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Coherent spin-transfer dynamics in diluted magnetic semiconductor quantum wells even after optical excitation with zero net angular momentum

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A quantum kinetic study of correlated spin transfer between optically excited electrons and Mn atoms in a ZnMnSe quantum well is presented. The simulations predict genuine signatures of non-Markovian spin dynamics which are particularly pronounced for special two-color laser excitations with a zero net angular momentum where a Markovian theory predicts an almost zero total electron spin for all times. In contrast, in the quantum kinetic simulations a sizable total electron spin builds up. Subsequently, a coherent oscillatory exchange of spin between the electron and Mn subsystems is observed.

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Recent experimental progress gives access to a coherent nonthermal regime of spin dynamics in solid state systems[1,2] and thus has paved the way towards a coherent all-optical control of magnetic properties.[3–7] A coherent spin control is of special interest because it holds the promise to overcome intrinsic limitations of spin manipulation schemes that rely on incoherent processes. For example, all-optical protocols for a coherent preparation of spin states in a single quantum dot doped with a single Mn atom[8,9] are able to switch between all quantum states of the Mn atom on a time scale that is much faster than achievable by incoherent methods.[10] Moreover, such protocols allow for the preparation of quantum mechanical superpositions which is out of reach for most incoherent schemes. Crucial for the control discussed in Refs. 8 and 9 is the fact that the spin that is optically induced in the electronic subsystem of the quantum dot is coherently transferred to the Mn atom. In contrast to quantum dots, studies of coherent spin dynamics in extended Mn doped diluted magnetic semiconductors (DMSs) have been almost exclusively restricted to investigations of spin precession, i.e., a process where no spin is transferred between the carrier and Mn subsystem.[11–13] The spin transfer has so far been regarded as a purely incoherent process that can be captured by Markovian rate equations.[14–17] For the spin transfer coherent features are widely unexplored. It is worthwhile to note that the description of coherent spin transfer requires a treatment beyond the mean-field theory, while coherent spin precession is well described on the mean-field level.[18]

In this Rapid Communication, we shall demonstrate signatures of coherent nonthermal spin-transfer dynamics appearing in optically driven DMS quantum wells. While such signatures can be found for different excitation conditions, particularly striking are the spin dynamics resulting from an excitation by two short laser pulses with different central frequencies and opposite circular polarization vectors. Such pulses realize an excitation where no net angular momentum is transferred from the laser to the semiconductor but still, at different band energies, finite spin distributions are prepared. We find in the subsequent dynamics a strong buildup of the total electron spin s^e_{tot} which reflects the spin exchange with the Mn atoms. Recalling that under these conditions both the rate and mean-field approaches would predict a constant zero total spin, we have to conclude that the observed spin dynamics is a genuine non-Markovian effect that is driven by correlations between carrier and Mn degrees of freedom.

Theory. Our studies are based on a recently developed quantum kinetic theory (QKT) which describes the correlated spin dynamics in Mn doped DMSs.[18] Here, we shall treat the case of a $Zn_{0.93}Mn_{0.07}Se$ quantum well of thickness $d = 4$ nm. As usual for intrinsic (II,Mn)VI materials, the system is strongly paramagnetic due to the Mn doping. While a detailed derivation of our theory can be found in Ref. 18, here we shall only give a short summary of its essential ingredients. The starting point is a Hamiltonian that comprises the band energies of the carriers in the host material, the exchange interaction between the carrier and Mn spins, as well as the dipole coupling to an external laser field. The exchange interaction has been identified to be the dominant spin relaxation mechanism for the electrons in (II,Mn)VI materials[19] which allows us to concentrate on this mechanism. A finite set of equations of motion has been obtained for all dynamical variables of interest within a density matrix approach by using a correlation expansion. The final equations also involve an average over a random distribution of the Mn positions and describe an on average spatially homogeneous system.

First applications of this approach have been restricted to the dynamics in a single band starting from an initially prepared nonequilibrium spin distribution.[20] There, it was shown that the difference between the quantum kinetic and the Markovian spin transfer arises mainly due to the redistribution of the carriers in k space according to the energy-time uncertainty relation, since the redistribution is suppressed in the Markovian case. Here, however, the situation is much more complicated, since the heavy holes and the interband coherences are included in the calculations as well as a time dependent laser field, whereas in Ref. 20, the electron excitation was modeled by suitable initial conditions.

