"Correlated" bands in oxides with wave-function based methods

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Our goal

- compute *energy bands* with quantum chemical accuracy
- long-term objective: strong correlations in transition-metal compounds — *magnetism, satellite structures* etc.

Motivation

- the limitations of the DFT-based methods:

  band gaps, "strong correlations" in $3d$ and $4f$ solid-state compounds (Mott insulating states, magnetism etc.)

Our approach

quasiparticle picture, local Hamiltonian formalism

first step: all-electron Hartree-Fock calc. for the *periodic system*
$\longrightarrow$ HF bands, localized Wannier orbitals (WO's) [CRYSTAL program]

second step: the correlation treatment [MOLPRO package]

- *finite fragment* $\mathcal{C}$ cut from the infinite solid (up to 100 sites, to include the tails of the "active" orbitals)
- use the data from the periodic Hartree-Fock (HF) calculation
  - localized WO's at the atomic sites of the finite cluster
  - HF embedding potential due to the rest of the crystal (the surrounding HF electron "sea")

$$V^{\mathrm{emb}}_{\alpha\beta} = F^{\mathrm{crys}}_{\alpha\beta} - F[P_{\mathcal{C}}]_{\alpha\beta}\,, \qquad P_{\mathcal{C}} = 2\sum_{\nu}^{\mathrm{occ}} |w_\nu\rangle\langle w_\nu|\,, \qquad \alpha,\beta,\nu \in \mathcal{C}$$

Starting point: Hartree-Fock

The fundamental gap: $(N+1)/(N-1)$ el. addition/removal states

$$|\Phi^{N+1}_{\mathbf{R}c\sigma}\rangle = c^{\dagger}_{\mathbf{R}c\sigma}|\Phi\rangle \quad \text{and} \quad |\Phi^{N-1}_{\mathbf{R}v\sigma}\rangle = c_{\mathbf{R}v\sigma}|\Phi\rangle$$

For clusters which are large enough, the HF bands of the periodic crystal can be recovered by diagonalizing **k**-dependent matrices of the form:

$$H^{\mathrm{HF}}_{nn'}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} \left(\langle \Phi^{N\mp1}_{\mathbf{0}n\sigma}|H|\Phi^{N\mp1}_{\mathbf{R}n'\sigma}\rangle - E^{\mathrm{HF}}_0 \delta_{\mathbf{0R}}\delta_{nn'} \right)$$

Diagonal terms (R=0): on-site Koopmans excitation energies, i.e.,

ionization potentials $\mathrm{IP}^{\mathrm{HF}}_{vv}(\mathbf{0}) = \langle \Phi^{N-1}_{\mathbf{0}v\sigma}|H|\Phi^{N-1}_{\mathbf{0}v\sigma}\rangle - E^{\mathrm{HF}}_0 = -\epsilon^{\mathrm{HF}}_{\mathbf{0}v} > 0$ and

electron affinities $\mathrm{EA}^{\mathrm{HF}}_{cc}(\mathbf{0}) = E^{\mathrm{HF}}_0 - \langle \Phi^{N+1}_{\mathbf{0}c\sigma}|H|\Phi^{N+1}_{\mathbf{0}c\sigma}\rangle = -\epsilon^{\mathrm{HF}}_{\mathbf{0}c} < 0$

Off-diagonal (R≠0): *tight-binding hopping matrix elements (ME's)*

$$t^{\mathrm{HF}}_{nn'}(\mathbf{R}) = \langle \Phi^{N\mp1}_{\mathbf{0}n\sigma}|H - E^{\mathrm{HF}}_0|\Phi^{N\mp1}_{\mathbf{R}n'\sigma}\rangle$$

Including correlations

Short-range relaxation and polarization : *separate SCF optimizations*, orbitals in *the immediate neighborhood* of the additional electron (hole)

[the $(N \pm 1)$ Wannier orbital is kept frozen]

Loss of ground-state correlations : small effect, not discussed here

Long-range polarization :
the approximation of a *dielectric continuum*

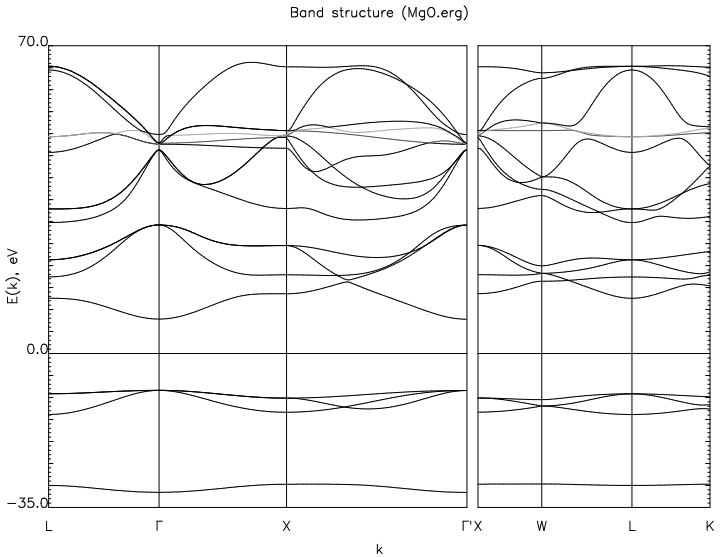
$$\Delta E(\infty) = \Delta E(R_i) - C/R_i \ , \quad C = \frac{\epsilon_0 - 1}{2\epsilon_0} e^2$$

C : by computing $\Delta E(R_1)$, $\Delta E(R_2)$ for two different radii R_1, R_2

$\longmapsto$ **"correlated" wave-functions, renormalized real-space ME's:**

$$\boxed{H_{nn'}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} \left(\langle \Psi^{N\mp 1}_{\mathbf{0}n\sigma} | H | \Psi^{N\mp 1}_{\mathbf{R}n'\sigma} \rangle - E_{\mathbf{0}} \delta_{\mathbf{0R}} \delta_{nn'} \right)}$$

