Ultrafast phenomena in nanomaterials from visible to Xrays

Jean-Yves Bigot

Institut de Physique et Chimie des Matériaux de Strasbourg
CNRS - Université De Strasbourg -
I. Ultrafast processes: formal description
* Light matter interaction in the dynamical regime
* Two levels system and time dependent polarization
* Four wave mixing and photon echoes

II. Examples of molecular systems
* Probing primary events with ultrashort laser pulses
* Wave packet dynamics: example of polydiacetylene
* Green florescent protein and proton transfer dynamics

III. Simple features of femtosecond laser spectroscopy
* Temporal and spectral characteristics
* Density of excitation

IV. Ultrafast magnetization dynamics
* Generalities on electron and spins relaxation
* Demagnetization induced by laser pulses
* Spin precession and damping
* Ultrafast confocal magneto-optical microscopy

V. Xrays femtosecond and attosecond spectroscopy

Winter School 2010 - IPCMS - QMMRC
How can we model dynamical processes in the femtosecond regime?

Light-Matter interaction with ultrashort optical pulses
Maxwell

\[ \nabla \cdot \mathbf{E}(r, t) = \frac{1}{\varepsilon_0} \rho(r, t) \]

\[ \nabla \cdot \mathbf{B}(r, t) = 0 \]

\[ \nabla \times \mathbf{E}(r, t) = -\frac{\partial}{\partial t} \mathbf{B}(r, t) \]

\[ \nabla \times \mathbf{B}(r, t) = \frac{1}{c^2} \frac{\partial}{\partial t} \mathbf{E}(r, t) + \frac{1}{\varepsilon_0 c^2} \mathbf{j}(r, t) \]

Newton-Lorentz

\[ m_i \frac{d^2}{dt^2} \mathbf{r}_i(t) = q_i [\mathbf{E}(\mathbf{r}_i(t), t) + \mathbf{v}_i(t) \times \mathbf{B}(\mathbf{r}_i(t), t)] \]

\[ \frac{\partial}{\partial t} \rho(r, t) + \nabla \cdot \mathbf{j}(r, t) = 0 \]

\[ Q = \int d^3 r \rho(r, t): \text{is conserved} \]

Constants of motion

\[ H = \sum_i \frac{1}{2} m_i \mathbf{v}_i^2(t) + \frac{\varepsilon_0}{2} \int d^3 r \left[ \mathbf{E}(r, t) + c^2 \mathbf{B}(r, t) \right]^2 \]

\[ \mathbf{P} = \sum_i m_i \mathbf{v}_i(t) + \varepsilon_0 \int d^3 r \mathbf{E}(r, t) \times \mathbf{B}(r, t) \]

\[ \mathbf{J} = \sum_i \mathbf{r}_i(t) \times m_i \mathbf{v}_i(t) + \varepsilon_0 \int d^3 r \mathbf{r} \times [\mathbf{E}(r, t) \times \mathbf{B}(r, t)] \]

Energy

Total momentum

Total kinetic momentum
Two main problems:

1. Quantum nature of the system is not considered

**OK, Newton-Lorentz replaced by:**

\[ \text{Schrödinger} \]

\[ \frac{\partial \Psi(t)}{\partial t} = -\frac{i}{\hbar} H(t) \Psi(t) \]

With appropriate “choice” of \( H(t) \)

2. How does the external field relates to the densities of charges and current?

**In principle everything is determined with:**

\[ \rho(r,t) = \sum_{i} q_i \delta[r - r_i(t)] \quad \text{and} \quad j(r,t) = \sum_{i} q_i v_i(t) \delta[r - r_i(t)] \]

But we need some hypothesis for the interaction between the field and the charges!
Alternatively one can introduce response functions instead of considering $\rho(r,t)$ and $j(r,t)$

$$f(r_1, t) = -\nabla V(r_1(t), t)$$

Classical: add to Lorentz a force $f(r_1, t)$

Quantum: interaction included in Hamiltonian $H = H_0 + H_{int}$

$$\rho_{tot} = \rho_{ext} + \rho_{int} ; \quad \rho_{int} = -\nabla P$$

$P$: polarization of the medium

$D(r, t) = \varepsilon_0 E(r, t) + P(r, t)$

$B(r, t) = \mu_0 H(r, t) + M(r, t)$

$M$: magnetization ...
It is tempting to write: \( \mathbf{D}(\mathbf{r},t) = \varepsilon \mathbf{E}(\mathbf{r},t) \) and \( \mathbf{B}(\mathbf{r},t) = \mu \mathbf{M}(\mathbf{r},t) \)
or: \( \mathbf{P}(\mathbf{r},t) = \chi_e \mathbf{E}(\mathbf{r},t) \) and \( \mathbf{M}(\mathbf{r},t) = \chi_m \mathbf{H}(\mathbf{r},t) \)

\( \varepsilon \) dielectric and \( \mu \) permeability constants
\( \chi_e \) dielectric and \( \chi_m \) magnetic susceptibilities

\[
\chi_e = \chi_e^{(1)} \otimes \mathbf{E} + \chi_e^{(2)} \otimes \mathbf{E}^2 + \ldots
\]
Nonlinear Optics

\[
\chi_m = \chi_m^{(1)} \otimes \mathbf{H} + \chi_m^{(2)} \otimes \mathbf{H}^2 + \ldots
\]
Nonlinear Magnetism

