Coulomb-bound few-particles states in semiconductor quantum wells

Coulombgebonden weinig-deeltjestoestanden in halfgeleider kwantumputten

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Chapter 1

Introduction

Being the materials of choice in the important field of microelectronics, semiconductor materials have been widely studied over the years, both theoretically and experimentally. The development of microelectronics, and in particular the desire to implement faster chips and a growing number of components on a single chip created a demand for smaller and smaller electronic components. This fact has posed new challenges to the experts in the field. Besides the purely technological problems of creating smaller and smaller components, some of the assumptions underlying the theory used to describe classical semiconductors are broken.

Together with new theories apt to better describe such reduced dimensionality semiconductor structures, the improved experimental techniques and the consequently high resolution achieved in the experiments allowed the researchers to observe features that had not yet been observed in bulk materials. Some of those features are not exclusive to low dimensional structures, even if the reduced dimensionality increases the energy of those features making them “more visible”. This and much more made the physics of low dimensional systems a very popular research topic in recent years [1, 2].

In this thesis, I will concentrate on a particular variety of semiconductors with reduced dimensionality: the type I semiconductor quantum wells. Type I semiconductor quantum wells are structures in which one semiconductor with lower chemical potential, e.g. GaAs, has been sandwiched between two layers of another semiconductor with higher chemical potential, e.g. Al_xGa_{1-x}As. Therefore, the profile of the potential felt by an electron in the structure has the shape of a well. The typical thickness of the central layer, which is normally referred to as width of the quantum well, varies from a few to a few hundred Angström. The width of the quantum well is, thus, smaller or at times comparable to the phase-coherent length of the electron. As a consequence the system cannot be treated classically but requires a quantum treatment, from which the name quantum well (QW) derives.
The electrons confined in a quantum well have a higher probability to bind to the impurities which are naturally or artificially present in the semiconductor and to the holes, which may have formed in the valence band, compared to the electrons in a bulk semiconductor. As a result of the confinement, the resulting bound states will be stable at higher temperature and will have an increased binding energy with respect to the corresponding bulk states, therefore they will be easier to detect. Eventually, by replacing an atom in the barrier with a new atom which has an extra electron in the outer shell, i.e. a donor impurity, it is possible to create an excess of electrons in the quantum well. In the presence of relatively high electron densities there is a good chance to observe states in which one or more extra electrons are bound to an already bound electron-impurity (electron-hole) couple, thus forming a charged donor (charged exciton). If however the density of electrons is too high the Coulomb interaction is screened preventing the formation of such charged donor (exciton). The interest for such systems is not only limited to condensed matter physics. In fact when an electron binds to an ionic donor, forming a neutral donor, or to an hole forming an exciton, it will form an atomic-like system. To these systems an extra electron can be attached relatively easily, as it has already been said. Because of their similarity with the hydrogen atom and its ions and molecules, those systems offer an interesting occasion to study, in a simple experimental set up, theories and calculation that can be easily applied to much more complex problems. For example it is an interesting astrophysical problem to study the dynamics of the surface and the core of the stars, and of course to do so one fundamental step in this direction is to understand the behaviour of the Hydrogen molecular ion. The $H^-$ in stars is subjected to rather extreme conditions like magnetic fields that are very large compared to the magnetic field expressed in natural units, i.e. in terms of the electron mass and of the dielectric constant. Such fields are of the order of $10^7$ Tesla. However, the same condition of “very large magnetic fields” for the atomic-like systems in semiconductors is satisfied for fields of the order of a few Tesla, due to the different masses and dielectric constant that come into play, this means that those systems undergo at laboratory magnetic fields changes similar to the ones of the Hydrogen ion in stars. Last but not least new bound states in semiconductors, especially GaAs, are very interesting for applications in opto-electronics like optical switches.

In particular in this thesis I will calculate and investigate the existence of hydrogen-like systems in semiconductor quantum wells, focusing the attention on GaAs/AlGaAs quantum wells which are extensively studied experimentally. I will also investigate the influence of the material parameters and of an external magnetic field on such systems. First I will discuss the charged donor system, i.e. two electrons bound to a donor impurity. This system is the simplest system in which the electron-electron interaction is non-trivial. It offers a unique occasion to study the electron-electron interaction, both theoretically, for the simplicity of its Hamiltonian, and experimentally, since already through simple spectroscopy experiments the nature of the electron-electron interaction can be revealed, unlike the artificial atoms which are their direct concur-
rent as a mean to study the electron-electron interaction. In particular thanks to the introduction of the magnetic field and the opportunity to engineer the system offered by the available techniques, I will show how under particular conditions the equilibrium between electron-electron and electron-donor interaction is broken and the bound system can be made unbound. Second, I discuss the charged exciton system, i.e. two electrons are bound to a hole or two holes are bound to an electron. This system adds to the problem the finiteness of the mass of the hole. This makes the problem, technically, much more difficult to solve, in which it is a non-trivial 3 body problem in a quasi-2D geometry. The charged exciton problem bears similarity with the charged positron problem. I will discuss both the situation in which no external magnetic field is applied to the confined charged exciton and the case when an external magnetic field is applied in the direction parallel to the quantum well growth axis. I also show how this system due to its larger mobility and spatial extension in the quantum well is quite sensitive to the structural imperfection of the quantum well. Last I will discuss how the effect of the quantum well interface irregularity are important in a molecular exciton systems, i.e. biexciton. Showing how this effect may have to be taken into account in systems that have a large spatial extension.

In this chapter the general background of this work is presented. To gain a better understanding of the quantum wells I will briefly discuss the techniques used to built and engineer a quantum well. The concept of shallow donor impurity and the concept of exciton are introduced through some fundamental concepts as band structure, the effective mass approximation in a bulk system and its validity in the quantum well structure. Lastly, the techniques used to solve the Hamiltonian of the system, i.e. the finite-difference method and the stochastic variational method, are discussed.

1.1 Fabrication process (Growth of the quantum wells)

The first heterojunctions were created, in the 50s, by alloying the elements to create a first layer, which was then overlaid to produce a new layer at the surface [2]. This way of proceeding would give almost no control on the quality of the interface and a very poor control on the number of 'unwanted' impurities present. The doping of the material (introduction of impurities at selected sites), made in order to modify the optical and/or electrical properties of the system, was done, during the beginning of the 60s, via ion implantation, a technique which is still used today. Ions of dopant are fired at the host wafer, with the velocity and in the quantity needed to achieve the required doping density at a given distance from the surface. However this technique tends to destroy the lattice, in fact the ions of dopants do not sit precisely at the lattice sites and an annealing process is required to restore the lattice.

The introduction of the epitaxial techniques in the late 60s has greatly improved the state of the art in this field. Epitaxial techniques, as the name suggests, are
1. Introduction

Figure 1.1: The set-up of a Molecular Beam Epitaxy process [from Ref. [15]].

Based on the principle of overgrowing crystals on a suitable substrate changing the relative percentage of the elemental species used in the process, depending on the desired doping in the grown crystal. There are different epitaxial techniques. I will briefly discuss, as an example, the Molecular Beam Epitaxy (MBE) [3, 4] which is, at present, one of the leading techniques to grow high quality samples.

In Fig. 1.1 a set up of an MBE process is shown. The vacuum chamber in which the growth takes place is a stainless steel vessel with a diameter of approximately 1 m. The vacuum is about $10^{-11}$ torr. On one side of the chamber there are effusion cells containing the vapours of the elemental species for the growth of the semiconductor (e.g. Ga, As, Al) as well as the ones used as dopants (e.g. Si as 'donors' and B as 'acceptors'), in Fig. 1.1 they are indicated as MBE sources. The vapours are obtained by thermal evaporation of the elemental sources. Those vapours form beams which cross the vacuum chamber to reach the substrate, which is situated at the other side of the chamber. The beams from different elements can be allowed in the chamber or not thanks to shutters which are in front of the effusion cells. Often, the process is interrupted for a few seconds in order to allow the surface species to settle and form in this way a more regular interface. The substrate on which the semiconductor is grown
contains a heater that provides the ions deposited on the substrate with an energy sufficient to migrate to the correct lattice sites. The flux rate is controlled changing the temperature in the effusion cells. With this technique one is able to control the chemical composition and the level of doping to less than one nanometer. In spite of this great accuracy, imperfections in the growth of the semiconductor samples are still present and while they are negligible for large semiconductor samples, they cannot be neglect in the physics of quantum well structures (see Fig. 1.2). In fact a barrier defect even of 5 Å (approximately the distance between two different layers of atoms in a GaAs crystal) on a typical quantum well of width 100 Å, corresponds to an uncertainty in the quantum well width of 5%.

1.2 Experimental detection techniques

The experimental analysis of atomic-like systems in quantum well structures, unlike the case of artificial atoms, i.e. electrons trapped in a parabolic quantum dot, does not present a particular technical challenge. In fact in the case of the artificial atoms the fact that the center-of-mass contribution can be exactly separated in the Hamiltonian makes the spectra of such electron systems identical to the one of the single electron, Kohn’s theorem [6], thus uninteresting. However, in quantum wells the center-of-mass can never be exactly separated due to the presence of the single particle quantum
well confinement making spectroscopy techniques suitable for the investigation of such structures. The energy of the radiation and the technique used to examine the sample will of course depend on the phenomena that the experimenter is interested in investigating.

A much more interesting experimental problem that accompanies the detection of atomic-like states in quantum wells is the creation of an excess of carriers in the quantum well. I will here very briefly list some of those techniques (see Fig. 1.3): (i) the barrier material is doped far from the quantum well edge, so that the presence of the dopant is not felt in the quantum well. The dopant produces carriers that will migrate towards the quantum well due to the potential difference between well and barrier [7, 8, 9]; (ii) the sample is illuminated with radiation in order to free carriers from the impurities naturally present in the barrier, who then migrate towards the quantum well due to the internal electric field [10, 11]; (iii) The structure is specially engineered in such a way that a smaller quantum well is built near the one under examination. From this narrower quantum well the extra carriers created can tunnel to the one that is being analyzed [10].

1.3 Basic theoretical concepts

I will now briefly go through some of the basics concepts used to study and describe semiconductors in general and quantum wells in particular.
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1.3.1 Band structure of a bulk crystal

A crystal is a periodic array of atoms which can be described through a Bravais lattice with a basis [12]. The periodical position of the atoms is due to the nature of the bonding. In the binding process neighbouring atoms share only a few outer electrons, while their cores remain on the sites that define the periodical lattice.

If we neglect the impurities in the crystal (ideal crystal) and we consider the cores fixed at their lattice sites (adiabatic approximation), those shared electrons feel a periodic potential generated from the ionic cores in the underlying lattice. Thus, the Hamiltonian of a single outer-shell electron in the lattice is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 + U(\vec{r}), \tag{1.1}$$

where $m_e$ is the mass of the electron and $U(\vec{r})$ is the periodic potential with periodicity equal to the lattice constant. The Bloch theorem [13] tells us that the solution of the Schrödinger equation associated to the Hamiltonian of Eq. (1.1) can be written in the form

$$\phi_{n\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{n\vec{k}}(\vec{r}), \tag{1.2}$$

where $u_{n\vec{k}}(\vec{r})$ has the same periodicity of the lattice and $\vec{k}$ has the dimension of a momentum, in units of $\hbar = 1$, and is known as crystal momentum. The vector $\vec{k}$ is related to the translational invariance of the system and in particular is the corresponding of the vector $\vec{r}$ in the reciprocal lattice, i.e. the lattice which is built from the original one in such a way that if the lattice constant of the Bravais lattice in the space is $a$, the lattice constant of the reciprocal lattice is $\pi/a$.

For each value of $\vec{k}$ we obtain a set of eigenvalues $E_n(\vec{k})$ which constitutes the electronic spectrum for an electron with a given momentum $\vec{k}$. When we vary $n$ and $\vec{k}$, a discrete series of continuum intervals of allowed values for the energy of the electron is described. These intervals can be ordered, the lowest being the one with the lower minimum for the energy. These intervals are normally referred to as electronic bands for the crystal and are represented with $\vec{k}$ in the first Brillouin zone, see Fig. 1.4 [12, 13]. Thus, using only the translational invariance of the crystal lattice, one can derive the band structure of the system. Even though this is a simplified picture and many properties of the band structure cannot be explained in this simplified way, it serves well the scope of giving an idea of the concept of band structure of a crystal. A more precise and detailed explanation can be found in many review papers and books [14]. The calculation of the exact band structure is, still today, a subject of research and refinement. As an example of a realistic band structure, I show the one of GaAs in Fig. 1.5.
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Figure 1.4: Energy band representation in the extended zone (a) and in the reduced zone (b), $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$, of a 1-dimensional reciprocal lattice.

1.3.2 Semiconductors

The electrons in a crystal fill the electronic bands starting from the lowest one and at $T=0$ the highest occupied band is either completely or partially filled. When the bands are completely filled, no current can be transported, i.e. the material is an insulator, when one of the band is partially filled, there is the possibility of current transport, i.e. the material is a metal.

The difference in energy between the minimum of the first empty band and the maximum of the highest filled band is referred to as energy band gap, i.e. gap, and is the minimum quantum of energy required to trigger an interband transition. When the temperature is non zero, the electrons can move from the highest filled band to the first empty band with a probability given by $\exp[-E_g/T]$, where $E_g$ is the energy gap and $T$ the absolute temperature. Thus if the energy gap is small enough some electrons will jump for a finite temperature to the first empty band and the material will become conducting. In this case we will say that the material is a semiconductor. The energy band gap, $E_g$, of a semiconductor is typically of the order of 1eV, e.g. $E_g$ is equal to 1.42 eV for GaAs at $T=300$ K.

The completely filled band at $T=0$ is called the valence band. The first empty band at $T=0$ is called the conduction band. We show the band structure of GaAs at $T=300$K in Fig. 1.5. Note that in GaAs both the minimum of the conduction band and the maximum of the valence band fall at the the same point, i.e. in this case the $\Gamma$ point, thus GaAs is what is called a direct gap semiconductor. This denomination refers to the fact that there are semiconductors which have a band structure such that
the maximum of the valence band falls at a different point in k-space with respect to the minimum of the conduction band, e.g. Si, and this kind of semiconductor are referred to as \textit{indirect gap semiconductor}. Such semiconductors will not be discussed further in the present work.

In GaAs the valence band is threefold degenerate at the Γ point (neglecting the spin). This means that when we perturb the state of one electron in the Γ point it will behave differently depending on which of the three bands it belongs to. The degeneracy of the band is partially lifted when the spin-orbit correction is taken into account, i.e. one takes into account the interaction of the electron with spin \( \frac{1}{2} \) moving in the electric field generated by the underlying lattice. The corresponding band originated is referred to as the split-off band, see Fig. 1.6. This effect is relativistic and can be ultimately written as \( \Delta = \lambda \cdot s \) were \( \lambda \) is a multiplicative constant known as spin-orbit coupling, \( l \) is the angular momentum of the charged particle and \( s \) its spin. It is then clear that this interaction resolves the degeneracy in the total angular momentum \( j \). In particular for the valence band in GaAs which is generated by p-orbitals, i.e. \( l=1 \), the spin-orbit interaction splits the states \( j=3/2 \) from the states \( j=1/2 \). The band with \( j=1/2 \) is referred to as split-off band and it is separated by

![Figure 1.5: The GaAs band structure [from Ref. [15]].](image)
the band with $j=3/2$ by an amount of energy that for most semiconductors is large compared to the energies of the systems of central interest in the present thesis, i.e. in GaAs is $\Delta = 0.34\text{eV}$. For this reason we will from now on neglect the split-off band.

### 1.3.3 The effective mass approximation

In general the study of the properties of a crystal requires the study of the collective motion of the arrays of atoms, i.e. nuclei and electrons, forming the crystal itself. However, if one is allowed to consider only an electron with momentum $\vec{k}$ in the vicinity of a critical point labelled $\vec{k}_e$, its energy $E(\vec{k})$ can be written using a Taylor
series expansion around \( \tilde{k}_c \),

\[
E(\tilde{k}) = E(\tilde{k}_c) + \sum_{i,j=1}^{3} \frac{\partial^2 E}{\partial k_i \partial k_j} (\tilde{k})|_{\tilde{k}=\tilde{k}_c} (k_i - k_{ci}) (k_j - k_{cj}),
\]

where \( \frac{\partial^2 E(\tilde{k})}{\partial k_i \partial k_j} |_{\tilde{k}=\tilde{k}_c} \) is a tensor that does not depend on \( \tilde{k} \). This tensor can be used in order to define a “new” mass of the electron called \( m^*_e \), such as

\[
\frac{\partial^2 E}{\partial k_i \partial k_j} (\tilde{k})|_{\tilde{k}=\tilde{k}_c} = \frac{\hbar^2}{2m^*_e (k)_{ij}} |_{\tilde{k} = \tilde{k}_c}.
\]

If we substitute Eq.(1.4) in Eq. (1.3) we obtain

\[
E(\tilde{k}) = E(\tilde{k}_c) + \sum_{i,j=1}^{3} \frac{\hbar^2}{2m^*_e (k)_{ij}} |_{\tilde{k} = \tilde{k}_c} (k_i - k_{ci}) (k_j - k_{cj}),
\]

this expression is very similar to the one of a free electron with a renormalised mass. In particular if we choose a particular direction, i.e. \( \hat{a} \), we obtain

\[
E(\tilde{k})|_{\hat{a}} = E(\tilde{k}_c) + \frac{\hbar^2}{2m^*_{e\hat{a}}} k_a^2,
\]

where \( m^*_{e\hat{a}} \) is the effective mass of the electron along the direction \( \hat{a} \). Eq.(1.6) describes a particle of mass \( m^*_{e\hat{a}} \) moving along a line.

In particular for GaAs, the material of central interest in this thesis, an expansion of the conduction band about the minimum energy is approximately parabolic [16], due to the s-type symmetry of the minimum at the \( \Gamma \) point. This defines an effective mass which is independent from the direction. The effective mass of the electron is \( m^*_e = 0.067 m_0 \), where \( m_0 \) is the free-electron mass. For the valence band the situation is more complicated due to its symmetry at the \( \Gamma \) point. Indeed following Dresselhaus [17] the band structure at the \( \Gamma \) point can be written as

\[
E(k) = E(k_{TV}) \pm (Bk^4 + C (k_x k_y + k_y k_z + k_z k_x))^{1/2},
\]

where \( k_{TV} \) is the value of \( k \) for which the valence band has a maximum, \( k - k_{TV} = (k_x, k_y, k_z) \) and \( B, C \) are constants. Notice that the value of the effective mass will, in this case, not only depend on the direction along which it is calculated, but also on which of the two degenerate bands the particle belongs to. However, spherical approximations for the effective mass are available also for the valence band. In the particular case of the holes, they will be called light-hole (if + is chosen in Eq. 1.7), heavy-hole (if - is chosen in Eq. 1.7), depending on which band originates them. For, eg., in GaAs the values of the light-hole mass and the one of the heavy-hole
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mass are $0.09m_0$ and $0.34m_0$ respectively [18]. In particular, as the effective mass is inversely proportional to the curvature of the band in the point, the band with the smallest curvature generates the heavy-hole (see Fig. 1.6). The symmetric effective mass approximation, although a strong approximation, will be used through all this thesis. When the problem requires it, a comparison with the asymmetric effective mass approximation will be made, and the reasons and the limitation of the approximation made will be discussed.

1.3.4 The concept of exciton

It is known that in a ideal case and at low temperature all the electrons in the crystal sit in the “valence band”. The question is what will happen if we excite one of those valence electrons? The electron will jump to the conduction band, if the energy of the excitation is larger or equal to the energy band gap. It is, however, wrong to think that if the energy of the excitation is smaller than the energy gap there will be no transition at all. In Fig. 1.7 we show the absorption spectra observed for a bulk GaAs sample near the band gap at different temperatures [19]. Notice that the absorption coefficient does not increase continuously for energies larger that the gap energy gap, as it would be expected if the electron could only be promoted to the conduction band, but presents a peak below the energy band gap which suggests the presence of discrete states in the gap.

Figure 1.7: Absorption spectra from a GaAs sample near its band gap at different temperatures [from Ref. [19]].
Figure 1.8: In (a) we show the conduction band in which an extra N+1-electron would sit in a semiconductor with N electrons in the full valence band and in (b) the excitonic state which arises when the excited Nth-electron problem is correctly treated.

It must be noticed that the conduction band is not built considering the allowed energy values for the excited states of a N electrons system, but it is built considering the allowed energy values for the N + 1 electron in a system with N + 1 electrons (see Fig. 1.8). From the correct treatment of the N particles problem a new state in the gap arises, i.e. the excitonic state. I will show now how this state arises and how it can be schematically described as the bound state of an electron in the conduction band interacting with a positive charge in the valence band, i.e. a hole, and I will show that this state lies in the gap.

Consider the Hamiltonian associated to the electronic motion in a crystal using the adiabatic approximation, i.e. the ionic cores (nuclei + internal electrons) are considered fixed at their equilibrium position and only the N external electrons in each elementary cell of the crystal are taken into account,

$$\hat{H} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{e^2}{2} \sum_{i,j=1}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{e^2}{2} \sum_{i,j=1}^{N,M} \varepsilon_0 |\vec{r}_i - \vec{R}_l| Z_l$$  \hspace{1cm} (1.8)
where \( \vec{r}_i \) and \( m_e \) are the vector position and the mass of the electron \( i \), \( M \) is the number of ions and \( \vec{R}_i \) and \( Z_i \) are the position and the charge in units of the electron charge, \( e \), for the \( l \)-th ion. Such Hamiltonian can be studied using the Hartree-Fock method (H-F) where an excited state of the \( N \) electrons can be written in terms of Bloch functions as,

\[
\Phi_{\psi_{\vec{k}\alpha, \beta}} (\vec{r}) = A\{\psi_{\vec{k}\alpha} (\vec{r})\alpha(1), \ldots, \psi_{\vec{k}\beta} (\vec{r}), \ldots, \psi_{\vec{k}\alpha} (\vec{r})\beta(2N)\}, \tag{1.9}
\]

where \( \psi_{\vec{k}\alpha} (\vec{r}) \) is the Bloch function relative to the electron with momentum \( \vec{k}_\alpha \) in the valence band, and \( \psi_{\vec{k}\beta} (\vec{r}) \) is the Bloch function of an electron of momentum \( \vec{k}_\beta \) in the conduction band; \( \alpha \) and \( \beta \) are the functions relative to the spin state of the system; \( A \) is the antisymmetrization operator. Thus, the energy relative to the excitation is given by the difference between the energy relative to \( \Phi_{\psi_{\vec{k}\alpha, \beta}} (\vec{r}) \) and the energy of the ground state of the crystal,

\[
\Delta E_{ex} = \left< \Phi_{\psi_{\vec{k}\alpha, \beta}} (\vec{r}) \left| \hat{H} \right| \Phi_{\psi_{\vec{k}\alpha, \beta}} (\vec{r}) \right> - \left< \Phi_0 \left| \hat{H} \right| \Phi_0 \right> \tag{1.10}
\]

\[
\begin{align*}
\Delta E_{ex} & = \left< \Psi_{\psi_{\vec{k}\alpha, \beta}} \left| \hat{H} \right| \Psi_{\psi_{\vec{k}\alpha, \beta}} \right> - \left< \Psi_0 \left| \hat{H} \right| \Psi_0 \right> \\
& = \left< \psi_{\vec{k}\alpha} \left| \hat{H}_c \right| \psi_{\vec{k}\alpha} \right> + \sum_{\vec{k}} \left[ I_{\vec{k}, \vec{k}} - J_{\vec{k}, \vec{k}} \right] \\
& \quad - \left< \psi_{\vec{k}\alpha} \left| \hat{H}_c \right| \psi_{\vec{k}\alpha} \right> + \sum_{\vec{k}} \left[ I_{\vec{k}, \vec{k}} - J_{\vec{k}, \vec{k}} \right] \\
& \quad - \left[ \left< \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} e^2/\varepsilon_{0r_{12}} \left| \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} \right> - \left< \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} e^2/\varepsilon_{0r_{12}} \left| \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} \right> \right) \right],
\end{align*}
\]

where \( \Phi_0 \) indicates the ground state of the system, \( \hat{H}_c \) is the single particle Hamiltonian, and

\[
I_{\vec{k}, \vec{k}} = \left< \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} \frac{e^2}{\varepsilon_{0r_{12}}} \left| \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} \right> ,
\]

\[
J_{\vec{k}, \vec{k}} = \left< \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} \frac{e^2}{\varepsilon_{0r_{12}}} \left| \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} \right> ,
\]

are the Hartree (direct) and the Fock (exchange) potentials for the particle of momentum \( \vec{k}_\alpha \) in the conduction band and \( I_{\vec{k}, \vec{k}}, J_{\vec{k}, \vec{k}} \) are the equivalent Hartree and the Fock potentials for the particle of momentum \( \vec{k}_\beta \) in the valence band, \( r_{12} \) is the distance between the two interacting particles. From Eq. (1.10), if \( \psi_{\vec{k}\alpha} \) is a solution of the H-F problem with \( N + 1 \) particle, we obtain

\[
\Delta E_{ex} = E_c (\vec{k}_\alpha) - E_a (\vec{k}_\alpha) \\
\quad - \left< \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} e^2/\varepsilon_{0r_{12}} \left| \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} \right> \right) \\
\quad + \left< \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} e^2/\varepsilon_{0r_{12}} \left| \psi_{\vec{k}\alpha} \psi_{\vec{k}\alpha} \right> \right) , \tag{1.11}
\]
with $E_j(\vec{k}_i)$ solutions of the H-F problem relative to the Bloch function $\psi_j(\vec{k})$. It is clear then that an excited state where one electron is promoted to the conduction band can be treated as a two particles problem where one of the particle has charge equal to the electron charge, $e$, and sits in the conduction band with energy $E_c(\vec{k}_c)$ and the other one has charge opposite to the electron charge and sits in the valence band with energy $E_v(\vec{k}_v)$. We call the particle in the valence band a hole. It is a missing chemically bound electron. When one takes into account the Coulomb interaction, the two particle form a composite particle: “the exciton”. Notice that in materials like GaAs the hole originates from a $j = \frac{3}{2}$ band. As the hole, in this picture, is a “free” particle it will have $l = 0$ and consequently, spin $s = \frac{3}{2}$.

