29 Nov. '07
Moments and Multiplets in Mott Materials
@ KITP UCSB

Impurity Effects in Orbital Ordered Systems

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Acknowledgment

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Outline

1. Randomly diluted e_g orbital system
   PRL 95, 2672048 (2005)

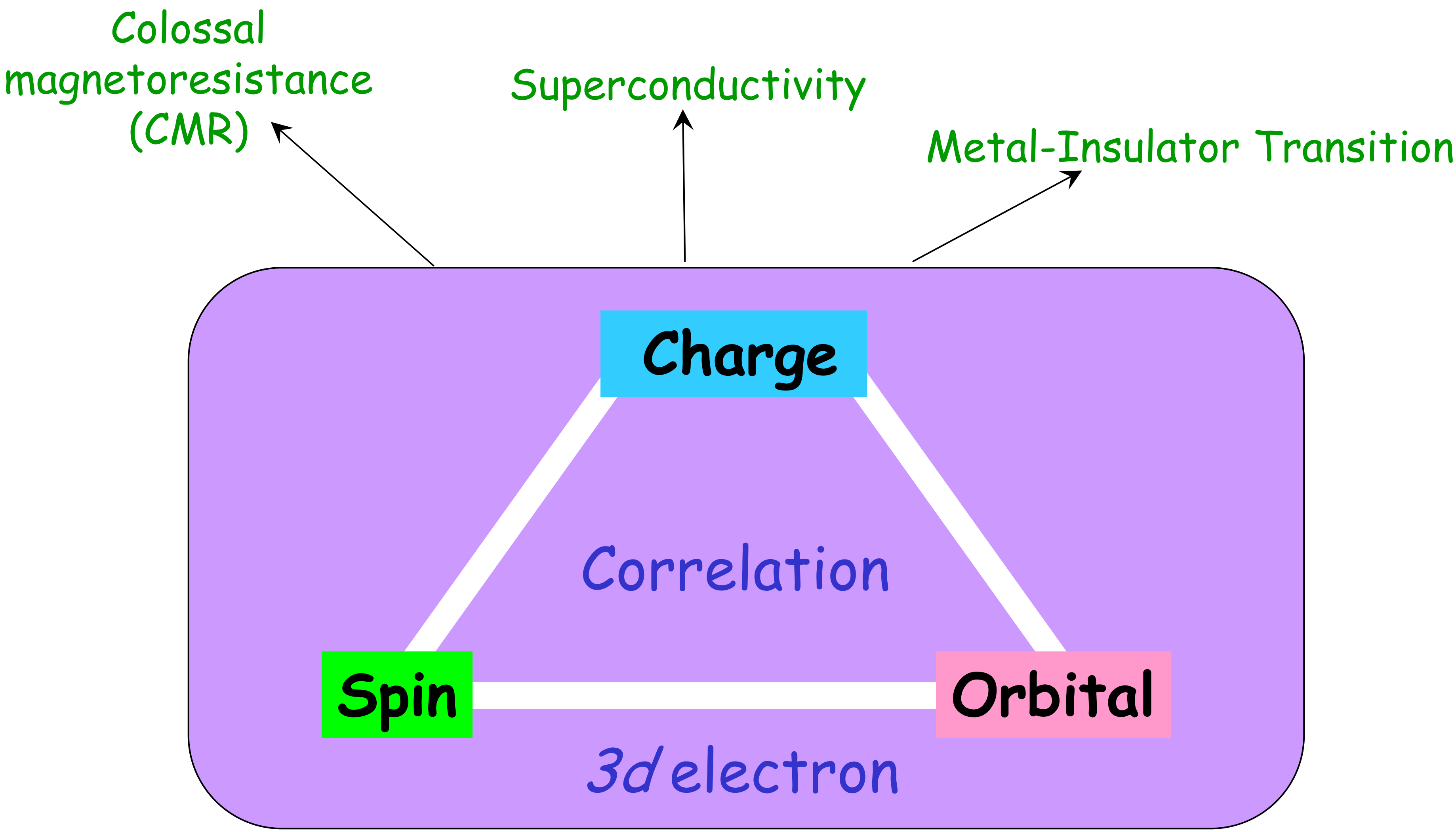
2. Spin state in dilute orbital system
   in preparation

