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Excitons in II-VI Quantum Wells

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Abstract

We present a systematic theoretical study of exciton binding energy in II-VI wide gap quantum wells based in ZnSe. We examine three different cases: first, systems with marginal valence band potential such as ZnSe/(Zn,Cd)Se/ZnSe where confinement of holes is almost negligible. Second, systems with marginal potential at the conduction band such as ZnS/(Zn(S,Se)/ZnS, in which the electrons are nearly free. Third, systems where ZnSe is the well material and barriers are semimagnetic semiconductors like (Zn,Mn)Se/ZnSe/(Zn,Mn)Se with vanishing valence band offset. The binding-energy features for all three cases are discussed. Special attention is paid to quantum wells with semimagnetic barriers in presence of external magnetic field, in which the transition from quantum well type I to type II has been detected. Our results are in good agreement with recent experimental reports.

Keywords: Quantm wells, Binding energy, Excitons, II-VI Semimagnetic Semiconductors

Introduction

In recent years II-VI quantum well systems based on wide gap semiconductors have been heavily studied because of their extensive application in blue light emitters [1].From the fundamental point of view the problem of the long range interaction between charged particles constitutes one of the most important aspects in solid state physics. Since the works of Frenkel and Peierls [2], who introduced the notion of free exciton to define the first excited state of an ideal crystal, such elementary excitation has been studied and its theory has been developed on the basis of approximations similar to those applied in the description of electrons in the band formalism.

Excitons play a much more prominent role in quantum wells than in bulk semiconductors, with respect to optical properties. An intense research effort is currently been devoted to clarify the optical properties of wide-gap II-VI semiconductor heterostructures. Blue-green laser based on ZnSe have been recently examined and found strong non-linear excitonic properties. However, a preliminary thorough understanding of the linear excitonic properties together with the evaluation of several important band parameters as fraction of the band gap difference, which appears in the valence or in the conduction band and effective masses. Band offsets in particular play a central role in determining electron and hole confinements energies and therefore strongly influence the excitonic optical properties. Excitons in quantum wells with one marginal potential are interesting in order to find out the variation of binding energy as function of band-offsets. For common anion heterostructures are the holes much less confined than the electrons but for common cation heterostructures are the electrons the delocalized particles. In ZnSe/(Zn,Cd)Se/ZnSe a possible explanation of optical gain and laser emission is the exciton nature of the transitions [3]-[6]. Optical absorption coeffcient in ZnSe/ZnS superlattices shows clearly excitonic features, in this system with the hole strongly confined]7]-[9].

Semiconducting systems with controlled quantity of magnetic elements -as well impurities as components of alloys- have been intensively studied in bulk. Quantum wells constituted on these materials are more interesting than the non-magnetic ones, due to the additional control mechanism offered through the strong splitting of electronic energy states caused by magnetic ions. The observed effects have been explained by introducing influence of the system of Mn-ions on exciton or band electron states by means of exchange interaction.[9]-[15].

In this paper we show numerical results calculated using Green's function technique for binding energy in finite wells, properly taking into account the singularities of the Coulomb potential in the momentum space. We compare the numerical results of the exciton Green's function method with those using the variational method. We find that the variational method may give very accurate results for the binding energy of the lowest bound exciton in the quantum well if the chosen trial function is adequate. In case of marginal potential systems the calculation must contain at least two variational parameters. In many works are reported one variational parameter in the wave function and the other as the depth of the well, which leads to a controversy because the problem so solved although auto-consistent, is quantum mechanical each time a different one. We follow the variation of the exciton binding energy as function of the well-width and band-offset in all cases. In addition we perform a study of the behavior of semimagnetic quantum wells as function of magnetic field. We observe the transition from quantum well type I to type II as magnetic field increases. Our agreement with experiment is very satisfactory.

The present report is organized as follows: In sec. I we outline the method of calculation, then in sec.II we discuss the results for marginal valence band potential, while sec.III is dedicated to the systems with marginal conduction band potential. In sec. IV we study the semimagetic quantum wells case without and with external magnetic field. Finally in sec. V we present the conclusions.