Not always right. Particularly in the ultrafast regime!
The polarisation response to a perturbation field is not instantaneous

\[ P^{(n)}(t) = \varepsilon_0 \int_{-\infty}^{+\infty} dt' \, R^{(n)}(t, t') \otimes E(t') \]

\[ R^{(n)}(t, t') = R^{(n)}(t' - t) \]

\[ R^{(n)}(t' - t) = 0 \quad \text{if} \quad t < t' \]

\[ P^{(n)}(t) = \varepsilon_0 \int dt'_1 \ldots \int dt'_n \, R^{(n)}(t'_1 - t, \ldots, t'_n - t) \otimes E(t'_1) \ldots E(t'_n) \]

Linear response

Time invariance

Causality

n\textsuperscript{th} order response

In practice one has to distinguish between the adiabatic and transient regimes for the response function (compare pulse duration versus relaxation times of the physical processes).

The response is also non-local in space and may not be invariant by space translation! 

Important for the study of nanostructures

\[ \Rightarrow \text{Density Functional Theory} \]
What are the measurable quantities?

N dipoles simultaneously excited at time \( t = 0 \)

- Population relaxation
- Phase relaxation

How can we measure them?

- **Pump-probe measurement**
  
  \[ \frac{T(\tau) - T(-\infty)}{T(-\infty)} \approx \exp(-\tau/T_1) \]
  
  \( T_1 \) : lifetime (population)

- **Four-Wave Mixing measurement**
  
  \[ S(\tau) \approx \exp(-2\tau/T_2) \]
  
  Observed in direction \( k_2 \)
  
  \( T_2 \) : dephasing (coherence)
How can we model the phase and population dynamics?

Example of two levels system:

Density matrix for two levels system:

\[ \frac{d \rho(t)}{dt} = \left[ H(t), \rho(t) \right] \]
\[ \rho(t) = |\psi(t)\rangle \langle \psi(t)| \]

\[ \frac{d \rho_{12}}{dt} = \left( i \omega - \frac{i}{T_2} \right) \rho_{12} + \frac{i}{\hbar} E (\rho_{22} - \rho_{11}) \]

Dynamics of coherence with \( T_2 \) relaxation time:

\[ \frac{d \rho_{12} - \rho_{21}}{dt} = \frac{2i}{\hbar} E (\rho_{12} - \rho_{21}) - \frac{[ (\rho_{12} - \rho_{21}) - (\rho_{22} - \rho_{11}) ]}{T_1} \]

Dynamics of populations with \( T_1 \) relaxation time:

Assume semiclassical approximation and dipolar interaction:

\[ H = H_0 - \mu E \]
\[ \langle \rho \rangle = \begin{pmatrix} 0 & \rho^* \\ \rho & 0 \end{pmatrix} \]

\[ T_1 \rho = 1 \]
Typical configuration: two incident fields which relative temporal variation can be changed with a stepper motor (step \( \delta x \)) : \( \delta x = c \frac{\tau}{2} \) for \( \delta x = 0.1 \, \mu m \) \( \tau = 0.6 \, fs \)

\[
\mathcal{E}(\vec{r}, t) = \frac{i}{2} \left[ \mathcal{E}(\vec{r}, t) e^{-i\omega t} + c.c. \right]
\]

\[
\mathcal{E}(\vec{r}, t) = \mathcal{E}_0(t) e^{i\vec{k}_1 \cdot \vec{r}} + \mathcal{E}_1(t-z) e^{i\vec{k}_2 \cdot \vec{r}}
\]

Measuring the dephasing times: polarization dephasing and photon echoes

Observing signal in direction \( 2k_1-k_2 \):

solve equations to 3rd order in E

and retain terms in \( E_1E_1E_2^* \)

\[
\langle P \rangle = NT_\alpha \left[ P \right]
\]

\[
\langle P \rangle(t, z) = e^{-2z} \frac{\delta \omega(t-z)}{T_\text{k}} e^{-\frac{t}{\tau}} H(z) H(t-z)
\]

Winter School 2010 - IPCMS – QMMRC
homogeneous linewidth : $\omega_0$

$$S(\tau) = \int_{-\infty}^{+\infty} \langle P(\tau, z) \rangle dt$$

$$S(\tau) = S(0) e^{-\frac{2\tau}{T_2}} \quad \text{if } \tau > 0$$
$$= 0 \quad \text{if } \tau < 0$$

Polarization free decay by analogy with atomic systems

Winter School 2010 – IPCMS - QMMRC
inhomogeneous linewidth: $g(\omega_0)$

\[
S_{inh}(\tau) = \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} d\omega \langle P(t, \tau, \omega) \rangle g(\omega) \exp(-2t/T_2)
\]

\[
g(\omega_0) = \frac{C}{\pi^2}
\]

\[
S(\tau) = S(0) e^{-4\tau/T_2} \quad \text{if} \quad \tau > 0
\]

\[
= 0 \quad \text{if} \quad \tau < 0
\]

Photon echo: a “burst” of light is emitted when the dipoles get together in phase. It occurs $2\tau$ after the excitation of the medium by the 1st pulse.

