Coherent spin and lattice dynamics studied with femtosecond x-ray diffraction

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- Why x-rays?
- Principles of scattering and diffraction
- Sources of short x-ray pulses
- Time-resolved scattering
- Time-resolved diffraction
Why x-rays?
X-ray region of spectrum

- Wavelength: 0.1-100 Å
- Photon energy: 100 eV - 100 keV
X-ray region of spectrum

- Wavelength: 0.1-100 Å
- Photon energy: 100 eV - 100 keV
X-ray scattering / diffraction

- Use interference of scattered radiation to infer electronic charge distribution, atomic structure
- Measure “cuts” of Fourier Transform space
Vibrational dynamics

- Speed of sound (condensed media) $\sim 2000 \text{ m/s}$
- Typical interatomic spacing $\sim 1 \text{ Å}$
- $\Delta t \sim (1 \times 10^{-10} \text{ m})/(2000 \text{ m/s}) = 50 \text{ fs}$
  (tomorrow: spin and valence dynamics)
Principles of scattering and diffraction
Interactions: EM radiation & matter

- Hamiltonian for a free particle with mass m and charge q (non-relativistic)

\[ H = \frac{\left| \mathbf{P} - \frac{q \mathbf{A}}{c} \right|^2}{2m} = \frac{\mathbf{P}^2}{2m} - \frac{q}{mc} (\mathbf{A} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{A}) + \frac{q^2 |\mathbf{A}|^2}{2mc^2} \]

\[ \mathbf{A} = \hat{\epsilon} \sqrt{\frac{\hbar}{2\epsilon_0 V \omega}} \left( a_k^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}} + a_k e^{i\mathbf{k} \cdot \mathbf{r}} \right) \]

KE term

inelastic (dipole, quad, etc.)

Thomson scattering

photon creation

photon annihilation
Interactions: EM radiation & matter

- Per atom elastic scattering weak, \( \sim 10^{-26} \text{ m}^2 \)
- Typically weaker than incoherent contributions…but maintains phase coherence

Coherence

• To use interference as a probe, coherence essential
• What is coherence?

\[
\mu(r_1, r_2) = \frac{\langle E(r_1, t)E(r_2, t)^* \rangle}{\sqrt{\langle |E(r_1, t)|^2 \rangle \langle |E(r_2, t)|^2 \rangle}}
\]

Spatial coherence: “Complex coherence factor”

“Incoherent”
\[ \mu \rightarrow 0 \]

“Coherent”
\[ \mu \rightarrow 1 \]

Ability of waves at different locations to interfere
Coherence

\[
\mu(\mathbf{r}_1, \mathbf{r}_2) = \frac{\langle E(\mathbf{r}_1, t)E(\mathbf{r}_2, t)^* \rangle}{\sqrt{\langle |E(\mathbf{r}_1, t)|^2 \rangle \langle |E(\mathbf{r}_2, t)|^2 \rangle}}
\]

- Coherence volume: volume of space such that
  \[|\mu(0, \mathbf{r})| > 1/2\]

- Usually divided into “longitudinal” and “transverse”

![Diagram of coherence volume with notation: \(t_{coh} \sim 1/d\), \(l_{coh} = \lambda^2 / 2\Delta\lambda\), and \(d\) is an apparent source size)
Coherence and order

Source coherence volume vs. Sample order

- Low source coherence: Diffuse scattering
- High source coherence: Coherent imaging
Diffuse scattering

• Coherence volume small compared with illuminated sample volume
• Coherence volume large compared to interatomic spacings

Look at the average distances between atoms within the coherence volume dimensions
Diffuse scattering

Structure factor

\[ F(Q) = \sum_j f_j e^{iQ \cdot r_j} \]

... a Fourier transform

Phase difference

\[ Q = k_f - k_i \]

\[ \text{Phase difference} = r \cdot k_f - r \cdot k_i \]

\[ \frac{I_s}{I_0} = |F(Q)|^2 \]
Diffuse scattering

- How to get structure? (assume orientational disorder)

\[
S(Q) = \sum_k N_k f_k(Q)^2 \sum_{l \neq k} N_k f_k(Q) N_l f_l(Q) \int 4\pi r^2 \rho_0 (g_{kl}(r) - 1) \frac{\sin(Qr)}{Qr}
\]

