Disorder induced e – h correlation in photoexcited transients in semiconductors

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Abstract. In mixed semiconductor crystals, the alloy disorder in the valence and conduction bands is statistically correlated. This leads to kinematical correlations in the motion of electrons and holes analogous to exciton effects. This mechanism long known to affect the linear optical response is presently shown to act also in the non-linear regime induced by strong short light pulses. A direct numerical solution of the Kadanoff–Baym equations for non-equilibrium Green functions (employing a self-consistent and conserving single-site approximation) is used to demonstrate the onset and a ripe stage of correlations between the electron and hole photoexcited populations, and the influence of the transient light induced band hybridization.

1 Introduction

Short time optical transients of electrons in semiconductors as induced by sub-picosecond light pulses are one of the dynamically developing areas of research, because of their importance for semiconductor physics, but also as a prototype case of fully quantum transient phenomena far from equilibrium [1], [2]. Improved experimental and theoretical techniques provide an access to rather subtle phenomena, including the formation of correlations in many-electron systems. A sample recent work concerning transient exciton phenomena, that is the time evolution of the electron–hole correlations, is [3].

Our previous research in this area was oriented on the sub-problem of optical transients in disordered semiconductors, in which, in particular at the early stages of the transient process, scattering on the static random potential in the disordered sample may be dominant. This leads to important modifications of the physical picture and formal tools for its description as compared with the crystal case. The necessary formal tools and numerical methods based on the use of non-equilibrium Green’s functions are described and illustrated on a few case studies in [4]. The specific systems we have in mind are random III-V semiconductor alloys, materials of special importance in optoelectronics [5]; the actual models used are simplified, however, in that it is assumed that the valence and conduction wave functions are not mutually mixed by disorder [6]. The alloy case is better susceptible to a theoretical treatment than the other important class of disordered materials, the amorphous semiconductors, because of the availability of effective approximations of the CPA family, as discussed in the references given above.

The specific problem addressed in this lecture is the effective electron-hole "interaction" representing the spatial correlation in the propagation of an $e-h$ pair moving in the same random environment. This phenomenon is known from linear optics, and it has been found as crucial for understanding the absorption edges of amorphous semiconductors, in particular their exponential ("Urbach") tails. There, it combines with the excitonic interactions proper, and a quasiclassical theory of the doubly correlated $e-h$ motion was worked out decades ago. Summaries can be found in two chapters, 2 and 8, of [7]. In chapter 8 of this book, a comparison is made also with the case of short range disorder of the alloy type, which is similar on the one hand, but quite different on the other one, because of its fully quantum nature. In the linear theory, the $e-h$ correlation was expressed in terms of the so-called optical vertex defined in terms of the configuration average of two propagators. Schematically, $\langle G^{(e)} \otimes G^{(h)} \rangle = \langle G^{(e)} \rangle \otimes \langle G^{(h)} \rangle + \langle G^{(e)} \rangle \times \text{vertex} \times \langle G^{(h)} \rangle$. A number of papers devoted to an actual construction of this vertex within the CPA formalism could be given, but we single out just one paper [8], to which it will be frequently referred below.

These authors transfer the notion of a correlated and anticorrelated disorder, introduced originally for the quasiclassical disorder in amorphous semiconductors, to the case of a disorder on the atomic scale and obtain the corresponding optical response. The atomic disorder in two bands, conduction and valence, is said to be correlated/anticorrelated, if the underlying quasiatomic levels fluctuate in parallel, or against each other. Each case leads to a different type of the $e-h$ correlation.

We generalize all these notions to the transient non-linear behavior. The effect of the kinematical $e-h$ correlation is predicted to be perhaps even more pronounced than in the case of linear response. At the same time, it is found that this correlation develops gradually. Thus, we find that it has the nature of a final state interaction, just like the genuine excitons. Changing the pulse strength (measured by a compound characteristic, the Rabi phase), we obtain a marked variation of the degree of correlation in the $e-h$ transient. Altogether, it is found that the kinematic $e-h$ correlation is a basic phenomenon in the optical transients in semiconductor alloys.

Sec. 2 serves to give a qualitative picture of the optical transitions in disordered systems. In Sec. 3, we introduce our alloy model and contrast the case of the linear response and of the non-linear transients employing the simple density matrix language. Next section 4 gives a brief overview of the NGF technique used, and the final Sec. 5 shows the computed response of our model to two pulses, one comparatively weak, the other moderately strong, both lasting about 100 fs.

2 Qualitative picture of disorder effects in the optical response of semiconductors

The format of lectures at this meeting allows to present the background motivation of the reported research in more detail and more deeply than is usually possible, and we take the liberty to place our problem into the context of several broader areas: linear optical properties of crystalline semiconductors, non-linear response to short light pulses, and disordered systems. Linear optics of semiconductors is a classical field, and it is reviewed in advanced text-books [9]. A point of departure for us will be the simplest case of the interband transitions across the gap between just two ideal bands $\epsilon_c(\mathbf{k})$, $\epsilon_v(\mathbf{k})$. The absorptive part of complex permittivity is in this case given by a Golden Rule expression as

$$\varepsilon_2(\omega) = 4\pi(N\Upsilon_0\epsilon_0)^{-1} \sum_{\mathbf{k} \in \text{BZ}} |ex_{vc}|^2 \delta(\hbar\omega - [\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})]). \quad (1)$$

Here, N is the number of primitive cells, Υ_0 the cell volume, the dipole matrix element ex_{vc} should in general depend on $\mathbf{k}$. For simplicity, we assume that it is constant throughout the paper.

If, first, we want to generalize this expression to incorporate the effect of phonon emission and absorption, it is necessary to consider the evolution of the photoexcited $e - h$ pair as a motion of two particles which interact with the phonons independently. This interaction leads to relaxing the vertical selection rule $\mathbf{k}_c = \mathbf{k}_v = \mathbf{k}$ (indirect transitions) and to a broadening in the region of direct transitions. Both these effects amount to the transformation of the bare particles to the respective polarons and can be taken into account by introducing the polaron spectral functions $A_b(\mathbf{k}, \omega)$, $b = c, v$. With them, $\varepsilon_2(\omega)$ becomes a convolution,

$$\varepsilon_2(\omega) = 4\pi(N\Upsilon_0\epsilon_0)^{-1} \int d\eta \sum_{\mathbf{k} \in \text{BZ}} |ex_{vc}|^2 A_v(\mathbf{k}, \eta) A_c(\mathbf{k}, \eta + \hbar\omega). \quad (2)$$

If, now, the electron-phonon interactions is turned off, the spectral functions have the limit $A_b(\mathbf{k}, \omega) \rightarrow \delta(\hbar\omega - \epsilon_b(\mathbf{k}))$ and (2) reduces to the ideal crystal case (1).