We want now to go further and derive the excitonic Hamiltonian in the effective mass approximation. An exciton is an excited state of the crystal and, as electrons are indistinguishable, the excitonic state can be written as a linear combination of the states in Eq.(1.9) diagonalized with respect to the spin operator, with the constraint that the excitonic momentum $\vec{k}_X = \vec{k}_h - \vec{k}_e$ is conserved:

$$\Psi_{\vec{k}_X, S}(\vec{r}) = \sum_{\vec{k}_h \neq \vec{k}_e} A \left( \vec{k}_h, \vec{k}_e \right) \Phi_{\vec{k}_h, \vec{k}_e, S}(\vec{r}).$$

(1.12)

Applying the Hamiltonian in Eq.(1.8) to the excitonic function, where $\vec{k}_h, \vec{k}_e$ are re-written as $\vec{k}_h = \vec{k} + \frac{1}{2}\vec{k}_X$, $\vec{k}_e = \vec{k} - \frac{1}{2}\vec{k}_X$, one obtains the following equation for $A \left( \vec{k} \right)$,

$$\left[ E_c \left( \vec{k} + \frac{1}{2}\vec{k}_X \right) - E_v \left( \vec{k} - \frac{1}{2}\vec{k}_X \right) - E_X \right] A \left( \vec{k} \right) + \sum_{\vec{k}} \left[ - \int d\vec{r} \frac{e^2}{\varepsilon_0 \varepsilon_{0r}} \exp \left[ -i \left( \vec{k} - \vec{k}' \right) \cdot \vec{r} \right] + J_{kx} \delta_{S,0} \right] A \left( \vec{k}' \right) = 0,$$

(1.13)

where $J_{kx}$ is the Fock integral which is non negligible only if the possibility of finding the two particles at the same place is non negligible, i.e. singlet states. Considering the Fourier transform of $A \left( \vec{k} \right)$, i.e. $F(\vec{r})$, and taking into account that we are interested in strongly delocalized excitons, i.e. Wannier excitons, we derive an hydrogen-like equation for $F(\vec{r})$,

$$\left[ - \frac{\hbar^2}{2m_e^*} \left( -i \nabla - \vec{q} + 1/2\vec{k}_X \right)^2 - \frac{\hbar^2}{2m_h} \left( -i \nabla - 1/2\vec{k}_X \right)^2 - E_X \right] F(\vec{r}) = 0,$$

(1.14)

with the assumption that the maximum of the valence band falls at $\vec{k} = 0$ and the minimum of the conduction band around $\vec{k} = \vec{q}$. The Fock term can be neglected since
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<table>
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<th>D-center</th>
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<td>12.5</td>
</tr>
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<td>1.0</td>
<td>0.067</td>
<td>0.067</td>
</tr>
<tr>
<td>$m^*_h/m_0$</td>
<td></td>
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<td></td>
</tr>
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<td>120</td>
<td>98.7</td>
</tr>
</tbody>
</table>

Table 1.1: Comparison between different characteristic parameters for the Hydrogen atom, for the exciton and for the neutral donor-center.

its effect is mostly to generate two series of eigenvalues: the spin-singlet ones and the spin-triplet ones. For direct band gap semiconductors $q = 0$, and in particular for GaAs, which is the material of interest in the present thesis, $k_X = 0$. Then Eq. (1.14) can be re-written as

\[
\left[ -\frac{\hbar^2}{2m^*_e} \left(-i\nabla\right)^2 - \frac{\hbar^2}{2m^*_h} \left(-i\nabla\right)^2 - E_X \right] F(\vec{r}) = 0, \tag{1.15}
\]

Notice that a parabolic approximation for the energy band has been used, i.e. $E(k) = ak^2$. Such approximation is not always correct and deviation from the parabolicity law, also called “band non parabolicity” can in some cases not be neglected, e.g. for GaAs [16] narrow quantum wells.

Energy states associated to the excitonic Hamiltonian lay in the energy gap. The energy spectrum and the dimension of the exciton are in fact easily obtained by the one of the hydrogen atom, when in the Hamiltonian the electron mass is replaced by the reduced exciton effective mass, $\mu^* = m^*_e m^*_h/(m^*_e + m^*_h)$. The characteristic energy of an exciton can consequently be defined through the effective Rydberg, $R^*_\mu = e^2/2\varepsilon_0 a^*_B$, and its characteristic length through the effective Bohr radius, i.e. $a^*_B = \hbar^2 \varepsilon_0 / \mu^* e^2$. In Table 1.1 we compare the typical values for the Rydberg and the effective Bohr radius for the exciton with the one for the Hydrogen atom. Notice that the characteristic length is large enough to justify the assumption that the particles see an uniform macroscopic dielectric medium, hence justifying the use of $\varepsilon_0$, and that the characteristic energy is much smaller than the band energy gap, thus, assuring that the exciton states lie in the gap.

Excitons in semiconductors can also bind an extra electron (hole) from the back ground of carriers the system formed, i.e. a charged exciton, has (in the case the extra
carrier is an electron) the following Hamiltonian,

\[
H = \left[ -\frac{\hbar^2}{2m^*_e} \left( -i \nabla^2 \right) - \frac{\hbar^2}{2m^*_h} \left( -i \nabla^2 \right) + \frac{\hbar^2}{2m^*_e} \left( -i \nabla^2 \right) \right]
+ \left[ \frac{e^2}{\varepsilon_0 |\vec{r}_{1e} - \vec{r}_{1h}|} - \frac{e^2}{\varepsilon_0 |\vec{r}_{2e} - \vec{r}_{1h}|} + \frac{e^2}{\varepsilon_0 |\vec{r}_{1e} - \vec{r}_{2e}|} \right]
\]  \hspace{1cm} (1.16)

which it has been shown [20] that gives rise to bound states with a binding energy of about 0.2 meV for the \( X^- \).

1.3.5 The concept of donor

The perfect crystal is only an ideal system. Consider for example the case of a GaAs-crystal. In the ideal case we have a regular structure of Ga and As atoms, in reality it is not uncommon that Ga atoms are replaced by another atom which has an extra electron in the outer shell, e.g., Ge. In such cases there will be an extra positive charge on some lattice sites and an extra electron in the crystal.

One can then assume that the “donor electron” feels a crystal potential which is changed with respect to the one of the pure crystal by replacing the charge \( Z_\ell \) of the ion in the position \( \ell \) with the charge \( Z_\ell + 1 \), using an H-F approach the \( N+1 \) electronic crystal state can be written in term of the \( N \) valence Bloch states and one conduction Bloch state. Following the same approach used for the exciton it is easy to show that an hydrogen-like equation can be derived also for a donor [15, 21]:

\[
\left( -\frac{\hbar^2}{2m^*_e} \nabla^2 + \frac{e^2}{\varepsilon_0 \ell} \right) F(\vec{r}) = E F(\vec{r}).
\]  \hspace{1cm} (1.17)

It is easy to show that energy states associated to this Hamiltonian lay in the energy gap, see Tab. 1.1. The characteristic energy of these states is reduced with respect to the one of the hydrogen atom by a factor \( m^*_e/\varepsilon^*_0 \), which is about \( 4 \times 10^{-4} \) in the case of GaAs and it is thus a value much smaller than the one of the energy band gap. At the same time the effective radius of the orbital states is increased by a factor \( \varepsilon_0/m^*_e \), which gives \( a_F^* = 98.7 \) meV for GaAs. This ensures us that the orbit is large enough for the extra electron to effectively see an uniform macroscopic dielectric medium.

However, life is not always as simple and not all donor impurities can be described using the Hydrogenic Hamiltonian. Hydrogenic donors are normally shallow donors, e.g. donors were the core of the impurity atoms resembles the core of the atoms that is replaced. However, for some deep donors, i.e. donors that induce strongly localized deformation in crystal potential, the lowest electronic levels can still be described as the one of a shallow donor, i.e. using the Hydrogenic Hamiltonian. Si is such an example of donor with very different behaviour in GaAlAs alloys or under pressure [15].
1. Introduction

In the present thesis the focus will be on negatively charged donors, i.e. $D^-$, which are neutral donors to which an extra electron is bound. The Hamiltonian of such systems resembles the one of a charged Hydrogen atom

$$H = \left( -\frac{\hbar^2}{2m_e^*} (\nabla_1^2 + \nabla_2^2) + \frac{e^2}{\varepsilon_0 r_1} + \frac{e^2}{\varepsilon_0 r_2} - \frac{e^2}{\varepsilon_0 [r_1 - r_2]} \right),$$  \hspace{1cm} (1.18)

where $\vec{r}_i$ is the vector position of the particle $i$. Lampert [20] also demonstrated that this state is bound with an energy of about 0.3 meV in GaAs.

1.3.6 The quantum well

When different materials are brought in contact with each other (e.g. heterojunction), the periodicity of the system, so important to derive the band structure of a crystal is destroyed or at the very least perturbed. If indeed we imagine to bring in contact two materials with a very different lattice constant, the two structures will hardly form a periodical lattice again in the interface region. When instead the two materials have similar lattice constants an infinite periodical lattice is obtained. This is reflected on the band structure which does not get destroyed but only deformed (band-bending) to allow the band structures of the materials to match. This is the case for GaAs and AlAs two materials whose lattice constants are very similar, i.e. a difference of only about 0.2% [22]. In this thesis I will mainly discuss the GaAs/AlGaAs quantum well, for which the lattice mismatch is even smaller. In fact, the lattice constant of Al$_x$Ga$_{1-x}$As is a linear combination of the one of the two binary-materials, AlAs and GaAs, which depends on the concentration $x$ of Al (Vegards Law). For this reason I will from now on consider that no strain is present in the quantum well under examination.

Assuming that the periodical structure of the lattice is maintained, the Hamiltonian of, e.g., an electron, in the quantum well can be written as the Hamiltonian of an electron with a given effective mass $m^*$ into a potential well:

$$H = -\frac{\hbar^2}{2m_e^*} \nabla^2 + V(z),$$  \hspace{1cm} (1.19)

where $V(z)$ is the confinement potential due to the quantum well assuming the $z$-direction to be coincident with the confinement axis. Depending on the different band offset, i.e. the difference in energy between the corresponding band edges of the materials forming the quantum well, the potential can be represented using a finite or infinite potential well. The associated Schrödinger equation has then simple and well known solutions, see Fig. 1.9. The typical value for the band offsets in a GaAs/Al$_x$Ga$_{1-x}$As quantum well are $\Delta E_c = 0.6 \Delta E_g$ and $\Delta E_v = 0.4 \Delta E_g$ for the conduction and the valence band respectively, with $\Delta E_g = (1.155x + 0.37x^2)$ meV the band gap difference.
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The same approach can be used with other and more complex systems as exciton, molecular excitons and donor, and the Hamiltonian of the hydrogenic system becomes

\[
H = H_0 + \sum_{i=1}^{P} V_i(z_i),
\]

where \( H_0 \) is the hydrogenic Hamiltonian, \( V_i(z_i) \) is the single particle confinement potential of the \( i \)-th particle due to the presence of the quantum well and \( P \) is the number of particles. We have seen that the effect of the confinement on the electron results in a series of subbands where the electron can be situated. In general, the presence of an interaction, in this case the Coulomb interaction, mixes the different subbands. However, if the strength of the Coulomb interaction is sufficiently small the different subbands will not be mixed and in this case it can be useful to retain the subband wave functions in order to describe the particles in the confinement direction. It must be pointed out, however, that the effective mass approximation Hamiltonian for hydrogen-like systems has only been rigorously derived for an infinite crystal. The use of the effective mass approximation in the case of quantum wells is only justified by the fact that it works. It is, thus, empirical.

When I discussed the MBE technique I already mentioned that even the best interfaces have irregularities which result in deformations of the quantum well edges (see Fig. 1.2). These irregularities are referred to as surface corrugation. Such irregularities change the well width of the QW and as a consequence the ground state of, e.g., an electron in the quantum well will have an energy \( \frac{\hbar^2}{2m} \) (infinite potential barrier) in
1. Introduction

Figure 1.10: A schematic picture showing the quantum well irregularities and their effect on the confinement levels.

the region A in Fig. 1.10. In region B the same electron will have an energy of \( \frac{e^2}{\epsilon L} \). As a consequence the electron in region A sees a potential barrier when moving in the direction indicated with \( x \) in Fig. 1.10. Thus, the electron is more localized in a real quantum well than it would be in an ideal one. Those irregularities are typically a few hundred Angström apart from each other, as a consequence they are felt only by systems with a comparable spatial extension, e.g. the systems studied in this thesis. Other types of imperfections can have the same effect, for example the fluctuation in the composition of the alloy forming the barrier induces local changes in the barrier height with effects similar to the one due to the well width fluctuations.

1.3.7 The magnetic field

The properties of atomic-like systems both in bulk and quantum well systems are changed when an external field is applied. In particular in this thesis I will study the effect of an uniform magnetic field applied along the confinement direction on the atomic-like system in a quantum well. In the presence of a magnetic field the Hamiltonian of a particle with charge \( q \) becomes

\[
H = \frac{1}{2m} \left( \vec{p} - \frac{q}{c} \vec{A}(\vec{r}) \right)^2 ,
\]

with \( m \) the mass of the particle and \( A(\vec{r}) \) the vector potential associated to the field \( B \). If the particle has spin \( \vec{s} \) then this will interact with the magnetic field and the
following contribution will have to be added to the Hamiltonian

$$\Delta s = -g_e \frac{\mu_B}{\hbar} s_z B,$$

where we are assuming that the direction of the magnetic field $B$ coincides with the $\hat{z}$-direction, $g_e$ is the gyromagnetic factor of the electron and $\mu_B = \frac{e\hbar}{2m_e}$. The solutions of this Hamiltonian are well known and are normally referred to as Landau levels [24]. Sometimes the formalism in terms of Landau levels is retained also to describe atomic-like systems. This approach is especially satisfying at high magnetic fields, where the separation between different Landau levels of the same particle is such that Coulomb interaction couples one or at most a few Landau levels. Such an approach will not be followed in this thesis since it is my interest to develop a calculation which is appropriate both for the high and the low magnetic field regime, however comparison with theories using the Landau levels approach will be made.

The Hamiltonian of an atomic-like system in an uniform magnetic field is

$$H = \sum_{i=1}^{num.\ part.} \frac{1}{2m_i} \left( \vec{p}_i - \frac{q_i}{c} \vec{A}(\vec{r}_i) \right)^2 + \sum_{i,j} \frac{q_i q_j}{|r_i - r_j|^2} + \sum_i g_i \mu_B \vec{B} \cdot \vec{S}_i.$$

(1.23)

In 3D systems it is known that the presence of a magnetic field resolves the degeneracy with respect to the components along the magnetic field of the total angular momentum, $J_z = L_z + S_z$. This effect is known as the Zeeman effect. In a quantum well $J$ is not a good quantum number. Nevertheless, the spatial asymmetry of the problem ensures that $L_z$, the orbital angular momentum along the confinement axis, is conserved, while the degeneracy with respect to the spin component of the system remains. This degeneracy is lifted by the introduction of an external magnetic field, i.e. along the $z$-direction. The correction due to the Zeeman effect can be taken into account perturbatively [12].

### 1.4 State of the Art

I will now give a brief history of the physics of the charged donor, of the charged exciton and of the biexciton systems in semiconductors, together with the state of the art. The existence of the charged donor and of the charged exciton was hypothesized for the first time in 1938 by Lampert [20]. In his article, published in the first volume of Physical Review Letters, Lampert discussed the existence of bound charged donor and bound charged excitonic systems in analogy with the $H^-$ ion. After this common start, the two systems have a separate, however, parallel history. Continuous comparison between the two systems is made, still today.
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Figure 1.11: In (a) we show an on-center donor and in (b) an off-center donor.

1.4.1 The charged donor.

The problem of a charged donor confined in a quantum well lies between the exactly two-dimensional problem and the three-dimensional one. The 3D problem is well known and was first solved by Chandrasekhar [25] in his paper on the bound states of the Hydrogen molecular ion. The 2D case was solved by Phelps and Bajaj [30]. In both studies it was found that the ground state was a spin-singlet state, i.e. the total spin of the electrons was zero. However, it has been proven [26, 27, 28, 29] that when a magnetic field is applied the system has also bound spin-triplet states. The results from the different calculations also showed that the binding energy of the charged donor is about one order of magnitude larger in a 2D system than in a 3D one. This suggested that charged donor centers are more easily detectable in quasi two-dimensional systems compared to their bulk counterpart. The early studies on charged donors in quantum well systems both experimental [33, 34] and theoretical [35, 36, 37, 38], were concentrated on on-center donors, i.e. donors situated at the center of the quantum well, see Fig. 1.11. However it is clear that different properties can be expected depending on the position of the donor center with respect to the quantum well center, i.e on-center or off-center. In fact the translational invariance, typical of crystals, is in this case broken both due to the presence of the quantum well and to the presence of the donor center. Thus, while the position of the well and the position of the donor relative to the bulk crystal are not essential, their position relative to each other is expected to play a role. In fact, for the on-center charged donor the binding energy of the singlet state is always larger than the one of the excited triplet states even for increasing magnetic fields. It has been shown that for a off-center $D^-$ a transition to a spin-triplet ground state is expected [39]. Fox and Larsen [40] showed that more spin-singlet to spin-triplet transitions are observed at least for
the case in which the electrons are confined and move in a perfect plane and the
donor center is displaced outside the plane. As much as 5 transitions were observed
for this system, and eventually for high enough magnetic field the charged donor
would become unbound, i.e. magnetically evaporates. Similar results were obtained
for a spatially separated charged donor in a double quantum well [41]. Experimental
evidence of the negatively charged exciton spin-singlet and spin-triplet states has been
reported by Jiang et al. [8]. The attribution of the experimental features to these
states was confirmed by the theoretical calculation reported in this thesis, for a donor
in a realistic quantum well structure. The effect of the electron-phonon interaction
has not been included in my calculation, however it has been shown [42] that for
large magnetic fields and for a superlattice this interaction gives a contribution to
the binding energy of the system, due to the fact that the neutral donor polaron
correction is 4 times smaller than the one of the charged donor. The influence of
this correction on the transition energies between different charged donor states is,
however very small.

1.4.2 The charged exciton

The first calculation for charged excitons in bulk materials which takes into account
the finite hole mass was performed by Stébé et al. [44]. Notice that the results from
Ref. [20] and from this last work are comparable and give a very small value for the
binding energy of the negatively charged exciton, i.e. about 0.1 meV. The low binding
energy found theoretically is consistent with the inability of the experimentalists to
report clear evidences of the existence of charged excitons in bulk semiconductors. In
the eighties, with the increased interest for low dimensional systems, the first paper
regarding 2D charged excitons appeared [43]. The 2D calculation pointed out that
the decreased dimensionality increases the binding energy of the negatively charged
exciton with about an order of magnitude with respect to the bulk case. This result
is especially interesting as a larger binding energy makes the systems easier to be
observed experimentally.

The first clear observation of negatively charged excitons was reported in the
middle nineties by Kheng et al. [9] in a CdTe/CdZnTe quantum well. Starting from
this first observation a lot of research on the charged exciton both experimental [7, 10,
46, 47, 48, 51, 52, 53, 54, 55, 56, 57] and theoretical [58, 59, 60, 61, 62, 63, 101, 65] has
been done. A great deal of these experiments was focused on GaAs-based structures.

Photoluminescence studies of quantum well structures have shown that the quenching
of the excitonic line, i.e. the line in the spectrum associated to a transition from
the exciton, which is observed when the density of electrons in the quantum well
increases is associated to the formation of a new line, which has been attributed to
the negatively charged exciton [7, 52, 49], see Fig. 1.12. This attribution has been
supported by the fact that such a line needs an excess of electrons to exist and that
it disappears when the temperature is increased, i.e suggesting that the line must
be attributed to a feature with a relatively low dissociation energy. Studies of the
magnetic field dependence [48, 52] of the optical spectra of quantum wells in which an excess of electrons is present, i.e. quasi two dimensional electron gases (Q2DEG), have shown that another line between the one attributed to the $X^-$ and the one attributed to $X$ appears when a magnetic field is applied. Such a line has been attributed to the so called $X^-$ spin-triplet state (see Fig. 1.12). To understand what we mean as spin-triplet state for a system of two electrons and a hole it may be convenient to make use of a diagram see Fig. 1.13. It is clear that when we have two fermions in a system they have to satisfy the Pauli exclusion principle. We will then be able to have a singlet state in which the two fermions are antiparallel to each other, which is split in a doublet by the extra spin of the hole, and a triplet state in which the two fermions are parallel to each other, which hides a set of 5 degenerate states. The degeneracy is lifted by the interaction with the magnetic field and when a circularly polarized light is applied the transitions shown by the vertical lines in Fig. 1.13 are possible. Studies similar to the ones that allowed the observation of $X^-$ in Q2DEG have also been carried out on quasi-two dimensional hole gases (Q2DHH) showing a singlet and triplet state for the positive charged exciton [10, 52, 50], see Fig. 1.14. Particularly
interesting is the PL study by Glasberg et al. [10] who thanks to an especially designed structure, have been able to observe negatively and positively charged excitons in the same quantum well, depending on the condition of illumination. Their results brought to light a remarkable difference between the $X^{-}$ and $X^{+}$. It was, in fact, found that at least for $B < 10$ T, the binding energy of the $X^{+}$ is almost constant with the magnetic field, while the binding energy of the $X^{-}$ increases fastly up to a certain magnetic field were it seems to saturate, see Fig. 1.15(a). Notice however that it has been found that in ZnSe the binding energy of the negative trion is almost constant with the magnetic field [67] in contrast to what is found in GaAs. The experiment also showed a singular dependence on the magnetic field of the gyromagnetic factor of the exciton and of the negatively and positively charged exciton, see Fig. 1.15(b). These results are still not understood, however they show evidence that the gyromagnetic factor of the neutral exciton and of the excitonic ions are not the same in contrast to what has been believed until recently. More recent experiments seem also to show a transition between the spin-singlet ground state regime and the spin-triplet ground state regime [57].

Theoretically, it has been found by many authors that the ground state of a charged exciton in a quantum well at $B=0$ is a spin singlet state, i.e. the two electrons have parallel spin. More over, it was shown [68] that due to the so called “hidden symmetry”, which is due to the equal strength of the electron-electron and electron-hole interaction, the exciton does not bind an extra electron at high magnetic field. However the hidden symmetry is broken in quantum wells [60], due, e.g., to the fact that the envelop function of the electrons and of the holes differs more than for a change of sign. As a consequence of this breaking of the “hidden symmetry” the charged exciton at high magnetic fields is bound. It has been proven that the
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Figure 1.14: PL spectra that shows the evolution of the $X$ and $X^+$ peaks for different magnetic fields for a 300 Å GaAs/AlGaAs structure [from Ref. [50]].

system has then only one spin-triplet bound state [59, 60]. However, it is known that a systems of charged particles, like the charged exciton, in an uniform magnetic field $B$, is invariant for translations generated by the vector $\hat{K} = \sum_i K_i$ with $K_i = \hat{\pi}_i - \frac{\hbar}{e^2 c} \hat{r}_i \times \hat{B}$ where $\hat{\pi}$ the magnetic angular momentum of the system [69]. In particular, for charged excitons in quantum wells this property holds along the plane without confinement. It has been proven that this symmetry results into a conservation rule for magneto-optical transitions [70]. An interesting consequence of this selection rule is that the spin-triplet state is optically dark, i.e. it cannot be observed in spectroscopic experiments. This theoretical result is clearly in contrast with the experimental results. However it has also been shown that irregularity of the quantum well, such as well width fluctuations, break the magnetic translational invariance and thus the selection rule that forbids the optical transitions for the $X^-$ triplet states is relaxed.

As at $B=0$ the ground state of the system is a spin-singlet state and at high magnetic field it is a spin-triplet state a ground state transition must happen at some critical magnetic field. Such transition has been theoretically predicted by Whittaker and Shields [62] for a quantum well of width $W = 100$ Å at a magnetic field of $B=30$ T. However their theory did not agree with the available experimental results. It did however show the importance of going beyond the Lowest Landau Level approximation and of including more quantum well subbands in the calculation. The approach of Whittaker and Shields [62] has however still the limit of starting from
1. Introduction

Figure 1.15: Experimental data for a 200 Å GaAs/AlGaAs structure [from Ref. [10]].

single particle wave functions and it becomes too heavy when one wants to increase
the number of Landau levels and quantum well subbands included.

The group of Stébé used, in different works on charged excitons in quantum wells
with or without magnetic field, a variational approach in order to take into account
the interaction among the particles. However, all those works involve a certain degree
of approximation in the Hamiltonian of the system.

Interesting although some time contrasting results have also been obtained by
Wojs, Hawrylak and co-workers. It seems in fact that two new bound states have
been theoretically found for the charged exciton: an optically bright triplet [71] and
an optically dark singlet [111]. It has been argued that the existence of this bright
triplet could explain why until now no crossing between the spin-singlet and the spin-
triplet peak has been observed. In fact all the theoretically predicted spin-singlet to
spin-triplet transition involve the dark spin-triplet state. The fact that the less bound
“bright” triplet would be seen instead of the more strongly bound “dark” triplet,
would be consistent with the fact that the transition from the “dark” triplet has
a long relaxation time. Calculation have been made to consider the displacement on
two different planes of the electron(s) and the hole(s) provoked, e.g., by the application
on an electric field during the experiment [72]. It has been found, in agreement with
the experiment, that the binding energy of the system decreases [111, 63].

I will present in this thesis a calculation that, taking into account the correlation
between the particles both in the confinement direction and in the non-confined plane,
solves the exact Hamiltonian of the problem, both in the case with and without
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magnetic field.

1.4.3 The biexciton

The interest for the physics of biexcitons in quantum wells was awoken by experimental results that showed a splitting of the excitonic peak in the PL spectrum of the quantum wells, which was consistent with the biexcitonic behaviour [75]. However the binding energy associated to this peak was much larger than the calculated biexciton 3D energy [76, 77]. Preliminary theoretical results on perfect 2D biexcitons showed that their binding energy is indeed increased as compared to the 3D case. Those results did however report binding energies which are about a factor of two smaller than the one experimentally measured for quantum wells. The theoretical results by Kleinman [18] seemed to solve the discrepancy between theory and experiment. However subsequent experiments [78] did report a binding energy of the biexciton which was larger than the one calculated in Ref. [18]. On the other hand it was recently pointed out [79] that the theoretical results of Ref. [18] were even overestimating the biexciton binding energy due to an unfortunate error in the calculation, see Fig. 1.16. It has been claimed [11] that probably the assignment of the low-energy peak as due to the biexciton has been too easily made and that the same peak could also originate from positively charged excitons. However Adachi et al. [22] showed that through the correct choice of the polarization of the excitation light it is possible to discriminate between the biexciton transition and the transition originated by other excitonic states.

