Charge and spin responses under pump-probe excitations in comparison with single pump excitations

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Conventional pump-probe experiments are very powerful to time-resolve ultrafast spin dynamics in ferromagnetic metals. Recently, a question is raised how the spin and polarization changes differ from those induced by a single pump. Here, we show that the difference is not intrinsic and depends on the laser pulses themselves. If the laser pulse duration is as short as ten femtoseconds, the difference in polarization is very small, at least within the single-particle approximation. However, if the laser pulses are long, the difference becomes much more pronounced, and it also depends on the time delay between the pump and probe. This difference directly results from the fact that the same laser frequencies are used for both pump and probe pulses and the same portion of electronic states are excited. If pump and probe pulses are detuned slightly away from each other, the difference in the polarization disappears. Different from the polarization, the spin moment change is almost immune to different excitation conditions whether it is from one pump pulse or two pulses (pump and probe). This finding finally clarifies the effect of the number of laser pulses on polarization and spin moment changes in femtosecond magnetism.

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I. INTRODUCTION

In the traditional continuous wave (cw) optics, a single light beam impinges onto a sample; a single detector is used to monitor the change in reflected or transmitted light or both. If the sample is ferromagnetic, the reflected light's polarization is rotated with respect to the incident polarization. This is called Kerr effect (see Fig. 1). If the transmitted light is probed, this effect is called the Faraday or Voigt effect. Figure 1 shows some of the typical geometries frequently used in experiments. If the light intensity is very strong or the system is excited by multiple pulses, the nonlinear optical effect becomes important.[1–3] From the beginning of the nonlinear optics, it is almost always fascinating to see whether one can link the high order nonlinear susceptibilities to lower order susceptibilities. Among the earliest attempts, the Miller's rule aims to link the second-order susceptibility to the linear susceptibility, with some success. In the classical limit, at least in the aharmonic potential, the third-order susceptibility has been linked to the first-order susceptibility via

$$\chi^{(3)}(\omega_4 = \omega_1 + \omega_2 + \omega_3) \propto \chi^{(1)}(\omega_4)\chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2)\chi^{(1)}(\omega_3), \quad (1)$$

where ω_{1-3} are the incident light frequencies and ω_4 is the radiated one. It is clear that higher-order responses are indeed closely related to the lower order ones.

However, these cw techniques do not provide a time resolution. With advent of the ultrafast laser pulses, multiple pulses are used. In a typical pump-probe experiment, two laser pulses are used, where a pump pulse impinges a sample first, and after a time delay, a probe pulse detects a change in polarization induced by the pump. The system interacts with the pump twice and the probe once. In other words, the signal is in the second order of the pump pulse field and the first order of the probe pulse field. The experimental time is a delay time between pump and probe. Theoretically, by contrast, one pulse is enough to investigate the time-dependent polarization change since at any time the density matrices are known and all the subsequent quantities such as charge and spin change can be computed. Here, the time is real time. Therefore it is interesting to ask whether there is any major difference between the polarization change induced by a single pump pulse and that induced by two pulses such as pump and probe. This issue has been raised in a recent review[4] on femtosecond magnetism.[5–7]

There are additional differences between the experiment and theory. In the pump-probe geometry, often only the signal propagating along the $\vec{k}_1 + \vec{k}_2 - \vec{k}_1$ direction is detected,[8] where $\vec{k}_1$ and $\vec{k}_2$ are the wave vectors of the pump and probe fields, respectively. Since this signal is only one of 81 components in the third-order nonlinear optical process,[3] this raises an experimental question how good this signal represents the true polarization change. In other words, whether the experimental results are component dependent. This directly affects the second-order harmonic generation measurement, and its subsequent interpretation as a magnetic signal.

By contrast, the theory has a unique advantage. At least within a single-particle picture, the exact polarization can be calculated once the density matrices are known. It is our goal to investigate whether the polarization change induced by a single pump pulse really differs from that by one pump and one probe pulses, and more importantly whether there is any difference in the spin moment change. We aim to, at least partially, resolve this issue.

This paper is arranged as follows. Section II is devoted to the theoretical formalism, with the results and discussions presented in Sec. III. Finally, we conclude the paper in Sec. IV.

