

Wannier Functions and Applications to Magnetic Insulators

{Ku, Rosner, Pickett, Scalettar, *PRL*, ca. Oct 2002}
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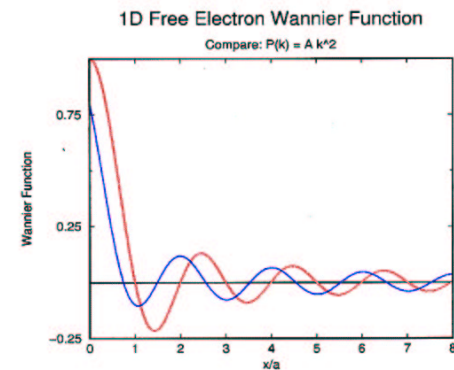
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- Helge Rosner
- Richard Scalettar
- Michelle Johannes

Outline of Talk

- General comments about Wannier functions
- Calculation of all-electron, full potential WFs
- Application to magnetic insulators
 $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$, $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$
- Case of overlapping bands: cerium
- Peculiar case of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (if there's time)

Local Orbitals: What do You Want?

- Just another basis set?
- Some physical meaning?
- Orthogonal? it costs in localization
- Maximally localized? any physics in this?
- Symmetric or no



Wannier Functions: Generalities

Given an isolated set of bands with Bloch wfn's $\{\psi_{k,n}\}$, Wannier functions are given by

$$W_m(r - R) = \sum_k \sum_j U_{mj}(k) \psi_{k,j}(r) e^{ik \cdot R}$$

- $U(k)$ is any k -dependent unitary transformation
- $\{R\}$ labels the unit cells
- Indices run over orbitals in the subspace
- Single band: $U(k) \rightarrow e^{iP(k)}$ where P is real
- $P(k)$ affects the localization of $W(r)$
- If $\{\psi_{k,n}\}$ are orthonormal, then

$$\int d^3r W_i^*(r - R_1) W_j(r - R_2) = \delta_{ij} \delta_{R_1 R_2}.$$

$U(k)$ provides much flexibility: maximally localized WFs are popular and, without other considerations, are more efficient than alternatives.

Wannier Functions: Single Band

Given a single band, what can we say about the (single) Wannier function?

$$\hat{h} \psi_k = \varepsilon_k \psi_k; \quad \varepsilon_k = \sum_R t_R e^{ik \cdot R}$$

- $\{t_R\}$ is unique (Fourier transform of ε_k)
- hence, the “extent” of the Wannier function is determined
- $|W(r - R)|^2$, and $\langle (r - R)^2 \rangle$, depends on the phase choice $P(k)$

Thus even for a simple $S = \frac{1}{2}$ spin-orbital, the degree of localization is somewhat flexible (so the orbital is not unique), but its extent (hopping range) is unique.

For multiband systems, progressively less can be said in general about the flexibility of their localization.

Symmetric Projection of Wannier Functions

Given an isolated set of Bloch wvfns $\{\psi_{k,n}\}$

- choose (symmetry-related) orbitals $\{g_j\}$
- form the projections $\langle g_j | \psi_{k,n} \rangle = M_{j,n}(k)$
- construct unitary transformation

$$M(M^\dagger M)^{-1/2} = U$$

$$U^\dagger U = (M^\dagger M)^{-1/2} M^\dagger M (M^\dagger M)^{-1/2} = 1$$

- transform to Wannier functions

$$\{\psi_{k,n}\} \rightarrow W(r-R) = \sum_k e^{ik \cdot R} U(k) \psi_k(r)$$

- produces symmetric orthonormal Wannier functions if $\{g\}$ are symmetric
- conserves the density of the subspace

$$\sum_{R,m} |W_m(r-R)|^2 = \rho(r) = \sum_{k,n} |\psi_{k,n}(r)|^2$$

- additional phase factors not yet investigated

Wannier Functions: Applications

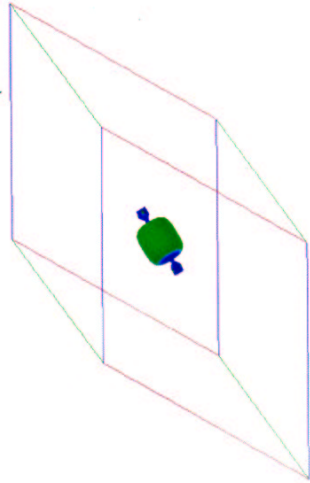
Given a set of Wannier functions (or any local orbitals) it is straightforward to calculate

