Optical control of the spin state of two Mn atoms in a quantum dot

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(Dated: May 1, 2014)

We report on the optical spectroscopy of the spin of two magnetic atoms (Mn) embedded in an individual quantum dot interacting with either a single electron, a single exciton and single trion. As a result of their interaction to a common entity, the Mn spins become correlated. The dynamics of this process is probed by time resolved spectroscopy, that permits to determine the optical orientation time in the range of a few tens of ns. In addition, we show that the energy of the collective spin states of the two Mn atoms can be tuned through the optical Stark effect induced by a resonant laser field.

Single atom quantum devices1, i.e., systems whose macroscopic properties depend on the quantum state of a single atom, have been demonstrated in several systems, like single donor Silicon transistor2, single Mn doped quantum dot (QD)3, a single magnetic atom in a surface4 or a single NV center in nano diamond.5 The manipulation of the spin state of a single atom has been shown both by optical pumping6,7 and in transport experiments.8 These systems permit to test matter at a fundamental scale and, in some instances, already have practical applications like room temperature magnetometry with nanometer resolution.9,10 A controlled upscale of this primary units would permit to test new physical phenomena and to find new applications. In this regard, the study of chains of a few magnetic atoms deposited on a metal is already giving promising results along this line.11 Here we report on the first step in that direction in the case of Mn atoms in semiconductor QDs.

When Mn atoms are included in a II-VI semiconductor QD (CdTe in ZnTe)12, the spin of the optically created electron-hole pair (exciton) interacts with the 5d electrons of the Mn (total spin S=5/2). In the case of a singly Mn doped QD, this leads to a splitting of the once simple photoluminescence (PL) spectrum of an individual QD into six (2S+1) components.11

In contrast to the case of magnetic atoms in a metal, semiconductors afford the unique opportunity of controlling the exchange interaction between distant magnetic dopants by varying the carrier density of the host. This has been shown in quantum wells13 but in quantum dots the effect is expected to be stronger and to take advantage of the discreteness of the charge addition.14,15 Thus, in a neutral dot containing 2 Mn atoms, the spins are only coupled via a very short range supercharge, which would be only relevant for first or second neighbors.10,17 The injection of a single electron, whose wave function is spread along the entire dot, couples the 2 Mn and the electron spin ferromagnetically, resulting in a ground state with S = 11/2. This contrasts with the addition of a single exciton on the neutral dot, for which the Mn spins also couple ferromagnetically, but the strong spin-orbit coupling of the hole breaks spin rotational invariance. The addition of an exciton on the negatively charged dot, puts the 2 electrons in a singlet state so that the 2 Mn interacting with a single hole.

Here we show how we can address and investigate the magnetic properties of 2 Mn atoms which are coupled to optically injected carriers. The fine structure of a confined exciton (X) and negatively charged exciton (X−) in the exchange field of the 2 Mn atoms are analyzed and modeled in detail. We show that the 2 Mn spins can be optically oriented by the injection of spin polarized carriers in a few ns. Finally, we demonstrate that the energy of the spin states of the 2 Mn atoms can be tuned by a resonant laser field.

The low temperature (T=5K) PL and the PL excitation (PLE) spectra of a CdTe/ZnTe QD containing 2 Mn atoms are presented in Fig. [1]. As in non-magnetic or singly Mn-doped QDs, the emission of the X, X− and biexciton (X2) is observed simultaneously.21 Each excitonic complexe, X-2Mn, X−2Mn and X2-2Mn, is split by the exchange interaction with the 2 Mn spins. The spin structure of this system is better illustrated by the detailed spectrum of the X-2Mn presented in Fig. [2]. As each Mn sits in a different position in the QD, the overlap between the carrier wave function and each Mn atom is different. In this case, 36 PL lines are expected for the X-2Mn complex. The higher and lower PL lines correspond to the total spin projection of the 2 Mn Mz = ±5 coupled to the bright exciton (±1). The next lines correspond to the situation where the less coupled Mn spin has flipped its spin projection component by one unit (Mz = ±4). The emission structure becomes more complex as Mz decreases (towards the center of the emission structure) because different configurations of the 2 Mn spins interacting with the exciton spin are very close in energy.

The details of the PL are compared to a model based on an effective spin Hamiltonian that can be derived from the sp − d model for confined electrons and holes exchanged coupled to the Mn spin.18,19 The spin interacting part of the Hamiltonian of a QD describing the
The small energy correction produced by the Mn-Mn interaction mediated by the presence of the two electrons in the initial state \( E_{\text{eff}} \) is neglected here.

The calculated spectra are presented in Fig. 2. The main feature (i.e. overall splitting, position of PL lines, linear polarization) of the experimental spectra can be well reproduced by this spin effective model. The QD presented here corresponds to a situation where the coupling with one Mn is about twice the coupling with the other (the parameters are listed in the caption of Fig. 2). To reproduce the intensity distribution in the PL spectra, a thermalization on the X-2Mn levels with an effective temperature \( T=40\text{K} \) is included in the model. The inset show the Mn-Mn correlation function calculated for the model presented in the text (exciton) compared with the spin-spin correlation function for a Heisenberg model for two \( S=\frac{5}{2} \).