Winter School 2010 - IPCMS - QMMRC
Influence of vibrational motion

\[ \hbar \omega_{ij} \]

Considering several excited states

It is easy to show that:

\[ S(\tau) = S(0) \left[ \sum_i \left( \langle j | H_{ij} \rangle \langle i | \right) \cos \omega_{ij} \tau \right]^2 e^{-\frac{2\tau}{T_2}} \]

\[ S(\tau) \]

\[ \exp(-2t/T_2) \]

\[ 2\pi/\omega_{ij} \]
I. Ultrafast processes: formal description
   * Light matter interaction in the dynamical regime
   * Two levels system and time dependent polarization
   * Four wave mixing

II. Examples of molecular systems
   * Probing primary events with ultrashort laser pulse
   * Wave packet dynamics: example of polydiacetylene
   * Green florescent protein and proton transfer dynamics

III. Simple features of femtosecond laser pulses
   * Temporal and spectral characteristics
   * Density of excitation

IV. Ultrafast magnetization dynamics
   * Generalities on electron and spins relaxation
   * Demagnetization induced by laser pulses
   * Spin precession and damping
   * Ultrafast confocal magneto-optical microscopy

V. X-rays femtosecond and attosecond spectroscopy
The detection of primary events in the time evolution of many physical, chemical or biological systems require a femtosecond temporal resolution.

Example: chlorination of methane
Probing transition states:
The case of NaI (A. Zewail et al.)

A. Zewail, 1999 Nobel price in chemistry for his studies of the transition states of chemical reactions using femtosecond spectroscopy

Winter School 2010 - IPCMS - QMMRC
Estimates of the typical timescales associated with the energies involved in molecular systems

Electronic energy: \( E_e = p^2/2m_e \sim \hbar^2/m_e r_0^2 \)

In SI units:

\( m_e \sim 10^{-30} \); \( \hbar \sim 10^{-34} \); \( r_0 \sim 3 \times 10^{-10} \):

\( E_e \sim 10^{-19} \text{ J} \sim 1 \text{ eV} \)

The corresponding timescale is: \( T \sim \hbar/E \quad 1 \text{eV} \Leftrightarrow 10^{-15} \text{ s} = 1 \text{ femtosecond} \)

Energy of vibration stretch: The force binding the two nuclei is comparable to the one of the electron bound to the molecule. Considering classical oscillators:

\[
E_{\text{vib}} = \sqrt{k/M} \; ; \; E_e = \sqrt{k/m_e} \; ; \; E_{\text{vib}} = E_e \sqrt{m_e/M} \quad \text{with:} \quad \frac{1}{M} = \frac{1}{M_1} + \frac{1}{M_2} \quad \text{E}_{\text{vib}} \sim 10^{-2} \text{ eV} \quad \text{T}_{\text{vib}} \sim 100 \text{ fs}
\]
Wave-packet dynamics in molecular systems

- Excited state absorption (100 fs)
- Vibronic coupling (~100 fs)
- Inter-system crossing: (10 – 50 fs), with tunneling to ground state or spin orbit interaction: Population of triplet states
- IVR: intra-molecular vibrational relaxation (>1 ps)
- Rotational motion (10-100 ps)
- Luminescence (1 ns)
Example of a conjugated polymer: Polydiacetylene (p-DCH)

Structure of p-DCH

linear absorption spectrum

excitons vibronic states

Absorbance

Energy (eV)

Winter School 2010 – IPCMS - QMMRC
Dynamics of polymer backbone

\[ \Delta T/T \]

23 fs  C=C stretch - 1500 cm\(^{-1} \)

damping of wave-packet: \[ T_{2,C=C} \sim 120 \text{ fs} \]

Population relaxation: \[ T_{1,X} \sim 2 \text{ ps} \]


Winter School 2010 - IPCMS - QMMRC
Wave packet motion

Excited state absorption of polydiacetylene

Winter School 2010 - IPCMS - QMMRC
Quantum chemistry computation of the fundamental and excited states of a trimer diacetylene ring


Schematic of electron delocalization along the polymer backbone

\[
\begin{align*}
\text{10 fs Pulse} & \\
\text{PDA backbone vibrations} & \\
(\star) & 
\end{align*}
\]

Energy (eV)

\[
\begin{align*}
\delta (\text{angstroms}) & \\
\text{acetylenic butatrienic} & 
\end{align*}
\]
Dephasing dynamics of polymer backbone

Dephasing of excitons: $T_{2,X} \sim 50$ fs


Winter School 2010 - IPCMS - QMMRC
Dynamics of bio-compatible fluorescent markers

Aequorea victoria

Winter School 2010 - IPCMS - QMMRC
Green fluorescent protein

β barrel (polypeptides)

Chromophore:

Absorbance (arb. un)

Wavelength (nm)

Fluo. (arb. un)

GFPuv
GFPwt
Fluo.
Mechanism for the green emission (1)

How fast is the excited state proton transfer?

Dynamics of proton transfer

Neutral form

Unrelaxed anionic form

Weak transient absorption


Winter School 2010 - IPCMS - QMMRC
Probing the dynamics of antibodies-GFP fusions

* Emission dynamics is sensitive to protein folding
* GFP-uv used as reporter of folding (solubility) of fragments of antibodies.

