X-ray Studies of Quantum Materials
1. Preamble - Properties of X-rays
What I’m going to talk about:

Using bright, accelerator-based x-ray facilities to perform photon-in, photon-out studies of quantum materials.
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Using bright, accelerator-based x-ray facilities to perform photon-in, photon-out studies of quantum materials.

What I’m NOT going to talk about:

Photo-emission, x-ray “home labs”, UV / IR / THz, details of sources / optics
What I’m going to talk about:

Using bright, accelerator-based x-ray facilities to perform photon-in, photon-out studies of quantum materials.

Goals for these lectures:

(i) Help you become discriminating consumers of x-ray data

(ii) Introduce techniques that are potentially useful for your research

(iii) Recruit quantum materials users for the light sources; maximize our “slice of the pie”
1. Preamble

Single X-ray photon properties of interest

Energy
\[ E = \left( \frac{hc}{\lambda} \right) \]

Wavelength
\[ \lambda \]

Polarization
\[ \hat{\epsilon} \]

Vector Momentum
\[ \vec{k} \]
### Single X-ray photon properties of interest

<table>
<thead>
<tr>
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### X-ray beam properties of interest

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<tbody>
<tr>
<td>Bandwidth</td>
<td>$\frac{\Delta E}{E}$</td>
</tr>
<tr>
<td>Size, Divergence</td>
<td>$s, \nu$</td>
</tr>
<tr>
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<td>$P$</td>
</tr>
<tr>
<td>Coherence Length</td>
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</tr>
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1. Preamble

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For an ideal x-ray expt, all of these properties would be tunable for \(|\vec{k}_i\rangle\) and resolvable for \(|\vec{k}_f\rangle\). Typically, the more desirable beams have more similar (~identical) incident photons.
What is achievable? Typical beam properties at a modern synchrotron x-ray light source:

\[ E = \left( \frac{hc}{\lambda} \right) \]

- 0.2 keV - 200 keV  \hspace{1cm} Electron binding energies
- 60 Å - 0.06 Å  \hspace{1cm} Atomic scale
- 10^{-2} - 10^{-7}  \hspace{1cm} Resolution / Resolving Power
- 50 nm - 5 mm  \hspace{1cm} Mesoscale, domains, phase sep.
- 3 \mu rad - 300 \mu rad  \hspace{1cm} Intrinsic rocking curves
- Tunable linear / circular  \hspace{1cm} Dichroism, magnetism
- microns  \hspace{1cm} Mesoscale, domains, phase sep.
- \( 10^9 - 10^{14} \) ph/s  \hspace{1cm} Trade flux for precision
- picoseconds
- MHz
Table 1-1: Electron binding energies

Table 1-2: Energies of x-ray emission lines

Section 2: Details of synchrotron radiation generation

Section 4: X-ray optics and detectors

http://cxro.lbl.gov/x-ray-data-booklet
## Notes on “X-ray Notation”

The notation for X-ray emissions is given as:

\[ n \ell_m s \text{ X-ray } (n, \ell, m+s) \]

<table>
<thead>
<tr>
<th>( n \ell_m s )</th>
<th>( \text{X-ray} )</th>
<th>( (n, \ell, m+s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d(_{5/2})</td>
<td>( M_5 )</td>
<td>(3,2,5/2)</td>
</tr>
<tr>
<td>3d(_{3/2})</td>
<td>( M_4 )</td>
<td>(3,2,3/2)</td>
</tr>
<tr>
<td>3p(_{3/2})</td>
<td>( M_3 )</td>
<td>(3,1,3/2)</td>
</tr>
<tr>
<td>3p(_{1/2})</td>
<td>( M_2 )</td>
<td>(3,1,1/2)</td>
</tr>
<tr>
<td>3s(_{1})</td>
<td>( M_1 )</td>
<td>(3,0,1/2)</td>
</tr>
<tr>
<td>2p(_{3/2})</td>
<td>( L_3 )</td>
<td>(2,1,3/2)</td>
</tr>
<tr>
<td>2p(_{1/2})</td>
<td>( L_2 )</td>
<td>(2,1,1/2)</td>
</tr>
<tr>
<td>2s(_{1})</td>
<td>( L_1 )</td>
<td>(2,0,1/2)</td>
</tr>
<tr>
<td>1s(_{1})</td>
<td>( K )</td>
<td>(1,0,1/2)</td>
</tr>
</tbody>
</table>

s: \( \ell = 0 \)
p: \( \ell = 1 \)
d: \( \ell = 2 \)
f: \( \ell = 3 \)
Summary: Properties of X-rays

- X-rays penetrate into the bulk of a material, and probe average structure / chemistry
- X-rays interact strongly with electron charges, and more weakly with spins and nuclei
- Flux, polarization, bandwidth, and coherence can be prepared to order, within limits, using accelerator-based sources and crystal optics
- X-ray energies are comparable to electronic energy levels in atoms
- X-ray wavelengths are comparable to size of atoms and unit cells
2. X-ray Light Sources
World-wide suite of light sources: More than 50 user facilities, various specialties
Accelerate electrons to relativistic speed, wiggle them to produce x-rays

lightsources.org
X-ray User Facilities in the Americas: Small group of world-class facilities with distinct roles

USA, High Energy Storage Rings

USA, Low/Mid Energy Storage Rings

USA, Free Electron Laser

Canada & Brazil, Mid-Energy Storage Rings
X-ray User Facilities in the Americas: Small group of world-class facilities with distinct roles

USA, High Energy Storage Rings

~ 6 GeV Rings
Best choice for E > 10 keV

USA, Low/Mid Energy Storage Rings

USA, Free Electron Laser

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X-ray User Facilities in the Americas: Small group of world-class facilities with distinct roles

