Exciton-exciton interactions in quantum wells. Optical properties and energy and spin relaxation.

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Abstract

The gas of interacting excitons in quantum wells is studied. We obtain the Hamiltonian of this gas by the projection of the electron-hole plasma Hamiltonian to exciton states and an expansion in a small density. Matrix elements of the exciton Hamiltonian are rather sensitive to the geometry of the heterostructure. The mean field approximation of the exciton Hamiltonian gives the blue shift and spin splitting of the exciton luminescence lines. We also write down the Boltzmann equation for excitons and estimate the energy and spin relaxation time resulting from the exciton-exciton scattering. Making use of these calculations we succeeded to explain some recent experimental results which have not been explained so far.
I. INTRODUCTION

Optical properties of dense exciton gas in quantum wells had been studied intensively both experimentally and theoretically in the past decade. Originally, attempts to obtain dense exciton gas were motivated by a desire to reach Bose-Einstein condensation of excitons. However, the fascinating observed physical phenomena and the promising potential for device application had made the exciton gas a very interesting system by itself.

Recent experiments have stressed the importance of exciton-exciton interaction of two-dimensional (2D) excitons in quantum wells. Exciton-exciton interaction affects exciton photoluminescence, breaks the symmetry between excitons with different spin components, contributes to depolarization of the exciton gas, and controls spin and momentum relaxation in the exciton system. A thorough investigation of exciton-exciton interaction is crucial for understanding of a number of experimental results in exciton gas.

Blue shift of the exciton luminescence line with growing exciton density was reported in single quantum wells [1,2], multiple quantum wells [3,4] and coupled quantum wells where electrons and holes are spatially separated [5,6]. The blue shift is attributed to the net exciton-exciton repulsion interaction in quantum wells [7–9].

Other interesting interaction induced phenomena are related to exciton spin. Here we use the term spin for the projection of the total angular momentum of the exciton to the direction perpendicular to quantum well plane (the growth direction). In quantum wells size quantization leads to an energy separation between heavy and light holes. Therefore one can treat the ground state exciton as a bound state of a conduction electron with spin $\pm 1/2$ and a heavy hole with spin $\pm 3/2$. So, in the ground state, i.e., s-state exciton, the spin can take the values $\pm 1$ and $\pm 2$. Total momentum conservation allows only states with spin projection $\pm 1$ to be optically active in single photon experiments.

Spin $+1$ and spin $-1$ excitons can be created independently by pumping circular polarized light. A spontaneous energy splitting between the two different components of spin-polarized exciton gas in zero magnetic field was observed in multiple quantum wells [10,13] and in
coupled quantum wells [14]. The splitting increased with the exciton density and decreased with the separation of the electron and hole induced by external electric field in coupled quantum wells. The splitting was explained by the exciton-exciton exchange interactions [8].

At high exciton densities the decay of the exciton luminescence cannot be characterized by one decay time. Initially the decay is very fast and then it is followed by a slower relaxation. [15–17] Similar results were obtained for the decay of luminescence polarization. [16,17] A very careful analysis of the luminescence intensity and polarization by Baylac, Amand et al. [16,17] and two-pulse experiments performed by Le Jeune et al. [12] proved that the short decay time can be explained only by exciton-exciton scattering. In dense exciton gas exciton-exciton scattering can also be the leading mechanism of momentum relaxation. [18]

The active investigation of exciton-exciton interaction and many new experimental results makes it difficult to overestimate the importance of theoretical description of this interaction. Such a description, however, encounters significant difficulties even when the exciton density is small and the interaction between excitons could be considered with the help of perturbation theory. Indeed, let us consider two electron - hole pairs (e1,h1) and (e2,h2) bound in excitons. One could expect that the Coulomb interaction within pairs (i.e., the interaction between e1 and h1 and the interaction between e2 and h2) has to be taken into account exactly because it provides bound states, while the Coulomb interaction between particles belonging to different excitons (e.g., the interaction between e1 and h2 and the interaction between e2 and h1) can be considered as a perturbation. However, due to electron-electron and hole-hole exchange it is impossible to say if bound pairs are really (e1,h1) and (e2,h2) or (e1,h2) and (e2,h1). For this reason it is not clear what part of the Coulomb interaction is the interaction between excitons and can be considered as a perturbation.

A few approaches have been developed which formally related the gas of electron-hole pairs to a Bose gas and avoided such difficulty. Hanamura [19] made use of the Usui trans-
formation, [20] that makes a correspondence between the space of fermion pairs and a "hypothetical" boson space. The transformed Hamiltonian still contained Fermi operators. To eliminate them the commutators of this Hamiltonian with Bose operators averaged over the ground state of the fermion system were declared to be equal to the commutators of the target boson Hamiltonian with Bose operators. The harmonic part of the resulting boson Hamiltonian immediately led to the known exciton states. Thus, it was natural to assume that the anharmonic part describes exciton-exciton interaction. Haug and Schmitt-Rink [21] (see also Ref. [8]) modified this approach introducing creation and annihilation operators as linear combinations of pairs of Fermi operators. Commutation relations of new operators are different from those of Bose operators by terms proportional to the density of bosons. The coefficients of the linear combination were found from a variation principle and appeared to be single-exciton wave functions corrected by interactions between bosons. Stolz et al. [22] used another approach where they represented wave functions of the electron-hole plasma as linear combinations of products of single-exciton wave functions. Then again a variational principle was used to find the single-exciton wave function. In all these works the exciton-exciton interaction was calculated in the leading order in the exciton density.

In this paper we develop a theory of exciton-exciton interaction in quantum wells which is free of a formal definition of exciton creation and annihilation operators. We do not use a variational method, the accuracy of which is difficult to control. The physical basis to our approach is that we consider a system of equal number of electrons and holes at low enough temperature and low density, when all the particles are bound in excitons. If the density is not small then excitons overlap and the Coulomb interaction between particles of different excitons is of the same order as the electron-hole interaction within one exciton. In such a case the identity of excitons is lost and the electron-hole plasma can hardly be considered as gas of excitons. If the other limitation, i.e., small kinetic energy of excitons is not met then excitons can be ionized and the system can not be described as the gas of excitons only. Experimentally small exciton kinetic energy is achieved by resonant excitation at lattice temperature much lower than the binding energy [3,12,15,17].
Technically our approach resembles that of Stolz et al. [22]. However, we don’t rely on a variational principle but use a systematic expansion in small exciton density. Finally, we arrive at an expression for the second quantized exciton Hamiltonian with coefficients that are expressed in terms of the free single-exciton wave function. This function, and so the coefficients, strongly depend on the geometry of the heterostructure.

We use the exciton Hamiltonian for the calculation of the blue shift of the exciton luminescence line and the energy splitting between excitons with different spin projection. These phenomena are described by Hamiltonian matrix elements which are diagonal with respect to occupation numbers of exciton states. Off-diagonal matrix elements of the Hamiltonian describe exciton-exciton scattering. We use them to write down the Boltzmann equation for the excitons and estimate the relaxation time in the exciton gas. For numerical calculation of the coefficients of the Hamiltonian we use the variational single-exciton wave function that we suggested earlier [23].

We are not trying to reach an exact numerical matching of our theory with experiments. This would require an accurate calculation of the single-exciton wave function for different geometries. Our goal is rather to explain semi-quantitatively (i.e., with an accuracy better than the order of magnitude) as many experiments as possible. In other words, we are trying to show that our theory is able to describe all so far detected phenomena in the exciton gas of a small density which are related to exciton-exciton scattering.

The structure of the paper reflects the specifics of the problem. We consider electrons and holes confined in quantum wells. Their motion in the growth direction is strongly quantized (we assume that only the ground electron and hole states are occupied) and the problem is essentially two-dimensional. So, in the next section we reduce the three-dimensional (3D) Hamiltonian of electrons and holes to a 2D one. In Sec. II we present the main assumptions of our approach and give the derivation of the exciton Hamiltonian. Some cumbersome details of the derivation are transferred to appendices. In Sec. IV we calculate the blue shift of the exciton luminescence line and the energy splitting of excitons with opposite spins. In Sec. V we estimate the exciton-exciton relaxation time with the
help of the Boltzmann equation. We discuss our results and compare them to experiments in Sec. VII. Our conclusions are presented in Sec. VII.

II. THE HAMILTONIAN OF 2D ELECTRON - HOLE PLASMA

Due to a strong quantization of the electron and hole motion in the growth direction the dynamics of electrons and holes is essentially two-dimensional. For this reason excitons in quantum wells sometimes are considered as purely 2D [7–9]. In this approximation, however, it is impossible to describe effects of the geometrical parameters of quantum wells on the exciton binding energy and their interaction. So we use a more realistic model which takes into account the geometry of the heterostructure.

In quantum wells, light and heavy holes are split off in energy. We consider only heavy holes, assuming that the splitting is much larger than kinetic energies of all involved particles and the interaction between them. Therefore, light hole states are not occupied and the Hamiltonian of the plasma of $N$ electrons and $N$ heavy holes in quantum wells is

$$\mathcal{H}_{3D} = \sum_j \left[ T_{ej} + T_{hj} + U_{0e}(z_{ej}) + U_{0h}(z_{hj}) \right]$$

$$+ \sum_{ij} U_{eh}(|\vec{r}_{ei} - \vec{r}_{hj}|, z_{ei}, z_{hj}) + \frac{1}{2} \sum_{ij} \left[ U_{ee}(|\vec{r}_{ei} - \vec{r}_{ej}|, z_{ei}, z_{ej}) + U_{hh}(|\vec{r}_{hi} - \vec{r}_{hj}|, z_{hi}, z_{hj}) \right].$$

Here $\vec{r}_e$ and $z_e$ are electron coordinates in the quantum well plane and in the growth direction respectively, $\vec{r}_h$ and $z_h$ is the same for holes,

$$T_e = -\frac{\hbar^2 \nabla_e^2}{2m_e} - \frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z_e^2},$$

$$T_h = -\frac{\hbar^2 \nabla_h^2}{2m_{\parallel}} - \frac{\hbar^2}{2m_{\perp}} \frac{\partial^2}{\partial z_h^2},$$

are the operators of the electron and hole kinetic energy, $m_e$ is the electron mass, $m_{\parallel}$ and $m_{\perp}$ are in-plane and perpendicular hole effective masses, $\nabla_e$ and $\nabla_h$ are the derivatives with respect to in-plane coordinates of electron and hole, $U_{0e}(z_e)$ and $U_{0h}(z_h)$ are the heterostructure potentials that confine electrons and holes in quantum wells, and $U_{eh}, U_{ee},$ and $U_{hh}$ are
the electron-hole, electron-electron, and hole-hole Coulomb interaction energies respectively. If the difference between dielectric constants in wells and barriers is negligible then

\[ U_{eh}(|\vec{r}_1 - \vec{r}_2|, z_1, z_2) = -\frac{e^2}{\kappa \sqrt{(z_1 - z_2)^2 + (\vec{r}_1 - \vec{r}_2)^2}}, \]  

(2.3a)

\[ U_{ee}(|\vec{r}_1 - \vec{r}_2|, z_1, z_2) = U_{hh}(|\vec{r}_1 - \vec{r}_2|, z_1, z_2) = \frac{e^2}{\kappa \sqrt{(z_1 - z_2)^2 + (\vec{r}_1 - \vec{r}_2)^2}}, \]  

(2.3b)

where \( \kappa \) is the dielectric constant.

The method that we develop can be applied to a single quantum well or to coupled quantum wells with all possible well and barrier widths. In this paper we use it only for coupled quantum wells where electrons and holes are spatially separated. We neglect the electron-hole exchange \([24,25]\) which is very small in general \([26,27]\) and is further reduced in coupled quantum wells due to the smaller electron-hole wave function overlap. We also neglect the reduced symmetry of quantum well - barrier interfaces since this effect is very small. \([28]\) As a result, Hamiltonian \([2.1]\) does not depend on electron and hole spins.

The Hamiltonian \([2.1]\) contains an information about particle confinement in quantum wells which makes the study of in-plane states of the particles more difficult. Fortunately, in the most interesting cases the in-plane motion can be separated and the problem is simplified. Typically the interaction energy between the lowest level in a quantum well and the first excited one (a few tens of meV or even larger) is much larger than Coulomb interaction between particles (a few meV). For this reason at low enough temperature particles are confined at the lowest quantization level. A distortion of the wave functions caused by an admixture with the next level due to Coulomb interaction between the particles can be neglected. In such a case \( z \)-dependence of electron and hole wave functions is described by \( \zeta_e(z) \) and \( \zeta_h(z) \) respectively, which satisfy the equations

\[ -\frac{\hbar^2}{2m_e} \frac{\partial^2 \zeta_e}{\partial z^2} + U_{0e}(z)\zeta_e = E_{0e}\zeta_e, \]  

(2.4a)

\[ -\frac{\hbar^2}{2m_\perp} \frac{\partial^2 \zeta_h}{\partial z^2} + U_{0h}(z)\zeta_h = E_{0h}\zeta_h. \]  

(2.4b)

Here \( E_{0e} \) and \( E_{0h} \) are the electron and hole confinement energies respectively. The wave
function of the gas is a product of all single particles wave functions $\zeta_e$ and $\zeta_h$ and a many-particle wave function describing the in-plane state. The Hamiltonian that controls the in-plane dynamics of the gas is obtained from the Hamiltonian, (2.1), by averaging with the functions $\zeta_e$ and $\zeta_h$, and has the form

$$\mathcal{H} = \sum_j \left( -\frac{\hbar^2 \nabla^2_{ej}}{2m_e} - \frac{\hbar^2 \nabla^2_{hj}}{2m_h} \right) + \sum_{ij} u_{eh}(|\vec{r}_{ei} - \vec{r}_{hj}|) + \frac{1}{2} \sum_{ij} [u_{ee}(|\vec{r}_{ei} - \vec{r}_{ej}|) + u_{hh}(|\vec{r}_{hi} - \vec{r}_{hj}|)], \quad (2.5)$$

where

$$u_{ij}(r) = \int U_{ij}(r, z_1, z_2) \zeta^2_i(z_1) \zeta^2_j(z_2) dz_1 dz_2. \quad (2.6)$$

All details of the derivation of 2D Hamiltonian, (2.5), from 3D one, (2.1), in the case of two particles are given in Ref. [23]. The derivation of many particle Hamiltonian can be done in the same way.

Thus to study electron - hole gas confined in quantum wells it is enough to consider only a 2D problem described by Hamiltonian, (2.5).

**III. DERIVATION OF THE EXCITON HAMILTONIAN**

In this section we derive the 2D Hamiltonian of exciton gas starting from the 2D Hamiltonian of electrons and holes, Eq. (2.5). We begin this derivation with a discussion of the necessary conditions for considering the electron - hole gas as exciton gas.

Not in any state the electron - hole gas can be represented as a gas of excitons. To make this possible, two conditions are necessary. The first one is a small enough concentration of electrons and holes, $n$. Under this condition all electrons and holes can be bound in excitons and the excitons are far from each other. That is

$$na^2 \ll 1 \quad (3.1)$$

where $a$ is the exciton radius. If this condition is not met then excitons overlap and the Coulomb interaction between electrons and holes of different excitons becomes of the order
of the interaction within one exciton. In such a case it is impossible to identify excitons, and the electron-hole plasma hardly can be described as a gas of excitons.

The other condition is that typical exciton kinetic energy is much smaller than the absolute value of the exciton binding energy, \( \epsilon_b \),

\[
\frac{\hbar^2 \vec{K}^2}{2M} \ll \epsilon_b.
\]  

(3.2)

Here \( \vec{K} \) and \( M \) are the exciton wave vector and the exciton mass respectively. If this condition is not met then as a result of collisions between excitons they can be excited from the ground state or even be ionized into free electrons and holes. Then it is necessary to consider excitons interacting with each other and with free electrons and holes. We are not going to consider this case. Strictly speaking, the accurate condition for ground state excitons contains the energy separation between the ground state and the first excited state of exciton in the right hand side of Eq. (3.2). But this difference is of the order of \( \epsilon_b \) and we can use Eq. (3.2) as it is.

To derive the exciton Hamiltonian we construct a basis for the space of all electron-hole states from products of single exciton wave functions. Under the conditions (3.1) and (3.2) we expect that only the ground state exciton wave function is important. So of all matrix elements of Hamiltonian (2.3) only the elements between the states constructed of these functions should be kept. Such a program in an accurate form is carried out in Sec. IIIA, where we show how to calculate all matrix elements of the exciton Hamiltonian. Due to inequality (3.1) some of these matrix elements are small. Namely, matrix elements describing triple and higher order interaction between excitons are proportional to higher power of the exciton concentration than matrix elements describing pair interaction, and we neglect them. For the calculation of the pair interaction matrix elements it is enough to consider the system of only two excitons. This calculation is performed in Sec. IIIB. Finally, in Sec. IIIC, we use these matrix elements to write down the Hamiltonian of the exciton gas in the second quantized form.
A. Reduction of the electron - hole Hamiltonian to the exciton Hamiltonian

1. Exciton basis

The starting point of our derivation is the Hamiltonian of many electrons and holes, (2.3). The general idea of the derivation is that we reduce the space of all electron-hole states to the subspace of ground state excitons states only, and project the Hamiltonian to this subspace. The first step in this direction is the construction of a basis in which this subspace can be separated.

