Ultrafast Spin Dynamics in Nickel

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The spin dynamics in Ni is studied by an exact diagonalization method on the ultrafast time scale. It is shown that the femtosecond relaxation of the magneto-optical response results from exchange interaction and spin-orbit coupling. Each of the two mechanisms affects the relaxation process differently. We find that the intrinsic spin dynamics occurs during about 10 fs while extrinsic effects such as laser-pulse duration and spectral width can slow down the observed dynamics considerably. Thus, our theory indicates that there is still room to accelerate the spin dynamics in experiments.

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The potential application of ferromagnetic materials on ultrafast time scales is attractive for information storage. Both experimentally and theoretically the ultra-short time behavior of spin dynamics in transition metals is a new and challenging area. Vaterlaus et al. [1] were the first to study the spin dynamics in ferromagnetic Gd. Employing spin- and time-resolved photo-emission with 60 ps probe pulses they found a spin-lattice relaxation (SLR) of 100±80 ps. Using femtosecond optical and magneto-optical pump-probe techniques, Beaurepaire et al. [2] have studied the relaxation processes of electrons and spins in ferromagnetic Ni. They reported that the magnetization of a 22 nm thick film drops rapidly during the first picosecond and reaches its minimum after 2 ps. Recently, by time-resolved second harmonic generation (SHG), Hohlfeld et al. [3] found that even when electrons and lattice have not reached a common thermal equilibrium, the classical M(T) curve can be reproduced for delay times longer than the electron thermalization time of about 280 fs. On the other hand, the transient magnetization reaches its minimum ≈50 fs before electron thermalization. Both groups used polycrystalline Ni but different pulse durations: 60 fs [2] vs 150 fs [3]. Recently even faster spin decays have been observed [4].

At present, not even the mechanism for this ultrafast spin relaxation is known. Moreover, it is of great importance to know whether these results already reflect the intrinsic spin relaxation time scale or not. Theoretically, even the static ferromagnetism in transition metals has been a challenging topic as the electron correlation is very strong in these systems [5]. The theoretical treatment of the spin dynamics is limited. On the longer time scales, SLR been studied previously [5], and the theory yielded a relaxation time of 48 ps for Gd, in good agreement with the above mentioned experiment [2]. On this time scale, the main contribution results from anisotropic phonon-magnon interaction. To our knowledge, so far no theoretical study has been performed about the spin dynamics of transition metals on the femtosecond time scale, which is apparently needed.

For the theoretical description of ultrafast nonequilibrium charge and spin dynamics, one can either rely on the Baym-Kadanoff-Keldysh Green’s function approach [6] or employing an exact diagonalization framework. In this Letter, we prefer the latter method, which does not involve perturbation theory. Thus it is more suitable to optical excitations far from equilibrium, especially in the presence of strong electron correlations. We start from a spin-independent single-electron Ni bandstructure (monolayer to mimic a thin film geometry) and use an intra-electron-electron interaction. As shown previously [7], to ensure that the interaction possesses the correct atomic symmetry, it is necessary to go beyond the simplest and most commonly used form [7] by including general contributions from four different indices. We also take into account spin-orbit coupling (SOC) as an important effect [8]. Then the total Hamiltonian reads

$$H = \sum_{i,j,k,l,\sigma,\sigma',\sigma'',\alpha''} U_{i\sigma,j\sigma',l\sigma'',k\sigma''} \epsilon_{i\sigma}^\dagger \epsilon_{j\sigma'}^\dagger c_{k\sigma''} c_{l\sigma''} + \sum_{\nu,\sigma,K} \mathcal{E}_\nu(K)n_{\nu\sigma}(K) + H_{SO}$$