Excitonic interactions represent the other limiting type of modification of the interband formula (1). Again, a bare $e - h$ pair is photogenerated, but now the mutual interaction between both particles, as they fly off, is important, and the final state of the process is modified; this is the so-called final state interaction. The correlated $e - h$ motion leads to a change in the absorption strength, while the energy and total momentum of the final scattering states does not change. As shown first in [10], the simple interband formula (1) is modified twofold: there may exist bound excitonic states, and the continuous part of the ε_2 spectrum differs from (1) by the appearance of the so-called Elliott factor $(1 + \Gamma(\mathbf{k}))$:

$$\begin{aligned} \varepsilon_2(\omega) = 4\pi(N\Upsilon_0\epsilon_0)^{-1} \Big\{ & [\text{BOUND STATES}] \\ & + \sum_{\mathbf{k} \in \text{BZ}} |ex_{vc}|^2 (1 + \Gamma(\mathbf{k})) \delta(\hbar\omega - [\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})]) \Big\}. \end{aligned} \quad (3)$$

The Elliott factor is seen to modify, appropriately enough, the effective transition matrix element, while the energies of the two particle excitations remain without change.

We will not continue in this review, leaving thus aside the general case of combined exciton-phonon processes, interband phonon induced correlations, etc.

Our main goal is to characterize the effects of disorder on the electrons in semiconductors, and to draw an analogy with the genuine phonon and exciton effects. Disorder affects the electrons through many channels, but we have in mind the modification of the one-electron orbitals caused by a random potential, in which the electrons move. We will consider a moderately pronounced disorder, for which it will be productive to think about its effect in a perturbative manner, with a reference crystal in mind. This approach makes sense for both major classes of disordered semiconductors, amorphous and glassy semiconductors on the one hand, mixed crystals, i.e., random alloys, in which crystal nodes are occupied by different atoms in an irregular way, on the other one. Presently, we are interested in the latter, alloy, case. We have to mention the amorphous semiconductors, however, for several reasons. Firstly, the exciton-like disorder-induced kinematical $e-h$ correlations in the linear optical response of electrons in amorphous semiconductors were, in their time, a seminal problem for the whole disorder area. These phenomena were then studied in detail, in connection with the problem of the optical absorption edge in disordered amorphous semiconductors. We refer the reader to two chapters, 2 and 8, of the book [7]. The disorder in question was a consequence of smooth random fields, due either to space charges, or to internal strains, both typical for amorphous semiconductors. This case can be treated using the effective mass picture combined with a quasiclassical approximation. This is easy to visualize, and we will use it for illustrative purposes. We must stress that near the absorption edge the kinematic effect combines with a true screened Coulomb interaction between both particles, and this makes the problem substantially more difficult. At higher excitation energies, however, the dynamic effect becomes negligible and the kinematic coupling prevails. This is especially true for a sufficiently strong disorder, and we will refer to this remark to justify that we work later in a purely one-electron approximation.

Let us gradually introduce disorder into the reference crystal. The crystal symmetry is lowered, so that neither of the quantum numbers b , $\mathbf{k}$ is preserved. In particular, the electrons do not have a sharp k -vector, and their eigenfunctions are inhomogeneously distributed in space. In general, also the bands are intermixed. For simplicity, we neglect this latter blurring of the band index b . This defines the so-called model of independent bands. Most of the existing work on linear optics of disordered semiconductors uses this model expressly or tacitly. A general expression for ε_2 then reads

$$\varepsilon_2(\omega) = 4\pi(N\mathcal{T}_0\epsilon_0)^{-1} \sum_i \sum_f |\langle vi | e\hat{x}_{vc} | cf \rangle|^2 \delta(\hbar\omega - [\epsilon_{cf} - \epsilon_{vi}]). \quad (4)$$

The random eigenfunctions have the form

$$\begin{aligned} |vi\rangle &= \sum_{\mathbf{k} \in \text{BZ}} a_{vi} |v\mathbf{k}\rangle \\ |cf\rangle &= \sum_{\mathbf{k} \in \text{BZ}} a_{cf} |v\mathbf{k}\rangle \end{aligned} \quad (5)$$

by assumption, while the transition operators look like

$$\begin{aligned} e\hat{x}_{vc} &= ex_{vc} \sum_{\mathbf{k} \in \text{BZ}} |v\mathbf{k}\rangle \langle c\mathbf{k}| \\ &\equiv ex_{vc} \Pi_{vc} \end{aligned} \quad (6)$$

The eigenfunction expansions may be wild, in particular for energies at the band edge, where the Anderson localization may be expected. Deeper in the band, however, we assume that a signature of the parent Bloch function will be apparent. We use this remark to illustrate schematically the origins of the analogy of the polaron effect. Physically speaking, the random potential may be considered as a distortion of an original periodic potential due to immobile, "frozen phonons". Assuming that the valence band states are practically undistorted and the disorder only smeared the conduction states, we may rewrite (4) with the use of (5) and (6) in the form

$$\varepsilon_2(\omega) = 4\pi(N\gamma_0\epsilon_0)^{-1} |ex_{vc}|^2 \int d\eta \sum_f \sum_{\mathbf{k} \in \text{BZ}} \delta(\eta - \varepsilon_v(\mathbf{k})) \delta(\hbar\omega + \eta - \epsilon_{cf}) |a_{cf}(\mathbf{k})|^2 \quad (7)$$