It has been argued that the discrepancy between theory and experiment for the binding energy of the biexciton must be attributed to the localization effect due to interface fluctuations [31] and statistical disorder in alloys [96]. The main effect of the fluctuation is to restrict the biexciton center of mass rather than change the nature of the exciton-exciton interaction. This is the so called weak localization regime, which has been shown to increase the biexciton binding energy in structures of all dimensionality.

I will present in this thesis a calculation for the biexciton in a quantum well which takes into account the quantum-well width fluctuations as modeled through a parabolic potential.

1.5 Numerical Techniques

Once the Hamiltonian of the system is known, in principle, also the eigenstates and the eigenvalues of the system are known. However to diagonalize a Hamiltonian is almost never a trivial task. We present in this section the two techniques used in the present work. The first, the finite difference technique, exactly diagonalizes the Hamiltonian with the help of numerical algorithms. The second one, the stochastic variational
method, finds, through the use of the variational principle, suitable approximations to the eigenvalues and the eigenstates of the given Hamiltonian.

1.5.1 The finite difference technique.

The finite difference approach is the direct approach to solve numerically a given Hamiltonian $H$.

The problem of solving the partial differential equation $H\phi = E\phi$ is reformulated into the problem of finding the solution of the matrix equation $A_H \phi = E\phi$. Let us consider a grid with $N$ points per coordinate, so that for a 3D problem $x = lh, y = mh, z = qh$, with $h$ the step of the grid and $l, m, n$ three integers smaller than $N$. With this convention the function $\phi_{l,m,n} = \phi(x,y,z)$ is written, using the Taylor formula, as

$$\phi_{l+1,m,n} = \phi_{l,m,n} + h \frac{\partial \phi_{l,m,n}}{\partial x} + \frac{h^2}{2} \frac{\partial^2 \phi_{l,m,n}}{\partial x^2} + \ldots$$

(1.24)

The same can be done for $\phi_{l-1,m,n}, \phi_{l+1,m,q}, \ldots$, i.e. the wave function in the other grid points. In this way we are able to easily write the derivatives of $\phi_{l,m,n}$ as function
1. Introduction

of the value of \( \phi \) in the other points of the multidimensional grid. As an example of how the problem is re-written in this formalism, let us consider the second derivative with respect to, e.g., \( x \). Through the finite difference representation one obtains,

\[
\frac{\partial^2 \phi_{l,m,q}}{\partial x^2} = \frac{2}{h^2} \phi_{l,m,q} - \frac{1}{h^2} \phi_{l-1,m,q} - \frac{1}{h^2} \phi_{l+1,m,q} + O \left( h^2 \right).
\]  

(1.25)

If we define the vector \( \phi \equiv [\phi_{1,1,1}, \ldots, \phi_{N-1,N-1}]^T \) to designate the \((N - 1)^3\) unknown values, we can re-write the equation \( H \phi = E \phi \) as \( A_H \phi = b \) where the vector \( b \) contains the boundary condition of the problem. In this thesis, this technique is applied to Dirichlet problems, i.e., problems for which the constraints for the wave function are expressed on the boundary. In particular, as I am generally looking for bound states, the wave function has to go to zero at infinity, i.e., \(|\vec{r}| \rightarrow \infty\) with \( \vec{r} = (x, y, z) \). In order to correctly approximate this behaviour I assume an asymptotic exponentially decreasing behaviour for the wave function. Considering more explicitly an Hamiltonian of the form \( H = \hbar^2 / 2m \sum \nabla_i + V(\vec{r}) \) the choice of boundary condition is

\[
\phi \sim \exp\left(-\sqrt{\frac{2m}{\hbar^2}} (V_0 - E) r^2 \right) = \exp[-\zeta]
\]  

(1.26)

with

\[
V_0 = \lim_{|r| \rightarrow \infty} V(|r|),
\]  

(1.27)

and

\[
\zeta = \sqrt{\frac{2m}{\hbar^2}} (V_0 - E) r^2.
\]  

(1.28)

This condition re-written in terms of the finite difference approach becomes \( \phi_{l+i,m,q} = \phi_{l,m,q} \exp \left( \zeta_{l,m,q} - \zeta_{l+i,m,q} \right) \), with \( l_i \) the number of mesh points in the \( x \) direction and \( \zeta_{l,m,q} \) is \( \zeta \) as defined in Eq.(1.28) relative to the position \( \vec{r} \) defined by the indices \((l,m,q)\) on the grid. The same boundary condition can be used, if instead of considering only the kinetic term, one considers the generalized momentum \( \vec{p} \), which eventually includes the magnetic field. At this point the problem is transformed into a diagonalization problem. To find the eigenvalues and eigenvectors of the matrix \( A_H \), one can think to use the inverse iteration technique. However, this approach is rather slow for large matrices. To accelerate the convergence of the diagonalization procedure one uses the Gauss-Siedel method. While using the Jacobi method the wave function at iteration \( k \) is found as a function of the wave function at iteration \( k-1 \) following the relation:

\[
\phi_i^k = \sum_j J_{ij} \phi_j^{k-1}
\]  

(1.29)
Figure 1.17: An example of a non uniform grid, with parameter $h$ and $a$.

where $J = I - A_H$ and $j = (l,m,q)$. In the Gauss-Seidel method, if the function in the grid point specified through the index $j$ has already been calculated at the iteration $k$, the new value will be used instead of the one from iteration $k - 1$. The error residual, difference between the wave function in a point between one iteration and the previous one, in the $k$-th iteration is

$$
\| e^k \| = J_{max}^2 \| e^{k-1} \|
$$

where $J_{max}$ is the maximum eigenvalue allowed for the matrix $J$. Nevertheless it is clear that such a technique can prove rather heavy and time consuming for large systems in which large matrices have to be solved.

Another problem intrinsic in the approach is the systematic introduction of an error of the order of $h^2$ for every spatial direction in which the calculation is made and for every particle. As I am dealing with Hydrogenic problems in which the interaction potential decreases slowly, $h$, which also defines the dimension of the grid cannot be taken too small, typically it is taken of the order of 0.1 a.u. Using such a value of $h$ we would obtain for a spatial three dimensional three particle problem and error of the order of $3 \times 3 \times 0.1^2 = 0.09$ a.u. on the energy which would be unacceptable when compared to the energies of the systems of interest in this thesis.

To partially resolve this problem, I have used in this thesis a non uniform space grid (see Ref. [84]) as it is shown in Fig. 1.17 for an unidimensional situation: a uniform part of the grid with points spaced by $h$ among each other and a non-uniform part whose spacing increases with $a^n$ where $a$ is the parameter of non-uniformity of the
grid. This choice allows, when possible to make a guess on the form of the solution, to have a large grid limiting the number of total points by having a larger density of points in the region were the wave function is expected to be more relevant and having a more sparse distribution of grid point as we move farther from the “relevant” region. This approach is particularly suitable when the wave function is expected to be localized around one point as for the charged donors or when the center of mass cannot be exactly separated.

Notice that the finite difference technique has been successfully applied in this thesis to quasi-two dimensional problems, i.e., problems in which the effect of the Coulomb interaction along the confined direction can be averaged out, but not neglected. In this case the Hamiltonian can be reduced to an effective two dimensional Hamiltonian. In the case of the charged donor this has especially been applied at first to the neutral donor Hamiltonian and subsequently to the charged donor Hamiltonian which was diagonalized on a basis of neutral donor wave functions. For an exact three dimensional problem consisting of 3 or 4 particle this technique becomes rather heavy and the error which is introduced increases unacceptably.

1.5.2 The Stochastic Variational Method (SVM) [89]

The variational method

When the exact way to diagonalize a given Hamiltonian is unknown, one way to find one of its solutions is to make a guess for its eigenfunction and see if it is correct. This is somehow the idea behind the variational method, however there are theorems which show us the way to proceed in our search for a good wave function.

The Ritz Theorem states that: for any function $\phi$ of the Hilbert space the mean value of the Hamiltonian, $H$, satisfies the relation $\langle \phi | H | \phi \rangle / \langle \phi | \phi \rangle \geq E_1$, where the equality holds if $\phi$ is eigenstate of $H$ with eigenvalue $E_1$, with $E_1$ the true value of the lowest eigenvalue of the given Hamiltonian. Moreover a generalized version of this theorem ensures us that the mean value of $H$ has a minimum around its eigenvalues. Thus, if we consider a function $\phi(\alpha)$, which depends on some parameter $\alpha$, the set of eigenvalues obtained for different values of $\alpha$ will define a function $E(\alpha)$. If $E(\alpha)$ has minima, they will be approximate values for the eigenvalues $E_n$. At least for the ground state, $E_1$, one knows that the estimated value is an upper limit to the true value of the ground state energy. If one makes sure that states relative to different minima are orthogonal to each other, it will also hold that the approximated eigenvalue $E(m)$ is an upper limit for the true value of the energy of the $m$-th excited state.

Consider the trial function to be of the following form,

$$
\psi(\alpha) = \sum_{i=1}^{K} C_i \Phi(\alpha_i),
$$

(1.31)
where $K$ is the number of independent states that we consider to write our eigenstates into, i.e. we restrict ourselves to a subspace of dimension $K$. In this case it can be proven that: if $E_1, \ldots, E_K$ are the first $K$ eigenvalues of the Hamiltonian $H$ and $\varepsilon_1, \ldots, \varepsilon_K$ are the $K$ eigenvalues of $H$ in the subspace of dimension $K$ defined by the functions $\Phi(\alpha_i)$, then $E_l \leq \varepsilon_l \quad \forall l \in \{1, \ldots, K\}$ (Mini-Max Theorem). It is also easy to show that if one considers a subspace of dimension $K+1$ one obtains a better approximation for the energy than considering a subspace of dimension $K$.

Choosing a wave function like in Eq. (1.31) and increasing the number of states which are included we can improve our approximation for the energy levels. But what can be said about the quality of the wave function? When we know the true eigenfunction $\Psi$ of an Hamiltonian $H$, the Virial Theorem ensures us that if $T$ is the kinetic part of the Hamiltonian and $V$ the part which expresses the interaction potential, then the equality

$$2 \langle \Psi | T | \Psi \rangle - \left\langle \Psi \left| \sum_{i=1}^{N} r_i \partial V/\partial r_i \right| \Psi \right\rangle = 0$$

holds. The quantity

$$2 \langle \Psi | T | \Psi \rangle / \left\langle \Psi \left| \sum_{i=1}^{N} r_i \partial V/\partial r_i \right| \Psi \right\rangle$$

is known as the virial of the system. If we apply the virial theorem to a system for which the potential $V$ is the Coulomb potential, it translates into the virial of the system being equal to $1$. Thus, for a system of particles interacting through the Coulomb potential we can assume that: the closer the virial, as calculated using our approximated wave function $\phi(\alpha)$ is to one, the better $\phi(\alpha)$ approximates the true eigenfunction.

The stochastic variational method

The choice of the functions $\Phi(\alpha_i)$ in (1.31) is called basis optimization and consists in choosing functions that meet the needs of our problem. Firstly, we want $\Phi(\alpha_i)$'s which are easily extended to an N-body problem. In fact we are going to treat excitons as well as charged excitons and biexcitons, and we would prefer not to modify too much our wave function from one case to the other. Secondly, the basis has to be flexible enough so that it can even approximate rapidly changing functions and that it can be easily adapted to satisfy the symmetries of our problem. On top of this we search for functions whose matrix elements of the Hamiltonian can be easily calculated, in order not to slow down the numerical calculation too much.

We choose the following functions
1. Introduction

where now instead of one variational parameter we have a tensor $\hat{A}$ of variational parameters, $\mathbf{r}_l$ is the vector position of the particle $l$ and $N$ is the total number of particles in the system. Such functions are a generalization of the well known correlated Gaussian functions. These functions are very often used in atomic and molecular physics [73, 74]. In the present work the possibility that the coupling between two particles depends on the spatial direction has been introduced. This generalization is much needed as we are going to study quantum well structures, which are for their nature anisotropic in space.

The wave function has to this point $3N(N - 1)/2$ parameters, e.g. which if $N=3$, like for the trions, it is 9, and if we need a basis set with dimension $K = 400$, we will have to solve a problem involving $3KN(N - 1)/2 = 3600$ variational parameters. The choice of those parameters can be made using a deterministic procedure or a stochastic procedure. The deterministic procedure, which is not used in the present work, always moves towards the same minimum given a starting point for the calculation and can prove to be very dangerous in the neighborhood of a local minimum. Deterministic algorithms are well-known and used already for a long time. They work very well when the form of the wave function is selected more ad hoc than it is done here.

If we want to find a global minimum in the presence of local minima, stochastic methods are better suited. The simplest way to perform a stochastic optimization is by trial and error. A range of values in which the parameters have to be chosen is assigned, in this space random points are picked up, trying to find the ones that give the minimum. This is the procedure we are going to use. This method has, unfortunately, the drawback that sometimes the dimension of the basis can be unjustifiably large. The dimension of the basis can be, in a second time, reduced by picking up the $K$ states which give the lowest estimate for the energy among the $K$ that form the basis.

Applying the random distribution method can, sometimes, prove too heavy because of the computational time required, if we intend to optimize the complete basis at each step. What the stochastic method does is to completely optimize a small initial basis set, i.e. $K = 20$, then add one by one the other basis functions. While increasing the number of basis states the optimization is only made for the last state added. In practice, to select the $K + 1$ state a number $n$ of different sets of parameters $\hat{A}_{k+1}^i$, $i = 1, \ldots, n$ is generated randomly. The energies $E_{k+1}^i$ corresponding to each parameter set are calculated. The set $\hat{A}_{k+1}^{m}$ which gives the lowest energy is selected. One, can then proceed to search for the state $K + 2$.

Notice that even if our problem involves typically 3600 variational parameter, all

$$
\Phi(\hat{A}_i) = \exp \left[ \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \mathbf{r}_i \cdot \hat{A}_{i,j} \cdot \mathbf{r}_j \right],
$$

(1.34)
Chapter III, IV

Chapter III, V

Chapter VI

1. Introduction

Figure 1.18: The different chapters of the present thesis deal with different numbers of interacting particles, starting with the three particle problem of the $D^-$, in which one particle can be considered at rest and ending with the four mobile particles problem of the biexciton.

the wave functions are chosen in such a way that all matrix elements of the Hamiltonian with the basis states can be calculated analytically. And that the diagonalization problem is reduced to the one of diagonalizing a $400 \times 400$ matrix, at most. The diagonalization is needed in order to find the coefficients of the linear combination in Eq. (1.31). Notice also that it is not really necessary to calculate all coefficients at each iteration step. In fact if the first $K$ states of the basis set are known. The eigenvalues can be found as roots of the equation:

$$E - h_{k+1} = \sum_{i=1}^{K} \frac{|h_i|^2}{E - \varepsilon_i}.$$  

(1.35)

where $h_i$ is the matrix element of the Hamiltonian between the state $i$ and the state $K + 1$ and $\varepsilon_i$ for $i = 1, \ldots, k$ are the first $K$ eigenvalues calculated with $K$ basis states [89].
1.6 Organization of the thesis

In this thesis the ground state and the lower excited states of different atomic-like systems in a quantum well are studied.

In the second chapter I present a calculation based on the finite difference method for the ground and excited states of the negatively charged donor in a quantum well with and without an applied magnetic field.

In the third chapter using the stochastic variational technique I calculated the ground state energy of the exciton and of the negatively and positively charged excitons in a quantum well at $B = 0$.

In the fourth and fifth chapter using the same approach used in the third chapter but modifying the wave function to include the angular dependence, I calculate, respectively, the behaviour of the negatively and positively charged exciton (also called “trion”) in a quantum well in the presence of a magnetic field along the confinement direction.

In the sixth chapter again using the stochastic variational method I study the behaviour of the biexciton system in a quantum well, taking into account the localization effect induced by the corrugation of the quantum well.
Chapter 2

Off-center $D^{-}$ centers in a quantum well in the presence of a perpendicular magnetic field.

In this chapter we investigate the effect of the position of the donor in the quantum well on the energy spectrum and the oscillator strength of the $D^{-}$ system in the presence of a perpendicular magnetic field. As a function of the magnetic field we find that when $D^{-}$ centers are placed sufficiently off-center they undergo singlet-triplet transitions which are similar to those found in many-electron parabolic quantum dots. The main difference is that the number of such transitions depends on the position of the donor and only a finite number of such singlet-triplet transitions are found as function of the strength of the magnetic field. For sufficiently large magnetic fields the two electrons system becomes unbound. For the near center $D^{-}$ system no singlet-triplet and no unbinding of the $D^{-}$ is found with increasing magnetic field. A magnetic field vs. donor position phase diagram is presented that depends on the width of the quantum well.

The results presented in this chapter were published in:

2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

2.1 Introduction

In multilayer and quantum well structures, such as GaAs/Al$_x$Ga$_{1-x}$As, the electrons bound to donor impurities situated in the barrier tend to migrate into the well, due to the favorable potential gap. There they are trapped by impurity donors, such as Si, that are naturally or artificially present in the material. The trapping of one electron by a donor does not completely screen the charge of the donor itself, thus bounded states of negative charged donors are possible in principle and in practice [33].

A great deal of attention has been given in recent years to the formation and stability of negative donor centers in semiconductors. Those systems, indeed, being the simplest many-body systems, represent an interesting occasion to study the electron-electron interactions in solids.

In previous experimental and theoretical studies the dependence of the binding energy of the $D^-$ on the magnetic field strength and on the dimension of the quantum well have been investigated. While a great part of these works consider the on-center $D^-$ problem [36, 35, 80], i.e., when the impurity donor is at the center of the well, the study of the off-center, i.e., when the impurity donor is displaced from the center of the well, and the barrier $D^-$ problem, i.e., when the donor is in the barrier, are much less investigated. On the theoretical side, Zhu and Xu [39] studied the spin-singlet $L=0$ and the spin-triplet $L=-1$ states for a quasi-2D $D^-$ while Fox and Larsen [40] studied the barrier $D^-$ in which the electrons are moving in a perfect 2D plane. The dependence of the properties of a $D^-$ system on the position of the donor with respect to the center has been partly investigated in Ref. [41]. The authors considered the problem of a double quantum well in which one of the two wells hosts, in its center, the donor, while the other contains the electrons. On the experimental side, we point out the work of Jiang et al. [8], in which experimental evidence of an off-center $D^-$ system was presented. All these studies on off-center and barrier $D^-$ show spin-singlet spin-triplet transitions of the ground state with increasing strength of the magnetic field. But the situation studied in previous works differs from the real problem of the off-center $D^-$. The work of Zhu and Xu [39] is most close to the real experimental situation but they studied only the first two states of the $D^-$ system. Such singlet-triplet transitions have also been observed in electron systems confined in quantum dots, and are known as magic magnetic number ground-state transitions [81]. In quantum dots the electrons are held together by a parabolic or hard wall confinement potential, which for the $D^-$ problem is replaced by the Coulomb potential of the donor impurity. Thus it seems that the appearance of singlet-triplet transitions is a characteristic feature of confined electronic systems, and in this paper we will shed more light on the condition under which such transitions appear in the $D^-$ system. The $D^-$ problem has the added flexibility that the singlet-triplet transition can be influenced by changing the position of the donor with respect to the center of the quantum well. It is even possible that for certain donor positions there is no singlet-triplet transition at all.

In the present paper we study the properties of the off-center $D^-$ as function of
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

the position of the donor in the well, and as function of the quantum-well width in the quasi-2D approximation. In Sec. 2.2 we present our model and explain how we obtain the wave function and energy of the different $D^0$ and $D^-$ levels. Next, in Sec. 2.3, we present and discuss the energy spectral behavior for quantum wells of width 200 Å and 100 Å. Then, we compare the results of the two calculations in order to have a better understanding of the reasons that underlie the different behaviors of the two energy spectra. Next, in Sec. 2.4, we evaluate and study the dependence of the oscillator strength and of the transition energies on the magnetic field and on the position of the donor with respect to the center of the well. In Sec. 2.5 we use our model to explain the cyclotron-resonance experiment of Jiang et al.[8]. Our conclusions are presented in Sec. 2.6.

2.2 The model

The properties of the off-center $D^-$ in a finite-height quantum well under the influence of a perpendicular magnetic field will be treated in the present paper. In the framework of the effective mass approximation the Hamiltonian of the $D^-$ system is given by

$$ H_{D^-} = H^D_1 + H^D_2 + V_{ee}(|\mathbf{r}_1 - \mathbf{r}_2|), $$

(2.1)

where $H^D_i$ is the Hamiltonian for the $i$-th one electron $D^0$ system and $V_{ee}$ is the electron-electron repulsive Coulomb interaction. Using cylindrical coordinates and the effective Bohr radius $a_B = \hbar^2 e_0/m^* e^2$, and the effective Rydberg $R_y = e^2/2\alpha a_B$, as units of length and energy, respectively, the neutral donor Hamiltonian $H^D_{D^-}$ and the electron-electron Coulomb potential assume the form

$$ H^D_i = -\nabla^2 + \gamma \frac{\partial}{\partial \phi_i} + \frac{1}{4} \frac{\gamma^2 r_i^2}{|\mathbf{r}_i - \zeta|^2} + V_{QW}(z), $$

(2.2)

$$ V_{ee}(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{2}{|\mathbf{r}_1 - \mathbf{r}_2|}, $$

(2.3)

where the vector potential is taken in the symmetric gauge $\mathbf{A} = \mathbf{r} \times \mathbf{B}/2$. The magnetic field is expressed in the dimensionless quantity $\gamma = \hbar \omega_c/2R_y$, with $\omega_c = eB/m^* e$ the cyclotron frequency; $\zeta$ is the position of the donor along the $z$ axis, as measured from the center of the well, and $V_{QW}(z)$ is the confining potential due to the quantum well of width $W$. For GaAs/Al$_x$Ga$_{1-x}$As with $x = 0.25$, we took $\epsilon = 12.5$, and obtain $a_B = 98.7$ Å, $R_y = 5.83$ meV, and $\gamma = 0.148B(T)$. We took the mass of the electron equal in the well and in the barrier, namely, $m^* = 0.067m_0$, and the height of the barrier is given by $V_b = 0.6 \times (1.155x + 0.37x^2)$ eV.

The strong confinement along the $z$ axis allows to neglect the correlation induced by the Coulomb interaction in the $z$-direction, thus we can write the wave functions
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

for the $D^-$ as follows

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1, \vec{r}_2) f_1(z_1) f_1(z_2), \quad (2.4)$$

with $f_1(z_i)$ the 1D ground state wave function for the electron confined in a quantum well of height $V_0$ [82].

The two-electron function $\psi(\vec{r}_1, \vec{r}_2)$ expresses the correlation between the two electrons, and is obtained by diagonalizing the Hamiltonian (2.1) in which the electron-electron $V_{ee}$ and the electron-donor $V_{ed}$ Coulomb interaction are replaced by their average along the $z$ axis, $V_{ee}(\vec{r}_1 - \vec{r}_2) = \int dz_1 \int dz_2 |f_1(z_1)|^2 |f_1(z_2)|^2 \frac{2}{\sqrt{(\vec{r}_1 - \vec{r}_2)^2 - (z_1 - z_2)^2}}, \quad (2.5)$

and

$$V_{ed}(\vec{r}_1 - \vec{r}_2) = \int dz |f_1(z)|^2 \frac{2}{\sqrt{\rho^2 + (z - \zeta)^2}}, \quad (2.6)$$

respectively. In a previous work [83] it was shown that in the case of hard wall confinement Eq. (2.5) can be replaced by the expression

$$V_{ee}(\vec{r}_1 - \vec{r}_2) = \frac{2}{\sqrt{2\pi} \lambda} e^{\frac{-|\vec{r}_1 - \vec{r}_2|^2}{4\lambda^2}} K_0(\frac{|\vec{r}_1 - \vec{r}_2|^2}{4\lambda^2}), \quad (2.7)$$

where $\lambda \approx 0.2W$ and $K_0(x)$ is the modified Bessel function of the third kind. In the present paper we use the same expression for a finite height quantum well in which $\lambda$ is determined by fitting Eq. (2.7) to Eq. (2.5). A comparison between the potential (2.5) that was evaluated numerically and the approximate expression (2.7) is shown in Fig. 2.1(a) for a quantum well of width $W = 200 \, \AA$ where the fitting parameter was found to be $\lambda = 0.607a_B$. On the other hand, no simple analytic approximation of Eq.(2.6) could be found. This is shown in Fig. 2.1(b) for an off-center donor with $\zeta = 0.7a_B$ and $W = 200 \, \AA$ where we compare Eq. (2.6) which we fitted to the potential (2.7) with $\lambda = 0.92a_B$ (solid curve) and the screened Coulomb potential $1/\sqrt{\rho^2 + \lambda^2}$ with $\lambda = 0.803a_B$ (dashed curve). None of the two fits give a good approximation to Eq. (2.6) in the small $\rho$ region. Therefore, in the Hamiltonian we retain the numerical expression for Eq. (2.6).

Using a finite difference technique, as explained in Ref. [84], the Schrödinger equation associated to the Hamiltonian (2.2) was numerically solved on a non uniform grid in $\rho$ space, and the eigenvalues and eigenvectors $R_{n_l} (\rho) e^{il\phi}$ for the $D^0$ were found for different values of $\zeta$ and arbitrary magnetic field strength. The eigenfunctions for the $D^-$ can then be constructed as a linear combination of the $D^0$ wave functions. Due to the rotational symmetry in the $\rho$-plane of the Hamiltonian (2.2),
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Figure 2.1: Comparison between the numerical evaluation and the analytical fitting of the average in-plane potentials for a quantum well of width $W = 200$ Å. In (a) the e-e potential (2.5) is fitted to Eq. (2.7) (dashed curve). In (b) the e-d potential (2.6) is fitted to Eq. (2.7) (solid curve) and to $1/\sqrt{\rho^2 + \lambda^2}$ (dashed curve).
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

The $z$-component of the orbital angular momentum, $L$, is a good quantum number for those functions, and therefore the $D^-$ wave functions are taken as

$$
\psi_L(\tilde{\rho}_1, \tilde{\rho}_2) = \sum_{k=k_m}^{k=+k_m} \sum_{n=n_m}^{n=+n_m} \sum_{l=l_m}^{l=+l_m} C_{kn}^l R_{n,(L+l)/2}(\rho_1) R_{k,(L-l)/2}(\rho_2) e^{i(k \phi_1 + \phi_2 + L(\phi_1 + \phi_2))/2},
$$

where $\sum'$ indicates the summation is only over even (odd) values of the index $l$ when $L$ is even (odd).

