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Exponential tails in optical absorption and electro-absorption of disordered systems—a one-dimensional model

H Overhof† and K Maschke‡

† Institut für Theoretische Physik, Universität Paderborn, D-4790 Paderborn, Federal Republic of Germany

‡ Ecole Polytechnique Fédérale de Lausanne, Institut de Physique Appliquée, CH-1015 Lausanne, Switzerland

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Abstract. We investigate the influence of short-range and long-range disorder on the exponential tails in absorption and electro-absorption. The numerical calculations are performed for a two-band one-dimensional Anderson Hamiltonian with diagonal disorder. The long-range disorder is described by a Gaussian distribution function. It is correlated, i.e. the disorder potentials are the same for valence and conduction bands. The distribution function for the short-range disorder is rectangular and uncorrelated. We find that exponential absorption tails are due to correlated long-range disorder. Similarly, a significant change in the absorption spectrum in the presence of an external electric field is only found in the presence of such correlated long-range disorder. In this case, we obtain a quadratic dependence of the electro-absorption signal on the external field, and in comparison with the absorption tail we find a somewhat smaller slope for the electro-absorption.

1. Introduction

Exponential absorption tails or Urbach (1953) edges are commonly found in many crystalline systems, where the slope of the tails depends drastically on the temperature. In contrast, the slopes of the exponential absorption edges observed in amorphous semiconductors show only a rather weak temperature dependence. In this case the absorption tails are generally attributed to the presence of the disorder, which in a simple model can be considered to be short ranged and statistically uncorrelated for valence and conduction bands, respectively (Economou *et al* 1985), leading to exponential tails in the density of states. The exponential absorption tails are then interpreted in terms of convoluted exponential valence and conduction tail density-of-states distributions (Picket *et al* 1983, Tauc *et al* 1966). Since in most cases the disorder potential distribution $p(V)$ is essentially Gaussian, the resulting density-of-states distributions $\rho(E)$ are not strictly exponential and hence one finds only approximate exponential tails in a rather limited energy range (see, e.g., Abe and Toyozawa 1981). The idea that exponential tails can be caused by random potentials was proposed by Tauc (1970).

Recently, Dersch *et al* (1987) have considered the case of a potential with long-range disorder (LRD) and with a Gaussian distribution. When the spatial variations in this

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potential are identical for the conduction and the valence band, a much larger exponential tail is obtained. This is primarily due to the behaviour of the transition matrix elements, which depend strongly on the energy of the involved initial and final states, since states near the maximum of the valence band are separated in space from states near the minimum of the conduction band. Since in that paper the short-range disorder (SRD) was entirely neglected, the question arises as to the extent to which the presence of an additional SRD suppresses the exponential tails. It is evident that ultimately, for extreme SRD, the effects of LRD will become negligible. This question will be investigated in the present paper. We further study the more complicated question of electro-absorption, i.e. the modulation of the absorption spectra due to a quasi-static external electric field. Experimental data for hydrogenated amorphous silicon (a-Si:H) and amorphous selenium (a-Se) have been presented recently (Mescheder 1985, Weiser *et al* 1988). The result is a quite pronounced electro-absorption in the tail region, which is proportional to the square of the external field. Again we shall investigate the effect of the electrostatic external field in the presence of both SRD and LRD potentials.

We have restricted our numerical studies to one-dimensional (1D) chains for several reasons. The first reason is that a LRD potential requires sample sizes which exceed the length scale of this potential considerably, a requirement that can be met best for 1D models. The second reason is that we are interested in the absorption tails only, i.e. we want a large ratio of tail states to band states. Again 1D systems are best suited to this purpose. There is also a vast numerical advantage. For 1D systems, we can cast the Hamiltonian into a band matrix, which can be diagonalised in a very efficient manner (see, e.g., Wilkinson 1965). This allows us to treat rather large matrices with tolerable numerical effort, and to perform configurational averages to such a degree that we can sufficiently reduce the amount of statistical noise.

