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LETTER TO THE EDITOR

## Excitonic–biexcitonic polaritons—new quasiparticles in semiconductors

Z G Koinov†

Department of Physics, Higher Institute for Transport Engineering, 1574 Sofia, Bulgaria

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**Abstract.** The existence of new quasiparticles in semiconductors, formed by the coupling of photons with excitons and biexcitons, is theoretically predicted. This elementary excitation (excitonic–biexcitonic polaritons) manifests itself as a common pole of photon, and two- and four-particle electron–hole Green functions. The dependence of the dielectric function on the existence of biexcitons is discussed in the case of  $Z_{12}$  exciton resonance of CuBr.

The last two decades of semiconductor research have been characterized by a large number of studies, which have considered the problem of light propagation in crystals as polaritons propagating through the crystals. From the theoretical point of view the polariton modes are formed by the interaction of light with the polarization in crystals. The polarization can be caused by atomic displacements or it can be of electronic origin. In the first case the light and the lattice vibrational modes are coupled into a set of normal modes. These new modes are called phonon polaritons. In what follows we will consider the ions to be fixed at their equilibrium positions, i.e. we assume that the polarization is caused by the collective electronic excitations. In an ideal crystallized semiconductor, excitons and biexcitons are the lowest energetically electronic excitations. In what follows we will show that in the system under consideration the light, excitons and biexcitons are coupled into a set of normal modes. We call these new modes excitonic–biexcitonic polaritons.

Turning our attention to the theoretical description of biexcitons we find that two basic approaches have been proposed. According to the first one, which is called a phenomenological approach, the excitons are boson excitations and the biexcitons are considered as compound particles formed by the coupling of two excitons due to the exciton–exciton attractive potential (Ivanov *et al* 1991, Keldysh 1992, Ivanov and Haug 1993, 1995a, b). But, if only the attractive potential between the boson particles (excitons) is taken into account, the system of Bose particles is unstable against spontaneous contraction. In order to avoid this difficulty one has to introduce two equivalent types of exciton with the same parameters, both with total spin zero. The only distinction is that the excitons of the different types attract each other whereas excitons of the same type have a repulsive interaction. The main problem with the phenomenological approach arises due to the fact that excitons and biexcitons are not truly independent boson particles. In the second approach the explicit introduction of boson creation and annihilation operators for the exciton states is avoided. The second method, which is a completely microscopic treatment, is based on the assumption that the biexcitons are four-particle (two electrons and two holes) bound states (Combescot

† E-mail: ann@phys.uni-sofia.bg; fax: +359-2-971-10-58.

and Combescot 1989, Ivanov *et al* 1991). The main problem with this approach is that the equations for the corresponding many-particle Green functions are too complicated, but the method is very suitable for accounting for the changes of the biexciton properties and parameters due to the Coulomb interactions.

In this letter we formulate a microscopic Green function method for describing the elementary excitation spectra in a system of interacting photons and electrons taking into account not only the two-particle electron-hole bound states, but also the four-particle (two electrons and two holes) bound states as well. The method is based on the field-theoretical technique which naturally leads to the Legendre transforms of the generating functional. Using the functional technique combined with the method of Legendre transforms we derive a set of nine independent exact equations for the photon, two- and four-particle electron-hole Green functions. Knowledge of the solutions of the above equations provides the excitation energies of the quasiparticles. In this letter we report two main results.

(i) In the system of interacting electrons and photons, there exist well-defined composite quasiparticles (excitonic-biexcitonic polaritons) formed by the coupling of photons, excitons and biexcitons. The excitonic-biexcitonic polaritons are manifested as common poles of the Fourier transforms for the photon, and two- and four-particle electron-hole Green functions. Although this result is to be expected for general reasons, it has not been derived in previous papers. A similar problem has been analysed recently by Ivanov and Haug (1993, 1995a, b). In these studies the authors proposed the so-called 'bipolariton concept' which treats the excitonic molecule as two polaritons quasi-bound through the Coulomb interaction, rather than the two-exciton complex. The starting Hamiltonian for this model has the form

$$H = H_{pt}^{(0)} + H_{exc}^{(0)} + H_{exc-pt} + H_{exc-exc}$$

where  $H_{pt}^{(0)}$  and  $H_{exc}^{(0)}$  are the Hamiltonians for the system of non-interacting photons and excitons. They can be expressed in terms of Bose creation and annihilation operators for the photon and exciton states. The coupling of the photons and excitons into excitonic polaritons is due to the exciton-photon interaction  $H_{exc-pt}$ . The coupling of two excitons of the polariton waves into bipolaritons is due to the last term in the above equation.

