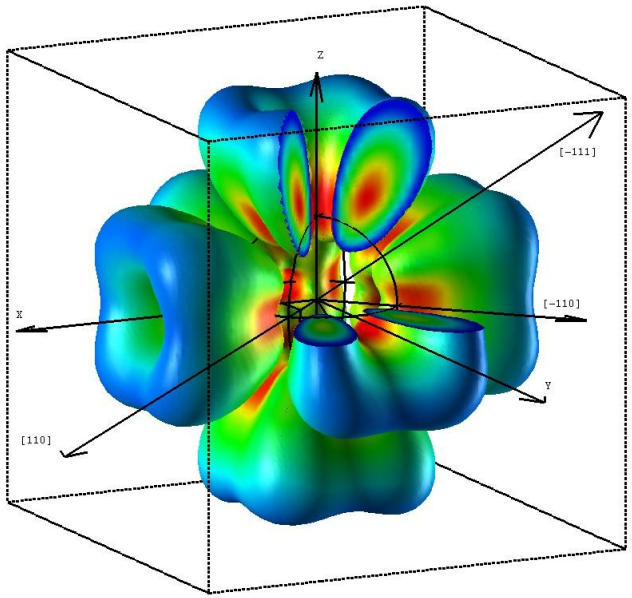
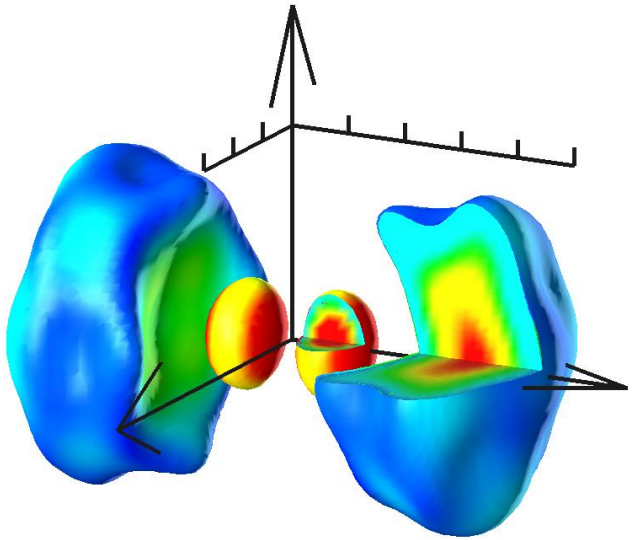
Simplifying Excitations in Charge-Transfer Insulators





Wei Ku

Brookhaven National Lab & SUNY Stony Brook

Acknowledgement

Funding sources

- Basic Energy Science, Department of Energy
- DOE-CMSN
- Taiwanese Student Fellowship

Theoretical works

- Chi-Cheng Lee (BNL & Tamkang Univ.) ← about to move on
- Chen-Lin Yeh (BNL & Tamkang Univ.)
- Hung-Chung Hsueh (Tamkang Univ.)

Experiments

- Ben C. Larson (ORNL) – PRL 2007
- Igor Zaliznyak (BNL) – Nature Physics 2009
- Peter Abbamonte (UIUC) – PNAS 2008

Discussions

- George Sawatzky (UBC)
- Adolfo G. Eguiluz (UT-Knoxville / ORNL)

Outline

- Recent X-ray experiments
  - Sort wave length → sensitivity to local excitations
  - Strong anisotropy → sensitivity to orbitals orientation
- Strong local interaction & short-range correlation

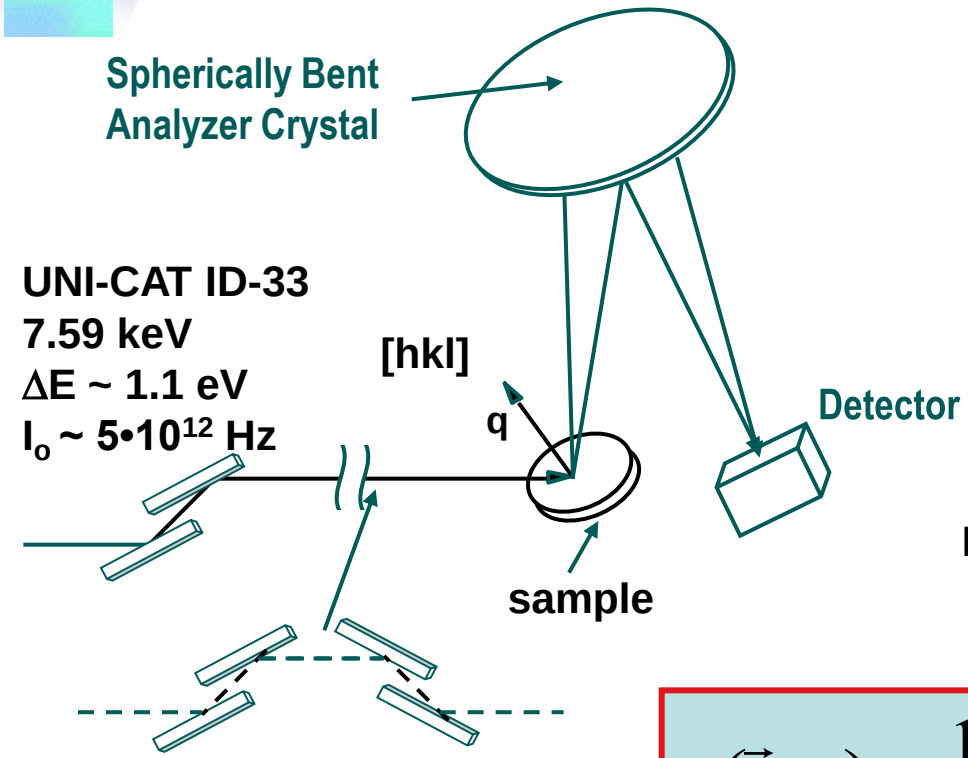
  →Local approach
- Fundamental difficulty of charge-transfer insulators

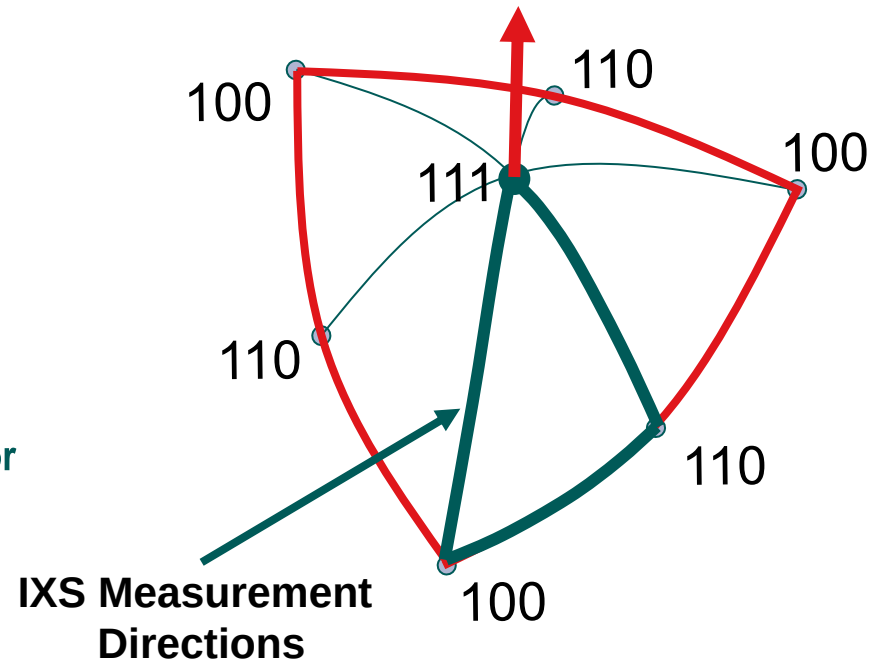
  → Defining “local” in a crystal with “natural” symmetry
- Simple understanding of anisotropy from local picture
- 70% missing spectral weight in INS
- Treating local problem via TDDFT: TD-LDA+*U*
- Treating local problem beyond perturbation
- Propagation of local excitations

For the Purists & the Rest

- In a many-body system, G_1, G_2, …, G_N not apparently related
  - → Band structure (or DOS) is not sufficient
  - → At least linear response is necessary
- TD-DFT: time evolution of density is legally accessible

Non-Resonant Inelastic X-Ray Scattering (NIXS)





$$s(\vec{q},\omega) = \frac{1}{V} S(\vec{q},\omega) = -2\hbar \,\mathrm{Im}\,\chi_{\vec{G}\vec{G}'}(\vec{q}-\vec{G},\omega)$$

