Resonant Inelastic X-ray Scattering

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Synchrotrons and Free Electron Lasers

NSLS II, Brookhaven NY

ESRF, France
A few references

- **RIXS review:**
  

- **Crystal field excitations in cuprates (direct RIXS):**
  
  Sala et al., New Journal of Physics 13, 043026 (2011)

- **Shake-up RIXS vs. S(q,w):**
  

- **XAS:**
  

- **The atomic multiplet Hamiltonian:**
  
  Racah, Physical Review 61, 186 (1942)

- **RIXS in the EUV:**
  

- **Quantum interference and fs dynamics in the RIXS process:**
  
Outline

1. A challenge: to learn the atomic-scale quantum structure of material systems
   - Spatial scales of many-body states
   - Resonant X-rays as a tool

2. Spectroscopic pictures of local electronic correlations
   - XAS: Atomic-scale electron entanglement
     - Correlated physics of a mixed-valence battery cathode
   - RIXS: a powerful and local low energy probe
     - Many-body excitation spectra
     - Long-lived single atom excitons
   - Examples: VO$_2$ and Hundness
     - Atomic and local cluster excitations
     - RIXS vs. Raman
     - Other shake-up
     - The local-to-nonlocal crossover

3. Future technologies and science
   - QERLIN (ALS), QRIXS (ALS/LCLS), SIX/CENTURION (NSLS II)
   - Dynamics on the scale of $K_B T$
   - Spectromicroscopy
   - Pump-probe RIXS
Microscopic Building Blocks

| Å-scale | nm-scale | Å + nm + ...
<table>
<thead>
<tr>
<th></th>
<th></th>
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<tbody>
<tr>
<td>Atomic wavefunctions</td>
<td>Resonating valence bonds...</td>
<td>URu$_2$Si$_2$: “Hidden order” in a sea of itinerant electrons</td>
</tr>
<tr>
<td>...in a high $T_c$ superconductor</td>
<td>...or a quantum spin liquid</td>
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**Wish list:**

- ~<1nm spatial resolution
- $10^{-15}$s time resolution
- ~1eV perturbation ($10^6$V/mm)
Light as a Tool

http://www-als.lbl.gov
Absorption (excitation) edges covered by soft x-ray

**$K$-edges: $1s$-$2p$**

- Li
- Be
- B
- C
- N
- O
- Ne
- Mg
- Na
- F

**$L$-edges: $2p$-$3d$ states**

- Na
- Mg
- Al
- Si
- S
- Cl
- Ar
- K
- Ca
- Sc
- Ti
- V
- Cr
- Mn
- Fe
- Co
- Ni
- Cu
- Zn
- Ga
- Ge
- As
- Se
- Br
- Kr
- Xe

(S -K: 2472eV – “tender”)
### Resonant X-rays: \textit{XAS, XES(RIXS)}

**Two Particle Response --- Correlation Function**

<table>
<thead>
<tr>
<th>Process</th>
<th>Formula</th>
<th>Probability</th>
<th>Interaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon excites core-electrons to <strong>Unoccupied States</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Auger+2\textsuperscript{nd}ary Emission</td>
<td>\textit{XAS}</td>
<td>99%</td>
<td>Photon-In-Electron-Out</td>
</tr>
<tr>
<td>X-ray Fluorescence</td>
<td>\textit{XAS, XES, RIXS}</td>
<td>&lt;1%</td>
<td>Photon-in-Photon-out</td>
</tr>
</tbody>
</table>

- **Excited state** is an entangled, atomically localized object
  - Dipole selection rule!

- **Decay after \(~1\text{fs}\)** can leave an electronic or magnetic excitation.