We construct such a basis of symmetrized products of single exciton wave functions. Single exciton wave functions are eigenfunctions of the Hamiltonian

\[ \mathcal{H}_{1eh} = -\frac{\hbar^2 \nabla^2_e}{2m_e} - \frac{\hbar^2 \nabla^2_h}{2m_\parallel} + u_{eh}(|\vec{r}_e - \vec{r}_h|) . \]  

(3.3)

Since the Hamiltonian (3.3) is independent on electron and hole spins, a single exciton wave function can be written as

\[ \Psi_{\vec{K}\alpha,s}(\vec{r}_e,\vec{r}_h) = g_s(\sigma)\psi_{\vec{K}\alpha}(\vec{r}_e;\vec{r}_h) . \]  

(3.4)

Here, \( \psi_{\vec{K}\alpha}(\vec{r}_e;\vec{r}_h) \) is the eigenfunction of Hamiltonian, (3.3), and the spin wave function,

\[ g_s(\sigma) = \delta_{s,\sigma} , \]  

(3.5)

can be represented as the product of the electron and hole spin functions, \( g_s(\sigma) = g_{se}(\sigma_e)g_{sh}(\sigma_h) \). The projection of electron and hole spins to z-direction can take the values \( s_e = \pm 1/2 \) and \( s_h = \pm 3/2 \) respectively. The exciton spin projection to the same direction is \( s = s_e + s_h \) and it can take the values \( \pm 1, \pm 2 \). The spin variables, \( \sigma = \sigma_e + \sigma_h \), take the same values. There is one to one correspondence between the set of electron and hole spins and the exciton spin, i.e., each exciton spin corresponds to a single combination of electron and hole spins.

The in-plane exciton wave function is

\[ \psi_{\vec{K}\alpha}(\vec{r}_e;\vec{r}_h) = \frac{1}{\sqrt{S}} e^{i\vec{K}\cdot\vec{R}} \phi_\alpha(|\vec{r}_e - \vec{r}_h|) . \]  

(3.6)
Here, $\vec{R} = (m_e \vec{r}_e + m_\parallel \vec{r}_h)/M$ is the exciton center of mass coordinate, $M = m_e + m_\parallel$ is the exciton mass, $S$ is the normalization area, and the function, $\phi_\alpha(r)$ is an eigenfunction of the Hamiltonian

$$H_{1eh} = -\frac{\hbar^2 \nabla^2}{2\mu} + u_{eh}(r) ,$$

where

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_\parallel} ,$$

is the reduced mass.

The functions $\Psi_{K,\alpha,s}(\vec{r}_e, \sigma_e; \vec{r}_h, \sigma_h)$ form a complete basis for electron-hole pair states. That means that a complete basis for the gas consisting of $N$ electrons and $N$ holes can be constructed of these functions. This basis consists of correctly symmetrized products of single exciton functions, [22]

$$\Phi_{\{\nu\}}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1}; \ldots; \vec{r}_{eN}, \sigma_{eN}; \vec{r}_{hN}, \sigma_{hN}) = \frac{1}{N!} \sum (-1)^P \prod_{j=1}^{N} \Psi_{\nu_j}(\vec{r}_{ej1}, \sigma_{ej1}; \vec{r}_{hj2}, \sigma_{hj2}) .$$

(3.9)

Here $\nu$ stands for the set of quantum numbers $(K, \alpha, s)$, $\{\nu\} = \nu_1, \nu_2, \ldots, \nu_N$, the summation is carried out over all transpositions of electrons and holes, $j_1$ and $j_2$, and $P$ is the parity of a transposition. Basis (3.3) is very convenient for our purpose because it easily allows us to separate the subspace of wave functions containing only ground state excitons. This subspace contains those $\Phi_{\{\nu\}}$ in which all $\alpha$ correspond to the ground state. We enumerate this subspace as 1 and the subspace of functions containing at least one excited exciton as 2.

It is necessary to note that the functions $\Phi_{\{\nu\}}$ are not orthogonal, in spite of the orthogonality of the single exciton functions $\Psi_{\nu}$. [22] Let us, for instance, consider the integral of the product of two functions $\Phi_{\{\nu_1\}}$ and $\Phi_{\{\nu_2\}}$ which differ by only one of all the quantum numbers $\nu$, e.g., $\nu_1$ in the first function is replaced by $\nu_1' \neq \nu_1$ in the second one. Comparing these two wave functions we see that for each term in the sum (3.9) of one wave function there are terms
in the sum of the other that differ by exchange of pairs of electrons and holes in such a way that the identity of excitons is not violated [e.g., \( \Psi_{\nu_1}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1})\Psi_{\nu_2}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h2}, \sigma_{h2}) \) and \( \Psi'_{\nu_1}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h2}, \sigma_{h2})\Psi'_{\nu_2}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1})\)]. The integrals of the products of these terms equal zero because of the orthogonality of single exciton wave functions. But there are also terms that differ by a transposition of electrons or holes which violates the exciton identity, e.g., \( \Psi_{\nu_1}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1})\Psi_{\nu_2}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h2}, \sigma_{h2}) \) and \( \Psi_{\nu_1}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1})\Psi_{\nu_2}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h2}, \sigma_{h2}) \). The integral of the product of these terms is nonzero. From the definition of the single exciton wave functions, Eq. (3.6), we see that this integral, contains the factor \( a^2/S \).

If functions \( \Phi_{\{
u\}} \) and \( \Phi'_{\{
u\}} \) differ by more than just one value of \( \nu \) or the transposition mixes more than a pair of excitons, the integral of \( \Phi_{\{
u\}}\Phi'_{\{
u\}} \) contains the factor of \( a^2/S \) to a higher power. Eventually, in the calculation of observable quantities each factor of \( 1/S \) is accompanied by a sum over occupied states of the system which gives the factor of \( N \). So that the nonorthogonality of the basis is characterized by the parameter \( na^2 \).

The basis (3.9) is not normalized. The normalization integral of any of the basis functions, \( \int |\Phi_{\{
u\}}|^2 \prod_j d^2r_{ej}d^2r_{hj} \), contains integrals of the same type of exchange that leads to the nonorthogonality. Thus this integral is different from unity by terms of the order of \( na^2 \).

2. Wave equation for excitons

After the characterization of the basis (3.9) we begin the derivation of the exciton Hamiltonian. We write down the Schrödinger equation for the gas of \( N \) electrons and \( N \) holes, \( \mathcal{H}\Psi = E\Psi \), in the matrix form in basis (3.9). To do this we need to represent the eigenfunction \( \Psi \) as an expansion in the functions \( \Phi_{\{
u\}} \), and to obtain equations for the coefficients of this expansion. For this purpose we multiply the Schrödinger equation by the functions complex conjugated to \( \Phi_{\{
u\}} \) and integrate over all variables. To write down the result in the matrix form we introduce the notation \( \Psi_1 \) for the column of the expansion coefficients of the basis function belonging to subspace 1 (only ground state excitons) and the notation \( \Psi_2 \) for the column of the expansion coefficients of the basis function belonging to subspace...
2 (including also excited states). Then the matrix equation takes the form

\begin{align}
(H_{11} - N_{11}E)\Psi_1 + (H_{12} - N_{12}E)\Psi_2 &= 0 , \\
(H_{21} - N_{21}E)\Psi_1 + (H_{22} - N_{22}E)\Psi_2 &= 0 ,
\end{align}

(3.10a)

(3.10b)

where \(H_{ij}\) are the matrices with elements \(\langle \Phi_{\{\nu\}} | H | \Phi_{\{\nu'\}} \rangle\) and \(N_{ij}\) are matrices with elements \(\langle \Phi_{\{\nu\}} | \Phi_{\{\nu'\}} \rangle\), where \(\Phi_{\{\nu\}}\) and \(\Phi_{\{\nu'\}}\) belong to \(i\) and \(j\) subspaces respectively. We use Eq. (3.10b) in order to express \(\Psi_2\) in \(\Psi_1\), substitute the result in Eq. (3.10a) and come up with the equation

\[(H_{11} - N_{11}E)\Psi_1 - \mathcal{H}^{(ex)}\Psi_1 = 0 , \]

(3.11)

where the effect of excited states is described by

\[\mathcal{H}^{(ex)} = (H_{12} - N_{12}E)(H_{22} - N_{22}E)^{-1}(H_{21} - N_{21}E) . \]

(3.12)

Although Eq. (3.11) contains only \(\Psi_1\) it does not have the form of the Schrödinger equation because \(\mathcal{H}^{(ex)}\) is a nonlinear function of the energy \(E\). The reason is that Eq. (3.11) is equivalent to Eq. (3.10) and describes the general situation, where electrons and holes can occupy excited states. To describe a system where all electrons and holes are bound in ground state excitons we make use of the small parameters (3.1) and (3.2).

### 3. Exciton Hamiltonian

Here we start from Eqs. (3.11) and (3.12), neglect small terms and obtain the Hamiltonian and the Schrödinger equation for the exciton gas.

First we note that \(N_{11}\) and \(H_{11}\) contain terms of different order in \(a^2/S\). The estimate of both \(N_{11}\) and \(H_{11}\) can be done in the same way. The larger the overlap between \(\Phi_{\{\nu\}}\) and \(\Phi_{\{\nu'\}}\), the larger the matrix element \(\langle \Phi_{\{\nu\}} | H | \Phi_{\{\nu'\}} \rangle\) is. As we explained above, matrix elements between states that differ by a transposition of two electrons or two holes contain the factor \(a^2/S\) and describe two-exciton interaction in
$H_{11}$. Matrix elements between the states that differ by a transposition of three electrons or three holes, e.g. $\Psi_{\nu_1}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1})\Psi_{\nu_2}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h2}, \sigma_{h2})\Psi_{\nu_3}(\vec{r}_{e3}, \sigma_{e3}; \vec{r}_{h3}, \sigma_{h3})$ and $\Psi_{\nu_1}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h2}, \sigma_{h2})\Psi_{\nu_2}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h3}, \sigma_{h3})\Psi_{\nu_3}(\vec{r}_{e3}, \sigma_{e3}; \vec{r}_{h1}, \sigma_{h1})$, contain $(a^2/S)^2$. In $H_{11}$ they describe a triple exciton interaction that is not reduced to pair interaction. We neglect such and other high order terms both in $N_{11}$ and $H_{11}$.

Matrix elements of $N_{12}$, and $N_{21}$ are nonzero only because of the nonorthogonality of basis functions (3.9). As we showed above $\langle \Phi_{\nu}\mid \Phi_{\nu'} \rangle \approx a^2/S$ when $\nu \neq \nu'$. The matrix elements of $H_{12}$ and $H_{21}$ contain the same parameter. To prove this, let us examine the largest matrix elements of $H_{12}$. The maximal overlap between subspace 1 and subspace 2 is achieved when the state from subspace 2 is such that all electrons and holes are bound in ground state excitons except from one pair which is bound in an excited exciton state. From the orthogonality of single exciton wave functions (3.4) with different $\alpha$ it follows that there are only two kinds of non vanishing terms. The first are the terms that describe Coulomb interaction between different excitons,

$$\int |\psi_{K,\alpha}(\vec{r}_{e1}, \vec{r}_{h1})|^2|\psi_{K,\alpha'}(\vec{r}_{e2}, \vec{r}_{h2})|^2d\vec{r}_{e1}d\vec{r}_{h1}d\vec{r}_{e2}d\vec{r}_{h2} \times [u_{ee}(\vec{r}_{e1} - \vec{r}_{e2}) + u_{hh}(\vec{r}_{h1} - \vec{r}_{h2}) + u_{eh}(\vec{r}_{e1} - \vec{r}_{h2}) + u_{eh}(\vec{r}_{e2} - \vec{r}_{h1})].$$

(3.13)

This integral converges at large distance, $R$, between the excitons (dipole-dipole interaction falls off as $1/R^3$) and it is of the order of $(a^2/S)e_b$. The second kind are the terms where the identity of the exciton is violated. We gave an example for those terms when we discussed the nonorthogonality and saw that they contain the small parameter $a^2/S$. Other non-vanishing terms, e.g. for states with smaller overlap between subspace 1 and subspace 2 contain higher powers of $a^2/S$.

From the above arguments we see that the matrix $H^{(exex)}$ contains the small parameter $a^2/S$ coming from $N_{12}$, $N_{21}$, $H_{12}$ and $H_{21}$. For this reason, in the leading order, all other contributions to $H^{(exex)}$ containing this small parameter can be neglected. In particular, in the summation over intermediate states in Eq. (3.12) we consider only diagonal terms of $(H_{22} - N_{22}E)^{-1}$, and in these terms neglect the interaction between excitons. In other
words, \( \mathcal{H}_{22} - \mathcal{N}_{22} E \) can be replaced with the diagonal matrix \( E_\mu - E \), where \( E_\mu \) is the sum of the energies of \( N \) excitons with at least one of them excited or ionized.

From this expression the importance of inequality (3.2) is immediately seen. If this inequality is not satisfied then the energy of the ground state excitons \( E \) can be close to \( E_\mu \) due to the high ground state exciton kinetic energy. In such a case some matrix elements of \( \mathcal{H}^{(exex)} \) contain a small denominator and become anomalously large. When condition (3.2) is met the exciton kinetic energy can be neglected and \( E \approx -N\epsilon_b \). As a result, matrix elements of \( \mathcal{H}^{(exex)} \) are

\[
\mathcal{H}_{\nu\nu'}^{(exex)} = \sum_\mu \left( \mathcal{H}_{12} + \mathcal{N}_{12} N\epsilon_b \right)_{\nu\mu} \left( \mathcal{H}_{21} + \mathcal{N}_{21} N\epsilon_b \right)_{\mu\nu'} \frac{E_\mu + N\epsilon_b}{E_\mu + N\epsilon_b} .
\] (3.14)

We would like to add one more comment concerning the neglect of the exciton-exciton interaction in the intermediate states. The radius of highly excited exciton states can be of the order of the distance between different excitons and the interaction between excitons in this case is of the order of the electron-hole interaction within the same exciton. However, such highly excited states are very close to states of free electrons and holes where Coulomb interaction can be neglected compared to the kinetic energy.

Eq. (3.11) with \( \mathcal{H}^{(exex)} \) determined by Eq. (3.14) is now linear in the energy \( E \), and different from Schrödinger equation just by the non-diagonal matrix \( \mathcal{N}_{11} \). The transformation that reduces Eq. (3.11) to the regular Schrödinger equation is equivalent to the introduction of an orthogonal and normalized basis, \( \tilde{\Phi}_\nu \),

\[
\Phi_\nu = \mathcal{V}_{\nu\nu'} \tilde{\Phi}_{\nu'} ,
\] (3.15)

where the matrix \( \mathcal{V} \) is not unitary. (Note that this matrix is defined only in subspace 1). The corresponding transformation of the \( \mathcal{N} \) matrix is

\[
\mathcal{V}^\dagger \mathcal{N} \mathcal{V} = I ,
\] (3.16)

where \( I \) is the unit matrix. Since the difference between \( \mathcal{N} \) and the unit matrix is small, we can write
\[ N = I + A, \quad (3.17) \]

where \( A^\dagger = A \) and \( A \propto a^2 / S \). That is, \( V \) can be found from Eq. (3.16) with the help of the perturbation theory, assuming that \( V = I + V_1 \), where \( V_1 \approx a^2 / S \). It is necessary to note that the transformation (3.16) is not unique because an orthogonal and normalized basis can be chosen by many ways which differ by unitary transformations. So we chose a simplest solution to Eq. (3.16) that produces minimal modification of the basis constructed of single exciton wave functions, namely, \( V_1^\dagger = V_1 \). This immediately gives

\[ V = 1 - \frac{1}{2} A. \quad (3.18) \]

After the transformation to the orthogonal basis, Eq. (3.11) takes the following form

\[ V^\dagger (H_{11} - H^{(exex)}) V \Psi_1 = E \Psi_1. \quad (3.19) \]

The matrix \( H_{11} \) can be represented as

\[ H_{11} = H_0 + H_1, \quad (3.20) \]

where \( H_0 \) describes free excitons and \( H_1 \) describes their interaction, \( H_1 \propto a^2 / S \). We neglect terms of the second and high order in \( a^2 / S \), so Eq. (3.19) is reduced to

\[ H_{ex} \Psi_1 = E \Psi_1, \quad (3.21a) \]

\[ H_{ex} = H_{11} - \frac{1}{2} (A H_0 + H_0 A) + H^{(exex)}. \quad (3.21b) \]

Eq. (3.21a) is the Schrödinger equation for the gas of \( N \) excitons and Eq. (3.21b) is the expression for the exciton Hamiltonian that includes exciton-exciton interaction.

The necessity of the transition to a new basis, Eq. (3.15), means that exciton-exciton interaction changes single exciton wave functions. Such a change appears also in other approaches [19,21,22].

