Chapter 3

Optical transitions in the $D^0 - D^0X$ system in n-GaAs

This chapter provides an introduction into the variety of optical transition that exist for low-doped n-GaAs. The main focus is on excitation of free excitons (X) and donor-bound excitons (D^0-D^0X system), and their dependence on magnetic field.

3.1 Neutral donor D^0, free exciton X and donor-bound exciton D^0X

When it comes to the optical transitions in GaAs with donor or acceptor atoms at a low concentration, one can think of the following transitions:

- Excitation of the free electron-hole pairs. The minimal photon energy that is required is equal to the gap energy, $\hbar\omega = E_g$.
- Excitation of free excitons (X), which is an electron-hole pair bound together by the attractive Coulomb potential. The photon energy that is required for this transition is less than the gap energy by the amount of the exciton binding energy E_X, leading to $\hbar\omega = E_g - E_X$.
- Excitation of the neutral donor-bound exciton complex D^0X. This requires less energy than the excitation of free excitons by the amount the binding energy E_{D^0X} of the exciton to the donor. This yields $\hbar\omega = E_g - E_X - E_{D^0X}$.
- Excitation of an exciton bound to an ionized donor (D^+X) or acceptor-bound excitons (A^0X). These require even less photon energy due to the stronger binding for the exciton.

In this chapter we will focus on the optical properties of the donor-bound excitons D^0X since these will form the key object for the studies of coherent optical manipulation in this thesis.

3.1.1 Neutral donor: D^0

In GaAs doped with silicon, *Si* dopants usually play the role of donor by donating their excess electron to the electron ensemble in the conduction band. At low temperatures, however, the electron remains bound to the donor. If the concentration of dopants is sufficiently low the electron wave-functions of the neighboring donors do not overlap, and this results a system of localized non-interacting electrons in hydrogen-like orbitals. The temperature below which the donors are not ionized and the radius of the electron wavefunction can be found quite accurately with the effective mass theory [1]. This allows for writing the equation of motion for the electron's envelope wave-function $F_n(\vec{r})$ as:

$$\left(-\frac{\hbar^2\nabla^2}{2m_e^*} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right) F_n(\vec{r}) = E_n F_n(\vec{r}) \tag{3.1}$$

where $m_e^* = 0.067 m_e$ is the effective mass of the electron in the conduction band of GaAs, m_e is the free electron mass, e is the elementary charge, $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m is the vacuum permittivity constant and $\varepsilon_r = 12.56$ is the relative permittivity constant for GaAs.

Equation 3.1 is a hydrogenic Schrödinger equation of motion in the Coulomb potential of the ionized donor, which results in following spectrum of eigenenergies:

$$E_n = -\frac{m_e^*}{m_e}\frac{1}{\varepsilon_r^2}\frac{R_H}{n^2} \tag{3.2}$$

where $R_H = 13.6$ eV is the Rydberg constant of the hydrogen atom and the energy E_n is defined with respect to the bottom of the conduction band.

The ground state ($n = 1$) of the D^0 electron lies 5.8 meV below the bandgap of the GaAs $E_g = 1.519$ eV (value for at 0 K). This means that donors are not ionized for temperatures well below ≈ 70 K.

The Bohr radius r_n of the n^{th} level can be approximated by:

$$r_n = \frac{m_e}{m_e^*}\varepsilon_r n^2 a_H \tag{3.3}$$

where $a_H = 5.29177 \times 10^{-11}$ m is the Bohr radius of the hydrogen atom. This gives $r_1 \approx 100$ Å. This size sets an upper limit of 10^{-14} cm^{-3} for the concentration of donors if one aims to work with an ensemble of non-interacting donor-bound electrons (this number is also supported by the experimental observations from Chapter 6 of this thesis).

The first excited state ($n = 2$) has a binding energy of 1.4 meV (again with respect to the bottom of conduction band) and a Bohr radius $r_2 = 396$ Å. The difference in energy between the ground $n = 1$ and the first excited $n = 2$ state is 4.4 meV. For the optical transitions of the D^0-D^0X system this translates into difference in wavelength of 20 Å. This is important to keep in mind since optical emission by a D^0X system from a transition to a D^0 state with $n = 2$ can be observed in luminescence experiments, and these luminescence side peaks are often referred to as two electron satellites (TES).

