Tuning the laser-induced ultrafast demagnetization of transition metals

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Abstract

The ultrafast demagnetization (UFD) dynamics of itinerant ferromagnets is theoretically investigated as a function of the characteristics of the initial laser excitation. A many-body $pd$-band Hamiltonian is considered which takes into account hybridizations, Coulomb interactions, spin-orbit interactions and the coupling to the laser field on the same electronic level. In this way, a fruitful connection is established between the non-adiabatic quantum dynamics and the well-known equilibrium statistical mechanics of itinerant-electron ferromagnets. The time evolution during and after the pulse absorption is determined exactly by performing numerical Lanczos propagations on a small cluster model with parameters appropriate for Ni. The most relevant laser parameters, namely, the fluence $F$, wave length $\lambda$, polarization $\hat{\varepsilon}$ and pulse duration $\tau_p$ are varied systematically. The results show how $F$, $\hat{\varepsilon}$ and $\tau_p$ allow one to control the total absorbed energy, the spectral distribution of the initial excitation, and the subsequent magnetization dynamics. The calculations show that reasonable changes in these parameters do not affect the UFD dynamics qualitatively and have only a minor influence on the time scale $\tau_{dm}$ which characterizes the initial demagnetization. In contrast, our model predicts that the degree of demagnetization $\Delta S_z/S_0^z$ achieved for $t \gtrsim \tau_{dm}$ correlates well with the average number of electrons excited by the laser or average number of absorbed photons $n_{ph}$, which can be tuned by varying the fluence, spectral distribution and polarization of the laser pulse. The theoretical results are discussed by comparing them with available experiments. From a fundamental perspective, the robustness of the ultrafast demagnetization effect is theoretically demonstrated, as a phenomenon reflecting the intrinsic dynamics of the metallic $3d$ valence electrons. A wide variety of well-focused possibilities of tailoring the efficacy of the ultrafast demagnetization process is thereby opened.
I. INTRODUCTION

Over the past twenty years, a wide range of different time-resolved experiments have demonstrated that the excitation of magnetic transition metals (TMs) and rare earths with short laser pulses triggers an ultrafast demagnetization (UFD) of the material on a sub-picosecond or picosecond time scale. This remarkable effect offers new possibilities of ultrafast control and manipulation of the magnetization, which could find multiple applications in spin-electronic devices and storage media. Understanding the non-trivial quantum physics behind this phenomenon is obviously crucial for any knowledge-oriented material design. Therefore, several mechanisms explaining the UFD have been proposed in the literature. On the one hand, one finds models in which the central role is played by the coupling between the narrow-band electrons responsible for magnetism and some distinct, a priori nonmagnetic degrees of freedom or field. In this context, let us mention the mechanisms based on electron-phonon spin-flip scattering, on the transport of spin-polarized electrons, and on the coherent relativistic interaction between the photon field and the electronic spins. On the other hand, two purely electronic theories have also been proposed, in which the essential part of the demagnetization takes place within the electronic system, as a result of the coupling between the spin and translational degrees of freedom in the presence of the lattice potential. To this category belong the time-dependent density-functional studies reported in Refs. These explain the UFD as a throughout breakdown of the spin density and local magnetic moments in all unit cells, which involves spin-orbit driven spin flips and spin currents. An alternative approach, which is particularly relevant for the present paper, is the many-body electronic model Hamiltonian proposed in Ref. In this case the experimentally observed demagnetization is explained as the consequence of an ultrafast breakdown of the FM correlations between the local 3d magnetic moments which remain highly stable at all times. From the latter investigations the following microscopic picture of the magnetization dynamics emerges: (i) At the start the laser excitation changes the occupation of the valence-electron states by inducing mainly 3d-to-4p electronic transitions, thus creating holes in the magnetically relevant 3d band. During this process the total magnetization of the sample remains essentially unchanged, since spin is conserved in optical transitions. (ii) These changes in occupations trigger the dynamics by opening so far Pauli-blocked new channels for spin-orbit coupling
(SOC) induced local angular-momentum transfers, dominantly from the atomic $d$-electron spins $\vec{s}_i$ to the $d$-orbital moments $\vec{l}_i$. Taking into account that the local spin moments are initially large and the orbital moments almost quenched, this process alone would tend to enhance $\langle \vec{l}_i \rangle$ at the expense of $\langle \vec{s}_i \rangle$, since the total local angular momentum $\vec{j}_i = \vec{l}_i + \vec{s}_i$ is conserved by the SOC. (iii) However, the perpetual motion of electrons in the lattice due to interatomic hopping quenches most efficiently any incipient increase of the average orbital angular momentum $\langle \vec{L} \rangle = \sum_i \langle \vec{l}_i \rangle$ on a time scale of the order of one femtosecond. The result of these three simple fundamental processes is the rapid decrease of the average electronic angular momentum $\langle \vec{J} \rangle = \sum_i \langle \vec{j}_i \rangle$ and magnetization of the sample as a function of time. The demagnetization occurs essentially at the same rate as the spin-to-orbital angular momentum transfer, which is governed by the SOC and thus corresponds to a characteristic demagnetization time $\tau_{dm}$ of the order of 100 fs. Notice, moreover, that the sum of the angular momenta associated to the electronic and ionic degrees of freedom is strictly preserved by the electron-lattice interactions. Therefore, the decrease of $\langle \vec{J} \rangle$ is exactly compensated by an increase of the lattice angular momentum $\vec{L}_{\text{lat}}$, occurring at the same rate. The fact that high local-moment stability, electron delocalization, and spin-orbit interactions are all inherent features of itinerant-electron magnetism explains the experimentally observed universality of the UFD effect. Further details on the electronic mechanism of UFD are discussed in Ref. [45].

In past years a considerable research activity has been focused on the role of the initial excitation in the UFD process, and on the possibilities of controlling the spin dynamics by tuning the laser-pulse characteristics. For example, it has been recently demonstrated that the degree of demagnetization can in principle be controlled by changing the shape and spectral distribution of the pump pulse. It is therefore most interesting to correlate the degree of demagnetization with the material parameters and electronic structure. Furthermore, one would like to understand how the efficiency of the demagnetization process depends on the degree of excitation of the ferromagnet. Varying the intensity of the pumping pulse at a given frequency allows us to adjust the number of absorbed photons, excited electrons and absorbed energy. Changing the laser frequency for a given absorbed energy one should be able to discern the role of the number of excitations, and thus gain further insight into thermalization effects. In addition, one may also consider different circularly and linearly polarized light, in order to explore how an initial transfer of angular momentum
upon laser absorption may affect the subsequent dynamics. Finally, adjusting the laser-pulse duration \( \tau_p \), from ultrashort highly-intense excitations to values of \( \tau_p \) comparable with SOC relaxation time, should help us to reveal any specific spin dynamics taking place while the laser field is active, and which may result from SOC-laser interference effects.\(^{38-40} \) It is the purpose of this paper to investigate the role of the initial laser excitation on the magnetization dynamics of ferromagnetic TMs and to quantify the possibilities of tuning the ultrafast demagnetization by its means. To this aim we consider a many-body electronic theory in which the dynamics of the electronic translational, orbital and spin degrees of freedom, as well as their coupling to the external electric field, are described quantum mechanically and on the same footing.\(^{45} \)

The remainder of the paper is organized as follows. The theoretical background, including a derivation of the model Hamiltonian, the involved approximations, and the parameters used for the calculations, is presented in Sec. II. Exact numerical results for the magnetization dynamics as a function of the fluence, wave length, polarization and duration of the laser pulse are presented and discussed in Sec. III. Finally, Sec. IV summarizes the main conclusions and perspectives.

II. THEORETICAL BACKGROUND

In the following we first derive the electronic model\(^{45} \) used in the present investigations of the laser-induced magnetization dynamics by explicitly pointing out all the involved approximations. The complete many-body problem, which includes both electronic and ionic degrees of freedom, is simplified by using the Born Oppenheimer approximation, which decouples the electronic and ionic dynamics.\(^{49} \) This is justified, as usual, by the large ion-to-electron mass ratio, and the resulting differences in the corresponding time scales. Since we are interested in the dynamics of the magnetization, which is given by the spin and orbital electronic contributions, we focus on the electronic degrees of freedom so that the ion coordinates appear only as parameters of the quantum many-electron problem. Although the lattice dynamics is ignored in all the calculations reported in Sec. III we shall return to it at the end of this section and in Sec. IV when discussing the conservation of total (lattice plus electron) angular momentum and the possible role of the coupling to phonons.

The spin and orbital magnetic moments of transition metals are known to be dominated
by the $3d$-electron contributions. Moreover, the prime optical excitations of the $3d$ states, which result from the pumping laser, involve transitions to the nearby $4p$ orbitals. Therefore, in order to capture the main physics of laser-excited $3d$ electrons in ferromagnetic TMs, it is reasonable to concentrate on the correlated-electron dynamics within these two bands. The corresponding many-body $pd$ Hamiltonian is given by

$$
\hat{H} = \hat{H}_0 + \hat{H}_C + \hat{H}_{SO} + \hat{H}_E(t) ,
$$

where

$$
\hat{H}_0 = \sum_{i\sigma} \varepsilon_\alpha \hat{n}_{i\alpha\sigma} + \sum_{ij} \sum_{\alpha\beta\sigma} t_{ij}^{\alpha\beta} \hat{c}_{i\alpha\sigma}^{\dagger} \hat{c}_{j\beta\sigma}
$$

describes the single-particle electronic structure of the $3d$ and $4p$ bands. In the usual notation, $\hat{c}_{i\alpha\sigma}^{\dagger}$ ($\hat{c}_{i\alpha\sigma}$) creates (annihilates) an electron at atom $i$ with radial and orbital quantum numbers $\alpha = nlm$ and spin $\sigma$ ($nl$ refers to $3d$ and $4p$). The corresponding electron number operator is $\hat{n}_{i\alpha\sigma}$. For simplicity, the energy levels $\varepsilon_\alpha$ of the atomic-like $3d$ and $4p$ orbitals $|\varphi_{i\alpha}\rangle$ are assumed to be independent of $m$. The interatomic hopping integrals $t_{ij}^{\alpha\beta}$ describe the delocalization of the electrons throughout the lattice. Formally, they are given by $t_{ij}^{\alpha\beta} = \langle \varphi_{i\alpha}|(-\hbar^2\nabla^2/2\mu + \phi^{\text{lat}})|\varphi_{j\beta}\rangle$, where $\mu$ stands for the electron mass and $\phi^{\text{lat}}$ for the effective lattice potential, which depends on all atomic positions $\vec{R}_i$. Notice that the hoppings $t_{ij}^{\alpha\beta}$, but also the energy levels $\varepsilon_\alpha = t_{ii}^{\alpha\alpha}$, incorporate the leading contribution to the electron dynamics resulting from the electron-lattice interaction as given by $\phi^{\text{lat}}$. In the following, the hopping integrals $t_{ij}^{\alpha\beta}$ are determined by using the two-center approximation, which takes into account the most important terms in $\phi^{\text{lat}}$ due to the ions $i$ and $j$. In this case $t_{ij}^{\alpha\beta}$ depends only on the relative vector $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$, as well as on the radial and orbital quantum numbers $nlm$ of the orbitals $\alpha$ and $\beta$. Further details on the calculation of $t_{ij}^{\alpha\beta}$ may be found in Appendix A.

