Wannier Function Based First Principles Method for Disordered Systems

Tom Berlijn

Stony Brook University &

Brookhaven National Laboratory

Excitations in Condensed Matter:
From Basic Concepts to Real Materials
November 23 2:00pm
KITP Santa Barbara

Acknowledgements

- Collaborators: Dmitri Volja & Wei Ku

- Funding: DOE BNL + LDRD (John Hill & Wei Ku)

U.S. DEPARTMENT OF ENERGY

BROOKHAVEN NATIONAL LABORATORY

Outline

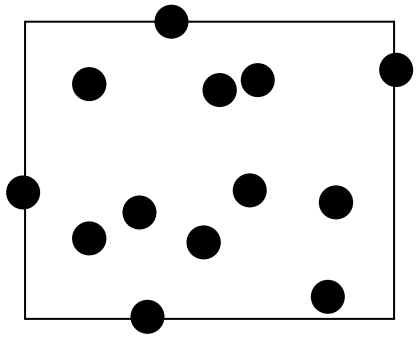
- Introduction: Super Cell Approximation
- Method 1: Unfolded Bandstructure (Wannier function)
- Method 2: Effective Hamiltonian (Wannier function)
- Results: Disordered Na_xCoO_2 & $Zn_{1-x}Cu_xO_{1-y}$

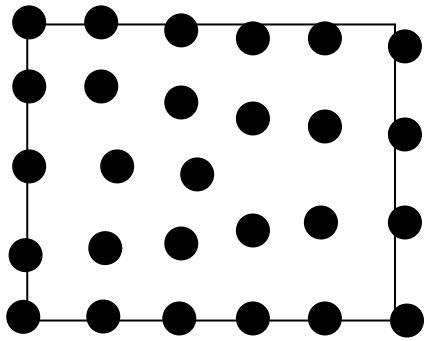
Introduction:

Super Cell Approximation

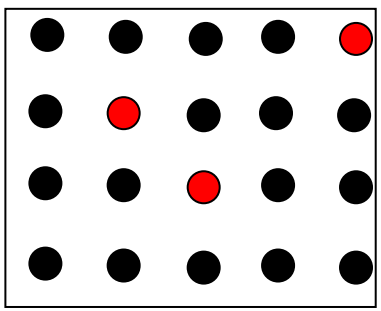
What kind of disorder?

Not like

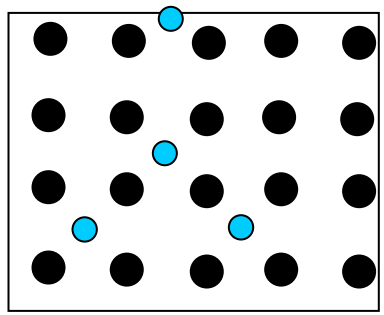




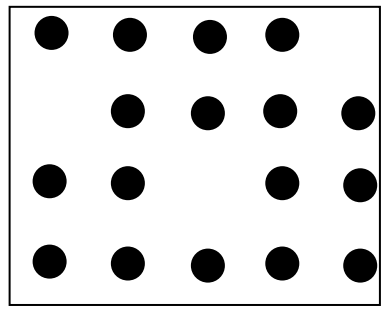
But like



substitution



interstitial



vacancy

Goal: average Green function of disordered systems from first principles

$$\langle G \rangle = \sum_{\text{config } i} G_i$$

1) Indirect Method

2) Direct Method

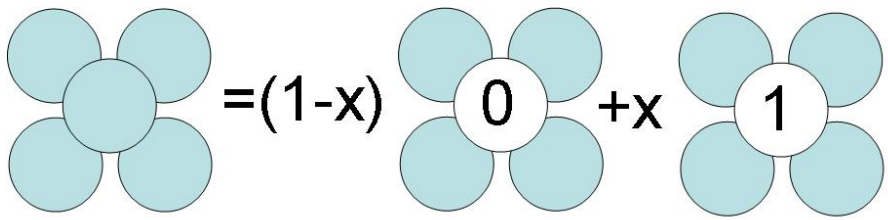
1) Indirect Methods[1]

VCA: Virtual Crystal Approximation

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

no scattering

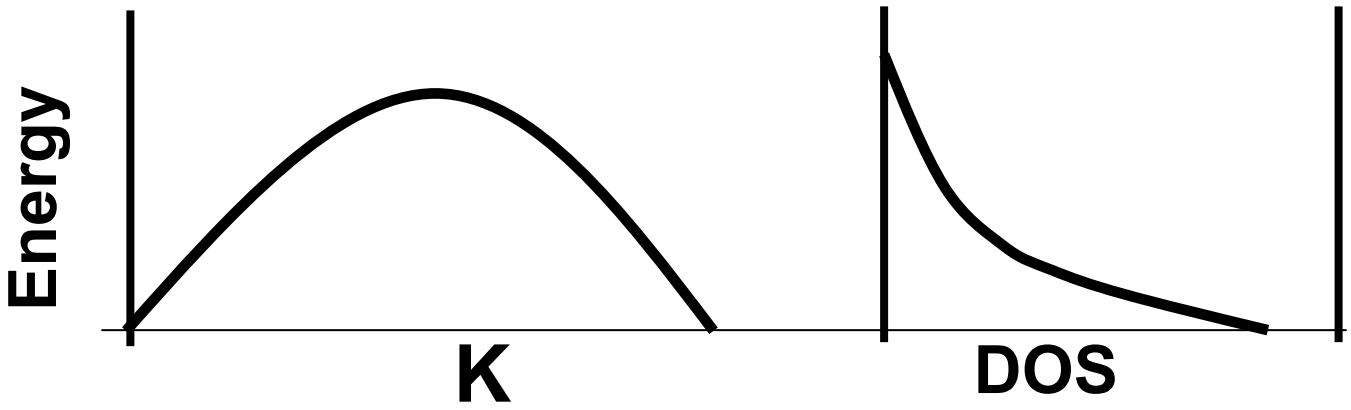
CPA: Coherent Potential Approximation



no cluster-scattering

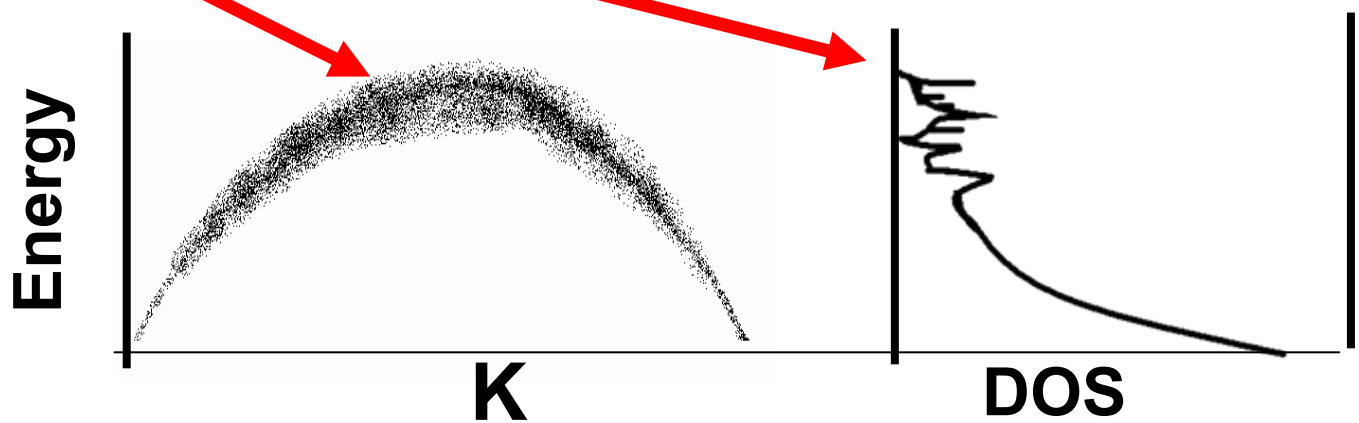
1) A. Gonis, “Green functions for ordered and disordered systems” (1992)

Example 1: States at the band edge

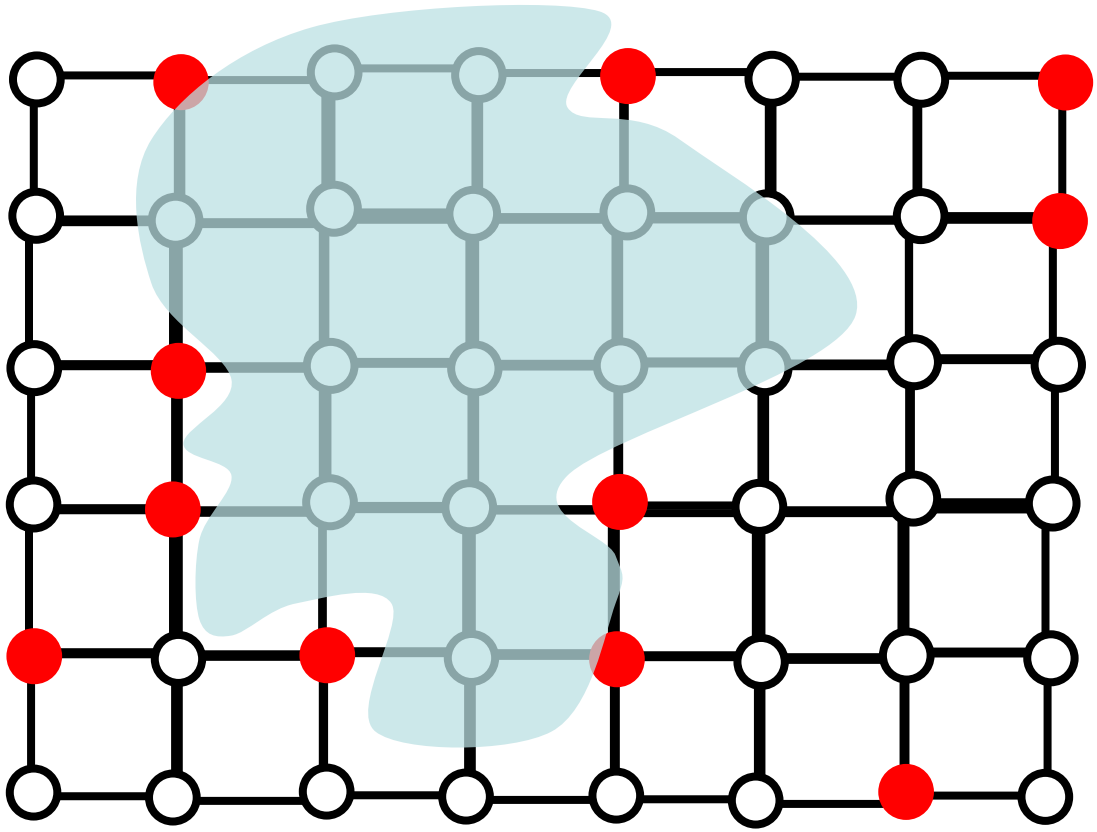


disorder

cluster-scattering important



Example 2: Large-sized impurity states



2) Direct Method

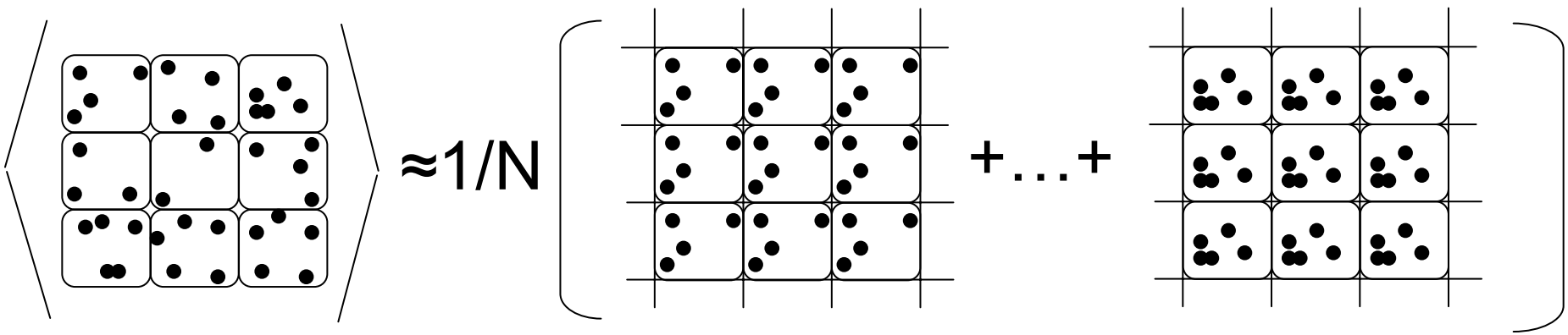
SCA: Super Cell Approximation

$$\langle G \rangle \approx 1/N(\quad G_1 \quad + \ldots + \quad G_N \quad)$$

disordered system

configuration 1

configuration N



Wannier Function Based Methods

1. Unfolded Bandstructure

2. Effective Hamiltonian

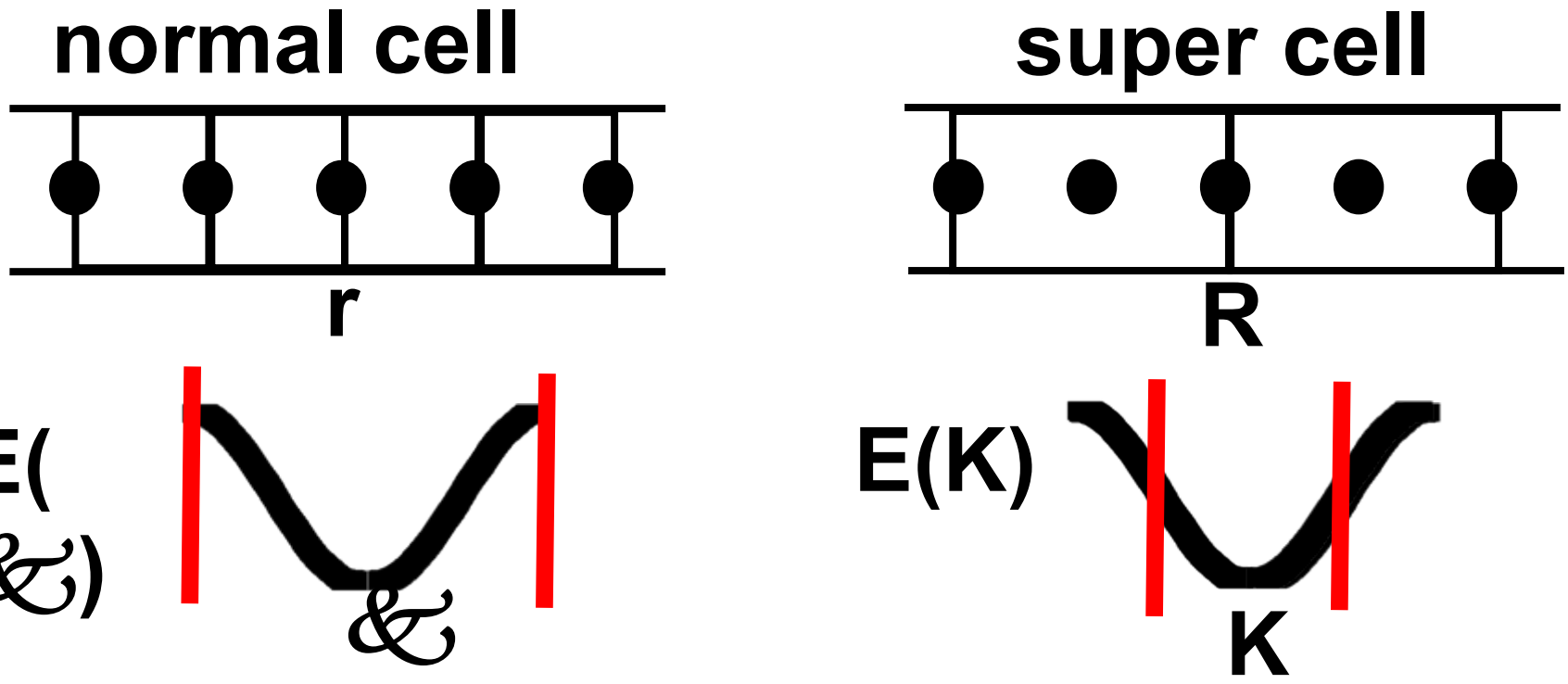
Method 1:

Unfolded Bandstructure

Notation

normal cell	**super cell**	
& crystal momentum	**K crystal momentum**	**J band index**
r lattice vector	**R lattice vector**	**$\|\text{☞}_{KJ}\rangle$ Bloch state**
n Wannier index	**N Wannier index**	

Folded Bandstructure



normal cell	super cell	
& crystal momentum	K crystal momentum	J band index
r lattice vector	R lattice vector	$\|\hat{\psi}_{KJ}\rangle$ Bloch state
n Wannier index	N Wannier index	

Spectral Function

$$A_n(\bullet,\&) = -\,\mathrm{Im}\,\langle \&n|G(\bullet)|\&n\rangle$$

$$= -\,\mathrm{Im} \sum_{KJ} |\langle \&n|\☞_{KJ}\rangle|^2 \langle \☞_{KJ}|G(\bullet)|\☞_{KJ}\rangle$$

Spectral Weight

Green's function on Eigen basis

normal cell	**super cell**	
& crystal momentum	K crystal momentum	J band index
r lattice vector	R lattice vector	$\|\☞_{KJ}\rangle$ Bloch state
n Wannier index	N Wannier index	

Green's function on Eigen basis

$$< \text{☞}_{KJ} |G(\blacklozenge)| \text{☞}_{KJ} > = (\blacklozenge - E_{KJ} + i0^{+})^{-1}$$

Eigenvalue

normal cell	super cell	
& crystal momentum	K crystal momentum	J band index
r lattice vector	R lattice vector	$\lvert \text{☞}_{KJ} \rangle$ Bloch state
n Wannier index	N Wannier index	

Spectral Weight

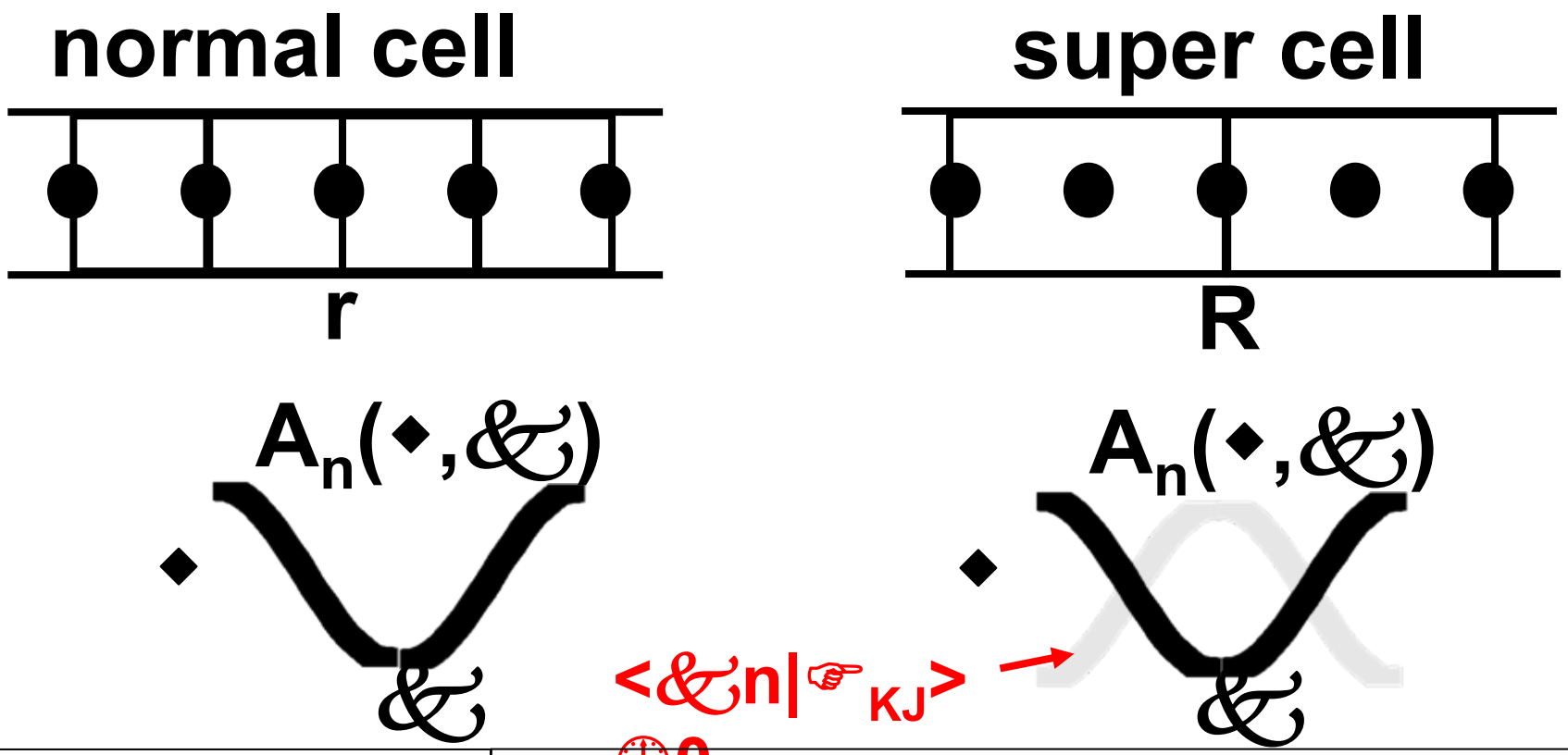
$$\langle \& n | \hat{\psi}_{KJ} \rangle = \sum_{RN} \langle \& n | RN \rangle \langle RN | KN \rangle \langle KN | \hat{\psi}_{KJ} \rangle$$

$$= \sum_{} (R/r)^{3/2} e^{-i \& \cdot r} \Omega_{nm} \Omega_{K \&} \langle KN | \hat{\psi}_{KJ} \rangle$$

Eigenvector

normal cell	super cell	
& crystal momentum	K crystal momentum	J band index
r lattice vector	R lattice vector	$\lvert \hat{\psi}_{KJ} \rangle$ Bloch state
n Wannier index	N Wannier index	

Unfolded Bandstructure



normal cell	super cell	
& crystal momentum	K crystal momentum	J band index
r lattice vector	R lattice vector	$\|\text{☞}_{KJ}\rangle$ Bloch state
n Wannier index	N Wannier index	

