Microscopic Theory of Excitonic Signatures in Semiconductor Photoluminescence

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Luminescence in a quantum well is studied theoretically using a consistent quantum description of light interacting with Coulomb correlated carriers. The buildup of excitonic luminescence during the plasma cooling process is analyzed for an initially hot electron-hole plasma. [S0031-9007(98)07252-4]

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The detailed analysis of the excitonic resonance features and their dynamics in either absorption or photoluminescence (PL) spectra are the subject of many current semiconductor experiments. Since the excitonic resonances are energetically below the band edge, it is interesting to investigate the buildup of excitonic features for a situation where an interband excitation creates a free carrier plasma with excess kinetic energy well above the band gap. Such investigations are often designated to extract information about energy relaxation and exciton formation dynamics [1].

There have been several theoretical attempts [2] to determine the exciton formation time by evaluating the coupled dynamics of electron $f^e_{\mathbf{k}}$, hole $f^h_{\mathbf{k}}$, and often phenomenologically introduced exciton $n^{ex}_{\mathbf{k}}$ occupation probabilities. The observed light emission I with momentum $\mathbf{q}$ and energy $\hbar c|\mathbf{q}|$ is then related in an *ad hoc* manner to the exciton population with the same energy via Fermi's golden rule

$$I(\mathbf{q}) \propto |\mathcal{M}_{g,e}|^2 n^{ex}_{E=\hbar c|\mathbf{q}|}\,, \tag{1}$$

where $\mathcal{M}_{g,e}$ is the transition matrix element between excited (e) and ground state (g) of hydrogen-atom-like bound states. This way the build-up of the excitonic resonance in photoluminescence has been interpreted as direct evidence for exciton formation [1].

A more systematic approach is to investigate excitonic signatures in the semiconductor luminescence by starting from the many-body Hamiltonian where Coulomb interaction of electrons and holes is included [3] and then derive the relevant quantities either with the Green's function or the density matrix approach. In such a description, exciton properties can be determined by solving a two-body problem involving expectation values of four Fermionic carrier operators $a_{\mathbf{s}}$

$$\langle a^\dagger_{\mathbf{1}} a^\dagger_{\mathbf{2}} a_{\mathbf{3}} a_{\mathbf{4}}\rangle = \langle a^\dagger_{\mathbf{1}} a^\dagger_{\mathbf{2}} a_{\mathbf{3}} a_{\mathbf{4}}\rangle|_{HF} + \delta\langle a^\dagger_{\mathbf{1}} a^\dagger_{\mathbf{2}} a_{\mathbf{3}} a_{\mathbf{4}}\rangle\,, \tag{2}$$

where the first term is the Hartree-Fock decoupling and the second term contains the higher order correlations. The simplest approximation is to keep the first term of Eq. (2) which leads to the Hartree-Fock semiconductor Bloch equations (SBE) when the light is treated classically. The resulting semiconductor absorption correctly shows excitonic resonances [3] even though no predictions for the formation of exciton populations can be made at this level. Much attention has been paid to a systematic improvement of the Hartree-Fock approximation scheme, [4,5], where the effects of carrier and polarization scattering have been included, e.g., at the level of a second order Born approximation.