(1)

where $U_{i\sigma,j\sigma',l\sigma'',k\sigma''}$ is the electron interaction, which can be described in full generality by the three parameters Coulomb repulsion $U$, exchange interaction $J$, and the exchange anisotropy $\Delta J$, for the details see Ref. [7]. $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) are the usual creation (annihilation) operators in the orbital $i$ with spin $\sigma$ ($\sigma = \uparrow, \downarrow$). $\mathcal{E}_\nu(K)$ is the single-particle energy spectrum for band $\nu$. $n_{\nu\sigma}(K)$ is the particle number operator in $K$-space. $H_{SO}$ is the spin orbit coupling [7]. Such kind of Hamiltonian is general enough to address the spin dynamics on the ultrafast time scale as it contains the necessary ingredients, such as the electronic Coulomb interaction, exchange interaction, and the nature of the bands. However it is not possible to solve it without further approximation. Fortunately, in the magneto-optical process, vertical (momentum conserving) transitions dominate the whole spectra. The
momentum crossing terms in the electron interaction are less important, especially on the ultrafast time scale. For simplicity, we ignore those terms, which are off-diagonal in \( K \), but keep all the off-diagonal terms of the orbitals in position space. The single-particle band structure and spin-orbit coupling parts are treated exactly. Under the above approximation, we are able to solve the Hamiltonian by the exact diagonalization scheme.

The parameters affecting femtosecond spin dynamics fall in two classes: intrinsic (material specific) and extrinsic (experiment specific). Intrinsic parameters are: (i) Coulomb interaction \( U \), (ii) exchange interaction \( J \), (iii) exchange anisotropy \( \Delta J \), (iv) SOC \( \lambda \), and (v) band structure \( \mathcal{E}(K) \). Extrinsic parameters include: (vi) the photon frequencies for the pump and probe pulses, (vii) different optical techniques such as pump-probe spectroscopy of reflectivity and magneto-optics, SHG, or two-photon photoemission (TPPE), (viii) flux of the pulse, (ix) laser spectral width, and (x) optical pulse duration. For a given sample, one can vary these external parameters to actively tune the spin dynamics rather than to only passively observe it. In this Letter we focus on the effects of (ii), (iv), (v), and (ix).

Experimentally when the system is pumped, the initial distribution of states is formed. We populate the states according to a Gaussian distribution, which mimics the real experimental pulse. The center of the populated states is around 2 eV above the ground state. The initial state will evolve with time according to Schrödinger’s equation. We track the relaxation at 2 eV.

For the charge and spin dynamics, the response functions are different. The diagonal element \( \chi^{(1)}_{xy}(\omega, t) \) of the optical susceptibility mainly reflects the contribution from the charge dynamics while \( \chi^{(1)}_{zz}(\omega, t) \) mostly reflects the contribution from the spin dynamics. With the help of those two functions, we are able to address the different characters of the charge and spin dynamics separately.

First we switch off spin-orbit coupling. Then \( \{S^2, S_z\} \) are good quantum numbers. Before we go further, it is worth checking whether our Hamiltonian reasonably describes transition metals such as nickel. Firstly, the band structure is correctly reproduced. Second, the atomic symmetry is well preserved, yielding the correct degeneracies. Thirdly, with nonzero Coulomb interaction \( U \) and exchange interaction \( J \), the ground state is ferromagnetic \( \| \), which is consistent with the ferromagnetism of the Ni thin film. However, for \( U = J = 0 \), the ground state is a singlet. It is interesting to note that the ferromagnetism exclusively results from the Coulomb and exchange interactions. This is a nontrivial result.

In the following we monitor both charge and spin dynamics on the fs time scale and investigate the influence of different intrinsic and extrinsic parameters. We start with the generic set of parameters, which is \( U_0 = 12 \text{ eV}, J_0 = 0.99 \text{ eV}, \) and \( (\Delta J)_0 = 0.12 \text{ eV} \) as given by the spectroscopic data for Ni. The band structure is parameterized in the usual tight-binding form \( \mathcal{E}(k) \). The Gaussian width is taken as broad as 20 eV in order to reveal the intrinsic charge and spin responses. In Figs. (b) and (d), \( \chi^{(1)}_{xy}(\omega, t) \) and \( \chi^{(1)}_{zz}(\omega, t) \), as measured by typical pump-probe experiments, are shown, which represent the spin and charge dynamics, respectively. \( \omega = 2 \text{ eV} \) hereafter. This basic result indicates already a much faster charge and spin dynamics than seen in all existing experiments so far. Consequently, there is room to accelerate both charge and in particular spin dynamics in experiments. The second important result is that the spin dynamics lags behind the charge dynamics by 1 fs, which is an appreciable effect on a time scale of 3 fs. This result is very important for possible applications in magnetic storage technology, as it guarantees a separate non-equilibrium spin memory time. We note in passing that, at no stage of our calculation, we had to invoke the notion of either electron or spin temperature. Particularly the concept of spin temperature is questionable not only due to the heavy non-equilibrium, but also due to the absence of any well-defined quasi-particle statistics for the spins.

