Influence of Coulomb interaction on the photon echo in disordered semiconductors

D. Bennhardt, P. Thomas, and A. Weller
Fachbereich Physik und Wissenschaftliches Zemtrum für Materialwissenschaften, Phillips-Universität Marburg, Renthof 5, D-3550 Marburg, Federal Republic of Germany

M. Lindberg
Optical Sciences Center, University of Arizona, Tucson, Arizona 85721

S. W. Koch
Optical Sciences Center and Department of Physics, University of Arizona, Tucson, Arizona 85721
(Received 8 November 1990)

The photon-echo signal in disordered semiconductors is treated including the electron-hole Coulomb attraction. The amplitude of the spontaneous photon echo is calculated up to third order in the external-field amplitude using the semiconductor Bloch equations. Several idealized situations are analyzed showing the significance of a critical correlation of the polarization dynamics in the two time intervals preceding and following the second excitation pulse. Strong photon-echo decay is predicted for short-range disorder without Coulomb interaction. The inclusion of electron-hole attraction leads to a stabilization of the echo signal. For the case of long-range disorder with Coulomb interaction, we predict slow decay in the diffusive limit.

I. INTRODUCTION

During the past decades the near-band-gap optical response of semiconductors has been studied in great detail both experimentally and theoretically. The theoretical analysis clearly shows the important influence of the electron-hole Coulomb interaction on the linear and nonlinear, cw and femtosecond-time-resolved optical-absorption and refractive-index spectra.[1-3] In most of the theoretical studies, a more or less perfect semiconductor crystal has been assumed and the imperfections present in real materials have been dealt with by introducing phenomenological broadenings and/or decay rates. Even though such an approach is well justified for an analysis of experimental results obtained with high-quality semiconductor crystals, it is clearly a poor approach for most amorphous or disordered materials. Actually, basically all semiconductors posses a certain degree of static disorder. This is evident for alloy semiconductors like $Al_xGa_{1-x}As$ or CdS_xSe_{1-x}, for amorphous semiconductors like amorphous Si:H, but also for quantum wells, quantum wires, quantum dots, and superlattices due to interface roughness. Since, in general, the quasiparticle interaction strength depends on static disorder, it is necessary for a complete theory to consider static disorder and electron-hole Coulomb interaction on an equal footing.

As a first approach to study the combined influence of Coulomb and disorder effects, we investigate in this paper the process of optical dephasing for statically disordered semiconductors. After an ultrashort laser pulse excites a semiconductor a variety of dynamical processes occur which each develop on their characteristic time scales. Phase relaxation of optical excitations can be considered as one of the earliest developments in such a situation. The theoretical description of these processes requires a thorough treatment of a highly complex interacting many-particle system in a nonequilibrium situation.

Experimentally a wide range of phase-relaxation times has been reported, ranging from femtoseconds in GaAs (Ref. 4) to hundreds of picoseconds in CdS_xSe_{1-x} (Ref. 5) mixed crystals. The interpretation of this enormous range of T_2 times provides a challenging theoretical problem. As a first step it seems to be in order to treat the influence of static disorder on optical phase relaxation exclusively, omitting all quasiparticle interactions. This is the purpose of this work. Since quasiparticle interactions destroy the phase coherence of optical excitations, our present treatment provides a lower limit for the phase-relaxation rate.

We consider in particular a spontaneous-photon-echo experiment, which gives information about the irreversible phase relaxation of optical excitations. In such an experiment a coherent optical polarization is produced in the sample, say, at time $t=0$ by a short laser pulse No. 1 (with k vector $\mathbf{k}_1$). This coherent polarization develops in time under the influence of many-body Coulomb effects and interaction with the static disorder. After a time delay τ a second pulse No. 2 with k vector $\mathbf{k}_2$ is applied. A spontaneous-photon-echo signal[6] is then emitted in the direction $2\mathbf{k}_2-\mathbf{k}_1$ at a time 2τ if an inhomogeneous distribution of oscillators has been excited. The decay of the echo signal is then monitored as a function of the delay time τ. Assuming optically thin samples, the echo amplitude is proportional to the nonlinear optical polarization $P(t)$. For an ensemble of inhomogeneously distributed two-level absorbers

$$P(2\tau) \propto \exp\left[-\frac{2\tau}{T_2}\right], \tag{1}$$

where T_2^{-1} is the phenomenologically introduced dephasing rate.[7] This particular system closely resembles the case of the well-known spin echo, and many results obtained for the latter can directly be transferred to the optical case. However, the analogy no longer holds if we consider a semiconductor which in a tight-binding description can be modeled by an ensemble of two-level absorbers, which are mutually coupled by quantum-mechanical transfer rates and the Coulomb interaction.[1,2,3,8,9]

Recently we have shown that a treatment along these lines of the photon echo in a disordered semiconductor without Coulomb interactions yields a decay of the photon-echo amplitude, which is in general nonexponential and depends on the ratio of coupling and disorder.[10] In particular, it turned out that the Anderson localization determines the long-time behavior of the photon-echo signal. The decay of the photon-echo amplitude in this situation can be related to irreversible phase relaxation in ensembles of n-level systems, of which quantum beats in three-level absorbers is the simplest example.

These findings are relevant for disordered semiconductors where the Coulomb interaction is of minor importance, as, e.g., in amorphous semiconductors. Most experiments, on the other hand, are performed on semiconductors characterized by excitonic excitations. It is, therefore, necessary to include this interaction in the theory. We find, as a result of the electron-hole coupling, that the phase coherence is enhanced. For the particular case of a long-range correlated disorder potential we obtain (for a suitable configuration of excitation pulses) no decay of the photon-echo amplitude at all. This result can be explained in terms of phase reconstruction by phase conjugation in a situation where the scattering system and the nonlinear system are identical.

This paper is organized as follows. In Sec. II we introduce the model Hamiltonian used in our study. In the next section we derive the relevant equations of motion, which are a generalization of the semiconductor Bloch equations for inhomogeneous systems. For our present purposes we neglect the exchange contributions. The photon-echo signal is computed in Sec. IV leading to a general but formal result. This result is then evaluated for the cases of short-range disordered in Sec. V and for long-range disorder in Sec. VI. Instead of using the formal result of Sec. IV in the Appendix an alternative derivation for the long-range disorder case is presented based on the equations of motion of the physical expectation values of the polarization and densities. In this equivalent formulation the physical interpretation of the approximations is more transparent.

II. MODEL

Disorder usually is related to spatial inhomogeneities of the local material properties, such as, for example, irregularities in compositions or bondings. Hence one cannot use a theory that is based on the homogeneity of the material. Therefore we use a site representation of our model semiconductor, where we assume that there is only one resonant transition at each atomic site. However, it is possible for optically excited electrons and holes to be transferred from site to site. The transfer dynamics of a single electron (hole) is described with the Hamiltonian matrix T_{ij}^{c} (T_{ij}^{v}), the indices i and j going through the optically active sites in the material. The diagonal elements of the matrix T are the local energies which are determined by the levels of an isolated atom plus the shifts due to the interaction among neighboring atoms. The off-diagonal elements describe the transition between the different sites which gives rise to kinetic motion. The matrix T is nondiagonal because the site basis which is appropriate for purely localized electrons and holes does not describe the eigenstates of delocalized electrons and holes. A diagonalization of the matrix T would lead to the introduction of energy bands and the corresponding eigenstates would be more or less localized or delocalized.

When the interaction between neighboring atoms is not regular throughout the total system we expect the diagonal elements to vary as a function of the site index. In that case also the off-diagonal elements vary in a form that is typical for the specific type of mechanism causing the disorder. In what follows we assume that the disorder induced modifications are more important for the energy shifts than for the transfer rates. We take for T the general form

$$\begin{aligned} T_{ii} &= e_i \ , \\ T_{ij} &= t_{i-j} \ , \quad \text{for } i \neq j \ . \end{aligned} \tag{2}$$

In the continuum limit, site-dependent diagonal elements cause position-dependent energy levels, i.e., a local disorder potential. More general expressions for T are possible but certainly would complicate the problem.

The total sample in our model is described as an interacting gas of electrons and holes. We assume that the Coulomb interaction in the medium has the general free space form even though the strength might be changed in the disordered material. Our tight-binding model Hamilton operator takes the form (in Hartree approximation)

$$\begin{aligned} \hat{H} = &\sum_{i,j} (T_{ji}^{c} \hat{a}_i^{\dagger} \hat{a}_j + T_{ji}^{v} \hat{b}_i^{\dagger} \hat{b}_j) + \tfrac{1}{2} \sum_{i,j} u_{ij}^{e} \hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_j \hat{a}_i \\ &+ \tfrac{1}{2} \sum_{i,j} u_{ij}^{h} \hat{b}_i^{\dagger} \hat{b}_j^{\dagger} \hat{b}_j \hat{b}_i - \sum_{i,j} u_{ij} \hat{a}_i^{\dagger} \hat{b}_j^{\dagger} \hat{b}_j \hat{a}_i \ , \end{aligned} \tag{3}$$

where $\hat{a}$ and $\hat{b}$ are the fermion annihilation operators of the electrons and holes, respectively, and u's are the Coulomb matrix elements. In general they are all different but for the sake of simplicity we take them to be equal. In contrast to the ordinary electron gas problem, our model has no translational invariance because of the site dependence of the diagonal elements in the matrix T.