II. THEORY

Quantum mechanically, in the literature, there are only a few limited cases where a comparison between the first- and third-order susceptibilities (in the frequency domain) is possible. The analytic results are ever fewer. Moreover, they are not

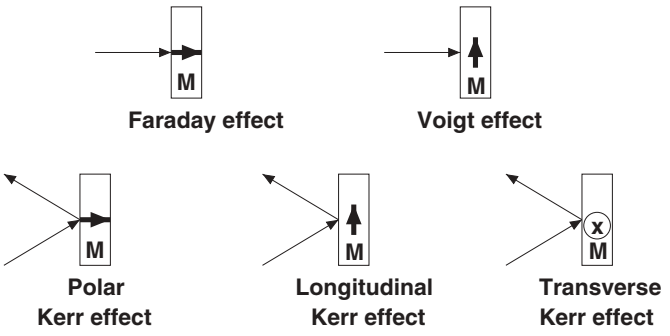

FIG. 1. Typical experimental geometry of the magneto-optical measurements. (Top) Faraday and Voigt geometries. (Bottom) Polar Kerr, longitudinal Kerr, and transverse Kerr effects.

generic nor time dependent, but they do show some intrinsic connection between the first- and third-order processes. For instance, in a two-level system (level a and level b), if the system is driven by a single cw laser, within the rotating wave approximation (RWA),[1]

$$\chi^{(3)} = -\frac{4|\mu_{ba}|^2 T_1 T_2}{3\hbar^2\left(1+\Delta^2 T_2^2\right)}\chi^{(1)}, \tag{2}$$

where μ_{ba} is the transition matrix element, T_1 and T_2 are the longitudinal and transverse relaxation times, respectively, and $\Delta = \omega - \omega_{ba}$ is the detuning factor. Other quantities have their usual meanings. This equation shows clearly that $\chi^{(3)}$ is linearly proportional to $\chi^{(1)}$. But it is unclear how these results will hold in a multiple pulse excitation in the real-time domain. This is where the numerical simulation is a must.

Numerically, we want to simulate the dynamics as realistically as possible. Therefore we choose a ferromagnetic fcc Ni as an example.[9,10] We do not include the electron correlation effects explicitly so the results can be directly assigned to the pump and probe effects. Our theoretical calculations start with the first-principles density functional calculation as implemented in the WIEN2K code[11] which has been heavily modified by us[12] to compute both the spin and orbital moment matrices and the optical transition matrices.[13] Simulating optical responses in metals requires a huge number of k points to fully converge the results.[9,14] The total number of k points used is 104^3 in the Brillouin zone.[15] To minimize the linearization error, we fine tune the linearization energy. After a self-consistency is reached, we proceed to dynamic simulation.

Dynamically, we introduce two laser fields: one is the pump pulse $\mathbf{E}_p(t)$ and the other is the probe pulse $\mathbf{E}_b(t)$. Both fields have a Gaussian envelope function $|\mathbf{E}_{p(b)}| = A_{p(b)}\exp[-(t - T_{p(b)})^2/\tau_{p(b)}^2]\cos(\omega_{p(b)}t)$, but they can take different photon energies $\hbar\omega_{p(b)}$, field amplitudes $A_{p(b)}$, pulse durations $\tau_{p(b)}$, and delay times $T_{p(b)}$. Since the results only depend on the relative time delay, in the following, we choose $T_p = 0$ fs so we only have one time delay T_b or T. A negative time delay means that the probe pulse is fired ahead of the pump; a positive one means behind the pump.

Before we can compute the polarization and spin moment change, we first calculate the time-dependent density matrices. Within the dipole approximation, the density matrix is diagonal in the crystal momentum k space, or $\rho_{k,k'} = \rho_{k,k}\delta_{k,k'}$.[16] Therefore we can represent the density matrix as $\rho_{k;i,j}$, where $i(j)$ is the band index. The Liouville equation is

$$i\hbar\dot{\rho}_{k;i,j} = [H_0 + H_I, \rho_{k;i,j}]. \tag{3}$$

Here, H_0 is the original system Hamiltonian. H_I is the interaction between the system and laser field $\mathbf{E}(t) = \mathbf{E}_p(t) + \mathbf{E}_b(t)$. In our calculation, we do not explicitly include damping and decoherence since the decay to external heat bath occurs on a much longer time scale. With nearly half-million differential equations, we must resort to the massively parallel algorithm,[10] which has been successfully implemented in our code. With the density matrix in hand, we can compute both the polarization and spin moment via

$$P_{\text{pump}}(t) = \sum_k \sum_{i,j} \rho_{k;i,j}(t) D_{k;j,i}, \tag{4}$$

$$M^z_{\text{pump}}(t) = \sum_k \sum_{i,j} \rho_{k;i,j}(t) S^z_{k;j,i}. \tag{5}$$