Green Fluorescent Protein (UV mutant)

Fragment of antibody

Solubility Ratio $\equiv$ Gain/Excited state absorption

scFvs binding in vitro to oncoprotein E6. A good solubility requires that the fragments are well folded.
I. Ultrafast processes: formal description
   * Light matter interaction in the dynamical regime
   * Two levels system and time dependent polarization
   * Four wave mixing

II. Examples of molecular systems
   * Probing primary events with ultrashort laser pulse
   * Wave packet dynamics: example of polydiacetylene
   * Green fluorescent protein and proton transfer dynamics

III. Simple features of femtosecond laser pulses
   * Temporal and spectral characteristics
   * Density of excitation

IV. Ultrafast magnetization dynamics
   * Generalities on electron and spins relaxation
   * Demagnetization induces by laser pulses
   * Spin precession and damping
   * Ultrafast confocal magneto-optical microscopy

V. Xrays femtosecond and attosecond spectroscopy
Some characteristic numbers making understand why ultrafast spectroscopy is interesting:

* A sound wave propagating over a distance $x = 10$ nm in a metal: $v \sim 10^4$ m/s

$$T_{\text{acoustic}} = \frac{x}{v} \sim 10^{-12} \text{s} \quad \text{(acoustic waves: 1 picosecond)}$$

* Optical phonons in dielectric and semiconductors: $T_{\text{phon}} \sim 100 - 200$ fs

* Electron-hole pair breaking in a semiconductor:
  Binding energy of excitons $E_b \sim 20$ meV; $T_{\text{exc}} \sim 500$ fs

* Surface plasmons dynamics: $\hbar \Omega_{\text{Plasm}} \sim 2$ eV and $\delta \Omega \sim 200$ meV; $T_{\text{plasm}} \sim 50$ fs

* Light interferometry: $\lambda = 1$ μm; $c = 3 \times 10^8$ m/s; $T_{\text{light}} = \frac{\lambda}{c} \sim 3$ fs

* For magnetic systems:
  Spin orbit interaction: $E_{\text{SO}} \sim 50$ meV; $T_{\text{SO}} \sim 200$ fs
  Anisotropy energy: $E_{\text{MA}} \sim 20$ meV; $T_{\text{MA}} \sim 500$ fs
  Exchange interaction: $U \sim 0.5$ eV; $T_{\text{exch}} \sim 20$ fs
Time versus frequency domains

\[ \delta(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} d\omega \]

An ideal \( \delta \)-function pulse contains an infinite spectrum!

In practice: \( \Delta\omega \Delta\tau \geq 2\pi C \) (if equality: Fourier transform pulse)

\begin{align*}
\text{Pulse duration} & \quad \text{Spectrum} \\
12 \text{ fs pulse} & \quad \exp[-4\ln(2(t/\Delta\tau)^2)] \quad C = 0.441 \\
& \quad 1/[1 + (2t/\Delta\tau)^2] \quad C = 0.221 \\
& \quad 1/[\cosh(1.76t/\Delta\tau)]^2 \quad C = 0.315
\end{align*}

→ time dependent spectroscopy is accessible in a very large bandwidth of the optical spectrum

Winter School 2010 – IPCMS - QMMRC
Ultrafast spectroscopy performed with femtosecond pulses allows studying the dynamics of chemical and biological molecules as well as a variety of materials in condensed matter physics. The technical challenge is then to generate control and measure femtosecond pulses in a broad spectral band width.

Note that there is more than just temporal and spectral considerations!
Density of electromagnetic field

Typical energy of a low power CW laser (beam pointer): 1 mW

The same energy in 10 fs: $10^{11}$ Watt (still only 1 mJ / pulse)

Power density focused on a spot of 10 μm diameter: $10^{17}$ Watt/cm$^2$

Actual high power laser facilities:

$1$-$10$ J / pulse $\rightarrow$ $10^{20}$ – $10^{21}$ Watt/cm$^2$
$10^9$-$10^{12}$ W/cm$^2$ : Conventional Nonlinear Optics + Time resolved spectroscopy
Material processing (electron plasma) + medical applications
New laser design : self phase modulation, self focusing
Study of dynamical properties of nanostructures

$10^{12}$-$10^{16}$ W/cm$^2$ : High intensity Nonlinear Optics
High harmonic generation – Xray sources
Attosecond lasers

$10^{16}$-$10^{20}$ W/cm$^2$ : Relativistic plasma physics
Inertial confinement
Two-photon fluorescence and imaging

One photon excitation: $h\nu$

Two-photon excitation: $2x(h\nu/2)$

Application to bio-imaging:
Maybe one of the largest success of femtosecond Titanium Sapphire laser!