In the leading order in \( na^2 \) only matrix elements describing two exciton interaction should be kept in Eq. (3.21). To calculate them it is enough to consider the Hamiltonian of only two excitons. This is the subject of the next subsection.
B. Two-exciton Hamiltonian

The Hamiltonian of two electrons and two holes has the following form

\[
H_{2eh} = -\frac{\hbar^2 \nabla^2_{e1}}{2m_e} - \frac{\hbar^2 \nabla^2_{h1}}{2m_h} - \frac{\hbar^2 \nabla^2_{e2}}{2m_e} - \frac{\hbar^2 \nabla^2_{h2}}{2m_h} + u (\vec{r}_{e1}, \vec{r}_{h1}, \vec{r}_{e2}, \vec{r}_{h2}) .
\]

where

\[
u (\vec{r}_{e1}, \vec{r}_{h1}, \vec{r}_{e2}, \vec{r}_{h2}) = u_{ee}(|\vec{r}_{e1} - \vec{r}_{e2}|) + u_{eh}(|\vec{r}_{e1} - \vec{r}_{h1}|)
+ u_{eh}(|\vec{r}_{e1} - \vec{r}_{h2}|) + u_{eh}(|\vec{r}_{e2} - \vec{r}_{h1}|) + u_{hh}(|\vec{r}_{h1} - \vec{r}_{h2}|).
\]

For the calculation of matrix elements of \(H_{11}\) and \(N_{11}\) it is necessary to know only the wave function (3.9) of two ground state excitons. Explicitly, this function is

\[
\Phi_{K_1,s_1;K_2,s_2}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1}; \vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h2}, \sigma_{h2}) = \frac{1}{2}
\times \left[ \Psi_{K_1,s_1}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1}) \Psi_{K_2,s_2}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h2}, \sigma_{h2})
- \Psi_{K_1,s_1}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h1}, \sigma_{h1}) \Psi_{K_2,s_2}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h2}, \sigma_{h2})
- \Psi_{K_1,s_1}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h2}, \sigma_{h2}) \Psi_{K_2,s_2}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h1}, \sigma_{h1})
+ \Psi_{K_1,s_1}(\vec{r}_{e2}, \sigma_{e2}; \vec{r}_{h2}, \sigma_{h2}) \Psi_{K_2,s_2}(\vec{r}_{e1}, \sigma_{e1}; \vec{r}_{h1}, \sigma_{h1}) \right].
\]

Hereafter the quantum number \(\alpha\), characterizing an internal exciton state, will be omitted in the case of the ground state. The unity matrix elements in the space of two ground state excitons are

\[
I_{\vec{K}_1,s_1;\vec{K}_2,s_2;\vec{K}_3,s_3;\vec{K}_4,s_4} = \delta_{s_1,s_3} \delta_{s_2,s_4} \delta_{\vec{K}_1,K_3} \delta_{\vec{K}_2,K_4} + \delta_{s_1,s_4} \delta_{s_2,s_3} \delta_{\vec{K}_1,K_4} \delta_{\vec{K}_2,K_3} .
\]

The two products of \(\delta\)-symbols appear because the states are symmetric with respect to the transposition of single exciton quantum numbers.

The matrix \(N_{11}\) in the subspace of two excitons states is

\[
N_{\vec{K}_1,s_1;\vec{K}_2,s_2;\vec{K}_3,s_3;\vec{K}_4,s_4} = \langle \Phi_{\vec{K}_1,s_1;\vec{K}_2,s_2} | \Phi_{\vec{K}_3,s_3;\vec{K}_4,s_4} \rangle.
\]

According to the two exciton wave functions definition, \(\Phi_{\vec{K}_1,s_1;\vec{K}_2,s_2}\), Eq. (3.17) has now the form

\[
N_{\vec{K}_1,s_1;\vec{K}_2,s_2;\vec{K}_3,s_3;\vec{K}_4,s_4} = I_{\vec{K}_1,s_1;\vec{K}_2,s_2;\vec{K}_3,s_3;\vec{K}_4,s_4} + A_{\vec{K}_1,s_1;\vec{K}_2,s_2;\vec{K}_3,s_3;\vec{K}_4,s_4},
\]

where
\[ A_{K_{1s1},K_{2s2};K_{3s3},K_{4s4}} = \frac{1}{S} \delta_{K_{1}+K_{2},K_{3}+K_{4}} \]
\[ \times (\delta_{s_{1e}s_{3e}}\delta_{s_{2e}s_{3e}}\delta_{s_{1h}s_{3h}}\delta_{s_{2h}s_{3h}} + \delta_{s_{1e}s_{3e}}\delta_{s_{2e}s_{4e}}\delta_{s_{1h}s_{4h}}\delta_{s_{2h}s_{4h}}) A , \] (3.26)

where \( s_{je} \) and \( s_{jh} \) are electron and hole spins respectively of the exciton with the spin \( s_{j} \), and

\[ A = - \int \phi_{q} \frac{d\vec{q}}{(2\pi)^2} , \] (3.27)

is the Fourier transform of the wave function. The reduction of the overlap integral to such a simple form is possible due to the small parameter, Eq. (3.2). Details of the calculation are given in Appendix A.1.

For the calculation of the matrix elements of \( H_{11} \) it is convenient to separate them into two terms,

\[ (H_{11})_{K_{1s1},K_{2s2};K_{3s3},K_{4s4}} = H^{(d)}_{K_{1s1},K_{2s2};K_{3s3},K_{4s4}} + H^{(e)}_{K_{1s1},K_{2s2};K_{3s3},K_{4s4}} . \] (3.29)

The first part, \( H^{(d)} \), contains matrix elements between initial and final states where excitons consist of the same particles. This part consist of 8 integrals which have similar form. The grouping of terms which are different only by the notation of integration and summation variables leads to

\[ H^{(d)}_{K_{1s1},K_{2s2};K_{3s3},K_{4s4}} = \sum_{\sigma_{e1}\sigma_{e2}\sigma_{h1}\sigma_{h2}} \int d\vec{r}_{e1} d\vec{r}_{h1} d\vec{r}_{e2} d\vec{r}_{h2} \]
\[ \times \Psi^{*}_{K_{1s1}}(\vec{r}_{e1}\sigma_{e1},\vec{r}_{h1}\sigma_{h1}) \Psi^{*}_{K_{2s2}}(\vec{r}_{e2}\sigma_{e2},\vec{r}_{h2}\sigma_{h2}) H_{2eh} \Psi_{K_{3s3}}(\vec{r}_{e1}\sigma_{e1},\vec{r}_{h1}\sigma_{h1}) \Psi_{K_{4s4}}(\vec{r}_{e2}\sigma_{e2},\vec{r}_{h2}\sigma_{h2}) \]
\[ + \sum_{\sigma_{e1}\sigma_{e2}\sigma_{h1}\sigma_{h2}} \int d\vec{r}_{e1} d\vec{r}_{h1} d\vec{r}_{e2} d\vec{r}_{h2} \]
\[ \times \Psi^{*}_{K_{1s1}}(\vec{r}_{e1}\sigma_{e1},\vec{r}_{h1}\sigma_{h1}) \Psi^{*}_{K_{2s2}}(\vec{r}_{e2}\sigma_{e2},\vec{r}_{h2}\sigma_{h2}) H_{2eh} \Psi_{K_{3s3}}(\vec{r}_{e1}\sigma_{e1},\vec{r}_{h1}\sigma_{h1}) \Psi_{K_{4s4}}(\vec{r}_{e2}\sigma_{e2},\vec{r}_{h2}\sigma_{h2}) . \] (3.30)

The second part, \( H^{(e)} \), contains matrix elements between initial and final states where excitons consist of different particles. Again we have 8 integrals that can be grouped to the following form
\begin{equation}
H_{K_1 s_1, K_2 s_2, K_3 s_3, K_4 s_4}^{(x)} = - \sum_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} \int d \vec{r}_1 d \vec{r}_h d \vec{r}_2 d \vec{r}_h_2 \times \Psi_{K_1 s_1}^* (\vec{r}_1 \sigma_1, \vec{r}_h \sigma_1) \Psi_{K_2 s_2}^* (\vec{r}_2 \sigma_2, \vec{r}_h \sigma_2) H_{2eh} \Psi_{K_3 s_3} (\vec{r}_2 \sigma_2, \vec{r}_h \sigma_2) \Psi_{K_4 s_4} (\vec{r}_1 \sigma_1, \vec{r}_h \sigma_2) - \sum_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} \int d \vec{r}_1 d \vec{r}_h d \vec{r}_2 d \vec{r}_h_2 \times \Psi_{K_1 s_1}^* (\vec{r}_1 \sigma_1, \vec{r}_h \sigma_1) \Psi_{K_2 s_2}^* (\vec{r}_2 \sigma_2, \vec{r}_h \sigma_2) H_{2eh} \Psi_{K_3 s_3} (\vec{r}_1 \sigma_1, \vec{r}_h \sigma_2) \Psi_{K_4 s_4} (\vec{r}_2 \sigma_2, \vec{r}_h \sigma_1). \tag{3.31}
\end{equation}

There is a confusion in the literature about the term ”exchange” in the description of interaction (see, however, Ref. [9], where clear definitions are given). For elementary particles, the first term in Eq. (3.30) is usually called ”Hartree interaction” and the second is called ”exchange interaction” while \(H^{(x)}\) does not exist. In the case of excitons \(H^{(d)}\) is called ”direct interaction” and \(H^{(x)}\) is called ”exchange”. We stick to this last terminology.

In the direct part, (3.30), there are terms of \(H_{2eh}\) which do not mix between the two excitons, i.e., the kinetic energy of all the particles and the potential energy between particles belonging to the same exciton. These terms will result with the unity operator (3.25) multiplied by the single exciton energy. The other parts of \(H_{2eh}\) are the Coulomb interaction between the two excitons. The details of the calculation are given in Appendix A2 and the result is

\begin{equation}
H_{K_1 s_1, K_2 s_2, K_3 s_3, K_4 s_4}^{(d)} = \left( \delta_{s_1 s_3} \delta_{s_2 s_4} \delta_{\vec{K}_1 \vec{K}_3} \delta_{\vec{K}_2 \vec{K}_4} + \delta_{s_1 s_4} \delta_{s_2 s_3} \delta_{\vec{K}_1 \vec{K}_4} \delta_{\vec{K}_2 \vec{K}_3} \right) (E_K + E_{K'}) + \frac{1}{S} \delta_{\vec{K}_1 + \vec{K}_2 + \vec{K}_3 + \vec{K}_4} U_{K_1 s_1, K_2 s_2, K_3 s_3, K_4 s_4}^{(d)}, \tag{3.32}
\end{equation}

where \(E_K = -\epsilon_b + h^2 K^2/2M\) is the single exciton energy, and

\begin{equation}
U_{K_1 s_1, K_2 s_2, K_3 s_3, K_4 s_4}^{(d)} = \delta_{s_1 s_3} \delta_{s_2 s_4} U^{(d)} (|\vec{K}_1 - \vec{K}_3|) + \delta_{s_1 s_4} \delta_{s_2 s_3} U^{(d)} (|\vec{K}_1 - \vec{K}_4|). \tag{3.33}
\end{equation}

Here

\begin{equation}
U^{(d)} (q) = u_{ee} (q) \left[ \phi^2 \right]_{qmh/M}^2 + u_{hh} (q) \left[ \phi^2 \right]_{qm/\sqrt{M}}^2 + 2 u_{eh} (q) \left[ \phi^2 \right]_{qmh/M} \left[ \phi^2 \right]_{qmh/\sqrt{M}}, \tag{3.34}
\end{equation}

where \(u_{ij} (q)\) is the Fourier component of the Coulomb potential,

\begin{equation}
u_{ij}(q) = \int u_{ij}(r) e^{-iqr} dr, \tag{3.35}
\end{equation}

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and \([\phi^2]_q\) is the Fourier transform of the wave function squared, according to the general definition,

\[
[\phi \phi_\alpha]_q = \int e^{-i\vec{q} \cdot \vec{r}} \phi(\vec{r})\phi_\alpha(\vec{r}) d\vec{r}.
\]  

(3.36)

In the exchange part of the Hamiltonian matrix element, (3.31), all the terms mix between the excitons since the initial and final state consist of different particles and therefore corresponds to different pairs of excitons. The single exciton energy \(E_K\) is now multiplied by the factor \(A\) which reflects the small overlap between the initial and final states. The result of the calculation is

\[
H^{(x)}_{\vec{K}_1s_1, \vec{K}_2s_2, \vec{K}_3s_3, \vec{K}_4s_4} = U^{(x)} - 4A\epsilon_b \frac{\delta_{\vec{K}_1+\vec{K}_2, \vec{K}_3+\vec{K}_4}}{S} \times \left( \delta_{s_1s_4}s_{s_3s_5}s_{s_2s_5}s_{s_2s_5} + \delta_{s_1s_4}s_{s_3s_5}s_{s_2s_5}s_{s_2s_5} \right),
\]  

(3.37)

where \(A\) was defined in Eq. (3.27) and

\[
U^{(x)} = \frac{\hbar^2}{\mu} \int \phi_q^4 q^2 \frac{d\vec{q}}{(2\pi)^2} - \int [u_{ee}(r) + u_{hh}(r)] \left[ \int \phi_q^2 e^{i\vec{q} \cdot \vec{r}} \frac{d\vec{q}}{(2\pi)^2} \right]^2 d\vec{r}.
\]  

(3.38)

Details of the calculation are given in Appendix A3.

Apparently, the first term in \(H^{(d)}_{\vec{K}_1s_1, \vec{K}_2s_2, \vec{K}_3s_3, \vec{K}_4s_4}\), Eq. (3.32), describes free excitons. According to the notation of Eq. (3.20) this is a matrix element of \(H_0\). In other words,

\[
H_0^{\vec{K}_1s_1, \vec{K}_2s_2, \vec{K}_3s_3, \vec{K}_4s_4} = \left( \delta_{s_1s_3}s_{s_2s_4}s_{s_3s_5}s_{s_2s_5} + \delta_{s_1s_3}s_{s_2s_4}s_{s_3s_5}s_{s_2s_5} \right) (E_{\vec{K}_3} + E_{\vec{K}_4}).
\]  

(3.39)

The second term in \(H^{(d)}_{\vec{K}_1s_1, \vec{K}_2s_2, \vec{K}_3s_3, \vec{K}_4s_4}\) as well as \(H^{(x)}_{\vec{K}_1s_1, \vec{K}_2s_2, \vec{K}_3s_3, \vec{K}_4s_4}\), describe exciton-exciton interaction and, according to the same notation, are parts of the matrix element of \(H_1\).

Matrix elements \(H^{(exex)}_{\nu\nu'}\) seem to be of higher order in the small parameter, \(a^2/S\), since it contains the product of two off-diagonal matrix elements, \((H_{12} + N_{12}N\epsilon_b)_{\nu\nu'} (H_{21} + N_{21}N\epsilon_b)_{\mu\mu'}\), each of which is proportional to \(a^2/S\). However, the additional factor of \(a^2/S\) is cancelled by the summation with respect to the momentum of intermediate states in Eq. (3.14). Therefore the order of magnitude of \(H^{(exex)}_{\nu\nu'}\) is the same as of other matrix elements describing
Appendix A 4. The result has the form

\[ H_{\text{ex}}^{(\text{ex})} = \frac{1}{S} \delta_{\bar{K}_1 + \bar{K}_2, \bar{K}_3 + \bar{K}_4} \times \left( \delta_{s_1 s_3} \delta_{s_2 s_4} + \delta_{s_1 s_4} \delta_{s_2 s_3} \right) V_1 \]

\[ - \left( \delta_{s_1 s_3} \delta_{s_1 s_4} \delta_{s_2 s_3} + \delta_{s_1 s_4} \delta_{s_2 s_3} \right) V_2 \],

where

\[ V_1 = 2 \sum_{\alpha_1, \alpha_2} \int \frac{|D^{(d)}_{\alpha_1 \alpha_2}(\vec{q})|^2 + |D^{(x)}_{\alpha_1 \alpha_2}(\vec{q})|^2}{E_{\alpha_1} + E_{\alpha_2} + \hbar^2 q^2 / M + 2 \epsilon_b} \frac{d\vec{q}}{(2\pi)^2}, \]

\[ V_2 = 2 \sum_{\alpha_1, \alpha_2} \int \frac{D^{(d)}_{\alpha_1 \alpha_2}(\vec{q})D^{(x)*}_{\alpha_1 \alpha_2}(\vec{q}) + D^{(d)*}_{\alpha_1 \alpha_2}(\vec{q})D^{(x)}_{\alpha_1 \alpha_2}(\vec{q})}{E_{\alpha_1} + E_{\alpha_2} + \hbar^2 q^2 / M + 2 \epsilon_b} \frac{d\vec{q}}{(2\pi)^2}. \]