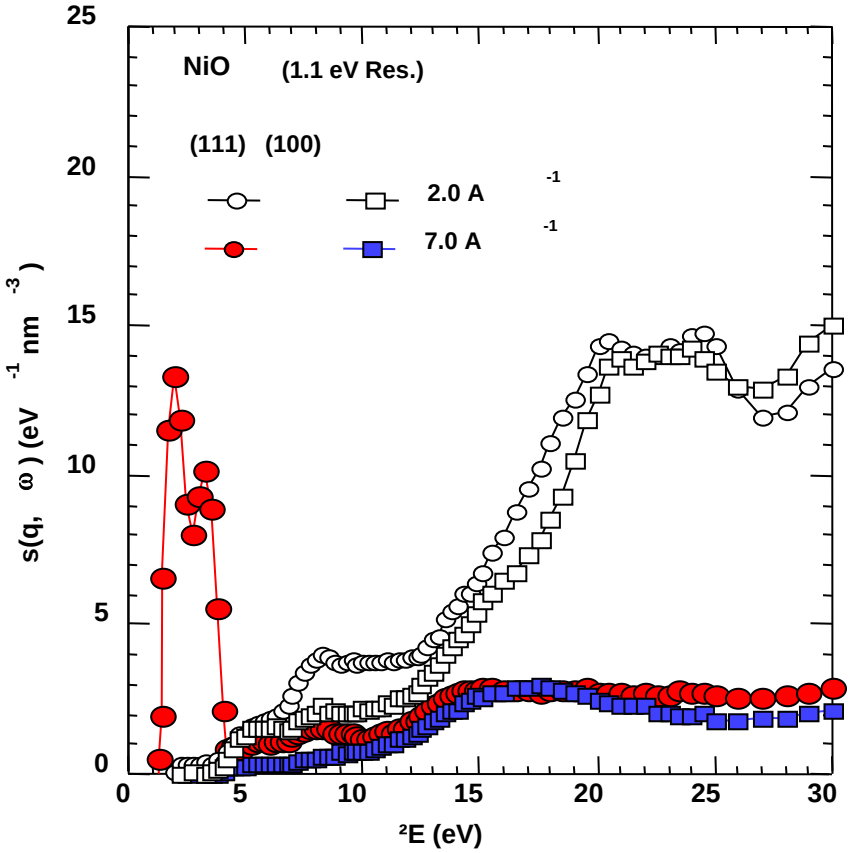
Absolute IXS Measurements

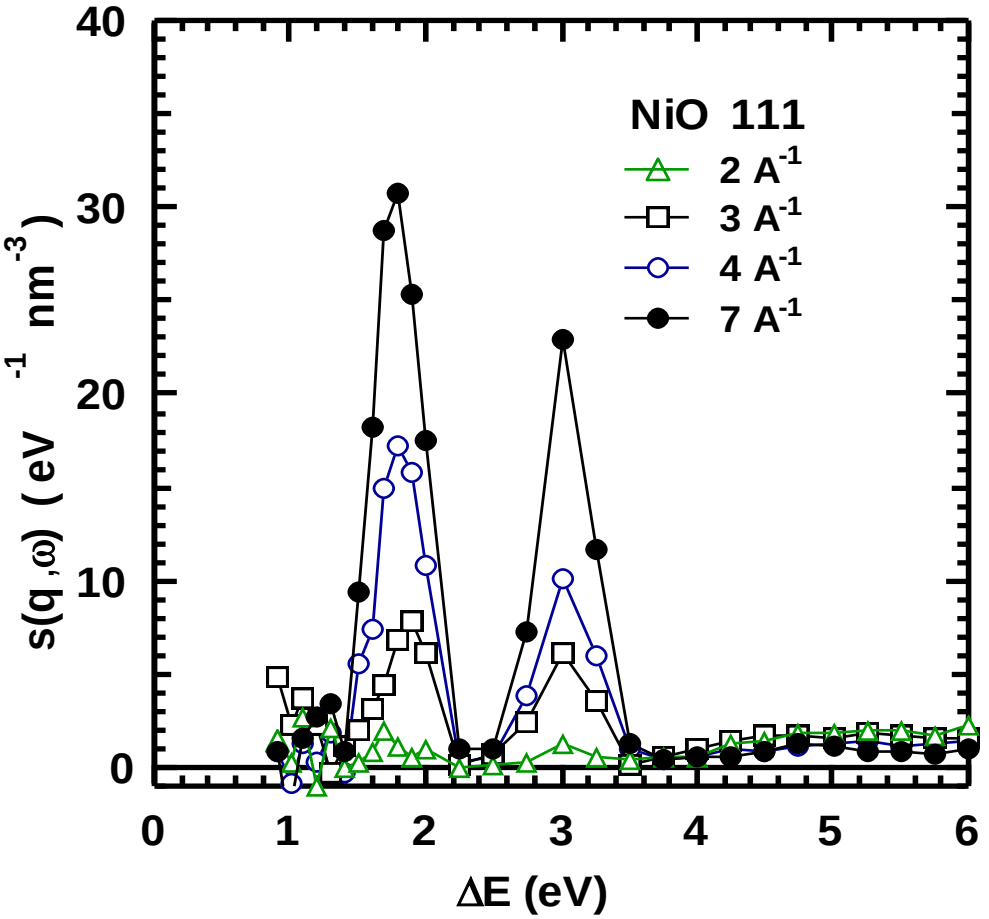
$$\frac{d^2\sigma}{d\Omega d\omega} =: r_0^2 \left(\vec{e}_i \cdot \vec{e}_f\right)^2 \left(\frac{\omega_f}{\omega_i}\right) S(\vec{q},\omega)$$

Absolute Response Calculations

$$S(\vec{q},\omega) = -2\hbar V \,\mathrm{Im}\,\chi_{\vec{G},\vec{G}}(\vec{q}-\vec{G},\omega)$$

Local Excitations in the Mott Gap in NiO





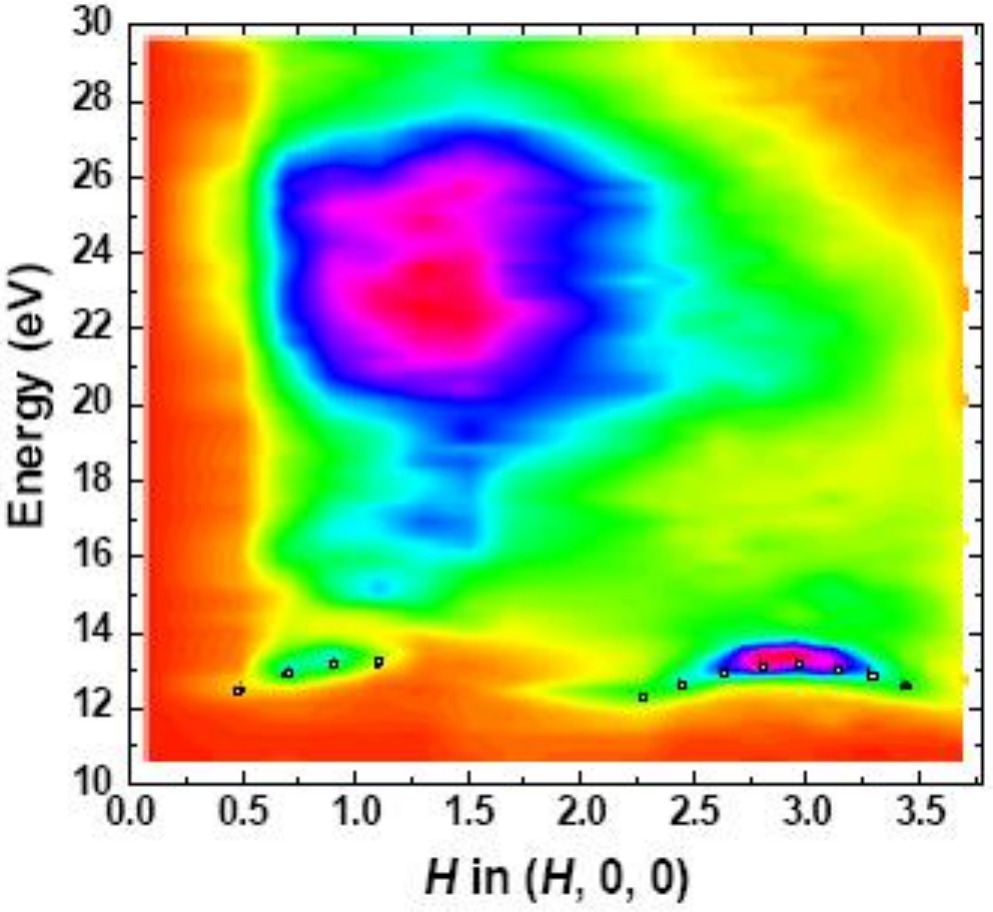
- New features at large q in the Mott gap! B. C. Larson et al.,PRL 2007
- Short wave length → local excitations (small exciton)
- Strong angular dependence: (100) != (111)

Tightly-Bound Excitons in Charge Transfer Insulators: case study of LiF

- Tightly bound exciton
- Charge transfer insulator
  → p-h in different atoms
- Frenkel or Wannier exciton ?
- Simple dispersion
  → propagation in space/time

Inelastic X-ray scattering

- Structured spectral weight
- Clear dispersion at large *q* !
- observe *fs* dynamics



P. Abbamonte et al.,PNAS 2008

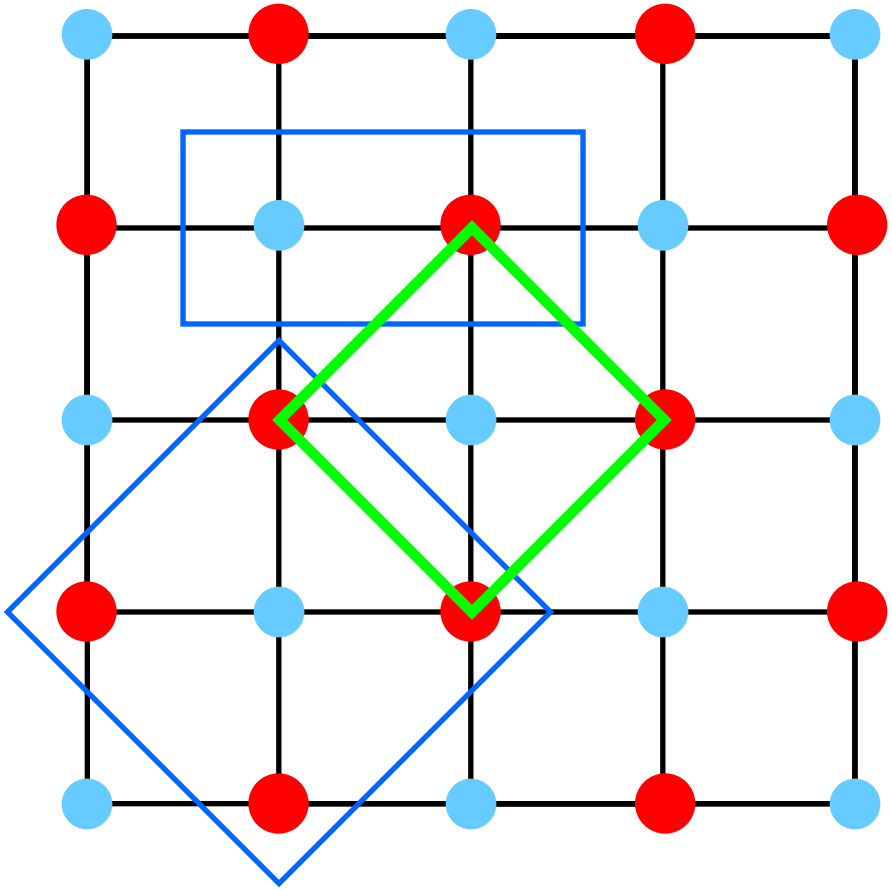
Local Picture for Strongly Correlated Systems

$$H = H_0 + V = H_{local} + H_{nonlocal}$$

- V too big for perturbation
- Maximize the terms in the "local" part

  → symmetric Wannier Representation → defines "local"
- Treat local part "accurately" and leave non-local part as modification

How to define “local” in CT-insulators?

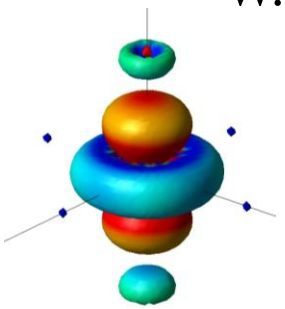


- Periodic symmetry
- Point group symmetry
- Simultaneously keep both? How to split the Hilbert space?

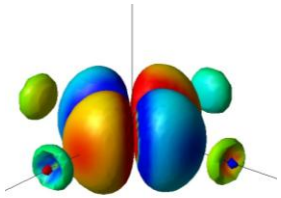
Symmetric Wannier Functions for CT-Insulators

W. Ku et al., Phys. Rev. Lett. **89**, 167204 (2002).
R. L. Barnett et al., Phys. Rev. Lett. **96**, 026406 (2006).
W.-G. Yin et al, Phys. Rev. Lett. **96**, 116405 (2006).

