# Theory of photoluminescence in semiconductors

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A theory is presented that relates the luminescence signal of a semiconductor to the current-density correlation function. It allows the calculation of the luminescence spectrum for nonthermal carrier distributions by means of solving the Bethe-Salpeter equation for the polarization. The present method passes important consistency checks and overcomes some limitations and shortcomings of previous approaches. A detailed comparison is made with previous results and numerical examples are presented to demonstrate the usefulness of the present method.

### I. INTRODUCTION

Spontaneous emission, stimulated emission, and absorption in atoms and molecules have been studied since the early days of quantum mechanics.<sup>1</sup> Although photoluminescence measurements are frequently used to characterize the optical transitions in bulk semiconductors or in lowdimensional structures, very few works on a rigorous theory of luminescence in semiconductors have been published so far.

We shall briefly mention important milestones towards a theory of luminescence in semiconductors. Important theoretical contributions to understanding the spectral measurement of fluctuating quantities were made by Butcher and Ogg.<sup>2</sup> This theory was applied by Enderlein *et al.* to optical processes in semiconductors and the statistical properties of the secondary emission were traced back to correlation functions of the electronic system.<sup>3</sup> During the last fifteen years, the method of Green's functions has been successfully applied to optical properties in semiconductors, including Coulomb interaction.<sup>4</sup> Recent theoretical papers used these concepts for the description of the luminescence properties.<sup>5</sup> The effect of Coulomb interaction has been treated approximately by truncating the Bethe-Salpeter equation first order in the Coulomb potential.<sup>6,7</sup> Pereira and Henneberger calculated the luminescence spectrum by generalizing the Kubo-Martin-Schwinger relation for quasiequilibrium, when valence and conduction electrons have equal temperatures but different chemical potentials.<sup>8,9</sup> Piermarocchi et al. found an exact solution in the case when the Coulomb interaction is replaced by a constant in momentum space, but the result is limited to one-dimensional models.<sup>10,11</sup> A different approach has been used by Kuhn and Rossi<sup>12</sup> and by Kira et al.,<sup>13,14</sup> who calculate the change in the photon number by means of photonassisted density matrices.

Despite the recent progress, the theoretical understanding of the luminescence from semiconductors is not yet satisfactory. Some solutions rely on restrictions of the theoretical model or the quantum-statistical properties. Others do not allow for bound states or tend to produce artifacts. An important problem is the calculation of the luminescence signal for nonthermal distributions. Such distributions may arise in polar semiconductors, when the dominating relaxation mechanism is LO-phonon scattering, or in low-dimensional semiconductors, because of bottleneck effects.

In this paper we present a rigorous formulation for the luminescence signal in terms of current-density fluctuations. Then the spontaneous emission, including Coulomb effects, can be derived by explicitly solving the Bethe-Salpeter equation. This approach treats absorption and luminescence on equal footing and allows us to calculate the luminescence spectrum for arbitrary nonthermal distributions.

The paper is organized as follows. After this introduction, in Sec. II we derive a relation between the luminescence spectrum and the polarization function. In Sec. III we give a solution of the Bethe-Salpeter equation and an explicit expression for the luminescence signal. We discuss some important properties and also examine previous results in the light of the new findings. To illustrate the usefulness of our approach, numerical solutions will be presented in Sec. IV. A summary is given in Sec. V.

## **II. BASIC EQUATIONS**

We follow the theory on measurement of fluctuating quantities by Butcher and Ogg,<sup>2</sup> where the field amplitudes are passed through a spectral filter and the intensity after the filter is measured during a time interval of length *T*, in the limit  $T \rightarrow \infty$ . As result, the measured signal is proportional to the integral of the spectrometer function and the autocorrelation function of the field amplitudes.

According to Enderlein *et al.*,<sup>3</sup> the Poynting vector of the electromagnetic radiation  $\langle \hat{\mathbf{E}} \times \hat{\mathbf{H}} \rangle$  consists of a coherent part  $\langle \hat{\mathbf{E}} \rangle \times \langle \hat{\mathbf{H}} \rangle$  and an incoherent part  $\langle \Delta \hat{\mathbf{E}} \times \Delta \hat{\mathbf{H}} \rangle$ . While the coherent part describes the propagation of macroscopic electromagnetic fields, the incoherent part contains the secondary emission. We therefore concentrate on the incoherent part, which results from the quantum fluctuations  $\Delta \hat{\mathbf{E}} = \hat{\mathbf{E}} - \langle \hat{\mathbf{E}} \rangle$  and  $\Delta \hat{\mathbf{H}} = \hat{\mathbf{H}} - \langle \hat{\mathbf{H}} \rangle$  of the electromagnetic field. If the semiconductor is not coherently excited or in a resonator, all electromagnetic radiation is incoherent.