USA, High Energy Storage Rings

USA, Low/Mid Energy Storage Rings

USA, Free Electron Laser

Canada & Brazil, Mid-Energy Storage Rings

1 - 3 GeV Rings
Best choice for E < 10 keV
Most coherence @ NSLS-II
X-ray Studies of Quantum Materials

2. X-Ray Light Sources

X-ray User Facilities in the Americas: Small group of world-class facilities with distinct roles

USA, High Energy Storage Rings

USA, Low/Mid Energy Storage Rings

USA, Free Electron Laser

Canada & Brazil, Mid-Energy Storage Rings

2.5 - 17 GeV LINAC
Coherent, brilliant, femtosecond pulses, 100Hz rep rate, $E < 10$ keV.
X-ray User Facilities in the Americas: Small group of world-class facilities with distinct roles

USA, High Energy Storage Rings

USA, Low/Mid Energy Storage Rings

USA, Free Electron Laser

Canada & Brazil, Mid-Energy Storage Rings

1 - 3 GeV Rings
Best for $E < 10$ keV
Some specialized beamlines
QUESTION 1:

You have synthesized a novel cuprate compound. You want to perform x-ray absorption spectroscopy studies of the Cu L-edges, to understand doping of the d-bands. The next round of user experiments will occur in February. Choose a suitable light source where you would apply for beam time.

A) CHESS
B) Argonne
C) ALS
D) LNLS
E) LNLS
What is a “beamline”?

(i) Insertion device to make x-rays

(ii) Optics to condition the beam

(iii) Hutch to perform experiments without irradiating ourselves

(iv) Experimental equipment (Diffractometers, spectrometers, magnets, lasers, fridges, etc.)
**Lightsources represent a massive investment in science!**

Total US expenditures by state and federal agencies on the construction and operation of lightsources is of order **$1B / year**. There are ~200 beamlines in operation in the Americas.

These facilities are almost exclusively run as free, open resources for academic users, with beam time and new instrument construction based on merit of scientific proposals from domain scientists like you.

Lightsources are interdisciplinary facilities, where quantum science competes for resources against life science, chemistry, engineering, medicine, etc.

Getting involved with lightsources can enrich your research, while also making sure that a larger share of these resources are allocated towards the problems you find most interesting.
2. X-Ray Light Sources

Commercial break:

Storage Ring (CESR):
- 768 m circumference
- 5 stories under ground
- 5.3 GeV (1 of 5 in world)
- 120 mA of both e⁻ and e⁺

CHESS:
- 1,300 user visits/year
- 11 Experimental stations
- 3,800 hours/year of user operations

CHESS is one of 5 high-energy synchrotrons in the world, specializing in hard x-rays (5-100 keV). It is also the only synchrotron located on a university campus in the US. CHESS has a strong focus on teaching early career scientists and developing novel x-ray techniques.
Commercial break:

Currently, the lab is undergoing a $15M upgrade (CHESS-U), which began on June 4. (Sorry, no tour!) After the upgrade, CHESS will deliver among the best high energy x-ray beams available anywhere worldwide. In addition to upgrades of the storage ring, CHESS-U will build out 6 new undulator beamlines for x-ray science.
Commercial break:

Two of the new beamlines will address forefront research problems in quantum materials.

<QM>²: Q-Mapping for Quantum Materials. Optimized for speed and ease of use, we will map extensive regions of Q-space, using resonant and non-resonant elastic scattering. Uncover intertwined quantum correlations of spins, charges, and orbitals, from high to low temperatures and spanning entire phase diagrams.

PIPOXS: Photon-In, Photon-Out X-ray Spectroscopy. Spectroscopic studies of valence electronic states in functional materials, operable by domain scientists who are not synchrotron X-ray experts. The facility will enable in situ spectroscopic measurements of manmade catalysts and enzymes, research on fuel-cells, batteries, and electronic excitations in quantum materials.
Commercial break:

Beamline information is available at www.chess.cornell.edu

Proposals for user experiments can be submitted at userdb.chess.cornell.edu

Commissioning experiments will begin in early 2019.

If you want to take advantage of your x-ray facilities, but aren’t sure how, feel free to contact me directly with inquiries: jruff@cornell.edu
Summary: Light Sources

• X-ray light sources are a key component of international scientific infrastructure

• They are a worldwide multi-billion dollar investment in interdisciplinary science

• Engaging with the light sources as a quantum scientist is good for the light sources, and good for quantum science.

• Light sources are also a great place to build your network as an early career researcher (Meet more collaborators, give more seminars, etc.)
3. X-ray Interactions with Matter
X-rays interact strongly with all of the electrons in the bulk. What are the possible outcomes when an x-ray is incident on a material?

Elastic (Unmodified / Thomson) Scattering
Electron is accelerated by EM wave, and re-radiates at the same frequency. Spherical wave. Elastic and coherent.

Scattering plane perpendicular to $\mathbf{\hat{e}}$:

$$ I = I_0 \frac{e^4}{m^2 c^4 R^2} $$

Scattering plane contains $\mathbf{\hat{e}}$:

$$ I = I_0 \frac{e^4}{m^2 c^4 R^2} \cos^2(\phi) $$

Where $\phi$ is the angle between $\mathbf{k}_i$ and $\mathbf{k}_f$ in the plane of $\mathbf{\hat{e}}$. 

\[3. X-Ray Interactions with Matter\]
X-rays interact strongly with all of the electrons in the bulk. What are the possible outcomes when an x-ray is incident on a material?

**Inelastic (Modified / Compton) Scattering**
Electron and Photon exchange energy and momentum. Inelastic and incoherent.

**Klein-Nishina Formula**

\[
I = I_0 \left[ \frac{\hbar \alpha}{mcR} \right]^2 Q^2(E_i, \theta) \left[ \frac{1}{Q(E_i, \theta)} + Q(E_i, \theta) - 2 + 4\cos^2(\theta) \right]
\]

Where

\[
Q(E_i, \theta) = \frac{E_f}{E_i} = \frac{1}{1 + (E_i/mc^2)(1 - \cos \theta)}
\]
X-rays interact strongly with all of the electrons in the bulk. What are the possible outcomes when an x-ray is incident on a material?

