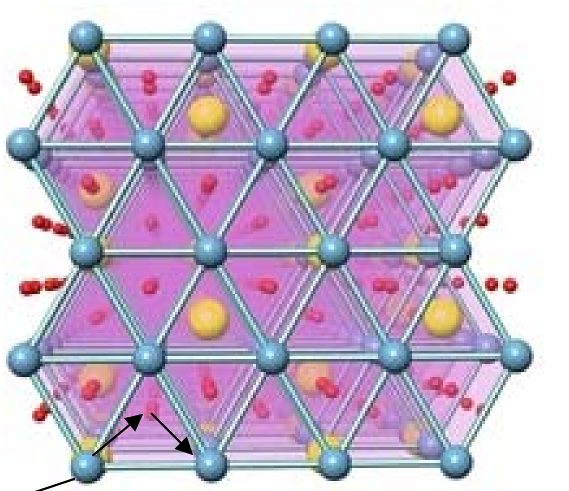
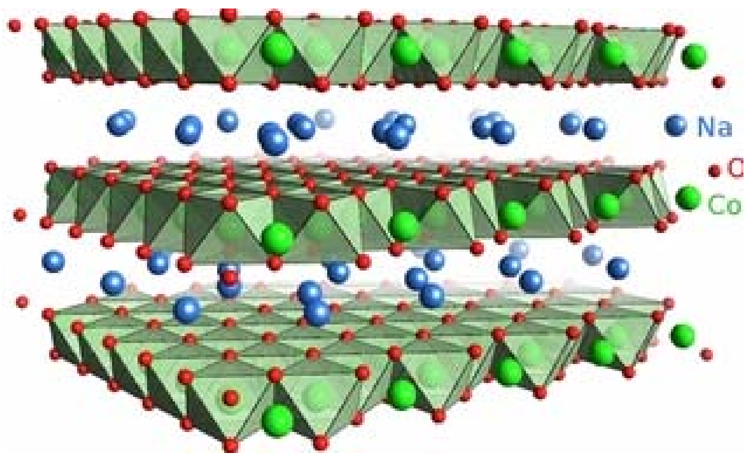
Layered cobaltates : CoO_2 planes filled by a variable number of electrons

CoO_2 slabs

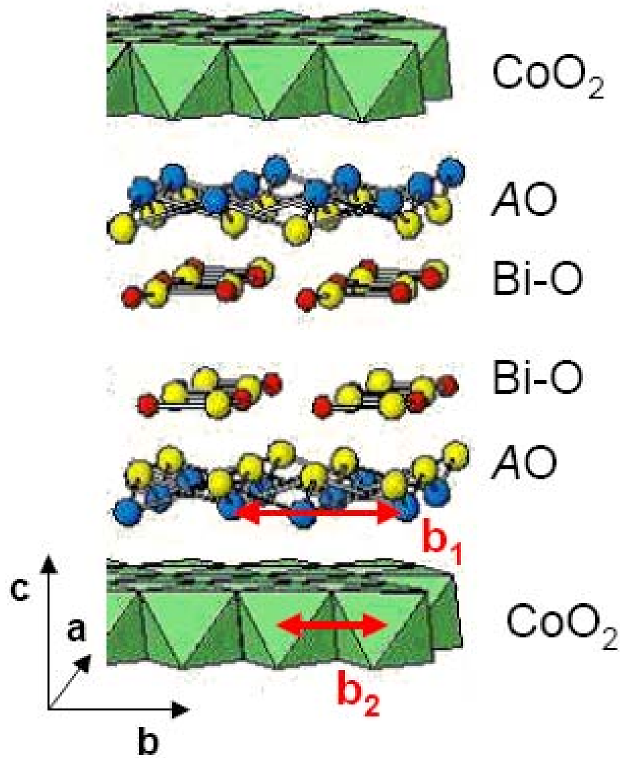


Co

Na cobaltates



Misfit cobaltates



Edge-shared octahedra, 90-degree Co-O-Co bonds

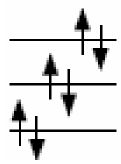
Layered cobaltates

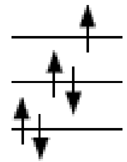
- *Extraordinary narrow (~200 meV) qp-bands*
- *Large thermopower, magn.field sensitive*
- *Magnetic and charge orderings*
- *Superconductivity (NaCoO)*

⇨ Strongly correlated CoO_2 planes

Two relevant valence states:

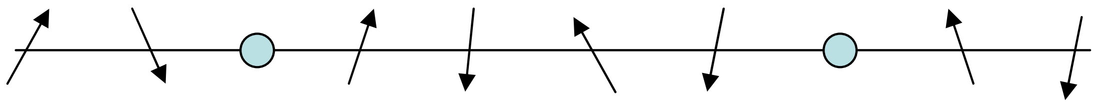
Co^{3+} (t_{2g}^6 S=0) & Co^{4+} (t_{2g}^5 S=1/2)





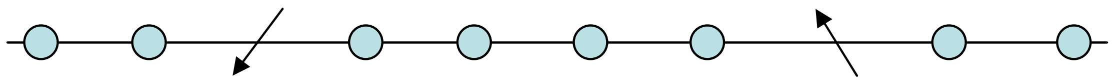
Two regimes accessible:

⇨ **Small x**: ***many*** **S=1/2 Co^{4+}**, ***few S=0*** **Co^{3+}** („***doped Mott insulator***“)



(strong corr.)

⇨ **Large x**: ***few*** **S=1/2 Co^{4+}**, ***many S=0*** **Co^{3+}** („***doped band insulator***“)



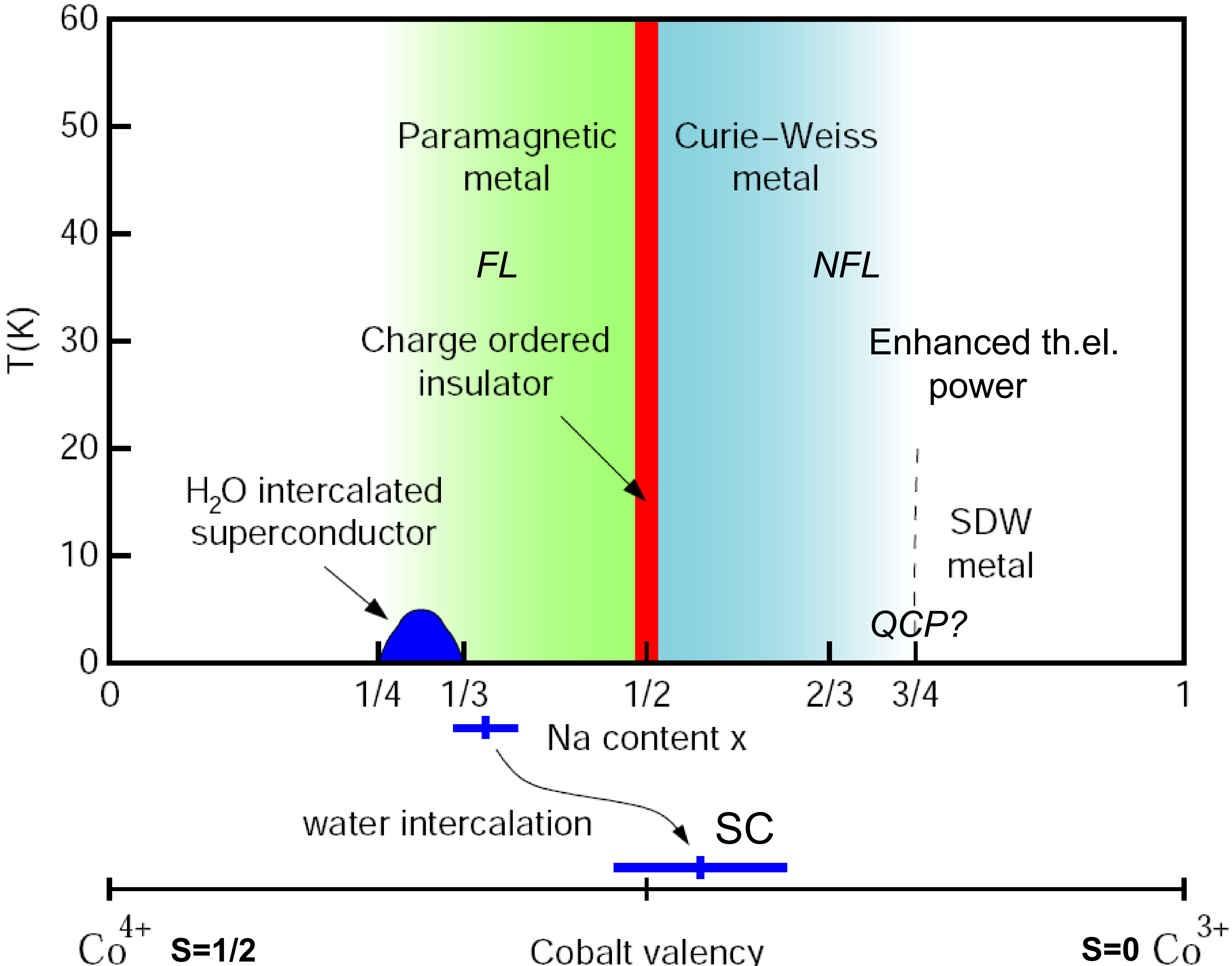
(weak corr.)

Experiment:

Small x → ***paramagnetic metal, Pauli susceptibility, FL***

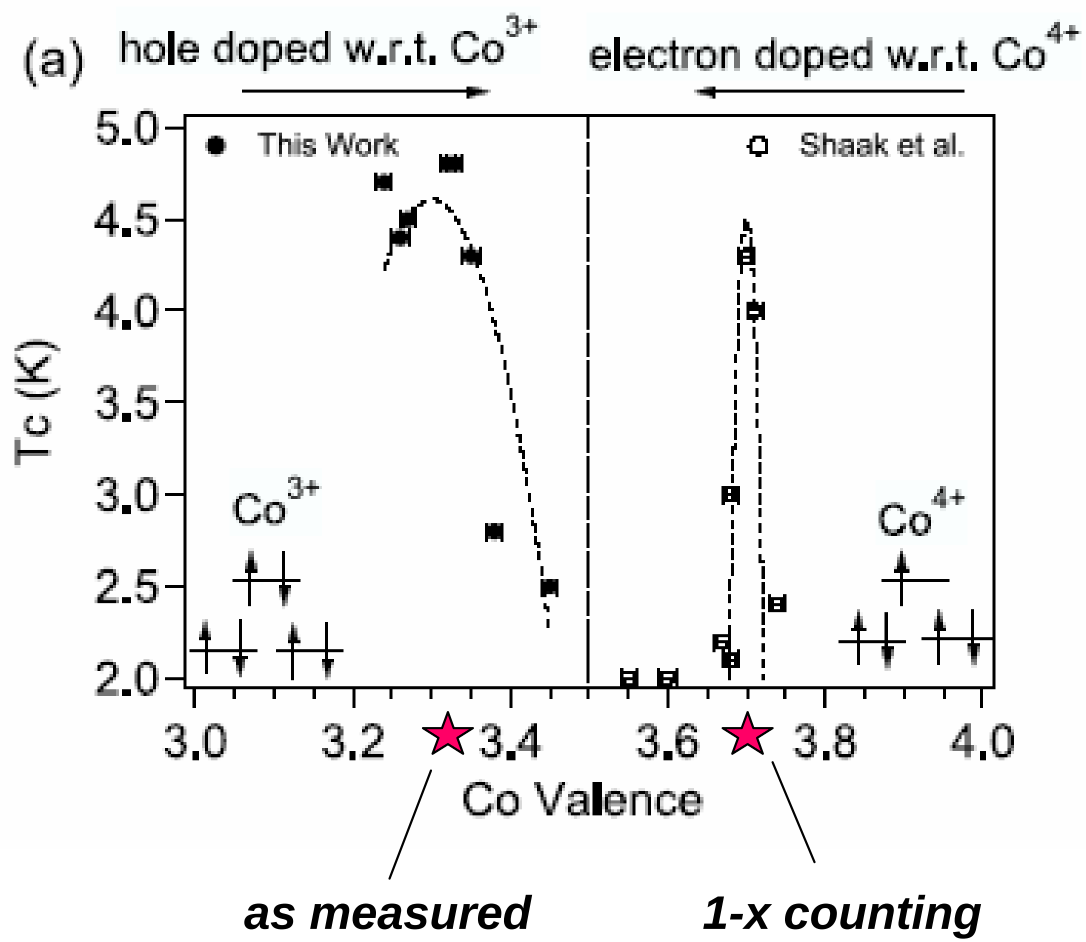
Large x → ***magn. order, enhanced thermopower, NFL, QCP…***

…opposite trend to what expected !