The relevant dynamical variables describing the correlated spin transfer in a paramagnetic single band system without an external magnetic field are[20]

$$M^{n_2}_{n_1} := \langle \hat{P}^I_{n_1 n_2} \rangle, \tag{1}$$

$$C^{l_2}_{l_1 \mathbf{k}} := \langle c^\dagger_{l_1 \mathbf{k}} c_{l_2 \mathbf{k}} \rangle, \tag{2}$$

$$\bar{K}_{C^{l_2 n_2 \mathbf{k}_2}_{l_1 n_1 \mathbf{k}_1}} := V \delta \langle c^\dagger_{l_1 \mathbf{k}_1} c_{l_2 \mathbf{k}_2} \hat{P}^I_{n_1 n_2} e^{i(\mathbf{k}_2 - \mathbf{k}_1)\mathbf{R}_I} \rangle, \tag{3}$$

where V is the sample volume. $\hat{P}^I_{n_1n_2}$ is defined as $\hat{P}^I_{n_1n_2} := |n_1,I\rangle\langle n_2,I|$, where $|n,I\rangle$ is the eigenstate of the z component of the Mn spin located at the position $\mathbf{R}_I$ with the eigenvalue $n\hbar$ and $n \in \{-\frac{5}{2},\ldots,\frac{5}{2}\}$. $M^{n_2}_{n_1}$ is the average of $\hat{P}^I_{n_1n_2}$ involving the quantum mechanical average as well as the ensemble average over a spatially homogeneous Mn distribution. Due to the ensemble average, $M^{n_2}_{n_1}$ is independent of the position $\mathbf{R}_I$. While $M^{n_2}_{n_1}$ describes the dynamics of the Mn spins, the dynamics of the band electrons are captured by $C^{l_2}_{l_1\mathbf{k}} := \langle c^\dagger_{l_1\mathbf{k}} c_{l_2\mathbf{k}}\rangle$, where $c^\dagger_{l\mathbf{k}}$ ($c_{l\mathbf{k}}$) are Fermi operators creating (destroying) an electron with in-plane wave vector $\mathbf{k}$ in the conduction band l. $\bar{K}_C$ is related to the corresponding expectation value $\langle c^\dagger_{l_1\mathbf{k}_1} c_{l_2\mathbf{k}_2} \hat{P}^I_{n_1n_2} e^{i(\mathbf{k}_2-\mathbf{k}_1)\mathbf{R}_I}\rangle$ by subtracting from the latter all possible factorizations into factors involving expectation values of fewer operators. Its lengthy explicit definition can be found in Eq. (13) of Ref. 18. Thus, $\bar{K}_C$ accounts for the correlations between the electron and Mn degrees of freedom.

In this Rapid Communication, we are interested in the laser driven dynamics. Therefore, we have to extend the single band model to include the optically coupled valence bands. Here, we account for the heavy hole bands which are typically the valence bands with the highest energies in quantum wells. This brings in these dynamical variables

$$D^{v_2}_{v_1\mathbf{k}} := \langle d^\dagger_{v_1\mathbf{k}} d_{v_2\mathbf{k}}\rangle, \tag{4}$$

$$\bar{K}_{D\,v_1n_1\mathbf{k}_1}{}^{v_2n_2\mathbf{k}_2} := V\delta\langle d^\dagger_{v_1\mathbf{k}_1} d_{v_2\mathbf{k}_2} \hat{P}^I_{n_1n_2} e^{i(\mathbf{k}_2-\mathbf{k}_1)\mathbf{R}_I}\rangle, \tag{5}$$

which are the valence band analogs of the conduction band variables in Eqs. (2) and (3). In addition, due to the laser induced coupling of valence and conduction bands, we also have to account for interband coherences,

$$Y^{l_2}_{v_1\mathbf{k}} := \langle d_{v_1\mathbf{k}} c_{l_2-\mathbf{k}}\rangle, \tag{6}$$

and interband correlations,

$$\bar{K}_{Y\,v_1n_1\mathbf{k}_1}{}^{l_2n_2\mathbf{k}_2} := V\delta\langle d_{v_1\mathbf{k}_1} c_{l_2\mathbf{k}_2} \hat{P}^I_{n_1n_2} e^{i(\mathbf{k}_2+\mathbf{k}_1)\mathbf{R}_I}\rangle. \tag{7}$$

As noted already in studies of the optically induced spin precession on the mean-field level,[3,21] during the pulse the coherences Y may induce coherent spin dynamics which are superimposed to the spin relaxation. The interplay between such laser induced coherences and the correlated non-Markovian spin transfer is explored here. The coupled nonlinear equations of motion for the dynamical variables defined in Eqs. (1)–(7) have been derived in Ref. 18 and are given explicitly in the Appendix of that paper.