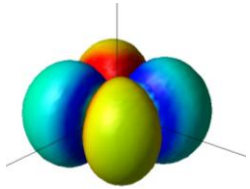
Ni



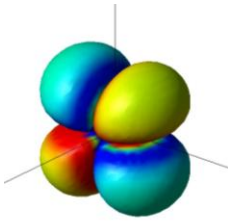
$3z^2 - r^2$



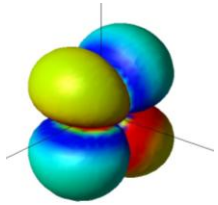
$\sqrt{3}(x^2 - y^2)$



xy

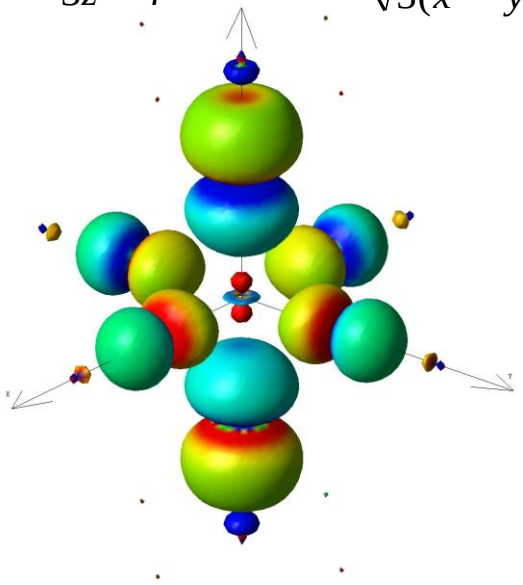


yz

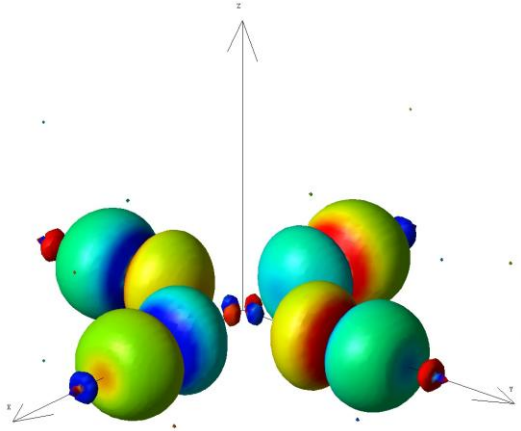


xz

O



$3z^2 - r^2$



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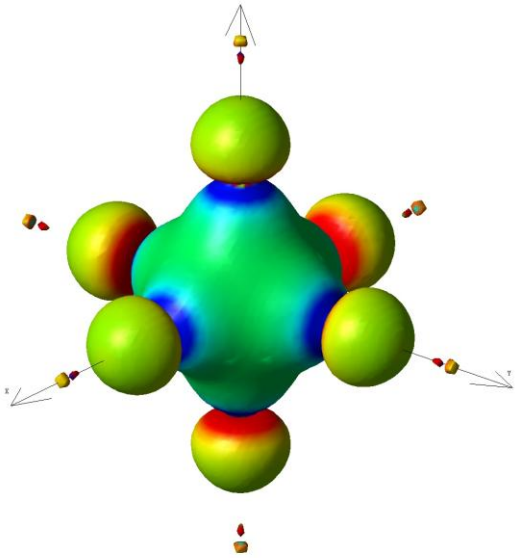
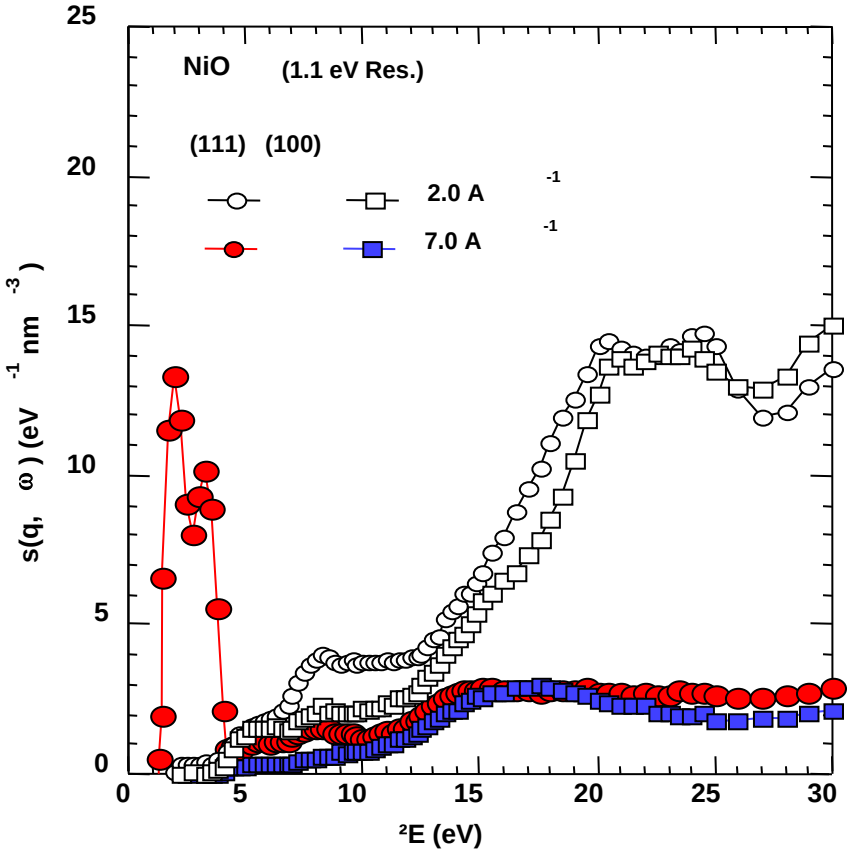
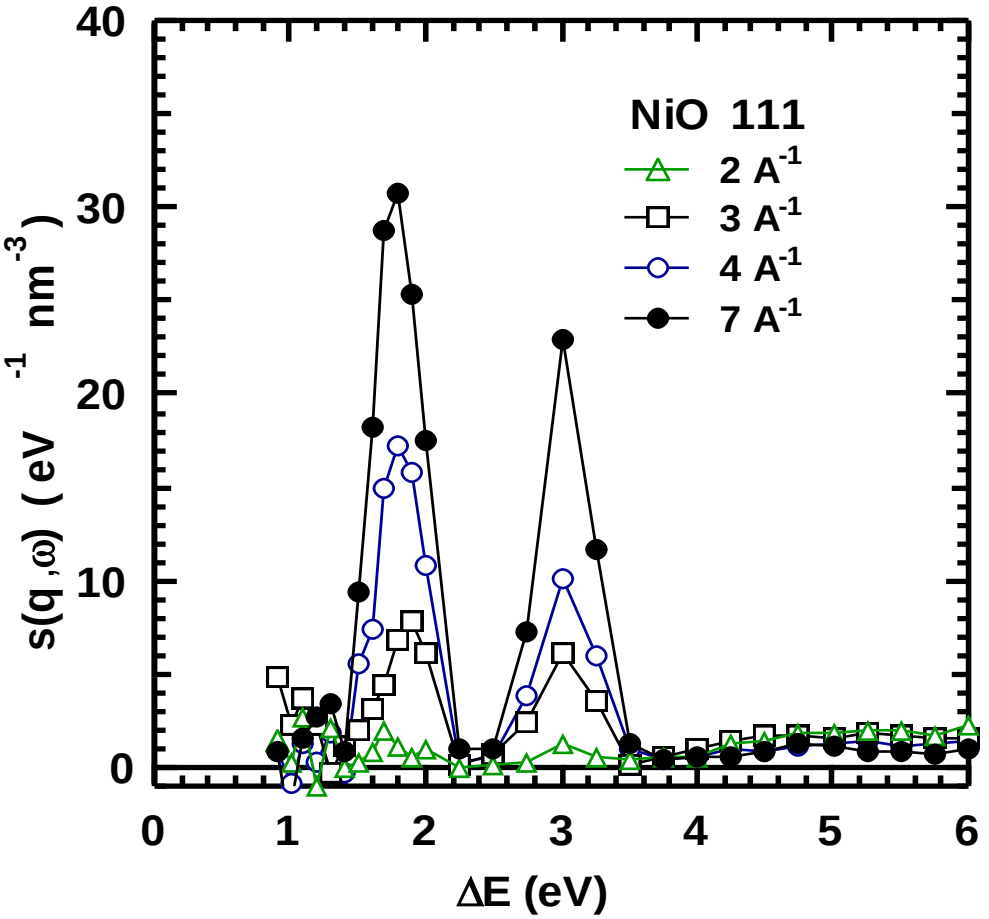


s wave

- O-*p* orbitals → additional Ni-*d* orbitals (no double counting of O orbitals)
- "local" is now defined by this "super-atom"

Local Excitations in the Mott Gap in NiO



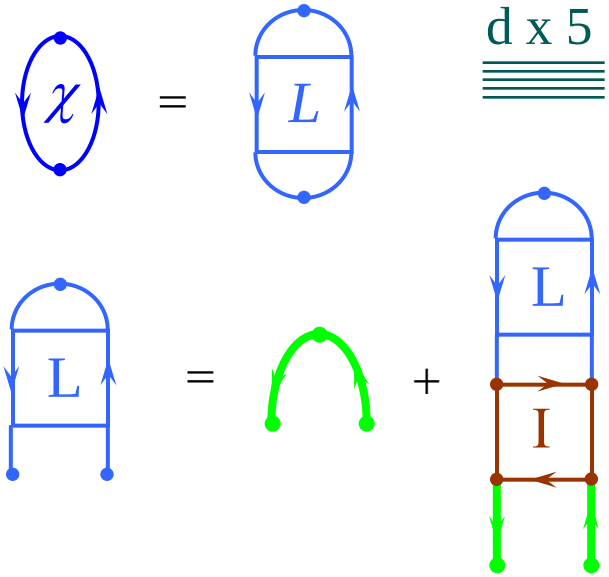


- New features at large *q* in the Mott gap!
- Short wave length → local excitations
- Strong angular dependence: (100) != (111)