The emission spectrum of the X$^{-2}$Mn can be computed using a similar spin effective Hamiltonian. It corresponds to the optical transitions between an initial state where the 2 Mn spins interact with a hole spin and two paired electron spins and a final state where the remaining electron is exchanged coupled with the 2 Mn spins.

FIG. 1: PL spectrum showing the coexistence of the neutral exciton (X-2Mn), the negatively charged exciton (X$^{-2}$Mn) and biexciton (X$^2$-2Mn) exchanged coupled to 2 Mn atoms in a CdTe/ZnTe QD. Inset: PL excitation spectra detected on the low energy line of X-2Mn and X$^{-2}$Mn.

FIG. 2: Experimental (top panels) and calculated (bottom panels) spectra of X and X$^{-2}$Mn exchanged coupled to 2 Mn in a QD. See text for details of the calculations performed with \( I_{c,1}=-55, I_{h,1}=150, I_{c,2}=-90, I_{h,2}=270, I_{\Delta}=600\mu eV \), an effective valence band mixing parameter \( \rho/\Delta_{ih}=0.025 \) and \( \theta=0 \). A thermalization (effective temperature \( T=40\text{K} \)) is included for the X-2Mn and hole-2Mn complexes. A broadening of the lines of 40 \( \mu eV \) is included in the calculated spectra. The inset show the Mn-Mn correlation function calculated for the model presented in the text (exciton) compared with the spin-spin correlation function for a Heisenberg model for two \( S=\frac{5}{2} \).

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interaction of the electron spin \( \vec{\sigma} \), the heavy hole spin \( \vec{J} \), and two Mn spins \( \vec{S}_{1,2} \) reads:

\[
\mathcal{H} = \vec{\sigma} \cdot \left( I_{c,1} \vec{S}_1 + I_{c,2} \vec{S}_2 \right) + \vec{J} \cdot \left( I_{h,1} \vec{S}_1 + I_{h,2} \vec{S}_2 \right) + I_{ch} \vec{\sigma} \cdot \vec{J} + I_{12} \vec{S}_1 \cdot \vec{S}_2 \quad (1)
\]

where the hole spin operator, represented in the basis of the two low energy heavy hole states, are related to the Pauli matrices \( \tau \) by \( J_\tau = \eta \tau \) and \( J_z = \frac{3}{2} \tau_z \), with \( \eta = -2\sqrt{\frac{\Delta_{ih}}{2\hbar \rho}} \), \( \rho \) the coupling energy between heavy-holes and light-holes split by \( \Delta_{ih} \) and \( \theta \) the angle relative to the [110] axis of the principal axis of the anisotropy responsible for the valence band mixing. \( I_{h,i} \) \( (I_{c,i}) \) is the exchange integral of the hole (electron) with the Mn atom \( i \), \( I_{ch} \) the electron-hole exchange interaction and \( I_{12} \) the short ranged anti-ferromagnetic Mn-Mn interaction. This latter coupling is only comparable with the carrier-Mn energy when the 2 Mn are positioned closed to each other \( (I_{Mn,Mn}=0.5\text{meV} \) for neighboring atom)\footnote{\cite{16}}, it is neglected in the following because the carrier-Mn interaction is different for the two atoms indicating that they are far apart in the QD.

The emission spectrum of the X$^{-2}$Mn can be computed using a similar spin effective Hamiltonian. It corresponds to the optical transitions between an initial state where the 2 Mn spins interact with a hole spin and two paired electron spins and a final state where the remaining electron is exchanged coupled with the 2 Mn spins.
\[ \chi_{1,2}(k_B T) \equiv \langle \vec{S}_1 \cdot \vec{S}_2 \rangle = \sum_n P_n(k_B T) \langle \Psi_n | \vec{S}_1 \cdot \vec{S}_2 | \Psi_n \rangle \]  

where \( P_n = e^{-E_n/k_B T}/\langle \sum_n e^{-E_n/k_B T} \rangle \) is for the Boltzmann occupation function. The curve \( \chi_{1,2}(k_B T) \) is shown in the inset of Fig. 2, together with the analogous curve for a Heisenberg model \( J_{\text{eff}} \vec{S}_1 \cdot \vec{S}_2 \). The \( \chi_{12} \) for the Heisenberg model depends only on the ratio \( J_{\text{eff}}/k_B T \) so that we take \( J_{\text{eff}} \) as the one that minimize difference between the two correlation curves. This procedure permits to extract an energy to characterize the indirect Mn-Mn correlation. When we use this procedure for the case of 1 electron Heisenberg coupled to 2 Mn, we find \( J_{\text{eff}} = -6 \mu\text{eV} \), for the parameters given in the caption of figure 2 and a scaling of \( J_{\text{eff}}/\sqrt{\Delta \varepsilon_1 \varepsilon_2} \approx -0.05 \), in agreement with the effective coupling derived by one of us.\(^{14}\) For the same parameters, in the case of the exciton mediated effective interaction, we find \( J_{\text{eff}} = -42 \mu\text{eV} \) and a scaling \( J_{\text{eff}}/\sqrt{\Delta \varepsilon_1 \varepsilon_2} \approx -0.2 \).