60
50
40
30
20
10
0
T(K)
Paramagnetic metal
Curie–Weiss metal
FL
NFL
Charge ordered insulator
Enhanced th.el. power
H_2O intercalated superconductor
SDW metal
QCP?
0
1/4
1/3
1/2
2/3
3/4
1
Na content x
water intercalation
SC
Co^{4+} S=1/2
Cobalt valency
S=0 Co^{3+}

Co-valence in superconducting Na_xCoO_2+ H_2O



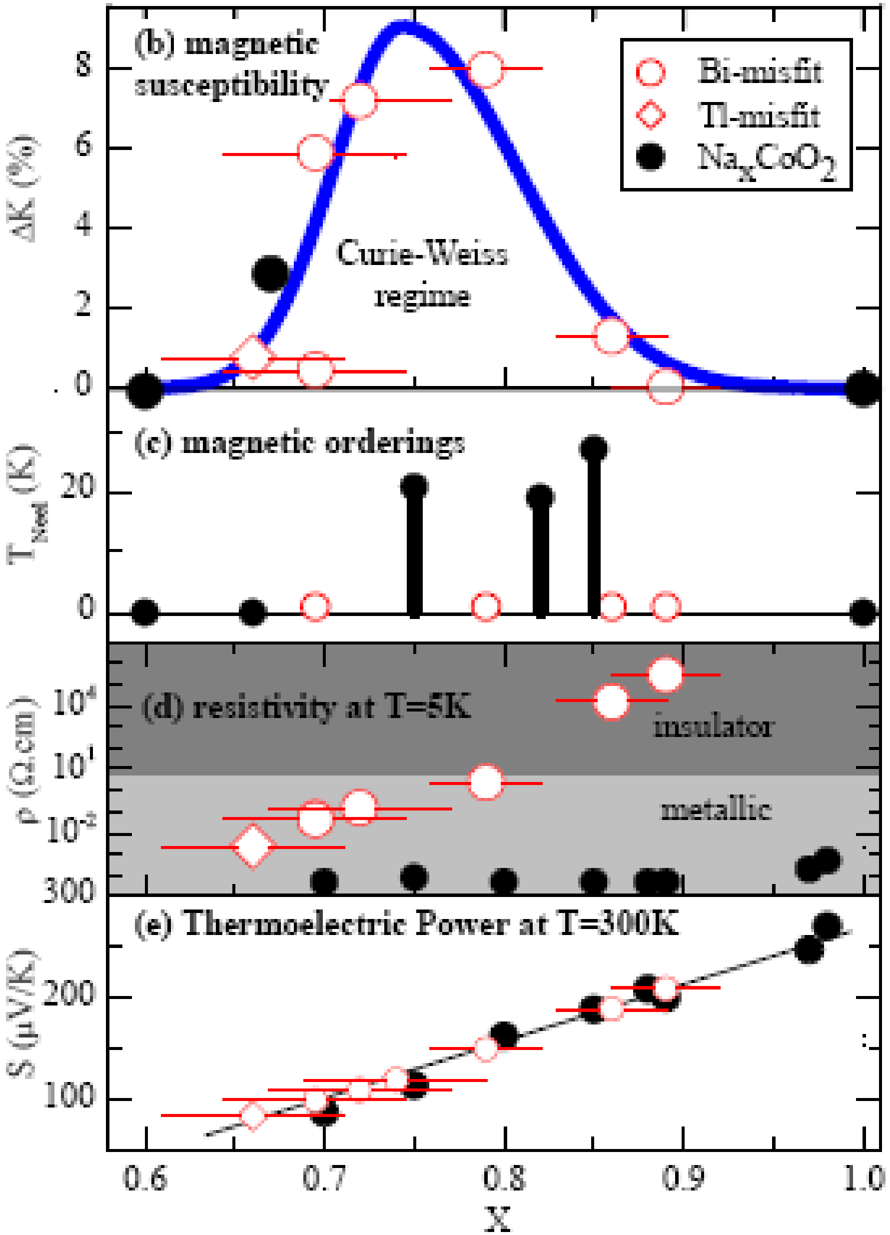
Milne *et al*. PRL (2004): Water intercalation addes electrons into CoO_2

→ *SC-dome located far away from the Mott limit*

Similar conclusion: Takada *et al.* (2004)
Karppinen *et al.* (2004)

Different result: NMR by Alloul *et al.*

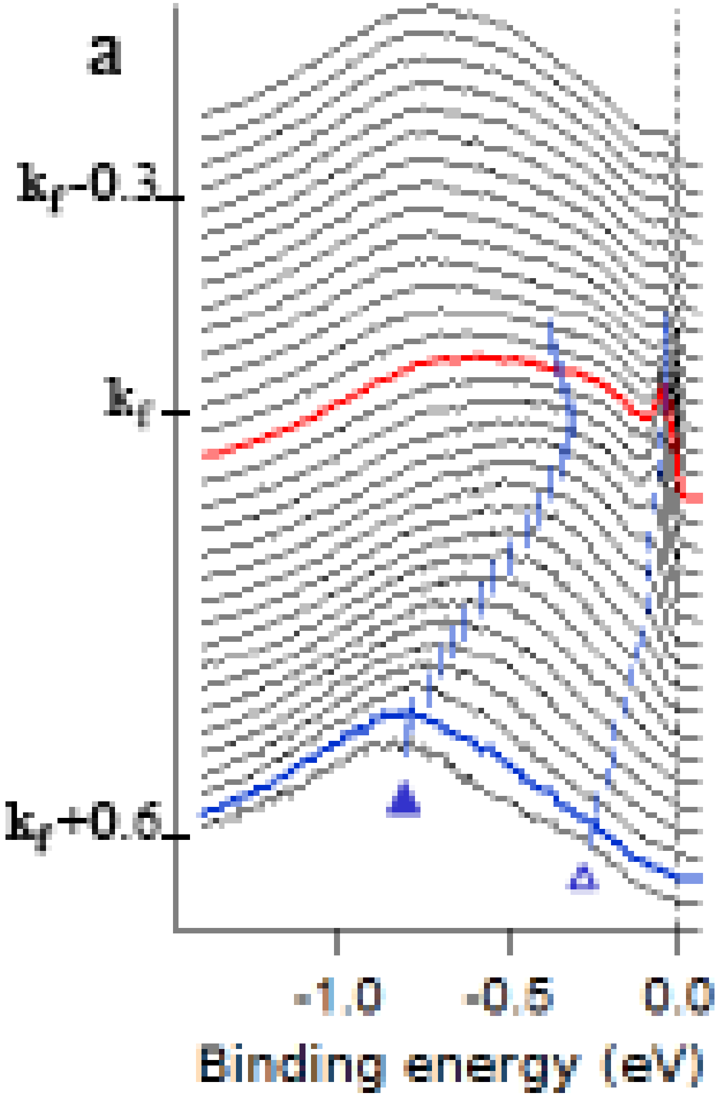
Bobroff *et al.*, 2007



Strong correlations develop at large x, near the band insulator (!) limit

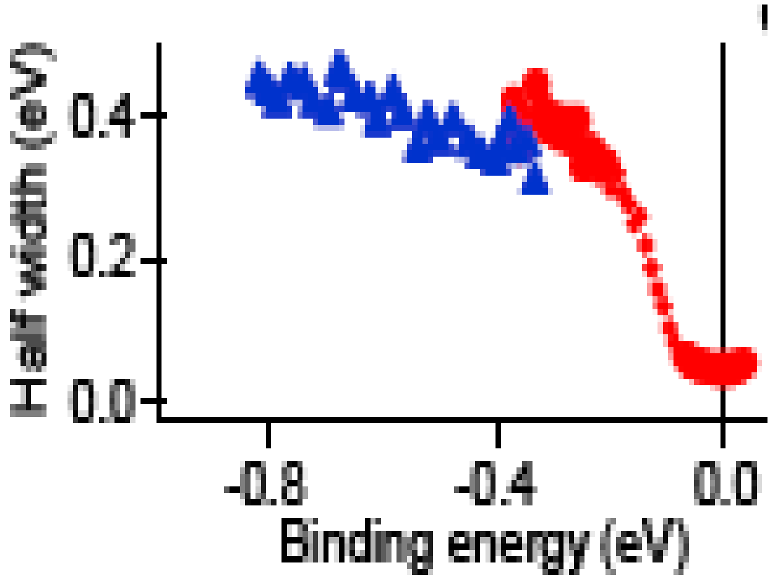
ARPES in misfits near the band insulator regime (x~0.7)

Brouet *et al.*, 2007



(a) *peak-dip-hump structure*
(b) *strongly renorm. qp-band*

qp-damping



(c) *strong scattering at ~150 meV*

?

Spin-diluted system but correlations as strong as in doped Mott insulators

Experiment:

- Correlations are enhanced at large x, *near* the spinless band-insulator limit
- SC dome is located at valence compositions *far away* from the Mott limit

....things are very different from cuprates!

⇒ *Different origin & functionality of correlations*

„no double occupancy“ principle as in cuprates is insufficient

Oxide families

- *Ti, V* – weak JT t_{2g} orbital ⟶ (*orbital fluctuation*)
- *Cr,Mn* – large spin, DE ⟶ (*half metallicity*)
- *Mn* – JT e_g orb., polarons ⟶ (*CMR effect*)
- *Fe,Ni* – proxim. to M/I trans. ⟶ (*spin-helix order*)
- *Co* – spin-state degen. ⟶ (*high th.el.power*)
- *Cu* – quant.spin, no orbital ⟶ (*high-Tc SC)*

Correlations: *universal*
Functionality: *different*

valence orbital spin lattice str.

local Hilbert space ***communication rules***

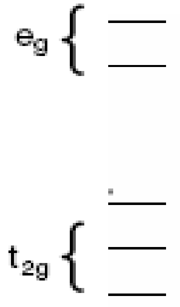
The origin of strong correlations in layered cobaltates

A. Spin-state quasidegeneracy of Co ions
B. Edge-sharing octahedra, 90° d-p-d path

G.Khaliullin & J.Chaloupka

Phys. Rev. Lett., *in press (2007)*

A. Spin-state quasidegeneracy in cobaltates

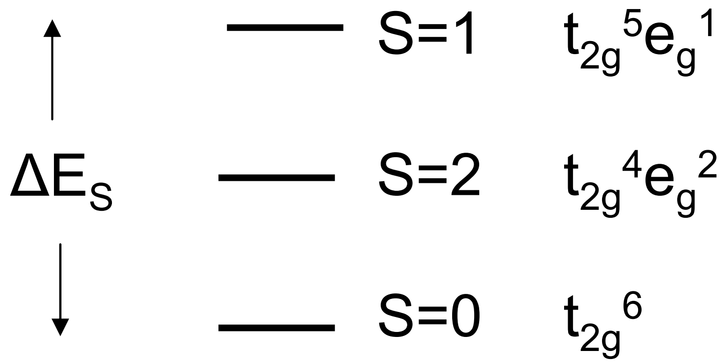


Co^{2+}: high-spin 3/2 (***Hund coupling dominates***)

Co^{4+}: low-spin 1/2 (***favored by 10Dq crystal field***)

⇨ **Co^{3+}: S = 0, 1, 2 states are energetically close !**

$Co^{3+}O_6$ octahedron:

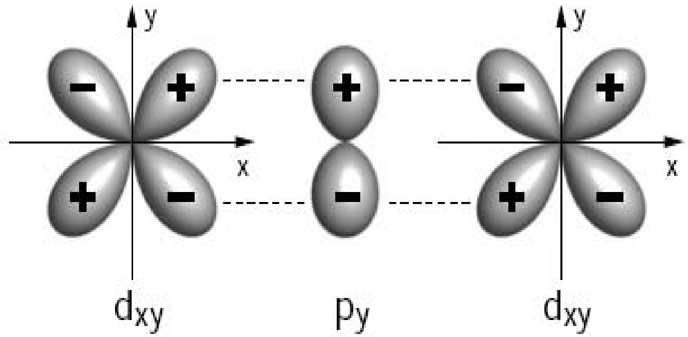


$\Delta E_S \sim 10Dq - 2J_H$ *is small, fraction of eV only*

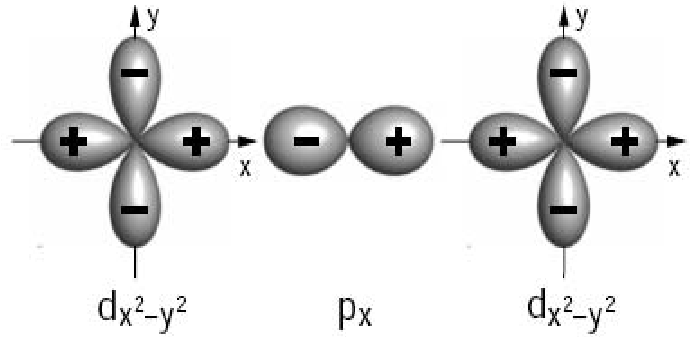
⇨ **SPIN-STATE TRANSITIONS** *driven by temperature, doping* **($LaCoO_3$…)**

180° Co-O-Co bond (t$_{2g}$ and e$_g$ sectors separated)

t$_{2g}$-t$_{2g}$



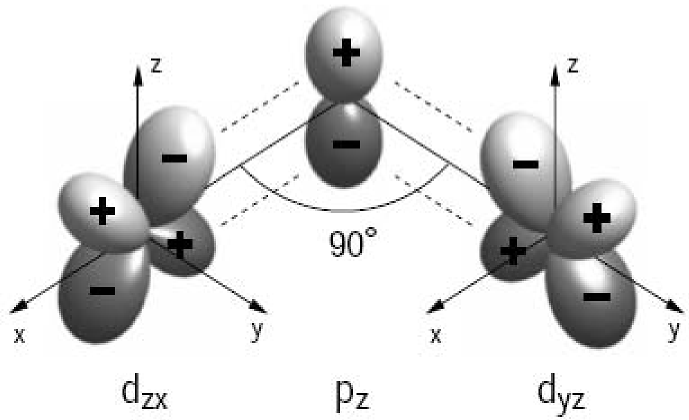
e$_g$-e$_g$



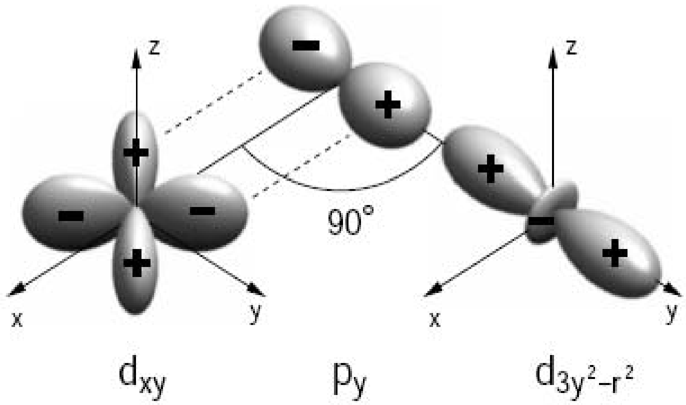
B.