Of course, most electrons in a solid are not free

Binding energy keeps electrons in particular orbitals, unless they are photo-excited via x-ray absorption. They can still contribute to coherent unmodified (Thomson) scattering, but we expect some frequency response (forced damped oscillations). Scattering near absorption edges is more complicated - more on that later.
X-ray Studies of Quantum Materials

X-rays interact strongly with all of the electrons in the bulk. What are the possible outcomes when an x-ray is incident on a material?

**Elastic Scattering**
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

**Absorption / Emission**
Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

**Resonant Scattering**
Incident photon excites a core electron into an empty state. The “same electron” returns to (or fills) the core hole, and emits a photon with close to the initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probes the valence band, i.e. magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

**Non-Resonant Inelastic Scattering**
Incident photon transfers some finite amount of energy and momentum to the sample, creating an elementary excitation. [Compton, HERIX, X-ray Raman]
Elastic Scattering
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Elastic scattering from an atom
Sum up plane-wave scattering from each volume element of each electron cloud. This is the Atomic Form Factor.

$$f_0 = \int \rho(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d\vec{r} ; \quad \text{where} \quad \vec{q} = \vec{k}_i - \vec{k}_f$$

$$f_0(|\vec{q}| \to 0) = Z \quad \text{(No. of electrons)}$$

$$f_0 \text{ falls off for large values of } |\vec{q}|, \text{ but remains finite}$$

Elastic Scattering
Momentum is transferred the sample, but not energy. \( E_i = E_f \). Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Elastic scattering from a solid, made of atoms
Sum up scattering from each atom. This is the Structure Factor. Measured Intensity follows the square of the structure factor.

\[
F(\vec{q}) = \sum_{m}^{\text{atoms}} f_{0m} e^{i\vec{q} \cdot \vec{R}_m}; \quad \text{where} \quad \vec{q} = \vec{k}_i - \vec{k}_f
\]

and atoms are at positions \( \vec{R}_j \)

\[
I(\vec{q}) \propto F^*F = \sum_{m,n}^{\text{atoms}} f^*_{0n} f_{0m} e^{i\vec{q} \cdot (\vec{R}_m - \vec{R}_n)}
\]

X-Ray diffraction measures the Fourier transform of the 2-body correlation function between pairs of atoms in a material.
Elastic Scattering

Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Elastic scattering from a crystalline solid, made of repeating unit cells of atoms

Measured Intensity follows the square of the structure factor. Correlation of pairs of atoms. For idealized crystals, intensity is only non-zero when $\vec{q}$ is a vector in the reciprocal lattice.

\[
I(\vec{q}) \propto F^* F = \sum_{m,n} f_{0n}^* f_{0m} e^{i\vec{q} \cdot (\vec{R}_m - \vec{R}_n)}
\]

\[
\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3
\]

\[
I(\vec{q}) \neq 0 \quad \text{only if} \quad \vec{q} \in G(h, k, l) = (hb_1 + kb_2 + lb_3)
\]

i.e. \[
e^{i\vec{G} \cdot \vec{R}} = 1
\]

This is the basis of x-ray crystallography, and average unit-cell structure determination.
Elastic Scattering
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Methods for x-ray structure solution at light sources
(a) Powder diffraction
Measure a statistical distribution of crystal orientations. Refine structures using Rietveld method. (GSAS, Fullprof)

http://11bm.xray.aps.anl.gov/
3. X-Ray Interactions with Matter

**Elastic Scattering**
Momentum is transferred the sample, but not energy. \( E_i = E_f \). Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

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**Methods for x-ray structure solution at light sources**

(b) Single Crystal Diffraction
Collect thousands of Bragg intensities from a single, highly perfect crystal. 360° rotations. Refine structures using open source software (shelx)

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Goal is to generate a list of H,K,L and Intensity values, and “solve” the structure.

A solution is typically (i) a space group; (ii) a list of atoms along with fractional coordinates in the unit cell; (iii) Thermal parameters.
Elastic Scattering
Momentum is transferred the sample, but not energy. \( E_i = E_f \). Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Example structural solution, from ICSD, for Sr\(_2\)RuO\(_4\).
3. X-Ray Interactions with Matter

Elastic Scattering
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Beyond Crystallography:
Elastic scattering can tell us much more than just the average unit cell.

Key Ideas: Resolution, Coverage, Dynamic Range

Synchrotron X-ray diffraction has high resolution, can see subtle lattice distortions
High energy X-ray scattering can cover wide ranges of Q space - comprehensive data
Extremely high flux of synchrotron sources lets us observe intense and weak features simultaneously
Elastic Scattering
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

**Beyond Crystallography: Phase transitions**

Parameterize a single Bragg peak as a function of temperature. Observe splitting at tetra-ortho transition.

Twinning: Diffraction resolves mesoscale structures and microscopic order parameter simultaneously.

Direction of x-ray momentum transfer
3. X-Ray Interactions with Matter

**Elastic Scattering**
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

**Beyond Crystallography: Thin Films and heterostructures**
Simultaneously resolve scattering from substrate, film, and interface.

Hard x-rays fully penetrate an epitaxial layer, so scattering is recorded from both film and substrate in reflection geometry.

Very high energy x-rays transmit through the substrate as well, allowing transmission geometry measurements.

2D interface structure also generates a unique scattering signature. Fourier transform of 2D object is 1D in reciprocal space.
Elastic Scattering
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Beyond Crystallography: Thin Films and heterostructures
Simultaneously resolve scattering from substrate, film, and interface.