Similarly to the singly Mn doped QD,\(^{23}\) the overall splitting of the \( X^-\text{-}2\text{Mn} \) observed experimentally is larger than the one obtained with the values of exchange integrals deduced from the calculation of the X-2Mn spectra. This can be understood by the enhancement of the hole-Mn overlap through the increase of the Coulomb attraction of the hole by the two strongly confined electrons.

Figure 5 reveals the linear polarization rate which is observed in the center of the X-2Mn and X^-2Mn PL spectra. This polarization can be explained by the presence of a valence band mixing. This mixing, combined with the short range electron-hole exchange interaction, couples the bright excitons +1 and -1 associated with the same Mn spins configurations\(^{21}\). As in non-magnetic QDs, this mixing creates linearly polarized eigenstates. This mechanism is more efficient in the center of the X-2Mn PL structure where \( M_z \) is smaller and the +1 and -1 exciton close in energy. In the absence of electron-hole exchange interaction (situation of a negatively charged QD) the valence band mixing allows simultaneous hole-exciton optical transition. These mixed states are at the origin of the linear polarization in the spectra of the charged exciton.\(^{21}\) The linear polarization is well reproduced by the spin effective model (Fig. 3(bottom panel)) for both the X-2Mn and X^-2Mn if a weak effective valence band mixing (\( \rho/\Delta \varepsilon = 0.025 \)) is introduced.

The 2 Mn spins can be optically oriented by the injection of spin polarized carriers.\(^{15,16}\) To optically pump the Mn spins, the QD is excited with a tunable continuous wave laser on resonance with the excited state corresponding to the strong PLE peak at 2143.5 meV (Fig. 1(b)).\(^{22}\) The relative intensity of the PL lines of the X-2Mn state depends strongly on the correlation between the polarization of the excitation and detection (Fig. 4(a)). As each line corresponds to a given \( M_z \), this shows that the whole process of spin injection and relaxation creates a non-equilibrium distribution of the two Mn spin states. In opposition to the observation in QDs containing a large number of magnetic atoms,\(^{23}\) the polarization of X-2Mn is almost fully conserved during the lifetime of the exciton. Nevertheless, an exciton spin relaxation time of about 10 ns can be extracted from the time decay of the circular polarization rate of the exciton (exponential fit in Fig. 4(b)).

The main features of time resolved optical orientation experiments are reported in Fig. 4(c-f) where the polarization of the excitation laser is modulated between two circular states by an electro-optic modulator with a rise time of 10 ns combined with a quarter-wave plate. Under these excitation conditions, switching the circular polarization of the laser produces a change of the PL intensity with two transients (Fig. 4(c)): first an abrupt one, reflecting the population change of the spin-polarized excitons; then a slower transient with opposite signs on the two extreme PL lines (Fig. 4(c)) (i.e., when monitoring the Mn spin states \( M_z = +5 \) or \( M_z = -5 \)) and a character-
Orientation increases as soon as a magnetic field, \( B_z \), is applied in the Faraday configuration (Fig. 4(d)). This is the signature of an optical precession of the Mn spins away from the optical axis (QDs growth axis), so that the average spin polarization, \( \sigma_z \), decays completely erase the optical pumping (Fig. 4(e)).

Finally, it is shown in Fig. 5 that a selective addressing of the X-2Mn complex can be achieved with a control laser on resonance with one of the PL line and the energy of the 2 Mn spins tuned optically\(^2\). When a control single mode laser is tuned to the high energy line of X-2Mn in \( \sigma^+ \) polarization, a splitting is detected in \( \sigma^- \) polarization on the low energy line of X-2Mn. The control laser field mixes the states with a 2Mn spin component \( M_z = +5 \) in the presence (X-2Mn) or absence (2Mn alone) of the exciton. At resonance, hybrid matter-field states are created (Fig. 5(b)). As the laser detuning increases, the optically active transitions asymptotically approach the original excitonic transitions where the remaining energy offset is the optical Stark shift. The use of a resonant laser field allows to individually address any spin state of the 2 Mn if the corresponding excitonic transition is sufficiently isolated from the others (Fig. 5(c) and (d)).

In summary, we demonstrated the possibility to access the spin state of 2 Mn atoms embedded in a CdTe/ZnTe QD. The two spins can be optically oriented and their energy tuned by a resonant laser field. As each of these spins is exchanged coupled to the confined carriers, one would expect to be able to control their mutual interaction. Each Mn spin could be individually addressed by a resonant microwave excitation while their coupling could be turned on by the controlled injection of an individual carrier.

This work is supported by the French ANR contract QuAMOS, Fondation Nanoscience (RTRA Grenoble) and EU ITN project Spin-Optronics. JFR ac-
knowledges funding from Ministerio de Economia, grants FIS2010-21883-C02-01, Plan Nacional de I+D, codigo FIS- No. FIS2010-21883-C02-01, and CONSOLIDER CSD2007-0010, and from Generalitat Valenciana, grant Prometeo 2012-011.

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