The second term, $\hat{H}_C$ in Eq. (1), refers to the electron-electron interaction. For simplicity, we approximate it by taking into account only the dominant intra-atomic terms among the $3d$ electrons, which are known to be responsible for the magnetic behavior of TMs. Starting from the general intra-atomic expression

$$
\hat{H}_C = \frac{1}{2} \sum_i \sum_{\alpha\beta\gamma\delta E3d} \sum_{\sigma\sigma'} V_{\alpha\beta\gamma\delta} \hat{c}_{i\alpha\sigma}^{\dagger} \hat{c}_{i\beta\sigma'} \hat{c}_{i\gamma\sigma'} \hat{c}_{i\delta\sigma} ,
$$

we consider only the largest two-orbital integrals, namely, the direct terms $U_{\alpha\beta} = V_{\alpha\beta\alpha\beta}$ and the exchange terms $J_{\alpha\beta} = V_{\alpha\beta\alpha\beta}$ ($\alpha \neq \beta$), which are the most important for the magnetic
behavior. Moreover, the orbital dependences of $U_{\alpha\beta}$ and $J_{\alpha\beta}$ are neglected by setting them equal to their average values $U_{\alpha\beta} = U$ and $J_{\alpha\beta} = J$. While the orbital dependences of the intra-atomic $d$-electron repulsions are known to be important for a quantitative description of orbital magnetism, they are not essential for describing the total spin polarization within the 3$d$ band, even as a function of temperature. Taking into account these simplifications one obtains the particularly transparent form:

$$\hat{H}_C = \frac{1}{2} \left( U - \frac{J}{2} \right) \sum_i \hat{n}^d_i (\hat{n}^d_i - 1) - J \sum_i \hat{s}^d_i \cdot \hat{s}^d_i + \frac{J}{2} \sum_{i\alpha\in3d} \hat{n}_{i\alpha} (2 - \hat{n}_{i\alpha}) + \frac{J}{4} \sum_i \hat{n}^d_i . \quad (4)$$

Here, $\hat{n}^d_i = \sum_{\alpha\in3d,\sigma} \hat{n}_{i\alpha\sigma}$ denotes the operator for the total number of 3$d$ electrons at atom $i$, $\hat{s}^\alpha_i (\hat{n}_{i\alpha})$ is the spin (number) operator for the orbital $\alpha$ at atom $i$, and $\hat{s}^d_i = \sum_{\alpha\in3d} \hat{s}^\alpha_i$ the total 3$d$-electron spin operator at atom $i$. The first terms, proportional to the number of pairs of $d$ electrons, take into account the changes in the Coulomb energy resulting from charge fluctuations. Although important for correlations, they have a visibly non-magnetic character. The second terms, proportional to $(\hat{s}^d_i)^2$, favor a parallel alignment of all the 3$d$ spins at each atom (Hund’s first rule). They are responsible for the formation and strong stability of the local spin moments ($J \sim 1$ eV). Part of the energy gain upon local moment formation (33–50% depending on the number of unpaired electrons) is compensated by the third terms, which are proportional to $\hat{n}_{i\alpha}(2 - \hat{n}_{i\alpha})$. These terms are actually ignored in the subsequent dynamics, since their contribution results in an effective reduction of the exchange integral $J$, and since they are unaffected by the relative orientation of the unpaired spins. Finally, the last terms amount to an unimportant constant energy shift which can be incorporated in the definition of the bare levels $\varepsilon_{3d}$ [see Eq. (2)].

For the sake of compactness it is useful to define a new direct Coulomb repulsion parameter $U$ as the average repulsion $U - J/2$ between $d$ electrons having parallel and antiparallel spins. In this way one obtains the model interaction in its final form:

$$\hat{H}_C = \frac{U}{2} \sum_i \hat{n}^d_i (\hat{n}^d_i - 1) - J \sum_i \hat{s}^d_i \cdot \hat{s}^d_i . \quad (5)$$

Notice that $\hat{H}_C$, as the full Coulomb interaction, conserves both the spin $\hat{s}^d_i$ and orbital $\hat{l}_i$ angular momenta of the atoms, since the rotational invariance of the first-principles interaction is not altered by the local approximations. In this context it is useful to recall that this model has been successfully applied in numerous previous studies of the equilibrium ground-state and finite-temperature properties of transition-metal magnetism.
The third term in Eq. (1) is the spin-orbit coupling operator

$$\hat{H}_{SO} = \xi \sum_i \sum_{\alpha \alpha' \in 3d} \sum_{\sigma \sigma'} (\vec{l}_i \cdot \vec{s}_i)_{\alpha \sigma, \alpha' \sigma'} \hat{c}_{i \alpha \sigma} \hat{c}_{i \alpha' \sigma'}^\dagger$$

in an intra-atomic approximation within the 3d band, where the parameter $\xi$ denotes the SOC strength. The matrix elements $(\vec{l}_i \cdot \vec{s}_i)_{\alpha \sigma, \alpha' \sigma'}$ of $\hat{H}_{SO}$ at atom $i$ couple the spin and orbital degrees of freedom, thereby conserving the total local angular momentum $\vec{j}_i = \vec{l}_i + \vec{s}_i$.

The last term $\hat{H}_E$ in Eq. (1) introduces the interaction with the external laser field, which is treated in the intra-atomic dipole approximation. For linearly polarized light we have

$$\hat{H}_E(t) = e\vec{\epsilon} \cdot \vec{E}(t) = e|\vec{E}(t)| \sum_{i \alpha \beta \sigma} \langle \alpha | \hat{\vec{r}} | \beta \rangle \hat{c}_{i \alpha \sigma} \hat{c}_{i \beta \sigma} ,$$

where $\vec{E}(t)$ refers to the uniform classical electric field, $\hat{\vec{r}}$ denotes a dimensionless normalized polarization vector, and $e > 0$ is the electron charge. In the case of circularly polarized laser pulses $\hat{H}_E$ is replaced by the operator $\hat{H}_E^\sigma$, which describes an electric field with helicity $\sigma = \pm 1$ carrying an angular momentum $\sigma \hbar$ along the $z$ axis. This is given by

$$\hat{H}_E^\sigma(t) = e|\vec{E}(t)| \hat{P}_\sigma (\hat{\vec{r}} \cdot \hat{\vec{r}}^\dagger) \hat{P}_\sigma + h.c. ,$$

where $\hat{P}_d$ ($\hat{P}_p$) denotes the projection operator onto the 3d (4p) orbitals and $\hat{\vec{r}} = (\hat{\vec{e}}_x \pm i\hat{\vec{e}}_y)/\sqrt{2}$ is the complex polarization vector. As usual, $\hat{\vec{e}}_x$ and $\hat{\vec{e}}_y$ stand for the unit vectors along the $x$ and $y$ axis. Since the dipole matrix elements $\langle \alpha | \hat{\vec{r}} | \beta \rangle$ satisfy the atomic selection rule $\langle nlm | \hat{\vec{r}} | n' l' m' \rangle = 0$ unless $l - l' = \pm 1$, the optical excitation involves only 3d-4p transitions. A more detailed account of the dipole matrix elements is given in Appendix B.

The operator $\hat{H}_E^\pm$ can be interpreted as follows. The first term in Eq. (8) describes the absorption of a photon which transfers an angular momentum $+\hbar$ to a 3d electron making a transition to a 4p orbital ($m \rightarrow m + 1$). Hermiticity, as ensured by the second term in Eq. (8), implies the emission of a photon with angular momentum $\hbar$ in the reverse electronic transition from a 4p to a 3d orbital ($m \rightarrow m - 1$). Analogously, the operator $\hat{H}_E^-$ with the opposite helicity $\sigma = -1$ describes the absorption (emission) of an angular momentum $-\hbar$ in the optical transitions from 3d to 4p (4p to 3d) orbitals.

Before closing the discussion of the model, it is worth recalling that the field-free Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_C + \hat{H}_{SO}$ represents a purely electronic model, which describes the dynamics of electrons within the lattice potential $\phi_{\text{lat}}$ generated by the ions at given fixed positions.
Since $\phi^{\text{lat}}$ is obviously not isotropic, the electronic angular momentum $\vec{L} + \vec{S}$ is not conserved, where $\vec{L} = \sum_i \vec{l}_i$ ($\vec{S} = \sum_i \vec{s}_i$) stands for the total electronic orbital (spin) angular momentum. However, the combined system of electrons and ions represents a closed and therefore rotationally invariant system. Consequently, it is clear that the total angular momentum of electrons and ions $\vec{J} = \vec{L} + \vec{S} + \vec{L}^{\text{lat}}$ remains a formally rigorous constant of motion, where $\vec{L}^{\text{lat}}$ denotes the angular momentum of the lattice. An explicit account of the time dependence of the lattice angular momentum would require to consider the dynamics of the ionic degrees of freedom, which is beyond the scope of the present work.

### A. Model simplifications and parameters

In order to achieve an exact numerical solution of the many-body dynamics without involving often hardly controllable and symmetry breaking mean-field approximations, we keep the $pd$-band model as transparent as possible by introducing two simplifications. First, we reduce the orbital degeneracy by considering only the $3d$ orbitals having $|m| \leq 1$ and the $4p$ orbital having $m = 0$. This approximation reduces the numerical effort involved in the exact numerical propagation without affecting significantly the $3d$-$4p$ optical absorption process, the electronic delocalization and exchange interactions responsible for magnetism, or the angular-momentum transfer between spin and orbital degrees of freedom induced by the SOC. Similar reductions of the local orbital degeneracy have often been used in the context of electron correlations and itinerant magnetism, in particular, in connection with the Hubbard model.\textsuperscript{57-59}

The second approximation consists in performing the numerical propagations on a small cluster model. In this work, we consider equilateral triangles ($N_a = 3$ atoms) having $N_e = 4$, 5 and 7 electrons, and an equilateral $N_a = 4$ rhombus with $N_e = 5$, where the length of the short diagonal equals the side length. This allows us to explore various geometries and band fillings having different electronic structures. As we shall see in Sec. III, the validity of this approximation can be justified \textit{a posteriori} by the local character of the mechanism responsible for angular momentum transfer and ultrafast demagnetization.