2. The model

Our 1D model system is similar to that studied by Dersch *et al*. It is described by the two-band Anderson Hamiltonian

$$H_0 = \sum_\alpha H_0^\alpha \tag{1}$$

where

$$H_0^\alpha = \sum_i \varepsilon_{i\alpha} n_{i\alpha} + t_\alpha \sum_{i,j=i\pm 1} c_{i\alpha} c_{j\alpha}^+ . \tag{2}$$

The index $\alpha \equiv \mathrm{v}, \mathrm{c}$ denotes the valence and conduction band, respectively. The single-band Hamiltonians H_0^α describe a finite chain of N atoms on a regular 1D lattice with lattice spacing a. t_α describes the nearest-neighbour coupling. The disorder is introduced via the fluctuating site energies $\varepsilon_{i\alpha}$. We note that the above Hamiltonian H_0 neglects electron–hole interactions as well as any coupling between valence and conduction bands other than by a correlation of the site energies. The site energies $\varepsilon_{i\alpha}$ are written as

$$\varepsilon_{i\alpha} = \varepsilon_\alpha + V_{i\alpha}^{\mathrm{SR}} + V_{i\alpha}^{\mathrm{LR}} \tag{3}$$

where $\varepsilon_\mathrm{c} = -\varepsilon_\mathrm{v} = E_\mathrm{g}^0/2$ is the centre of the conduction band, ε_v is the centre of the valence band and $V_{i\alpha}^{\mathrm{SR}}$ and $V_{i\alpha}^{\mathrm{LR}}$ describe the SRD part and the LRD part, respectively, of the disorder. The SRD is described by the rectangular distribution function of width Δ:

$$p(V_{i\alpha}^{\mathrm{SR}}) = \begin{cases} \Delta^{-1} & \text{for } -\Delta/2 \leqslant V_{i\alpha}^{\mathrm{SR}} \leqslant \Delta/2 \\ 0 & \text{otherwise.} \end{cases} \tag{4}$$

The disorder felt by valence and conduction band states, respectively, is assumed to be uncorrelated, i.e.

$$\langle V_{ic}^{\mathrm{SR}} V_{iv}^{\mathrm{SR}} \rangle = 0. \tag{5}$$

The LRD is characterised by the Gaussian distribution function

$$p(V_{i\alpha}^{\mathrm{LR}}) = (1/\sqrt{\pi\delta^2}) \exp[-(V_{i\alpha}^{\mathrm{LR}}/\delta)^2]. \tag{6}$$

The long-range character of the fluctuations is described by the correlation length $L = na$, which is defined by

$$\langle V_{i\alpha}^{\mathrm{LR}} V_{i+n,\alpha}^{\mathrm{LR}} \rangle / \langle V_{i\alpha}^{\mathrm{LR}} V_{i\alpha}^{\mathrm{LR}} \rangle = \tfrac{1}{2}. \tag{7}$$

Following Dersch *et al* (1987), we assume that the long-range potential fluctuations are of an electrostatic nature and that fluctuations in the valence and conduction bands are correlated in space, i.e.

$$V_{iv}^{\mathrm{LR}} = V_{ic}^{\mathrm{LR}}. \tag{8}$$

The construction of $V_{i\alpha}^{\mathrm{LR}}$ is described by Dersch *et al.* In our numerical calculations, we have used the parameters $L = 17.5a$, $N = 1000$, $t_c = -t_v = 1$ eV, $E_0 = 2$ eV and $\delta = 0.1$ eV. The SRD potential was varied in the range $0\ \mathrm{eV} \leqslant \Delta \leqslant 0.5\ \mathrm{eV}$. Eigenvalues and eigenvectors are obtained by direct diagonalisation of the Hamiltonians H_0^{v} and H_0^{c}, respectively. The optical absorption is then calculated using Fermi's golden rule, where the transition matrix elements are obtained within the on-site approximation (see, e.g., Abe and Toyozawa 1981), i.e. the interaction with the electromagnetic field is described by

$$H' = -\boldsymbol{E} \cdot \boldsymbol{P}. \tag{9}$$

$\boldsymbol{E}$ is the electric field vector of the electromagnetic field, and $\boldsymbol{P}$ the dipole operator:

$$\boldsymbol{P} = \boldsymbol{\Pi}\left(\sum_i c_{ic}^{+} c_{iv} + c_{iv}^{+} c_{ic}\right) \tag{10}$$

where $\boldsymbol{\Pi}$ is the transition dipole moment.