2.3 The energy spectrum

First we solve our model for an off-center donor in a GaAs/Al$_{0.3}$Ga$_{0.7}$As quantum well with width $W = 200$ Å ($\approx 2a_B$) and height of the potential barrier $V_0 = 0.23$eV. The dependence of the energy on the position of the donor with respect to the center of the well is investigated numerically.

The binding energy of the $D^-$ state, with $z$-component of the orbital angular momentum equal to $L$, is defined as

$$
E_n^B(D^-, L) = E_0(D^0, 0) + E(e, 0) - E_n^0(D^-, L),
$$

where $E_0(D^0, 0)$ is the energy of the ground state of the $D^0$ in the well, $E(e, 0) = \gamma$ is the energy of a free electron in the $N = 0$ Landau level and $E_n^0(D^-, L)$ is the $n$-th energy level of the $D^-$ with $L$ the $z$-component of the orbital angular momentum.

The results of our numerical calculation are plotted in Fig. 2.2 for $W = 200$ Å. The binding energies of the first $L=0$ state, a spin-singlet, and of the state $L=-1$, a spin-triplet, are plotted against the magnetic field for different positions, $\zeta$, of the donor with respect to the center of the well.

We note, first, that the binding energy decreases when the donor center is displaced from the center of the quantum well. The reason for this is that the electron-donor interaction decreases with increasing $\zeta$. This is because, due to the strong confinement along the growth axis of the well, the electrons tend, even in the case of an off-center donor system, to be localized in the center of the quantum well, although the donor is displaced at a distance $\zeta$ from the center.

A second feature to be noted is that the magnetic field dependence of the binding energy changes qualitatively with increasing $\zeta$. For sufficiently large $\zeta$, we find that $E_n^B(D^-, L)$ has a maximum, as function of $\gamma$. The binding energy starts to decrease after this maximum, and for sufficiently large $\gamma$ it can even become negative, indicating an unbinding of the $D^-$ state.

Third, in the absence of a magnetic field the ground state of the $D^-$ is, regardless of the position of the donor, the spin-singlet state. When increasing the magnetic field, the ground state for a well-center $D^-$, i.e., $\zeta = 0$, remains the singlet one. In
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Contrast, the ground state of the off-center $D^-$ with $\zeta > 0.45a_B$ shows a transition to a spin-triplet state for large enough magnetic fields. The magnetic field at which the singlet-triplet transition occurs depends on the position of the donor as it appears from Fig. 2.2. This dependence will be studied further below where it is found that the magnetic field at which the transition occurs decreases with increasing $\zeta$.

Fox and Larsen [40] investigated the ideal 2D problem, neglecting the finite extension of the electron wave function in the z-direction, i.e., $f_1(z) = \delta(z)$, and calculated the $D^-$ spectrum for a donor out of the plane in the limit of high magnetic fields and found an infinite number of singlet-triplet transitions. The situation for a quasi-2D off-center $D^-$ is quite different. In this case, in contrast to the 2D case, the extension of the electron wave function in the z-direction is taken into account, together with the finite height of the barrier. Let us investigate more deeply the behavior of the energy spectrum of such a system, with, e.g., $\zeta = 0.7a_B$. The results for the binding energy of the different levels, i.e., different angular momentum states, are shown in Fig. 2.3(a), for the case of a quantum well of width $W = 200$ Å. Note that different
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Figure 2.3: In (a) the binding energies for different values of the z-component of the angular momentum are shown for a $D^-$ with the donor placed at $\zeta = 0.7a_B \approx 70 \, \text{Å}$ from the center of the quantum well. In (b) the binding energies for a barrier $D^-$ are displayed, with $\zeta = 1.4a_B \approx 140 \, \text{Å}$. 
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Figure 2.4: Phase diagram for a quantum well of width $W = 200$ Å. The curves show the magnetic fields at which the singlet-triplet transitions occur for given position of the donor as well as the field at which the $D^-$ system evaporates.

transitions occur at higher magnetic fields. The ground state exhibits a singlet-triplet transition at $\gamma = 1.5$ and a triplet-singlet transition at $\gamma = 16.1$. For $\gamma > 22.7$, which corresponds to $B > 154 \text{T}$, the $D^-$ ground state unbinds, i.e., the $D^-$ magnetically evaporates.

While for the ideal 2D system an infinite number of singlet-triplet transitions are found for a quasi-2D system only a finite number of such transitions are possible as is clearly visible from Fig. 2.3(a,b). The critical $\gamma$’s at which the singlet $\leftrightarrow$ triplet transitions occur depend on the position of the donor [see Fig. 2.3(b)]. The $\gamma - \zeta$ phase diagram for the ground state of a quantum well of width $W = 200$ Å is given in Fig. 2.4. We found that for $\zeta < 0.45a_B$ the ground state is a singlet for all magnetic fields, for $0.45a_B < \zeta < 0.65a_B$ only one singlet-triplet transition (see Fig. 2.4) is possible and for $\zeta > 0.65a_B$ there are two such transitions. Increasing $\zeta$ further, such that the donor is in the barrier (i.e., $\zeta > 1.01a_B$), the number of singlet-triplet transition does not increase as illustrated in Fig. 2.3(b) for $D^-$ with $\zeta = 1.4a_B$.

The physical origin of the singlet-triplet transitions is related to the decrease of the electron-donor attraction with the displacement of the donor from the center of the well when compared to the constant electron-electron repulsion. The corresponding electron-donor and electron-electron in-plane potentials are shown in Fig. 2.5 for two values of $\zeta$. For small values of $\zeta$ (e.g., $\zeta = 0.$ in Fig. 2.5) the attractive single electron-
donor potential, is larger than the electron-electron potential and consequently the $D^-$ system "prefers" a configuration in which the two electrons are as close as possible to the donor in order to enhance the binding energy, i.e., the $L=0$ state is favored. When $\zeta$ is sufficiently large (e.g., $\zeta = 0.7a_B$ in Fig. 2.5) the repulsive electron-electron interaction dominates the attractive single-donor potential at small distances and the $D^-$ can have bound states only when the two electrons are sufficiently apart to render the repulsive inter-electrons interaction lower than or of the same order as the attractive electron-donor potential. For small magnetic fields this can still be realized in the $L=0$ state. Increasing the magnetic field brings the electrons closer to $\rho = 0$ which will also increase the electron-electron repulsive energy. For sufficiently small $\zeta$ this can still be compensated for by the attractive electron-donor energy. For $\zeta$ sufficiently large the electron-electron repulsive energy increases faster then the electron-donor energy with increasing $B$. The $D^-$ system can decrease its energy in this case by placing the electrons further apart, which is achieved by placing the electrons in higher $L$ states. Similar singlet-triplet transitions have recently been found in quantum dots systems [81, 84, 85]. The quantum dot system is an extreme case in which the electron-donor potential is replaced by the confinement potential which is usually taken of a quadratic form, i.e., $V_{cd} \propto \omega^2 \rho^2$.

In Fig. 2.6 the pair-correlation function $< \delta(\rho - |\vec{\rho}_1 - \vec{\rho}_2|) >$ is shown for the spin-singlet $L=0$ [Fig. 2.6(a)] and spin-triplet $L=-1$ [Fig. 2.6(b)] states for different values of the magnetic field for an on-center (i.e., $\zeta = 0$) $D^-$ system and an off-
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

![Graph](image)

Figure 2.6: The pair correlation function of the $D^-$. In (a) the correlation function of the spin-singlet $L=0$ state is presented for different values of the magnetic field both for the off-center (dotted curves) as well as for the center $D^-$ (solid curves). In (b) the same plot as in (a) is made but now for the spin-triplet $L=-1$ state.
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Figure 2.7: The binding energies for a $D^-$ with $\zeta = 0.7a_B$ in a 100Å quantum well, for different values of $L$. Four transitions occur before the $D^-$ system evaporates which occurs for $\gamma = 13.5$.

center (i.e., $\zeta = 0.7a_B$) $D^-$ system. The magnetic field behavior of the two states is essentially the same for both the center and the off-center $D^-$ system. The magnetic field tends to localize the wave function with increasing magnetic field. For the $L=0$ state the pair correlation function becomes more and more peaked at $\rho = 0$, which means that the electrons are closer and closer to each other with increasing magnetic fields. For the $L=-1$, the peak of the correlation function is shifted towards $\rho = 0$ with increasing $B$, and, thus, the magnetic field localizes the electrons further. The effect of the electron-electron repulsion can be seen in the shape of the correlation function itself. For the off-center system the pair-correlation function is broader than the one for the center $D^-$ system, even for increasing magnetic fields, and thus the electrons tend to repel each other more, which is a consequence of the diminished electron-donor interaction.

When the dimension of the well is reduced the localization of the electrons in the center of the well is increased. For example, if we neglect the penetration of the electrons in the barrier, the width of the $f_1(z)$ is equal to $L$. Thus the electron-electron repulsion increases and, at the same time, for the off-center case, the electron spends more time far from the position where the donor is located. Thus we expect that systems with a smaller well width will show more spin-singlet to spin-triplet transitions with increasing magnetic field, and that these transitions will occur at smaller fields.
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Indeed, for a $W = 100$ Å quantum well, with again $\zeta = 0.7a_B$, we observe (see Fig. 2.7) as much as 4 transitions before the $D^-$ evaporates at a magnetic field of $B \approx 81$ T (i.e., $\gamma \approx 12.0$). The full phase diagram for those transitions is shown in Fig. 2.8. The well width dependence of the singlet-triplet transitions and of the evaporation magnetic field are shown in Fig. 2.9 for $\zeta = 0.7a_B$. Notice that the critical magnetic field for the same transitions, e.g., for the spin-singlet $L=0$ to spin-triplet $L=-1$ state, decreases with decreasing well width. At the same time, the number of transitions increases. But the evaporation magnetic field first decreases and then, for $W < 140$ Å, increases again. An explanation of this feature is that other transitions are allowed for small well width and this ensure stability of the $D^-$ up to higher magnetic fields. The increase of the number of singlet-triplet transitions with decreasing dimensions of the quantum well, explains the larger number of transitions found by Larsen et al. [40] in the ideal 2D system with respect to the smaller number found in the present study of realistic quasi-2D systems.

2.4 Cyclotron resonance transitions

The oscillator strength for cyclotron transitions, in the present units, is defined as

$$F_{i,f} = (E_f - E_i) |\langle \Psi_f | \sum_j \frac{1}{2} \rho_j e^{\pm i\phi_j} |\Psi_f \rangle|^2$$

(2.10)
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure2.9}
\caption{The phase diagram for a fixed donor position, $\zeta = 0.7a_B$, as function of the well-width $W$.}
\end{figure}

\begin{align*}
E_f, E_i & \text{ are, respectively, the final and initial-state energies and } \psi_f, \psi_i \text{ are, respectively, the final and initial-state wave functions. The } \pm \text{ sign in Eq. (2.10) refers to circular left/right polarization of the light. Note that the perturbation induced by the electric field is spin-independent, thus the initial and final-states conserve the total spin, i.e., they are both spin-triplet or both spin-singlet states. Eq. (2.10) leads to the selection rules } \Delta L = \pm 1, \text{ while no selection rule is present for the quantum number } n. \\

\text{We have studied the oscillator strength for cyclotron resonance transitions from the first singlet } L=0 \text{ state } (n,L,S)=(1,0,0) - \text{ to the } (1,-1,0) \text{ and the } (1,1,0) \text{ states in the range } 2-15T. \text{ The transition energies and oscillator strengths, for } \zeta = 0.7a_B, \text{ are plotted in Fig. 2.10 against the magnetic field and are compared to the one for } \zeta = 0. \text{ We recall that for a two-electron atom the oscillator strength satisfies the sum-rule } \sum_i F_{ij} = 2. \text{ We observe that the off-center and the center } D^- \text{ have rather similar qualitative magnetic field dependence.}

\text{Cyclotron resonance transition from the ground state should show a discontinuous behavior in the cyclotron transition energies as a function of the magnetic field at the singlet-triplet transition points. In Fig. 2.11 the transition energies for a donor at position } \zeta = 0.85a_B \text{ are shown. Respectively, the transition energies for } (1,0,0) \rightarrow (1,1,0) \text{ and } (1,-1,1) \rightarrow (1,0,1) \text{ and } (1,-2,0) \rightarrow (1,-1,0) \text{ are plotted. The solid curve shows the transition energy which we expect to observe if the system makes a cyclotron resonance transition starting from the ground state. Thus steps in the cyclotron resonance energy should be observed at those magnetic fields at which the}
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Figure 2.10: The transition energies, (a), and the oscillator strengths, (b), for the $(1,0,0) \rightarrow (1,-1,0)$ and for the $(1,0,0) \rightarrow (1,1,0)$ transitions. The values for the donor placed at $\zeta = 0.7a_B$ are compared to the values for a well-center $D^-$. The dotted line is the free electron cyclotron transition energy, $\hbar \omega_c$. 

\[ \text{singlet } \zeta = 0 \]
\[ \zeta = 0.7a_B \sim 70 \, \text{Å} \]

L=0 $\rightarrow$ L=1
L=0 $\rightarrow$ L=-1

\[ B(\text{T}) \]

\[ F_{\omega} \]

\[ 0 \leq B(\text{T}) \leq 16 \]
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Figure 2.11: The cyclotron resonance transition energies for a donor at $\zeta = 0.85a_B$ are shown by the dashed curves for the first three lowest states. The solid curve represents the expected transition energy from the ground state as function of the magnetic field at zero temperature.

singlet-triplet transition takes place. In real experiments, as we will see later, not always transitions only from the ground state are seen in the neighborhood of the critical field which is due to the fact that in a real experiment the temperature is non zero. Indeed, when the old ground-state, i.e., the state that was before the transition the ground-state, and the new ground-state, i.e., the state that is after the transition the ground-state, have a comparable binding energy they can both be thermally populated.

2.5 Comparison with experiment

In this section we present a comparison between our theoretical results and the experimental data reported by Jiang et al. [8] The experiment of Jiang et al. was performed on multi-layers of GaAs/Al$_{0.3}$Ga$_{0.7}$As with well width of 200 Å and barrier width of 600 Å. Such a system can be considered as an ensemble of single quantum wells. The wells were nominally $\delta$-doped at 3/4 of the distance between the center of the well and its edge. In the model discussed in this paper this means that $\zeta = 0.75a_B$.

A comparison between the theoretical and the experimental transition energies is reported in Fig. 2.12. The observed transitions are the $D^0$ (1, 0) $\rightarrow$ (1, 1) and the $D^-$ singlet $(1, 0, 0) \rightarrow (1, 1, 0)$ and triplet $(1, -1, 1) \rightarrow (1, 0, 1)$ transitions. Our theoretical
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

![Graph](image)

Figure 2.12: The experimental data of Jiang et al. [8] for the cyclotron resonance transition energy (symbols) are compared to our theoretical results (curves), for the $D^0$ and the singlet and triplet $D^-$. The donor is at $\zeta = 0.75\alpha_B$ and the well width is $W = 200\text{Å}$.

Results are given by the three different curves. Note that our results fit well the data at low magnetic fields. The deviations between theory and experiment observed for $B > 9 \text{T}$ can be attributed to band non-parabolicity and polaron effects. Both effects decrease the transition energy [36] but are not taken in account in this paper.

In cyclotron resonance experiments the integrated absorption intensities can be measured. The integrated absorption intensities are proportional to the oscillator strength times the population densities of the levels involved in the transition. To compare our results with the experimental data we have to make an assumption on the form of the population density. We assume that only the initial level of the transition is populated. Thus for the off-center $D^-$ the population density of the level is proportional to $e^{E_B/kT}$, where $E_B$ is the binding energy of the initial state. We remark that for off center $D^-$ in this range of magnetic fields the energies of the triplet and the singlet states are comparable. For the well-center $D^-$, instead, we consider only the L=0 spin-singlet state to be populated, i.e., the population density is 1. The results for the relative integrated intensities of the singlet transition as evaluated in our calculation and the experimental results are plotted in Fig. 2.13 and are in good agreement, both for the well-center as well as for the off-center $D^-$. The temperature in the experiment was $T = 4.3 \text{ K}$. Note that the different magnetic field dependence for the center $D^-$ (i.e., increase with $B$) and for the off-center
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

Figure 2.13: Comparison of the relative integrated absorption intensity between the experimentally measured (symbols) and the present theoretical results (curves). The donor position is at $\zeta = 0.75a_B$. The dotted curve takes into account a displacement of the donor from the position at which the well is nominally $\delta$-doped, i.e., $\zeta = 0.7a_B$. $D^-$ (i.e., decrease with B) is correctly described. The errors bars for the off-center intensities are rather large. A slight discrepancy is observed at certain values of the magnetic field for the off-center $D^-$ but we observe that moving the donor in our model slightly closer to the center of the well, i.e., $\zeta = 0.7a_B$, the relative integrated intensity changes from the solid to the dotted curve in Fig. 2.13 and now matches the experimental data in the magnetic fields region in which there was not such a good agreement before. Thus the apparent discrepancy in the integrated intensity, with $\zeta = 0.75a_B$, in the range $5 – 14$ T is explained by considering a small distribution of donors around the point of intended $\delta$-doping.

2.6 Summary and Conclusion

We presented a theoretical study of the off-center $D^-$, where special attention was paid to the dependence of the binding energy on the well width and the donor position. We found that the magnetic field induces spin-singlet to spin-triplet transitions in the ground-state of the off-center $D^-$. The number of those transitions depends both on the position of the donor and on the width of the well. In contrast to the ideal 2D system and to quantum dots only a finite number of transitions are found. If the donor is near the center of the quantum well no such singlet-triplet transitions occur.
2. Off-center $D^-$ centers in a quantum well in the presence of a perpendicular magnetic field.

When such singlet-triplet transitions occur we find that at sufficiently large magnetic field the $D^-$ system becomes unbound and consequently one observes a magnetic evaporation of the $D^-$ system. We calculated also the oscillator strength for the off-center $D^-$ as function of the magnetic field and compared it to the results for a center $D^-$. We restrain ourselves to the study of the optical transitions $(1,0,0) \rightarrow (1,-1,0)$, $(1,0,0) \rightarrow (1,1,0)$, and we observed that the off-center and the center $D^-$ have similar magnetic behavior. Our results were used to explain the experimental results recently reported by Jiang et al. on the cyclotron resonance transition energy and the absorption intensity of the off-center $D^-$ system for magnetic fields up to $15 \, \text{T}$.

In conclusion, the $D^-$ center is a natural quantum dot system which is confined by the Coulomb potential of the impurity and consequently is more closely related to real atomic systems. A remarkable feature of the $D^-$ centers in quantum wells is the controllability of the effective confinement potential which is Platzmann-like for a donor in the center of the well and screened Coulomb-like when the donor is placed far away from the quantum well center. In the latter case the potential is parabolic near the center of the quantum well plane and thus resembles the confinement potential of quantum dots. In this case singlet-triplet transitions are found as function of the magnetic field. A crucial difference with the quantum dots is that only a finite number of such a transitions occur and that for sufficiently large magnetic fields the $D^-$ system becomes unbound, i.e., magnetically evaporates.
Chapter 3

Excitons and charged excitons in a semiconductor quantum well and in a magnetic field

A variational calculation of the ground state energy of neutral excitons and of positively and negatively charged excitons (trions) confined in a single quantum well is presented. We study the dependence of the correlation energy and of the binding energy on the well width and on the hole mass. The conditional probability distribution for positively and negatively charged excitons is obtained, providing information on the correlation and the charge distribution in the system. A comparison is made with available experimental data on trion binding energies in GaAs, ZnSe and CdTe based quantum well structures which indicates that trions become localized with decreasing quantum well width.

Part of the results presented in this chapter were published in:

3. Excitons and charged excitons in a semiconductor quantum well and in a magnetic field

3.1 Introduction

The stability of charged excitons in bulk semiconductors was proven theoretically by Lampert [20] in the late fifties. After the initial work by Lampert charged excitons in bulk semiconductors [44] as well as in an exactly two-dimensional (2D) configuration [45] were systematically studied theoretically. These studies revealed that, due to confinement, the 2D charged excitons have binding energies which are an order of magnitude larger than the charged excitons in the corresponding bulk materials. The increased binding energy in reduced dimensionality systems together with the improved experimental techniques has recently allowed the experimentalists to observe them in quantum well structures [9, 52, 48]. Recently, several theoretical works were published on charged excitons [86, ?, 87, 88] in a high magnetic field [61, 62] or in the presence of an electric field [63].

In our previous papers [87, 88] on charged exciton in quantum wells we have shown how using the stochastic variational method we could find the solution of our problem without making any approximation. We want to present here a calculation for the excitons and charged exciton in a uniform magnetic field, which uses the same technique.

In the present paper we study the $X^-$ and $X^+$ systems in a single quantum well (QW) with a finite height of the potential barrier in the presence of a magnetic field parallel to the quantum well axis, i.e., $z$-axis. In the first section we present the Hamiltonian of the problem. In the second section we discuss the dependence of the charged exciton correlation energy on the well width and on the hole mass. We compare our results with those of Stébé et al. [86], where a variational technique with a 66-terms Hylleraas trial wave function was used. In this section we also present our results for the binding energy of the $X^-$ and $X^+$ and we discuss the pair correlation functions and the probability density of the system. Our results are compared with available experimental data from the literature. In the last section we summarize our results and give our conclusions.

3.2 The model

In the effective mass approximation the Hamiltonian describing a charged exciton, i.e., $X^-$, in a uniform magnetic field $B$ applied along the $z$-axis is the Hamiltonian for a charged exciton in a quantum well and in the presence of a magnetic field is:

$$H = \sum_{i=1}^{N} \frac{1}{2m_i} (\mathbf{p}_i + \frac{e_i}{c} \mathbf{A}_i)^2 + \sum_{i=1}^{N} U(\mathbf{r}_i) + \sum_{i<j}^{N} \frac{e_i e_j}{\varepsilon |\mathbf{r}_i - \mathbf{r}_j|},$$

(3.1)

where $\mathbf{A}_i = \frac{e_i}{c} \mathbf{r}_i \times \mathbf{B}$, with $B$ the applied magnetic field; $m_i, e_i$ are the masses and charges of the interacting particles; $\varepsilon$ is the dielectric constant;

$$U(\mathbf{r}) = 0 \quad \text{if} \quad -W/2 < z < W/2 \quad \text{and} \quad U(\mathbf{r}) = U_0 \quad \text{if} \quad W < |z|,$$

(3.2)
3. Excitons and charged excitons in a semiconductor quantum well and in a magnetic field

where \( W \) is the quantum well width, and the reference systems is taken such as the quantum well axis is considered as \( z \) axis and the origin is at the center of the quantum well. If we consider the case where the magnetic field is applied along the growth axis of the well then the magnetic field is \( \mathbf{B} = (0,0,B) \), the Hamiltonian becomes:

\[
H = \sum_{i=1}^{N} \frac{1}{2m_i} \left( -\hbar^2 \Delta_i + \frac{e_i^2B^2}{4e^2}(x_i^2 + y_i^2) + \frac{e_i\hbar B}{c} z_i \right) + \sum_{i=1}^{N} U(r_i) + \sum_{i<j} \frac{e_ie_j}{\varepsilon r_{ij}},
\]

where \( l_zi \) is the component along \( z \) of the orbital momentum of the \( i \)-th particle.

From the Hamiltonian appears that it is possible to use atomic units, i.e. for the energy in \( 2R^* = \frac{\varepsilon^2}{\varepsilon_{\infty}} \) and for the length \( a^* = \frac{\hbar^2}{m^* \varepsilon} \). In the case of GaAs/AlGaAs \( \varepsilon = 12.5 \) and \( m^* = 0.067 m_0 \), thus \( 2R^* = 11.6 \) meV and \( a^* = 98.7 \) Å. The magnetic field can then be expressed using \( \gamma = \hbar \omega_c/2R^* = 0.148B \) with \( B \) measured in Tesla.

\[
\hat{H} = T_{1e} + T_{2e} + T_h + V_C + V_{1e} + V_{2e} + V_h,
\]

where \( 1e, 2e \) indicate the electrons and \( h \) the hole; \( V_{1e}, V_h \) are the quantum well confinement potentials; \( T_i \) is the kinetic energy operator for particle \( i \),

\[
T_i = \frac{\hat{p}_i^2}{2m_i},
\]

with \( m_i \) the mass of the \( i \)-th particle; \( V_C \) is the sum of the Coulomb electron-electron and electron-hole interactions,

\[
V_C = \frac{e^2}{\varepsilon} \left( \frac{1}{|r_{1e} - r_{2e}|} - \frac{1}{|r_{1e} - r_h|} - \frac{1}{|r_{2e} - r_h|} \right),
\]

with \( e \) the elementary charge and \( \varepsilon \) the static dielectric constant. For a GaAs/Al\(_{x}\)Ga\(_{1-x}\)As quantum well the heights of the square well confinement potentials are \( V_{1e} = 0.57 \times (1.155x + 0.37x^2) \) eV for the electrons and \( V_h = 0.43 \times (1.155x + 0.37x^2) \) eV for the hole.

The Hamiltonian is then solved using the stochastic variational method. The trial function, for the variational calculation, is taken as a linear combination of “deformed” correlated Gaussian functions,

\[
\phi_0(\vec{r}_{1e}, \vec{r}_{2e}, \vec{r}_h) = \sum_{n=1}^{K} C_n \Phi_{n0}(\vec{r}_{1e}, \vec{r}_{2e}, \vec{r}_h),
\]

\[
\Phi_{n0}(\vec{r}_{1e}, \vec{r}_{2e}, \vec{r}_h) = \mathcal{A} \left\{ \exp \left[ -\frac{1}{2} \sum_{\begin{subarray}{c} i,j \in \{1e, 2e, h\} \end{subarray}} A_{nij} \xi(1e, 2e, h) \right] \xi(1, 2, 3) \right\},
\]
where \( r_{ik} \) gives the position of the \( i \)-th particle in the direction \( k \); \( \mathcal{A} \) is the antisymmetrization operator and \( \{ C_{n0}, A_{nij0} \} \) are the variational parameters, and \( \xi(1, 2, 3, \ldots) \) is the spin function. The '0' in Eqs. (3.7) refers to the ground state. Note that in contrast with the "classical" correlated Gaussians here, the parameter \( A_{nij0} \) which expresses the correlation among the particle \( i \) and the particle \( j \) in the direction \( k \), is allowed to be different from the parameter \( A_{mij0} \) which couples the same two particle \( i \) and \( j \) in a different direction \( k' \). This additional degree of freedom in the calculation allows us to take into account the asymmetry introduced in the 3D space by the presence of the quantum well. The dimension of the basis, \( K \), is at first increased until the energy is accurate to the second digit, a typical value of \( K \) in this calculation is \( 300 \), and then is refined to increase the accuracy. The refinement is made by replacing the \( n \)-th state with a new state, i.e. with a state built using new parameters \( C_{n0}, A_{nij0} \) in such a way that it lowers the total energy. The process is reiterated multiple times for all the \( K \) states, until the energy reaches the desired accuracy. One can get faster convergence by taking into account the cylindrical symmetry choosing \( A_{nij0} = A_{mij0} \).

