Angular Momentum Conservation for Coherently Manipulated Spin Polarization in Photoexcited NiO: An *Ab Initio* Calculation

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In an ultrafast laser-induced magnetization-dynamics scenario we demonstrate for the first time an exact microscopic spin-switch mechanism. Combining *ab initio* electronic many-body theory and quantum optics analysis we show in detail how the coherently induced material polarization for every elementary process leads to angular-momentum exchange between the light and the irradiated antiferromagnetic NiO. Thus we answer the long-standing question where the angular momentum goes. The calculation also predicts a dynamic Kerr effect, which provides a signature for monitoring spin dynamics, by simply measuring the transient rotation and ellipticity of the reflected light.

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Ever since the ultrafast all-optical demagnetization in ferromagnetic materials was discovered [1], it has attracted worldwide attention. As hope for technological applications grows, the investigation is enormously intensified. Laser-induced spin manipulated devices will be employed in future computers, with increased speed and reduced size. New experiments demonstrate the delicate interplay between laser pulses and the magnetic state, which varies for different magnetically ordered materials. In ferromagnets, not only demagnetization but time-resolved (TR) spin trajectories have been observed [2], while in antiferromagnetic materials spins can be coherently driven to point in specific directions [3,4], or to oscillate around designated axes [5]. Furthermore, several experimental TR techniques have been implemented thus far, like nonlinear magneto-optics [6], TR photoemission [7,8], and TR x-ray magnetic circular dichroism [9].

However, it is still an open theoretical and experimental question about what the fate of the angular-momentum surplus is during demagnetization in both space and time (naturally underlying a conservation law), which has to be preserved by getting passed to a different subsystem, and eventually absorbed by a bath, e.g., lattice, light, or carriers. Up to now, several mechanisms have been proposed. The Elliot-Yafet mechanism highlights the coupling of the spins to the lattice [10], a mechanism that has been disputed for the demagnetization of metallic ferromagnets in several cases [11,12]; the *sp-d* model emphasizes the coupling of the localized spins to the carrier spins [13], as well as classical Gilbert-damping-based mechanisms [14] and precessional dynamics [15]. None of these mechanisms directly address the angular-momentum transfer at the first-principles level. This is particularly important for the inverse Faraday effect where the angular-momentum exchange plays a pivotal role [5]. Recently Bigot *et al.* showed that in a ferromagnetic material one can distinguish between three temporal regimes: (i) the laser-induced coherent (spin) dynamics, (ii) the electron and spin thermalization where incoherent processes occur, and (iii) the incoherent regime in which the phonon and magnon baths become important [16]. Here we discuss the coherent temporal regime in an insulator (NiO) (no thermalization).

The indirect connection between light and spin subsystems through the spin-orbit coupling (SOC) renders a first-principles description mandatory, as it is free of any empirical parameter. Until now, we have not explicitly considered the fate of the angular momentum, although the only possible way it can follow on very short time scales (coherent regime before the lattice gets involved) is per construction of the emitted light. Here, based on a full *ab initio* calculation for an ultrafast laser-induced spin switch in NiO, we explicitly show that the light acts as the main angular-momentum reservoir. The key idea is the consideration of the induced time-dependent polarization in the material. By introducing the Stokes parameters we describe the polarization state of the emitted wave, while in the Kerr measurements the polarization state of the reflected rather than emitted wave is studied.

We examine the angular-momentum transfer on a doubly embedded (effective core potentials plus charge point field) NiO_5^{-8} cluster which represents one site of the antiferromagnetic (001) surface of NiO [17] and the highly correlated complete active space self-consistent field method, to which SOC is added in a perturbative way. Thus we obtain not only accurate results for the energies for the discrete dispersionless intragap *d*-character levels, but symmetry-obeying many-body wave functions, which are indispensable for computing the optics [18]. The wave functions are then propagated under the influence of the laser field within the interaction picture [19]. Optimization of the laser parameters (incidence geometry, duration, and intensity) is performed with a specially developed genetic algorithm.