We treat the coupling between the semiconductor and the external light field semiclassically assuming that the light couples to the induced, local dipoles at each site. Furthermore, we assume that the local-dipole matrix element does not depend on the site index. The local-dipole operator is given by the product $\hat{a}_i \hat{b}_i$. Using the dipole approximation at each site, we obtain the interaction

Hamiltonian in the form

$$\hat{H}_{\rm int} = -\mu \sum_l [E_l(t)\hat{a}_l^\dagger \hat{b}_l^\dagger + E_l(t)\hat{b}_l \hat{a}_l] \ . \tag{4}$$

Note that the dependence of the interaction Hamiltonian on the local field also introduces a force, the so-called light pressure force,[11] that causes translational motion of the induced dipoles in addition to the oscillatory motion. When a photon is absorbed not only its energy but also its momentum (determining the spatial phase factor of the field) must be absorbed. As long as the site dependence of the field is treated with equal footing to the site dependence of the electron and hole kinetic energies this effect is included. The continuum limit is taken by replacing the sums in the Hamiltonian (3) by integrals and the discrete site index by continuous position variables to be integrated over.

Our main goal in this paper is to represent a theory for the detected signal in a photon-echo experiment when the detector is in the phase conjugated direction. We neglect the absorption of the scattered field. According to classical electromagnetic theory the far field E_f is related to the source polarization distribution P by

$$E_f^*(\mathbf{r},t) \propto \frac{e^{i(kr-\omega t)}}{r} \int d\mathbf{r}' P(\mathbf{r}',t) e^{-i\mathbf{k}\cdot\mathbf{r}'} \ , \tag{5}$$

where $k=\omega/c$ and $\mathbf{k}$ points from the source to $\mathbf{r}$. The integral determines the radiation pattern in different directions, and its square gives the intensity measured by the detector at $\mathbf{r}$ if the detector is not looking in the directions of the incoming pump beams. Quantum mechanically we can evaluate $P(\mathbf{r},t)$ as the sum of the oscillating local dipole moments $\langle \hat{a}_i \hat{b}_i \rangle$ of the sample which are induced by the two pump fields. The observed intensity in the discrete site case is then given by

$$I_{\rm obs} \propto \left| \sum_i \langle \hat{a}_i \hat{b}_i \rangle e^{-i\mathbf{k}\cdot\mathbf{r}_i} \right|^2 . \tag{6}$$

III. EQUATIONS OF MOTION

Using the Hamiltonian (3) we follow the method of Ref. 12 to derive the Hamiltonian equations of motion. We apply the time-dependent Hartree-Fock approximation by factorizing all expectation values in terms of two operator expectation values. The loss of translation invariance, however, complicates the problem in comparison to Ref. 12 since, e.g., now

$$\langle \hat{a}_i \hat{b}_j \rangle \neq \langle \hat{a}_{i+k} \hat{b}_{j+k} \rangle \ . \tag{7}$$

Introducing a notation consistent with Ref. 12, we define

$$p_{ij} = \langle \hat{b}_i \hat{a}_j \rangle \ , \tag{8}$$

$$n_{ij}^h = \langle \hat{b}_j^\dagger \hat{b}_i \rangle \ , \tag{9}$$

$$n_{ij}^e = \langle \hat{a}_i^\dagger \hat{a}_j \rangle \ . \tag{10}$$

Since the derivation of the dynamic equations is straightforward but lengthy, we omit those details. If we formally treat the expectation values (8)–(10) as components of matrices, we can write the resulting generalization of the Bloch equations in the compact form

$$\begin{aligned}
&\partial_t p + \frac{i}{\hbar}(pT_{\rm eff}^c + T_{\rm eff}^{vt} p) = \frac{i}{\hbar}(F_{\rm eff} - n^h F_{\rm eff} - F_{\rm eff} n^e) \ , \\
&\partial_t n^e + \frac{i}{\hbar}[n^e, T_{\rm eff}^c] = -\frac{i}{\hbar}(F_{\rm eff}^\dagger p - p^\dagger F_{\rm eff}) \ , \\
&\partial_t n^h + \frac{i}{\hbar}[T_{\rm eff}^{vt}, n^h] = -\frac{i}{\hbar}(pF_{\rm eff}^\dagger - F_{\rm eff} p^\dagger) \ .
\end{aligned} \tag{11}$$

At first sight, these equations look just like the linear density matrix equations of motion for two-level systems. In reality, however, Eqs. (11) are a set of nonlinear matrix equations, where the many-body effects are hidden in the definitions of the effective energy matrices $T_{\rm eff}$ and effective field matrix $F_{\rm eff}$,

$$\begin{aligned}
(T_{\rm eff})_{ij}^c &= T_{ij}^c - \sum_l u_{il}(n_{ll}^h - n_{ll}^e)\delta_{ij} - u_{ij} n_{ij}^e \ , \\
(T_{\rm eff})_{ij}^v &= T_{ij}^v - \sum_l u_{il}(n_{ll}^e - n_{ll}^h)\delta_{ij} - u_{ij} n_{ji}^h \ , \\
(F_{\rm eff})_{ij} &= \mu E_i(t)\delta_{ij} + u_{ij} p_{ij} \ .
\end{aligned} \tag{12}$$

$T_{\rm eff}$ and $F_{\rm eff}$ describe the many-body renormalizations of the energy and the local light field.

In the case of the photon-echo problem to be analyzed the light field E consists of two components

$$\begin{aligned}
E_j(t) &= E_{j,1}(t) + E_{j,2}(t) \\
&= \tilde{E}_1(t)(e^{i\mathbf{k}_1\cdot\mathbf{R}_j - i\omega t} + e^{-i\mathbf{k}_1\cdot\mathbf{R}_j + i\omega t}) \\
&\quad + \tilde{E}_2(t)(e^{i\mathbf{k}_2\cdot\mathbf{R}_j - i\omega t} + e^{-i\mathbf{k}_2\cdot\mathbf{R}_j + i\omega t}) \ ,
\end{aligned} \tag{13}$$

where $\mathbf{R}_j$ is the position of site j. Within the rotating wave approximation we keep only the first terms in the parentheses on the right-hand side of Eq. (13). The amplitudes can be written as

$$\begin{aligned}
\tilde{E}_1(t) &= \Theta_1 \delta(t) \ , \\
\tilde{E}_2(t) &= \Theta_2 \delta(t-\tau)
\end{aligned} \tag{14}$$

because we are interested in the case where the pulse duration is smaller than all other relevant time scales in the problem except the optical frequency.

In what follows we shall assume that the exciting fields are weak enough that we can treat Eqs. (11) perturbatively. We especially neglect all products of polarizations and populations, which allows us to write the equations in the form

$$\begin{aligned}
&\partial_t p_{ij} + \frac{i}{\hbar}[(pT^c + T^{vt}p)_{ij} - u_{ij}p_{ij}] \\
&\qquad = \frac{i\mu}{\hbar}(E_i\delta_{ij} - E_j n_{ij}^h - E_i n_{ij}^e) \ , \\
&\partial_t n_{ij}^e + \frac{i}{\hbar}[n^e, T^c]_{ij} = -\frac{i\mu}{\hbar}(E_i p_{ij} - E_j p_{ji}^*) \ , \\
&\partial_t n_{ij}^h + \frac{i}{\hbar}[T^{vt}, n^h]_{ij} = -\frac{i\mu}{\hbar}(E_j p_{ij} - E_i p_{ji}^*) \ .
\end{aligned} \tag{15}$$

The remaining term proportional to the Coulomb matrix element u describes the attraction between the electrons

and holes, which produces the exciton structure in the optical-absorption spectrum.

A handy notation is obtained if we understand $E_i(t)$ as a component of the diagonal matrix $\mathcal{E}$ and define operators $\mathcal{V}$ and $\mathcal{H}^\dagger$ operating on matrices by setting

$$[\mathcal{V}(X)]_{ij}=u_{ij}X_{ij} \tag{16}$$

and

$$\mathcal{H}^\dagger(X)=\frac{1}{\hbar}[XT^c+T^{vt}X-\mathcal{V}(X)] . \tag{17}$$

With these definitions the equations of motion take the form

$$\begin{aligned}
&\partial_t p+i\mathcal{H}^\dagger(p)=\frac{i\mu}{\hbar}[\mathcal{E}(t)-n^h\mathcal{E}(t)-\mathcal{E}(t)n^e] ,\\
&\partial_t n^e+\frac{i}{\hbar}[n^e,T^c]=-\frac{i\mu}{\hbar}[\mathcal{E}^\dagger(t)p-p^\dagger\mathcal{E}(t)] ,\\
&\partial_t n^h+\frac{i}{\hbar}[T^{vt},n^h]=-\frac{i\mu}{\hbar}[p\mathcal{E}^\dagger(t)-\mathcal{E}(t)p^\dagger] .
\end{aligned} \tag{18}$$

IV. PHOTON-ECHO SIGNAL

In this section we solve the semiconductor Bloch equation (18) perturbatively up to third order. For the photon-echo configuration considered, the echo signal travels in the direction $2\mathbf{k}_2-\mathbf{k}_1$. Hence we have to obtain the polarization p up to second order in Θ_2 and first order in Θ_1, together to third order in the field amplitudes. We solve the equations iteratively.