B. C. Larson et al.,PRL 2007

q-dependence of Localized Excitons

Energy-resolved Wannier states

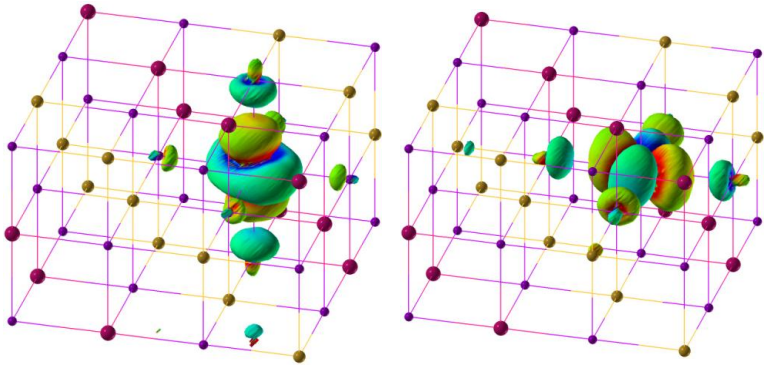


d x 5

e_g x 2

$e_g\ 1 \propto 3z^2 - r^2$

$e_g\ 2 \propto \sqrt{3}\left(x^2 - y^2\right)$

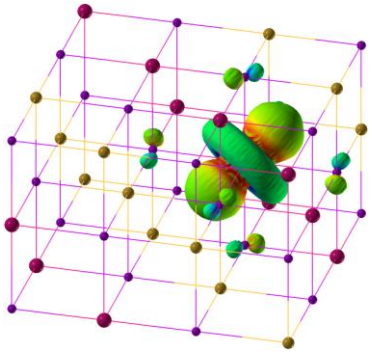


E_F of NiO

t_{2g} x 3

a_{1g} x 1

$a_{1g} : 2\left(yz + zx + xy\right)$

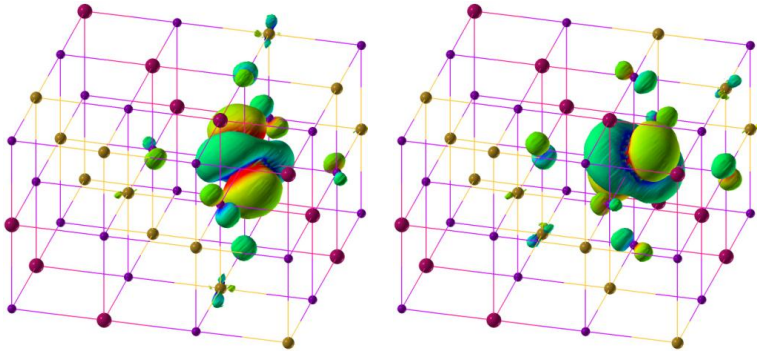


E_F of CoO

e'_g x 2

$e'_g\ 1 \propto \left(1+\sqrt{3}\right)yz + \left(1-\sqrt{3}\right)zx - 2xy$

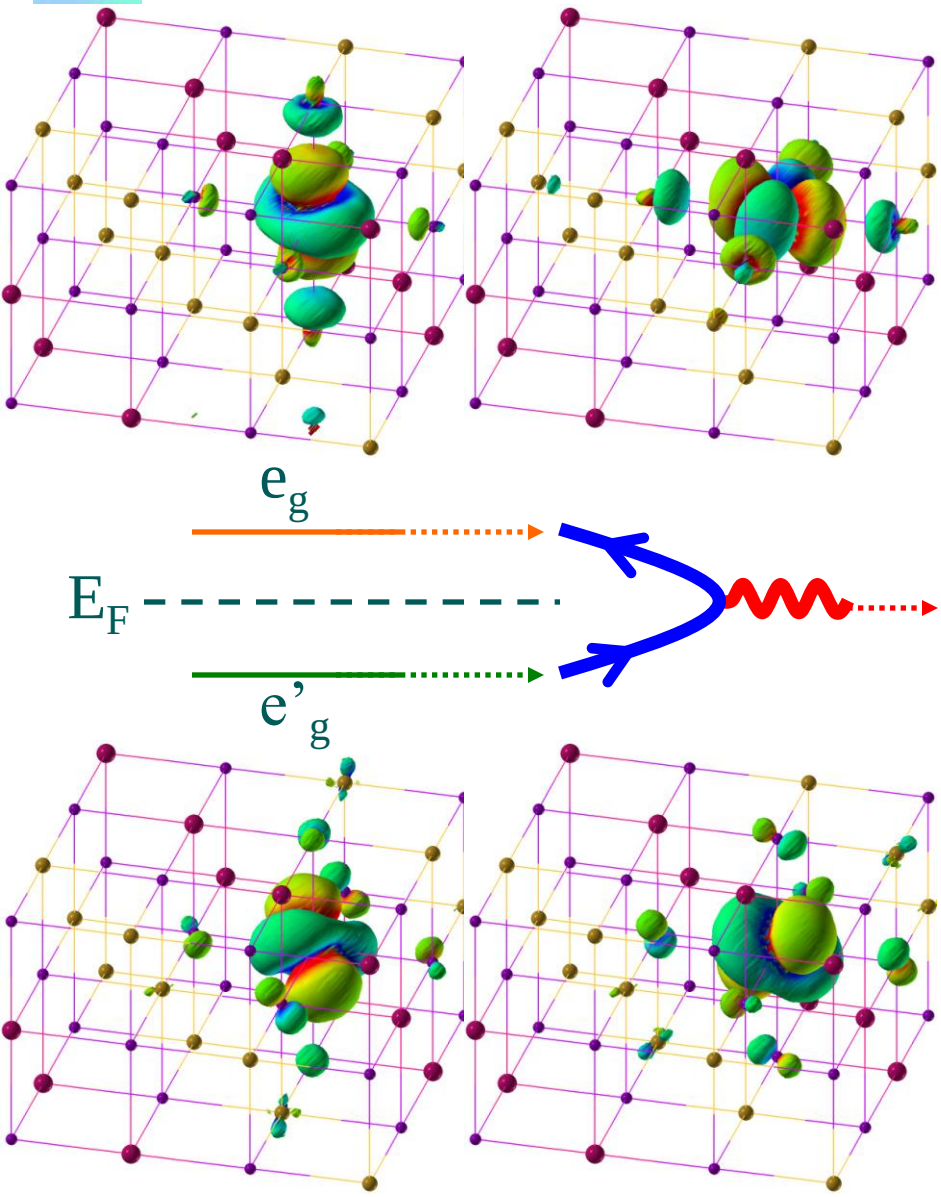
$e'_g\ 2 \propto \left(1-\sqrt{3}\right)yz + \left(1+\sqrt{3}\right)zx - 2xy$



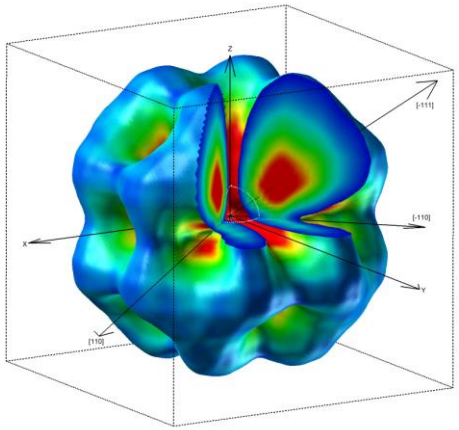
$$\chi\left(\mathbf{q},\mathbf{q}';w\right) = \sum_{11'} \left\langle 1\left| e^{-i\mathbf{q}\cdot\hat{\mathbf{x}}} \right| 1' \right\rangle \left\langle 1'\left| e^{i\mathbf{q}'\cdot\hat{\mathbf{x}}} \right| 1 \right\rangle L\left(1,1';1',1;w\right)$$

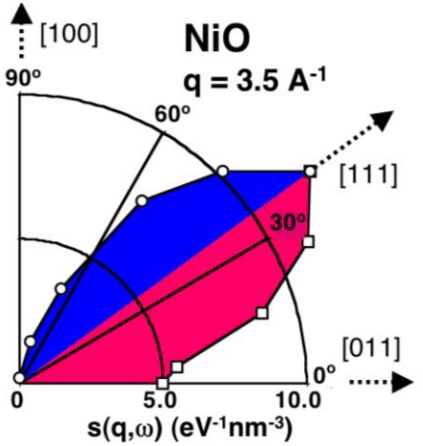
Local Excitations in NoO and CoO

Point group symmetry and new selection rules



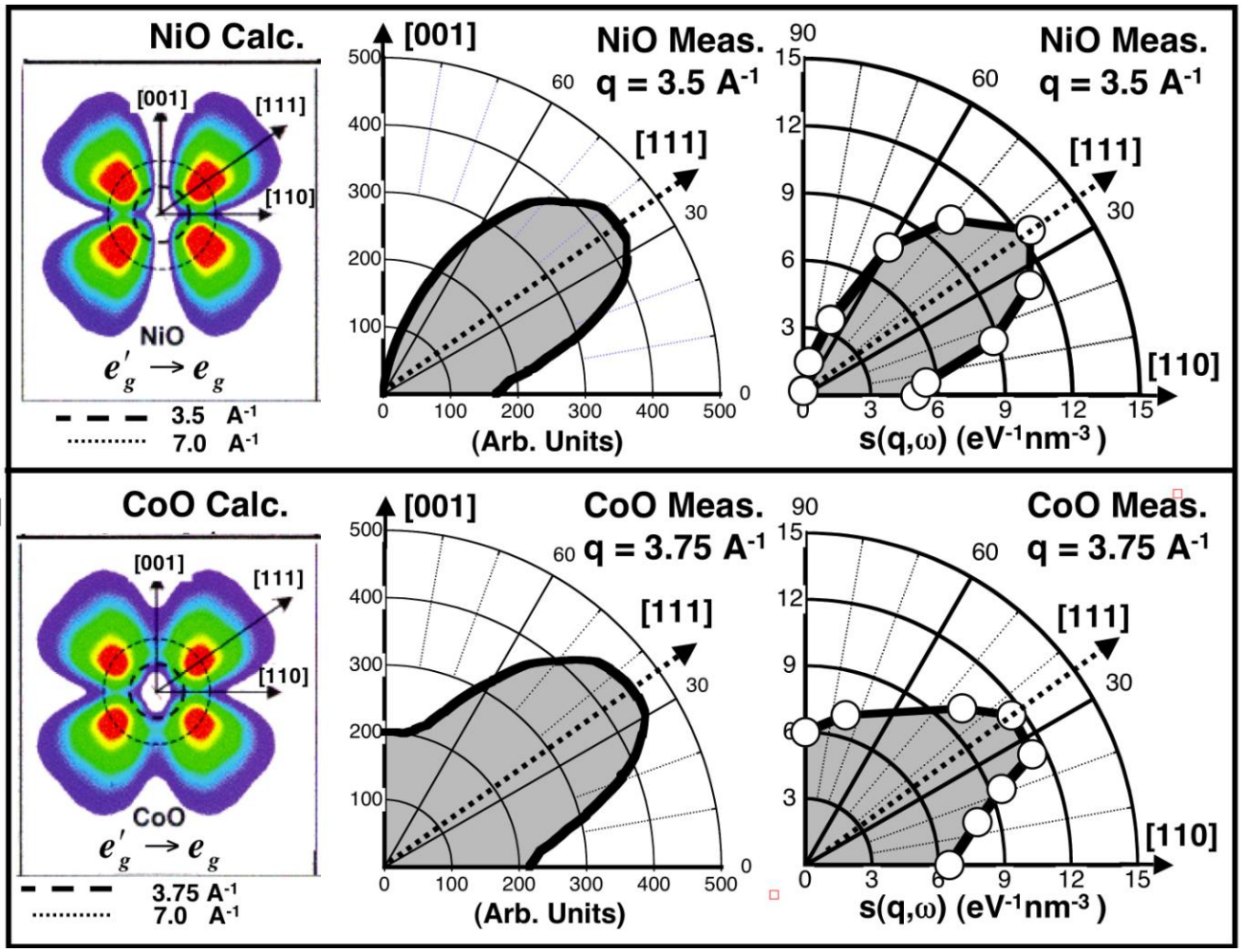
- Local cubic point group symmetry
  - → nodal directions
  - → new selection rules





Decoupling 6D exciton WF into sum over small number of pair of 3D WF

Angular Dependence of Local Excitations

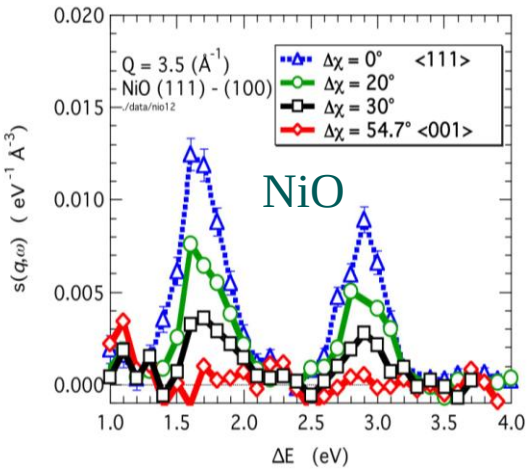


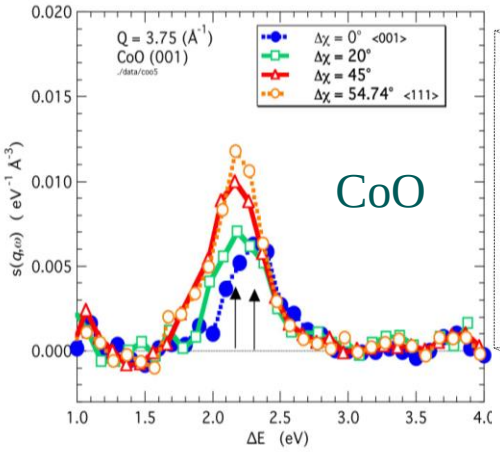
- Nodal direction ← point group symmetry
- Lack of [100] node in CoO → weak symmetry breaking

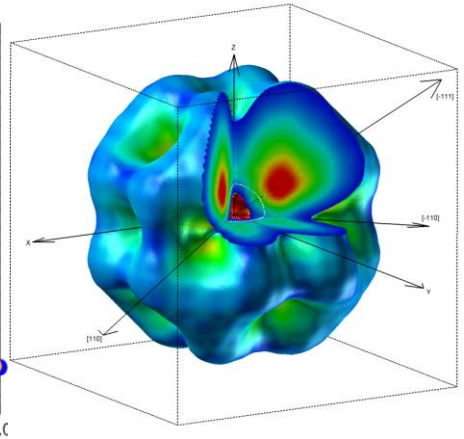
B. C. Larson, Wei Ku, Tischler, Chi-Cheng Lee, *et al.*, PRL **99**, 026401 (2007)

