First principles approach to binding energies of excitons, trions and biexcitons in quantum wells

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We present first-principle path integral Monte-Carlo (PIMC) studies of strongly correlated electron-hole complexes such as excitons, trions (charged excitons) and biexcitons in $Al_xGa_{1-x}As$ quantum-well structures. The correlation and binding energies are calculated as function of quantum well width L, for $10\text{Å} \leq \text{L} \leq 250\text{Å}$ and compared with available experimental [1] and theoretical [2, 3, 4] data. As in the experiments, we observe a maximum of the binding energies in GaAs/AlGaAs quantum well samples around $L = 40\text{Å}$ the physical reason of which is the non-monotonic dependence of the electron (hole) confinement on the well width. The developed method is a powerful tool for further systematic investigation of the influence of temperature and many-body effects on bound states in heterostructures (e.g. depedence on finite exciton, biexciton densities) and disorder (e.g. well-width fluctuations).

1 Introduction. With recent developments in semiconductor technology quasi one-dimensional and thin-layer structures have attracted much attention. These systems show nontrivial Coulomb correlation effects leading to interesting optical and transport characteristics which are not seen in bulk materials. For example, a strong increase of exciton binding energies has been found experimentally [1] at specific quantum well (QW) widths. Also, crystallization of electrons in quantum dots with a finite number of particles has recently been predicted theoretically using PIMC simulations [5].

In this paper we investigate Coulomb correlations in electron-hole systems in QW's and clearly show that the observed effect of the increase of the binding energies in these systems is connected with changes in the effective in-plane interaction potential. We develop a novel first-principles approach based on PIMC simulations which does not involve expansions in terms of basis functions or any symmetry assumptions and is, thus, expected to allow for an efficient treatment of complex experimental systems in the future.

2 Quantum well model. We consider a single quantum well consisting of a thin semiconductor film of thickness L. In the effective-mass approximation the electron-hole Hamiltonian reads

$$H = \sum_{i=1}^{N_e,N_h} \left[-\frac{\hbar^2}{2m_i}\nabla^2 + V_{e\,(h)}(z_i) \right] + \sum_{i<j} \frac{e_i\, e_j}{\epsilon |\mathbf{r_i} - \mathbf{r_j}|}, \tag{1}$$

where m_i and e_i are masses and charges of particles, and we take dielectric constants ϵ of the well and barrier materials to be the same. The confinement potential for electrons in the conduction band, V_e, and holes in the valence band, V_h, is modeled as a square well of finite width L and depth ΔV, where for a

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$GaAs/Al_xGa_{1-x}As$ QW, we use: $\Delta V_e = 0.57 \times (1.155x + 0.37x^2)\ eV$ and $\Delta V_h = 0.43 \times (1.155x + 0.37x^2)\ eV$. In the numerical simulations below we use an Al concentration of $x = 0.3$ as well as $\epsilon = 12.58$, $m_e = 0.067\, m_0$, $m_h = 0.34\, m_0$ (m_0 is the free electron mass), and the spatial and energy scales are given by $a_B = \hbar^2\epsilon/m_e\, e^2 = 99.7$ Å and $Ry^* = e^2/(2\epsilon\, a_B) = 5.79\ meV$. Further, to simplify our Monte Carlo simulations we use an *adiabatic approximation* and neglect the influence of in-plane electron-hole correlations on their motion in the z-direction perpendicular to the QW plane. This assumption appears to be valid due to strong quantization in square wells of widths $L \le a_B$ where $\Delta E^z_{e\,(h)} \gg E_c, E_b^X, E_b^{XX}, \ldots$, with $\Delta E^z_{e\,(h)}$ denoting the level spacing in the QW and $E_c, E_b^X, E_b^{XX}, \ldots$ being the correlation and binding energy of exciton, biexciton, respectively.