Can collect volumetric 3D datasets with $>2^{10}$ distinct measurements of I(q) ($\text{Sr}_2\text{RuO}_4$ thin film on oxide substrate). Only 20 mins data collection.
3. X-Ray Interactions with Matter

**Elastic Scattering**
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

**Beyond Crystallography: Thin Films and heterostructures**
Simultaneously resolve scattering from substrate, film, and interface.

(A) Film peak; (B) Truncation rod; (C) Substrate peak; (D) Diffuse Scattering, most likely Substrate phonon modes; (E) Textured epitaxial defect phase
3. X-Ray Interactions with Matter

**Elastic Scattering**
Momentum is transferred to the sample, but not energy. \( E_i = E_f \). Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

**Beyond Crystallography: Thin Films and heterostructures**
Simultaneously resolve scattering from substrate, film, and interface.
Elastic Scattering
Momentum is transferred the sample, but not energy.  \( E_i = E_f \). Probe symmetry and order via Fourier transform of the 3D electron density.  [X-ray Diffraction]

Beyond Crystallography: Thin Films and heterostructures
Simultaneously resolve scattering from substrate, film, and interface.

COBRA: Coherent Bragg Rod Analysis. Transform and fit 1D rods of scattering to resolve surface / interface structure.  [Gustafson, Science 343 6172 (2014)]
QUESTION 2:
Your suspect that your sample harbors spin-Peierls physics at low temperature. Theory suggests that above $T_{SP}$, there are 1D chains of atoms with spin-1/2 moments running along the $\hat{C}$ direction, which dimerize to form spin-singlets. This doubles the unit cell along the chain direction, but there are no correlations between the chains. Then, below $T_{SP}$, the dimerization of the different chains locks in phase, and there is a long range 3D distortion of the lattice. If the theory is correct, what new features would you see in the elastic scattering, besides the Bragg peaks from the average structure?

(A) Rods of scattering along L at integer (H,K) positions above $T_{SP}$
New Bragg peaks at $(1/2,1/2,1/2)$ below $T_{SP}$

(B) Sheets of scattering in the (H,K) planes at half-integer L positions above $T_{SP}$
New Bragg peaks at $(0,0,1/2)$ below $T_{SP}$.

(C) Rods of scattering along L at half-integer (H,K) positions above $T_{SP}$
New Bragg peaks at $(0,0,1/2)$ below $T_{SP}$.

(D) No new scattering above $T_{SP}$
New Bragg peaks at $(1/2,0,0)$ below $T_{SP}$.

(E) None of the above.
Elastic Scattering
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Beyond Crystallography: Charge Density Waves
Lattice is sympathetic to electronic symmetry breaking - electron-phonon, excitonic, etc

UBt$_2$Si$_2$

Ubiquitous CDW distortions
Small distortion gives weak peak!
**Elastic Scattering**

Momentum is transferred the sample, but not energy. \( E_i = E_f \). Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

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**Beyond Crystallography: Charge Density Waves**

Lattice is sympathetic to electronic symmetry breaking - electron-phonon, excitonic, etc

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<table>
<thead>
<tr>
<th>Table 1. Refinement of the single crystal neutron diffraction data, carried out at 50 K, on as-grown UPt₂Si₂, with the CaBe₂Ge₂ lattice (space group ( P4/nmm )).</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
</tr>
<tr>
<td>U</td>
</tr>
<tr>
<td>Pt(1)</td>
</tr>
<tr>
<td>Pt(2)</td>
</tr>
<tr>
<td>Si(1)</td>
</tr>
<tr>
<td>Si(2)</td>
</tr>
</tbody>
</table>

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Crystallography “fails” for weakly modulated structures, but these failures are not always obvious! “Disorder” can be a convenient excuse, leading us to overlook interesting physics.
3. X-Ray Interactions with Matter

**Elastic Scattering**
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

**Beyond Crystallography: Charge Density Waves**
Lattice is sympathetic to electronic symmetry breaking - electron-phonon, excitonic, etc

Underdoped YBCO. CDW formation causes all the ions to shift slightly in the lattice.

Forgan, Nat. Comms. 6: 10064 (2015)
3. X-Ray Interactions with Matter

**Elastic Scattering**

Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density.

[X-ray Diffraction]

**Beyond Crystallography: Incommensuration**

No more 3D space group or unit cell, if $n \tau \neq m \alpha$, where $m,n$ are integers

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**Bi-2212: Castellan**

*PRB 73, 174505 (2006)*

**Kogar**

*PRL 118, 027002 (2017)*
Elastic Scattering
Momentum is transferred the sample, but not energy. \( E_i = E_f \). Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Beyond Crystallography: Short-ranged local order
Pair correlations without Bragg Peaks, 1D and 3D PDF

Linear scale - Similar Scattering, Avg. Structure.
**Elastic Scattering**
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

**Beyond Crystallography: Short-ranged local order**
Pair correlations without Bragg Peaks, 1D and 3D PDF

Log scale - “Charge Ice” Diffuse Scattering

Courtesy B.D. Gaulin
Elastic Scattering
Momentum is transferred the sample, but not energy. \( E_i = E_f \). Probe \textit{symmetry} and \textit{order} via Fourier transform of the 3D electron density.

Beyond Crystallography: Short-ranged local order
Pair correlations without Bragg Peaks, 1D and 3D PDF

Need extensive Q coverage for PDF analysis. High energy x-rays, large detectors.
Elastic Scattering
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe symmetry and order via Fourier transform of the 3D electron density. [X-ray Diffraction]

Beyond Crystallography: Short-ranged local order

$$G(r) = \frac{2}{\pi} \int Q[I(Q) - 1] \sin(Qr) dQ$$
3. X-Ray Interactions with Matter

**Elastic Scattering**
Momentum is transferred the sample, but not energy. $E_i = E_f$. Probe *symmetry* and *order* via Fourier transform of the 3D electron density. [X-ray Diffraction]

**Beyond Crystallography: Short-ranged local order**
3. X-Ray Interactions with Matter

**Elastic Scattering**
Momentum is transferred the sample, but not energy. \( E_i = E_f \). Probe *symmetry* and *order* via Fourier transform of the 3D electron density.