We assume temporal homogeneity and incorporate the detection time T in the Fourier expansions for fluctuating quantities:

$$\Delta \hat{\mathbf{E}}(\omega) = \lim_{T \to \infty} \frac{1}{\sqrt{T}} \int_{-T/2}^{+T/2} dt e^{+i\omega t} \Delta \hat{\mathbf{E}}(t).$$
(1)

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It is important to know that not all terms from the Poynting vector contribute to the measured intensity. In classical stochastics, for a given frequency  $\omega > 0$ , terms that oscillate with  $\exp(\pm 2i\omega t)$  will not appear in the signal, because of the time average.<sup>2</sup> For quantized fields, the operators also need to be in normal order and the part of the Poynting vector, which reflects the measurable intensity is equal to  $\frac{1}{2}\hat{\mathbf{E}}^{(+)} \times \hat{\mathbf{H}}^{(-)} + \text{H.c.}$ , where the superscripts  $\pm$  denote the Fourier components oscillating with  $\exp(\pm i\omega t)$ .<sup>15</sup>

According to Poynting's theorem, the source term (divergence) of the Pointing vector is equal to  $-\mathbf{j} \cdot \mathbf{E}$ , where  $\mathbf{j}$  is the current density. Therefore, the emitted light power per frequency and sample volume  $\Omega$  is equal to

$$p(\omega) = -\frac{1}{2\pi} \frac{1}{\Omega} \int d^3 \mathbf{r} \langle \Delta \hat{\mathbf{j}}^{\dagger}(\mathbf{r}, \omega) \cdot \Delta \hat{\mathbf{E}}(\mathbf{r}, \omega) + \text{H.c.} \rangle \quad (2)$$

and the total emitted power per volume is the positivefrequency integral of  $p(\omega)$ . To evaluate expression (2), we express the operator of the electric field by the current operator. In Coulomb gauge, it holds that

$$\Delta \hat{\mathbf{E}}(\mathbf{r},\omega) = i\omega\Delta \hat{\mathbf{A}}(\mathbf{r},\omega)$$
$$= i\omega\mu_0 \int d^3\mathbf{r}' e^{+i\omega|\mathbf{r}-\mathbf{r}'|/c_0} \frac{\Delta \hat{\mathbf{j}}^T(\mathbf{r}',\omega)}{4\pi|\mathbf{r}-\mathbf{r}'|}, \quad (3)$$

where  $\mu_0$  is the vacuum permeability,  $c_0$  is the vacuum speed of light, and the subscript *T* refers to the transverse current density. In the optical limit of small photon wave numbers  $\omega/c_0$ , the exponential term can be expanded and the spectral power density takes the form

$$p(\boldsymbol{\omega}) = \frac{\boldsymbol{\omega}^2 \boldsymbol{\mu}_0}{4 \, \pi^2 c_0} \frac{1}{\Omega} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \langle \Delta \hat{\mathbf{j}}^{T\dagger}(\mathbf{r}, \boldsymbol{\omega}) \cdot \Delta \hat{\mathbf{j}}^T(\mathbf{r}', \boldsymbol{\omega}) \rangle.$$
<sup>(4)</sup>

From the explicit expression it follows that  $p(\omega)$  is positive semidefinite. By virtue of the definition (1) the above quantity is equal to

$$p(\omega) = \frac{\omega^2 \mu_0}{4 \pi^2 c_0} \frac{1}{\Omega} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \int_{-\infty}^{+\infty} dt e^{i\omega(t-t')} \\ \times \langle \Delta \hat{\mathbf{j}}^T(\mathbf{r}, t') \cdot \Delta \hat{\mathbf{j}}^T(\mathbf{r}', t) \rangle,$$
(5)

in accordance with the Wiener-Khintchine theorem.

We mention that the same result as above can be obtained by integrating the Poynting vector over the surface of a sphere. The Poynting vector also provides information about the angular dependence of the radiation<sup>3</sup> and allows us to derive a general expression of the luminescence signal.

The expressions considerably simplify if the medium is assumed to be isotropic. This is the case, e.g., for cubic semiconductors in the spherical approximation. Then the restriction to transverse currents is equivalent to summing over two out of three polarizations, for example,  $\alpha = x, y$  (linear polarization) or  $\alpha = +, -$  (circular polarization). If the currentdensity operators are expressed by creation and annihilation operators of Bloch electrons, the current-density correlation function on the right-hand side of Eq. (5) takes the form

$$\int d^{3}\mathbf{r} \int d^{3}\mathbf{r}' \langle \Delta \hat{j}_{\alpha}^{T}(\mathbf{r},t') \cdot \Delta \hat{j}_{\alpha}^{T}(\mathbf{r}',t) \rangle$$

$$= \frac{e^{2}}{m_{0}^{2}} \sum_{j_{1}j_{1}'j_{2}j_{2}'} \langle j_{1} | \hat{p}_{\alpha} | j_{1}' \rangle \langle j_{2} | \hat{p}_{\alpha} | j_{2}' \rangle$$

$$\times \sum_{\mathbf{k}_{1}\mathbf{k}_{2}} i\hbar L_{-+j_{1}j_{1}'j_{2}j_{2}'}(\mathbf{k}_{1},t,\mathbf{k}_{2},t'), \qquad (6)$$

where we have replaced the momentum matrix elements by their values at the band edge. The symbols e > 0,  $m_0$  denote the elementary charge and the electron mass, respectively, and *L* is the density correlation function, defined on the Keldysh contour as