3.1.2 D^0 in a magnetic field

When no magnetic field is applied, the $n = 1$ ground state is two-fold degenerate due to the spin of the electron. When a magnetic field B is applied this degeneracy is lifted and a two-level system is formed. The energy of the spin-up state $|\uparrow\rangle$ is

lower than the energy of the spin-down state $|\downarrow\rangle$ by an amount:

$$\Delta E = g_e \mu_B B \tag{3.4}$$

where $g_e \approx -0.42 \pm 0.02$ [2, 3] is the g-factor for the electron of the GaAs D^0 system, and $\mu_B = 5.79 \cdot 10^{-5}$ eV/T is the Bohr magneton. In a magnetic field $B = 9$ T, $\Delta E = 0.23$ meV. For the optical transitions of the D^0-D^0X system this translates into a difference in wavelength $\Delta\lambda = 1.2$ Å. It would require a temperature below $T \simeq \Delta E / k_B = 2.7$ K, where k_B is the Boltzman constant, to thermally depopulate the $|\downarrow\rangle$ state. If one operates at liquid Helium temperature ($T = 4.2$ K), both states are populated with a ratio of about 2 : 1 for thermal equilibrium.

3.1.3 Free exciton: X

A free exciton X can be described as a weakly bound electron-hole pair. Even though the free exciton is not a localized state, the correlated motion of the electron and hole does follow the hydrogenic equation of motion. For the mass one now has to use the reduced electron-hole mass $m_r = (1/m_e^* + 1/m_h^*)^{-1} = 0.05\ m_e$, where $m_h^* = 0.2 m_e$ of the weighted average of the heavy and light hole effective masses in GaAs [1]. The binding energy of the $n = 1$ free exciton $E_X = 4.3$ meV and the corresponding Bohr radius is $r_X = 133$ Å. The optical transitions associated with excitation of free excitons require an energy equal to bandgap energy E_g minus the binding energy of the exciton E_X, corresponding to $\lambda_X \simeq 818$ nm in zero magnetic field.

3.1.4 X in a magnetic field

When a magnetic field is applied the wavefunction of the free exciton is perturbed and the binding energy decreases [1]. In weak fields, where Coulomb attraction between an electron and a hole is larger than the cyclotron orbit energy, the magnetic field is treated as a perturbation to the excitons wavefunction resulting in a diamagnetic shift for the exciton energy that scales as $\propto B^2$:

$$\Delta E_d = + \frac{e^2}{12 m_r} r_X^2 B^2 \tag{3.5}$$

For the values given above this yields an energy shift $\Delta E_d \sim 0.052$ meV/T^2.

In strong magnetic fields, the cyclotron energy is stronger than the electron-hole Coulomb interaction and both electrons and holes form Landau levels. Now

the Coulomb interaction can be treated as a perturbation. In this regime the dependence of the exciton energy on magnetic field becomes linear and corresponds to the difference in energy between the electron and hole Landau levels:

$$\Delta E_L = +\frac{\hbar e}{m_r} B \tag{3.6}$$

The expected energy shift with magnetic field follows $\Delta E_L \sim 2.3$ meV/T.

Even though this description of the diamagnetic shift of X using the reduced mass m_r provides a good indication of the system's behavior, understanding high-resolution spectroscopy of this system requires a more detailed description that takes into account the difference in mass for light holes and heavy holes, and the Zeeman splittings of all particles involved. A complete picture of the energy shifts of free excitons is therefore rather complicated, and beyond the scope of this thesis. It is, however, important to note that the energy of optical transitions associated with the creation or destruction of free excitons increases with magnetic field, since the cyclotron shifts are typically larger than the Zeeman splitting.

3.1.5 Neutral donor-bound exciton: D^0X

The neutral donor forms an attractive potential to which an exciton can be bound, thus creating the donor-bound exciton complex D^0X. This is a three-body complex (two electrons and one hole) around an ionized Si^+ donor core. The lowest energy levels of this system have the two electrons in a singlet state.

The energy of the optical transition associated with excitation of a D^0X complex is (besides the fine structure) equal to the energy for exciting a free exciton X minus the binding energy of the exciton to the neutral donor D^0. The binding energy for an exciton to the D^0 system (with both systems in their ground state)is for $B = 0$ T approximately 0.9 meV (corresponding to a difference in wavelength between such X and $D^0 - D^0X$ excitation of $\Delta\lambda = 55$ Å) [2–9].

3.1.6 Neutral donor-bound excitons D^0X in a magnetic field

Since the energy for exciting free excitons X increases with magnetic field, also the energy of the $D^0 - D^0X$ transitions increase according to similar diamagnetic-shift laws. The optical spectra of the donor-bound exciton also shows a fine structure due to Zeeman splitting of the electron and the hole's spin. For the transitions with lowest energy this concerns the Zeeman splitting of the D^0 electron spin, and the Zeeman and the orbital energy of the hole in the D^0X complex which has a spin $J = 3/2$ character (heavy hole) [1, 3]. The spin of electron in the D^0X complex can be disregarded since the two electrons are in a singlet state.