1.Method

Up to now most of the theoretical calculations for exciton binding energy and the linear absorption coefficient are based on the variational method. Only the bound 1s exciton and the pure two dimensional Coulomb enhancement factor for the continuum states within the parabolic model are taken into account. Besides that the Coulomb potential is calculated only approximately. We present a method in which the Coulomb interaction is calculated in an exact way. An outline of the method is presented as follows, for detailed calculation see [16]

The approach we use is based on the a Green's function, which satisfies an inhomogeneous Coulomb wave function for an electron-hole pair with the dipole moment as the source term. The equation is similar to the exciton wave equation and contains terms such as the single particle electron and hole hamiltonians with the Coulomb interaction.

With this method we calculate the Coulomb matrix elements

$$<nm|\ V(k-k')|\ n'm'>$$

in an exact way.

The calculation itself proceeds as following:

1) obtention of eigenvalues and eigenfunctions for a finite quantum well as function of the well width and the depth of the well.

2) Set up the matrix in k space, A_{ij}, which is a matrix j x j, being j the number of different in-plane k values, which are parabolic at k=0 for no interaction in the well case. The greater the number of k values the more continuos curve $E(k_X,k_Y)$ is obtained. We take only the ground state value n=1

3) By diagonalizing the matrix A, we get its eigenvalues and eigenfunctions.

4) Calculation of the susceptibilily as function of the light frequency. Here we sum over all components of the eigenvectors for each eigenvalue and then we applied:

$$\varepsilon_0 \chi(\omega) =$$

$$2/V \Sigma_X [\ |\ \Sigma_{nmk} \phi^X_{nm}(k) \mu^*_{nm}(k)\ |^2 / (E_X - h\omega - i\Gamma)]$$

5) We sum over all eigenvalues for each frequency.

6) To solve the exciton Green's function satisfying

$$[E_{nm}(k) - W]\ G_{nm}(k,W) - \Sigma_{n'm'k'} <nm|\ V(k-k')|\ n'm'>$$
$$G_{n'm'}(k',W) = \mu_{nm}(k)$$

the singularity of the Coulomb potential must be taken into account properly. Here we assume that the Green's function G depends on the magnitude of k only, since only the s states of the exciton wave functions contribute to the linear absorption. This equation can be written as

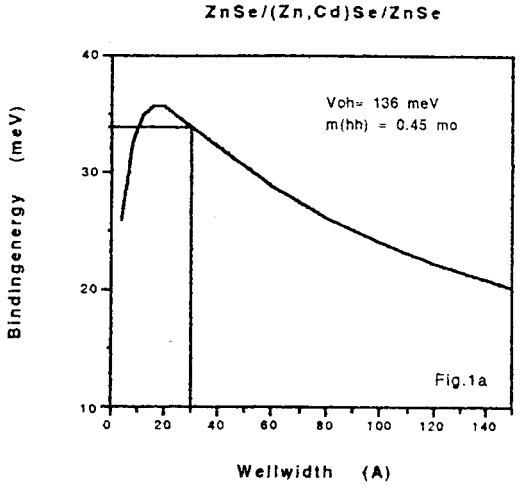
$$\Sigma_{n'm'j} (A_{i,j}^{nm,n'm'} - W \delta_{nn'}\delta_{mm'}\delta_{ij})\ G_{n'm'}(j) = \mu_{nm}(i)$$

and the imaginary part of dielectric function as

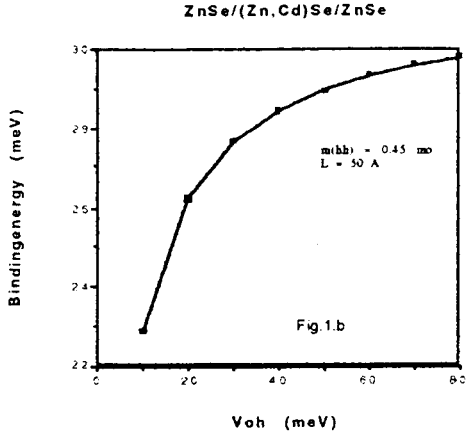
$$\varepsilon_2 = Im[2/V \Sigma_{nmk} \mu^*_{nm}(k)\ G_{nm}(k, h\omega + i\Gamma)].$$