- $\varepsilon_j = \int W_j^*(r-R) \hat{h} W_j(r-R)$
- $t_{i,j}(R) = \int W_i^*(r-R) \hat{h} W_j(r)$
- $U_{i,j}^\circ = \int |W_i^*(r-R)|^2 \frac{e^2}{|r-r'|} |W_j(r-R)|^2$
- $J_{i,j}^\circ(R) = \int \int W_i^*(r-R) W_i^*(r'-R) \frac{e^2}{|r-r'|} W_j(r') W_j(r)$

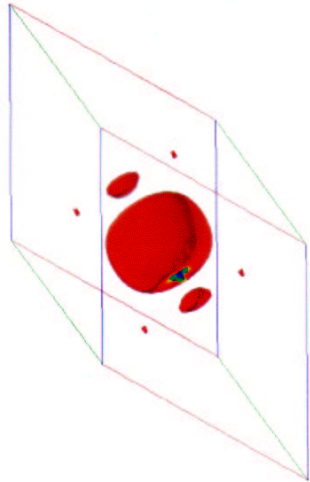
and other more specific integrals.

Silicon

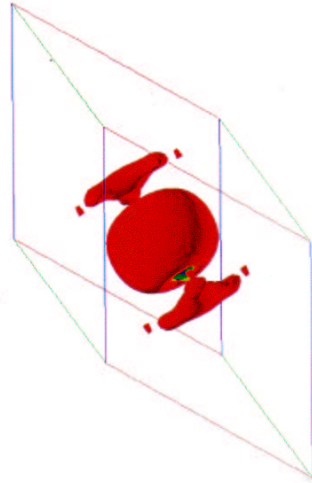
$\rho = 0.02$



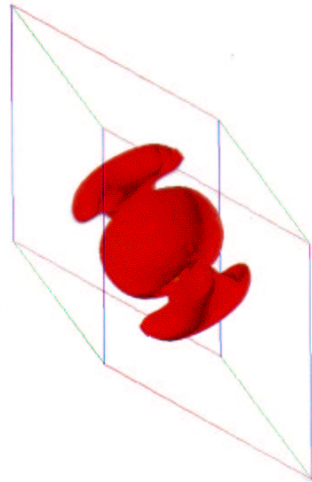
$\rho = 0.0007$



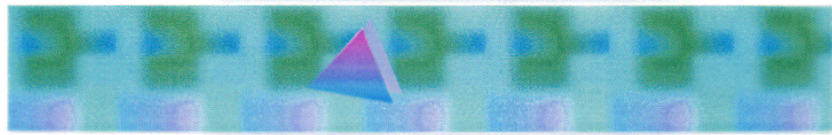
$\rho = 0.0005$



$\rho = 0.0002$



Wannier State Analysis of
Insulating Ferromagnetism in $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$



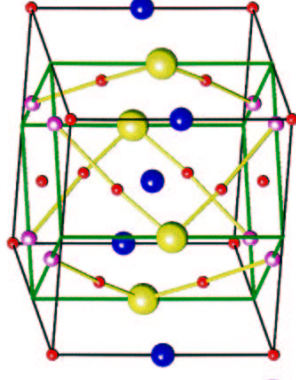
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Ferromagnetic Order of Insulating $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$