To first order we have

$$\partial_t p^{(1)}+i\mathcal{H}^\dagger(p^{(1)})=\frac{i\mu}{\hbar}\mathcal{E}_1(t) . \tag{19}$$

Since both pulse envelopes were assumed to be δ functions in time, we write

$$\mathcal{E}_1(t)_{ij}=(\mathcal{E}_1)_{ij}\delta(t)=\Theta_1\delta_{ij}e^{i\mathbf{k}_1\cdot\mathbf{r}_i}\delta(t) \tag{20}$$

and similarly for the second pulse. The integration can be formally performed and we obtain the first-order contribution to the polarization in the form

$$p^{(1)}(t)=\frac{i\mu}{\hbar}e^{-it\mathcal{H}^\dagger}(\mathcal{E}_1)\Theta(t) . \tag{21}$$

In the next step we solve the second-order contribution for the populations. Because of the short pulse duration, we neglect all transfer effects during the pulse. Keeping only the components that are relevant for the photon echo, we obtain

$$\partial_t n^{e(2)}=\frac{i\mu}{\hbar}p^{(1)\dagger}\mathcal{E}_2(t) , \tag{22}$$

$$\partial_t n^{h(2)}=\frac{i\mu}{\hbar}\mathcal{E}_2(t)p^{(1)\dagger} . \tag{23}$$

The solutions of these equations are given by

$$\begin{aligned}
&n^{e(2)}(t)=\frac{\mu^2}{\hbar^2}[e^{i\tau\mathcal{H}}(\mathcal{E}_1^*)\mathcal{E}_2]\Theta(t-\tau) ,\\
&n^{h(2)}(t)=\frac{\mu^2}{\hbar^2}[\mathcal{E}_2e^{i\tau\mathcal{H}}(\mathcal{E}_1^*)\Theta(t-\tau)] .
\end{aligned} \tag{24}$$

In the third-order equation for the polarization we again neglect on the right-hand side all the terms irrelevant for the photon echo and obtain

$$\partial_t p^{(3)}+i\mathcal{H}^\dagger(p^{(3)})=-\frac{i\mu}{\hbar}[\mathcal{E}_2(t)n^{e(2)}+n^{h(2)}\mathcal{E}_2(t)] \tag{25}$$

or, after an integration,

$$p^{(3)}(t)=-\frac{i2\mu^3}{\hbar^3}e^{-i(t-\tau)\mathcal{H}^\dagger}[\mathcal{E}_2e^{i\tau\mathcal{H}}(\mathcal{E}_1^*)\mathcal{E}_2] . \tag{26}$$

As discussed in Sec. II the detected signal can be computed from the polarization density. The local polarization at site i is given by $p_{ii}^{(3)}$ for the phase conjugated component. Using Eq. (6), we find the observed signal traveling in the direction of $\mathbf{k}$ from the source as

$$I_{\rm obs}\propto\left|\sum_i p_{ii}^{(3)}(t)e^{-i\mathbf{k}\cdot\mathbf{r}_i}\right|^2 . \tag{27}$$

The maximum signal for the photon echo is expected to come approximatively a time delay τ after the second pulse. By defining a diagonal matrix,

$$(\Lambda_{\mathbf{k}})_{ij}=\delta_{ij}e^{i\mathbf{k}\cdot\mathbf{r}_i} , \tag{28}$$

which has on the diagonal the phase factors at each site we can write the maximum signal in the form

$$\begin{aligned}
I_{\rm obs}&\propto|{\rm Tr}[\Lambda_{\mathbf{k}}^\dagger e^{-i\tau\mathcal{H}^\dagger}(\Lambda_{\mathbf{k}_2}e^{i\tau\mathcal{H}}(\Lambda_{\mathbf{k}_1}^\dagger)\Lambda_{\mathbf{k}_2})]|^2\\
&=|{\rm Tr}[e^{-i\tau\mathcal{H}}(\Lambda_{\mathbf{k}}^\dagger)\Lambda_{\mathbf{k}_2}e^{i\tau\mathcal{H}}(\Lambda_{\mathbf{k}_1}^\dagger)\Lambda_{\mathbf{k}_2}]|^2 ,
\end{aligned} \tag{29}$$

where the second step follows since

$${\rm Tr}[B\mathcal{H}^\dagger(A)]={\rm Tr}[\mathcal{H}(B)A] \tag{30}$$

for any matrices A and B.

If we can separate the length scales of the light wavelength and the disorder by assuming, for example, that the wavelength of the light is large in comparison to the length scale of the disorder, we can perform the summation independently for the phase factors and the dynamical evolution. It is easy to see that a nonvanishing contribution for the signal is only obtained in the direction $\mathbf{k}=2\mathbf{k}_2-\mathbf{k}_1$. The approximation, which allows one to separate the length scales, is equivalent to neglecting the mechanical effect related to the momentum of the light. Another way of looking at this approximation is to say that within each wavelength of light there is place for several regions, which already contain all the characteristics of the total sample. For example, if the system is completely localized by the disorder, an ensemble average taken within a wavelength gives the same result as taken over the whole system. In this limit the field has only a parametric spatial dependence. The observed intensity is given by

$$I_{\rm obs}\propto|{\rm Tr}[e^{-i\tau\mathcal{H}}(\overleftrightarrow{1})e^{i\tau\mathcal{H}}(\overleftrightarrow{1})]|^2\delta_{\mathbf{k},2\mathbf{k}_2-\mathbf{k}_1} . \tag{31}$$

The results (29) and (31) are formal and, hence, very general in nature. The excitonic effects due to the electron-hole Coulomb attraction are included. No assumptions about the nature of the disorder have been made. In the

following sections we evaluate the theory in some limiting cases.

V. SHORT-RANGE DISORDER

First we study the case of short-range disorder, i.e., the parameter region where Eq. (31) is valid. For the case of amorphous semiconductors, where excitonic effects seem to be masked by disorder, we completely neglect the Coulomb interaction in the lowest-order approximation. It is generally accepted that the disorder potential in amorphous semiconductors is short range (i.e., on a typical length scale of 5 Å) and strong (of the order of 0.1 eV). A further simplification can be introduced if we excite the amorphous semiconductor by photons with energy well below the mobility gap. Then most excited electron-hole pairs are in states where one of the particles is localized in deep tail states, and the other is energetically close to the mobility edge. This situation can be modeled by taking $T^v_{ij}=0$ for $i\neq j$. Then the holes are strongly localized, which in the theory is manifested by the absence of the hole transfer. To be more realistic we also investigate the effect of the Coulomb interaction between electrons and holes in this case. The opposite limit, a nearly perfectly ordered crystal, is not treated here. In this case the photon-echo amplitude decays if we introduce scattering by disorder because the decay rate is simply related to the scattering rate, i.e., to the conductivity.[10]

If we neglect the Coulomb interaction, the time evolution operator can explicitly be written as

$$e^{i\tau\mathcal{H}}(X)=e^{i\tau T^c}Xe^{i\tau T^{vt}} \tag{32}$$

yielding

$$I_{\rm obs}\propto|{\rm Tr}(e^{-i\tau T^c}e^{-i\tau T^{vt}}e^{i\tau T^c}e^{i\tau T^{vt}})|^2 . \tag{33}$$

Equation (33) shows that the photon-echo amplitude does not decay if we have

$$[T^c,T^{vt}]=0 . \tag{34}$$

The relation (34) holds for an ensemble of uncoupled two-level absorbers, since T^c and T^v are site diagonal. In this case the mechanisms included in our theory do not lead to any dephasing. Because of Eq. (34) there exists a common set of eigenvectors $\mathbf{a}^\lambda$ with real eigenvalues ϵ^v_λ and ϵ^c_λ. It can easily be seen that the corresponding unitary transformation also diagonalizes the interaction with the external field indicating a selection rule for optical transitions. We can therefore state that whenever we have an optical selection rule, then there is no irreversible dephasing. Apart from the trivial case of uncoupled two-level absorbers we mention as examples the somewhat academic case of a perfect crystal without Coulomb interaction. This system can be viewed as an ensemble of inhomogeneously distributed two-level absorbers, each labeled by a k vector. Other examples are ensembles of dimers.[10]

In a general disordered system Eq. (34) does not hold. As a representative example we treat the case where the holes are completely localized, i.e.,

$$T^v_{ij}=\delta_{ij}\varepsilon^v_i . \tag{35}$$

We keep the Coulomb term to obtain a generalization of Eq. (33) for the electron motion. Inserting Eq. (35) into Eq. (31) we obtain

$$I_{\rm obs}\propto\left|\sum_{l,m}e^{-i(\varepsilon^v_l-\varepsilon^v_m)\tau}U_{lm}(\tau)U_{ml}(-\tau)\right|^2 , \tag{36}$$

where the matrix $U(\tau)$ obeys the equation

$$\partial_\tau U(\tau)=i[T^cU(\tau)-\mathcal{V}(U(\tau))]$$
$$\text{with } U(\tau=0)=\overleftrightarrow{1} . \tag{37}$$