The bipolariton concept contradicts our result that the new quasiparticles (excitonic-biexcitonic polaritons) exist in the system of interacting photons and electrons. In order to clarify how our result is connected with the bipolariton model the following critical remarks should be made. The bipolariton model describes the non-linear propagation of the polariton waves. In the case where the non-linearities can be neglected there exist two polariton branches, which are the roots of the equation  $\omega^2 \varepsilon(\mathbf{Q}, \omega) = c^2 Q^2$ , where  $\varepsilon$  is the dielectric function. If one takes into account the exciton-exciton interaction, then not only are the bipolaritons formed, but also the existence of the bipolaritons modifies the dielectric function. In the studies mentioned above the bipolaritons do not modify the excitonic-polariton dispersion. For this reason the photon and exciton Green functions have common poles (upper and lower polariton branches), while the poles of the two-exciton (bipolariton) Green function depend on the bipolariton binding energy. The authors stated that the Bethe-Salpeter equation for the bipolariton Green function can be derived from the Heisenberg equations for the photon, exciton and biexciton creation and annihilation operators, when the non-linear term in the corresponding Heisenberg equation (the third term in the right-hand side of equation (34) in a paper by Ivanov and Haug 1993) is neglected. But, this term is responsible for the exciton-exciton interaction and the non-linear polariton absorption is governed by the neglected term. If the authors neglected the exciton-exciton interaction simply in order to obtain explicit results, then one may well ask whether this neglected

term does not change the form of the Bethe–Salpeter kernel and, therefore, the numerically calculated bipolariton binding energy.

(ii) The second result concerns the fact that the formation of biexcitons may modify the dielectric function and, therefore, the excitonic–polariton dispersion. In order to obtain a simple understanding of this problem we consider the eightfold-degenerate exciton ground state for the  $Z_{12}$  series of CuBr. In this case the exciton states are formed by  $\Gamma_6$  conduction and  $\Gamma_8$  valence band. The splitting of the exciton ground state is caused by the Elliott exchange interaction and yields the exciton states  $\Gamma_3 \oplus \Gamma_4$  and  $\Gamma_5$ . The  $\Gamma_5$  exciton dispersion

$$E_{\Gamma_5}(\mathbf{Q}) = E_{\Gamma_5} + \hbar^2 Q^2 / 2M_{exc}$$

where  $E_{\Gamma_5} = E_{\Gamma_3 \oplus \Gamma_4} + \Delta_E$ ;  $\Delta_E$  is the splitting caused by the Elliott exchange interaction. The dielectric function  $\varepsilon(\mathbf{Q}, \omega)$  can be expressed in the following form:

$$\varepsilon(\mathbf{Q}, \omega) = 1 - \frac{4\pi\hbar c^2}{\omega^2} \Pi^{(L)}(\mathbf{Q}, \omega)$$

where  $\Pi^{(L)}$  is the proper self-energy part of the long-wavelength photons, and it can be calculated by means of the corresponding Green function  $K_M^E$ . In diagrammatic language  $K_M^E$  can be obtained by subtracting from the two-particle Green function any diagrams that may be separated into two parts by cutting only a long-wavelength photon line. In the case where the existence of the biexciton states can be neglected,  $K_M^E$  assumes the form of the two-particle Green function for ‘mechanical’ excitons when the Elliott exchange interaction is included, and the dielectric function takes the following form:

$$\varepsilon(\mathbf{Q}, \omega) = \varepsilon_b \left( 1 + \frac{\Delta_{LT}}{E_{\Gamma_5}(\mathbf{Q}) - \hbar\omega} + \frac{\Delta_{LT}}{E_{\Gamma_5}(\mathbf{Q}) + \hbar\omega} \right)$$