90° Co-O-Co bond → **strong mixing between t$_{2g}$ and e$_g$**

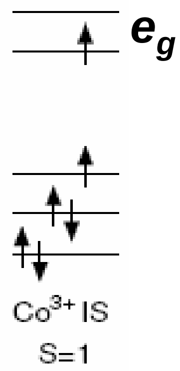
t$_{2g}$-t$_{2g}$



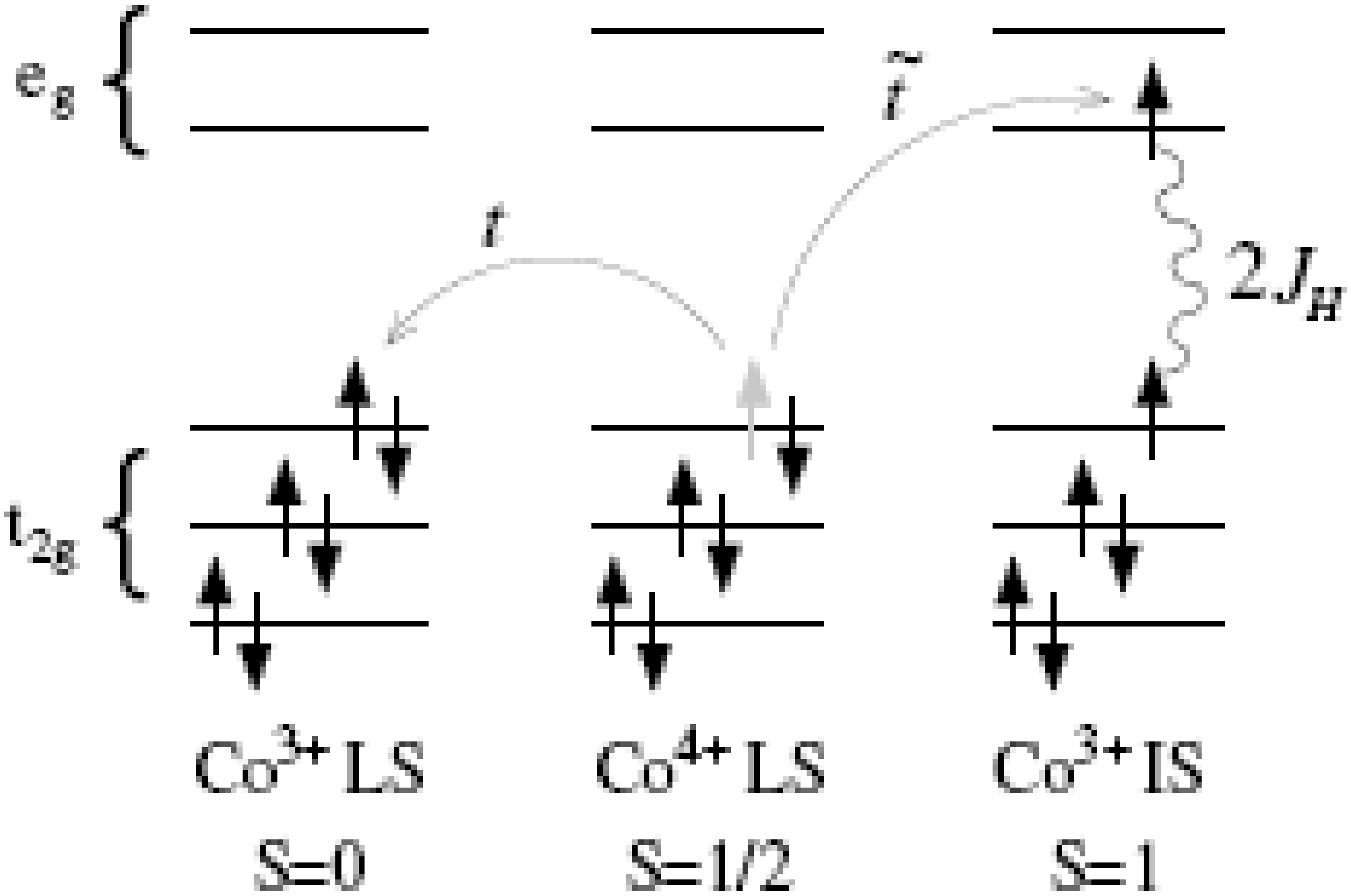
t$_{2g}$-e$_g$



t$_{2g}^5$e$_g$ S=1 states are generated by this hopping



Spin-state fluctuations → ***spin-polaron physics***



e_g
t_{2g}
t
$\tilde{t}$
$2J_H$
Co^{3+} LS
S=0
Co^{4+} LS
S=1/2
Co^{3+} IS
S=1

Electron transfer matrix depends on Me—O—Me bond angle

180-degree

	e_g	t_{2g}
e_g	1	0
t_{2g}	0	$\sim \frac{1}{3}$

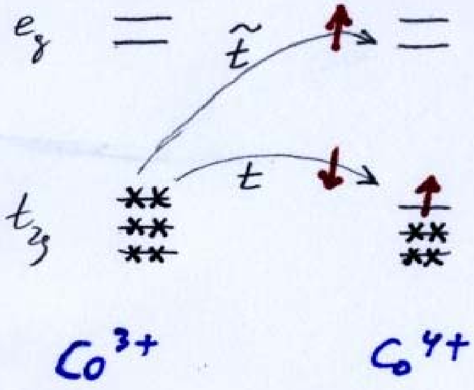
Units: t_{σ}^2/Δ_{pd}

90-degree

	e_g	t_{2g}
e_g	0	~ 2
t_{2g}	~ 2	1

t_{π}^2/Δ_{pd}

t_{2g}– e_g overlap: *the largest element*

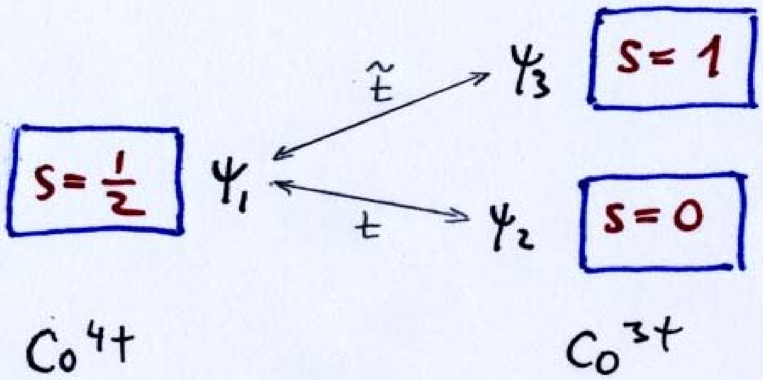


$$\frac{\tilde{t}}{t} \sim \frac{t_\sigma}{t_\pi} \sim 2$$

t-process generates $Co^{3+}(t_{2g}^6, S=0)$

$\tilde{t}$-process generates $Co^{3+}(t_{2g}^5 e_g, S=1)$

Relevant Hilbert space $\{\psi_1\ \psi_2\ \psi_3\}$:



$$H\{\psi_1, \psi_2, \psi_3\}$$

Model

$$H = H_t + H_{\tilde{t}}$$

t_{2g}--t_{2g}

t_{2g}--e_g

accompanied by S=1 exciton

(present in $NaCoO_2$ but not in $LaCoO_3$)

$$H_{\tilde{t}} = \frac{\tilde{t}}{\sqrt{3}} \sum_{ij} \Big[\mathcal{T}^{\dagger}_{+1,\gamma}(i)\, f^{\dagger}_{j\downarrow} f_{i\uparrow} - \mathcal{T}^{\dagger}_{-1,\gamma}(i)\, f^{\dagger}_{j\uparrow} f_{i\downarrow}$$

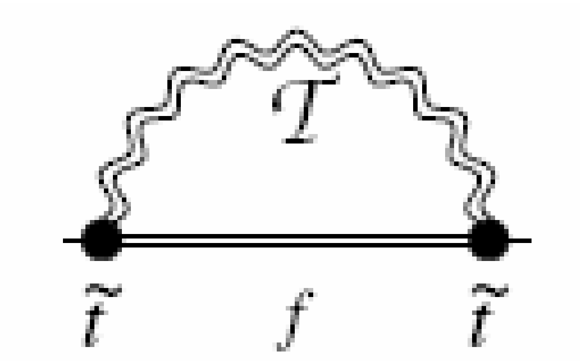
$$+ \mathcal{T}^{\dagger}_{0,\gamma}(i)\, \frac{1}{\sqrt{2}} \Big(f^{\dagger}_{j\uparrow} f_{i\uparrow} - f^{\dagger}_{j\downarrow} f_{i\downarrow} \Big) + \text{h.c.} \Big]$$

S=1 exciton ($\mathcal{T}$) — e_g-orbital label (γ)

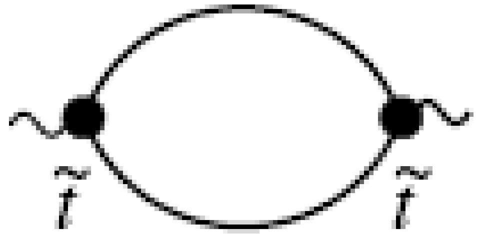
Fermions dressed by spin-state fluctuations