[X-ray Diffraction]

---

**Coherent Beams: X-ray Photon Correlation Spectroscopy**

Dynamics of domains  

---

DW Domains in Cr - Speckle Dynamics vs Temp. & Time
Summary: Elastic Scattering

- Long-standing, classic technique. After 100+ years, diffraction is still the “killer app” for x-rays. Vast majority of beamlines are dedicated to this.

- Elastic x-ray scattering is a premier probe of symmetry, order, disorder, and critical phenomena.

- Looking beyond crystallography, elastic scattering exploiting high energy, high dynamic range, and high coherence can be highly informative for quantum materials research.

- Understanding structural data without a space group and unit cell remains a daunting challenge
Homework:

• Tomorrow, we will talk about resonant scattering and inelastic scattering, and possibly discuss sample environments and pumps/perturbations.

• I’d also like to open up discussion about what x-ray research at synchrotrons might have to offer to your research. I propose a Q&A.

• If you are interested, please fill out your card with the following information:

  Name
  Email address (optional)
  Question

I will collect them before lecture tomorrow, and try to answer several of them. If we run out of time, I will email a response.

Example (made up) questions:
• “I study skyrmions. Can I use x-rays to see them?”
• “Which is the best beamline for magnetic scattering studies of Ytterbium?”
• “How do I get beam time at the LCLS?”
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

Note: This section contains blatant theft from other talks and reviews by M. Newville, G. Bunker, and S. De Beer.
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

Key Ideas: High Spectral Flux, Tunable Energy, Narrow Bandwidth

For absorption / emission studies, we need bandwidth comparable to the intrinsic core-hole lifetimes in atoms.

We also need to be able to reliably tune the energy at the sub-eV level, and resolve the final energy with similar precision.

Synchrotron sources with perfect crystal optics are unique sources of such photons.
### Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

**Table 1-1.** Electron binding energies, in electron volts, for the elements in their natural forms.

<table>
<thead>
<tr>
<th>Element</th>
<th>K 1s</th>
<th>L 1s</th>
<th>L 2 2s</th>
<th>L 2 3p&lt;sub&gt;1/2&lt;/sub&gt;</th>
<th>L 3 2p&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>M 1 3s</th>
<th>M 2 3p&lt;sub&gt;1/2&lt;/sub&gt;</th>
<th>M 3 3p&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>M 4 3d&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>M 5 3d&lt;sub&gt;5/2&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td>V</td>
<td>5465</td>
<td>626.7</td>
<td>519.8</td>
<td>512.1</td>
<td>66.3</td>
<td>37.2</td>
<td>37.2</td>
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<td></td>
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<tr>
<td>Cr</td>
<td>5989</td>
<td>696.0</td>
<td>583.8</td>
<td>574.1</td>
<td>74.1</td>
<td>42.2</td>
<td>42.2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mn</td>
<td>6539</td>
<td>769.1</td>
<td>649.9</td>
<td>638.7</td>
<td>82.3</td>
<td>47.2</td>
<td>47.2</td>
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<td></td>
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<tr>
<td>Fe</td>
<td>7112</td>
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<td>91.3</td>
<td>52.7</td>
<td>52.7</td>
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<td></td>
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<tr>
<td>Co</td>
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<td>101.0</td>
<td>58.9</td>
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<tr>
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<td>1782</td>
<td>1596</td>
<td>1550</td>
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<td>182</td>
<td>70</td>
<td>69</td>
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</tr>
<tr>
<td>Rb</td>
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<td>1921</td>
<td>1730.9</td>
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<td>292.8</td>
<td>222.2</td>
<td>214.4</td>
<td>95.0</td>
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<tr>
<td>Sr</td>
<td>15200</td>
<td>2065</td>
<td>1864</td>
<td>1804</td>
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<td>248.7</td>
<td>239.1</td>
<td>113.0</td>
<td>112</td>
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<tr>
<td>I</td>
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<td>2216</td>
<td>2007</td>
<td>1940</td>
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<td>280.3</td>
<td>270.0</td>
<td>136.0</td>
<td>134.2</td>
<td></td>
</tr>
</tbody>
</table>

Energy

\[ I_1 = I_0 e^{-\mu(E)t} \]

\[ \mu(E) \propto \log \left( \frac{I_0}{I_1} \right) \]

Geometric Information

\[ E_i > E_b \]

Electronic (and Geometric) Information

\[ E_i < E_b \]
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

\[
\mu(E) \propto \left| \langle i | \hat{\mathbf{r}} \cdot \mathbf{r} e^{i\mathbf{k}_i \cdot \mathbf{r}} | f \rangle \right|^2
\]

Where initial state has (incident x-ray + core electron), final state has (core hole + photo-excited electron), and interaction is \( \sim \) the leading dipole term.

We expect low-lying density of empty final states to determine the shape and intensity of the absorption edge.


Consider the difference between Ir L₃ spectra in the 5d⁷, 5d⁶, and 5d⁵ configurations. (Ir⁰, Ir³⁺, and Ir⁴⁺)

Dipole selection rules for L₃ prefer \( \Delta l = \pm 1 \)

So, L₃ preferentially sensitive to 2p - 5d transitions.
QUESTION 3:

Which spectrum is which?
(IrO$_2$ is 5d$^5$, Ir metal is 5d$^7$, IrCl$_3$ is 5d$^6$)

(A) IrCl$_3$, IrO$_2$, Ir
(B) IrCl$_3$, Ir, IrO$_2$
(C) IrO$_2$, IrCl$_3$, Ir
(D) Ir, IrCl$_3$, IrO$_2$
(E) Ir, IrO$_2$, IrCl$_3$

Clancy, PRB 86 195131 (2012)
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

\[
\mu(E) \propto \left| \langle i | \hat{\epsilon} \cdot \vec{r} e^{i \vec{K}_i \cdot \vec{r}} | f \rangle \right|^2
\]

Where initial state has (incident x-ray + core electron), final state has (core hole + photo-excited electron), and interaction is \( \sim \) the leading dipole term.