Different from the single pulse excitation, to simulate the pump-probe excitation, it is necessary to perform two separate calculations for all the calculations: one with the pump and the other without the pump. The induced change is computed from

$$\Delta P(t) = P_{\text{pump+probe}}(t) - P_{\text{probe}}(t), \tag{6}$$

$$\Delta M^z(t) = M^z_{\text{pump+probe}}(t) - M^z_{\text{probe}}(t). \tag{7}$$

These changes are then compared with the changes under a single pump excitation, i.e., $P_{\text{pump}}(t)$ and $M^z_{\text{pump}}(t)$.

III. RESULTS AND DISCUSSIONS

In the pump-probe configuration, there are many possible combinations. We choose three representative cases. Case A: both pump and probe have the same photon energy and laser pulse duration, but only differ in the laser field amplitude. Case B: similar to A, but both pulses have a longer pulse duration. Case C: the pump and probe have different photon energies.

A. Excitation with 12-fs pump and probe pulses

Figure 1 shows our first results for our pump-probe calculation. Here, both τ_p and τ_b are 12 fs. The inset on the top of Fig. 2(a) shows the profile of our laser pulse. The amplitude of the pump is 0.05 V/Å, while the probe is five times smaller, 0.01 V/Å. The photon energies are the same, $\hbar\omega_{p(b)} = 2.0$ eV. Under a single pump excitation [see the first curve in Fig. 2(a)], the polarization $P_{\text{pump}}(t)$ increases quickly with the laser field and reaches its extreme around 0 fs. It has rapid beating, consistent with our earlier results.[9] After the extreme, there is a small recurrence around 25 fs. This recurrence becomes much weaker as time progresses.

Next, we compute $\Delta P(t)$ under both pump and probe excitations. The pump-probe technique introduces a new time variable, the time delay T. It is necessary to scan several different delays between pump and probe to develop a whole picture of the polarization change. At $T = -20$ fs, $\Delta P(t)$ is very similar to $P_{\text{pump}}(t)$. The main difference appears at the first recurrence around 25 fs. At other time delays, its structure remains same, but after $T = 20$ fs, the peak becomes slightly

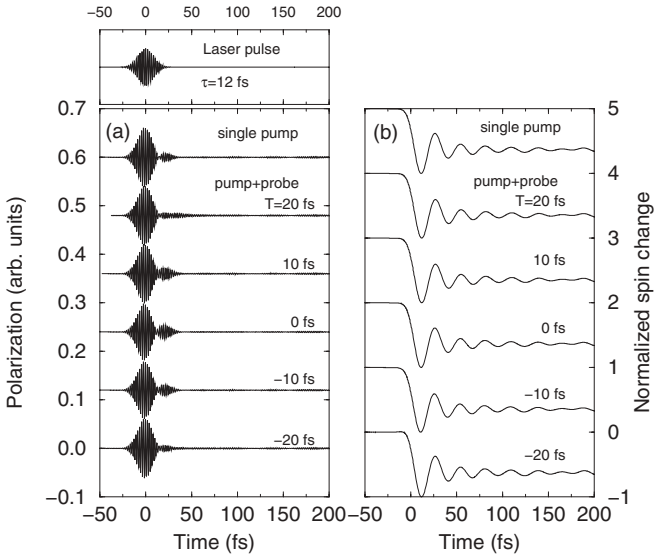

FIG. 2. (a) Polarization change as a function of time for a single pump excitation (the first curve) and pump-probe excitation at five different delay times from −20 to 20 fs (from bottom to top). Here, the laser pulse duration is 12 fs for both pump and probe pulses. Both their photon energies are 2 eV. The profile of the laser field is shown on the top. (b) Magnetic moment change as a function of time. The delay times are the same as (a). The spin moment change for the single pump excitation is also shown on the top.