Here in the sums with respect to the internal exciton quantum number \( \alpha \) at least one of \( \alpha_1 \) and \( \alpha_2 \) corresponds to an excited state. The remaining matrix elements are

\[ D^{(d)}_{\alpha_1 \alpha_2}(\vec{q}) = u_{ee}(\vec{q}) \left[ \phi_{\alpha_1} - m q / M \right] \left[ \phi_{\alpha_2} - m q / M \right] \]

\[ + u_{eh}(\vec{q}) \left[ \phi_{\alpha_1} - m q / M \right] \left[ \phi_{\alpha_2} - m q / M \right] \]

\[ D^{(x)}_{\alpha_1 \alpha_2}(\vec{q}) = \int \left[ \phi_{\alpha_1, \vec{k} - \vec{q}} m / M \phi_{\alpha_2, \vec{k} - \vec{q}} m / M \right] u_{ee}(\vec{K} - \vec{q} + \vec{K}_2) \]

\[ + \phi_{\alpha_1, \vec{k}} m / M \phi_{\alpha_2, \vec{k}} m / M u_{eh}(\vec{K} - \vec{q} + \vec{K}_2) \]

\[ + \left( \phi_{\alpha_1, \vec{k}} m / M \phi_{\alpha_2, \vec{k}} m / M \right) u_{eh}(\vec{K} - \vec{q} + \vec{K}_2) \]

\[ + \int \phi_{\alpha_1, \vec{k} - \vec{q}} m / M \phi_{\alpha_2, \vec{k} - \vec{q}} m / M u_{eh}(\vec{K} - \vec{q} + \vec{K}_2) \]

\[ + \phi_{\alpha_1, \vec{k}} m / M \phi_{\alpha_2, \vec{k} - \vec{q}} m / M u_{eh}(\vec{K} - \vec{q} + \vec{K}_2) \]

\[ + \phi_{\alpha_1, \vec{k}} m / M \phi_{\alpha_2, \vec{k} - \vec{q}} m / M u_{ee}(\vec{K} - \vec{q} + \vec{K}_2) \]

According to Eq. (3.21), to complete the calculation of the interaction Hamiltonian it is necessary to calculate \( \mathcal{A}\mathcal{H}_0 + \mathcal{H}_0\mathcal{A} \). Both \( \mathcal{A}_{\nu_1 \nu_2, \nu_3 \nu_4} \) and \( \mathcal{H}_{0\nu_1 \nu_2, \nu_3 \nu_4} \) are symmetric with respect to transpositions of the first and the second pair of subscripts, i.e.,

\[ \mathcal{A}_{\nu_1 \nu_2, \nu_3 \nu_4} = \mathcal{A}_{\nu_2 \nu_1, \nu_3 \nu_4} = \mathcal{A}_{\nu_1 \nu_2, \nu_4 \nu_3} \]

\[ \mathcal{H}_{0\nu_1 \nu_2, \nu_3 \nu_4} = \mathcal{H}_{0\nu_2 \nu_1, \nu_3 \nu_4} = \mathcal{H}_{0\nu_1 \nu_2, \nu_4 \nu_3} \].
They are defined in the symmetric space, i.e., \((\nu_1\nu_2)\) and \((\nu_2\nu_1)\) describe the same two-exciton state. Because of this, the summation with respect to intermediate states in \(A_{\nu_1\nu_2,\nu_3\nu_4} H_{0\nu_3\nu_4,\nu_5\nu_6}\) has to be carried out over all different pairs of \(\nu_3\nu_4\), but not independently with respect to \(\nu_3\) and \(\nu_4\). Actually, due to continuous spectrum of \(\vec{K}\) the contribution of diagonal states, where \(\nu_3 = \nu_4\), can be neglected and then the independent summation respect to \(\nu_3\) and \(\nu_4\) is equivalent to double counting of each pair \(\nu_3\nu_4\). As a result it is possible to sum independently with respect to \(\nu_3\) and \(\nu_4\) and then to divide the result by 2. This leads to

\[
(\mathcal{A} H_0 + H_0 A)^{(x)}_{\vec{k}_1s_1,\vec{k}_2s_2,\vec{k}_3s_3,\vec{k}_4s_4} = \frac{A}{S} \delta_{\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4} \times \left( \delta_{s_1s_4}\delta_{s_2s_3}\delta_{s_1s_3h}\delta_{s_2s_4h} + \delta_{s_1s_3h}\delta_{s_2s_4}\delta_{s_1s_3s_4h} \right) 
\times \left( E_{\vec{k}_1} + E_{\vec{k}_2} + E_{\vec{k}_3} + E_{\vec{k}_4} \right) 
\approx \frac{4A\epsilon_b}{S} \delta_{\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4} \times \left( \delta_{s_1s_4}\delta_{s_2s_3}\delta_{s_1s_3h}\delta_{s_2s_4h} + \delta_{s_1s_3h}\delta_{s_2s_4}\delta_{s_1s_3s_4h} \right). 
\]

Here we used again the assumption of a small exciton kinetic energy, \((3.2)\).

Finally, we can present matrix elements of the two-exciton Hamiltonian in the form

\[
H_{2\text{ex}} = H_0\delta_{\vec{k}_1s_1,\vec{k}_2s_2,\vec{k}_3s_3,\vec{k}_4s_4} + \frac{1}{S} \left( U_{\vec{k}_1s_1,\vec{k}_2s_2,\vec{k}_3s_3,\vec{k}_4s_4}^{\text{ex-ex}} + U_{\vec{k}_1s_1,\vec{k}_2s_2,\vec{k}_3s_3,\vec{k}_4s_4}^{\text{ex-ex}} \right),
\]

where matrix elements of \(H_0\) are defined by Eq. \((3.38)\) and matrix elements of \(U_{\text{ex-ex}}\) are

\[
U_{\vec{k}_1s_1,\vec{k}_2s_2,\vec{k}_3s_3,\vec{k}_4s_4}^{\text{ex-ex}} = \delta_{\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4}\delta_{s_1s_3}\delta_{s_2s_4} \left[ U^{(d)}(|\vec{k}_1 - \vec{k}_3|) + V_1 \right] 
+ \delta_{\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4}\delta_{s_1s_4}\delta_{s_2s_3}\delta_{s_1s_3h}\delta_{s_2s_4h} \left[ U^{(x)}(2\epsilon_b - V_2) \right].
\]

In this form we still keep a trace of non-elementary nature of excitons in the spin \(\delta\)-symbols. The corresponding expression in exciton spins is quite cumbersome. We overcome this disadvantage in the many-exciton Hamiltonian in the next subsection.
C. Hamiltonian of exciton gas with pair interaction

The matrix form of the Hamiltonian of the exciton gas (3.21b) is practically inconvenient. It is desirable to reduce it to the second quantized form. There is a standard way to obtain the second quantized form of the Hamiltonian of a gas of elementary bosons. To make use of this way we show that the Hamiltonian of two excitons (3.45) is equivalent to a Hamiltonian of two elementary bosons. Then, keeping only pair exciton interaction, we can immediately write down the Hamiltonian of \( N \) excitons.

The Hamiltonian of two elementary bosons with masses \( M \) and the interaction \( \hat{U} \) can be written as

\[
H_{\text{ex}} = -2\epsilon_b - \frac{\hbar^2}{2M} \nabla_1^2 - \frac{\hbar^2}{2M} \nabla_2^2 + \hat{U},
\]  
(3.47)

where \( \epsilon_b \) is the energy necessary to create a boson.

As a basis for wave functions we chose plane waves so that wave function of two bosons can be written as

\[
\Psi_{\mathbf{K}_1s_1, \mathbf{K}_2s_2} = \frac{1}{\sqrt{2S}} \left[ g_{s_1}(\sigma_1)g_{s_2}(\sigma_2)e^{i(\mathbf{K}_1\mathbf{R}_1+\mathbf{K}_2\mathbf{R}_2)} + g_{s_1}(\sigma_2)g_{s_2}(\sigma_1)e^{i(\mathbf{K}_1\mathbf{R}_2+\mathbf{K}_2\mathbf{R}_1)} \right],
\]  
(3.48a)

when at least one of the inequalities \( s_1 \neq s_2, \mathbf{K}_1 \neq \mathbf{K}_2 \) is satisfied and

\[
\Psi_{\mathbf{K}_1s_1, \mathbf{K}_1s_1} = \frac{1}{S} g_{s_1}(\sigma_1)g_{s_1}(\sigma_2)e^{i\mathbf{K}_1(\mathbf{R}_1+\mathbf{R}_2)},
\]  
(3.48b)

when both spins and wave vectors of the bosons are equal.

Matrix elements of the Hamiltonian, (3.47), between functions, (3.48a), are identical to the matrix elements, (3.45), if we identify the matrix elements of \( \hat{U} \) between wave functions, (3.48a), \( \hat{U}^{\text{ex}-\text{ex}}_{R_1s_1,R_2s_2,R_3s_3,R_4s_4} + \hat{U}^{\text{ex}-\text{ex}}_{R_1s_1,R_2s_2,R_4s_4,R_3s_3} \) with \( U^{\text{ex}-\text{ex}}_{R_1s_1,R_2s_2,R_3s_3,R_4s_4} + U^{\text{ex}-\text{ex}}_{R_1s_1,R_2s_2,R_4s_4,R_3s_3}, \) Eqs. (3.45)-(3.46). This last identification is the definition of \( \hat{U} \). The nontrivial spin structure of these matrix elements means that the operator \( \hat{U} \) is spin-dependent. [One should remember that \( s_j = s_{je} + s_{jh}, \sigma_j = \sigma_{je} + \sigma_{jh}, \) and \( g_4(\sigma) = g_{se}(\sigma_e)g_{sh}(\sigma_h). \).] Due to the continuity of \( \tilde{K} \), the contribution of matrix elements with \( \tilde{K}_1 = \tilde{K}_2 \) and with \( \tilde{K}_3 = \tilde{K}_4 \) to all effects is negligible and we don’t consider them.
Now we have two-exciton Hamiltonian with known matrix elements of the pair interaction operator. The many excitons Hamiltonian with pair interaction in the second quantized form is usually written with the help of a non-symmetrized matrix element, \[ U_{K_1 s_1, K_2 s_2, K_4 s_4, K_3 s_3}^{\text{ex-ex}} = \frac{1}{S} \sum_{\sigma_1 \sigma_2} g_{s_1}(\sigma_1) g_{s_2}(\sigma_2) \times \int d\vec{R}_1 d\vec{R}_2 e^{-i(\vec{R}_1 + \vec{R}_2)} \hat{U}_{\text{ex-ex}} e^{i(\vec{R}_3 + \vec{R}_4)} g_{s_3}(\sigma_1) g_{s_4}(\sigma_2) . \]

Due to commutation relations of Bose operators it is possible to write down this Hamiltonian also with the symmetrized matrix element, \( (1/2) (\hat{U}_{K_1 s_1, K_2 s_2, K_4 s_4, K_3 s_3}^{\text{ex-ex}} + \hat{U}_{K_1 s_1, K_2 s_2, K_4 s_4, K_3 s_3}^{\text{ex-ex}}) \). That is, an additional factor of 1/2 appears in the interaction term of the many exciton Hamiltonian

\[
H_{\text{ex}} = \sum_{K,s} E_K c_{K,s}^\dagger c_{K,s} + \left. \frac{1}{4S} \sum_{K_1, K_2, K_3, K_4 \atop s_1, s_2, s_3, s_4} \right\} \left\{ \left| (U^{(d)}(K_1 - K_3)) + V_1 \right| \delta_{s_1, s_3} \delta_{s_2, s_4} + \left| (U^{(d)}(K_1 - K_4)) + V_1 \right| \delta_{s_1, s_4} \delta_{s_2, s_3} \right\} + V_x \left( \delta_{s_1, s_4} \delta_{s_2, s_3} \delta_{s_1, s_3} \delta_{s_2, s_4} \right) + \delta_{s_1, s_4} \delta_{s_2, s_3} \delta_{s_4, s_2} \delta_{s_3, s_1} \right\} \times \delta_{K_1 + K_2, K_3 + K_4} c_{K_1, s_1}^\dagger c_{K_3, s_3} c_{K_2, s_2} c_{K_4, s_4}.
\]

where \( c_{K,s} \) and \( c_{K,s}^\dagger \) are exciton annihilation and creation operators respectively, and

\[
V_x = U^{(x)} - 2Ae_b - V_2 .
\]

Now we make use of the one to one correspondence between electron and hole spins and the exciton spin, in order to express the \( \delta \)-symbols containing separately electron and hole spins, in \( \delta \)-symbols containing exciton spin only. Details of this calculation are given in Appendix 3, and the result is

\[
H_{\text{ex}} = \sum_{K,s} E_K c_{K,s}^\dagger c_{K,s} + \frac{1}{2S} \sum_{K_1, K_2, q \atop s_1, s_2} \left[ U^{(d)}(q) + V_1 \right] c_{K_2, s_2}^\dagger c_{K_1, s_1} c_{K_1 - q, s_1} c_{K_2 + q, s_2}
\]

\[
+ \frac{V_x}{4S} \sum_{K_1, K_2, q \atop s_1, s_2} \left[ \sum_{s_1 s_2} c_{K_1 s_1}^\dagger c_{K_2 - s_1} c_{K_1 - q s_2} c_{K_2 + q - s_2} c_{K_1 s_1}^\dagger c_{K_2 - s_1} c_{K_1 - q s_2} c_{K_2 + q - s_2} + 2 \sum_{s_1 s_2} c_{K_1 s_1}^\dagger c_{K_2 s_2} c_{K_1 - q s_1} c_{K_2 + q - s_2} \right].
\]
Hamiltonian, (3.52), is the main result of this section. In the following sections we use this Hamiltonian to study the density dependent luminescence line shift and exciton-exciton relaxation. To do this we calculate numerically the matrix elements of the Hamiltonian for a number of structures. The calculation of $V_1$ and $V_2$ is extremely difficult because it involves all exciton excited states. Fortunately, for the most of the structures that we consider $V_1$ and $V_2$ are numerically small compared to other matrix elements. The reason behind this is that the wave functions of excited states oscillate in the region where the wave function of the ground state is smooth. Our estimates show that the value of $\mathcal{H}_{\nu\nu'}^{(exex)}$ is smaller then 10% of $A\epsilon_b$ or $U^{(x)}$. So in the following calculation $V_1$ and $V_2$ are neglected.

IV. MEAN FIELD APPROXIMATION. LUMINESCENCE LINE SHIFT

In the mean field approximation the exciton scattering is neglected and only the shift of the exciton energy due to interaction is taken into account. This means that only terms diagonal with respect to occupation number $n_{\vec{K}s} = c_{\vec{K}s}^\dagger c_{\vec{K}s}$ are kept in the Hamiltonian. Then the energy of the system of $N$ excitons is

$$E_N = \sum_{\vec{K},s} E_{\vec{K}} n_{\vec{K}s} + \frac{V_b}{2S} N^2 + \frac{V_x}{4S} \sum_s (N_s - N_{-s})^2$$

$$+ \frac{1}{2S} \sum_{\vec{K}_1,\vec{K}_2,s} U^{(d)}(|\vec{K}_1 - \vec{K}_2|) n_{\vec{K}_1,s} n_{\vec{K}_2,s}$$

(4.1)

where $N_s = \sum_{\vec{K}} n_{\vec{K}s}$ is the number of excitons with spin $s$, $N = \sum_s N_s$, and

$$V_b = U^{(d)}(0) + V_x.$$  

(4.2)

The recombination energy $\epsilon_{\vec{K},s}$ of an exciton with momentum $\vec{K}$ and spin $s$ equals the change of the energy of the exciton system when the occupation number $n_{\vec{K}s}$ decreases by one, $\epsilon_{\vec{K},s} = E_N(n_{\vec{K}s}) - E_N(n_{\vec{K}s} - 1) \approx \frac{\partial E_N}{\partial n_{\vec{K}s}}$. Neglecting the photon wave vector we can put $\vec{K} = 0$ and then Eq. (4.1) leads to

$$\epsilon_s = -\epsilon_b + V_b n + V_x (n_s - n_{-s}) + \int \frac{d^2K}{(2\pi)^2} U^{(d)}(K) n_{\vec{K},s}.$$  

(4.3)
where \( n_s = N_s/S \) is the density of excitons with spin \( s \) and \( n = N/S \) is the total exciton density. The energy splitting between optically active excitons with spins +1 and -1 is

\[
\Delta E_{1,-1} = \epsilon_1 - \epsilon_{-1} = 2V_x(n_1 - n_{-1}) + \int \frac{d^2K}{(2\pi)^2} U^{(d)}(K)(n_{\vec{K},1} - n_{\vec{K},-1}).
\]  

(4.4)

Eqs. (4.3) and (4.4) are complicated to use due to the integral term. To calculate it, the exciton concentration is not enough, it is necessary to know the energy distribution of excitons. These expressions can be simplified if the typical exciton wave vector is much smaller than the typical wave vector of \( U^{(d)}(K) \). The last one is characterized by the wells width, \( L \) and the width of the barrier, \( w \) (see Appendix C). The exciton wave vector is small in the case of resonant pumping at low temperature \( T \). Then it is of the order of the photon wave vector \( K_{ph} \) or of the thermal wave vector \( K_T \sim \sqrt{2MT}/\hbar \). So, if both \( K_{ph} \) and \( K_T \) are much smaller than \( 1/L \) and \( 1/w \) then \( U^{(d)}(K) \) in Eq. (4.1), (4.3) and (4.4) can be replaced with \( U^{(d)}(0) \). As a result we have

\[
E_N = \sum_{K,s} E_K n_{\vec{K}s} + \frac{V_b}{2S} N^2 + \frac{V_x}{4S} \sum_s (N_s - N_{-s})^2 + \frac{U^{(d)}(0)}{2S} \sum_s N_s^2 ,
\]

(4.5)

and

\[
\epsilon_s = -\epsilon_b + V_b n + V_x (n_s - n_{-s}) + U^{(d)}(0)n_s ,
\]

(4.6a)

\[
\Delta E_{1,-1} = V_{es}(n_1 - n_{-1}) ,
\]

(4.6b)

where \( V_{es} = 2V_x + U^{(d)}(0) \). An expression similar to Eq. (4.6a) was suggested phenomenologically by Amand et al. [4]. This expression differs from Eq. (4.6a) by a relation between the coefficients in two last terms.