In this Letter, we use a quantum theory of the interacting photon electron-hole system to study excitonic signatures in the photoluminescence without the need to address the full exciton formation problem. The approach describes the quantum statistical features of the light by a boson operator $b_{\mathbf{q}}$ for each independent field mode $\mathbf{u}_{\mathbf{q}\sigma}(\mathbf{r})$ identified with a wave vector $\mathbf{q}$ and polarization direction $\mathbf{e}_{\mathbf{q}}$. Since we are investigating the bare quantum well (QW) luminescence the mode functions can be chosen to be plane waves $\mathbf{u}_{\mathbf{q}\sigma}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}}\mathbf{e}_{\mathbf{q}}$. For notational simplicity, we include the polarization index with $\mathbf{q}$. The quantum properties of the carrier system are determined by Fermion operators $e_{\mathbf{k}}$ and $h_{\mathbf{k}}$ for conduction band electron and valence band hole, respectively, having the in-plane momentum $\mathbf{k}$. The noninteracting photons are described with the harmonic oscillator Hamiltonian [6] and for the carrier subsystem we use the standard [3] many-body Hamiltonian including Coulomb interaction. The quantized form of the dipole interaction between the photons and carriers is described, e.g., in Ref. [7]. To investigate photoluminescence properties of the interacting electron-hole-photon system (see Fig. 1), we determine the dynamics of the photon number $\langle b^\dagger_{q,\mathbf{q}_{\|}} b_{q,\mathbf{q}_{\|}}\rangle$, where $\mathbf{q}_{\|}$ is the photon momentum in the QW plane, together with the electron occupation $f^e_{\mathbf{k}} = \langle e^\dagger_{\mathbf{k}} e_{\mathbf{k}}\rangle$ and the hole occupation $f^h_{\mathbf{k}} = \langle h^\dagger_{-\mathbf{k}} h_{-\mathbf{k}}\rangle$. Because of the light-matter interaction Hamiltonian, these expectation values are coupled via the quantity $\langle b^\dagger_{q,\mathbf{q}_{\|}} h_{-\mathbf{k}} e_{\mathbf{k}+\mathbf{q}_{\|}}\rangle$ describing the amplitude of photon assisted electron-hole pair recombination. In the following, we want to study a situation where an incoherent electron-hole plasma has been generated and the radiative carrier recombination is observed as PL. When external driving fields are absent in the spectral region where the PL is observed, we have $\langle b_{\mathbf{q}}\rangle = 0$ and $\langle h_{-\mathbf{k}} e_{\mathbf{k}'}\rangle = 0$. Such a situation is realized, e.g., for an optical pump pulse high above the band gap, where carrier relaxation leads to a rapid loss of coherence. Using a Hartree-Fock level decoupling scheme [7], the Heisenberg equations of motion for $\langle b^\dagger_{q,\mathbf{q}_{\|}} h_{-\mathbf{k}} e_{\mathbf{k}+\mathbf{q}_{\|}}\rangle$, $\langle b^\dagger_{q,\mathbf{q}_{\|}} b_{q',\mathbf{q}_{\|}}\rangle$, $f^e_{\mathbf{k}}$, and $f^h_{\mathbf{k}}$ lead to the closed set of equations

$$i\hbar \frac{\partial}{\partial t} \langle b_{\mathbf{q}}^{\dagger} h_{-\mathbf{k}} e_{\mathbf{k}+\mathbf{q}_{\|}} \rangle = (\epsilon_{\mathbf{k},\mathbf{q}_{\|}} - \hbar\omega_{\mathbf{q}} - i\gamma) \langle b_{\mathbf{q}}^{\dagger} h_{-\mathbf{k}} e_{\mathbf{k}+\mathbf{q}_{\|}} \rangle + (f_{\mathbf{k}+\mathbf{q}_{\|}}^{e} + f_{\mathbf{k}}^{h} - 1)\Omega_{\mathbf{k},\mathbf{q}} + f_{\mathbf{k}}^{h} f_{\mathbf{k}+\mathbf{q}_{\|}}^{e} \Omega_{\mathbf{q}}^{\mathrm{SE}}, \tag{3}$$

$$\frac{\partial}{\partial t} \langle b_{q,\mathbf{q}_{\|}}^{\dagger} b_{q',\mathbf{q}_{\|}} \rangle = i(\omega_{\mathbf{q}} - \omega_{\mathbf{q}'}) \langle b_{q,\mathbf{q}_{\|}}^{\dagger} b_{q',\mathbf{q}_{\|}} \rangle + \frac{1}{\hbar} \sum_{\mathbf{k}} [\mathcal{F}_{\mathbf{q}} \langle b_{\mathbf{q}'} e_{\mathbf{k}+\mathbf{q}_{\|}}^{\dagger} h_{-\mathbf{k}}^{\dagger} \rangle + \mathcal{F}_{\mathbf{q}'} \langle b_{\mathbf{q}}^{\dagger} h_{-\mathbf{k}} e_{\mathbf{k}+\mathbf{q}_{\|}} \rangle], \tag{4}$$

$$\frac{\partial}{\partial t} f_{\mathbf{k}}^{e} = -\frac{2}{\hbar} \sum_{q,\mathbf{q}_{\|}} \mathrm{Re}[d_{cv}^{\star} \mathcal{F}_{\mathbf{q}} \langle b_{q,\mathbf{q}_{\|}}^{\dagger} h_{-\mathbf{k}-\mathbf{q}_{\|}} e_{\mathbf{k}} \rangle] + \frac{\partial}{\partial t} f_{\mathbf{k}}^{e}|_{\mathrm{rel}} + \frac{\partial}{\partial t} f_{\mathbf{k}}^{e}|_{\mathrm{SBE}}, \tag{5}$$