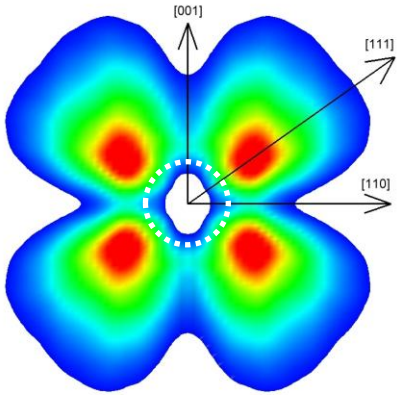
Local Excitations in NoO and CoO

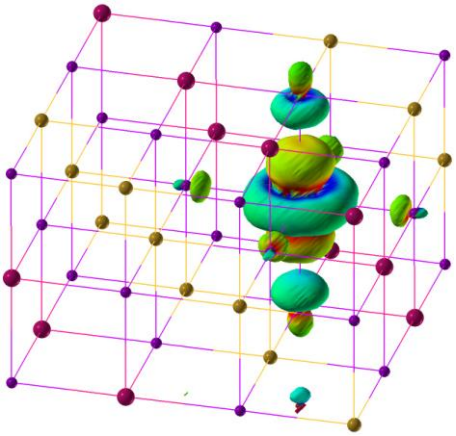
Sensitive probe of weak symmetry breaking



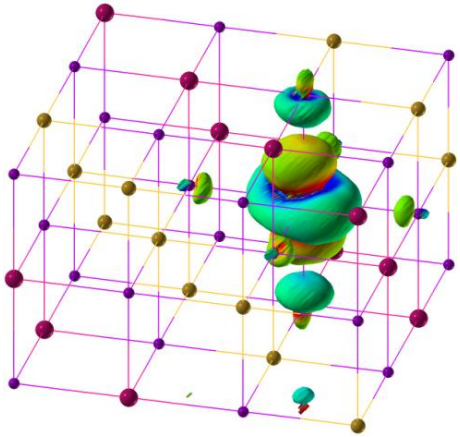




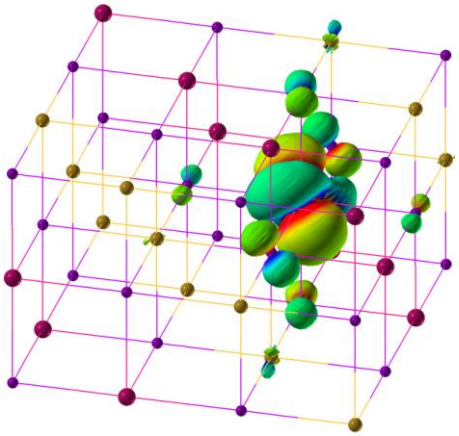




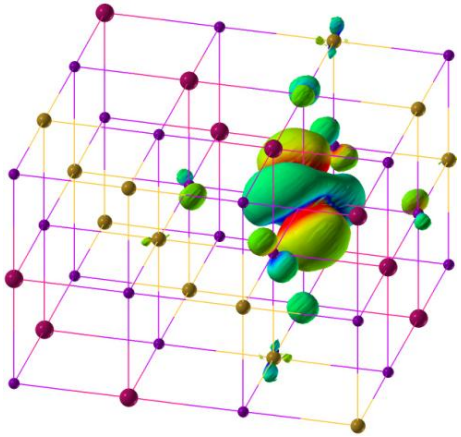
NiO



CoO



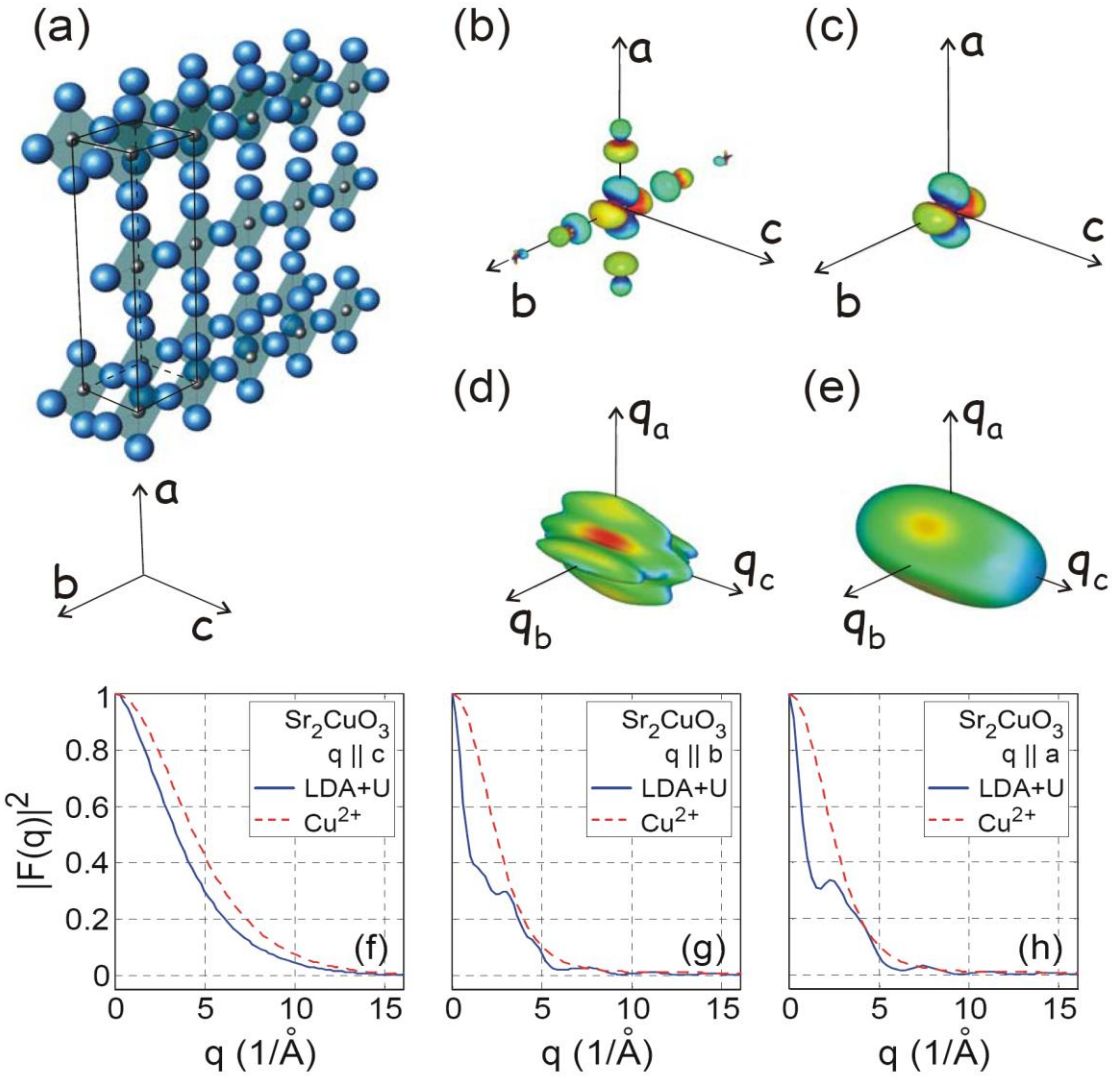
NiO



CoO

- Lost of nodal directions : extremely sensitive to weak symmetry breaking
- Visualization of symmetry breaking via Wannier functions

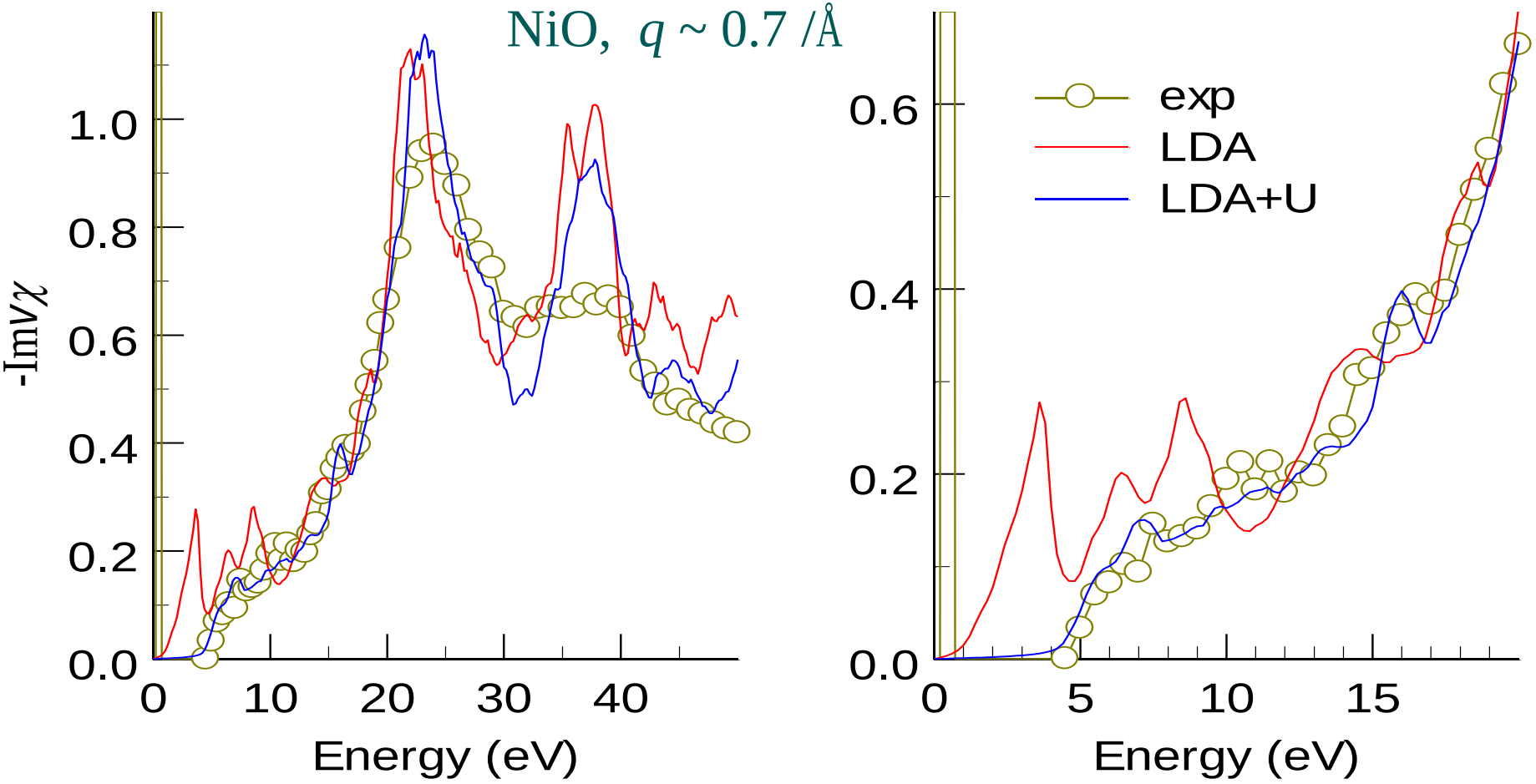
70% Missing Spectral Weight of INX in Cuprates



Igor Zaliznyak *et al*., Nature Physics 2009 (in print)