MgO: the HF data

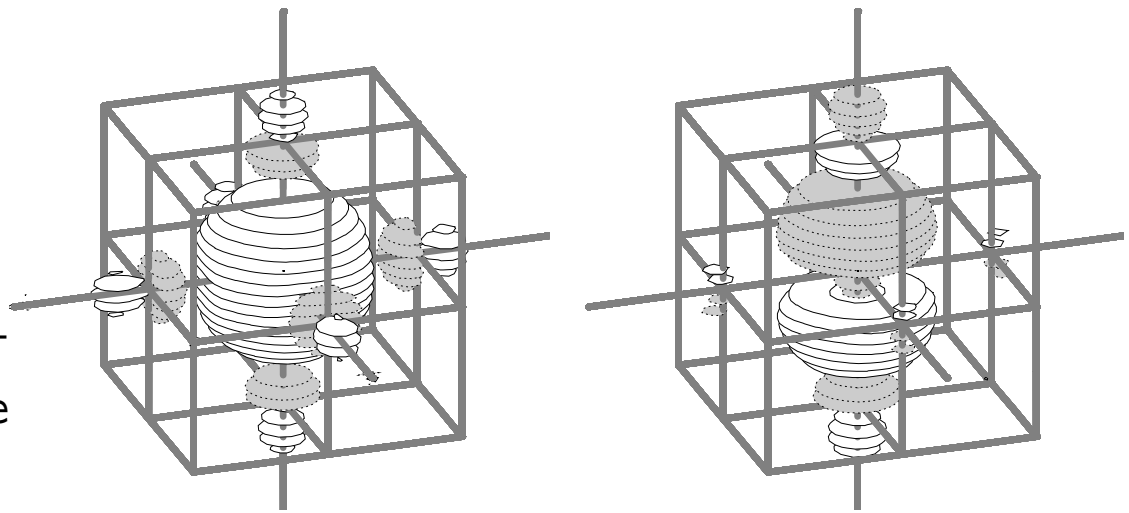


- HF gap : 16.20 eV; Exp.: 7.8 eV
  (Basis sets: Mg – TZ; O – TZ + pol.)
- low-lying conduction bands : Mg $3s$–$3p$
- valence-band states : oxygen $2p$

Conduction-band Wannier orbitals (WO's) :

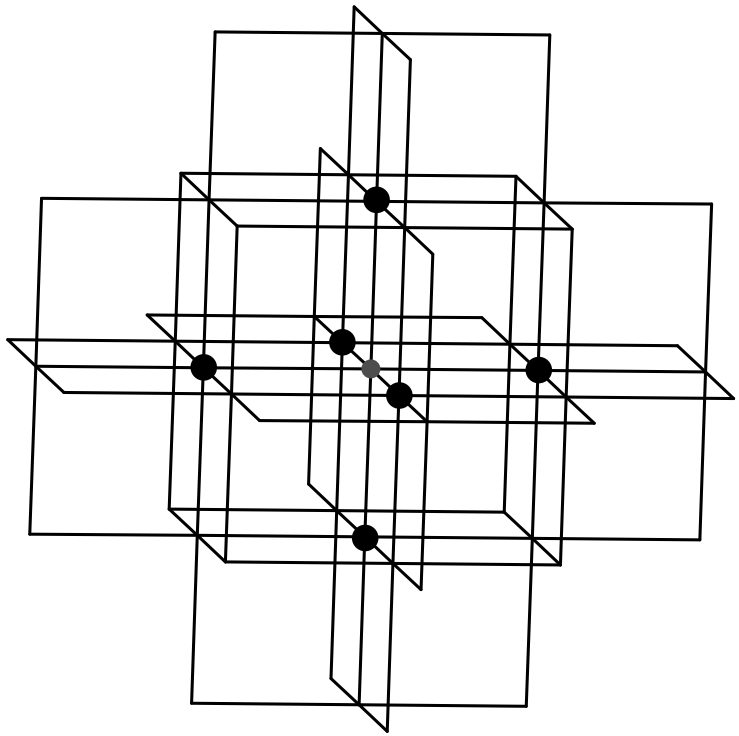
- the most diffuse

after projection onto the finite cluster, their norms are $>98.5\%$ of the orig. WO's



Short-range relaxation and polarization effects

- *separate SCF optimizations*, orbitals in the immediate neighborhood of the additional electron/hole
- the "$(N \pm 1)$"th Wannier orbital is frozen



$\Delta H_{nn}(\mathbf{0})$	O $2s$	O $2p$	Mg $3s$	Mg $3p$
On-site orb. relaxation	-2.64	-2.04	—	—
NN orb. relaxation	-1.23	-1.20	-0.81	-0.84
NNN orb. relaxation	-0.18	-0.18		

(O $2s/2p$ WO's: 12 NN O's; Mg $3s/3p$ WO's: 6 NN O's, see figure)

Long-range polarization

The approximation of a *dielectric continuum*:

$\Delta E(\infty) = \Delta E(R_i) - C/R_i$

- $\Delta E(R_i)$: short-range relax./pol. within a sphere of radius R_i
- C: a) $C = \frac{\epsilon_0 - 1}{2\epsilon_0} e^2 \longrightarrow C = 0.45$ a.u. $(\epsilon_0 = 9.7)$

  b) by computing $\delta E_{ji} = \Delta E(R_j) - \Delta E(R_i)$

  R_i: NN's; R_j: NN's + NNN's (*previous page*)

  $C \sim \frac{R_i R_j}{R_j - R_i} \delta E_{ji} \longrightarrow C = 0.41$ a.u.