We expect low-lying density of empty final states to determine the shape and intensity of the absorption edge.


Consider the difference between Ir L3 spectra in the 5d⁷, 5d⁶, and 5d⁵ configurations. (Ir⁰, Ir²⁺, and Ir³⁺)

Dipole selection rules for L₃ prefer \( \Delta l = \pm 1 \)

So, L₃ preferentially sensitive to 2p - 5d transitions.
Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

(After S. DeBeer)

Crystal environment shifts energy levels of unoccupied states.
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

\[ k_{pe} = \sqrt{\frac{2m(E_i - E_b)}{\hbar^2}} \]

Photo-electron ejected with more momentum for incident photon energies farther from the edge. These electrons can backscatter from adjacent atoms. Probe radial local environment, akin to PDF. This is EXAFS.

P-wave photoelectron from isolated atom

P-wave photoelectron with interference from backscattering neighbors

(After G. Bunker)
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

\[
\mu(E) = \mu_0(E)[1 + \chi(E)]
\]

\[
\chi(k_{pe}) = \frac{f(k_{pe})}{k_{pe}R^2} \sin[2k_{pe}R + \delta(k_{pe})]
\]

(After M. Newville)

“Fundamentals of XAFS”

User-friendly software exists for exafs analysis.

https://bruceravel.github.io/demeter/
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

The emitted photons are not only useful as a monitor of absorption. The energy structure of x-ray emission is a powerful spectroscopy in its own right. Learn about the excited state core hole energetics in the final state. Note nomenclature for lines.
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

Local moments in Fe-SCs. [Gretarsson, PRB 84 100509 (2011)]

\( K_\beta \) emission can resolve the instantaneous local moment on transition metals. This is key information when trying to resolve local vs. itinerant quandaries in SDW metals.
Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]


Use curved, backscattering crystal optics to collect emission over a large solid angle with fine energy resolution. (CHESS-U - PIPOXS Beamline)
3. X-Ray Interactions with Matter

Absorption / Emission

Incident photon is absorbed by an atom, causing a core electron to be excited into a valence band hole. A different core electron annihilates with (or fills) the core hole, and emits a lower energy photon. Probe chemistry, bands, local moments. [XANES, EXAFS, XES, XMCD]

X-Ray Magnetic Circular Dichroism

p-d L-edge transitions with circular light, probe spin+orbital atomic moment.

Difference in absorption when helicity is flipped.

Polarize atoms with magnetic field, measure susceptibility with atomic and orbital specificity.

Sum rules deconvolve L, S.

\[
\langle S \rangle \propto A - 2B \\
\langle L \rangle \propto A + B
\]
Summary: XAS/XES/XMCD

- Core electron spectroscopy can access many details of structure, chemistry, and spin/orbital configuration.

- X-rays are a uniquely appropriate probe at these energy scales.
Resonant Scattering

Incident photon excites a core electron into an empty energy level. The “same electron” returns to (fills) the core hole, and emits a photon with close to the initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]
3. X-Ray Interactions with Matter

Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

\[ I = I_0 \frac{e^4}{m^2 c^4 R^2} \]

Go back to the atomic form factor, with more sophistication. (No more taking the easy way out.)

Recall - back on slide 30 we said:
(1) There should be frequency dependence to the form factor
(2) Scattering near the edges will be complicated

We’ve ignored this so far…
Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

\[
\begin{align*}
\hat{H}_1 &= \sum_{\alpha} \frac{e^2}{2m} \left[ \bar{A}(\vec{r}_\alpha, t) \right]^2, \\
\hat{H}_2 &= -\sum_{\alpha} \frac{e^2}{2mc^2} \bar{s}_\alpha \cdot \left[ \partial_t \bar{A}(\vec{r}_\alpha, t) \times \bar{A}(\vec{r}_\alpha, t) \right], \\
\hat{H}_3 &= -\sum_{\alpha} \frac{e}{m} \left[ \bar{A}(\vec{r}_\alpha, t) \cdot \vec{p}_\alpha \right], \\
\hat{H}_4 &= -\sum_{\alpha} \frac{e}{m} \bar{s}_\alpha \cdot \left[ \vec{\nabla} \times \bar{A}(\vec{r}_\alpha, t) \right].
\end{align*}
\]

\[
I(\omega) \propto \left| \sum_j e^{i\vec{Q} \cdot \vec{R}_j} \left( f_j^{(0)} + f_j^{(0m)} + f_j(\omega) + i f'_j(\omega) \right) \right|^2 |S(\vec{Q})|^2
\]

\[
\equiv |F(\vec{Q})|^2 |S(\vec{Q})|^2,
\]

Following di Matteo - Dirac Hamiltonian, in the proper limits for elastic scattering, x-ray + bound electron. Recover Thomson term, a weak spin-scattering term, and two resonant terms.