The matrix Eq. (37) is equivalent to a set of Schrödinger equations for a particle moving in the potential of a local point charge in various positions. The matrix element U_{ij} is the ith component of the wave function for an electron, which started initially from the site j, where the attracting point charge lies. For the subsequent discussion it is instructive to use the notation

$$H^j_{kl}\equiv T^c_{kl}-u_{kj}\delta_{lk} . \tag{38}$$

The Hamiltonian matrix is only parametrically dependent on the site j of the attracting charge. Since the hole energies ε^v_l are assumed to be randomly distributed we replace the exponent in the sum on the right-hand side of Eq. (36) by its configurational average. Furthermore we choose the matrix elements of T^c to be real. This leads to

$$I_{\rm obs}\propto\Big|[1-g(\tau)]\sum_l U_{ll}(\tau)U_{ll}(-\tau)$$
$$+g(\tau){\rm Tr}[U(\tau)U(-\tau)]\Big|^2 \tag{39}$$

where $g(\tau)=|\langle e^{-\varepsilon^v\tau}\rangle|^2$. The physical contents of the sum of the product of the diagonal terms are better shown if we manipulate it into the form

$$\sum_l U_{ll}(\tau)U_{ll}(-\tau)=\sum_j{\rm Tr}[e^{iH^j(\tau)}\rho^j(0)e^{-H^j(\tau)}\rho^j(0)]$$
$$=\sum_j{\rm Tr}[\rho^j(0)\rho^j(\tau)]\equiv\Phi_{00}(\tau) , \tag{40}$$

where $[\rho^j(0)]_{lm}=\delta_{lj}\delta_{jm}$ is the initial density matrix for the single-particle problem determined by the Hamiltonian (38). Hence Eq. (40) describes a kind of configurational sum of density-density correlation functions for electrons in the conduction band attracted to localized holes.

The result for the particular case when the Coulomb interaction is neglected has been derived and discussed previously.[10] Here we note that the density-density correlation function of particles in a band with diagonal disorder has well-known properties as revealed by various theories of Anderson localization. These properties are reflected in the nonlinear optical response, if the model assumptions of this section are met. The strongly localized conduction-band case ($T^c_{ij}=0$, $i\neq j$) evidently gives

$$\Phi_{00}(\tau)=N , \tag{41}$$

since the electrons are unable to move and the system

reduces to an ensemble of uncoupled two-level absorbers. For finite coupling, however, still in the localized regime, $\Phi_{00}(\tau)$ decays initially and attains a finite saturation value, which can be shown to be roughly proportional to $\xi_{\rm loc}^{-2}$, where $\xi_{\rm loc}$ is the localization length.[10] The signal finally decays to zero if the Anderson transition is reached. The decay rate for intermediate times in the delocalized regime is given by the diffusion constant. The fastest decay follows if we take as an extreme case a perfectly ordered conduction band. If only nearest-neighbor coupling J_c in the conduction band is considered the density-density correlation function is given by

$$\Phi_{00}(\tau)=NJ_0^{2d}(2J_c\tau) , \tag{42}$$

where d is the spatial dimension and J_0 is the zeroth-order Bessel function.

In order to understand the behavior of the photon-echo amplitude it is instructive to consider the photon echo in an ensemble of n-level absorbers. Let $n=1$ be the ground state, which is optically coupled to all higher states. We assume that all transition energies ω_{1i} are inhomogeneously distributed. Let us start with $n=3$. One particular three-level absorber produces quantum beats with a beat frequency given by the energy separation $\Delta\omega=\omega_{13}-\omega_{12}$. For an inhomogeneous distribution of such systems the signal initially decays with a rate given by the distribution function of $\Delta\omega$ and attains a constant long-time value. Qualitatively the same behavior is found for $n>3$ systems; the long-time limit of the photon-echo signal, however, decreases with increasing n. For $n\rightarrow\infty$ there can be irreversible phase relaxation even in a single n-level system.[13]

There is a close analogy of the n-level ensemble with our semiconductor model with strongly localized holes. The ground state $n=1$ corresponds to the localized hole state, while the excited states are the eigenstates, to which the hole state is optically coupled. For strongly localized electrons only the excited state corresponding to the same site is coupled to the hole state, and there is no dephasing. Increasing coupling (and decreasing disorder) leads to localized states with larger and larger spatial extent. This implies that a given site contributes to more and more eigenstates, i.e., n increases and the long-time value of the photon echo decreases. The photon echo for long time vanishes if the electronic eigenstates become delocalized, since then every (or nearly every) site contributes to infinitely many eigenstates. In this case complete irreversible phase relaxation occurs as for n-level absorbers in the limit $n\rightarrow\infty$.

Note that the appearance of a density-density correlation function in Eq. (39), which is conceptually related to transport, does not mean that particle *transport* is responsible for dephasing in this particular situation. It rather indicates a correlation of *amplitude* propagation in two distinct time intervals due to the static disorder. The propagation in the interval $[0,\tau]$ is correlated with the propagation in the interval $[\tau,2\tau]$. Formally this correlation reflects itself in the appearance of the correlation function.

It is interesting to speculate how inelastic interactions with dynamical degrees of freedom, e.g., with phonons, destroy optical phase coherence in the situation at hand. Since the electron-phonon interaction tends to delocalize carriers, it will induce an increased decay rate of the photon echo. Phonon-induced delocalization is most pronounced close to the mobility edge, where the localization length exceeds the inelastic scattering length.[14] Excitations involving states close to the mobility edges, therefore, will reveal phase-relaxation rates due to phonons which are much larger than those related to strongly localized states.

The stabilizing action of the Coulomb potential on the phase coherence can be demonstrated most easily for strongly localized holes and an ordered conduction band. Because of the translational symmetry of the conduction-band Hamiltonian we have

$$\begin{aligned} T^c_{i,j}&=T^c_{i-j,0} ,\\ u_{i,j}&=u_{i-j,0} . \end{aligned} \tag{43}$$

In this case Eq. (39) simplifies to

$$I_{\rm obs}\propto\{[1-g(\tau)]|U_{00}(\tau)|^2+g(\tau)\}^2 , \tag{44}$$

where the matrix $U(\tau)$ obeys Eq. (37). The solution can be expressed in terms of excitonic envelopes (not necessarily hydrogenic),

$$T^c\Psi^n-\mathcal{U}\Psi^n=\varepsilon_n\Psi^n , \tag{45}$$

where we have $\mathcal{U}_{lm}=\delta_{lm}u_{l0}$. The matrix U is then given by

$$U(t)=\sum_n e^{i\varepsilon_n t}\Psi^n\Psi^{n\dagger} . \tag{46}$$

The expression for $|U_{00}(\tau)|^2$ can be evaluated and we obtain

$$|U_{00}(\tau)|^2=\left|\sum_n|\Psi_0^n|^2e^{i\varepsilon_n\tau}\right|^2 . \tag{47}$$

The sum contains the discrete and the continuous spectrum of Eq. (45). For long times the continuous spectrum does not contribute because it decays to zero. Also $g(\tau)$ vanishes for long times and we, therefore, obtain for large τ

$$I_{\rm obs}\propto\left|\sum_n^{\rm discrete}|\Psi_0^n|^2e^{i\varepsilon_n\tau}\right|^4 . \tag{48}$$

To illustrate the situation we solve the eigenvalue problem for two simple cases. First for a contact Coulomb potential in one dimension, $u_{l,0}=u\delta_{l,0}$ and $T^c_l=-T^c\delta_{l,\pm1}$. The problem can be solved in the discrete case too but the results in the continuum limit are more instructive. The spectrum has a band and a single bound state which has the binding energy

$$E\approx-\frac{u^2}{4T^c}\rightarrow-\frac{\hbar^2}{2m^*r_B^2} \tag{49}$$

with the corresponding eigenstate

$$\Psi_j \approx \left[\frac{u}{2T^c}\right]^{1/2} e^{-(u/2T^c)|j|} \rightarrow \left[\frac{1}{r_B}\right]^{1/2} e^{-|x|/r_B} . \quad (50)$$

In the long-time limit the photon-echo signal approaches the limit

$$I_{\text{obs}} \propto \left[\frac{u}{2T^c}\right]^4 \propto \frac{1}{|j|^4} \propto \frac{1}{r_B^4} , \quad (51)$$

i.e., a constant value given by the reciprocal Bohr radius r_B to the fourth power. A true $1/r$ potential in three dimensions in the continuum limit has the binding energies for the bound states given by

$$E_n = -\frac{\hbar^2}{2m^* r_B^2}\frac{1}{n^2} \quad (52)$$

and the corresponding eigenstates at the origin have the values

$$\Psi_{n,l=0}(\mathbf{r}=0) \propto \left[\frac{1}{r_B^3 n^3}\right]^{1/2} . \quad (53)$$

This yields the photon-echo signal proportional to

$$I_{\text{obs}} \propto \frac{1}{r_B^{12}} . \quad (54)$$

In the long-time limit we have included the leading term only. The general behavior is the same as in the one-dimensional case. After a very fast initial decay, determined by the spread of excitonic energies, the amplitude approaches a constant value given by the Bohr radius to power $-4d$, where d is the dimension. This result indicates that the Coulomb interaction tends to stabilize the phase of an optical excitation in a disordered semiconductor.