Winter School 2010 - IPCMS - QMMRC
Ablation of matter by lattice heating versus electron plasma

Nanosecond

Femtosecond

Laser fabrication of 100 μm hole made in steel with nanosecond and femtosecond pulses

Winter School 2010 - IPCMS - QMMRC
Femtosecond pulse generation

Oscillator:
- Broad band laser medium (Titanium Sapphire: 700 nm – 1 μm)
- Mode locking (phase coincidence of all spectral components)

Amplifier:
- Example: regenerating amplification by seeding in a sub-cavity pumped by high power high repetition rate laser (importance of chirped pulse amplification – prevents damage of Amplifying medium)

Typical performances: 50 fs, 1 mJ/pulse, 5 kHz, 700-900 nm tunability
Tunability (change of wavelength) requires nonlinear optical process

Self Phase Modulation: continuum generation - visible

Frequency doubling or tripling: near UV

Optical parametric amplification: visible near IR – 1 - 2 μm

Difference frequency mixing: 10 μm

Optical rectification: TeraHertz

High harmonic generation with plasma: X-UV
### Self phase modulation: generation of white light continuum

**Kerr nonlinear index**

\[ n = n_0 + n_2 I(t) + \ldots \]

**Phase of propagating laser pulse**

\[ \delta \phi(t) = n_2 I(t) \frac{\omega z}{c} \]

**Instantaneous frequency**

\[ \delta \omega(t) = -\frac{d\phi(t)}{dt} = -n_2 \frac{\omega z}{c} \frac{dI(t)}{dt} \]

If \( n_2 > 0 \): when \( I \) increases (leading part of pulse) \( \omega \) decreases, red colors are generated. When \( I \) decreases (falling part of pulse) \( \omega \) increases, blue colors are generated.

![Diagram of laser pulse and Kerr medium](image-url)
I. Ultrafast processes: formal description
   * Light matter interaction in the dynamical regime
   * Two levels system and time dependent polarization
   * Four wave mixing

II. Examples of molecular systems
   * Probing primary events with ultrashort laser pulse
   * Wave packet dynamics: example of polydiacetylene
   * Green fluorescent protein and proton transfer dynamics

III. Simple features of femtosecond laser pulses
   * Temporal and spectral characteristics
   * Density of excitation

IV. Ultrafast magnetization dynamics
   * Generalities on electron and spins relaxation
   * Demagnetization induces by laser pulses
   * Spin precession and damping
   * Ultrafast confocal magneto-optical microscopy

V. Xrays femtosecond and attosecond spectroscopy
Time scales of magnetization dynamics

Optically induced Precession in Cobalt ferromagnetic film

Demagnetization of Nickel ferromagnetic film

Ultrafast demagnetization and damping

Femtomagnetism

Micromagnetism

Centro de Nanomagnetismo

- Spin-orbit coupling
- Coulomb interactions
- Spin scattering at surfaces – Spin-Phonon scattering
- Coupling with the photons: TeraHertz emission

Winter School 2010 – IPCMS – QMMRC
Lattice
Molecular vibrations, Phonons

Electrons
Charges, plasmons

Electrons
Spins, magnons

Laser field
Photons
\((E, V; A, \Phi)\)

Photons :
High Harmonics & Xrays
TeraHertz emission (charges); Raman scattering
Luminescence
...

Internal Vibrational Relaxation
Heat propagation (internal & to environment: substrate ...)
...

Micro-magnetic interactions :
Precession and damping:
Spin torque; Nucleation propagation & pinning of domain walls

Fluctuations :
Superparamagnetic fluctuations
Domain fluctuations

Winter School 2010 - IPCMS - QMMRC
Physical mechanisms for ultrafast charge and spin dynamics

\[ \rho(E, T_e) : \text{Fermi-Dirac} \]

electron/spin and lattice dynamics

two temperatures model

\[ C_e(T_e) \frac{dT_e(t, r)}{dt} = G_{el}(T_i(t, r) - T_e(t, r)) + P(t, r) + \nabla \kappa_e \nabla T_e(t, r) \]

\[ C_l \frac{dT_l(t, r)}{dt} = G_{el}(T_e(t, r) - T_l(t, r)) + \nabla \kappa_l \nabla T_l(t, r) \]

Laser pulse

Temperature (K)

Time (ps)

Winter School 2010
IPCMS - QMMRC

Dissipation into environment
Probing $T_{\text{spins}}$ with a Femtosecond resolution

$E(r,t)$

Time resolved spin thermometer

Winter School 2010 - IPCMS - QMMRC
Principles of time resolved magneto-optical experiment

15 nm nickel film
Excitation : 100 fs pulses


Q1. Can one induce a full demagnetization of ferromagnets using femtosecond laser pulses?

Q2. How fast can it be?

Q3. What is the mechanism that induces a change of the spins angular momentum?
Ultrafast ferro-paramagnetic phase transition

CoPt$_3$ thin film ($M_\perp$)


Q1 : Yes we can !
**How fast is the demagnetization?**

experiments made with 20 fs laser pulses

21 nmCoPt$_3$/Al$_2$O$_3$

Spins dynamics: real and imaginary transverse
Magneto-Optical dielectric tensor

The “magnetization” has changed after 54 fs

Charges dynamics
Transmission and reflectivity

The electron thermalize to the Fermi level in 55 fs

Q2. For low densities of laser excitation the de-magnetization occurs during thermalization of charges ~50 femtoseconds


Winter School 2010 - IPCMS - QMMRC
Magnetization trajectory
and Time domain Ferromagnetic Resonance

\[ \frac{d\vec{M}}{dt} = -P(t)\vec{M}(t) + \gamma \vec{M}(t) \times \vec{H}_{\text{eff}}(t) - \frac{d\vec{M}}{dt}_{\text{damp}} \]