**Diagram:**
- **Tunable photon**
- **Emitted electron**
- **Emitted photon**

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6/13/2019 Simons Many Electrons
X-ray absorption (XAS): Projecting an unknown atomic state onto a known set of resonance states

\[ F(n, hv, P_0) = \langle n | D | g \rangle / (hv - E_n + i \Gamma_n), \quad I(hv, P_0) = \sum_n |F(n, hv, P_0)|^2 \]
Cycling a LiFePO$_4$ cathode

X.S. Liu, W.L. Yang, Nat. Comm. 4, 2568 (2013)

Prussian blue battery


Atomic multiplet Hamiltonian: Racah, Physical Review 61, 186 (1942);
Correlated electronic states of a Prussian Blue-based battery

Identifying features

Model based on de Groot JACS 128, 10442 (2006)

Charge/discharge chemistry

W. Yang, LAW, JACS (2014)

XAS is great for symmetry characterization, but core hole obscures the low energy Hamiltonian.
Resonant inelastic X-ray scattering (RIXS): powerful microscopic manipulation of quantum states
Resonant Inelastic X-ray Scattering (RIXS)

- Non-electron quasiparticles
- Probing strong correlations

- Orbital fluctuations: ~ 100 meV - 1.5 eV
- Multiphonons/magnons ~ 50-500 meV
- Pseudogap ~ 30-300 meV
- quasi e-h pairs ~ 1-250 meV
- Collective modes from competing order (QCP, Aslamazov-Larkin) ~ 1-150 meV
- Optical Phonons: ~ 10 - 70 meV
- Single Magnons: ~ 10 meV - 40 meV
- Superconducting gap ~ 1 - 35 meV
RIXS on Cuprates

Q-resolution of the cuprate Mott gap

M.Z. Hasan, Science 2000

Magnon dispersion of single layer La$_2$CuO$_4$

M. Dean, J. Hill, Nat. Mat. 2012

E&Q resolution of 1D “spin-orbiton separation”

J. Schlappa, Nature 2012
The RIXS Process

Kramers-Heisenberg Equation:

\[
\mathcal{F}_{fg}(k, k', \epsilon, \epsilon', \omega_k, \omega_{k'}) = \sum_n \frac{\langle f | D'^\dagger | n \rangle \langle n | D | g \rangle}{E_g + \hbar \omega_k - E_n + i \Gamma_n} \\
I_{fg} = |F_{fg}|^2
\]

Here, the D photon operators implicitly encode photon polarization, and cause an electron to transition between the core and valence orbitals. (e.g. 2p to 3d)

Q1: Another way to describe the variables is: \( q, \Delta E, h\nu, P_0, P_F' \). What does this emphasize?
Q2: How would you distinguish between elastic and inelastic scattering?
Q3: How would you factor in temperature?
Q4: Under what conditions could you get a 2p to 3d core transition? How about 1s to 3d?

Two Paradigms for RIXS

Kramers-Heisenberg Equation:

\[
\mathcal{F}_{fg}(\mathbf{k}, \mathbf{k}', \epsilon, \epsilon', \omega_k, \omega_{k'}) = \sum_n \frac{\langle f \mid D^\dagger \mid n \rangle \langle n \mid D \mid g \rangle}{E_g + \hbar \omega_k - E_n + i \Gamma_n}
\]

\[
D = \sum_{ij} \langle v_i \mid \mathbf{E} \cdot \mathbf{r} \mid c_j \rangle v_i^\dagger c_j
\]

Q1: Why does it matter that there are multiple intermediate states?
Q2: How would quantum interference show up?
Q3: What would the short- and long-core hole lifetime limits represent?

These extreme scenarios have names that we’ll see on the next slides!

A diagram of RIXS scattering
Two Paradigms for RIXS (1): Shake-up

Kramers-Heisenberg Equation:

\[
\mathcal{F}_{fg}(\mathbf{k}, \mathbf{k}', \epsilon, \epsilon', \omega_{\mathbf{k}}, \omega_{\mathbf{k}'}) = \sum_n \frac{\langle f | D^\dagger | n \rangle \langle n | D | g \rangle}{E_g + \hbar \omega_{\mathbf{k}} - E_n + i \Gamma_n}
\]

(or \(q, \Delta E, \hbar v, P_0, P_F\))

Q1: The intensity of shake-up RIXS (relative to ‘photon operator RIXS’) goes as \(I \sim U^2/\Gamma^2\). What do you think this means for resonant elastic scattering?

Q2: Can you think of a shake-up mechanism for exciting phonons? How about magnons?

Q3: Shake-up RIXS is characterized by destructive quantum interference. What does this mean?

Q4: What will happen if I perturb a 3d\(^6\) weakly correlated metal with a strong, long-lived core hole?

Q5: What if the material is an insulator?