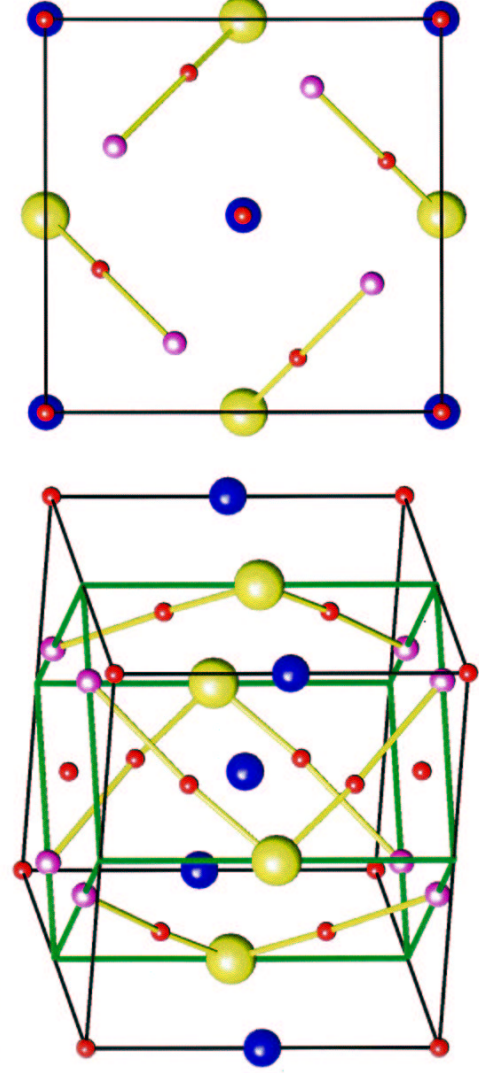
- “Brown phase”: byproduct of High- T_c CuO material
 - Large on-site repulsion
 - Narrow bandwidth
 - Half-filling
→ ~ Mott-Hubbard insulator
 - Structurally identical to $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$
- But**
- $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$: ferromagnetic (FM) order
 - $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$: anti-ferromagnetic (AF) order



What is the underlying microscopic mechanism?



Crystal Structure of $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$



Reformulation of *Ab Initio* 2nd-Quantized Hamiltonian

$$H = \varepsilon_{\mu\alpha} n_{\mu\alpha} - t_{\mu\nu} c_{\mu\alpha}^{\dagger} c_{\nu\alpha} + U_{\mu} \tilde{n}_{\mu\uparrow} \tilde{n}_{\mu\downarrow} + \frac{1}{2} C_{\mu\nu} \tilde{n}_{\mu\alpha} \tilde{n}_{\nu\beta} - J_{\mu\nu} \left(\mathbf{S}_{\mu} \cdot \mathbf{S}_{\nu} + \frac{1}{4} n_{\mu\alpha} n_{\nu\beta} \right)$$

+other $\left(c_{\mu\alpha}^{\dagger} c_{\nu\beta} \right) \left(c_{\nu\beta}^{\dagger} c_{\mu\alpha} \right)$ terms + constant terms

$$\varepsilon_{\mu\alpha} \equiv \langle \mu | h^{DFT} - v^{xc} | \mu \rangle - U_{\mu} \langle n_{\mu\alpha} \rangle^{DFT}$$

$$t_{\mu\nu} \equiv - \left(\langle \mu | h^{DFT} - v^{xc} | \nu \rangle - J_{\mu\nu} \langle c_{\nu\beta}^{\dagger} c_{\mu\beta} \rangle^{DFT} \right) (1 - \delta_{\mu\nu})$$

$$U_{\mu} \equiv \langle \mu\mu | v | \mu\mu \rangle; \quad C_{\mu\nu} \equiv \langle \mu\nu | v | \mu\nu \rangle (1 - \delta_{\mu\nu}); \quad J_{\mu\nu} \equiv \langle \mu\nu | v | \nu\mu \rangle (1 - \delta_{\mu\nu})$$

$$\tilde{o} \equiv o - \langle o \rangle^{DFT}$$

- Inclusion of long-range Coulomb repulsion $\rightarrow \tilde{n}_{\mu\alpha}$
(in mean-field approximation $\rightarrow 0$)
- Self-interaction eliminated in $\varepsilon_{\mu\alpha}$
- Quality of h^{DFT} : LDA & LSDA+U (for Nd-f states)
- Spin independence of $|\mu\rangle$