From Eq. (4.3) we see that for a constant exciton number, \( N \), the ground state of the exciton gas can be paramagnetic or ferromagnetic, depending on the sign of \( V_{es} \). When \( V_{es} \) is positive the minimal total energy of the system is reached when the number of excitons with opposite spins is equal, \( N_s = N_{-s} \). For negative \( V_{es} \), the system reaches its minimal energy when the difference, \( N_s - N_{-s} \), is maximal, which corresponds to ferromagnetic phase. The
possibility of these two phases for condensed excitons has been pointed out by Fernández-Rossier and Tejedor. [33] From Eq. (4.6b) we see that the same parameter, $V_{es}$, characterizes the spin energy splitting.

To make a quantitative comparison to experiments we evaluate the values of the Hamiltonian matrix elements for coupled quantum wells where electrons and holes are confined in different wells. Such a separation is usually reached by an external electric field applied in the growth direction. In the region of well widths that we consider the energy separation between the ground state and the first excited state in the wells is much larger than typical external potential drop across one well. This means that the electron and hole ground state wave functions can be taken as

$$
\zeta_e(z_e) = \sqrt{\frac{2}{L_e}} \sin \frac{\pi z_e}{L_e}, \quad -L_e < z_e < 0,
$$

$$
\zeta_h(z_h) = \sqrt{\frac{2}{L_h}} \sin \frac{\pi (z_h - w)}{L_h}, \quad w < z_h < w + L_h,
$$

where $L_e$ and $L_h$ and the widths of the electron and hole quantum wells respectively and $w$ is the width of the barrier. The expressions for the interaction energy $u_{ij}$ are cumbersome and their Fourier transforms are presented in Appendix C.

For the calculation of matrix elements we use the variational single-exciton wave function that gives a very good approximation [23],

$$
\phi(r) = \frac{1}{\sqrt{2\pi b(b + r_0)}} \exp \left\{ -\frac{\sqrt{r^2 + r_0^2 - r_0}}{2b} \right\},
$$

where $b$ and $r_0$ are variation parameters that are found by minimizing of the binding energy. The Fourier transform $\phi_q$ necessary for the calculation of $U^{(d)}(q)$ and $V_x$ is given in Appendix C.

For $U^{(d)}(0)$ it is possible to obtain a simple analytic expression without making use of the exciton wave function (Appendix C),

$$
U^{(d)}(0) = \frac{4\pi e^2}{\kappa} [w + 0.397(L_e + L_h)].
$$
We see that the direct interaction, \( U^{(d)}(0) \), grows with the separation between the wells, \( d = w + (L_e + L_h) / 2 \). This behavior is easy to understand. From the point of view of electrostatics, excitons resemble parallel dipoles of the size \( d \), and \( U^{(d)}(0) \) is a the dipole - dipole interaction. This interaction is a repulsion growing with the size of the dipoles. The coefficient of the second term in the square brackets is close to 0.5, for which \( U^{(d)}(0) \) corresponds to the plate capacitor approximation \[5,34,35\]. Typical value for \( U^{(d)}(0) \) for coupled quantum wells where the separation between the wells is \( d = 100 \text{ Å} \) is about \( 1.5 \times 10^{-10} \text{ meV} \cdot \text{cm}^2 \).

We present numerically calculated \( V_x \), \( V_b \) and \( V_{es} \) for a symmetric \( \text{Al}_x\text{Ga}_{1-x}\text{As} / \text{GaAs} / \text{Al}_x\text{Ga}_{1-x}\text{As} / \text{GaAs} / \text{Al}_x\text{Ga}_{1-x}\text{As} \) coupled quantum wells structure with the well widths \( L_e = L_h = L \). In the numerical calculations we use the electron effective mass \( m_e = 0.067 m_0 \), the hole effective masses \( m_\perp = 0.45 m_0 \) and \( m_\parallel = 0.126 m_0 \) (here \( m_0 \) is the free electron mass), and the dielectric constant \( \kappa = 12.5 \). In the previous paper \[23\] we have shown that the exciton wave function depends mainly on the distance between the centers of the wells and is not very sensitive to details of their geometry. We can expect the same from the parameters \( V_x \), \( V_b \) and \( V_{es} \). For this reason in Figs. \[1\] - \[4\] we present the dependence of \( V_x \), \( V_b \) and \( V_{es} \) on this distance, \( d = w + L \). To show the sensitivity of these parameters to the barrier width and the well width separately we give on Figs. \[1\] and \[3\] two curves, one for a given \( w \) (solid line) and the other for a given \( L \) (dotted line).

The parameter \( V_x \) can be positive or negative depending on the separation between the wells \( d \). To demonstrate this we presented its dependence on \( d \) for different ranges in Figs. \[1\] and \[4\]. The reason for the change of the sign is that \( V_x \) contains two contributions of different sign, the negative quantity \( U^{(x)} \) and the positive quantity \(-2A\epsilon_b\), Eq. \[3.31\] (we neglect \( V_2 \)). At small distances between the wells the second term dominates. When the separation between the wells increases \( U^{(x)} \) is just weakly affected while the binding energy \( \epsilon_b \) decreases, which leads to the change of the sign.

In Fig. \[8\] we present the parameter \( V_b \) which characterizing the overall shift of the exciton luminescence line. It is the combination of the direct interaction and the exchange term, \( V_x \),
Eq. (4.2). The direct interaction dominates and $V_b$ is always positive, which leads to the blue shift of the line.

To demonstrate the possibility of paramagnetic and ferromagnetic phases of the exciton gas we present the dependence of $V_{es}$ on $d$ in Fig. 4. We see that $V_{es}$ is a decreasing function of the separation. It becomes negative at large separation, which corresponds to ferromagnetic phase.

In a single infinite quantum well the electron and hole wave functions describing the confinement in the well are equal, and according to Eq. (3.34) $U^{(d)}(q)$ is identically zero.\[8,9\] For an estimate of the exchange matrix element $V_x$ in a single-well we can use two-dimensional model for which the exciton wave function is known (see, e.g., Ref. \[7\]) and which is typically used for such estimates.\[4,7–9\] In this case the wave function is a simple exponent, the absolute value of the binding energy is $\epsilon_b = \frac{2\mu e^4}{\hbar^2 \kappa^2}$ and

$$\epsilon_b A = -\frac{8\pi}{5} \frac{\hbar^2}{\mu} , \quad (4.10a)$$

$$V_x = \frac{4\pi\hbar^2}{\mu} \left( 1 - \frac{315\pi^2}{4096} \right) \approx 3.03 \frac{\hbar^2}{\mu} . \quad (4.10b)$$

The corresponding coefficient in the expression for the splitting, \[4.6b\] appears to be twice larger than in Ref. \[8\]. This difference comes from a different numerical factor in the Hamiltonian.

V. EXCITON-EXCITON RELAXATION TIME.

In this section we study exciton gas relaxation due to exciton-exciton collisions. In these collisions, the excitons change their momenta and can change their spins, however, the sum of exciton spins is conserved. For further calculation it is convenient to introduce the notation $M_{s_1 s_2}^{s_3 s_4}(q)$ for the scattering matrix element that describes the scattering from the state with spins $s_1$ and $s_2$ to the state with spins $s_3$ and $s_4$ ($s_1 + s_2 = s_3 + s_4$) with the transferred momentum $\hbar q$. In the Born approximation, according to Hamiltonian (3.52) the spin dependence of the matrix element is reduced to the separation of three cases. If the
sum of exciton spins is nonzero then the collision matrix element

\[ M_{s_1s_2}^{s_1s_2}(q) = U^{(d)}(q) + V_x, \quad s_2 + s_1 \neq 0. \]  \(5.1a\)

If the total spin is zero and spins in the final state are different from spins in the initial state then

\[ M_{s_1-s_1}^{s_2-s_2}(q) = \frac{V_x}{2}, \quad s_2 \neq s_1. \]  \(5.1b\)

If the total spin is zero and initial and final spins are the same then

\[ M_{s-s}^{s-s}(q) = U^{(d)}(q) - \frac{V_x}{2}. \]  \(5.1c\)

For 2D scattering, however, the Born approximation at low energies is not satisfactory and the matrix element can be strongly renormalized. \[36–38\] For a spin independent interaction between particles, \(U(\vec{r})\), the renormalization is reduced to the division of the Born matrix element by

\[ 1 - M \frac{\hbar^2}{K^2} \int \frac{1}{2i} \left[ \frac{1}{\pi} \left( C + \ln \left( \frac{K_r}{2} \right) \right) \right] U(\vec{r}) d\vec{r}, \]  \(5.2\)

where \(\hbar^2 K^2/M\) is the kinetic energy in the center of mass reference frame and \(C\) is the Euler constant. We don’t calculate the renormalization for a spin dependent potential since we use Eq. (5.2) only for estimates.

The spin relaxation in the exciton gas is usually described by simplified kinetic equations that ignore exciton momentum distribution. \[17,39\]. The Boltzmann equation that describes both spin and momentum relaxation has the form

\[
\frac{\partial n_{\vec{K}s}}{\partial t} = \frac{2\pi}{\hbar} \sum_{s_1 \neq -s} \int \left| M_{ss_1}^{s_1s}(q) \right|^2 \left[ (n_{\vec{K}s} + 1)(n_{\vec{K}1s_1} + 1)n_{\vec{K}+\vec{q}s}n_{\vec{K}1-\vec{q}s_1} 
- (n_{\vec{K}+\vec{q}s} + 1)(n_{\vec{K}1-\vec{q}s_1} + 1)n_{\vec{K}s}n_{\vec{K}1s_1} \right] 
\times \delta \left( E_K + E_{\vec{K}1} - E_{\vec{K}+\vec{q}} - E_{\vec{K}1-\vec{q}} \right) \frac{d^2K_1}{(2\pi)^2} \frac{d^2q}{(2\pi)^2} \\
+ \frac{2\pi}{\hbar} \sum_{s_1} \int \left| M_{s-s}^{s_1s}(q) \right|^2 \left[ (n_{\vec{K}s} + 1)(n_{\vec{K}1-s} + 1)n_{\vec{K}+\vec{q}s_1}n_{\vec{K}1-\vec{q}-s_1} \right] 
\times \delta \left( E_K + E_{\vec{K}1} - E_{\vec{K}+\vec{q}} - E_{\vec{K}1-\vec{q}} \right) \frac{d^2K_1}{(2\pi)^2} \frac{d^2q}{(2\pi)^2}
\]
\[ -(n_{\vec{K}+\vec{q}s_{1}} + 1)(n_{\vec{K}_1-\vec{q}-s_{1}} + 1)n_{\vec{K}s_{1}}n_{\vec{K}_1-\vec{q}} \]
\[ \times \delta \left( E_K + E_{K_1} - E_{\vec{K}+\vec{q}} - E_{\vec{K}_1-\vec{q}} \right) \frac{d^2 K_1}{(2\pi)^2} \frac{d^2 q}{(2\pi)^2}. \]  
\[ \text{(5.3)} \]

Numerical solution of Eq. (5.3) is much more difficult than its simplified versions that ignore momentum distribution. In general, the relaxation according to Eq. (5.3) cannot be exactly described by a relaxation time. To characterize the relaxation rate it is possible, nevertheless, to introduce an inverse relaxation time as the coefficient for \(-n_{\vec{K}s_{1}}\) in the collision operator

\[
\frac{1}{\tau_{Ks}} = \frac{2\pi}{\hbar} \sum_{s_1 \neq -s} \int \left| M^{ss_{1}}(q) \right|^2 \left[ (n_{\vec{K}+\vec{q}s_{1}} + n_{\vec{K}_1-\vec{q}s_{1}} + 1)n_{\vec{K}s_{1}} - n_{\vec{K}+\vec{q}s_{1}}n_{\vec{K}_1-\vec{q}s_{1}} \right] \]
\[ \times \delta \left( E_K + E_{K_1} - E_{\vec{K}+\vec{q}} - E_{\vec{K}_1-\vec{q}} \right) \frac{d^2 K_1}{(2\pi)^2} \frac{d^2 q}{(2\pi)^2} + \frac{2\pi}{\hbar} \sum_{s_1} \int \left| M^{s_{1}-s_{1}}(q) \right|^2 \left[ (n_{\vec{K}+\vec{q}s_{1}} + n_{\vec{K}_1-\vec{q}-s_{1}} + 1)n_{\vec{K}s_{1}} - n_{\vec{K}+\vec{q}s_{1}}n_{\vec{K}_1-\vec{q}-s_{1}} \right] \]
\[ \times \delta \left( E_K + E_{K_1} - E_{\vec{K}+\vec{q}} - E_{\vec{K}_1-\vec{q}} \right) \frac{d^2 K_1}{(2\pi)^2} \frac{d^2 q}{(2\pi)^2}. \]  
\[ \text{(5.4)} \]

This expression contains both linear and quadratic terms in exciton occupation numbers. Respectively, an order of magnitude estimate of the relaxation time contains linear and quadratic terms in the exciton concentration \(n\),

\[
\frac{1}{\tau_{Ks}} \sim \frac{n^2 + nK^2}{\hbar(h^2 K^2/\mu)} \left| M^{ss_{1}}(K) \right|^2. \]  
\[ \text{(5.5)} \]

The relaxation time \(\tau_{Ks}\) characterizes energy and momentum relaxation in the exciton gas. The same time characterizes also a partial spin relaxation. The spin relaxation due to collisions cannot be complete because of the total spin conservation in collisions. Formally it is described by the identity

\[
\frac{\partial}{\partial t} (n_s - n_{-s}) = 0, \]  
\[ \text{(5.6)} \]

that follows from Eq. (5.3). Here \(n_s\) is the concentration of excitons with spin \(s\). That is, the only spin relaxation due to collisions is the relaxation between dark excitons, (excitons with spin \(\pm 2\)), and bright excitons, (excitons with spin \(\pm 1\)) (see also Ref. [4]).
follows from here that spin relaxation in the exciton gas is characterized by few relaxation times which correspond to different relaxation mechanisms. If the exciton concentration is not very small then the fastest relaxation is the dark - bright exciton relaxation characterized by $\tau_{Ks}$. Complete relaxation can take place due to processes that involve D’yakonov - Perel mechanism of electron spin relaxation, light - heavy hole mixing, or electron - hole exchange. All these mechanisms contain their respective small coupling constants and are activated by scattering. So, if the main exciton scattering mechanism is exciton-exciton scattering then the complete spin relaxation has to be much slower than dark - bright exciton relaxation. The relation between the relaxation times can be different for a very small exciton concentration when other scattering mechanisms, e.g., phonon, impurity or surface roughness scattering are important.

VI. DISCUSSION

In this section we compare our results with a few experiments. We consider the shift of the exciton luminescence line, the energy splitting between exciton with different spins, the polarization of the exciton gas, and the exciton-exciton scattering time.

As we already mentioned in the introduction, the density dependence of the exciton luminescence line shift, the time dependence of line spin splitting and the luminescence depolarization proved that all these phenomena come from exciton-exciton interaction. A theoretical study of these phenomena has been done by Fernández-Rossier et al. [8,33], Ciuti et al. [9], Amand et al. [17], and Maialle et al. [39]. Here we consider only some features of the experiments which have not found a clear explanation so far.

The density dependent blue shift of the exciton line in GaAs/Al$_x$Ga$_{1-x}$As symmetric coupled quantum wells, where electrons and holes are spatially separated by external gate voltage, has been recently measured by Butov et al. [3] and Negoita et al. [3]. Butov et al. detected blue shift of 1.6 meV at zero magnetic field for wells width $L = 80$ Å and barrier width of $w = 40$ Å. They used the plate capacitor expression for the direct
interaction, neglecting the exchange, to calculate the exciton density of \( n = 9 \times 10^9 \text{ cm}^{-2} \).

To compare our results with their measurements we calculate the concentration according to Eq. (4.3) and check the importance of the corrections. For the described geometry we obtain \( V_b = 8.7 \times 10^{-11} \text{ meV} \cdot \text{cm}^{-2} \). The temperature of this experiment, 50 mK, is so low that we can use Eq. (4.6) instead of Eq. (4.3), where \( U^{(d)}(0) = 1.5 \times 10^{-10} \text{ meV} \cdot \text{cm}^{-2} \).