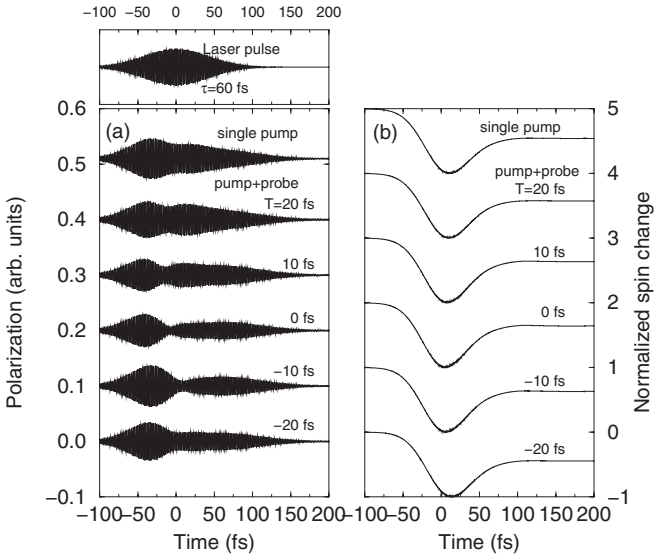

FIG. 3. (a) Polarization change as a function of time for a single pump excitation (the first curve) and pump-probe excitation at five different delay times from −20 fs to 20 fs (from bottom to top). A clear difference is observed at different delays. Here, the laser pulse duration is 60 fs for both pump and probe pulses. The profile of the laser field is shown on the top. (b) Magnetic moment change as a function of time. The delay times are the same as (a). The spin moment change for the single pump excitation is also shown on the top.

more dispersive. From this, we conclude that there is no major qualitative difference in polarization between a single pump excitation and pump-probe excitation. Since our polarization includes all the orders of optical responses, our results are exact.

However, experimentally, what is unknown is how the spin moment change depends on the number of pulses. We compute the spin moment changes under single pump as well as pump-probe excitations. This result is shown in Fig. 2(b). As before, we plot the spin moment change for the single pump pulse at top. Here for an easy comparison, we normalize the spin moment change to its minimum. Different from the polarization change, the spin change has no rapid beating, and more importantly the effect of the time delay between the pump and probe is virtually nonexistent, and all the spin changes are almost identical.

B. Excitation with 60-fs pump and probe pulses

Experimentally, pulses within twenty femtoseconds have been available for a long time,[17] but up to now, these pulses are rarely used to investigate spin dynamics in ferromagnets, with very few exceptions.[18] The majority of experiments use very long laser pulses. To address those experiments, we use two longer pulses with a duration of 60 fs,[19] with its temporal shape shown in the top inset of Fig. 3(a). All the other parameters are the same as above. Figure 3(a) shows that for a single pump excitation, $P_{\text{pump}}(t)$ shows a similar rapid oscillation, but its envelope is much broader temporally, due to multiple excitations. Here, the multiple excitations refer to the fact that the electrons have enough time to undergo several transitions among more energy levels before the pulse is over. This is an excellent example to show why the longer pulses normally are unsuitable for the ultrafast dynamics.

The polarization change in the pump-probe configuration shows a strong dependence on the time delay T. For instance, at $T = -20$ fs, although the general shape is similar, the polarization $\Delta P(t)$ starts to deviate from $P_{\text{pump}}(t)$. $P_{\text{pump}}(t)$ is "fatter" than $\Delta P(t)$. At $T = 0$ fs, the difference is much more pronounced. The reason for this difference is easy to understand. Since both pump and probe have the same frequency, they excite the same portion of the electronic states and the coherence induced by the pump is directly felt by the probe, or visa versa. This constitutes a major concern for excitation using a long pulse, which will be discussed further below. By contrast, the spin moment change is largely immune to the delay time. Figure 3(b) shows that independent of time delay, $\Delta M^z(t)$ and $M^z_{\text{pump}}(t)$ are very similar to each other.