$$L_{j_{1}j_{1}'j_{2}j_{2}'}(\mathbf{k}_{1},\underline{t}_{1},\mathbf{k}_{2},\underline{t}_{2}) = \frac{1}{i\hbar} [\langle \mathrm{T}\hat{\rho}_{j_{1}j_{1}'}(\mathbf{k}_{1},\underline{t}_{1})\hat{\rho}_{j_{2}j_{2}'}(\mathbf{k}_{2},\underline{t}_{2})\rangle - \langle \hat{\rho}_{j_{1}j_{1}'}(\mathbf{k}_{1},\underline{t}_{1})\rangle \langle \hat{\rho}_{j_{2}j_{2}'}(\mathbf{k}_{2},\underline{t}_{2})\rangle],$$
(7)

where we used the abbreviation  $\hat{\rho}_{jj'}(\mathbf{k},t) = \hat{a}_{j'}^{\dagger}(\mathbf{k},t)\hat{a}_{j}(\mathbf{k},t)$ and *T* denotes the time-ordering symbol. For interband transitions under consideration, and no macroscopic polarization, the second contribution in Eq. (7) is zero.

For the explicit calculation we will consider the  $\Gamma_{1c}$  $\rightarrow \Gamma_{15v}$  transition in a zinc blende semiconductor without spin-orbit interaction assuming parabolic bands. This is equivalent to the model of a two-band semiconductor. The nonvanishing momentum matrix elements are  $\langle c|p_x|v,X \rangle$  $= \langle c|p_y|v,Y \rangle = \langle c|p_z|v,Z \rangle = p_{cv}$ . We choose one valence band and identify the band indices in Eq. (6) as  $j_1 = j'_2 = c$ ,  $j'_1 = j_2 = v$ , which corresponds to positive frequencies. A prefactor ("band-structure factor") f = 4 appears because of two polarizations and the spin degeneracy.

In order to keep resonant one-photon processes for which  $E_c(\mathbf{k}) - E_v(\mathbf{k}) \approx \hbar \omega$  but to take into account nonresonant transitions via static screening, we replace the density correlation function by  $L = P/\varepsilon$ , where the polarization function *P* is the irreducible part of *L* and  $\varepsilon$  is the static screening constant. With the abbreviation  $P = P_{cvvc}$  for the interband polarization function, the final result takes the form

$$p(\omega) = \frac{f\omega^2 \mu_0 e^2 |p_{cv}|^2}{4\pi^2 c_0 \varepsilon m_0^2} \frac{1}{\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2} i\hbar P_{-+}(\mathbf{k}_1, \mathbf{k}_2, \omega). \quad (8)$$

The relation between luminescence spectrum and the polarization function  $P_{-+}$  appears in various forms in the literature.

#### **III. SOLUTION OF THE BETHE-SALPETER EQUATION**

In this section we derive an explicit expression for the polarization function  $P_{-+}$  in the presence of Coulomb interaction between electrons and holes. This has to be done using the method of nonequilibrium Green's functions. Green's functions have been applied to various optical properties in semiconductors.<sup>4</sup> By means of the Keldysh formalism, most of the concepts can be generalized to nonequilibrium. For an introduction, see, e.g., the textbook of Landau and

Lifschitz.<sup>16</sup> The fundamental equations for nonequilibrium are also derived in the papers by Pereira and Henneberger.<sup>7,8</sup>

The one-particle Green's functions in Bloch representation are defined as

$$G_{j_1j_2}(\mathbf{k}_1, t_1, \mathbf{k}_2, t_2) = \frac{1}{i\hbar} \langle \mathrm{T}\hat{a}_{j_1}(\mathbf{k}_1, t_1)\hat{a}_{j_2}^{\dagger}(\mathbf{k}_2, t_2) \rangle, \quad (9)$$

where t denotes a time on the Keldysh contour, consisting of the ordinary time t and a Keldysh index A which specifies the branch on the Keldysh contour, - for the upper branch and + for the lower branch. In fact, for each pair of band indices  $j_1, j_2$ , Eq. (9) defines four functions, which can be considered as matrix elements  $G_{AB}$  with respect to the Keldysh indices, each one depending on two ordinary times.

In general, the one-particle Green's functions have a complicated frequency dependence due to the correlation part of the self energy. In the case of stationarity, when the correlation self-energy is assumed static, the elements of G can be expressed in terms of single-particle energies  $E_j$  and occupation numbers  $f_i$  according to:

$$G_{j_{1}j_{2}-+}(\mathbf{k}_{1},t_{1},\mathbf{k}_{2},t_{2})$$

$$= -\frac{1}{i\hbar}e^{E_{j_{1}}(\mathbf{k}_{1})(t_{1}-t_{2})/i\hbar}f_{j_{1}}(\mathbf{k}_{1})\delta_{j_{1}j_{2}}\delta_{\mathbf{k}_{1}\mathbf{k}_{2}} \quad (10)$$

$$G_{j_{1}j_{2}+-}(\mathbf{k}_{1},t_{1},\mathbf{k}_{2},t_{2})$$

$$= \frac{1}{i\hbar} e^{E_{j_1}(\mathbf{k}_1)(t_1 - t_2)/i\hbar} [1 - f_{j_1}(\mathbf{k}_1)] \delta_{j_1 j_2} \delta_{\mathbf{k}_1 \mathbf{k}_2}.$$

While the solution of the Bethe-Salpeter equation does not depend on the specific form of G, the above approximation allows us to derive a particularly simple expression for the luminescence signal in terms of an effective Hamiltonian.