In our realistic calculation we irradiate the cluster with linearly polarized light (σ_0) of a duration of 200 fs, energy

of 0.443 eV (optimal although not unique choice), and maximum field amplitude of 8.0×10^9 V/m (lower intensities would lead to slower times [19]) and reverse the spin magnetization by more than 99%. In order to define the spin in the C_{4v} symmetry of the cluster we apply an infinitesimal static magnetic field which also coincides with the quantization axis z of our cluster. The localized intragap d-character states of NiO_5^{-8} mainly consist of the atomic d orbitals of the central Ni, intermixed due to strong correlations and hybridizations with some p orbitals of both the Ni and the surrounding oxygens. The correlations and the high multiplicity of the electronic ground state of the cluster (triplet) allow for spin-charge decoupling [20]. Moreover, using the Clebsch-Gordan coefficients, it can be theoretically shown that for d orbitals only with triplets it is possible to satisfy the optimization condition that the two transition matrix elements be equal. The switching is achieved via excitation to an intermediate state and deexcitation to a final state with opposite spin expectation value [a Λ process, see Fig. 1(b)] [19]. During the process, the expectation value of the time-dependent induced polarization in the material $\langle \mathbf{P}(t) \rangle$ gyrates [see Fig. 1(c)–1(e)], and thus the material can radiate light with different polarizations and different frequencies. The importance of the correlations becomes obvious for within the Hartree-Fock approximation the lowest excitation is at 4.5 eV, and thus the laser pulse of 0.443 eV is so off resonant that no dynamics whatsoever is observed.

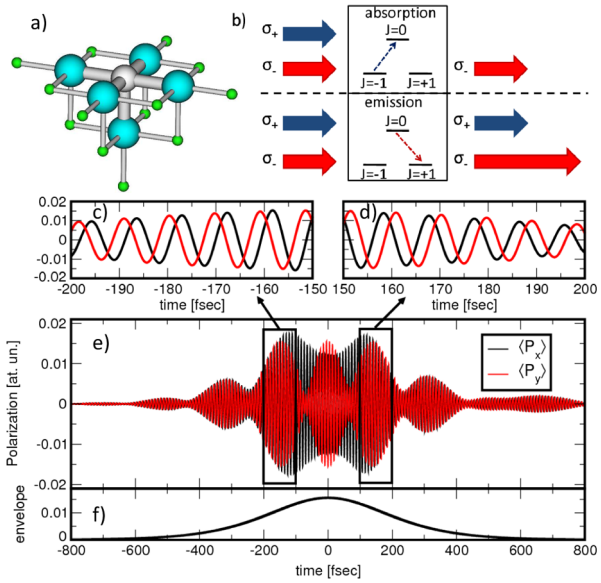

FIG. 1 (color online). Time-dependent polarization. Panel (a) shows the NiO_5^{-8} cluster and panel (e) its induced polarization throughout the whole Λ process. In panels (c) and (d) two time windows are magnified and one can see that the phase difference between $\langle P_x(t) \rangle$ and $\langle P_y(t) \rangle$ changes sign, which corresponds to different helicities of the participating light. Panel (f) shows the envelope of the laser pulse. Panel (b) is a schematic view of the angular-momentum flow during absorption and emission; the cluster has always a net change of $\Delta J = +1$ and the reflected light a net total helicity of σ_-.

Next, in order to qualitatively describe the interaction of light and matter we calculate $\langle \mathbf{P}(t) \rangle$ (see Fig. 1). The main idea is that two perpendicular dipoles oscillating with the same frequency but phase shifted absorb or emit elliptically polarized radiation. Thus after Fourier transforming the light-induced material polarization, we perform a polarization analysis of the spectrum; i.e., we compute the Stokes vector $\mathbf{S} = (I, Q, U, V) = (|P_x|^2 + |P_y|^2, |P_x|^2 - |P_y|^2, 2\,\mathrm{Re}(P_x P_y^*), 2\,\mathrm{Im}(P_x P_y^*))$ and analyze the sign of V which indicates right- or left-handed circularly polarized light (σ_+ or σ_-, respectively). Note that here P_x, P_y, and P_z are the components of $\langle \mathbf{P}(\omega) \rangle$, which contrary to $\langle \mathbf{P}(t) \rangle$ is a complex quantity.