ARPES spectra

1. Self-consistent Born approximation

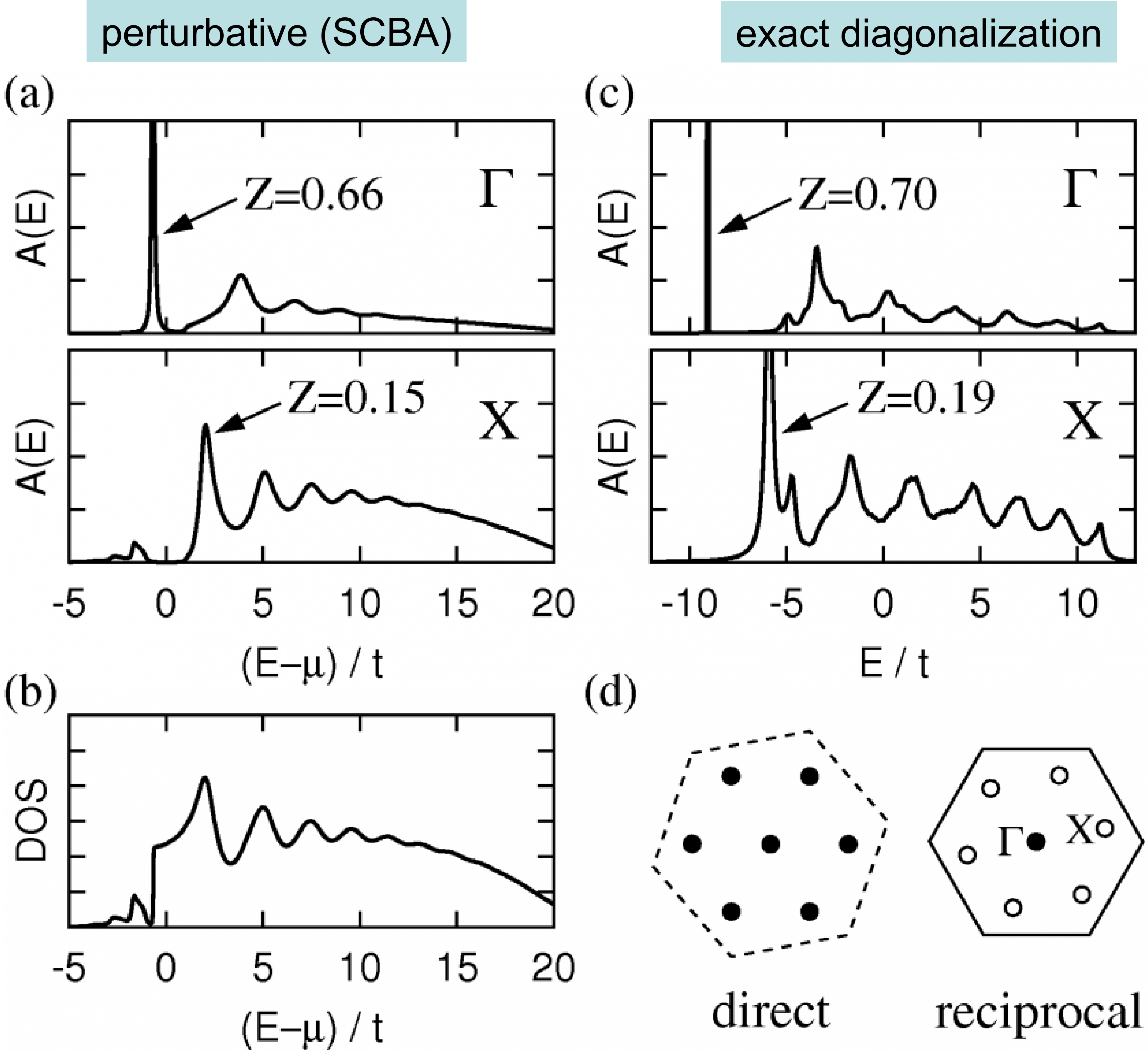


Fermion selfenergy



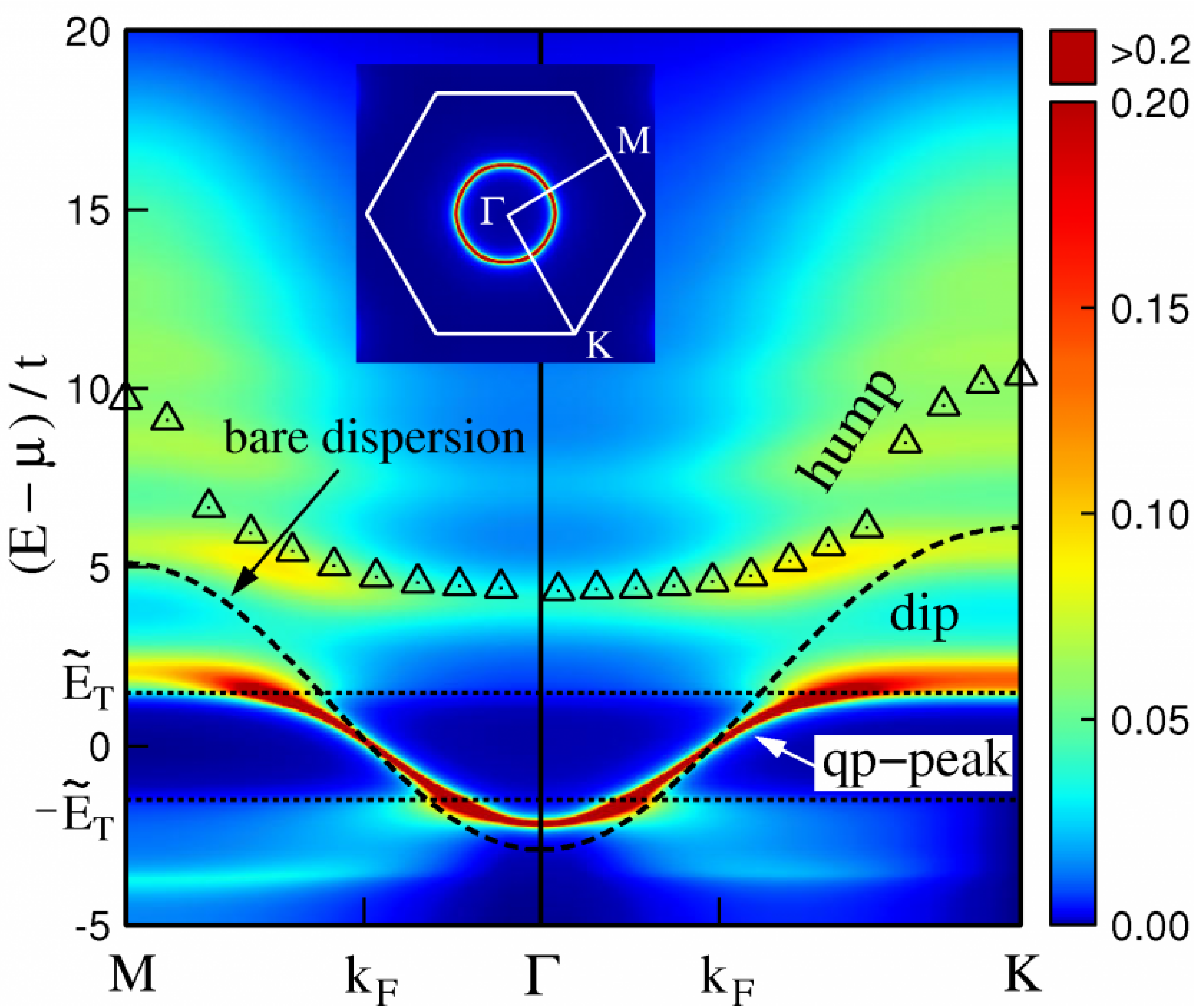
Spin-exciton selfenergy

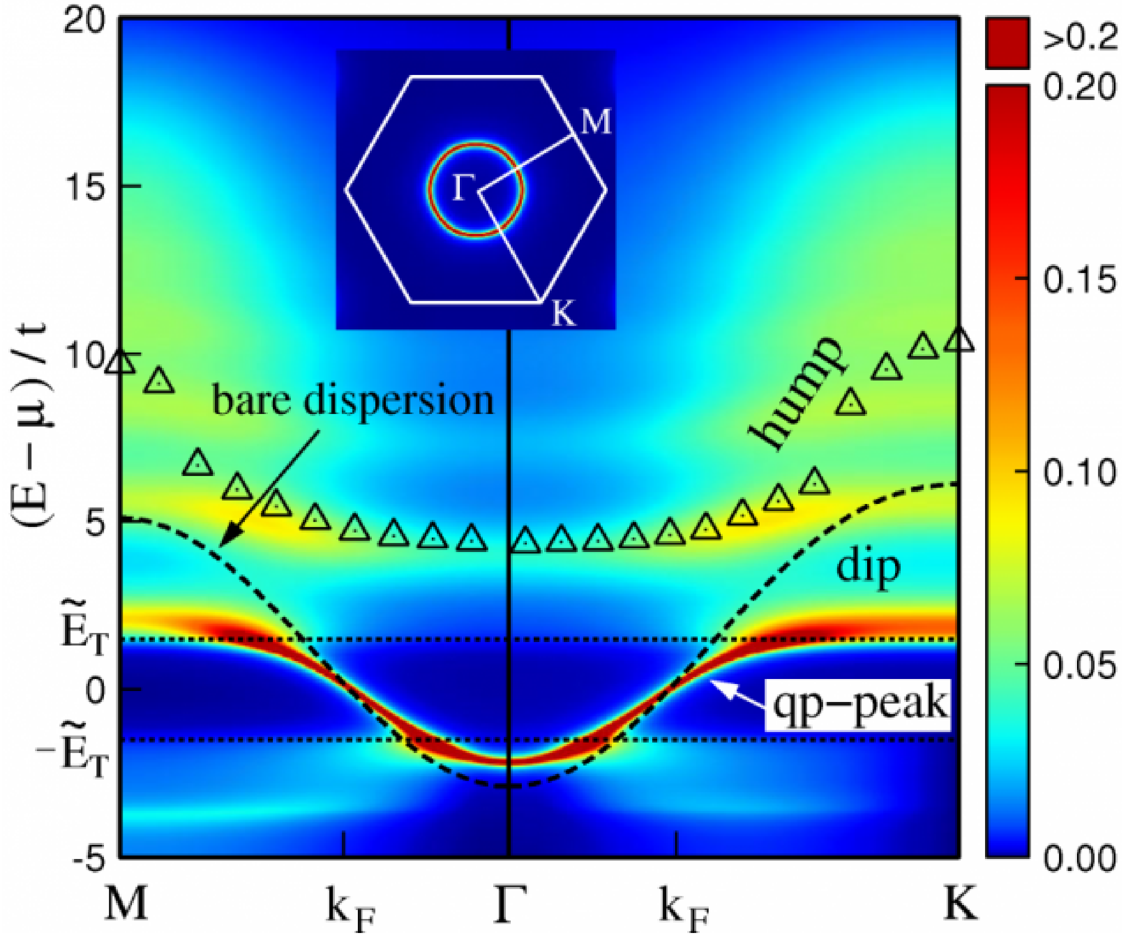
2. Exact diagonalization (one s=1/2 hole on a hexagon)



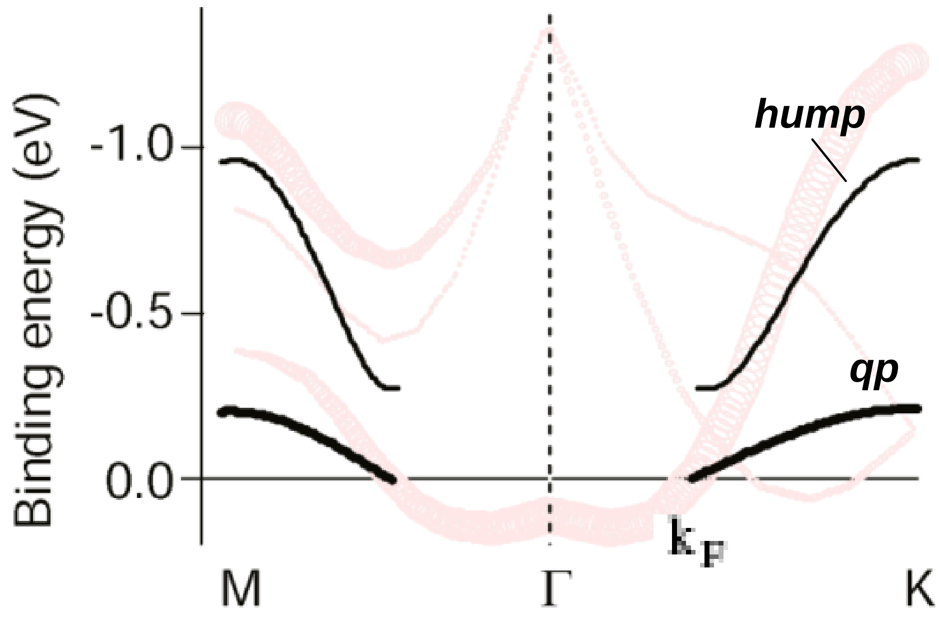
perturbative (SCBA)
exact diagonalization
(a)
(c)
Z=0.66
Γ
Z=0.70
Γ
Z=0.15
X
Z=0.19
X
A(E)
-5
0
5
10
15
20
(E−μ) / t
-10
-5
0
5
10
E / t
(b)
(d)
DOS
-5
0
5
10
15
20
(E−μ) / t
Γ
X
direct
reciprocal

Im G(E,k) **at x = 0.7 (fermionic density = 0.3)**





theory (x=0.7)



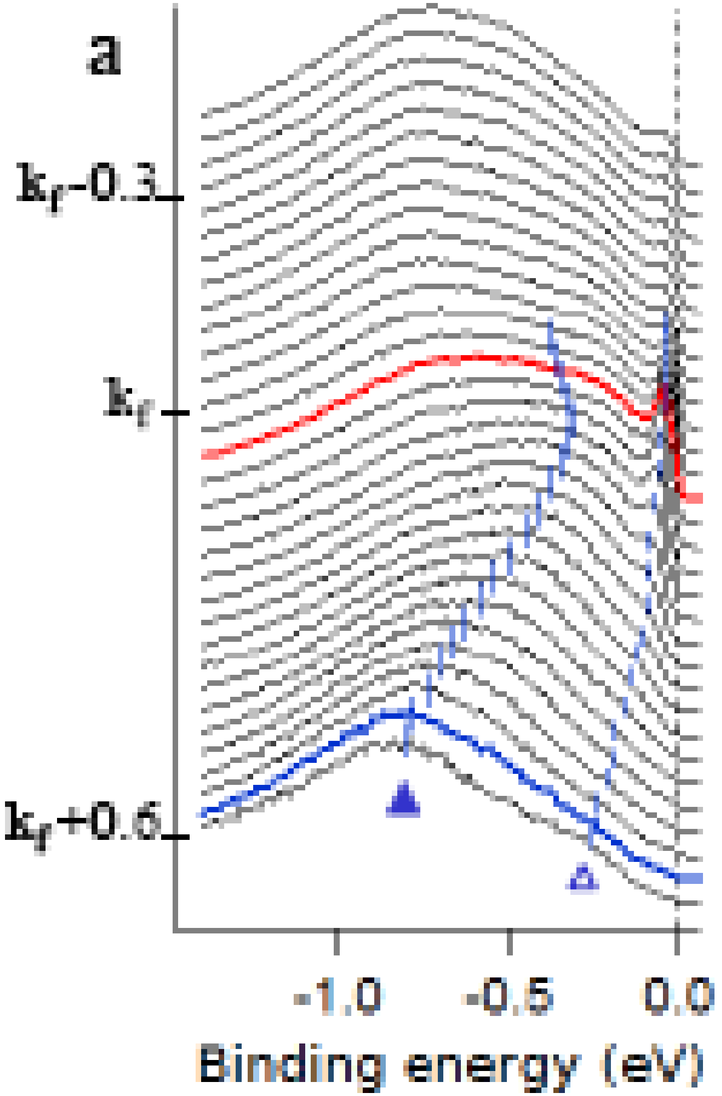
Exp: ***ARPES in misfits x~0.7***

Brouet *et al*. (2007)

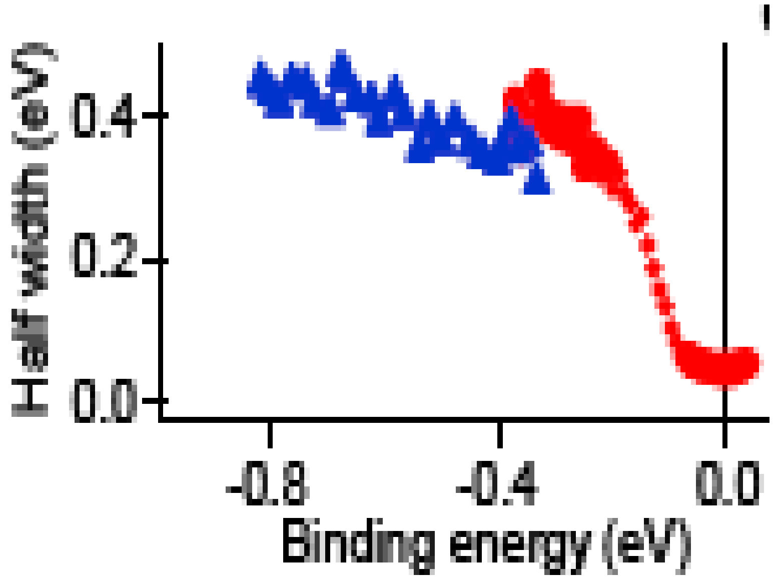
⇨ With t ~ 100 meV, theory reproduces both qp- and hump dispersion

consistent with LDA value

Brouet *et al.* ARPES in misfits near the band insulator regime (x~0.7)

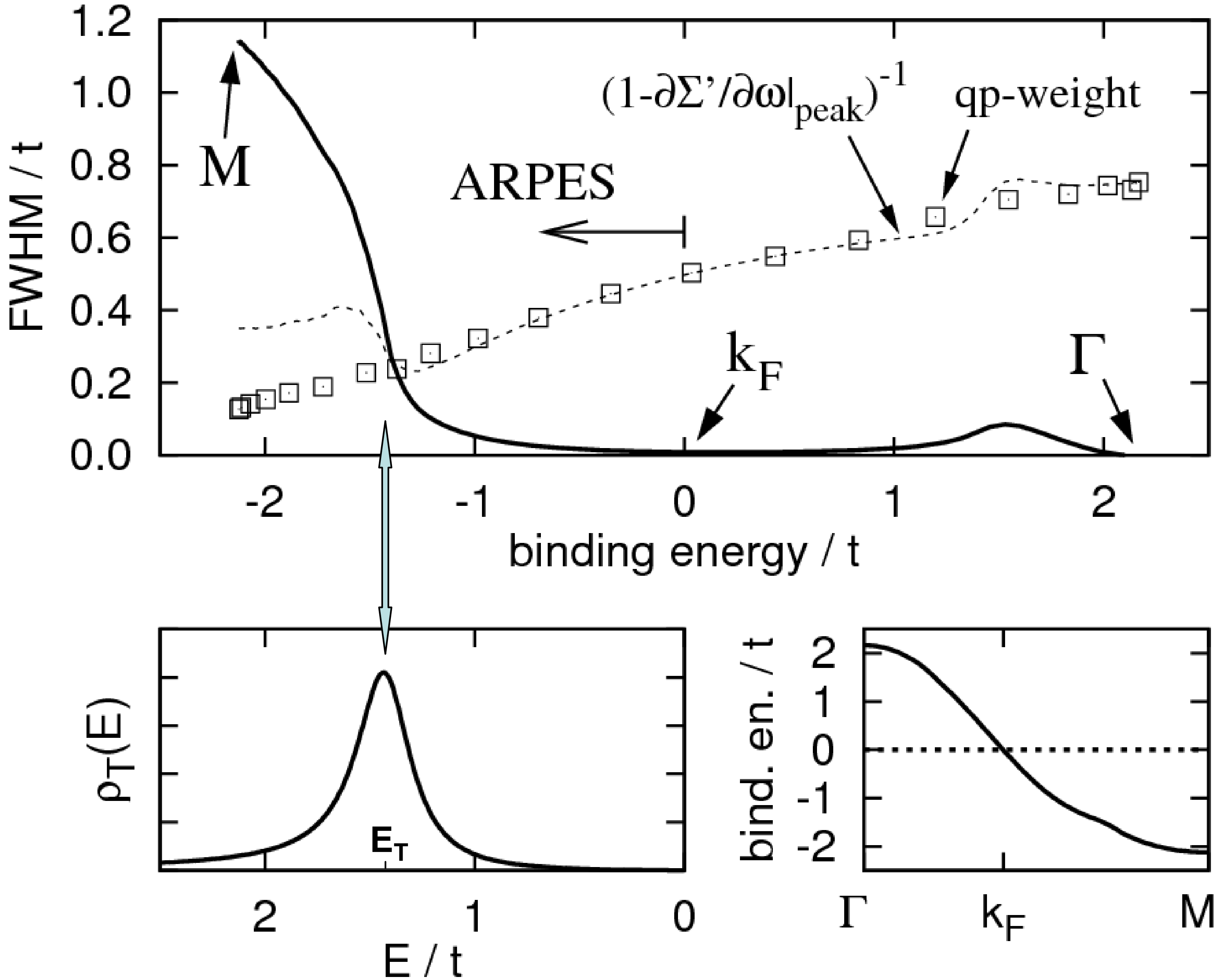


quasiparticle damping



experiment: strong scattering at ~150 meV

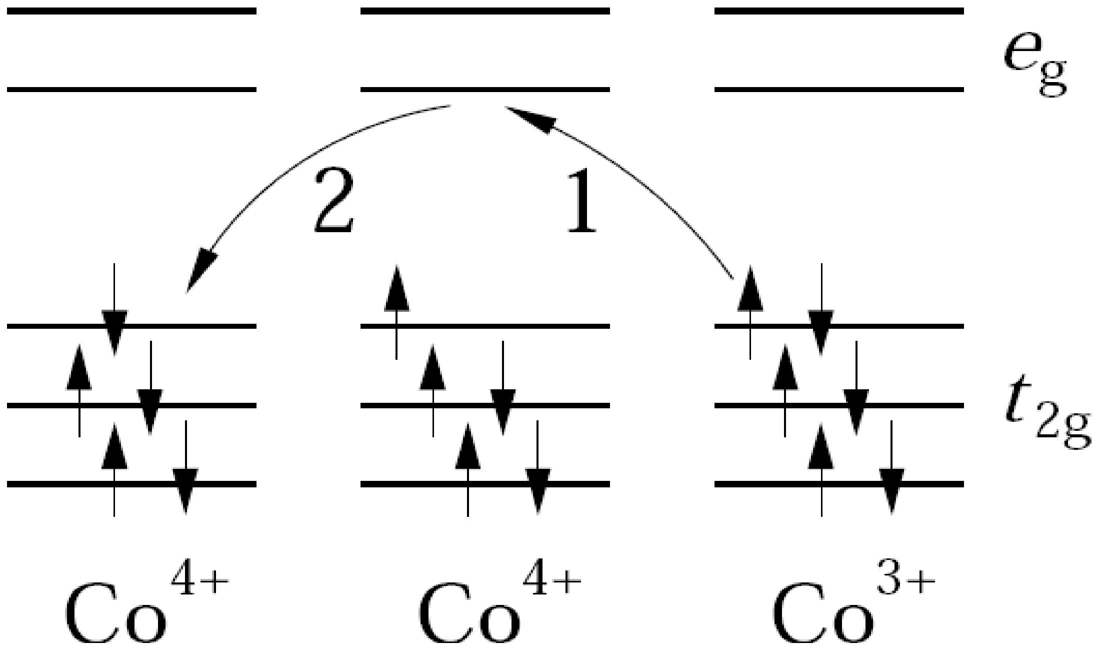
theory suggests: S=1 virtual state energy