The backward integration in time on the lower branch on the Keldysh contour implies a product of the Keldysh matrices of the form  $(FG)_{AB} = F_{A-}G_{-B} - F_{A+}G_{+B}$ . It is therefore useful to introduce upper indices  $G_A{}^B = \pm G_{AB}$  for  $B = \mp$  and to adopt a sum convention for upper and lower indices. Then we obtain the ordinary matrix product  $(FG)_A{}^B = F_A{}^-G_-{}^B + F_A{}^+G_+{}^B = :F_A{}^CG_C{}^B$ . For functions on the Keldysh contour, it is common to define retarded and advanced functions

$$F_{\rm ret} = F_{--} - F_{-+} = F_{+-} - F_{++}, \tag{11}$$

$$F_{adv} = F_{--} - F_{+-} = F_{-+} - F_{++},$$

where  $F_{\text{ret}}(t_1, t_2) = 0$  for  $t_1 < t_2$  and  $F_{\text{adv}}(t_1, t_2) = 0$  for  $t_1 > t_2$ . Furthermore, the above relations show that the elements of the Keldysh matrix are not independent of each other.

The polarization function from the last section can be calculated from the single-particle Green's functions by means of the Bethe-Salpeter equation (BSE). In the ladder approximation with a statically screened potential V, this equation simplifies to an integral equation in **k** space,

$$P_{A}^{B}(\mathbf{k}_{1},\mathbf{k}_{2},\omega) = L_{0A}^{B}(\mathbf{k}_{1},\mathbf{k}_{2},\omega)$$
$$-\frac{1}{\Omega}\sum_{\mathbf{k}'\mathbf{k}''}L_{0A}^{C}(\mathbf{k}_{1},\mathbf{k}',\omega)$$
$$\times V(\mathbf{k}'-\mathbf{k}'')P_{C}^{B}(\mathbf{k}'',\mathbf{k}_{2},\omega), \quad (12)$$

where the frequency  $\omega$  plays the role of a parameter. If the screened Coulomb potential is not static, the solution is considerably more complicated, and very few solutions have been published so far.<sup>17</sup> The function  $L_0$  is defined as

$$L_{0AB}(\mathbf{k}_{1}, t_{1}, \mathbf{k}_{2}, t_{2})$$
  
=  $L_{0 \ cvvc \ AB}(\mathbf{k}_{1}, t_{1}, \mathbf{k}_{2}, t_{2})$   
=  $-i\hbar G_{cc \ AB}(\mathbf{k}_{1}, t_{1}, \mathbf{k}_{2}, t_{2})G_{vv \ BA}(\mathbf{k}_{2}, t_{2}, \mathbf{k}_{1}, t_{1}),$ 

and is equal to the polarization function in the absence of Coulomb interaction. From the single-particle Green's functions (10) one obtains

$$L_{0-}^{+}(\mathbf{k}_{1},\mathbf{k}_{2},\omega) = 2if_{c}(\mathbf{k}_{1})[1-f_{v}(\mathbf{k}_{1})] \times \pi \delta[\hbar \omega - E_{c}(\mathbf{k}_{1}) + E_{v}(\mathbf{k}_{1})]\delta_{\mathbf{k}_{1}\mathbf{k}_{2}},$$
(13)

$$L_{0 \text{ ret}}(\mathbf{k}_{1},\mathbf{k}_{2},\omega) = \frac{f_{v}(\mathbf{k}_{1}) - f_{c}(\mathbf{k}_{1})}{\hbar(\omega + i\epsilon) - E_{c}(\mathbf{k}_{1}) + E_{v}(\mathbf{k}_{1})} \,\delta_{\mathbf{k}_{1}\mathbf{k}_{2}},$$
$$L_{0 \text{ adv}}(\mathbf{k}_{1},\mathbf{k}_{2},\omega) = \frac{f_{v}(\mathbf{k}_{1}) - f_{c}(\mathbf{k}_{1})}{\hbar(\omega - i\epsilon) - E_{c}(\mathbf{k}_{1}) + E_{v}(\mathbf{k}_{1})} \,\delta_{\mathbf{k}_{1}\mathbf{k}_{2}}.$$

Here,  $\epsilon = +0$  is a positive infinitesimal. Physically and numerically,  $\epsilon > 0$  plays the role of a finite lifetime and the delta function is replaced by a Lorentzian according to  $\delta(E) = \frac{1}{\pi} (\hbar \epsilon) / [E^2 + (\hbar \epsilon)^2].$ 