Results. The simplest way to optically induce spin-transfer dynamics is to excite an unmagnetized DMS without an external magnetic field by a single short circularly polarized laser pulse. In this case no precession can take place and the spin dynamics reflects the transfer between the carrier and dopant spins. Displayed in Fig. 1 are the results of simulations of the laser driven dynamics[25] quantum well by a single circularly σ^- polarized Gaussian pulse with a duration of 1.7 ps full width at half maximum (FWHM) of the intensity. The central frequency is set to the band edge[26] and the pulse area corresponds to a π pulse for a transition at the central frequency. As sketched in the inset of Fig. 1(a), such an excitation generates spin polarized electrons near the band edge of the conduction band. The heavy holes that

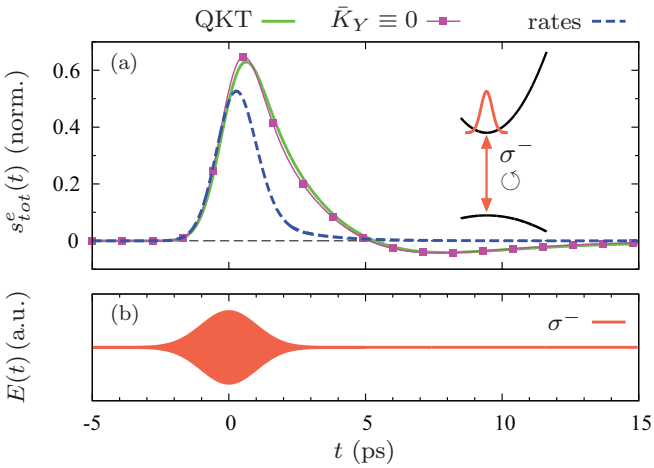

FIG. 1. (Color online) Time evolution of (a) the total electron spin $s^e_{\rm tot}$ in the conduction band calculated with the quantum kinetic model (green solid line), with $\bar{K}_Y$ switched off by hand (pink line with squares), and Markovian rate equations (blue dashed line); (b) the electric field $E(t)$ of the σ^- polarized incident laser pulse. $s^e_{\rm tot}$ has been divided by the total number of electrons in the conduction band after the optical excitation sketched in the inset of (a). We use the following material parameters for ZnMnSe: $J_{sd} = 12$ meV nm^3, $J_{pd} = -60.5$ meV nm^3 (exchange constants) (Ref. 22); $E_P = 24.2$ eV (dipole energy), $E_g = 2.82$ eV (band gap), $m_h = 1.44$ (effective heavy hole mass) (Ref. 23); $m_e = 0.21$ (effective electron mass) (Ref. 24).

are also generated by this pulse cannot change their spins via the exchange interaction with Mn spins as the light hole bands which are necessarily involved as intermediate states are energetically well separated. We will thus not discuss the hole spin in the following. Shown in Fig. 1(a) is the time evolution of $s^e_{\rm tot}$ spin in the conduction band obtained from the QKT (green solid line) together with results corresponding to the Markovian limit of the spin-transfer dynamics (blue dashed line). Here we have used the standard rates for the spin transfer in the conduction band[27,28] while the influence of the exchange interaction on the coherences Y has been neglected in the Markovian limit. We have checked that the latter is not important in our case by performing quantum kinetic calculations where all exchange induced terms in the equations for Y have been switched off by hand [cf. pink squares in Fig. 1(a)]. Obviously, the QKT deviates significantly from the Markov limit. It predicts an enhanced generation of spin polarization which stays in the system much longer than the pulse duration [cf. Fig. 1(b)] and changes its sign after the pulse. In contrast, in the Markovian dynamics the spin production is weaker and the total spin is gone after the pulse without a sign change. As shown in single band calculations for initially spin polarized electrons,[20] i.e., calculations without laser driving and interband coherences Y, the energy-time uncertainty enables energetic redistributions of the carriers which are suppressed in the Markov limit. Here, this also holds for holes even though the valence band spins are pinned. These redistributions reduce the Pauli blocking and thus explain the enhanced spin generation in the QKT. In addition, these redistributions slow down the decay of the spin polarization. The sign change has already been identified in the single band

