Connecting real materials to low-energy effective Hamiltonian: applications of symmetry-respecting Wannier functions

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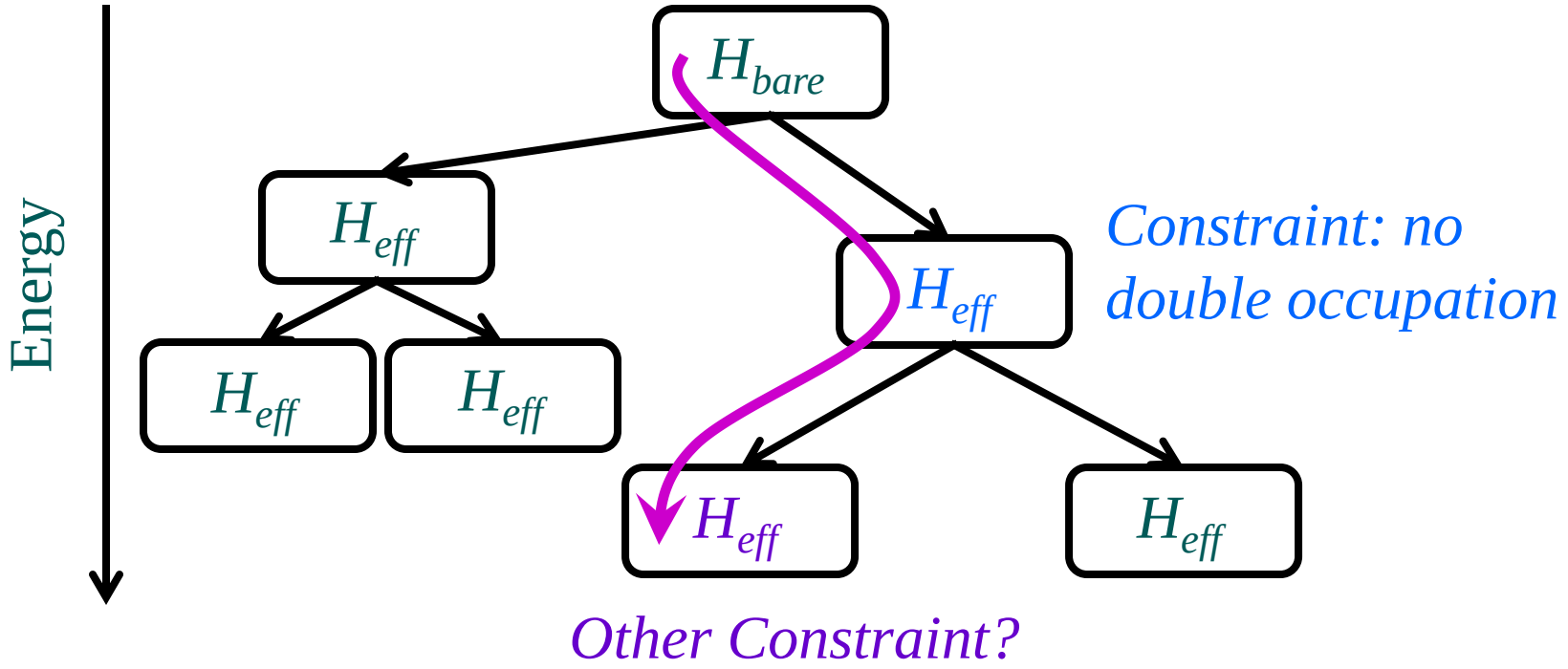
Outlines

- Simple illustrations:
  - Orbital order in $LaMnO_3$
  - Gapless CDW in $TaSe_2$
  - Ferro-orbital order in Fe-SCs
- Interacting problems:
  - Local excitations
  - Propagation and decay of local excitations
- Effects of disordered impurities in Fe-SCs:
  - Substitution of Fe: doping or not?
  - Fe vacancy: “violation” of Luttinger theorem
  - Ru substitution: realization of superdiffusion

RG perspective: bifurcation of many-body systems

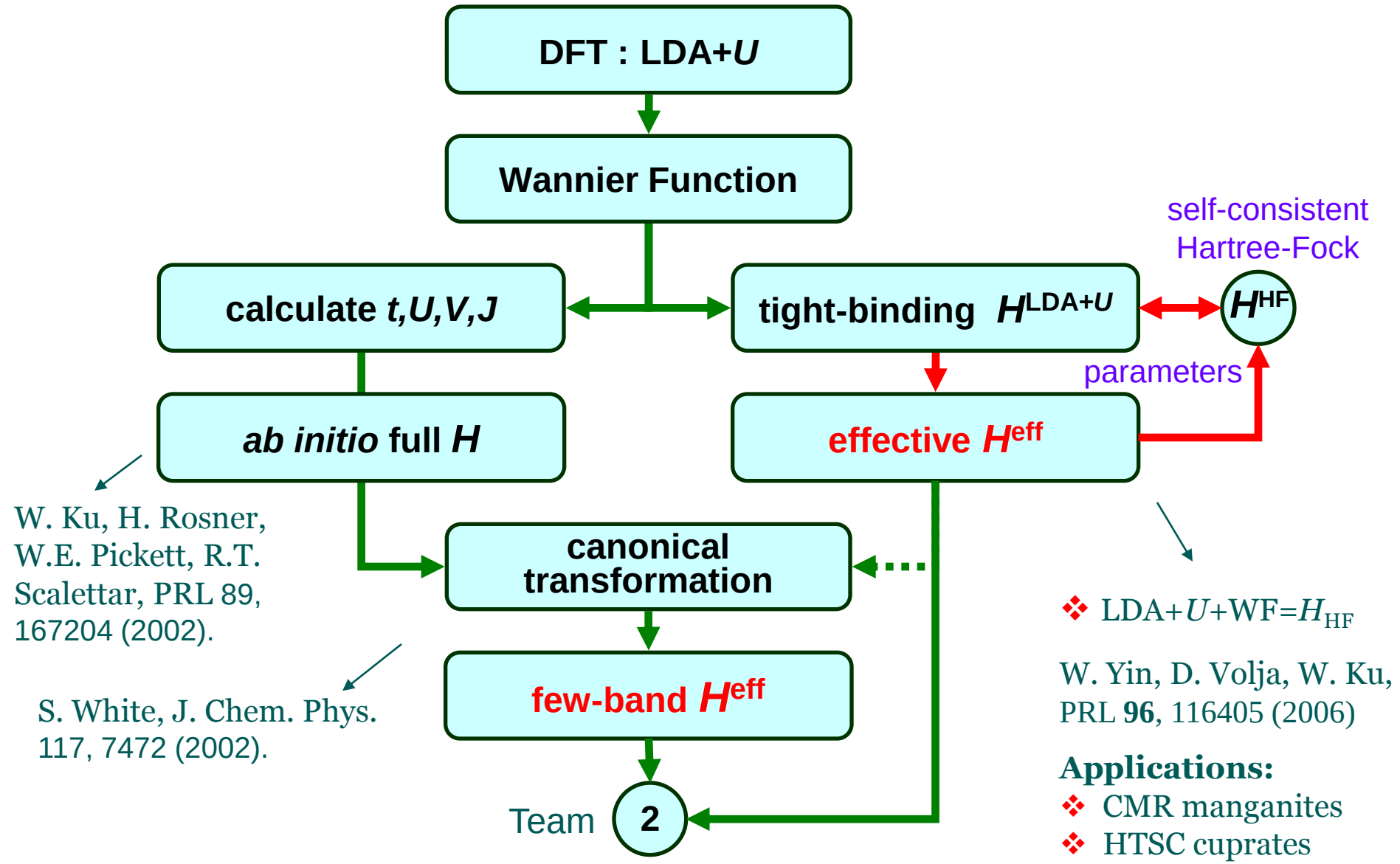


- Lagrangian: integrate out high-energy sectors

vs.

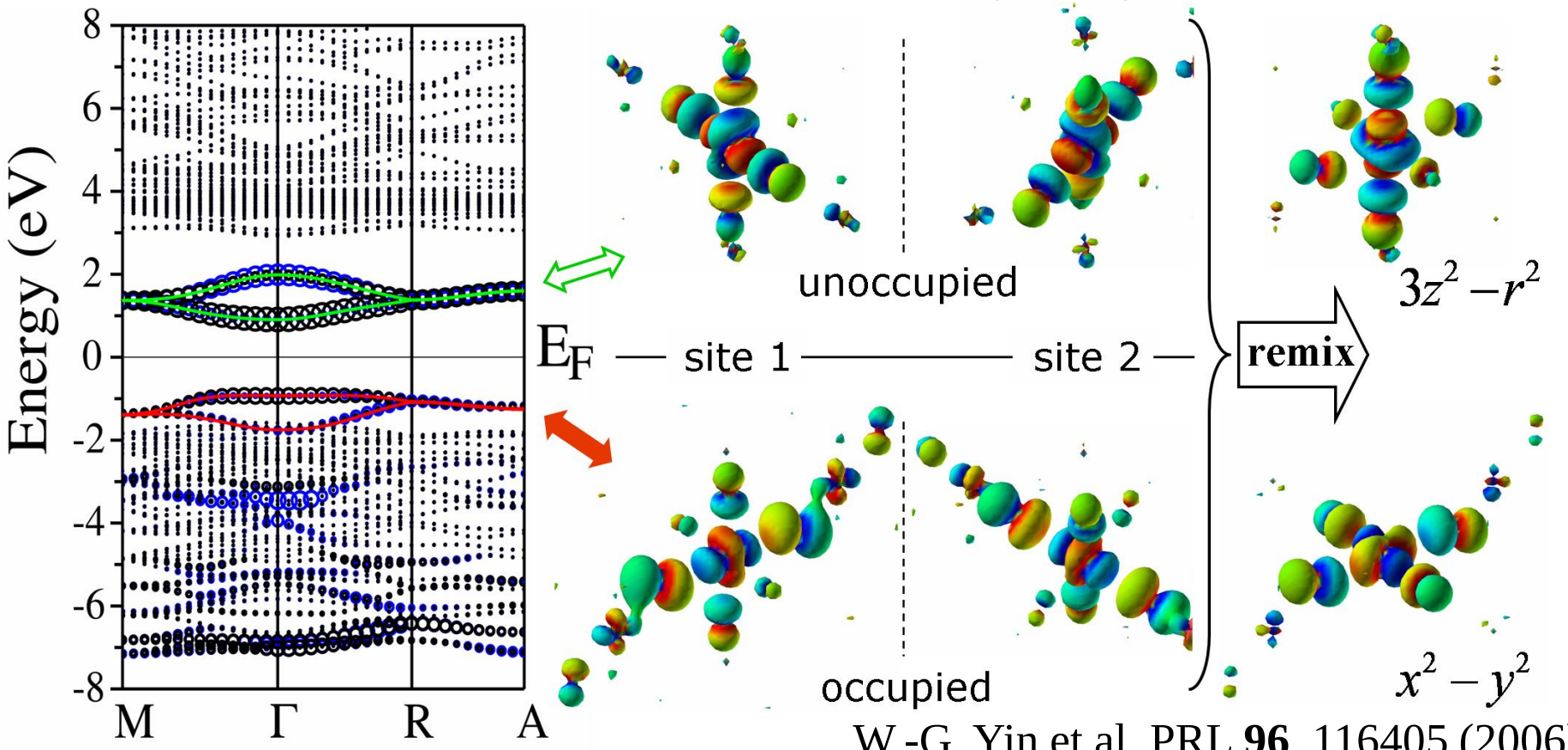
- Hamiltonian: block diagonalize low-energy sctors

Direct mapping to effective Hamiltonian



Orbital Ordering in $LaMnO_3$

e-e vs. e-l interactions & effective many-body H^{eff}



W.-G. Yin et al, PRL **96**, 116405 (2006)

- Large O component → nature of charge transfer gap
- Systematic study of e-e vs. e-l interactions in ordering orbitals

$$H = \sum_{\langle ij\rangle \gamma\gamma'} t_{ij}^{\gamma\gamma'} d_{j\gamma'}^{\dagger} d_{i\gamma} - g\sum_i \vec{T}_i \cdot \vec{Q}_i + \frac{K}{2}\sum_i \vec{Q}_i \cdot \vec{Q}_i + U_{\text{eff}} \sum_i n_{i\uparrow} n_{i\downarrow} - E_z \sum_i T_i^z .$$

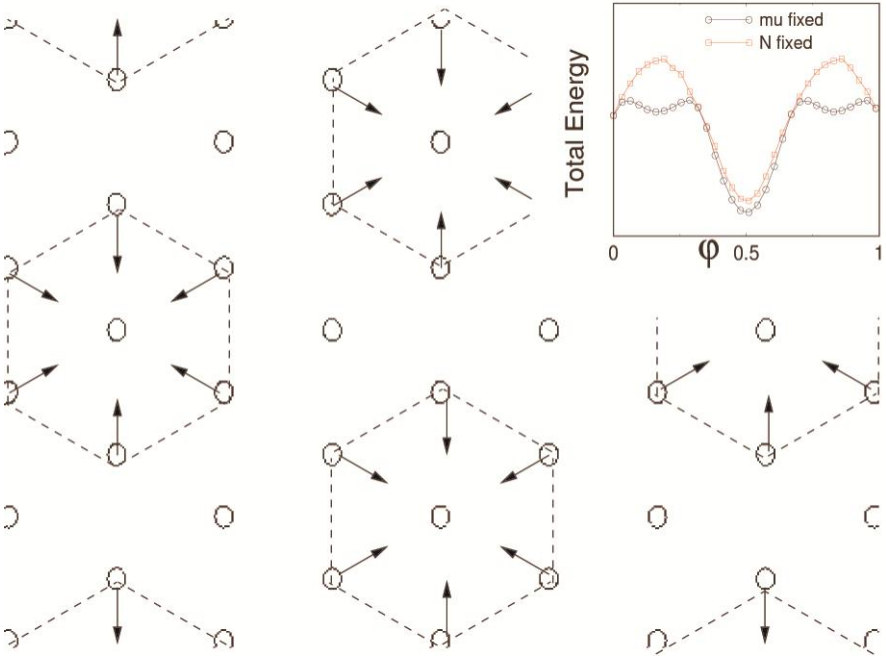
pseudo-spin: $T_i^z = \frac{1}{2}(d_{i\uparrow}^{\dagger} d_{i\uparrow} - d_{i\downarrow}^{\dagger} d_{i\downarrow}),\ T_i^x = \frac{1}{2}(d_{i\uparrow}^{\dagger} d_{i\downarrow} + d_{i\downarrow}^{\dagger} d_{i\uparrow}).$

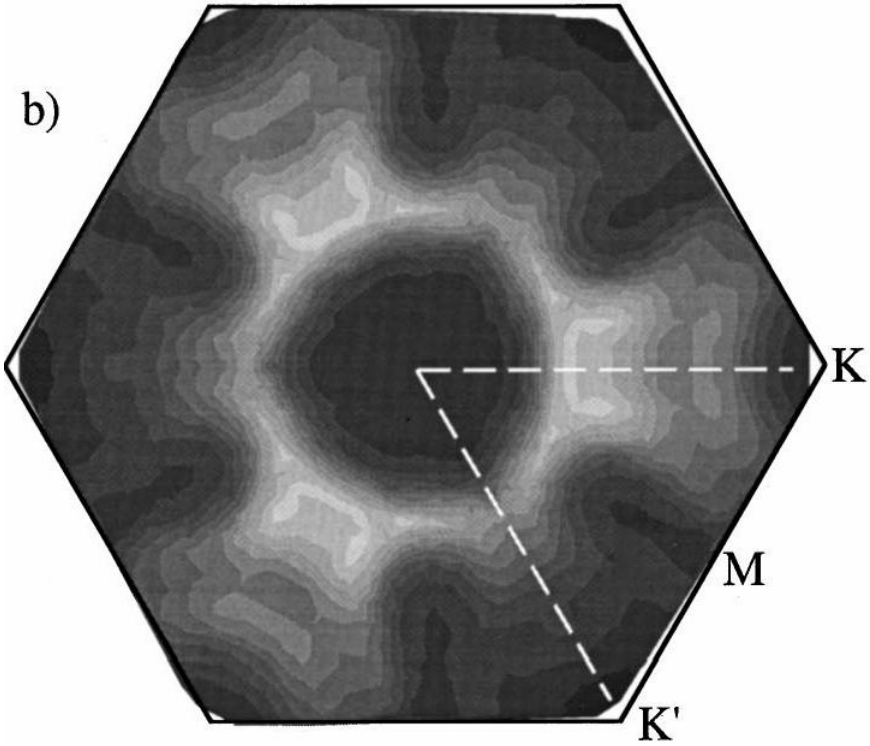
Gapless charge density wave in $TaSe_2$

R. L. Barnett, A. P., E. Demler, W.-G. Yin, and Wei Ku

Phys. Rev. Lett. **96**, 026406 (2006)

Gapless Charge-Density Wave in $TaSe_2$

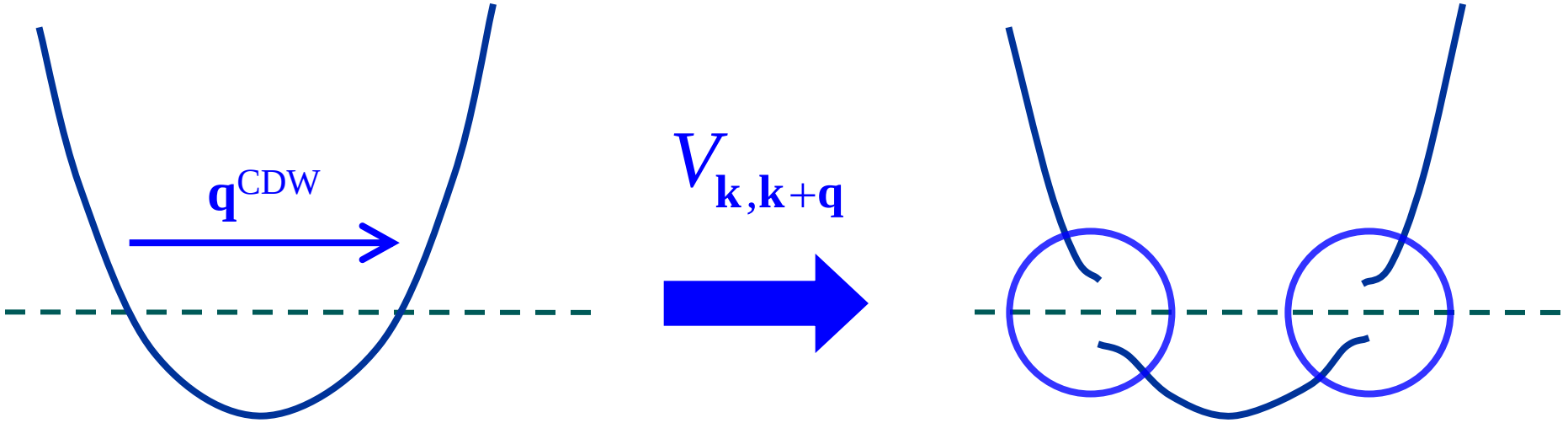




- commensurate CDW
- gapless excitations throughout the whole Fermi surface in CDW phase ?
- Fermi surface Nesting vector too large for q^{CDW} ?

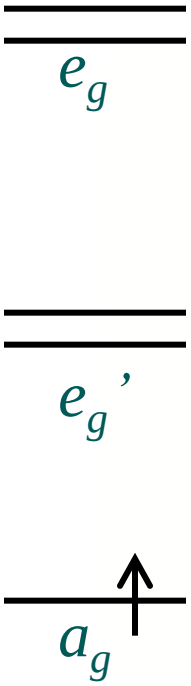
R. Liu, et. al. Phys. Rev. B, 5212 (2000)

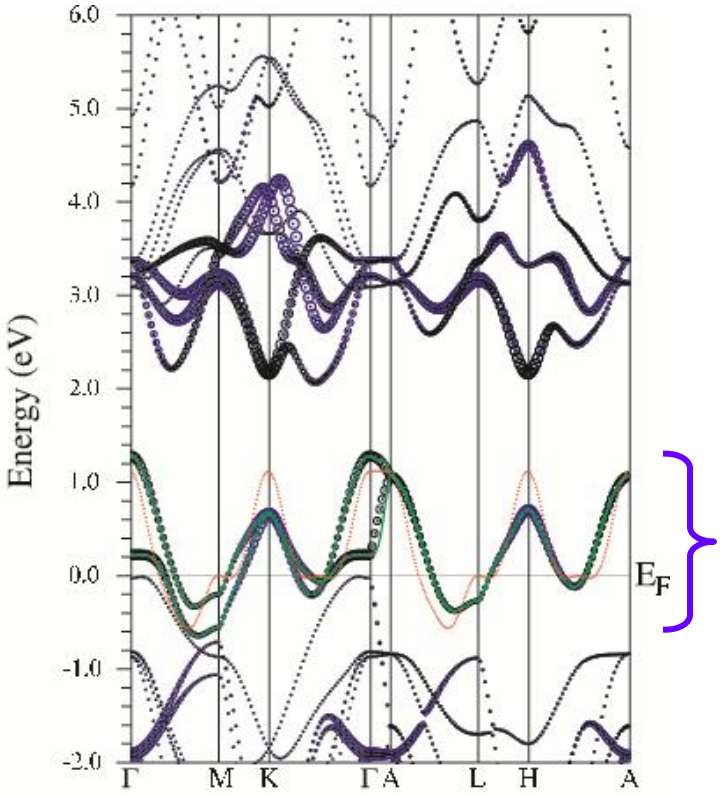
Conventional gapped CDW picture

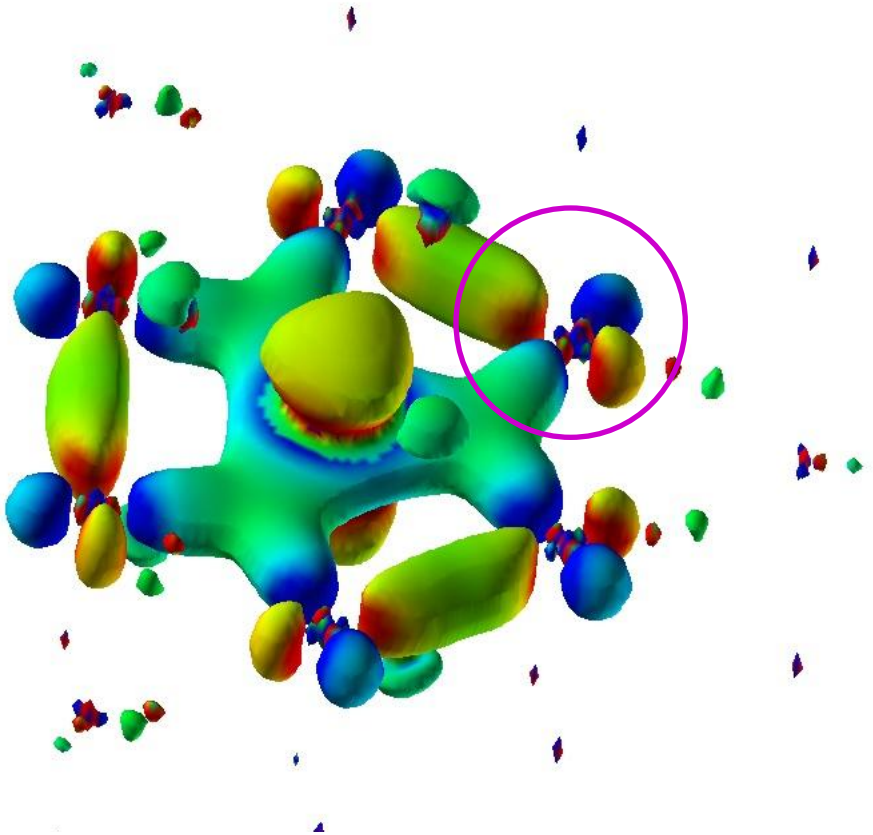


- Fermi surface instability
  - → divergent $\chi\left(\mathbf{q}^{\mathrm{CDW}}, \omega \to 0\right)$
  - → nesting preferred
- gap → energy gain

Local Picture: Low-Energy Wannier Function







- $3z^2 – r^2$ (a_g) symmetry near EF, noticeable hybridization with e_g'
- WS in one site contains complete information of the full k-space
- center: a_g symmetry; tail: e_g' symmetry

Surprising Hopping Path

$$t^{DFT}_{Rn,R'n'} = \left\langle Rn \left| h^{DFT} \right| R'n' \right\rangle$$

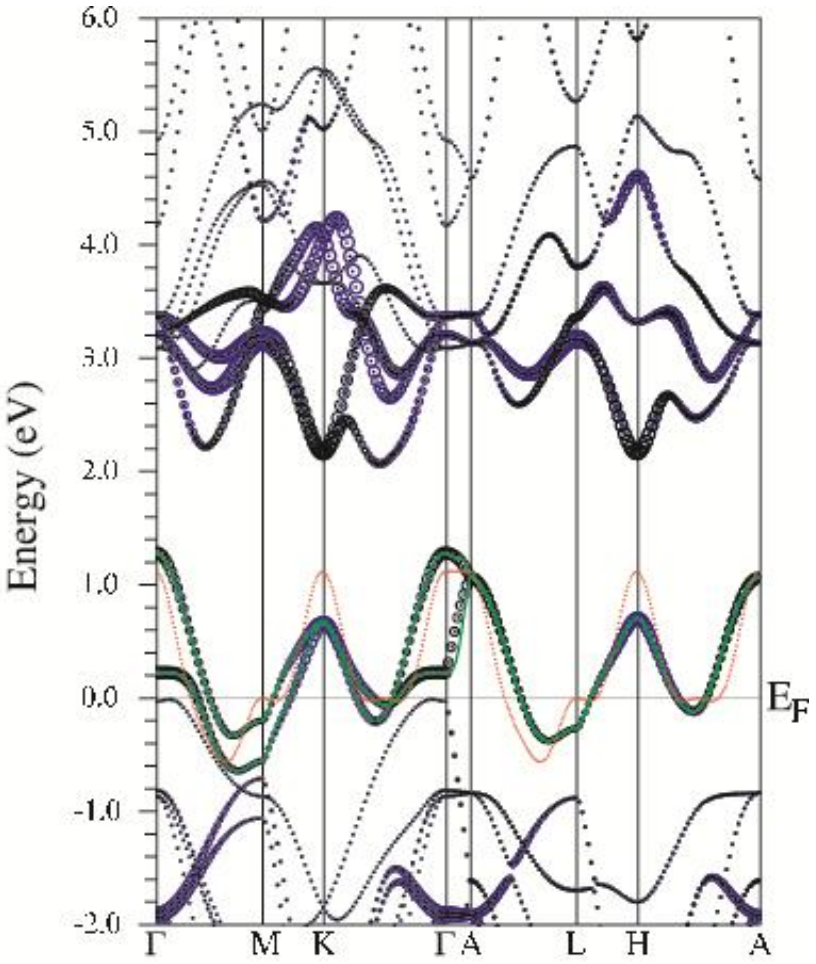
$$t_1 = 38\,(\text{meV})$$

$$t_2 = 115\,(\text{meV})$$

$$t_{\perp,1} = 29\,(\text{meV})$$

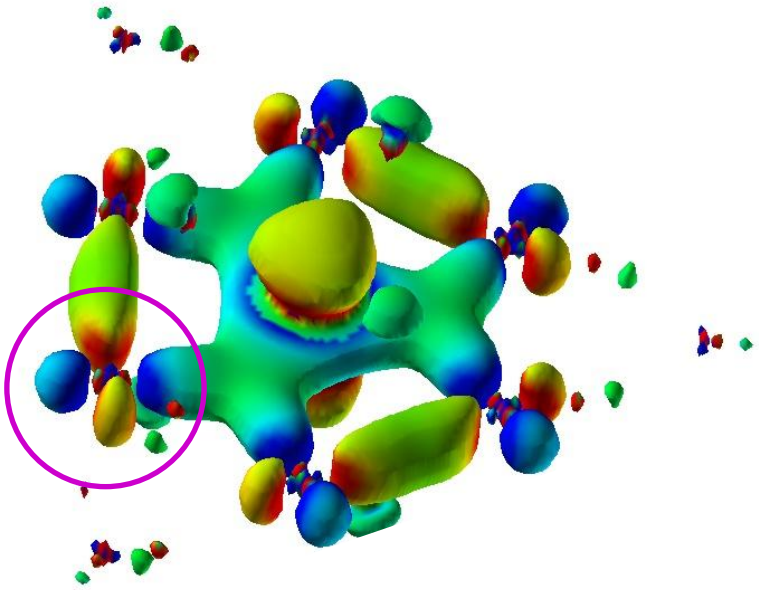
$$t_{\perp,2} = 23\,(\text{meV})$$

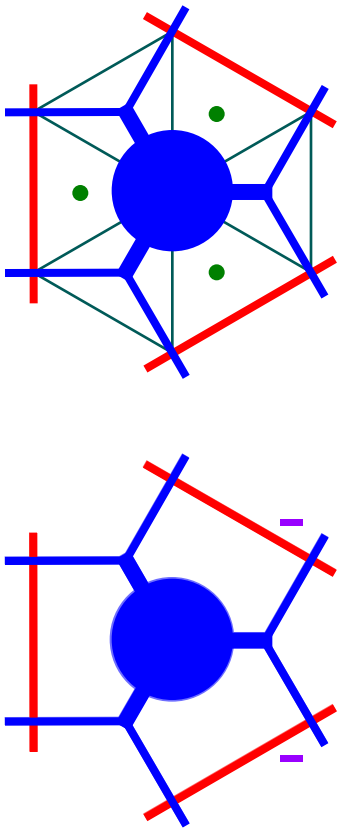
$$t_2 \gg t_1 !$$



- perfect tight-binding “fit” to the band structure
- surprising hopping strength to 2nd nearest neighbors

Why $t_2 >> t_1$?