From L. Ament Rev. Mod. Phys. 83, 705 (2011)
Two Paradigms for RIXS (2): Photon Operator

Kramers-Heisenberg Equation:

\[ F_{fg}(k, k', \epsilon, \epsilon', \omega_k, \omega_{k'}) = \sum_n \frac{\langle f \mid D^\dagger \mid n \rangle \langle n \mid D \mid g \rangle}{E_g + \hbar \omega_k - E_n + i\Gamma_n} \]

(or q, \(\Delta E\), hv, \(P_0, P'\))

Q1: What are a couple of excitations you could create in this way?
Q2: What's an excitation that would be hard to create?
Q3: When do you think this process occurs?

“Photon-operator RIXS”
Or “direct RIXS” (Ament Review)
Mott Insulator: A diagonalization problem
No gapless charge modes, separation of energy scales for charge and spin degrees of freedom

Electron gas: A DFT problem
RIXS spectrum determined by occupied/unoccupied band structure convolution

The RIXS process for an atomic multiplet

FeTe, J. Hancock, PRB 2010

The “Direct RIXS” process for an itinerant system

BKFA, K. Zhou, Nat. Comm. 2013
Soft X-rays are Gentle X-rays

\[ U \approx 10 \text{ eV} \]

Hard X-ray
\[ U > \Delta_{CT} \gg \Delta_{SC} \]

\[ 3d^{n+2}, 3d^{n+1} \]

\[ U \approx 1 \text{ eV} \]

Soft X-ray
\[ \Delta_{SC} \geq \Delta_{CT} - U \]

\[ 3d^{n+1}, 3d^{n+2} \]

\[ U \approx 0.1 \text{ eV} \]

VUV resonance
\[ \Delta_{SC} \gg U \]

\[ 3d^{n+1} \]

Shake-up in the VUV:

Augustin, LAW, JESRP 2016
http://dx.doi.org/10.1016/j.elspec.2016.12.004
VO$_2$: a Tipping Point for Localization

A 3d$^1$ cousin of the cuprates?


Samples from: J. W. Jeong, A. X. Gray, S. S. P. Parkin
What are the Core Questions?

Simpler than cuprates: M1-phase dimerization

Charge gap is complex: Not a 1-band Hubbard model

Why RIXS? (and only RIXS)
- Coupling to spin and/or specific orbital transitions
- Momentum transfer along the chain
- ~>100meV wide excitation at 0.46 eV

Common issues for moderately correlated materials!
What does a RIXS model need?

A) Multiplet physics
   \((2p^63d^1 \rightarrow 2p^53d^2)\)

B) 2 or more vanadium sites

- In 2010-2014, no simulation codes were well set up to model this near-trivial scenario.

- To model 2-sites with no charge transfer takes a basis of \(6840\) states. With up to 2 electrons transferred, it takes \(36M\) states. \((36M/6840)^3=1.45e11\)
RIXS vs. Raman

RIXS, showing 1-atom-triggered excitations on vanadium!

He, LAW, PRB 94, 161119(R) (2016)

Raman (metal)

Raman (insulator)

None of the features correspond

Tomczak and Biermann, PRB 80, 085117 (2009)
The incident energy axis is simplest

RIXS incident energy dependence comes from core hole states split on a multi-eV scale
First direct observation of singlet bonds in VO$_2$

$polarization matrix elements$

$I(1)/(I(1)+I(2))$

<table>
<thead>
<tr>
<th>Theory</th>
<th>Experiment</th>
</tr>
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<tbody>
<tr>
<td>4.5%</td>
<td>8%</td>
</tr>
<tr>
<td>19.3%</td>
<td>23%</td>
</tr>
</tbody>
</table>

Huihuo Zheng and Lucas K. Wagner

(Received 19 December 2017; published 31 January 2018)

DOI: 10.1103/PhysRevLett.120.059901

We predicted that the insulating state in VO$_2$ would have a singlet-triplet excitation around 123(6) meV. Recently, inelastic x-ray scattering measurements [1] found this excitation at 460 meV. It has been noted that this result is far from the quantum Monte Carlo result we obtained [1,2]. On reanalysis of our original computational data, we noticed two errors that bring the results in closer alignment. The first error was due to a confusion of formula units and crystallographic units, and the second has to do with the interpretation of the calculation. The corrected value of the singlet-triplet gap from our quantum Monte Carlo calculation is 440(24) meV, which agrees with the experimental result within statistical error.
Open Questions: What About Other Shake-up?