In order to characterize the diamagnetic shifts and the fine structure of the GaAs exciton complexes we have performed magneto-photoluminescence experiments (see also Chapter 5). Results of this study are shown in the gray scale plot of Fig. 3.1.

The fine structure of the neutral donor was described earlier. To describe the energy levels of the D^0X complex in magnetic field one has to account for an interplay between the Zeeman splitting of the hole spin and formation of cyclotron orbits. This requires a rather complicated theoretical treatment [1], which goes beyond the scope of this thesis. Instead, we will focus on an empirical study of the

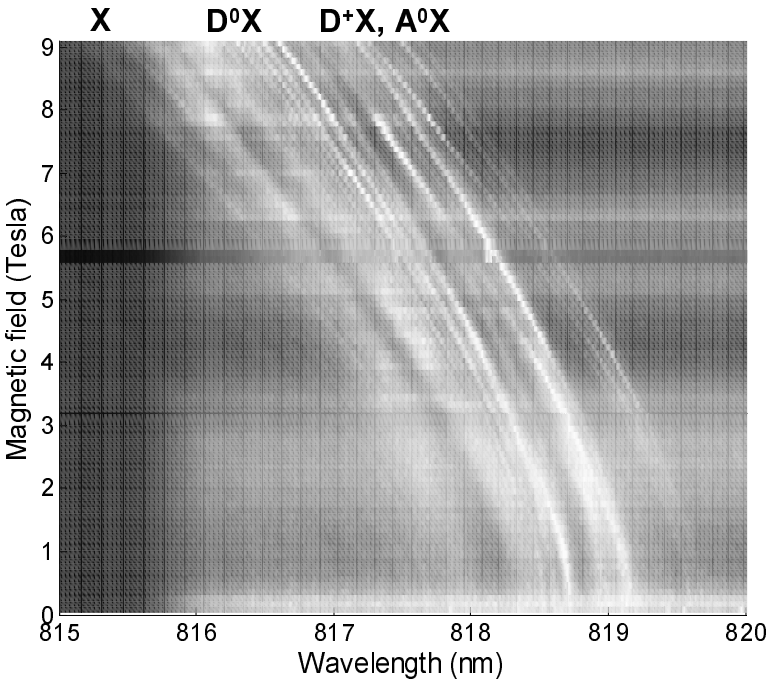

Figure 3.1: Grayscale plot with magneto-photoluminescence spectrums for a range of magnetic fields B, for a GaAs sample with Si doping at $n_{Si} = 3 \times 10^{13}$ cm^{-3}. Dark represents strong luminescence, light represent weak luminescence. The leftmost broad transition corresponds free-exciton luminescence (X). The narrow lines that start for $B = 0$ T at 818.7 nm and evolve into rich spectrum of transitions is the $D^0 - D^0X$ system. Other transitions that are observed (as labeled) are due to acceptor-bound excitons ($A^0 - A^0X$) and ionized donor-bound excitons ($D^+ - D^+X$).

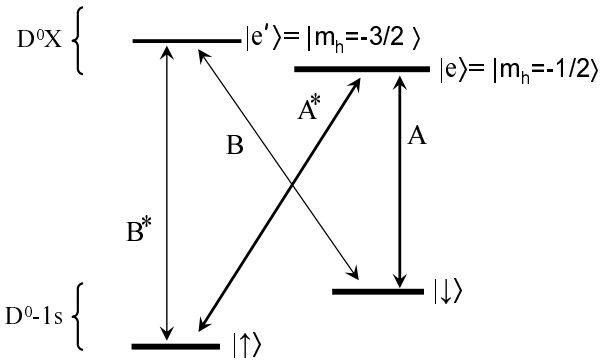

Figure 3.2: Schematic with energy levels and optical transitions associated with excitation of a donor-bound exciton D^0X in an external magnetic field. The ground state of the system (neutral donor D^0, with an electron in a hydrogen-like $1s$ orbital) Zeeman split and labeled as $|\uparrow\rangle$ and $|\downarrow\rangle$. The excited states are donor-bound excitons states (D^0X), with two electrons in a singlet state and a hole that can have various z-projections for its total angular momentum. The lowest D^0X level $|e\rangle$ this is $m_h = -1/2$ due the hole's spin and orbital state $L = 1$. For the second-lowest D^0X level $|e'\rangle$ this is expected to be a $m_h = -3/2$ and $L = 0$ hole's state [7] The two pairs of optical transitions $A-A^*$ and $B-B^*$ form so-called Λ-systems. Such pairs of transitions can be used for implementing EIT.

lowest energy levels of the D^0X complex. This provides adequate information for the investigations later in this thesis. Notably, the associated optical transitions show very strong polarization dependent selection rules [3].