3. Dilution effect in two-dimensional quantum orbital system
   PRL 98, 256402 (2007)

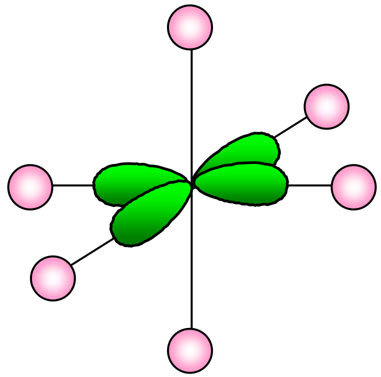
3d Transition-Metal Compounds

High-Tc cuprates $La_{2-x}Sr_xCuO_4$

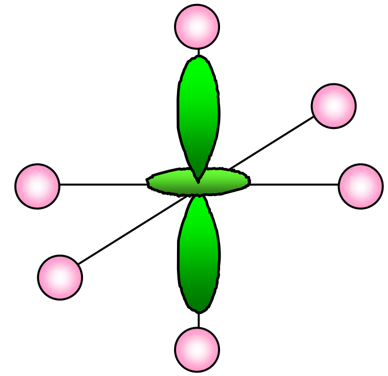
CMR manganites $La_{1-x}Sr_xMnO_3$



Orbital degree of freedom



$d(x^2-y^2)$

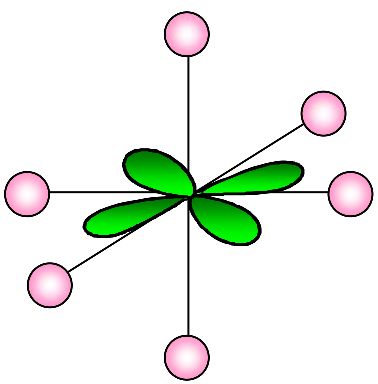


$d(3z^2-r^2)$

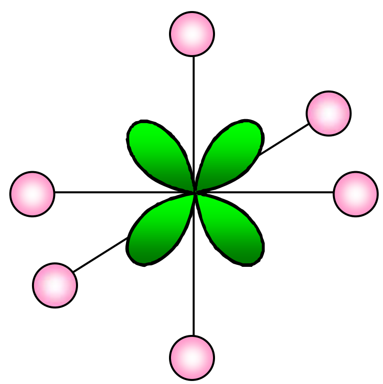
d orbital

$$l=2$$

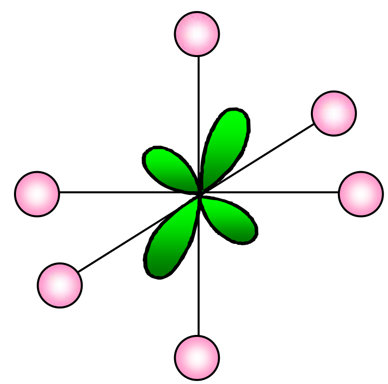
$$2l+1=5$$



$d(xy)$



$d(yz)$



$d(zx)$

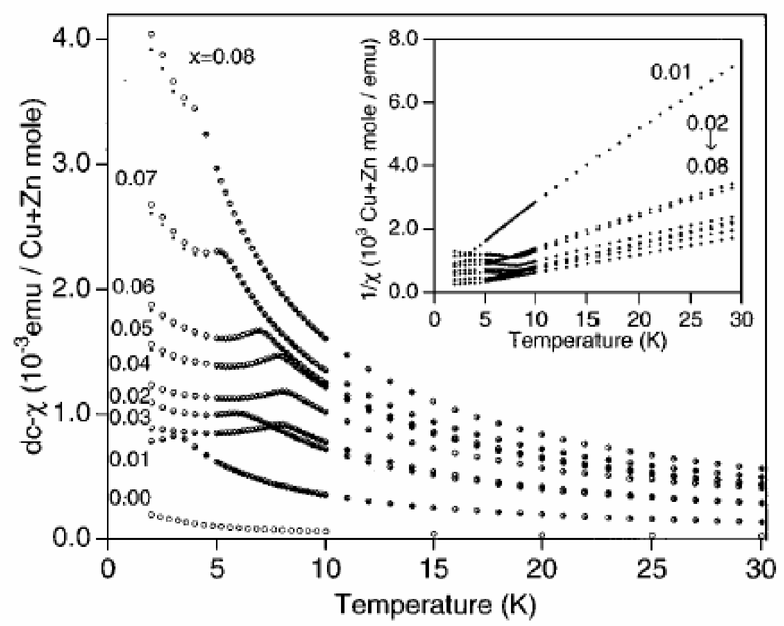
Impurity effects in correlated systems

$Sr(Cu_{1-x}Zn_x)_2O_3$

- Impurity in high Tc cuprates

  $La_{2-x}Sr_x(Cu_{1-x}Zn_x)O_4$

  Rapid quench of Superconductivity



Azuma et al. PRB ('97)