$\longrightarrow$ the approx. of a dielectric continuum works quite well

$\Delta H_{nn}(\mathbf{0})$	O $2s$	O $2p$	Mg $3s$	Mg $3p$
Long-range polarization	-1.80	-1.80	-2.25	-2.25

Correlation-induced corrections to the gap

$\Delta H_{nn}(\mathbf{0})$	O 2s	O 2p	Mg 3s	Mg 3p
On-site orb. relaxation	−2.64	−2.04	—	—
NN orb. relaxation	−1.23	−1.20	−0.81	−0.84
Long-range polarization	−1.80	−1.80	−2.25	−2.25
Total	−5.67	**–5.04**	**–3.06**	**–3.09**

- **valence bands:** shift *upwards* by approx. 5 eV
- **conduction bands:** *downwards* shift, approx. 3.1 eV

- "correlated" gap: 8.1 eV; exp.: 7.8 eV
- LDA gap: 5.0 eV [CRYSTAL package]

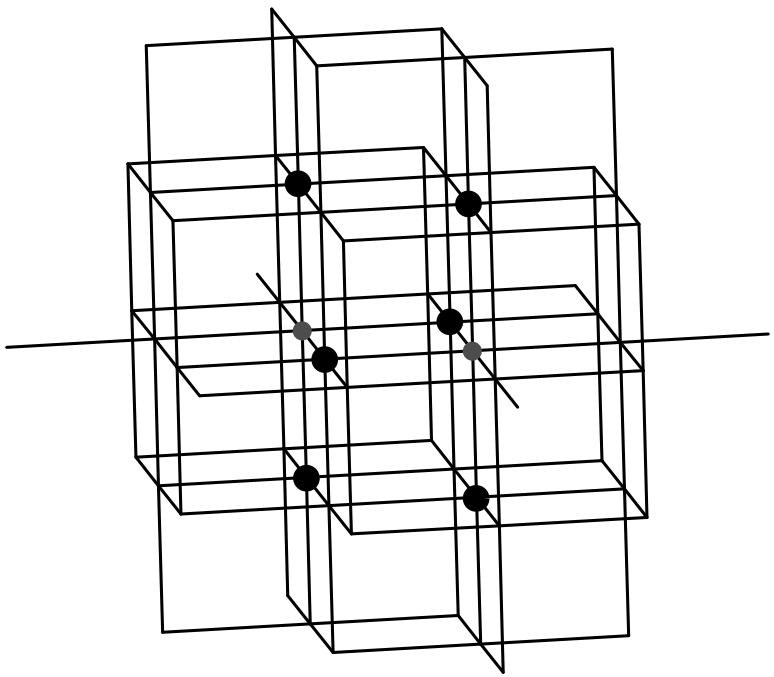
95% of the difference between HF and experiment !!

Renormalized hoppings, band widths

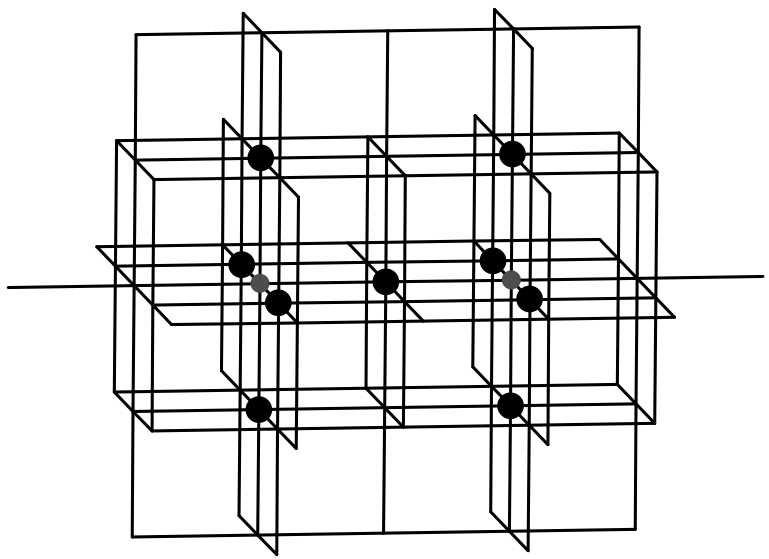
less affected, as compared to the diagonal (on-site) matrix elements

- separately optimized $(N \pm 1)$ wave-functions $\Psi^{N\pm1}_{\mathbf{0}\,i}$, $\Psi^{N\pm1}_{\mathbf{R}\,j}$
  (relaxation effects in the immediate vicinity of the extra particle)
- $t_{ij} = (H_{ij} - S_{ij}H_{ii})/(1 - S_{ij}^2)$ [2×2 secular problem in terms of non-orthog. sets of orbitals (Non-Orthog. Config.-Interaction, NOCI)]

$t_{NN} \longrightarrow \mathbf{R}_{NN} = (1,1,0)a/2$



$t_{NNN} \longrightarrow \mathbf{R}_{NNN} = (1,0,0)a$



Conduction-band hopping matrix elements

Conduction-band states (Mg $3s$–$3p$): changes **within** $\sim 5\%$

$t_{ij}(\mathbf{R})$	HF (frozen orb. CI)	**NOCI (relaxed orbs.)**
t_{NN} :		
$3s - 3s$	0.41	0.42
$3p_{x(y)} - 3p_{x(y)}$	0.66	0.69
$3p_{x(y)} - 3p_{y(x)}$	**0.72**	**0.77**
$3p_z - 3p_z$	0.13	0.13
t_{NNN} :		
$3s - 3s$	0.36	0.37
$3p_x - 3p_x$	**0.77**	**0.74**
$3p_{y(z)} - 3p_{y(z)}$	0.13	0.12