This on-site approximation is convenient for the calculation of optical properties. However, it does not describe the observed polarisation effects due to an external electric field (Weiser *et al* 1988). This is certainly a weakness of the present approach, which cannot be overcome within the two-band Anderson model, however.

The electro-absorption is caused by an additional electrostatic field which is described by

$$H_1 = -e\boldsymbol{F} \cdot \boldsymbol{a} \sum_n n \sum_{\alpha \equiv \mathrm{c,v}} c_{n\alpha} c_{n\alpha}^{+}. \tag{11}$$

The change $\Delta\alpha$ in the optical absorption in the presence of an external electric field is calculated as

$$\Delta\alpha(\boldsymbol{F}) = \alpha(\boldsymbol{F}) - \alpha(\boldsymbol{0}). \tag{12}$$

The statistical noise problem generally inherent in Monte Carlo calculations becomes particularly serious if differences in the Monte Carlo calculations are to be considered. In order to reduce this noise, we had to use rather large electrostatic fields F = 1–3 mV/a, which for a lattice constant of a = 3 Å is equivalent to 3×10^4–10^5 V cm^{-1}. It is worthwhile to mention that our Hamiltonian is still bounded in the presence of an external electric field F and that our eigenstates remain stationary, since our system is finite.

For the numerical calculations, it is important to note that the electric field leads to a spatial separation of the highest valence band and the lowest conduction band states towards the extrema of the considered chain. The calculation of $\Delta\alpha$ at the band edge thus requires the knowledge of almost all eigenstates in the valence band and in the conduction band. This complication limits the maximum chain length for which the calculation can be performed, owing to the drastic increase in the eigenvectors that must be stored and to the computational effort for calculating the transition matrix elements. Therefore, the presented data exhibit a significantly larger statistical noise than those published previously for absorption alone (Dersch *et al* 1987).

3. Results

In figure 1, we show the absorption spectra for chains consisting of 1000 sites with the LRD fixed to $\delta = 0.1$ eV. The full symbols correspond to $\Delta = 0$ (i.e. no SRD), while the open symbols correspond to $\Delta = 0.5$ eV (i.e. the SRD exceeds the mean LRD). We observe two features. In the absence of SRD the absorption shows a pronounced kink at $E = E^0_\mathrm{B}$. This is a remnant of the singularity of the absorption at the band edge for a 1D crystalline system. A slight LRD potential removes the singularity and transforms it into a kink which is preceded by the exponential tail. This tail can be traced over five to eight orders of magnitude. For even lower photon energies, there is a transition to a

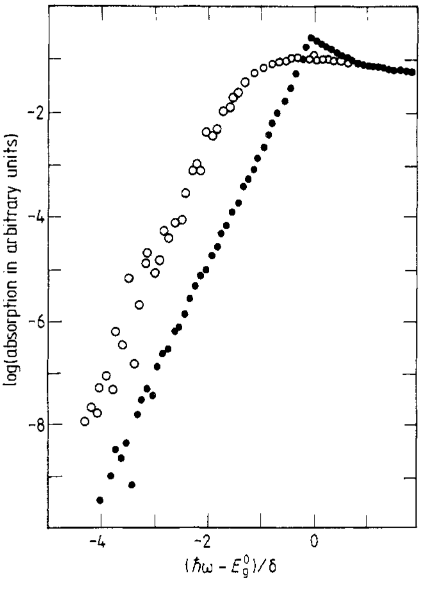

Figure 1. Calculated absorption spectra: ●, no SRD (Δ = 0 eV); ○, with SRD (Δ = 0.5 eV).

second exponential tail with a somewhat larger slope, as discussed by Dersch *et al* (1987). For our present study of rather short chains, we ignore this part of the spectrum as it is almost lost in the numerical noise.