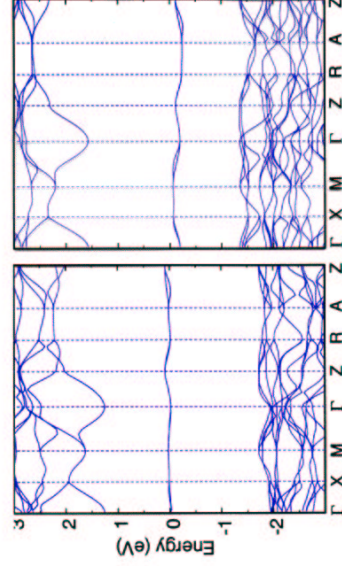
Wannier States as Basis

$$|Rn\rangle \equiv |\bar{k}n\rangle e^{-i\bar{k}\cdot R} / \sqrt{\#}$$

$$|kn\rangle' = |\bar{k}\bar{m}\rangle \langle \bar{k}\bar{m} | kn \rangle'$$

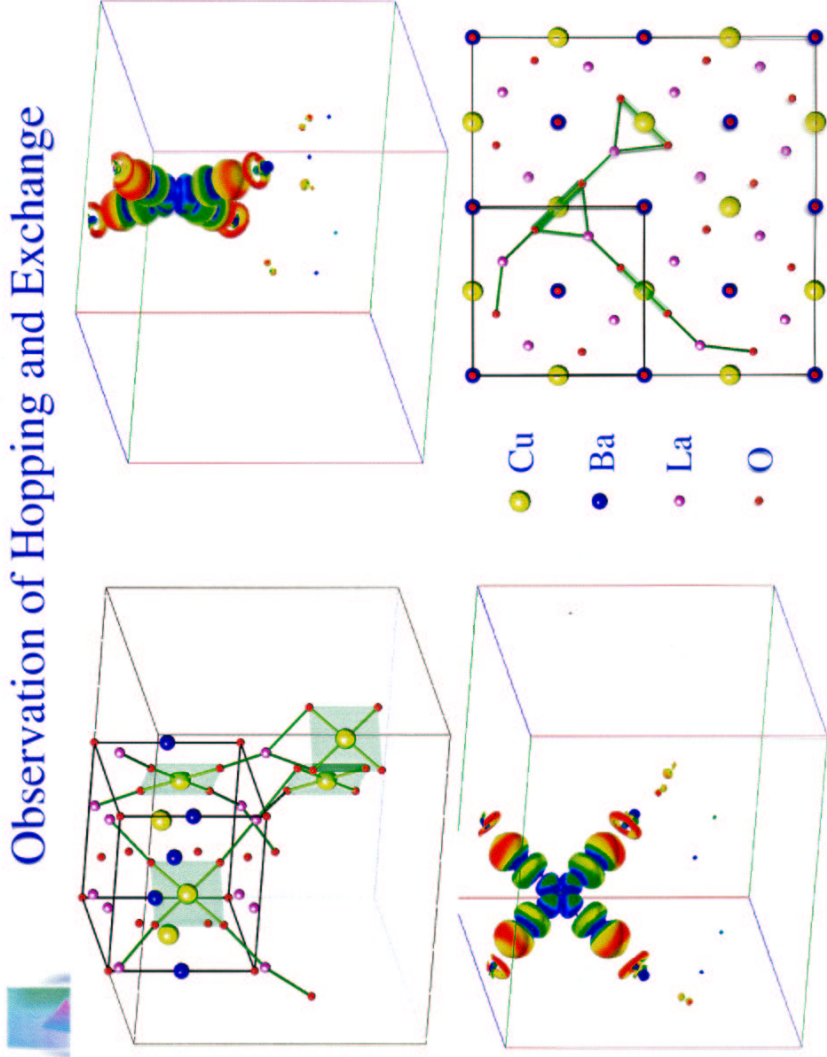
$$\langle km | kn \rangle' = \langle km | g_{\bar{n}} \rangle M_{\bar{n}n}$$

$$M_{\bar{n}n}^{-2} \equiv \langle g_{n'} | \bar{k}\bar{m} \rangle \langle \bar{k}\bar{m} | g_n \rangle$$



- Localized picture (desired for spin analysis)
- Orthonormal + Complete (unlike atomic orbitals)
- **Energy resolution** (chosen band indices)
 - One per Cu site (two per unit cell) \rightarrow simpler picture
 - Half-filled
- All-electron wave function

Observation of Hopping and Exchange



Wannier representation of H

- Partial spin density:
Cu : 50%, O : 4 x 10%, La : 4 x 2% → hyperfine structure in NMR
- t_{ij} is *calculated*, not fitted. (perfect “downfolding”)
- U_i and J_{ij} are evaluated via 6D numerical integration
- AF via superexchange

$$\mathcal{J}_z^{SX} \sim \sum \mathcal{J}_{ij}^{SX} \sim \sum -4t_{ij}^2/W_i; \quad W_i \sim U_i/2 \quad (\text{leading hopping paths})$$
- FM via direct exchange

$$\mathcal{J}_z^{DX} \sim \sum J_{ij}^{SX}/2$$



Calculated Parameters for $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$