- some hoppings are enlarged, some are reduced by correlations

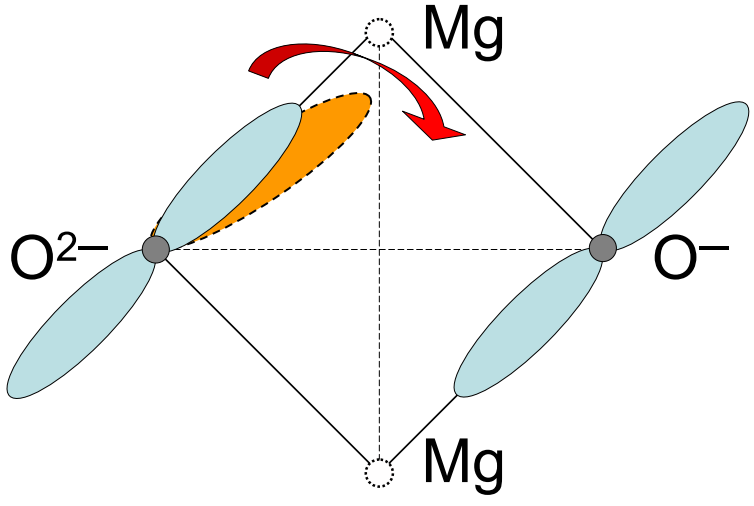
O 2p valence bands

- correlation-induced **broadening, by** $10-15\%$

$t_{ij}(\mathbf{R})$	HF (FO-CI)	NOCI (relaxed orbitals)	
		Two-site	Two-site, NN O's
t_{NN} :			
$2p_{x(y)} - 2p_{y(x)}$	0.42	**0.49**	0.47
$2p_{x(y)} - 2p_{x(y)}$	0.32	**0.37**	0.36
$2p_z - 2p_z$	0.12	**0.14**	0.13
t_{NNN} :			
$2p_x - 2p_x$ (σ-ov.)	0.06	0.06	—

- main effect :
  "bending" of the p orbitals due to the adjacent O hole $\longrightarrow$
  increased inter-site overlap

- $w_{2p}^{\Gamma L} = 8t_{xx}^{110} + 8t_{xy}^{110} - 4t_{xx}^{011} + \ldots$
  $w_{2p}^{\Gamma L}$: 5.5 (HF) $\longrightarrow$ 6.2 (HF + correl.)



O valence bands : comparison to experiment

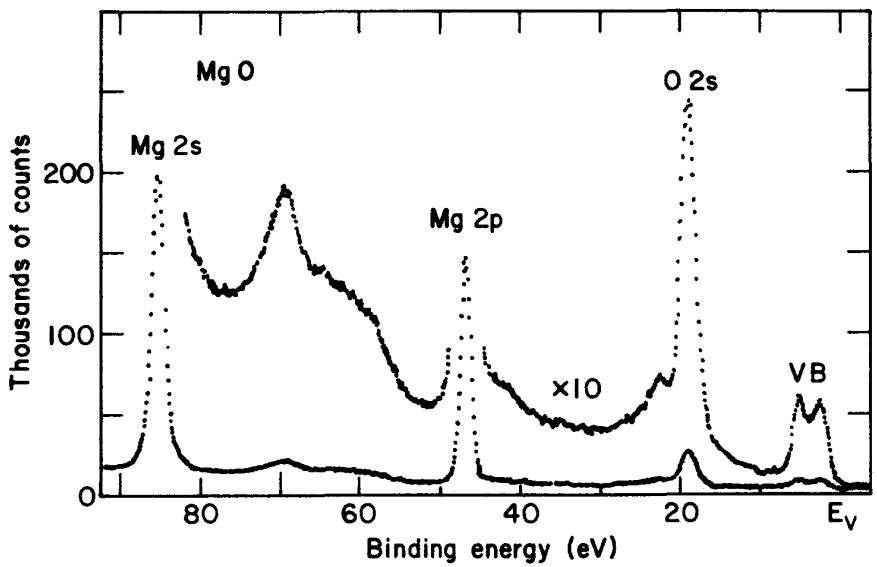
	HF	**HF + correl.**	PES	LDA
$w(2p)$	5.5	**6.2**	$\sim$ 6.5 [1,2]	4.7
$\Delta E_{2p}^{1,2}$	3.5	**...**	3.5 [2]	3.0
ΔE_{2s2p}	15.9	**14.8**	14.0 [1]	10.7

[1] S. Kowalczyk, D. A. Shirley *et al.*, Solid State Commun. **23** (1977).

[2] L. H. Tjeng *et al.*, Surf. Sci. **235** (1990).

$\Delta E_{2p}^{1,2}$: separation between the two O $2p$ peaks

ΔE_{2s2p} : O $2s$ – bottom of the $2p$ bands



MgO :

- **charge relaxation** effects are essential for computing accurate band gaps
- band widths are less affected

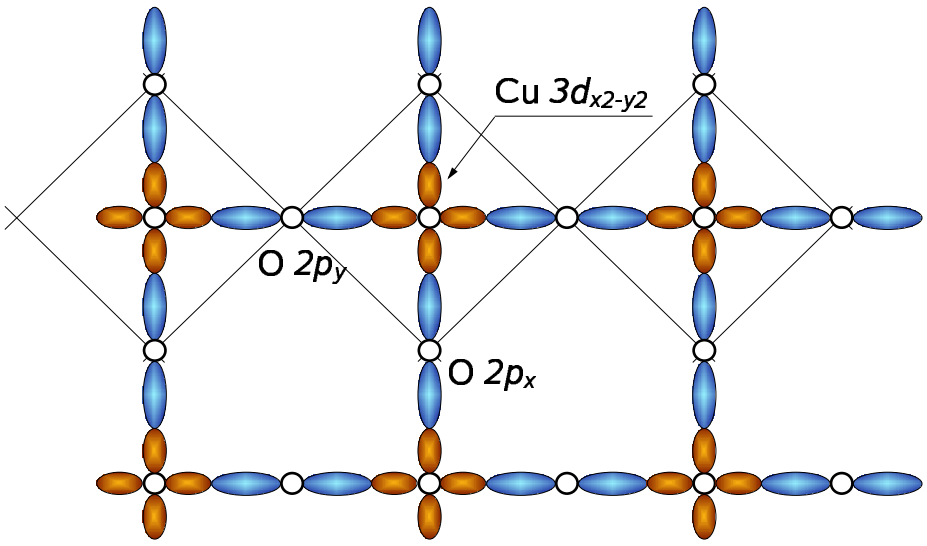
What about spin polarization and relaxation ?