Scattering on spin-state fluctuations ⟹ *qp destroyed below E_T~ 150 meV*

Interaction between t_{2g} holes mediated by $S=1$ excitations

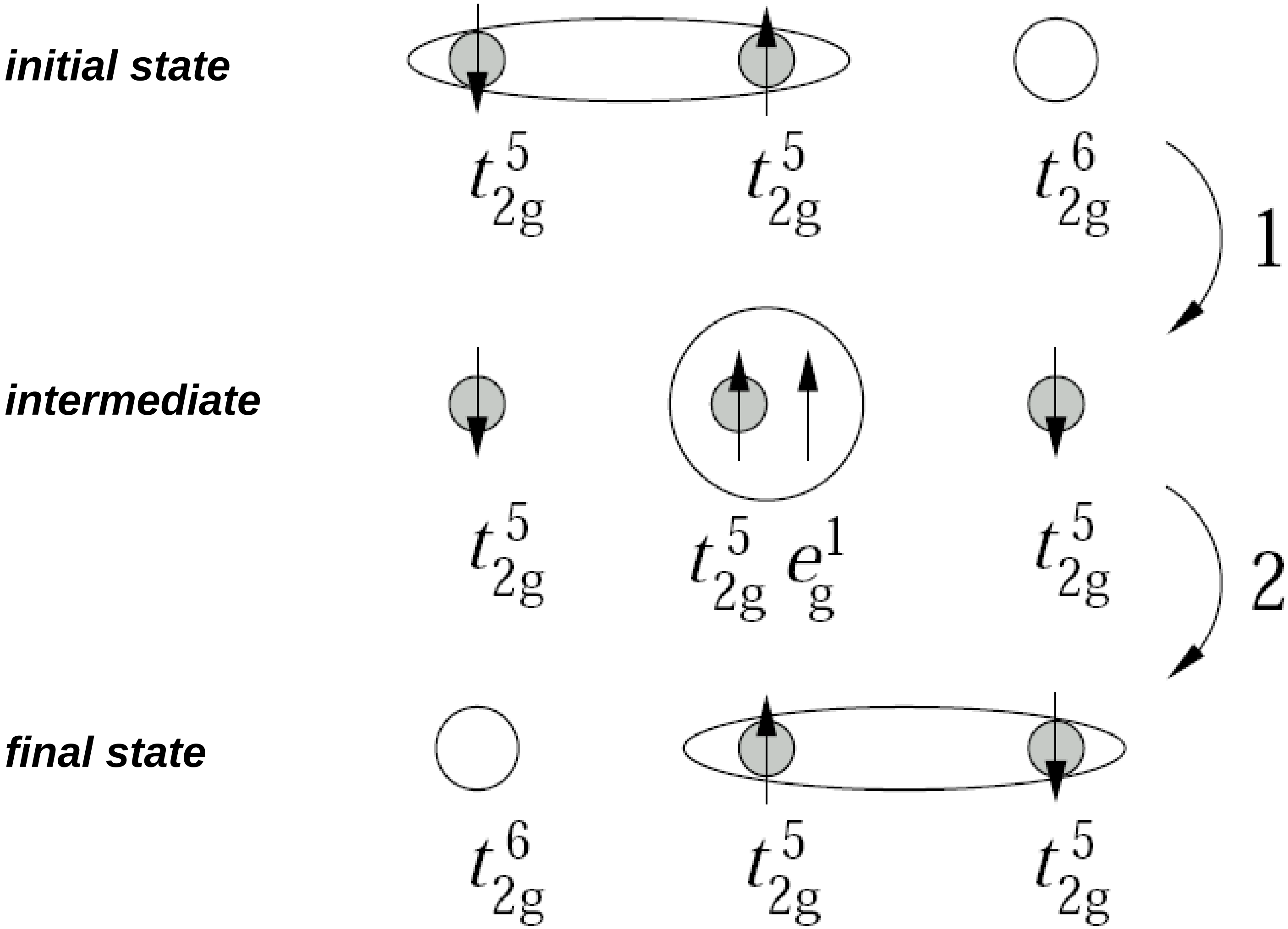
Spin-correlated hopping via the S=1 intermediate states



Step 1 : S=1 exciton formed
Step 2 : Exciton relaxed

Process sensitive to the spin orientation of holes

⟹ **Effective interaction between fermions**



Exchange by S=1 exciton ⟶ fermionic pair-hopping

Interaction between t_{2g}-fermions in terms of:

- ⟹ *singlet S_{ij} and triplet T_{ij} dimer-hopping* ***(SC pairing)***
- ⟹ *nonlocal charge and spin interactions* ***(spin/ch. order)***

$$H_{\text{eff}} = \frac{1}{2} V \sum_{\langle ijk \rangle} \cos(\phi_{ij} - \phi_{jk}) \left[\hat{S}^{\dagger}_{ij} \hat{S}_{kj} + \frac{1}{3} \hat{\boldsymbol{T}}^{\dagger}_{ij} \hat{\boldsymbol{T}}_{kj} \right]$$

$$= V \sum_{\langle ijk \rangle} \cos(\phi_{ij} - \phi_{jk}) \left[n_j n_{ik} - \frac{1}{3} \boldsymbol{s}_j \boldsymbol{s}_{ik} \right]$$

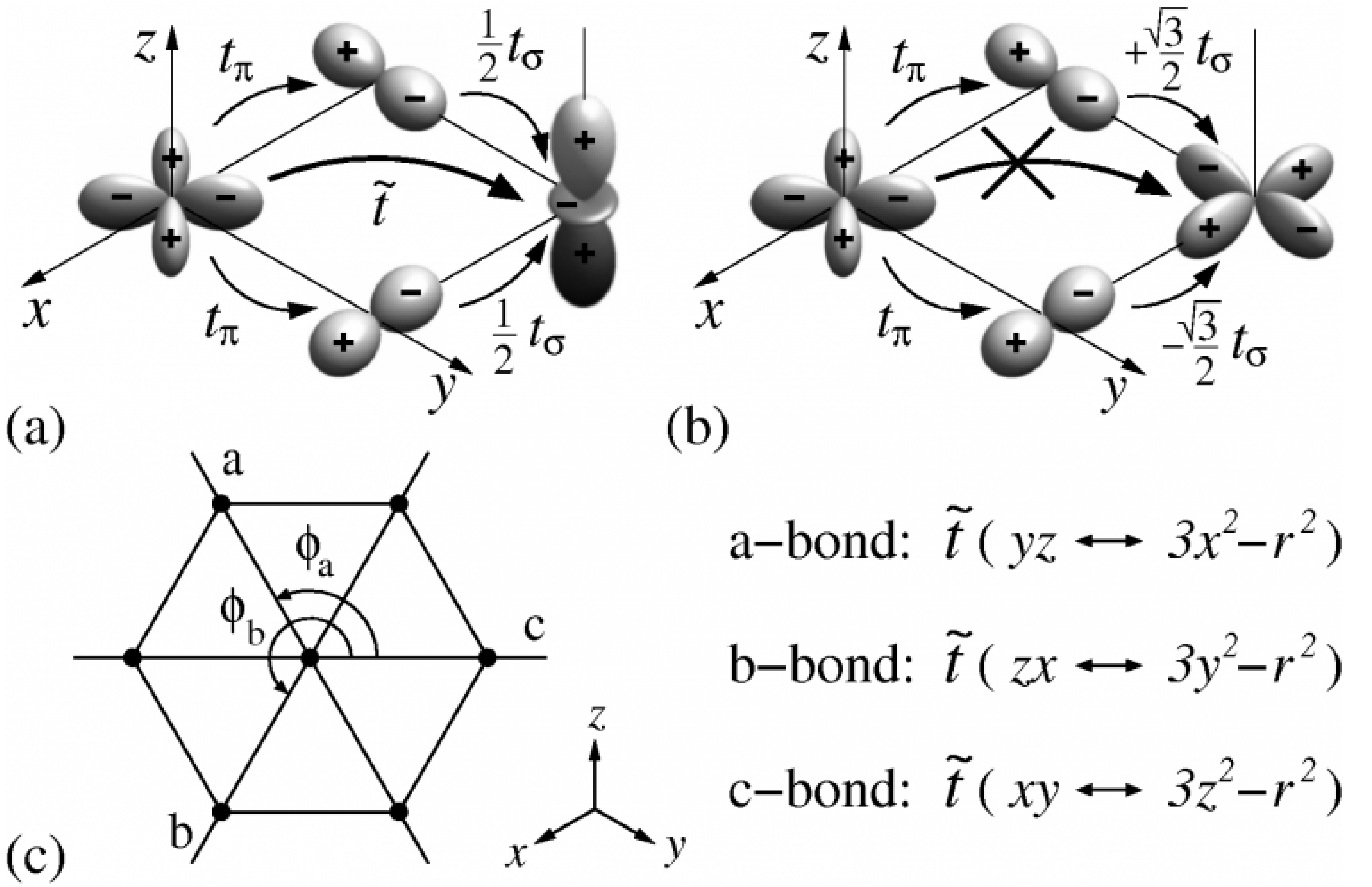
bond-charge & bond-spin

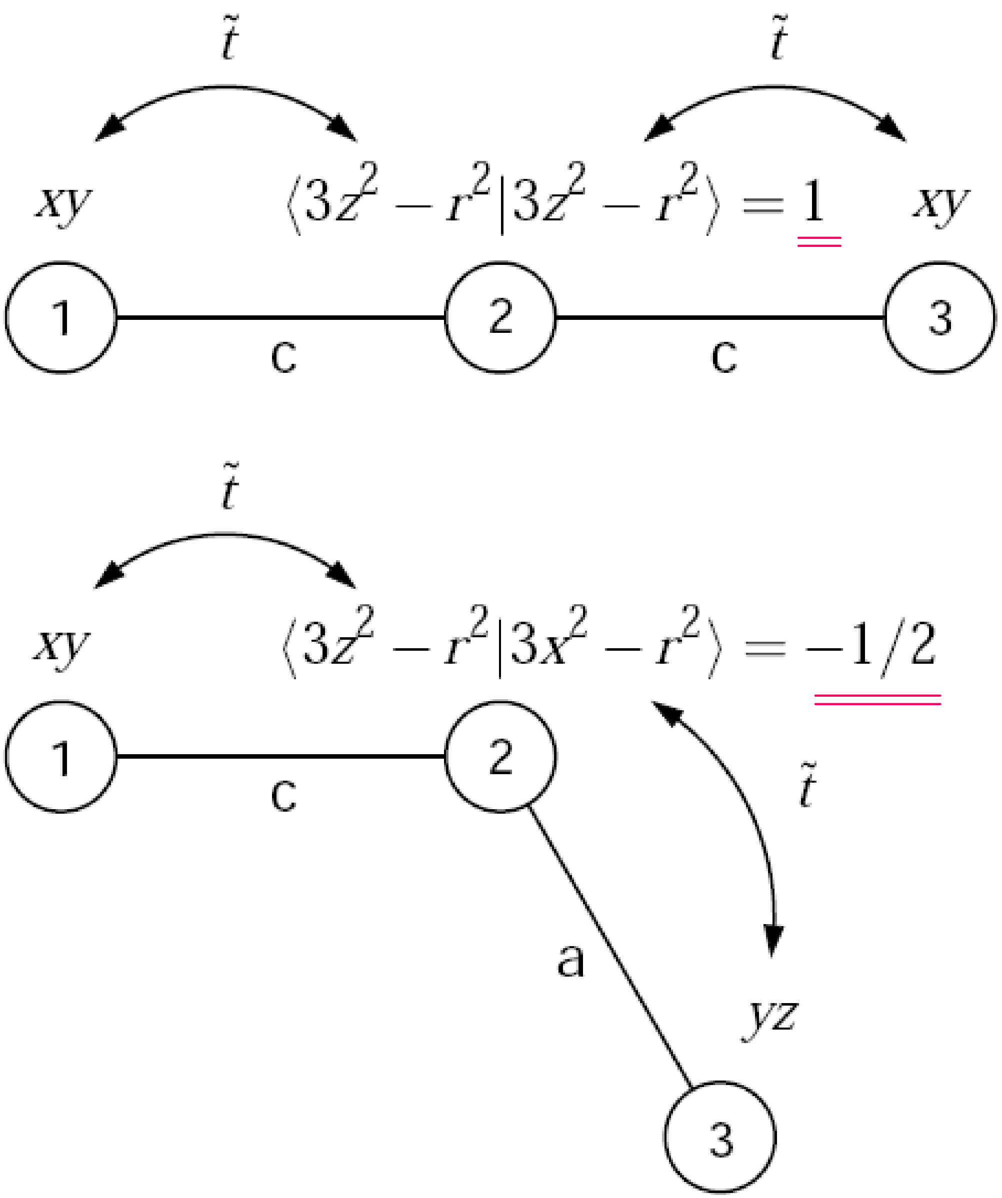
$V = \tilde{t}^2 / E_T$

(i) 1/3 factor: *Singlets move faster and gain more kinetic energy*

(ii) cos-factor: *Frustration*

t_{2g}—e_g hopping is orbital selective





origin of $\tilde{t}^{\,2} \cos(\phi_{12} - \phi_{23})$ factor
due to e_g orbital overlap