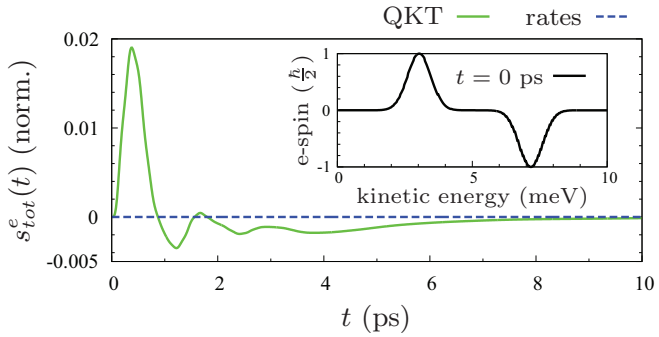

FIG. 2. (Color online) Time evolution of $s^e_{\rm tot}$ in the conduction band after the initial preparation of the electron spin distribution sketched in the inset obtained from the QKT (green solid line) and Markovian rate equations (blue dashed line).

calculations as a signature of non-Markovian dynamics.[20] Our present results demonstrate that this feature is clearly visible in the laser driven case where the spin-transfer dynamics competes with the dynamics of laser induced coherences.

While the simple excitation with a single circularly polarized pulse has already revealed qualitative signatures of non-Markovian dynamics in the spin transfer, the deviation of the QKT from its Markovian limit is even more dramatic in the special situation that we are going to discuss now. To set the stage we shall first analyze the spin-transfer dynamics in a single band of the ZnMnSe quantum well starting with an initial spin distribution with $s^e_{\rm tot} = 0$. To be specific, we consider the initial situation sketched in the inset of Fig. 2, where a Gaussian spin-up distribution of FWHM of 1 meV centered 3 meV above the band gap is combined with a Gaussian spin-down distribution of the same width but shifted by 4 meV to higher energies such that $s^e_{\rm tot}$ sums up to zero. According to the Markovian rate dynamics, the electron spin evolves independently at each kinetic energy in the form of an exponential decay. Recalling that the Markovian spin-transfer rates in quantum wells do not depend on the kinetic energy of the electrons,[20,27] we find for the initial preparation sketched in the inset of Fig. 2 that in a given time the reduction of the spin-up distribution at lower energies equals exactly the reduction of the spin-down distribution at higher energies. Thus, within the Markovian limit $s^e_{\rm tot}$ stays zero for all times under these conditions. This is confirmed by the numerical solution of the corresponding rate equations, which is depicted in Fig. 2 (blue dashed line). In contrast, the prediction of the QKT for this case (green solid line in Fig. 2) is a strong buildup of $s^e_{\rm tot}$ followed by an oscillatory decay. This is no violation of the conservation of angular momentum since spin is transferred between the Mn and electron system. As shown in Ref. 20, the redistributions of electron energies that are enabled by the energy-time uncertainty involve, in general, spin changes and do depend on the excess energy (unlike the rates). In particular, the change of $s^e_{\rm tot}$ is larger for a near band-edge distribution than for distributions high up in the band. This explains why for our initial preparation a finite total spin builds up.