The polarization dependent transmission spectroscopy, that will be described later in the thesis (Chapter 5) provides a very strong indication that the lowest D^0X level corresponds to a state with $m_h = -\frac{1}{2}$ for the z-projection of the hole spin. This also agrees recent reports by Fu *et al.* [7] (this also provides an example of the complex character of the D^0X complex, since one expects in fact $m_h = -\frac{3}{2}$ lowest hole level). A schematic picture of the two lowest D^0X levels together with the two D^0 Zeeman-split electron spin states is shown in Fig .3.2. Each pair of transitions that start from the two D^0 spin states to a particular D^0X level form a so-called Λ-system that can be applied in studies of EIT.

3.2 Polarization selection rules of the optical transitions in $D^0 - D^0X$ system

The strength of optical transition is determined by the magnitude of the dipole moment associated with this transitions, which in general form is written as:

$$\langle \vec{\mu} \rangle = \langle i|\hat{\mu}|f\rangle \tag{3.7}$$

where $|i\rangle$ and $|f\rangle$ are the initial and the final state of the optical transitions and $\hat{\mu} = e \cdot \vec{r}$ is a quantum mechanical dipole operator where e is the charge of electron. Owing to the presence of the $\vec{r}$ in the dipole's operator, the expectation value of the dipole moment is also expected to be a vector.

Knowing the dipole moment, the interaction Hamiltonian for light-matter interaction can be written as:

$$\hat{V}_{int} = -\vec{\mu} \cdot \vec{E} \tag{3.8}$$

where $\vec{E} = E_0 \cdot \vec{e}$ with E_0 being an amplitude of the electric field associated with the optical excitation and $\vec{e}$ is an unitary cartesian vector that describes a polarization of the optical field.

Using the expression for the optical field and the dipole operator the expectation value of the interaction Hamiltonian can be written as:

$$\langle i|\vec{V}_{int}|f\rangle = qE_0\langle i|\vec{r}\cdot\vec{e}|f\rangle = qE_0\langle i|(x\cdot\vec{e_x} + y\cdot\vec{e_y} + z\cdot\vec{e_z})|f\rangle \tag{3.9}$$

The non-zero value of the expectation value in the angled brackets will result in the optical transition that is dipole allowed.

It is often possible to determine whether the interaction Hamiltonian results in zero expectation value based on the principles of symmetry, which creates a basis for sets of polarization and other selection rules.

Lets consider the interaction of the optical field with a donor bound electron spin D^0 that can be excited to the donor-bound exciton complex D^0X. The initial and the final states for the optical transitions of the $D^0 - D^0X$ type can be factorized in the product of the envelope wavefunction and the Bloch wevefunction amplitude as $F(\vec{r}) \cdot \Psi(\vec{r})$. Since the amplitude of the dipole oscillations is comparable to the period of the lattice, while the spread of the envelope function is much larger then that [1] the expectation value in the equation 3.9 can be approximated as:

$$\langle i|\vec{V}_{int}|f\rangle = qE_0F_i(\vec{r})\cdot F_f(\vec{r})\,\langle\Psi_i(\vec{r})|(x\cdot\vec{e_x} + y\cdot\vec{e_y} + z\cdot\vec{e_z})|\Psi_f(\vec{r})\rangle \tag{3.10}$$

The expression $F_i(\vec{r}) \cdot F_f(\vec{r})$ is a scalar product of two functions in integral sense (product integral) and is non-zero only when both functions have the same parity, which demonstrates an example of the parity optical selection rules.

On the other hand, the product $\langle \Psi_i(\vec{r}) | (x \cdot \vec{e_x} + y \cdot \vec{e_y} + z \cdot \vec{e_z}) | \Psi_f(\vec{r}) \rangle$ is interesting from the spherical symmetry point of view. The angular part of the Bloch wavefunctions $\Psi_{i,f}(\vec{r})$ that describes the electron's or the hole's spin is the spherical harmonics of the type $Y_l^m(\theta, \phi)$, where l is the orbital momentum quantum number and m is the projection momentum quantum number. Exact expressions in terms of the angles ϕ and θ for the spherical harmonics can be found in most textbooks on quantum mechanics [10].

Electron spin, for example, which possess an angular momentum of $1/2$ is described by the $Y_{1/2}^{\pm 1/2}$ spherical harmonics. The spherical part of the heavy hole's spin, that has an angular momentum of $3/2$ and therefore four projections, will be a set of four functions $Y_{3/2}^{-3/2..+3/2}$.