$$\frac{\partial}{\partial t} f_{\mathbf{k}}^{h} = -\frac{2}{\hbar} \sum_{q,\mathbf{q}_{\|}} \mathrm{Re}[d_{cv}^{\star} \mathcal{F}_{\mathbf{q}} \langle b_{q,\mathbf{q}_{\|}}^{\dagger} h_{-\mathbf{k}} e_{\mathbf{k}+\mathbf{q}_{\|}} \rangle] + \frac{\partial}{\partial t} f_{\mathbf{k}}^{h}|_{\mathrm{rel}} + \frac{\partial}{\partial t} f_{\mathbf{k}}^{h}|_{\mathrm{SBE}}, \tag{6}$$

where $\epsilon_{\mathbf{k},\mathbf{q}_{\|}}$ is the kinetic energy of the electron-hole pair with the Coulomb renormalization, $\omega_{\mathbf{q}}$ is the frequency of the field mode, and $\frac{\partial}{\partial t} f_{\mathbf{k}}^{e(h)}|_{\mathrm{SBE}}$ contains the carrier generation dynamics described by the semiconductor Bloch equations. We have introduced a dephasing rate γ and carrier relaxation rate $\frac{\partial}{\partial t} f_{\mathbf{k}}^{e(h)}|_{\mathrm{rel}} = \sum_{\mathrm{rel}} (f_{\mathbf{k}}^{e(h)} - f_{\mathbf{k},\mathrm{rel}}^{e(h)})/T_{\mathrm{rel}}$ where carrier distribution relaxes toward thermal distribution $f_{\mathbf{k},\mathrm{rel}}^{e(h)}$ with rate T_{rel}. Both T_{rel} and γ are obtained from a separate calculation of correlation contributions in the second Born approximation [5]. The effective mode strength at the QW position is given by $\mathcal{F}_{\mathbf{q}} = \mathcal{E}_{\mathbf{q}} \int |\xi(z)|^2 e^{iqz}\, dz$ with the QW confinement function $\xi(z)$ and the vacuum field amplitude $\mathcal{E}_{\mathbf{q}}$. Equation (3) is driven by a spontaneous emission term,

$$\Omega_{\mathbf{q}}^{\mathrm{SE}} = i\mathcal{F}_{\mathbf{q}} d_{cv}, \tag{7}$$

where d_{cv} is the dipole matrix element. The electron-hole recombination is also influenced by a renormalized stimulated process described by

$$\Omega_{\mathbf{k},\mathbf{q}} = d_{cv} \left[\sum_{q'} i\mathcal{F}_{\mathbf{q}'} \langle b_{\mathbf{q}}^{\dagger} b_{q',\mathbf{q}_{\|}} \rangle - \sum_{\mathbf{k}'} P d_{cv}^{\star} \langle b_{\mathbf{q}}^{\dagger} h_{-\mathbf{k}'} e_{\mathbf{k}'+\mathbf{q}_{\|}} \rangle \right] + \sum_{\mathbf{k}'} V_{\mathbf{k}'-\mathbf{k}} \langle b_{\mathbf{q}}^{\dagger} h_{-\mathbf{k}'} e_{\mathbf{k}'+\mathbf{q}_{\|}} \rangle, \tag{8}$$

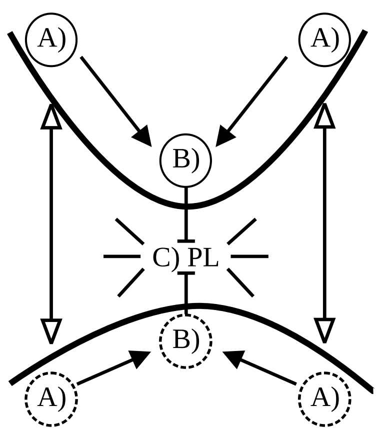

FIG. 1. Schematic picture of electron-hole PL: (*A*) Excitation of electron-hole plasma energetically high in the bands; (*B*) carrier relaxation toward low momentum states; (*C*) PL resulting from the recombination of low momentum electrons and holes.

where the two first terms are the unrenormalized stimulated contribution. Here P defines strength of the photon assisted polarization $\sum_{\mathbf{k}'} d_{cv}^{\star} \langle b_{\mathbf{q}}^{\dagger} h_{-\mathbf{k}'} e_{\mathbf{k}'+\mathbf{q}_{\|}} \rangle$, and $V_{\mathbf{k}}$ is the quantum well Coulomb matrix element. Equations (3)–(6) are the *semiconductor luminescence equations*.