The imaginary part of the retarded polarization function is responsible for the optical absorption/gain. From the definition of the retarded function (11) it follows for the product of two Keldysh matrices  $(FG)_{ret} = F_{ret}G_{ret}$ . Applying this rule to Eq. (12) we find

$$P_{\rm ret} = L_0 \,_{\rm ret} - L_0 \,_{\rm ret} V P_{\rm ret} \,. \tag{14}$$

We shall briefly review different ways of solving Eq. (14) in view of generalizations for the solution of the complete BSE (12). First, a direct solution of the form

$$P_{\rm ret} = (L_0^{-1} + V)^{-1} \tag{15}$$

is not possible in the general case, because the operator  $L_{0 \text{ ret}}$ is singular in the case of population inversion, i.e., if  $f_c(\mathbf{k}) > f_v(\mathbf{k})$  for some **k**. This problem can be avoided by taking the inverse only of the first part of  $L_{0 \text{ ret}} = [\hbar(\omega + i\epsilon) - E_c + E_v]^{-1} (f_v - f_c)$ . This leads to the common expression

$$P_{\text{ret}} = -[H - \hbar(\omega + i\epsilon)]^{-1} (f_v - f_c), \qquad (16)$$

where

$$H(\mathbf{k}_{1},\mathbf{k}_{2}) = [E_{c}(\mathbf{k}_{1}) - E_{v}(\mathbf{k}_{1})] \delta_{\mathbf{k}_{1}\mathbf{k}_{2}}$$
$$-[f_{v}(\mathbf{k}_{1}) - f_{c}(\mathbf{k}_{1})] \frac{1}{\Omega} V(\mathbf{k}_{1} - \mathbf{k}_{2}). \quad (17)$$

This effective Hamiltonian is non-Hermitian unless  $f_v(\mathbf{k}) - f_c(\mathbf{k}) = \text{const.}$  For simplicity, we also used some straightforward matrix notation. For example,  $f_v - f_c$  stands for a diagonal matrix with elements  $[f_v(\mathbf{k}_1) - f_c(\mathbf{k}_1)] \delta_{\mathbf{k}_1 \mathbf{k}_2}$ . An alternative solution is found by iterating the BSE (14). In this case  $P_{\text{ret}}$  becomes

$$P_{\text{ret}} = \sum_{n=0}^{\infty} (-L_{0 \text{ ret}} V)^n L_{0 \text{ ret}} = (1 + L_{0 \text{ ret}} V)^{-1} L_{0 \text{ ret}}.$$
(18)

The operator  $1 + L_{0 \text{ ret}}V$  is regular for each  $\omega$ . The equivalence of the solutions (16) and (18) is obvious from the explicit expression of  $L_{0 \text{ ret}}$  (13). Analogous relations can also be established for  $P_{\text{adv}} = P_{\text{ret}}^{\dagger}$ .

Now we proceed to solve the BSE (12) for the whole Keldysh matrix *P*. Again, a solution in the form  $P = (L_0^{-1} + V)^{-1}$ , in analogy to Eq. (15), is not possible. For, by conservation of difficulty, the operator  $L_0$  is also singular. Its determinant is equal to  $L_0 \operatorname{ret} L_0 \operatorname{adv}$  and, therefore, proportional to  $(f_c - f_v)^2$ . Furthermore, a separate treatment of  $f_c - f_v$  is not possible since none of the matrix elements of  $L_0$  explicitly contains a factor  $f_c - f_v$ . There is, in principle, a cure for this problem: the Keldysh matrices in Eq. (12) can be transformed into triangular form, <sup>16</sup> and a retarded and advanced function, both containing the factor  $f_c - f_v$ , appear in the corners.

The generalization of Eq. (18) is straightforward to give immediately

$$P = (1 + L_0 V)^{-1} L_0 \tag{19}$$

and  $1+L_0V$  is always regular. Even though Eq. (19) provides a method of calculating  $P_-^+$ , we shall also derive an explicit expression, which allows us to analytically deduce important properties.

From the definition of retarded and advanced functions (11) it follows that  $(FG)_{-}^{+} = F_{ret}G_{-}^{+} + F_{-}^{+}G_{adv}$ , which can be generalized by recursion to the product of any number of Keldysh matrices. Application to the BSE (12) yields

$$P_{-}^{+} = L_{0-}^{+}$$

$$-L_{0-}^{+} VL_{0 adv} - L_{0 ret} VL_{0-}^{+}$$

$$+L_{0-}^{+} VL_{0 adv} VL_{0 adv} + L_{0 ret} VL_{0-}^{+} VL_{0 adv}$$

$$+L_{0 ret} VL_{0 ret} VL_{0-}^{+}$$

$$\mp \cdots . \qquad (20)$$

After rearranging the power series,

$$P_{-}^{+} = \sum_{n=0}^{\infty} (-L_{0 \text{ ret}} V)^{n} L_{0 -}^{+} \sum_{n=0}^{\infty} (-V L_{0 \text{ adv}})^{n}$$
$$= (1 + L_{0 \text{ ret}} V)^{-1} L_{0 -}^{+} (1 + V L_{0 \text{ adv}})^{-1}, \qquad (21)$$

using the definition of the effective Hamiltonian (17) and the form of  $L_0$   $_{-}^{+}$  (13), we obtain the result

$$P_{-}^{+} = 2i[H - \hbar(\omega + i\epsilon)]^{-1}\hbar\epsilon f_{c}(1 - f_{v})$$
$$\times [H - \hbar(\omega + i\epsilon)]^{-1}^{\dagger}.$$
(22)