$i-j$	(001)	(111)	(201)	(021)
t_{ij}	3.4	3.6	4.8	-0.10
J_{ij}	1.3	~0	~0	~0

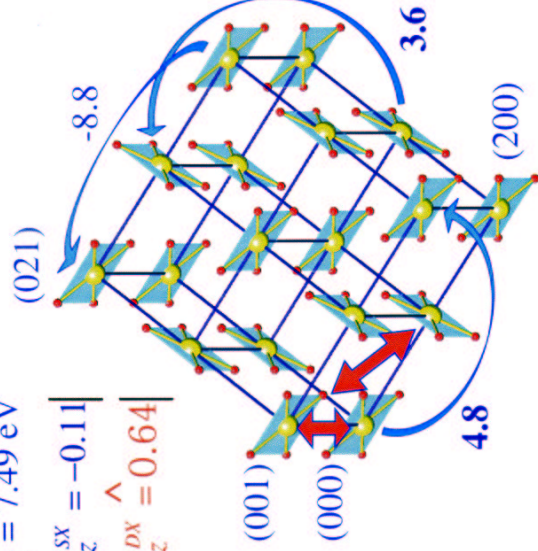
$i-j$	(101)	(100)
t_{ij}	0.0	0.0
J_{ij}	1.1	0.4

$i-j$	(200)	(020)	(210)	(211)
t_{ij}	-8.8	0.71	± 0.84	± 0.64

$$U_i = 7.49 \text{ eV}$$

$$|\mathcal{J}_z^{\text{SX}}| = -0.11$$

$$|\mathcal{J}_z^{\text{DX}}| = 0.64$$



- **DX** overwhelms SX: (001) & (101)
- in-plane coupling is *not* nearest-neighbor



Calculated Parameters for $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$

$i-j$	(001)	(111)	(201)	(021)
t_{ij}	-31	7.8	8.0	-0.087
J_{ij}	2.1	~0	~0	~0

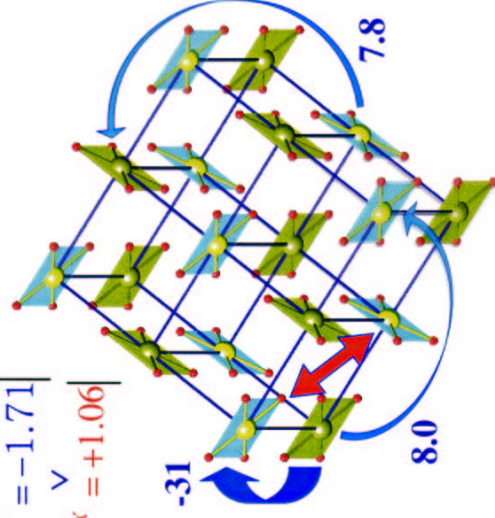
$i-j$	(101)	(100)
t_{ij}	0.0	0.0
J_{ij}	1.4	1.1

