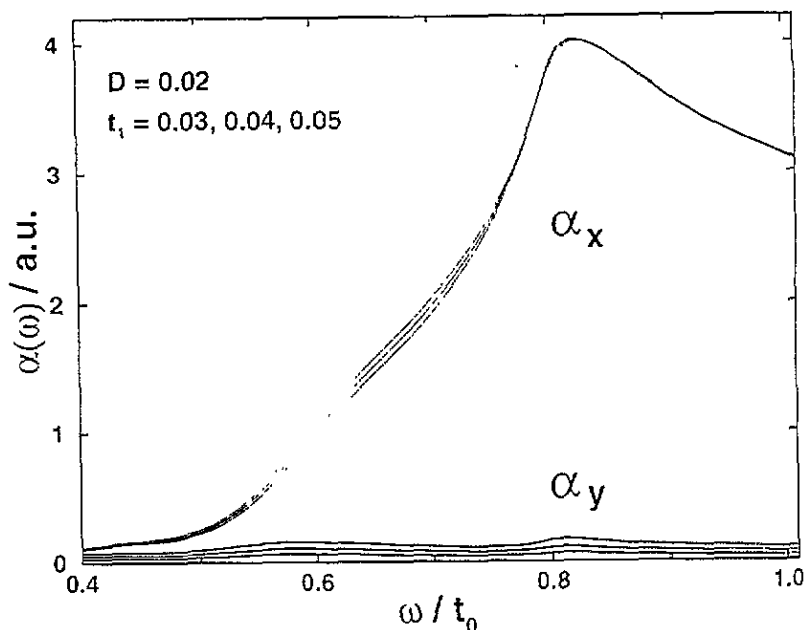**Figure 2.** DOS taken from the imaginary part of the Green function.

Figure 3. Anisotropic optical absorption α_x and α_y for light polarized in the chain direction and perpendicular to it, respectively.

seem to be in contrast to the physical condition of small fluctuations $D \ll t_1^2$. To explain the absorption curve α_y additional contributions to D originating from intrachain disorder effects have to be taken into account.

Here we have ascribed the shoulder in the absorption spectrum as being caused only by electronic effects, namely the two-dimensional interchain coupling. The coupling of

electronic excitations to vibrational modes also leads to additional structures at the absorption edge. In our present model we have not taken these effects into account as experimental techniques are available to suppress these features. In principle by a more generalized approach a calculation of these properties seems feasible.

Of special importance in the case of conjugated polymers are inherent effects such as the zero-point motion of the lattice, leading to a considerable amount of bond type disorder (fluctuations in the intrachain coupling) [15], and the finite conjugation length of the individual polymer chains. These effects are not considered explicitly in our model; however, in earlier one-dimensional calculations [16, 17] it was found that different kinds of disorder have very similar consequences for the Green functions. Generalizing these conclusions for the two-dimensional case of the polymer film the disorder parameter D can be interpreted as an effective disorder strength, modelling not only the fluctuations in the interchain coupling but also the lattice fluctuations and finite-chain-length effects mentioned above.

In order to describe the line broadening due to lattice vibrations and disorder effects it is commonly accepted to use a Gaussian line shape. In our field theoretical approach such a Gaussian characteristic is introduced in a natural way via the auxiliary HS field $\bar{q}$. It allows a direct relation of the broadening to the disorder strength D. If we want to compare our results with the experimental situation exact data of angle resolved measurents of the optical absorption coefficients α_x and α_y are required. In the case of PA such data are available [10]; for other polymer materials we would appreciate such measurements.

5. Conclusions

In summary, we are able to describe the main effects of a stochastic interchain coupling strength in a model of a disordered polymer film upon the electronic properties. Using a supersymmetric path integral approach we can derive an exact expression for the disorder averaged one- and two-particle Green functions determining the electronic DOS and the anisotropic optical absorption $\alpha_x(\omega)$, $\alpha_y(\omega)$. Our main results are a change in the dimensionality, which can be seen in the DOS as a shoulder of width $2t_1$, and a shift of the van Hove singularity, which occurs even without disorder. From the anisotropy of the optical absorption α_x/α_y which is nearly independent of fluctuating contributions t_1 can be fixed accurately. Both the value of $t_1 = 0.045$ and the qualitative shape of $\alpha(\omega)$ are in good agreement with band structure calculations and experimental results. We have not reported our results for the electric DC conductivity given through $\lim_{\omega \to 0} \sigma(0, \omega)$. To describe the electric transport appropriately local relaxation of the lattice, charge transfer from remaining impurities and additional intrinsic disorder effects as discussed in the last section should be taken into account. This is beyond the scope of this paper.

Acknowledgment

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