The explicit expressions allow us to deduce some general properties. First, the operator  $-iP_{-}^{+}$  is positive semidefinite. It is thus guaranteed that the luminescence signal is

non-negative. Second, the elements of the Keldysh matrix for *P* fulfill the compatibility relations (11). This is because an analogous relation to Eq. (21) can also be established for  $P_{+}^{-}$  and for the difference  $P_{\text{ret}} - P_{\text{adv}}$  (but not for  $P_{\text{ret}}$  and  $P_{\text{adv}}$  separately).

Another conclusion can be drawn: the difference  $P_{\text{ret}} - P_{\text{adv}}$ , responsible for absorption/stimulated emission, can be expressed as

$$P_{\rm ret} - P_{\rm adv} = -2i[H - \hbar(\omega + i\epsilon)]^{-1}\hbar\epsilon(f_c - f_v)$$
$$\times [H - \hbar(\omega + i\epsilon)]^{-1\dagger}.$$
(23)

Equations (22) and (23) generalize the expressions for the free-particle case  $L_0$ , in a nonobvious way.

An important point is the validity of the Kubo-Martin-Schwinger (KMS) relation, which connects the elements of Pby the Bose function g and can be viewed as the pendant to the relation between the Einstein coefficients. The solution (21) preserves the KMS relation, i.e., if  $L_0$  +  $P_{-}^{+} = -g(\hbar\omega)(P_{\text{ret}})$  $= -g(\hbar \omega)(L_0 \operatorname{ret} - L_0 \operatorname{adv}),$ then  $-P_{adv}$ ). However, as a consequence of the approximate Green's functions (10), the KMS relation for  $L_0$  (13) is fulfilled only in the limit  $\epsilon = +0$ . In order to take into account effects of dynamic correlation, the exchange-correlation selfenergy has to be calculated in T-matrix approximation, consistently with the ladder approximation for the BSE. In this case, the illustrative concept of an effective Hamiltonian becomes void.

It is worthwhile to discuss the relationship between previous results and the results of this paper. In early publications on this subject,<sup>6,7</sup> a truncation of the BSE according to

$$P_{-}^{+} = L_{0-}^{+} - L_{0 \text{ ret}} V L_{0-}^{+} - L_{0-}^{+} V L_{0 \text{ adv}}$$
(24)

was proposed for high densities and the difference to the free-particle luminescence was expressed by a Coulomb enhancement factor. Besides the fact that this approximation does not allow for bound states, the truncation of Dyson or Bethe-Salpeter equations is never recommended because of a tendency to produce artifacts.

Pereira and Henneberger<sup>8,9</sup> used the KMS relation to calculate  $P_{-}^{+}$  from  $P_{\text{ret}} - P_{\text{adv}}$  for quasiequilibrium. By calculating the chemical potentials in a T-matrix approximation, consistently with the BSE, a positive luminescence signal is obtained. For quasiequilibrium, the approach in Refs. 8 and 9 is comparable to the present approach, but also allows for effects of dynamic correlation.

For one-dimensional systems, when the Coulomb potential is approximated by a constant in k space (delta function in real space), the  $k_1$  sum in  $P(k_1, k_2, \omega)$  can be carried out and Eq. (12) goes over into an algebraic equation. This has been done successfully by Piermarocchi *et al.*<sup>10</sup> These authors also calculated the self-energy in T-matrix approximation, which is important for the discussion of densitydependent broadening and band-gap renormalization in quantum wires.<sup>11</sup>

From the equations-of-motion for photon-assisted density matrices, Kuhn and Rossi derived an expression for the spontaneous emission of the form<sup>12</sup>

$$p(\boldsymbol{\omega}) \propto -i \frac{1}{\Omega} \sum_{\mathbf{k}_{1}\mathbf{k}_{2}} \left\{ \left[ H - \hbar(\boldsymbol{\omega} + i\boldsymbol{\epsilon}) \right]^{-1} \times (\mathbf{k}_{1}, \mathbf{k}_{2}) f_{c}(\mathbf{k}_{2}) \left[ 1 - f_{v}(\mathbf{k}_{2}) \right] - \text{H.c.} \right\}, \quad (25)$$

which corresponds to the approximation

$$P_{-}^{+} = [H - \hbar(\omega + i\epsilon)]^{-1} f_{c}(1 - f_{v})$$
  
-  $f_{c}(1 - f_{v})[H - \hbar(\omega + i\epsilon)]^{-1}^{\dagger}.$  (26)

The same result is obtained using the semiconductor luminescence equations<sup>13,14</sup> with the unrenormalized source term proportional to  $f_c(1-f_v)$ . It is worthwhile to note that expression (26) contains only part of the terms of Eq. (21). It does also not guarantee a positive luminescence signal, as we will see in the next section.