Pair correlation function

liquid K-Bi

[example from: Hochgesand, Physica B 276-278, 425 (2000)]
Diffuse scattering

- Advantages:
  - Given a structural model, easy to calculate diffraction
  - Selective, only sensitive to structure

- Disadvantages:
  - Requires a model (not invertible)
  - Interaction with all electrons in sample (solvents)
  - In normal use, just the pair correlation function (no higher orders)
• For now, we discuss systems with true long-range order (no quasicrystals or incommensurate superlattices)
• Unit cell: arrangement of atoms (basis)
• Vectors $t$ describe translational symmetry, can be used to “build” the crystal from a unit cell
Diffraction: crystals

\[
\frac{I_s}{I_0} = |F(Q)|^2
\]

\[
F(Q) = \sum_R f_R e^{iQ \cdot R}
\]

\[
F(Q) = \sum_t \left( \sum_j f_j e^{iQ \cdot r_j} \right) e^{iQ \cdot t} = \sum_t F_c(Q) e^{iQ \cdot t}
\]

\[
F_c(Q) = \sum_j f_j e^{iQ \cdot r_j} \quad \text{Unit cell structure factor}
\]
**Diffraction: crystals**

\[ \frac{I_s}{I_0} = |F(Q)|^2 \quad F(Q) = \sum_t F_c(Q)e^{iQ \cdot t} \]

- For a large crystal (many unit cells), strong peaks when

\[ Q \cdot t / 2\pi \in I \]

- We call values of Q that satisfy this for all t *reciprocal lattice vectors* G

\[ G = h b_1 + k b_2 + l b_3 \]

h, k, l integers; \( b_1, b_2, b_3 \) reciprocal primitive vectors
Diffraction: crystals

Reciprocal space

2D case (easily generalized)

Direct space

\[ a_i = \sum_j a_{ij} x_j \]

Reciprocal space

\[ b_i = \sum_j b_{ij} x_j \]

\[
\begin{bmatrix}
  b_{11} & b_{21} \\
  b_{21} & b_{22}
\end{bmatrix}
= \left(2\pi
\begin{bmatrix}
  a_{11} & a_{21} \\
  a_{21} & a_{22}
\end{bmatrix}^{-1}\right)^T
\]
Diffraction: crystals

Reciprocal lattice

Direct space

Reciprocal space

Lattice planes represented by $G$:

$$G = h\mathbf{b}_1 + k\mathbf{b}_2$$

...where $h, k$ are integers

Direction: orientation of plane

$$|G| = \frac{2\pi}{d}$$
Ewald sphere (circle)

...A graphical way to predict where in reciprocal space Bragg peaks appear

\[ k_f = k_i + G \]

Determined only by long range translational order
Diffraction: crystals

- Determining average structure from diffraction:
  - Find sets of $Q$ that can lead to reflections
  - Practically, involves rotating crystal or changing x-ray wavelength to sweep the Ewald sphere around in reciprocal space
Diffraction: crystals
Diffraction: crystals

• Now we know the translational symmetry (shape of u.c.)
• For unit cell structure, need to measure $|F_c(G)|^2$ for several reflections
• “Systematic absences”: additional symmetries
• In principle, results in a system of nonlinear equations to solve
• Sometimes ambiguous, need tricks (e.g. anomalous diffraction, see tomorrow)

$$F_c(Q) = \sum_j f_j e^{iQ \cdot r_j} \quad \text{Unit cell structure factor}$$
Short pulse x-ray sources
Overview of fs x-ray sources

Laser-based

Plasma

HHG

“Plasma-wiggler”