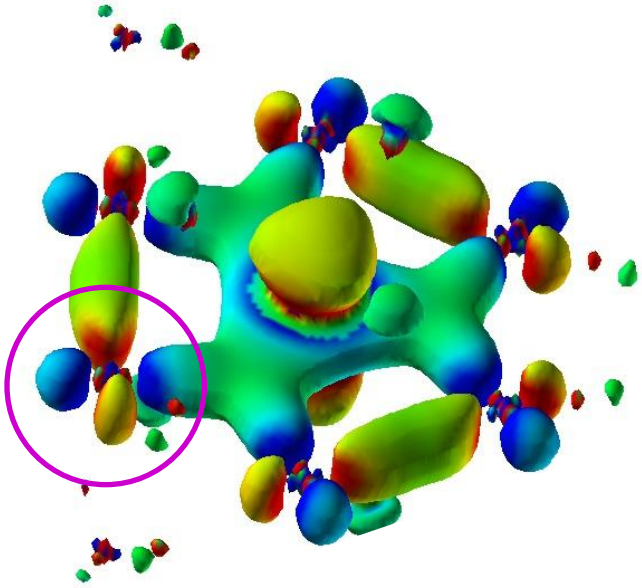


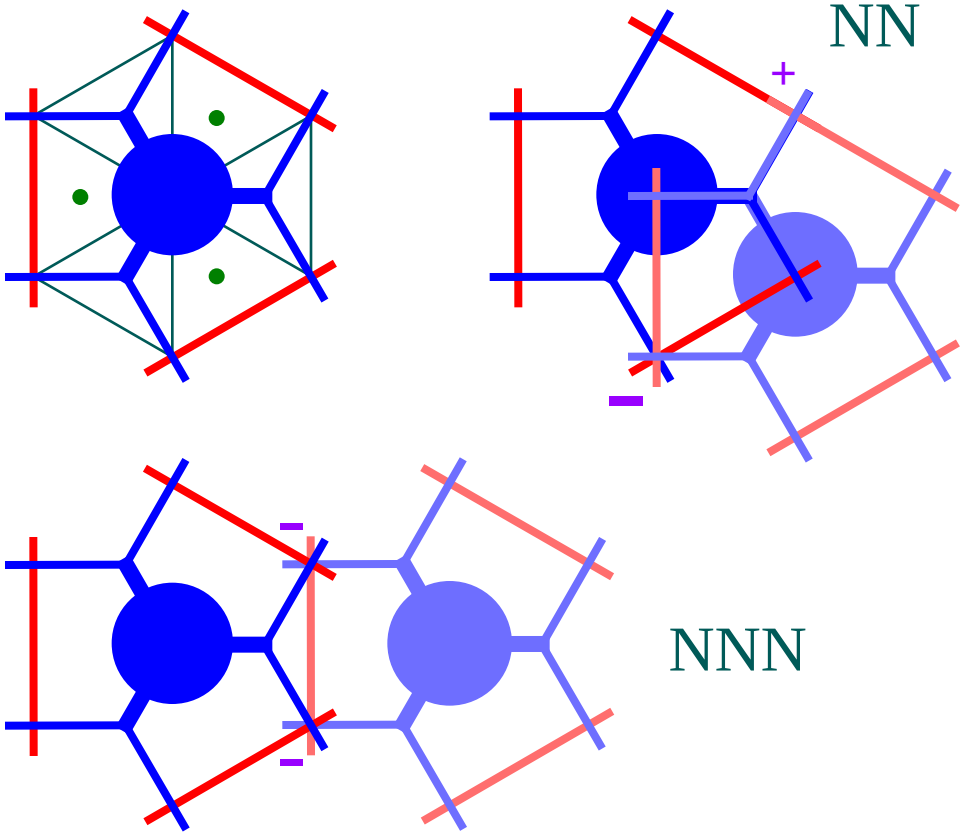


NN

NNN

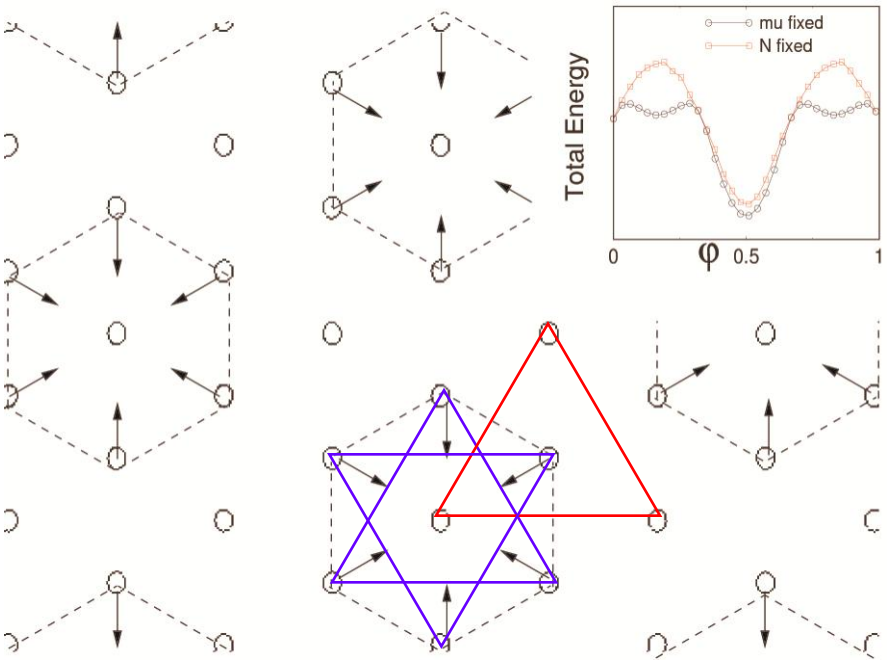
Why $t_2 >> t_1$?

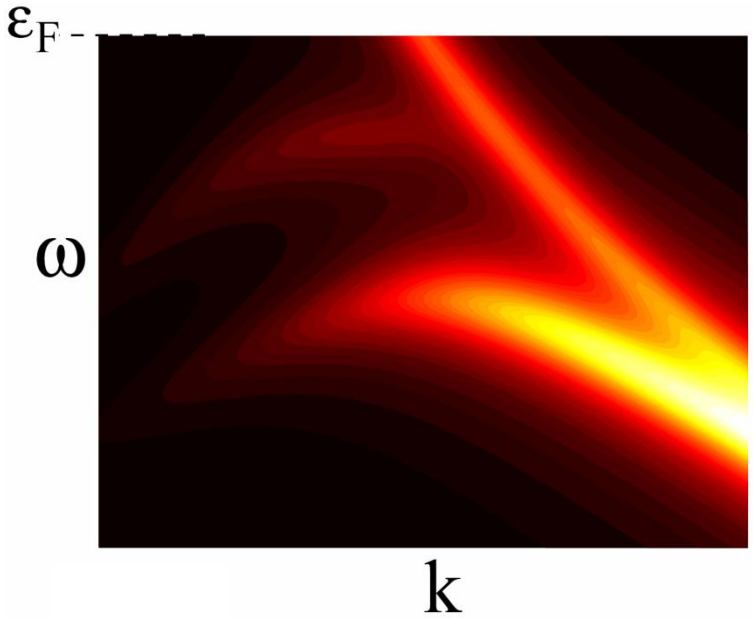




- phase interference from e_g' hybridization tail → $t_2 \gg t_1$

Gapless Charge-Density Wave in $TaSe_2$





- x^2-y^2 hybridization → $t_2 \gg t_1$ → decoupling of 3 sublattices
- minimization of tight-binding *H* against distortion
  - → one sublattice undistorted
  - → gapless band structure

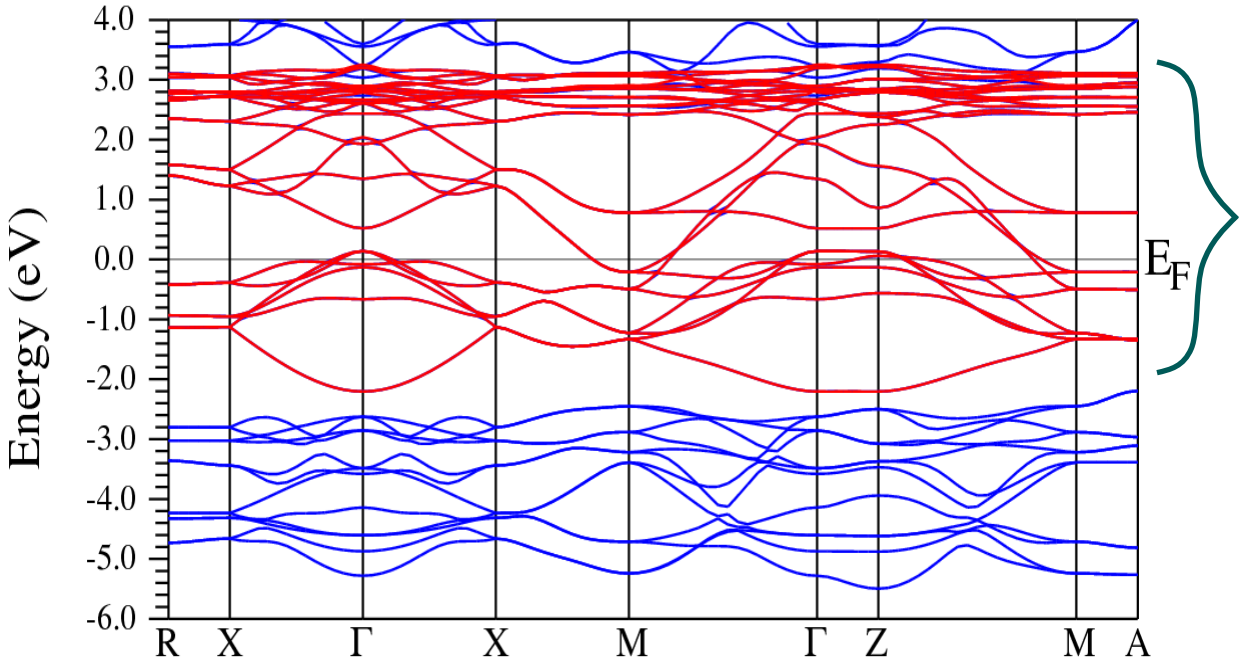
R. L. Barnett et al, PRL **96**, 026406 (2006)

Ferro-orbital order & anisotropic magnetic structure in 1111 (&122)

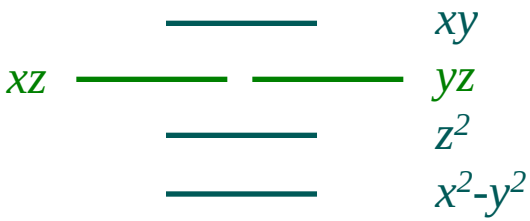
Chi-Cheng Lee, Wei-Guo Yin & Wei Ku

Phys. Rev. Lett. **103**, 267001 (2009)

Energy resolved, symmetry respecting Wannier function

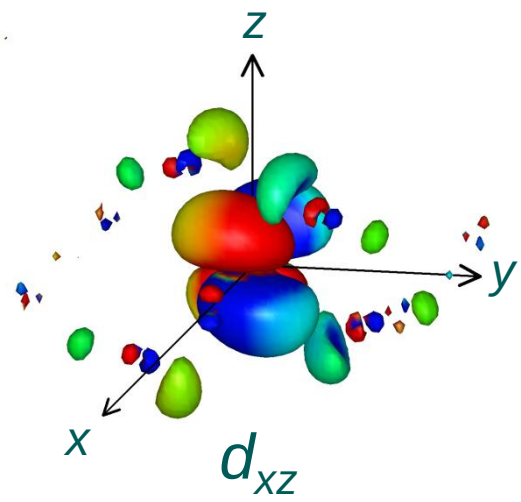


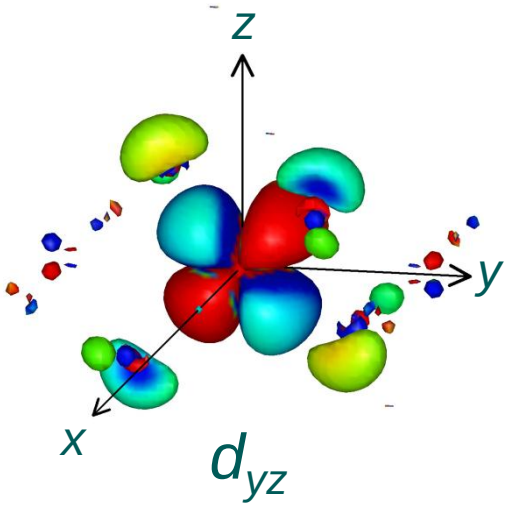
$$|\vec{R}n\rangle = \sum_{\vec{k}m}^{(\text{energy window})} |\vec{k}m\rangle\langle\vec{k}m|\vec{R}n\rangle$$
$$= \frac{1}{\sqrt{N_{cell}}}\sum_{\vec{k}m}|\vec{k}m\rangle e^{-i\vec{k}\cdot\vec{R}}U_{mn}^{(\vec{k})}$$
$$= \frac{1}{\sqrt{N_{cell}}}\sum_{\vec{k}}\left(\sum_{m}U_{mn}^{(\vec{k})}|\vec{k}m\rangle\right)e^{-i\vec{k}\cdot\vec{R}}$$



NM onsite energy (eV)

z^2	-0.03
x^2-y^2	-0.20
yz	0.10
xz	0.10
xy	0.34



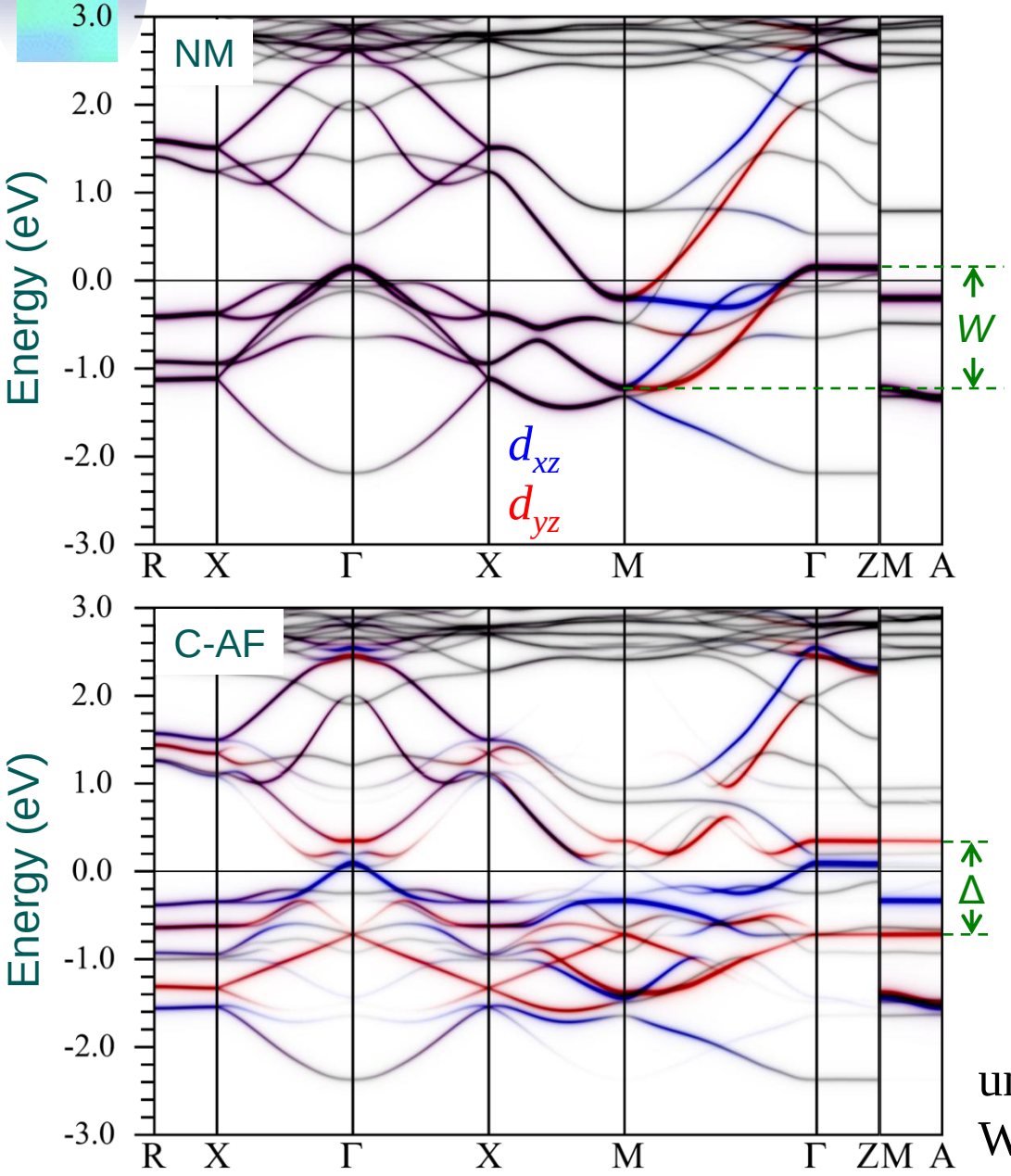


- small crystal field splitting
- degenerate *xz* and *yz*

→ orbital freedom !

methods see: W. Ku et al., PRL 89, 167204 (2002); W. Yin et al., PRL 96, 116405 (2006)

Comparing LDA band structures



- in NM 1st-BZ
- d_{xz} & d_{yz} most relevant to the low-E
- Only d_{yz} splits strongly near E_F
- d_{yz} more spin polarized ~0.34μ_B than d_{xz} (~0.15μ_B)
- more different with U=2eV
  0.58 vs. 0.23μ_B

→ orbital symmetry broken

- $\Delta \sim W$

→ large (ω,**k**)-space involved

→ local picture more suitable

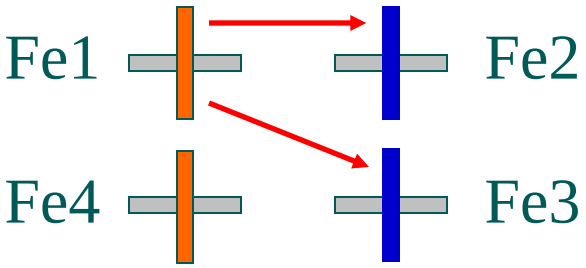
→ Fermi surface nesting not essential

→ SDW less convenient

unfolding methods see:
Wei Ku *et al.*, PRL **104**, 216401 (2010)

Anti-intuitive hopping parameters

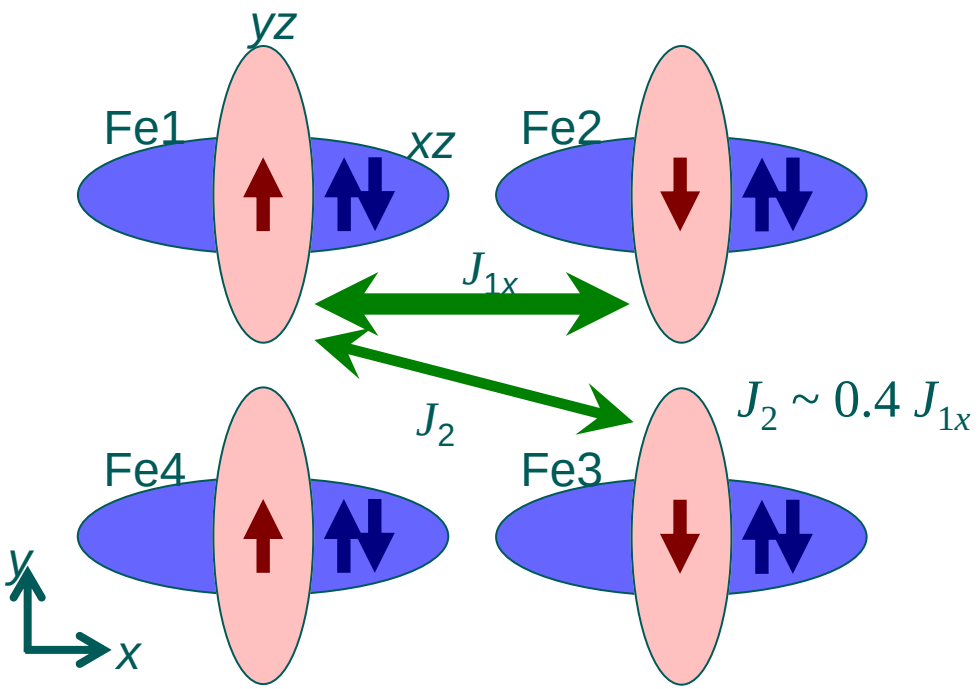
<WFs|H|WFs>	Fe1 z^2	x^2-y^2	yz	xz	xy
Fe2 (Fe4) z^2	0.13	0.31 (-0.31)	-0.10 (0.00)	0.00 (0.10)	0.00
x^2-y^2	0.31 (-0.31)	-0.32	0.42 (0.00)	0.00 (0.42)	0.00
yz	-0.10 (0.00)	0.42 (0.00)	-0.40 (-0.13)	0.00	0.00 (0.23)
xz	0.00 (0.10)	0.00 (0.42)	0.00	-0.13 (-0.40)	-0.23 (0.00)
xy	0.00	0.00	0.00 (0.23)	-0.23 (0.00)	-0.30
Fe3 z^2	0.06	0.00	-0.08	0.08	0.26
x^2-y^2	0.00	-0.10	0.12	0.12	0.00
yz	0.08	-0.12	0.25	-0.07	-0.05
xz	-0.08	-0.12	-0.07	0.25	0.05
xy	0.26	0.00	0.05	-0.05	0.16

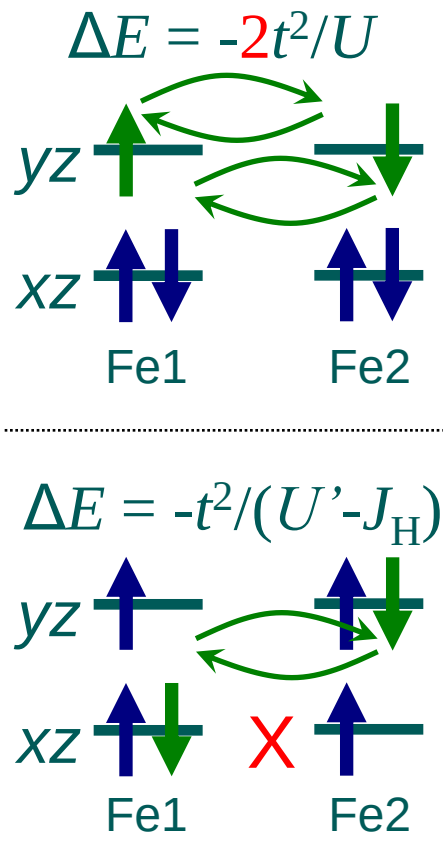


- Unusual coupling direction
- Cubic symmetry broken seriously by As
  → Fe-As phonon modes important
- Perpendicular hopping direction!

Chi-Cheng Lee *et al.*, PRL **103**, 267001 (2009)

C-AF magnetic structure and ferro-orbital order





- Strongly anisotropic super-exchange: $J_{1x} > J_2 >> J_{1y}$
  - → no competition with G-AF at all ! $J_1 \sim 2J_2$ irrelevant !
  - → single orbital Heisenberg model inadequate
- Orbital polarization and ferro-orbital correlation important
  - → rotational symmetry breaking
- Unusual coupling direction and strong anisotropic hoppings !
  - → common staggered OO loses
  - → *a* > *b*: AF across long bond (rare)

Chi-Cheng Lee *et al.*, PRL **103**, 267001 (2009)

Outlines

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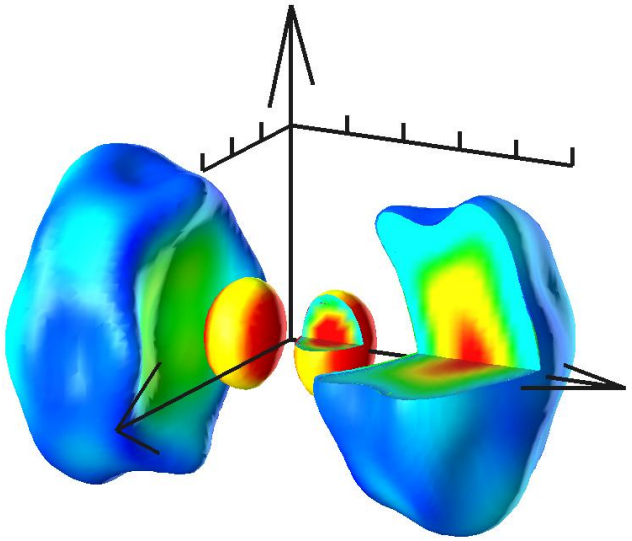
Propagation of local excitations in strongly correlated materials



P. Abbamonte *et. al.*, PNAS **105**, 12159 (2008)
C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

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- Chen-Lin Yeh (BNL & Tamkang Univ.)
- Hung-Chung Hsueh (Tamkang Univ.)

Chi-Cheng Lee
Sinica

Experiments

- Peter Abbamonte, Xiaoqian M. Chen, Yu Gan (UIUC)
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- John Hill (BNL), Young Cai (BNL)
- Andrivo Rusydi (NUS, Singapore)
- Young-June Kim (U. Toronto, Canada)
- Nozomu Hiraoka (Sping-8, Japna)

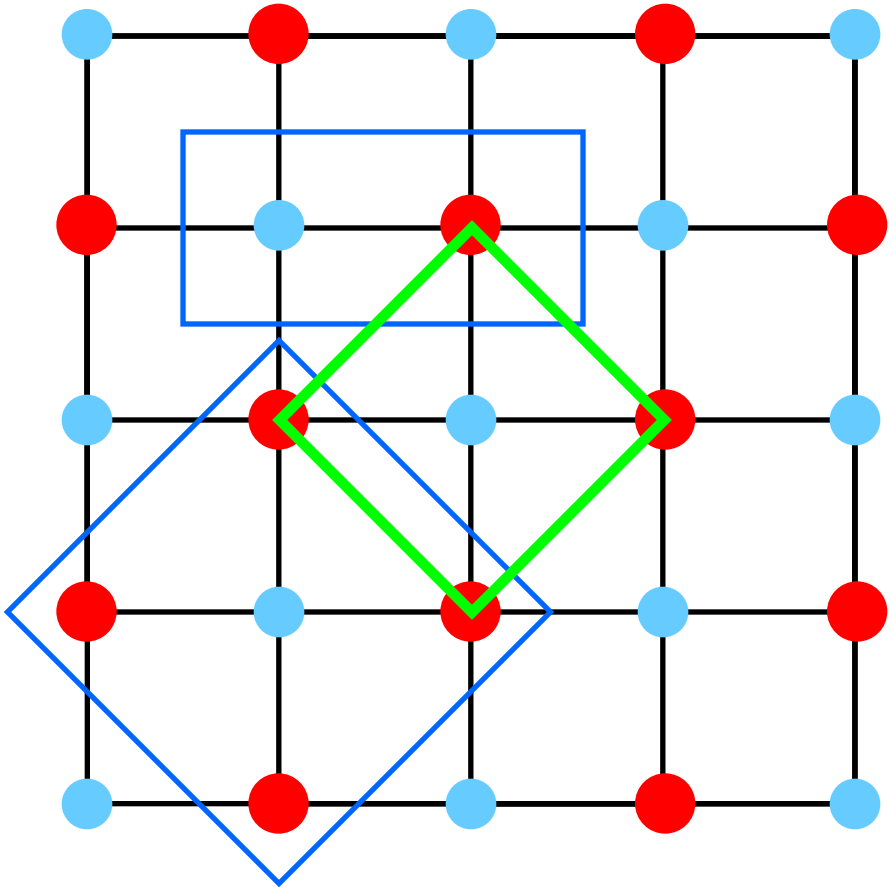
Local Picture for Strongly Correlated Systems

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

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

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

How to define “local” in CT-insulators?

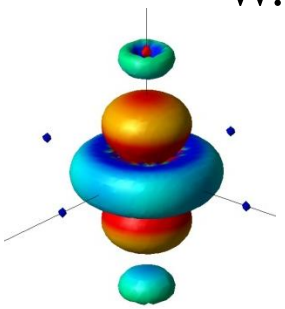


- Periodic symmetry
- Point group symmetry
- Simultaneously keep both? How to split the Hilbert space?

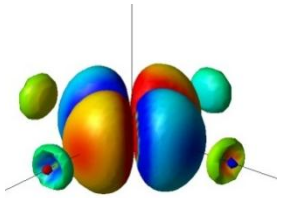
Symmetric Wannier Functions for CT-Insulators

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).