Illustrative example :

doped hole (electron) in the cuprate antiferromagnetic lattice
(*reduction by a factor of 4 of the band widths*)

"Correlated" bands in layered Cu oxides

Formal valence states for the undoped layer:
$Cu^{2+}\ 3d^9\ (S=1/2)$; $O^{2-}\ 2p^6$



180^o Cu – O – Cu interactions
$d_{x^2-y^2} - p_{x,y}$ σ-bonds

Superconductivity: both *hole* and *electron* doping
(e.g., $La_{2-x}Sr_xCuO_4$ vs. $Sr_{1-x}Nd_xCuO_2$)

Dressed carriers: strong correlation effects (charge, spin, ...)

Method

Ab initio wave-function based approach

Finite fragments (up to 11 CuO_4 plaquettes) :

all-electron, multiconfiguration calculations [MOLCAS package]

(Static) embedding :

- *Madelung field* $\longleftarrow$ *point charges*
- *finite charge distrib. of NN's* $\longleftarrow$ *effective ion potentials*
- less rigorous as compared to the study on MgO

Multiconfiguration approach : CAS SCF

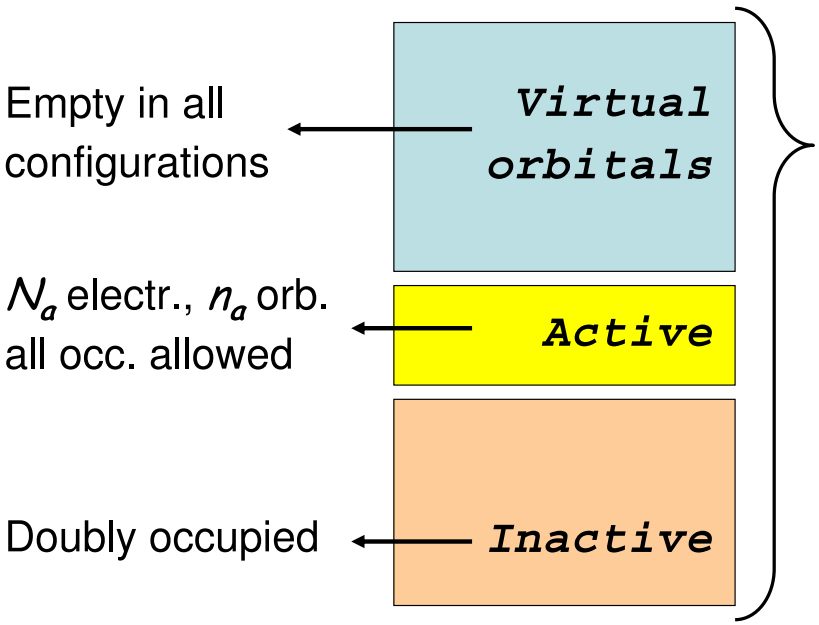
The minimal active space in cuprates :
one $3d_{x^2-y^2}$ orbital per Cu site

- provides the correct antiferromagnetic (AFM) ground-state configuration (*Anderson superexchange mechanism*)

Multiconfiguration approach : CAS SCF

The N-electron wave-function : complete active space (CAS)

"full" Configuration Interaction (CI) within a relatively small set of "active" orbitals (e.g., one $3d_{x^2-y^2}$ per Cu site) $\longrightarrow$ $\Psi = \sum_k^{\mathrm{CAS}} C_k \Phi_k$



The orbital variational space :

Gaussian-type basis functions $\longrightarrow$

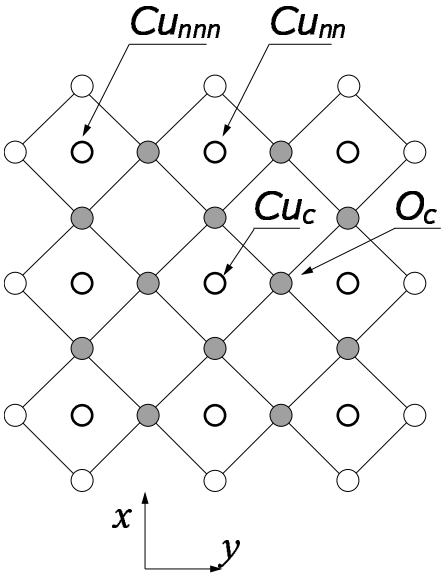
AO's $\chi_p(\mathbf{r}) = \sum_\nu a_{\nu p}\, \mu_\nu(\mathbf{r}) \longrightarrow$

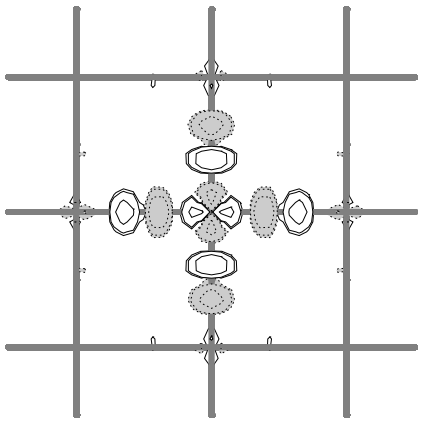
LCAO's

- highly flexible: *orbitals* and *CI coefficients* are both variationally optimized
- *near-degeneracy (static) correlation effects* :
  competing valence structures, bond breaking, magnetism (Anderson superexchange, double exchange) etc.