The model parameters are specified as follows. The hopping integrals $t_{\alpha\beta}^{\alpha\beta}$ are determined by considering nearest-neighbor (NN) Slater-Koster integrals $(dd\sigma) = 0.6$ eV, $(dd\pi) = -0.3$ eV, $(pp\sigma) = 1.5$ eV and $(pd\sigma) = -0.4$ eV. These values are similar to those obtained
in Ref. [60] by fitting the experimental Ni band structure. Notice that the largest pp-integral is roughly three times larger than the dd-integrals. This corresponds to a rather broad sp-band and a narrow 3d-band, as found in 3d TMs such as Ni. Moreover, the NN pd-hopping $(p_d\sigma) = -0.4$ eV is also considerably large, almost of the same order of magnitude as the difference between the 4p and the 3d energy levels $\varepsilon_p - \varepsilon_d = 1.4$ eV. This leads to a significant pd-hybridization and a small but not negligible p-level ground-state occupation, which is consistent with the spd-hybridization found in 3d TMs.

The largest energy scale is given by the direct Coulomb integral $U = 8.0$ eV, a value taken from experimental photoemission spectra and theoretical calculations of the Ni density of electron states.

The intra-atomic exchange integral $J$ yields stable FM ground states whose easy magnetization direction defines the z axis. For the rhombus having $N_a = 4$ atoms and $N_e = 5$ electrons, we use $J = 1.5$ eV and obtain a ground-state off-plane spin polarization $S^0_z = 2.15\hbar$. For the triangular clusters having $N_e = 4$, 5 and 7 we use $J = 0.8$–1.0 eV. The ground states of the $N_e = 4$ and 5 triangles exhibit off-plane easy magnetization axes and spin polarizations of $S^0_z = 1.96\hbar$ and $S^0_z = 1.34\hbar$, while the ground state of the $N_e = 7$ triangle exhibits an in-plane easy magnetization plane and $S^0_z = 1.52\hbar$.

The smallest energy scale in the model is the spin-orbit coupling strength $\xi = -80$ meV. Typical values for 3d TMs are in the range $|\xi| = 50$–100 meV. Notice that the sign of $\xi$ has been changed for systems having a less than half-filled d band, in order to reproduce the parallel alignment between $\vec{L}$ and $\vec{S}$ found in Ni, Co and Fe. This corresponds to performing the electron-hole transformation $\hat{h}_{i\sigma\alpha} = \hat{c}_{i\sigma\alpha}^\dagger$, which does not affect the Coulomb interaction and only changes the sign of the hopping integrals. Explicit calculations show that changing the sign of $\xi$ does not affect the time dependence of the discussed observables in any significant way.

The spin dynamics is triggered by an optical pump pulse having a Gaussian form

$$\vec{E}(t) = \vec{\varepsilon} \cdot E_0 \cos(\omega t) \exp(-t^2/\tau^2_p) \ ,$$

where $\omega = 2\pi c/\lambda$ is the laser frequency. The pulse, centered at $t = 0$, has a duration characterized by the pulse width $\tau_p$. The intensity of the electric field can be measured by the maximal amplitude $E_0$ of $\vec{E}(t)$, which is related to the energy flow per unit area or fluence $F$: $E_0 = (2/\pi)^{1/4}\sqrt{2F/(c\varepsilon_0\tau_p)}$, where $\varepsilon_0$ is the vacuum permittivity. In order to investigate the role of the pump-pulse parameters in the laser-induced magnetization
dynamics, we vary $F$, $\bar{\varepsilon}$ and $\tau_p$ systematically. In this way we quantify the dependence of the spin relaxation on the initial laser excitation. In cases where $F$, $\tau_p$ or $\bar{\varepsilon}$ are not explicitly mentioned, we use $F = 40$ mJ/cm$^2$, $\tau_p = 5$ fs and a linear in-plane polarization $\bar{\varepsilon}$ along one NN bond in the triangle or along the long diagonal in the rhombus. These reference values correspond approximately to the typical numbers of absorbed photons per atom and pulse durations considered in experiments.$^{[B3]}$ Finally, the strength of the coupling between the electronic degrees of freedom and $\vec{E}$ is characterized by the reduced matrix element $\langle 3d||\hat{T}^{(1)}||4p \rangle$ [see Eqs. (B5) and (B6) in Appendix B]. For the calculations throughout this work we set $\langle 3d||\hat{T}^{(1)}||4p \rangle = 0.5\AA$, which corresponds to the typical extension of $3d$ and $4s$ orbitals in $3d$ TMs. The precise value of $\langle 3d||\hat{T}^{(1)}||4p \rangle$ is not important for our conclusions.

In the following section we investigate the consequences of the laser excitation on the FM ground state $|\Psi_0\rangle$ by propagating $|\Psi(t)\rangle$ numerically under the action of the time-dependent electric field. The time evolution is calculated by using the short-time iterative Lanczos propagation method.$^{[67]}$ Once the many-body wave function $|\Psi(t)\rangle$ is obtained we compute the expectation values $O(t) = \langle \Psi(t)|\hat{O}|\Psi(t)\rangle$ of the observables $\hat{O}$ of physical interest, for example, the total spin magnetization $\hat{S}_z$, the local spin and orbital moments $\hat{s}_i$ and $\hat{l}_i$, and the spin-correlation functions $\hat{s}_i \cdot \hat{s}_j$.

III. RESULTS AND DISCUSSION

Before solving and analyzing the dynamics it is important to keep in mind that the hybridizations due to the electron-lattice interaction, the Coulomb interactions and the laser-absorption processes, which are described by $\hat{H}_0$, $\hat{H}_C$ and $\hat{H}_E$, all conserve the total spin $\hat{S} = \sum_i \hat{s}_i$, i.e., $[\hat{H}_0, \hat{S}] = [\hat{H}_C, \hat{S}] = [\hat{H}_E, \hat{S}] = 0$. The spin-rotational invariance is broken only by the SOC since $[\hat{H}_{SO}, \hat{S}] \neq 0$. However, the SOC operator $\hat{H}_{SO}$ commutes with the sum $\hat{l}_i + \hat{s}_i$ of the local orbital and spin angular momenta at each TM atom. Therefore, any spin-flip process induced by SOC necessarily involves a local angular momentum transfer between $\hat{s}_i$ and $\hat{l}_i$, in which the sum $\hat{l}_i + \hat{s}_i$ is conserved. This local intra-atomic symmetry notwithstanding, neither the local orbital moment $\hat{l}_i$ nor the total orbital angular momentum $\hat{L} = \sum_i \hat{l}_i$ are conserved throughout the dynamics, since the lattice potential is not rotationally invariant (i.e., $[\hat{H}_0, \hat{l}_i] \neq 0$ and $[\hat{H}_0, \hat{L}] \neq 0$). This can be traced back to the fact that the interatomic hoppings $t_{ij}^{\alpha\beta}$ connect orbitals with different azimuthal quan-
tum numbers \( m \) at different atoms. The previous fundamental symmetry considerations are essential for understanding the ultrafast magnetization dynamics from a microscopic quantum perspective. The use of time-dependent mean-field approximations to the dynamics seems very questionable in this context, because they artificially break the spin-rotational invariance with respect to \( \hat{H}_0, \hat{H}_C \) and \( \hat{H}_E \). In contrast, exact time propagations—although limited in their application to small finite systems—have the clear advantage of complying with all fundamental conservation laws. They should therefore allow us to derive rigorous conclusions.

The purpose of this Section is to investigate the dynamics of ferromagnetic TMs as a function of the laser fluence \( F \), photon energy \( \hbar \omega \), electric-field polarization \( \hat{\varepsilon} \) and pulse duration \( \tau_p \), in order to quantify to what extent these experimentally tunable parameters can be used to taylor the magnetization dynamics. Results for different model systems and band fillings are contrasted. The correlations between degree of initial electronic excitation, absorbed energy, demagnetization time and degree of demagnetization are analyzed. General trends are inferred.

A. Laser fluence

The laser fluence \( F \) is naturally expected to play an important role in the subsequent spin relaxation since it controls the level of electronic excitation. In order to quantify its effect we have determined the magnetization dynamics \( S_z(t) \) for different representative values of \( F \) and for different structures and number of electrons \( N_e \). This also gives us the opportunity to explore the dependence of the ultrafast demagnetization on band filling. Since the excitation spectrum depends on the precise structure and band filling of the model, and in order that the results can be compared, we have chosen the laser wave length such that it matches the absorption spectrum. The results of Figs. 1 and 2 show that similar laser-induced demagnetizations take place for all considered geometries and band fillings. One observes that \( S_z(t) \) decreases rapidly after the pulse passage at \( t = 0 \) (\( \tau_p = 5 \) fs) reaching values close to the long-time limit \( S_z^\infty \) in 50–100 fs. The characteristic demagnetization time scale \( \tau_{dm} \) can be obtained by fitting an exponential law of the form

\[
S_z(t) = S_z^\infty + (S_z(0) - S_z^\infty) \exp\{-t/\tau_{dm}\}
\]

to the exact calculated numerical propagations, where \( S_z(0) \) is the spin polarization at the time \( t = 0 \) when the electric field amplitude \( E(t) \) reaches its maximum. The pulse shape is
FIG. 1. Time dependence of the spin magnetization in an equilateral triangle with $N_e = 4$, 5 and 7 electrons, after excitation using a linearly polarized 5 fs laser pulse with wave length $\lambda = 1051$ nm, 556 nm and 849 nm, respectively. The considered laser fluences $F$ are indicated together with the corresponding absorbed energies per atom $\Delta E$. The left insets show the demagnetization times $\tau_{dm}$ as a function of $F$, as obtained from exponential fits to $S_z(t)$ given by the dashed curves in the main panels. The right insets show, for all considered values of $F$, the nearly identical time dependences of the corresponding scaled spin magnetization $S_{sc}(t) = [S_z(t) - S_z^\infty]/\Delta S_z$. In the bottom panel the amplitude $E(t)$ of the triggering electric field is illustrated.