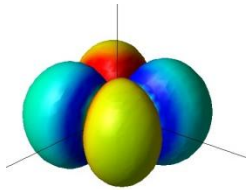
Ni



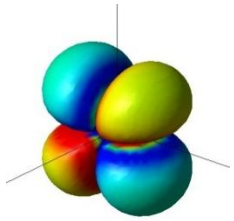
$3z^2 - r^2$



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



xy



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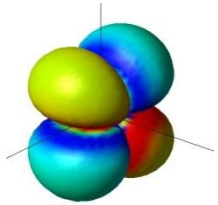
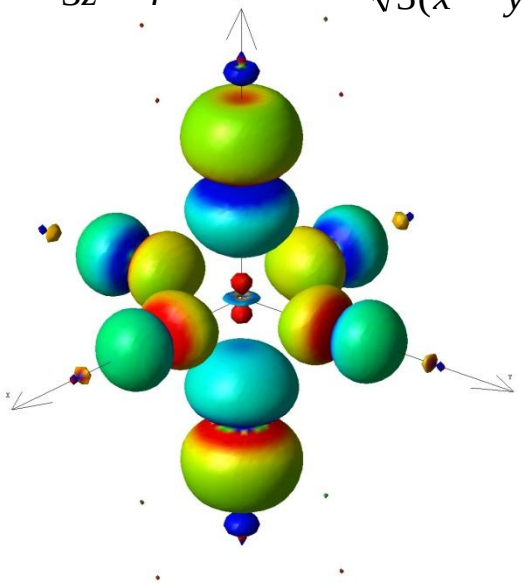
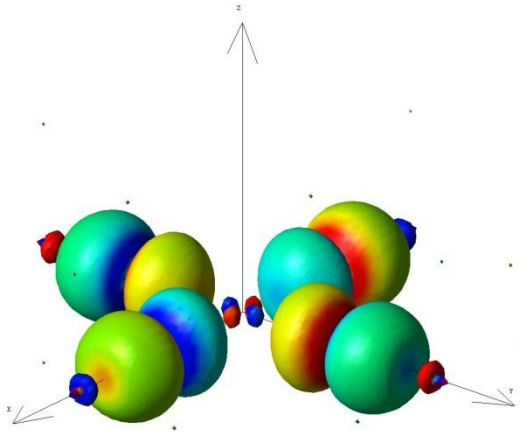


xz

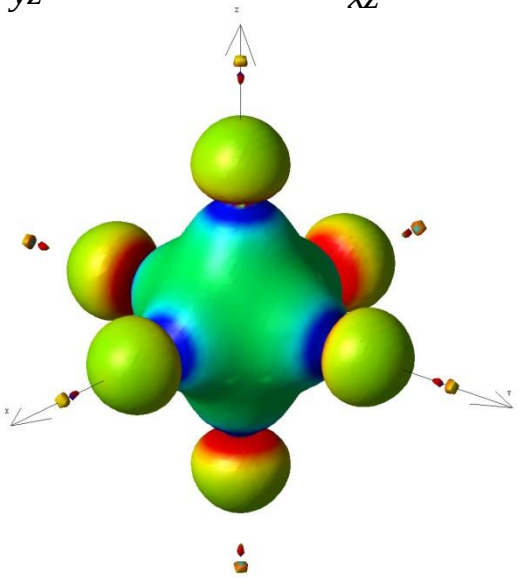
O



$3z^2 - r^2$



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

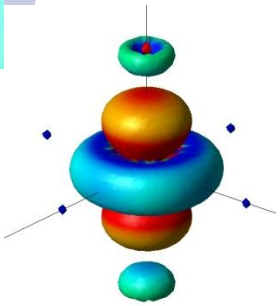


s wave

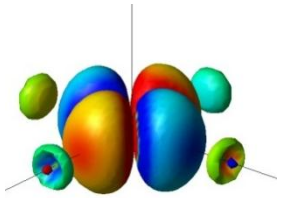
- O-*p* orbitals → additional Ni-*d* orbitals (no double counting of O orbitals)
- "local" is now defined by this "super-atom"

Super Atom for Charge Transfer Insulator

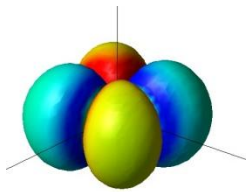
Ni



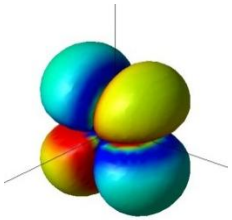
$3z^2 - r^2$



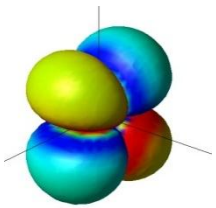
$\sqrt{3}(x^2 - y^2)$



xy

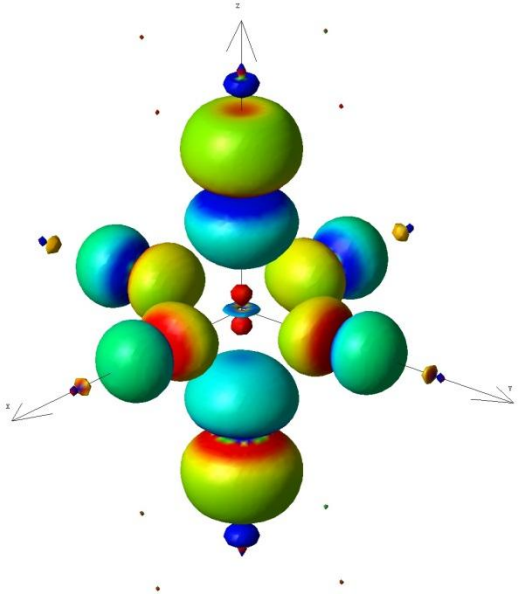


yz

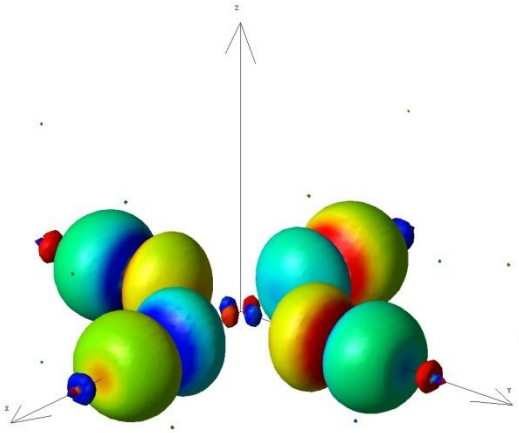


xz

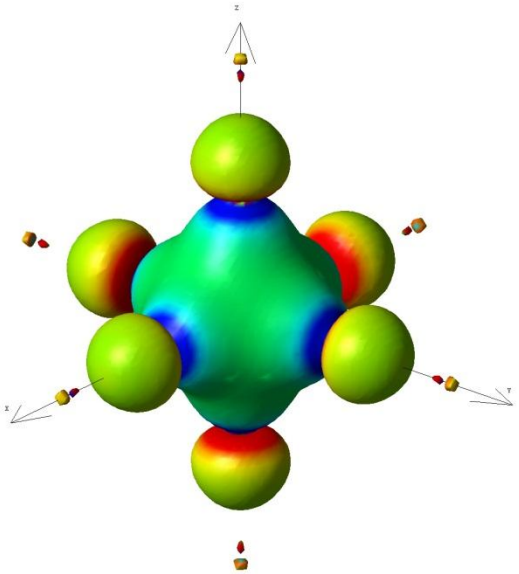
O



$3z^2 - r^2$



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



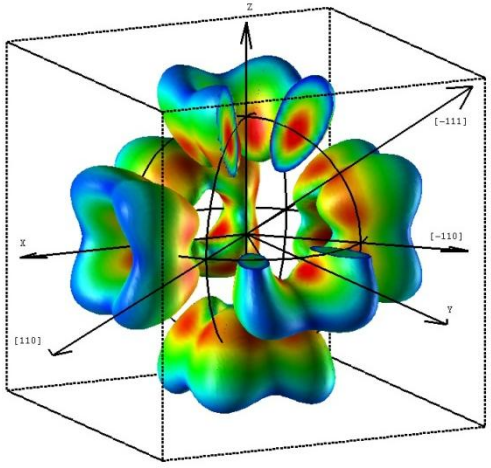
s wave

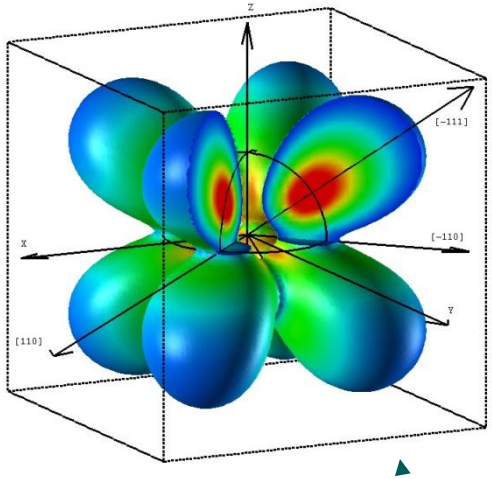
$$H = H_{local} + H_{nonlocal}$$

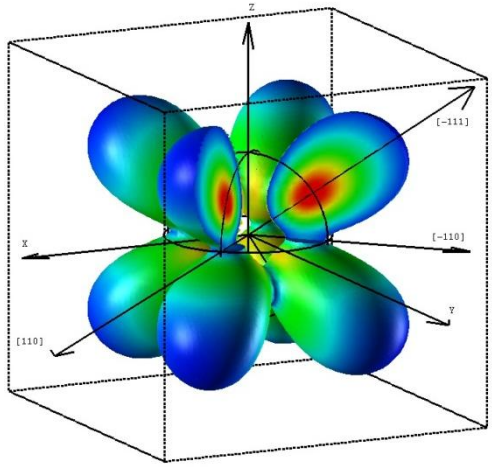
(exact) **(modification)**

Maximize the contributions of “local atom”

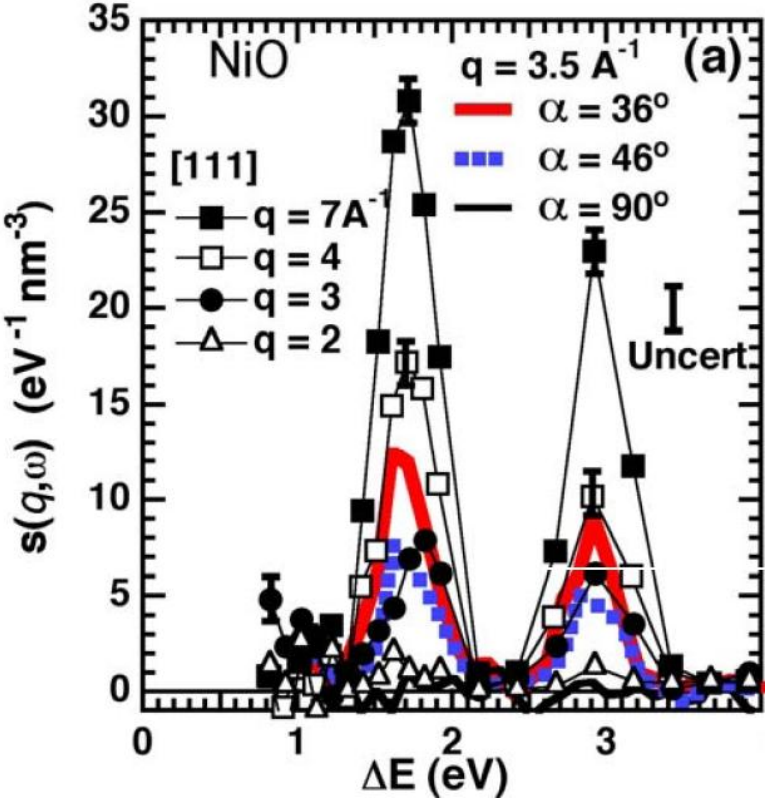
Density response for super atom (eg-t2g=0.65eV)

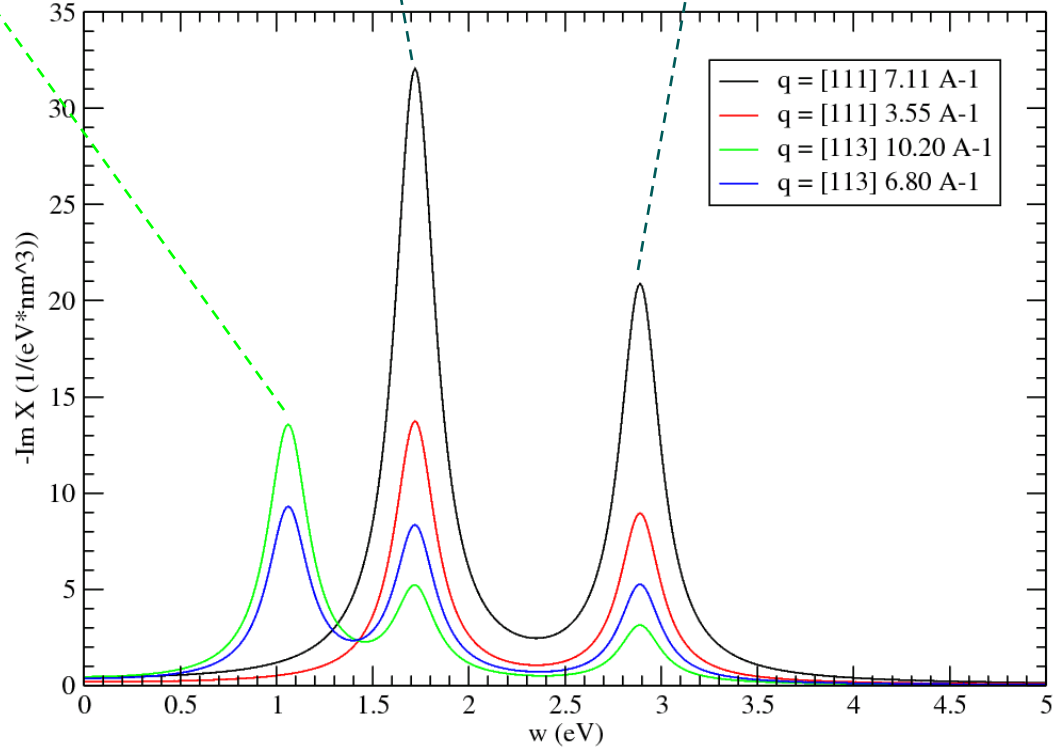






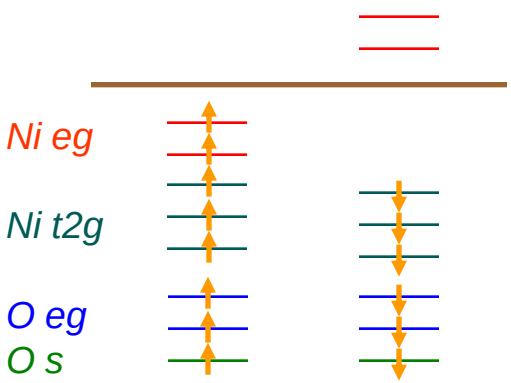
(antibonding-type)



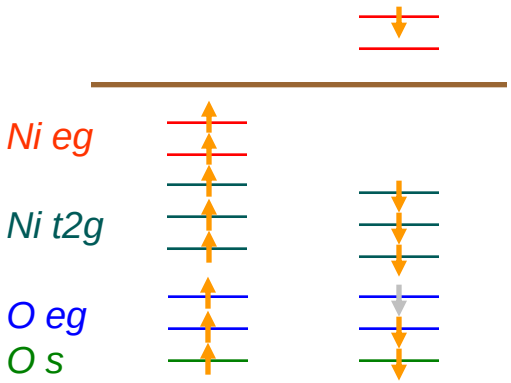


Multiplet Splitting Made Possible with MB Hilbert Space

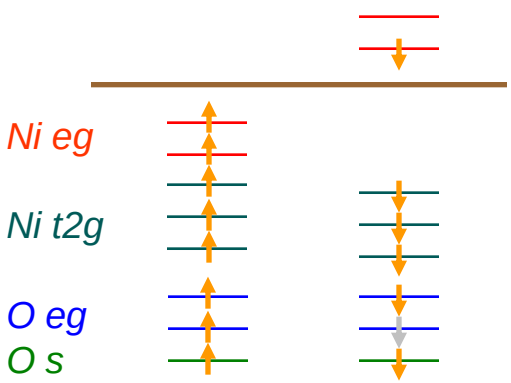
GS



(0.9484)

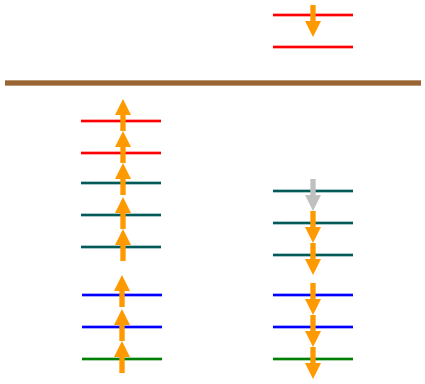


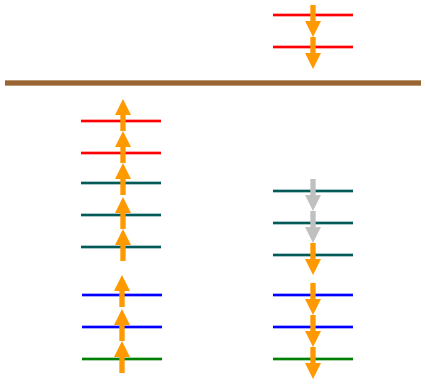
(-0.2226)

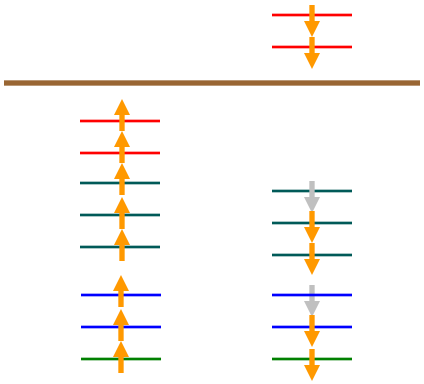


(0.2226)

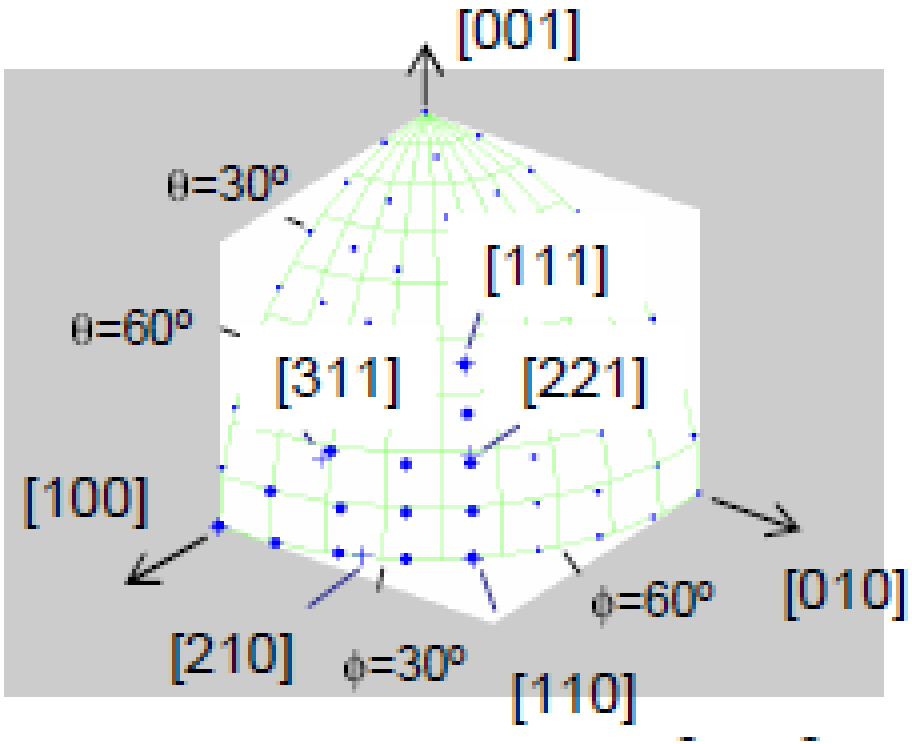
T_{1g}

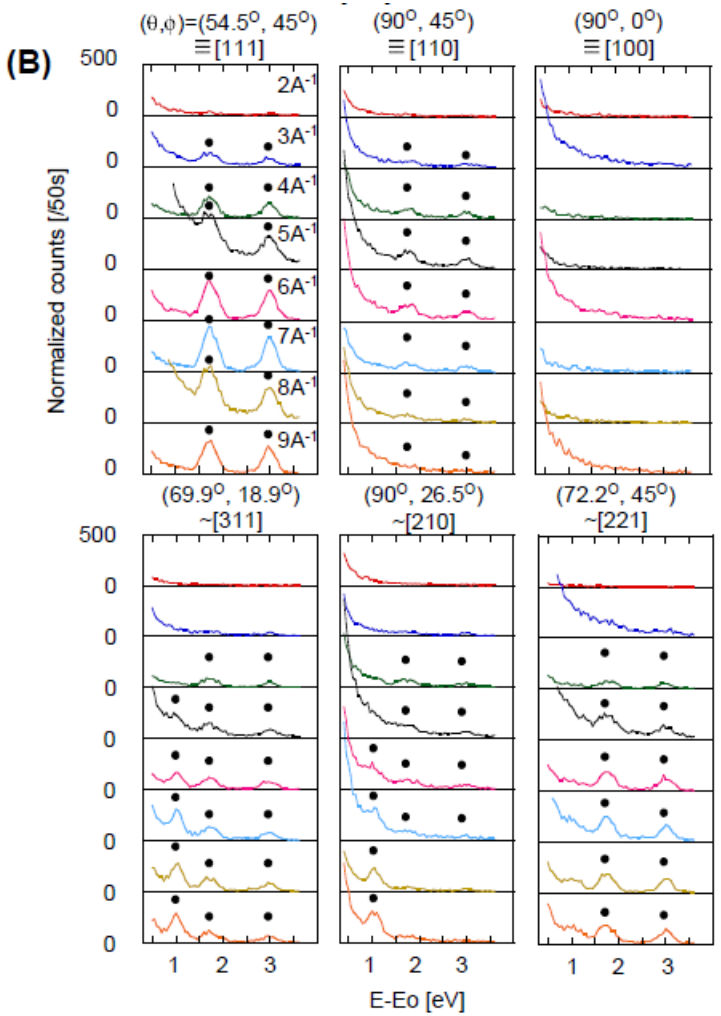






3D Map of Local Excitations in the Mott Gap in NiO

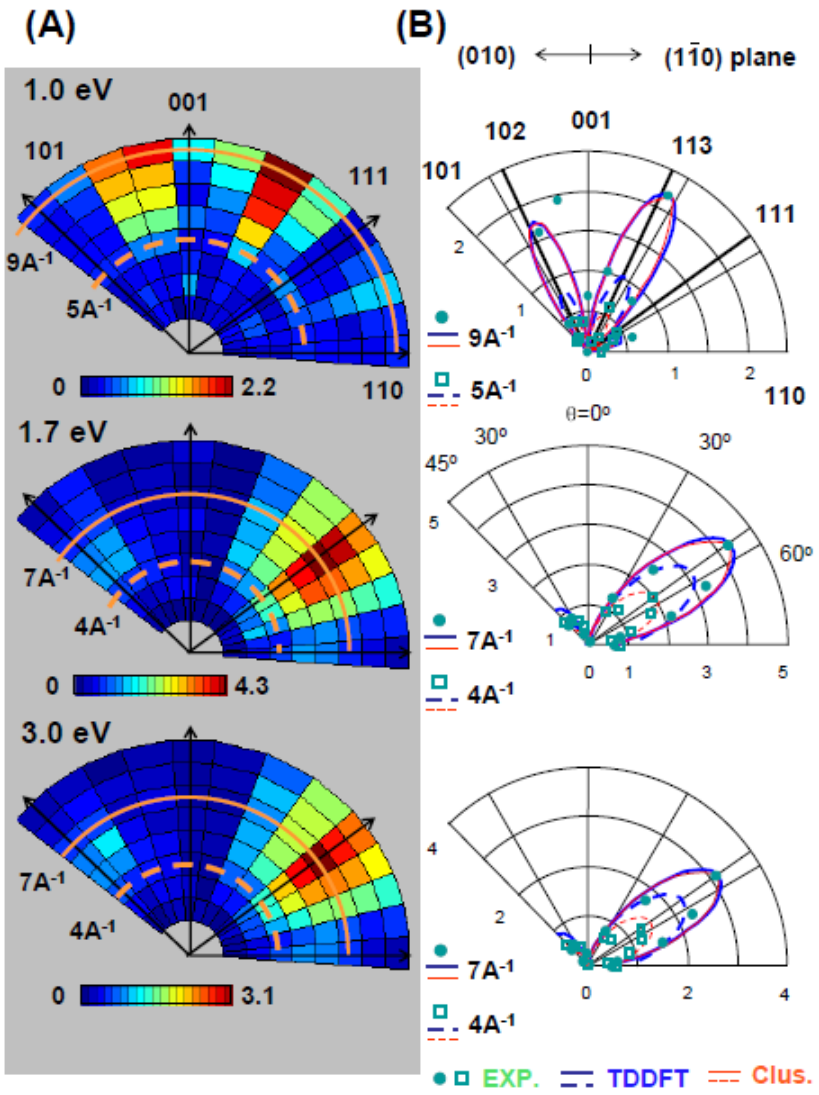


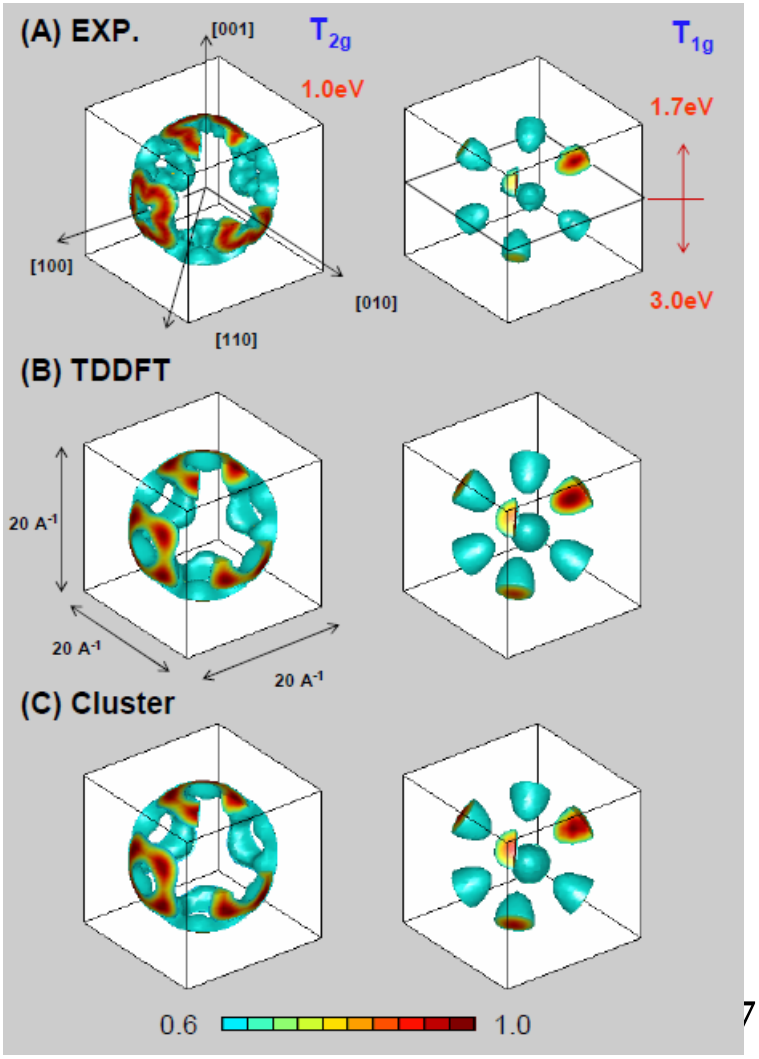


- 1eV excitation found !
- very different q-dependence of spectral weight

Nozomu Hiraoka *et al*, Europhys. Lett. **96**, 37007 (2011)

3D Map of Local Excitations in the Mott Gap in NiO





- Detailed comparison: exp vs. TD-LDA+*U* & cluster model
  - good general agreement with some discrepancies in details

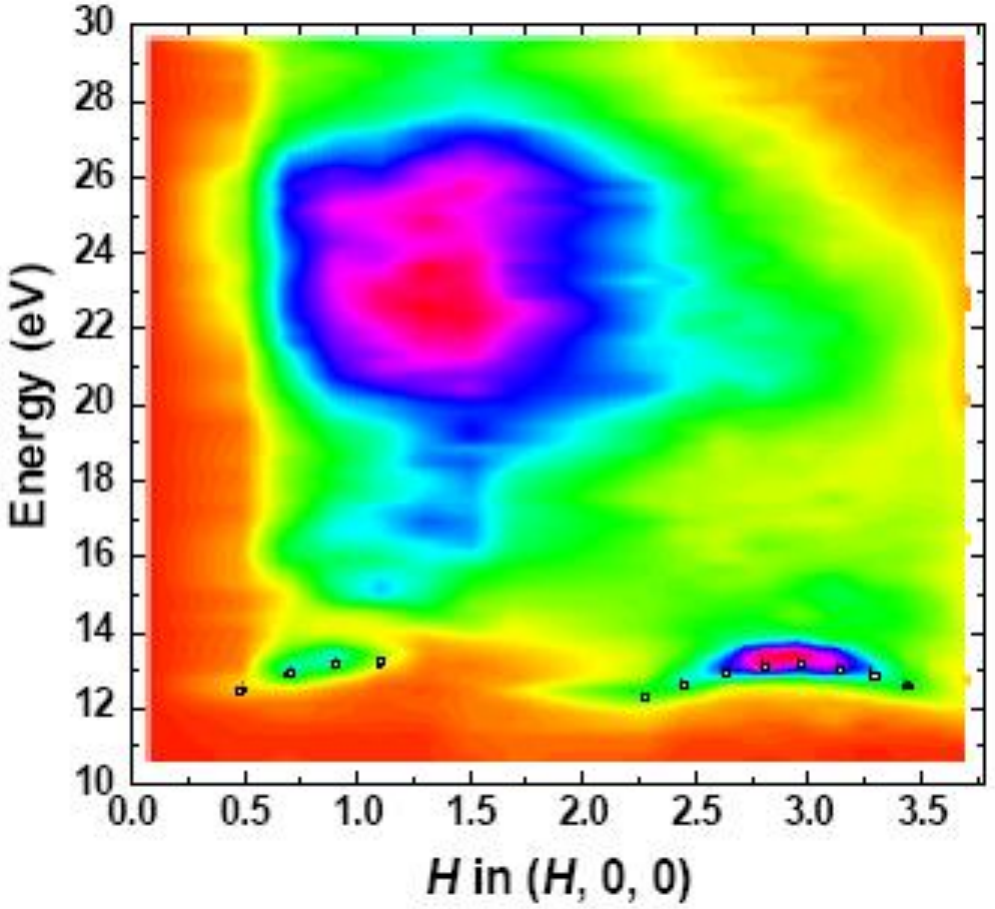
How does the local excitations propagate and decay?