VI. LONG-RANGE DISORDER POTENTIALS AND WANNIER EXCITONS

In this section we study the limit of long-range disorder, assuming that the length scale, in which the disorder changes the material properties, exceeds the Bohr radius of the exciton. We no longer assume that the photon momentum is negligible and, as a consequence, the exciton which is interacting with the light also must change its center-of-mass state. We use here the formal result of Eq. (29), but for instructive reasons we show in the Appendix how to obtain the same results from the semiconductor Bloch equations in the continuum representation.

We write Eq. (29) explicitly and obtain

$$\mathrm{Tr}[e^{-i\tau\mathcal{H}}(\Lambda_k^\dagger)\Lambda_{\mathbf{k}_2} e^{i\tau\mathcal{H}}(\Lambda_{\mathbf{k}_1}^\dagger)\Lambda_{\mathbf{k}_2}] = \sum_{i,j} e^{i\mathbf{k}_2\cdot(\mathbf{r}_i+\mathbf{r}_j)}[e^{-i\tau\mathcal{H}}(\Lambda_k^\dagger)]_{ij}[e^{i\tau\mathcal{H}}(\Lambda_{\mathbf{k}_1}]_{ji} . \quad (55)$$

In the continuum limit $\mathbf{r}_i$ and $\mathbf{r}_j$ will be continuous variables denoted by $\mathbf{r}_1$ and $\mathbf{r}_2$ and consequently we have to express the Hamiltonian in the continuum representation. In the long-range disorder case we assume the Hamilton operators to take the form describing a particle in a potential caused by the disorder

$$\mathcal{H}(X)(\mathbf{r}_1,\mathbf{r}_2) = \left[\omega_g - \frac{\hbar}{2m_e}\nabla_1^2 - \frac{\hbar}{2m_h}\nabla_2^2\right]X(\mathbf{r}_1,\mathbf{r}_2) - \frac{1}{\hbar}[V_c(|\mathbf{r}_1-\mathbf{r}_2|) - \Phi_c(\mathbf{r}_1) - \Phi_v(\mathbf{r}_2)]X(\mathbf{r}_1,\mathbf{r}_2) . \quad (56)$$

Here m_e and m_h are the electron and hole masses, respectively. V_{eh} denotes the Coulomb potential and Φ_c and Φ_v are the local disorder potentials for electrons and holes, respectively.

For this purpose we introduce the center-of-mass and relative coordinates. Our goal is to describe the system in terms of internal and center-of-mass motion and to separate the variables in the Hamiltonian (56). First we relate the coordinate $\mathbf{r}_1$ to the electron and $\mathbf{r}_2$ to the hole motion, respectively. The standard notation,

$$\mathbf{r}_1 = \mathbf{R} - \frac{m_h}{M}\mathbf{r} , \quad \mathbf{r}_2 = \mathbf{R} + \frac{m_e}{M}\mathbf{r} , \quad \mu_{\text{ex}} = \frac{m_e m_h}{M} , \quad M = m_e + m_h , \quad (57)$$

is used and in addition we denote $\alpha = (m_e - m_h)/M$. The sums in Eq. (55) are transformed into integrals over $\mathbf{r}$ and $\mathbf{R}$. In the new coordinates the Hamiltonian $\mathcal{H}$ is defined by the equation

$$\mathcal{H}(X)(\mathbf{r},\mathbf{R}) = \left[\omega_g - \frac{\hbar}{2M}\nabla_R^2 - \frac{\hbar}{2\mu_{\text{ex}}}\nabla_r^2 - \frac{1}{\hbar}V_c(|\mathbf{r}|)\right] \times X(\mathbf{r},\mathbf{R}) + \frac{1}{\hbar}\left[\Phi_c\left[\mathbf{R} - \frac{m_h}{M}\mathbf{r}\right] + \Phi_v\left[\mathbf{R} + \frac{m_e}{M}\mathbf{r}\right]\right]X(\mathbf{r},\mathbf{R}) . \quad (58)$$

At this point we use the assumption that the disorder is of long range, i.e., the disorder potential does not vary appreciably within an exciton Bohr radius, allowing us to neglect the $\mathbf{r}$ dependence in the disorder potentials. Physically this means that an exciton is not deformed but only changes its center-of-mass state as a consequence of the disorder. With this assumption the Hamiltonian $\mathcal{H}$ is approximatively separable and the time evolution operator can be given in the form

$$e^{-i\tau\mathcal{H}}(\Lambda_k^\dagger)(\mathbf{r},\mathbf{R}) \approx e^{-i\tau[w_g - (\hbar/2\mu_{ex})\nabla_r^2 - (1/\hbar)V_c(|\mathbf{r}|)]}[\delta(\mathbf{r})]e^{-i\tau[(-\hbar/2M\nabla_R^2 + \Phi_c(\mathbf{R}) + \Phi_v(\mathbf{R})]}(e^{-i\mathbf{k}\cdot\mathbf{R}}) . \quad (59)$$

The other factor that potentially is able to deform the excitons is the light field. Its effect is manifested by the fact that in Eq. (55) the sites i and j and consequently in the continuum limit the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ are reversed in the second time evolution operator. The internal motion is disturbed by the imbalance of the momentum transfer to the electron and the hole in the optical process. When transformed into relative and center-of-mass coordinates the first coordinate is going to be $-\mathbf{r}$ instead of $\mathbf{r}$ and the second coordinate $\mathbf{R}+\alpha\mathbf{r}$ instead of $\mathbf{R}$. We see that in the signal the internal and the center-of-mass motion are still coupled. We now argue that, because the range of $\mathbf{r}$ is restricted inside a Bohr radius and because the features we study take place on a larger spatial scale, we can neglect this coupling by setting $\alpha=0$ (note if $m_e=m_h$ the decoupling is exact). The phase factor is then also given in terms of $\mathbf{R}$ only,

$$e^{i\mathbf{k}_2\cdot(\mathbf{r}_1+\mathbf{r}_2)}=e^{i\mathbf{k}_2\cdot(2\mathbf{R}+\alpha\mathbf{r})}\approx e^{i2\mathbf{k}_2\cdot\mathbf{R}} . \tag{60}$$

After this approximation the internal and the external motion are completely decoupled and only the center-of-mass motion is affected by the disorder in the environment. With these approximations we have reduced the system to a set of induced oscillating dipoles propagating through the sample. The center-of-mass propagation of these dipoles is influenced by the interaction with both the photons and the disorder in the sample.

We write the Hamiltonians for the relative and center-of-mass motion (CM) as

$$\begin{aligned}\hat{H}_{\rm ex}(\mathbf{r})&=\omega_g-\frac{\hbar}{2\mu_{\rm ex}}\nabla_r^2-\frac{1}{\hbar}V_c(|\mathbf{r}|) ,\\ \hat{H}_{\rm CM}(\mathbf{R})&=\frac{-\hbar}{2M}\nabla_R^2+\Phi_c(\mathbf{R})+\Phi_v(\mathbf{R}) .\end{aligned} \tag{61}$$

The Hamiltonians are Hermitian so that the time evolution operator (59) is essentially formed of two wave functions, one for the internal dipole oscillation and the second for the center-of-mass motion. Inserting the approximations in the expression of the signal we obtain the result

$$\begin{aligned}I_{\rm obs}&\propto\left|\int d\mathbf{r}\,e^{-i\tau\hat{H}_{\rm ex}(\mathbf{r})}[\delta(\mathbf{r})]\right|^2\left|\int d\mathbf{R}\,e^{i2\mathbf{k}_2\cdot\mathbf{R}}e^{-i\tau\hat{H}_{\rm CM}(\mathbf{R})}(e^{-i\mathbf{k}\cdot\mathbf{R}})e^{i\tau\hat{H}_{\rm CM}(\mathbf{R})}(e^{-i\mathbf{k}_1\cdot\mathbf{R}})\right|^2\\ &\propto\left|\int d\mathbf{R}\,e^{i2\mathbf{k}_2\cdot\mathbf{R}}e^{-i\tau\hat{H}_{\rm CM}(\mathbf{R})}(e^{-i\mathbf{k}_1\cdot\mathbf{R}})e^{i\tau\hat{H}_{\rm CM}(\mathbf{R})}(e^{-i\mathbf{k}_1\cdot\mathbf{R}})\right|^2 .\end{aligned} \tag{62}$$

The last step follows from the conversation of the normalization for the wave functions. For the detection direction $\mathbf{k}$ we can write the signal in the Dirac bracket form

$$I_{\rm obs}\propto|\langle\mathbf{k}|e^{-i\hat{H}_{\rm CM}\tau}e^{i2\mathbf{k}_2\cdot\hat{R}}e^{i\hat{H}_{\rm CM}\tau}|-\mathbf{k}_1\rangle|^2 . \tag{63}$$

The phase conjugated signal is obtained in the direction $\mathbf{k}=2\mathbf{k}_2-\mathbf{k}_1$. Note that the exponential operator of $\mathbf{k}_2\cdot\mathbf{R}$ is a momentum shift operator describing the absorption of the momentum of the second pulse. No dephasing takes place if no disorder exists and $\hat{H}_{\rm CM}$ is just a function of momentum operators.