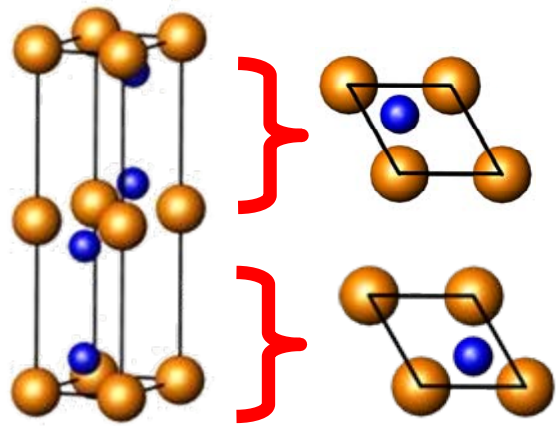
Unfolded Bandstructure

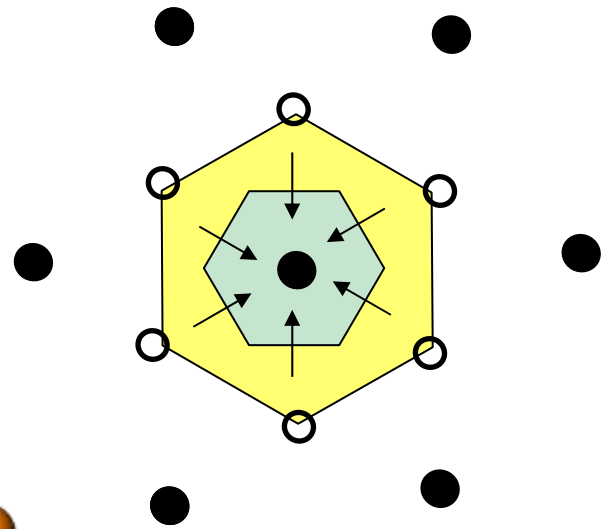
Example 1: $Na_2Co_6O_{12}$

Unfolded Bandstructure Example 1: Na_xCoO_2

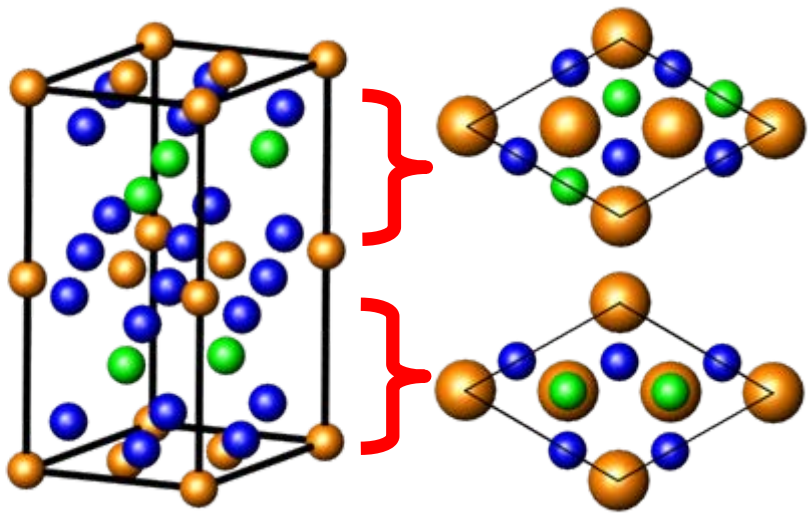
Brillouin zone

normal cell
Co_2O_4





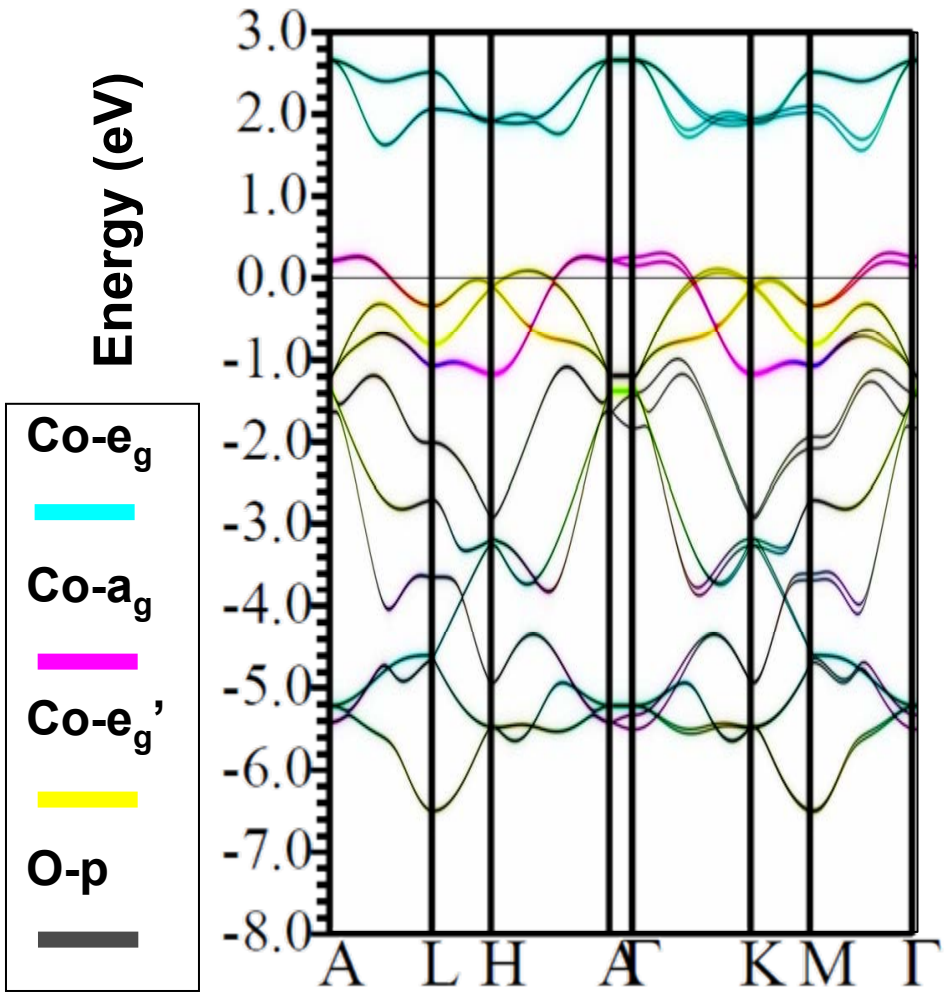
super cell
$Na_4Co_6O_{12}$

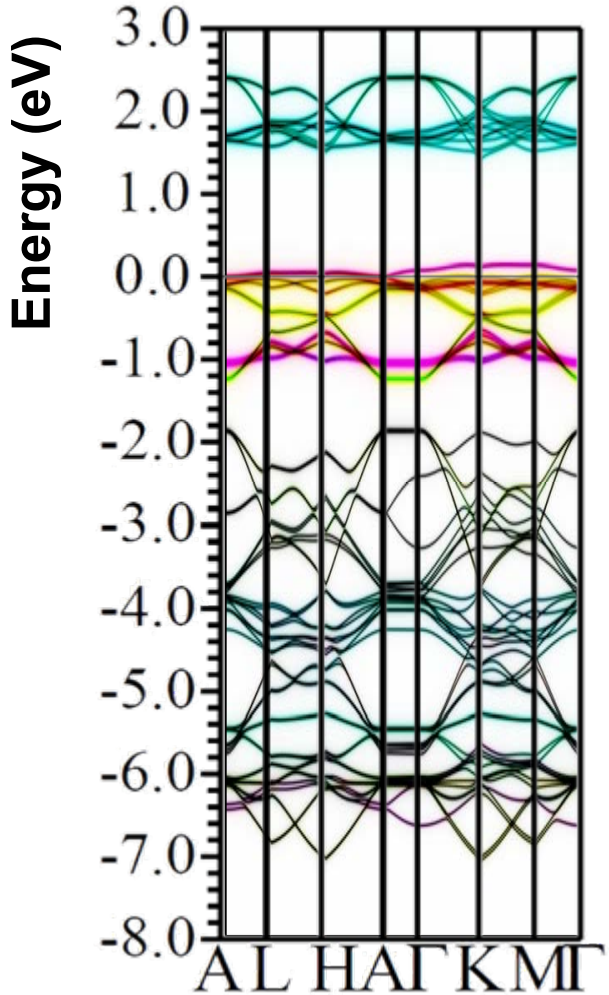


Backfolded Bandstructure

normal cell: Co_2O_4

super cell: $Na_4Co_6O_{12}$

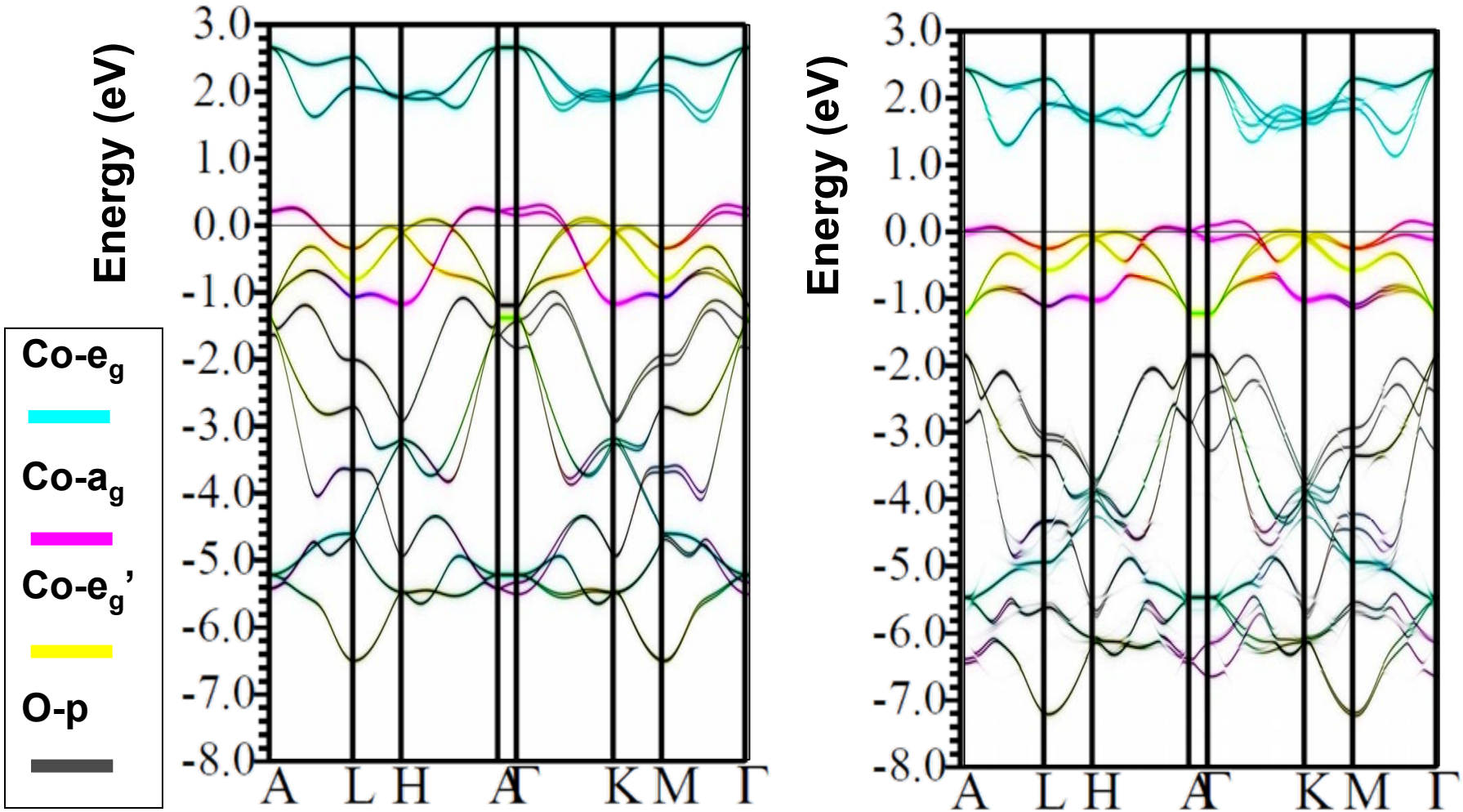




Unfolded Bandstructure

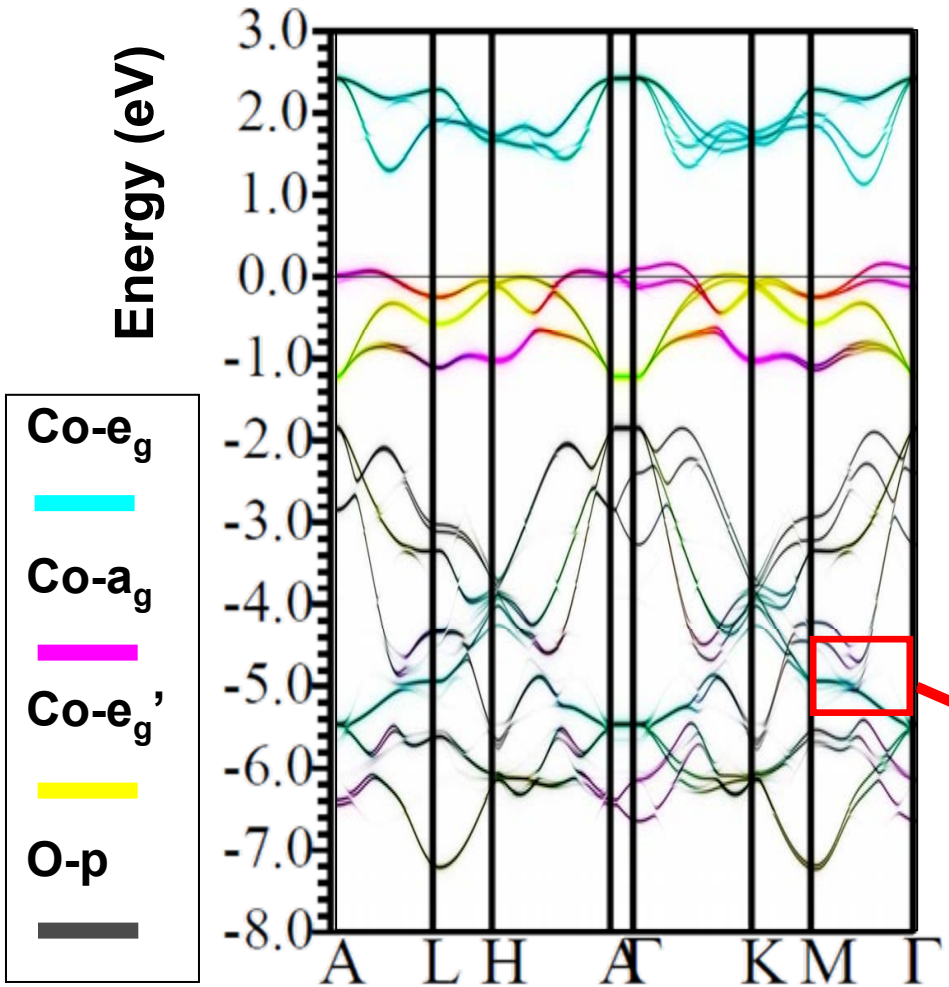
normal cell: Co_2O_4

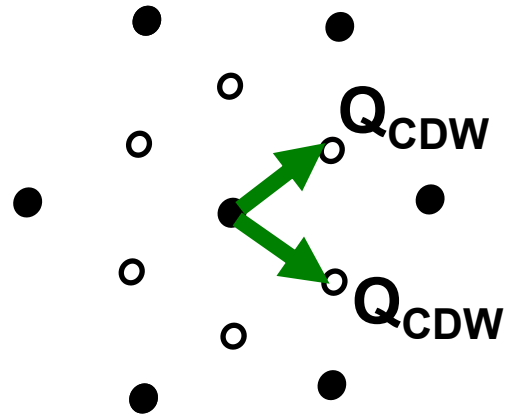
super cell: $Na_4Co_6O_{12}$



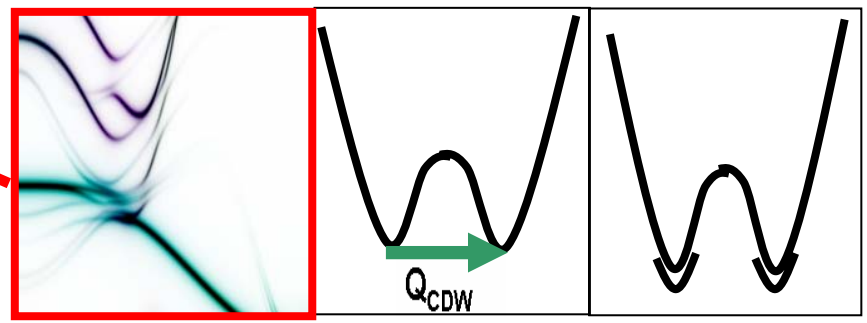
Unfolded Bandstructure

super cell: $Na_4Co_6O_{12}$





$$|k'>=\sum_{q_{CDW}}|k+q_{CDW}>\frac{<k+q_{CDW}|V_{Na}|k>}{\epsilon_k-\epsilon_{k+q_{CDW}}}$$