The Zhang-Rice (ZR) -like state

- crystal structure : $La_{1.85}Sr_{0.15}CuO_4$
- 3×3 9-plaquette cluster, one "doped" hole
- CASSCF calculations : 10 active orbitals, 10 electrons (9 $d_{x^2-y^2}$, 1 p_σ^{ZR})

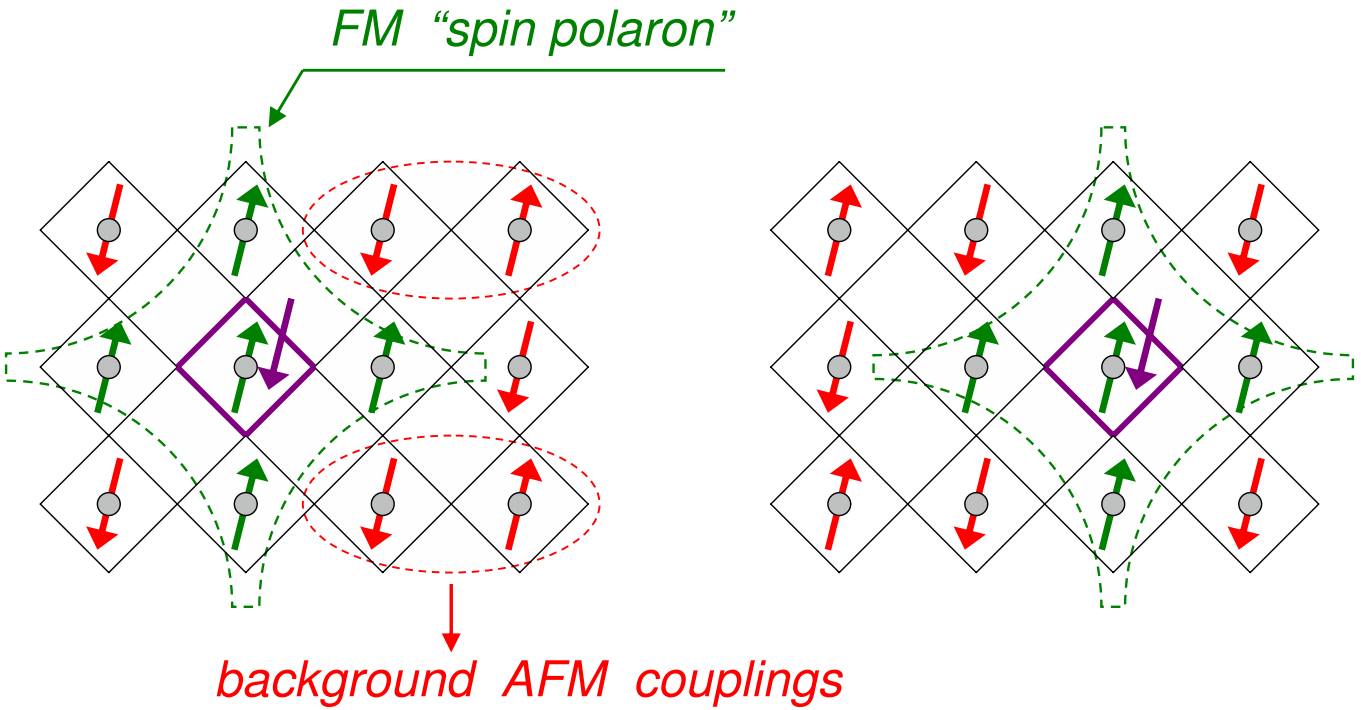




An O $2p$, ZR-like hole induces *ferromagnetic correlations* among the *adjacent* Cu $d_{x^2-y^2}$ spins : FM "spin polaron"

Relevant AOs	Mulliken charge	Mulliken spin
Cu_c $3d_{x^2-y^2}$	1.17	0.06
$O_c^{x,y}$ $2p_{x,y}$	1.62	−0.01
$Cu_{nn}^{x,y}$ $3d_{x^2-y^2}$	1.27	0.31
Cu_{nnn}^{xy} $3d_{x^2-y^2}$	1.28	−0.32

Nonlocal spin correlations, effective hoppings



Effective hoppings (QP picture): $t = (H_{LR} - S_{LR}H_{LL})/(1 - S_{LR}^2)$

$H_{LR} = \langle \Psi_L | H | \Psi_R \rangle$, $S_{LR} = \langle \Psi_L | \Psi_R \rangle$

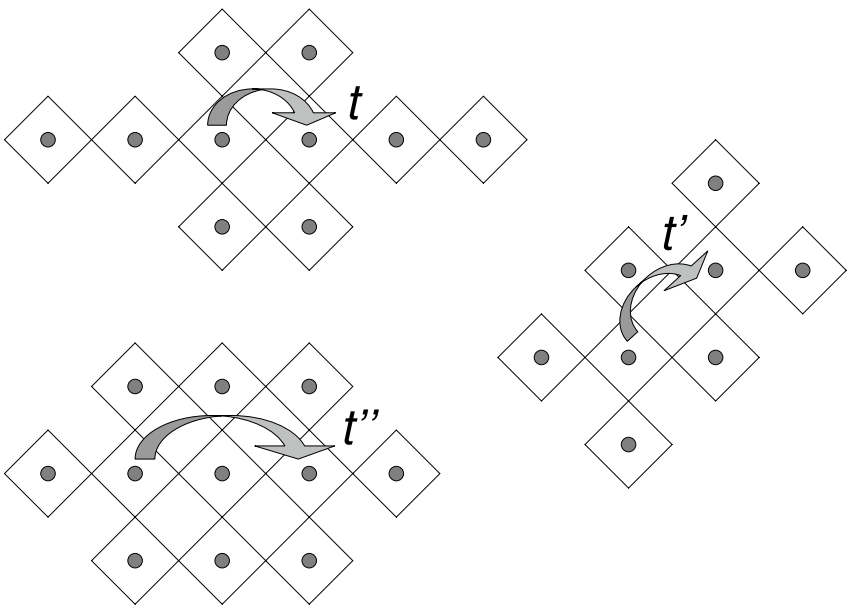
Ψ_L, Ψ_R : *separately optimized*, localized ZR-like solutions (CASSCF) $\longrightarrow$ *both charge and spin relaxation ("readjustment") on neighboring plaquettes*