The above analysis suggests that dramatic non-Markovian features in the spin transfer can be expected after the preparation of equal numbers of up and down spins at different energies. However, the preparation of spin states with the required spectral characteristics takes a finite time during which the spin dynamics already sets in. Thus, although the assumption of having, at a given time, spectrally sharp spin distributions with total spin zero is rather idealized, it is possible to realize excitations where essentially the same physics takes place. This can be achieved with two Gaussian pulses of opposite circular polarizations centered at different frequencies. In order to find an excitation that, in the absence of exchange induced spin transfer, would come close to a constant zero $s^e_{\rm tot}$, we have chosen pulse areas close to π at the central frequencies and have adjusted the relative amplitudes of the two pulses to obtain low values of $s^e_{\rm tot}$ for a ZnSe quantum well of the same thickness but without Mn dopants. Of course, also in real quantum wells without Mn dopants spin dynamics will take place during the excitation due to spin relaxation processes other than the exchange coupling to Mn atoms. But typical relaxation times are of the order of several nanoseconds[29] and thus can be neglected on the short times we are interested in here. Figure 3 shows results of simulations of the electron spin dynamics in ZnMnSe quantum wells induced by the so adjusted laser pulses. The green solid line represents the QKT while the blue dashed line is the Markovian result. Indeed, in the Markovian limit there is practically no net spin induced under these conditions. In contrast, this specific two-color excitation gives rise to a large spin response in the quantum kinetic simulations. A sizable $s^e_{\rm tot}$ builds up during the pulses and persists long after the pulses are gone (cf. Fig. 3). The decay of $s^e_{\rm tot}$ exhibits pronounced oscillations which represent a coherent exchange of spin back and forth between the electron and Mn subsystems. Comparing Fig. 3(a) with Fig. 2, it is seen that the resulting amplitude of $s^e_{\rm tot}$ for the laser driven case is similar to the initial value single band calculations (note that both curves have been normalized to the total final electron number which allows a quantitative comparison). Moreover, also the time evolution of $s^e_{\rm tot}$ is similar in both

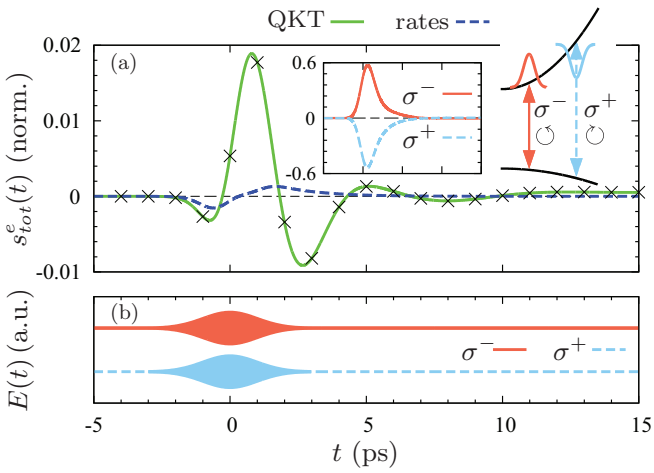

FIG. 3. (Color online) Time evolution of (a) $s^e_{\rm tot}$ calculated within the quantum kinetic model (green solid line) and Markovian limit (blue dashed line); (b) the electric field of the σ^- (red solid line) and σ^+ (light blue dashed line) polarized laser pulses with a duration of 1.7 ps FWHM of the intensity I with $I_{\sigma^+}/I_{\sigma^-} = 1.04$. The excitation is sketched in the right inset of (a) while the left inset shows $s^e_{\rm tot}(t)$ when the σ^+ or the σ^- pulse acts alone. Crosses in (a) mark the sum of the curves in the left inset.

cases. We thus can conclude that the physics responsible for the non-Markovian coherent spin dynamics seen in Fig. 3(a) has the same origin as in the single band case, namely, spin dependent energetic redistributions of electrons enabled by the energy-time uncertainty that depend on the excess energy in the band. Indeed, it turns out that $s^e_{\rm tot}(t)$ shown in Fig. 3(a) almost coincides with the sum of the electron spins induced individually by each of the two pulses [see crosses and the inset in Fig. 3(a) (Ref. 30)], although the dynamics is nonlinear in the laser amplitudes. If the spin relaxation would be independent of the excess energy, the compensation of these two contributions would be complete as in the Markovian limit.

Conclusion. We have performed simulations of the spin dynamics in a ZnMnSe quantum well exposed to short laser pulses within a quantum kinetic theory which accounts for electron-Mn correlations beyond the mean-field level. Our results reveal a number of significant signatures of genuine non-Markovian spin-transfer dynamics. Most striking is the buildup of a sizable net electron spin after a two-color excitation with two oppositely circularly polarized pulses, where in the Markovian limit the total electron spin is expected to stay almost zero for all times. After the buildup a coherent oscillatory exchange of spin between the Mn and electron subsystems is observed, which is not related to spin precession. Thus, we have identified excitation conditions that allow for a coherent nonthermal manipulation of spin-transfer processes in extended DMS which may open different perspectives for a short time coherent spin control.

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