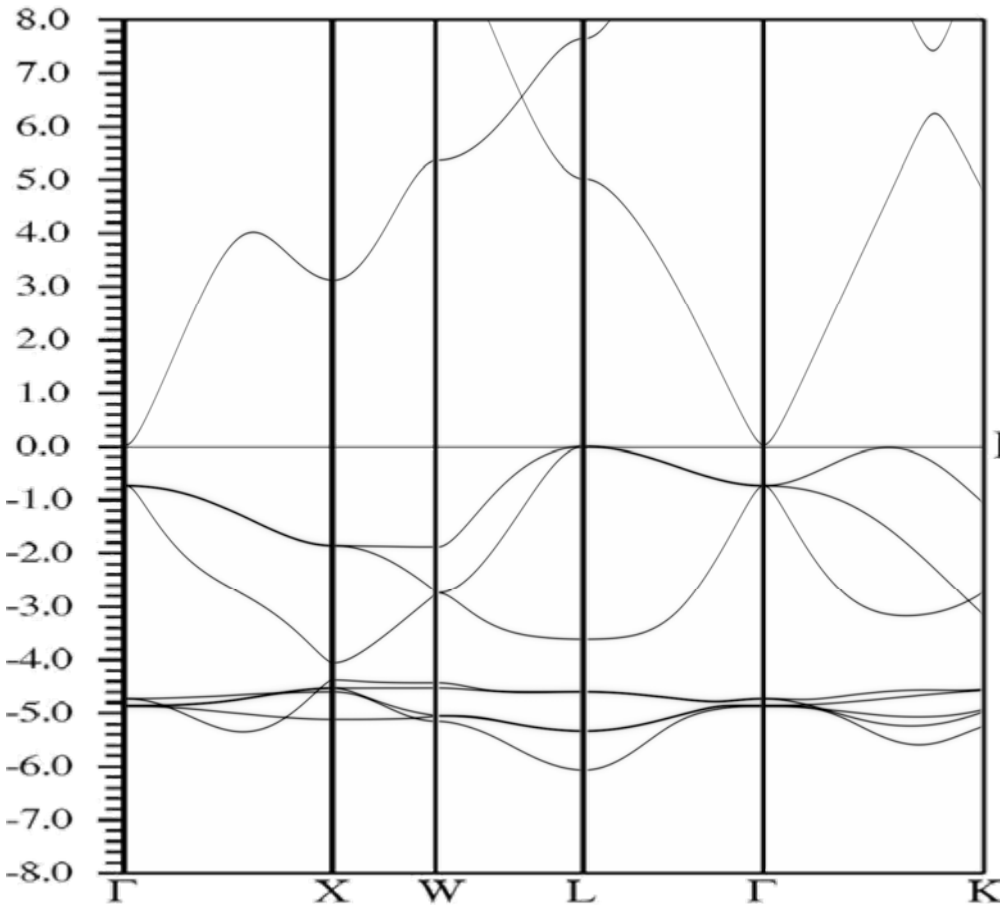


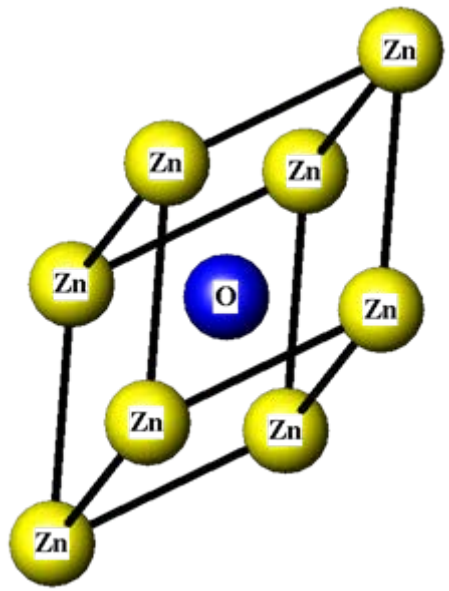
Unfolded Bandstructure

Example 2: $Zn_{1-x}Cu_xO$ LDA+U spin$\downarrow$

$Zn_{1-x}Cu_xO$ LDA+U spin ↓

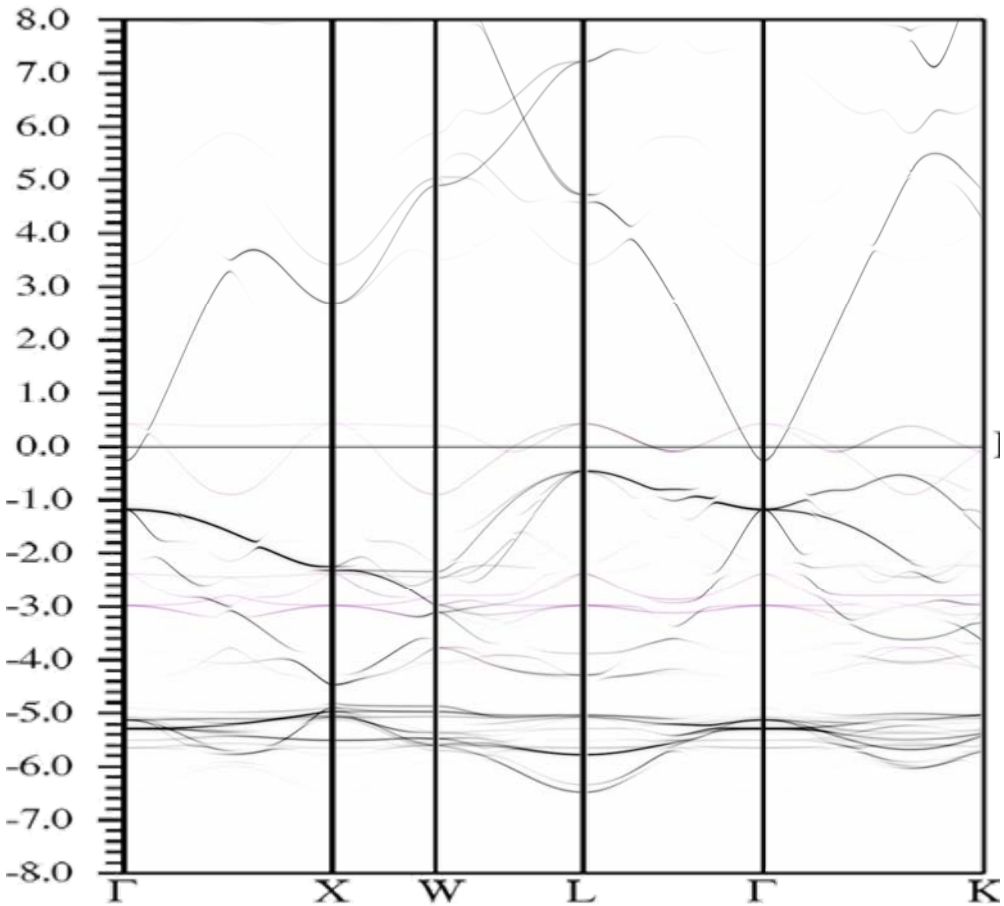
X =0

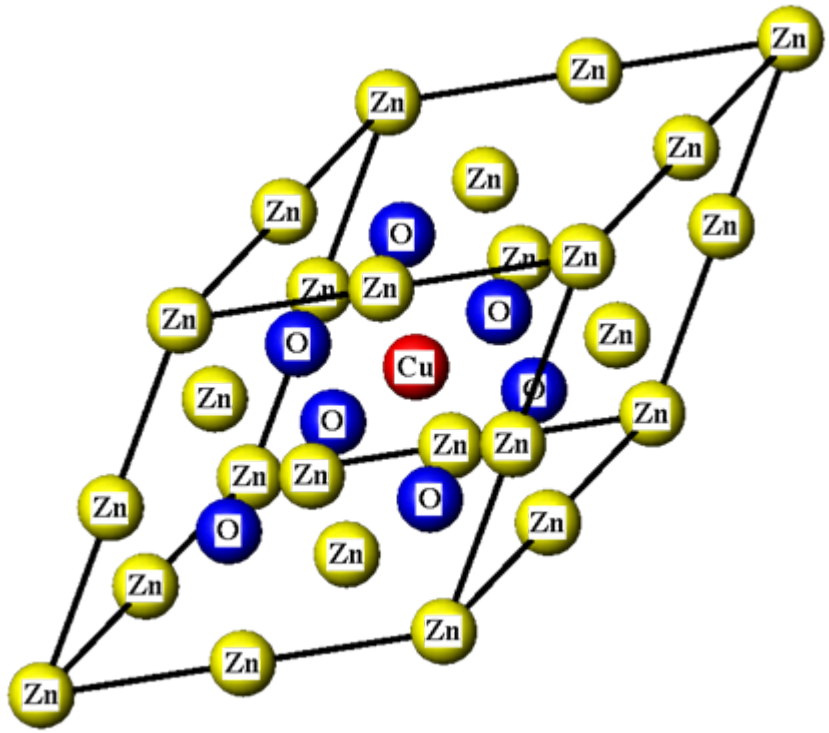




$Zn_{1-x}Cu_xO$ LDA+U spin ↓

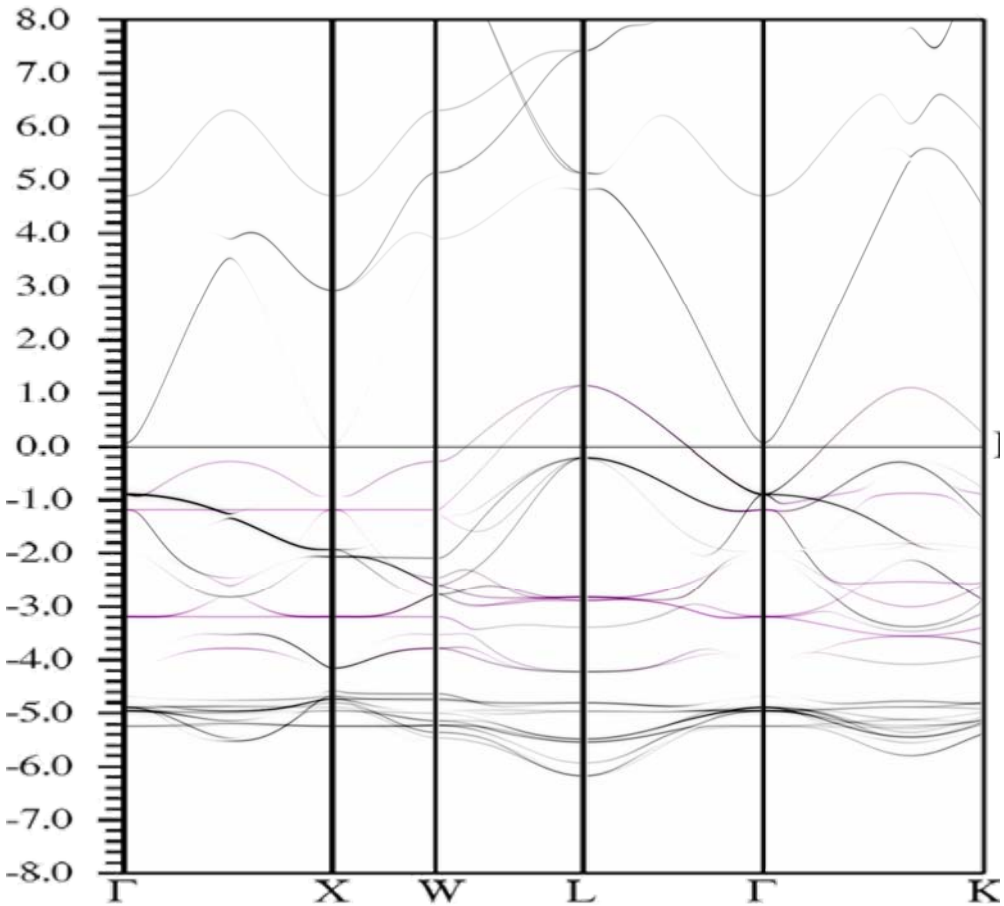
X =1/8

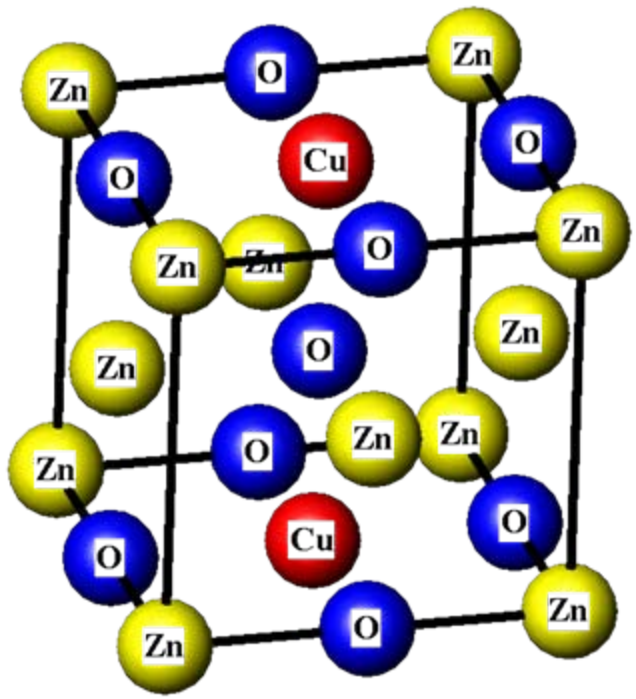




$Zn_{1-x}Cu_xO$ LDA+U spin ↓

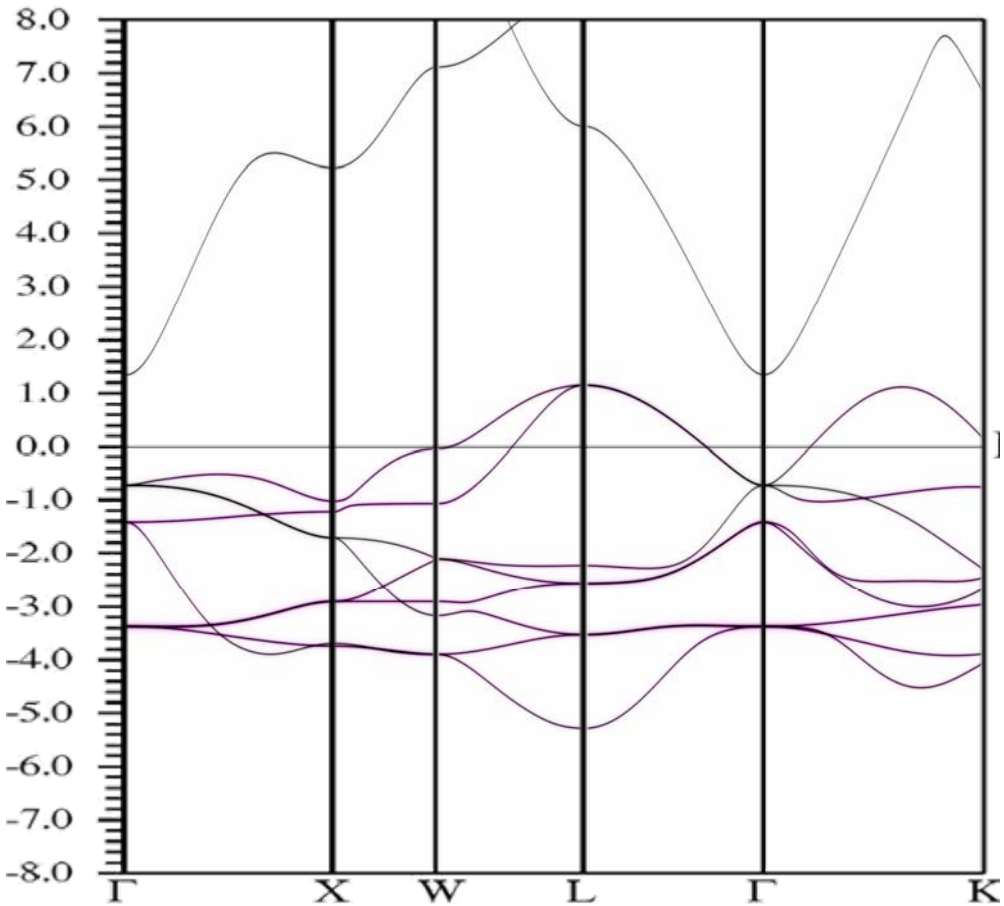
X =1/4

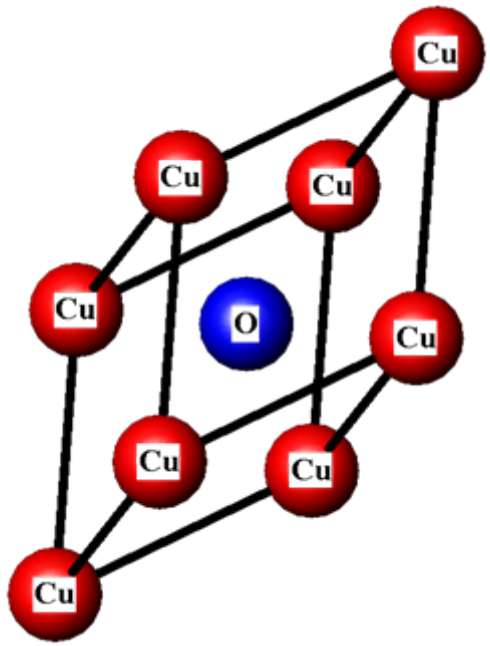




$Zn_{1-x}Cu_xO$ LDA+U spin ↓

X =1





Method 2:

Effective Hamiltonian

Concept: Linearity

Drop impurity correlations in Hamiltonian
(not in solutions)

$\longrightarrow$ Influence impurity = linear

$$\mathbf{H} = \mathbf{H_0} + \sum_{\mathbf{i}=1}^{\mathbf{N}} \frac{\delta \mathbf{H}}{\delta \mathbf{I_i}} \mathbf{\Delta I_i}$$

$$+ \sum_{\mathbf{i,j}=1}^{\mathbf{N}} \frac{\delta^2 \mathbf{H}}{\delta \mathbf{I_i} \delta \mathbf{I_j}} \mathbf{\Delta I_i \Delta I_j} + \dots$$

drop impurity correlations in Hamiltonian

(not in solutions)

$$\frac{\delta \mathbf{H}}{\delta \mathbf{I_i}} = \left(\frac{\delta \mathbf{V_{ex}}}{\delta \mathbf{I_i}} + \frac{\delta [\mathbf{T} + \mathbf{V_H} + \mathbf{V_{xc}}]}{\delta \mathbf{I_i}} \right)$$

$$\frac{\delta^{\mathbf{n}} \mathbf{H}}{\delta \mathbf{I_{i_1}} \dots \delta \mathbf{I_{i_n}}} = \frac{\delta^{\mathbf{n}} [\mathbf{T} + \mathbf{V_H} + \mathbf{V_{xc}}]}{\delta \mathbf{I_{i_1}} \dots \delta \mathbf{I_{i_n}}} \; ; \; \mathbf{n} \geq \mathbf{2}$$