Two aspects deserve consideration here. (i) Looking at the spectral splitting of the two transitions of the Λ process (since the initial and the final state are energetically slightly shifted by the small magnetic field due to the Zeeman effect) we expect the ellipticities for the two frequencies to differ in sign. This is indeed the case as shown in Fig. 2. Note that this analysis cannot distinguish between the absorption (excitation) or emission (deexcitation), it only indicates the transition channel. Therefore it is essential that the analysis be done on processes where absorption and emission can be clearly separated by alternative means (in our case by following the expectation value of the energy of the cluster, see Fig. 3 upper panel). (ii) Since the whole process is highly dynamical, a simple Fourier transformation of $\langle \mathbf{P}(t) \rangle$ yields no information about the frequency evolution of the process. To that end we perform a Fourier transformation convolved with a Gaussian function $h(t - t')$ which ensures that temporally distant points do not contribute to the frequency spectrum as much as close ones [21],

$$\langle \tilde{\mathbf{P}}(\omega, t) \rangle = \int_{-\infty}^{\infty} \langle \mathbf{P}(t') \rangle h(t - t') e^{i\omega t} dt'. \qquad (1)$$

This way we can follow the power spectrum in time. Note that here the same laser pulse both pumps and probes the strongly nonthermalized material.

Figure 3 shows the TR and energy-dispersed circular polarization of the emitted light. Strikingly, the material,

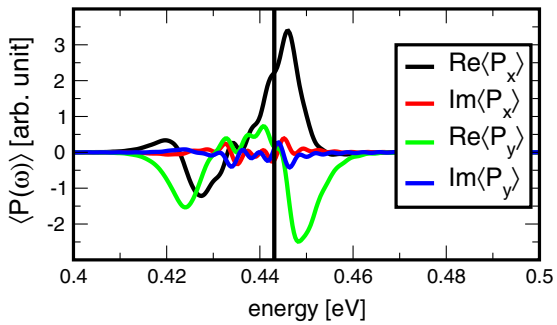

FIG. 2 (color online). Fourier transform of the laser-induced polarization in the material (compare also with Fig. 1).

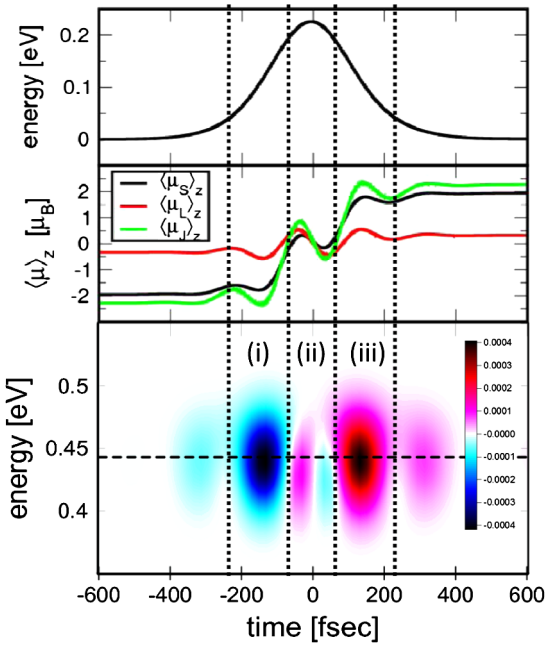

FIG. 3 (color online). Upper panel: Expectation value of the energy of the cluster. Middle panel: Expectation values of the spin, orbital angular momentum, and total angular momentum. Lower panel: Contour plot of the polarization of the emitted light at frequencies around that of the incident light as a function of energy and time. Blue [black in phase (i)] means σ_+ and red [gray in phase (iii)] σ_- light (color code in atomic units). The horizontal dashed line indicates the energy (0.443 eV) of the incident σ_0 light. One can clearly distinguish the change of the polarization when going from absorption to emission (compare upper and lower panel). The four vertical dashed lines roughly indicate phases (i), (ii), and (iii) (see text).