Accelerator-based

Slicing

ERL

XFEL

Laser-produced plasmas

Basic idea: very high energy fs ablation
Laser-produced plasmas

Basic idea: very high energy fs ablation
Laser-produced plasmas

High energy electrons sent into cold material
Core level ionization of atoms causes x-ray line emission; Bremsstrahlung radiation gives a continuum background.
Laser-produced plasmas: properties

- Integrated flux: $\sim 3 \times 10^8$/pulse at Ti Kα line (10 Hz system)
- Collimation: none (emits in all directions)
- Brilliance: $\sim 5 \times 10^4$ photons/mm$^2$/mrad$^2$/0.1% BW/pulse
- Wavelength: Depends on target; most flux at atomic emission lines, but there is a continuum background esp. for high Z targets
- Pulse duration: $\sim 300$ fs (set by plasma dynamics)
- Rep rate: 10-1000 Hz (depends on laser)
- Stability: not formally characterized, but very sensitive to laser
Synchrotron radiation

Light from accelerated relativistic electrons


Synchrotron radiation

Insertion devices: more bends for more light

Wiggler:
large angular excursions, essentially a series of bends

Undulator:
small angular excursions, interference phenomena

Synchrotron radiation

Insertion devices: more bends for more light
Synchrotron radiation

Time structure of synchrotron X-rays

- Electrons in bunches, spacing \( \sim 2 \) ns
- Stability of electron beam (e-e scattering) requires \( \sim 100 \) ps long bunches
- For femtosecond x-rays, create a transient short bunch...
Slicing

1. Modulation

2. Separation

3. Radiation

Wiggler

Dispersive element(s)
(e.g. bend magnets)

Undulator
Slicing

1. Modulation

2. Separation

3. Radiation

[Diagram showing the process of slicing with Wiggler, Dispersive element(s) (e.g. bend magnets), and Undulator]
• E-field of laser transverse to direction of propagation
• Efficient energy exchange requires transverse component of electron momentum … undulator!
Slicing

- E-field of laser transverse to direction of propagation
- Efficient energy exchange requires transverse component of electron momentum ... undulator!
Slicing

\[ \frac{dE}{dt} = \mathbf{F} \cdot \mathbf{v} \geq 0 \]
\[ \frac{dE}{dt} = \mathbf{F} \cdot \mathbf{v} \leq 0 \]
Slicing

1. Modulation
2. Separation
3. Radiation

- Wiggler
- Dispersive element(s) (e.g. bend magnets)
- Undulator

Dispersive element(s) (e.g. bend magnets)
Slicing

1. Modulation
2. Separation
3. Radiation
Free electron laser

Like slicing, but long undulator → positive feedback → microbunching

Initial facilities (LCLS, SwissFEL, EU-XFEL, ...) seeded by noise
Free electron laser

\[ P = N \, P_1 \]

\[ E = N \, E_1 \]

\[ P = N^2 \, P_1 \]

\[ N \approx 10^9 \]
Free electron laser

- Low gain
- Exponential gain (high-gain linear regime)
- Non-linear

Result: coherent, bright, short (< 10 fs) x-ray pulses
Free electron laser

- Photons per pulse: $\sim 10^{12}$
- Wavelength: $\sim 1$-100 Å
- Pulse duration: $\sim 10$-100 fs (shorter “spikes”)
- Rep rate: highly variable, from $\sim 10$ Hz to $\sim 1$ MHz “bursts”
- Collimation: $\sim 1$-10 μrad divergence
- Brilliance: $\sim 10^{20}$ ph/mrad²/mm²/0.1% BW/pulse
- Spatially coherent
- Stability poor (so far)

(recall: $\sim 10^5$ for plasma source!!)
Time-resolved diffraction
“Indirect” control:

Electronically induced symmetry changes
Idea: driving symmetry changes

- Electronic excitation changes free energy surface for ions
- What if new surface has a different (lower) symmetry?