Construction

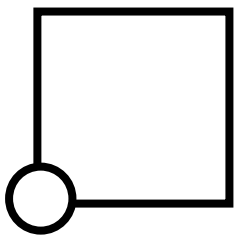
1. DFT doped & undoped
2. Wannier-transformation
3. Linear superposition

1) Density Functional Theory

two DFT Calculations

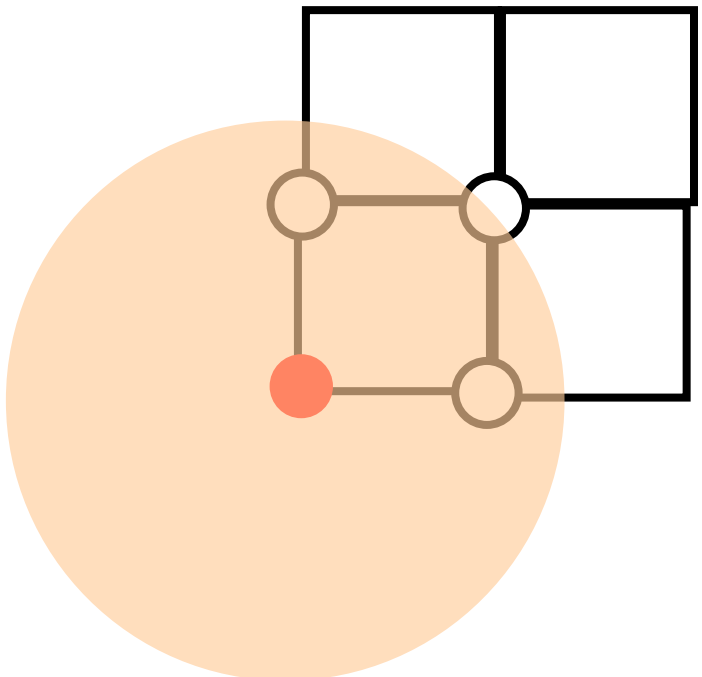
undoped

(normal cell)



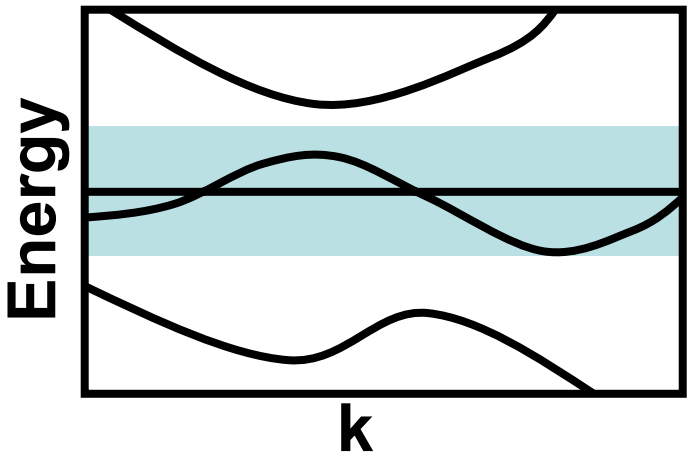
1 impurity

(per super cell)

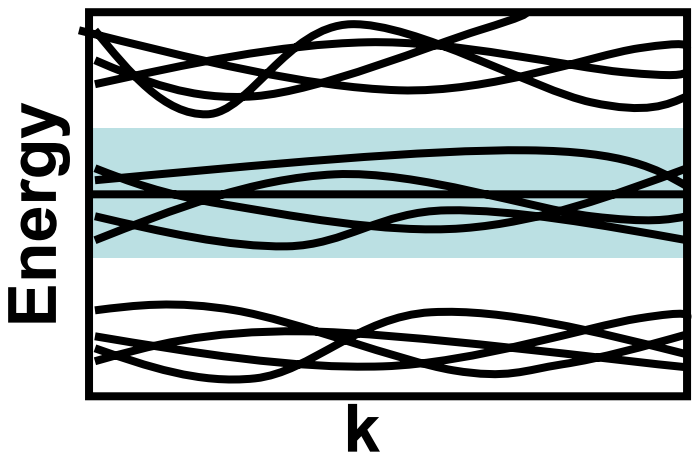


2) Wannier transfomation

DFT undoped

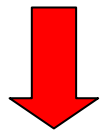


DFT 1 impurity



2 Wannier transformations

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



2 Tight Binding Hamiltonians

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

3) Linear Superposition

Influence 1 impurity: $\mathbf{\Delta^i = P^i \otimes (H^1_{DFT} - H^0_{DFT})}$

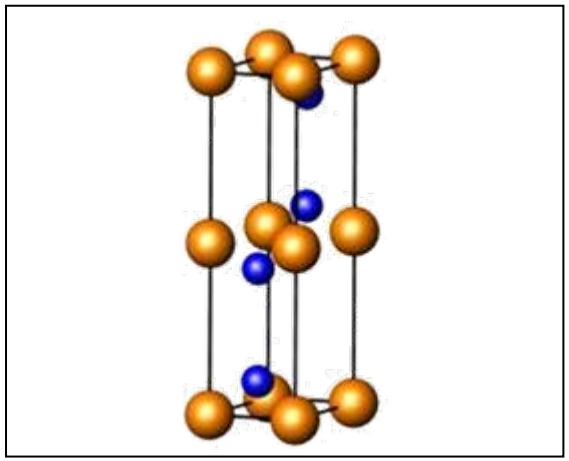
Hamiltonian N impurities: $\mathbf{H^{\{1,\ldots,N\}}_{eff} = H^0_{DFT} + \sum_{i=1}^{N} \Delta^i}$

Testing
DFT v.s. effective Hamiltonian

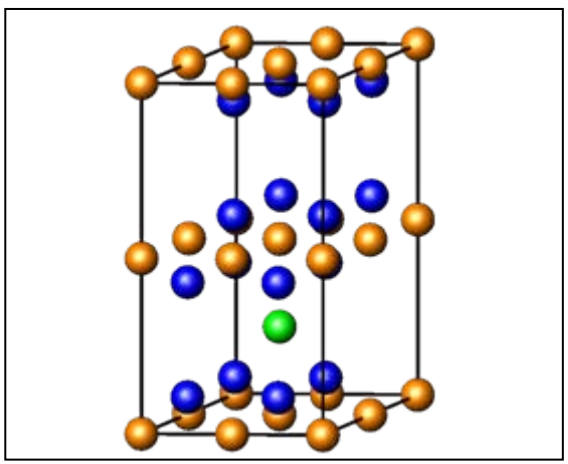
1. Linearity: $x^1_{dft} > x_{eff}$
2. Partition: H_{eff} break symmetry H^1_{dft}

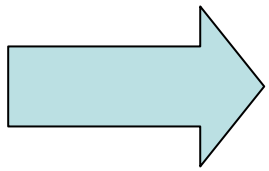
Test Linearity & Partition: Na_xCoO_2

$\mathbf{H}^{0}_{\mathrm{dft}}$ x=0

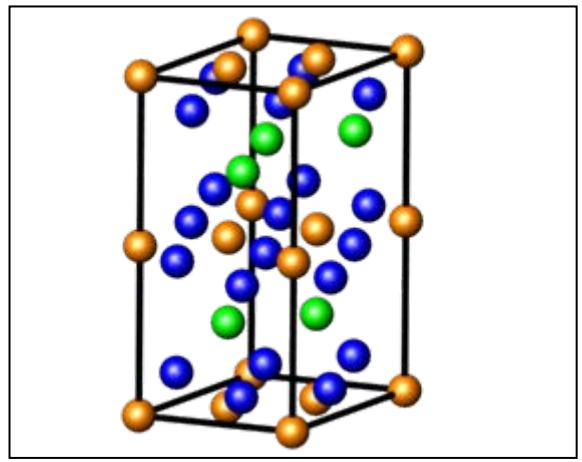


$\mathbf{H}^{1}_{\mathrm{DFT}}$ x=1/8

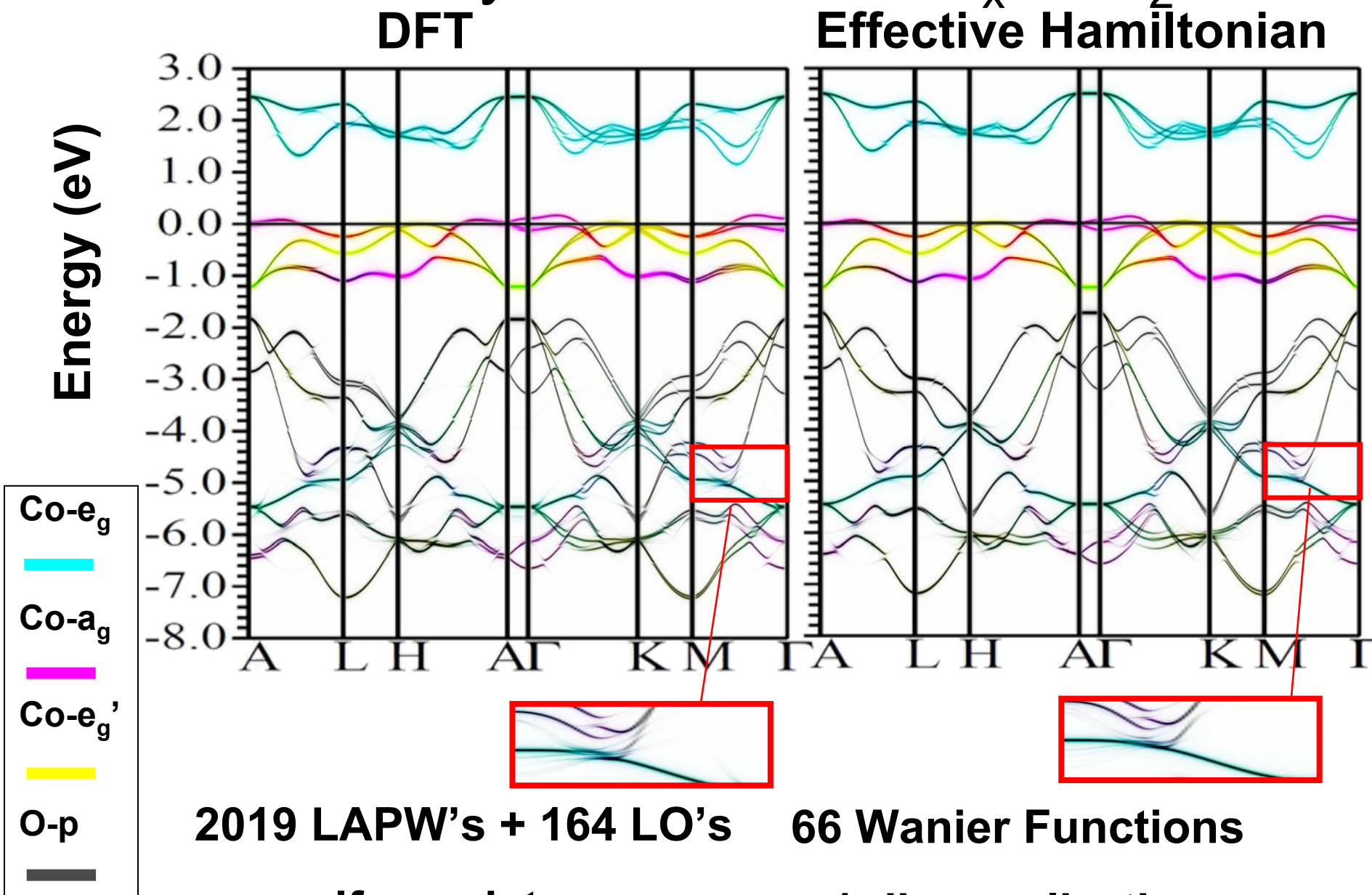




$\mathbf{H}_{\mathrm{eff}}$ x=2/3



Test Linearity & Partition: Na_xCoO_2



2019 LAPW's + 164 LO's

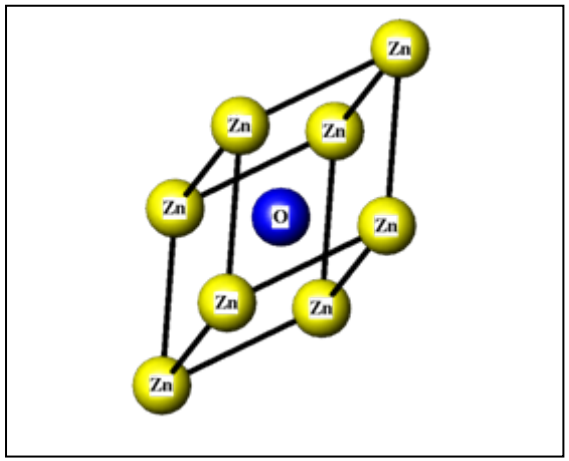
self consistency

66 Wanier Functions

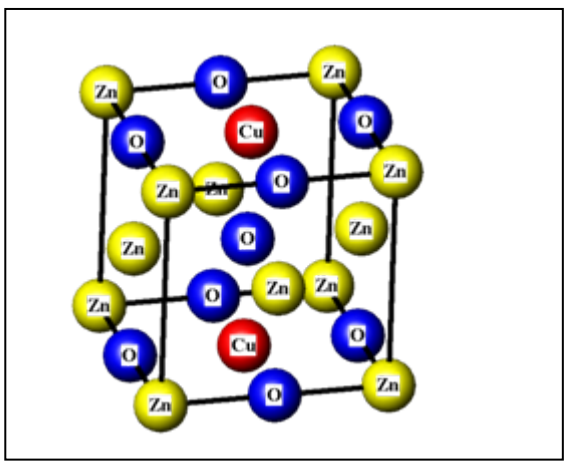
1 diagonalization

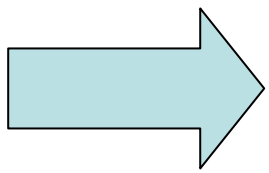
Test Linearity $Zn_{1-x}Cu_xO$ (rock salt)