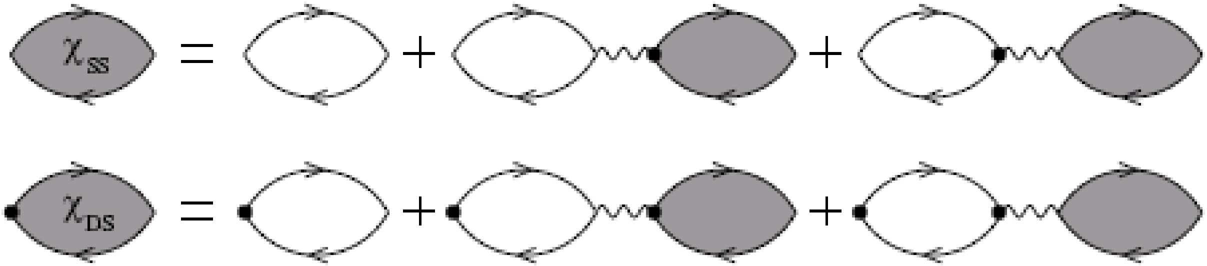
Spin susceptibility

$$H_{spin} = -\frac{1}{3}\frac{\tilde{t}^2}{E_T}\sum_{\boldsymbol{R},\delta\neq\delta'} \cos(\phi_\delta - \phi_{\delta'})\,\hat{S}_{\boldsymbol{R}}\cdot\hat{S}_{\boldsymbol{R}+\delta,\boldsymbol{R}+\delta'}$$

$$= -\lambda\sum_{\boldsymbol{q}} \hat{S}_{-\boldsymbol{q}}\cdot\hat{D}_{\boldsymbol{q}} =$$  $$\lambda = \tilde{t}^2/3E_T$$

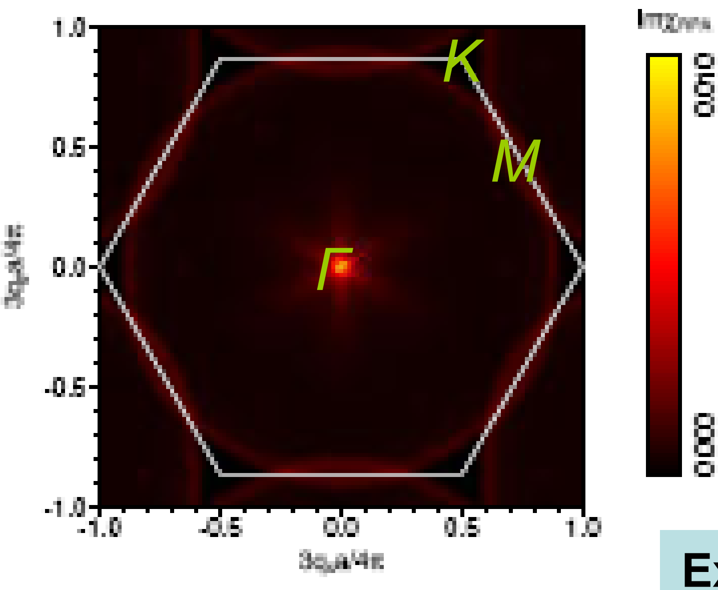
S_q: on-site spin
D_q: bond-spin

RPA:



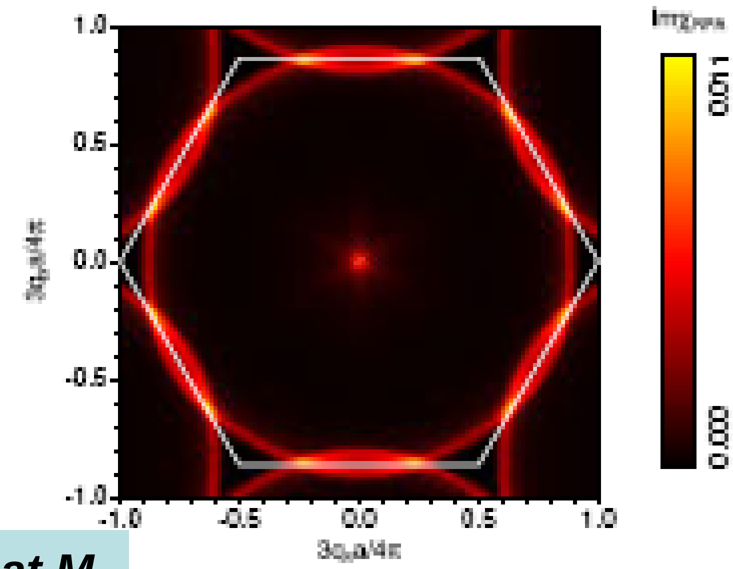
$2k_F$-fluctuations enhanced

bare



x=0.5

$\lambda = t$



Exp: *Bragg peak at M*

Interaction between t_{2g}-fermions in terms of pair hopping

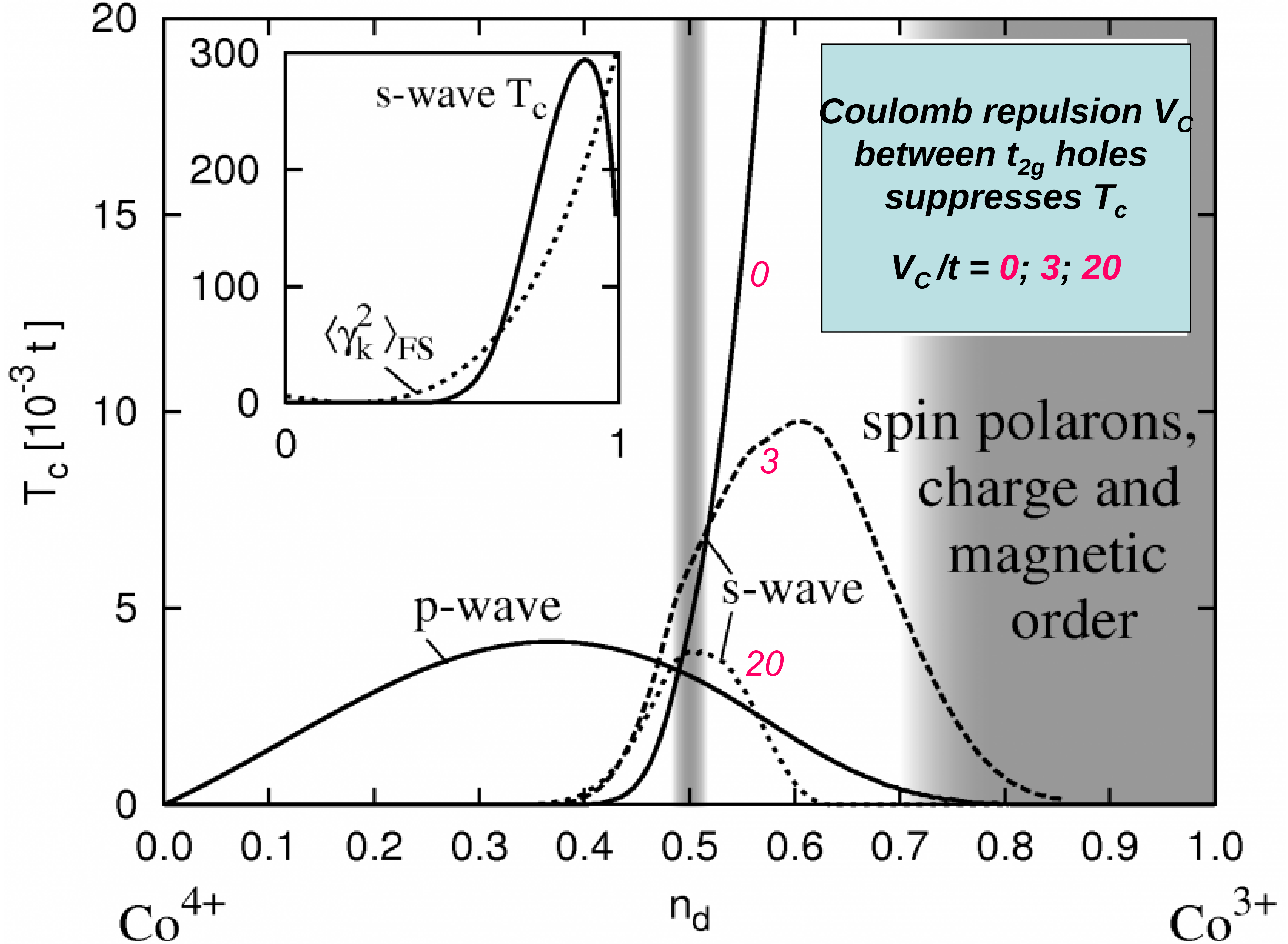
$$H_{\text{eff}} = \frac{1}{2} V \sum_{\langle ijk \rangle} \cos(\phi_{ij} - \phi_{jk}) \left[\hat{S}^{\dagger}_{ij} \hat{S}_{kj} + \frac{1}{3} \hat{\boldsymbol{T}}^{\dagger}_{ij} \hat{\boldsymbol{T}}_{kj} \right]$$

Singlets *Triplets*

$V = \tilde{t}^2 / E_T$

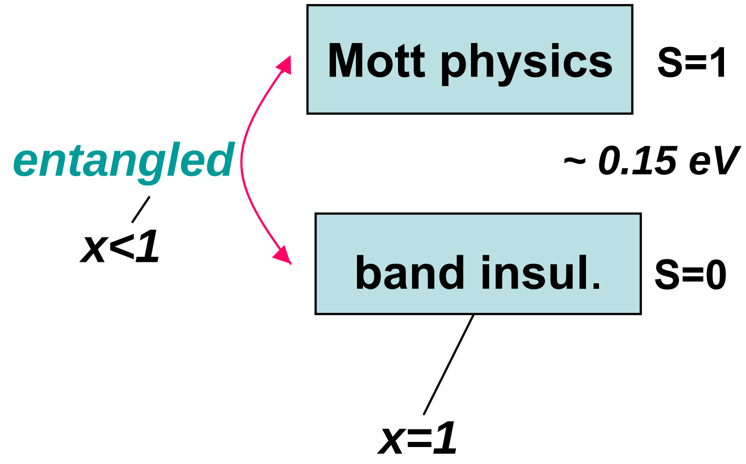
(i) 1/3 factor: *Singlets move faster and gain more kinetic energy*

(ii) cos-factor: *Frustration*



Coulomb repulsion V_C between t_{2g} holes suppresses T_c
V_C/t = 0; 3; 20
s-wave T_c
$\langle \gamma_k^2 \rangle_{FS}$
0
3
20
p-wave
s-wave
spin polarons, charge and magnetic order
T_c [10^{-3} t]
n_d
Co^{4+}
Co^{3+}
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
5
10
15
20
300
200
100
0
1

Summary



- Spin-state quasidegeneracy of Co^{3+}:

  ⇒ *proximity to the Mott physics*

- 90° d-p-d bonding in $NaCoO_2$:

  ⇒ *S=1 states accessible by t_{2g}- e_g hopping, spin-polarons, incoherent ARPES, …*

- Superconductivity:

  ⇒ *pairing mediated by spin-state fluctuations*

Coulomb repulsion between holes:

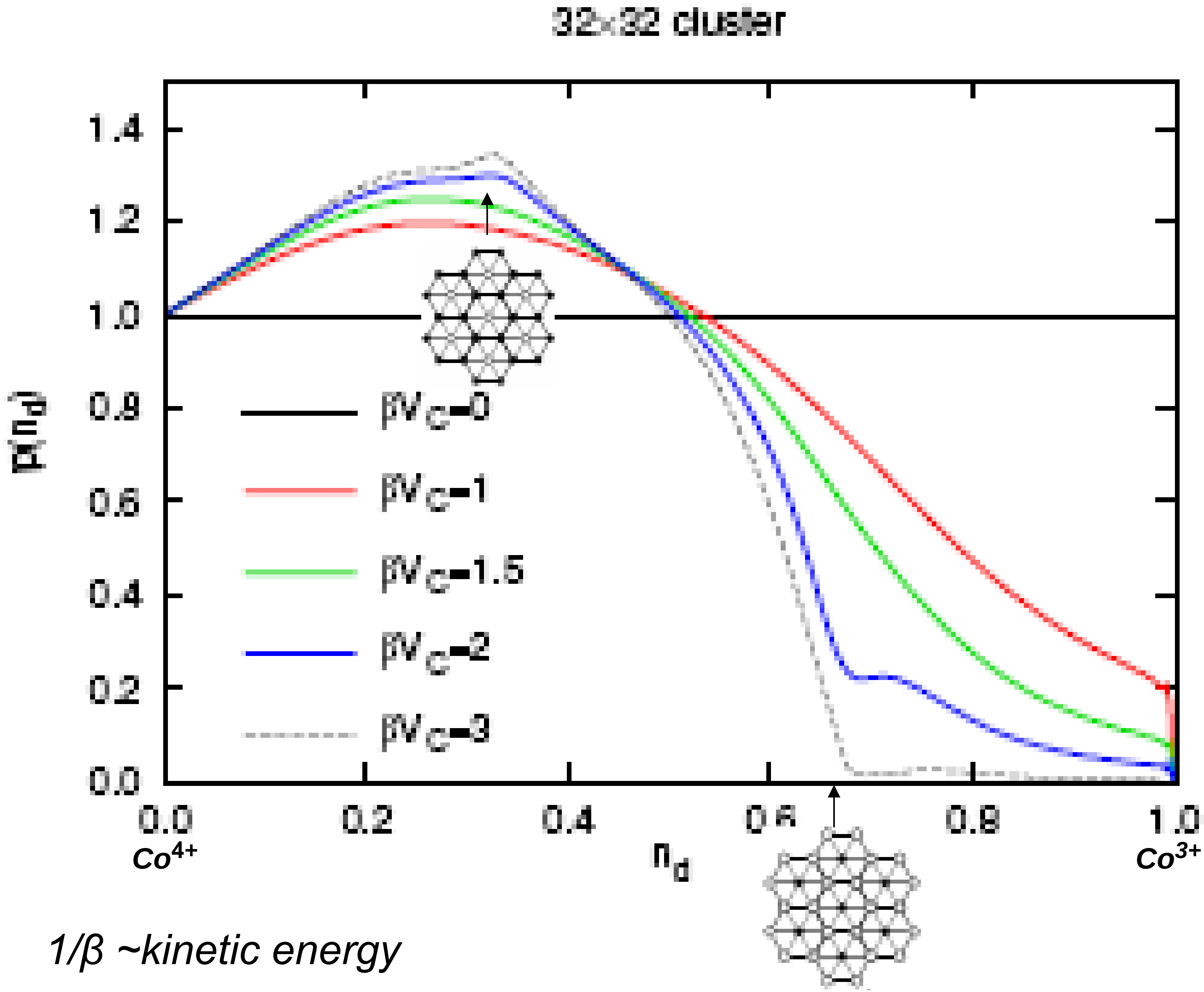
- **reduces the pair-hopping process: $V = p(n_d)V$**
- **spatially separated spin-polarons (trapped by a random Na-potential)**
- **supports magnetic and charge order, suppresses SC**

$$p(n_d) = \frac{P(\circ_i \uparrow\!\bullet_j \downarrow\!\bullet_k)\big|_{V_C \neq 0}}{P(\circ_i \uparrow\!\bullet_j \downarrow\!\bullet_k)\big|_{V_C = 0}}$$