Fig. 1a suggests an interpretation of the formula. In the crystal, along the depicted line in the k -space, only one sharply defined wave vector at the crossing of ϵ_c and of $\epsilon_v + \hbar\omega$ led to an interband transition. In the disordered case, this sharp selection rule is relaxed. In principle, for a selected $\hbar\omega$, there always exists a transition between any of the cf states and some $v\mathbf{k}^*$ state whose energy is $\epsilon_v(\mathbf{k}^*) = \hbar\omega - \epsilon_{cf}$. The transition strength is weighted by $|a_{cf}(\mathbf{k}^*)|^2$. This is a clear picture of "non-direct", or non-vertical transitions. For a systematic theory, it is preferable to make another rearrangement, summing first over the final states. This internal sum is

$$\begin{aligned} &\sum_f \delta(\hbar\omega + \eta - \epsilon_{cf}) |a_{cf}(\mathbf{k})|^2 \\ &= \langle c\mathbf{k} | \left\{ \sum_f |cf\rangle \delta(\hbar\omega + \eta - \epsilon_{cf}) \langle c\mathbf{k}| \right\} | c\mathbf{k} \rangle \\ &\equiv A_c(\mathbf{k}) \end{aligned} \quad (8)$$

By these rearrangements, we introduce the spectral density function $A_c(\mathbf{k})$ for the conduction band. This is a random quantity, of course, but, unlike the individual orbitals and energies, it is self-averaging. This term means that for very

Fig. 1. **a** Left panel: $\mathbf{k}$ is not conserved in non-direct transitions between sharp energy levels for one alloy configuration **b** Right panel: $\mathbf{k}$ conservation is restored for direct transitions to a broadened ("complex") quasiparticle band after configuration average

large samples of the random medium, the value of the spectral density will have a vanishingly small statistical dispersion, so that it will be practically independent of the particular choice of the configuration, that is a realization of the randomly generated sample. In that case, these individual values can be replaced by their statistical, or, as the term goes, configuration average. The dielectric function then assumes a form fully resembling the polaron case (2):

$$\varepsilon_2(\omega) = 4\pi(N\gamma_0\epsilon_0)^{-1} \int d\eta \sum_{\mathbf{k} \in \text{BZ}} |ex_{vc}|^2 A_v(\mathbf{k}, \eta) A_c(\mathbf{k}, \eta + \hbar\omega). \quad (9)$$

Here, of course, the valence band spectral function is sharp: $A_v(\mathbf{k}, \eta) = \delta(\eta - \epsilon_v(\mathbf{k}))$. The physical picture obtained is sketched in Fig. 1b. The configuration average implicit in the procedure restores the translational invariance of the sample. The $\mathbf{k}$ -vector becomes sharp again, and the interband transitions can be visualized as vertical. The transition energies become blurred, however, so as to capture the disorder effect.

Finally, we come to the basic situation studied in this paper. Disorder causes a random potential acting in each of the bands separately and differently in general. The assumed dynamical decoupling of both bands does not preclude a statistical coupling; the two random fields are a result of the same random environment in the sample, so that they should show some degree of statistical correlation. While this feature does not reflect itself in static properties of the electrons, it plays an important role for the interband transitions, where the

statistically correlated initial and final states are linked through the transition matrix element $\langle ci|\Pi_{vc}|vf\rangle$. Without entering into details, we quote [6], [8], [11], [12] the general configuration averaged form of ε_2 :

$$\varepsilon_2(\omega) = 4\pi(N\Upsilon_0\epsilon_0)^{-1} \int d\eta \sum_{\mathbf{k}} |ex_{vc}|^2 A_v(\mathbf{k}, \eta) A_c(\mathbf{k}, \eta + \hbar\omega) (1 + \Gamma(\eta, \eta + \hbar\omega, \mathbf{k})). \quad (10)$$

As compared to (9), a new $1 + \Gamma$ factor appears. For an uncorrelated disorder in the two bands, $\Gamma \rightarrow 0$, and only the two convoluted spectral functions remain. Thus, the polaron-like disorder broadening is always present. The additional correlation related factor is, in the Green's function language, a vertex part. Very clearly, it stems from the statistical correlations in the transition matrix element, and it also modifies the transition strength multiplicatively. A comparison with (3) shows that it plays exactly the role of the Elliott factor for excitons, only now it depends, in addition to the $\mathbf{k}$ dependence, also on the energies of both one-particle excitations.

Fig. 2. Smooth random potentials acting in the conduction and the valence bands. Upper row: the two potentials positively correlated (left panel). A negative correlation of the e and h WKB wave functions results (right panel). Lower row: for negatively correlated potentials, the wave functions are correlated positively.

The analogy with the Elliott factor is not only formal. It may be said that the statistical correlation of the potentials leads to a kinematic correlation between the electron and the hole whose appearance resembles an effective interaction. Depending on the type of correlation, this interaction may be attractive or repulsive, as sketched in Fig. 2 for the case of smooth random fields. Two situations

are sketched. In the first case, the potentials fluctuate in parallel (as corresponds to a fluctuating electric field). These are the so-called correlated potentials [8]. In the other case, the potentials fluctuate against each other (... elastic strains), the anti-correlated potentials. For energies moderately remote from the band edges, the wave function can be found using the WKB approximation easily, $\psi(x) \sim \sqrt{k(x)} \exp(\pm i \int dx' k(x'))$ with $k(x) = \hbar^{-1} \sqrt{2m_b(E - V_b(x))}$. We only have to recall that the valence band effective mass is negative. This is just like to say that for the hole its mass and energy are positive, while the potential changes sign. Then, it is easily found that, in the correlated case, the two particles prefer to "meet" at the common minima of their potentials. This means an effective attraction. For the anticorrelated potential, the behavior is the opposite, and an effective repulsion results. By analogy with the exciton case, we may expect that this will lead to an enhancement of the optical absorption in the correlated case, to a reduction in the other one.