The product of the type $\vec{r} \cdot \vec{e}$ can be written as a sum of the spherical harmonics by using the following set of transformations [10]:

$$\sqrt{\frac{3}{4\pi}} z = r \cdot Y_1^0(\theta, \phi) \tag{3.11}$$

$$\sqrt{\frac{3}{4\pi}} x = \frac{r}{\sqrt{2}} \cdot \left[Y_1^{-1}(\theta, \phi) - Y_1^{-1}(\theta, \phi) \right] \tag{3.12}$$

$$-i\sqrt{\frac{3}{4\pi}} y = \frac{r}{\sqrt{2}} \cdot \left[Y_1^{-1}(\theta, \phi) + Y_1^{-1}(\theta, \phi) \right] \tag{3.13}$$

Using the spherical representation of the wavefunctions and operators, the expectation value of the interaction Hamiltonian for the optical transitions of the type $D^0 - D^0X$ reduces to calculating a following integral product:

$$\langle \hat{V}_{int} \rangle \sim \langle Y_{1/2}^{\pm 1/2} | Y_1^{1,0,-1} | Y_{3/2}^{-3/2..+3/2} \rangle \tag{3.14}$$

A conservation of the angular momentum requires that $\Delta l = 0, \pm 1$ and $\Delta m = 0$. The first condition is always satisfied in GaAs owing to the fact that in the process of electron-hole pair generation the spin of electron is $1/2$, the maximum angular momentum of the hole's spin is $3/2$ and the angular momentum carried by the photon is $1 \cdot \hbar$. The second condition depends on the choice of the polarization of the optical field and on the actual projection of the electron's and hole's spin that are participating in the transition.

Lets consider a situation, where an external magnetic field is applied along the $\vec{z}$ direction, which sets a quantization axis for electron's and hole's spins. A light is

propagating along the direction that is collinear with the applied field. If polarization of the light is a right-circular then its polarization state is $\vec{e_x} + i \cdot \vec{e_y}$, which leads to the calculation of the expectation value that is $x + i \cdot y$. In terms of the spherical harmonics this expression is proportional to the Y_1^1 function and when using it in the expression 3.14, the only non-zero products will be obtained between the pair of states $Y_{1/2}^{-1/2}$ (electron spin $m_h = -1/2$) and $Y_{3/2}^{+1/2}$ (heavy hole's spin $m_h = +1/2$) and the pair $Y_{1/2}^{+1/2}$ (electron $m_h = +1/2$) and $Y_{3/2}^{+3/2}$ (heavy hole $m_h = +3/2$). The result of this exercise could have been easily predicted on a basis of the fact that right-circularly polarized photon is inducing an optical transitions with a change in projection of angular momentum by $+\hbar$. In a similar fashion one can show that the left-circularly polarized light induces an optical transition with a change of angular momentum of $-\hbar$. The left and the right circular light's polarization are often referred to as σ^+ and σ^- respectively.

It is interesting to note that in the geometry where the propagation direction of light is along the direction of magnetic field no transitions without change in projection of angular momentum are possible since light can not have polarization vector that is along the propagation direction. If, however, light propagates along the $\vec{x}$ or $\vec{y}$ - direction that is orthogonal to the magnetic field, it can be linearly polarized along the direction of the field - $\vec{z}$-direction. This polarization state leads to the integration of the z function, which is described by the Y_1^0 spherical harmonic. When using it in the expression (3.14) we obtain that only the transitions between $Y_{1/2}^{-1/2}$ and $Y_{3/2}^{-1/2}$ and between $Y_{1/2}^{+1/2}$ and $Y_{3/2}^{+1/2}$ are allowed. These transitions do occur without a change in the total projection of angular momentum and polarization of light that is used is often referred to as a π polarization.

It is quite evident that when light is linearly polarized and orthogonal to both magnetic field and propagation direction it will be seen by the spins system as a superposition of σ^+ and σ^- polarizations, which we will label as σ polarization later in this thesis.

Throughout this thesis we are using the orthogonal to magnetic field light propagation geometry which allows us to selectively address transitions from the D^0 spin $|\uparrow\rangle (m_e = +1/2)$ and D^0 spin $|\downarrow\rangle (m_e = -1/2)$ states to the common excited state D^0X that has $m_h = -1/2$ by using two orthogonal linear polarization of the excitation light.

We also utilize the ability to map polarization state of light on the polarization state of the electron's spin and we show in the Chapter 7 of this thesis that together with coherent optical driving any spin state on the Bloch sphere can be generated.

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