Renormalized hoppings

When moving through the AFM lattice, the O $2p$ hole must drag along the spin polarization "cloud" at nearby Cu sites $\longrightarrow$ *strong renormalization of the hoppings*
(essentially, non-dynamical correlation)

CASSCF and State-Interaction (CAS SI) calculations :

- 2(3)-plaquette "central" region (L,R) + adjacent plaquettes
- "bare" t : a) the Cu^{2+} $3d^9$ ($S = 1/2$) neighbors $\longrightarrow$ Zn^{2+} $3d^{10}$ ($S = 0$)
  b) FM "lattice"



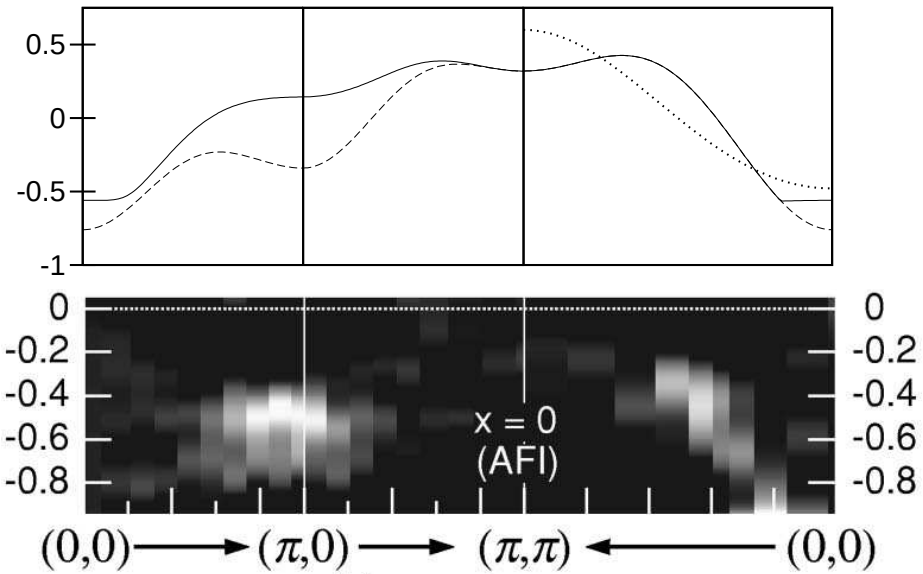
	Bare values	Renorm.
t	0.450/0.540	0.133
t'	0.262/0.305	0.014
t''	0.107/0.113	0.073

[LDA: $t \approx 0.45$ eV; Fits of PES data: $t \approx 0.15$]

Tight-binding dispersion $\epsilon(\mathbf{k})$:

$-2t\,(\cos k_x + \cos k_y) + 4t' \cos k_x \cos k_y$
$-2t''(\cos 2k_x + \cos 2k_y) + \ldots$

The ZR-like band



- *Full line*: lowest (renormalized) electron-removal band
- Dots: $t'' = 0$
- *Experiment*: AR-PES, Ino et al., PRB **62** (2000).

All important details of the experimental spectrum are faithfully reproduced in the theoretical results:

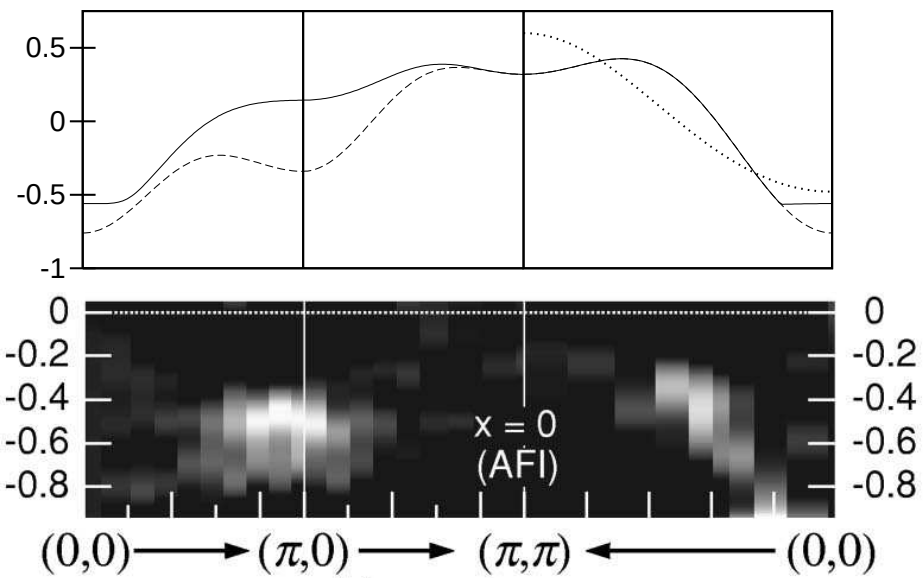
- overall width of $\approx$1 eV
- flat dispersion near the (π,0) point
- maximum close to the ($\pi/2$,$\pi/2$) region

States at higher binding energies: z^2 holes

- Significant nearest-neighbor mixing between the ZR-like and z^2 hole states : $t_m(\cos k_x - \cos k_y)$; $t_m = 0.15$, $\Delta\epsilon = 0.60$ (eV)
  [CASSCF/State-Interaction (CAS SI)]

Mulliken charge	$d_{x^2-y^2}$	$d_{3z^2-r^2}$	σ p_x/p_y (x4)	apex p_z
ZR hole	**1.05**	2.00	**1.60**	1.95
$d_{3z^2-r^2}$ hole	**1.40**	**1.15**	**1.70**	1.85