The SRD, in addition to the LRD, leads to a broadening of the density of states in the tail region. The kink in the absorption spectrum, therefore, is gradually broadened until it finally disappears. The broadening of the density-of-states distribution, however, is not reflected by a concomitant change in the slope of the exponential absorption tail. This fact, which may depend somewhat on the dimensionality of the system and the particular slope of the SRD distribution function, is due to two effects which compensate each other. With increasing SRD the tails are broadened, which should lead to a broadening of the absorption tail. At the same time the states deep in the tail become more localised, which reduces the absorption between tail states centred at different sites, thus increasing the slope of the absorption tail. The principal reason for the occurrence of exponential tails, however, does not arise from the SRD but from the LRD. The latter gives rise to 'pockets' in the bands where the LRD potential has its maxima or minima. Valence and conduction states localised at different pockets can have a relatively small energy difference and still extend over a relatively large spatial region, such that the overlaps (and hence the transition matrix elements) between the states are non-negligible. If we lower the energy difference, the number of states which according to the joint density of states could contribute to the optical transitions does not decrease very drastically. It is thus the decreasing overlap which leads to the exponential tail. An additional SRD broadens the tails in the density of states and thus leads to a red shift of the exponential tail but does not change its slope.

If we include the electrostatic field and calculate $\Delta\alpha$ according to equation (12), we obtain the results shown in figures 2 and 3 with the corresponding absorption data for comparison. Since the electro-absorption data arise from a small difference of two

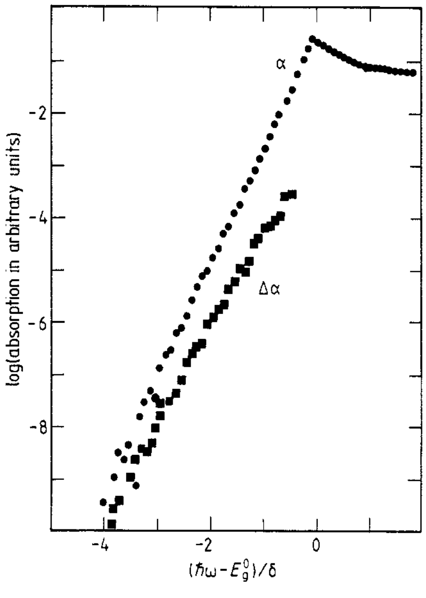

Figure 2. Calculated absorption α (●) and electro-absorption spectra $\Delta\alpha$ (■) without SRD (Δ = 0 eV).

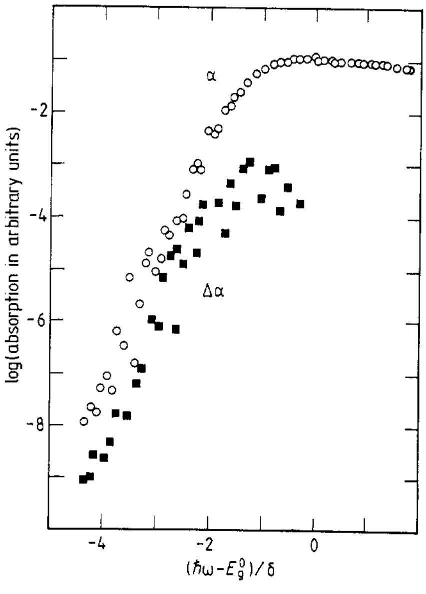

Figure 3. Calculated absorption α (○) and electro-absorption spectra $\Delta\alpha$ (■) with SRD (Δ = 0.5 eV).

essentially independent large quantities, the former data exhibit a much larger scatter than do the latter. This limits the range of fields that can be used for our Monte Carlo calculations. In order to reduce this noise, it would be convenient to increase the electrostatic field but, as evident from figure 2, the electro-absorption signal, which is proportional to F^2, readily exceeds the absorption itself at lower energies, in contrast with the spirit of modulation spectroscopy.