It is interesting to compare this simple picture with the calculations of Abe and Toyozawa [8] in more detail. The situation they consider is far from being quasiclassical, but quite close to our model alloy, as the randomness in their two-band model is represented by a Gaussian distribution of the "atomic" levels in the Wannier representation. The random levels may be positively correlated, uncorrelated, or negatively correlated, as described by a parameter γ , which assumes a corresponding value 1, 0, and -1. The authors demonstrate, using the CPA, that the sharp crystal absorption edge is paraexponentially smeared and they find that this so-called Urbach tail of the absorption edge is enhanced/reduced for an anticorrelated/correlated potential. This appears like the exact opposite of the above qualitative conclusion. We reproduce their Figure 6. to clarify this

Fig. 3. Reproduction of Fig. 6 of the paper [8]. $I(E)$ is the absorption profile for photon energies around the direct optical gap of a reference crystal. B 's and W are quantitative parameters of the model. Important are the labels $\gamma = 0, +1, -1$ which specify the uncorrelated, correlated, and anticorrelated disorder in both bands. The crystal absorption edge is at $E = 0$. The part of the spectrum relevant to the present discussion is not the tail region (negative E), but the main absorption band, $E \geq 0$, as discussed in the main text.

seeming contradiction. In this picture, see Fig. 3, the optical absorption $I(E)$ is shown as a function of energy E measured from the crystal energy gap. The tails then appear for negative E , and they behave precisely as the authors describe. The ordering of the absorption curves becomes reverted, however, already around $E = 0$. There, it agrees with the prediction resulting from Fig. 2, which also holds only for energies somewhat above the gap. Thus, the quasiclassical reasoning has some bearing also on the fully quantum case.

3 Model Alloy and its linear and non-linear response

In this section, we formalize the qualitative model outlined above and define the physical questions we will address in a straightforward manner employing the language of the one-electron density matrix.

3.1 Model semiconductor alloy

The model used is schematic, but possessing most of the salient features of the realistic systems we mimic here, namely the mixed semiconductor crystals thoroughly characterized in [5]. In these systems, one of the sublattices is randomly occupied by atoms which are isoelectronic and chemically similar. In the basic approximation, such alloying can best be described in an LCAO language by random shifts of the corresponding quasiatomic levels. Our model is even cruder, and its justification is outlined in [4].

Following [4], we consider a completely random binary alloy $A_{c^A}B_{c^B}$ with $c^A + c^B = 1$. The semiconductor has a two-band electron structure with the gap between two isotropic parabolic band edges at the center of the Brillouin zone ("*standard band structure*"). All many-body interactions are ignored. The disorder potential acts in each band separately, it is not mixing states of both bands ("*independent bands*"). The effect of the optical pulse is restricted to a non-random interband dipole coupling treated in the rotating wave approximation (RWA). The initial condition is a fully occupied valence band and a completely empty conduction band before the arrival of light.

The notion of independent bands is formalized by introducing the band projectors which are non-random and diagonal in both the Bloch and the Wannier (site) basis, labeled by $\mathbf{k}$ and i , respectively:

$$P_b = \sum_{\text{BZ}} |b\mathbf{k}\rangle \langle b\mathbf{k}| = \sum_{\text{lattice}} |bi\rangle \langle bi|, \quad b = c, v. \quad (11)$$

The full one-electron Hamiltonian for one configuration of our alloy has the following structure:

$$\mathcal{H} = W_v + W_c + \mathcal{V}_c + \mathcal{V}_v + U(t) \equiv \mathcal{H}_c + \mathcal{H}_v + U(t) \equiv \mathcal{H}_{\text{DARK}} + U(t). \quad (12)$$

The non-random configuration independent or averaged quantities are denoted by italics, while the configuration dependent ones by rounded ("*\code{cal}*") characters. The dark Hamiltonian $\mathcal{H}_{\text{DARK}}$ is band diagonal, as both the Bloch Hamiltonians W_b and the random potentials $\mathcal{V}_b$ are assumed to obey the rule $\mathcal{O}_b = P_b \mathcal{O}_b P_b$

with $b = c, v$. The interaction with the pulse is taken as purely interband, that is off-diagonal; with the linear polarization in the x direction, the basic frequency Ω , and in the Rotating Wave Approximation, it reads

$$\begin{aligned} U(t) &= U_{cv}(t) + U_{vc}(t) \\ &= -Q \cdot \Phi(t) \left\{ \sum_{\mathbf{k}} |c\mathbf{k}\rangle e^{-i\Omega t} \langle v\mathbf{k}| + \sum_{\mathbf{k}} |v\mathbf{k}\rangle e^{i\Omega t} \langle c\mathbf{k}| \right\} \\ &\equiv -Q \cdot \Phi(t) \{ \Pi_{cv} e^{-i\Omega t} + \Pi_{vc} e^{i\Omega t} \} \end{aligned} \quad (13)$$

where $Q = ex_{cv}E_m$ is the strength of the pulse, ex_{cv} a real constant electric dipole matrix element and E_m the peak electric field of the pulse; $\mathcal{E}_x(t) = E_m \Phi(t) \geq 0$ is the pulse envelope. The $\Pi_{bb'}$ operators were already defined in (6). The RWA is not fully quantitative for short pulses, but it is still well justified in our model, where the transition energies across the gap are about 1.5 eV corresponding to periods about 4 fs, while the pulse duration is of the order of 100 fs.

3.2 Transient optical response

Our model treats electrons as independent particles. In such case, the natural quantity describing time evolution of the photoexcited transient is the one-electron density matrix ϱ of a single random alloy configuration. It evolves according to a Liouville equation

$$\begin{aligned} i\hbar\varrho &= [\mathcal{H}(t), \varrho(t)] \\ &= [\mathcal{H}_{\text{DARK}}, \varrho(t)] + [U(t), \varrho(t)] \end{aligned} \quad (14)$$

The *initial condition* is $\varrho(t_0) = P_v$ for t_0 in a distant past; this initial condition is non-random. A formal solution of (14) is expressed in terms of the usual evolution operator $\mathcal{S}(t, t')$ for the full Hamiltonian (12):

$$\begin{aligned} \varrho &= \mathcal{S}(t, t_0) \varrho(t_0) \mathcal{S}(t_0, t) \\ &= \mathcal{S}(t, t_0) P_v \mathcal{S}(t_0, t) \end{aligned} \quad (15)$$

All effect of the external optical field is contained in the evolution operator in a closed non-linear fashion.

In general, the macroscopic optical response is given by the electric polarization $\mathbf{P}$ induced by the electric field $\mathbf{E}$ of incident light. In our isotropic case, we need

$$P_x(t) = (N\Upsilon_0\epsilon_0)^{-1} \text{Tr} \langle e\hat{x} \cdot \varrho(t) \rangle \quad (16)$$

with $\hat{x} = x_{cv} \{ \Pi_{cv} + \Pi_{vc} \}$. Macroscopic observables should not depend on a particular configuration; hence they should be given by a configuration average. The symbol $\langle \dots \rangle$ indicates such averaging over all random configurations. N is the number of primitive cells, Υ_0 the cell volume. The electric field enters through the time dependence of ϱ . Clearly, for $\varrho(t_0) = P_v$ in the distant past, $P_x(t_0) = 0$. All polarization is an induced transient.