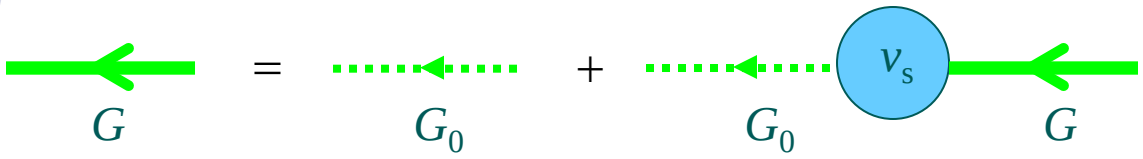
Charge Excitations in NoO and CoO

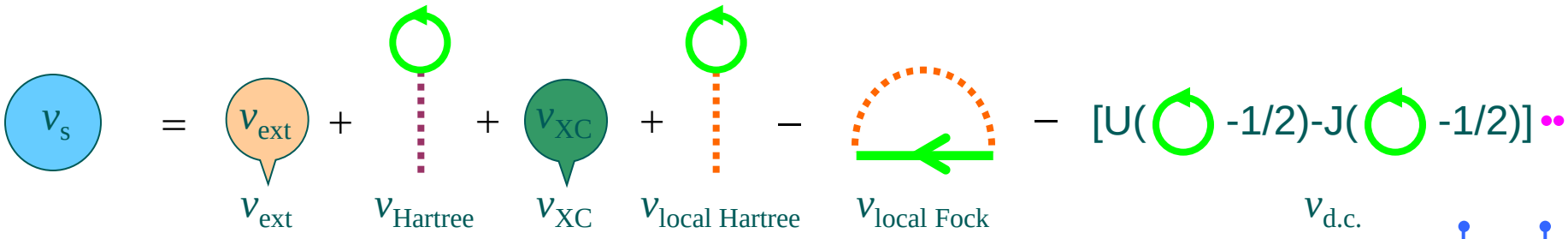
Small momentum transfer



- Small q → inter-site excitations
- LDA+U approximation greatly improves the gap and line shape
- Good agreement at small q in absolute unit

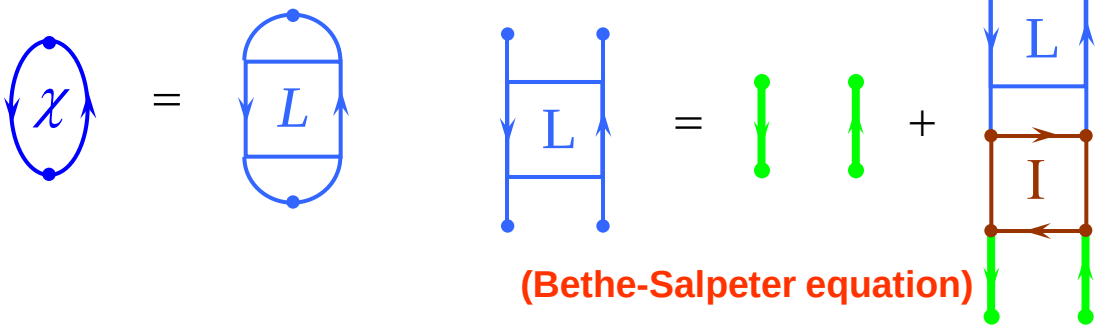
TDDFT via LDA+U Functional (TD-LDA+U)

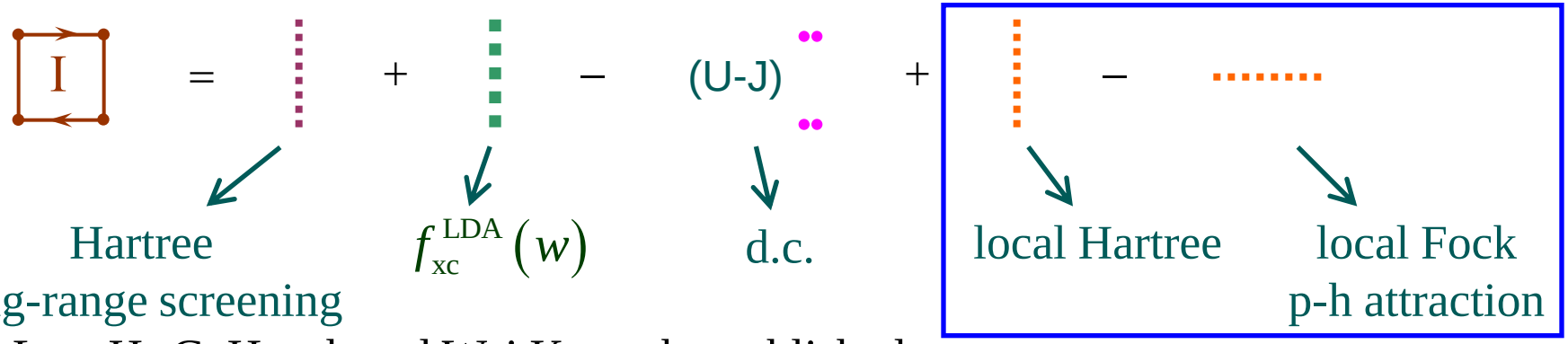




response function

$$L = \frac{\delta G}{\delta v_{ext}} = -G\frac{\delta G^{-1}}{\delta v_{ext}}G$$

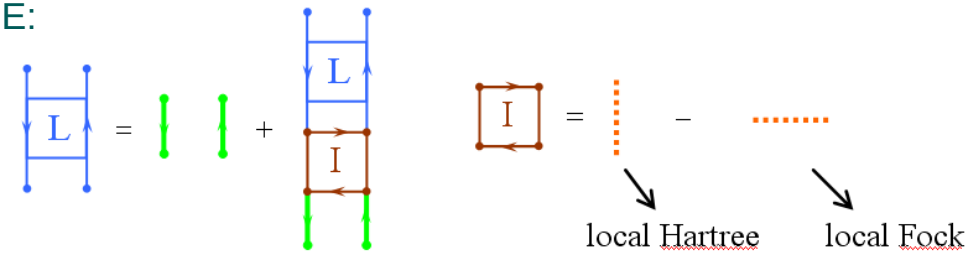




C.-C. Lee, H.-C. Hsueh and Wei Ku, to be published

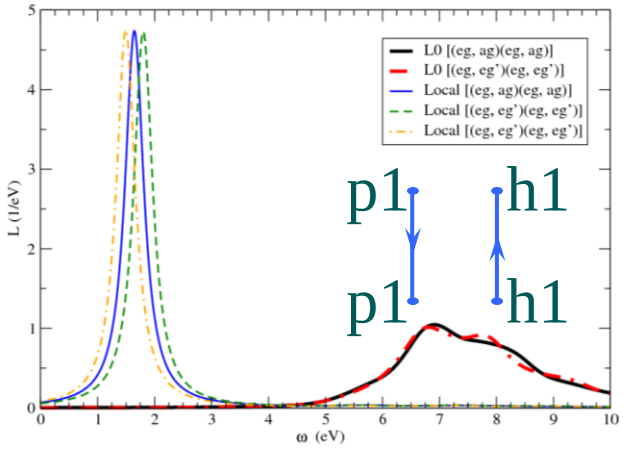
Formation of Frenkel Excitons in Local Picture

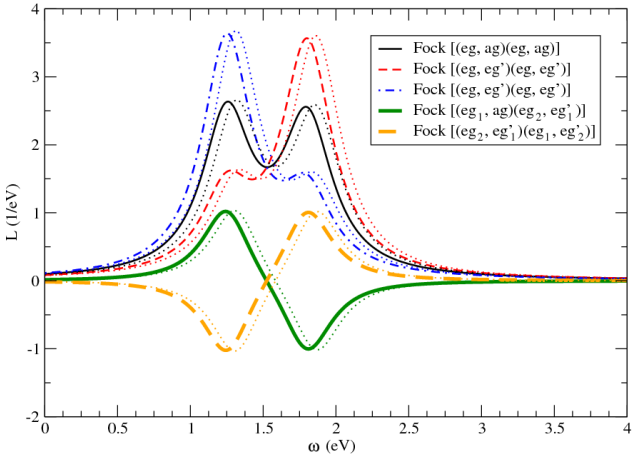
BSE:

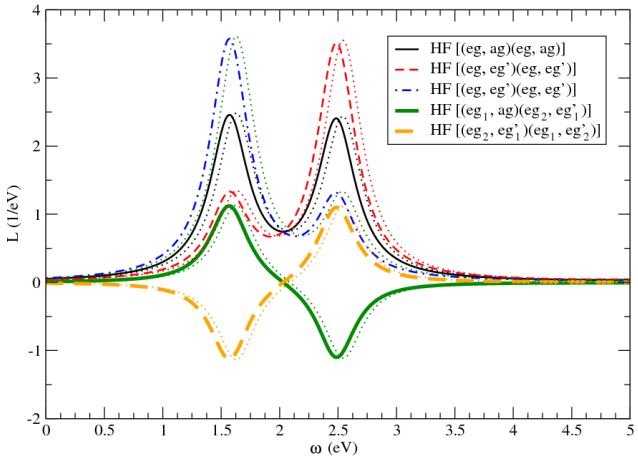


(Wannier basis, laptop done all the job)