II. Systems with marginal valence band potential

We start with the most interesting technologically wide-gap II-VI system: ZnSe/ZnCdSe/ZnSe. It has been demonstrated that the quasi-two-dimensional confinement of electron-hole pairs leads to enhancement of exciton oscillator strength and its binding energy, so that the latter exceeds the longitudinal optical (LO) phonon energy. Given the very large Froehlich interaction in this relatively ionic materials a good reference energy for the exciton binding energy is the LO-phonon one. The bulk exciton binding energy in ZnSe is 22 meV and its Bohr radius is 38 A. We obtain for a well of 20 A and 20% CdSe a binding energy of 34 meV. Because of the relatively delocalization of holes in these materials, specially for Cd-concentrations that do not exceed 20%, the valence band-offset is the most important parameter for a given well-width. Varying the band discontinuity value we find the eigen-energy of the hole in the well and then we calculated the exciton binding energy. In order to approach adequately this value we suppose first that as common anion system the valence band-offset should be zero. But due to strain at the interfaces energy-shift and splitting should be considered, which can be calculated based on the difference on lattice constants of both constituents. For the alloy in the well a = 6.1588 A and for the barriers a = 5.6680 A, and thus for thin wells we only take into account the diminishing of the lattice constant of the well material to fit the one of the barriers. It produces lifting of the degeneracy at Γ-point in heavy and light holes with a larger confinement for the heavy holes (73 meV). Therefore we perform a calculation varying the band-offset between 0 and 80 meV and find out that the binding energy saturates above this value. Cingolani [18] reports for a Cd-concentration range from 0.10 to 0.26 a variation in the binding energy from 30 to 38 meV in a 30 A well. Our calculation gives for the same system energies between 25 and 35 meV.



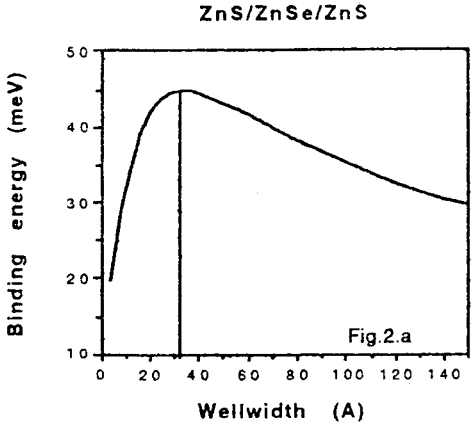
In Fig.1a we show the obtained dependence of exciton binding energy with well-width, which has its maximum at 20 A almost half the value of Bohr radius in bulk and the maximal binding energy reaches twice the value in bulk. For 30 A our predicted binding-energy is 34 meV with a fixed valence-band-offset of 73 meV. It fits very well the experimental reported data. If we calculate the binding-energy for a band-discontinuity of 76 meV we obtain a value slightly above 29 meV. We observe that the exciton strengths with confinement. However, for very shallow wells its binding energy turns to be again the bulk value due to hole delocalization. As the well becomes very thin the eigen-energy shifts to the continuum, which



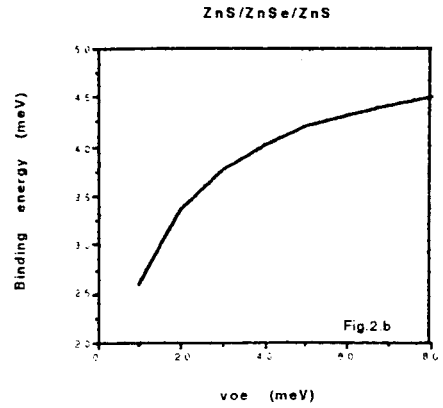
means the hole becomes free again. We also calculate the binding energy as function of valence band-offset in a relevant range (0-80 meV) as shown in Figure 1b, where we see that the bindng energy increases from cero to the saturation value of 30 meV, which corresponds to the binding energy for well-width of 50A as shown in Fig.1a.

III. Systems with marginal conduction band potential

On the other hand we study the case of almost free electron while the hole is strongly confined in the example ZnS/ZnSe/ZnS. From the work of Satoshi Hohnoki [19] we take some important parameters for ZnSe: ε = 8.1, the free exciton energy is 18 meV in bulk.



The conduction band-offset is less than 40meV and it is not very much affected by strain. The Luttinger parameters γ_1= 3.77, γ_2= 1.24, γ_3= 1.67 para ZnSe and γ_1= 2.54, γ_2= 2.75, γ_3= 1.09 para ZnS and effective conduction masses of $0.17m_0$ for ZnSe y $0.39m_0$ for ZnS. We use for the band-offset the one obtained in a previous work [20] in which the splittings due to strain are found.