### 3.3 Theoretical results

The correlation energy of a charged exciton is defined as

\[
E_C(X^-) = E(X^-) - 2E_e - E_h, \quad (3.8)
\]
\[
E_C(X^+) = E(X^+) - 2E_h - E_e, \quad (3.9)
\]

with \( E(X^\pm) \) the energy level of the charged exciton and \( E_e \) and \( E_h \) the energy levels of the free electron and hole, respectively, in the quantum well. Thus, \( E_C \) is the energy due to the Coulomb interaction between the charged particles. We discuss here the results obtained for a GaAs/Al\(_x\)Ga\(_{1-x}\)As quantum well with \( x = 0.3 \), where the value of the masses used are \( m_e = 0.0667m_0, m_{hh} = 0.34m_0 \), i.e. GaAs masses, with \( R_y = h/m_e a_B = 5.79 \) meV, the donor effective Rydberg, and \( a_B = \hbar^2/\epsilon m_e e^2 = 99.7 \) Å, the donor effective Bohr radius. The results for the correlation energy of the exciton and the \( X^- \) are shown in Fig. 3.1 and compared with the theoretical results of others. We observe that the correlation energy of the exciton, \( E_C(X) = E(X) - 2E_h - E_e \), (dotted line in Fig. 3.1) increases in absolute value for well widths up to \( L = 30\) Å, where it reaches a minimum \( E_C(X) = -11.7 \) meV. For \( L < 30\) Å and with decreasing \( L \) the exciton correlation energy decreases in magnitude due to the fact that the electron, and to a lesser extent, the hole wave functions spill over into the barrier material of the quantum well. Consequently the exciton becomes more extended in the z-direction and the Coulomb interaction among the particles is diminished. At \( L = 0 \) we obtain \( E_C(X) = -4.80 \) meV which compares with the correlation energy of an exciton in bulk GaAs, i.e. \( E_C^{DP}(X) = -4.84 \) meV. For \( L > 30\) Å and increasing \( L \) the correlation energy decreases in magnitude with \( L \), which is due to the fact that the
3. Excitons and charged excitons in a semiconductor quantum well and in a magnetic field

The correlation energy of the exciton and the negatively charged exciton vs. the quantum well width.

Figure 3.1: The correlation energy of the exciton and the negative charged exciton vs. the quantum well width.

The correlation energy of the negatively charged exciton has the same qualitative L-dependence as the exciton. It reaches a minimum at about 30 Å with $E_C(X^-) = -13.2$ meV. For $L > 30$ Å it proceeds almost parallel to $E_C(X)$, in the region shown. For the $X^-$ we obtain $E_C^{3D}(X^-) = -4.95$ meV as 3D correlation energy.

We compare our results for the $X$ in GaAs/Al$_{0.3}$Ga$_{0.7}$As to the ones reported in Ref. [90] (short-dashed curve in Fig. 3.1), which are derived using the theory in Ref. [91]. The theory of Andreani and Pasquarello [91] also includes the non-isotropy of the masses, the non-parabolicity of the conduction band and the dielectric constant mismatch. Moreover the values for the heights of the potential barrier used are slightly different with respect to ours. However, a comparison between the two calculations can still be made. We observe that our results and the ones in Ref. [90], are very close in the range 70-120 Å. For $L < 70$ Å, our values for the correlation energy are much smaller, in absolute value, than the ones reported in Ref. [90], which is due to the band non-parabolicity which is known from Ref. [91] to be the major factor responsible for
the steep decrease of the correlation energy at small quantum well widths. We want now to estimate, although in a naive way, the effect of band non-parabolicity on our results. From Ref. [91] we estimate that for a quantum well \( L=30 \text{Å} \), and \( x=0.3 \) the parallel mass of the electron is about \( 0.08m_0 \). If we consider, in a very simplified picture, that: a) the contribution to the correlation energy strongly depends on the mass along the growth direction, namely the confinement energy, which has been subtracted out in the correlation energy, and that b) the energy of the exciton is largely dominated by the mass of the electron, through the change in the Rydberg which re-scales the energy. Such a procedure gives \( E_C = -13.9 \text{ meV} \), for the case of a quantum well of width \( L=30 \text{Å} \), which compares very well with the value \(-14 \text{ meV}\) given for a quantum well of width \( L=27 \text{Å} \) in Ref. [90].

Both for the cases of an X and of an X\(^-\) in a GaAs/Al\(_{0.3}\)Ga\(_{0.7}\)As quantum well we compare our results to the one obtained in Ref. [86]. Our calculation gives qualitatively the same correlation energy both for the X and for the X\(^-\) as compared to the one given by Stébé et al.[86] However while for the exciton we find that the correlation energy is lower than the one obtained in Ref. [86], thus indicating that the Coulomb correlation is more fully included in our approach, for the negatively charged exciton our approach gives a higher correlation energy (about 4\% for \( L=100 \text{Å} \)). The latter can be understood as follows: in Ref. [86] the Coulomb potential along the \( z\)-direction was approximated by an analytical form and Hylleras-type functions were used for the wave function. They calculated the Coulomb potential matrix between any two basis states \((s_1, s_2)\) by integrating it over the \( p\)-plane thus obtaining a potential matrix \( V_{s_1,s_2}(z) \). Then \( V_{s_1,s_2}(z) \) was replaced by the analytical expression

\[
-\gamma/|\delta + |z_1e - z_2e|\rangle - \gamma/|\delta + |z_1e - z_2e|\rangle + \gamma/|\beta + |z_1e - z_2e|\rangle
\]

where \( \gamma, \delta \) and \( \beta \) were determined in such a way that it reproduces the correct behavior of the Coulomb potential matrix in the limit of zero and infinite distance between the particles in the \( z\)-direction. This approximation leads, as the authors of Ref. [86] noted, to an error in the exciton correlation energy which was estimated to increase its absolute value by approximately 5\%. Our present results for the exciton energy are about 8\% lower than those of Stébé et al.[86] For the charged exciton energy the authors of Ref.[86] did not report an estimate of the error which was introduced through the approximations made. However, we find a smaller correlation energy of about 4\% as compared to those of Ref. [86]. We think that this result is not in conflict with the one obtained for the exciton. Indeed, while in the exciton case in Ref. [86] only the attractive interaction between the electron and hole was underestimated, for the charged exciton case the repulsive interaction between the electrons will also be underestimated. The difference is that the former interaction has the effect of increasing the bonding of the particle while the latter has the effect to diminish it. Our result indicates that a larger error is made in the electron-electron repulsive interaction in Ref. [86] as compared to the error in the electron-hole attractive interaction.

The approximation by Stébé et al.[86] consisted in averaging the wave function in the \( xy\)-plane in order to find an effective Hamiltonian describing the exciton and
the trion in the z-direction. This is similar to an adiabatic approximation which is valid when the motion in the xy-plane is faster than the one in the z-direction. We believe that it is more natural to do the reverse and average over the particle motion in the z-direction which is due to the quantum well confinement and which will be much faster. Such an approach is equivalent to neglect the particle-particle correlation along the z-direction which we expect to be valid when \( E_{e(h)} \gg E_{C}^{X^-} \). For both the exciton and the trion this relation is satisfied for \( L < 150 \, \text{Å} \). Averaging Eq. (3.4) over \( z \) we obtained an effective 2D Hamiltonian, in which the effective Coulomb potential was replaced by the analytical form \( \frac{e^2}{\epsilon} \left( \lambda + (\vec{p}_i - \vec{p}_j)^2 \right)^{1/2} \), where \( \lambda \) was obtained by fitting this analytical form to the numerical results for the effective Coulomb interaction. The correlation energy for the exciton and the charged exciton is in this case lower than the one we obtain with our more exact calculation presented above, e.g. in the frame of the model presented in this paper we find \( E_C(X) = -10.1 \, \text{meV} \) and \( E_C(X^-) = -10.9 \, \text{meV} \) for a 100 Å wide quantum well, and \( E_C(X) = -10.7 \, \text{meV} \) and \( E_C(X^-) = -11.6 \, \text{meV} \) for a 80 Å wide quantum well, while using the screened 2D Coulomb potential we found \( E_C(X) = -10.4 \, \text{meV} \) and \( E_C(X^-) = -11.4 \, \text{meV} \) for a 100 Å wide quantum well and \( E_C(X) = -11 \, \text{meV} \) and \( E_C(X^-) = -12.2 \, \text{meV} \) for a 80 Å wide quantum well. Consequently, such an approach leads to larger correlation energies and also to slightly larger binding energies.

In Fig. 3.1 we also report the result of a simplified model (open diamonds) for the study of the energy of a trion which we proposed in Ref. [55]. This model is derived from the one used for a D^- system[7] and it assumes that the hole is fixed at the center of the well, i.e. it has an infinite mass. The effect of the hole is reflected in the renormalization of the mass of the electron, i.e. \( m_{e} \) is replaced by the reduced mass \( \mu = m_{e} m_{h} / (m_{e} + m_{h}) \). This model gives for the correlation energy of the charged exciton results that are, at first, surprisingly close to the one obtained by Stébé et al., [86] at least down to well widths of about 40 Å. This seems to suggest that the procedure of averaging the potential in the plane adopted in Ref. [86] is almost equivalent to localize the hole in the \( p \)-plane. For smaller well width the magnitude of the correlation energy becomes much larger as compared both to our present result and to the one of Ref. [86]. As shown in Fig. 3.1 the result we obtain in the \( L=0 \)-limit is dramatically different from the one found in the present work: \( E_C = -3.2 \, \text{meV} \). The reason is that for small well widths the hole may no longer be considered as a "fixed" particle and the penetration of the hole in the barrier can no longer be neglected.

To prove further the accuracy of our calculation and to check the quality of our wave function for the \( X^- \) we calculated the virial which is defined as

\[
v = 2 \frac{\langle \phi_N | T | \phi_N \rangle}{\langle \phi_N | W | \phi_N \rangle},
\]

with \( T \) the total kinetic energy operator and \( W = \sum_{i=1}^{N} r_i \partial V / \partial r_i \). It is known[12] that for a system of particles interacting through the Coulomb interaction this quantity has to be 1 for the exact wave function. We obtained a value of 0.999 for almost
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Figure 3.2: The correlation energy of the negative charged exciton vs. the quantum well width, for the case of constant masses in the well and in the barrier, and for the case of different electron and hole masses in the well and in the barrier of a GaAs/Al0.3Ga0.7As quantum well. In the inset the wave function for both the electron and the hole are shown.

all the quantum well widths studied, which suggests that our wave function is well chosen.

Next we investigate the effect of taking a different mass of the particles in the well (GaAs) and in the barrier (AlxGa1−xAs) material, which is expected to be important in the narrow well regime where the electron and hole wave functions penetrate into the barrier (see inset of Fig. 3.2). The values for the GaAs-masses, i.e. the masses for the electron and the hole, are taken equal to the one used in the previous calculation. The values for the masses in AlxGa1−xAs are $m^*_e = 0.067 + 0.083x$, $m^*_h = 0.34 + 0.42x$, where $x$ indicates the percentage of Al present in the alloy. If we assume, as a first approximation, that part of the electron and the hole wave function is in the quantum well and the rest is in the barrier we may take the total effective mass of
the electron and the hole as given by
\[
\frac{1}{m_i} = \frac{P_{iw}}{m_{iw}} + \frac{P_{ib}}{m_{ib}},
\]
(3.10)
where \(m_{iw}, m_{ib}\) are the masses of the \(i\)-th particle in the barrier and in the well, and \(P_{iw}, P_{ib}\) are the probabilities of finding the \(i\)-th particle in the well and in the barrier, respectively. The results of this calculation are shown in Fig. 3.2 for \(x = 0.3\). The correlation energy increases in absolute value and this is consistent with the fact that the effective masses are now larger. The effect of the mass mismatch is important only in the narrow quantum well regime, i.e. \(L < 40 \text{ Å}\), where it leads to a substantial increase of the magnitude of the correlation energy. In the \(L=0\) limit we obtain now \(E_C(X^-) = -7.5\text{ meV}\) which compares to the 3D correlation energy of a trion in Al\(_{0.3}\)Ga\(_{0.7}\)As which we found to be \(E_C^D(X^-) = -6.6\text{ meV}\). The minimum of the correlation energy is now obtained at \(L=17 \text{ Å}\).

We also studied the dependence of the total energy on the hole mass for a \(100 \text{ Å}\) and a \(200 \text{ Å}\) wide quantum well. The result, reported in Fig. 3.11, shows that the total energy decreases as the hole mass increases. The energy of the negatively charged exciton approaches the energy of the \(D^-\) in the same quantum well from above and they become practically equal when \(m_b/m_e > 16\) for the \(200 \text{ Å}\) quantum well. Note that for large values of the hole mass the \(X^+\) energy is practically parallel to the one of the \(X^-\). In fact, if the hole mass is large its confinement energy contribution to the total energy is negligible, and the difference between the \(X^+\) and \(X^-\) total energies is just the confinement energy of one electron, which of course does not depend on the hole mass.

Next we studied the correlation energy of the positively charged exciton. In Fig. 3.3 we plot the correlation energy of the \(X^-\) and \(X^+\) systems as function of the well width. Note that the correlation energy of the \(X^+\) is equal to the one of \(X^-\) (within the numerical accuracy). This is in agreement with recent experimental data[52] where the binding energy of the \(X^+\) was found to be equal to the one of the \(X^-\). In fact we have
\[
E_C(X^-) - E_C(X^+) = E(X^-) - E_e + E_h - E(X^+)
= [E(X^-) - E(X)] - [E(X^+) - E(X) - E_h]
= E_B(X^-) - E_B(X^+),
\]
(3.11)
where \(E_B(X^\pm)\) is the binding energy of a charged exciton system referred to the one of the exciton plus one free electron (hole) system,
\[
E_B(X^\pm) = E(X) + E_{e(h)} - E(X^\pm),
\]
(3.12)
where \(E(X)\) is the energy of the exciton, \(E_{e(h)}\) is the energy of the free electron (hole) and \(E(X^\pm)\) is the charged exciton total energy. Consequently, if the \(X^-\) and the \(X^+\)
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Figure 3.3: The correlation energy of the negatively charged exciton (symbols) and the one of the positively charged exciton (solid curve) vs. the well width. The correlation energy of the exciton (dotted curve) is given as reference.

correlation energy are the same, the corresponding binding energies will also be the same.

Last we study the wave function of the negatively and positively charged exciton and the correlation between the different particles. The pair correlation function, \( g_{ij}^{2D}(r) = \langle \delta (r - |r_i - r_j|) \rangle \), for a 100 Å wide quantum well is shown in Fig. 3.4. This function gives the probability to find particle \( i \) and particle \( j \) at a distance \( r \) from each other. Notice that \( g_{eh}^{2D}(r) \) is the same for both \( X^- \) and \( X^+ \) (dashed curve in Fig. 3.4) and in both cases the electron and the hole tend to be close to each other. A similar result is obtained for the exciton (dot-dashed curve in Fig. 3.4). The fact that the intensity of the correlation function for the exciton is higher than the one of the charged exciton is a direct consequence of the normalization of the wavefunction to one. The situation is very different for the correlation between particles having the same charge. For the \( X^- \) electrons \( g_{ee}^{2D}(r) \) (dotted curve in Fig. 3.4) shows that the two electrons avoid each other at small distances and have the highest probability of sitting at a distance of \( 25 \text{ Å} \approx a_B/4 \). For the holes in \( X^+ \) \( g_{hh}^{2D}(r) \) (solid curve
Figure 3.4: 3D pair correlation function for different pairs of particles in $X^-$ and in $X^+$ vs. the distance between the particles for a quantum well of width 100 Å. In the inset the 2D pair correlation function is shown. The curve convention is the same in the two plots.
in Fig. 3.4) shows that the two holes avoid each other at small distances and have
the highest probability of sitting at a distance of 80 Å ≈ 4a_B/5, thus farther from
each other than the electron-couple in X-. However the average distance, ⟨|r_i − r_j|⟩,
of the two electrons in X-, does not differ much from the average distance between
the holes in X+. We found 250 Å and 216 Å respectively. The average distance
between the electron and the hole is 150 Å and is found to be the same in the X-
and in the X+. In the inset of Fig. 3.4 we show the 2D-pair correlation function,
\[ g_{ij}^{2D}(\rho) = \langle \delta(\rho - |\tilde{\rho}_i - \tilde{\rho}_j|) \rangle, \]
for a 100 Å wide quantum well, where the same curve conventions are used as for the 3D pair correlation functions. These 2D correlation functions express more clearly the Coulomb correlation between the particles. In the 3D correlation functions the z-direction is still involved. In this direction the quantum well potential forces the particles towards the middle of the well. As a consequence all 2D correlation functions are more spread out as compared to their 3D counterpart. The peaks in the electron-electron and hole-hole correlation functions are shifted towards larger distances. The average distances in the \( \rho \)-plane of the electrons in X- and of the holes in X+ is \( \langle |\tilde{\rho}_i - \tilde{\rho}_j| \rangle = 249 \) Å and 214 Å respectively. This result differs only by a few angstroms as compared to the 3D result, suggesting that the charged exciton, for \( L=100 \) Å , is almost bidimensional.

We now look at the 2D correlation function for different well widths (see Fig. 3.5). Notice that the peak of the correlation function for the electron-electron couple in X- slowly shifts towards smaller distances as the well width decreases (see Fig. 3.5(a)), at the same time the tail of the function becomes smaller. The peak of the electron-hole correlation function also increases (see Fig. 3.5(b)) but is still centered around zero. With decreasing well width the X- becomes less extended. A similar behavior was observed for X+.

In Fig. 3.6 we show the contour plots of \( |\phi_0(\tilde{r}_{1e}, \tilde{r}_{2e}, \tilde{r}_h)|^2 \) for a negatively charged exciton in a quantum well of width 100 Å, where lighter regions correspond to lower probability. In Figs. 3.6(a,b) we plot the projection of the electron probability density in the xy- and xz-plane when the hole is fixed at \( \tilde{r}_h = (0,0,0) \) and one of the two electrons is fixed at \( \tilde{r}_{1e} = (1.5a_B,0,0) \). The distance between the particles is equal to the average electron-hole distance in the X-. The two symbols show the positions of the two fixed particles. The second electron sits close to the hole and the fixed electron sees an exciton consisting of the hole-second electron couple. Notice, from Fig. 3.6(b), that the second electron slightly penetrates the barrier. In Figs. 3.6(c,d) we plot the projection of the probability density in the xy- and xz-plane when the hole is fixed at \( \tilde{r}_h = (0,0,0) \) and one of the two electrons is fixed at \( \tilde{r}_{1e} = (a_B,0,0) \). Thus, the distance between the electron and the hole is now smaller than the average distance. We observe that this situation does not present substantial differences with the one in which the particles are separated by the average distance.

In Fig. 3.7 we show the contour plots of \( |\phi_0(\tilde{r}_{1h}, \tilde{r}_{2e}, \tilde{r}_e)|^2 \) for a positively charged exciton in a quantum well of width 100 Å. In Figs. 3.7(a,b), we plot the projection of the electron probability density function on the xy- and the xz-plane where we fixed
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Figure 3.5: The pair correlation function for the electron-electron (a) and electron-hole (b) in X− for different quantum well widths.
Figure 3.6: Contour maps of the conditional probability for the $X^-$ in a quantum well of width $100 \text{Å} \approx a_B$. The fixed particles are indicated by symbols (circle with a cross for the hole and circle with a minus sign for the electron). The dotted lines indicate the quantum well boundaries.
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Figure 3.7: Contour maps of the conditional probability for the X\(^+\) in a quantum well of width 100 Å \(\approx a_B\). The fixed particles are indicated by symbols (circle with a cross for the hole and circle with a minus for the electron). The dotted lines indicate the quantum well boundaries.

the two holes at \(\vec{r}_{1h} = (0, 0, 0)\) and \(\vec{r}_{2h} = (2.2a_B, 0, 0)\). The distance between the holes is now equal to their average distance. We observe that even if the electron in the X\(^+\) has a higher probability of sitting on top of the two holes, it also has a comparable probability to sit between the two holes. This ensures the binding of the system. Notice also (see Fig. 3.7(b)) that the electron does slightly penetrate into the barrier, similarly to what happens for hole in the X\(^-\). In Fig. 3.7(c), we show again the projection of the probability density function on the xy-plane, where now the second hole is fixed at \(\vec{r}_{2h} = (1.5a_B, 0, 0)\). As in the case of the X\(^-\) we do not observe a substantial difference with the case in which the particles are separated by the average distance. In Fig. 3.7(d) we fix the position of the electron \(\vec{r}_e = (0, 0, 0)\) and the first hole \(\vec{r}_{1h} = (1.5a_B, 0, 0)\), such that the average distance is equal to the electron-hole pair average distance. The second hole is now centered around the electron which is the same as the behavior of the second electron in X\(^-\) (see Fig. 3.6(a)). We found that the contour plot of the probability density of finding the hole in a X\(^-\) at a position \(\vec{r}\)
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Figure 3.8: The wave function of the hole in X− when the two electrons are fixed (dotted curve) and of the electron in X+ when the two holes are fixed (dashed curve) along the direction [1,0,0]. The two solid dots indicate the two equally charged fixed particles.

when the two electrons are fixed, is practically the same as the one for the electron in the X+ with the two holes fixed (see Fig. 3.7(a)).

In Fig. 3.8 we show the wave function of the hole in X− and the electron in X+ along the x-axis when the two particles having the same charge are fixed (solid circles in Fig. 3.8). The trions are both in a singlet state, the spin part of the wave function is antisymmetric and consequently the spatial part of the wave function is symmetric for reflections around the mid-point between the two fixed particles. The reason is that the interchanging the two fixed particles must result in a sign change of the wave function. Remark that the electron in X+ is slightly more localized on the two holes as compared to the hole in X− which is spread out over the two electrons.

For the nature of the wavefunction between the two fixed particle it seems reasonable to conclude that the interaction between the three particles can be viewed as "chemical bonding"-like. It seems then reasonable to say that in the same way in which the X− can be described as an exciton with an extra electron moving around
the electron-hole couple and weakly bound to it, the $X^+$ can be viewed as an exciton in which an extra hole moves in an orbit around the electron-hole couple. The latter picture is different from a system in which two holes bind through an electron, i.e. $H_2^+$-like. Another confirmation for this picture comes from the pair correlation functions. Suppose that the electron, for $X^-$, is in the origin, then the hole will be near the origin as indicated by the electron-hole correlation function and the other electron will be situated around the position of the peak in the electron-electron pair correlation function. So the picture we get is an electron-hole pair with an extra electron moving around it. If we switch the role of hole and electron, a similar picture can be imagined for the $X^+$, with the only difference being that now the extra hole sits even further from the electron-hole couple than in the $X^-$. Thus, the charged exciton is similar to the charged positron. The similarity in the structure of the two different species of charged excitons is consistent with the fact that their correlation energy is found to be equal.

3.4 Comparison with experiments

Experimental data in zero magnetic field were reported for the binding energy of the $X^-$ in a 100 Å [93], 200 Å [52], 220 Å [?] and in a 300 Å [?] quantum well. The reported values are 2.1, 1.15, 1.1±0.1 and 0.9±0.1 meV respectively and are compared in Fig. 3.9 with our theoretical results. The value of $E_B = 2$ meV for a 80 Å well is for a GaAs/AlAs quantum well and was measured by Yan et al.[47]. The theoretical results for the binding energy are represented by a shaded region which gives the accuracy of our calculation for the binding energy. Note that the accuracy obtained for the total energy is better than 1%, however, its error propagates and increases because of the subtractions (see Eq. (3.12)) which have to be made in order to obtain the binding energy, which is one order of magnitude lower than the total energy. An important consequence of this observation is that any approximation made in the calculation of $E(X^\pm)$ may lead to substantial errors in the binding energy. For comparison we also report (open squares) the theoretical result obtained by Tsuchiya and Katayama[94] using the quantum Monte Carlo method. Notice that the results of Ref.[94] agree very well with ours, however our calculation goes down to smaller well width. The binding energy first increases with increasing quantum well width and then, after reaching a maximum of $E_B = 1.6$ meV at $L \approx 35$ Å starts to decrease. The decrease becomes very slow for quantum well width above 70Å. The increase of the binding energy with decreasing quantum well width agrees qualitatively with the experimental data, but the experimental increase is much faster than the one we find theoretically. The inclusion of the conduction band non-parabolicity would increase the binding energy only slightly. We believe that the increased discrepancy between theory and experiment with decreasing well width is a consequence of the localization of the trion due to the presence of quantum well width fluctuations, as was also found for biexcitons[95, 96]. This is consistent with the fact that for $L=300\text{Å}$
our result agrees with the experiments and that the effect of the quantum well width modulation on the localization of the exciton and the trion increases with decreasing well width.

A similar calculation was done for CdTe quantum well structures (Fig. 3.10(a)) and ZnSe based quantum well structures (Fig. 3.10(b)). The binding energy versus the well width in these materials is shown in Figs. 3.10(a,b) (solid curve) and is compared to experimental data [9, 53, 56] (symbols in Figs. 3.10(a,b)). The parameters used in the calculation for CdTe based structures are \( V_e = 216.4 \) meV, \( V_h = 163 \) meV, \( m_e = 0.096m_0 \), \( m_h = 0.19m_0 \), \( a_B = 54 \) Å, which results into \( R_y = 13.8 \) meV. The value of the parameters are taken from Ref. [53]. Notice that for this structure we have the same potential barrier heights than for the GaAs case, however the ratio between the mass of the electron and the mass of the hole is very different, namely \( m_e/m_h = 0.505 \) (CdTe) as compared to \( m_e/m_h = 0.196 \) (GaAs). In the range \( 200 \) Å \( < L < 600 \) Å the theoretical curve is shifted by about 1 meV with respect to the experimental results. Below \( 200 \) Å the experimental results increase faster with decreasing \( L \) as compared to the experimental data which is probably a consequence of the above mentioned increased localization of the trion.