Assuming equal concentration of excitons with different spins, \( n_s = n_{-s} = n/4 \), we have \( \delta \epsilon_s = V_b n + U^{(d)}(0)n/4 \) and for \( \delta \epsilon_s = 1.6 \text{ meV} \) we obtain \( n = 1.3 \times 10^{10} \text{ cm}^{-2} \), which is close to the concentration obtained from the simple plate capacitor expression without the exchange correction.

The comparison with the results of Negoita et al. [6] is more interesting because there the excitation concentration was measured from the excitation intensity, independently of the blue shift. The measurements were made in symmetric coupled quantum wells, where the wells width was \( L = 60 \text{ Å} \) and the barrier width was \( w = 42 \text{ Å} \). The lattice temperature was 2 K and the concentration was in the range \( 10^9 - 10^{12} \text{ cm}^{-2} \). For low density, linear blue shift of \( 5 \times 10^{-11} \text{ meV} \cdot \text{cm}^2 \), was observed. For this geometry we have \( V_b = 7.8 \times 10^{-11} \text{ meV} \cdot \text{cm}^2 \). In the case, \( n_s = n_{-s} = n/4 \), with \( U^{(d)}(0) = 1.3 \times 10^{-10} \text{ meV} \cdot \text{cm}^{-2} \) we get from Eq. (4.6) linear shift of \( 1.1 \times 10^{-10} \text{ meV} \cdot \text{cm}^2 \). The difference between this value and the experimental one can result from our assumption that electrons and holes are completely confined in separate wells which increases the direct interaction \( U^{(d)} \). Another reason can be the presence of free carriers in the experiment, which screen the Coulomb potential and make exciton-exciton interaction weaker. The later possibility is supported by the luminescence line width which is larger than the exciton binding energy.

In the same structure, in a weak magnetic field, Snoke et al. [40] observed a red shift of the exciton luminescence line which grew with the gate voltage that separated electrons and holes. The most striking result is that the red shift reaches values of 10 or 20 meV (depending on the gate voltage) at magnetic field around 1 T. Such a magnetic field is not strong enough to induce a significant blue diamagnetic line shift. [41,42] The explanation that we suggest is based on a very narrow line of the pumping laser. Even a weak magnetic
field can split the exciton lines with different polarizations so much that they go away from the resonance with the pumping laser. This leads to a reduction of the exciton density, resulting, according to Eq. (4.7), with a red shift of the luminescence line. An increase of the external electric field increases the separation between electrons and holes leading to larger values of the coefficients $V_b$ and $U^d(0)$. As a result, the red shift also increases, as it is observed in the experiment. The effect is symmetric to the direction of the magnetic field, which is also in agreement with the experiment. The magnitude of the effect depends only on the absolute concentration change, $\Delta n$, so the relative change $\Delta n/n$ in the luminescence intensity, can be small.

Another phenomenon related to exciton-exciton interaction is a spontaneous energy splitting between excitons with opposite spins. A typical experimental way to produce a polarized exciton gas, (i.e., a gas where $n_{-s} \neq n_{s}$) is pumping by polarized light. In Refs. [10–13], the energy spin splitting was measured in multiple quantum wells where the electrons and holes are in the same well. This corresponds to zero separation between the carriers and therefore zero $U^{(d)}(0)$ and positive $V_{es}$. In all the experiments the spin majority excitons had higher energy than the minority and the difference increased with the density, as we would expect from positive $V_{es}$. Another evidence for $V_{es}$ being positive in multiple quantum well systems is the depolarization of the initially polarized exciton gas, that was reported by different authors [3,10,12,13,17]. According to the results of Sec. [V], when $V_{es}$ is positive the system is paramagnetic, and the minimal energy of the system is reached when the exciton gas is depolarized.

In a double well structure Aichmayr et al. [14] detected an energy spin splitting dependence on the gate voltage that separated electrons and holes. As the voltage increased, the energy splitting decreased from 4 meV to zero. This behavior corresponds to Eq. (4.6b), where with the increase of the electron and the hole separation, the coefficient $V_{es}$, being positive, decreases to zero (see Fig. [4]). A more detailed consideration, with the help of Eq. (4.6a), can describe a different behaviour of the minority and majority exciton luminescence lines which is presented in Fig.2 of Ref. [14]. At low gate voltage the lines are split nearly
symmetrically (the shift of the majority line is positive while the shift of the minority line is negative) with respect to the value to which both of them relax with the time constant $\tau_{sd} = 180$ ps. With increase of the voltage the shift of the majority line does not change while the shift of the minority line decreases, becomes positive and at a very high voltage the splitting disappears. First of all it is necessary to note that the luminescence decay time (400 ps for the low voltage and 1000 ps for the high voltage) is a few times larger than $\tau_{sd}$. The luminescence decay characterizes the decrease of the exciton concentration and the comparatively small value of $\tau_{sd}$ means that the reason the splitting relaxation is not decrease of the exciton concentration but spin relaxation, probably due to light and heavy hole mixing. So the line shift due to exciton polarization under the condition of constant total concentration can be calculated according to $\Delta \epsilon_s = V_x(n_s - n_{-s}) + U^{(d)}(0)n_s$. At low gate voltage the separation between electrons and holes is small, the direct interaction $U^{(d)}(0)$ is negligible and the shifts of the majority (+1) and minority (-1) lines are $\Delta \epsilon_{\pm 1} = \pm V_x(n_{+1} - n_{-1})$. This is a symmetric shift in agreement with the experiment. With increase of the voltage the separation between electrons and holes grows leading to growth of $U^{(d)}(0)$ and decrease of $V_x$. Given the concentrations, at some intermediate voltage $V_x = U^{(d)}(0)n_{-1}/(n_{+1} - n_{-1})$ and then $\Delta \epsilon_{+1} = U^{(d)}(0)(n_{+1} + n_{-1})$ while $\Delta \epsilon_{-1} = 0$. This corresponds to Fig.2b of Ref. [14]. At high voltage $V_x$ is negative, and if $V_x \approx -U^{(d)}(0)/2$ then $\Delta \epsilon_{\pm 1} = U^{(d)}(0)(n_{+1} + n_{-1})/2$ which corresponds to Fig.2c of Ref. [14]. That is Eq.$(4.6a)$ completely describes the behavior of both minority and majority lines. It makes sense to note that $U^{(d)}(0)$ at the intermediate field is smaller than at high field so the majority line does not shift much, which also corresponds to the experiment.

The last physical phenomena we want to discuss here is the exciton-exciton relaxation time. For the estimate of the relaxation time we make use of Eq. $(5.3)$. The time necessary for an exciton to emit or absorb a phonon is around hundreds of ps [13] which is much longer than short luminescence relaxation times with electrons and hole in the same well (a few tens of ps). That means that under the condition of resonant excitation the exciton momentum is around that of an exciting photon, $K \sim 2 \times 10^5$ cm$^{-1}$. So for concentrations
of the order or smaller than \(4 \times 10^{10} \text{ cm}^{-2}\) we can use for an estimate only the second term in the numerator of Eq. (5.3). Since the relevant experiments have been done in multi quantum wells structures, where electrons and holes are confined in the same layer, we make use of the 2D model that we have discussed in the end of Sec. IV and estimate the interaction matrix element according to Eq. (4.10b). In the renormalization factor (5.2) only the logarithmic term can be important and it is \(\sim 1 - (M/\pi \hbar^2)V_x \ln(Ka) \approx 8.7\) for the exciton radius \(a \approx 80\ \text{Å}\). This leads to \(1/\tau \approx 0.12(\hbar n/\mu)\) and \(\tau \sim 8\ \text{ps}\) which is close to the experimental spin relaxation time measured by Le Jeune et al. [12], Baylac et al. [16], and Amand et al. [17].

Wang et al. [18] measured the exciton momentum relaxation rate in the concentration region between \(10^9\) to \(1.5 \times 10^{10} \text{ cm}^{-2}\) in multiple quantum wells of 130 Å width. They obtained the relaxation rate that grew with the concentration from 0.5 to 2 \(\text{ps}^{-1}\) that is about an order of magnitude larger than Eq. (5.5) gives. Such a big difference cannot be attributed to a deviation for 2D model for exciton. It is likely that a contribution of other elastic scattering mechanisms (e.g., surface roughness) was substantial in this experiment.

VII. CONCLUSION

We derived the Hamiltonian of exciton gas in quantum wells by the projection of the electron-hole plasma Hamiltonian to exciton states and expansion in a small exciton density. Matrix elements of the exciton Hamiltonian are expressed in terms of a single exciton wave function which is not modified by exciton-exciton interaction and is rather sensitive to the geometry of the heterostructure. With the help of the exciton Hamiltonian we estimated the blue shift and spin splitting of the exciton luminescence line and their dependence on the heterostructure parameters. We also wrote down the Boltzmann equation for excitons and estimated the energy and spin relaxation time resulting from the exciton-exciton scattering. We succeeded to give an explanation to some recent experimental results that have not been explained so far.
VIII. ACKNOWLEDGEMENTS

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APPENDIX A: CALCULATION OF MATRIX ELEMENTS

In this Appendix we present the detailed calculation of the matrix elements that determine the exciton-exciton pair interaction. The Appendix contains four subsections where the overlap integral \( A_{\vec{k}_1s_1,\vec{k}_2s_2;\vec{k}_3s_3,\vec{k}_4s_4} \), the direct part of the matrix element \( H^{(d)}_{\vec{k}_1s_1,\vec{k}_2s_2;\vec{k}_3s_3,\vec{k}_4s_4} \), (3.30), the exchange part of the matrix element \( H^{(e)}_{\vec{k}_1s_1,\vec{k}_2s_2;\vec{k}_3s_3,\vec{k}_4s_4} \), (3.31), and the contribution from the excited states, \( H^{(ex)}_{\vec{k}_1s_1,\vec{k}_2s_2;\vec{k}_3s_3,\vec{k}_4s_4} \), are calculated. In this calculation we omit \( z \)-dependent part of the kinetic and potential energy in \( H_{2eh} \). This part gives only the size quantization energy of free particles which is our energy reference point.

1. Overlap integral

The substitution of functions (3.24) in the definition (3.17) gives

\[
A_{\vec{k}_1s_1,\vec{k}_2s_2;\vec{k}_3s_3,\vec{k}_4s_4} = \frac{1}{S} \delta_{\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4} \times \left( \delta_{s_1e,\bar{s}_4e} \delta_{s_2e,\bar{s}_3e} \delta_{s_1h,\bar{s}_4h} \delta_{s_2h,\bar{s}_3h} A_{\vec{k}_1\vec{k}_2,\vec{k}_3\vec{k}_4} + \delta_{s_1e,\bar{s}_4e} \delta_{s_2e,\bar{s}_3e} \delta_{s_1h,\bar{s}_4h} \delta_{s_2h,\bar{s}_3h} A_{\vec{k}_1\vec{k}_2,\vec{k}_3\vec{k}_4} \right),
\]

(A1)

\( s_{je} (s_{jh}) \) is the electron (hole) spin of the exciton with spin \( s_j \), and

\[
A_{\vec{k}_1\vec{k}_2,\vec{k}_3\vec{k}_4} = -\int d\vec{R}d\vec{r}_{ee}d\vec{r}_{hh} \exp \left[ -i(\vec{k}_1 - \vec{k}_4)\vec{r}_{ee} - i(\vec{k}_1 - \vec{k}_3)\vec{r}_{hh} \right] \times \phi \left( \vec{R} + \frac{\vec{r}_{ee} - \vec{r}_{hh}}{2} \right) \phi \left( \vec{R} - \frac{\vec{r}_{ee} - \vec{r}_{hh}}{2} \right) \phi \left( \vec{R} - \frac{\vec{r}_{ee} + \vec{r}_{hh}}{2} \right) \phi \left( \vec{R} + \frac{\vec{r}_{ee} + \vec{r}_{hh}}{2} \right). \tag{A2}
\]

The overlap integral (A2) has an obvious property, \( A_{\vec{k}_1\vec{k}_2,\vec{k}_3\vec{k}_4} = A_{\vec{k}_1\vec{k}_2,\vec{k}_4\vec{k}_3} \). The reduction of the overlap integral to this form has been made with the help of the relative electron-hole coordinates.
\[ \vec{r}_{ee} = \vec{r}_{e1} - \vec{r}_{e2} , \quad \vec{r}_{hh} = \vec{r}_{h1} - \vec{r}_{h2} , \quad (A3a) \]

\[ \vec{R} = \left( \vec{r}_{e1} + \vec{r}_{e2} - \vec{r}_{h1} - \vec{r}_{h2} \right) / 2 . \quad (A3b) \]

The characteristic values of \( R, r_{ee}, \) and \( r_{hh} \) in integral (A3) are of the order of the exciton radius \( a \). On the other hand, inequality (3.2) is equivalent to \( aK \ll 1 \). This means that all exponential factors in the integrand can be replaced by unity and

\[ A_{K_1K_2K_3K_4} = A \equiv - \int d\vec{R} d\vec{r}_{ee} d\vec{r}_{hh} \]

\[ \phi \left( \vec{R} + \frac{\vec{r}_{ee} - \vec{r}_{hh}}{2} \right) \phi \left( \vec{R} - \frac{\vec{r}_{ee} - \vec{r}_{hh}}{2} \right) \phi \left( \vec{R} + \frac{\vec{r}_{ee} + \vec{r}_{hh}}{2} \right) . \quad (A4) \]

The substitution here of the Fourier transform of the wave function, (3.28), immediately leads to Eq. (3.27).

2. The direct part.

After the summation over spin variables, Eq. (3.30) becomes

\[ H^{(d)}_{K_1s_1, K_2s_2, K_3s_3, K_4s_4} = \delta_{s_1,s_3} \delta_{s_2,s_4} \int \psi^*_{K_1}(\vec{r}_{e1}, \vec{r}_{h1}) \psi^*_{K_2}(\vec{r}_{e2}, \vec{r}_{h2}) \mathcal{H}_{2eh} \]

\[ \times \psi_{K_3}(\vec{r}_{e1}, \vec{r}_{h1}) \psi_{K_4}(\vec{r}_{e2}, \vec{r}_{h2}) d\vec{r}_{e1} d\vec{r}_{h1} d\vec{r}_{e2} d\vec{r}_{h2} \]

\[ + \delta_{s_1,s_4} \delta_{s_2,s_3} \int \psi^*_{K_1}(\vec{r}_{e1}, \vec{r}_{h1}) \psi^*_{K_2}(\vec{r}_{e2}, \vec{r}_{h2}) \mathcal{H}_{2eh} \]

\[ \times \psi_{K_3}(\vec{r}_{e1}, \vec{r}_{h1}) \psi_{K_4}(\vec{r}_{e2}, \vec{r}_{h2}) d\vec{r}_{e1} d\vec{r}_{h1} d\vec{r}_{e2} d\vec{r}_{h2} . \quad (A5) \]

The following part of the Hamiltonian (3.22)

\[ - \frac{\hbar^2 \nabla^2_{e1}}{2m_e} - \frac{\hbar^2 \nabla^2_{h1}}{2m_{\parallel}} + u_{eh}(|\vec{r}_{e1} - \vec{r}_{h1}|) - \frac{\hbar^2 \nabla^2_{e2}}{2m_e} - \frac{\hbar^2 \nabla^2_{h2}}{2m_{\parallel}} + u_{eh}(|\vec{r}_{e2} - \vec{r}_{h2}|) \quad (A6) \]

is the sum of the Hamiltonians of two free excitons consisting of the pairs \((e1,h1)\) and \((e2,h2)\). This part of the matrix element gives the sum of the two free excitons energies, \( E_{K_3} + E_{K_4} \) multiplied by the unit matrix, (3.25). Here \( E_K = -\epsilon_b + \hbar^2 K^2 / 2M \). For the calculation of the other terms of the Hamiltonian, it is convenient to change the in-plane variables of the integration to the center of mass coordinate,
\[ \vec{R}_c = [m_e(\vec{r}_{e1} + \vec{r}_{e2}) + m_r(\vec{r}_{h1} + \vec{r}_{h2})]/2M , \]  \hspace{1cm} \text{(A7a)}

the distance between the exciton centers of mass,

\[ \bar{\rho} = [m_e(\vec{r}_{e1} - \vec{r}_{e2}) + m_r(\vec{r}_{h1} - \vec{r}_{h2})]/M , \]  \hspace{1cm} \text{(A7b)}

and relative coordinates,

\[ \vec{r}_1 = \vec{r}_{e1} - \vec{r}_{h1} , \quad \vec{r}_2 = \vec{r}_{e2} - \vec{r}_{h2} . \] \hspace{1cm} \text{(A7c)}

Then the integration with respect to \( \vec{R}_c \) results in Eq. (3.32), where

\[
U^{(d)}_{K_1s_1, K_2s_2, K_3s_3, K_4s_4} = \delta_{s_1s_3} \delta_{s_2s_4} \int \exp \left[ i(-\vec{K}_1 + \vec{K}_2 + \vec{K}_3 - \vec{K}_4)\bar{\rho} \right] \frac{\phi^2(r_1)\phi^2(r_2)d\vec{r}_1d\vec{r}_2d\bar{\rho}}{2} \]

with the help of the momentum conservation that is expressed by \( \delta_{\vec{K}_1 + \vec{K}_2, \vec{K}_3 + \vec{K}_4} \) in Eq. (3.32), we come up with Eq. (3.33) where

\[
U^{(d)}(q) = \int e^{-i\vec{q}\bar{\rho}} \left[ u_{ee} \left( \left| \bar{\rho} + M\frac{\vec{r}_1 - \vec{r}_2}{M} \right| \right) + u_{hh} \left( \left| \bar{\rho} - M\frac{\vec{r}_1 - \vec{r}_2}{M} \right| \right) 
+ u_{eh} \left( \left| \bar{\rho} + M\frac{\vec{r}_1 - \vec{r}_2}{M} \right| \right) + u_{eh} \left( \left| \bar{\rho} - M\frac{\vec{r}_1 - \vec{r}_2}{M} \right| \right) \right] \phi^2(r_1)\phi^2(r_2)d\vec{r}_1d\vec{r}_2d\bar{\rho} \]

The Fourier transformation with the help of notations, (3.33) - (3.36), easily reduces this expression to Eq. (3.34).