Gilbert damping: \( \alpha \)

Co/Al\(_2\)O\(_3\)

Pump: \( P(t) \)

Probe

Femtosecond optical pulses

Winter School 2010 - IPCMS - QMMRC
Ferromagnetic resonance induced with femtosecond optical pulses

16 nm Co/Al$_2$O$_3$ MBE grown

Winter School 2010 – IPCMS - QMMRC
Ultrafast Magnetization Dynamics visualized in 3D

16 nm Co/Al$_2$O$_3$

Winter School 2010 - IPCMS - QMMRC
Precession dynamics in Co: \textit{perpendicular} and \textit{parallel} anisotropies

Co/Al$_2$O$_3$ $H_{Anis} \perp$ sample

Co/MgO $H_{Anis} \parallel$ sample

\textbf{Winter School 2010 – IPCMS - QMMRC}
Model of time dependent magnetization dynamics with anisotropy

* **Electron/spin and lattice dynamics: two temperatures model**

\[ C_e(T_e) \frac{dT_e}{dt} = G_e(T_e(t) - T_e(t)) + P(t) - \kappa_e \nabla^2 T_e(t, \vec{r}) \]
\[ C_l \frac{dT_l}{dt} = G_e(T_e(t) - T_l(t)) - \kappa_l \nabla^2 T_l(t, \vec{r}) \]

* **Bloch equation or LL (without assuming conservation of \(|M(t)|\))**

\[ \frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H}_{\text{eff}}(T_e(t), T_l(t), \vec{M}(t)) - \left( \frac{d\vec{M}}{dt} \right)_{\text{relax}} \]
\[ \vec{H}_{\text{eff}}(t) = \vec{H}_0 - \vec{N} \otimes \vec{M}(t) + \vec{H}_a(t) \]

* **Temperature dependent magnetization modules**

\[ |\vec{M}(T_e(t))| = M_s \sqrt{1 - \left( \frac{T_e}{T_c} \right)^2} \text{ for } T_e \leq T_c \text{ and } |\vec{M}| = 0 \text{ for } T_e > T_c \]

* **Temperature dependent magneto-crystalline anisotropies**

\[ K_a(T_l) = K_a(0) \left( \frac{|\vec{M}(T_l)|}{M_s} \right)^10 \]
Dots with perpendicular magnetization
Multi-domains structure

MFM imaging of CoPt$_3$ dots

(d=1 µm)  (d=250 nm)

Some are mono-domains
Many are mono-domains

Winter School 2010 – IPCMS - QMMRC
Femtosecond magneto-optical confocal microscope

Optics letters 32, 936-398 (2007)

Winter School 2010 - IPCMS - QMMRC
Individual 500 nm CoPt₃ dot

Photo-induced dot on 15 nm film of CoPt₃/Al₂O₃

Optics letters 32, 936-398 (2007)

IPCMS

Winter School 2010 – IPCMS - QMMRC
Dynamical imaging of a CoPt$_3$ dot (1 mm)
Dynamics of an individual CoPt₃ dot (d = 1 μm)
Remagnetization through spin-lattice & thermal diffusion

Winter School 2010 – IPCMS - QMMRC
Magnetization dynamics of a single Permalloy dot
(5 x 5 \( \mu \text{m}^2 \) on glass substrate)

Precession period = 230 ps
\( \tau_{\text{damping}} = 946 \text{ ps} \)

\[ \Delta M / M \]

\[ \text{Delay (ps)} \]

\[ P = 8 \text{ mJ cm}^{-2} \]

\[ \text{Delay (ns)} \]
Laser induced writing-reading-erasing

Winter School 2010 – IPCMS - QMMRC
Writing a 150 nm single domain without external field CoPt/glass

Laser intensities: 4 mJcm\(^{-2}\)  
8 mJcm\(^{-2}\)

Pump 600 nm

Kerr Images

MFM Images

Winter School 2010 – IPCMS - QMMRC
Structure of magnetic domains on different substrates

<table>
<thead>
<tr>
<th>CoPt$_3$/Sapphire $MBE$</th>
<th>$I_p = 4$ mJ.cm$^{-2}$</th>
<th>$I_p = 8$ mJ.cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labyrinth</td>
<td>$D_{average} = 250$ nm</td>
<td></td>
</tr>
<tr>
<td>0.9 μm</td>
<td>1.8 μm</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CoPt/glass $polycrystalline$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-domain $d = 250$ nm</td>
</tr>
<tr>
<td>0.5 μm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CoPt/glass $polycrystalline$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-domain structure $D_{average} = 175$ nm</td>
</tr>
</tbody>
</table>
What about Question Q3?