bind energy ~ 8 eV







\+ p1 h1 / p1 h1 **binding**

same pair

p-h attraction

\+ p2 h2 / p1 h1 **scattering**

local Fock

\+ p1 h1 / p1 h1 **screening**

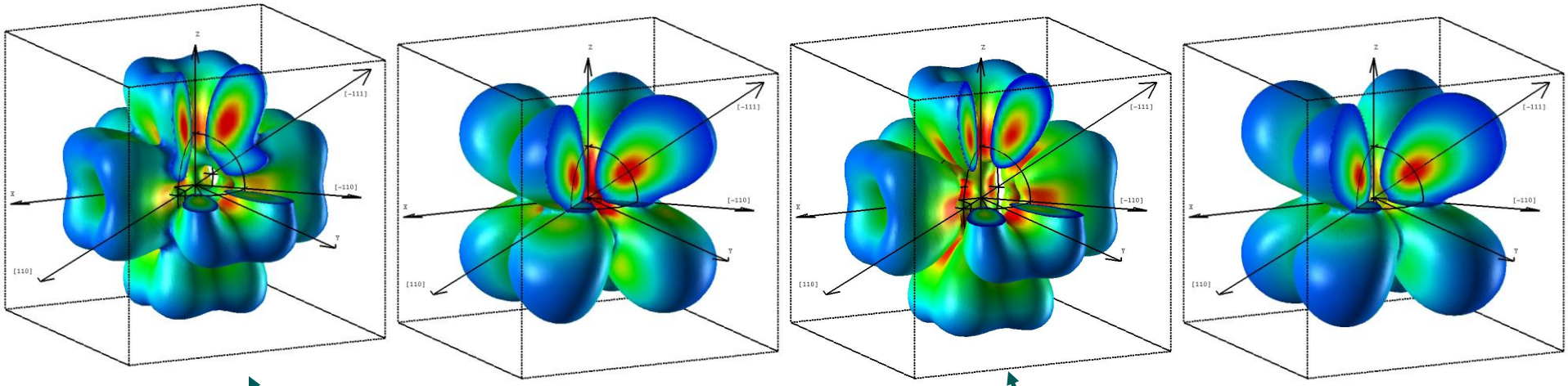
local Hartree

➔ Exciton energy in reasonable agreement with experiment

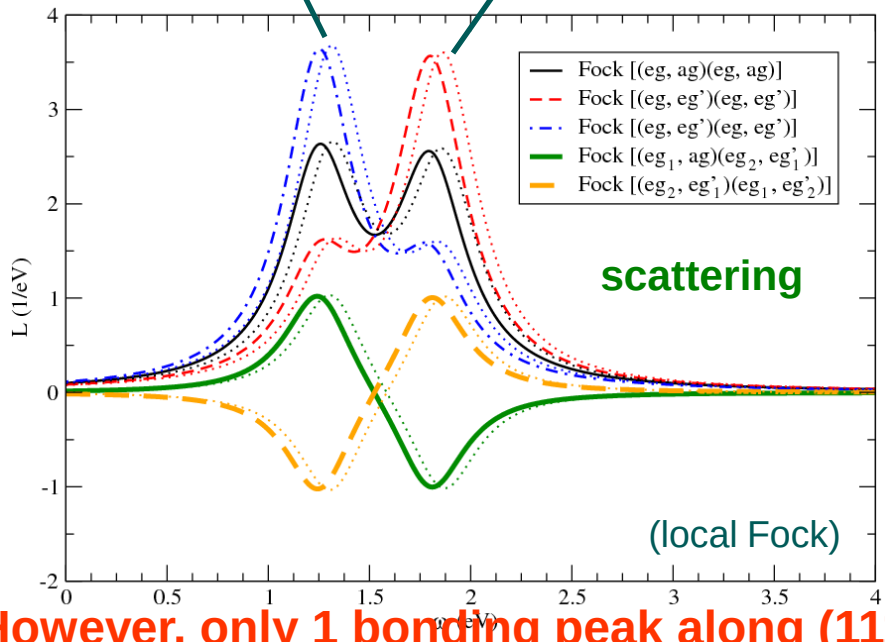
➔ Strongly hybridized Frenkel excitons

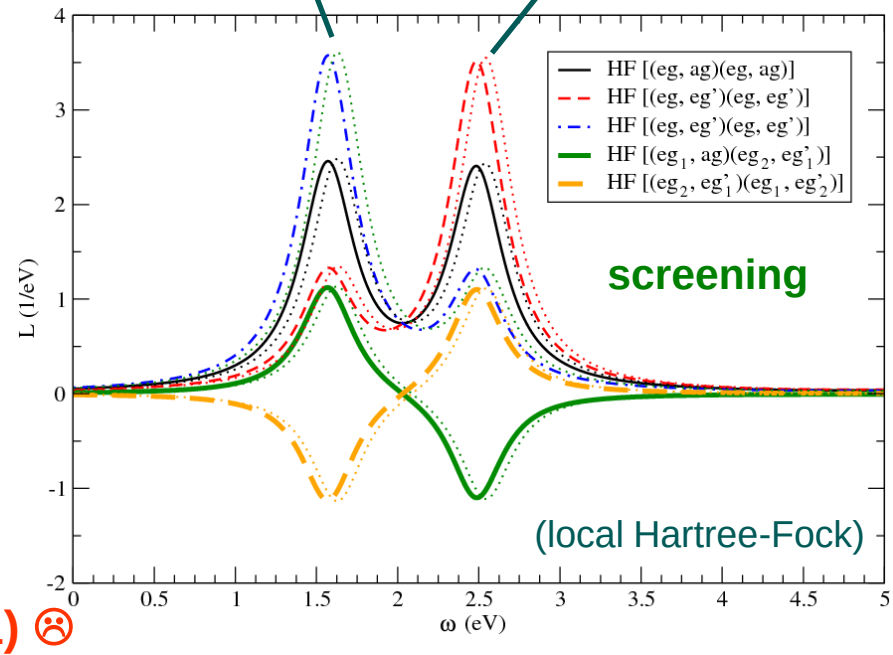
C.-C. Lee, H.-C. Hsueh and Wei Ku, to be published

Capability and Limitation of the Approximate Functional



(anti-bonding) (bonding) (anti-bonding) (bonding)





However, only 1 bonding peak along (111) ☹

← Generic problem in solving BSE with simple kernel or with QP approximation

Solving Local Interacting Problem Accurately

1. Map to an interacting Hamiltonian

   W.-G. Yin, D. Volja and Wei Ku, Phys. Rev. Lett. **96**, 116405 (2006).

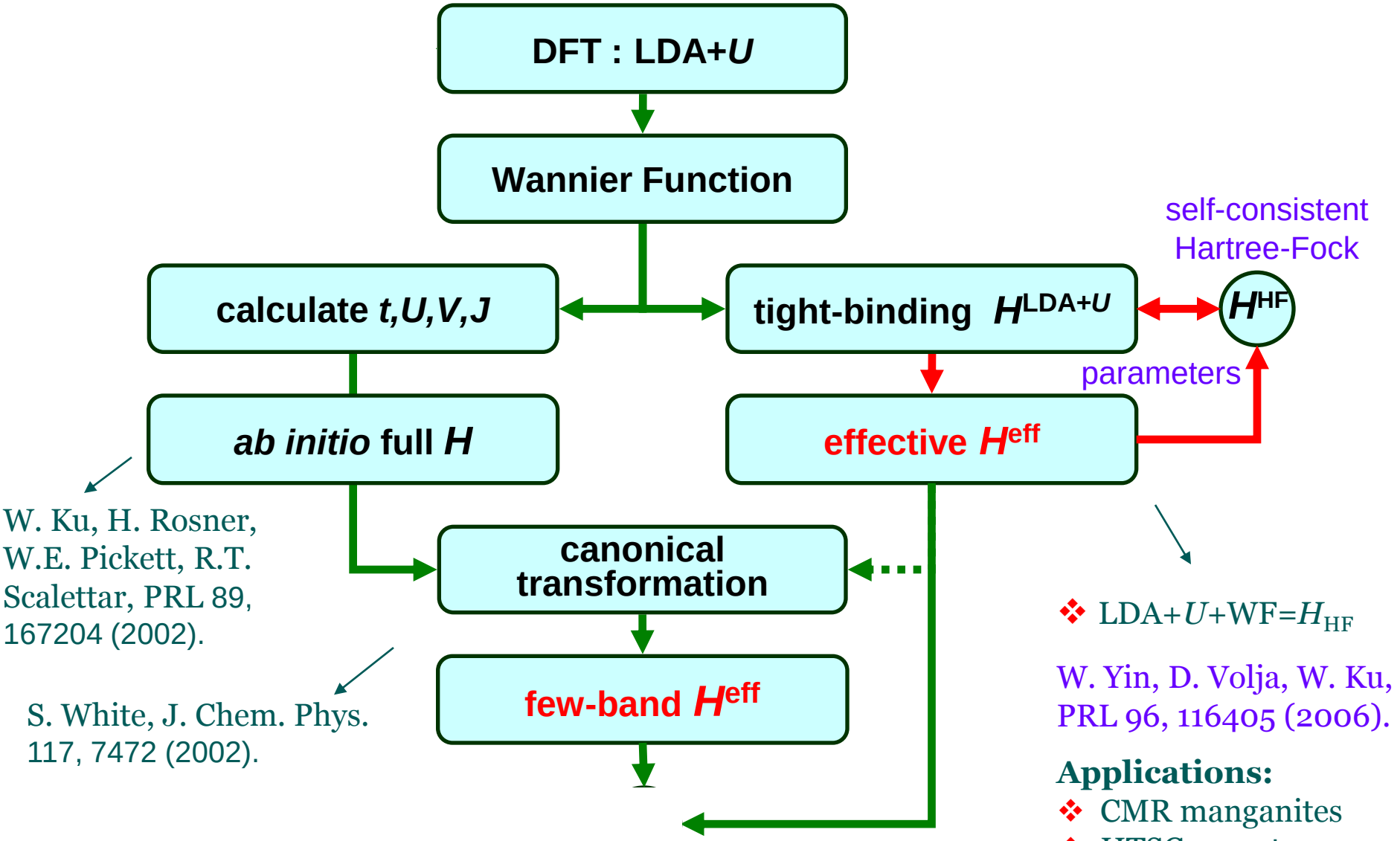
2. Solve local part exactly

3. Add non-local part via

   1) effective kinetic energy for the excitons

   2) extended Hubbard X-operator (powerful but demanding)

Direct mapping to effective Hamiltonian



W. Ku, H. Rosner, W.E. Pickett, R.T. Scalettar, PRL 89, 167204 (2002).

S. White, J. Chem. Phys. 117, 7472 (2002).

- LDA+U+WF=H_{HF}

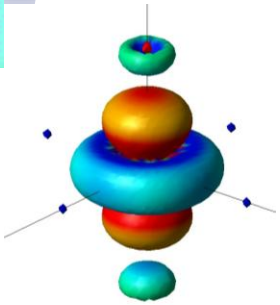
W. Yin, D. Volja, W. Ku, PRL 96, 116405 (2006).

Applications:

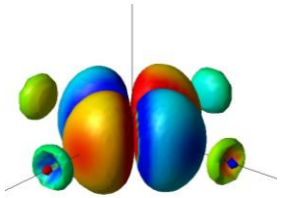
- CMR manganites
- HTSC cuprates

Super Atom for Charge Transfer Insulator

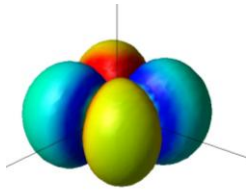
Ni



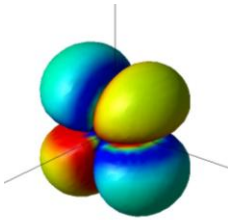
$3z^2 - r^2$



$\sqrt{3}(x^2 - y^2)$



xy



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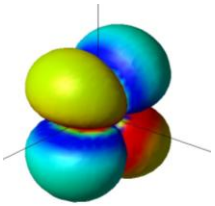
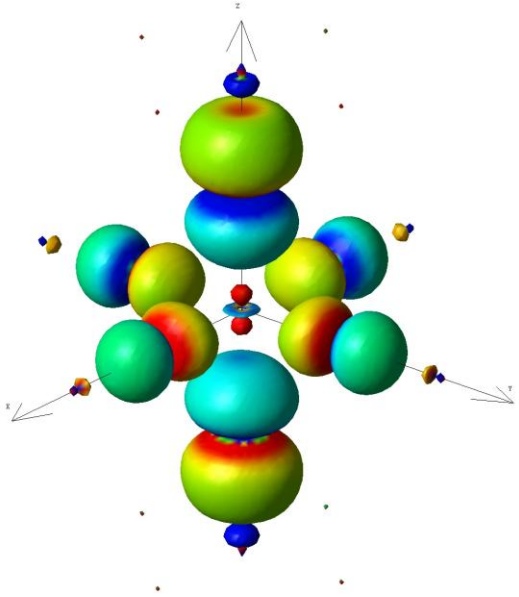
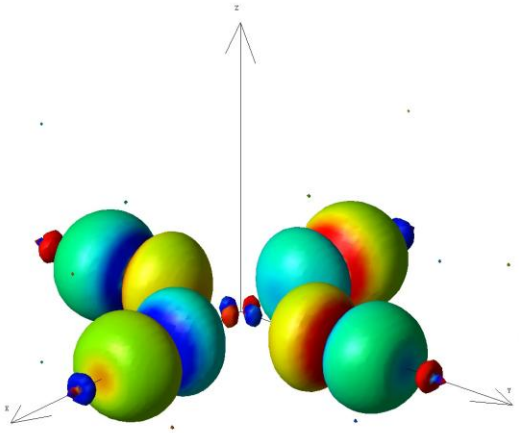