Breaking a dimer means phonons

The phonon component may have a larger energy scale for VO$_2$! Best if the process is fast, or if you measure at the leading edge of resonance.

See LAW, PRB 91, 035131 (2015)
RIXS and “Hundness”
Hund’s Rules (one version)

For an isolated atom

1. Align electron spins (top priority)

2. Align orbital angular momentum

3. Point the spin and orbital angular momentum in opposite directions

4. Satisfy Pauli exclusion

\[ m_L = \begin{array}{c} +1 \\ 0 \\ -1 \end{array} \]

Hund’s ground state of Si
Hund’s Rules Meet Itinerancy

Rapid electronic itinerancy jumbles the spin alignment, and supports band insulator states with 0 angular momentum.
Hund’s Rule Gaps

**Singlet-triplet Hund gap:**

- **Mn**\(^{2+}\): 3.3 eV
- **Fe**\(^{2+}\): 2.2 eV
- **Si**: 1.1 eV
- **U**\(^{4+}\): 0.6 eV

**This calls for a multi-band Hubbard model!**

“I would rather change careers than try to meet your spec.”

**1. Align spin angular momentum**

**2. Align orbital angular momentum**

**3. Antialign spin and orbital moments**
"Hundness" and DMFT

3-band Mott+Hund model


See also:

But: no multiplet-resolving spectral functions (XAS/RIXS) yet from theory!
What can experiments look for? A fundamental question is: do we have Hund gaps?
RIXS sees **Gapped Local Degrees of Freedom**

**What have strong correlations removed from the basis?**

Q-resolution of the cuprate Mott gap


Magnon dispersion of single layer La$_2$CuO$_4$

M. Dean, J. Hill, *Nat. Mat.* 2012

Atomic multiplet excitations

LAW, Chuang, *PRB* 2012

**Double occupancy**

**Misaligned angular momentum states**

**Flipped spins**
Hund gaps: is it Mottness or Hundness?

What is gapped out of the URu$_2$Si$_2$ ground state?

LAW PRL 114, 236401 (2015)
So is there a Hund gap?

A Guess, in 2015: What if Hundness “melts”?


H. He, L. Miao, G. Kotliar, LAW (in prep)
A New Kind of Quantum Critical Threshold?

E. Hassinger et al., PRL 105, 216409 (2010)
The next “world’s best”?  

NSLS II CENTURION beamline  
180-2300eV photons  
~15meV energy resolution @ 1keV  

Resolution better than $k_B T$!!!
New Dimensions of Spectroscopic Study

The ARI beamline design proposed for NSLS-II offers 100nm resolution from mirror optics for ARPES and RIXS.

The ALS QERLIN RIXS beamline will map an extra dimension of energy.
<30 meV resolution RIXS (ALS MERLIN, NSLS-II SIX)
- Beamlines accesses shallow core holes
  (less shake-up, strong multiplet structure)

**Multiplexed** RIXS (QERLIN):
- Increased efficiency from extra dimensions of measurement
- Important for metals/interfaces/heterostructures
- ‘Free’ time-domain information

**FEL**-based RIXS (e.g. QRIXS):
- Current pulses <~3fs at LCLS!
- Pump-probe manipulation of dynamics
- Improved resolution for femtosecond scale dynamics
- Stimulated RIXS (multiwave mixing)
- QRIXS shared by LCLS and future LCLS-II
Summary: Simplicity, “Chaos”, and Emergence

Simple: RIXS probes charge-neutral quasiparticles
• Phonons
• Magnons
• Small excitons and atomic multiplets
• Mott gap excitations
• More: superconducting gap excitations?

“Chaos”: RIXS final states *often* do not look like single particle excitations
• Strangely weighted multi-particle continua
• Multi-excitation (e.g. phonon) ‘broadening’ tails
• Lower energy X-rays or fast resonance can help avoid this

Emergence
• Simple excitations can persist and evolve in complex metallic environments (spin excitations, Hund gaps, Mott gaps, multiplet modes)
• Polarization and incident energy can help to parse the excitation symmetries
• Knowing excitation symmetries tells you what correlations gap out of the ground state