- Non-magnetic impurity in spin-gap systems

Two-leg ladder	$Sr(Cu_{1-x}Zn_x)_2O_3$
Spin Peierls	$(Cu_{1-x}Mg_x)GeO_3$

Long-range AF order appears

Impurity in CMR manganites

- Cr doping in charge/orbital order

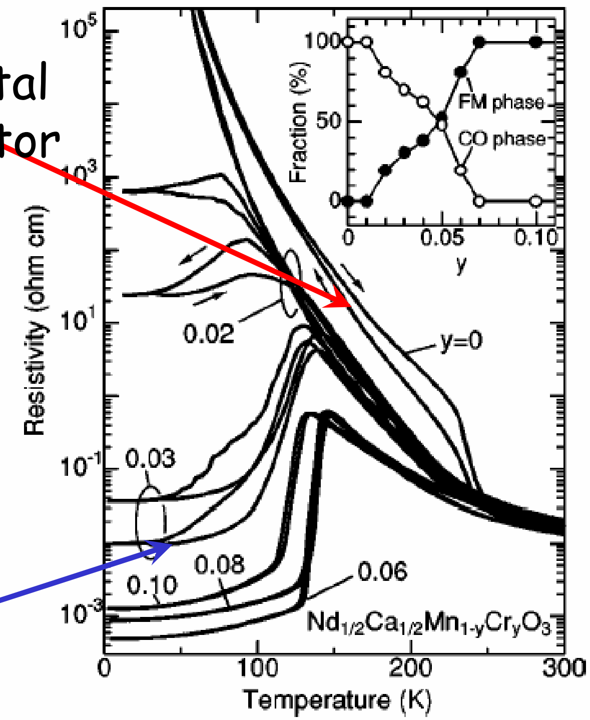
$La_{1/2}Ca_{1/2}Mn_{1-y}Cr_yO_3$

$$(t_{2g})^3(e_g)^1 \rightarrow (t_{2g})^3(e_g)^0$$

Charge/orbital order rapidly collapses by Cr doping

$La_{1/2}Ca_{1/2}Mn_{1-y}Cr_yO_3$