For the ZnSe structure we use the parameters of the ZnSe/ZnBeMgSe structures, \( \Delta V = 230 \) meV with \( V_e = 0.70\Delta V \), \( V_h = 0.30\Delta V \), \( m_e = 0.16m_0 \), \( m_h = 0.8m_0 \), \( a_B = 30.05 \) Å, which results in \( R_y = 53.34 \) meV. The results are qualitatively similar to the one obtained for the GaAs/AlGaAs quantum wells. The agreement with experiment is also in this case not satisfactory (see Fig. 3.10(b)) except for the 200 Å wide quantum well.

To understand the fact that the theoretical results for CdTe- and ZnSe-based structures underestimate so much the experimental data even for large well widths, we have to take into account that these materials are strongly polar. In the present work we are neglecting polaronic effects and it is known, at least for the case of excitons, that this leads to an underestimation of the binding energy of the system [97]. Currently only a calculation of the polaron correction to the ground state of a D− system is available[109] but no calculation for the trion system has been published. For the D− system we know that the polaron correction equals the 3D polaron correction down to rather small well widths. When, we shift the results in Figs. 3.10(a,b) by the constant values \( 1.1 \) meV and \( 1.6 \) meV, respectively (dotted curve in Figs. 3.10(a,b)), they agree very well with the experimental results over a large range of quantum well widths. We believe that these shifts are due to polaron effects. Shi et al.[109] obtained an upper limit of \( \approx 0.4a\alpha\hbar\omega_{LO} \) to the polaron contribution to the binding energy of the D− system in a wide quantum well (\( \alpha \) is the electron-phonon coupling constant and \( \hbar\omega_{LO} \) is the optical phonon energy). In an X− system the hole is not localized which will strongly reduce the polaron effect to an estimated value of \( 0.1 \)-\( 0.2 \) \( a\alpha\hbar\omega_{LO} \). For CdTe quantum wells with \( \alpha = 0.3 \) and \( \hbar\omega_{LO} = 21.1 \) meV this gives \( 0.6 \)-\( 1.2 \) meV while for ZnSe[98] we have \( \alpha = 0.42 \) and \( \hbar\omega_{LO} = 31.5 \) meV and consequently \( 1.3 \)-\( 2.6 \) meV. These value are comparable to the shifts in Fig. 3.10(a,b), and agree with the
fact that the shifts for the ZnSe quantum wells is larger than for CdTe quantum wells.

3.5 Conclusion

In this paper we applied the stochastic variational method to study the ground state of the exciton and the charged exciton in a quantum well. This is the first time, to our knowledge, that a calculation fully includes the effect of the Coulomb interaction and the confinement due to the quantum well, and thus the particle-particle correlation in both the direction of the quantum well and the confinement direction. The results obtained do not show a big qualitative difference from the one already present in the literature, however substantial quantitative differences are found. This difference leads to an improvement in the agreement with experimental data. However, the experimentally measured binding energy for a negatively charged exciton increases much faster with increasing well width at small well width than our theoretical results. We believe that this discrepancy is a consequence of the increased localization of the exciton and trion with decreasing well width. A similar conclusion was also reached recently for biexcitons [96, 95]. For CdTe- and ZnSe-based quantum wells the polaron effect, which was not included in our approach, is expected to lead to a substantial shift (≈ 1 meV) of the binding energy to larger values. Also in this case the trapping of the trions on the quantum well width fluctuations is probably responsible for the rapid increase of the trion binding energy below L ≈ 100 Å. The study of the conditional probability distribution of the particles in the system and of the pair correlation functions lead us to conclude that a charged exciton is similar to a charged positron. This conclusion is important as it supports the fact that the correlation energy for X− and X+ is found to be equal.

3.6 Acknowledgment

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Figure 3.9: The theoretical (shaded curve) and experimental (open circles) binding energies of the negatively charged exciton in a GaAs/AlGaAs quantum well vs. the well width. The theoretical results of the quantum Monte Carlo calculation of Ref. 22 are shown by the open squares.
3. Excitons and charged excitons in a semiconductor quantum well and in a magnetic field

![Graph showing energy levels as a function of well width](image_url)
Figure 3.11: The total energy of the negative charged exciton and the positive charged exciton vs. $m_h/m_e$ for a 200 Å wide quantum well and for a quantum well of width 100 Å (inset). The total energy of a $D^-$ in the same quantum well is given by the dash-dotted line for comparison.
Chapter 4

Magnetic field dependence of the energy of negatively charged excitons in semiconductor quantum wells.

A variational calculation of the spin-singlet and spin-triplet state of a negatively charged exciton (trion) confined to a single quantum well and in the presence of a perpendicular magnetic field is presented. We calculated the probability density and the pair correlation function of the singlet and triplet trion states. The dependence of the energy levels and of the binding energy on the well width and on the magnetic field strength was investigated. We compared our results with the available experimental data on GaAs/AlGaAs quantum wells and find that in the low magnetic field region ($B < 18$ T) the observed transition are those of the singlet and the dark triplet trion (with angular momentum $L_z = -1$), while for high magnetic fields ($B > 25$ T) the dark trion becomes optically inactive and possibly a transition to a bright triplet trion (angular momentum $L_z = 0$) state is observed.

The results presented in this chapter were published in:

4. Magnetic field dependence of the energy of negatively charged excitons in semiconductor quantum wells.

4.1 Introduction

After the initial work by Lampert [20], who proved the stability of the charged exciton complexes, charged excitons in bulk semiconductors [44] as well as in an exactly two-dimensional (2D) configuration [45] were studied theoretically. These studies revealed that, due to the confinement, the 2D charged excitons have binding energies which are an order of magnitude larger than charged excitons in the corresponding bulk materials. The increased binding energy in reduced dimensionality systems together with the improved experimental techniques have allowed the experimentalists to observe them in quantum well structures [9, 49, 52]. Many of the experimental results reported in the literature are for charged excitons in the presence of a perpendicular magnetic field [52, 10, 99, 100, 66, 48]. Up to recently, there was little or no agreement between the experimental results and the available theories [62, 101].

Lately, however, progress were made in the direction of bringing theoretical prediction and experiments closer to each other. Stèbe and Moradi [101] used a variational method which was valid in the low magnetic field regime and explained the minimum around 1 Tesla observed experimentally by Shields et al. [48] in the charged exciton singlet transition energy for a 300 Å wide quantum well. Recently Mutenau et al. [102] found a transition between the singlet ground state and the triplet ground state at $B = 35$ T for a 200 Å wide asymmetric quantum well, similar to the one predicted earlier by Whittaker and Shields [62] for a 100 Å wide symmetric quantum well.

The triplet transition energies which have been so far identified are assigned to the angular momentum $L_z = -1$ triplet state. In exactly 2D systems with translational invariance this state was shown [103, 104] to be an optically dark state. As a consequence, one would expect that such a state is ‘dark’ also in quasi-2D systems, particularly in narrow quantum wells. The fact that the $L_z = -1$ triplet is observed in quantum wells suggests that a breaking of symmetry occurs and in particular that the system is no longer invariant under a magnetic translation. Recently, the existence of a bound bright triplet state, i.e. $L_z = 0$ was predicted [71]. Due to its small binding energy, this triplet state could be difficult to detect. The possible existence of such a triplet state may force us to review the assignment that has been made of some of the photoluminescence lines.

Our previous works [87, 88] on charged excitons in quantum wells was limited to the case of zero magnetic field and showed that the stochastic variational method (SVM) is an efficient technique for solving the effective mass Hamiltonian of exciton complexes without involving any approximations. In Ref. [88] we showed that approximations made by Stèbe et al. [105] in the Coulomb matrix elements lead to an overestimation of the trion binding energy. The latter approximation aimed to convert the problem into an effective 2D problem. In our approach no simplifying approximations are made and the full 3D nature of the quantum well problem is retained. Here we extend our previous work to the important experimental situation in which an uniform magnetic field is applied along the quantum well growth axis. Our results for the magnetic field dependence of the trion singlet binding energy agrees,
for the first time, with available experimental results on 100 Å and 300 Å wide GaAs/AlGaAs quantum wells. Furthermore we find that the earlier predicted bright triplet is unbound for the 300 Å wide quantum well and probably marginally bound for the 100 Å wide quantum well.

The present paper is organized as follows. In Sec. 4.2 we present the Hamiltonian of the problem and outline our method to obtain the energy of the exciton and charged exciton. The conditional probability density function of the trion, its pairs correlation functions and the average distance between the different particles in the trion are discussed in Sec. 4.3 In Sec. 4.4 we compare our results for the transition energy and in Sec. 4.5 for the binding energy with available experimental data on symmetric GaAs/AlGaAs quantum wells and with the theoretical results of Whittaker and Shields [62]. In the last section we summarize our results and present our conclusions.

4.2 The model

In the effective mass approximation the Hamiltonian describing a negative charged exciton, i.e. X−, in an uniform magnetic field B is given by

\[
H = \sum_{i=1}^{3} \frac{1}{2m_i} \left( \frac{\hat{p}_i^2}{c} - \frac{e_i}{\varepsilon} \hat{A}_i \right)^2 + \sum_{i=1}^{3} V(\hat{r}_i) + \sum_{i<j} \frac{e_i e_j}{\varepsilon |\hat{r}_i - \hat{r}_j|},
\] (4.1)

where \( \hat{A}_i = \frac{1}{2} \hat{r}_i \times B \) is the vector potential; \( m_i, e_i \) are the masses and charges of the interacting particles; \( \varepsilon \) is the dielectric constant; the confinement potential is \( V(\hat{r}_i) = 0 \) if \(|z| < W/2\) and \( V(\hat{r}_i) = V_i \) if \(|z| > W/2\), with \( W \) the quantum well width. The reference system is taken such that the origin of the coordinate system is at the center of the quantum well. For a GaAs/AlxGa1−xAs quantum well the heights of the square well confinement potentials are \( V_e = 0.57 \times (1.155x + 0.37x^2) \) eV for the electrons and \( V_h = 0.43 \times (1.155x + 0.37x^2) \) eV for the hole. If we consider the case where the magnetic field is applied along the growth axis of the well, i.e. \( \hat{B} = (0, 0, B) \), the Hamiltonian becomes:

\[
H = \sum_{i=1}^{3} \frac{1}{2m_i} \left( -\hbar^2 \Delta_i + \frac{e_i^2 B^2}{4\varepsilon^2}(x_i^2 + y_i^2) - \frac{e_i \hbar B}{c} l_{zi} \right) + \sum_{i=1}^{3} V(\hat{r}_i) + \sum_{i<j} \frac{e_i e_j}{|\hat{r}_i - \hat{r}_j|},
\] (4.2)

where \( l_{zi} = -i\partial/\partial \phi_{zi} \) is the z-component of the orbital momentum of the \( i \)--th particle. The Hamiltonian under examination has cylindrical symmetry with respect to the quantum well axis, i.e. z-axis, which implies that the z-component of the total orbital angular momentum, \( L_z \), is a conserved quantity, i.e. a good quantum number. The spin interaction is not explicitly included in our Hamiltonian. The total spin of the electrons, \( S_e \), and the spin of the hole, \( S_h \), and their projections along the
4. Magnetic field dependence of the energy of negatively charged excitons in semiconductor quantum wells.

z-axis, $S_{z}$ and $S_{z}$, are conserved quantities. Notice that the state of the system is not degenerate with respect to the total electron spin. In fact the two electrons obey Fermi-Dirac statistics which means that the electronic part of the total wave function must be antisymmetric, i.e. when $S_{e} = 0$ the spatial part of the electronic wave function must be symmetric and when $S_{e} = 1$ the spatial part of the electronic wave function must be anti-symmetric. Thus, $S_{e}$ can be used as a quantum number which indicates the parity of the state. Once the projection along $z$ of the total orbital momentum, $L_{z}$, and the electron spin $S_{e}$ are fixed we obtain, after solving our Hamiltonian, a series of energy levels which we indicate by the quantum numbers $(n, L_{z}, S_{e})$, where $n$ is the principal quantum number. These levels are degenerate with respect to the quantum number $S_{h}, S_{z}$ and $S_{z}$.

The Hamiltonian (4.2) is solved using the stochastic variational method which was outlined in Ref. [89]. The trial function, for the variational calculation, is taken as a linear combination of “deformed” correlated Gaussian functions (DCG),

$$
\phi_{N}(\vec{r}_{1e}, \vec{r}_{2e}, \vec{r}_{h}) = \sum_{m=1}^{K} C_{qN} \Phi_{qN}(\vec{r}_{1e}, \vec{r}_{2e}, \vec{r}_{h}),
$$

with

$$
\Phi_{qN}(\vec{r}_{1e}, \vec{r}_{2e}, \vec{r}_{h}) = \mathcal{A} \left\{ \sum_{r=1}^{M} \prod_{i=1}^{3} \varphi_{q_{mi}N}(\vec{\beta}_{i}) \exp \left[ -\frac{1}{2} \sum_{j, l \in \{1e, 2e, h\}, k \in \{x, y, z\}} \beta_{q_{ji}N}^{k}(\vec{r}_{j} - \vec{r}_{l})^{2} \right] \chi(1, 2, 3) \right\},
$$

and

$$
\varphi_{q_{mi}N}(\vec{\beta}_{i}) = \xi_{q_{mi}N}(\vec{\beta}_{i}) \exp \left( -\sum_{k \in \{x, y, z\}} \beta_{q_{ii}N}^{k} \vec{r}_{i}^{2} \right),
$$

where $r_{ik}$ gives the position of the $i$-th particle in the $k$-direction; $\mathcal{A}$ is the antisymmetrization operator and $\{ C_{qN}, \beta_{q_{mi}N}^{k} \}$ are the variational parameters, $\chi(1, 2, 3)$ is the three particle spin function, and $\xi_{q_{mi}N}(\vec{\beta}) = (x + iy)^{m_{r}}$ with $m_{r}$ integers such that $L_{z} = m_{1r} + m_{2r} + m_{3r}$ for each value of $r$, with $L_{z}$ the projection of the total angular momentum along the z-axis; $M$ is the number of channels used to obtain our state; $N$ indicates for brevity the set of quantum numbers which characterizes our state, i.e. $(n, L_{z}, S_{e})$. Note that in contrast to the “classical” correlated Gaussians, here, the parameter $\beta_{q_{ji}N}^{k}$ which expresses the correlation among the particle $j$ and the particle $l$ in the direction $k$, is allowed to be different from the parameter $\beta_{q_{ji}N}^{k}$ which couples the same two particles $j$ and $l$ in a different direction $k'$. This additional degree of
freedom in the calculation allows us to take into account the asymmetry introduced in the 3D space by the presence of the quantum well and of the magnetic field.

A basis of dimension $K$, e.g. 10, is at first selected using the stochastic procedure. This does not ensure that the best basis set is found, so a refinement procedure is carried out on the basis set in order to improve it. The refinement is made by replacing the $m$-th state with a new state, i.e. with a state built using new parameters $\{C_{mN}, \beta_{mN}^k\}$ in such a way that the total energy is lowered. When the refinement process does not change the total energy significantly, the number of basis states is further increased. The process is reiterated multiple times for different and increasingly larger dimensions of the basis set, until the energy reaches the desired accuracy. The final dimension of the basis set consists typically of 400 states. Faster convergence is obtained by taking into account the cylindrical symmetry, i.e. by choosing $\beta_{mN}^\pi = \beta_{mN}^\varphi$. Notice also that with respect to the case without magnetic field, less basis states have to be used because the magnetic field localizes the particles around the magnetic center of mass leading to a faster convergence of the energy. The number of channels used depends on the magnetic field. For example, for the case $L_z = 0$, we found that for low magnetic fields we already obtain good results using one channel, which actually gives the largest contribution, while for large fields we have to use up to 7 channels, to obtain a reasonable convergence. On the other hand, for small magnetic fields we need larger number of states $K$ in order to accurately describe the trion energy.

### 4.3 Theoretical results

Our numerical results are given for a GaAs/Al$_x$Ga$_{1-x}$As quantum well. The parameter used in our calculation are $x = 0.3$, $\varepsilon = 12.58$ and $m_e = 0.067 m_0$, which give for our unit of length $a_B = \hbar^2/\varepsilon m_e = 99.3$ Å and energy $2R_y = \varepsilon^2/\varepsilon a_B = 11.58$ meV. Notice that $R_y$ and $a_B$ are calculated for the donor problem and do not depend on the hole mass which we took to be $m_h = 0.34 m_0$. Often one uses $a_B^* = \varepsilon^2/\varepsilon^2 \mu$ and $R_y^* = e^2/\varepsilon a_B^*$ where $\mu$ is the exciton reduced mass, i.e. $1/\mu = 1/m_e + 1/m_h$, which for our problem is $\mu = 0.056 m_0$ corresponding to $a_B^* = 118$ Å and $R_y^* = 4.8$ meV.

First we studied the magnetic field dependence of the inter-particle average distance. In Fig. 4.1 we present the 2D average distance, $d_{ij} = \langle \rho_{ij}^2 \rangle^{1/2}$, vs. the magnetic field for the electron-electron pair and for the electron-hole pair, both in the $(n = 0, L_z = 0, S_e = 0)$ state, i.e. the singlet (solid curves) and in the $(n = 0, L_z = -1, S_e = 1)$ state, i.e. the triplet (dashed curves) for a 100 Å wide quantum well. As a comparison we show also the exciton electron-hole inter-particle distance vs. magnetic field. For the exciton problem the electron and the hole are more strongly bound and the inter-particle distance decreases more slowly than for the trion’s singlet and triplet state. Nevertheless, it decreases by 50% over the magnetic field range shown in the figure. For the negatively-charged exciton the electron-electron average distance is always larger than the electron-hole average distance both
4. Magnetic field dependence of the energy of negatively charged excitons in semiconductor quantum wells.

Figure 4.1: The 2D average inter-particle distance vs. the magnetic field for the exciton, and the singlet and triplet state of the charged exciton in a quantum well of width 100 Å.

for the electron spin-singlet state and for the electron spin-triplet state. This of course is a consequence of the repulsive electron-electron interaction, while the electron-hole is attractive. Notice that for \( B = 0 \) the electron-hole distance for the negative charged exciton is about twice the exciton one. The triplet state is more than 20 times larger than the singlet-state in the small magnetic field range where the triplet state is, in fact, unbound. The size of the charged exciton decreases with increasing magnetic field. This decrease is faster in the low magnetic field region, and it is faster for the triplet than for the singlet state. The reason is that the triplet state is more extended, it is less bound, and consequently an external magnetic field will have a larger effect on its size. Notice also that for both states, i.e. singlet and triplet, the curves for \( d_{ee} \) and \( d_{eh} \) are almost parallel to each other, but nevertheless with increasing magnetic field the distance between them slowly decreases.

Next we calculated the 1D pair correlation function, \( g_{ij}^{2D}(\rho) = <\delta(|\vec{\rho}_i - \vec{\rho}_j| - \rho) > \), for the spin-singlet and spin-triplet state of a charged exciton in a quantum well of width 100 Å in a magnetic field of \( B = 13.7 \) T, see Fig. 4.2. We notice that the electron-hole pair correlation function both for the spin-singlet state (dashed curve) and for the spin-triplet state (dash-dotted curve) has its maximum when the distance between the particles is zero. This means that in both states the electron and hole have the tendency of staying close to each other. Notice that the triplet electron-hole pair has a longer tail compared to the singlet one, indicating that the triplets is more
extended but, nevertheless, the particles in this state are still correlated even at large distances. On the other hand the electron-electron pair correlation function in the singlet state (solid curve) shows that, even though the electrons have a significant probability of being close to each other, the correlation is maximal for \( \rho = 0.35a_B \) which is a consequence of the Coulomb repulsion between the electrons. In the triplet state the pair correlation function is zero if the particles are in the same position in space, which is an expression of the Pauli exclusion principle, and has a maximum at \( \rho = 7.32a_B \).

To gain further understanding on how the system is influenced by the presence of a magnetic field, we studied the conditional probability, which gives the probability of finding one of the three particles in position \( \mathbf{r} \) when the other two particles are fixed at \( \mathbf{r}_{1,0} \) and \( \mathbf{r}_{2,0} \). Notice that by fixing two of the particles we obtain information on the positional correlation of the third particle. We focus on the \( xy \)-correlation since the effect of the applied magnetic field along the quantum well axis is larger in the plane orthogonal to the quantum well axis. Along the \( z \)-direction the probability is mainly determined by the confinement potential. Because the \( x \)- and \( y \)-axis are equivalent due to the cylindrical symmetry of the problem we take \( \mathbf{r} = (x, 0, 0) \) for all three particles and for brevity we will indicate \( \Phi(\mathbf{r}, \mathbf{r}_{1,0}, \mathbf{r}_{2,0}) \) by \( \Phi(x, 0, 0) \). In Fig. 4.3(a,b,c) we plot \( |\Phi(x, 0, 0)|^2 \) for a negatively charged exciton in a 100 Å wide quantum well when the two electrons are fixed at a distance given by their average
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Figure 4.3: The projection on the x-axis of the conditional probability for the charged exciton for $B = 0 \, \text{T}$ (a), $B = 13.7 \, \text{T}$ (b) and for $B = 54 \, \text{T}$ (c) in a quantum well of width 100 Å. The symbols represent the fixed electrons.

Distance $d_{ee} = \langle \rho_{ee}^2 \rangle^{1/2}$. Notice that for $B = 0 \, \text{T}$ (Fig. 4.3(a)) the hole is centered around each of the two electrons, while for $B = 13.7 \, \text{T}$ and for $B = 54 \, \text{T}$ (Fig. 4.3(b,c)) the hole is mostly situated in the region between the two electrons. For $B = 0 \, \text{T}$ there is a smaller but non-zero probability that the hole is between the two electrons. This binds the two electrons together. When a magnetic field is applied the electrons are on average closer to each other and as a consequence the two “hole clouds” around the electrons overlap. The hole has almost the same probability of sitting on top of the two electrons or between them. Notice, that when a magnetic field is applied the conditional probability still shows two “kinks” at the position of the two electrons, which are memories of the two peaks present in the conditional probability function at $B = 0 \, \text{T}$. Furthermore, for increasing $B$ the hole wave function decays much faster when the hole moves away from the electron. The increased probability for the hole to sit between the two electrons leads to an increased bonding between
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Figure 4.4: The projection along the x-axis of the conditional probability for the charged exciton, for $B = 0$ T (a), $B = 13.7$ T (b) and for $B = 54$ T (c) in a quantum well of width 100 Å. The symbols represent the fixed electron and the hole.

The electrons. This behavior is consistent with the fact that the binding energy of the charged exciton increases when a magnetic field is applied.

In Fig. 4.4(a,b,c) we plot $|\Psi(x,0,0)|^2$ for a charged exciton in a 100Å wide quantum well when the hole and one electron are fixed at a distance equal to their average position $d_{eh} = \langle \rho_{eh}^2 \rangle^{1/2}$, for the $B = 0$ T case (Fig. 4.4(a)), the $B = 13.7$ T case (Fig. 4.4(b)) and the $B = 54$ T case (Fig. 4.4(c)). The qualitative difference, between the situation when a large magnetic field is applied and when a low magnetic field is applied is not very pronounced, except for the length scale. However, we observe that for $B = 0$ T the probability of having the second electron near the fixed electron is zero, while in the case in which a magnetic field is applied there is a finite probability for the second electron to be at the position of the first electron. Since the charged exciton is in the singlet state, the spin function is asymmetric for an interchange of the two electrons and consequently there is no Pauli exclusion principle to forbid the two electrons to be at the same position in space. Only the electron-electron interaction
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Figure 4.5: The projection on the x-axis of the conditional probability function for the triplet state, when the electrons are fixed (a) and when one electron and the hole are fixed (b), in quantum well of width 100 Å and for $B = 13.7$ T. The symbols represent the fixed particles.

will make the latter probability as small as possible. This result is consistent with the result obtained for the pair-correlation functions.

Next we consider the triplet state and limit ourselves to the magnetic field $B = 13.7$ T. Notice, that the triplet state is not bound for small magnetic fields. We plot $|\Phi(x, 0, 0)|^2$ for a charged exciton in a 100 Å wide quantum well when the two electrons are fixed (Fig. 4.5(a)) and when one electron and the hole are fixed (Fig. 4.5(b)). Notice that there is not much qualitative difference between the conditional probability function of the triplet state and of the singlet state (see Fig. 4.3(b)). Quantitatively there are two major differences: i) the average distance between the particles is substantially larger, and ii) the probability to find the second electron at the same spatial position as the first one (see Fig. 4.5) is zero, while this is not the case for the singlet
state. The latter is consistent with the fact that in the triplet state the electronic part of the wave function is antisymmetric under the exchange of the two electrons, which is also consistent with the fact that the electron-electron pair-correlation function is zero at the origin.

### 4.4 Comparison of the transition energies with experiments

In comparing our theoretical results with the available experimental data we assume that the observed peaks in the PL spectra are associated with an exciton, in which the electron and the hole recombine with emission of light, or with a recombination of a negatively-charged exciton, which leaves behind an electron in the lowest Landau level. Consequently, the transition energies are defined as

\[
E_X = E_g + E(X), \quad (4.5)
\]

\[
E_{X^-} = E_g + E(X^-) - E_e(W,B), \quad (4.6)
\]

where \(E_g\) is the energy band gap and \(E_e(W,B)\) is the energy of a free electron in a quantum well of width \(W\) and in a magnetic field of strength \(B\); \(E(X)\) and \(E(X^-)\) are, respectively, the exciton and charged exciton total energy. We will also take into account the Zeeman splitting induced by the magnetic field, under the assumption that the transitions observed follow the energy diagram discussed in Ref. [66]. We also assume that the electron gyromagnetic factor, \(g_e\), and the hole gyromagnetic factor are the same for the exciton as well as for the charged exciton. The total Zeeman splitting of each transition can then be written, in agreement with the results presented in Ref. [122], as

\[
\Delta E_z = (g_e + g_h) \mu_B B, \quad (4.7)
\]

where \(\mu_B\) is the Bohr magneton. Notice also that the gyromagnetic factor is defined using the same conventions as in Ref. [122], i.e. the hole is considered to have an effective spin of \(S_h = 1/2\) instead of the real hole spin \(S_h = 3/2\). As a consequence of this Zeeman effect each transition line \(E\) is split into two lines, i.e. \(E^\pm = E \pm \Delta E_z/2\), associated to a change of 1 and -1 in the \(z\)-projection of the total angular momentum \(\vec{J} = \vec{L} + \vec{S}\), i.e. \(J_z\), respectively.