In the diffusive limit when the localized character of the excitons is dominant we should use the position representation. We can write

$$\begin{aligned}I_{\rm obs}\propto\Bigg|\int d\mathbf{R}\,d\mathbf{R}_1d\mathbf{R}_2e^{-i(2\mathbf{k}_2-\mathbf{k}_1)\cdot\mathbf{R}}e^{i2\mathbf{k}_2\cdot\mathbf{R}_1}e^{-i\mathbf{k}_1\cdot\mathbf{R}_2}\\ \times\langle\mathbf{R}|e^{-i\hat{H}_{\rm CM}\tau}|\mathbf{R}_1\rangle\langle\mathbf{R}_1|e^{i\hat{H}_{\rm CM}\tau}|\mathbf{R}_2\rangle\Bigg|^2 .\end{aligned} \tag{64}$$

In the diffusive limit only those combinations of the matrix elements of the time evolution operator are dominant in the configurational average, which start and end in the same point. This reduces one integral and we have

$$\begin{aligned}I_{\rm obs}\propto\Bigg|\int d\mathbf{R}\,d\mathbf{R}_1e^{-i2\mathbf{k}_2\cdot(\mathbf{R}-\mathbf{R}_1)}\\ \times\langle|\langle\mathbf{R}_1|e^{i\hat{H}_{\rm CM}\tau}|\mathbf{R}\rangle|^2\rangle_{\rm conf}\Bigg|^2 .\end{aligned} \tag{65}$$

Because of the stochasticity of $\hat{H}_{\rm CM}$, the matrix elements in average are translationally invariant so that we obtain

$$I_{\rm obs}\propto\left|\int d\mathbf{R}\,e^{i2\mathbf{k}_2\cdot\mathbf{R}}\langle|\langle\mathbf{R}|e^{i\hat{H}_{\rm CM}\tau}|\mathbf{R}=0\rangle|\rangle_{\rm conf}\right|^2 . \tag{66}$$

The result is, hence, a spatial Fourier transform of the transition probability for moving under the influence of the disorder potential a distance $|\mathbf{R}|$ from the starting point in time τ. In the diffusive limit this probability has the typical exponential form

$$\langle|\langle\mathbf{R}|e^{-i\hat{H}_{\rm CM}\tau}|\mathbf{R}=0\rangle|^2\rangle_{\rm conf}=\left[\frac{1}{4\pi D\tau}\right]^{3/2}e^{-R^2/4D\tau} , \tag{67}$$

which, after the Fourier transformation, gives

$$I_{\rm obs}\propto e^{-8k_2^2D\tau}=e^{-(4/3)k_2^2\langle\mathbf{R}^2(\tau)\rangle} , \tag{68}$$

where $\langle\mathbf{R}^2(\tau)\rangle$ is the mean-square displacement

$$\langle\mathbf{R}^2(\tau)\rangle=6D\tau . \tag{69}$$

The dephasing time is given by the time the exciton needs to diffuse over distances comparable to the wavelength of light. If, on the other hand, the disorder potential produces localization of excitons, the transition probability has a finite long-time value implying a long-time value of the photon-echo amplitude, in this particular situation.

In the following we will neglect the possibility of the photon-echo amplitude to decay due to diffusion, which

can be a rather slow process,[15] by taking $\mathbf{k}_2=0$. Experimentally this situation can be realized by applying at time $t=\tau$ two pulses from opposite directions $\mathbf{k}_2$ and $-\mathbf{k}_2$ simultaneously. We are faced with the following question. Why is there no dephasing, although disorder of arbitrary strength is still present? Formally the answer follows simply from Eq. (63) when $\mathbf{k}_2=0$. The two time evolution operators cancel each other. It is instructive to interpret this result physically. At time $t=0$ a plane wave (light or excitonic) is prepared which then develops in time. At the time of the second pulse, which in order to have $\mathbf{k}_2=0$ is applied from two opposite directions simultaneously, the excitation has developed random phases and reads

$$\sum_{\mathbf{k}} |\mathbf{k}\rangle\langle\mathbf{k}|e^{-i\hat{H}_{\mathrm{CM}}\tau}|\mathbf{k}_1\rangle \ .$$

Now the nonlinear interaction produces an excitation proportional to

$$\sum_{\mathbf{k}} |\mathbf{k}\rangle\langle -\mathbf{k}|e^{-i\hat{H}_{\mathrm{CM}}\tau}|\mathbf{k}_1\rangle^* \ ,$$

which further develops in time according to

$$\sum_{\mathbf{k}} e^{-i\hat{H}_{\mathrm{CM}}(t-\tau)}|\mathbf{k}\rangle\langle -\mathbf{k}|e^{-i\hat{H}_{\mathrm{CM}}\tau}|\mathbf{k}_1\rangle^* \ .$$

This is essentially the initial wave with $\mathbf{k}_1$ replaced by $-\mathbf{k}_1$. The situation is equivalent to the case where an initial plane wave is scattered in a nonlinear medium. The nonlinear interaction conjugates the phase of the scattered wave, which is then transformed back into the phase conjugated plane wave at time 2τ. A similar case, in a stationary situation, however, has recently been treated by Kravtsov *et al.*,[16] Our result is a further manifestation of the reconstructive property of the phase conjugated wave. As a consequence, purely kinematic effects on the center of mass of exciton do not cause dephasing. Dephasing is caused by mixing of the internal states, which occurs due to a short-range disorder or in lesser degree by taking the photon momentum fully into account.

What happens if the disorder potential fluctuates on length scales comparable to or shorter than the Bohr radius? The excitonic transitions do not remain independent anymore. The internal dipole is excited always into a coherent mixture leading to stronger dephasing of the photon-echo signal for similar reasons to those explained in Sec. V. The dephasing rate will again be determined by the energetic range of the excitonic states and can therefore be rather large. A further cause of excitonic dephasing is a mass asymmetry ($\alpha>0$) together with a short-range disorder potential because it causes internal exciton states to mix and the effect is similar to that caused by the disorder. Notice that the mass imbalance causes mixing even if the disorder is not present. Clearly, more work is needed to investigate the influence of short-range potentials on Wannier excitons in detail.

VII. CONCLUSIONS

We have discussed the influence of static disorder on the decay of the spontaneous photon-echo amplitude in disordered semiconductors. The most important contribution of the Coulomb interaction, the attraction between electrons and holes, is included. One might be surprised that static disorder produces irreversible phase relaxation at all. Scattering on impurities is a purely coherent process, there is no phase relaxation whatsoever. Also Anderson localization is a coherent constructive interference of enhanced backscattering of partial waves.

The key for understanding this puzzle is provided by looking at quantum beats in n-level systems. We have pointed out that whenever more than one state is dipole coupled to a given ground state, quantum beats occur, which for an inhomogeneous infinite ensemble of such systems add up to a decaying nonlinear signal. There is a finite long-time value of the nonlinear signal, if only a finite number of states is dipole coupled to a given ground state. On the other hand, complete relaxation occurs if infinitely many excited states with a dense energy spectrum are coupled to a given ground state. This corresponds to delocalization within a disordered conduction band. The argument also applies if a single excited state is dipole coupled to more than one ground state. We can also have the dipole coupling of several ground states to a group of excited states. An optical selection rule has been shown to lead to a nondecaying signal. Special cases are an ensemble of uncoupled two-level absorbers and a perfect crystal, both without Coulomb interaction.

The Coulomb interaction has been shown to stabilize the photon-echo amplitude. The special case of Wannier excitons in a long-range disorder potential closely resembles a time-resolved configuration, where a plane wave is reconstructed within the scattering nonlinear medium due to phase conjugation. This corresponds to a constant photon-echo amplitude. Again in this situation there is no mixing of more than one exciton state in an optical dipole transition. All interactions which lead to an admixture of different excitonic states, in particular a short-range disorder potential, produce a decay of the photon echo. It remains an open question, whether the exchange contributions to the Coulomb interaction, which have been ignored in the present treatment, can be an additional source of phase relaxation. This problem seems to require heavy computation work which is in progress to find a definite answer.

Finally we may speculate as to what one should expect in various real situations. First of all one must remember that we have neglected all other relaxation mechanisms except the scattering due to disorder. Hence our results are describing only situations in which disorder scattering is the dominating decay mechanism. We base our speculation on the simple trends obtained; fast dephasing is related to short-range disorder and slow decay is related to long-range disorder. Amorphous semiconductors are characterized by a strong short-range disorder, which seems to mask excitonic effects. In addition, for not too high photon energies electrons and holes are located energetically in states with quite different character. Either the electrons are localized and the holes are free or vice versa. We expect a very fast phase relaxation in this case. If one were able to produce electrons and holes, both in localized states, we expect an initially decaying signal

with a finite long-time value which increases with increasing localization. This situation can be expected in mixed crystals, which have band tails of finite width. A small enough photon energy then excites only localized particles.