$\mathbf{H}^{0}_{\mathrm{dft}}$ x=0

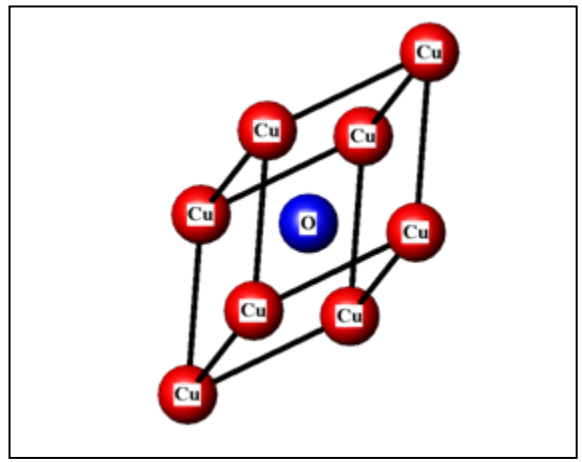


$\mathbf{H}^{1}_{\mathrm{DFT}}$ x=1/4



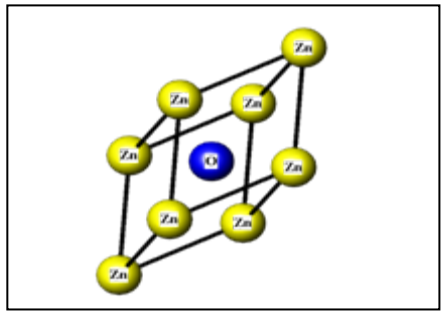


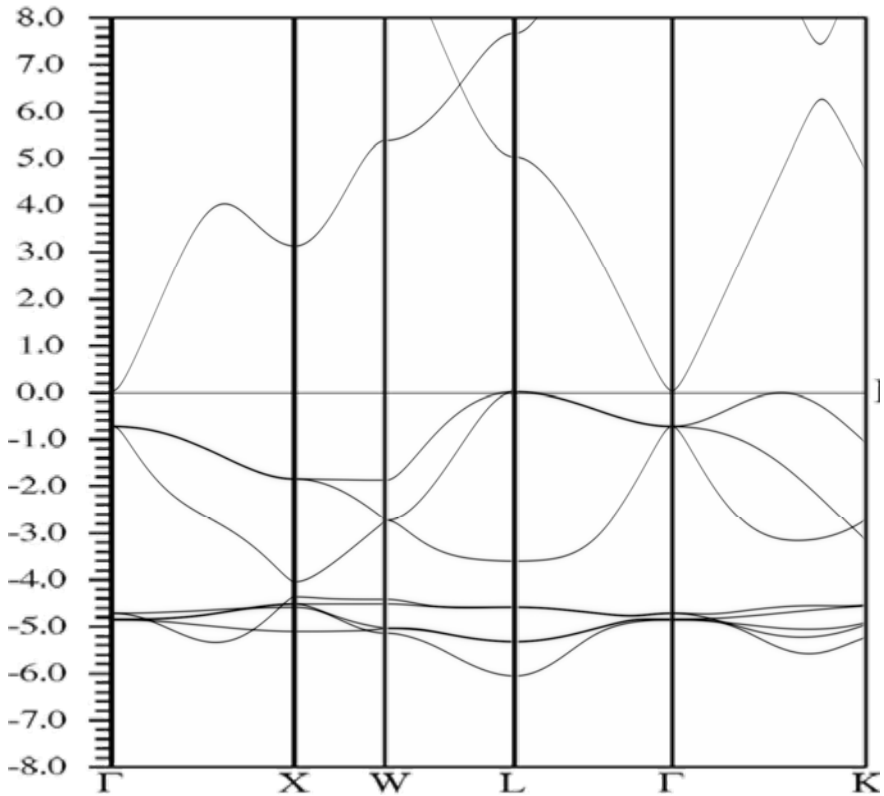
$\mathbf{H}_{\mathrm{eff}}$ x=1



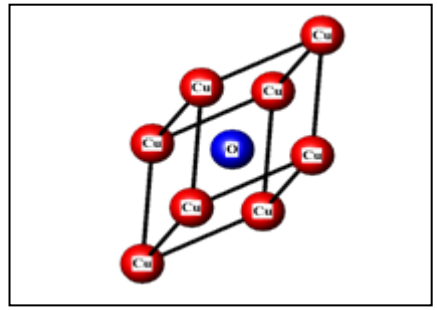
Reminder

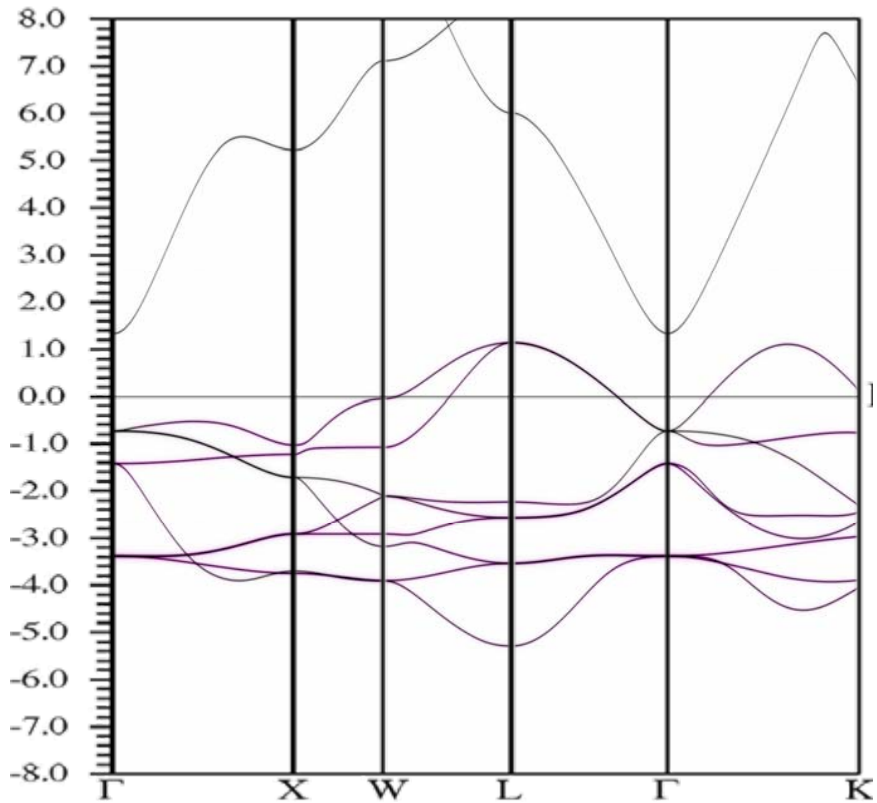
ZnO



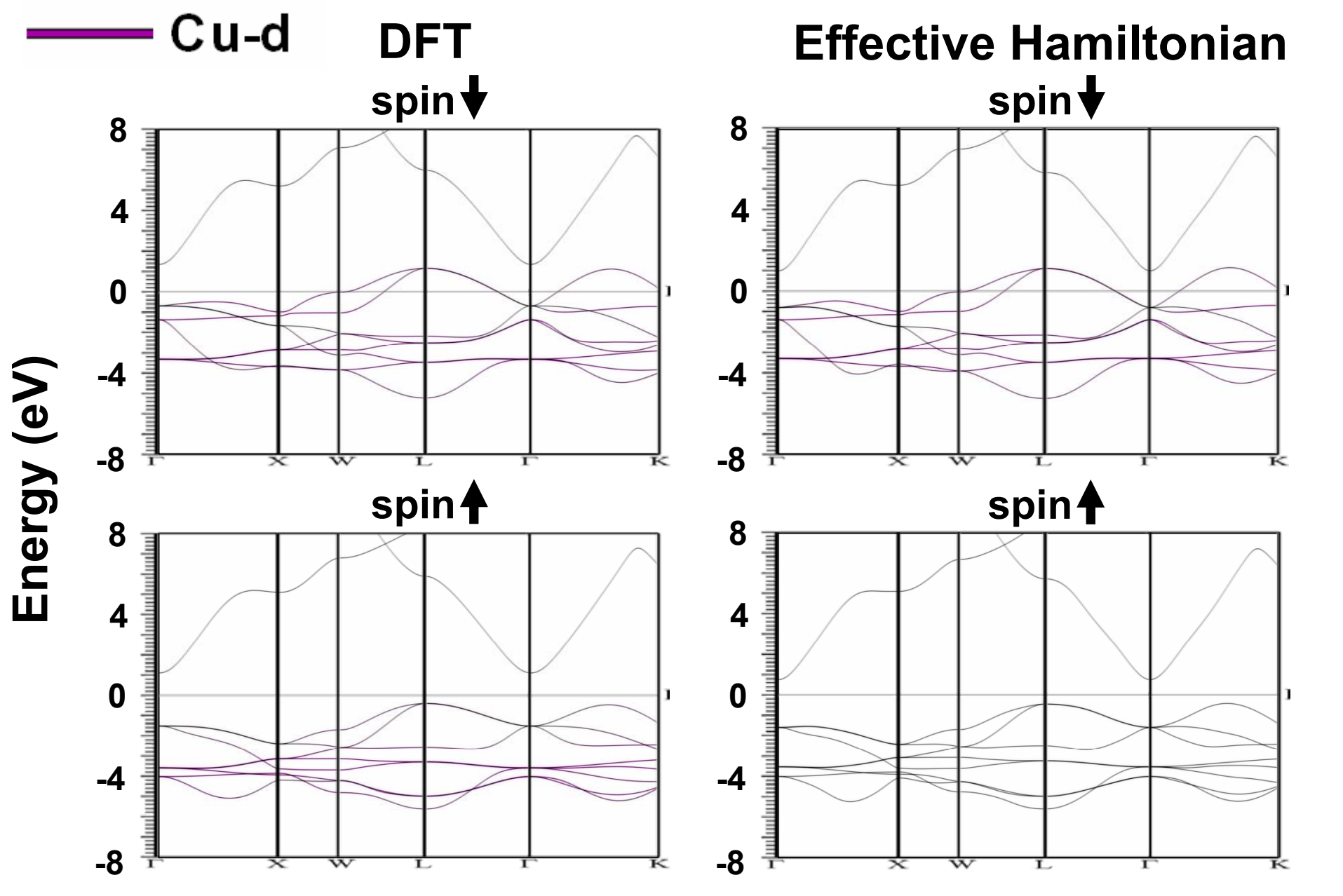


CuO



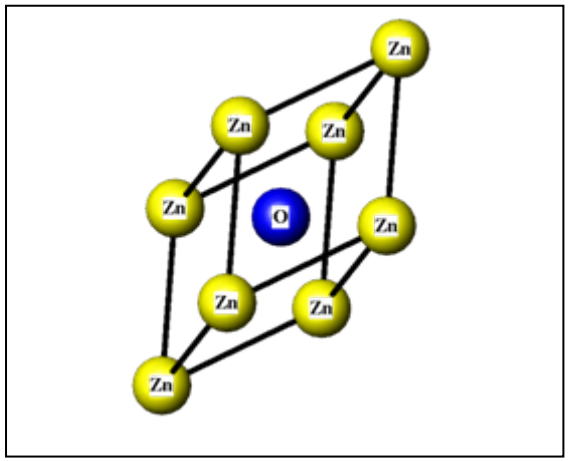


Test Linearity : Zn1-xCuxO (rock salt)

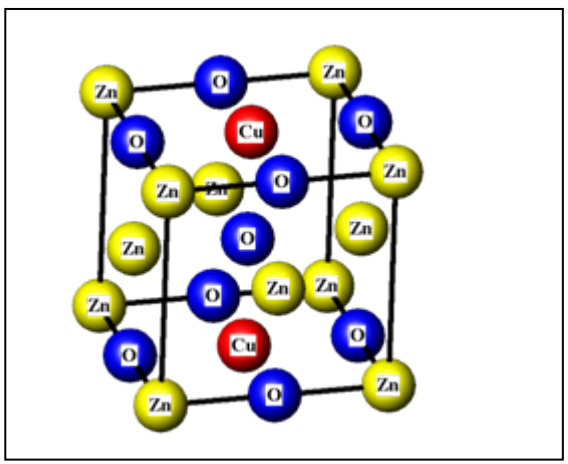


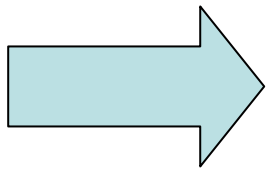
Test Partition $Zn_{1-x}Cu_xO$ (rock salt)