C. Excitation with pump and probe pulses of two different colors

So far, the only difference between the pump and probe pulses is their field amplitudes. As seen above, since they both have the same photon energy, this leads to a clear difference in the polarization change from a simple pump excitation. We examine whether it is possible to eliminate these differences for long pulses. To realize this, we employ two colors of pulses, i.e., pump and probe pulses having different photon energies. The probe photon energy is chosen to be $\hbar\omega_b = 1.6$ eV, which is slightly detuned away from that of the pump $\hbar\omega_p = 2.0$ eV. The time delay is fixed at 20 fs. Figure 4(a) shows that there is almost no difference in the spin moment change between the

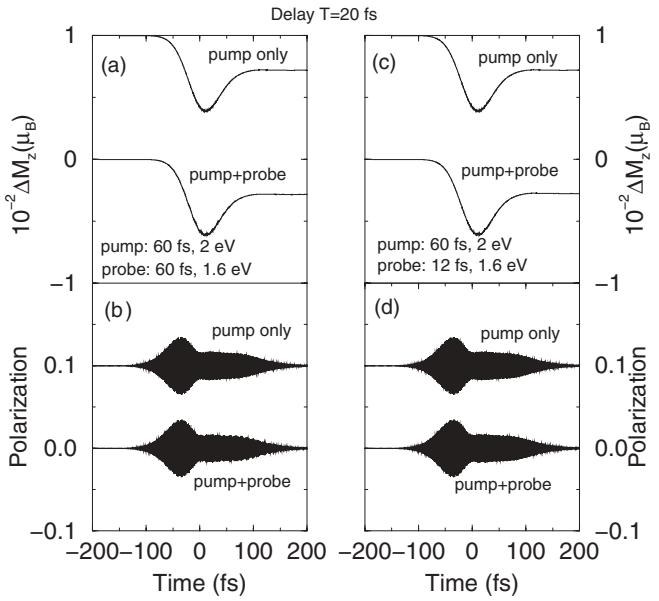

FIG. 4. Excitation with pulses of two different colors. The time delay between the pump and probe is fixed at 20 fs. (a) Spin moment change as a function of time. Both pump and probe have the same pulse duration of 60 fs, but their photon energies are detuned from each other. (b) Polarization change. (Top) Polarization under a single pump excitation. (Bottom) Polarization change under a pump-probe excitation. (c) Spin moment change. The probe pulse is 12 fs long, while the pump pulse is still 60 fs. The photon energies for pump and probe are also different. (d) Polarization as a function of time. The laser pulses are same as (c).

single pump pulse and pump-probe excitations. Amazingly, there is no major difference in the polarization either [see Fig. 4(b)]. Therefore we finally succeed to find a solution for those long pulse experiments. Our results remain true even if we use two different laser pulse durations for the pump and the probe. In Figs. 4(c) and 4(d), our probe pulse's duration is 12 fs, while the pump duration is 60 fs long. Quantitatively, by comparing the absolute values of the polarization and spin moments, we find that the percent difference is only 0.3% for the spin moment change and is 0.5% for the polarization change. We also test the results at delay time $T = 0$ and find no difference.

The reason why two-color excitations tend to have a smaller effect on the spin and polarization is because the density matrices beat at different frequencies and the coherence can not be built up easily for either pulse. Electronically, the pump and probe now excite different groups of electronic states; as a result, this eliminates multiple excitations originating from the same electronic states. This way, the difference between the single pump excitation and the pump-probe excitation can be avoided entirely.

IV. CONCLUSION

We have performed a first-principles calculation to investigate whether and how the polarization and spin moment change behave differently if excited by one single pump pulse or by two pulses (pump and probe). Our results show that when the laser pulses are short, within ten of femtoseconds, both the polarization and spin moment changes are insensitive to the number of pulses used. In both cases, the polarization and spin moment are similar. However, when pulses are longer, the polarization starts to deviate, and the degree of deviation depends on the pump-probe time delay. A longer delay leads to less deviation. The reason for this deviation originates from the single-color excitation. When both pump and probe have the same frequency, coherence between them is established, which induces multiple excitations. This problem can be easily overcome if pump and probe pulses use different frequencies. We show that by slightly detuning the laser frequency of the probe away from that of the pump, the polarization under the pump-probe configuration faithfully follows the polarization in a single pump excitation. This result remains true if pump and probe pulses have different laser pulse durations. When the laser frequencies are detuned from each other, the time delay between pump and probe almost has no effect on the polarization change either. In all the test cases, the spin moment change is much less sensitive to whether the spin is excited by a single pump pulse or pump and probe pulses. Therefore our calculation, at least partially, resolves the issue how the number of laser pulses affects the spin and polarization changes.

Note added in proof. After this paper was accepted for publication, we became aware of a new publication by Vonesch and Bigot[20] who nicely computed the magneto-optical response in a hydrogenlike atom. Their results compliment with our results well.

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