Illustrated at the bottom panel of Fig. 1. From the fits, shown as thin dashed curves in the figures, one obtains $\tau_{dm} \simeq 23$ fs for the rhombus and $\tau_{dm} \simeq 20$–50 fs for the triangles. These values, which correspond to $|\xi| = 80$ meV, are 3–5 times longer than the spin-orbit time scale $\hbar/\xi = 8$ fs. In Ref. 45 it has been shown that $\tau_{dm} \propto \hbar/\xi$ and that the rate of spin-to-orbital angular momentum transfer controls the UFD dynamics. Notice, moreover, that the spin relaxation occurs essentially after the passage of the laser pulse. In particular,
FIG. 2. Time dependence of the spin magnetization in a rhombus having $N_e = 5$ valence electrons. The excitation at $t = 0$ corresponds to a linearly polarized 5 fs laser pulse with wave length $\lambda = 385$ nm. See the caption of Fig. 1.

$\tau_{dm}$ is always much larger than the considered pulse duration $\tau_p = 5$ fs. This implies that the demagnetization effect is not the direct result of the interaction with the laser electric field, but rather the consequence of an intrinsic process occurring within the excited electronic system. The same previous work shows that the interplay between the electronic motion in the lattice and the SOC is at the origin of the ultrafast demagnetization. The spin-orbit interactions acting on the excited electrons bring about a local flow of angular momentum from the atomic spins $\vec{s}_i$ to the atomic orbits $\vec{l}_i$ on a time scale of the order of $\hbar/\xi = 8$ fs. At the same time, the hopping of the electrons between different atoms quenches any incipient increase of the total orbital angular momentum $\vec{L} = \sum_i \vec{l}_i$ on a very short time scale of only $\hbar/c_{jk} \lesssim 1$ fs. This prevents any accumulation of the transferred spin angular momentum in the orbital degrees of freedom. The local character of the above discussed mechanism of angular momentum transfer, including the laser excitation dominated by intra-atomic dipole transitions, supports the physical validity of the present small-cluster exact-propagation approach (see Sec. II A).

Figures 1 and 2 clearly show that the larger the fluence $F$ the larger the demagnetization $\Delta S_z = S_z^0 - S_z^\infty$, where $S_z^0$ denotes the initial spin polarization. For instance, in the triangle with $N_e = 7$ electrons the long-time spin polarization decreases from $S_z^\infty = 0.36 \hbar$ to $S_z^\infty = 0.09 \hbar$ per atom when the fluence is increased from $F = 10$ to 80 mJ/cm$^2$. However, the characteristic shape of $S_z(t)$, and in particular the demagnetization time $\tau_{dm}$, depend weakly on $F$. To clarify this point, the insets in Figs. 1 and 2 show, on the right hand side, the scaled spin magnetization $S_{sc}(t) = [S_z(t) - S_z^\infty]/\Delta S_z$ as a function of time $t$ for
all considered fluences $F$. In addition, on the left hand side, the demagnetization time $\tau_{\text{dm}}$ is given as a function of $F$. One observes that for all considered systems $S_{\text{sc}}(t)$ and $\tau_{\text{dm}}$ are essentially independent of $F$, i.e., of the degree of excitation ($10 \text{ mJ/cm}^2 \leq F \leq 80 \text{ mJ/cm}^2$). However, $\tau_{\text{dm}}$ depends to some extent on the lattice structure and band filling, although it always remains in the range of a few tens of femtoseconds for $|\xi| = 80 \text{ meV}$. This can be understood by recalling that the coupling between spin and translational degrees of freedom, which results from spin-orbit interactions, can be very sensitive to the details of the electronic structure. In fact, it is well-known that the magneto-crystalline anisotropy energy, easy magnetization axis, and orbital moments of transition-metal systems depend strongly on lattice structure and band filling. Furthermore, notice that weak oscillations are superimposed to the general exponential decrease of the calculated $S_z(t)$. These become somewhat weaker (stronger) for shorter (longer) pulse durations $\tau_p$, as the laser-field spectrum becomes broader (narrower) and the final excited state involves a larger (smaller) number of eigenfrequencies. They are possibly a consequence of the discreteness of the energy spectrum of the small cluster models used for the numerical time propagations.

It is instructive to compare our theoretical results for the fluence dependence of the UFD effect with available experiments. The measurements on Ni by Koopmans et al. have shown that with increasing fluence the relative demagnetization becomes stronger and the demagnetization time $\tau_{\text{dm}}$ increases. While the former is in agreement with our trends, the latter is in clear contrast. However, more recent experiments on Ni by Tengdin et al. show a qualitatively different fluence dependence, namely, a fluence-independent demagnetization time, which coincides with the predictions of our model (see Figs. 1 and 2). Interestingly, Tengdin et al. fitted their experimental magnetization data by using up to three distinct exponential functions: The first one describes the initial laser-triggered magnetization decrease, which is investigated in this paper, whereas the remaining ones correspond to the subsequent magnetization recovery. In this way, they were able to separate the time scale of the ultrafast magnetization collapse from the much slower magnetization recovery. Concerning the latter process, both experimental groups have clearly observed that it depends qualitatively and quantitatively on the fluence of the pumping laser, and thus, on the absorbed energy. It is therefore possible that the fluence dependence of $S_z(t)$ observed in Ref. and the demagnetization time inferred using a single exponential fit, are partly affected by these energy dissipation processes, particularly as the level of excitation increases.
FIG. 3. Spectral density $D_\Psi(\epsilon)$ of the excited many-body state $|\Psi(t)\rangle$ after the laser-pulse passage ($t \geq 15$ fs) as a function of excitation energy $\epsilon = E - E_0$. Results are given for the equilateral triangle having $N_e = 4$ and representative laser fluences $F$. The laser wave length is $\lambda = 1051$ nm ($\hbar \omega = 1.18$ eV). The discrete spectral lines have been broaden with a finite width $\delta = 20$ meV for the sake of clarity. The ground-state energy and the excitation energies corresponding to the absorption of one and two photons are indicated by the dashed lines.

It is interesting to investigate the experimentally observed increase of the demagnetization $\Delta S_z$ with increasing fluence $F$ by analyzing the spectral distribution of the many-body state $|\Psi(t)\rangle$ after the pump-pulse passage (e.g., $t \geq 15$ fs for a 5 fs laser pulse). For this purpose, we expand $|\Psi\rangle = \sum_k \alpha_k |\psi_k\rangle$ in the stationary states $|\psi_k\rangle$ of the field-free Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_C + \hat{H}_{SO}$ satisfying $\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle$. The spectral distribution of $|\Psi\rangle$ is then given by

$$D_\Psi(\epsilon) = \sum_k |\langle \psi_k |\Psi(t)\rangle|^2 \delta(\epsilon - \epsilon_k),$$

where $\epsilon = E - E_0$ is referred to the ground-state energy $E_0$ and $\epsilon_k = E_k - E_0$. Notice that $\hat{H}$ and thus the spectral distribution $D_\Psi(\epsilon)$ of $|\Psi(t)\rangle$ are independent of $t$ once the pulse has passed (e.g., $t \geq 3\tau_p$). Fig. 3 shows $D_\Psi(\epsilon)$ for a triangle with $N_e = 4$, which has been excited with a 5 fs laser pulse of wave length $\lambda = 1051$ nm ($\hbar \omega = 1.18$ eV) and fluences $F = 10, 20, 40$ and $80$ mJ/cm$^2$. Three main peaks or groups of nearby peaks are distinguished around $\epsilon = 0$, $\hbar \omega$ and $2\hbar \omega$. They correspond to the ground state and to the absorption of 1 and 2 photons. One observes how the spectral weight of the excited-state manifolds around $\hbar \omega$ and $2\hbar \omega$ increases with increasing $F$ at the expense of the ground-state
contribution $|\langle \Psi_0 | \Psi(t) \rangle|^2$. This reflects the growing level of electronic excitation and can be directly related to the degree of demagnetization $\Delta S_z / S_z^0 = (S_z^0 - S_z^\infty) / S_z^0$ achieved at long times $t \gg \tau_{\text{dm}}$. Indeed, a simple argument allows us to approximately express $\Delta S_z / S_z^0$ in terms of the angle $\alpha = \arccos \langle \Psi_0 | \Psi(t) \rangle$ between the excited state $|\Psi(t)\rangle$ at $t \geq 3\tau_p$ and the ground state $|\Psi_0\rangle$. Writing

$$|\Psi(t)\rangle = \cos(\alpha) |\Psi_0\rangle + \sin(\alpha) |\Delta \Psi(t)\rangle$$

(11)

with $\langle \Psi_0 | \Delta \Psi(t) \rangle = 0$ and $\langle \Delta \Psi(t) | \Delta \Psi(t) \rangle = 1$ we have

$$S_z(t) = \cos^2(\alpha) S_z^0 + \sin^2(\alpha) \langle \Delta \Psi(t) | \hat{S}_z | \Delta \Psi(t) \rangle.$$  

(12)

The demagnetization in the long-time limit is then given by

$$\Delta S_z = \sin^2(\alpha) \left[ S_z^0 - S_z^\ast(\infty) \right],$$

(13)

where $S_z^\ast(t) = \langle \Delta \Psi(t) | \hat{S}_z | \Delta \Psi(t) \rangle$ is the magnetization in the excited states at time $t$. This shows that $\Delta S_z / S_z^0$ is proportional to the spectral weight $\sin^2(\alpha)$ transferred to the excited states or, in other words, to the level of excitation. Since $S_z^\ast(0) \simeq S_z^0$ (i.e., essentially no change in the spin polarization occurs during the pulse passage) the proportionality factor $S_z^0 - S_z^\ast(\infty) = S_z^\ast(0) - S_z^\ast(\infty)$ gives a measure of the efficiency of the demagnetization in the excited-state manifolds. It is interesting to observe that the dynamics of the many-electron system yields a remarkably effective reduction of the excited-state magnetization $S_z^\ast(t)$. In fact, in some cases (e.g., a triangle having $N_e = 7$ electrons) the quenching of $S_z^\ast(t)$ is nearly complete (i.e., $S_z^\ast(\infty) \simeq 0$). While it is tempting to interpret this in terms of the statistical hypothesis of equal a priori probability, there are many examples where no full excited-state quenching is found. For instance, in a triangle having $N_e = 4$ or 5 electrons, as well as the rhombus, one finds that $S_z^\ast(\infty)$ is significantly larger than zero ($S_z^\ast(\infty) \simeq 0.06-0.13 \hbar$ per atom, see Sec. III B).