In order to pinpoint the origin of the spin dynamics, we first vary the exchange interaction while the Coulomb interaction \( U \) is fixed at 12 eV. For reduced \( J = J_0/10 \) (Figs. 1 (a) and (c)), one can see a more clearly different behavior between spin and charge dynamics. For \( \chi^{(1)}_{xy}(\omega, t) \), the main peak is much broader than for \( \chi^{(1)}_{zz}(\omega, t) \). With increasing \( J \), the spin dynamics begins earlier, but still lags behind the charge dynamics while the latter is virtually unaffected by the variation of \( J \) (see Figs. 1 (c) and (d)). \( \chi^{(1)}_{xy}(\omega, t) \) always reaches its maximum after \( \chi^{(1)}_{zz}(\omega, t) \). An onset of this effect has already been found in \( \mathcal{E}(k) \). The exchange interaction does not only affect the position of the maximum, but also its subsequent decay: with the decrease of \( J \) from \( J_0 \) to \( J_0/10 \) the relaxation time for spin dynamics increases from 2.2 to 3.4 fs. (see Figs. 1 (a) and (b)).

Our calculations show that the relaxation time can be changed by tuning the exchange strength. Physically ferromagnetism mainly results from the exchange interaction, but it has been unknown how the exchange affects the spin dynamics on the ultrafast time scale. Here we clearly see that it accelerates the relaxation: since in the ferromagnetic system the energy scales roughly as \( J \), the relaxation time scales as \( 1/J \). Without SOC, the total spin is a good quantum number, yet the spin dynamics exclusively results from the loss of the quantum coherence due to the dephasing of the initial state. This occurs on different time scales for charge and spin dynamics. Consequently the spin dynamics is delayed as compared to the charge dynamics due to the exchange coupling \( J \).

When the spin-orbit coupling \( \lambda \) is turned on to its generic value \( \lambda_0 = 0.07 \text{ eV} \), the relaxation time of spin dynamics is determined by both \( \lambda \) and \( J \). To see the
effect of SOC on the relaxation process more clearly, we set \( J = \Delta J = 0 \) eV and choose \( \lambda = 0.07, 1.0 \) eV. Fig. 2 shows that the relaxation time becomes shorter if \( \lambda \) is larger while the main peak of the spectrum becomes narrower. Thus for noble metals, such as gold, or rare earths, where SOC is much larger than in Ni, optical alignment could favorably make use of this enhanced SOC and generate an ultrafast spin dynamics in TPPE in this way even from nonmagnetic metals \(^{13}\).

Next we study how bandstructure changes spin and charge dynamics to demonstrate its material sensitivity. We change the bandstructure multiplying all the hopping integrals by a factor of 0.1. A smaller hopping integral corresponds to a more atom-like material. Here \( \{ A_0 \} \) stand for the original hopping integrals for Ni \(^{13}\). Figs. 3 (a) and (b) show the spin and charge dynamics, respectively. Comparing Figs. 1(b) and (d) with the solid curves in Figs. 3 (a) and (b), one may note that upon decreasing the hopping integral from \( A_0 \) to \( A_0/10 \), the recurrent features in both \( |\chi_{xy}(\omega, t)| \) and \( |\chi_{(1)}(\omega, t)| \) are more obvious and the relaxation time for the spin dynamics increases up to more than 20 fs for \( A_0/10 \) (note the different abscissa scales). Thus a small hopping integral as appearing in nanostructured thin films, islands, clusters, or some impurities in the material, slows down the spin dynamics. Besides, the reduction of the pulse width from 20 eV to 0.2 eV further prolongs the relaxation time to 100 fs (long dashed curves in Figs. 3(a) and 3(b)), which is close to the experimentally observed relaxation time. So the laser width (spectral and temporal) has a very important impact on the relaxation time.