Undoped system, Mulliken charges of the σ p_x/p_y O orbitals: $\approx$1.85



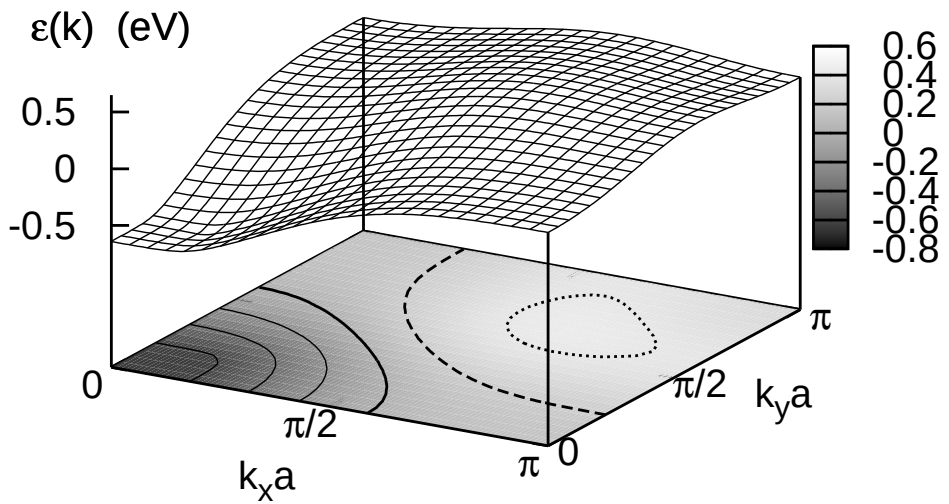
- Dashed line: ZR dispersion
- *Full line*: lowest renormalized electron-removal band including the ZR–z^2 mixing
- Dots: $t'' = 0$

- *Experiment*: AR-PES, Ino et al., PRB **62** (2000).

Fermi "surface": doping dependence

- Undoped cuprates: Mott insulators
- With doping: uniform shift of the Fermi level across the valence/conduction bands (ARPES, core-level XPS, optical absorption); *rigid-band picture*

The evolution of the FS with (hole) doping, as seen in ARPES and magneto-transport measurements, follows directly from our ab initio results:



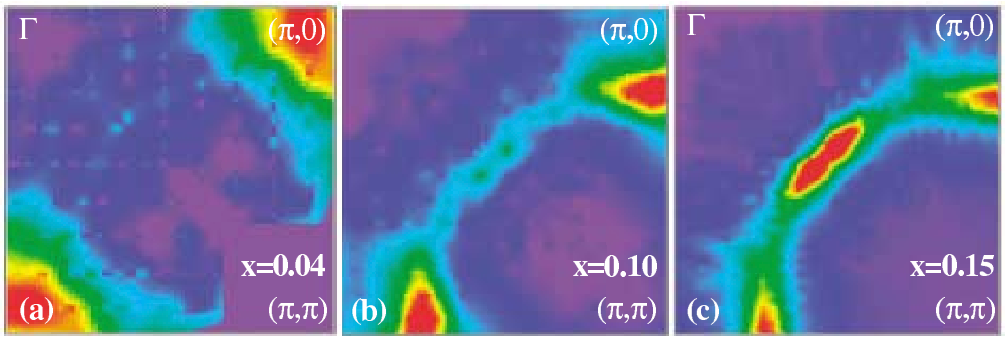
- deeply underdoped regime: *small hole pockets around $(\pi/2,\pi/2)$; d-wave "pseudogap"*
- intermediate doping: *hole-like FS; d-wave pseudogap*
- overdoped region: *gapless electron-like FS*

New insight into the nature of the pseudogap state !

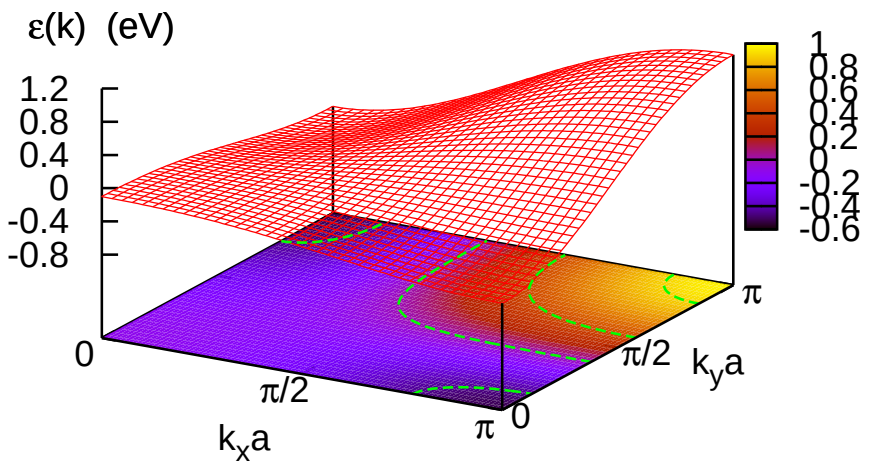
(no need to invoke exotic mechanisms such as charge "stripes")

Electron doped cuprates

— ARPES measurements [Armitage et al., PRL **88** (2000)]:



— CASSCF/SI: in a rigid-band picture, confirm the ARPES data



- low (electron) doping $\longrightarrow$ *small pockets at* $(\pi,0)$
- larger dopings $\longrightarrow$ *hole-like FS, d-wave pseudogap*

($3d^{10}$ "QP" on the $3d^9$ "lattice"; compared to the ZR band, different ratios among the effect. hoppings)

Conclusions

- transparent formalism, *controlled* approximations
- For MgO, a simple closed-shell ionic insulator :
  - *good understanding* of the major effects that determine the electronic band structure
  - *good agreement* with the experiment
- Next: dressed carriers in strongly correlated Cu oxides
  - renormalized hoppings of the ZR-like quasiparticle, *not accessible by DFT*
  - ZR physics : *richer than in the t-J picture*
  - reproduce and explain the ARPES data *(quasiparticle dispersion, topology of the Fermi surface)*

[PRB **76**, 085109 (2007); PRB **75**, 174505 (2007); cond-mat:0707.4648]