xz

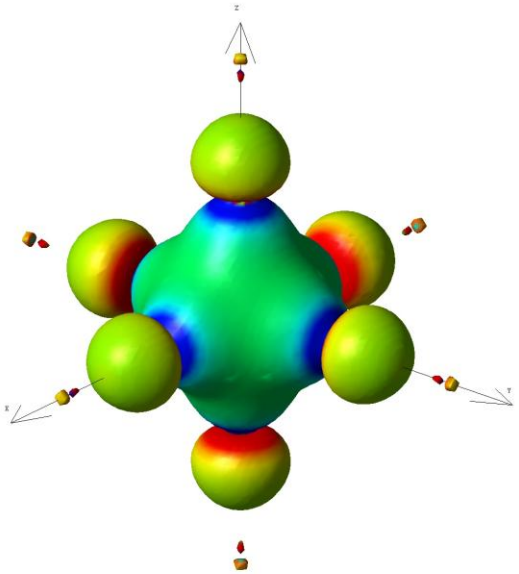
O



$3z^2 - r^2$



$\sqrt{3}(x^2 - y^2)$



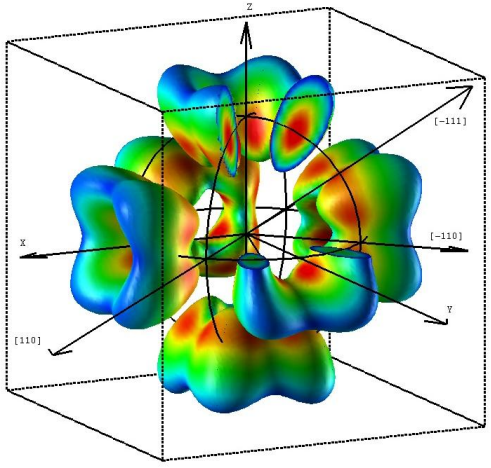
s wave

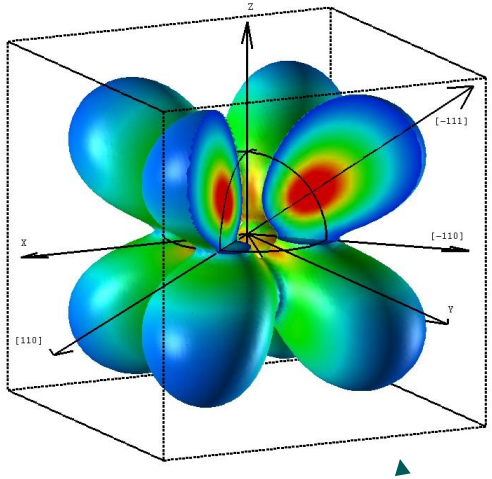
$$H = H_{local} + H_{nonlocal}$$

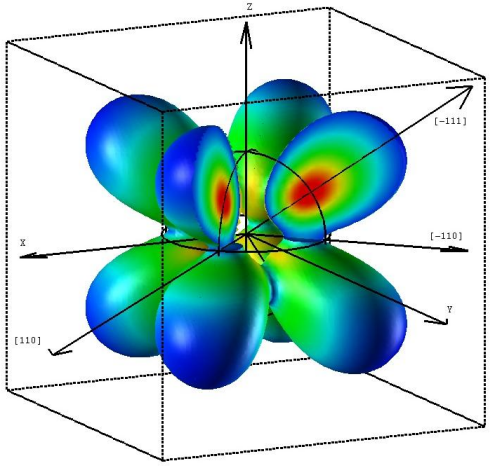
(exact) **(modification)**

Maximize the contributions of “local atom”

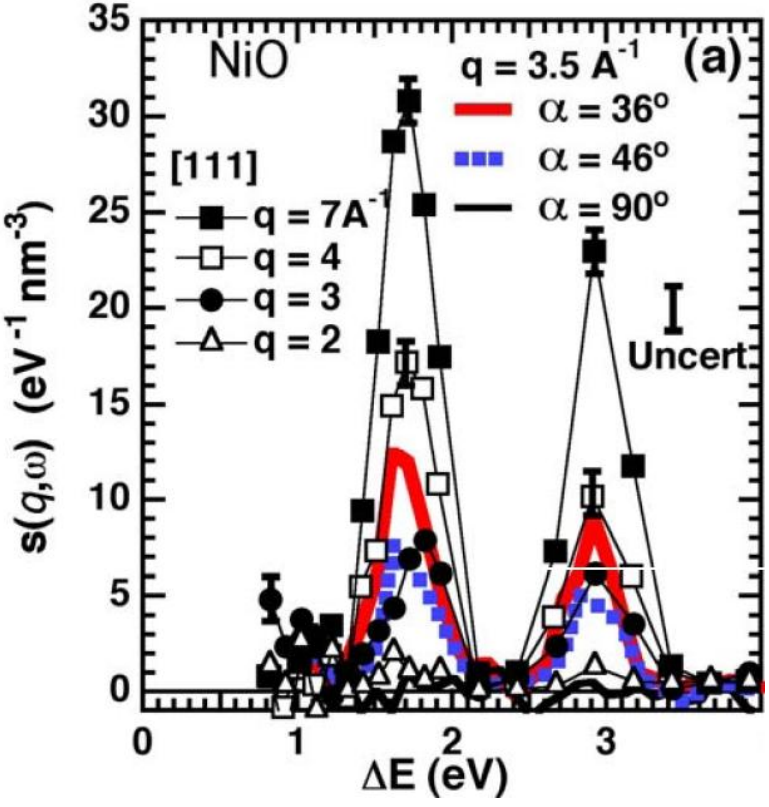
Density response for super atom (eg-t2g=0.65eV)

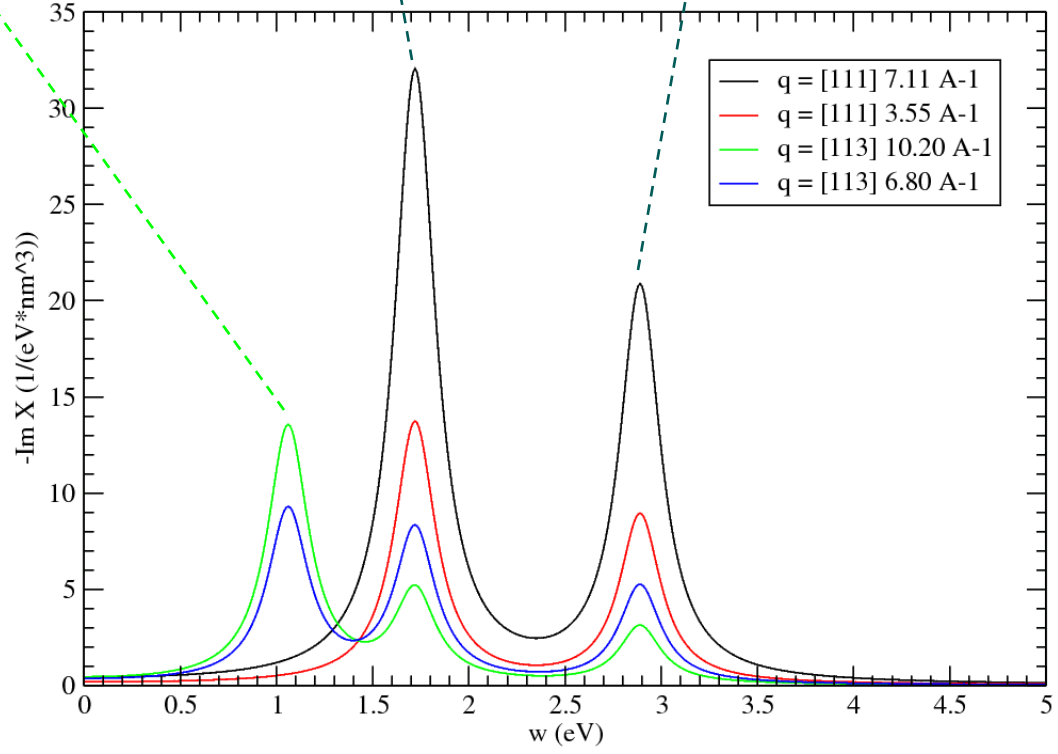






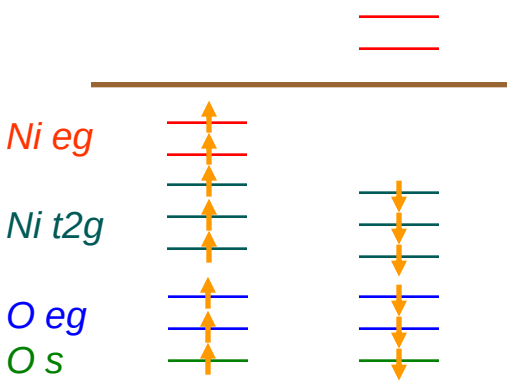
(antibonding-type)



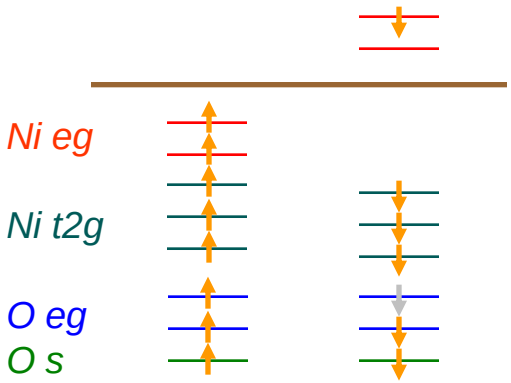


Multiplet Splitting Made Possible with MB Hilbert Space

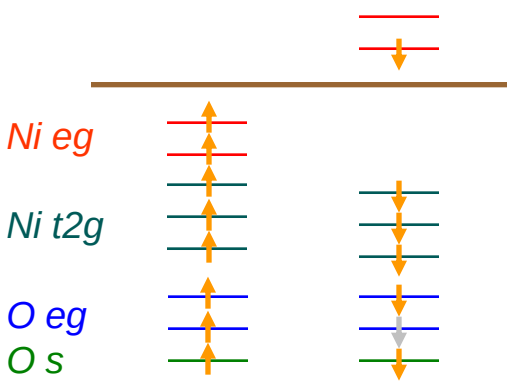
GS



(0.9484)

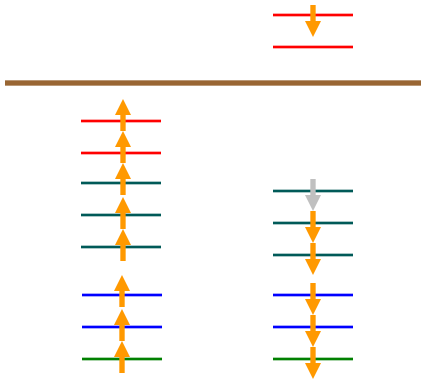


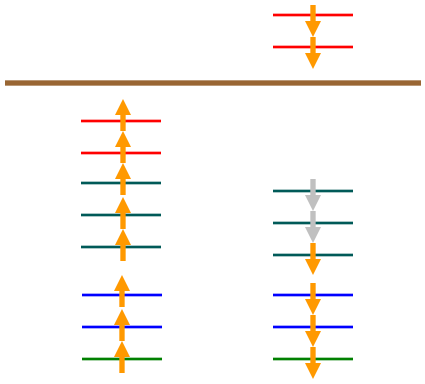
(-0.2226)

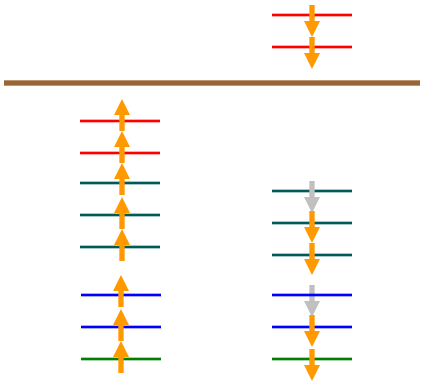


(0.2226)

T_{1g}







Summary

- Recent X-ray experiments
  - Sort wave length → sensitivity to local excitations
  - Strong anisotropy → sensitivity to orbitals orientation
- Strong local interaction & short-range correlation
  → Local approach
- Defining "local" in a crystal with "natural" symmetry
  → Symmetric Wannier functions
- Simple understanding of anisotropy from local picture
  → Single p-h pair (Frenkel exciton within super atom)
- 70% missing spectral weight in INS
- Treating local problem via TDDFT: TD-LDA+*U*
  - Easy visualization of physics, good energy scale
  - Generic limitation of adiabatic approximation of current *ab initio* approx.
- Treating local problem beyond perturbation
- Propagation of local excitations
  → p-h kinetic kernel