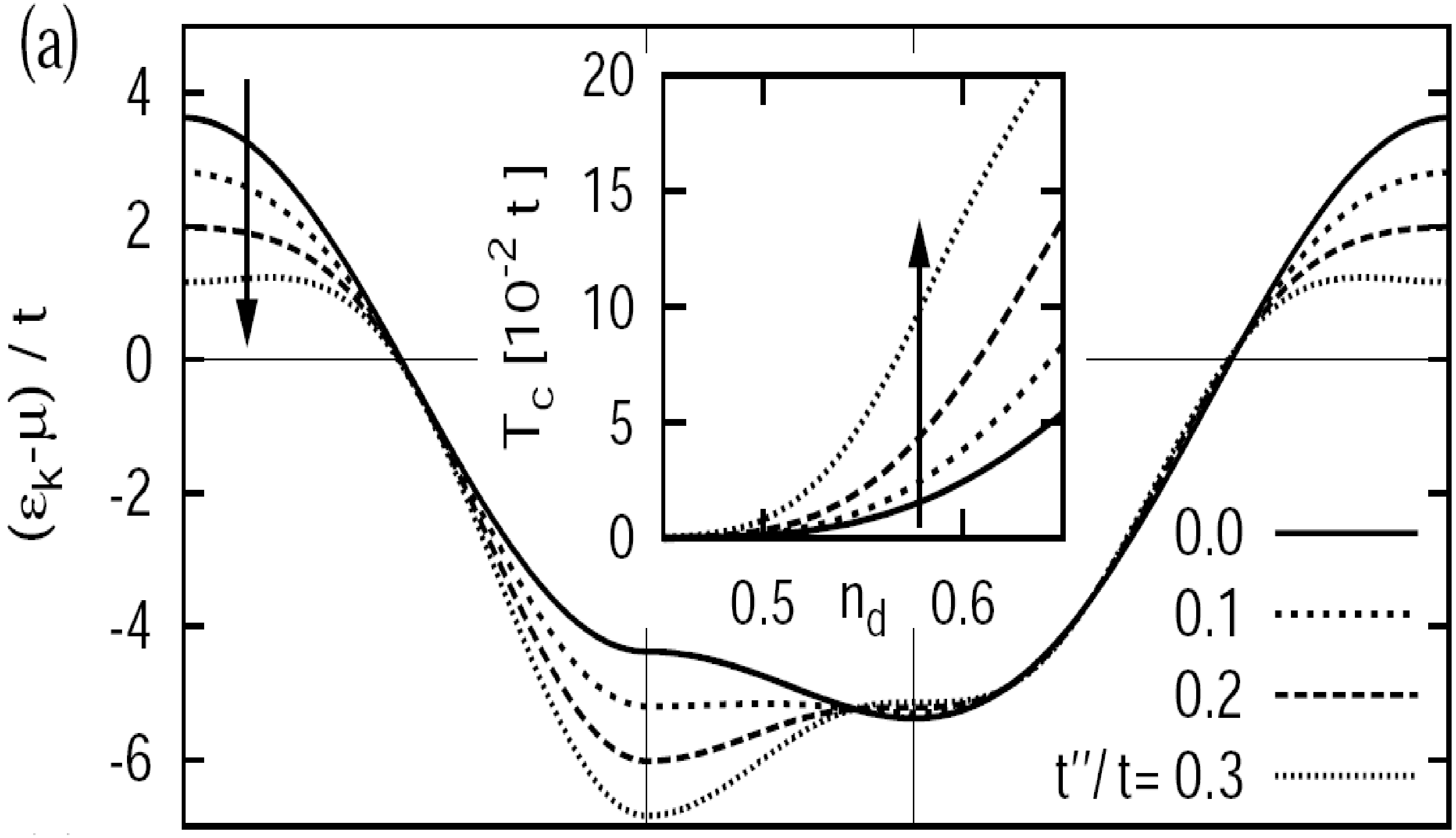
classical Monte-Carlo

…enjoying pair-hopping process

How good are the conditions for pair-hopping interaction?

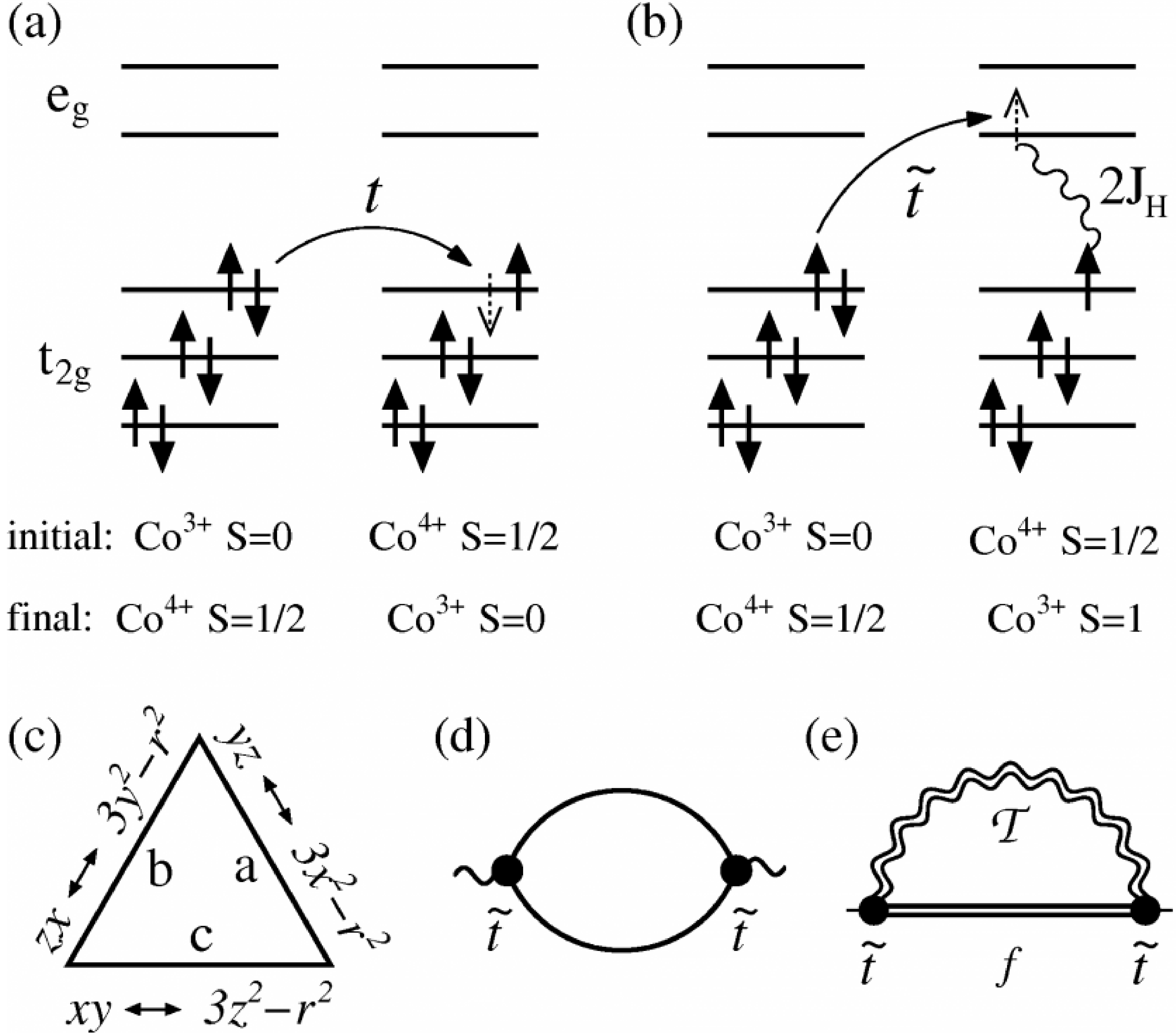


1/β ~kinetic energy



LDA suggests: ***band-flattening when water is present***

Model predicts: ***singlet s-wave T_c enhanced***

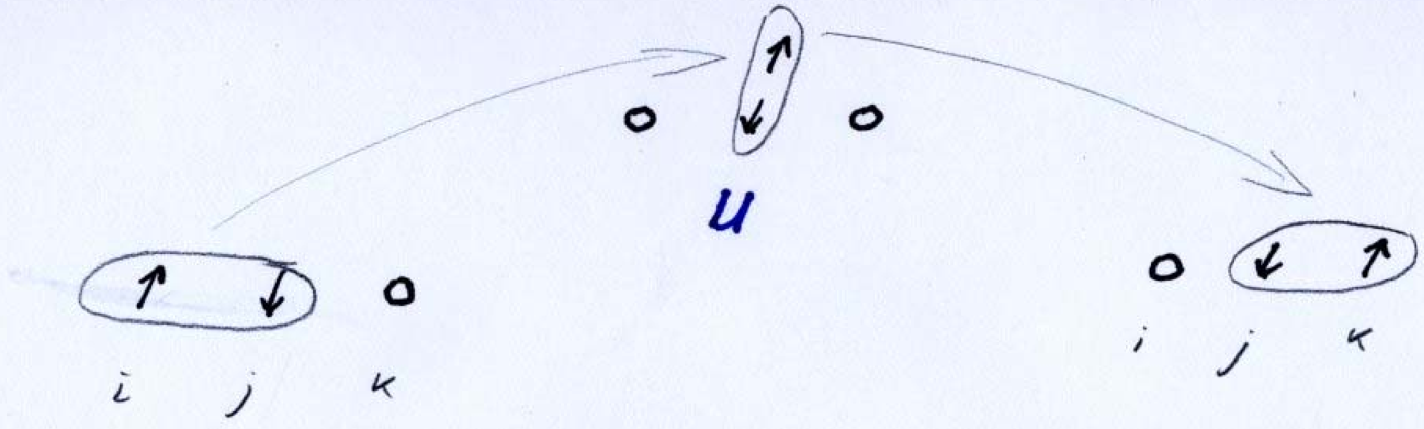


(a)
(b)
e_g
t_2g
t
t̃
2J_H
initial: Co^3+ S=0
Co^4+ S=1/2
Co^3+ S=0
Co^4+ S=1/2
final: Co^4+ S=1/2
Co^3+ S=0
Co^4+ S=1/2
Co^3+ S=1
(c)
(d)
(e)
3y^2−r^2
yz
3x^2−r^2
zx
xy
3z^2−r^2
a
b
c
t̃
t̃
𝒯
f
t̃
t̃

T_c equation (both the pair-hopping V and dispersion are renormalized by the Gutzwiller factor):

$$1 = \sum_{|\bar{\xi}_{\boldsymbol{k}}| \le E_T} \frac{\bar{V}_\alpha |\gamma_\alpha(\boldsymbol{k})|^2}{2\bar{\xi}_{\boldsymbol{k}}} \tanh \frac{\bar{\xi}_{\boldsymbol{k}}}{2T_c}$$

Pair-hopping term in cuprates is small



$$\frac{t^2}{U} \cdot s^{+}_{ij} \, s_{jk}$$

order of J, minor effect

- Na_xCoO_2 : $\frac{\tilde{t}^2}{E_T}$ is large

$\tilde{t} \sim 2t$

$E_T \ll U$

Pairing field $\propto \frac{\tilde{t}^2}{E_T} \gg J$

t_{2g}^6 systems

NOT simple band insulators !!

$LaCoO_3$
$NaCoO_2$
$SrRh_2O_4$

SPINLESS MOTT INSULATORS

spin gap $\ll$ charge gap

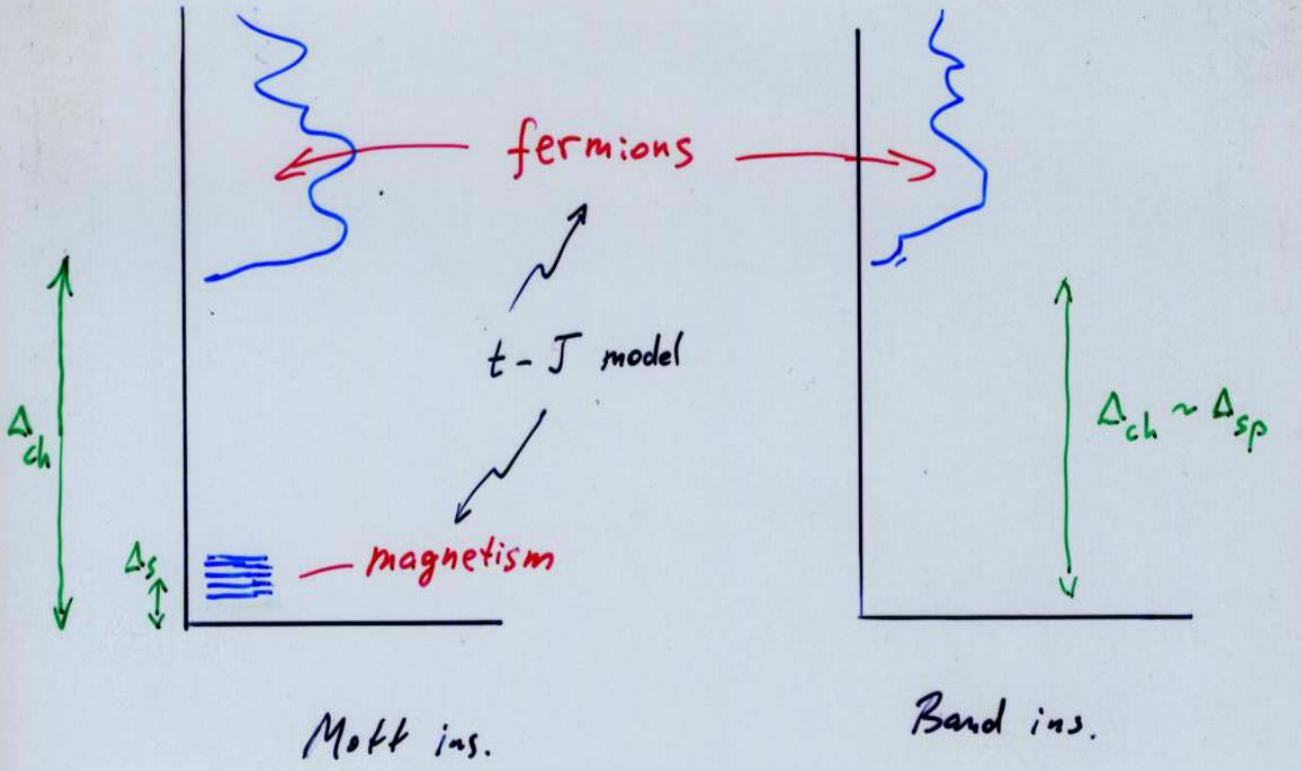
$\wr$ 10 – 100 meV $\wr$ ~1–2 eV

$\langle \bar{S}_i^2 \rangle \neq 0$

Δ_{spin}

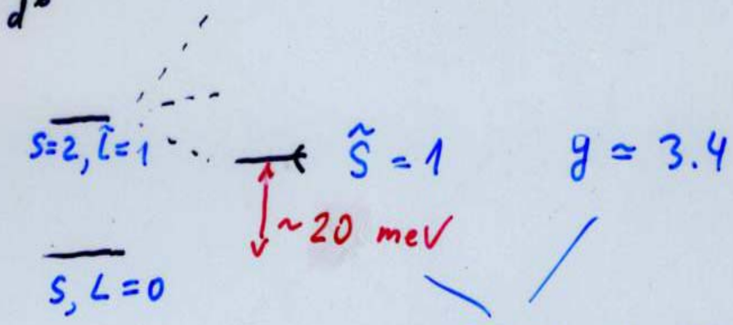
$\langle \bar{S}_i^2 \rangle \equiv 0$

G.Kh. Prog.Theor.Phys.Suppl.(2005)