Propagation of Tightly-Bound Excitons: case study of LiF

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

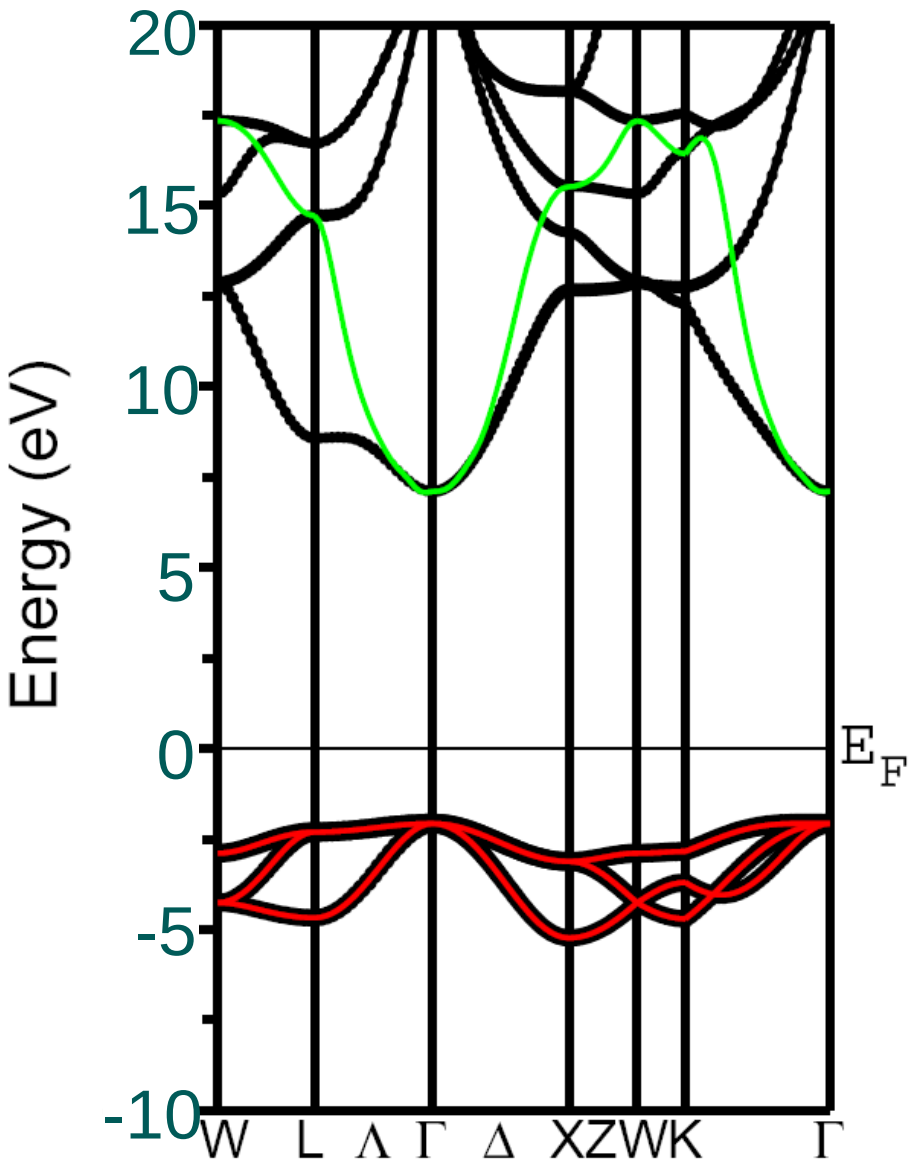
Inelastic X-ray scattering

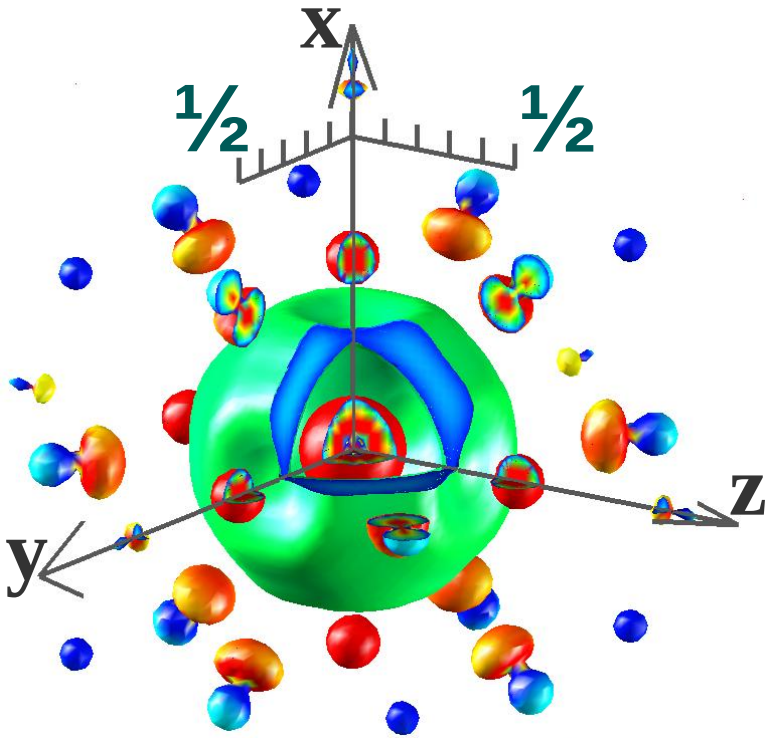
- Structured spectral weight
- Clear dispersion at large *q* !
- observe *fs* dynamics

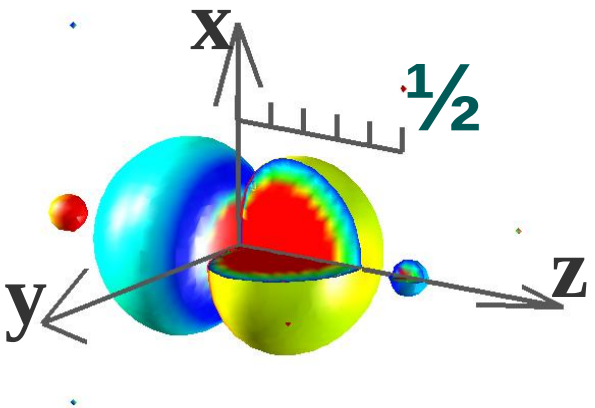


P. Abbamonte *et. al.*, PNAS 2008

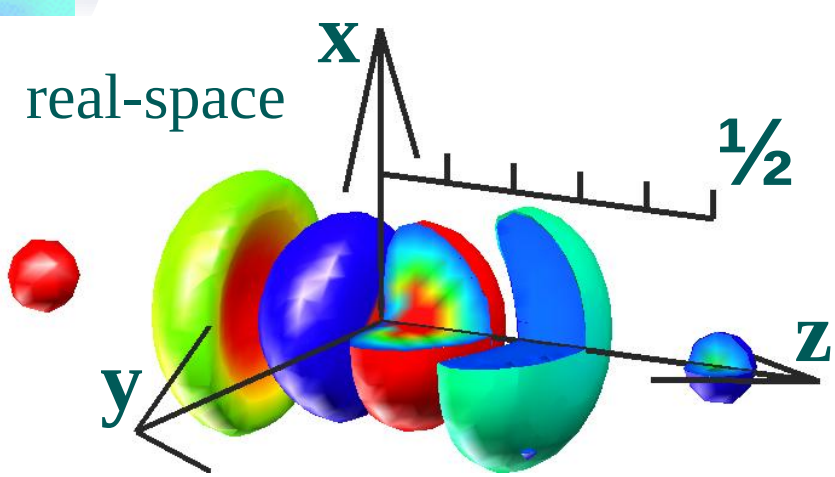
Excitons in LiF as a Frenkel Exciton in a "Super Atom"

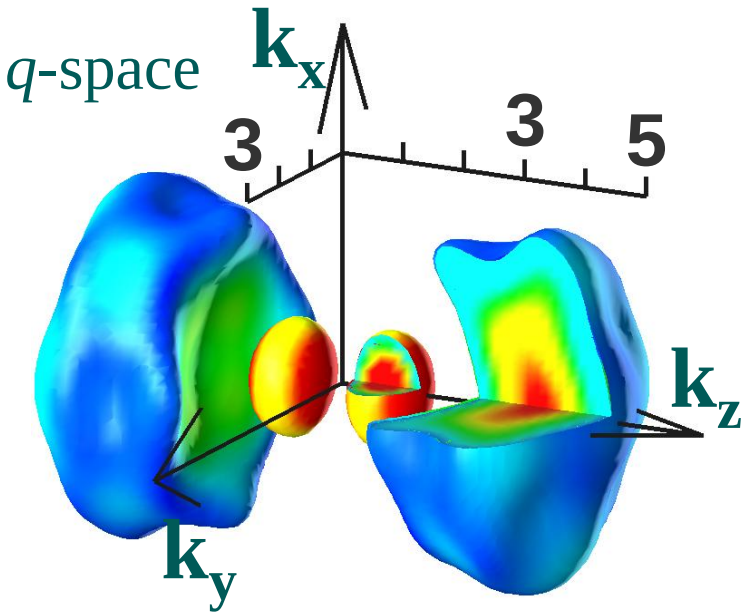


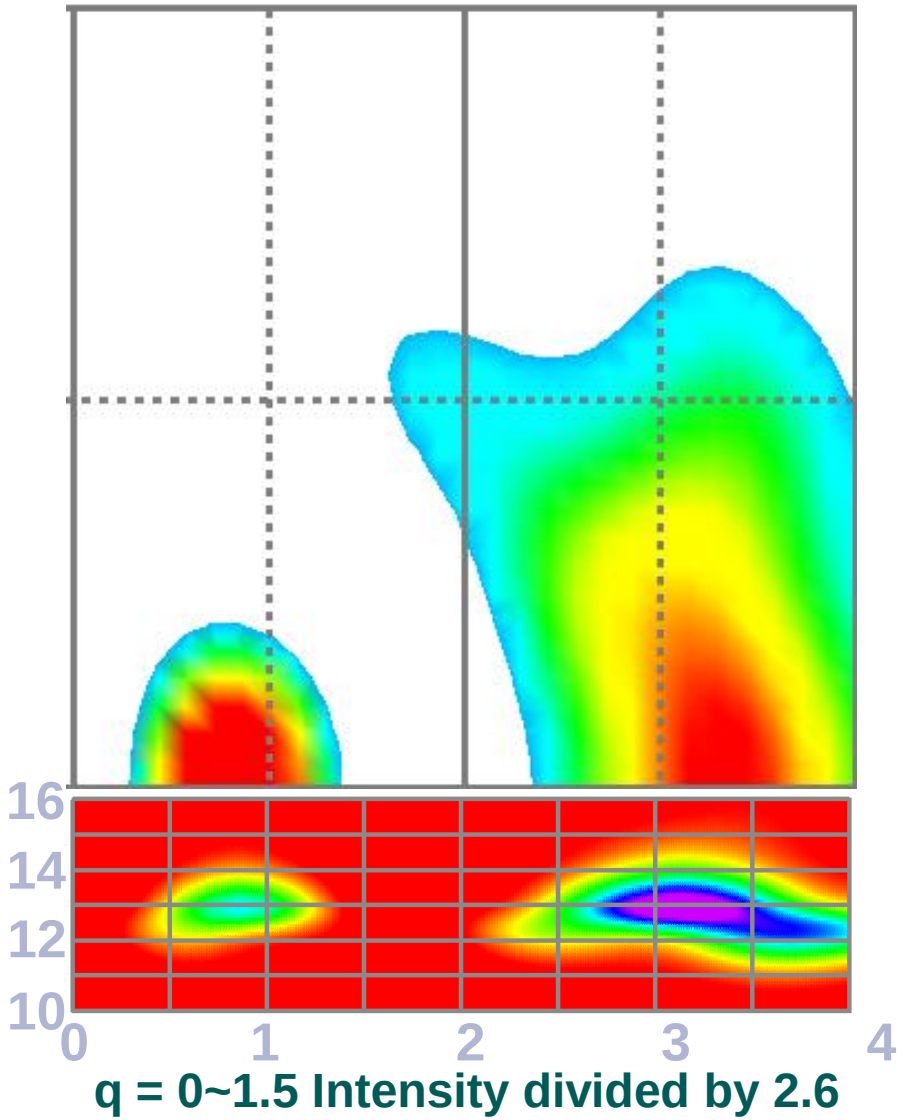




Matrix Element and Structure in *q*-space







P. Abbamonte *et al.*, PNAS 2008

Propagation of tightly bound excitons

- Treat tightly bound excitons (and other local excitations) as a composite boson. Define its propagation kinetic kernel T via local and full propagator $D[H_L]$ and $D[H]$:

$$D[H] = D[H_L] + D[H_L]TD[H]$$

- T integrates out all the pair fluctuation in space and encapsulates propagation and decay processes.
- We then approximate T using unbound exciton propagator

$$T = D^{-1}[H_L] - D^{-1}[H] \sim D_0^{-1}[G[H_L]] - D_0^{-1}[G[H]]$$

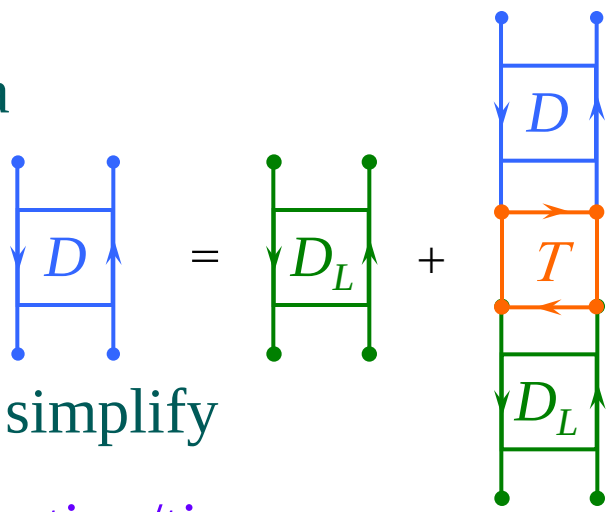
- Separation of local many-body problem from non-local propagation
- Many orders of magnitudes cheaper than Bethe-Salpeter equation

C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

Effective Two-Particle Hopping

Define effective two particle kinetic kernel T via

$$D[H] = D[H_L] + D[H_L]TD[H]$$



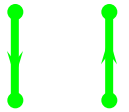
in the basis of local bound pair $b^{+}_{RN} \equiv c^{+}_{Rp} c_{Rh}$ and simplify

same location/time → *Rpt Rht*

$$\begin{aligned} T &= D^{-1}[H_L] - D^{-1}[H] \\ &= \left(D_0^{-1}\left[G[H_L]\right] - I[H_L]\right) - \left(D_0^{-1}\left[G[H]\right] - I[H]\right) \\ &\simeq D_0^{-1}\left[G[H_L]\right] - D_0^{-1}\left[G[H]\right] \end{aligned}$$

using the empty bubble

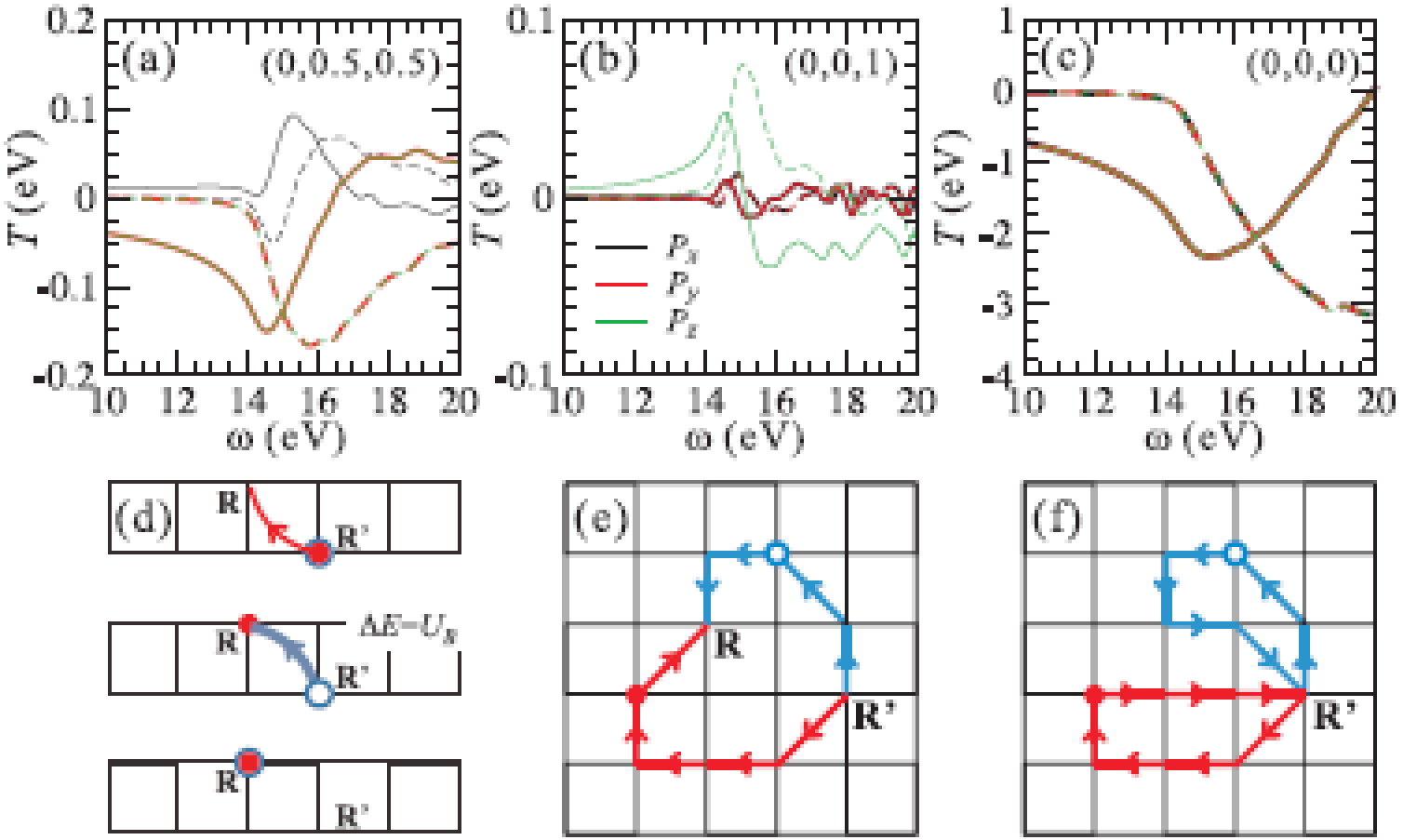
$$D_0(RN, R'N'; t, t') = G(Rp, R'p'; t, t')\, G(R'h', Rh; t', t)$$



T gives hopping of p-h pair in real space → dispersion in q-space

C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

Effective Two-Particle Hopping in LiF



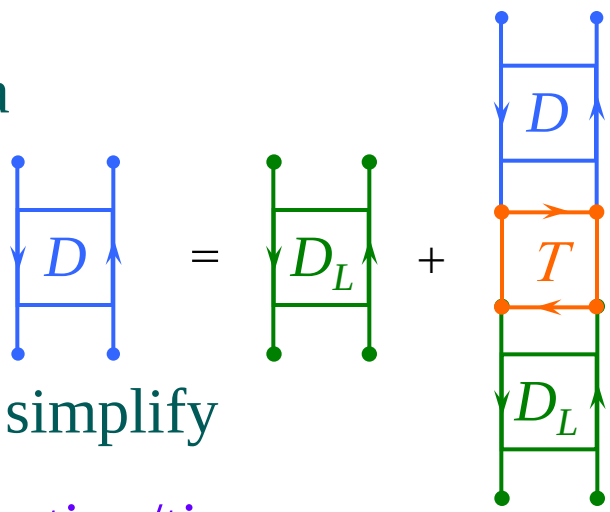
$T(\omega)$ is complex and strongly ω-dependent to fully account for

1. Landau continuum (integrating out virtual pair breaking processes) → exact for $E_b = 0$
2. Lower mobility with stronger p-h binding → correct t^2/E_b behavior
3. Renormalization of on-site energy from kinetic energy

Effective Two-Particle Hopping

Define effective two particle kinetic kernel T via

$$D[H] = D[H_L] + D[H_L]TD[H]$$



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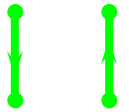
same location/time → Rpt Rht

$$\begin{aligned} T &= D^{-1}[H_L] - D^{-1}[H_L] \\ &= \left(D_0^{-1}[G[H_L]] - I[H_L]\right) - \left(D_0^{-1}[G[H]] - I[H]\right) \\ &\simeq D_0^{-1}[G[H_L]] - D_0^{-1}[G[H]] \end{aligned}$$

using the empty bubble

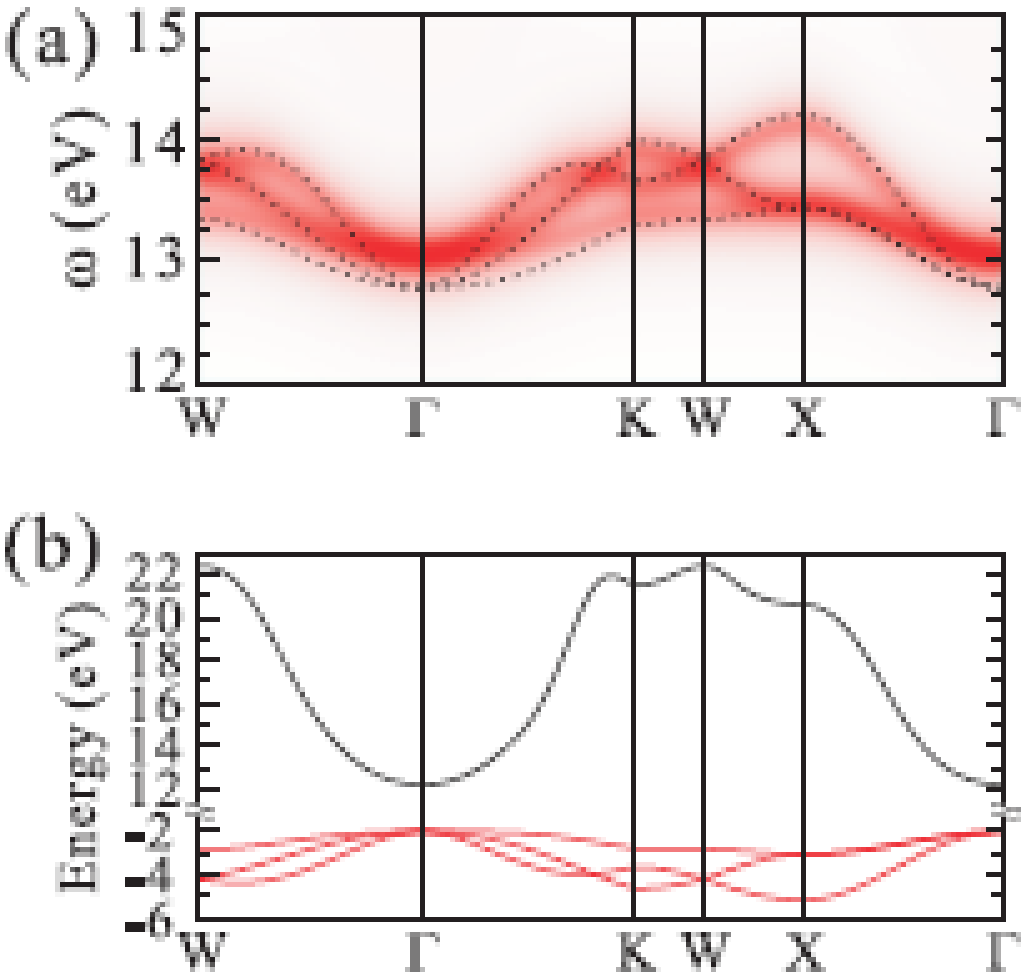
$$D_0(RN, R'N'; t, t') = G(Rp, R'p'; t, t')\, G(R'h', Rh; t', t)$$



T gives hopping of p-h pair in real space → dispersion in q-space

C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

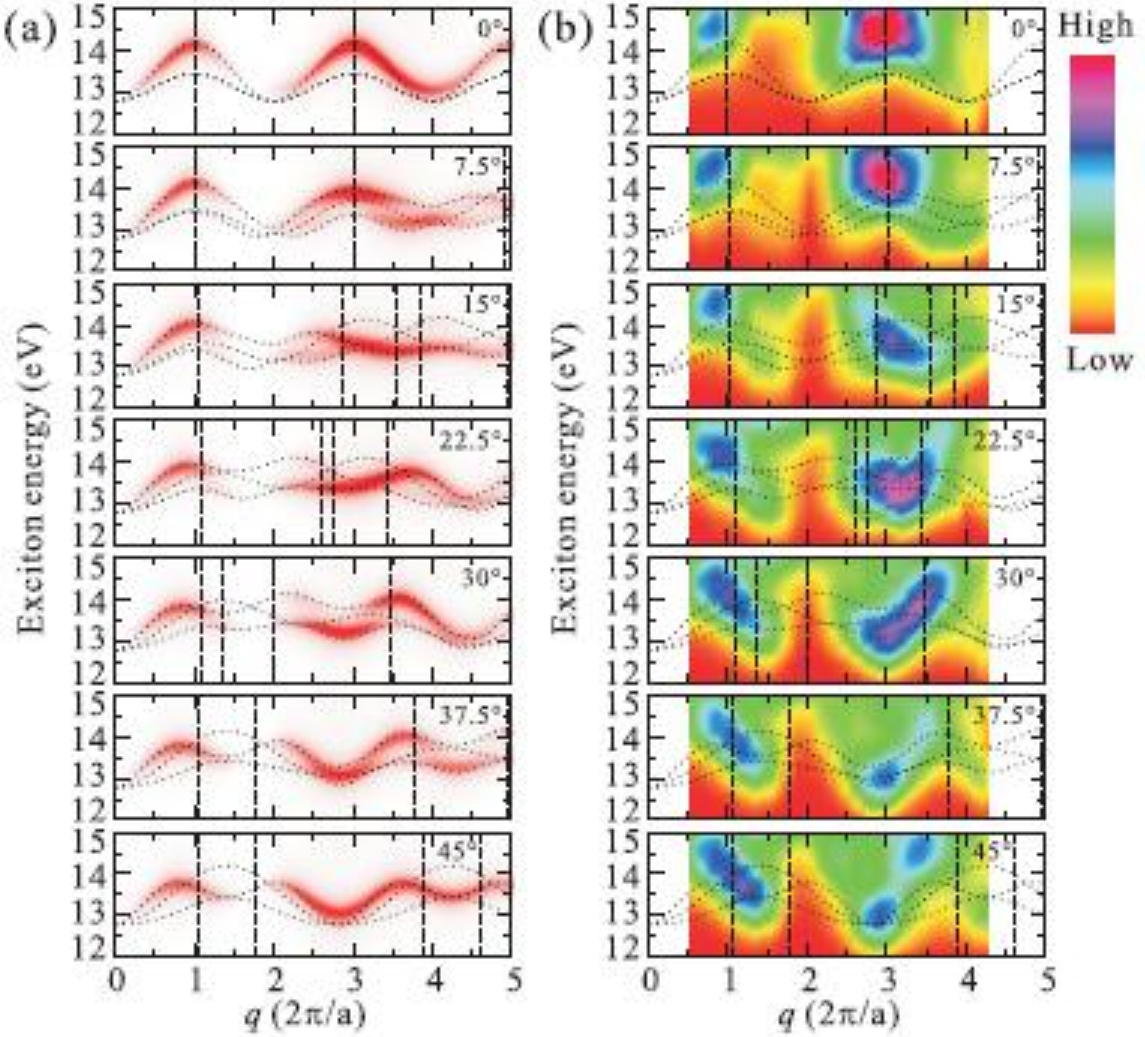
Exciton Band Structure



1. Full results similar to the diagonalization of $\omega_{exciton} + \mathrm{Re}\,T\left(\tilde{\omega}_{exciton}\right)$
2. Similar dispersion to the F *p*-bands (same symmetry)