By using our Green's function method we present in Fig.2a the variation of exciton binding energy as function of well-width and we find the same trend as in previous case of almost free holes, the maximum at 45 meV corresponds to a well of L = 30 A, which is exactly the Bohr radius, while the variational method predicts 49 meV for a 20A well. In addition we study also the dependence of exciton binding energy as function of conduction band-offset and we find that the binding energy saturates to the value 45 meV starting from band-discontinuities greater than 30 meV, but it decreases rapidly for shallow wells due to the vanishing electron localization. By using a variational method we obtain the maximum at L= 20A with an energy of 50 meV, which is the same reported value [21]

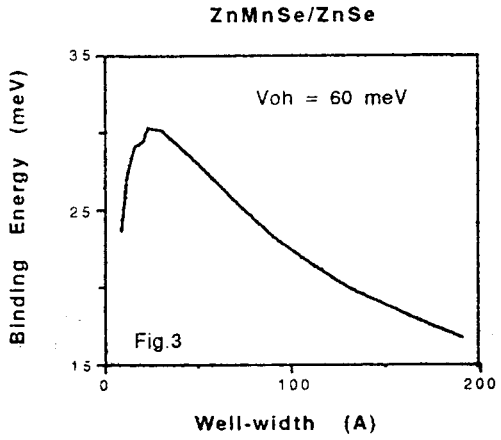
Also in this system, we observe that for very thin wells the binding energy turns to be the bulk value as expected from vanishing electron confinement in the well. The corresponding energy eigenvalue in the well is close to the continuum and the electron becomes delocalized.

However, we notice a binding energy, which is higher in this sytems as in ZnSe/ZnCdSe/ZnSe because electrons have very small effective mass are less localized than holes, and the Coulomb interaction is the main responsible force for the high binding energy. Therefore in wells of 5A (one atomic radius) the electron does not feel confinement but it remains bound to the hole forming a bulk exciton with 20 meV binding energy. For discontinuities larger than 30 meV, binding energy is twice the value in bulk and saturates at 45 meV.

For well-width is the exciton binding-energy higher in case of electron delocalization, it means marginal conduction potential, which can be explained through Coulomb interaction and hole localization. Due to lighter effective mass of the electron, hole localization is more important and we obtain for the heavy hole binding energy varying very little with confinement, because of its greater effective mass.

IV. Excitons in Semimagnetic Quantum Well Structures

Diluted magnetic semiconductors (DMS) or semimagnetic semiconductors are semiconducting alloys whose lattice is made up in part of subtitutional magnetic atoms. The band-gap of the alloy is greater than the band-gap of ZnSe, thus we study quantum wells in which the barriers are (DMS) and the well is no-magnetic: (Zn,Mn)S/eZnSe/(Zn,Mn)Se. Thus, we have now a new interaction of magnetic origin in the barriers, the exchange interaction between the carriers and the fixed magnetic ions.



The exciton binding energy is studied as function of well-width and we find the same behaviour as the observed in non-magnetic quantum wells. Only the binding energies are smaller [14]-[15]. The parameter we can vary very easily to control the binding energy is the valence band-offset. In this case the value of discontinuity depends also on the external magnetic field.

The energy split due to strain is such that the heavy hole is less confined than the light-hole, as can be seen in Fig.4, for the binding energy of heavy and light hole as function of well-width is shown. By applying a magnetic field one can control the barrier height.

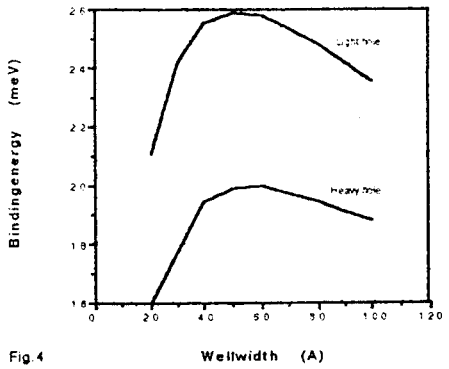
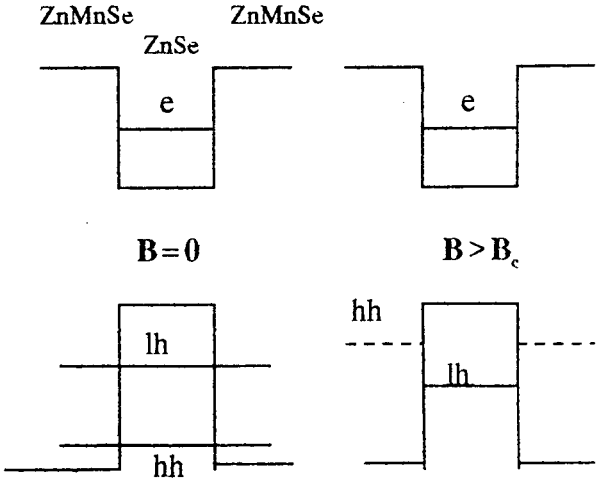
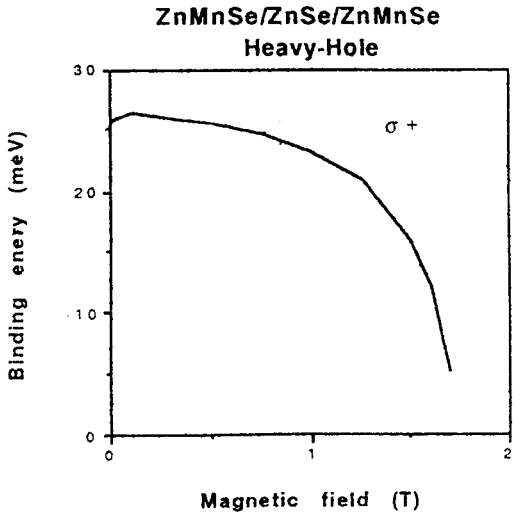