# **IV. EXAMPLES**

As luminescence is always related to the presence of electron-hole pairs, the effective Hamiltonian (17) is non-Hermitian and no simple analytical expression can be given in terms of eigenvalues and eigenfunctions. On the other hand, the numerical calculations are not difficult at all; when the Hilbert space is properly discretized, the application of the operator  $H^{-1}$  is transformed into the solution of a linear set of equations. Prior to treating specific examples, we also did some consistency checks: we verified that Eqs. (16) and (23) give identical results for the absorption and that the numerical results of Eq. (19) and Eq. (22) for the luminescence are identical.

The results of the previous section are rather general and do not depend on the specific form of the potential V and the band dispersions  $E_j$ . In order to model realistic situations, we take into account screening and band-gap renormalization. We use Thomas-Fermi screening, which can be generalized to nonthermal distributions:<sup>18</sup>

$$V(\mathbf{k}) = \frac{e^2}{\varepsilon_0 \varepsilon (k^2 + k_s^2)}; \quad k_s^2 = -\frac{e^2}{\varepsilon_0 \varepsilon} \sum_{j=c,v} \frac{2}{\Omega} \sum_{\mathbf{k}} \frac{df_j(\mathbf{k})}{dE_j(\mathbf{k})}.$$
(27)

The band dispersions in the effective Hamiltonian (17) are renormalized accordingly:<sup>4</sup>

$$E_{c}(\mathbf{k}) - E_{v}(\mathbf{k}) = E_{g} + \frac{\hbar^{2}k^{2}}{2m_{e}} + \frac{\hbar^{2}k^{2}}{2m_{h}} + \frac{1}{\Omega} \sum_{\mathbf{k}'} V(\mathbf{k} - \mathbf{k}')[f_{v}(\mathbf{k}') - f_{c}(\mathbf{k}') - 1] + \frac{1}{\Omega} \sum_{\mathbf{k}'} \left[ V(\mathbf{k} - \mathbf{k}') - \frac{e^{2}}{\varepsilon_{0}\varepsilon|\mathbf{k} - \mathbf{k}'|^{2}} \right].$$

$$(28)$$

For the calculation of the Thomas-Fermi screening wavenumber (27) we use the unrenormalized dispersions, because the main effect of the band-gap renormalization is a shift of the band edges. With the results for the polarization function from the last section we calculate the absorption coefficient

TABLE I. Parameters of the calculation.

| Case | ρ                         | $T_{e}$ | $T_h$ | $E_p - E_g$ | $\Delta E_p$ | $k_s a_B$ |
|------|---------------------------|---------|-------|-------------|--------------|-----------|
| а    | $10^{16} \text{ cm}^{-3}$ | 77 K    | 77 K  |             |              | 0.77      |
| b    | $10^{16} \text{ cm}^{-3}$ | 300 K   | 300 K |             |              | 0.40      |
| с    | $10^{16} \text{ cm}^{-3}$ | 77 K    | 300 K |             |              | 0.61      |
| d    | $10^{16} \text{ cm}^{-3}$ |         |       | 18.8 meV    | 4.7 meV      | 0.71      |
| e    | $10^{16} \ cm^{-3}$       |         |       | 56.4 meV    | 4.7 meV      | 0.40      |

$$\alpha(\omega) \propto i \frac{1}{\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2} \left[ P_{\text{ret}}(\mathbf{k}_1, \mathbf{k}_2, \omega) - P_{\text{adv}}(\mathbf{k}_1, \mathbf{k}_2, \omega) \right]$$
(29)

and the luminescence spectrum

$$p(\boldsymbol{\omega}) \propto -i \frac{1}{\Omega} \sum_{\mathbf{k}_1 \mathbf{k}_2} P_-^+(\mathbf{k}_1, \mathbf{k}_2, \boldsymbol{\omega}).$$
(30)

The explicit calculations are done with GaAs parameters  $E_g(0K) = 1.52 \text{ eV}$ ,  $m_e = 0.067m_0$ ,  $m_h = 0.442m_0$ , and  $\varepsilon = 13.1$ , leading to an exciton binding energy  $E_B = 4.7 \text{ meV}$  and Bohr radius  $a_B = 12 \text{ nm}$ . We consider different situations describing photoexcited semiconductors: electrons and holes at the same temperature (quasiequilibrium), electrons and holes at different temperature, and strongly nonthermal distributions with high-excess energy. Nonthermal distributions arise for optical excitation high above the band edge and can be determined solving kinetic equations.<sup>19</sup> For simplicity we assume Gaussian distributions centered at electron-hole-pair energy  $E_p$  with a width  $\Delta E_p$ .

Table I shows the parameters of the calculations for five different examples: the electron-hole-pair density  $\rho$ , electron and hole temperatures  $T_e$  and  $T_h$ , mean value of the electron energy  $E_p$ , energetic width  $\Delta E_p$ , and the Thomas-Fermi screening wave number as calculated from Eq. (27). Examples a-b correspond to a quasiequilibrium at 77 K and 300 K, respectively. In example c, the temperatures of the two Fermi gases are different: 77 K for electrons and 300 K for holes. Such a situation may occur when the relaxation is faster for one species than for the other. Examples d-e refer to strongly nonthermal states with different excess energies. To study the influence of the carrier distribution, the electron-hole-pair density was chosen to be the same for all examples. According to Eq. (27), a carrier distribution towards higher energies leads to a smaller screening wave number. In all cases, the excitation is below the Mott transition.