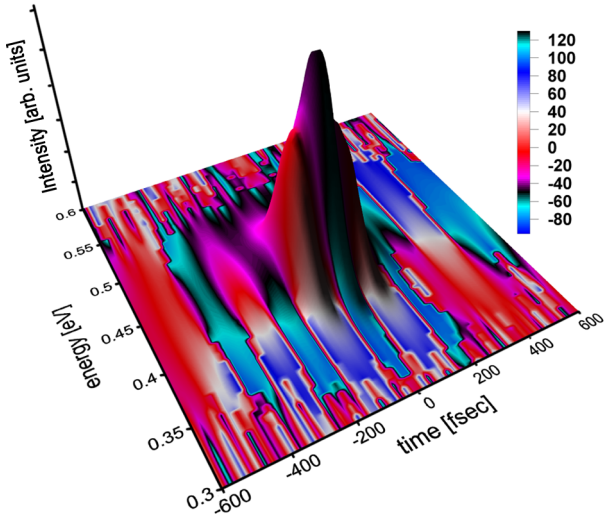

FIG. 4 (color online). Dynamical magneto-optical Kerr effect. The height of the peaks signifies the amplitude of the σ_0 light emitted or absorbed by the material. The color code indicates polarization angle in degrees (physically meaningful only in the presence of a peak). The peak is centered at the maximum of the pulse [phase (ii)] and is surrounded by two smaller peaks. The Kerr angle can become both negative and positive.

although irradiated with σ_0 light, absorbs σ_+ light during phase (i) and emits σ_- light during phase (iii). During phase (ii) both polarizations are present and thus the total polarization becomes almost linear (Fig. 4). Moreover, integrating over the total intensities for all three phases, one gets the correct total intensity relation 1:2:1 as would be expected for a model Λ system of the type $|l=1, m_l=-1\rangle \leftrightarrow |l=0, m_l=0\rangle \leftrightarrow |l=1, m_l=+1\rangle$, and can be understood as the "degree of the Λ character" of the process, which is perfect in our case. The difference here is that the light "absorbs" total angular momentum J_z, while due to the constancy of SOC the orbital angular momentum acts as a funnel through which spin goes over to light, as expected even in simple nonetheless very insightful two-level systems in which a constant $\langle S\rangle$:$\langle L\rangle$ branching ratio is shown [22]. In the opposite case $\langle L\rangle$ would increase at the expense of $\langle S\rangle$. Keep in mind that quantum theory does not allow for simultaneous calculation of spin eigenvalues in all three directions but only of their expectation values, and thus no classical analog exists. Note that we are always referring to the one-pulse process and the coherent temporal regime in the sense of Bigot *et al.* and Zhang *et al.* [16,23].

Most interestingly, the polarization of the material does not remain constant for all times and for all frequencies. This means (i) that the material can absorb one helicity but emit another and (ii) that the elementary processes need not rely on the irradiated polarization, as long as the "needed" one is present (remember that σ_0 is a superposition of both circular polarizations). Thus angular-momentum conservation now becomes a question of integrating over time and frequencies, and so although light does not necessarily take away the totality of the angular-momentum change in the material, it definitely takes away part of it and triggers its redistribution among frequencies and sites.