where  $\Delta_{LT}$  is the longitudinal–transverse splitting and  $\varepsilon_b$  is the ‘background’ dielectric constant. The exciton resonance at the point  $\mathbf{Q} = 0$  can be observed for the energy of exciting photons  $\hbar\omega_{\Gamma_5} = E_{\Gamma_3 \oplus \Gamma_4} + \Delta_E$ . Our calculations predict that the existence of biexcitons modifies the dielectric function, and the optical absorption of the photons of energy  $\hbar\omega_{pt} = E_{\Gamma_3 \oplus \Gamma_4} + \Delta_E - \Delta_{biexc}$  can be observed. The energy shift  $\Delta_{biexc}$  at the point  $\mathbf{Q} = 0$  can be calculated by means of the corresponding exciton–biexciton matrix element. Later, we will see that the order of magnitude of  $\Delta_{biexc}$  can be obtained from two-photon absorption measurements. It is worth noting that according to the bipolariton model this effect cannot be observed.

We now discuss the model and the method. The system under consideration consists of a radiation field, described by the action  $S_0^{(\omega)}$  and a material system. In this letter we will consider the ions fixed at their equilibrium positions. In this approximation the material system is the semiconductor, which can be described by the action for non-interacting electrons in a periodical lattice potential  $S_0^{(e)}$ . The radiation and the matter interact via an electron–photon interaction, described by the action  $S^{(e-\omega)}$ . In terms of the field theory we deal with a boson (photon) field  $A_\alpha(z)$  interacting with a fermion field  $\bar{\Psi}(y)$  (or  $\Psi(x)$ ) at finite temperatures. Here  $z = \boldsymbol{\rho}, v$ ,  $y = \mathbf{r}, \sigma, u$  and  $x = \mathbf{r}', \sigma', u'$  are composite variables, where  $\mathbf{r}, \mathbf{r}'$ ,  $\boldsymbol{\rho}$  are radius vectors and  $\sigma, \sigma'$  are spin indices. According to the finite-temperature field theory, invented by Matsubara (1955), the variables  $u, u', v$  range from 0 to  $\hbar\beta = \hbar(k_B T)^{-1}$ , where  $T$  is the temperature,  $k_B$  being the Boltzmann constant.

In the crystal optics approximation the action of the system has the following form (Koinov and Glinskii 1988):

$$S_1 = S_0^{(e)} + S_0^{(\omega)} + S^{(e-\omega)} + S^{(e-e)} \quad (1)$$

where

$$S_0^{(e)} = \bar{\Psi}(y)G^{(0)-1}(y, x)\Psi(x) \quad (2a)$$

$$S_0^{(\omega)} = \frac{1}{2}A_\alpha(z)D_{\alpha\beta}^{(0)-1}(z, z')A_\beta(z') \quad (2b)$$

$$S^{(e-\omega)} = \bar{\Psi}(y)\Gamma_\alpha^{(0)}(y, x|z)\Psi(x)A_\alpha(z) \quad (2c)$$

$$S^{(e-e)} = -\frac{1}{2}\bar{\Psi}(y)\Psi(x)\tilde{\Gamma}_\alpha^{(0)}(y, x|z)\tilde{D}_{\alpha\beta}^{(0)}(z, z')\tilde{\Gamma}_\beta^{(0)}(y', x'|z')\bar{\Psi}(y')\Psi(x'). \quad (2d)$$

Here and throughout we use the summation–integration convention that repeated variables are summed or integrated over. The action  $S^{(e-e)}$  describes the short-range part of the electron–electron interaction.  $G^{(0)-1}(y, x)$  is the inverse one-particle Green function for the system of non-interacting electrons in a periodical lattice potential.  $D_{\alpha\beta}^{(0)-1}(z, z')$  is the inverse free-photon propagator (in a gauge where the scalar potential is equal to zero).  $\Gamma_\alpha^{(0)}$  is the ‘bare’ electron–photon vertex.