3. The exchange part.

After the summation with respect to spin variables, Eq. (3.31) becomes
The fact that these terms correspond to the exchange of two electrons or two holes, so the initial and final two excitons are formed from different particles, makes the calculation more complicated than the calculation of the direct part. First, we cannot explicitly express products of the electron and hole spin \( \delta \)-symbols in the exciton spin as we did in the direct part, Eq. (A3). Second, it is harder to separate the single exciton energy \( E_K \) from the exciton-exciton interaction. Operating by Eq. (A6) on the wave functions \( \psi_{K_1}^* (\mathbf{r}_1, \mathbf{r}_2) \psi_{K_3} (\mathbf{r}'_1, \mathbf{r}'_2) \psi_{K_4}' (\mathbf{r}'_3, \mathbf{r}'_4) \) results in the sum of single exciton energies of the initial state, \( E_{K_1} + E_{K_3} \). However, operating by the same kinetic terms plus different terms of the Coulomb interaction, i.e.,

\[
H^{(z)}_{K_1 s_1, K_2 s_2, K_3 s_3, K_4 s_4} = - \delta_{s_1 s_3} \delta_{s_2 s_4} \delta_{s_1 h s_3} \delta_{s_2 h s_4} \int \psi^*_{K_1} (\mathbf{r}_1, \mathbf{r}_2) \psi^*_{K_3} (\mathbf{r}'_1, \mathbf{r}'_2) d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \\
\times \mathcal{H}_{2eh} \psi_{K_3} (\mathbf{r}'_1, \mathbf{r}'_2) \psi_{K_4} (\mathbf{r}'_3, \mathbf{r}'_4) d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \\
- \delta_{s_1 s_3} \delta_{s_2 s_4} \delta_{s_1 h s_3} \delta_{s_2 h s_4} \int \psi^*_{K_1} (\mathbf{r}_1, \mathbf{r}_2) \psi^*_{K_2} (\mathbf{r}'_1, \mathbf{r}'_2) d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \\
\times \mathcal{H}_{2eh} \psi_{K_2} (\mathbf{r}'_1, \mathbf{r}'_2) \psi_{K_4} (\mathbf{r}'_3, \mathbf{r}'_4) d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \
\]

(A10)

on the wave function \( \psi^*_{K_1} (\mathbf{r}_1, \mathbf{r}_2) \psi^*_{K_2} (\mathbf{r}'_1, \mathbf{r}'_2) \) results in the sum of single exciton energies of the final state, \( E_{K_1} + E_{K_2} \). We write the exchange part in a symmetric form so we add and subtract the kinetic terms to the Hamiltonian and reduce Eq. (A10) to
Appendix A 1. The result does not depend on the excitons momenta, \( \mathbf{r}_{ee} \) and \( \mathbf{r}_{hh} \), Eq. (A3), and the center of mass of the system \( \mathbf{R}_c \), Eq. (A11). After integration with respect to \( \mathbf{R}_c \) we obtain

\[
H^{(x)}_{K_1 s_1, K_2 s_2, K_3 s_3, K_4 s_4} = \frac{1}{S} \delta_{K_1 + K_2, K_3 + K_4} \left( E_{K_1} + E_{K_2} + E_{K_3} + E_{K_4} - \frac{\hbar^2 K^2}{4M} \right)
\]

\[
\times \left( \delta_{s_1 s_4} \delta_{s_2 s_3} \delta_{s_1 h s_3 h} \delta_{s_2 h s_4 h} A_{K_1 K_2, K_3 K_4} \right) + \frac{1}{S} \delta_{K_1 + K_2, K_3 + K_4} \times \left( \delta_{s_1 s_4} \delta_{s_2 s_3} \delta_{s_1 h s_3 h} \delta_{s_2 h s_4 h} U^{(x)}_{K_1 K_2, K_3 K_4} \right),
\]

where

\[
U^{(x)}_{K_1 K_2, K_3 K_4} = - \int d\mathbf{R} d\mathbf{r}_{ee} d\mathbf{r}_{hh}
\]

\[
\times \exp \left[ -i(\mathbf{K}_1 - \mathbf{K}_2) \frac{\mathbf{r}_{ee} + \mathbf{r}_{hh}}{2} \right] \phi \left( \mathbf{R} + \frac{\mathbf{r}_{ee} - \mathbf{r}_{hh}}{2} \right) \phi \left( \mathbf{R} - \frac{\mathbf{r}_{ee} - \mathbf{r}_{hh}}{2} \right)
\]

\[
\times \left[ u_{ee}(r_{ee}) + u_{hh}(r_{hh}) + \frac{\hbar^2}{4\mu} \nabla^2 + \frac{\hbar^2}{m_e} \nabla_{ee}^2 + \frac{\hbar^2}{m_h} \nabla_{hh}^2 \right]
\]

\[
\times \exp \left[ -i(\mathbf{K}_3 - \mathbf{K}_4) \frac{\mathbf{r}_{ee} - \mathbf{r}_{hh}}{2} \right] \phi \left( \mathbf{R} - \frac{\mathbf{r}_{ee} + \mathbf{r}_{hh}}{2} \right) \phi \left( \mathbf{R} + \frac{\mathbf{r}_{ee} + \mathbf{r}_{hh}}{2} \right). \quad (A14)
\]

From Eq. (A14) it follows that

\[
U^{(x)}_{K_1 K_2, K_3 K_4} = U^{(x)}_{K_3 K_4, K_1 K_2}. \quad (A15)
\]

The matrix element, \( U^{(x)}_{K_1 K_2, K_3 K_4} \), is simplified with the help of the low exciton energy assumption, (3.2). This is done in a similar way to the simplification of \( A_{K_1 K_2, K_3 K_4} \), in Appendix A1. The result does not depend on the excitons momenta,

\[
U^{(x)}_{K_1 K_2, K_3 K_4} = U^{(x)} \equiv - \int d\mathbf{R} d\mathbf{r}_{ee} d\mathbf{r}_{hh}
\]

\[
\times \phi \left( \mathbf{R} + \frac{\mathbf{r}_{ee} - \mathbf{r}_{hh}}{2} \right) \phi \left( \mathbf{R} - \frac{\mathbf{r}_{ee} - \mathbf{r}_{hh}}{2} \right)
\]

\[
\times \left[ u_{ee}(r_{ee}) + u_{hh}(r_{hh}) + \frac{\hbar^2}{4\mu} \nabla^2 + \frac{\hbar^2}{m_e} \nabla_{ee}^2 + \frac{\hbar^2}{m_h} \nabla_{hh}^2 \right]
\]

\[
\times \phi \left( \mathbf{R} - \frac{\mathbf{r}_{ee} + \mathbf{r}_{hh}}{2} \right) \phi \left( \mathbf{R} + \frac{\mathbf{r}_{ee} + \mathbf{r}_{hh}}{2} \right). \quad (A16)
\]
This integral takes a more compact form if it is expressed in Fourier transform of the wave function,

\[ U^{(x)} = \frac{\hbar^2}{\mu} \int \phi_q^4 q^2 \frac{d\vec{q}}{(2\pi)^2} - \int \phi_{q_1}^2 \phi_{q_2}^2 [u_{ee}(|\vec{q}_1 - \vec{q}_2|) + u_{hh}(|\vec{q}_1 - \vec{q}_2|)] \frac{d\vec{q}_1 d\vec{q}_2}{(2\pi)^4}. \] (A17)

This last integral can also be written in another form,

\[ U^{(x)} = \frac{\hbar^2}{\mu} \int \phi_q^4 q^2 \frac{d\vec{q}}{(2\pi)^2} - \int [u_{ee}(r) + u_{hh}(r)] \left[ \int \phi_q^2 e^{i\vec{q}\cdot\vec{r}} \frac{d\vec{q}}{(2\pi)^2} \right]^2 d\vec{r}. \] (A18)

Integral (A14) is of the order of \( \hbar^2/\mu \). Since \( \epsilon_b \sim \hbar^2/\mu a^2 \), the second term in Eq. (A13) is of the order of \( U^{(x)}/S \sim \epsilon_b(a^2/S) \). According to Eq. (A4), \( A \sim a^2 \), hence the first term in Eq. (A13) is of the same order as the second. The exciton kinetic energy in the first term can be neglected because its contribution to \( H^{(x)}_{\vec{K}_{1s_1},\vec{K}_{2s_2},\vec{K}_{3s_3},\vec{K}_{4s_4}} \) is of the order \( \epsilon_b(a^2/S)(\hbar^2 K^2/M) \), i.e., contains the product of two small parameters. As a result Eq. (A13) is reduced to Eq. (3.37).

**4. Contribution of excited states**

For two excitons the definition, (3.14), can be written as

\[ H^{(exs)}_{\vec{K}_{1s_1},\vec{K}_{2s_2},\vec{K}_{3s_3},\vec{K}_{4s_4}} = \sum_{\vec{q}_1,\vec{q}_2,\alpha_1,\alpha_2} \langle \vec{K}_{1s_1}\vec{K}_{2s_2}|H + 2\epsilon_b|\vec{q}_1\alpha_1 s_1'|\vec{q}_2\alpha_2 s_2' \rangle \]

\[ \times \left( E_{\alpha_1} + E_{\alpha_2} + \frac{\hbar^2 q_1^2}{2M} + \frac{\hbar^2 q_2^2}{2M} + 2\epsilon_b \right)^{-1} \langle \vec{q}_1\alpha_1 s_1'\vec{q}_2\alpha_2 s_2'|H + 2\epsilon_b|\vec{K}_{3s_3}\vec{K}_{4s_4} \rangle. \] (A19)

The matrix elements of the Hamiltonian between the ground state and excited states can be separated into the direct and exchange parts [compare Eqs. (3.29) - (3.31)],

\[ \langle \vec{K}_{1s_1}\vec{K}_{2s_2}|H + 2\epsilon_b|\vec{q}_1\alpha_1 s_1'|\vec{q}_2\alpha_2 s_2' \rangle = H^{(d)}_{\vec{q}_1\alpha_1 s_1',\vec{q}_2\alpha_2 s_2'}(\vec{K}_{1s_1},\vec{K}_{2s_2}) + H^{(d)}_{\vec{q}_1\alpha_1 s_1',\vec{q}_2\alpha_2 s_2'}(\vec{K}_{2s_2},\vec{K}_{1s_1}) - H^{(x)}_{\vec{q}_1\alpha_1 s_1',\vec{q}_2\alpha_2 s_2'}(\vec{K}_{1s_1},\vec{K}_{2s_2}) - H^{(x)}_{\vec{q}_1\alpha_1 s_1',\vec{q}_2\alpha_2 s_2'}(\vec{K}_{2s_2},\vec{K}_{1s_1}). \] (A20)

In the calculation of these matrix elements it is convenient to separate the sum of two single-exciton parts of the Hamiltonian, (A6), and to operate it on the left bracket [similar
to the calculation of $H^{(d)}_{K_1 s_1, K_2 s_2, K_3 s_3, K_4 s_4}$ and $H^{(x)}_{K_1 s_1, K_2 s_2, K_3 s_3, K_4 s_4}$. Then, after the neglect of the exciton kinetic energy,

$$H^{(d)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_1, \vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_2} (\vec{K}_1 s_1, \vec{K}_2 s_2) = \sum_{\sigma_1 \sigma_2 \sigma_1 \sigma_2} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_1 d\vec{r}_2 \Psi^{*}_{K_1, s_1} (\vec{r}_1, \sigma_1; \vec{r}_1, \sigma_1) \Psi^{*}_{K_2, s_2} (\vec{r}_2, \sigma_2; \vec{r}_2, \sigma_2) U (\vec{r}_1, \vec{r}_2, \vec{r}_1, \vec{r}_2) \Psi_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_1} (\vec{r}_1, \sigma_1; \vec{r}_1, \sigma_1) \Psi_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_2} (\vec{r}_2, \sigma_2; \vec{r}_2, \sigma_2) , \quad (A21a)$$

$$H^{(x)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_1, \vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_2} (\vec{K}_1 s_1, \vec{K}_2 s_2) = \sum_{\sigma_1 \sigma_2 \sigma_1 \sigma_2} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_1 d\vec{r}_2 \Psi^{*}_{K_1, s_1} (\vec{r}_1, \sigma_1; \vec{r}_1, \sigma_1) \Psi^{*}_{K_2, s_2} (\vec{r}_2, \sigma_2; \vec{r}_2, \sigma_2) U (\vec{r}_1, \vec{r}_2, \vec{r}_1, \vec{r}_2) \Psi_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_1} (\vec{r}_1, \sigma_1; \vec{r}_1, \sigma_1) \Psi_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_2} (\vec{r}_2, \sigma_2; \vec{r}_2, \sigma_2) . \quad (A21b)$$

where

$$U (\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) = u_{ex} (|\vec{r}_1 - \vec{r}_2|) + u_{eh} (|\vec{r}_2 - \vec{r}_1|)$$

$$+ u_{eh} (|\vec{r}_1 - \vec{r}_2|) + u_{eh} (|\vec{r}_2 - \vec{r}_1|) . \quad (A22)$$

After the substitution of the exciton wave function, Eqs. (3.4) - (3.6), in Eq. (A21), the spin factors are easily separated,

$$H^{(d)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_1, \vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_2} (\vec{K}_1 s_1, \vec{K}_2 s_2) = \delta_{s_1, s_1} \delta_{s_2, s_2} H^{(d)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2} (\vec{K}_1, \vec{K}_2) \quad (A23a)$$

$$H^{(x)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_1, \vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2, s_2} (\vec{K}_1 s_1, \vec{K}_2 s_2) = \delta_{s_1, s_1} \delta_{s_2, s_2} H^{(x)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2} (\vec{K}_1, \vec{K}_2) . \quad (A23b)$$

and

$$H^{(d)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2} (\vec{K}_1, \vec{K}_2) = \frac{1}{S^2} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_1 d\vec{r}_2 U (\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) \times \exp \left[ -i\vec{K}_1 \cdot M \frac{\vec{r}_1 \vec{r}_1}{M} + i\vec{K}_2 \cdot M \frac{\vec{r}_2 \vec{r}_2}{M} \right] \phi(|\vec{r}_1 - \vec{r}_1|) \phi(|\vec{r}_2 - \vec{r}_2|)$$

$$\quad \times \exp \left[ -i\vec{q}_1 \cdot M \frac{\vec{r}_1 \vec{r}_1}{M} + i\vec{q}_2 \cdot M \frac{\vec{r}_2 \vec{r}_2}{M} \right] \phi_{\alpha_1} (\vec{r}_1 - \vec{r}_1) \phi_{\alpha_2} (\vec{r}_2 - \vec{r}_2) , \quad (A24a)$$

$$H^{(x)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2} (\vec{K}_1, \vec{K}_2) = \frac{1}{S^2} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_1 d\vec{r}_2 U (\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) \times \exp \left[ -i\vec{K}_1 \cdot M \frac{\vec{r}_1 \vec{r}_1}{M} + i\vec{K}_2 \cdot M \frac{\vec{r}_2 \vec{r}_2}{M} \right] \phi(|\vec{r}_1 - \vec{r}_1|) \phi(|\vec{r}_2 - \vec{r}_2|)$$

$$\quad \times \exp \left[ -i\vec{q}_1 \cdot M \frac{\vec{r}_1 \vec{r}_1}{M} + i\vec{q}_2 \cdot M \frac{\vec{r}_2 \vec{r}_2}{M} \right] \phi_{\alpha_1} (\vec{r}_1 - \vec{r}_1) \phi_{\alpha_2} (\vec{r}_2 - \vec{r}_2) . \quad (A24b)$$
The integrals are simplified with the help of new integration variables. For the direct part
they are given by Eq. (A7) and for the exchange part they are the two-exciton center of
mass, \( \vec{R}_c \), Eq. (A7a), and the relative coordinates, Eq. (A3). After the integration with
respect to \( \vec{R}_c \)

\[
H^{(d)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2} (\vec{K}_1, \vec{K}_2) = \frac{1}{S} \delta_{\vec{K}_1 + \vec{K}_2, \vec{q}_1 + \vec{q}_2} D^{(d)}_{\alpha_1 \alpha_2} (\vec{K}_1, \vec{K}_2, \vec{q}_1, \vec{q}_2), \quad (A25a)
\]

\[
H^{(x)}_{\vec{q}_1 \alpha_1, \vec{q}_2 \alpha_2} (\vec{K}_1, \vec{K}_2) = \frac{1}{S} \delta_{\vec{K}_1 + \vec{K}_2, \vec{q}_1 + \vec{q}_2} D^{(x)}_{\alpha_1 \alpha_2} (\vec{K}_1, \vec{K}_2, \vec{q}_1, \vec{q}_2). \quad (A25b)
\]

In the remaining integrals, \( D^{(d)}_{\alpha_1 \alpha_2} \) and \( D^{(x)}_{\alpha_1 \alpha_2} \), it is possible to neglect \( K_1 \) and \( K_2 \) which
due to \( \delta \)-symbols in Eq. (A23) means also that \( \vec{q}_2 = -\vec{q}_1 \). This allows us to simplify the
notations, \( D^{(d)}_{\alpha_1 \alpha_2} (\vec{K}_1, \vec{K}_2, \vec{q}_1, \vec{q}_2) \equiv D^{(d)}_{\alpha_1 \alpha_2} (q_1) \), \( D^{(x)}_{\alpha_1 \alpha_2} (\vec{K}_1, \vec{K}_2, \vec{q}_1, \vec{q}_2) \equiv D^{(x)}_{\alpha_1 \alpha_2} (q_1) \). For further
simplification it is convenient to substitute the Fourier transform of the exciton functions,

\[
\phi_{\alpha, \vec{q}} = \int e^{-i\vec{q} \cdot \vec{r}} \phi_\alpha (\vec{r}) d\vec{r}.
\] (A26)

The calculations are a bit cumbersome but straightforward and they lead to Eqs. (3.40) -
(3.42).