$LaCoO_3$ ⇒ spinless Mott insulator

3+, d^6



ESR, INS on $\tilde{S}$-triplet

Cobaltates

- *Undoped*

$LaCoO_3$, 3D cubic : ***nonmagnetic insulator***

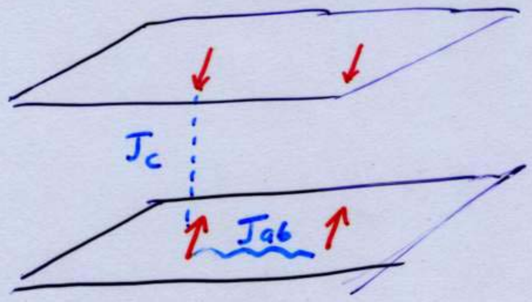
$NaCoO_2$, 2D triangular : ***nonmagnetic insulator***

- *Doped by holes*

$La_{1-x}Sr_xCoO_3$** :* ***spin-glass ⇨ ferromagnetic metal

$Na_{1-x}CoO_2$** :* ***spin-glass ⇨ ferro-planes metal (**$x < 0.25$**)
⇨ nonmagn. metal, supercond. (**$x > 0.25$**)

Similar ionic structure but different hopping geometry



$-J(\bar{S}_i \bar{S}_j)$

1. Spin-waves : $J_c \sim - J_{ab}$

(Keimer et al.
Boothroyd et al.)

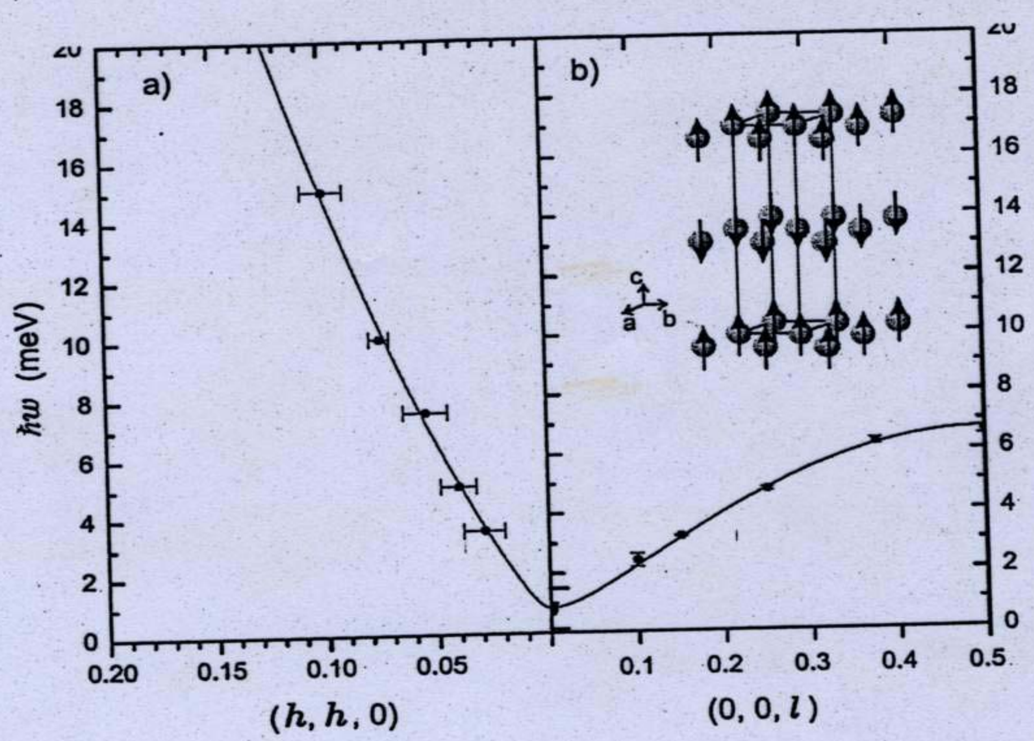
3D magn.
but 2D transport,
$\rho_{ab} \approx 10^{-2} \rho_c$

2. $\Sigma_R J(R) > 0 \rightarrow \theta > 0$ positive (SW-data)

however, $\Theta_{exp} \sim -200\,K$, negative

Different from $NaNiO_2$: $\left|\frac{J_{ab}}{J_c}\right| \simeq 15$, ~2D

A-AF



Spin waves in $Na_{0.8}CoO_2$ (Keimer et al. /cond-mat)

$J_{ab} = -4.5$ meV (Ferro)

$J_c = 3.3$ meV (AF)

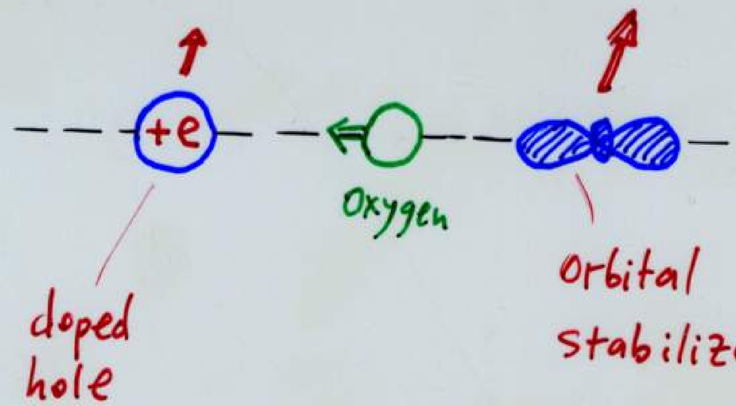
] A-type AF

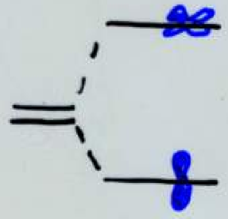
3D-magnetism / 2D-transport

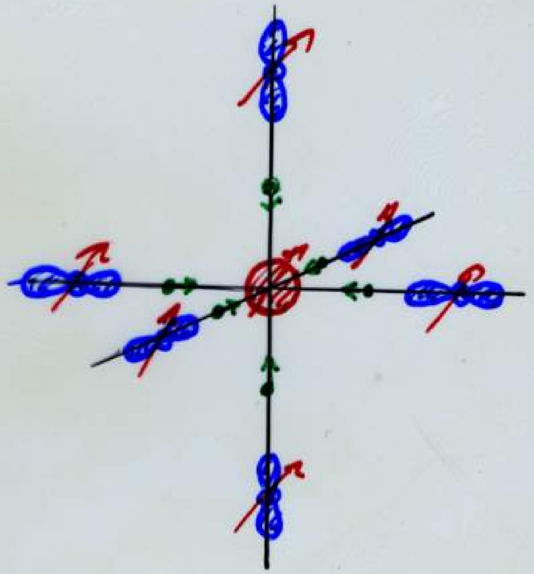
→ not simple SDW

ORBITAL POLARON

Kilian & G.Kh.
PRB (1999)





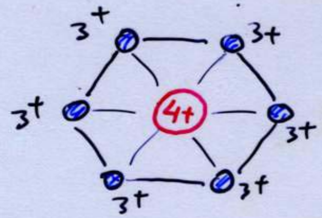


$E_{binding} \sim z \cdot \Delta_{orb-ch.}$

$E_b \gtrsim W$

polaron self-trapped

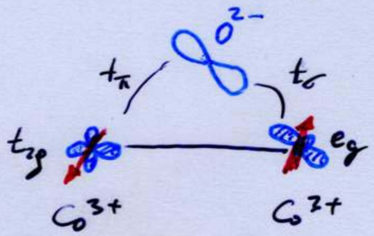
Doping of spinless Mott insulator $NaCoO_2$

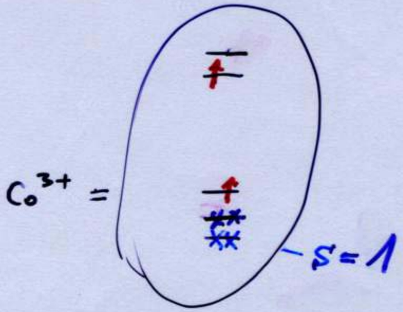


Spin/orbital structure:
- Different from that in $LaCoO_3$

90° Co - O - Co bonds !!!

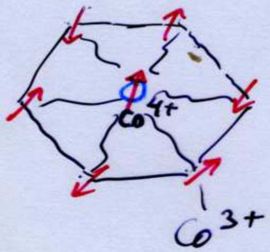
- $Co^{3+} - Co^{3+}$ bonds are strongly AF!





- $Co^{4+} - Co^{3+}$ bonds: competing F & AF

→ Groud state: NET SPIN $\frac{1}{2}$



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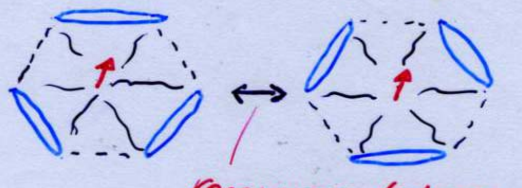
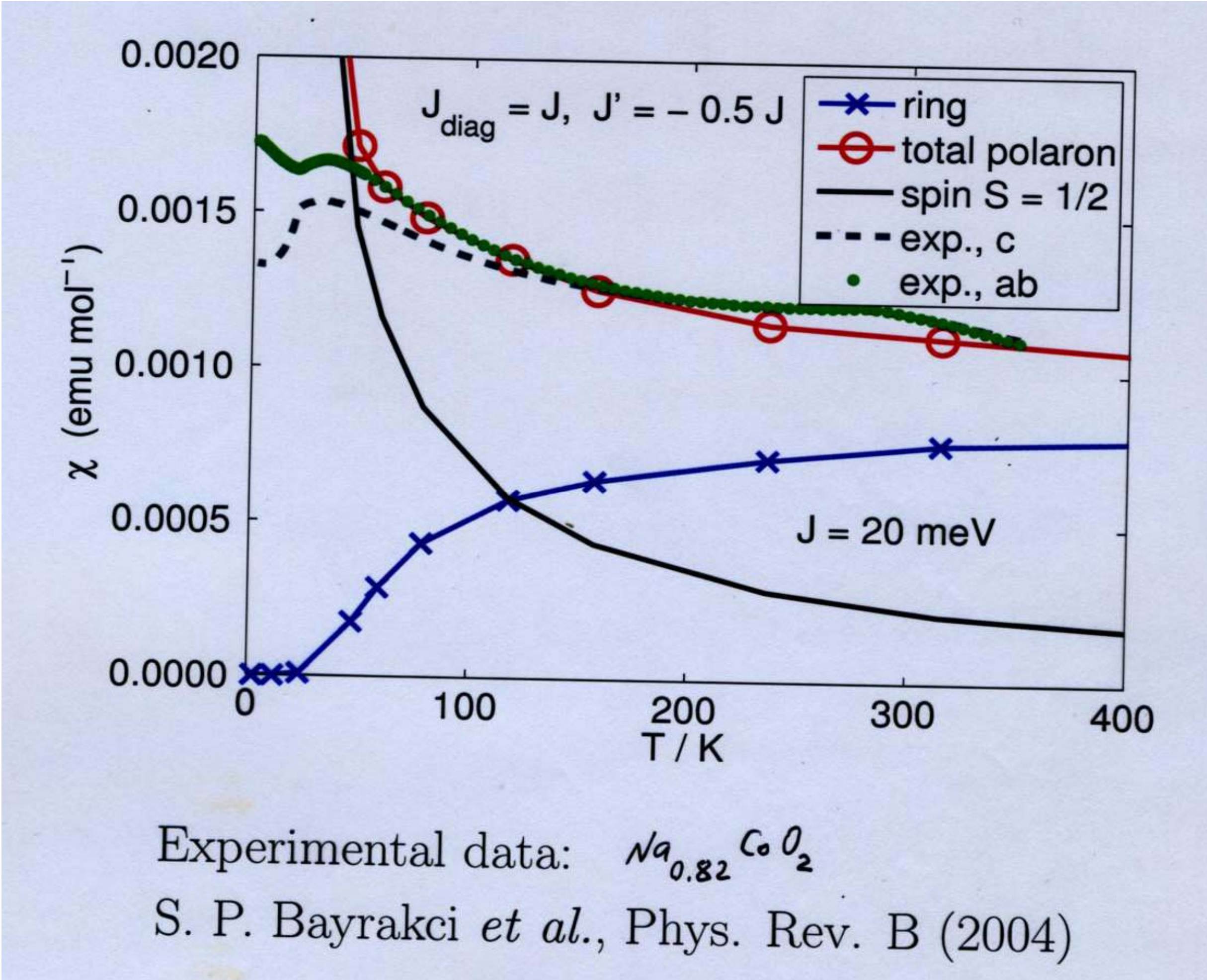


resonance between two configurations



Exact diagonalization:

M.Daghofer, P.Horsch, and G.Kh. (PRL 2006)

Two contibutions:
central-spin ½ and ring-spins 1

Key control factors in oxides

A. „Internal“ structure of TM ions (Ti,…Co,…Cu)

-- valence state, spin & orbital degeneracy

-- local Hilbert space $\{\psi_1, \psi_2, \psi_3, \ldots\}$

B. Lattice symmetry

-- dictates hopping geometry

-- communication rules / structure of Bloch states