Linear response Some understanding of (16) can be gained in the linear case. Then, $\mathbf{P}$ and $\mathbf{E}$ are linked by the dielectric function ε defined by a symbolic equation $\mathbf{P} = \epsilon_0(\varepsilon - 1) \cdot \mathbf{E}$. An explicit expression is obtained by expanding the field-dependent evolution operator $\mathcal{S}(t, t')$ in terms of the dark evolution operator $\mathcal{S}_D(t, t')$ and of the external field to the lowest order:

$$P_x(t) = 2 \operatorname{Re} \int_{t_0}^t d\bar{t} (ex_{cv})^2 (N\Upsilon_0)^{-1} \times \operatorname{Tr} \langle \mathcal{S}_{D;vv}(\bar{t} - t) \Pi_{vc} \mathcal{S}_{D;cc}(t - \bar{t}) \Pi_{cv} \rangle \underbrace{e^{-i\Omega\bar{t}} \mathcal{E}_x(\bar{t})}_{E_x(\bar{t})} \quad (17)$$

As indicated, the dark evolution operator only depends on the time difference $t - t'$, so the integral is, in fact, a convolution, and it neatly defines a linear response function. Its Fourier transform is the complex polarizability, and using the quoted macroscopic relations, the absorptive part of the complex permittivity for our model can be rewritten [6] in the form

$$\varepsilon_2(\omega) = 4\pi(N\Upsilon_0\epsilon_0)^{-1} \int d\eta \operatorname{Tr} \langle \delta(\eta - \mathcal{H}_v) \Pi_{vc} \delta(\eta + \hbar\omega - \mathcal{H}_c) \Pi_{cv} \rangle \quad (18)$$

It is easy to see that this is a configuration average of (4) written in a compact operator form. The last two equations (17), (18) are equivalent and lead to the following interpretation of the vertex corrections, that is the effective Elliott factors in (10). Before averaging, the electron and the hole move independently in their respective bands. Configuration average of the product of two δ -functions would not factorize in general, only if the randomness in both bands were uncorrelated. In a chemical environment common for both particles, a disorder induced optical vertex Γ_{vc} modifies the product of the averaged δ -functions $A_b(E) = \langle \delta(E - \mathcal{H}_b) \rangle$. Quantities $A_b(E)$ have the meaning of spectral densities in the individual bands. They describe the band broadening and shift, in other words the polaron-like effects of the disorder. In the time variable representation, the quantities to be factorized are the band diagonal components of the dark propagator. Again, correction factors will compensate for the simple factorization.

Generalization to the non-linear response In the non-linear case, the induced polarization $\mathbf{P}$ cannot be expressed in terms of the electric field $\mathbf{E}$ of incident light and of a response function; still, it is not difficult to obtain

$$P_x(t) = 2 \operatorname{Re} \int_{t_0}^t d\bar{t} (ex_{cv})^2 (N\Upsilon_0)^{-1} \times \operatorname{Tr} \langle \mathcal{S}_{vv}(\bar{t}, t) \Pi_{vc} \mathcal{S}_{cc}(t, \bar{t}) \Pi_{cv} + \mathcal{S}_{vc}(\bar{t}, t) \Pi_{cv} \mathcal{S}_{vc}(t, \bar{t}) \Pi_{cv} \rangle e^{-i\Omega\bar{t}} \mathcal{E}_x(\bar{t}) \quad (19)$$

Eqs. (19) and (17) are quite similar. In both equations, the external field amplitude is singled out in the integral. The other factor is thus of zeroth order, that

is field independent, in the linear response limit. The full expression (19) then reduces exactly to (17). There are also qualitative differences. The first term in (19) represents an $e-h$ correlation function, similarly to (17). The band diagonal blocks $\mathcal{S}_{vv}$, $\mathcal{S}_{cc}$ are dressed by the light, however. This can be interpreted simply as a non-linear effect. At the same time, it may be said that each of the particles is virtually excited into the other band and their identity is thus spurious. Even more striking is the appearance of the off-diagonal blocks $\mathcal{S}_{vc}$ in the second term in (19). Here, the band mixing is real, unlike the virtual mixing in the diagonal part. The phenomenon involved is the light induced hybridization of both bands and cannot be interpreted as a propagation of a well defined $e-h$ pair at all. The excitations in question are reminiscent of the Bogolyubov-Valatin anomalous propagators.

While these results are physically revealing, they offer no easy way for an actual evaluation, as is typically the case with a density matrix formulation. It is then preferable to turn to the NGF formulation.

4 Use of the Non-equilibrium Green's Functions

This section is going to be rather terse for two reasons. We use here the NGF technique in the form developed and explained at length in [4]. It is thus sufficient to recapitulate here several essential points. Besides, at this meeting, at the center of attention is physics rather than techniques. We work in the standard LW matrix form of NGF [13]. For example:

$$\mathbf{G} = \begin{Bmatrix} G^R & G^< \\ 0 & G^A \end{Bmatrix}; \quad \mathbf{\Sigma} = \begin{Bmatrix} \Sigma^R & \Sigma^< \\ 0 & \Sigma^A \end{Bmatrix}; \quad \mathbf{H} = \begin{Bmatrix} \mathcal{H} & 0 \\ 0 & \mathcal{H} \end{Bmatrix} \quad (20)$$

Among the reasons for using this variant is that, for the elastic alloy scattering, the equations for propagators decouple from the equations for the particle correlation function, a substantial advantage.