**APPENDIX B: SPIN SUMS IN THE EXCHANGE TERM**

In this appendix we reduce the spin sum in the exchange term of the many exciton
Hamiltonian, Eq. (3.52), to a simpler form. According to the definition, \( s_j = s_{ej} + s_{hj} \), and
there is one to one correspondence between the electron and hole spins on one side and the
exciton spin on the other. Therefore

\[
\sum_{s_1, s_2, s_3, s_4} (\delta_{s_{e1}, s_{e4}} \delta_{s_{e2}, s_{e3}} \delta_{s_{h1}, s_{h3}} \delta_{s_{h2}, s_{h4}} + \delta_{s_{e1}, s_{e3}} \delta_{s_{e2}, s_{e4}} \delta_{s_{h1}, s_{h4}} \delta_{s_{h2}, s_{h3}}) \times C_{K_2, s_2}^{\dagger} C_{K_1, s_1}^{\dagger} C_{K_1, -\vec{q}, s_3} C_{K_2 + \vec{q}, s_4}.
\]

\[
= \sum_{s_1, s_2, s_3, s_4} (\delta_{s_{e1}, s_{e4}} \delta_{s_{e2}, s_{e3}} \delta_{s_{h1}, s_{h3}} \delta_{s_{h2}, s_{h4}} + \delta_{s_{e1}, s_{e3}} \delta_{s_{e2}, s_{e4}} \delta_{s_{h1}, s_{h4}} \delta_{s_{h2}, s_{h3}}) \times C_{K_2, s_2}^{\dagger} C_{K_1, s_1 + s_{h1}}^{\dagger} C_{K_1, -\vec{q}, s_3} C_{K_2 + \vec{q}, s_4 + s_{h4}} =
\] (B1)
\[ \Sigma_1 = 2 \sum_{s_e, s_h} c_{K_2, s_e + s_h}^\dagger c_{K_1, s_e + s_h}^\dagger c_{K_1 - \vec{q}, s_e + s_h} c_{K_2 + \vec{q}, s_e + s_h}, \]  
\[ \Sigma_2 = \sum_{s_e, s_h} c_{K_2, s_e + s_h}^\dagger c_{K_1, s_e + s_h}^\dagger \left( c_{K_1 - \vec{q}, s_e + s_h} c_{K_2 + \vec{q}, s_e + s_h} + c_{K_1 - \vec{q}, s_e + s_h} c_{K_2 + \vec{q}, s_e + s_h} \right), \]  
\[ \Sigma_3 = \sum_{s_e, s_h} c_{K_2, s_e + s_h}^\dagger c_{K_1, s_e + s_h}^\dagger \left( c_{K_1 - \vec{q}, s_e + s_h} c_{K_2 + \vec{q}, s_e - s_h} + c_{K_1 - \vec{q}, s_e - s_h} c_{K_2 + \vec{q}, s_e + s_h} \right), \]  
\[ \Sigma_4 = \sum_{s_e, s_h} c_{K_2, s_e + s_h}^\dagger c_{K_1, s_e + s_h}^\dagger \left( c_{K_1 - \vec{q}, s_e + s_h} c_{K_2 + \vec{q}, s_e - s_h} + c_{K_1 - \vec{q}, s_e - s_h} c_{K_2 + \vec{q}, s_e + s_h} \right). \]  

The exchange term in the many exciton Hamiltonian, Eq. (B3a), has now the following form

\[ H^{(x)} = \frac{V_x}{4S} \sum_{\vec{K}_1, \vec{K}_2, \vec{q}} (\Sigma_1 + \Sigma_2 + \Sigma_3 + \Sigma_4), \]

Now we replace the summation over \( \vec{q} \) with the summation over \( Q = \vec{K}_1 - \vec{K}_2 - \vec{q} \) in the second term in both parentheses in \( \Sigma_2 + \Sigma_3 \) and see that it becomes equivalent to the
first term in the same parentheses. The same can be done with the two terms inside the parentheses in $\Sigma_4$. So the exchange term is

$$H^{(x)} = \frac{V_x}{4S} \sum_{K_1, K_2, q'} \left[ 2 \sum_{s_1, s_2} c_{K_2, s_2}^\dagger c_{K_1, s_1}^\dagger c_{K_1 - \vec{q}, s_1} c_{K_2 + \vec{q}, s_2} 
- 4 \sum_{s} c_{K_2, -s}^\dagger c_{K_1, s} c_{K_2 + \vec{q}, -s} + \sum_{s_1, s_2} c_{K_2, -s_1}^\dagger c_{K_1, s_1}^\dagger c_{K_1 - \vec{q}, s_2} c_{K_2 + \vec{q}, -s_2} \right].$$

(B5)

**APPENDIX C: FOURIER COMPONENTS OF THE INTERACTION POTENTIAL AND THE WAVE FUNCTION IN QUANTUM WELLS**

In this appendix we present some formulae necessary for the calculation of Hamiltonian matrix elements.

The expressions for $u_{ij}(r)$ that are obtained with the help of Eqs. (2.6) and (4.5) are quite complicated. But their Fourier components have a relatively simple form,

$$u_{eh}(q) = \frac{2\pi e^2}{\kappa} \frac{(8\pi)^2}{L_e L_h} \sinh \left( \frac{q L_e}{2} \right) \sinh \left( \frac{q L_h}{2} \right) e^{-q(w + L_e/2 + L_h/2)}, \quad (C1a)$$

$$u_{hh}(q) = \frac{2\pi e^2}{\kappa} \frac{q L_h}{L_h^2} \left[ \frac{2}{4\pi^2 + q^2 L_h^2} - \frac{32\pi^4(1 - \exp(-q L_h))}{q^2 L_h^2(4\pi^2 + q^2 L_h^2)^2} \right], \quad (C1b)$$

$$u_{ee}(q) = \frac{2\pi e^2}{\kappa} \frac{q L_e}{L_e^2} \left[ \frac{2}{4\pi^2 + q^2 L_e^2} - \frac{32\pi^4(1 - \exp(-q L_e))}{q^2 L_e^2(4\pi^2 + q^2 L_e^2)^2} \right]. \quad (C1c)$$

Each of these functions is singular at $q = 0$. But the direct interaction potential which contains the sum of them is finite,

$$U^{(d)}(0) = \frac{2\pi e^2}{\kappa} \left[ 2w + \left( \frac{2}{3} + \frac{5}{4\pi^2} \right)(L_e + L_h) \right]. \quad (C2)$$

This expression leads to Eq. (4.7).

The Fourier transform of single-exciton wave function, (4.8), necessary for the calculation of $U^{(d)}(q)$ and $V_x$, is

$$\phi_q = \sqrt{\frac{2\pi}{b(b + r_0)}} e^{r_0/2b} \frac{1}{2b} \left( \frac{1}{4b^2} + q^2 \right)^{-3/2} \left( 1 + r_0 \sqrt{\frac{1}{4b^2} + q^2} \right) \exp \left[ -r_0 \sqrt{\frac{1}{4b^2} + q^2} \right]. \quad (C3)$$
REFERENCES

[1] N. Peyghambarian, H. M. Gibs, J. L. Jewell, A. Antonetti, A. Migus, D. Hulin and A. Mysyrowics, Phys. Rev. Lett. 53, 2433 (1984).

[2] D. Hulin, A. Mysyrowics, A. Antonetti, A. Migus, W. T. Mazzeilink, H. Morkoc, H. M. Gibs and N. Peyghambarian. Phys. Rev. B 33, 4389 (1986).

[3] B. Dareys, X. Marie, T. Amand, J. Barrau, Y. Shekun, I. Razdobreed, and R. Planel, Superlatt. Microstr. 13, 353 (1993).

[4] T. Amand, X. Marie, B. Baylac, B. Dareys, J. Barrau, M. Brousseau, R. Planel, and D. J. Dunstan, Phys. Lett. A 193, 105 (1994).

[5] L. V. Butov, A. A. Shashkin, V. T. Dolgopolov, K. L. Campman adn A. C. Gossard, Phy. Rev. B 60, 8753 (1999).

[6] V. Negoita, D. W. Snoke and K. Eberl, Phys. Rev. B 61, 2779 (2000).

[7] S. Schmitt-Rink, D. S. Chemla and D. A. B. Miller, Phys. Rev. B 32, 6601 (1985).

[8] J. Fernández-Rossier, C. Tejedor, L. Muñoz and L. Viña, Phys. Rev. B 54, 11582 (1996).

[9] C. Ciuti, V. Savona, C. Piermarocchi, A. Quattropani and R. Schwendimann, Phys. Rev. B 58, 7926 (1998).

[10] T. C. Damen, Luis Viña, J. E. Cunningham, Jagdeep Shah and L. J. Sham, Phys. Rev. Lett. 67, 3432 (1991).

[11] L. Viña, L. Muñoz, E. Pérez, J. Fernández-Rossier, C. Tejedor and K. Ploog, Phys. Rev. B 54, 8317 (1996); L. Muñoz, E. Pérez, L. Viña, J. Fernández-Rossier, C. Tejedor and K. Ploog, Solid State Electron. 40, 755 (1996).

[12] P. Le. Jeune, X. Marie, T. Amand, F. Romstad, F. Perez, J. Barrau, and M. Brousseau, Phys. Rev. B 58, 4853 (1998).
[13] L. Viña, J. Phys. Condens. Matter, **11**, 5929 (1999).

[14] G. Aichmayr, M. Jetter, L. Viña, J. Dickerson, F. Camino and E. E. Mendez, Phys. Rev. Lett. **83**, 2433 (1999).

[15] A. Vinattieri, J. Shah, T. C. Damen, D. S. Kim, L. N. Pfeiffer, M. Z. Maialle and L. J. Sham, Phys. Rev. B **50**, 10868 (1994).

[16] B. Baylac, T. Amand, M. Brousseau, X. Marie, B. Dareys, G. Bacquet, J. Barrau, and R. Planel, Semicond. Sci. Tech. **10**, 295 (1995).

[17] T. Amand, D. Robart, X. Marie, M. Brousseau, P. Le Jeune and J. Barrau, Phys. Rev. B **55**, 9880 (1997).

[18] H. Wang, J. Shah, T. C. Damen and L. N. Pfeiffer Phys. Rev. Lett. **74**, 3065 (1995).

[19] E. Hanamura, J. Phys. Soc. Japan, **29**, 50 (1970); *ibid.* **37**, 1545 (1974); M.I. Sheboul and W. Ekardt, phys.stat.sol. (b) **73**, 165 (1976); E. Hanamura and H. Haug, Physics Reports, C **33**, 209 (1979).

[20] T. Usui, Progr. Theor. Phys. **23**, 787 (1957).

[21] H. Haug and S. Schmitt-Rink, Prog. Quant. Electr. **9**, 3 (1984).

[22] H. Stolz, R. Zimmermann, and G. Röpke, Phys. Stat. Sol. (b) **105**, 585 (1981).

[23] S. de-Leon and B. Laikhtman, Phys. Rev. B **61**, 2874 (2000).

[24] G.L. Bir and G.E. Pikus in *Symmetry and Strain-Induced Effects in Semiconductors* §26, (Wiley, New-York, 1974).

[25] M. Z. Maialle, E. A. de Andrada e Silva and L. J. Sham, Phys. Rev. B **47**, 15776 (1993).

[26] E. Blackwood, M. Snelling, M. J. Herley, R. T. Andrews and C. T. B. Foxon, Phys. Rev. B **50**, 14246 (1994).

[27] S. Glasberg, H. Shtrikman, I. Bar-Joseph, and P. C. Klipstein, Phys. Rev. B **60**, 16295
[28] I. L. Aleiner, E. L. Ivchenko, Pis’ma Zh. Eksp. Teor. Fiz. 55, 662 (1992) [JETP Letters 55, 692 (1992)]; E. L. Ivchenko, A. Yu. Kaminski, I. L. Aleiner, Zh. Eksp. Teor. Fiz. 104, 3401 (1993) [JETP 77, 609 (1993)].

[29] H. Haug, Z. Physik B 24, 351 (1976).

[30] B. Zimmermann, Phys. Stat. Sol. b 76, 191 (1976).

[31] P. Nozières and C. Comte, J. Phys. (Paris) 43, 1083 (1982).

[32] L. D. Landau and E. M. Lifshits, Quantum Mechanics: Nonrelativistic Theory, (Pergamon Press, Oxford, New York 1991).

[33] J. Fernández-Rossier and C. Tejedor, Phys. Rev. Lett. 78, 4809 (1997).

[34] D. Yoshioka and A. H. MacDonald, J. Phys. Soc. Jpn. 59, 4211 (1990).

[35] X. Zhu, P. B. Littlewood, M. S. Hybersten, and T. M. Rice, Phys. Rev. Lett. 74, 1633 (1995).

[36] M. Schick, Phys. Rev. A3, 1067 (1971).

[37] I. R. Lapidus, Am. J. Phys. 50, 64 (1982).

[38] V. N. Popov, Functional Integrals in Quantum Field Theory and Statistical Physics (D. Reidel Publishing Company, Dordrecht 1983).

[39] M. Z. Maialle and E. A. DE Andrada E Silva, Phys. Stat. Sol. (a) 178, 447 (2000).

[40] V. Negoita, D. W. Snoke and K. Eberl, Solid State Commun. 113, 437 (2000); D. W. Snoke, V. Negoita and K. Eberl, J. Lumin. 87-89, 157 (2000).

[41] Q. X. Zhao, B. Monemar, P. O. Holtz, M. Willander, B. O. Finland and K. Johannessen, Phys. Rev. B 50, 4476 (1994).
[42] K. Oettinger, Al. L. Efros, B. K. Meyer, C. Woelk and H. Brugger, Phys. Rev. B 52, 5531 (1995).

[43] T. Takagahara, Phys. Rev B 31, 6552 (1985); J. Luminesc. 44, 347 (1989).
FIGURES

FIG. 1. The dependence of the exchange coefficient, $V_x = U^{(x)} - 2|\epsilon_b|A$, on the separation between the wells, $d = w + L$. The continuous line is for fixed barrier width, $w = 42 \text{ Å}$, and changing wells width. The dashed line is for fixed wells widths, $L = 70 \text{ Å}$, and changing the barrier width.

FIG. 2. The dependence of the exchange coefficient, $V_x$, on the separation between the wells, $d = w + L$, where $w = 10 \text{ Å}$ and $L$ is changing. $V_x$ becomes positive for a small enough separation between the wells.

FIG. 3. The dependence of the coefficient, $V_b$, on the separation between the wells, $d = w + L$. The continuous line is for fixed barrier width, $w = 42 \text{ Å}$, and changing wells width. The dashed line is for fixed wells widths, $L = 70 \text{ Å}$, and changing the barrier width.

FIG. 4. The dependence of the energy splitting parameter, $V_{es}$, on the separation between the wells, $d = w + L$, where $L = 70 \text{ Å}$ and $w$ is changing.
Separation between the wells centers, $d = L + w$ [Å]
Fig. 2
Separation between the wells centers, $d = L + w$ [Å]

Fig. 3
Fig. 4

Separation between the wells centers, $d=L+w$ [Å]

$V_{es}$ [mev cm$^2$]

$L=70$ Å