(Terms quadratic in vector potential are non-resonant)

Results for diffraction still hold, but now the atomic form factor is complex. Terms can interfere.
Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

\[
f = f_0 + f_{\text{spin}} + f' (\omega) + if'' (\omega)
\]

As in XAS, the electric dipole (“E1”) and electric quadrupole (“E2”) transitions are the largest matrix elements, and give the dominant contribution to resonant scattering. Note that polarization is important now. Following Hill and McMorrow [Acta Cryst. (1996) A52 236]

\[
f_{EL}^e (\omega) = (4\pi / |k|) f_D \sum_{LM} \sum_{M=-L} [\hat{\mathcal{E}}^{*} \cdot Y_{LM}(\hat{k}') Y_{LM}(\hat{k}) \cdot \hat{\mathcal{E}}] F_{LM}^e (\omega)
\]

\[Y_{LM}^e (\hat{k}) \text{ are vector spherical harmonics}
\]

\[
F_{LM}^e (\omega) = \sum_{\alpha, \eta} [P_{\alpha} P_{\alpha} (\eta) \Gamma_x (\alpha M \eta; \text{ EL}) / \Gamma (\eta)] / [x(\alpha, \eta) - i]
\]
3. X-Ray Interactions with Matter

Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

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\[
f_{EL}^{e} (\omega) = (4\pi/|k|) f_{D} \sum_{M=-L}^{L} \left[ \hat{\varepsilon}^{*} \cdot Y_{LM}^{(e)} (\hat{k}') Y_{LM}^{(e)*} (\hat{k}) \cdot \hat{\varepsilon} \right] F_{LM}^{(e)} (\omega)
\]

\[Y_{LM}^{(e)} (\hat{k})\] are vector spherical harmonics

\[
F_{LM}^{(e)} (\omega) = \sum_{\alpha, \eta} [P_{\alpha} P_{\alpha} (\eta) \Gamma_{\chi} (\alpha M \eta; \text{EL}) / \Gamma (\eta)] / [x (\alpha, \eta) - i]
\]

Strength of resonance

Interaction with moment direction

Line width ratio

Distance from resonance

Probabilities from overlap integrals
Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

\[ f = f_0 + f_{\text{spin}} + f'(\omega) + if''(\omega) \]

Still following Hill and McMorrow [Acta Cryst. (1996) A52 236] - an example. L3 edge magnetic scattering from holmium ion. E1 term: (plug in VSH for L=1, M= -1,0,1)

\[ f_{nE1}^{\text{XRES}} = [(\hat{\epsilon}' \cdot \hat{\epsilon})F^{(0)} - i(\hat{\epsilon}' \times \hat{\epsilon}) \cdot \hat{Z}_n F^{(1)} + (\hat{\epsilon}' \cdot \hat{Z}_n)(\hat{\epsilon} \cdot \hat{Z}_n)F^{(2)}] \]

\[ F^{(0)} = (3/4k)[F_{11} + F_{1-1}] \]
\[ F^{(1)} = (3/4k)[F_{11} - F_{1-1}] \]
\[ F^{(2)} = (3/4k)[2F_{10} - F_{11} - F_{1-1}] \]
Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

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Still following Hill and McMorrow [Acta Cryst. (1996) A52 236] - an example. L3 edge magnetic scattering from holmium ion. E1 term: (plug in VSH for \( L=1, M=-1,0,1 \))

\[ f_{nE1}^{\text{XRES}} = [(\hat{e'} \cdot \hat{e})F^{(0)} - i(\hat{e'} \times \hat{e}) \cdot \hat{z}_n F^{(1)} + (\hat{e'} \cdot \hat{z}_n)(\hat{e} \cdot \hat{z}_n)F^{(2)}] \]

First term non-magnetic.

Second term rotates polarization, measures moment parallel to \( \vec{k}_f \).

Third term maximized for non-rotating polarization, measures moment along \( \hat{e} \).

Note - for vertical scattering planes, horizontal polarization is typically called \( \sigma \), while polarization in the scattering plane is typically called \( \pi \).
Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

Often we prepare a beam with pure incident linear $\sigma$ polarization, and analyze the $\pi$ component of the scattered beam, to probe the component of magnetic moment along $\vec{k}_f$.

This makes sense - it is the leading term with the simplest explanation. However, it is worth asking why the other transitions (E2, etc) and other terms are less frequently exploited.
3. X-Ray Interactions with Matter

### Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

Why the other transitions (E2, etc) and other terms are less frequently exploited:

---

X-ray Studies of Quantum Materials

On the other hand, the second terms allows $\alpha \rightarrow \pi$ scattering as well as $\pi \rightarrow \pi$ scattering, but $\pi \rightarrow \sigma$ scattering is forbidden and the matrix elements are:

$$
\begin{align*}
\langle \pi | \hat{M} | \sigma \rangle &= \frac{k \times \mathbf{E}}{\mathbf{k} \times \mathbf{E}} \\
\langle \sigma | \hat{M} | \pi \rangle &= \frac{k \times \mathbf{E}}{\mathbf{k} \times \mathbf{E}}
\end{align*}
$$

where $\theta$ is the Bragg angle. From (15), it possible to see which components of the magnetic moment contribute to the scattering for a given experimental geometry and, as we shall show in the next section, this is all that is required in many experiments. However, for a detailed comparison to be made between (15) and a data set, then it is necessary to compute the magnitude of the coefficients $F_{j\alpha}$. This is beyond the scope of this work, but the coefficients have been evaluated by Haller (1994) for several rare-earth elements.

### 3.2. Electric quadrupole transitions (E2)

We now carry out a similar procedure for the quadrupole transitions in the resonance cases. An example of such a transition is the $2p_{x} \rightarrow 2p_{y}$ transition in the $L_{2}$ edge of Cu. While the scattering from such processes is typically weaker than that due to dipole transitions, it is not insignificant. For example, in a nonmagnetic anisotropic material, the quadrupole terms produce zero magnetic moments.

Here we have observed experimentally (see, for example, Gibbs et al., 1993) that the scattering from mags in the $z$ direction is stronger than the magnetic moments in the $x$ and $y$ directions. We have not yet obtained the results from this scattering, but we have found some interesting results. For example, we have observed that the scattering from mags in the $z$ direction is stronger than the magnetic moments in the $x$ and $y$ directions.