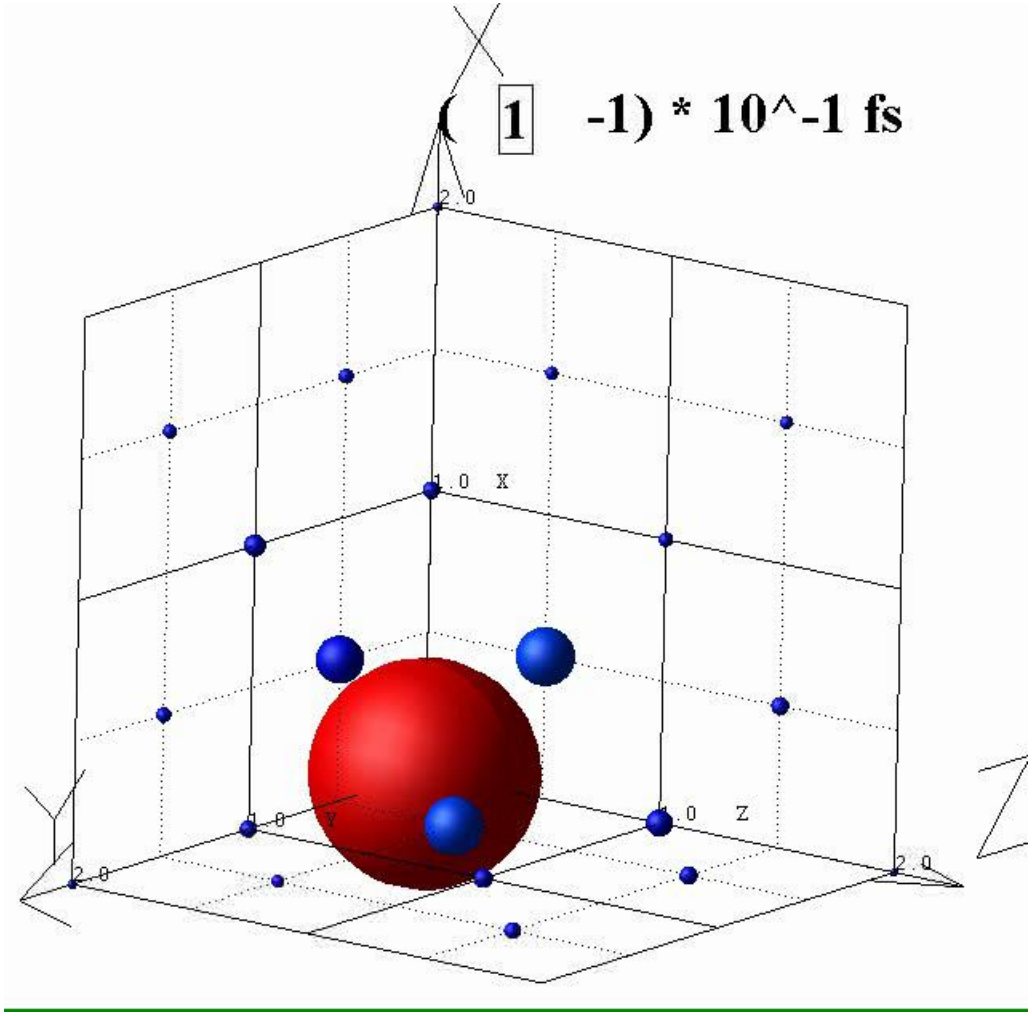
C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

Observation of Multiple Exciton Bands



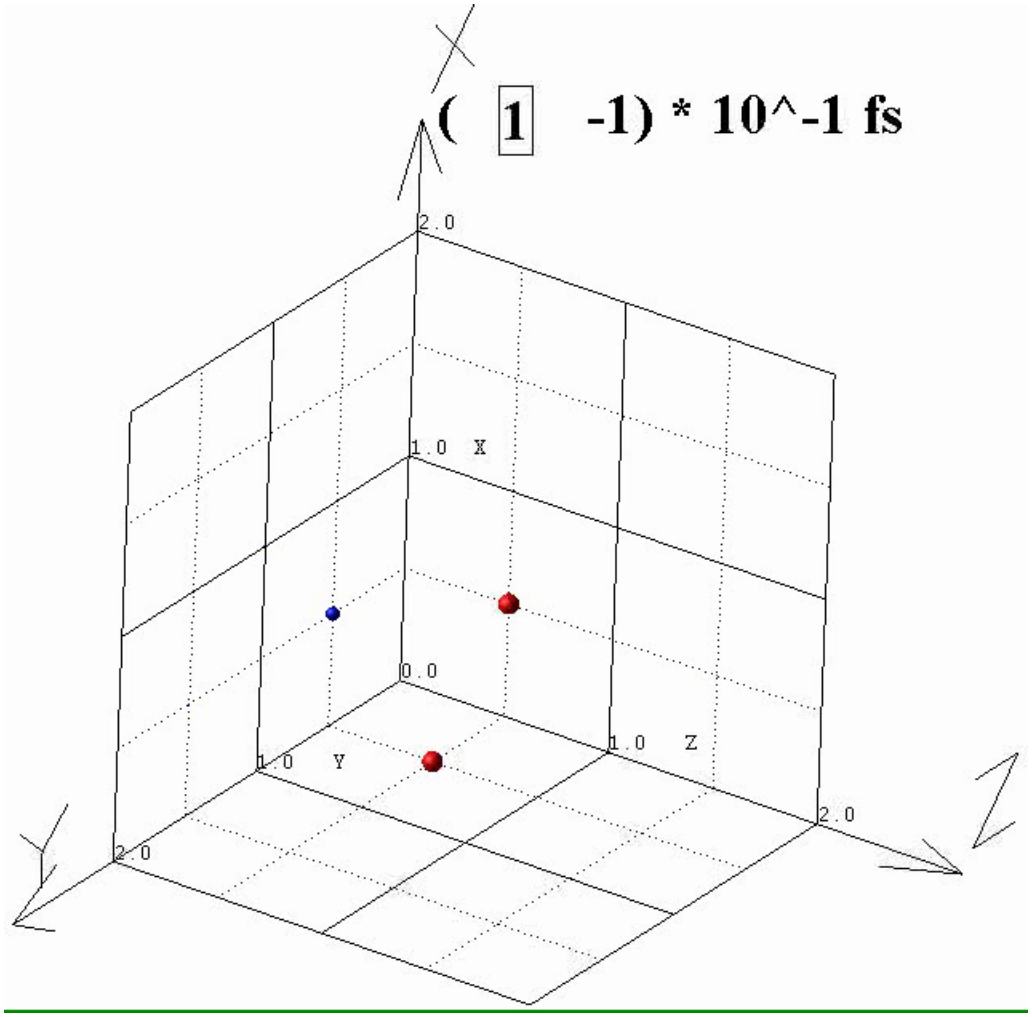
1. Similar weight in momentum space
2. Similar dispersion
3. Switching of bands (breaks in intensity)

Time Evaluation of Charge Fluctuation in LiF



- exp. 2D map of exciton propagation is in preparation

Time Evaluation of Charge Fluctuation in LiF



- exp. 2D map of exciton propagation is in preparation

Outlines

- Simple illustrations:
  - Orbital order in $LaMnO_3$
  - Gapless CDW in $TaSe_2$
  - Ferro-orbital order in Fe-SCs
- Interacting problems:
  - Local excitations
  - Propagation and decay of local excitations
- Effects of disordered impurities in Fe-SCs:
  - Substitution of Fe: doping or not?
  - Fe vacancy: “violation” of Luttinger theorem
  - Ru substitution: realization of superdiffusion

Treating materials with disordered impurities

T. Berlijn, D. Volja, and Wei Ku, PRL **106**, 077005 (2011)

For various applications, see

T.S. Herng, *et al*., *Phys. Rev. Lett.* **105**, 207201 (2010)

Tom Berlijn, *et al*., *Phys. Rev. Lett.* **108**, 207003 (2012)

Tom Berlijn, *et al*., *Phys. Rev. Lett.* **109**, 147003 (2012)

L.-M. Wang, *et al*., *Phys. Rev. Lett.* **110**, 037001 (2013)

Acknowledgement

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BNL

Limin Wang
BNL

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P. Hirschfeld, & H.-P. Chen, U of Florida

First-principles methods for disorder

Relevance

- Defects, vacancy, chemical substitution, doping & intercalation
- Thermal/quantum fluctuation induced spatial inhomogeneity
- Paramagnetic phase with disordered local moment

Different approaches

- Mean-field potential: virtual crystal approximation
- Mean-field scattering: coherent potential approximation
- Perturbation: diagrammatic summation
- Non-perturbed direct method: configuration average over super cells

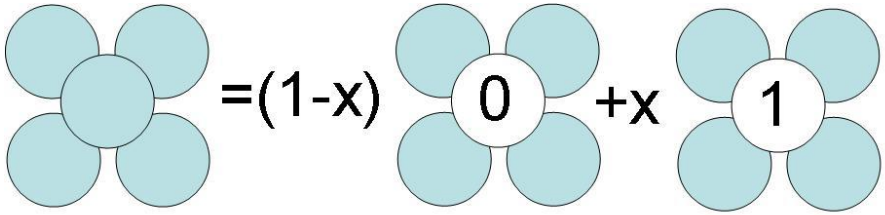
Mean-field approaches

VCA: Virtual Crystal Approximation

$$V_{\text{virtual crystal}} = (1-x)\ V_0 + x\ V_1$$

no scattering

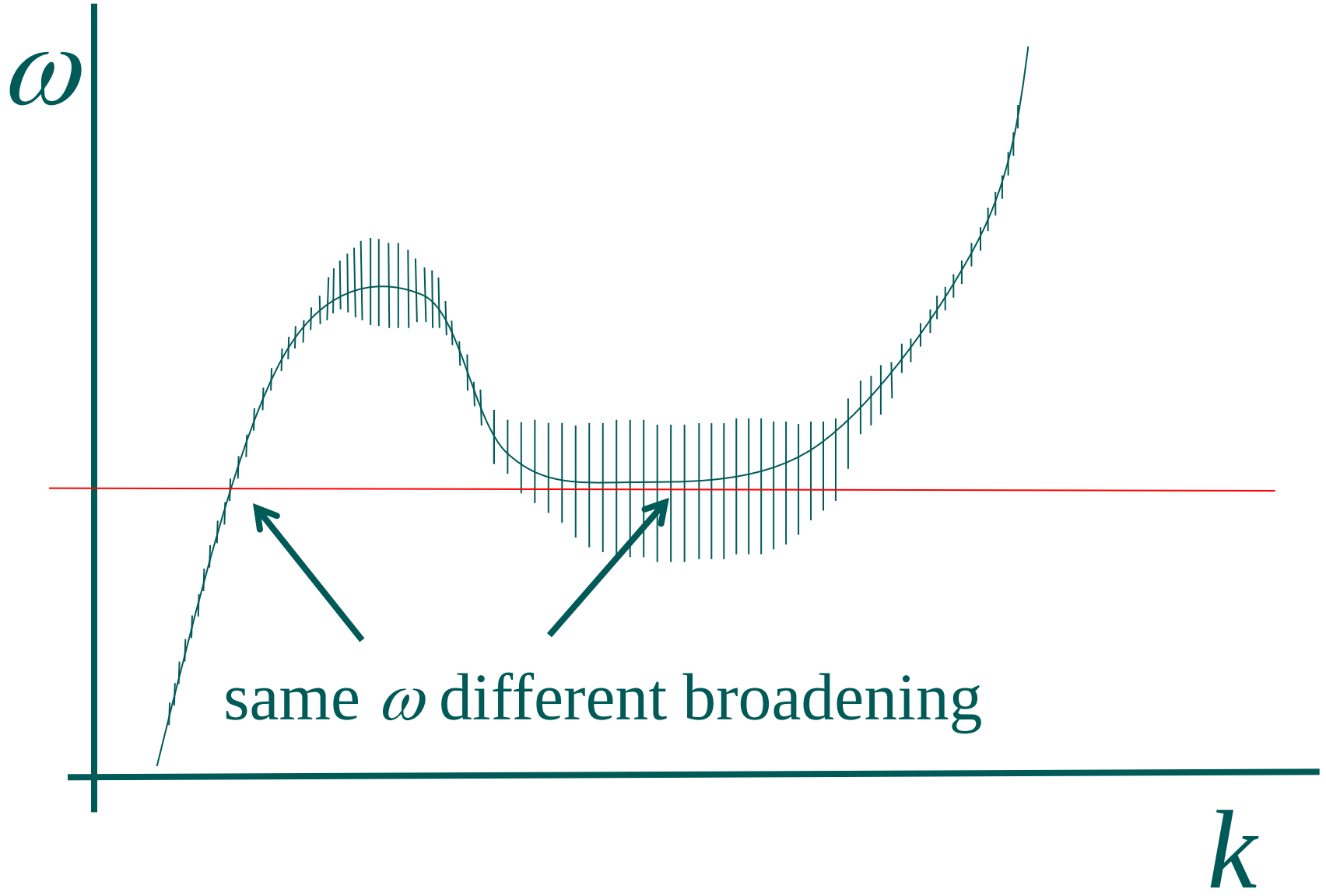
CPA: Coherent Potential Approximation



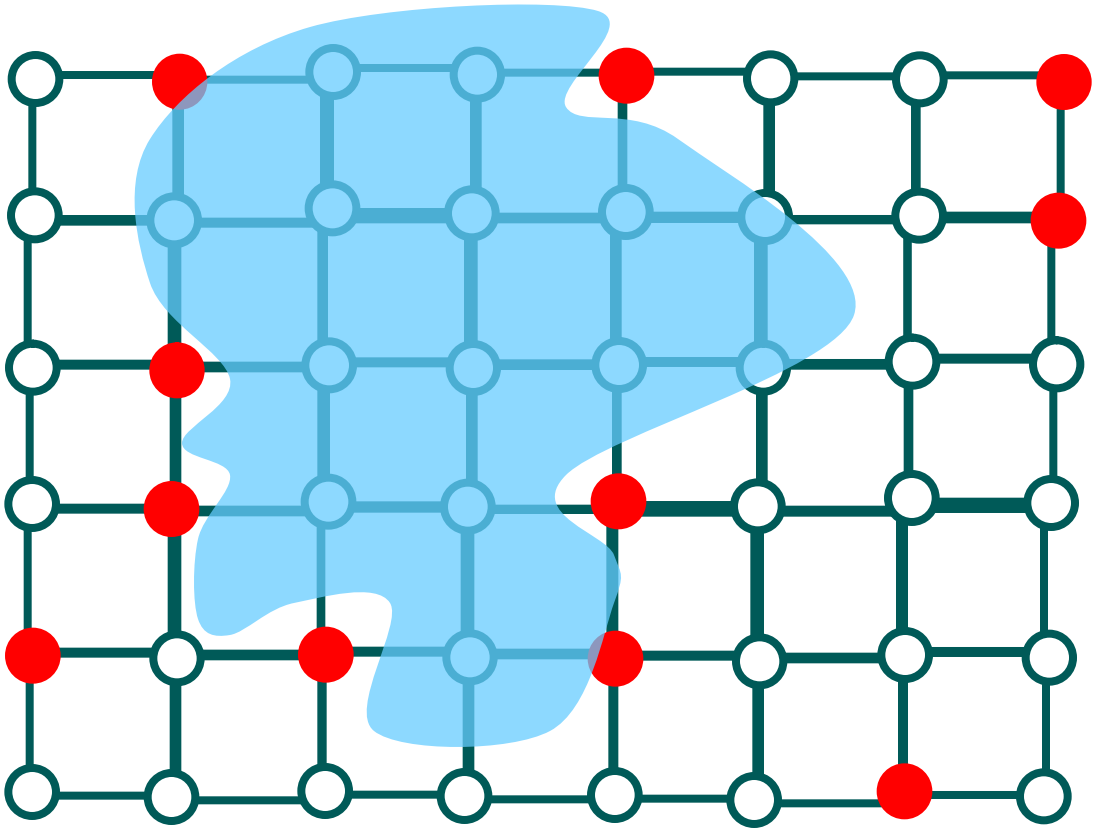
lack cluster-scattering

A. Gonis, “Green functions for ordered and disordered systems” (1992)

Non-local physics: *k*-dependent broadening

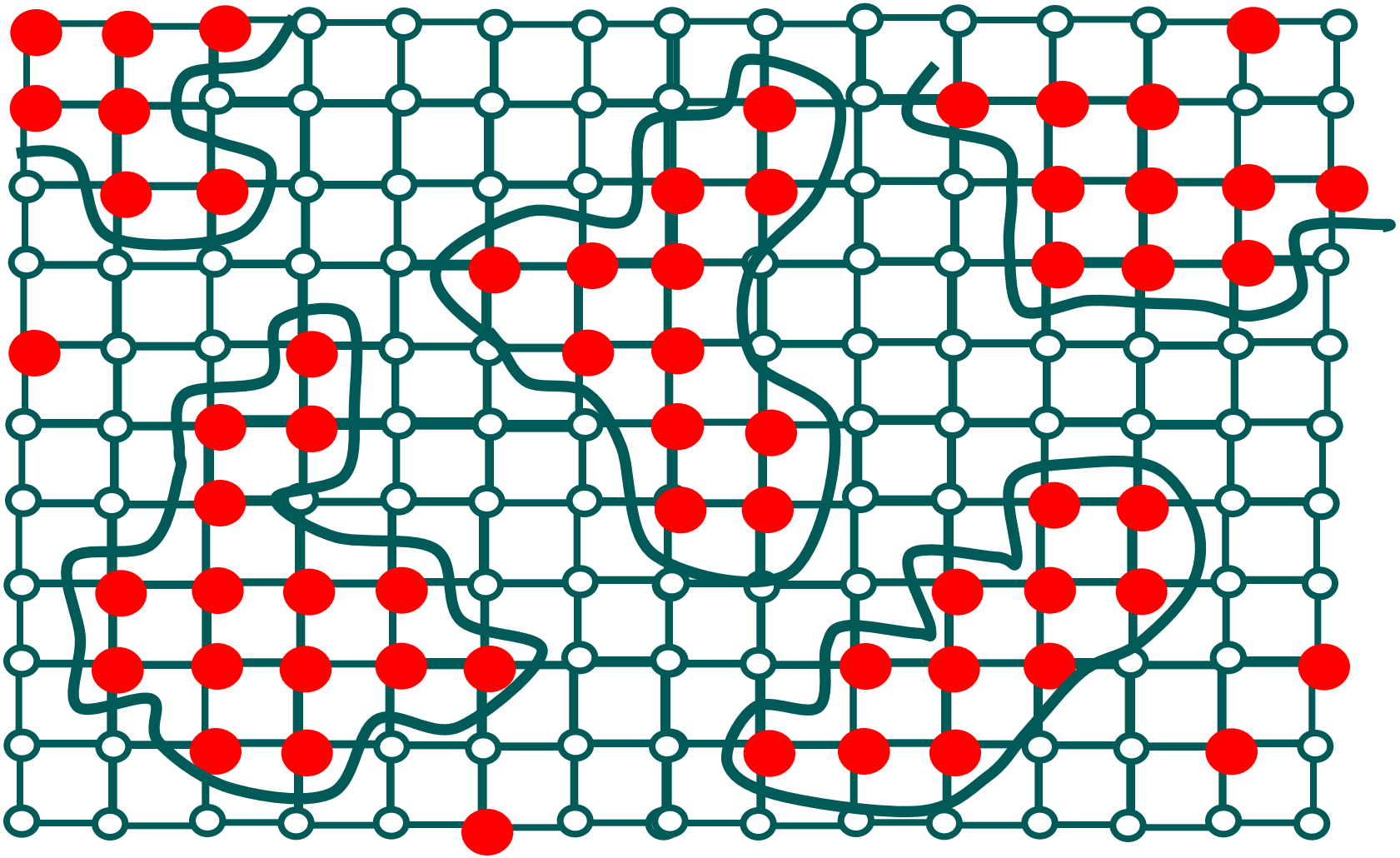


Non-local physics: large-sized impurity states



Anderson localization, multiple scattering required

Non-local physics: short-range order



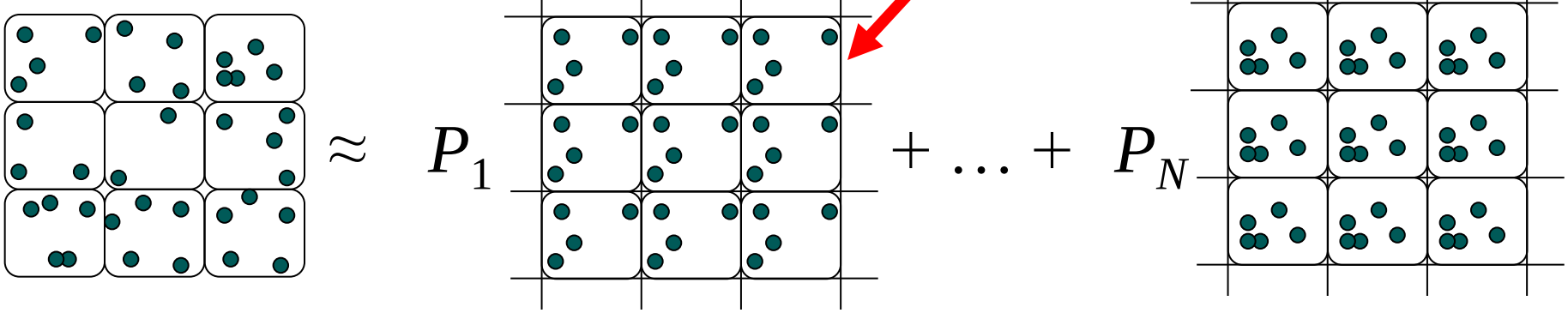
Configuration average over super cell

big super cells

disordered system

configuration 1

configuration N

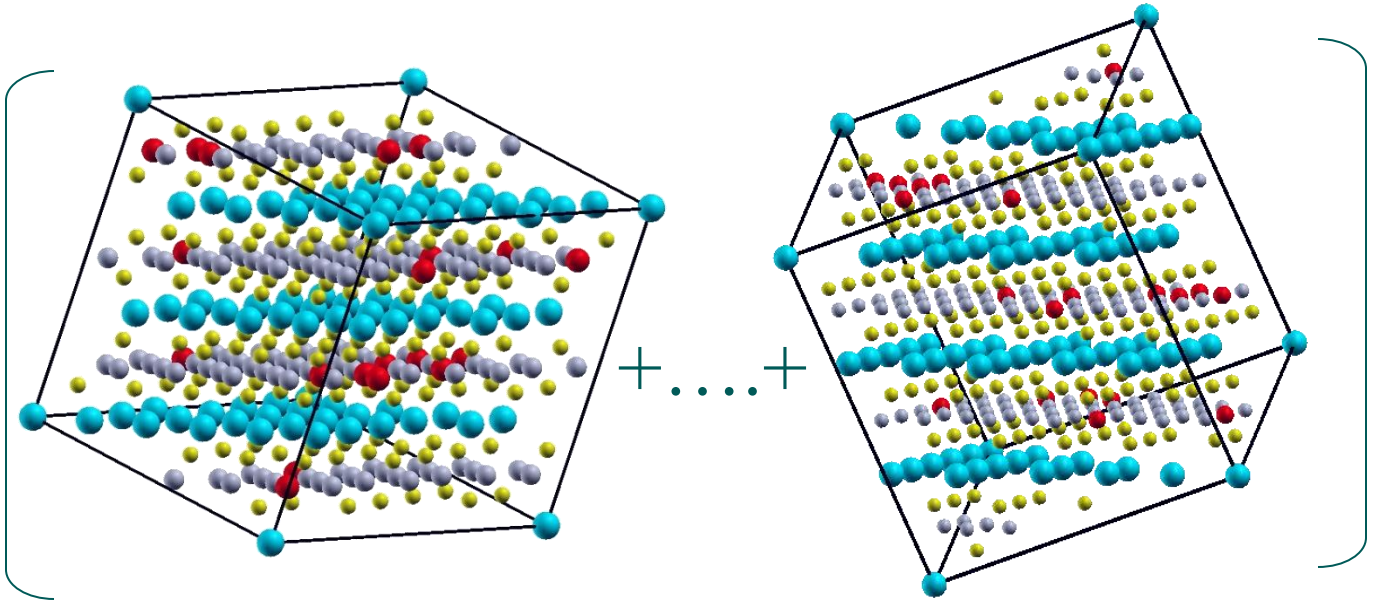


$$\langle G \rangle \approx P_1 G_1 + \ldots + P_N G_N$$

Challenge: solving many Hamiltonians with big super cells

Configuration average over super cell

big super cells (100 ~ 1000 of atoms)



$$\langle G \rangle \approx P_1 G_1 + \ldots + P_N G_N$$

Challenge: solving many Hamiltonians with big super cells

Constructing small and accurate effective H

Consider H from influence of impurities at $x_1, \ldots, x_N$

$$H^{(x_1,\ldots,x_N)} = H^0 + \sum_{i=1}^{N} \Delta^{(x_i)} + \sum_{i>j=1}^{N} \Delta^{(x_i,x_j)} + \ldots$$

1. Calculate $H^0, H^{(x_i)}$ & $H^{(x_i,x_j)}$ in same Wannier basis from DFT
2. Calculate Δ by taking difference of H^{DFT} in Wannier basis

$$\Delta^{(x_i)} = H^{(x_i)} - H^0; \quad \Delta^{(x_i,x_j)} = H^{(x_i,x_j)} - H^0 - \Delta^{(x_i)} - \Delta^{(x_i)}$$

3. Assemble H_c for each disorder configuration

$$\left\langle r'n' \middle| H^{((r_1,m_1),\ldots,(r_N,m_N))} \middle| r''n'' \right\rangle =$$

$$\left\langle r'-r'', n' \middle| H^0 \middle| 0n'' \right\rangle + \sum_{i=1}^{N} \left\langle r'-r_i, n' \middle| \Delta^{(m_i)} \middle| r''-r_i, n'' \right\rangle + \ldots$$

4. Solve H and unfold $A(k, \omega)$ to the normal cell unit
5. Average over configurations with different size & shape

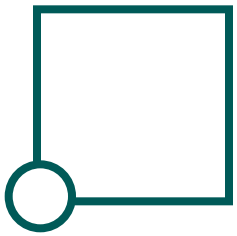
$$\langle A(k,w) \rangle = \sum_c P_c A_c(k,w)$$