The Coulomb interaction has an additional stabilizing effect on the photon-echo amplitude. For bound excitons, we found that there is a long-time value, which is proportional to the Bohr radius to the power $-4d$. No dephasing at all due to disorder is obtained for excitons in a long-range disorder potential, independent of the strength of the disorder amplitude. This result could explain the extremely long dephasing times observed in CdS_xSe_{1-x}.[5] If the disorder is due to Se and S clusters with linear dimensions larger than the Bohr radius, we would not expect a direct influence of disorder on the dephasing. There is, however, an indirect influence related to the electron-phonon coupling. This interaction is supressed for excitons strongly localized in the static potential fluctuations due to small spatial overlap of the states involved in the interaction (hopping). The puzzling result that $Al_xGas_{1-x}As$ shows a much faster photon-echo decay[17] [however, still slower than that of the binary system GaAs (Ref. 4)] suggests that the disorder in this ternary alloy might be of short-range character.

Finally we suggest that dephasing of excitons in quantum wells[18] or superlattices is not related directly to disorder. Interface roughness is usually reported to constitute a long-range disorder perturbation,[19] which has no direct dephasing influence on Wannier excitons according to our result. It is the exciton-exciton or exciton-phonon interaction which leads to dephasing. For quantum dots in a glass matrix very short dephasing times have been measured.[20] There the disorder is most certainly short range if compared to the relevant electron-hole length, i.e., the diameter of the dot. This could explain the short dephasing time. Electron-phonon (or exciton-phonon) interaction has not been treated explicitly here. We note that the interaction rate and thus the dephasing rate due to this quasiparticle coupling depend on disorder. Work is in progress to investigate this indirect influence of disorder on dephasing interactions.

ACKNOWLEDGMENTS

This work has been supported in part by the Deutsche Forschungsgemeinschaft. The Marburg group acknowledges fruitful discussions with E. O. Göbel, U. Siegner, A. Stahl, and S. Schmitt-Rink. The work of the Arizona group has been supported by the Optical Circuitry Cooperative, University of Arizona, NSF, and NATO.

APPENDIX

In this appendix we show how the results for Wannier excitons in Sec. VI can be obtained using the equations of motion for the macroscopic expectation values in the continuum limit. This approach is completely equivalent to that used in the main text. In this formulation the physical contents of some of the approximations made are more transparent. We describe the kinetic motion with an effective mass Hamiltonian and the disorder through effective disorder potentials for electrons and holes. The values of the disorder potentials have then a random character. The resulting equations of motion are given by

$$\partial_t p(\mathbf{r}_1,\mathbf{r}_2)+i\left[\omega_g-\frac{\hbar}{2m_h}\nabla_1^2-\frac{\hbar}{2m_e}\nabla_2^2-\frac{1}{\hbar}[V_c(|\mathbf{r}_1-\mathbf{r}_2|)-\Phi_v(\mathbf{r}_1)-\Phi_c(\mathbf{r}_2)]\right]p(\mathbf{r}_1,\mathbf{r}_2)$$
$$=\frac{i\mu}{\hbar}[\delta(\mathbf{r}_1-\mathbf{r}_2)E(\mathbf{r}_1,t)-E(\mathbf{r}_1,t)n^e(\mathbf{r}_1,\mathbf{r}_2)-E(\mathbf{r}_2,t)n^h(\mathbf{r}_1,\mathbf{r}_2)]\ ,$$
$$\partial_t n^e(\mathbf{r}_1,\mathbf{r}_2)+\left[\frac{i\hbar}{2m_e}(\nabla_1^2-\nabla_2^2)-\frac{i}{\hbar}[\Phi_c(\mathbf{r}_1)-\Phi_c(\mathbf{r}_2)]\right]n^e(\mathbf{r}_1,\mathbf{r}_2)=\frac{-i\mu}{\hbar}[E(\mathbf{r}_1,t)p(\mathbf{r}_1,\mathbf{r}_2,t)-E(\mathbf{r}_2,t)p^*(\mathbf{r}_2,\mathbf{r}_1)]\ , \tag{A1}$$
$$\partial_t n^h(\mathbf{r}_1,\mathbf{r}_2)+\left[\frac{i\hbar}{2m_h}(\nabla_2^2-\nabla_1^2)-\frac{i}{\hbar}[\Phi_v(\mathbf{r}_2)-\Phi_v(\mathbf{r}_1)]\right]n^h(\mathbf{r}_1,\mathbf{r}_2)=\frac{-i\mu}{\hbar}[p(\mathbf{r}_1,\mathbf{r}_2)E(\mathbf{r}_2,t)-p^*(\mathbf{r}_2,\mathbf{r}_1)E(\mathbf{r}_1,t)]\ ,$$

where m_h and m_e are the hole and electron effective masses. V_{eh} denotes the Coulomb potential and Φ_v and Φ_c are the local disorder potentials for holes and electrons, respectively.

Following the same iteration scheme as in Sec. IV we obtain the equations

$$\partial_t p(\mathbf{r}_1,\mathbf{r}_2)^{(1)}+i\left[\omega_g-\frac{\hbar}{2m_h}\nabla_1^2-\frac{\hbar}{2m_e}\nabla_2^2-\frac{1}{\hbar}[V_c(|\mathbf{r}_1-\mathbf{r}_2|)-\Phi_v(\mathbf{r}_1)-\Phi_c(\mathbf{r}_2)]\right]p(\mathbf{r}_1,\mathbf{r}_2)^{(1)}=\frac{i\mu}{\hbar}\delta(\mathbf{r}_1-\mathbf{r}_2)E_1(\mathbf{r}_1,t)\ ,$$
$$\partial_t n^e(\mathbf{r}_1,\mathbf{r}_2)^{(2)}+\left[\frac{i\hbar}{2m_e}(\nabla_1^2-\nabla_2^2)-\frac{i}{\hbar}[\Phi_c(\mathbf{r}_1)-\Phi_c(\mathbf{r}_2)]\right]n^e(\mathbf{r}_1,\mathbf{r}_2)^{(2)}=\frac{i\mu}{\hbar}E_2(\mathbf{r}_2t)\mathbf{p}^*(\mathbf{r}_2,\mathbf{r}_1)^{(1)}\ ,$$
$$\partial_t n^h(\mathbf{r}_1,\mathbf{r}_2)^{(2)}+\left[\frac{i\hbar}{2m_h}(\nabla_2^2-\nabla_1^2)-\frac{i}{\hbar}[\Phi_v(\mathbf{r}_2)-\Phi_v(\mathbf{r}_1)]\right]n^h(\mathbf{r}_1,\mathbf{r}_2)^{(2)}=\frac{i\mu}{\hbar}p^*(\mathbf{r}_2,\mathbf{r}_1)^{(1)}E_2(\mathbf{r}_1,t)\ , \tag{A2}$$
$$\partial_t p(\mathbf{r}_1,\mathbf{r}_2)^{(3)}+i\left[\omega_g-\frac{\hbar}{2m_h}\nabla_1^2-\frac{\hbar}{2m_e}\nabla_2^2-\frac{1}{\hbar}[V_c(|\mathbf{r}_1-\mathbf{r}_2|)-\Phi_v(\mathbf{r}_1)-\Phi_c(\mathbf{r}_2)]\right]p(\mathbf{r}_1,\mathbf{r}_2)^{(3)}$$
$$=\frac{-i\mu}{\hbar}[E_2(\mathbf{r}_1,t)n^e(\mathbf{r}_1,\mathbf{r}_2)^{(2)}+E_2(\mathbf{r}_2,t)n^h(\mathbf{r}_1,\mathbf{r}_2)^{(2)}]\ .$$