We begin, as before, with the expansion of the vector spherical harmonics (Harrow et al., 1984, Haller, 1994). For the $d_{z^{2}}$ and $d_{x^{2}-y^{2}}$ transitions, the matrix elements of the two different terms are:

$$
\begin{align*}
\langle d_{z^{2}} | \hat{M} | d_{z^{2}} \rangle &= \frac{k \times \mathbf{E}}{\mathbf{k} \times \mathbf{E}} \\
\langle d_{x^{2}-y^{2}} | \hat{M} | d_{x^{2}-y^{2}} \rangle &= \frac{k \times \mathbf{E}}{\mathbf{k} \times \mathbf{E}}
\end{align*}
$$

where the matrix elements of the two third-order terms are:

$$
\begin{align*}
\langle d_{z^{2}} | \hat{M} | d_{z^{2}} \rangle &= \frac{k \times \mathbf{E}}{\mathbf{k} \times \mathbf{E}} \\
\langle d_{x^{2}-y^{2}} | \hat{M} | d_{x^{2}-y^{2}} \rangle &= \frac{k \times \mathbf{E}}{\mathbf{k} \times \mathbf{E}}
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\langle d_{x^{2}-y^{2}} | \hat{M} | d_{x^{2}-y^{2}} \rangle &= \frac{k \times \mathbf{E}}{\mathbf{k} \times \mathbf{E}}
\end{align*}
$$

where $\theta$ is the Bragg angle. From (15), it possible to see which components of the magnetic moment contribute to the scattering for a given experimental geometry and, as we shall show in the next section, this is all that is required in many experiments. However, for a detailed comparison to be made between (15) and a data set, then it is necessary to compute the magnitude of the coefficients $F_{j\alpha}$. This is beyond the scope of this work, but the coefficients have been evaluated by Haller (1994) for several rare-earth elements.

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Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with \(~\) initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

We spent all last lecture assuming Thomson scattering was a legit description, and did plenty of good science. So, maybe E1 in $\sigma \rightarrow \pi$ isn’t so bad. Some examples:
Resonant Scattering

Incident photon excites core electron into empty state. “Same electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

\[ \text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4, \text{L edges}, \sigma \rightarrow \pi \]

[Clancy, PRB 89 054409 (2014)]
Resonant Scattering

Incident photon excites core electron into empty state. "Same electron" returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

Ca$_2$RuO$_4$, L edges, $\sigma \rightarrow \pi$

Zegkinoglu, PRL 95 136401 (2005)
QUESTION 4:

You are doing L$_3$ edge REXS measurements of an antiferromagnet with a simple tetragonal structure, looking at the (0,0,1/2) magnetic peak. You perform a scan of the azimuthal angle over a range from 0° to 360°. At the beginning and end of this scan the scattering plane is (H0L). What is the collinear axis of the moments?

(A) a-axis
(B) b-axis
(C) c-axis
(D) mixed
(E) unknowable
Resonant Scattering

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REXS to RIXS:
If we add the final-photon energy resolution from XES to our momentum-resolved resonant scattering, and narrow our incident bandwidth, we can gain sensitivity to elementary excitations in the sample (spin waves, etc). This is resonant inelastic x-ray scattering. Very precise and powerful technique, but very “photon hungry”.
3. X-Ray Interactions with Matter

Resonant Scattering

Incident photon excites core electron into empty state. “Similar electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

Elementary excitations to probe with x-rays.

These slides follow [Ament, Rev. Mod. Phys. 83 (2011)]
Resonant Scattering

Incident photon excites core electron into empty state. “Similar electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

Direct RIXS - dominant process if allowed

Indirect RIXS - dominant when direct processes are forbidden.
Resonant Scattering

Incident photon excites core electron into empty state. “Similar electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]
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MERIX on Sr$_2$IrO$_4$

[Kim, Nat. Comm. 5: 4453 (2014)]
Resonant Scattering

Incident photon excites core electron into empty state. “Similar electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

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Can also do non-resonant IXS:

If we narrow the incident and final energy resolutions to the absolute limit, we can look directly at non-resonant inelastic scattering processes. This lets us measure i.e. phonon dispersions with x-rays. Caution - even more “photon hungry”. Very long counting times.
Resonant Scattering

Incident photon excites core electron into empty state. “Similar electron” returns to (fills) the core hole, and emits a photon with ~ initial photon energy. Can think of this as a virtual fluctuation into an excited state for the ion. Probe magnetic, charge, orbital, and multipolar electronic ordering and excitations. [REXS, RIXS]

HERIX @ APS

Phonons in CuCrO2
[Bansal, PRB 95 054306 (2017)]
Question: Why not Neutrons?

- Many of the phenomena probed by resonant / inelastic scattering are also well studied by neutrons (phonons, magnetic order, spin waves).

- When neutrons work - they are often superior. Large crystals, non-absorbing elements, coherent neutron cross-sections.

- When neutrons won’t work, x-rays can be the only recourse: thin films, microcrystals, short timescales, “bad” elements for neutron work.

- Different cross sections can give complimentary information. Use both!
4. Sample Environments
Synchrotrons offer a wide variety of methods to perturb your samples

- Low temperatures: T>0.5K at few beamlines, T>4K at most beamlines.
- High Pressure: Diamond Anvil Cells are transparent to high-energy x-rays, and small probe volumes facilitate very high pressures. See HPCAT, HPSync @ APS.
- Magnetic fields: Up to 7T DC fields available at SSRL, NSLS-II, APS. Up to 30T pulsed fields available at APS and LCLS.
- Optical pump-probe: Dozens of laser and THz systems set up to pump materials for time resolved measurements in the ps regime (synchrotrons) or fs regime (FELs).
- In-situ growth chambers (PLD, CVD, MBE) operating at various beamlines as well.
- Several locations also specialize in accommodating custom setups (plug and play sample environments with partner users.)
4. Sample Environments