All Matsubara Green functions can be obtained by functional differentiation from the generating functional for the connected Green functions  $Z[J, M, N]$  which is defined as follows:

$$Z[J, M, N] = \ln W[J, M, N] \quad (3a)$$

where  $J$  is the source of the photon field;  $M$  and  $N$  are the two- and four-particle electron–hole sources, and

$$W[J, M, N] = \int D\mu(\bar{\Psi}, \Psi, A) \exp\{S + J_\alpha(z)A_\alpha(z) - \bar{\Psi}(y)M(y, x)\Psi(x) + \bar{\Psi}(y)\bar{\Psi}(y')N(y, y'; x, x')\Psi(x)\Psi(x')\}. \quad (3b)$$

In the last equation the measure  $D\mu$  is given by  $D\mu = \text{constant} \times d\bar{\Psi} d\Psi dA$ , where the normalization constant is chosen in such a manner that  $\int D\mu \exp(S) = 1$ . The source  $N(y, y'; x, x')$  is antisymmetric over the arguments  $y, y'$  and  $x, x'$ :  $N(y, y'; x, x') = -N(y', y; x, x') = -N(y, y'; x', x)$ .

The photon Green function and one-particle electron Green function can be defined as follows:

$$D_{\alpha\beta}(z, z') = -\langle \hat{T}_v \{A_\alpha(z)A_\beta(z')\} \rangle = -\frac{\delta^2 Z}{\delta J_\alpha(z) \delta J_\beta(z')} \quad (4a)$$

$$G(x, y) = -\langle \hat{T}_u \{\Psi(x)\bar{\Psi}(y)\} \rangle = -\frac{\delta Z}{\delta M(y, x)}. \quad (4b)$$

Here all functional derivatives over the fermion fields and over the sources of the fermion type are left-handed ones, and after the functional differentiation one should set  $J = M = N = 0$ . In a similar way we introduce the two- and four-particle electron–hole Green functions:

$$K \begin{pmatrix} x & y' \\ y & x' \end{pmatrix} = -\langle \hat{T}_u \{\bar{\Psi}(y)\Psi(x)\bar{\Psi}(y')\Psi(x')\} \rangle = -\frac{\delta^2 Z}{\delta M(y, x) \delta M(y', x')} \quad (4c)$$

$$R \begin{pmatrix} x_{21} & y_{43} \\ y_{21} & x_{43} \end{pmatrix} = -\frac{\delta^2 Z}{\delta N(y_{12}; x_{12}) \delta N(y_{34}; x_{34})} \\ = -\langle \hat{T}_u \{\bar{\Psi}(y_3)\bar{\Psi}(y_4)\Psi(x_3)\Psi(x_4)\bar{\Psi}(y_1)\bar{\Psi}(y_2)\Psi(x_1)\Psi(x_2)\} \rangle \quad (4d)$$

where  $\hat{T}$  is a  $u$  (or  $u', v$ ) ordering operator,  $y_{12} = \{y_1, y_2\}$ ,  $x_{12} = \{x_1, x_2\}$  are composite variables and the brackets  $\langle O \rangle$  on an operator  $O$  mean that the thermodynamic average is

taken. The other two functional derivatives of  $Z$  with respect to the sources are

$$R_\alpha(z) = -\frac{\delta Z}{\delta J_\alpha(z)} \quad \Delta(x_{21}; y_{21}) = -\frac{\delta Z}{\delta N(y_{12}; x_{12})} \quad (4e)$$

The basic idea in our method is to use the second Legendre transform in order to derive a set of exact equations for the Green functions and vertex functions.

It is convenient to treat equations (4b) and (4e) as definitions for functionals  $R[J, M, N]$ ,  $G[J, M, N]$  and  $\Delta[J, M, N]$ . If those functionals are invertible with inverses  $J[R, G, \Delta]$ ,  $M[R, G, \Delta]$  and  $N[R, G, \Delta]$ , then we define the second Legendre transforms by

$$V[R, G, \Delta] = Z[R, G, \Delta] - J_\alpha(z) \frac{\delta Z}{\delta J_\alpha(z)} - M(y, x) \frac{\delta Z}{\delta M(y, x)} - N(y_{12}; x_{12}) \frac{\delta Z}{\delta N(y_{12}; x_{12})}. \quad (5)$$

Furthermore, we based our treatment on the set of nine independent exact equations for corresponding vertex and Green functions. By using an important property of the second Legendre transform—its orthogonality—one can derive the following set of equations:

$$\frac{\delta^2 Z}{\delta A_i(x) \delta A_j(x')} \frac{\delta^2 V}{\delta B_j(x') \delta B_k(x'')} = -\delta_{ik} \delta(x - x''). \quad (6)$$