At this stage one may wonder whether the relation between the degree of long-time demagnetization and the level of excitation is not simply a consequence of the fact that with increasing fluence $F$ and increasing $\sin^2(\alpha)$ also the absorbed energy $\Delta E$ increases. In order to clarify this matter it is important to investigate the dynamical magnetic response as a function of the photon energy $\hbar \omega$.
B. Absorbed energy versus average number of absorbed photons

The preceding section has shown that the main consequence of increasing the level of electronic excitation is to enhance the degree of demagnetization $\Delta S_z = S_z^0 - S_z^\infty$ at long times, at least for the considered range of fluence $F$. A complementary way of investigating the dependence of ultrafast demagnetization on the level of excitation and on the absorbed energy $\Delta E$ is to vary systematically the photon energy $\hbar \omega$. In this way the importance of the absorbed energy and of the average number of electrons excited by the laser or of absorbed photons $n_{ph} = \Delta E/\hbar \omega$ can be tell apart.

In the following different laser frequencies are considered, for which the absorption probabilities are significant. The corresponding exact time dependences of $|\Psi(t)\rangle$ and $S_z(t)$ have been numerically determined. In all cases, the UFD effect is observed with demagnetization times $\tau_{dm} = 18–62$ fs for the triangle with $N_e = 4$ electrons, $\tau_{dm} = 23–62$ fs for the triangle with $N_e = 5$, $\tau_{dm} = 42–122$ fs for the triangle with $N_e = 7$, and $\tau_{dm} = 15–86$ fs for the rhombus with $N_e = 5$. This confirms that the UFD effect is an intrinsic characteristic of the correlated electronic system, which is qualitatively independent of the details of the triggering excitation. Nevertheless, notice that the precise value of $\tau_{dm}$ depends to some extent on the laser frequency $\omega$. This shows that different optical absorptions lead to different excited states, or more generally, different spectral distributions $D_\Psi(\epsilon)$, which exhibit their own specific many-body dynamics. Incidentally, this may also indirectly cause a fluence dependence of $\tau_{dm}$. Assuming a rapid thermalization of the electronic translational degrees of freedom after the laser absorption, one expects that the distribution of the excited many-body states should become broader as the fluence $F$ increases. This would render higher excitation energies accessible and could thus result in changes in $\tau_{dm}$ as a function of $F$. Unfortunately, this hypothesis cannot be quantified numerically in the present framework, since the cluster models accessible to exact time propagations are too small to allow a true thermalization or self-averaging.

The long-time limit of the demagnetization $\Delta S_z = S_z^0 - S_z^\infty$ has been derived for each $\hbar \omega$ from the numerical time propagations. The thus obtained relative demagnetizations $\Delta S_z/S_z^0$ are shown in Fig. 4 as a function of the absorbed energy $\Delta E$ (right-hand side) and of the average number of absorbed photons $n_{ph} = \Delta E/\hbar \omega$ (left-hand side). The scatter plot on the right-hand side of Fig. 4 is so disperse that no relation between $\Delta E$ and $\Delta S_z/S_z^0$ can
be established. $\Delta S_z$ is obviously not a function of $\Delta E$ alone. In contrast, the left-hand side figure reveals a remarkably simple, approximately linear dependence of $\Delta S_z/S_z^0$ on $n_{ph}$. For example, in the triangle with $N_e = 7$, $\Delta S_z/S_z^0$ are nearly the same for $\hbar \omega = 1.5$ eV and $\hbar \omega = 5.9$ eV although the absorbed energies $\Delta E = 1.0$ eV and $\Delta E = 4.1$ eV differ widely by a factor four. The corresponding $n_{ph} = 0.72$ and $n_{ph} = 0.69$ are very similar. In other cases,

![Figure 4](image_url)

**FIG. 4.** Correlation between the laser-induced degree of demagnetization $\Delta S_z/S_z^0$ at long times $t \gg \tau_{dm}$ and the absorbed energy $\Delta E$ (right) or the average number of absorbed photons $n_{ph} = \Delta E/\hbar \omega$ (left), where $\omega$ is the angular frequency of the exciting laser. The crosses are obtained from the exact calculated time evolution for (a) a rhombus with $N_e = 5$ electrons, and an equilateral triangle having (b) $N_e = 4$, (c) $N_e = 5$ and (d) $N_e = 7$ electrons. The laser fluence is always $F = 40$ mJ/cm$^2$, while the different photon energies $\hbar \omega$ are indicated in eV. The dashed straight lines on the left panels are fits to the approximate linear dependence of $\Delta S_z/S_z^0$ on $n_{ph}$. 18
for example in the triangle with \( N_e = 4 \), the absorbed energies are very similar (\( \Delta E = 0.9 \) eV for \( h\omega = 1.0 \) eV and \( \Delta E = 0.8 \) eV for \( h\omega = 2.5 \) eV) but the relative demagnetizations differ widely (\( \Delta S_z/S_z^0 = 0.81 \) and \( \Delta S_z/S_z^0 = 0.25 \), respectively). One concludes that the average number of absorbed photons \( n_{\text{ph}} \), or equivalently, the number of single-particle electronic excitations induced by the pumping pulse, rather than the absorbed energy, determines primarily the strength of the demagnetization. This is consistent with the discussion at the end of Sec. III A showing that \( \Delta S_z/S_z^0 \) is proportional to the spectral weight transferred to the excited states during the laser-pulse absorption.

The slope \( \gamma \) of the linear dependence \( \Delta S_z/S_z^0 \approx \gamma n_{\text{ph}} \) can be related to the efficiency of the demagnetization in the excited states \( S_z^*(\infty) \), which was introduced at the end of the Sec. III A. Assuming for simplicity that only the ground state and the lowest excited states around \( h\omega \) contribute to the spectral distribution of \( |\Psi(t)\rangle \) after the pump pulse, one can easily show that \( \sin^2(\alpha) \) in Eqs. (11)–(13) is equal to the average number of absorbed photons \( n_{\text{ph}} = \Delta E/h\omega \). Therefore, \( \gamma = [S_z^0 - S_z^*(\infty)]/S_z^0 \) represents the relative demagnetization efficiency in the excited states. Figure 4 (left) shows that \( \gamma \) and thus \( S_z^*(\infty) \) do not depend significantly on \( h\omega \). However, they depend somewhat on the considered cluster model and band filling. For example, for the triangle with \( N_e = 4 \) and 5 electrons, and for the rhombus with \( N_e = 5 \) electrons we find \( \gamma \approx 0.72 \)–0.88 < 1. This implies that the magnetic order in the excited states \( |\Delta\Psi\rangle \) is not fully destroyed as a result of the many-electron dynamics. In other words, \( |\Delta\Psi\rangle \) remains ferromagnetic to a small extent even at very long times. In contrast, for the triangle with \( N_e = 7 \), the FM correlations in \( |\Delta\Psi\rangle \) are fully lost along the dynamics. The demagnetization of \( |\Delta\Psi\rangle \) is in this case almost complete, namely, \( S_z^*(\infty)/S_z^0 \approx 0.03 \) or \( \gamma \approx 0.97 \).

According to our exact model calculations, the energy per atom \( \Delta E \), which is absorbed during the pump pulse, does not give the appropriate measure of the degree of excitation of the electronic system in relation to subsequent \( \Delta S_z/S_z^0 \). This is physically interesting, since it contrasts with the idea that the translational degrees of freedom of the electronic system should rapidly thermalize in a spin-conserving way. Indeed, if the latter were so, the energy absorbed in any field-induced single-particle transition would be rapidly redistributed among the electrons, thus erasing any memory of the details of the triggering excitation (e.g., the number of initial single-particle transitions or number of absorbed photons). Let us recall that the characteristic times involved in electron-lattice and electron-electron interactions
\( \hbar/t_{ij}^3 \) and \( \hbar/U \) are at least an order of magnitude shorter than the typical spin-orbit and demagnetization times. All these short-time dynamical processes are properly taken into account in our studies. Still, it is also true that our calculations are unable to describe the approach to thermal equilibrium, since the exact time propagations are performed for closed purely electronic systems (Neumann-Liouville theorem). The interactions with the environment are ignored and the considered models are too small to achieve self-averaging. It is unclear at present what would be the characteristic time involved in the thermalization of the translational electronic degrees of freedom of ferromagnetic metals, and how such a thermalization would affect the relation between \( \Delta S_z/S_0^z \) and the absorbed energy \( \Delta E \).

Extensions of our calculations by taking into account a spin-conserving coupling to a bath, which simulates the environment, as well as numerical time propagations of mixed states corresponding to translationally thermalized electronic states are therefore worthwhile.

C. Electric-field polarization

The dependence of the magnetization dynamics on the polarization \( \hat{\epsilon} \) of the incident laser pulse has been investigated by considering linearly and circularly polarized electric fields. Figure 5 shows the time dependence of the spin and orbital angular momenta in an equilateral triangle with \( N_e = 4 \) electrons. The pumping excitation has a duration \( \tau_p = 5 \text{ fs} \) and a wave length \( \lambda = 1051 \text{ nm} \). Three different electric-field polarizations \( \hat{\epsilon} \) are considered: linear polarization along a NN bond within the \( xy \)-plane containing the triangle (\( \sigma = 0 \)), right circular polarization (\( \sigma = + \)) and left circular polarization (\( \sigma = - \)). For \( \sigma = + \) (\( \sigma = - \)) the field carries an angular momentum of \( \hbar (-\hbar) \) which is parallel (antiparallel) to the ground-state spin magnetization \( S_0^z \) along the out-of-plane \( z \) direction. Figure 5(a) shows that \( S_z(t) \) depends weakly on the considered polarization, in agreement with experiment. In the limit of long times, the spin magnetization decreases to a somewhat larger (smaller) value \( S_\infty^z \) after the absorption of a right (left) circular pulse in comparison with the linear pulse. As we shall see, this can be ascribed to the rather small polarization dependence of the absorption cross section. One may also notice that the difference in \( S_z(t) \) between left and right polarized light increases at the early stages of the dynamics (\( t \lesssim \tau_{dm} = 19 \text{ fs} \)) showing some oscillations for \( t \geq \tau_{dm} \).