$\mathbf{H}^{0}_{\mathrm{dft}}$ x=0

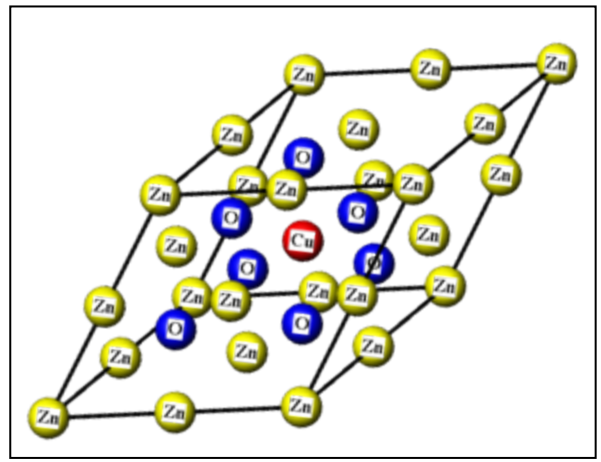


$\mathbf{H}^{1}_{\mathrm{DFT}}$ x=1/4

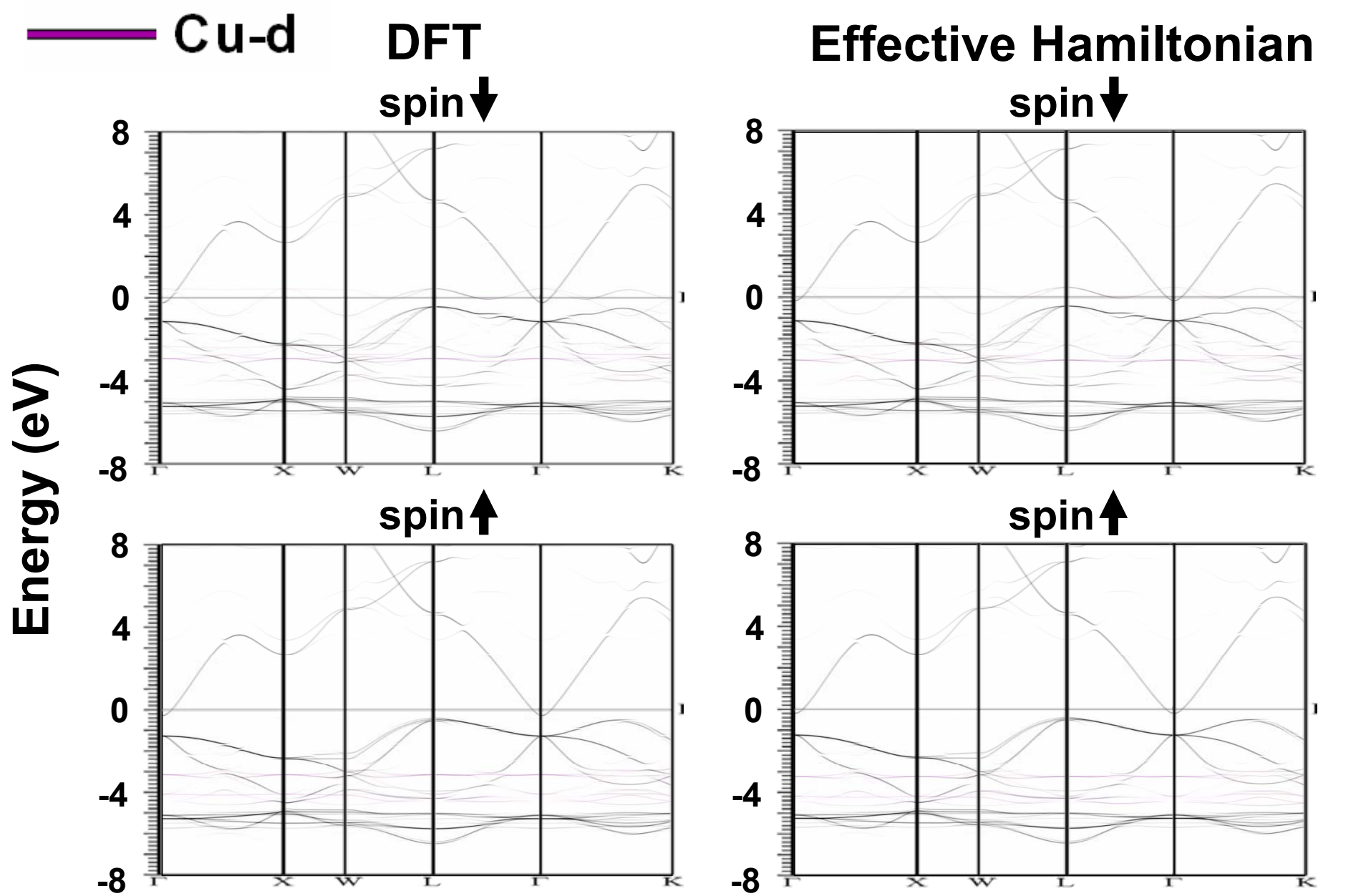




$\mathbf{H}_{\mathrm{eff}}$ x=1/8



Test Partition : Zn1-xCuxO (rock salt)

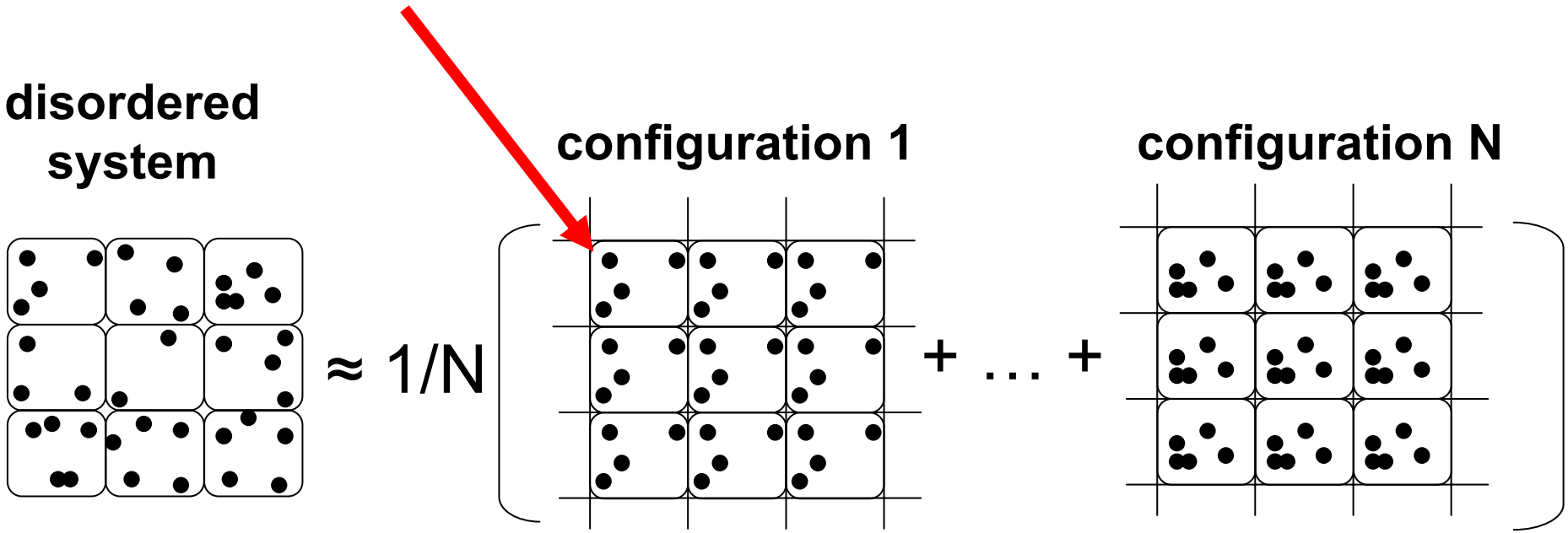


Disordered Results :

Na_xCoO_2 & $Zn_{1-x}Cu_xO_{1-y}$

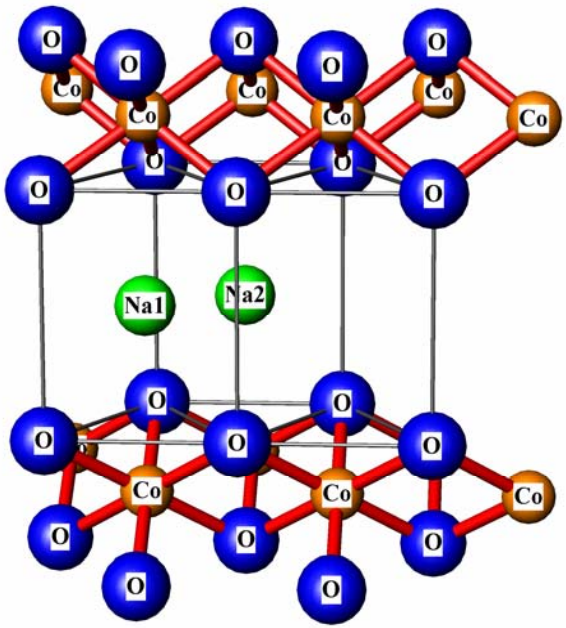
Disordered Results

big super cells (100's of atoms)

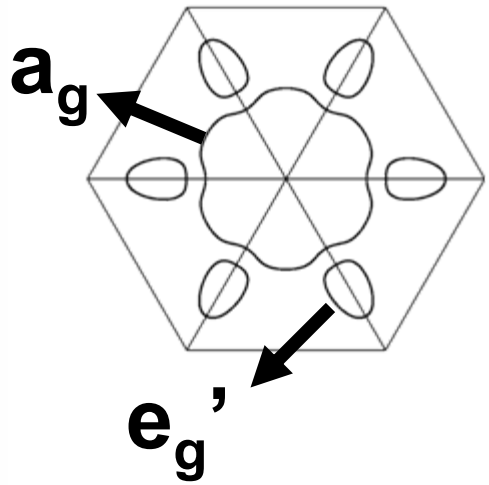


$$\langle G \rangle \approx 1/N(G_1 + \ldots + G_N)$$

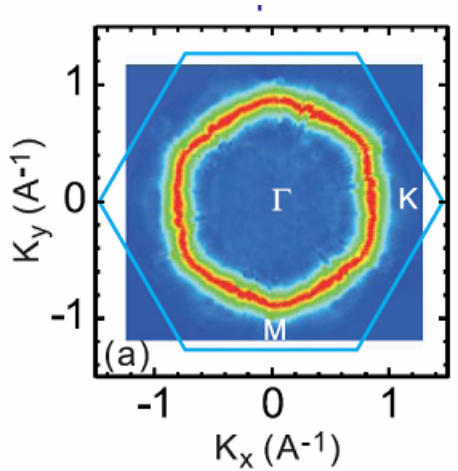
Intercalation: NaxCoO2



LDA[1]



ARPES[2]



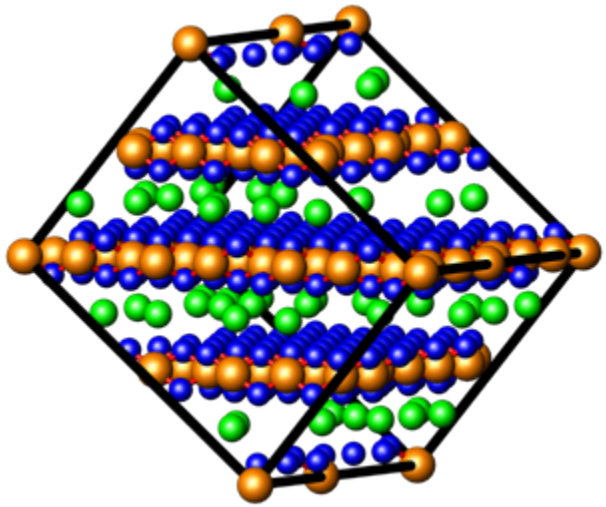
Q) Does Na disorder destroy e_g' pockets[3] ?

1) D.J. Singh, PRB 20, 13397 (2000)
2) D. Qian et al, PRL 97 186405 (2006)
3) David J. Singh et al, PRL 97, 016404-1 (2006)