Here  $A_1(x) = J_\alpha(z)$ ,  $A_2(x) = M(y, x)$ ,  $A_3(x) = N(y_{12}; x_{12})$  are the sources of the corresponding fields and  $B_1(x) = R_\alpha(z)$ ,  $B_2(x) = G(x, y)$ ,  $B_3(x) = \Delta(x_{21}; y_{21})$  are the corresponding dual quantities. Thus taking  $i = 1, 2, 3$  and  $k = 1, 2, 3$  we obtain a set of nine independent exact equations. Those equations allow us to formulate a microscopic theory of the propagation of a long-wavelength electromagnetic field through the crystal. Equations (6) allow us to obtain the following relationships between the three Green functions  $D_{\alpha\beta}$ ,  $K$  and  $R$ . The first one is a relationship between the photon propagator and two-particle Green function:

$$D_{\alpha\beta}(z, z') = D_{\alpha\beta}^{(0)}(z, z') + D_{\alpha\gamma}^{(0)}(z, z'') \Gamma_\gamma^{(0)}(y, x|z'') K \begin{pmatrix} x & y' \\ y & x' \end{pmatrix} \Gamma_\delta^{(0)}(y', x'|z''') D_{\delta\beta}^{(0)}(z''', z'). \quad (7a)$$

One can also obtain from equations (6) the relationship between two- and four-particle Green functions in the form

$$R \begin{pmatrix} x_{21} & y_{43} \\ y_{21} & x_{43} \end{pmatrix} = R_0 \begin{pmatrix} x_{21} & y_{43} \\ y_{21} & x_{43} \end{pmatrix} + R_0 \begin{pmatrix} x_{21} & y_{65} \\ y_{21} & x_{65} \end{pmatrix} \frac{\delta^2 V}{\delta \Delta(x_{65}; y_{65}) \delta G(x, y)} \times K \begin{pmatrix} x & y' \\ y & x' \end{pmatrix} \frac{\delta^2 V}{\delta G(x', y') \delta \Delta(x_{87}; y_{87})} R_0 \begin{pmatrix} x_{87} & y_{43} \\ y_{87} & x_{43} \end{pmatrix} \quad (7b)$$

where  $R_0$  is the four-particle electron–hole Green function when the polariton effects are neglected. The main result which follows from equations (7) is that in the system of interacting electrons and photons, there exist well-defined composite quasiparticles (excitonic–biexcitonic polaritons), which manifest themselves as common poles of the Fourier transforms of the three Green functions  $D_{\alpha\beta}$ ,  $K$  and  $R$  (Gell-Mann and Low 1951). Thus, any elementary excitation of wave vector  $\mathbf{Q}$  and energy  $\hbar\omega_v(\mathbf{Q})$  of the system under consideration manifests itself as a pole near the real axis in the frequency plane of the function

$$K \left( \begin{array}{cc|c} r_1\sigma_1 & r_3\sigma_3 & u_2 - u_1; u_4 - u_3; z \\ r_2\sigma_2 & r_4\sigma_4 & \end{array} \right).$$

The last one is obtained from the Fourier transform of the two-particle Green function

$$K \left( \begin{array}{cc} \mathbf{r}_1 \sigma_1 & \mathbf{r}_3 \sigma_3 \\ \mathbf{r}_2 \sigma_2 & \mathbf{r}_4 \sigma_4 \end{array} \middle| u_2 - u_1; u_4 - u_3; \frac{1}{2}(u_2 + u_1 - u_3 - u_4) \right)$$

by the analytic continuation of the set of points  $i\omega_p = i(2\pi/\hbar\beta)p$ ;  $p = 0, \pm 1, \pm 2, \dots$ , along the imaginary axis into the appropriate half of the  $z$ -plane. Similarly, one can define the analytic continuation of the photon and four-particle Green functions. If we restrict the range of frequencies  $\omega$  to the neighbourhood of position  $\omega_v(\mathbf{Q})$ , we may write

$$K \left( \begin{array}{cc} \mathbf{r}_1 \sigma_1 & \mathbf{r}_3 \sigma_3 \\ \mathbf{r}_2 \sigma_2 & \mathbf{r}_4 \sigma_4 \end{array} \middle| u_2 - u_1; u_4 - u_3; \omega \right) \approx \frac{\Phi^{vQ}(\mathbf{r}_2 \sigma_2; \mathbf{r}_1 \sigma_1; u_{21}) \Phi^{vQ^*}(\mathbf{r}_4 \sigma_4; \mathbf{r}_3 \sigma_3; u_{43})}{\omega - \omega_v(\mathbf{Q}) + i0^+} \quad (8a)$$