Virtual crystal and dark GF The Hamiltonians are split into their averaged (mean field, virtual crystal) and fluctuating parts:

$$\left. \begin{aligned} \mathcal{H} &= \langle \mathcal{H} \rangle + \mathcal{D} \\ \mathcal{H}_{\text{DARK}} &= \langle \mathcal{H}_{\text{DARK}} \rangle + \mathcal{D} \end{aligned} \right\} \mathcal{D} = \mathcal{D}_v + \mathcal{D}_c \equiv (\mathbf{V}_v - \langle \mathbf{V}_v \rangle) + (\mathbf{V}_c - \langle \mathbf{V}_c \rangle) \quad (21)$$

We might introduce the NGF $\mathcal{G}$ for each random configuration. For example, $\mathcal{G}^R = (i\hbar)^{-1} \mathcal{S}(t, t') \vartheta(t - t')$, etc. We will only need the averaged Green's functions, however, like $\mathbf{G} = \langle \mathcal{G} \rangle$. The self-energies are then defined with respect to the virtual crystal Green's functions. The latter GF are eliminated, however, as the Dyson equation for the full $\mathbf{G}$ is rewritten in terms of the dark Green's

function $\mathbf{G}_{\text{DARK}}$:

$$\begin{aligned}\mathbf{G}_{\text{DARK}}^{-1} &= i\hbar\partial_t\mathbf{1} - \langle\mathcal{H}_{\text{DARK}}\rangle - \Sigma_{\text{DARK}} \\ \mathbf{G}^{-1} &= i\hbar\partial_t\mathbf{1} - \langle\mathcal{H}_{\text{DARK}}\rangle - \mathbf{U} - \Sigma \\ &= \mathbf{G}_{\text{DARK}}^{-1} - \mathbf{U} - \underbrace{(\Sigma - \Sigma_{\text{DARK}})}_{\Sigma_{\text{IND}}}\end{aligned}\quad (22)$$

This transformation improves tremendously the stability and convergence of any numerical work, as the induced effect is a deviation from the equilibrium dressed by disorder. This (the so-called dark polaron effect [14]) is duly taken into account in the second form of (22) for $\mathbf{G}$.

Correlations in the self-consistent Born approximation The dark quantities are known beforehand and we solve numerically the Dyson equation in the second form together with the self-consistent Born approximation for the light induced part of the self-energy,

$$\begin{aligned}\Sigma_{\text{IND}} &= \langle\mathcal{D}(\mathbf{G} - \mathbf{G}_{\text{DARK}})\mathcal{D}\rangle = \\ \langle[\mathcal{D}_v + \mathcal{D}_c](\mathbf{G} - \mathbf{G}_{\text{DARK}})[\mathcal{D}_v + \mathcal{D}_c]\rangle &= \Sigma_{\text{IND};vv} + \Sigma_{\text{IND};vc} + \Sigma_{\text{IND};cv} + \Sigma_{\text{IND};cc}\end{aligned}\quad (23)$$

The off-diagonal parts of Σ_{IND} are the explicit source of the disorder induced correlation. It spreads, by self-consistence, also to the diagonal parts. We consider the case of a "diagonal disorder", when only the quasiautomic levels in the Wannier representation fluctuate at random and independently of each other:

$$\mathcal{D} = \sum_{b=c,v} \sum_{\text{lattice}} |b\rangle d_{bi} \langle b| \quad (24)$$

For a binary alloy, let the quasiautomic levels be $E_{cn} = E_c^A, E_c^B$; $E_{vn} = E_v^A, E_v^B$ at random and with average weights (concentrations) c^A, c^B . The fluctuating parts of the atomic potentials are $d_{bi} = E_{bi} - \langle E_{bi} \rangle$. The self-energy in the Born approximation is, according to (23) and (24), given by a 2×2 scalar matrix $\langle d_{bi} d_{b'i} \rangle \langle b| \mathbf{G} | b' \rangle$. The diagonal elements of $\langle d_{bi} d_{b'i} \rangle$ measure the intraband disorder strength, the off-diagonal elements pertain to the cross-correlation:

$$\begin{aligned}\langle d_{vi}^2 \rangle &= c^A c^B (E_v^A - E_v^B)^2 \equiv \lambda_v^2 \\ \langle d_{ci}^2 \rangle &= c^A c^B (E_c^A - E_c^B)^2 \equiv \lambda_c^2 \\ \langle d_{vi} d_{ci} \rangle &= c^A c^B (E_v^A - E_v^B)(E_c^A - E_c^B) \equiv \lambda_v \lambda_c \kappa \\ \langle d_{ci} d_{vi} \rangle &= c^A c^B (E_c^A - E_c^B)(E_v^A - E_v^B) \equiv \lambda_v \lambda_c \kappa\end{aligned}\quad (25)$$

Depending on the sign interplay of the level differences, the correlation parameter κ is ± 1 . We add in a formal manner the case $\kappa = 0$ and compare three cases:

$\kappa = -1$	0	1
anti-correlated	non-correlated	correlated

This terminology is the same as introduced in Sec. 2. As will be seen, the statistical correlation in the self-energy can be reformulated in terms of the "effective $e-h$ interaction" also in the non-linear case, although the interpretation is less straightforward than in the linear response.

Vertex in the particle correlation function The Green's functions for different correlation parameters will be distinguished by the left superscript: ${}^\kappa\mathbf{G}$ with $\kappa = 0, \pm 1$. To assess the effect of correlation, we compare ${}^{\pm 1}\mathbf{G}$ with ${}^0\mathbf{G}$. By (22), we have, putting $\bullet$ for ± 1 ,

$$\begin{aligned} \bullet\mathbf{G}^{-1} &= {}^0\mathbf{G}^{-1} - \bullet\Xi \\ \bullet\Xi &= \bullet\Sigma_{\text{IND}} - {}^0\Sigma_{\text{IND}} \end{aligned} \quad (26)$$

More explicitly, the quantities $\bullet\Xi_{bb'}^{R,A}(t, t')$, $\bullet\Xi_{bb'}^<(t, t')$ specify the propagators $\bullet G_{bb'}^{R,A}(k; t, t')$ and the particle function $\bullet G_{bb'}^<(k; t, t')$. There are differences, however. The propagators have, in fact, only an auxiliary role; at the same time, they satisfy a simple Dyson equation $\bullet G^{R,A} = {}^0 G^{R,A} + {}^0 G^{R,A} \bullet \Xi^{R,A} \bullet G^{R,A}$. The particle correlation function $\bullet G^<$ plays a central role, by contrast, as it directly yields the averaged one-particle density matrix. The expression for it has a more involved structure, permitting to define the desired correlation vertex, which is not simply $\bullet \Xi^<$. Skipping the straightforward, but lengthy derivation, we write directly the result.