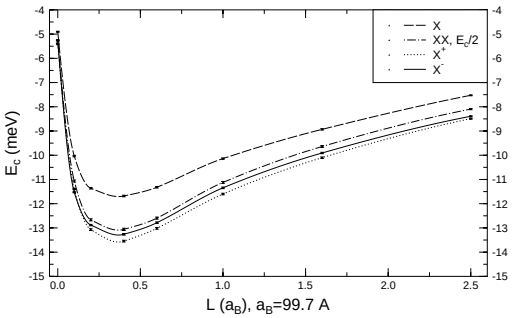

Fig. 1 Correlation energy of excitons (X), positive (X^+) and negative (X^-) trions and biexcitons (XX) vs. QW width L.

In the adiabatic approximation, the full N-particle density matrix (DM) factorizes

$$\rho(\mathbf{R}^{xyz}, \beta) = \rho(Z_e, \beta)\, \rho(Z_h, \beta)\, \rho(\mathbf{R}^{xy}, \beta), \tag{2}$$

where $\mathbf{R}^{xyz}$ ($\mathbf{R}^{xy}$) $= \{\mathbf{r}_{e\,1}, \mathbf{r}_{e\,2}, \ldots, \mathbf{r}_{e\,N_e};\ \mathbf{r}_{h\,1}, \mathbf{r}_{h\,2}, \ldots, \mathbf{r}_{h\,N_h}\}$ is a $3D$ ($2D$) vector of all particle coordinates, $Z_{e\,(h)}$ is the z coordinate of all electrons (holes), $\rho(Z_e, \beta)$ and $\rho(Z_h, \beta)$ are the DM's of free electrons and holes confined in the z direction by the square well and $\beta = 1/k_B T$. We underline that the DM $\rho(\mathbf{R}^{xy}, \beta)$ includes all in-plane electron-hole correlations and obeys the N-particle Bloch equation. Using (1) with (2) and averaging over Z, we obtain the two-dimensional Bloch equation which contains an effective 2D in-plane potential U_{eff}^{xy}

$$\frac{\partial}{\partial\beta}\, \rho(\mathbf{R}^{xy}, \beta) = \left(- \sum_{i=1}^{N_e, N_h} \frac{\hbar^2}{2m_i} \nabla^2_{xy} + U^{xy}_{\text{eff}} \right)\, \rho(\mathbf{R}^{xy}, \beta), \tag{3}$$

$$U^{xy}_{\text{eff}} = \int dZ_e\, dZ_h\, \sum_{i<j} \frac{e_i\, e_j}{\epsilon |\mathbf{r}_i - \mathbf{r}_j|}\, \rho(Z_e, \beta)\, \rho(Z_h, \beta) \left[\int dZ_e\, dZ_h\, \rho(Z_e, \beta)\, \rho(Z_h, \beta) \right]^{-1}. \tag{4}$$

3 Simulation idea. We numerically solve the Bloch equation (3) using the path integral representation of the DM in terms of M factors, each taken at an M times higher temperature,

$$\rho(\mathbf{R}, \mathbf{R}; \beta) = \int d\mathbf{R}_1 \ldots \int d\mathbf{R}_{M-1} \sum_P \frac{(-1)^{\delta P}}{N!} \langle \mathbf{R} | e^{-\tau \hat{H}} | \mathbf{R}_1 \rangle \times \cdots \times \langle \mathbf{R}_{M-1} | e^{-\tau \hat{H}} | \hat{P}\mathbf{R} \rangle, \tag{5}$$

where $\tau \equiv 1/(M k_B T)$, $\hat{P}$ is the N-particle exchange operator and $\rho(\mathbf{R}, \mathbf{R}'; \tau) = \langle \mathbf{R} | e^{-\tau \hat{H}} | \mathbf{R}' \rangle$ is the coordinate representation of the N-particle DM at the new inverse temperature τ.

To find the N-particle high-temperature DM we use its pair approximation which turns out to be valid for $\tau \le 1/(3\, Ha^*)$ (where the effective Hartree energy $Ha^* = 2\, Ry^*$),

$$\rho(\mathbf{R}, \mathbf{R}'; \tau) \approx \prod_i^N \rho^{[1]}(\mathbf{r}_i, \mathbf{r}'_i; \tau) \times \prod_{j<k} \frac{\rho^{[2]}(\mathbf{r}_j, \mathbf{r}_k, \mathbf{r}'_j, \mathbf{r}'_k; \tau)}{\rho^{[1]}(\mathbf{r}_i, \mathbf{r}'_i; \tau)\ \rho^{[1]}(\mathbf{r}_k, \mathbf{r}'_k; \tau)} + O(\rho^{[3]}), \tag{6}$$

where i, j are particle indices and $\rho^{[1]}$ ($\rho^{[2]}$) is the one(two)-particle density matrix. In the next step we obtain the DM $\rho^{[2]}$ from a direct solution of the two-particle Bloch equation, substitute it into Eq. (6) and perform a numerical integration in Eq. (5) with the use of Monte Carlo algorithms.