What is the mechanism that induces a change of the spins angular momentum?
Two beams – pump-probe experiment: coherent and incoherent contributions

\[ E_{\text{abs}} = 1.45 \text{ mJcm}^{-2} \]
\[ \text{Ni: 7.5 nm} \]

Two beams – experiment: coherent optical and magneto-optical response

*Nature Physics 5, 461 (2009)*

![Diagram](image)

**Distinction between the pump polarization and the external field orientation:**

- **Magnetic**
  - optic: \( \frac{1}{2} \left[ (S_{\theta_{pp}=0^\circ,+H} - S_{\theta_{pp}=0^\circ,-H}) - (S_{\theta_{pp}=90^\circ,+H} - S_{\theta_{pp}=90^\circ,-H}) \right] \)
  - magnetic: \( \frac{1}{2} \left[ (S_{\theta_{pp}=0^\circ,+H} + S_{\theta_{pp}=0^\circ,-H}) \right] \)
- **Optic**
  - \( \frac{1}{2} \left[ (S_{\theta_{pp}=0^\circ,+H} - S_{\theta_{pp}=0^\circ,-H}) - (S_{\theta_{pp}=90^\circ,+H} - S_{\theta_{pp}=90^\circ,-H}) \right] \)

Winter School 2010 - IPCMS - QMMRC
Coherent optical and magneto-optical response

Third order nonlinear response with Pump \(E(t)\) and probe \(e(t-\tau)\) fields:

Time ordered integration \(\Rightarrow\)

\[
\rho_{12}^{(3)}(t, \tau) \propto \frac{1}{4\hbar^2} \mu^3 \int \int \int dt_1 \, dt_2 \, dt_3 \, [H]_{\text{int}} \left[ E(t - t_1)E^*(t_1 - t_2)e(t_3 - t_2 - \tau) \right] \quad (1)
\]

\[
\left[ E(t - t_1)e(t_1 - t_2 - \tau)E^*(t_2 - t_3) \right] \quad (2)
\]

\[
\left[ e(t - t_1 - \tau)E(t_1 - t_2)E^*(t_2 - t_3) \right] \quad (3)
\]

(1) Charge population dynamics

(2) Coherent charge dynamics: dephasing time of electrons in the metallic film

(3) Pump perturbed free decay
Schematic vision of the ultrafast magneto-optical response

- Femtosecond laser pulse
- Coherent interaction between photons, charges and spins
- Thermalization of charges and spins
- Coupling with the phonon bath and THz photon emission
- Time: femtoseconds

- $T_{e,C}$
- $G_{e,l}$
- $G_{s,l}$
- $T_{s,C_s}$
- $T_{l,C_l}$

- e: electrons, s: spins, l: lattice

Winter School 2010 - IPCMS - QMMRC
I. Ultrafast processes: formal description
   * Light matter interaction in the dynamical regime
   * Two levels system and time dependent polarization
   * Four wave mixing

II. Examples of molecular systems
   * Probing primary events with ultrashort laser pulse
   * Wave packet dynamics: example of polydiacetylene
   * Green florescent protein and proton transfer dynamics

III. Simple features of femtosecond laser pulses
   * Temporal and spectral characteristics
   * Density of excitation

IV. Ultrafast magnetization dynamics
   * Generalities on electron and spins relaxation
   * Demagnetization induced by laser pulses
   * Spin precession and damping
   * Ultrafast confocal magneto-optical microscopy

V. Xrays femtosecond and attosecond spectroscopy

Winter School 2010 - IPCMS - QMMRC
Selection rules at the L2 and L3 threshold of Cobalt

\[ \begin{align*}
3d & \quad \text{L}_3 : 2p_{3/2} \\
& \quad \text{L}_2 : 2p_{1/2}
\end{align*} \]
Sum rules:

\[
    m_{\text{orb}} = - \left( \frac{L_3 + L_2}{3} \right) \int \omega (\mu_+ - \mu_-) \\
    m_{\text{spin}} = - \left( \frac{L_3 + L_2}{L_3 + L_2} \right) \int \omega (\mu_+ + \mu_-) \\
    \times (10 - n_{3d}) \left( 1 + \frac{7\langle T_z \rangle}{2\langle S_z \rangle} \right)^{-1}
\]

\[m_{\text{orb}}, m_{\text{spin}}: \text{orbital and spin moments (}\mu_B/\text{atom})\]
\[L_2 \text{ and } L_3: \text{integration contours near thresholds}\]
\[n_{3d}: 3d \text{ electron occupation number}\]

ALS femtosecond spectroscopy beamline layout. Femtosecond x-ray and laser pulses derive from a single 800-nm laser oscillator. Femtosecond x rays result from the interaction of a laser pulse with an electron bunch as it passes through the first of two insertion devices (the e-beam modulator) followed by the passage of the modified bunch through the second insertion device (the x-ray radiator), a technique known as laser slicing.
Observing how fast the spin-orbit interaction branches spin and orbital moments in solids.

C. Boeglin et al.
Submitted to Nature
Femtosecond evolution of the magnetic and electronic structure.

Time-resolved XMCD at the Co L3 and Co L2 edges measured on a 15nm Co$_{0.5}$ Pd$_{0.5}$ alloy film using femto-slicing.

C. Boeglin et al.
Submitted to Nature
Femtosecond evolution of the magnetic spin and orbital moments.

a. Sum rule extracted effective spin $S_z(t)$ and orbital magnetic $L_z(t)$ moments

b. Ratio $S_z(t)/L_z(t)$

The mechanism responsible for the ultrafast laser induced demagnetization in ferromagnetic films requires the concept of (SOI) and that the magneto-crystalline anisotropy energy is an important quantity to consider.

