Direct Imaging of Orbitals in Quantum Materials using non-resonant inelastic x-ray scattering (x-ray Raman)

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So far, information about orbital occupation / local wave functions is extracted from spectroscopy (= quantitative analysis of spectra)

- tedious at best (e.g. cluster full multiplet calculations need parameters)
- difficult if more than one site is involved (Ti_2O_3 , VO_2 , $LaNiO_3$)
- impossible if the system is very 'metallic' (large inter-site charge fluctuations)

Can we avoid spectroscopy ?!

Yes, we can !!



non-resonant inelastic x-ray scattering



me

dominant at absorption edges

core hole

dominant far away from absorption edges

non-resonant inelastic x-ray scattering, x-ray Raman

non-resonant inelastic x-ray scattering





W. Schülke "Electron dynamics by inelastic x-ray scattering" Oxford 2008

$$\begin{split} S(\vec{q},\,\omega) &= \sum_{f} |\langle f| e^{i\vec{q}\cdot\vec{r}} |i\rangle|^2 \delta(E_i - E_f + \hbar\omega) & \leftarrow \quad \text{Scattering function} \\ e^{i\vec{q}\cdot\vec{r}} &= 1 + i\vec{q}\cdot\vec{r} + (i\vec{q}\cdot\vec{r})^2 + \cdots \dots & \leftarrow \quad \text{Expansion of transition operator} \end{split}$$







Max-Planck P01 NIXS beamline PETRA III - Hamburg



hv = 6-18 keV, beam spot = $10 \mu m \times 10 \mu m$, bent spherical Si(660) analyzers |q| set to a large value (ca. 10 Å⁻¹) to optimize $s \rightarrow d$ transitions vs. $s \rightarrow p$ transitions



 $(\mathbf{s} \rightarrow d)$



 $(\mathbf{S} \rightarrow d)$

 $(s \rightarrow d)$





 $(\mathbf{S} \rightarrow d)$

NiO single crystal



Direct imaging of orbitals in quantum materials

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NiO single crystal



Why does the orientation dependence of $s \rightarrow d$ NIXS give directly the contour of the *d* hole density ?

no need for calculations!

 $(\mathbf{S} \rightarrow d)$

Energy (eV)

optical/x-ray absorption: orientation/polarization dependence



By rotating the *p* orbital, the $s \rightarrow p$ absorption intensity will vary and follow the shape of the *p* orbital

 \overrightarrow{E} is the only quantization axis

s-NIXS (X-ray Raman): orientation dependence

$$\begin{split} S(\vec{q},\omega) &= \sum_{f} |\langle f| e^{i\vec{q}\cdot\vec{r}} |i\rangle|^2 \delta(E_i - E_f + \hbar\omega) \\ e^{i\vec{q}\vec{r}} &= 1 + i\vec{q}\vec{r} + (i\vec{q}\vec{r})^2 + \cdots \dots \end{split}$$

s-orbital is spherical \overrightarrow{q} is the only quantization axis

By rotating the (p,d,f) orbital, the $s \rightarrow (p,d,f)$ NIXS intensity will vary and follow the shape of the p,d, or f orbital

 $(\mathbf{S} \rightarrow d)$

NiO single crystal



no need for resolution ! no need for calculations!



FAQs:

(1) only valid for insulating materials ? how about metallic systems ?
(2) how close can the empty *d*-states be to the Fermi level ?
(3) what is the influence of the core-hole on the empty *d*-density of states ?
(4) what is the effect of covalency ?
(5) why only the *d*-charge density, where are the *p*- or *s*-charge densities ?



$$S(\vec{q},\omega) = \sum_{f} |\langle f | \hat{O}(\vec{q}) | i \rangle|^2 \delta(Ei - Ef + \hbar\omega)$$

spectrum

to know

states

We have looked at the integrated intensity ("a sum-rule experiment")

$$\int S(\vec{q},\omega) \, d\omega = \sum_{f} |\langle f| \, \hat{O}(\vec{q}) \, |i\rangle|^2 = \sum_{f} \langle i| \, \hat{O}(\vec{q}) \, |f\rangle \, \langle f| \, \hat{O}(\vec{q}) \, |i\rangle$$

$$\vec{q} \text{ dependent expectation value of the ground/initial state} = \langle i| \, \hat{O}(\vec{q}) \hat{O}(\vec{q}) \, |i\rangle$$

$$= \langle i| \, \hat{O}_{sd}(\vec{q}) \hat{O}_{sd}(\vec{q}) \, |i\rangle$$

$$\text{there is absolutely no need anything about the final state}$$

 \vec{q} dependent

ground/ini

Orientation dependence of energy-integrated *s*-NIXS intensity

 \vec{q} dependent expectation value of the ground/initial state

$$= \langle i | \hat{O}(\vec{q}) \hat{O}(\vec{q}) | i \rangle$$

there is absolutely no need to know anything about the final states

we have done s-NIXS:

$$3s \rightarrow 3d$$
 transitions $\mathbf{qu}_{adrupole} = \langle i | \hat{O}_{3s3d}(\vec{q}) \hat{O}_{3s3d}(\vec{q}) | i \rangle$ local 3d charge density
we could do s-NIXS:
 $3s \rightarrow 4p$ transitions $\mathbf{dipole} = \langle i | \hat{O}_{3s4p}(\vec{q}) \hat{O}_{3s4p}(\vec{q}) | i \rangle$ local 4p charge density
we could do s-NIXS:
 $3s \rightarrow 4s$ transitions monopole $\langle i | \hat{O}_{3s4s}(\vec{q}) \hat{O}_{3s4s}(\vec{q}) | i \rangle$ local 4p charge density
local 4p charge density
local 4p charge density
local 4s charge density
local charge density
e^{iq} $\vec{r} = 1 + i\vec{q}\vec{r} + (i\vec{q}\vec{r})^2 + \cdots \dots$

s-NIXS



Yavas et al., Nat. Phys. 15, 559 (2019)



Amorese et al., PRX 11, 011002 (2021)

Leedahl et al., Nat. Comm. 10, 5447 (2019)



influence of covalency



PHYSICAL REVIEW X 11, 011002 (2021)

Selective Orbital Imaging of Excited States with X-Ray Spectroscopy: The Example of *a*-MnS

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Excited States: energy splitting = "effective" 10Dq (includes effect of hybridization)



direct imaging of orbitals: ground state of metals



direct imaging of orbitals: ground state of metals



Inelastic x-ray scattering beyond the dipole limit: a new powerful experimental method for *d*- and *f*- quantum materials

s-NIXS direct imaging : ground state orbital occupation

s-core hole is spherical \rightarrow direct imaging



- Information about the ground state : needs only integration over NIXS final states \rightarrow "sum-rule"
- No need for spectroscopic calculations; can be applied also for highly charge fluctuating systems

s-NIXS direct imaging : excited states ?

- Information from excited states : needs analyis of NIXS final states → spectroscopy !
- Identification of character of the excited states: from orbital imaging
- s-core hole is spherical → no extra orbital complexity in multiplet structure →
 Sugano-Tanabe-Kamimura can be used to extract energy parameters and character of ground state

 $(\mathbf{s} \rightarrow d)$

MnS rocksalt











 $(\mathbf{s} \rightarrow d)$





Andrea Amorese et al.











Ground State: spherical charge density



Andrea Amorese et al.





 $(\mathbf{s} \rightarrow d)$







Ground State: 3d⁵ high-spin (spherical charge density)







Excited States: $3d^5 + hv \rightarrow 3s^{-1}3d^6$

Andrea Amorese et al.







decomposition of excited states















M₁: $3d^5 \rightarrow 3s^{-1} 3d^6$ transition initial state = spherical \rightarrow final state = extra electron in t_{2g} or e_g















M₁: $3d^5 \rightarrow 3s^{-1} 3d^6$ transition initial state = spherical \rightarrow final state = extra electron in t_{2g} or e_g



Multiplets of Transition-Metal Ions in Crystals

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Academic Press New York and London 1970





FIG. 5.6. The energy level diagram for the N = 6 system



















 $S_{tot} = S_d - S_s$

 $(\hat{\mathbf{S}}_d \cdot \hat{\mathbf{S}}_s) = \Delta E \left[G_{3s-3d}^2 \right]$

0

s-core level does not add orbital angular momentum (on] \rightarrow Sugano-Tanabe-Kamimura tables can be directly us



s-core level does not add orbital angular momentum (only spin) → Sugano-Tanabe-Kamimura tables can be directly used !!!



Inelastic x-ray scattering beyond the dipole limit: a new powerful experimental method for *d*- and *f*- quantum materials

s-NIXS direct imaging : ground state orbital occupation //orbital character excited states

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- Information about the ground state : needs only integration over NIXS final states \rightarrow "sum-rule"
- No need for spectroscopic calculations; can be applied also for highly charge fluctuating systems
- Information from **excited states** : needs **analyis** of NIXS final states
- Identification of character of the excited states: from orbital imaging
- *s*-core hole is spherical → no extra orbital complexity in multiplet structure → Sugano-Tanabe-Kamimura can be used to extract energy parameters and character of ground state

NIXS spectroscopy : excitonic states // dichroism beyond dipole \rightarrow 4*f* and 5*f* systems