In Fig. 4.6 we compare our theoretical results for the transition energies of a \(X^-\) in a 300 Å wide quantum well (curves) with the experimental results of Shields et al. [49, 106] (symbols). We obtained the exciton gyromagnetic factor \(g_{ex} = g_e + g_h = 1.16\) from the measured splitting between the negatively \((\sigma_-)\) and the positively \((\sigma_+)\) circularly polarized lines of Ref. [49] using Eq. (4.7). This value of \(g_{ex}\) is consistent with the results by Ossau et al. [107] who found \(g_{ex} = 0.8\) for a 250 Å wide quantum well. The experimental data presented in Fig. 4.6 are from the emitted negatively
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Figure 4.6: Comparison between the experimental and theoretical transition energies for charged excitons and excitons in a 300 Å wide quantum well. The open symbols are the experimental results for $B > 8$ T shifted by 0.5 meV.

(\(\sigma^-\)) circular polarized light which results from transitions with $\Delta J_z = -1$. We choose the energy gap such that the exciton peak at $B = 0$ T coincides with the experimental exciton peak for $B = 0$ T, which leads to $E_g = 1521.55$ meV. Notice that for the singlet we reproduce the experimental behaviour, including the small minimum observed at low magnetic fields. Both for the exciton and for the triplet state of the charged exciton we find good agreement up to 8 T. At small magnetic fields: 1) the theoretical results slightly overestimate the singlet transition energy which is probably a consequence of the importance of localization as argued, e.g., in Ref. [88], and 2) the triplet state is unbound for small magnetic fields and consequently not observable. Notice also that the recently discussed [71] bright triplet (dotted curve) is not bound in the considered magnetic field region. None of the observed transitions can be associated to such a bright triplet. The data in the range 8-20 T are from Ref. [106] and are obtained under different experimental conditions as compared to those from Ref. [49] which were measured in the range 0-8 T. For example, an increase in electron density will shift the experimental photoluminescence towards larger energies [108]. If we perform an uniform shift of the experimental data by 0.5 meV in the 8-20 T range, which leads to the open symbols, a much better agreement with our theoretical results is obtained.

In Fig. 4.7(a,b) we compare our theoretical results for the transition energies of a 100 Å wide GaAs/AlGaAs quantum well with the experimental data obtained by
Figure 4.7: Comparison between the experimental and the theoretical transition energies for charged excitons and excitons in a 100 Å wide quantum well. For clarity, the low magnetic field region (a) and the high magnetic field region (b) are shown separately. The symbols represent the experimental data from Vanhoucke et al. [66].
Vanhoucke et al. [66] In Ref. [66] the Zeeman splitting was measured to be $\Delta E_z / B = 0.11 \text{ meV/T}$ leading to $g_{ex} = 1.85$ which is very different from the value $g_{ex} = 0.1$ obtained in Ref. [122] for a 115 Å wide quantum well. The energy gap is fixed by matching the $B = 5 \text{T}$ experimental and theoretical $X^-$ singlet transition energies which resulted into $E_g = 1.520.35 \text{ meV}$. We use for the electron and the hole mass $m_e = 0.067m_0$ and $m_h = 0.34m_0$, respectively. The lower transition line (squares) is in rather good agreement with our results for the charged exciton singlet transition energy. For $B < 3 \text{T}$ (see Fig. 4.7(a)) there is a substantial deviation between theory and experiment which again may be attributed to an enhancement of the negatively charged exciton binding energy due to localization of the trion. The higher transition line (circles) were attributed by the authors of Ref. [66] to the triplet charged exciton. Our theoretical results agree with this assignment at least for $B < 20 \text{T}$ (Fig. 4.7(a)). Notice that this magnetic field range, i.e. $B < 18 \text{T}$, is the same studied in Fig. 4.6 for the 300 Å quantum well. In the high magnetic field range (Fig. 4.7(b)), i.e. $B > 25 \text{T}$, the experimental results follow very closely the theoretical exciton transition energy, which coincides practically with the $X^-$ bright triplet transition energy. In the intermediate magnetic field range, i.e. $18 \text{T} < B < 25 \text{T}$ the results transit from the $X^-$ triplet to the exciton transition or bright triplet transition.

From the above comparison we may construct the following picture: 1) in the magnetic field range $B < 18 \text{T}$ quantum well width fluctuations and disorder break the translational invariance of the system which results into a breakdown of the optical selection rule, thus allowing the dark triplet negatively charged exciton state to be optically active; 2) only in the very small magnetic field range, i.e. $B < 5 \text{T}$, the localization of the trion due to quantum well width fluctuations leads to an increase of the singlet and triplet $X^-$ binding energy. For the 300 Å wide quantum well the effect of the quantum well width fluctuations on the trion energy is substantially smaller;[88] This agrees with Fig. 4.6 where the magnetic field range over which the singlet binding energy is strongly enhanced is much smaller, i.e. $B < 2 \text{T}$, and the size of the enhancement is also substantially smaller; 3) in the very large magnetic field range $B > 25 \text{T}$ the optical selection rule is restored and no transition from the $X^-$ dark triplet is observed. Because of the inhibition of the decay of the $X^-$ dark triplet it is possible that the bright triplet becomes sufficiently populated making it experimentally observable. We found that this $X^-$ bright triplet is at most marginally bound and therefore has almost the same transition energy as the exciton.

For $B > 40 \text{T}$ the experimental results are slightly lower in energy as compared to our theoretical results. A possible reason for this deviation may be the importance of band non-parabolicity at such large magnetic fields. For example, if we increase the hole mass to $m_h = 0.37m_0$ at $B = 50 \text{T}$, the $X^-$ singlet (exciton) transition energy becomes 1.5780 eV (1.5812 eV) which is almost 2 meV lower than the $m_h = 0.34m_0$ result 1.5796 eV (1.5824 eV), thus proving a strong dependence of the transition energy on the hole mass value. This is mainly due to the difference in confinement energy. Notice, that the binding energy only changes from $2.8 \pm 0.1 \text{ meV}$ to $3.2 \pm 0.1$
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Figure 4.8: The binding energy of a charged exciton in a 300 Å wide quantum well compared to the experimental data of Shields et al. [49, 106] and to the theoretical results by Whittaker and Shields [62].

meV, showing a less strong dependence on the hole mass.

4.5 Comparison of the trion binding energy with experiments and with other theoretical results

Finally we compute the binding energy of the negatively charged exciton and compare it with the available experimental results. The binding energy is defined as

\[ E_B(X^-, B) = E(X) + E_e(W, B) - E(X^-), \]  

where \( E(X) \) and \( E(X^-) \) are respectively, the total energy of an exciton and of a charged exciton in the quantum well and \( E_e(W, B) \) is the energy of a single electron in the quantum well of width \( W \).

In Fig. 4.8 we present our results for the binding energy of a negatively charged exciton in a 300 Å wide GaAs/Al\(_{0.3}\)Ga\(_{0.7}\)As quantum well and we compare it with the experimental binding energy obtained by Shields et al. [49, 106] (symbols) and with the theory of Whittaker and Shields [62] (dotted and dash-dotted curves). The error bars in the figure indicate the estimated accuracy of our results. Note that the electron spin-singlet binding energy (solid curve) increases with magnetic field, up to about 35 T, after which it saturates. The electron spin-triplet binding energy (dashed curves)
smoothly increases with magnetic field up to 60 T. Notice the very good agreement between our theory and the experimental binding energies both for the singlet and triplet state up to about 13 T. For the lower magnetic field range, $B < 2$ T, the binding energies are slightly underestimated theoretically. We believe that the larger binding energy obtained experimentally is a consequence of the localization of the trion, as already noticed for the $B = 0$ T case [88]. The effect of the magnetic field, however, decreases the discrepancy between theory and experiment. This is due to the fact that the magnetic field increases the localization of the charged exciton, which is then less sensitive to the well width fluctuations. In the range $8 \text{T} \leq B \leq 20 \text{T}$ the experimental binding energies show almost no magnetic field dependence which is in contrast to our theoretical results which still increases with $B$, although less fast than for $B \leq 8 \text{T}$. As already mentioned the $8 \text{T} \leq B \leq 20 \text{T}$ experimental results are measured under different experimental conditions than those in the region $B \leq 8 \text{T}$. Notice that our singlet binding energy is considerably larger than the one obtained by Whittaker and Shields [62], while the triplet binding energy is comparable to the one of Ref. [62] up to 15 T. For $B > 15$ T the present triplet binding energy becomes appreciably larger than the one of Ref. [62]. One of the reasons for this differences between our results and those of Whittaker and Shields are the different parameters used in Ref. [62]. They used $m_{\parallel}^e = 0.34m_0$, $m_{\perp}^e = 0.065m_0$ in the well, $m_{\parallel}^b = 0.45m_0$, $m_{\perp}^b = 0.07m_0$ in the barrier and $m_{\perp} = 0.18m_0$ in the well and in the barrier, which partially explains the lower binding energy.

The binding energy for a charged exciton in a 100 Å wide GaAs/Al$_{0.3}$Ga$_{0.7}$As quantum well is shown in Fig. 4.9 and compared to the theory of Whittaker and Shields [62] (dotted and dash-dotted curves). Notice that: i) we find substantial larger binding energies than Whittaker and Shields [62], ii) no crossing between the singlet and the triplet energies is found at least up to 70 T, while Whittaker and Shields predicted a singlet-triplet crossing near 30 T, and iii) the bright triplet is at most marginally bound for $B > 5$ T. We find a binding energy of $0.15 \pm 0.1 \text{meV}$ while Wójc et al. [71] obtained a binding energy of 0.75 meV for $B = 20$ T (in Ref. [111] a reduced binding energy of 0.37 meV was reported). For the 300 Å wide quantum well we found that the bright triplet state was unbound for the considered magnetic field range.

The quantitative discrepancy between our theoretical results and the one of Ref. [71] is probably a consequence of the approximations made by the authors of Ref. [71]: i) they replace the real quantum well $W$ with a hard wall quantum well with an effective width and only the lowest subband is retained, ii) the 3D problem is replaced by an effective 2D problem (in which the Coulomb interaction is approximated by the 2D screened interaction $\epsilon^2/\epsilon\sqrt{p^2 + \lambda^2}$), iii) the flat 2D quantum well geometry is replaced by a Haldane sphere, and iv) only the lowest 5 single particle Landau levels are included in their wave function. Previously we showed [88] for $B = 0$ T, that the approximations i) and ii) lead to an overestimation of the binding energy of the charged exciton [88]. Whittaker and Shields [62] showed that the inclusion of higher
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Figure 4.9: The binding energy of a charged exciton in a 100 Å wide quantum well calculated using the symmetric hole mass approximation (thick curves) and the asymmetric hole mass approximation (thin curves). The results are compared to the theoretical results by Whittaker and Shields [62].

subbands and of higher Landau Levels in the wave function substantially increases the high field singlet binding energy, while they have a smaller effect on the triplet binding energy.

Note that in agreement with Whittaker and Shields [62], and in contrast to the recent work by Stébé and Moradi [101], we find that the spin-triplet state is unbound for \( B = 0 \) T. This disagreement with the work of Stébé and Moradi [101] can be traced back to their poor variational function which gives an exciton energy which is about 8\% larger than ours, while the negatively charged exciton singlet energy is about 5\% lower than ours.

It has been argued that the hole mass is asymmetric and that the in-plane hole mass depends on the magnetic field. One expects that the hole mass in the z-direction, i.e. the confinement direction, will almost not influence the exciton and trion binding energies. This is different for the in-plane hole mass which, e.g. through the reduced exciton mass \( \mu \), will change the exciton and to a lesser extent the trion energies. In a recent cyclotron resonance experiment by Cole et al. [110] on p-doped (311)A GaAs quantum wells the measured hole mass varies from \( m_h \approx 0.15 - 0.18m_0 \) for \( B < 5 \) T to \( m_h \approx 0.35m_0 \) at higher fields for a 150 Å wide quantum well. For wider wells the large hole mass value was reached at smaller magnetic fields and therefore, this mass variation is expected not to be relevant for the 300 Å sample. In order to investigate
the influence of the value of the in-plane hole mass on the trion singlet and triplet binding energy we compare in Fig. 4.9 our results with those for the asymmetric hole mass (thin solid and dashed curves in Fig. 4.9) in which the in-plane hole mass was reduced to \( m_h = 0.18 m_e \). Notice that: i) the singlet trion binding energy is substantially reduced (about 0.5 meV); ii) the triplet binding energy is practically not altered and coincides with the Whittaker and Shields [62] results for \( B < 15 \) T, and iii) there is a singlet-triplet crossing at about 40 T. With this smaller hole mass the exciton reduced mass is diminished by 13% leading to a lower exciton binding energy and also to an increase of the trion total energies. This shifts the theoretical curves in Fig. 4.7 in such a way that an unrealistic low band gap of 1518.3 meV has to be assumed in order to match the experimental and theoretical \( B \approx 5 \) T trion transition energies. Furthermore, the agreement between theory and experiment is lost for \( B > 10 \) T and the experimental trion singlet energy for \( B < 3 \) T is now higher than the theoretical curve which disagrees with the idea of an enhanced trion binding energy in this low field region due to quantum well width fluctuations. These findings argue against such a reduced hole mass, even in the low magnetic field range.

It should also be noted that the use of a cyclotron mass in our calculation may be questionable. In a cyclotron resonance experiment, transitions between two Landau Levels are induced and from the transition energy \( h\omega^* = E_1 - E_0 \) one defines the cyclotron mass \( m_c^* = eB/c\omega^* \), where \( E_n \) is the energy of the \( n \)-th Landau Level. Notice that such a definition only corresponds to the effective hole mass if the hole mass is independent of the Landau Level. Furthermore, e.g., electric subband crossings and polaron effects may invalidate such an assignment. A further argument against the use of the low magnetic field cyclotron hole mass published by Cole et al. [110], is that those results are for the (311) GaAs plane while the experiments of Vanhoucke et al. [66] were performed on samples with quantum wells in the (100) plane. It is well known that in the latter crystallographic direction, with increasing density or increasing magnetic field, the hole mass very quickly reaches a value in the \( m_h \approx 0.3-0.5 m_0 \) range, the exact value depends on the quantum well width (see for example Ref. [121]). We believe that this argues in favor of the use of \( m_h = 0.34 m_0 \) in the important \( B > 4 \) T magnetic field region as we did.

For the 100 Å wide quantum well no experimental results on the trion binding energy are available. Therefore, we show in Fig. 4.10 the energy difference between the two transition lines as measured in Ref. [66] and compare them with: 1) the negatively charged exciton singlet binding energy (solid curve), 2) the energy difference between the negatively charged exciton dark triplet and singlet (dashed curve), 3) the energy difference between the negatively charged exciton bright triplet and singlet (dotted curve). To be complete we also show the negatively charged exciton bright triplet binding energy. This figure nicely illustrates how in the low magnetic field region, and more precisely in the range 6-18 T the experimental results are clearly not related to the binding energy of the \( X^- \)-singlet state but rather to the difference between the dark triplet state and the singlet state energy. In the high magnetic field region, i.e.
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4.6 Conclusion

We presented a calculation of the lowest energy levels of the negatively charged exciton spectrum in a quantum well and in the presence of a magnetic field which is perpendicular to the quantum well plane. Our approach is based on the stochastic variational method in which the trion wave function is expanded in deformed correlated Gaussian functions. The important correlation between the particles is built in this wave function and therefore such an approach is well suited for problems in which the binding of the system is a pure consequence of the particle-particle correlation as is the case for the trion. We do not observe any spin-singlet/spin-triplet transition using the symmetric mass approximation, however such a transition is found for the 100 Å wide quantum well if we use the asymmetric hole mass approximation (i.e. a substantially lower in-plane hole mass), in agreement with what was predicted by Whittaker and Shields [62]. The singlet-triplet transition is found to occur at about 40 T, in contrast to the predicted $B = 30$ T reported in Ref. [62]. We have argued

Figure 4.10: Comparison of the difference in energy between the upper and lower $\sigma^-$ transition lines in Ref. 64 (symbols) with our theoretical binding energy for the negative trion singlet state (solid curve), the energy difference between our theoretical dark triplet and singlet state (dashed curve) and the energy difference between our bright triplet and singlet state (dotted curve).

$B > 25$ T, the experimental results are closer to the singlet state binding energy and to the energy difference between the bright triplet state and the singlet state.
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that at such high magnetic fields the larger in-plane hole mass should be used and consequently we believe that this transition should not occur in reality for $B < 70$ T. Muntenau et al. [102] observed a spin-singlet/spin-triplet transition in an asymmetric quantum well in which electrons and holes are spatially separated. Such a singlet-triplet transition is then of the same nature as the one predicted for spatially separated charged donor systems [111, 41, 92].

A comparison between our theoretical results and available experiments gives good agreement for the trion singlet and triplet energy. Particular good agreement is achieved with the experimental results of Shields et al. [49, 106] on the 300 Å quantum well. For the results on the 100 Å quantum well we find good agreement for the trion singlet state while for the higher energy transition we find for $B < 20$ T that the results agree with the dark triplet transition, while for $B > 25$ T this transitions agrees more closely with the exciton transition energy or the bright triplet energy. Because the latter two have, in this magnetic field region, practically the same energy we are not able to make any definite assignment for this transition line.
Chapter 5

Positively charged magneto-excitons in a semiconductor quantum well.

A variational calculation of the lower singlet and triplet states of positively charged excitons (trions) confined to a single quantum well and in the presence of a perpendicular magnetic field is presented. We study the dependence of the energy levels and of the binding energy on the well width and on the magnetic field strength. Our results are compared with the available experimental data and show a good qualitative and quantitative agreement. A singlet-triplet crossing is found which for a 200 Å wide GaAs is predicted to occur for \( B = 15 \, \text{T} \).
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5.1 Introduction

In spite of the large number of theoretical\cite{20, 44, 45, 94, 62, 101, 103, 104, 71, 88, 112} and experimental\cite{9, 49, 7, 47, 52, 48, 11, 10, 99, 100, 66, 57} works published in recent years on the subject of charged excitons in quantum wells, only a very small number of them deals with positively charged excitons\cite{94, 101, 88, 7, 52, 11, 10}. Different authors\cite{94, 11} used the diffusion Monte Carlo technique to calculate the dependence of the binding energy of the positively charged exciton on the well width at zero magnetic field. Stébé and Moradi\cite{101} reported low magnetic field results for the positively charged exciton spin-singlet state, which was calculated using a deterministic variational technique. To our knowledge, this is the only theoretical calculation on the magnetic field dependence of the $X^+$ energy. In the present paper we go beyond the small magnetic field limit and present results for the whole magnetic field range not only for the singlet but also for the triplet state.

Experimental evidence of the positive trion ($X^+$) in GaAs/AlGaAs quantum wells was found by different groups\cite{7, 11, 52, 10}. These results confirm the existence of both the spin-singlet state and the spin-triplet state at non-zero magnetic field as was also found for the $X^-$. The magnetic field dependence of the binding energy, on the other hand, can be rather different for the $X^+$ as compared to the $X^-$. We extended our numerical technique, see Ref.\cite{112}, which we used for negatively charged excitons, to describe positively charged excitons in quantum wells under the influence of a magnetic field parallel to the quantum well axis. The present paper is organized as follows. In Sec. 5.2 we present the Hamiltonian of the problem. The dependence of the binding energy on the well width is discussed in Sec. 5.3. In Sec. 5.4 the magnetic field dependence is investigated and we discuss the dependence of the average distance between different pairs of particles in the system as a function of the magnetic field. We point out the differences and similarities between the $X^+$ and the $X^-$. The behaviour of the pair correlation functions is also studied for different magnetic fields. In Sec. 5.5 we compare our results with the experimentally measured transition and binding energies. Finally, in Sec. 5.6 we summarize our results and present our conclusions.

5.2 Hamiltonian

In the effective mass approximation the Hamiltonian describing a positively charged exciton, i.e. $X^+$, in an uniform magnetic field $B$ is:

$$ H = \sum_{i=1}^{3} \frac{1}{2m_i} \left( \vec{p}_i - \frac{e_i}{c} \vec{A}_i \right)^2 + \sum_{i=1}^{3} V(\vec{r}_i) + \sum_{i<j}^{} \frac{e_i e_j}{\varepsilon |\vec{r}_i - \vec{r}_j|} $$

(5.1)

where $\vec{A}_i = \frac{1}{2} \vec{r}_i \times \vec{B}$; $m_i, e_i$ are the masses and charges of the interacting particles and $\varepsilon$ is the dielectric constant of the medium the particles are moving in and is taken the
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same for the well and barrier material. The confining potential is

\[ V(r_i) = 0 \quad \text{if} \quad |z| < W/2 \quad \text{and} \quad V(r_i) = V_i \quad \text{if} \quad |z| > W/2, \]

where \( W \) is the quantum well width, and the reference system is taken such that the origin of the coordinate system is at the center of the quantum well. For a GaAs/Al\(_x\)Ga\(_{1-x}\)As quantum well the heights of the square well confinement potentials are \( V_e = 0.57 \times (1.155x+0.37x^2) \) eV for the electrons and \( V_h = 0.43 \times (1.155x+0.37x^2) \) eV for the hole. If we consider the case when the magnetic field is applied along the growth axis of the well, i.e., \( B = (0,0,B) \), the Hamiltonian becomes:

\[
H = \sum_{i=1}^{N} \left( -\hbar^2 \Delta_i + \frac{e^2 B^2}{4c^2} (x_i^2 + y_i^2) + \frac{e_i hB}{c} l_{zi} \right) + \sum_{i=1}^{N} U(r_i) + \sum_{i<j} \frac{e_i e_j}{|r_i - r_j|},
\]

where \( l_{zi} \) is the component along the \( z \)-axis of the orbital momentum of the \( i \)-th particle. The same considerations made in Ref. [112] for the \( X^- \) hold also in this case and the same functional form for the trial wave function which consists of a linear combination of deformed correlated wave functions is used to solve the Hamiltonian. However, here the variational parameters \( A_{ij} \) which enter in the definition of the deformed gaussian functions can assume also negative values. For our numerical calculation we focus on a GaAs/Al\(_x\)Ga\(_{1-x}\)As quantum well with \( x = 0.3 \). The parameters used are \( \epsilon = 12.58 \) and \( m_e = 0.067 m_0 \) and \( m_h = 0.34 m_0 \), which result in \( 2R_y = e^2/\varepsilon a_B = 11.58 \) meV and \( a_B = \varepsilon \hbar^2/\varepsilon^2 m_e = 99.3 \) Å.

5.3 Zero magnetic field trion energy

First, we study the binding energy of the positively charged exciton which is defined as

\[
E_B(X^+, B) = E(X) + E_h(W, B) - E(X^+),
\]

where \( E(X) \) and \( E(X^+) \) are respectively, the total energy of an exciton and of a positively charged exciton in the quantum well and \( E_h(W, B) \) is the energy of a free hole in the quantum well of width \( W \) in the presence of a magnetic field \( B \) directed along the confinement direction. The dependence of the binding energy of the positively charged exciton spin-singlet state on the well width is shown in Fig. 5.1 (solid curve) in the absence of a magnetic field. Our results are also compared with the Monte Carlo calculations of Ref. [94] (dotted curve). The results from the two theories differ by about 0.1 meV at \( W = 200 \) Å. One reason for this difference could be attributed to the different choice for the value of the static dielectric constant, we took it to be equal to 12.58 while in Ref. [94] it was taken equal to 12.5. Notice that while the binding energy is decreasing with increasing well width according to
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Figure 5.1: Dependence of the binding energy of the positively and negatively charged exciton on the well width at zero magnetic field. The symbols represent experimental data for the $X^+$ system from Ref. 18 (full circles), Ref. 14 (open circle) and Ref. 16 (triangle). Both theories our calculation shows a faster decrease of the positively charged exciton binding energy with increasing well width, this behaviour is particularly strong for the $X^+$ system. The symbols in Fig. 5.1 represent the experimentally measured values for the spin-singlet state binding energy of the $X^+$ for different quantum well width and in different experiments.[7, 52, 11] Notice that these results are in good agreement with the theory of Ref. [94], and agree with ours in the nominal error of the theory, i.e. ±0.1meV. This error is estimated considering the digit to which we round off our result for the total energies, however due to the very good convergence of the calculation we expect the “real error” to be smaller than the estimated one. In general we would expect that the experimental energies are larger than the theoretical calculated ones because: 1) a non zero density of holes leads to a non zero Fermi energy $E_F$ and it has been shown that the experimentally determined binding energy is in fact $E_F + E_B(X^+, B = 0)$; and 2) quantum well width fluctuations will localize the trion. Both effects lead to a larger binding energy with respect to the one calculated theoretically for a free translational invariant trion.

In Fig. 5.1, we also report the dependence of the negatively charged exciton binding energy on the well width (dashed curve). Notice that the $X^+$ binding energy is larger (about 20%) as compared to the $X^-$ binding energy, both for our theory and for
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Figure 5.2: The binding energy of a negatively and a positively charged exciton in a 100 Å wide quantum well as a function of the applied magnetic field.

the one of Ref. [94]. Moreover this result is also in agreement with the experimental results which showed that the energy of the $X^+$ is larger[49, 7] or equal[10] to the one of $X^-$. Stebé and Moradi[101] found, on the other hand, that for a 300 Å wide quantum well the binding energy of $X^+$ is lower than the one of $X^-$ which is opposite to our conclusion and to those of Ref. [94]. It should be stressed that the theoretical value for the trion binding energy depends not only on the obtained value for the trion energy but also on the exciton energy. In our theory, the latter are both upper bounds to the exact result and consequently the trion binding energy is neither an upper nor a lower bound to the exact value. For example, an overestimation of the exciton energy will lead to an overestimation of the trion binding energy.

5.4 Magnetic field dependence of the trion properties

Next, we compare the dependence of the binding energy of the positively charged exciton on the magnetic field with the one of the negatively charged exciton, for a quantum well of width 100 Å (see Fig. 5.2). Notice that while for $B < 1$ T we
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Figure 5.3: The binding energy of a negatively and positively charged exciton in a 200 Å wide quantum well. The open and full circles as well as the diamonds are the experimental data from Ref. [10], the triangles are experimental data from Ref. [111]. The bars represent the nominal error of our calculation.