In order to further investigate this effect as an example for the variation of the extrinsic parameters, we choose two different laser spectral widths, namely \( W = 20 \) eV (full curves in Figs. 4(a) and (b)) and 0.2 eV (long dashed curves). The other parameters are chosen as the generic values of Ni, namely, \( J = J_0, \Delta J = (\Delta J)_0, A = A_0, U = U_0 \), and \( \lambda = \lambda_0 \). With the increase of the width, the relaxation time is prolonged greatly. From Fig. 4(a), one may notice that for \( W = 20 \) eV, the decay of the spin dynamics is around 3.2 fs; for \( W = 0.2 \) eV, it prolongs to 14 fs. The pulse-width dependent relaxation is also obvious for the charge dynamics (see Fig. 4(b)). For \( W = 20 \) eV, it decays around 2 fs; for \( W = 0.2 \) eV, it lasts up to 13 fs. For real applications, the persistence of the slower decay of the spin dynamics is important as it sets the magnetic memory time. Thus one can change extrinsic parameters to influence the spin dynamics even if one does not change material parameters.

In conclusion, starting from a relativistic many-body Hamiltonian, we studied the spin dynamics on the femtosecond scale. For the intrinsic parameters, it is found that the increase of each of \( \lambda \) and \( J \) decreases the relaxation time, but the individual dependence on each of them is different. This ultrafast dynamics results from both the exchange interaction and SOC and does not involve the lattice \(^{13}\). This is very different from SLR in Ref. \(^1\). The SLR time in Ni is about 304 ps as calculated from a formalism similar to that applied to Gd before \(^{1}\), which can be compared with the experimental value of 400 ps in Ni \(^{14}\). From our calculation it is suggested that the high-speed limit of spin dynamics is about tens of femtoseconds, which is not yet exhausted by experiments. Thus, in total one has to distinguish four different relaxation processes: (a) electronic equilibration (1 fs, due to electron-electron interaction); (b) electron-spin relaxation (a few fs due to exchange interaction or SOC); (c) electron-lattice thermalization (\( \approx 1 \) ps, due to electron-phonon coupling); (d) SLR (\( \approx 100 \) ps due to SOC plus anisotropic crystal-field fluctuations). The hopping integral also has a very important effect on spin dynamics. A small hopping integral slows down the dynamics. This means that e.g. oxides \(^{17}\), exhibiting both dispersive bands and non-dispersive gap states, might be an ideal playground to tune the dynamical time scale at will, in particular, employing SHG or TPPE. For the extrinsic parameters, such as the laser pulse width, a small spectral width favors a slow decay of the spin dynamics. This is important for applications and further experimental studies.

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FIG. 1. Effect of exchange interaction $J$ ($J = J_0/10$ and $J_0$) on spin ((a), (b)) and charge dynamics ((c), (d)). Exchange interaction dominates the spin decay.

FIG. 2. Effect of spin orbit coupling $\lambda$ on spin dynamics. The solid curve is for $\lambda = 0.07$ eV while the dashed curve is for $\lambda = 1$ eV. SOC may speed up the spin dynamics only in heavy elements.

FIG. 3. Effect of hopping integral on (a) spin and (b) charge dynamics. The pulse width effect is also shown. Nanostructuring and selective population of resonances slow down the spin and charge dynamics.

FIG. 4. Effect of laser pulse-width $W$ on (a) spin and (b) charge dynamics for $W = 20$ and 0.2 eV. Monochromatic laser pulses slow down the dynamics.