T. Berlijn, D. Volja, and Wei Ku, PRL **106**, 077005 (2011)

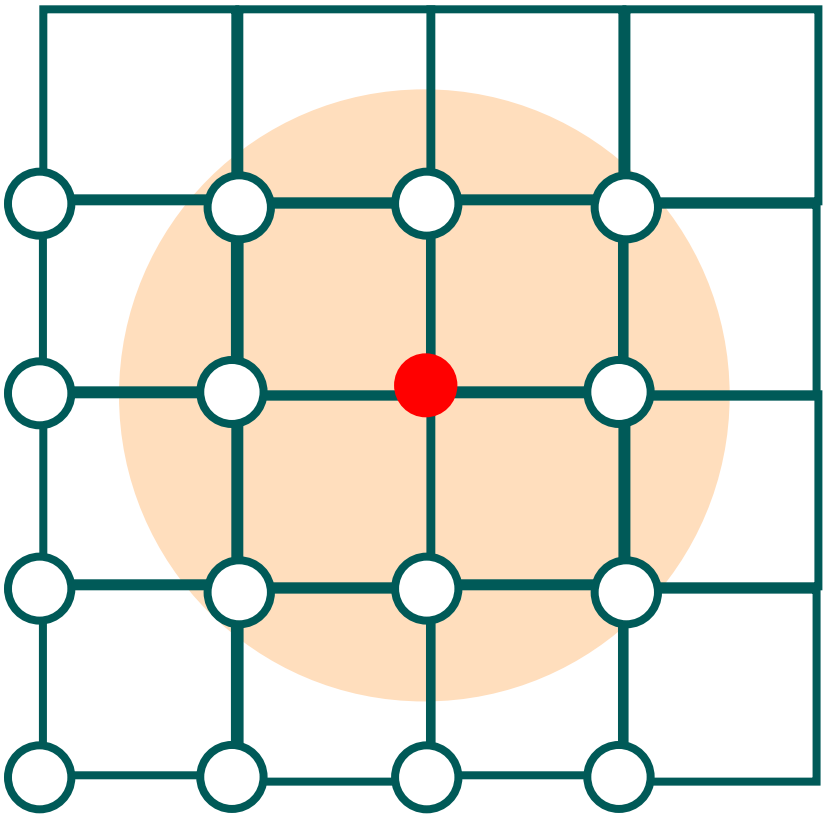
Including Effects in Density Functional Theory

two DFT Calculations

undoped normal cell

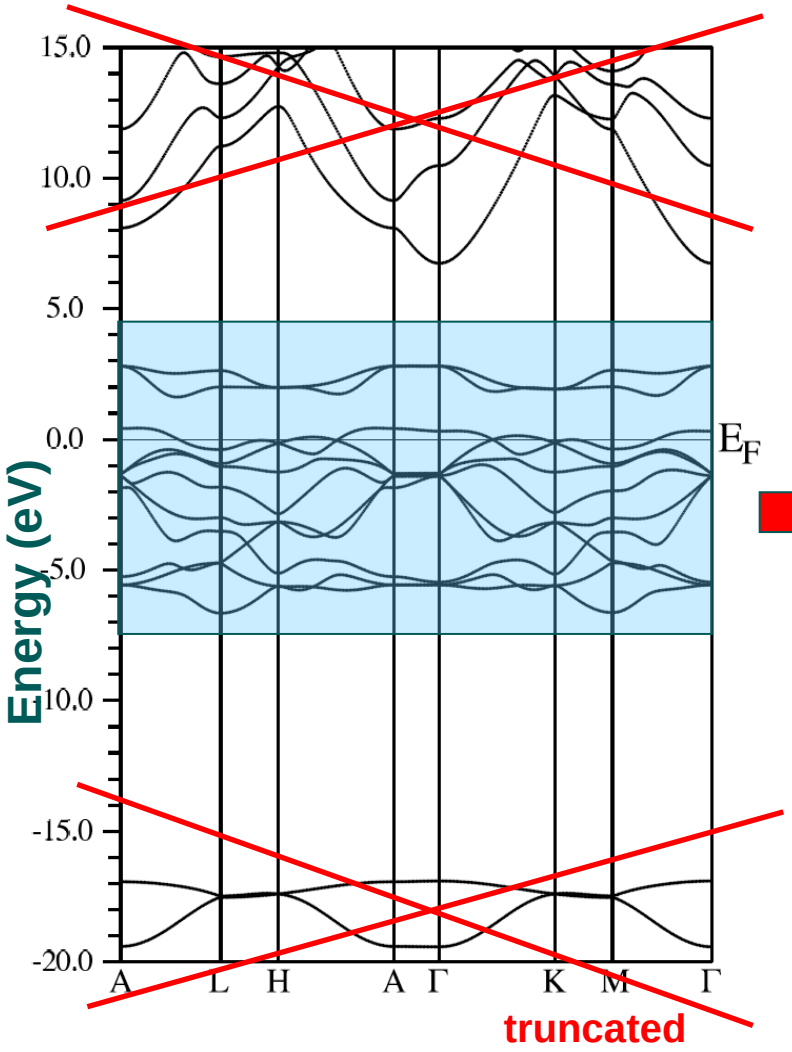


1 impurity in large super cell

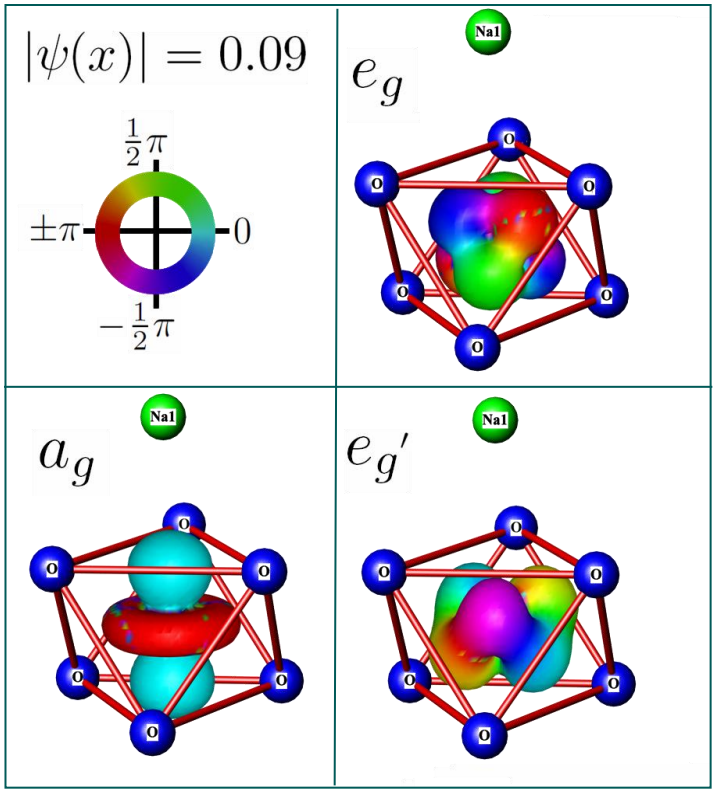


Reducing Hilbert Space via Wannier Transformation

DFT CoO_2

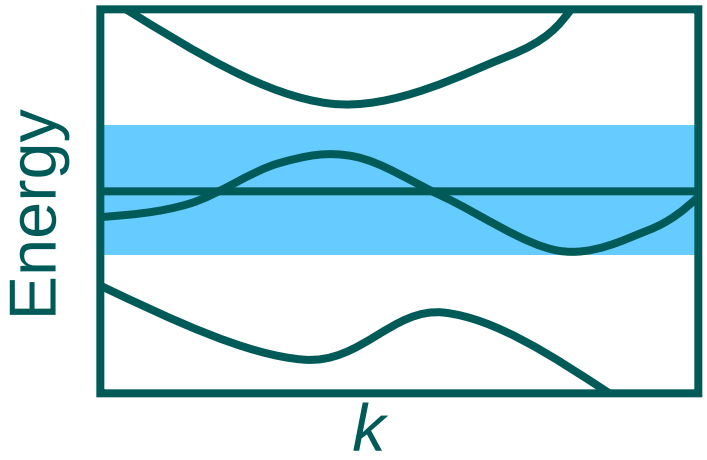


Wannier functions

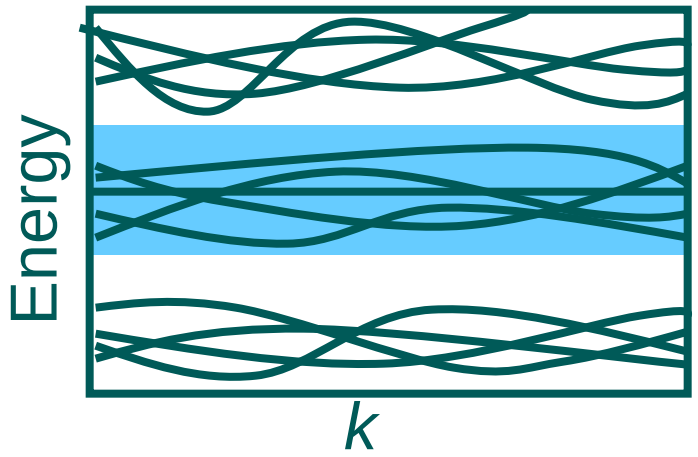


Obtain Effects of Impurities on H^{DFT}

DFT undoped



DFT 1 impurity



2 Wannier transformations

$$|\mathbf{Rn}>=\sum_{\mathbf{k,j}} \mathbf{e}^{-\mathbf{ik}\cdot\mathbf{R}}\mathbf{U_{nj}(k)}|\mathbf{kj}>$$

Reduced Hilbert space

2 Tight Binding Hamiltonians

undoped	1 impurity
$\mathbf{H}^{\mathbf{0}}_{\mathbf{DFT}}$	$\mathbf{H}^{\mathbf{1}}_{\mathbf{DFT}}$

$$\Delta^{(x_i)} = H^{(x_i)} - H^0$$

Constructing small and accurate effective H

Consider H from influence of impurities at $x_1, \ldots, x_N$

$$H^{(x_1,\ldots,x_N)} = H^0 + \sum_{i=1}^{N} \Delta^{(x_i)} + \sum_{i>j=1}^{N} \Delta^{(x_i,x_j)} + \ldots$$

1. Calculate $H^0, H^{(x_i)}$ & $H^{(x_i,x_j)}$ in same Wannier basis from DFT
2. Calculate Δ by taking difference of H^{DFT} in Wannier basis

$$\Delta^{(x_i)} = H^{(x_i)} - H^0; \quad \Delta^{(x_i,x_j)} = H^{(x_i,x_j)} - H^0 - \Delta^{(x_i)} - \Delta^{(x_i)}$$

3. Assemble H_c for each disorder configuration

$$\left\langle r'n' \middle| H^{((r_1,m_1),\ldots,(r_N,m_N))} \middle| r''n'' \right\rangle =$$

$$\left\langle r'-r'', n' \middle| H^0 \middle| 0n'' \right\rangle + \sum_{i=1}^{N} \left\langle r'-r_i, n' \middle| \Delta^{(m_i)} \middle| r''-r_i, n'' \right\rangle + \ldots$$

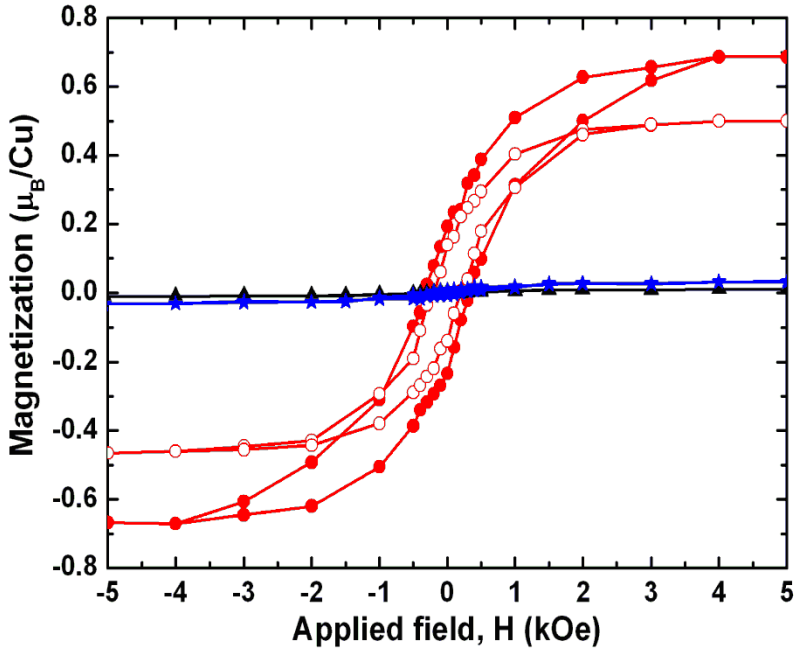
4. Solve H and unfold $A(k, \omega)$ to the normal cell unit
5. Average over configurations with different size & shape

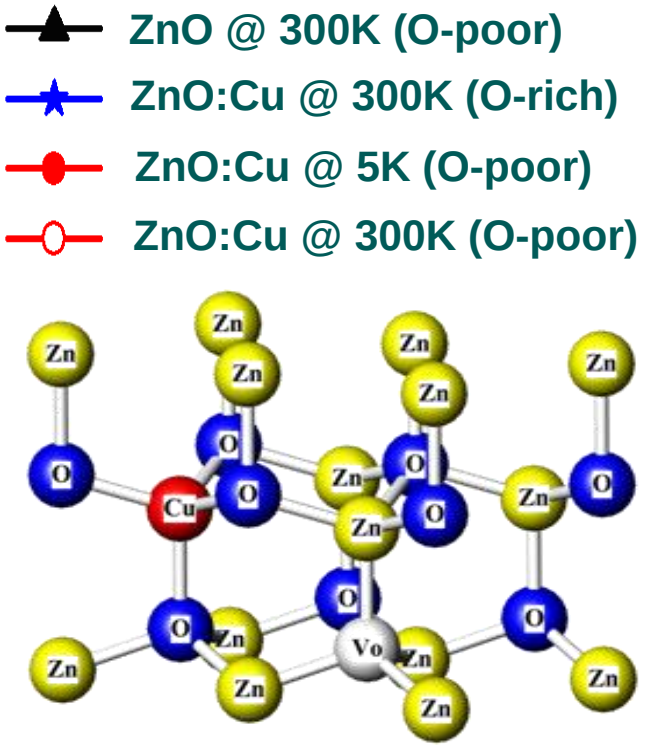
$$\langle A(k,w) \rangle = \sum_c P_c A_c(k,w)$$

T. Berlijn, D. Volja, and Wei Ku, PRL **106**, 077005 (2011)

Substitution & vacancies: $Zn_{1-x}Cu_xO_{1-y}$

SQUID

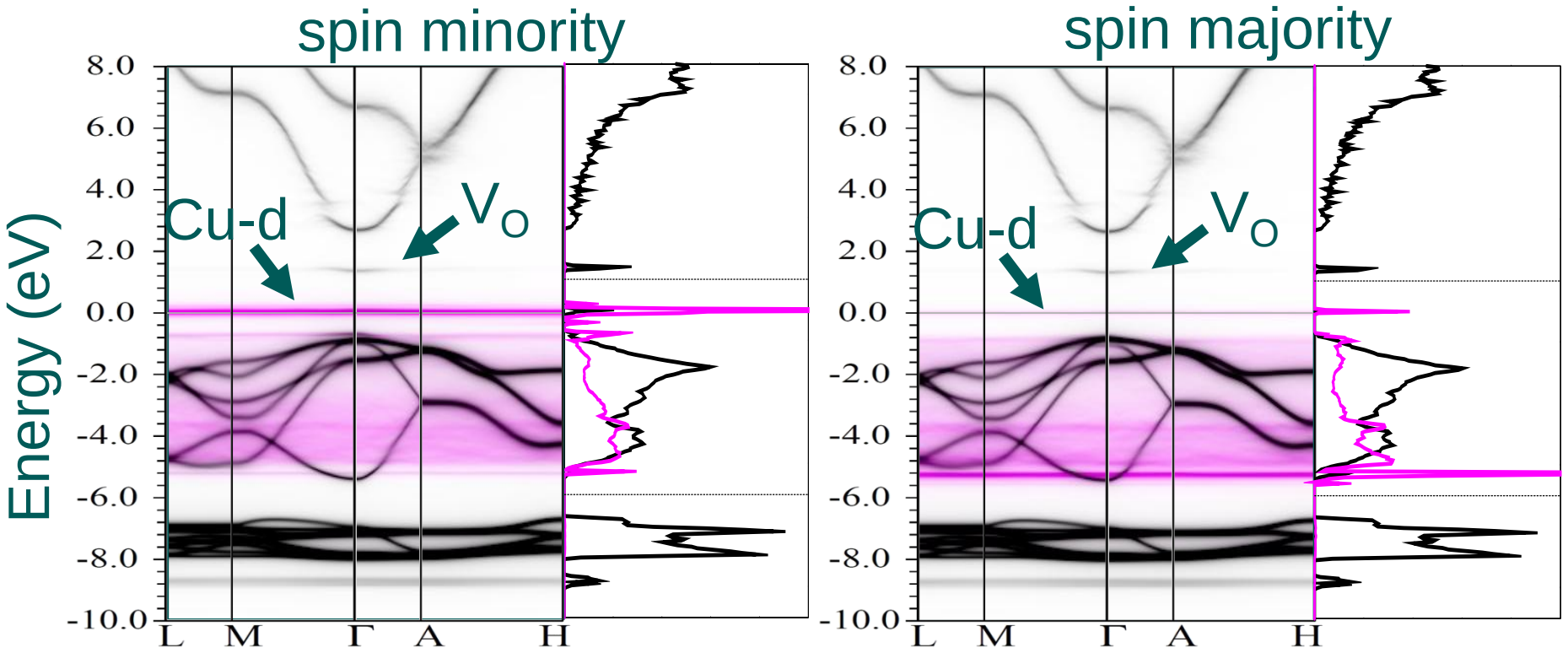




Q1) Where do the doped electrons reside?

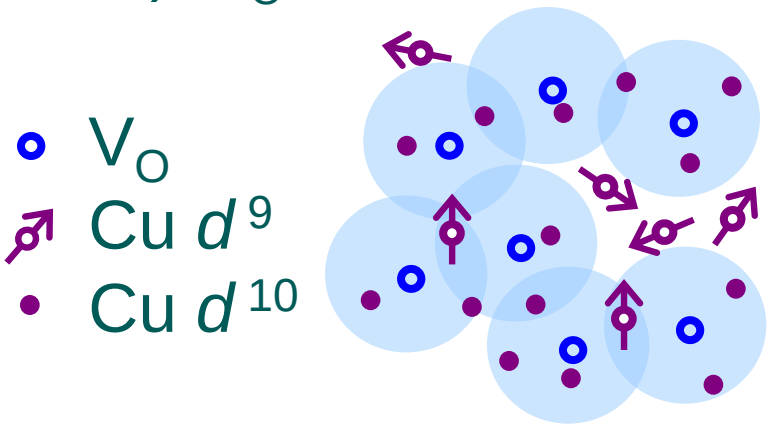
Q2) What is the role of oxygen vacancy?

T. S. Herng, *et. al*, PRL **105**, 207201 (2010)



A1) Doped electrons reside in Cu orbitals

A2) V_O mediates Cu moments



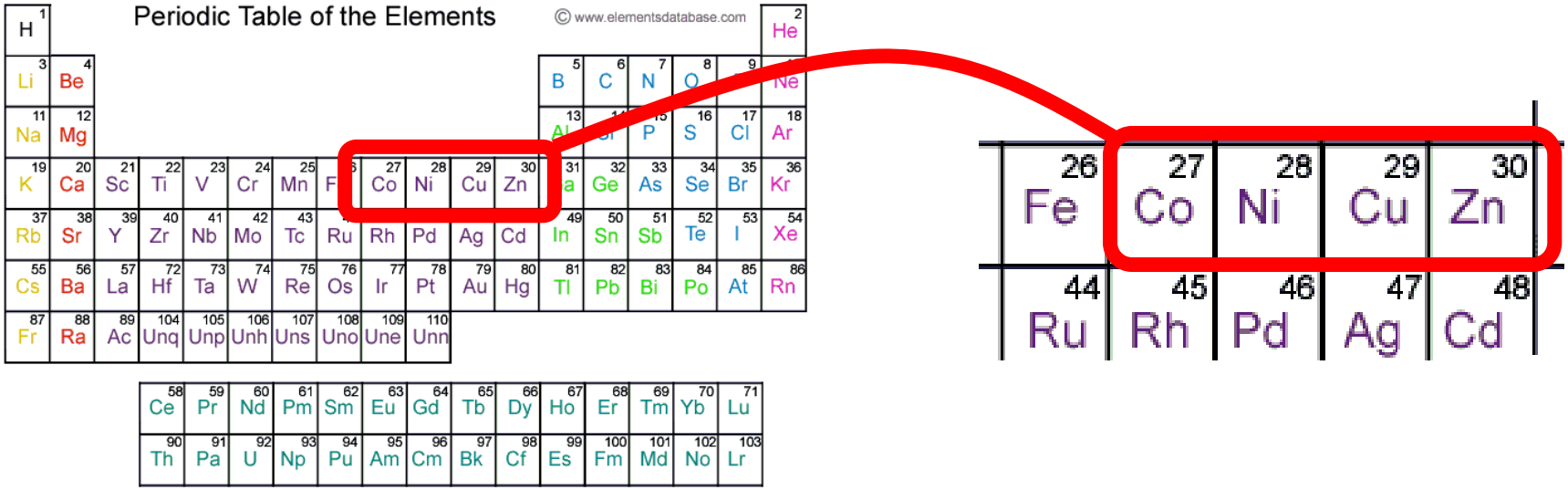
T. S. Herng, *et. al*, PRL **105**, 207201 (2010)

Do transition metal substitution dope carriers in Fe-based superconductors

T. Berlijn & Wei Ku

PRL **108**, 207003 (2012)

Do TM substitutions dope carriers in Fe-SC?



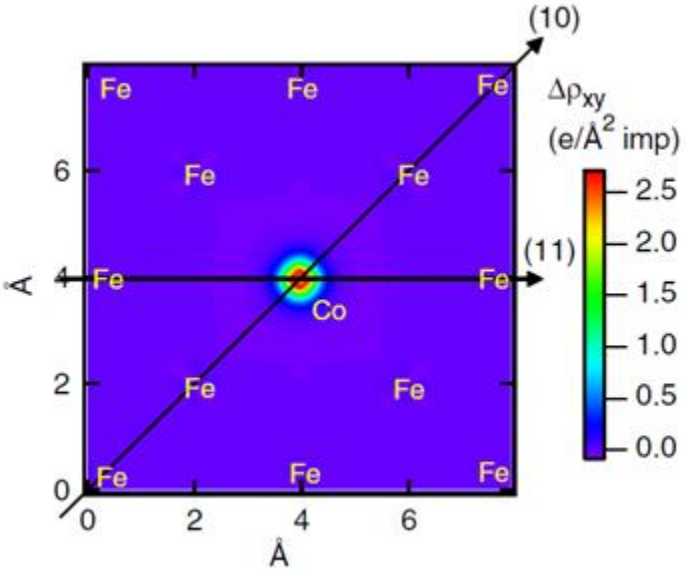
more valence electrons than Fe → expect electron doping

Additional Charge Residing in the Substituted Atoms in Fe-SC

Theory

DFT (density)

Co:122

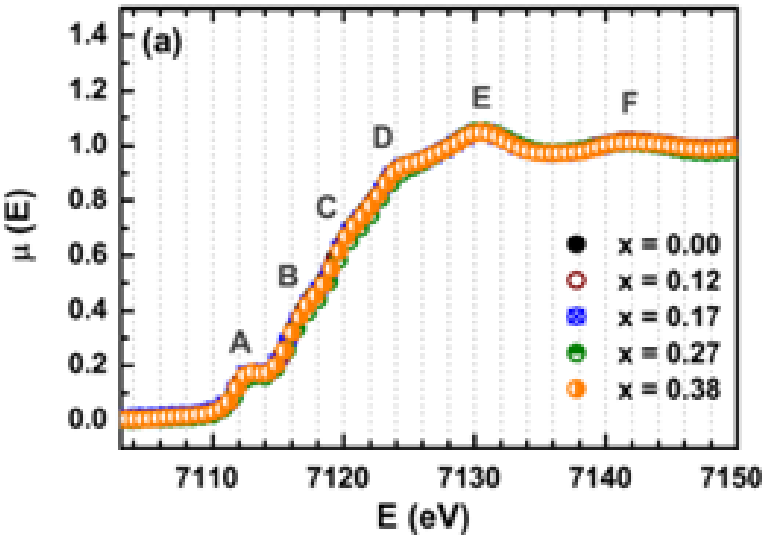


H. Wadati *et al*, PRL **105** (2010)

Experiment

XANES

Co:122



E. M. Bittar *et al*, PRL **107** (2011)

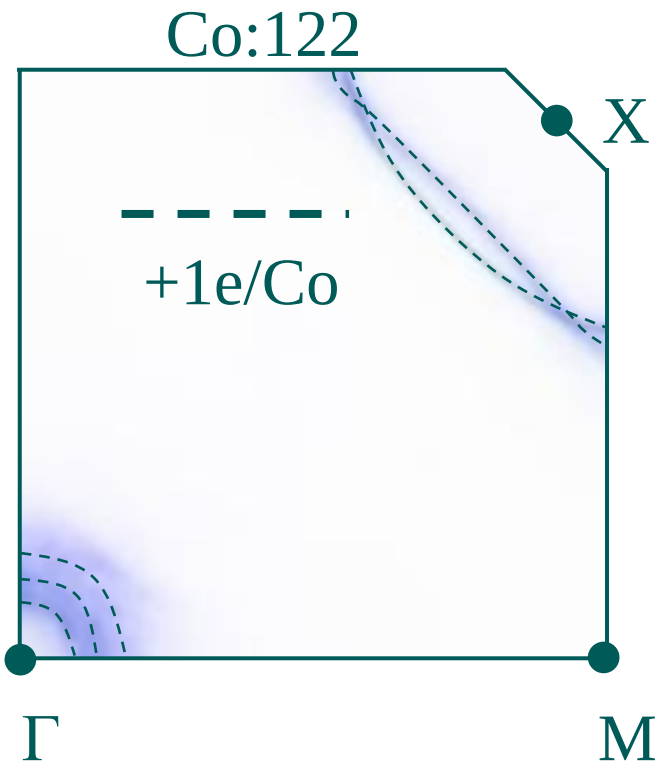
- Substitution does not dope the system (?)

12.5% Co Substituted $BaFe_2As_2$

$$\sum_{n\in\alpha}\int_{BZ} d^3k \int^{E_F} d\omega \langle A_n(k,\omega)\rangle$$

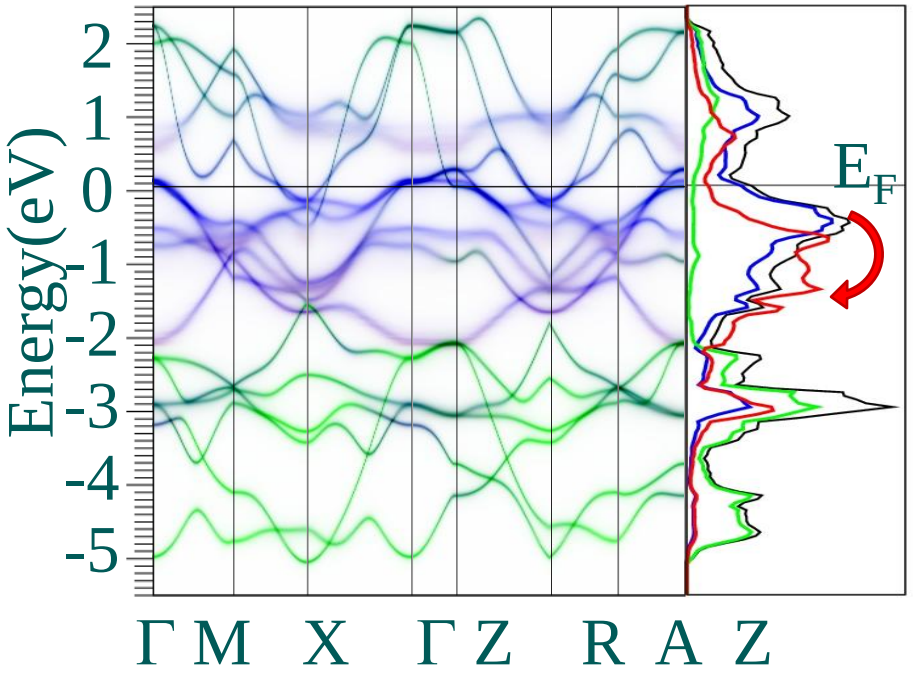
	α	
122	Fe	7.22
Co:122	Fe	7.19 x 7/8
Co:122	Co	8.40 x 1/8

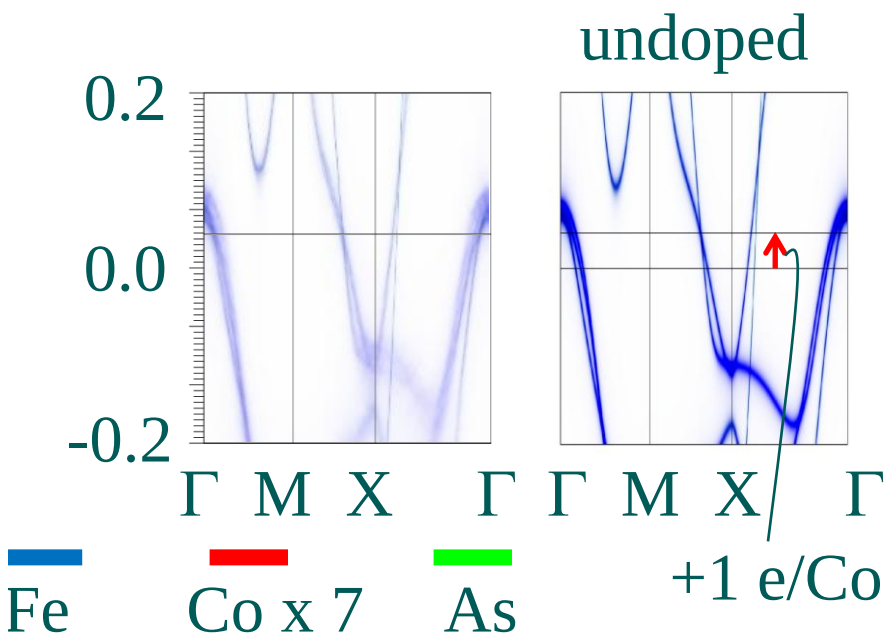
$$\langle A(k,\omega = E_F)\rangle$$



- Change of density in substituted atoms → not doping ?
- Enlarged Fermi surfaces & shift of chemical potential → doping?

Example: Does Co/Zn substitution dope Fe-SC?