Before we numerically solve the semiconductor luminescence equations, we briefly discuss the interplay of the different contributions. The term $f_{\mathbf{k}}^{h} f_{\mathbf{k}+\mathbf{q}_{\|}}^{e} \Omega_{\mathbf{q}}^{\mathrm{SE}}$ entering Eq. (3) is nonzero if carriers are excited in the QW. Hence, $\langle b_{\mathbf{q}}^{\dagger} h_{-\mathbf{k}} e_{\mathbf{k}+\mathbf{q}_{\|}} \rangle$ correlations start to build up even if the field-particle and the field-field correlations are initially taken to be zero. Thus, $f_{\mathbf{k}}^{h} f_{\mathbf{k}+\mathbf{q}_{\|}}^{e} \Omega_{\mathbf{q}}^{\mathrm{SE}}$ provides a spontaneous emission source to the recombination process. According to the factor $f_{\mathbf{k}}^{h} f_{\mathbf{k}+\mathbf{q}_{\|}}^{e}$, the spontaneous recombination takes place only if an electron at $\mathbf{k} + \mathbf{q}_{\|}$ and a hole at $-\mathbf{k}$ are simultaneously present. The quantity $\Omega_{\mathbf{q}}^{\mathrm{SE}}$ determines the rate of the recombination process in terms of the dipole matrix element d_{cv} of the transition multiplied by the effective mode strength $\mathcal{F}_{\mathbf{q}}$ at the QW. However, the observed photoluminescence is a result of the dynamic interplay of the field-field and field-particle correlations affected by spontaneous emission, stimulated contributions, as well as Coulomb correlations. When the light field changes are sufficiently slow, this PL is simply the photon flux passing the detector. In this adiabatic limit, the bare QW luminescence in direction $\mathbf{q}$ is $I(\mathbf{q}) = \frac{\partial}{\partial t} \langle b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} \rangle$.

To illustrate our approach we present in the following luminescence properties of a single 8 nm wide GaAs quantum well. Using the standard material parameters, we obtain the Bohr radius $a_0 = 12.5$ nm and the binding energy $E_B = 4.2$ meV for the 3D exciton. The QW exciton resonance occurs $2.5E_B$ below the unrenormalized band edge. The carrier generation is computed by solving the semiconductor Bloch equations for a 500 fs excitation pulse 16.7 meV above the unrenormalized band edge when the lattice temperature is initially 4 K. In the luminescence calculation, the contributions $\langle b_{\mathbf{q}}^{\dagger} h_{-\mathbf{k}} c_{\mathbf{k}+\mathbf{q}_{\|}} \rangle$ and $\langle b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} \rangle$ are initially zero and their dynamics is solved from Eqs. (3) and (4). The computed evolution of the carrier occupations and the PL spectrum for direction normal to the QW plane ($\mathbf{q}_{\|} = \mathbf{0}$) are shown in Fig. 2. The presented time resolved spectra can be directly related to temporal PL in experiments obtained, e.g., by upconversion techniques [8]. Inclusion of a specific detector model [9] basically introduces time resolution dependent weight and delay factors compared to the computed $\frac{\partial}{\partial t}\langle b_{\mathbf{q}}^\dagger b_{\mathbf{q}}\rangle$ spectra. When the pulse center is exactly at the QW ($t = 0$ ps), the electron and hole occupations are strongly non-thermal and peaked at the pump energy 16.7 meV. However, *the PL spectrum is already centered at the exciton* even though it is very broad. At the time $t = 0.5$ ps, the final carrier density $n = 1.8 \times 10^{11}$ cm^{-2} is reached and the carrier occupation functions approach Fermi-Dirac distributions where the low energy **k** states are increasingly populated. At the same time, the PL spectrum becomes considerably narrower and its peak value increases. After roughly $t = 4$ ps, the shape of the PL becomes time independent (quasistationary). For longer time scales, the peak value of the PL first increases due to the cooling carrier distributions and then decreases with the decaying carrier density.

To determine the origin of the excitonic PL we artificially switch off the Coulomb term in Eq. (8). The result is shown as a dashed line in Fig. 2. The computation leads to PL which is peaked at the renormalized band edge describing band-to-band luminescence. Thus, we conclude that the Coulomb correlation contribution to the photon assisted electron-hole recombination, $\sum_{\mathbf{k}'} V_{\mathbf{k}'-\mathbf{k}}\langle b_{\mathbf{q}}^\dagger h_{-\mathbf{k}'} e_{\mathbf{k}'+\mathbf{q}_\parallel}\rangle$, is responsible for the excitonic peak in the PL spectrum. The consistent quantum approach shows that the excitonic peak occurring in the PL spectrum is already well described without including a correlated exciton population. Neither can one apply the quantum regression theorem to relate one particle level semiconductor luminescence equation results to formation of two particle level exciton densities because we purposely have not included any phenomenological exciton formation processes in our analysis (see Fig. 1).