4 Correlation and binding energies in quantum wells. In this section we investigate the influence of the finite QW width L on bound states of the electron-hole system in a single layer. We study the correlation (E_c) and binding (E_b) energies of excitons $E_b(X)$, positive and negative trions ($E_b(X^{\pm})$) and biexcitons $E_b(XX)$ which are defined by $E_b(X) = E_e + E_h - E(X)$; $E_b(X^{\pm}) = E(X) + E_{h(e)} - E(X^{\pm})$ and $E_b(XX) = 2E(X) - E(XX)$, where the total energy of N_e electrons and N_h holes is defined as $E(N_e, N_h) = N_e E_e + N_h E_h + E_c(N_e, N_h)$, and $E_{e\,(h)}$ is the energy of a single free electron (hole).

The dependence of the correlation energy on the QW width L is shown in Fig. 1. This dependence is non-monotonic and has two important limits. First, for $L \gg a_B$, the QW confinement has practically no influence on the e-h bound states, and we simply recover the correlation energies and binding energies (see below) of the $3D$ system. In the opposite limit of a very narrow QW, $L \to 0$, the electron and hole wave functions extend significantly into the barrier material (see upper figures in Fig. 3). This case again results in a practically pure $3D$ solution for the e-h pair. Here the important note is that in a very narrow QW ($L \ll a_B$) approximation (2) cannot be applied. In QW's of finite height there is always a possibility for at least one bound state to exist, however, this bound state may be very close to the continuum. Even at zero temperature the e-h interaction can excite states of the continuum, and electrons with holes cannot be considered further to be at the center of the QW in the z-direction. For this reason, at $L = 0$, we performed a full $3D$ calculation. From Fig. 1 one can see that the influence of the confinement on the bound states becomes important for QW widths $L \leq a_B$, and at $L \approx 0.4\ a_B$ the correlation energies reach a minimum, in very good agreement with the results of Ref. [3]. Next, in Fig. 2 (a), (b) we show results for the exciton (X) and biexciton (XX) binding energies. These results demonstrate that our model and the accuracy of the PIMC simulations are sufficient to ensure quantitative agreement with available experimental data [1]. For a quasi-2D $Al_xGa_{1-x}As$ sample with $L \approx 0.4\ a_B$, we found that the biexction binding energy (2.8 meV) is about *four* times larger than in the same bulk material.

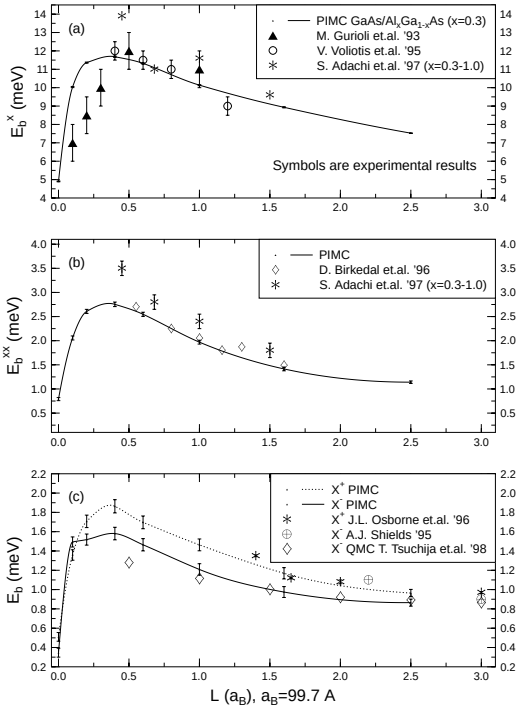

Fig. 2 PIMC results for binding energies $E_b(X)$ (a), $E_b(XX)$ (b), and $E_b(X^{\pm})$ (c) vs. QW width L together with experimental data [1] and simulations of [2].