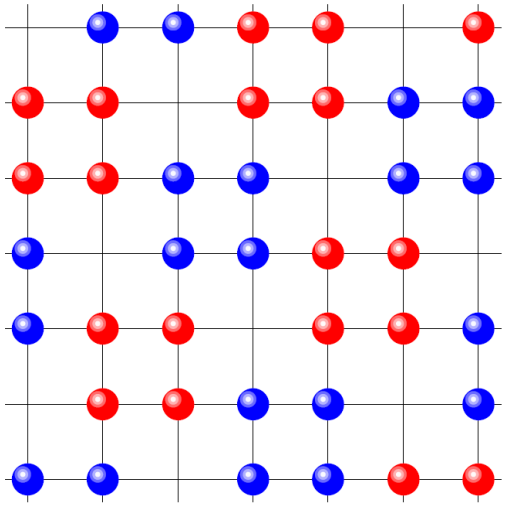
Most definitely yes, in the simplest manner,
but some carriers lose coherence!

Tom Berlijn, *et al.*, PRL **108**, 207003 (2012)

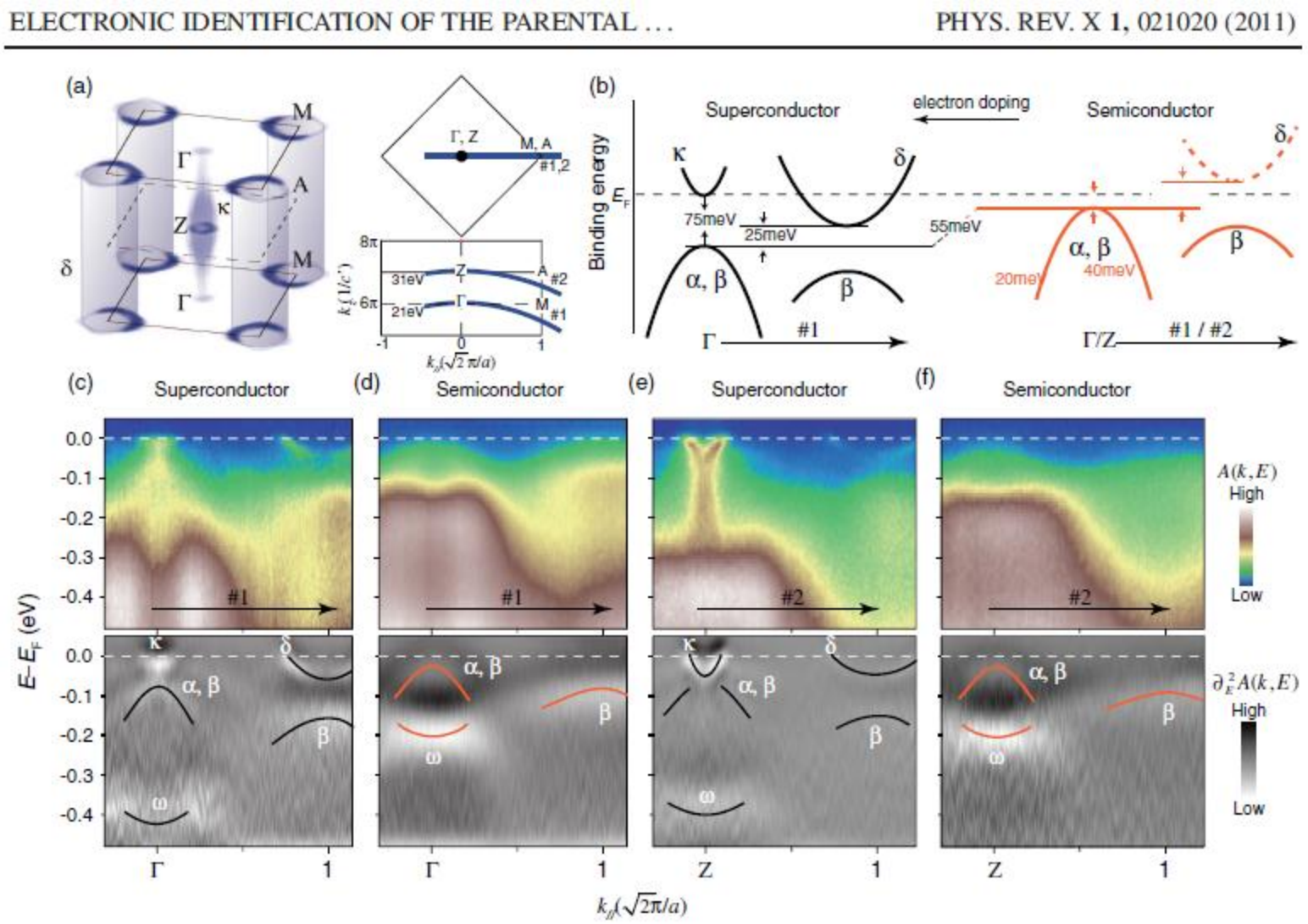
Fe vacancy in K2Fe4Se5

T. Berlijn, P. Hirschfeld, & Wei Ku

PRL **109**, 147003 (2012)

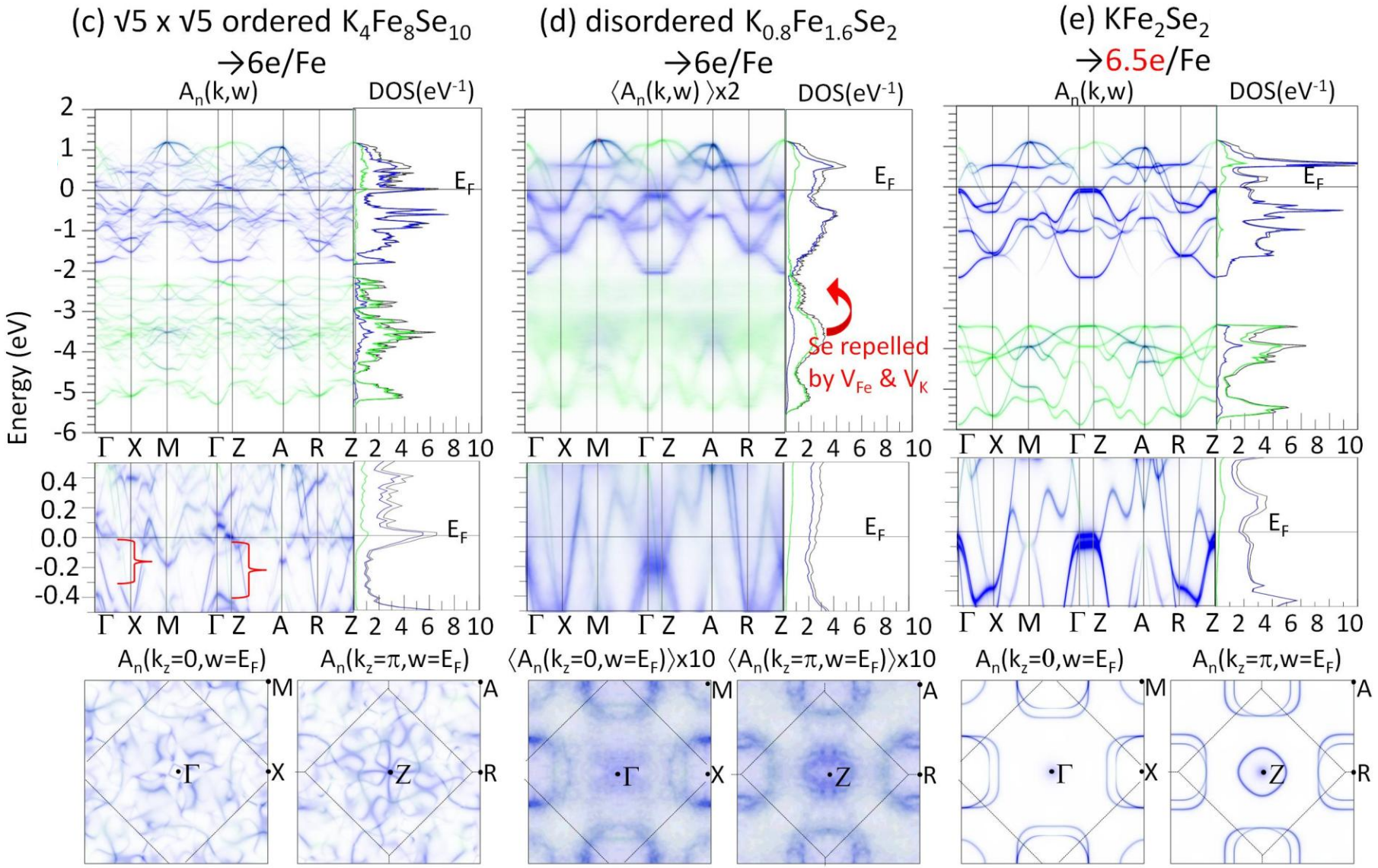


A heavily electron doped system?



F. Chen et al. Phys. Rev. X **1**, 021020 (2011)

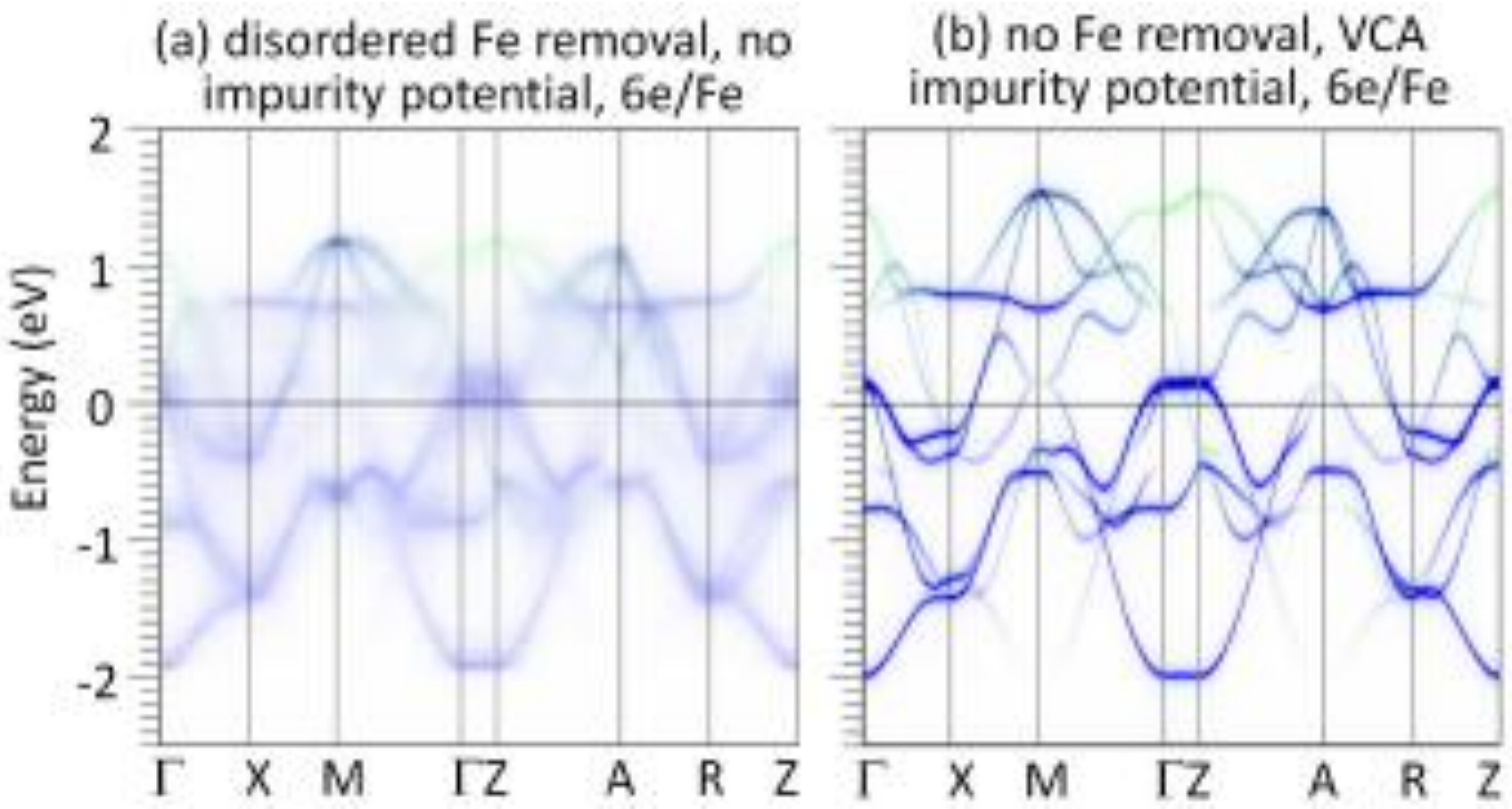
Effective "doping" with Fe vacancy: Luttinger theorem?



Appears to be heavily doped ~ 0.5 e / Fe with disordered Fe vacancy

Tom Berlijn, Peter Hirschfeld, and Wei Ku, **109**, 147003 (2012)

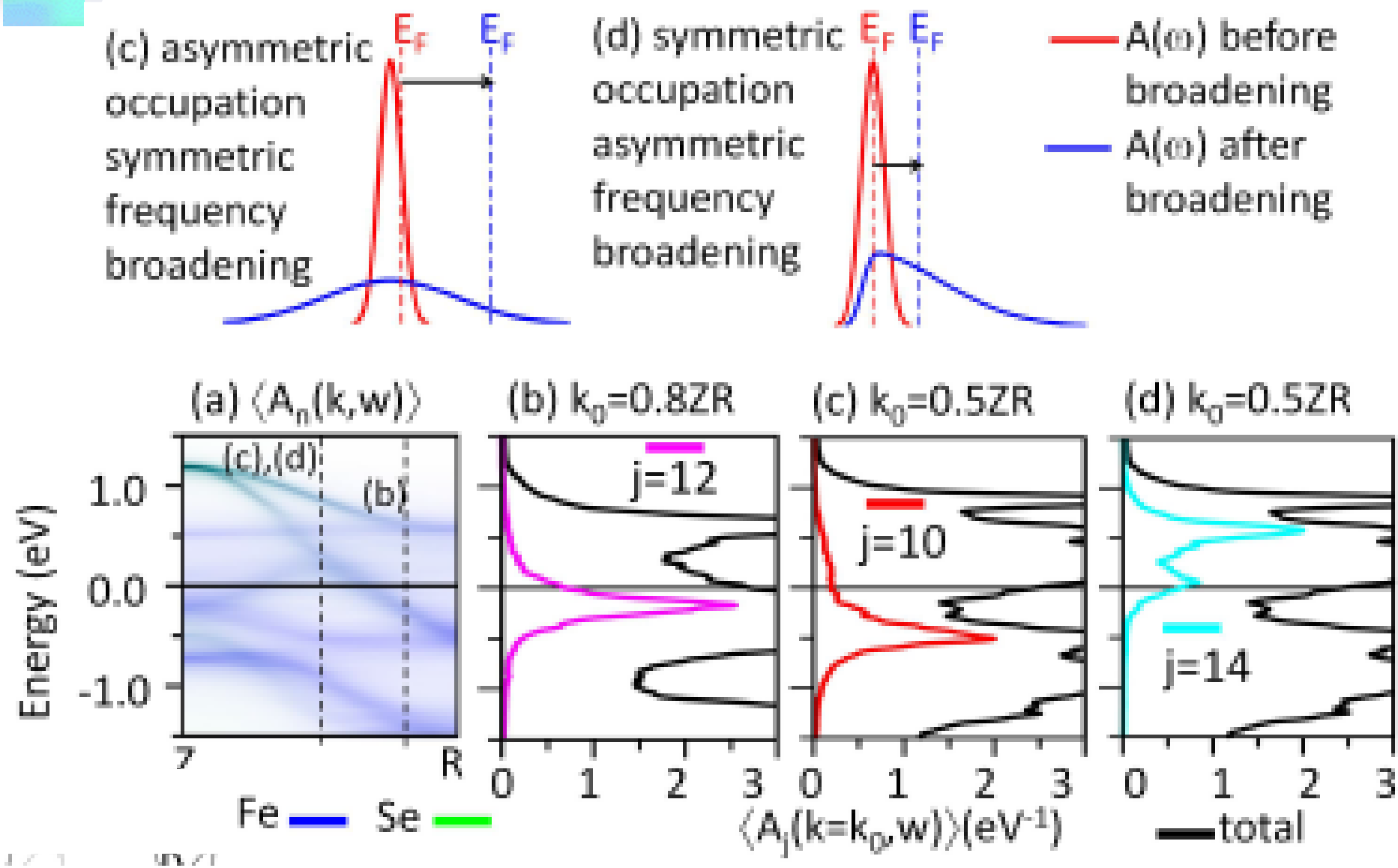
Origin of the effective "doping" with Fe vacancy



- Need both disorder and the impurity potential

Tom Berlijn, Peter Hirschfeld, and Wei Ku, **109**, 147003 (2012)

Effects of disordered impurity potential



Tom Berlijn, Peter Hirschfeld, and Wei Ku, **109**, 147003 (2012)

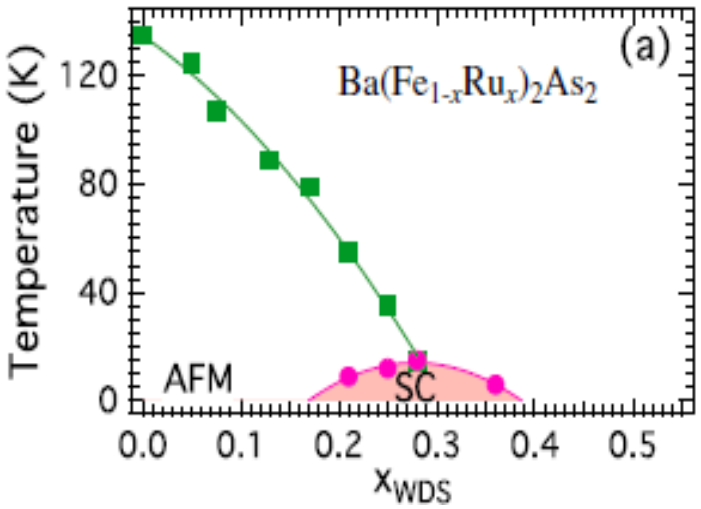
Ru substitution of BaFe2As2

Limin Wang, Tom Berlijn, Chia-Hui Lin, Yan Wang, Peter Hirschfeld,

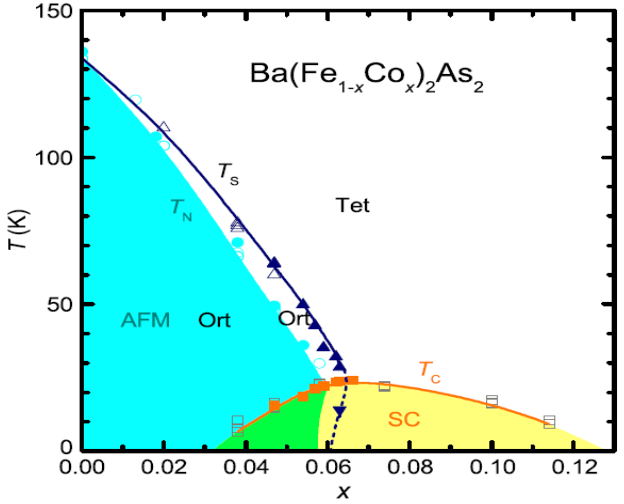
Wei Ku

PRL **110**, 037001 (2013)

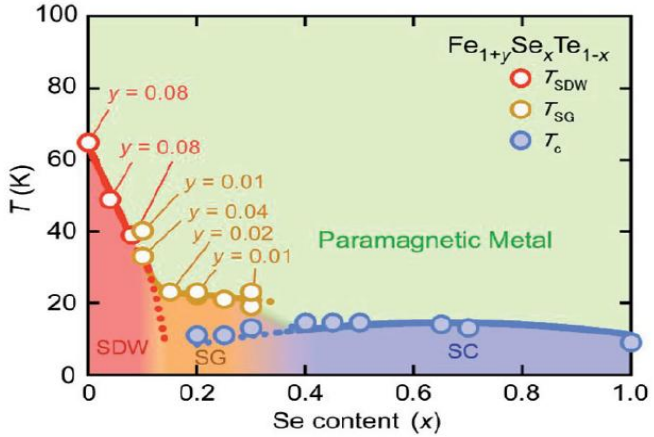
Temperature-composition phase diagram



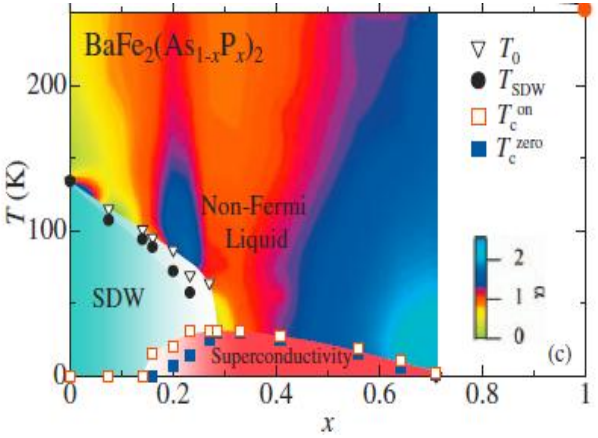
[R. S. Dhaka *et al*, PRL 107, 267002]



S. Nandi et al, PRL 104, 057006



[N. Katayama, et al , JPSJ 79,113702]



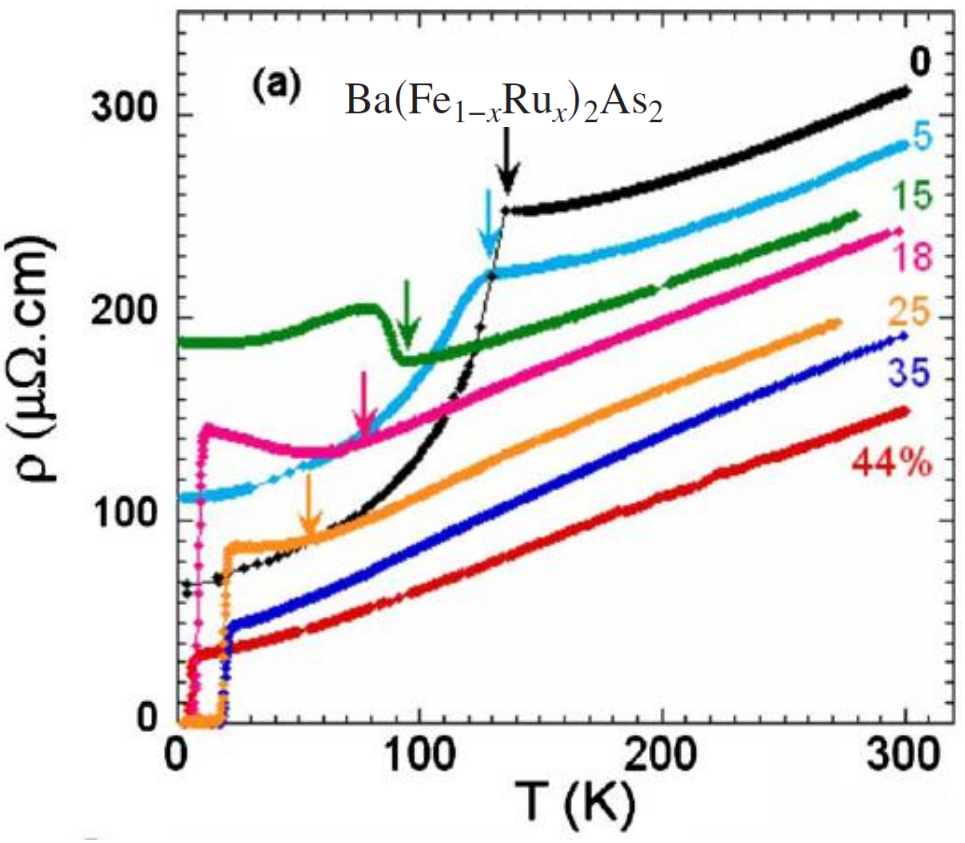
[S. Kasahara, et al , PRB 81 184519]

Ru/Co atoms replace the most essential Fe atom.

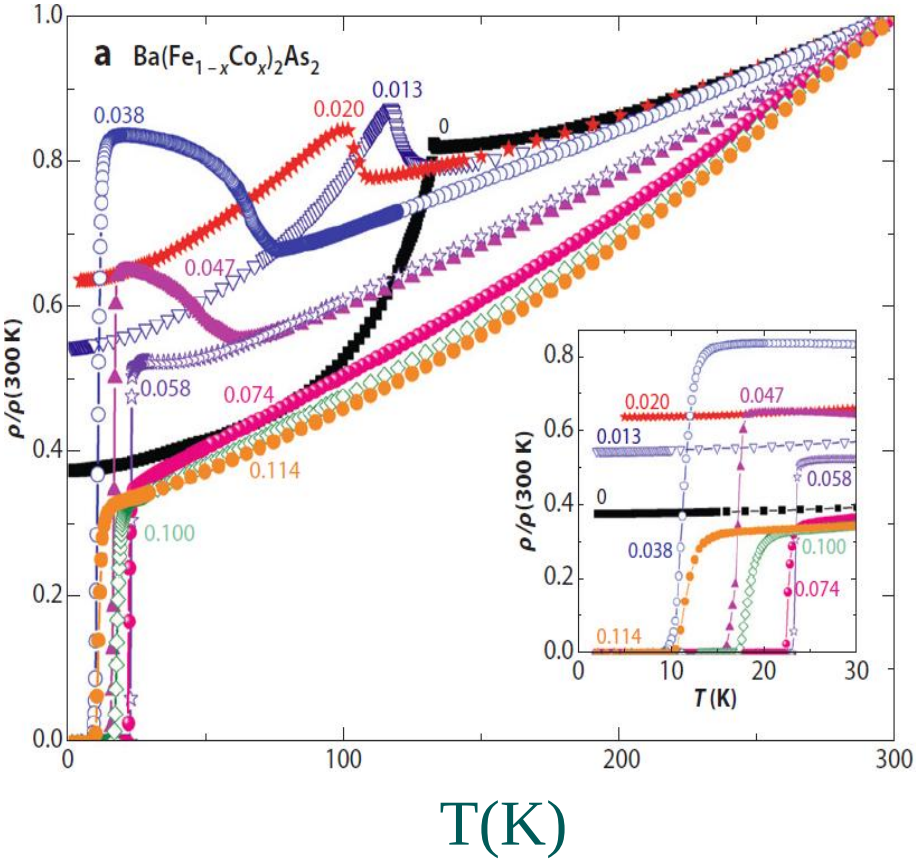
Superconductivity can survive even with 40% Ru substitution

Transport property

[F. Rullier-Albenque et al., PRB 81, 224503 (2010)]



[P. C. Canfield et al., Annu. Rev. Cond. Matt. 27 (2010)]



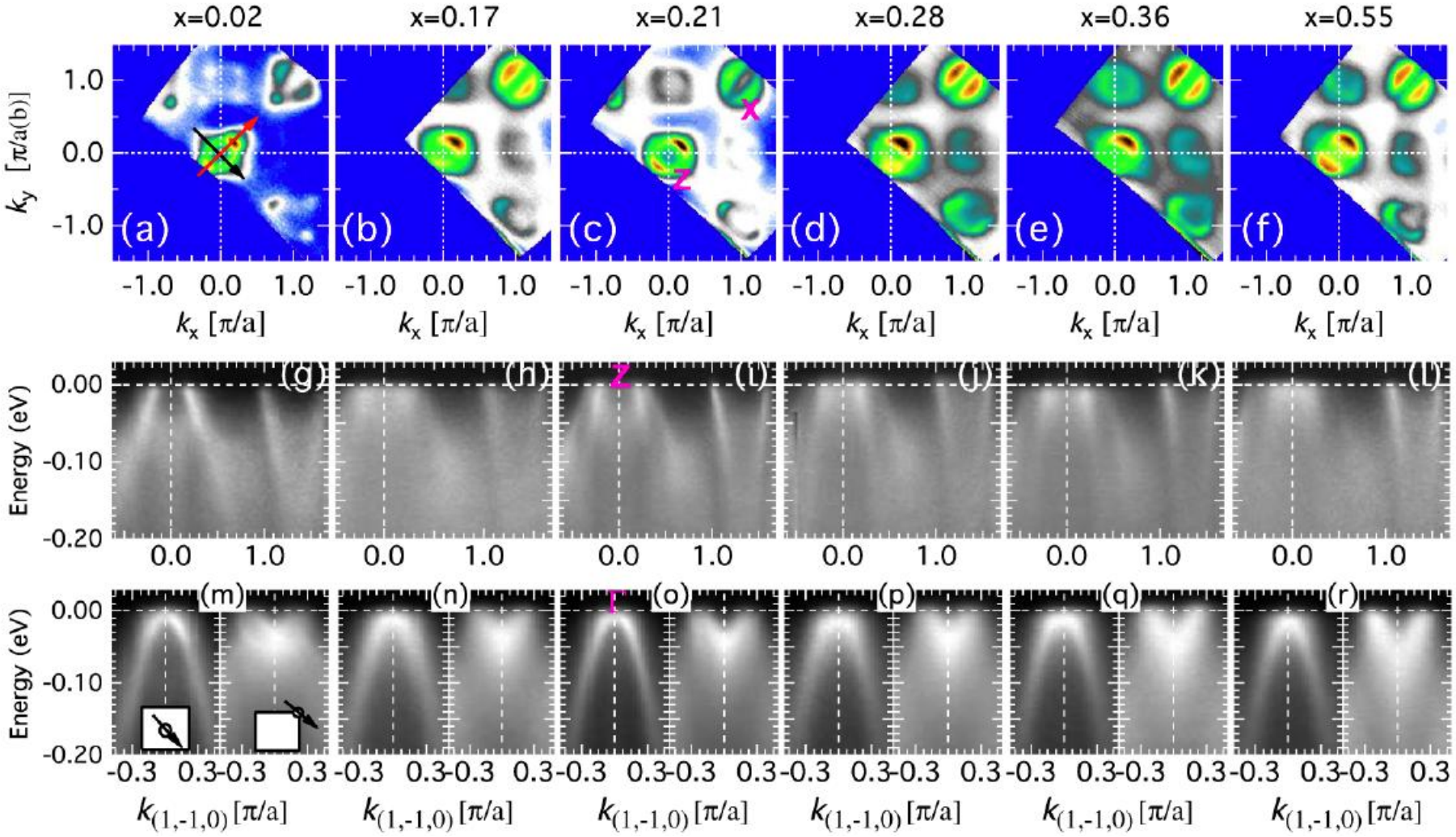
T(K)