$$\begin{aligned} \bullet G^< &= {}^0 G^< + {}^0 G^R \bullet \Theta^< {}^0 G^A \\ {}^0 G^< &= i\hbar {}^0 G^R P_v {}^0 G^A + {}^0 G^R {}^0 \Sigma^< {}^0 G^A \\ \bullet \Theta^< &= \bullet \Xi^< \\ &+ (1 + \bullet \Xi^R \bullet G^R) \bullet \Xi^< (1 + \bullet G^A \bullet \Xi^A) - \bullet \Xi^< \\ &+ (1 + \bullet \Xi^R \bullet G^R) {}^0 \Sigma^< (1 + \bullet G^A \bullet \Xi^A) - {}^0 \Sigma^< \end{aligned} \quad (27)$$

The form of ${}^0 G^<$, namely $G^< = G^R[i\hbar\varrho_0 + \Sigma^<]G^A$, is the usual Dyson equation expressing the full $G^<$ as a decomposition into its coherent and incoherent parts. The newly introduced quantity $\bullet \Theta^<$ plays clearly the role of a vertex transforming the uncorrelated particle function into the correlated one. It consists of several contributions. First, it is the corresponding change in the induced self-energy. The other two parts involve the correlated propagation. Particularly significant is the appearance of the last (third line) contribution, which only involves the correlation correction to the propagator, while the particle correlation proper, $\Xi^<$, does not enter at all. One last point should be made. This vertex correction Θ applies to a product of propagators, while the originally introduced Γ was correcting a product of spectral densities. This is not peculiar to our case, but rather a result already known from other physical problems.

5 Numerical study: onset and evolution of disorder induced correlations

To demonstrate the importance of the $e-h$ disorder induced correlation, we present here a few numerical results obtained by solving the Eqs. (22) and (23) using the method described in ref. [4]. We have directly calculated full Green functions ${}^\kappa G_{ab}^R(k; t, t')$, ${}^\kappa G_{ab}^<(k; t, t')$ and self-consistent self-energies ${}^\kappa \Sigma_{\text{IND},ab}^R(t, t')$, ${}^\kappa \Sigma_{\text{IND},ab}^<(t, t')$ for $a, b = c, v$ and $\kappa = 0, \pm 1$. We do not intend to analyze at this place the extensive results for the double time Green's functions and self-energies. The kinematical correlation is clearly revealed already in the behavior of much simpler single time observable quantities. All results are shown in the Galickii picture [4] suppressing the fast Ω -oscillations and extracting the envelopes characteristic of the pulse induced transients.

Calculations were performed for these parameters: $E_G = 1.5$ eV, $\hbar\Omega = 2$ eV, $m_v^* = .6$, $m_c^* = .4$; *disorder*: c - and v - band lifetimes $\tau_c = 160$ fs, $\tau_v = 240$ fs, $c^A = 0.05$; *pulse*: Gaussian, duration $\tau_m = 120$ fs, strength – two pulses used, "weak" with $Q = 0.0025$ eV and "strong" with $Q = 0.01$ eV. By this, their respective Rabi phase $3.3Q\tau_m/\hbar$ are adjusted to 0.48π , and 1.93π , in other words slightly below $\pi/2$, and 2π .

Fig. 4. Weak pulse, $Q = 0.0025$ eV: total one-electron density matrix (29) as a function of time. The diagonals are real, the off-diagonals are complex conjugate, and we show the real and the imaginary parts separately, as labeled. Three different cases of the $e-h$ correlation, $\kappa = 0, +1, -1$ (uncorrelated, correlated, and anticorrelated disorder), have a line code defined in the ρ_{cc}^{TOT} panel.

The central quantity is the averaged one-electron density matrix $\rho(t) = \langle \varrho(t) \rangle$. It is given by the time diagonal of $G^<$ as

$$\kappa \rho(t) = -i\hbar \kappa G^<(t, t) \quad (28)$$

It is k -, but not band-, diagonal. To further condense the information, we trace over the k -vectors and obtain the total excitation per unit cell,

$$\kappa \rho_{ab}^{\text{TOT}}(t) = N^{-1} \sum_{k \in \text{BZ}} \kappa \rho_{ab}(k, t), \quad a, b = c, v \quad (29)$$

The time dependent deviation from equilibrium $\kappa \rho^{\text{TOT}} - P_v$ for the weaker pulse is in Fig. 4. The diagonal elements are related to total photoexcited populations, namely $n_e = \rho_{cc}^{\text{TOT}}$, $n_h = 1 - \rho_{vv}^{\text{TOT}}$. Their sum should be zero (particle number conservation). This is reasonably satisfied considering that computationally the way to each of the elements is rather remote [4]. The effect of correlation is distinct, but not striking. Two features can be noticed. First, the correlation develops only gradually; at the early times the populations appear as κ independent. This is in agreement with the notion of "final state interactions" discussed in Sec. 2.

Physically more relevant are the off-diagonal elements linked with the electric polarization by $M_x(t) = ex_{cv} \cdot 2 \text{Re}[\rho_{cv}^{\text{TOT}} e^{-i\Omega t}]$ (the dipole moment of one cell) and $P_x = \Upsilon_0^{-1} M_x$. The populations and the polarization have in common that they are correlation insensitive early after the pulse arrival, while the differences are marked at later times, again in a qualitative agreement with the notion of final state $e - h$ interactions. This points to the important link between the correlation effects and the incoherent back-scattering which sets on gradually, but persists for long times. Formally, this is described by (27) which basically expresses the correlation vertex in terms of $\Sigma^<$.

The tendency is different, however: the diagonal elements increase with a stronger correlation, while the off-diagonal ones seem to decrease. In fact, this apparent discrepancy may be reconciled, if we notice that the late time overshoot in $\text{Im} \rho_{cv}^{\text{TOT}}$ is due to the coherent Rabi oscillation, which is then suppressed more, or less, depending on κ , and with the "correct" ordering. Finally, the tentatively suggested interpretation of this behavior is that *positive/negative* correlation *enhances/reduces* the incoherent backscattering, and, hence, the disorder effect on the optical response.