[Zijlstra, Tatarinova & Garcia, PRB 74, 220301 (2006)]
K_{0.3}MoO_3

- Quasi 1D Peierls system
- Below 180 K incommensurate superlattice
- Optical excitation excites coherent phonons related to transition
  e.g.: H. Schäfer et al. PRL 105, 066402 (2010)

Experiment team: $K_{0.3}MnO_3$

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Dynamics of incommensurate modulation

- Low fluence: coherent phonon in low-symmetry potential
- High fluence: symmetry change
- Anomalous damping

[A. T. Huber et al. PRL 113, 026401 (2014)]
Dynamics of incommensurate modulation

\[ V(x) = \frac{1}{2} \left( \eta \exp \left( -\frac{t}{\tau_{\text{disp}}} \right) - 1 \right) x^2 + \frac{1}{4} x^4 \]

- Time-dependent potential surface, relaxes as electrons equilibrate with lattice
- Time-dependent damping rate

\[
\frac{1}{\omega_{\text{DW}}^2} \frac{\partial^2}{\partial t^2} x - \left( 1 - \eta \exp \left( -\frac{t}{\tau_{\text{disp}}} \right) \right) x + x^3
+ \frac{2\gamma(t)}{\omega_{\text{DW}}^2} \frac{\partial}{\partial t} x = 0
\]

\[ \gamma(t) = \gamma_{\text{asym}} \left( 1 - e^{-t/\tau_{\gamma}} \right)^2 \]

[A. T. Huber et al. PRL 113, 026401 (2014)]

[Pouget et al. PRB 43, 8421 (1991)]
“Direct” control:

Spin dynamics of a large-amplitude coherent electromagnon
THz excitation: path to fast control of multiferroics?

TbMnO$_3$

excitations due to the electromagnetic coupling:

- Higher-harmonic, ellipticity, phonons
  - 0.7 THz
- Spin-spiral excitation, 1.8 THz

Im$\varepsilon$ vs $\omega$ [THz]

- [0, 1.2 THz]
- [1.2, 2.0 THz]

(g) 0 psec
- $C//a$
- $b^{-}$

(h) 1.2 psec
- $C//c$
- $C//a$

(i) 2-3.4 psec
- $C//a$
- $C//c$

(j) 6 psec
- $C//a$
- $b^{+}$

[Senff 2008]

[Y. Takahashi et al., PRL 101, 187201 (2008)]
Experiment concept

Pump electromagnon with THz, watch spins with resonant x-ray diffraction
X-ray pulses: probe spin order

- L$_{2,3}$-edge
  - 3d
  - 2p$_{3/2}$
  - 2p$_{1/2}$

- (0q0) reflection at Mn L-edges: only magnetic order

- Experiment at LCLS
- Pulses of < 80 fs duration
- Time-stamping for < 250 fs resolution

Experiment team: TbMnO$_3$

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Results: coherent electromagnon

- E-field of THz $\rightarrow$ coherent spin response
- Measured spin response delayed by half cycle
- Response suppressed in non-multiferroic phase

[T. Kubacka et al., Science 343, 1333 (2014)]
Analyzing the motion

4.2° ± 0.4° rotation of spin planes

Fig. 3. Spin-motion patterns analyzed to interpret the time-dependent data. Schematics on the left illustrate the movements of spins, where black (color) arrows denote the direction of spins in the ground (excited) state. Plots on the right show calculated \( I / I(45°) \) peak intensity assuming the azimuthal angle of 45°. (A) Antiphase oscillation within the spin-spiral plane, parameterized using the electromagnon coordinate \( M \). (B) Coherent rotation of the spin-spiral plane about the crystallographic \( b \) axis, parameterized with the angle of rotation \( M' \).

Even function

Odd function

\[ [T. \text{ Kubacka et al., Science 343, 1333 (2014)}] \]
Summary

- Blue bronze: time-dependent free energy + damping

- \(\text{TbMnO}_3\): Direct excitation of coherent electromagnon
  - See actual spin motions
  - Outlook: switching?
ESB station at SwissFEL

- Hard x-ray (4-12.4 keV)
- Time resolution to 10 fs
- Optimized THz pumping
- Support for low-T, high-B

[G. Ingold, P. Beaud]