The laser-polarization effects on the orbital magnetic moment \( L_z \) are found to be sig-
FIG. 5. Time dependence of the average (a) spin moment $S_z$ and (b) orbital moment $L_z$ following the excitation with a $\tau_p = 5$ fs laser pulse having a wave length $\lambda = 1051$ nm and a polarization $\hat{e}$ which is in-plane linear ($\sigma = 0$), right circular ($\sigma = +$) or left circular ($\sigma = -$). The full curves are obtained from the exact time evolution of the equilateral triangle model with $N_e = 4$ electrons. The dashed curves in (a) are exponential fits to $S_z(t)$ with a common demagnetization time $\tau_{dm} = 19$ fs. The inset in (a) shows the degree of demagnetization $\Delta S_z/S^0_z$ as a function of the average number of absorbed photons $n_{ph} = \Delta E/\hbar \omega$, together with the same linear approximation (dashed line) as the one found in Fig. 4(b) left.

significant only at very short times ($t \lesssim 10–15$ fs). The dynamics of the initially quenched moment $L_z \simeq 0.17 \hbar/\text{atom}$, which is parallel to $S_z$, is shown in Fig. 5(b) for different laser polarizations. For linear polarization ($\sigma = 0$), the orbital moment decreases to around $L_z \simeq 0.03 \hbar/\text{atom}$ during the action of the pulse, while in the case of a left (right) circularly polarized pulse $L_z$ decreases by around $0.26 \hbar/\text{atom}$ (increases by around $0.03 \hbar/\text{atom}$) on the same time scale. Notice that for $\sigma = -$, $L_z$ becomes even negative (i.e., antiparallel to $S_z$) for a very short time. The time lapse during which the polarization dependence of $L_z$ is significant is of the order of the pulse width, in the present case $\tau_p = 5$ fs.

In order to analyze the polarization effects on $L_z$, let us first notice that the absorption of
non-polarized $\sigma = 0$ pulses consists in electronic dipole transitions mainly from the $3d, m = \pm 1$ orbitals to the $4p, m = 0$ orbitals. Thus, the orbital-moment projection is reduced, which explains qualitatively the laser-induced decrease of $L_z$ observed for linearly polarized pulses [see Fig. 5(b)]. For $\sigma = - (\sigma = +)$ $L_z$ is further decreased (enhanced) by around 0.12–0.17 $\hbar$/atom in comparison with the $\sigma = 0$ dynamics ($t \lesssim 10–15$ fs). This polarization-dependent decrease (enhancement) is the consequence of the transfer of angular momentum from the laser field to the orbital electronic motion. The left (right) polarized light induces $m \rightarrow m - 1 (m \rightarrow m + 1)$ intra-atomic transitions, where the azimuthal quantum number $m$ gives the local contribution to $L_z$. Neglecting for a moment any spin-orbit transitions and interatomic electron hoppings, this would imply a change $\Delta L_z = \pm \hbar$ in the angular momentum per absorbed photon. Knowing that $n_{ph}/N_a \simeq 0.28$ ($n_{ph}/N_a \simeq 0.22$) for left (right) polarization, we conclude that the change in $L_z$ induced per absorbed photon explains qualitatively the observed short-time decrease (enhancement) of $L_z$ for $\sigma = - (\sigma = +)$. The polarization-dependent change $\Delta L_z$ is in fact somewhat smaller than $\pm n_{ph}\hbar/N_a$, since part of the effect is lost due to the rapid interatomic hoppings.

It is also important to remark that the changes in $L_z$ induced by the laser field, and the thus resulting differences in the time dependence of $L_z$ for different polarizations, rapidly vanish once the laser pulse passes. As shown in Fig. 5(b), already 18 fs after the pulse reaches its maximum ($t = 0$) the differences in $L_z(t)$ for different $\sigma$ are no longer distinguishable from the intrinsic oscillation of $L_z(t)$ due to the dynamics ruled by the field-free $\hat{H}$. The reason behind this is the motion of $3d$ electrons throughout the lattice, which does not conserve the atomic $l_{iz}$. In TMs $d$-electron delocalization actually quenches $L_z$ on a very short time scale of the order of $\hbar/t_{ij}^{\alpha\beta} \simeq 1$ fs, where $t_{ij}^{\alpha\beta}$ is the hopping integral between NNs. Thus, the electronic motion tends to wash out any change in the orbital angular momentum, irrespectively of its origin. The results show that the hopping-induced rapid quenching of $L_z$ applies equally well to an enhancement of $L_z$ due to the laser absorption ($\sigma = +$) and to the spin-to-orbital angular momentum transfer due to SOC in the excited states. This explains why the time dependences of $L_z(t)$ for the different laser polarizations are very similar after the pulse passage. The differences in the excited state for different $\sigma$, which are clearly visible in $L_z(t)$ for short times, have only a modest effect on the slower spin dynamics [see Fig. 5(a)]. The latter is actually governed by the spin-to-orbital transfer of angular momentum and the above-mentioned $L$-quenching electronic motion. As we shall
FIG. 6. Time dependence of the average (a) spin moment $S_z$ and (b) orbital moment $L_z$ corresponding to an excitation with a $\tau_p = 20$ fs laser pulse, having a wave length $\lambda = 1051$ nm and a polarization $\hat{\epsilon}$ which is in-plane linear ($\sigma = 0$), right circular ($\sigma = +$) and left circular ($\sigma = -$). See also the caption of Fig. 5.

In the present calculations the same fluence $F = 40$ mJ/cm$^2$ has been used for all electric-field polarizations. The obtained degrees of excitation, as measured by $n_{ph} = \Delta E/\hbar \omega$ and the long-time demagnetization $\Delta S_z/S^0_z$, are quantitatively similar for all $\sigma$ [see the inset in Fig. 5(a)]. Furthermore, Fig. 5(a) shows that the time dependences of $S_z(t)$ for different $\sigma$ can all be reasonably well fitted with exponential functions having the same demagnetization time $\tau_{dm} = 19$ fs (dashed curves). Our calculations show no significant effect of the laser polarization $\hat{\epsilon}$ on $\tau_{dm}$.

In order to investigate the interplay between spin-orbit coupling and laser-ferromagnet interaction, it is interesting to consider pulse durations $\tau_p$ that are larger than the time scale of the SOC ($\hbar/|\xi| = 8$ fs) for different laser polarizations. Figure 6 shows the time
dependences of $S_z$ and $L_z$ in an equilateral triangle ($N_e = 4$ electrons) which is excited with a laser pulse having $\tau_p = 20$ fs and $\lambda = 1051$ nm. One observes that $S_z(t)$ and $L_z(t)$ depend significantly on the considered polarization. In the case of $L_z$ the polarization-dependent changes resulting from direct optical absorption vanish very rapidly as the pulse passes ($t > \tau_p = 20$ fs). As already discussed, this is due to the rapid electron delocalization in the lattice [see Fig. 6(b)]. In contrast, the differences in $S_z(t)$ for the different considered $\hat{\varepsilon}$ remain significant during several hundreds of femtoseconds [see Fig. 6(a)], well beyond the point where the electric field has vanished. The results also show that at long times the circular $\sigma = - (\sigma = +$) pulse induces a more (less) efficient demagnetization $\Delta S_z/S_z^0$ than the linear $\sigma = 0$ pulse. The actual values of $\Delta S_z/S_z^0$ for different $\hat{\varepsilon}$ correlate well with the average number of absorbed photons, as shown in the inset of Fig. 6(a). As for shorter pulses, the demagnetization time $\tau_{\text{dm}} = 27$ fs is found to be essentially independent of $\hat{\varepsilon}$.

The small polarization dependence of the long-time demagnetization degree $\Delta S_z/S_z^0$ can be interpreted qualitatively in terms of the orbital occupations. Let us first recall that the initial state before the pulse absorption has a small positive orbital moment $L_z \simeq 0.17 \hbar$ per atom. This means that the $3d$ orbitals with $m > 0$ are in average more likely occupied than the orbitals with $m < 0$. This introduces an asymmetry in the absorption of left and right polarized light (dichroism). Since the orbital polarization of the final $4p$ states is negligible, and the optical matrix elements are invariant upon reversing the circular polarization and the sign of the initial-state $m$, a higher laser absorption is expected when the average occupation of the dominant initial states is larger. In the case of left (right) circularly polarized light the $m \rightarrow m-1$ ($m \rightarrow m+1$) selection rule implies that the absorption is dominated by the initial states having $m > 0$ ($m < 0$). Consequently, for $L_z > 0$ the absorption cross section for left-circularly polarized light should be somewhat larger. Our results confirm this trend and can be interpreted accordingly. For example, for a $\tau_p = 5$ fs laser pulse we obtain that the average number of absorbed photons is $n_{\text{ph}} = 0.83$ for left-circularly polarized pulses, while it is about $n_{\text{ph}} = 0.67$ for linearly or right-circularly polarized pulses. Similarly, for a $\tau_p = 20$ fs laser pulse we obtain $n_{\text{ph}} = 0.96$ for left polarization, $n_{\text{ph}} = 0.88$ for linear polarization, and $n_{\text{ph}} = 0.70$ for right polarization. The insets in Figs. 5 and 6 show the already discussed linear dependence between $\Delta S_z/S_z^0$ and $n_{\text{ph}}$. In fact, the slopes of the straight dashed lines in the insets of Figs. 5(a) and 6(a) are the same as in Fig. 4(b). One concludes that the dependence of $\Delta S_z/S_z^0$ on the laser polarization is mainly a consequence of the different
FIG. 7. Time dependence of the average spin moment $S_z$ in an equilateral triangle with $N_e = 4$ electrons resulting from laser-pulse excitations having wave length $\lambda = 1051$ nm and pulse durations $\tau_p = 1–50$ fs. The full curves are obtained from the exact time evolutions, while the dashed curves are the corresponding exponential fits to $S_z(t)$. The laser fluences are such that the average number of absorbed photons per atom is $n_{\text{ph}}/N_a = \Delta E/(N_a \hbar \omega) = 0.22$ for all $\tau_p$. The inset shows the demagnetization time $\tau_{\text{dm}}$ and the long-time demagnetization $\Delta S_z/S_z^0$ as a function of $\tau_p$.

absorption cross sections. It should be, however, noted that the orbital magnetic moments $\langle L_z \rangle$ in TMs are weak. In other words, the differences in the ground-state occupations for positive and negative $m$ are small. Therefore, the possibilities of taking advantage of dichroism in order to tune the degree of excitation and $\Delta S_z/S_z^0$ seem quantitatively limited.