Ru substituted samples exhibit a residual resistivity comparable to 8% substituted system at a much higher 35% substitution level

Experimental (ARPES) controversy

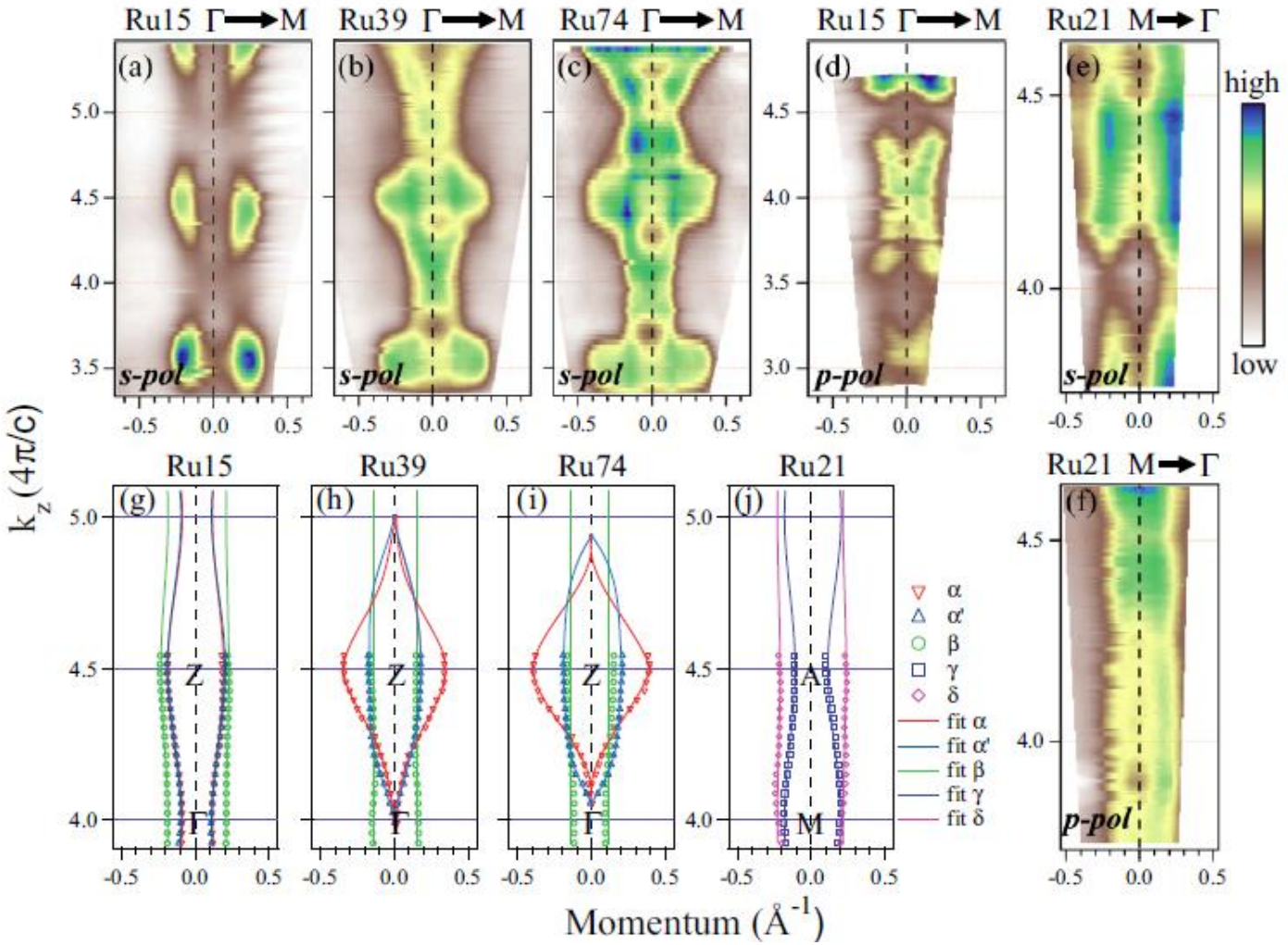
- Nearly substitution-independent FS

[R. S. Dhaka *et al*, PRL 107, 267002(2011)]

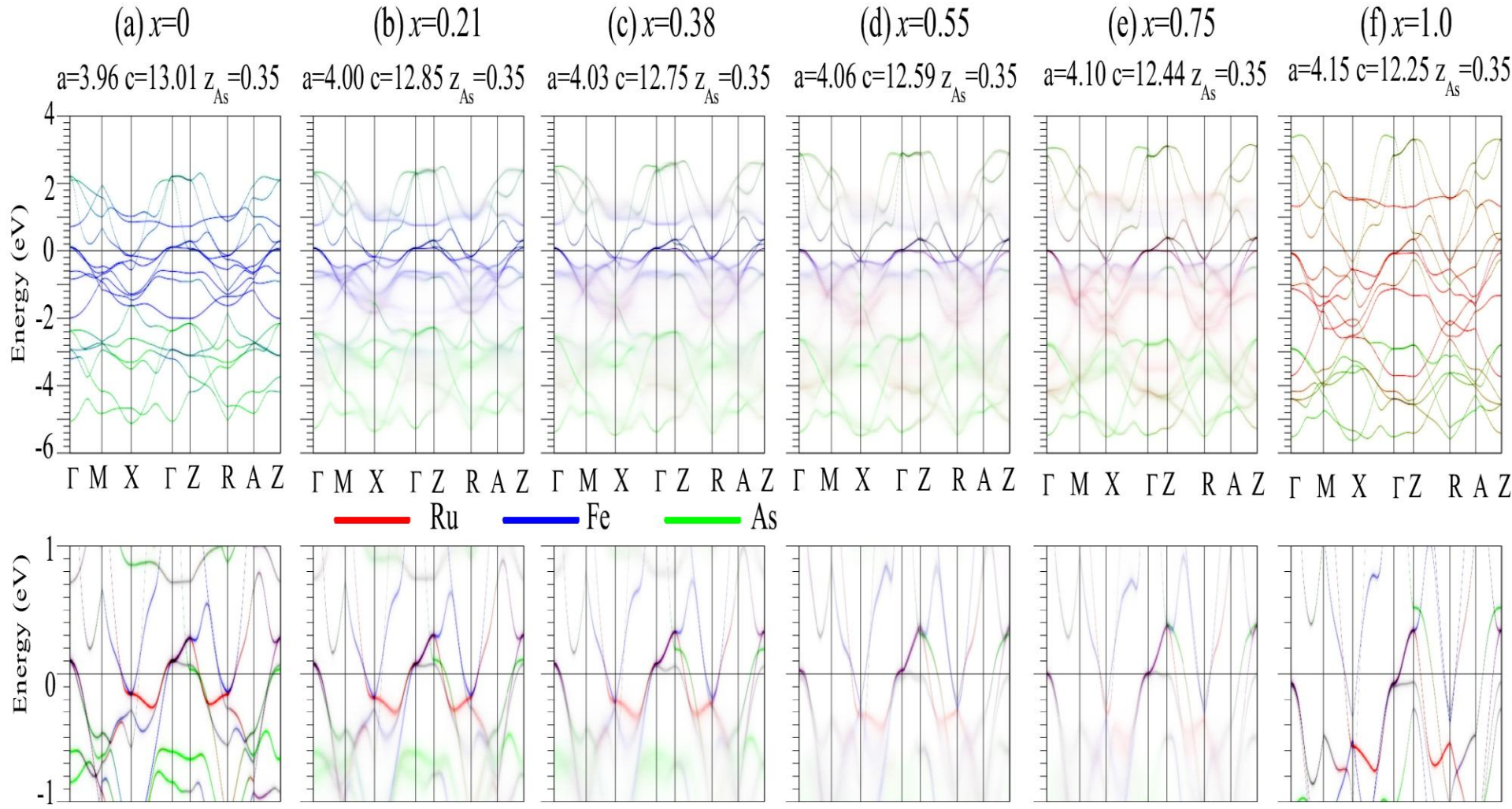


Experimental (ARPES) controversy

- A crossover from two-dimensional to three dimensional structure [N. Xu et al, PRB 86, 064505]

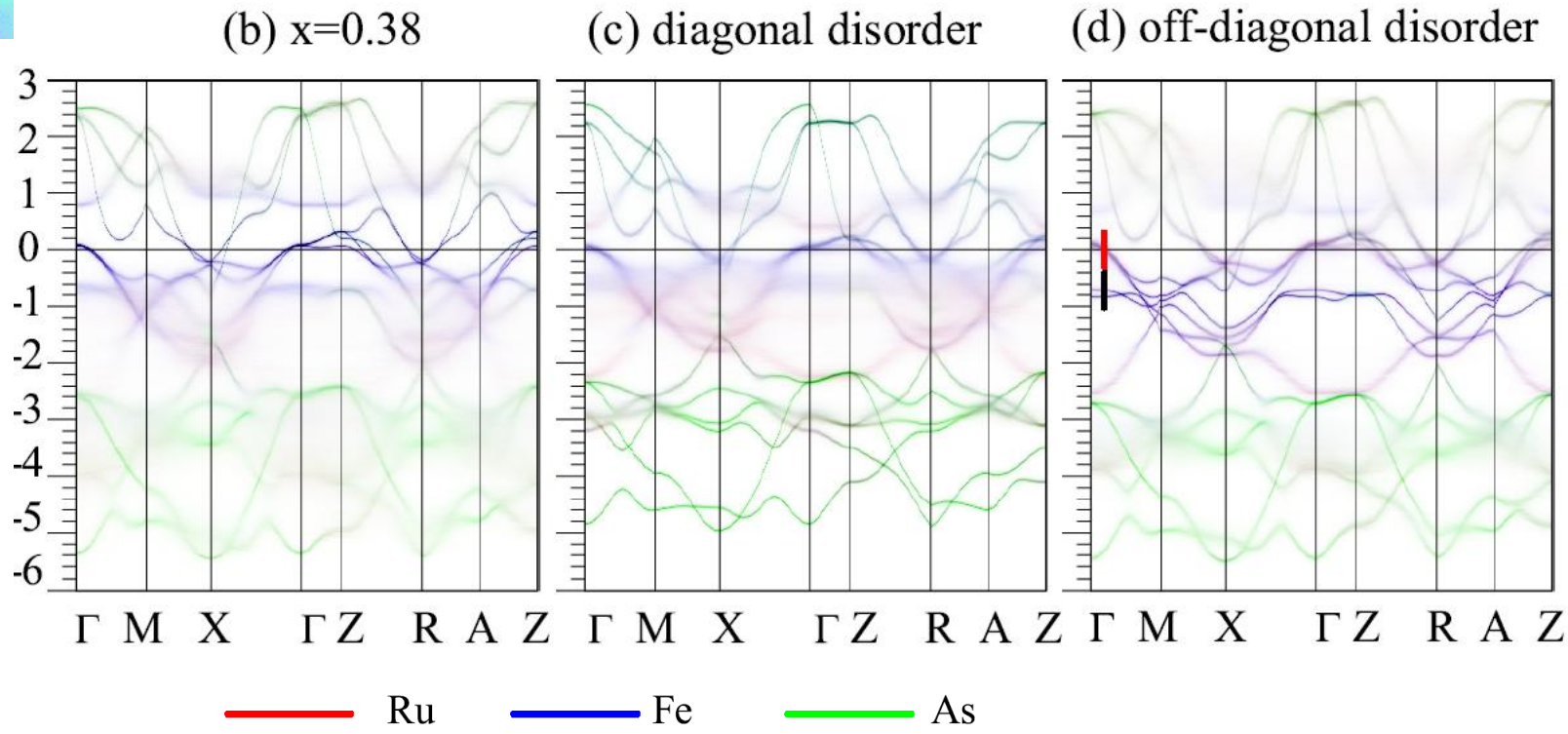


Band structure for different Ru substitution



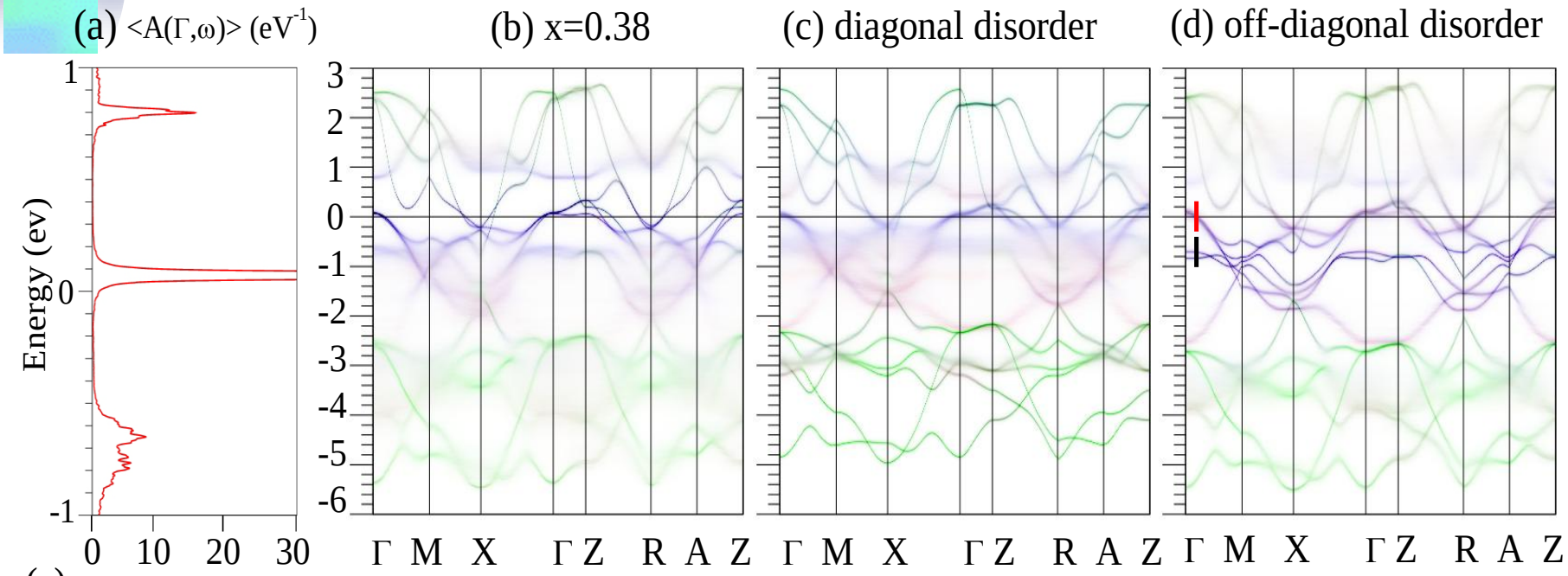
- The bands are heavily smeared.(-0.8eV)
- x=0.55 is the most disordered one.
- Fe bands around the Fermi level remain very sharp.

Origin of the superdiffusion around the Fermi level



- diagonal disorder only : strong smearing of the entire *d*-band
- off-diagonal disorder only : scattering diminishes near the center of the *d*-band.
- combined → weak impurity scattering near E_F

Origin of the superdiffusion around the Fermi level



(e)

k	j	k'	j'	$\langle kj\|\Delta\|k'j'\rangle$	$\langle kj\|\Delta_D\|k'j'\rangle$	$\langle kj\|\Delta_{OD}\|k'j'\rangle$
Γ	9	0.3ΓM	10	-0.0578	-0.3023	0.2445
Γ	8	0.3ΓM	7	-0.2938	-0.3316	0.0378

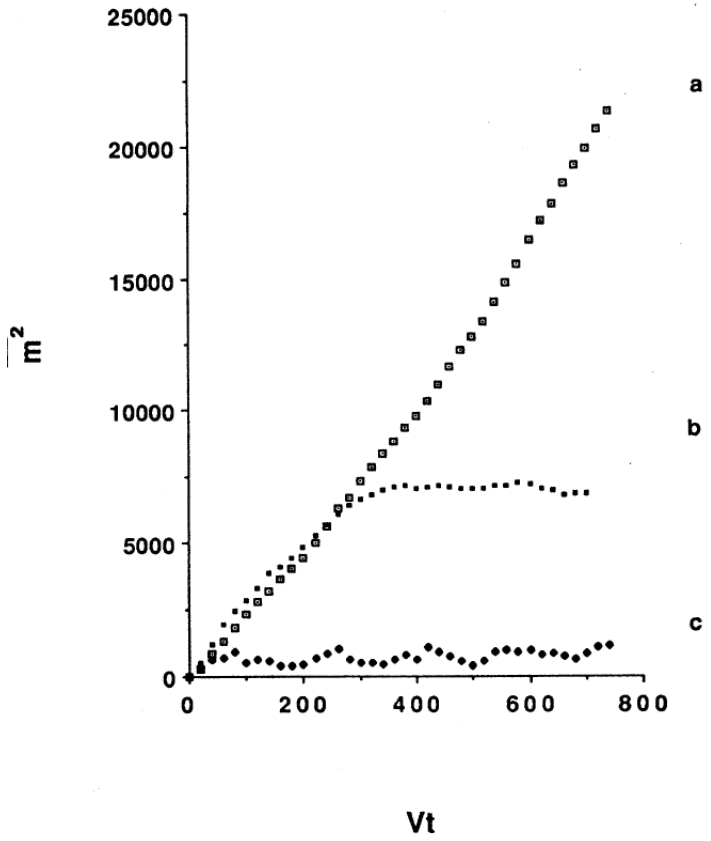
- The insensitivity originates from a coherent interference between on-site and off-site impurity effects.

Superdiffusion in 1D model

[D. H. Dunlap, K. Kundu, and P. Phillips, PRB 40, 10999 (1989)]

Single-particle Hamiltonian

$$H = H_{\text{lattice}} + \sum_{\mathbf{k}} \varepsilon_0 a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{k},\mu} 2V_{\mu} \cos(\phi_{\mu} - k_{\mu}) a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}}$$
$$+ \sum_{\mathbf{k},q,\mu} 2i[\gamma_{\mu} \sin(k_{\mu} - \theta_{\mu}) - \gamma_{\mu} \sin(k_{\mu} - q_{\mu} - \theta_{\mu})$$
$$- G_{\mu} \sin(q_{\mu})] x_q^{\mu} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}-\hat{\mu}q_{\mu}} , \qquad (1.2)$$



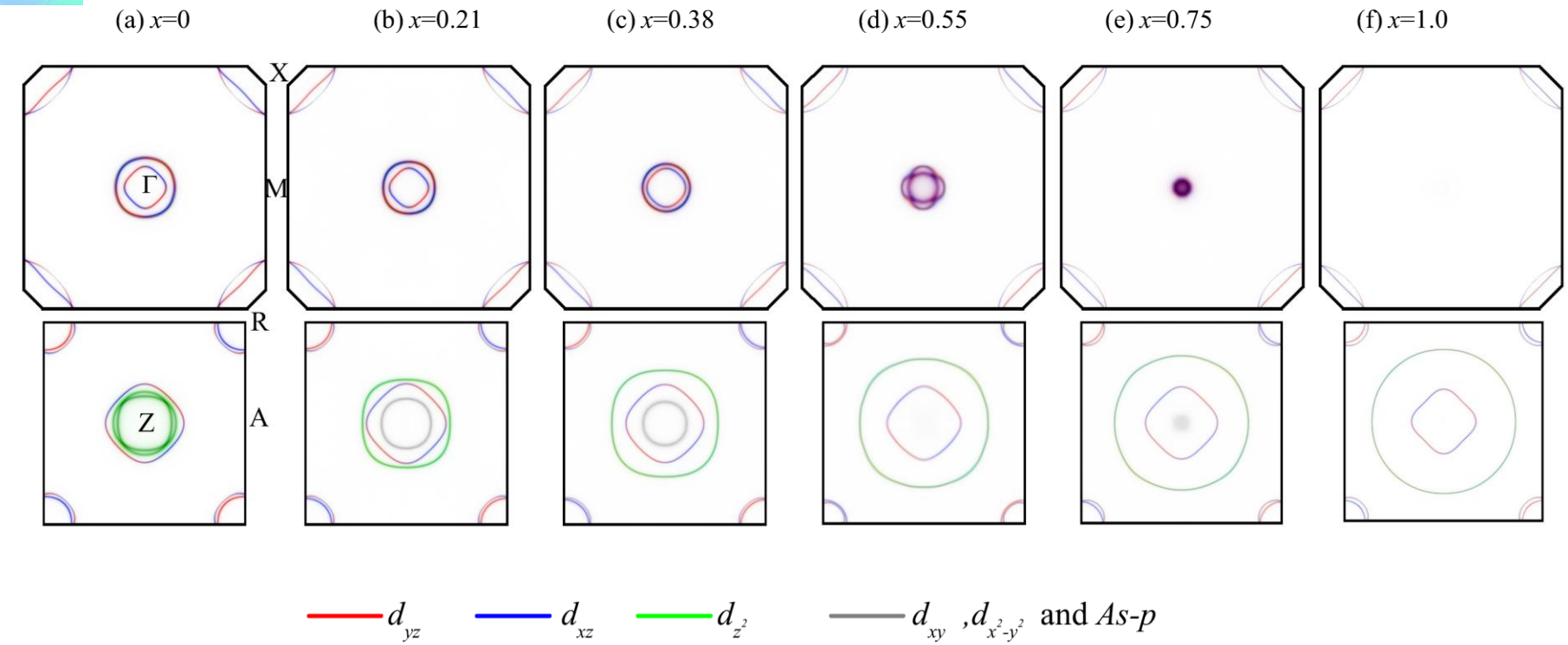
a correlated disorder ($\gamma = G$)

b site-diagonal disorder.

c site-off diagonal disorder.

- Correlations between site and off-diagonal disorder give rise to superdiffusion transport.

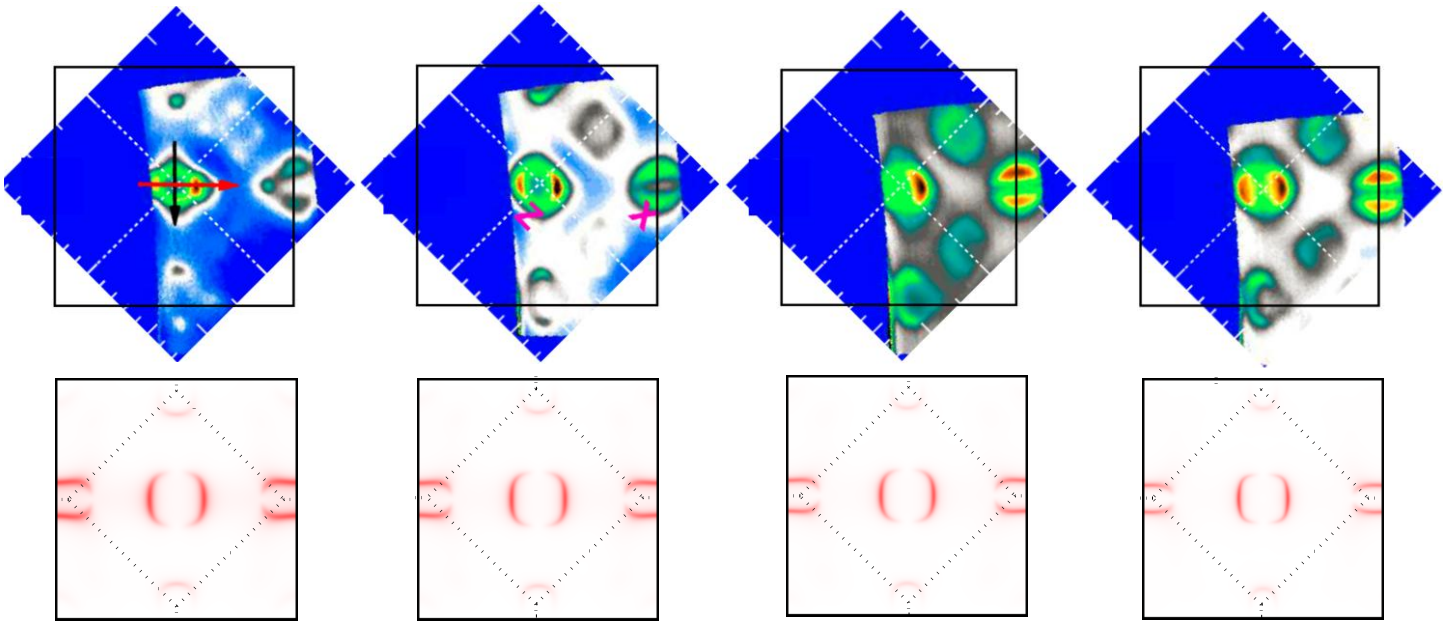
Fermi surface (2Fe) for different Ru substitution



- The hole pockets become more three dimensional
- The electron pockets show a slight substitution dependence.

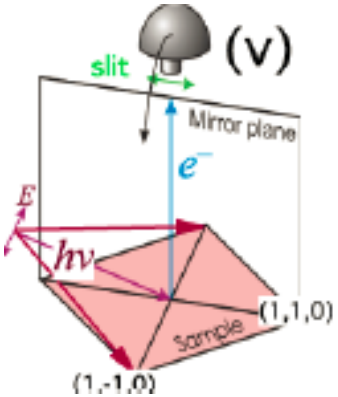
Resolution of the ARPES controversy

(a) x=0.02 (b) x=0.21 (c) x=0.36 (d) x=0.55



[R. S. Dhaka *et al*, PRL 107, 267002]

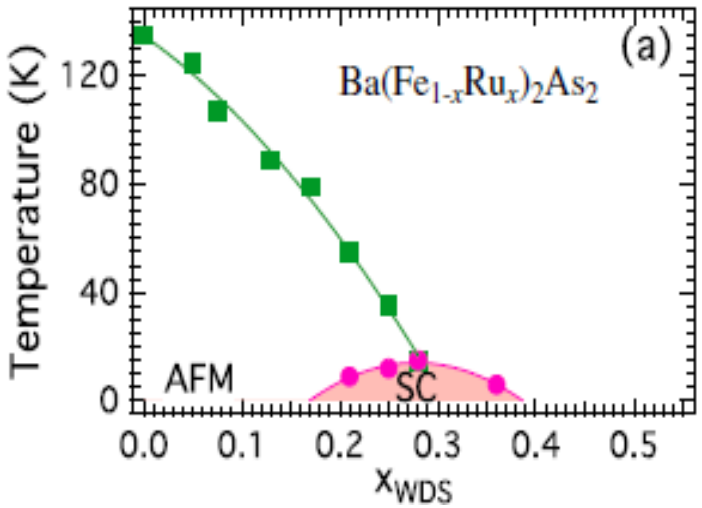
1Fe zone



- This photon polarization couples mostly to the *yz* orbital.
- The *yz* character of our unfolded BS also show little change.

Suppression of the long-range order

	$x = 0$	$x = 0.21$	$x = 0.38$	$x = 0.55$	$x = 0.75$	$x = 1.0$
$e/Fe = h/Fe$	0.162	0.151	0.142	0.127	0.123	0.120
$DOS(E_F)$	2.393	2.024	1.775	1.458	1.299	0.868



[R. S. Dhaka *et al*, PRL 107, 267002]

- Larger splitting between the conduction and valence bands → carrier reduction
- The reduced DOS & enhanced 3D nature → suppress the long-range orbital/magnetic order

Conclusions

- Symmetry-respecting Wannier function
  - Simple, flexible and efficient basis to describe physics
  - Intuitive microscopic picture + quantitative realism
- Unfolding 1st-principles band structures
  - Visualizing each band's coupling to the order parameters and other symmetry breakers
  - Useful for the study of extrinsic (doping, intercalation, vacancy, substitution, & defects) and intrinsic (CDW, SDW, OO, & structure distortion) effects on the electronic structure
  - Direct comparison with ARPES spectrum, built-in matrix elements effects
- A non-perturbative beyond-mean-field first-principles method for materials with disordered impurities
  - Defects, vacancy, chemical substitution, doping & intercalation
  - Thermal/quantum fluctuation induced spatial inhomogeneity
  - Paramagnetic phase with disordered local moments