In Fig. 2 (c) we report data for the L-dependence of the binding energies of negative and positive trions (solid and dashed lines respectively). Interestingly, the $E_B(X^+)$ is about 20% larger than $E_B(X^-)$. This can be explained by the fact that in the X^+ state we have two holes which are about *five* times heavier than the electron, and so the contribuion of zero point fluctuations of all three particles, which always act to destroy bound states, are smaller than in the case of X^-. In Fig. 2 (c) our PIMC results are compared with the variational Monte Carlo calculations of Ref. [2] (shown by diamonds) and experimental data from Ref. [1]. The results for the binding energies show that this quantity reaches a maximum around $L \approx 0.4\ a_B$. To explain this interesting feature of a strong increase of e-h correlations at $L = 40$ Å observed in all figures, let us return to the Bloch equation (3). The only quantity that may have the L-dependence is the effective potential $U_{\rm eff}^{xy}$. The L-dependence of this potential comes from the integration,

Eq. (4), over free electron and hole density matrices corresponding to solutions in the square well potential of varying width L.

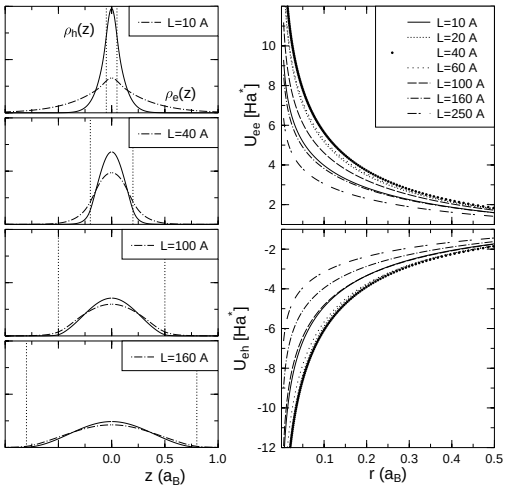

Fig. 3 *Left*: electron $\rho_e(z)$ and hole $\rho_h(z)$ density matrix in the QW (dotted lines indicate QW walls). *Right*: L-dependence of effective electron-electron (ee) and electron-hole (eh) potentials, Eq. (4).

In Fig. 3, we present the electron and hole density matrices in the square well confinement, the QW width is varied in the range $10\ \text{Å} \leq \text{L} \leq 160\ \text{Å}$. The left figures confirm that, due to the lighter mass, the electron is more delocalized than the hole and, at $L \leq 20\text{Å}$, most of the electron density matrix resides in the barrier material. (In cases where the dielectric constants of the well and barrier material are strongly different, this would have to be taken into account giving a significant effect in narrow QW's. In $GaAs/AlGaAs$ structures with close values of ϵ this effect is not so important.) As L approaches $a_B = 99.7$ Å the finite depth of the square well has practically no influence on the solutions, and the density matrix for both particles vanishes at the QW edges. The effective in-plane potential U_{eff}^{xy} is shown in the right set of figures. Obviously, it depends in a non-monotonic way on L reaching a maximum (absolute) value at $L = 40$ Å. It is this increase at intermediate L causing a growth of interparticle correlations and thus is the main reason for the increase of the binding energies at intermediate QW widths as observed experimentally and found in our simulations, cf. Fig. 2.

5 Conclusion. Using a path integral Monte Carlo approach, we have calculated the correlation and binding energies of excitons, trions and biexcitons in $GaAs/AlGaAs$ quantum wells of different widths which agree well with experimental results. Our method is based on first principles and does not invoke eigenfunction expansions and is not limit to certain symmetries. Thus it also yields the temperature dependence of the binding energies and all pair distribution functions [6]. The only assumption – the adiabatic approximation (2) – appears to be justified for the present application but it can be easily dropped. Thus, the extension of our method to more realistic situations, including disorder, well-width fluctuations etc. is straigtforward.

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