D. Pulse duration

The pulse duration $\tau_p$ is a central characteristic of the laser excitation whose role on the dynamics deserves to be investigated in some detail. To this aim, exact time propagations have been performed for a triangle having $N_e = 4$ electrons, which is excited with a laser having $\lambda = 1051$ nm and $1$ fs $\leq \tau_p \leq 50$ fs. This covers the range from narrow to broad pulses in comparison with the period of oscillation of the field $T = \lambda/c \simeq 3.5$ fs and the SO time scale $\hbar/|\xi| \simeq 8$ fs. Since the radiated energy is directly proportional to the pulse duration $\tau_p$, and the absorption efficiency depends strongly on the frequency distribution of the field, comparing the magnetization dynamics for the same fluence $F$ and different $\tau_p$ would be confusing. We have therefore scaled $F$ for each $\tau_p$ so that the absorbed energy $\Delta E$
and the average number of absorbed photons \( n_{\text{ph}} = \Delta E / \hbar \omega \) remain constant. In this way the role of the pulse duration can be effectively assessed. Figure 7 shows the time dependence of the average spin magnetization \( S_z(t) \) for \( \tau_p = 1-50 \) fs and \( F \) such that \( n_{\text{ph}} / N_a = 0.22 \). For relatively short pulses (\( \tau_p < 10 \) fs) the decrease of \( S_z(t) \) takes place sharply after the pulse passage. The excitation is sudden, since the electronic system has no time to evolve from a magnetic point of view (\( \tau_{\text{dm}} \approx 20 \) fs and \( \hbar / |\xi| = 8 \) fs for \( |\xi| = 80 \) meV). However, as the pulse duration is increased, one observes that a significant part of the demagnetization occurs while the laser field is still on. This is particularly clear for \( \tau_p = 50 \) fs, in which case almost half of the long-time demagnetization has already taken place when the laser pulse reaches its maximum at \( t = 0 \) (see Fig. 7).

The demagnetization time \( \tau_{\text{dm}} \) and the degree of demagnetization \( \Delta S_z / S_z^0 \) are obtained by fitting the exact calculated time dependences of \( S_z \) (full curves) for each \( \tau_p \) with simple exponential functions. The results, given in the inset of Fig. 7, show that \( \Delta S_z / S_z^0 = 0.62-0.68 \) is essentially independent of the pulse duration, provided that \( n_{\text{ph}} \) is kept constant. This holds even for pulse durations which are much longer than the spin-orbit time scale (\( \tau_p > \hbar / |\xi| = 8 \) fs), which is consistent with the fact that the long-time demagnetization \( \Delta S_z / S_z^0 \) is controlled primarily by the number of laser-induced single-particle excitations or absorbed photons (see Sec. III B). At least in these examples, the simultaneous action of the laser field and the spin-orbit interactions does not affect the degree of demagnetization at long times. Moreover, no significant interference effects between the laser field and the spin-orbit interactions are seen in \( S_z(t) \) and \( L_z(t) \).

The inset of Fig. 7 also shows the corresponding demagnetization time scales, which increase from \( \tau_{\text{dm}} \approx 20 \) fs for very short pulses (\( \tau_p \leq 5 \) fs) to \( \tau_{\text{dm}} \approx 38 \) fs for \( \tau_p = 50 \) fs. This trend can be qualitatively understood by recalling that longer pulses imply a narrower spectral distribution \( D_{\Psi}(\epsilon) \) and thus a slower time evolution of the many-body excited state \( |\Psi\rangle \). Moreover, in the limit of very short pulses, \( \tau_{\text{dm}} \approx 20 \) fs remains approximately constant since after a sudden excitation the demagnetization rate is controlled by the SOC (\( \tau_{\text{dm}} \propto \hbar / \xi \), see also Ref. 45). The results confirm that the laser-induced UFD of TMs reflects primarily the intrinsic dynamical behavior of the itinerant-electron many-body system, even in cases where the pulse duration is longer than \( \hbar / \xi \) and \( \tau_{\text{dm}} \).
IV. CONCLUSION

The laser-triggered dynamics of itinerant-electron magnetism has been investigated in the framework of a many-body $pd$ Hamiltonian which describes electron delocalization, Coulomb interactions, spin-orbit interactions and the coupling to the laser field on the same footing. The time-dependent many-body state of the system $|\Psi(t)\rangle$ has been exactly calculated by applying a numerical short-time Lanczos propagation method on small cluster models with parameters appropriate for Ni. Starting from the ground state $|\Psi_0\rangle$, the time evolution of $|\Psi(t)\rangle$ has been followed during and after the laser pulse. The relevant observables, in particular the average spin moment $S_z(t)$ and orbital moment $L_z(t)$, have been obtained for a wide range of representative excitation parameters: fluence $F$, wave length $\lambda$, linear and circular polarizations $\hat{\varepsilon}$, and pulse duration $\tau_p$. For all considered excitations, cluster models and band fillings, one observes that $S_z(t)$ decreases rapidly after the pulse passage reaching values close to its long-time limit $S_z^\infty$ in a very short characteristic demagnetization time $\tau_{dm}$ of the order of 20–100 fs. The actual value of $\tau_{dm}$ is found to scale with $\hbar/\xi$, where $\xi$ is the spin-orbit coupling strength, which controls the slowest electronic spin-to-orbital angular-momentum transfer. Furthermore, the observed general trends show that whenever the main ingredients of itinerant-electron magnetism are present, namely, band formation, strong intra-atomic $3d$ Coulomb interactions and spin-orbit coupling, the ultrafast demagnetization effect should take place. One concludes that the ultrafast demagnetization of ferromagnetic TMs reflects the intrinsic many-body dynamical behavior of itinerant magnetism. The universality of the effect has been theoretically demonstrated.

The present investigations indicate that ultrafast demagnetization can be regarded as an essentially local process which involves mainly the atomic spin and orbital $d$-electron degrees of freedom and their immediate local environment. While this justifies small-cluster modelizations, it is also clear that one would like to improve on this limitation by considering larger clusters and extended systems, not least in order to quantify the importance of intermediate- and long-range dynamical effects. Besides the possible consequences on the electronic correlations, improving on the cluster model would allow us to obtain a more quantitative account of the laser absorption efficiency, which has been shown to be crucial for predicting $S_z(t)$. Such improvements will most certainly involve mean-field or functional-integral static approximations of the Coulomb interactions, whose validity could
be checked by comparison with the exact results reported in this work. Moreover, our study suggests that the laser-induced ultrafast demagnetization effect, being an essentially local phenomenon, should also take place in ferromagnetic small clusters, nanoparticles and granular systems. It would be therefore most interesting to perform cluster-specific studies of ultrafast demagnetization in order to reveal its size and structural dependence.

Finally, from the fundamental perspective of understanding the underlying physical mechanisms of UFD, it is important to recall that there are other forms of spin-lattice relaxations (e.g., electron-phonon coupling) which have been ignored in the present electronic model and which are expected to contribute to the magnetization dynamics. It would be therefore very interesting to incorporate these contributions into the present many-body model, in order to quantify their role at the same level as the spin-orbit, Coulomb and hopping electronic effects. In addition, other excitation methods, for instance, involving hot electron injection, mixed thermalized states and indirect optical excitation, should also be investigated in order to challenge the reliability of the present model and the universal character of the ultrafast demagnetization effect.

Appendix A: Interatomic hopping integrals

The present Appendix describes the interatomic hopping integrals $t_{jk}^{\alpha\beta}$, which define the single-particle operator $\hat{H}_0$ and its band structure as given by Eq. (2). The matrix elements $t_{jk}^{\alpha\beta}$ are determined by applying the two-center approximation, which has found countless successful applications in the description of the electronic structure of solids. Since only the $3d$ and $4p$ valence bands are taken into account in the model, all hopping elements $t_{jk}^{\alpha\beta}$ in $\hat{H}_0$ are obtained in terms of the 7 independent Slater-Koster parameters $(dd\sigma)$, $(dd\pi)$,
\[ t_{jk}^{4p0,4p0} = \lambda_z^2 (pp\sigma) + (1 - \lambda_z^2) (pp\pi), \]
\[ t_{jk}^{4p0,4p\pm 1} = \mp \lambda_z (\lambda_x \pm i\lambda_y) [(pp\sigma) - (pp\pi)]/\sqrt{3}, \]
\[ t_{jk}^{4p\pm 1,4p\pm 1} = [(1 - \lambda_z^2) (pp\sigma) + (1 + \lambda_z^2) (pp\pi)]/2, \]
\[ t_{jk}^{4p\pm 1,4p-1} = - (\lambda_x - i\lambda_y)^2 [(pp\sigma) - (pp\pi)]/2, \]
\[ t_{jk}^{4p0,3d0} = \lambda_z [(3\lambda_x^2 - 1) (pd\sigma) + 2\sqrt{3} (1 - \lambda_x^2) (pd\pi)]/2, \]
\[ t_{jk}^{4p0,3d\pm 1} = \mp (\lambda_x \pm i\lambda_y) [\sqrt{3} \lambda_x^2 (pd\sigma) + (1 - 2\lambda_x^2) (pd\pi)]/\sqrt{3}, \]
\[ t_{jk}^{4p0,3d\pm 2} = \lambda_z [\sqrt{3} (1 - \lambda_x^2) (pd\sigma) + 2\lambda_x^2 (pd\pi)]/2, \]
\[ t_{jk}^{4p0,3d\pm 3} = \pm (\lambda_x \mp i\lambda_y) [(3\lambda_x^2 - 1) (pd\sigma) - 2\sqrt{3} \lambda_x^2 (pd\pi)]/\sqrt{8}, \]
\[ t_{jk}^{4p0,3d\pm 4} = \mp (\lambda_x \mp i\lambda_y)^2 [\sqrt{3} (pd\sigma) - 2 (pd\pi)]/4, \]
\[ t_{jk}^{4p\pm 1,3d\pm 1} = - \lambda_z (\lambda_x \pm i\lambda_y)^3 [(pd\sigma) - 2 (pd\pi)]/4, \]
\[ t_{jk}^{4p\pm 1,3d\pm 2} = \mp (\lambda_x \pm i\lambda_y)^2 (dd\sigma)/4 + 3\lambda_x^2 (1 - \lambda_x^2) (dd\pi) + 3(1 - \lambda_x^2) (dd\delta)/4, \]
\[ t_{jk}^{4p\pm 1,3d\pm 3} = \mp \lambda_x \sqrt{3} (\lambda_x \pm i\lambda_y) [(3\lambda_x^2 - 1) (dd\sigma) + 2(1 - 2\lambda_x^2) (dd\pi) - (1 - \lambda_x^2) (dd\delta)]/\sqrt{8}, \]
\[ t_{jk}^{4p\pm 1,3d\pm 4} = \sqrt{3} (\lambda_x \pm i\lambda_y)^2 [(3\lambda_x^2 - 1) (dd\sigma) - 4\lambda_x^2 (dd\pi) + (1 + \lambda_x^2) (dd\delta)]/\sqrt{3}., \]
\[ t_{jk}^{4p\pm 1,3d\pm 5} = [3\lambda_x^2 (1 - \lambda_x^2) (d,d; \sigma) + (4\lambda_x^4 - 3\lambda_x^2 + 1) (dd\pi) - (1 + \lambda_x^2) (dd\delta)]/2, \]
\[ t_{jk}^{4p\pm 1,3d\pm 6} = \mp \lambda_x (\lambda_x \pm i\lambda_y)^2 [3(1 - \lambda_x^2) (dd\sigma) + 4\lambda_x^2 (dd\pi) - 3 + \lambda_x^2 (dd\delta)]/4, \]
\[ t_{jk}^{4p\pm 1,3d\pm 7} = - (\lambda_x - i\lambda_y)^2 [3\lambda_x^2 (dd\sigma) - 4\lambda_x^2 (dd\pi) + (1 - \lambda_x^2) (dd\delta)]/2, \]
\[ t_{jk}^{4p\pm 1,3d\pm 8} = \mp \lambda_x (\lambda_x \mp i\lambda_y)^3 [3 (dd\sigma) - 4 (dd\pi) + (dd\delta)]/4, \]
\[ t_{jk}^{4p\pm 1,3d\pm 9} = [3(1 - \lambda_x^2)^2 (dd\sigma) + 4(1 - \lambda_x^2) (dd\pi) + (\lambda_x^4 + 6\lambda_x^2 + 1) (dd\delta)]/8, \]
\[ t_{jk}^{4p\pm 1,3d\pm 10} = (\lambda_x - i\lambda_y)^4 [3 (dd\sigma) - 4 (dd\pi) + (dd\delta)]/8, \]