C. Boeglin et al.
Submitted to Nature
Towards table top X-ray sources

Attosecond spectroscopy
**Generation of attosecond laser pulses: Three step model**

* Photo-excitation of one electron by tunneling effect
* Acceleration in the linearly polarized laser field
* Capture of the electron by the parent ion and emission of photon or ionization

Process \{tunnel-capture \rightarrow \text{emission}\} occurs every half period: harmonic spectra spaced by $2\omega_L$ (double of laser frequency) and odd harmonics (two photon transitions with two virtual intermediate states in a cento-symmetric system)
Characteristics of emission of UV-X photons

- Existence of energy threshold (cut off):
  
  Classically: maximum energy of accelerated electron
  \[ \hbar \nu_{\text{max}} = I_p + 3.17 \ U_p \]

  Ponderomotive energy: (mean energy in the laser field during one optical cycle)
  \[ U_p = \frac{<p^2>}{2m} = \frac{e^2E_L^2}{4m\omega_L^2} \]

- Typical laser density: \(10^{14} - 10^{16} \ \text{Wcm}^{-2}\)

- Requires ultrashort laser pulses with phase stabilization: single pulse generation

- Necessity of controlling the phase of the carrier envelope: CEP (Carrier Envelope Phase)
Spectrum and spectrogram

Spectrum obtained $\tau_L = 5\ \text{fs}$ and $\lambda_L = 750\ \text{nm}$

a) shape cosine of the CEP
b) shape sine of the CEP

Baltuska et al. 2003

Spectrograms $h\nu(T_{\text{cycle}})$ calculated with $\tau_L = 5\ \text{fs}$ and $\lambda_L = 800\ \text{nm}$
b) Spectrum for cosine CEP
d) Spectrum for sine CEP

Yakovlev et al. 2003

Winter School 2010
Generation and Control of laser pulses

• Generation of pulses
  ◦ Near IR – Titanium Sapphire oscillator 10 fs à ~800nm
  ◦ Multi-pass or regenerative amplification (a few mJ – 20-30 fs)
  ◦ Generation of continuum by self-phase modulation in a hollow fiber containing a rare gaz
    (record : 5.4 fs, 2.7 mJ in a fiber with gradient of pressure + focusing at the diffraction limit → $5 \times 10^{18} \text{Wcm}^{-2}$) A. Suda et al. APL, 86, 111116 (2005)

• Control of CEP
  ◦ Interferometry f-2f with active control of oscillator and amplifier
  ◦ passive control by frequency mixing : frequency difference
    $\phi_{\text{tot}} = \phi_1 - \phi_2 = \phi_{10} - \phi_{20} - (\phi_{\text{drift}} - \phi_{\text{drift}}) = \text{constant}$
    → combined with Optical Parametric Amplification : 1.mJ, 17 fs stabilized

• Generation of single pulses :
  ◦ Few cycles pulses (about 7-8 fs with cosine CEP)
  ◦ Polarization Gating : The recombination by capture on the parent ion depends on the polarization of the laser beam (linear).
    → combination of two pulses with polarizations $\sigma^+$ and $\sigma^-$ which give a linear polarization in a temporal window of the order of one optical cycle
Selection with a linear polarization window ("polarization gating")

Delay between ordinary and extra-ordinary wave

\[ \lambda/4 \text{ (multiple ordre)} \]

\[ \alpha = 45^\circ \]

\[ \lambda/4 \text{ (ordre 0)} \]

\[ \beta = 0^\circ : \text{Narrow window} \]

Width of the linear polarization window:

\[ \tau_G = \frac{\varepsilon \tau^2}{\delta |\cos 2\beta| \ln 2} \]
Temporal and spectral characterization of the pulses

Technique: « attosecond streak camera »: method FROG - CRAB

• Generation of a packet of electrons with the attosecond pulse by ionization of an atomic gas by 1 photon absorption. (out of resonance the packet of electrons is a replica of the attosecond pulse)

• Print a phase on the electronic wave packet in the field of an IR laser pulse

• Temporal correlation between the electronic wave packet and the femtosecond pulse (delay $\tau$).

Amplitude of transition: fundamental state $\rightarrow$ states of the continuum:

$$a_v(\tau) = -i \int_{-\infty}^{\infty} dt \ e^{i\Phi(t)} d_{p(t)} E_X(t - \tau) e^{i(W + I_p)t}$$

$\Phi(t)$: phase printed on the electronic wave packet by the IR pulse
$P = v + A(t)$ kinetic momentum of the electrons in the presence of the field
$A(t)$: Vector potential of the IR laser field
$d_p$ : dipolar moment of the transition

Winter School 2010 – IPCMS - QMMRC
\[ |a_v(\tau)|^2 \text{ is like a FROG correlation with a gate } G(t) = \exp[-i\Phi(t)]:\]

\[
S(\omega, \tau) = \left| \int_{-\infty}^{\infty} dt \ G(t)E(t - \tau)e^{i\omega t} \right|^2
\]

Photo-electron spectrum FROG-CRAB corresponding to a 130 as pulse generated by IR pulses of 5.7fs. Nisoli, Science 314 (2006) 443

Winter School 2010 - IPCMS - QMMRC
A new project at IPCMS supported by the European Research Council

Dynamique d’aimantation dans les systèmes magnétiques

Photonique de spins

Electro dynamique quantique relativiste

ATOMAG

Winter School 2010 - IPCMS - QMMRC