Fig.4

Two energies must be compared: the potential barrier provided by the band-offsets and the exchange energy available at the interface, which is function of the applied magnetic field. It is sufficient to examine these energies for holes since the electron exchange coupling in (Zn,Mn)Se is a factor five smaller. The band-offset for light-holes is substantially larger than that for heavy holes due to the tensile in-plane strain. When a magnetic field is applied perpendicular to the well we notice that depending on the polarization of the field we detect the spin up or the spin down state. The spin up is going down in energy making the heavy hole less localized, while the spin down state is going up in energy making the heavy hole more localized.



In Fig.5 we show a band-offset sketch,which illustrates the positions of the electron and hole energies without and with magnetic field. Bc is the critical value of magnetic field at which would detect binding energy cero.



The exciton binding energy goes to cero before the field reiches 2 T (see Fig. 6). It means it does not exists the exciton any more because the confinement energy balances the exchange energy and the confinement desappears. If the magnetic field continues increasing the decreasing of the band-offset energy is such that now we have the well in the old barrier material. It turns to be a quantum well type II

Experimentally has been demostrated that the exciton continues living but now is an exciton formed by a hole in the DMS and an electron in the non-magnetic material. It is a exciton magnetic polaron. We present a graph of

the exciton binding energy for σ^+-polarization in both holes heavy-hole and light hole. The σ^--polarization will present always a binding energy different from cero because the hole will be always confined in the well due to saturation of the exchange interaction for field greater than Bc.

The maximal binding energy we can expect in this example will be the heavy-hole exciton in σ-polarization, for which the valence band-offset reiches almost 200 meV and it means a great confinement of heavy-hole, although due to the depth the dependence of well-width is the same in shape but the binding enrgy increases because the eigenvalues in the well are more confined.

This case is interesting because it shows how to control the exciton binding-energy from outside by applying a magnetic field with a chosen polarization.

V.Conclusions

In this report we present results of exciton binding-energy in three cases, which are interesting from different points of view. 1) Marginal potential in valence band such as the well-known ZnSe/ZnCdSe/ZnSe quantum wells, in this case the exciton is formed by an well-confined electron and a relative delocalized hole. We find that the exciton binding energy can be controlled through the well-width for a given concentration. 2) Marginal potential in conduction band, electron almost free while the hole is strongly confined in the example ZnS/ZnSe/ZnS. Here the exciton binding energy is higher than in case of delocalized hole, although electron confinement plays a role as can be seen in Fig. 2a. Exciton binding energy decays as well-width increases, much less than in case of marginal potential at the valence band and we notice also a rapid decay for very thin wells. The binding energy decreases more than twice between 20 and 5 A well-width because confinement desappears. On the other hand for the case of heavy hole almost delocalized the exciton binding energy is less sensible to the change in well-width in the same range from 20 to 5 A.

Finally the quantum well with semimagetic barriers allows us to control the binding energy of exciton discriminating spin-polarization and having now a complete new open field, the predicted transition type I to type II is a very interesting feature of these systems. We present the exciton binding energy for the whole expected range type I and compare with experimental reported values [14-15], which agree completely. Thus a very new field of applications based on spin dependent transitions is open.

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