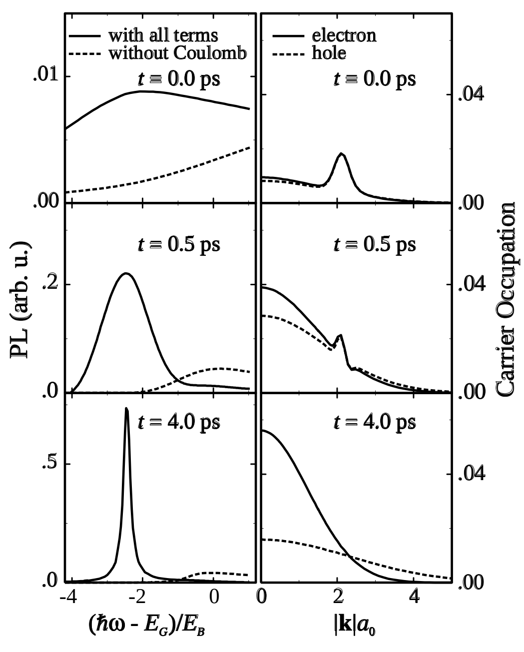

FIG. 2. The time evolution of bare QW luminescence with (solid line) and without (dashed line) the Coulomb Correlations are shown in the left column. The carrier occupations at the corresponding time are shown; the final carrier density is $n = 1.8 \times 10^{10}$ cm^{-2}. In the computations, the QW band gap energy is $E_G = 1.485$ eV and the dephasing constant is 0.4 meV determined from the independent quantum kinetic computations.

The semiconductor luminescence equations provide a rather general basis for analysis of semiconductor luminescence properties. For example, they allow a direct extension of the investigations to the nonlinear regime. As an illustration, we show in Fig. 3 the computed PL spectrum for a carrier density $n = 2.2 \times 10^{11}$ cm^{-2} when the exciton resonance is present and the carrier occupation functions have relaxed to 77 K Fermi-Dirac distributions. Even with such a high excitation the PL spectrum is still centered at the excitonic peak of Fig. 2. However, the spectrum is asymmetric due to nonlinearities caused by the free carrier plasma above the band edge. The PL spectrum is compared to the absorption spectrum at the same excitation conditions in Fig. 3b. We see that the excitonic absorption resonance is already bleached due to Coulombic and exchange effects in the electron-hole plasma. The computation without the Coulomb correlated electron-hole recombinations (dashed line Fig. 3a) shows once again PL at the renormalized band edge.

In summary, we present a rather general formalism that allows us to compute semiconductor luminescence properties. We demonstrate that the appearance of excitonic

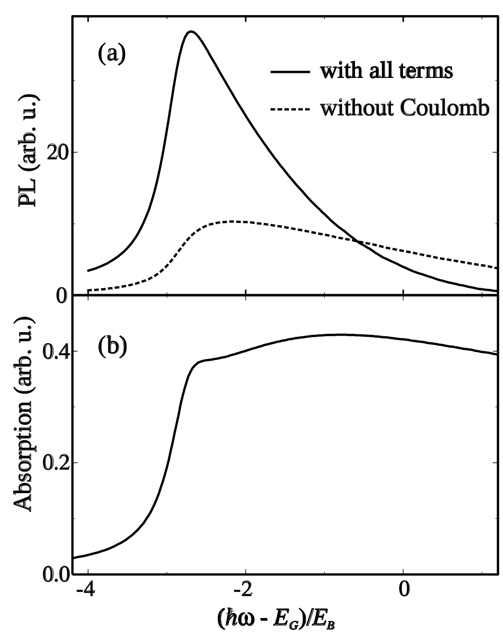

FIG. 3. (a) Computed steady state PL spectra with (solid line) and without (dashed line) the Coulomb correlations for carrier density $n = 2.2 \times 10^{11}$ cm^{-2}, and carrier temperature $T = 77$ K. (b) The corresponding absorption spectrum is also shown. The dephasing constant for this density is 1 meV.

signatures in the emission cannot simply be related to the formation of exciton population.

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