In figure 2 we show the results for the case with no SRD, and in figure 3 the corresponding data for a SRD with $\Delta = 0.5$ eV. The statistical noise of the electro-absorption data in the presence of SRD is much larger than for $\Delta = 0$, primarily because the number of states involved decreases with increasing widths of the tails, which in turn increase with increasing SRD. We emphasise that in both cases $\Delta\alpha$ depends exponentially on the photon energy as α itself, with a levelling off at the high-energy side of the tail. Deep in the tail the slope of $\Delta\alpha$ is somewhat smaller than that of α. This effect can be understood in the same way as the exponential tail itself. In the tail the absorption arises from pairs of pockets in the LRD potential which are some distance Λ apart. The external field $\boldsymbol{F}$ increases or decreases the energy difference between these pockets by $\pm e\boldsymbol{\Lambda}\cdot\boldsymbol{F}$, depending on the relative orientations of the field and the maximum or minimum of the LRD potential (in the two-dimensional or three-dimensional case, one has to perform an average over the relative angles). We therefore approximate

$$\begin{aligned}\Delta\alpha(\hbar\omega,\boldsymbol{F}) &\simeq \tfrac{1}{2}[\alpha(\hbar\omega + e\boldsymbol{\Lambda}\cdot\boldsymbol{F}) + \alpha(\hbar\omega - e\boldsymbol{\Lambda}\cdot\boldsymbol{F}) - 2\alpha(\hbar\omega)]\\ &= \tfrac{1}{2}(e\boldsymbol{\Lambda}\cdot\boldsymbol{F})^2\mathrm{d}^2\alpha(\hbar\omega)/\mathrm{d}(\hbar\omega)^2\end{aligned}$$

which gives us the field dependence observed in the Monte Carlo experiment as well as the slope of the calculated electro-absorption signal. The average distance Λ between the initial and final states decreases with increasing photon energy, which explains the fact that $\Delta\alpha$ rises with a smaller slope than α on the high-energy side of the tail.

If we increase the photon energy beyond E_0, the electro-absorption signal turns negative. This effect is more pronounced for the smaller Δ values. It is an artefact of our 1D model; already in the absence of any random potential, the field $\boldsymbol{F}$ leads to a drastic decrease in the absorption singularity at the band edge, i.e. to a large negative $\Delta\alpha$. For larger values of Δ the singularity is removed and, therefore, the decrease in $\Delta\alpha$ is significantly attenuated.

4. Discussion

The essential results of our model calculation for the absorption and the electro-absorption properties can be summarised as follows.

(i) The exponential absorption tail is caused by the LRD. Additional SRD leads to a shift of the absorption tail towards lower energies but virtually does not influence the slope of the tail.

(ii) A significant electro-absorption spectrum is obtained only in the presence of LRD. For SRD alone, we do not find any electro-absorption effect above the statistical noise.

For electro-absorption, we further find

(iii) an exponential tail of $\Delta\alpha$ with a slope about 30% smaller than that of α and

(iv) a quadratic dependence on the applied field $\boldsymbol{F}$.

Polarisation effects of the electro-absorption cannot be described within our two-band Anderson model. For this, one would have to consider field-induced inter-band mixing, which is completely neglected in our approach. Moreover, a realistic evaluation of the field dependence of the transition matrix elements would require us to go beyond the on-site approximation, which is not a straightforward extension, since the inter-site elements of the momentum operator cannot be specified from the two-band Anderson Hamiltonian.

Even if it is difficult to compare our model calculations for the electro-absorption with experimental results for realistic amorphous semiconductors (for a-Si:H and a-Se, see, e.g., Mescheder (1985) and Weiser *et al* (1988)), we note that our findings are in general agreement with the experiments. Experimentally the electro-absorption effect in the tail region is also found to be large and to depend quadratically on the applied field F. Further, the experimental electro-absorption signal shows a peak which is located roughly at the high-energy end of the exponential absorption tail. The experimental electro-absorption spectrum decays exponentially to lower photon energies in perfect agreement with the result of our model calculation. There is a slight difference, however; in the experiment the slope of the electro-absorption tail is somewhat larger than that of the absorption tail while in our model the absorption tail is slightly steeper. We do not consider this difference to be of any significance. Instead we propose that a correlation of the slope of the electro-absorption tail with the doping level should be observable. Transport measurements (Beyer and Overhof 1984) show that the long-range potential is significantly enhanced on moderate and high doping, in particular for compensated samples. Such a correlation would be welcome as additional evidence for the existence of long-range potential fluctuations in a-Si:H.

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