We obtain $E_B(X^+, B) > E_B(X^-, B)$, which is in agreement with the $B = 0$ T behaviour as shown in Fig. 5.1, for $B > 1$ T the relation between the two energies is reversed and the negatively charged exciton becomes more strongly bound. Moreover while the $X^-$ singlet binding energy quickly increases up to about 2.5 meV for $B = 10$ T after which it saturates, the $X^+$ binding energy increases slowly from about 1 meV at $B = 0$ up to about 1.1 meV for $B = 7$ T, where it starts to decrease slowly. We found a similar behaviour for the binding energy in the case of a quantum well of width 200 Å (see Fig. 5.3). For the latter quantum well width we also calculated the spin-triplet state with $L = 1$ (dashed-dotted line in Fig. 5.3). The triplet state is unbound at low magnetic field and then becomes bound around 1 T. We also find that the binding energy of this state increases rather fast with increasing magnetic field.
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and eventually we observe a crossing around $B = 15$ T. This behaviour is consistent with the one found for the negatively charged exciton where we found that when the hole mass was much larger than the electron one no spin-singlet spin-triplet transition was observed. However, when the hole mass was decreases considerably such singlet-triplet transition occurred. In that case the hole mass was always larger than the electron one, however it is reasonable to assume that decreasing further the hole mass the singlet-triplet transition would still be observed. Here the roles of the hole and the electron are switched and the electron mass is much smaller than the hole one. As a consequence this is then consistent with the fact that we now find a singlet-triplet transition.

The average distance between pairs of particles of the trion in the plane orthogonal to the quantum well axis, i.e. $\langle \rho_{ij}^2 \rangle^{1/2}$, is shown in Fig 5.4 as function of the magnetic field for quantum well of width 200 Å. Notice that for $B = 0$ the average distance between the positively charged exciton pairs, i.e. hole-hole and electron-hole ones, are smaller than the correspondent one for the negatively charged exciton. In particular the difference is more pronounced for the pair of particles with the same charge (i.e. hole-hole in case of $X^+$ versus electron-electron in $X^-$). Since the attractive and the repulsive contribution to the potential are inversely proportional
to the average interparticle distance, the behaviour at \( B = 0 \) explains the fact that we find a lower binding energy for the \( X^- \) than for the \( X^+ \) at \( B = 0 \). Notice that around \( 1 \) T the average distance of the electron-hole pair in \( X^- \) crosses the one of \( X^+ \), this is the same magnetic field at which the \( X^- \) binding energy becomes larger than the \( X^+ \) binding energy. For increasing magnetic field the ratio between the average distance between the electron-electron and electron-hole pair in \( X^- \) is rather constant. Looking at the corresponding pairs in \( X^+ \) we see that the distance between the electron and hole diminishes with increasing magnetic field but less than the one between the two holes. This could explain the slow increase and then the decrease already at low magnetic fields of the \( X^+ \) binding energy against the fast increase and saturation of the \( X^- \) binding energy.

We calculated also the pair correlation function for the positive trion in the confinement direction, \( g_i(z) = \langle \delta(z - |z_i - z_j|) \rangle \), and in the orthogonal plane, \( g_i(\rho) = \langle \delta(\rho - |\vec{\rho}_i - \vec{\rho}_j|) \rangle \), both at \( B = 0 \) and at \( B = 4 \) T (see Fig. 5.5). Notice that along the \( z \)-axis, Fig. 5.5(a), both the hole-hole and the electron-hole pair correlation function have a peak around the center of the quantum well, which is in agreement with the fact that the Coulomb interaction plays a minor role as compared to the confinement due to the presence of the quantum well. Notice also that, as expected, the presence of a magnetic field has only a very small influence on the correlation function in the \( z \)-direction. In the \( \rho \)-plane, Fig. 5.5(b), we observe that electron-hole pair correlation is peaked around zero, i.e. the electron and the hole maximize their interaction by staying as close as possible to each other. The hole-hole pair correlation function has instead a peak around the average pair inter-particle distance. When a magnetic field is applied the peak of the hole-hole pair correlation function is shifted towards lower \( \rho \). This is consistent with the fact that the average pair inter-particle distance decreases with increasing magnetic field.

5.5 Comparison with experiment

In Fig. 5.3, we compare the binding energy of the \( X^+ \) and of the \( X^- \) singlet state for a 200 Å wide quantum well with the experimental results obtained by Glasberg et al. [10] and Yusa et al.[?]. When comparing the experimental results with our theoretical results we observe that for \( B = 0 \) the experimental and theoretical result for the negatively charged exciton binding energy differ by about 0.3 meV, which may be due to a non-zero density effect and/or to localization induced by quantum well width fluctuation. In the range \( 1 \) T \(< B < 7 \) T there is very good agreement between theory and experiment. For \( B > 8 \) T the experimental binding energy saturates, while this occurs at higher fields for our theoretical results. The agreement of the \( X^- \) singlet energy with the very recent experimental results of the same group[?] is on the other hand remarkable. Not only theoretical but experimental results improve with time.

For the \( X^+ \) spin-singlet state binding energy, the agreement is rather good over
5. Positively charged magneto-excitons in a semiconductor quantum well.

Figure 5.5: The pair correlation function for the spin singlet state of the positively charged exciton in a 200 Å wide quantum well as function of the magnetic field.
the whole magnetic field range at which experimental results are available. However at low magnetic fields the theoretical binding energy underestimates the experimental value. It has been argued that this effect can be attributed to localization effects due to quantum well width fluctuations. Notice that localization effects are less important on the positively charged exciton than on the negatively charged exciton, which is consistent with the larger mass of the holes which leads to a less extended trion (see Fig. 5.4). For the $X^+$ spin-triplet state a comparison with the experimental data by Glasberg et al.\cite{10} shows a good agreement for magnetic fields up to about 3 T. Beyond 3 T the experimental energy saturates while the theory still predicts and increasing binding energy with increasing magnetic field.

5.6 Conclusion

The present work is the first theoretical work in which a detailed comparison is made between experimental and theoretical singlet and triplet binding energies of the positively charged exciton. The theoretical results explain the different magnetic field dependence of the $X^-$ and $X^+$ ground state binding energy, which was observed experimentally. Namely the $X^+$ singlet has a very weak magnetic field dependence while the $X^-$ singlet binding energy increases rapidly in the low magnetic field region and saturates at higher fields. We find good qualitative and quantitative agreement with the available experimental results. The $X^+$ triplet binding energy on the other hand increases with magnetic field and we predict for a quantum well of width 200 Å a singlet-triplet crossing at $B \approx 15$ T. The experiments of Ref. \cite{10} show a rather saturated triplet binding energy for $B > 3$ T, which we do not find in our theoretical results.
Chapter 6

Binding energy of localized biexcitons in quantum wells.

A variational calculation of the ground state energy of a biexciton in a GaAs/AlGaAs quantum well is presented. The well width fluctuations leading to trapping of the biexcitons are modeled by a parabolic potential. The results obtained for different well widths are compared with recent experimental data. Good agreement is obtained both for the biexciton binding energy and for the Haynes factor when using a reasonable quantum well width dependence for the strength of the parabolic confinement potential. We find that the structure of a biexciton is similar to the one of the $H_2$ molecule.

Part of the results presented in this chapter were published in:


6.1 Introduction

In the last few years considerable experimental progress was made in detecting biexcitons in semiconductor systems. A biexciton is a system consisting of two excitons which are bound together. Since the first observation of biexcitons in quantum wells reported by R.C. Miller et al. [75] there have been many studies, both experimental [75, 113, 114, 115, 116, 117, 78] and theoretical [18, 118, 119], on this subject. Kleinman [18] developed a variational model that gives results in agreement with the first experimental [75, 113] data. However later experimental studies, carried out with more advanced techniques, have reported substantial larger values for the binding energy [114, 115, 116, 117] as compared to the early experiments. For example the Haynes factor, \( f_H = E_{XX}^b / E_X^b \), which is the ratio between the biexciton binding energy \( (E_{XX}^b) \) and the exciton binding energy \( (E_X^b) \), found by Birkenal et al. [78] has a value in the range 0.19-0.22 for well widths between 80 and 160 Å, while Kleinman predicts a value in the range 0.11-0.12. In order to explain this difference between theory and experiment, calculations were carried out with different techniques as well as with new assumptions [118] on the spatial form of the biexciton. Singh et al. [118] assumed a square-like arrangement of the electrons and the holes in a two dimensional biexciton which resulted in \( f_H = 0.228 \). The latter approach is rather ad hoc and does not include the finite thickness of the biexciton and consequently is not able to explain the well width dependence of the biexciton binding energy.

The aim of the present paper is to explain the recent experimental results by considering localization effects on the biexciton. This localization can be a consequence of the modulation of the thickness of the quantum well. Indeed for a quantum well of width \( W \) a variation in well width of \( \Delta W \) produces a change in the zero point energy of the order of \( \Delta W^2 \pi^2 / (m \omega^2) \). For a quantum well of 160 Å a fluctuation of about 2.5 Å induces a zero point fluctuation of the order of 0.5 meV which compares to a biexciton binding energy of about 1.5 meV.

In Sec. 6.2 we present and discuss the Hamiltonian of the system. In Sec. 6.3 we present the results for the binding energy of the biexciton and discuss the choice of the confinement parameter. In Sec. 6.3 we also calculate and discuss some geometrical properties of the wave function. In Sec. 6.4 we present our conclusions.

6.2 The model

Using the effective mass approximation a biexciton in a quantum well laterally confined by a parabolic potential can be described by the Hamiltonian

\[
\hat{H}_{XX} = \hat{H}_{1X} + \hat{H}_{2X} + V_C(\rho) + V_{\text{conf}}(z) + \sum_{i=e,h} \sum_{j=1,2} \frac{1}{2} m_i \omega_i^2 \rho_{j,i}^2,
\]  

(6.1)
with

$$H_{iX} = -\frac{\hbar^2}{2m_i^*} \nabla_{i\epsilon}^2 - \frac{\hbar^2}{2m_h^*} \nabla_{ih}^2 - \frac{e^2}{|r_{i\epsilon} - r_{ih}|}$$

(6.2)

and

$$V_C(\vec{r}) = \frac{e^2}{|\vec{r}_{1\epsilon} - \vec{r}_{2\epsilon}|} + \frac{e^2}{|\vec{r}_{2\epsilon} - \vec{r}_{1h}|} = \frac{e^2}{|\vec{r}_{1\epsilon} - \vec{r}_{2\epsilon}|} + \frac{e^2}{|\vec{r}_{1h} - \vec{r}_{2h}|},$$

(6.3)

where the indexes 1, 2 indicate the first and second exciton, $m_i^*$ is the effective mass of the particle $i$, and $V_{con}(z)$ is the confining potential associated with the presence of the quantum well. $\omega$ is the frequency of the shallow parabolic confining potential in the quantum well plane that models the quantum well width fluctuations and $\tilde{\rho}$ is the projection of $\vec{r}$ in the plane orthogonal to the well axis. The confinement energy is much larger than the biexciton and exciton binding energy which allows us to treat the system as a quasi-two dimensional system, i.e. we can separate the contribution to the wave function along the quantum well axis, chosen as $z$-axis, from the contribution along the plane, the $\tilde{\rho}$-plane,

$$\Psi(\vec{r}_{1\epsilon}, \vec{r}_{2\epsilon}, \vec{r}_{1h}, \vec{r}_{2h}) = \mathcal{F}(z_1, z_2, z_a, z_b)\psi(\tilde{\rho}_{1\epsilon}, \tilde{\rho}_{2\epsilon}, \tilde{\rho}_{1h}, \tilde{\rho}_{2h}).$$

(6.4)

The component of the wave function along the $z$-axis is taken as a product of the 1D ground state wave functions for an electron (hole) in a hard wall quantum well. Averaging the Hamiltonian over the $z$-component $\mathcal{F}(z_1, z_2, z_a, z_b) = f(z_{1\epsilon}) f(z_{2\epsilon}) f(z_{1h}) f(z_{2h})$ we obtain the following effective 2D Hamiltonian

$$\tilde{H}_p = \frac{1}{1 + \sigma} (\sigma \Delta_a + \sigma \Delta_b + \Delta_1 + \Delta_2) + 2(U_{1, e} + U_{1, h} + U_{2, a} + U_{2, b} - U_{a, h} - U_{1, 2})$$

$$+ \frac{1}{4} (1 + \sigma) \frac{1}{\mu} \omega^2 (\rho_a^2 + \rho_b^2 + \rho_1^2 + \rho_2^2),$$

(6.5)

where $\sigma = m_e/m_h$ is the mass ratio between the electron and the hole and $U_{i, j}$ is the effective Coulomb potential obtained by averaging the real Coulomb potential over the wave functions along the $z$-direction. In Eq.(6.5) we expressed the energy in units of $R_y = e^2/2\varepsilon a_B$ and the length in units of $a_B = \varepsilon \hbar^2/e^2 \mu$ with $\varepsilon$ the static dielectric constant and $\mu$ the in-plane reduced mass of the electron-hole system. Using $\sigma = 0.68$, i.e. $m_e/m_0 = 0.067$, $m_h/m_0 = 0.099$, $\varepsilon = 12.1$ for a GaAs/AlGaAs with concentration of Al=25%, we find $R_y = 3.7 meV$ and $a_B = 160 \AA$.

It has been shown [83] that $U_{i, j}$ can be well approximated by $1/\sqrt{\lambda^2 + \rho_1^2}$, where $\lambda = 0.2 W$ with $W$ the width of the well which is valid for hard well confinement. The latter approach is a very good approximation for the wide quantum wells considered in the present paper. Using this approximation the Hamiltonian (6.5) was solved with
the stochastical variational technique of Ref. 12 with the trial wave function taken as a combination of correlated Gaussian functions,

$$\psi = \sum_{n=1}^{K} C_n \Phi_n,$$

$$\Phi_n = A \{ exp(-\frac{1}{2} \sum_{i,j=1}^{3} A_{nij} \vec{p}_i \cdot \vec{p}_j) \},$$

where $\vec{p}_1$ and $\vec{p}_2$ are the in-plane distance vectors between the hole and the electron in the first and in the second exciton respectively and $\vec{p}_3$ is the in-plane distance between the centers of mass of the two excitons and $A$ is the antisymmetrization operator. The interaction among the different particles is taken into account via the non diagonal terms of the matrix $A$. The best set of variational parameters $\{C_n, A_{nij}\}$ is found using a stochastical method. The dimension of the basis $K$ is increased until the required accuracy is achieved.

6.3 The binding energies and the structure of the biexciton

The biexciton binding energy is obtained as follows

$$E_{b}^{XX} = 2E^{X} - \tilde{E}^{XX},$$

where $E^{XX} = (E^{XX} - 4 \omega)$ is the biexciton ground state energy as referred to the four free particle in the shallow parabolic confinement potential and $E^{X}$ the ground state of a mobile exciton.

The quantum well width fluctuations ($\Delta W$) shift the zero point energy of the electrons and holes by $\Delta W \hbar^2 \pi^2/(mW^3)$ and thus it is reasonable to assume that the shallow confinement $\omega$ is inversely dependent on some power of the well width $W$. These considerations suggest to search for such a dependency in the form of $\omega(W) = a/W^n$. In order to do this we considered the experimental data reported in various experiments [114, 115, 116, 117, 78] and we used $\omega$ as a fitting parameter. The obtained confinement frequencies are plotted in Fig. 6.1. The influence of the confinement on the biexciton binding energy is shown in the inset of Fig. 6.1 for different values of the quantum well width. Note that $E_{b}^{XX}$ increases almost linearly with $\omega$. On the basis of the above zero point energy argument we expect that $\omega \propto W^{-3}$ which seems to agree with the experimental results for $W/a_B \leq 0.7$. Noticing that there is a lot of scatter between the different experimental results, it seems that the best overall behaviour of $\omega$ is given by $\omega = 0.06/W^{-1}$, although a constant value of $\omega = 0.068R_y \approx 0.26meV$ also agrees with the experimental results, at least for $W/a_B > 0.6$

In Fig. 6.2 we plot our $\omega = 0$ biexciton binding energies which are even smaller than those found by Kleinman this must be attributed to a missing factor of two in
Figure 6.1: The confinement trapping frequency as function of the quantum well width \( W \). The different symbols are the results obtained from the fitting to the experimental biexciton binding energy. The different curves show the inverse power law with \( a=0.06 \), \( b=0.03 \) and \( c=0.02 \) and \( W \) measured in Bohr radii. The inset shows the dependence of the biexciton binding energy on the confinement for different well width.

the calculation by Kleinman, as it has been recently found out [79]. Adding a shallow confinement potential in the quantum well plane increases the biexciton binding energy substantially (about a factor of 2) and brings the theoretical results in agreement with the experimental results. We show our results for a constant confinement of \( \hbar \omega = 0.068 R_y \) and for a well width dependent confinement of \( \hbar \omega / R_y = 0.06/(W/a_B) \). The latter gives a better overall agreement with the experimental data. We also report as comparison the “not-corrected” results from Kleinman (dash-dotted curve) and the results from Denschlag and Baltz [79]. Notice that our results without confinement and the one reported in Ref. [79] are practically coincident even though in Ref. [79] a different analytical approximation is chosen for the potential \( U_{i,j} \). This different choice allows the authors of Ref. [79] to solve the Hamiltonian analytically. We do not report the “corrected” Kleinman results, as they also agree very closely with the one from Ref. [79]. The different experimental results are from different quantum wells which have not been grown under the same conditions and consequently the well width fluctuations can also be substantially different.
Figure 6.2: Comparison between different theoretical results for the binding energy of the biexciton (curves) and the experimental data (symbols).

The Haynes factor, which is the ratio between the biexciton energy and the exciton energy, is found experimentally to be almost independent on the width of the quantum well. Our theoretical results, see Fig. 6.3, seem to confirm this and leads to \( f_H \approx 0.22 \) which compares to the value, \( f_H = 0.228 \), found by Singh et al. [118]. Although our theoretical results show a weak well width dependence they fall within the scatter of the experimental results.

Note that the previous calculation by Kleinman results into \( f_H = 0.13 \) which is about a factor of two smaller than the one found experimentally and very close to the value we found in the case \( \omega = 0 \).

In order to investigate the structure of the biexciton we evaluate the average distance between the two electrons, between the two holes and between the electron and hole which is defined as follows

\[
< \rho_{ij} > = \int |\psi(\vec{\rho}_1, \vec{\rho}_2, \vec{\rho}_{1h}, \vec{\rho}_{2h})|^2 d\vec{\rho}_1 d\vec{\rho}_2 d\vec{\rho}_{1h} d\vec{\rho}_{2h} ,
\]

with \( i, j = 1e, 2e, 1h, 2h \). The results are depicted in the inset of Fig. 6.4 as function of the well width. Note that the average electron-electron and the average hole-hole distances are comparable, and the average electron-hole distance is such that \( < \rho_{eh} > / < \rho_{ee} > \approx 1.35 \). For a square 2D biexciton as assumed by Singh et al. [118]
one has $\rho_{ee} = \rho_{hh} = \sqrt{2}\rho_{eh}$. Noticing that this equation is satisfied within 4% one may naively believe that the electrons and the holes are situated on the corner of a square.

Next we consider the pair correlation function for the electron-hole pair

$$P_{eh}(\rho) = \frac{1}{2} \sum_{i=1,2} \sum_{j=1,2h} <\delta(|\hat{\rho}_i - \hat{\rho}_j| - \rho)>,$$  \hspace{1cm} (6.10)

and the one of the electron-electron (hole-hole) pair

$$P_{ee}(\rho) = \frac{1}{2} \sum_{i=1,2e} \sum_{j=1,2h} <\delta(|\hat{\rho}_i - \hat{\rho}_j| - \rho)>,$$  \hspace{1cm} (6.11)

which is plotted in Fig. 6.4. Note that the electron is much more strongly correlated to the hole and that there is a high probability for the two particles to stay very close to each other. While electrons (holes) stay quite far from each other. This result argues against the model of a square biexciton proposed by Singh et al. [118] and

![Graph showing different pair correlation functions for a biexciton in a quantum well](image)

Figure 6.4: The different pair correlation functions, for a biexciton in a quantum well of width $W/a_B = 1$ and confinement energy $\hbar \omega / R_y = 0.068$, with $\rho_{ij} = |\vec{r}_i - \vec{r}_j|$. The inset shows the average distance between the different particles in the biexciton as function of the well width for a confinement energy $\hbar \omega / R_y = 0.068$.

suggests that the electrons and holes orbit around each other like in single excitons and that the centers of mass of the two excitons are a certain distance apart which is approximately equal to the average hole-hole (electron-electron) distance. This result is confirmed by the conditional probability of finding the two electrons at a certain distance $\rho$ if the holes are at a fixed distance that is taken equal to the average distance between the two holes, i.e. $< \rho_{hh} > = 1.61 \ a_B$. In fact from Fig. 6.5 it is clear that the two electrons have a probability distribution which is very similar to the one of a molecular system, i.e., the one of a $H_2$ molecule.

6.4 Conclusions

In conclusion, we found that in order to explain the experimentally available results on the biexciton binding energy in quantum wells we have to assume that the biexcitons are trapped. The trapping potential is assumed to be parabolic which models
the trapping potential induced by the well width fluctuations found in real systems. Our results indicate that the trapping potential frequency has a smaller well width dependence than expected from a pure monolayer well width behaviour, except maybe for the quantum wells which are smaller than 100 Å. The Haynes factor is practically independent from the well width in agreement with the experimental results. By investigating the interparticle correlation functions we found that the biexciton can be considered like a $H_2$ molecule rather than a square arrangement of electrons and holes as proposed by Singh et al. [118].
Chapter 7

Summary

Electrons in semiconductors will bind to available holes and impurities forming atomic-like systems, e.g., excitons, charged excitons, biexcitons and charged impurity states. In reduced dimensionality systems the binding energy of such impurity and exciton complexes is substantially enhanced making them more easy to observe than in bulk materials.

In this thesis, I studied the low energy spectrum of different atomic-like complexes in quantum wells. The obtained results shed light on the mechanism behind the formation of such few-particles Coulomb bound systems and have helped to better understand several experimental results.

In chapter 2, I dealt with the problem of the off-center charged donor. This was the first study which studied higher energy levels of an off-center charged donor in a realistic quantum well, i.e., non-zero well width quantum well. Through the study of the dependence of the energy levels on the well width, the donor position and the magnetic field strength, I was able to draw phase diagrams for the ground state of the charged donor system. In particular, I found that, depending both on the well width and the position of the donor, up to 4 spin-singlet to spin-triplet transitions are allowed. Furthermore, depending on the well width and the position of the donor the charged donor can evaporate (i.e. becomes unbound) for sufficiently large magnetic fields. I also calculated the oscillator strength for the lower charged donor transitions. This result helped to explain the experimental results by Jiang et al. [Phys. Rev. B 56, R1692 (1997) (SUNY at Buffalo, Buffalo, NY, USA)] and to definitively identify the triplet state of the off-center charged donor in the spectrum.

In chapter 3, I study a more complex system: the charged exciton. In this case all the three interacting particles are free to move in the quantum well. To do so, a more general and powerful technique was used: the stochastic variational method. I calculated the ground state energy for the exciton and for the negative and positive charged exciton (also called trion) in a given quantum well. This was the first calculation that, to our knowledge, fully includes the inter-particle Coulomb interaction, the quantum
well confinement and particle-particle correlation in all the three spatial dimensions. A comparison between theory and experimental results from the groups in Cambridge (U.K.) and in Rehovot (Israel), showed a good qualitative agreement. However, for narrow quantum well widths a discrepancy between theory and experiment was found, which we ascribed to the increasing importance of the localization effect for decreasing well widths. For the highly polar II-VI quantum wells a comparison between the theory and the experimental data, from the groups in Grenoble (France) and in Würzburg (Germany), showed a practically constant shift as a function of the quantum well width of the theoretical results with respect to the experimental ones which we attributed to the polaron correction, whose effect on charged trions has not yet been dealt with.

As in most experiments on charged trions a magnetic field is applied I extended the calculation of chapter 3 to include the effect of a magnetic field which is directed along the confinement direction. In chapter 4, using again the stochastic variational method, I studied the dependence of the lower energy states of the negatively charged exciton on the magnetic field as well as on the well width and the materials parameters. I found that the \( L = -1 \) spin-triplet state binding energy is almost independent of the hole mass, while the spin-singlet binding energy is largely influenced by the hole mass value. We showed that whether or not the previously predicted spin-triplet/spin-singlet transition can be observed for realistic magnetic field values strongly depends on the value of hole mass. In fact, in agreement with Whittaker and Shields [Phys. Rev. B 56, 15185 (1997), (Toshiba Cambridge Research Center, Cambridge, UK)], I found such a spin-singlet/spin-triplet transition, when I used the asymmetric mass approximation. This approximation implies the use of a lower mass for the hole in the plane perpendicular to the confinement. On the other hand if I use the symmetric mass approximation, which implies the use of a higher mass for the hole, I found no such transition for \( B < 70 \) T. I did, also, find that the negatively charged donor can have a weakly bound “bright”-triplet state. We found good agreement with the experimental results from the group in Cambridge (U.K.) for a quantum well of width 300 Å. We also gave an interpretation of the results from Vanhoucke et al. [Solid Stat. Commun. 115, 403 (2000), (KUL, Leuven, Belgium)] for a quantum well of width 100 Å. From our results we concluded that the lower energy transition in the observed spectra coincide with the spin-singlet state of the charged exciton over all the magnetic field range. The higher energy transition should be attributed to the “dark” triplet state for \( B < 20 \) T, when the translational invariance is broken due to quantum well width fluctuations (i.e. the selection rule which makes the triplet dark is broken). For higher magnetic fields the charged exciton is much more localized and as a consequence is less sensitive to the quantum well width fluctuations. In this case then, i.e. \( B > 25 \) T, the high energy transition line should be attributed to the exciton or eventually to the bright triplet. In this range of fields, in fact, the two states have practically the same energy (the bright triplet is only weakly bound) and we are not able to make a definite assignment for this transition line.
Comparing the positively charged exciton and the negatively charged exciton in the presence of a magnetic field, chapter 5, I found, in agreement with the experimental finding [Glasberg et al., Phys. Rev. B 59, R10 525 (1999), (The Weizmann Institute of Science, Rehovot, Israel)], that the behaviour of the two charged complexes is very different. In fact while the positively charged exciton binding energy is almost constant with the magnetic field the one of the negatively charged exciton increases fastly to saturate at higher magnetic fields. I explain this behaviour in the light of the wave function properties of the system.

In chapter 6 I studied the problem of four interacting particles in a quantum well, i.e. the biexciton problem. I found that the obtained theoretical binding energies are much lower than the experimental ones [from the group in Lyngby (Denmark); the group in Rehovot (Israel) and the group in Urbana-Champaign (Illinois,USA)]. As the biexciton is a rather “extended” system it seems reasonable to assume that the effect of the quantum well width fluctuations is much stronger for this system. We modeled these quantum well width fluctuations through a parabolic potential. I show that including the effect of the well width fluctuations increases the binding energies and brings them closer to the experimental results for reasonable values of the strength of the localization potential.
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