$$D_{\alpha\beta}(\mathbf{Q}, \omega) \approx \frac{A^{vQ}(\mathbf{Q}) A^{vQ^*}(\mathbf{Q})}{\omega - \omega_v(\mathbf{Q}) + i0^+} \quad (8b)$$

$$\begin{aligned} R^c \left( \begin{array}{cc} (\mathbf{r}, \sigma)_{21} & (\mathbf{r}, \sigma)_{65} \\ (\mathbf{r}, \sigma)_{43} & (\mathbf{r}, \sigma)_{87} \end{array} \middle| i\omega_{m_1}; i\omega_{m_2}; i\omega_{p_1} | i\omega_{m_3}; i\omega_{m_4}; i\omega_{p_2} | \omega \right) \\ \approx \Psi^{vQ}((\mathbf{r}, \sigma)_{43}; (\mathbf{r}, \sigma)_{21} | i\omega_{m_1}; i\omega_{m_2}; i\omega_{p_1}) \\ \times \frac{\Psi^{vQ^*}((\mathbf{r}, \sigma)_{87}; (\mathbf{r}, \sigma)_{65} | i\omega_{m_3}; i\omega_{m_4}; i\omega_{p_2})}{\omega - \omega_v(\mathbf{Q}) + i0^+} \end{aligned} \quad (8c)$$

where  $\Phi^{vQ}(\mathbf{r}_2 \sigma_2; \mathbf{r}_1 \sigma_1; u_{21})$ ,  $A^{vQ}(\mathbf{Q})$  and  $\Psi^{vQ}((\mathbf{r}, \sigma)_{43}; (\mathbf{r}, \sigma)_{21} | i\omega_{m_1}; i\omega_{m_2}; i\omega_{p_1})$  are the electron-hole, photon and four-particle amplitudes, respectively. Since the excitonic-biexcitonic polariton energy  $\hbar\omega_v(\mathbf{Q})$  is a pole of the photon Green function, it can be obtained from the corresponding Dyson equation for the photon Green function. In this way, one can obtain the Maxwell equations for the vector potential  $A_\alpha^{vQ}$  in the form

$$[(\omega_v/c)^2 \varepsilon_{\alpha\beta}(\mathbf{Q}, \omega_v) - \delta_{\alpha\beta} \mathbf{Q}^2 + \mathbf{Q}_\alpha \mathbf{Q}_\beta] A_\beta^{vQ}(\mathbf{Q}) = 0 \quad (9a)$$

where the tensor  $\varepsilon_{\alpha\beta}(\mathbf{Q}, \omega_v)$  has been defined as follows:

$$\varepsilon_{\alpha\beta}(\mathbf{Q}, \omega) = \delta_{\alpha\beta} - \frac{4\pi\hbar c^2}{\omega^2} \Pi_{\alpha\beta}^{(L)}(\mathbf{Q}, \omega). \quad (9b)$$

Here  $\Pi_{\alpha\beta}^{(L)}(\mathbf{Q}, \omega)$  is the Fourier transform of the proper self-energy part of the long-wavelength photons.  $\Pi_{\alpha\beta}^{(L)}$  can be calculated from the corresponding exciton Green function:

$$\Pi_{\alpha\beta}^{(L)}(z, z') = \Gamma_\alpha^{(0)}(y, x|z) K_M^E \begin{pmatrix} x & y' \\ y & x' \end{pmatrix} \Gamma_\beta^{(0)}(y', x'|z'). \quad (9c)$$

$$\begin{aligned} K_M^{E-1} \begin{pmatrix} y & x' \\ x & y' \end{pmatrix} &= K^{(0)-1} \begin{pmatrix} y & x' \\ x & y' \end{pmatrix} - \frac{\delta\Sigma(y, x)}{\delta G(y', x')} - 2 \frac{\delta\Sigma(y, x)}{\delta\Delta(x_{21}; y_2, y')} \Delta(x_{21}; y_{21}) G^{-1}(y_1, x') \\ &\quad - \frac{\delta\Sigma(y, x)}{\delta\Delta(x_{21}; y_{21})} R_0 \begin{pmatrix} x_{21} & y_{43} \\ y_{21} & x_{43} \end{pmatrix} \frac{\delta\Sigma(y', x')}{\delta\Delta(x_{43}; y_{43})}. \end{aligned} \quad (9d)$$

Here, the electron mass operator  $\Sigma$  is considered as a functional of  $R$ ,  $G$  and  $\Delta$  after going over from the functional  $Z$  to the second Legendre transform.