We may look at the effects of correlated disorder from a different angle by considering the energy balance. The "Joule heat" rate (actually, a non-dissipative energy transfer[4]) is

$$w = \mathbf{E} \cdot \mathbf{J} = \mathbf{E} \cdot \frac{\partial}{\partial t} \mathbf{P} \quad (30)$$

$$Q_{\max}=0.0025 \text{ eV}$$

Fig. 5. Weak pulse, $Q = 0.0025 \text{ eV}$: the absorbed power (left panel) and the integral energy gain (right panel) obtained as "Joule heat" from Eq. (31). Line code for different cases of the $e-h$ correlation, $\kappa = 0, +1, -1$, as in Fig. 1. Hatched profile: pulse intensity, arbitrary scale

As seen in Fig. 5, the gain is the least, and even becomes negative at the trailing side of the pulse, for $\kappa = -1$, while it is enhanced somewhat for $\kappa = 1$. By

$$W(t) = \int_{-\infty}^t dt' w(t') \quad (31)$$

this is transferred also on the integral energy transfer. Again, for $\kappa = \pm 1$ the incoherent backscattering is *enhanced/reduced*, which leads to the same tendency for the irreversible abduction of energy from the pulse into the bath.

Let us briefly look on the strong pulse. In this case, the coherent action of light overcomes better the disorder (kept at the same level), so that the off-diagonal of the density matrix, shown in Fig. 6, nicely manifests the single Rabi oscillation. The populations are first coherently excited and then fall to their saturation values. Clearly, all of the discussion for the weak pulse fully applies here, too, only the effects are more pronounced. In particular, we may observe that for the anticorrelated disorder the final population is rather small. Without disorder, we would expect that at the end of one Rabi oscillation, all of the excitation would precisely return back to zero. This indicates that the anti-correlated case reduces the disorder effect on the $e-h$ pair truly effectively. Similarly, the power gained from the pulse, Fig. 7, depends on κ ; while the positive gain is at first comparable for all three cases, the negative gain, when energy is returned to the electromagnetic field during the second half-cycle, is strongly correlation dependent, and the anti-correlation leads virtually to a full compensation. We may conclude that the 2π pulses are particularly suited for measuring the kinematical correlations of $e-h$ pairs in disordered systems.

$Q_{\max}=0.01$ eV

Fig. 6. Strong pulse, $Q = 0.01$ eV: total one-electron density matrix (29) as a function of time. The layout and coding of the figure is the same as in Fig. 4.

 $Q_{\max}=0.01$ eV

Fig. 7. Strong pulse, $Q = 0.01$ eV: the absorbed power (left panel) and the integral energy gain (right panel) obtained as "Joule heat" from Eq. (31). The layout and coding of the figure is the same as in Fig. 5.

6 Conclusion

To summarize our discussion, we may say first that indeed the statistical correlation of the disorder in a valence and a conduction band leads to a kinematical correlation between the particles in an $e-h$ pair, which is fully observable and qualitatively important for systems with parameters resembling real semiconductor alloys.

A second conclusion is that in order to develop an efficient theoretical description of the photoexcitation process in such semiconductor alloys, we found as the

most efficient way the use of Non-equilibrium Green's Function, which permit to define the correlation vertex and to evaluate the physical characteristics of such photoexcitation process in a straightforward numerical procedure.

In the course of the theoretical analysis and of the numerical work, we found a number of general conclusions concerning the behavior of the photoexcited electrons. The most interesting are as follows:

1. The stochastic correlation in motion of the photoexcited electron -hole pairs is predicted to have a strong effect on the absorption of light from a pulse
2. The theory developed presently extends the previous work for the linear response[8],[11] to non-linear transients[4]
3. Main effect of the $e - h$ kinematic correlation is to modify the late time asymptotic corresponding to the final state interaction in the linear theory and to the incoherent backscattering in the general non-linear case
4. correlated $e - h$ disorder enhances the effect ("attraction")
anticorrelated $e - h$ disorder reduces the effect ("repulsion")

There is a number of open questions for future work. An obvious one is to analyze in detail the structure and properties of the correlation vertex $\kappa\Theta$ and to obtain qualitative rules linking the behavior of this vertex with properties of the observable quantities.

More complicated is the question of improving the dynamical approximation for the self-energy beyond the Born approximation, and aiming at something like the coherent potential approximation.

A truly satisfactory theory leading to a picture permitting a direct comparison with experiments should, by necessity, incorporate also the real correlations due to the $e-p$ and the $e-e$ interactions. For this purpose, there is no theoretical framework available at present, however.

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References

1. H. Haug, and A.P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors*, (Springer, Berlin Heidelberg 1997), Vol.123
2. M. Bonitz, *Quantum Kinetic Theory*, (Teubner, Stuttgart Leipzig 1998)
3. T. Schmielau, G. Manzke, D. Tamme, K. Hennenberger, Phys. Stat. Sol.B 221,(1),215-219
4. A. Kalvová and B. Velický, *Phys. Rev B* **65** 155329 (2002)
5. AB Chen and A. Sher, *Semiconductor Alloys*, Plenum, New York 1995
6. B. Velický and A. Pieczonková, *Physica scripta* **T19**, 558 (1987)
7. B. Seraphin, Editor, *Optical properties of solids: New developments*, North Holland/ American Elsevier, Amsterdam 1976

8. S. Abe and Y. Toyozawa, *J. Phys. Soc. Japan* **50**, 2185 (1981)
9. P.Y. Yu, and M. Cardona, *Fundamentals of Semiconductors*, (Springer Verlag, Berlin Heidelberg 1999)
10. R. J. Elliott, *Phys. Rev.* **108**, 1384 (1957)
11. K. C. Hass, *Topics in the Electronic Theory of Disordered Semiconductors*, Thesis, Ch. VIII., Harvard University, Cambridge 1984
12. N. F. Schwabe and R. J. Elliott, *Phys. Rev.* **B 53**, 5301 (1996)
N. F. Schwabe and R. J. Elliott, *Phys. Rev.* **B 53**, 5318 (1996)
13. D. Langreth, and J.W. Wilkins, *Phys. Rev. B* **6**, 3189 (1972)
14. P. Gartner, L. Bányai, and H. Haug, *Phys. Rev. B* **60**, 14234 (1999)

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