where \( \hat{z} \) has been chosen as the \( m \)-quantization axis, and \( \lambda_\mu = \vec{R}_{jk} \cdot \hat{\mu}/R_{jk} \) denotes the direction cosine of the interatomic vector \( \vec{R}_{jk} = \vec{R}_j - \vec{R}_k \) (\( \hat{\mu} = \hat{x}, \hat{y} \) or \( \hat{z} \)). Notice that the hopping elements which are not explicitly given can be obtained by applying the relation \( t_{jk}^{\alpha \beta} = t_{jk}^{\beta \alpha} (\vec{R}_{jk}) = |t_{jk}^{\beta \alpha} (\vec{R}_{jk})|^* \). Further details may be found in Ref. [50].

As described in Sec. [1A], the \( pd \) model has been simplified in order to keep the dimension
of the many-body Hilbert space and the numerical effort involved in the exact time evolution tractable. Thus, the 3d orbitals are approximated by three degenerate levels having \( |m| \leq 1 \) and the 4p orbitals by a single level having \( m = 0 \). This reduction of the number of bands implies that only the four Slater-Koster parameters \((dd\sigma), (dd\pi), (pp\sigma)\) and \((pd\sigma)\) are necessary in order to determine all hopping integrals \( t_{jk}^{\alpha\beta} \). The corresponding expressions for \( t_{jk}^{\alpha\beta} \) are

\[
\begin{align*}
t_{jk}^{4p,4p0} &= (pp\sigma), \\
t_{jk}^{4p,3d0} &= \lambda_z (pd\sigma), \\
t_{jk}^{4p,3d\pm1} &= \mp (\lambda_x \pm i\lambda_y) (pd\sigma)/\sqrt{2}, \\
t_{jk}^{3d0,3d0} &= \lambda_z^2 (dd\sigma) + (1 - \lambda_z^2) (dd\pi), \\
t_{jk}^{3d0,3d\pm1} &= \mp \lambda_z (\lambda_x \pm i\lambda_y) [(dd\sigma) - (dd\pi)]/\sqrt{2}, \\
t_{jk}^{3d\pm1,3d\pm1} &= [(1 - \lambda_z^2) (dd\sigma) + (1 + \lambda_z^2) (dd\pi)]/2, \quad \text{and} \\
t_{jk}^{3d\pm1,3d\pm1} &= - (\lambda_x - i\lambda_y)^2 [(dd\sigma) - (dd\pi)]/2 .
\end{align*}
\]

The values of the Slater-Koster parameters are given in the main text.

**Appendix B: Electric dipole matrix elements**

The dominant intra-atomic dipole matrix elements \( \langle \alpha|\vec{r}|\beta \rangle \) characterizing the interaction \( \hat{H}_E \) with the laser field [see Eqs. (7) and (8)] can be expressed in terms of the irreducible spherical tensor operator \( \hat{T}_q^{(k)} \) of rank \( k = 1 \) and components \( q \) given by

\[
\begin{align*}
\hat{T}_1^{(1)} &= - \frac{1}{\sqrt{2}} (\hat{x} + i\hat{y}), \\
\hat{T}_1^{(1)} &= \frac{1}{\sqrt{2}} (\hat{x} - i\hat{y}), \\
\hat{T}_0^{(1)} &= \hat{z} .
\end{align*}
\]

The elements of \( \hat{T}_q^{(1)} \) between the atomic orbitals \( |nlm\rangle \) having principal quantum number \( n \), orbital angular momentum \( l \) and z-axis projection \( m \) are given by the Wigner-Eckart relation\(^{11}\)

\[
\langle nlm|\hat{T}_q^{(k)}|n'lm' \rangle = \langle l'k; m'q|lm \rangle \frac{\langle nl||\hat{T}_q^{(k)}||n'l' \rangle}{\sqrt{2l' + 1}} ,
\]

where \( \langle nl||\hat{T}_q^{(k)}||n'l' \rangle \) is the reduced matrix element and the scalar products \( \langle l'k; m'q|lm \rangle \) are the Clebsch-Gordan coefficients. Thus, the matrix element \( \langle nlm|\hat{T}_q^{(k)}|n'lm' \rangle \) in Eq. (B2) can
be interpreted as a projection resulting from the addition of the angular momenta $\hat{l}$ and $\hat{k}$ to $\hat{l}$ ($\hat{l} \oplus \hat{k} = \hat{l}$). Since $\langle nL||\hat{T}(1)||n'L'\rangle$ is independent of $n'$, $q$ and $m$, all the dipole matrix elements entering $\hat{H}_E$ are characterized by a single parameter $\langle 3d||\hat{T}(1)||4p\rangle$, the dependence on $m$, $m'$ and $q$ being given by the known Clebsch-Gordan coefficients. Since the operator $\hat{H}_E$ is given by a product of $\hat{r}$ and $\hat{E}$, the matrix element $\langle 3d||\hat{T}(1)||4p\rangle$ gives a measure of the strength of the coupling between the electronic translational degrees of freedom and the external electric field $\hat{E}$ [see Eqs. (7) and (8) of the main text].

The non-vanishing dipole matrix elements then read

$$\langle 3dm|\hat{\xi}|4pm'\rangle = (\delta_{m,m'-1} - \delta_{m,m'+1}) \left( \sqrt{|m|/12 + \delta_{m,0}/6} \right) \langle 3d||\hat{T}(1)||4p\rangle,$$

$$\langle 3dm|\hat{\gamma}|4pm'\rangle = i \left( \delta_{m,m'-1} + \delta_{m,m'+1} \right) \left( \sqrt{|m|/12 + \delta_{m,0}/6} \right) \langle 3d||\hat{T}(1)||4p\rangle,$$

$$\langle 3dm|\hat{\zeta}|4pm'\rangle = \delta_{m,m'} \left( |m|/\sqrt{6} + \sqrt{2/9} \right) \langle 3d||\hat{T}(1)||4p\rangle.$$  \hspace{1cm} (B3)

In the case of circular polarization $\hat{\xi}_{\pm}$ the relevant matrix elements are

$$\langle 4pm'|\hat{\xi}_{\pm} \cdot \hat{r}|3dm\rangle = \pm \delta_{m',m\pm1} \left( \sqrt{|m|/6} + \sqrt{2}\delta_{m,0}/6 \right) \langle 3d||\hat{T}(1)||4p\rangle^*.$$ \hspace{1cm} (B4)

Taking into account the reduction of the local orbital degeneracy introduced in Sec. II A the non-vanishing electric-dipole matrix elements are simplified as follows. For linear electric-field polarization, they read

$$\langle 3dm|\hat{\xi}|4p0\rangle = -m \langle 3d||\hat{T}(1)||4p\rangle/\sqrt{2},$$

$$\langle 3dm|\hat{\gamma}|4p0\rangle = i(1 - \delta_{m,0}) \langle 3d||\hat{\tilde{T}}(1)||4p\rangle/\sqrt{2},$$

$$\langle 3dm|\hat{\zeta}|4p0\rangle = \delta_{m,0} \langle 3d||\hat{\tilde{T}}(1)||4p\rangle,$$  \hspace{1cm} (B5)

while for circular polarization they are given by

$$\langle 4p0|\hat{\xi}_{\pm} \cdot \hat{r}|3dm\rangle = \pm \delta_{m,\pm1} \langle 3d||\hat{\tilde{T}}(1)||4p\rangle^*.$$  \hspace{1cm} (B6)

The value of $\langle 3d||\hat{\tilde{T}}(1)||4p\rangle$ is given in the main text.

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In practice, nearly the same fits are obtained by replacing $S_z(0)$ with the ground-state spin magnetization $S_0^z$, except when $\tau_p$ is comparable or larger than $\tau_{dm}$ as discussed in Sec. III D.

In addition, other different linear electric field polarizations $\hat{\varepsilon}$ have also been considered. For all $\hat{\varepsilon}$ within the triangle plane the optical absorptions and subsequent dynamics have been found to be quantitatively very similar. However, for $\hat{\varepsilon}$ normal to the triangle plane ($\hat{\varepsilon} = \hat{z}$) we obtain a strong reduction of the optical absorption. Thus, for a given $F$, the demagnetization strength is significantly smaller than in the case of in-plane polarizations.