The energy shift  $\Delta_{biexc}$  is due to the last term in (9d). Unfortunately, equation (9d) is so complicated that it is of almost no use in calculating the dielectric tensor  $\varepsilon_{\alpha\beta}$ . For this reason, as a first approximation, we can treat the effects of the four-particle states by using in the last term in equation (9d), the biexciton Green function, instead of  $R_0$ . The simplest case in which the calculation can be done is the case of the exciton resonance at the point  $\mathbf{Q} = 0$  in CuBr. In CuBr the lowest poles of the exciton Green function are the exciton states with symmetry  $\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$ , but only excitons with  $\Gamma_5$  symmetry

are dipole active. Thus, the energy of exciting photons has to be equal to the lowest dipole-active pole of the exciton Green function, i.e.  $E_{\Gamma_5}^{exc} = E_{\Gamma_3 \oplus \Gamma_4}^{exc} + \Delta_E$  where  $\Delta_E$  is the splitting caused by the Elliott exchange interaction. The lowest poles of the biexciton Green function in CuBr, i.e. the biexciton states at the point  $\mathbf{Q} = 0$  have  $\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$  symmetry. According to our theory, the existence of biexcitons modifies the dielectric function, and the optical absorption of the photons by excitation of exciton states at the point  $\mathbf{Q} = 0$  is determined by the lowest dipole-active pole of the Green function (9d) with  $\Gamma_5$  symmetry, i.e. the photon energy has to be equal to  $E_s(\mathbf{Q} = 0) = E_{\Gamma_5}$ . Since we are looking for the lowest dipole-active state, instead of the sum over all exciton bands, we take into account only the resonant term proportional to  $1/(E_{\Gamma_5}^{exc} - E_{\Gamma_5})$ . Furthermore, we take into account only the three lowest biexciton states with  $\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$  symmetry, assuming that  $E_{\Gamma_1}^{biexc} - E_{\Gamma_5} \approx E_{\Gamma_5}^{biexc} - E_{\Gamma_5} \approx E_{\Gamma_3}^{biexc} - E_{\Gamma_5} \approx E_0$ . In this approximation the pole of the Green function (9d) is given by

$$E_{\Gamma_5} = E_{\Gamma_5}^{exc} - \Delta_{biexc} \quad \Delta_{biexc} = \frac{1}{E_0} (|A_{\Gamma_1\Gamma_5}|^2 + |A_{\Gamma_5\Gamma_5}|^2 + |A_{\Gamma_3\Gamma_5}|^2) \quad (10a)$$

where the exciton–biexciton matrix element is defined as follows:

$$A_{mn} = \langle \Psi_{biexc}^{m\mathbf{Q}=0} | \delta\Sigma / \delta\Delta | F_{exc}^{n\mathbf{Q}=0} \rangle \quad (10b)$$

where  $F_{vc}^{n\mathbf{Q}}(k)$  and  $\Psi_{c,c',v,v'}^{m\mathbf{Q}}(\mathbf{k}, \mathbf{p}, \mathbf{q})$  are the exciton and biexciton wave functions. The matrix element (10b) describes a transition between an exciton and a biexciton state. It is worth noting that since our theory takes into account the non-linear polariton absorption in principle, the operator  $\delta\Sigma/\delta G$  should depend on the light intensity and on the exciton population in principle. But, it has a very complicated form, so at the present time the calculation of the exciton–biexciton matrix elements remains an open problem.