It is not possible to count photons within the semiclassical model, but only when quantizing the electromagnetic field as well. In this case we need to go over to the product of the Hilbert spaces for the electronic and the photonic part $\mathcal{H} = \mathcal{H}_{\mathrm{el}} \otimes \mathcal{H}_{\mathrm{ph}}$. In a simple approximation, and neglecting transitions when off resonance or with the wrong light polarization the matrix becomes

$$\hat{H} = \begin{pmatrix} E_{\mathrm{in}} + n_{\sigma_+}\hbar\omega_0 + (n_{\sigma_-}+1)\hbar\omega_0 & 0 & g d_{\sigma_+} \hat{a}^\dagger_{\sigma_+} \sqrt{n_{\sigma_+}+1} \\ 0 & E_{\mathrm{fi}} + (n_{\sigma_+}+1)\hbar\omega_0 + n_{\sigma_-}\hbar\omega_0 & g d_{\sigma_-} \hat{a}^\dagger_{\sigma_-} \sqrt{n_{\sigma_-}+1} \\ g d^*_{\sigma_+} \hat{a}_{\sigma_+} \sqrt{n_{\sigma_+}+1} & g d^*_{\sigma_-} \hat{a}_{\sigma_-} \sqrt{n_{\sigma_-}+1} & E_{\mathrm{exc}} + (n_{\sigma_+}+1)\hbar\omega_0 + (n_{\sigma_-}+1)\hbar\omega_0 \end{pmatrix}, \quad (2)$$

where E_{in}, E_{fi}, and E_{exc} are the energies of the initial, final, and intermediate state, n_{σ_+} and n_{σ_-} the numbers of the σ_+ and σ_- photons, d_{σ_+} and d_{σ_-} the transition matrix elements for σ_+ and σ_- light, $\hat{a}^\dagger_{\sigma_+}$, $\hat{a}^\dagger_{\sigma_-}$, $\hat{a}_{\sigma_+}$, and $\hat{a}_{\sigma_-}$ the creation and annihilation operators of σ_+ and σ_- photons, and ω_0 and g the frequency of the laser (same for both polarizations) and a cavity-dependent constant, respectively. For strong fields (large photon numbers) the above Hamiltonian becomes similar to that of the semiclassical Λ process. So we can identify the initial and the final states as connected to the number of photons present in the environment. Thus we know that at the end of the process we have one σ_+ photon less and one σ_- more, which amounts to $\Delta J_{\mathrm{ph}} = -2$. Note here that for high fields the decoherence of electronic states upon application of a quantized, coherent field can be made as small as desired by making the interaction time sufficiently short compared to the spontaneous decay time [24,25]. This concludes the bookkeeping of the angular momentum: the system evolves with a branching ratio (angular-momentum redistribution) of $\langle \Delta J_{\mathrm{ph}} \rangle_{\mathrm{tot}}$:$\langle \Delta S \rangle_{\mathrm{tot}}$:$\langle \Delta L \rangle_{\mathrm{tot}} = -2$:1.8:0.2.

Our final result is the dynamical Kerr effect. By calculating the angle of the σ_0 part of the emitted light, we find that it is both frequency- and time-dependent, and thus a TR measurement of the ellipticity and polarization angle of the reflected or reemitted light can perfectly monitor such complicated nonequilibrium processes [26]; Fig. 4 (compare with the off-diagonal suceptibility-tensor elements in Ref. [23]). The material clearly tends to emit in a polarization direction parallel to that of the laser pulse during phases (i) and (iii), and with larger Kerr angles during phase (ii) when it is more strongly nonthermalized (Fig. 4).

In conclusion, we have shown that for every elementary on-site process of optically induced magnetic switching, light acts on ultrashort time scales (before slower degrees of freedom such as phonons set in) as local angular-momentum reservoir. The transfer takes place with the use of the orbital angular momentum via SOC as a converter, as the induced material polarization indicates. The material absorbs and emits light as needed in order to obey selection rules, as long as the helicity needed is present in the environment (irradiating laser). The process evolves in a highly dynamical way, creating a dynamical far-from-equilibrium Kerr effect. The process becomes even more complex since the light absorbed at every single site consists not only of the driving laser pulse but also of the emitted light from neighboring sites. However, the single-site mechanism clearly points out the electromagnetic field as both a local reservoir and a trigger of spin or orbital angular-momentum redistribution. In an antiferromagnetic material, where the overall magnetic moment remains zero, the role of the light is mainly to trigger the exchange, while in a ferromagnetic one light can (at least to a large extent) carry away angular momentum.

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