$i-j$	(200)	(020)	(210)	(211)
t_{ij}	-1.7	1.1	± 1.4	± 0.38

$$U_i = 6.12 \text{ eV (smaller)}$$

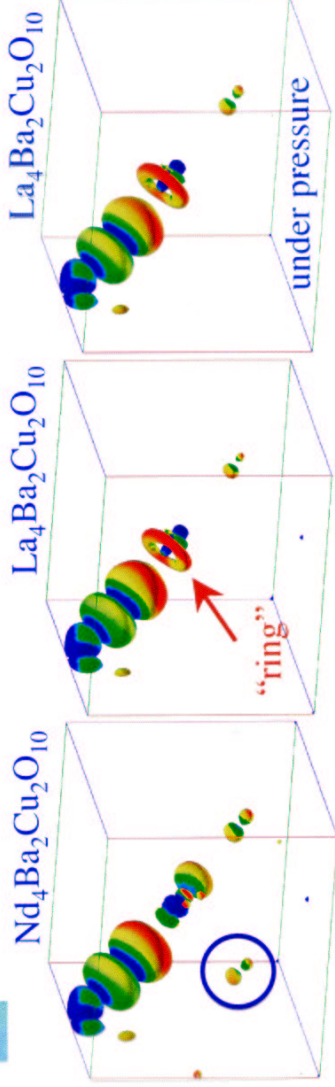
$$|\mathcal{J}_z^{\text{SX}}| = -1.71$$

$$|\mathcal{J}_z^{\text{DX}}| = +1.06$$



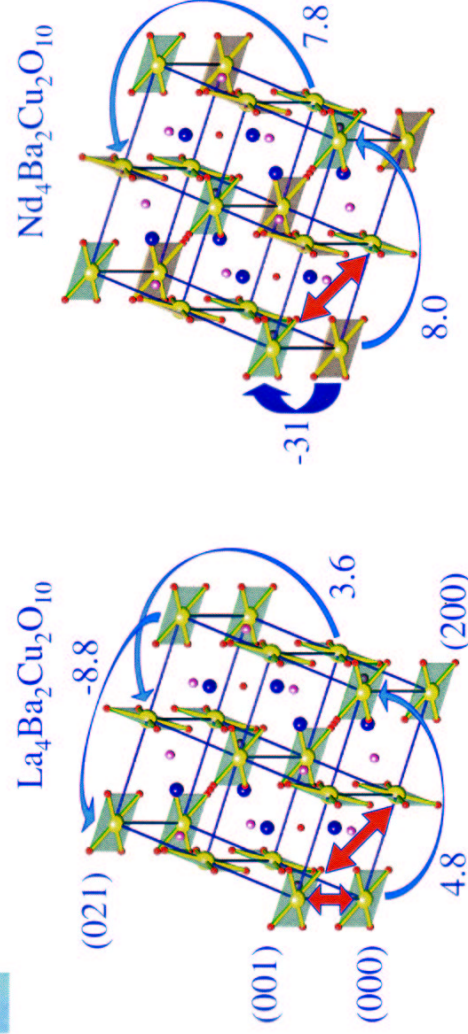
- Enhanced (001) hopping \rightarrow 1D AF chain along z-axis
- **(101) FM exchange \rightarrow in-plane AF order!**

Effect of Chemical Replacement



- Different (001) hopping path : Cu-O-O-Cu vs. Cu-O-La-O-Cu
- **Smaller lattice constant** → more extended orbitals
→ 20% difference in localization (smaller U , larger t and J)
- $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$ under pressure: chemical vs. **size effects**
- **Prediction**: pressure-induced **FM-to-AF** transition

Different Electronic Structure

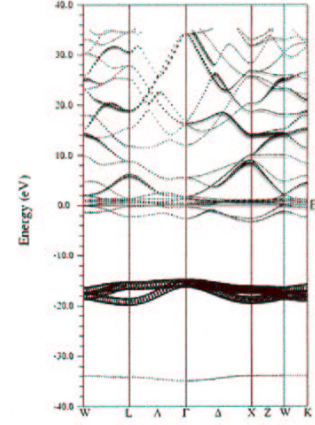
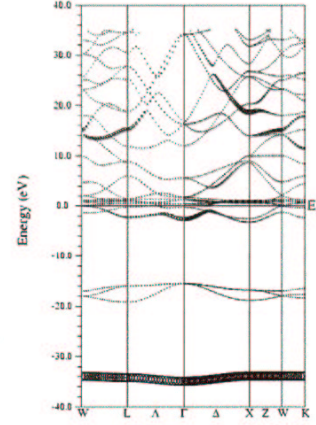


- two 3D **FM** sublattices
- all-directional **FM** coupling
- 1D **AF** chain along z-axis
- (101) **FM** coupling



Conclusion

- Novel *ab initio* scheme:
 - Reformulation of *ab initio* second-quantized H
 - Wannier state representation of the “fluctuation” H
 - Energy-resolved localized all-electron Wannier states
 - Intuitive microscopic picture + quantitative realism
- Unified picture of insulating magnetic structure:
 - Ferromagnetism in $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$:
 - Strong FM direct exchange near La/O
 - Anti-ferromagnetism in $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$:
 - Strong z-axis hopping induced superexchange
- FM (101) coupling \rightarrow in-plane FM/AF order in both cases. isostructural, yet very different electronic structure:
 - 3D FM sublattices vs. 1D AF chain



Ce LDA bands over large E range

WANNIER FUNCTIONS FOR
fcc Cerium METAL