We now proceed to a comparison with the experiment. Due to the valence band degeneracy, the biexciton ground state in CuBr is sixfold degenerate. For the centre-of-mass momentum  $\hbar\mathbf{Q} = 0$  of biexcitons, the different types of two-particle interaction (electron–electron, electron–hole and hole–hole) split the ground state according to the relation  $(\Gamma_6 \otimes \Gamma_6)^- \otimes (\Gamma_8 \otimes \Gamma_8)^- = \Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5$ . The biexciton binding energies  $E_{bi}^b(\Gamma_i) = 2E_{\Gamma_3 \oplus \Gamma_4} - E_{bi}(\Gamma_i)$  for the different ground states are given by the relation  $E_{bi}^b(\Gamma_i) = E_{bi}^0 + \Delta E(\Gamma_i)$ , where  $\Delta E(\Gamma_i)$  are the energy shifts of the states with symmetry  $\Gamma_i$  due to the hole–hole interactions and have the following forms (Honerlage *et al* 1985):

$$\begin{aligned} \Delta E(\Gamma_1) &= -\frac{15}{4}\beta_1 + 18\beta_2 + \frac{9}{4}\beta_3 & \Delta E(\Gamma_3) &= -\frac{3}{4}\beta_1 \\ \Delta E(\Gamma_5) &= -\frac{3}{4}\beta_1 - 18\beta_2 + \frac{3}{4}\beta_3. \end{aligned}$$

The energy  $E_{bi}^0$  can be written in the following form:

$$E_{bi}^0 = 2E_{\Gamma_3 \oplus \Gamma_4} + \frac{3}{4}\Delta_E + \frac{1}{4}\Delta_{LT} - (E_{bi}^d + 3\alpha_1)$$

where  $E_{bi}^d + 3\alpha_1$  is the contribution to the biexciton binding energy due to the diagonal terms of the biexciton Hamiltonian. This part of the biexciton energy can be calculated theoretically by using a biexciton wave function symmetric with respect to the exchange of two identical particles and neglecting all exchange interactions. The parameters for the  $Z_{12}$  exciton resonance of CuBr and the parameters of the biexciton states are (Honerlage *et al* 1985) as follows:

$$E_{\Gamma_5} = 2.9644 \text{ eV} \quad E_{bi}(\Gamma_1) = 5.9059 \text{ eV}$$



$$\begin{aligned}
 E_{\Gamma_3 \oplus \Gamma_4} &= 2.9627 \text{ eV} & E_{bi}(\Gamma_5) &= 5.9103 \text{ eV} \\
 \Delta_{LT} &= 0.0122 \text{ eV} & E_{bi}(\Gamma_3) &= 5.9128 \text{ eV}.
 \end{aligned}$$

From the experimental results (Honerlage *et al* 1981, 1985) one can obtain that the energy  $E_{bi}^0$  is equal to 5.9158 eV. If we assume that  $\Delta_E = E_{\Gamma_5} - E_{\Gamma_3 \oplus \Gamma_4} = 0.0017$  eV, we calculate that  $E_{bi}^d + 3\alpha_1$  is equal to 0.0139 eV. But, according to the theoretical calculations by Ekardt and Sheboul (1976), the energy  $E_{bi}^d + 3\alpha_1$  is equal to 0.0265 eV. The discrepancy between the energy  $E_{bi}^d + 3\alpha_1$  calculated theoretically by Ekardt and Sheboul and that obtained by Honerlage *et al* (1981, 1985) can be explained by making the assumption that the splitting due to the Elliott exchange interaction is not equal to 0.0017 eV, since the existence of biexcitons modifies the dielectric function and the exciton resonance can be observed for the energy of exciting photons  $\hbar\omega_{pt} = 2.9644 \text{ eV} = E_{\Gamma_3 + \Gamma_4} + \Delta_E - \Delta_{biexc}$ . The order of magnitude of the splitting due to the Elliott exchange interaction and energy shift  $\Delta_{biexc}$  can be obtained by assuming that  $E_{bi}^0$  is equal to 5.9158 eV and  $E_{bi}^d + 3\alpha_1$  is equal to 0.0265 eV. Then one can obtain for the splitting due to the Elliott exchange interaction  $\Delta_E = 0.0165$  eV and for the energy shift  $\Delta_{biexc} = 0.0148$  eV. Although the calculations by Ekardt and Sheboul should be corrected for the band-structure terms, screening effects, polaron masses, etc, we will still have an important Elliott exchange interaction which is then compensated by the energy shift  $\Delta_{biexc}$ .

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