Na_xCO_2 : x≈0.30

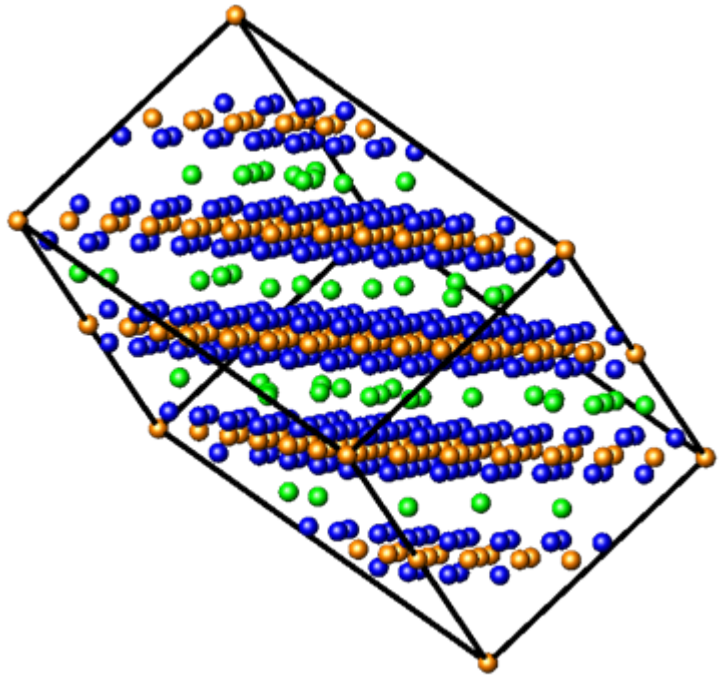
30 configurations of ~200 atoms

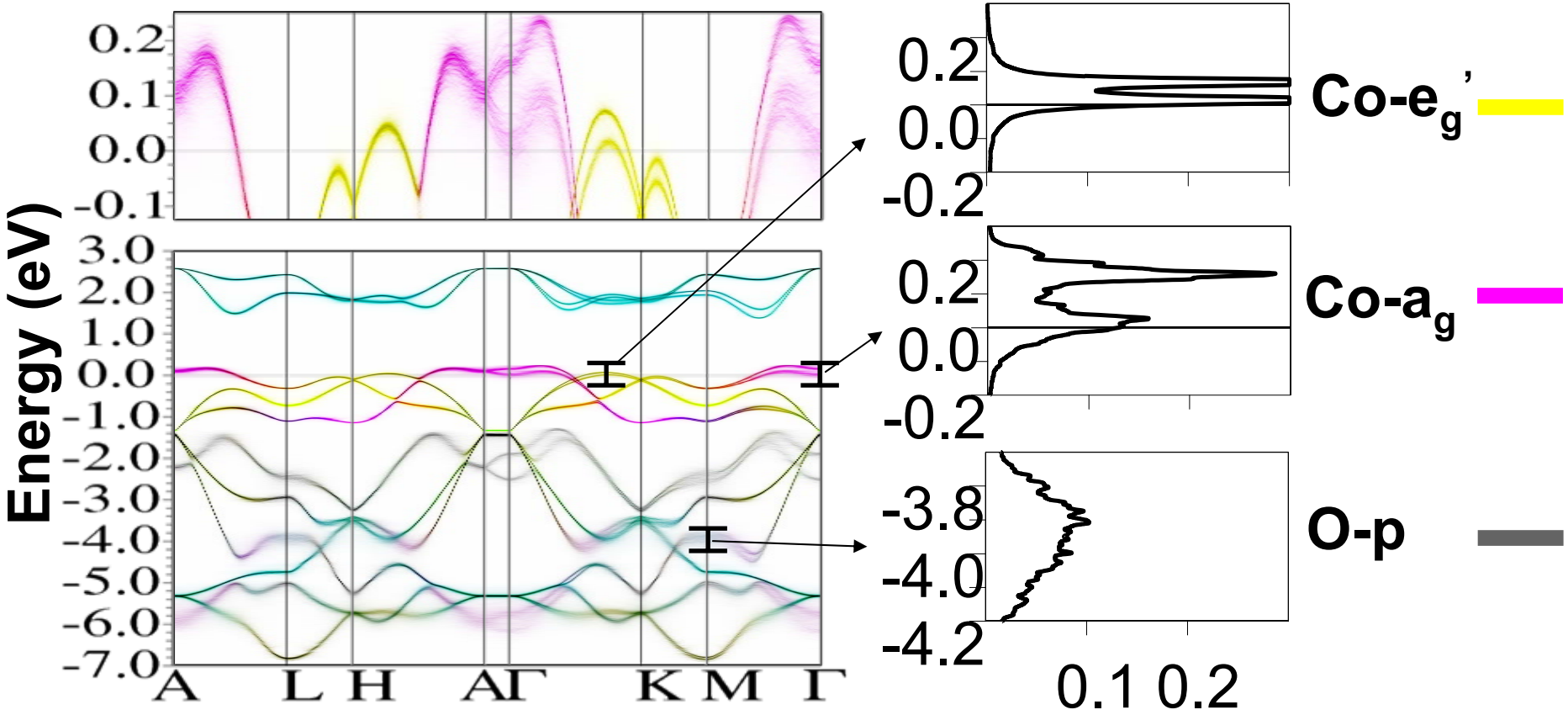
configuration 1



+ . . . +

configuration 30



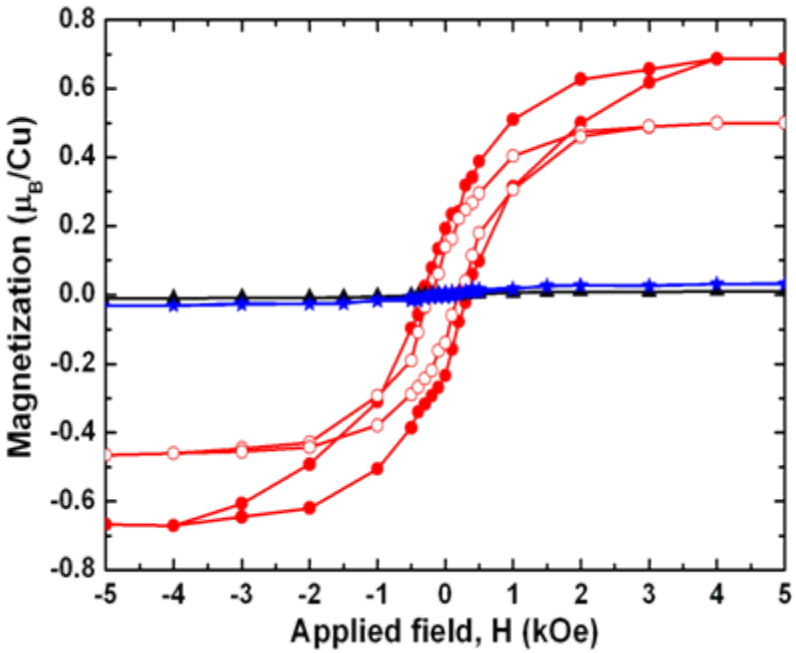


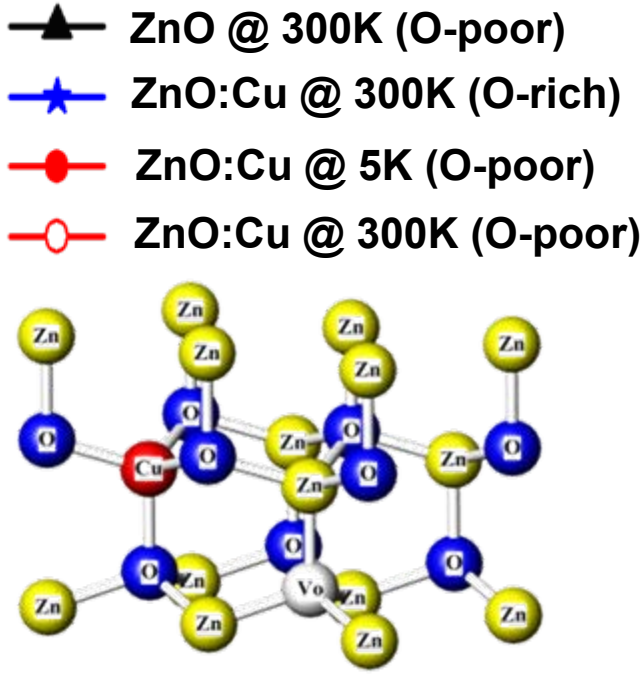
A) Na disorder does not destroy e_g' [1]

1) T. B., D. Volja, W. Ku, *to be published*

Substitution & Vacancies: Zn1-xCuO1-y

SQUID[1]





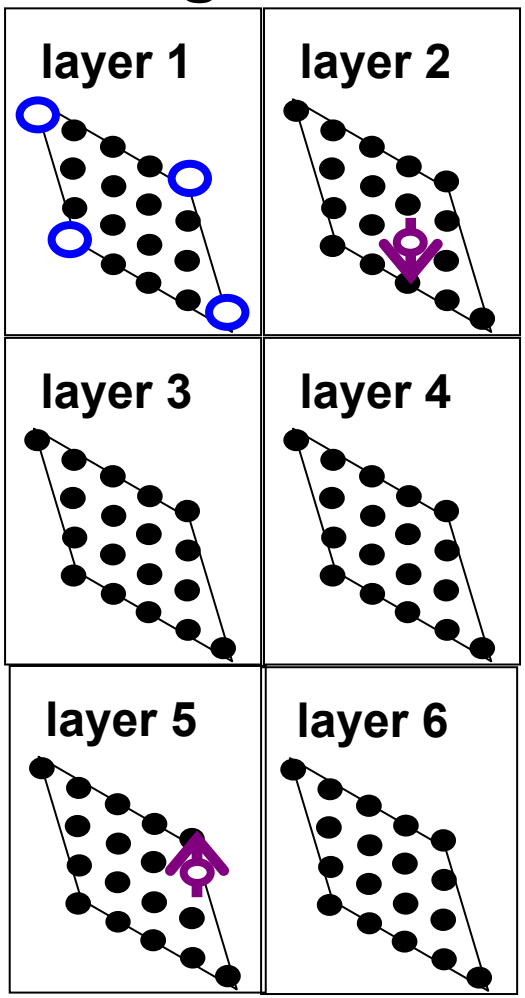
Q) What is the role of oxygen vacancy?

1) T. S. Herng, D.-C. Qi, T. B, J. B. Yi, K. S. Yang, Y. Dai, Y. P. Feng, I. Santoso, C. H. Sanchez, X. Y. Gao, A. T. S. Wee, W. Ku, J. Ding, A. Rusydi, *to be published*

$Zn_{1-x}Cu_xO_{1-y}$: x≈0.02, y≈0.01, M≈0.8μ_B/Cu

10 configurations of ~200 atoms

configuration 1



+ . . . +

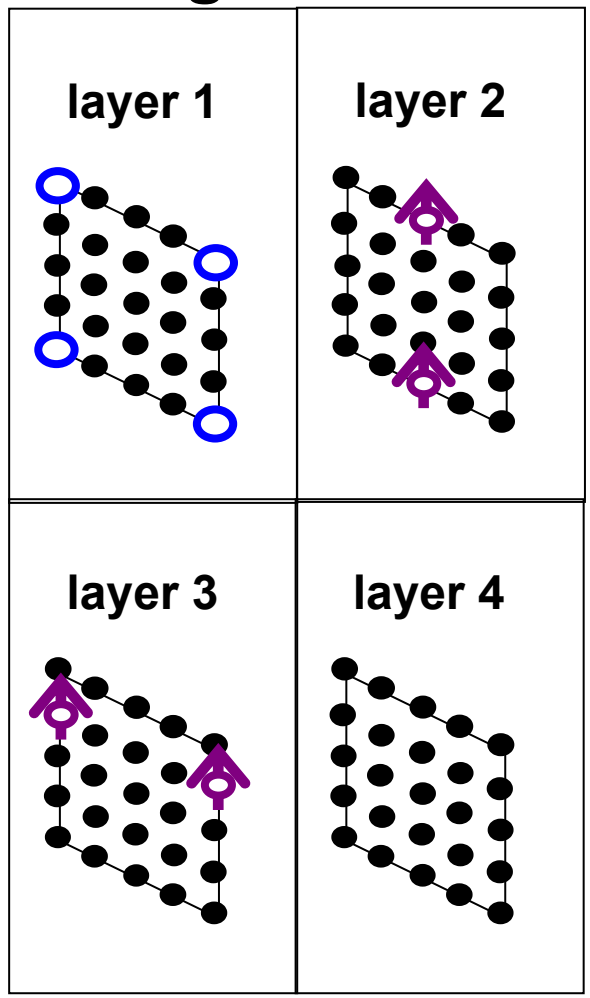
● = ZnO

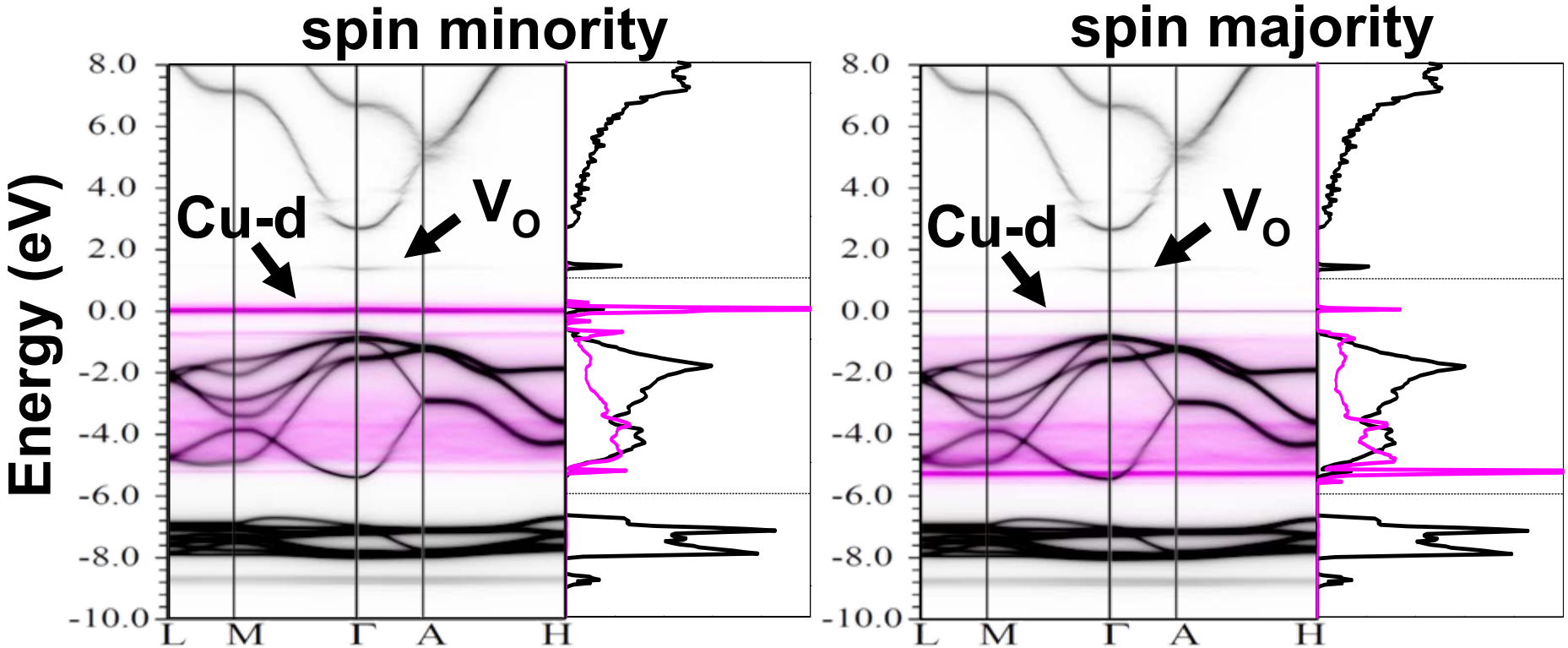
= Cu-up

= Cu-dn

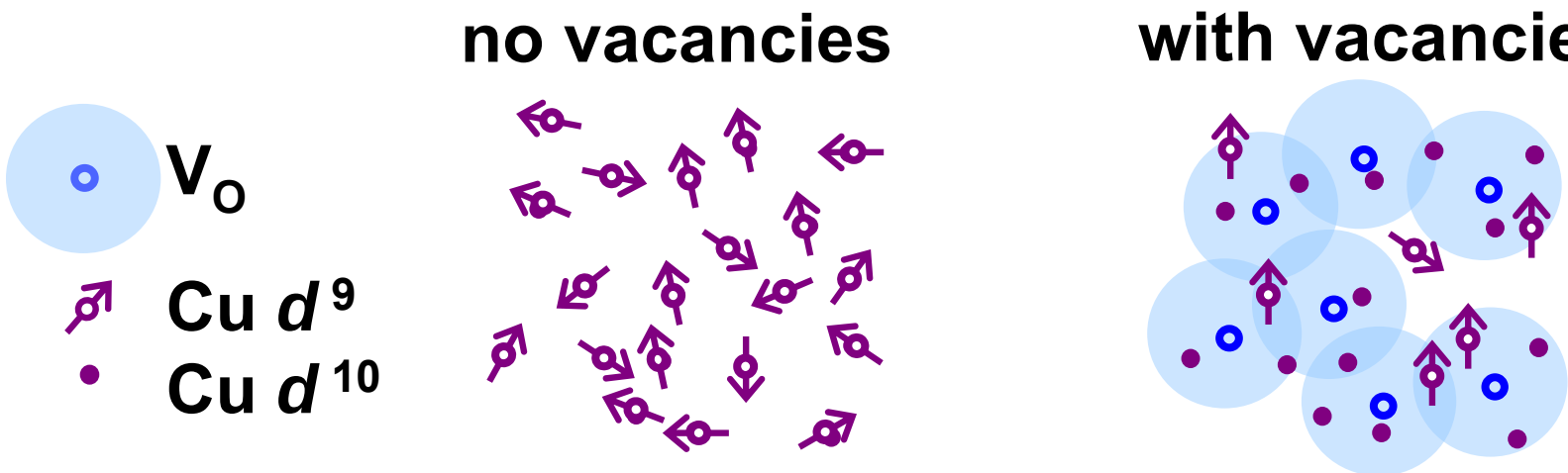
○ = Vo

configuration 10





A) To mediate Cu moments



Next

- New materials: CaC_6, $Fe_{1+y}Te_{1-x}Se_x$,
  (solid solution GaN/ZnO with Phil Allen & Li Li?)
- Short range order, 2-particle Green function
- Extensions of the method:
- Total energy
- Higher-order impurity correlations
- Self-consistency
- Relaxed atoms

Summary

- Introduction: Super Cell Approximation
- Method 1: Unfolded Bandstructure (Wannier function)
- Method 2: Effective Hamiltonian (Wannier function)
- Results: Disordered Na_xCoO_2 & $Zn_{1-x}Cu_xO_{1-y}$