For our treatment of the spontaneous photon echo we again have omitted all the contributions that do not influence the lowest-order signal. We continue by transforming the equations into relative and center-of-mass coordinates, which yield

$$\partial_t p(\mathbf{r},\mathbf{R})^{(1)}+i\left\{\omega_g-\frac{\hbar}{2M}\nabla_R^2-\frac{\hbar}{2\mu_{\rm ex}}\nabla_r^2-\frac{1}{\hbar}\left[V_c(|\mathbf{r}|)-\Phi_v\left[\mathbf{R}+\frac{m_e}{M}\mathbf{r}\right]-\Phi_c\left[\mathbf{R}-\frac{m_h}{M}\mathbf{r}\right]\right]\right\}p(\mathbf{r},\mathbf{R})^{(1)}$$
$$=\frac{i\mu}{\hbar}\delta(\mathbf{r})\tilde{E}_1(t)e^{i\mathbf{k}_1\cdot\mathbf{R}},$$

$$\partial_t n^e(\mathbf{r},\mathbf{R})^{(2)}=\frac{i\mu}{\hbar}\tilde{E}_2(t)e^{i\mathbf{k}_2\cdot[\mathbf{R}-(m_h/M)\mathbf{r}]}p^*(-\mathbf{r},\mathbf{R}+\alpha\mathbf{r})^{(1)},$$
$$\partial_t n^h(\mathbf{r},\mathbf{R})^{(2)}=\frac{i\mu}{\hbar}\tilde{E}_2(t)e^{i\mathbf{k}_2\cdot[\mathbf{R}+(m_e/M)\mathbf{r}]}p^*(-\mathbf{r},\mathbf{R}+\alpha\mathbf{r})^{(1)}, \tag{A3}$$

$$\partial_t p(\mathbf{r},\mathbf{R})^{(3)}+i\left\{\omega_g-\frac{\hbar}{2M}\nabla_R^2-\frac{\hbar}{2\mu_{\rm ex}}\nabla_r^2-\frac{1}{\hbar}\left[V_c(|\mathbf{r}|)-\Phi_v\left[\mathbf{R}+\frac{m_e}{M}\mathbf{r}\right]-\Phi_c\left[\mathbf{R}-\frac{m_h}{M}\mathbf{r}\right]\right]\right\}p(\mathbf{r},\mathbf{R})^{(3)}$$
$$=\frac{-i\mu}{\hbar}\tilde{E}_2(t)[e^{i\mathbf{k}_2\cdot[\mathbf{R}+(m_e/M)\mathbf{r}]}n^e(\mathbf{r},\mathbf{R})^{(2)}+e^{i\mathbf{k}_2\cdot[\mathbf{R}-(m_h/M)\mathbf{r}]}n^h(\mathbf{r},\mathbf{R})^{(2)}].$$

We have again neglected the internal dynamics in the equations for the populations, because we assumed that the pulse duration is so short that the system only responds to the pulse. We combine the two population equations by introducing a total population function f,

$$f(\mathbf{r},\mathbf{R},t)=e^{i\mathbf{k}_2\cdot(m_h/M)\mathbf{r}}n^e(\mathbf{r},\mathbf{R})+e^{-i\mathbf{k}_2\cdot(m_e/M)\mathbf{r}}n^h(\mathbf{r},\mathbf{R}). \tag{A4}$$

This substitution leads to

$$\partial_t p(\mathbf{r},\mathbf{R})^{(1)}+i\left\{\omega_g-\frac{\hbar}{2M}\nabla_R^2-\frac{\hbar}{2\mu_{\rm ex}}\nabla_r^2-\frac{1}{\hbar}\left[V_c(|\mathbf{r}|)-\Phi_v\left[\mathbf{R}+\frac{m_e}{M}\mathbf{r}\right]-\Phi_c\left[\mathbf{R}-\frac{m_h}{M}\mathbf{r}\right]\right]\right\}p(\mathbf{r},\mathbf{R})^{(1)}$$
$$=\frac{i\mu}{\hbar}\delta(\mathbf{r})\tilde{E}_1(t)e^{i\mathbf{k}_1\cdot\mathbf{R}},$$

$$\partial_t f(\mathbf{r},\mathbf{R})^{(2)}=\frac{i2\mu}{\hbar}\tilde{E}_2(t)e^{i\mathbf{k}_2\cdot\mathbf{R}}p^*(-\mathbf{r},\mathbf{R}+\alpha\mathbf{r})^{(1)}, \tag{A5}$$

$$\partial_t p(\mathbf{r},\mathbf{R})^{(3)}+i\left\{\omega_g-\frac{\hbar}{2M}\nabla_1^2-\frac{\hbar}{2\mu_{\rm ex}}\nabla_2^2-\frac{1}{\hbar}\left[V_c(|\mathbf{r}|)-\Phi_v\left[\mathbf{R}+\frac{m_e}{M}\mathbf{r}\right]-\Phi_c\left[\mathbf{R}-\frac{m_h}{M}\mathbf{r}\right]\right]\right\}p(\mathbf{r},\mathbf{R})^{(3)}$$
$$=\frac{-i\mu}{\hbar}\tilde{E}_2(t)e^{i\mathbf{k}_2\cdot(\mathbf{R}+\alpha\mathbf{r})}f(\mathbf{r},\mathbf{R})^{(2)}.$$

In this set of equations the internal and relative motion are still coupled as can be seen by the appearance of the factor α. So far no approximations concerning the properties of the disorder have been made. This set of equation is still equivalent with the formal result (29) in the continuum limit. Physically, however, the continuum limit can be used only if the disorder is of long range. The kick of the photon is manifested in this formulation by the appearance of the spatial-dependent phase factors which actually in quantum mechanics represent momentum shift operators.

With the assumptions discussed above we can solve Eqs. (A5) and we obtain for the third-order polarization at $t=2\tau$ the expression

$$p(\mathbf{r}_1,\mathbf{r}_2,2\tau)^{(3)}=-i\left[\frac{\mu}{\hbar}\right]^3\tilde{E}_2^2\tilde{E}_1^*\delta(\mathbf{r})e^{-i\hat{H}_{\mathbf{R}}\tau}$$
$$\times[e^{i2\mathbf{k}_2\cdot\mathbf{R}}e^{i\hat{H}_{\mathbf{R}}\tau}(e^{-i\mathbf{k}_1\cdot\mathbf{R}})], \tag{A6}$$

where the Hamiltonian is given by

$$\hat{H}_{\mathbf{R}}=-\frac{\hbar}{2M}\nabla_R^2+\Phi_v(\mathbf{R})+\Phi_c(\mathbf{R}). \tag{A7}$$

The polarization density needed for the evaluation of the observed intensity is obtained by setting $\mathbf{r}=0$. The formal divergence disappears because the expression must also be divided by the volume of the sample. A more careful evaluation gives the density as a multiplier. The observed intensity is, hence, given by

$$I_{\rm obs}\propto\left|\int d\mathbf{R}\,e^{-i\mathbf{k}\cdot\mathbf{R}}e^{-i\hat{H}_{\mathbf{R}}\tau}[e^{i2\mathbf{k}_2\cdot\mathbf{R}}e^{i\hat{H}_{\mathbf{R}}\tau}(e^{-i\mathbf{k}_1\cdot\mathbf{R}})]\right|^2$$
$$=|\langle\mathbf{k}|e^{-i\hat{H}_{\mathbf{R}}\tau}e^{i2\mathbf{k}_2\cdot\mathbf{R}}e^{i\mathbf{H}_{\mathbf{R}}\tau}|-\mathbf{k}_1\rangle|^2 \tag{A8}$$

as we obtained using the formal expression too.

[1]H. Haug and S. Schmitt-Rink, Prog. Quantum Electron. **9**, 3 (1984), and the given references.
[2]S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, Adv. Phys. **38**, 89 (1989).
[3]H. Haug and S. W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors* (World Scientific, Singapore, 1990).
[4]P. C. Becker, H. L. Fragnito, C. H. Brito Cruz, R. L. Fork, J. E. Cunningham, J. E. Henry, and C. V. Shank, Phys. Rev. Lett. **61**, 1647 (1988).
[5]G. Noll, U. Siegner, S. G. Shevel, and E. O. Göbel, Phys. Rev. Lett. **64**, 792 (1990).
[6]N. A. Kurnit, I. D. Abella, and S. R. Hartmann, Phys. Rev. Lett. **13**, 567 (1964).
[7]T. Yajima and Y. Taira, J. Phys. Soc. Jpn. **47**, 1620 (1979).
[8]S. Abe and Y. Toyozawa, J. Phys. Soc. Jpn. **50**, 2185 (1981).
[9]A. Stahl and I. Balslev, *Electrodynamics of the Semiconductor Band Edge,* Springer Tracts in Modern Physics Vol. 110 (Springer, Berlin, 1987).
[10]Ch. Lonsky, P. Thomas, and A. Weller, Phys. Rev. Lett. **63**, 652 (1989); see also Ch. Lonsky, Ph.D. thesis, Marburg, 1990.
[11]S. Stenholm. Rev. Mod. Phys. **58**, 699 (1986).
[12]M. Lindberg and S. W. Koch, Phys. Rev. B **38**, 3342 (1988).
[13]I. J. Yeh and J. H. Eberly, Phys. Rev. A **22**, 1124 (1980).
[14]H. Overhof and P. Thomas, *Electronic Transport in Hydrogenated Amorphous Semiconductors,* Springer Tracts in Modern Physics, Vol. 114 (Springer, Berlin, 1989).
[15]G. Noll, Ph.D. thesis, Marburg, 1989.
[16]V. E. Kravtsov, V. I. Yudson, and V. M. Agranovich, Phys. Rev. B **41**, 2794 (1990).
[17]U. Siegner, G. Noll, S. G. Shevel, E. O. Göbel, D. Bennhardt, P. Thomas, and A. Weller, Proceedings of the 30th International Conference on Semiconductors, Thessaloniki (1990) (to be published).
[18]L. Schultheis, M. D. Sturge, and J. Hegarty, Appl. Phys. Lett. **47**, 995 (1985).
[19]B. Deveaud, A. Regreny, J.-Y. Emery, and A. Chomette, J. Appl. Phys. **59**, 1633 (1986).
[20]N. Peyghambarian, B. Fluegel, D. Hulin, A. Migus, M. Joffre, A. Antonetti, S. W. Koch, and M. Lindberg, IEEE J. Quantum Electron. **QE-25**, 2516 (1989).