The optical absorption according to Eq. (29) for examples a-e is plotted in Fig. 1 as a solid line. For comparison, the absorption spectrum of the semiconductor in ground state is shown as a dashed curve. The absorption near the band edge is strongly correlated with the screening wave number (see Table I). It is plausible that the oscillator strength of the exciton is reduced with increasing  $k_s$ . The correlation between exciton position and screening wave number is due to the fact that the Coulomb-hole term [third line of Eq. (28)] is the dominant contribution to the band-gap renormalization. As there is no population inversion in any of the examples, there is no stimulated emission. For the highly-excited, non-thermal carriers (d–e), the carrier distribution manifests itself



FIG. 1. Absorption  $\alpha$  vs energy  $E = \hbar \omega$  for examples (a)–(e). Solid line: calculations for parameters from Table I. Dashed line: absorption of the semiconductor in ground state.

as differential gain, combined with a small induced absorption at the high-energy shoulder.

The corresponding luminescence spectra can be seen in Fig. 2. The results of the exact solution (22) correspond to the solid line. As the total intensities are different for each example, individual y-axis scalings have been chosen. For the thermal distributions (a-c), the main contribution to the luminescence stems from the exciton and there is a pronounced high-energy shoulder. The spectrum (c) in case of different electron and hole temperatures, 77 K and 300 K, respectively, is similar to the spectra for quasiequilibrium, and is somewhat in-between the spectra for 77 K (a) and 300 K (b). Nevertheless, the luminescence in case (c) could not be calculated by means of the KMS relation. The nonthermal distributions (d-e) are characterized by a luminescence signal from the continuum region. The maximum of the luminescence is near the change from differential gain to differential absorption. In contrast, the contribution from the exciton is vanishingly small, but would be seen in a logarithmic plot.

We now discuss the approximate solutions. The solution in first order in V [Eq. (24)] (dashed curve) goes over in the exact solution for high energies. For the thermal distributions this approximation completely fails, since the truncation of the BSE removes the bound states. In contrast, for the nonthermal distributions, the result of this approximation gives qualitatively the correct result, because the contribution of the bound states is suppressed. Even though the approximation (24) does not guarantee that  $-iP_{-}^{+}$  is positive semidefinite, a positive luminescence spectrum was observed in all cases.



FIG. 2. Luminescence p vs energy  $E = \hbar \omega$  for examples (a)–(e) according to Table I. Solid line: exact solution of the BSE (22). Dashed line: solution of the BSE in first order [Eq. (24)]. Dotted line: result from Eq. (25). The y axes are individually normalized.

In the approximation (25) (dotted line), the overall intensity is not correlated with the overall intensity of the exact solution, although for free-particles equations (22) and (26) give identical results. Nevertheless, for thermal distributions of carriers, where the exciton is dominant, the correct qualitative behavior is observed. However, there are also regions where the signal is slightly negative, even for quasiequilibrium situations (a). For nonthermal distributions with highexcess energy (d-e), this approximation completely fails: a negative signal is observed, which is of the same order as the positive signal, and the contribution of the exciton is drastically overestimated. A significant improvement is the calculation of the source term in a second Born approximation.<sup>14</sup> In this case, the result is much closer to the exact solution.<sup>20</sup> It is not yet clear whether the inclusion of Coulomb scattering in all orders would give the same result as Eq. (22).

### V. SUMMARY

In this paper we have derived a relation between the luminescence signal, the current-density correlation function and the polarization function. The Bethe-Salpeter equation for  $P_{-}^{+}$  was exactly solved for static screening. This allows us to calculate the luminescence signal for an arbitrary non-thermal distribution of carriers. The solution complies with the Kubo-Martin-Schwinger relation for thermal equilibrium and the compatibility relations relations between the components of the Keldysh matrix. Furthermore, it is guaranteed that the luminescence signal is non-negative.

Numerical studies were done for various thermal and non-

thermal distributions and the comparison was made with previous solutions. The solution of the Bethe-Salpeter equation first order in the Coulomb interaction by Jahnke *et al.* and Pereira and Henneberger gives a reasonable agreement in case that the luminescence signal stems from continuum states, but fails when the signal from the exciton is the dominating one. The solution by means of photon-assisted density matrices with unrenormalized source term gives the correct qualitative behavior when the signal is dominated by the exciton contribution, but completely fails when the signal is dominated by continuum states. Furthermore, the luminescence spectrum may become negative.

The formalism presented can be generalized to include

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microscopic polarization, i.e., nondiagonal elements of the density matrix, which is important for coherently excited semiconductors. The application to low-dimensional structures is also straightforward. At present, there is no rigorous proof for the equivalence of both approaches, Green's functions and photon-assisted density matrices. This question will be the subject of future research.

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