Charge & Orbital ordered Insulator

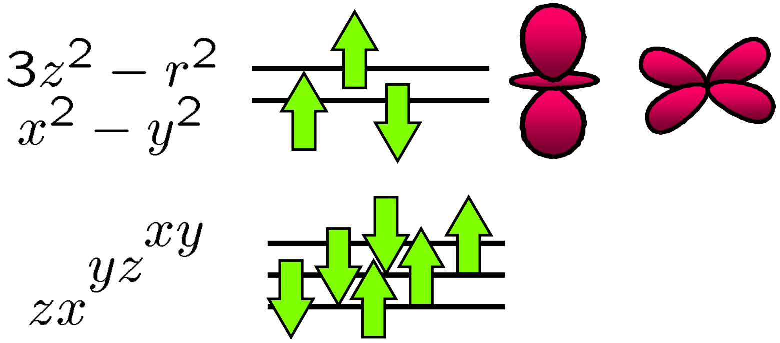


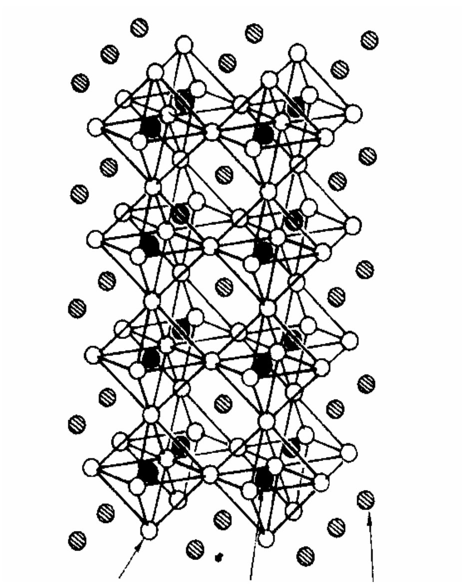
Ferromagnetic Metal

Kimura-Tokura and co-workers (2000)

$KCuF_3$

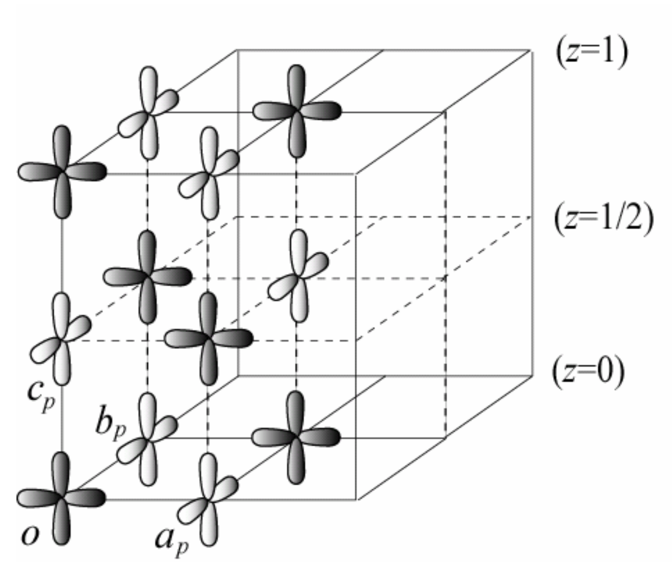
Cu^{2+} (d^9)





3-dim. Perovskite crystal

Orbital order with Jahn-Teller distortion



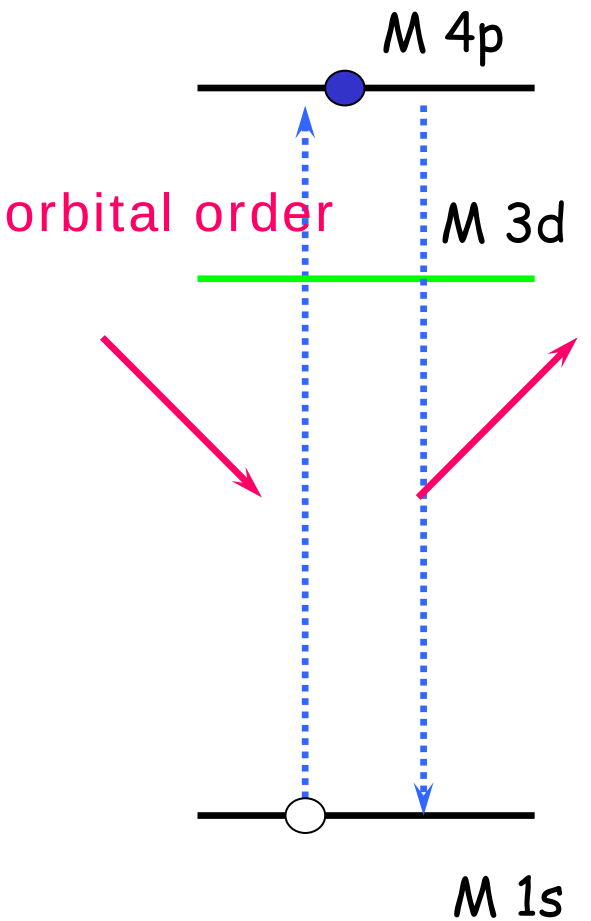
$d(y^2 - z^2)/d(z^2 - x^2)$ type

$$Q = (\pi, \pi, \pi)$$

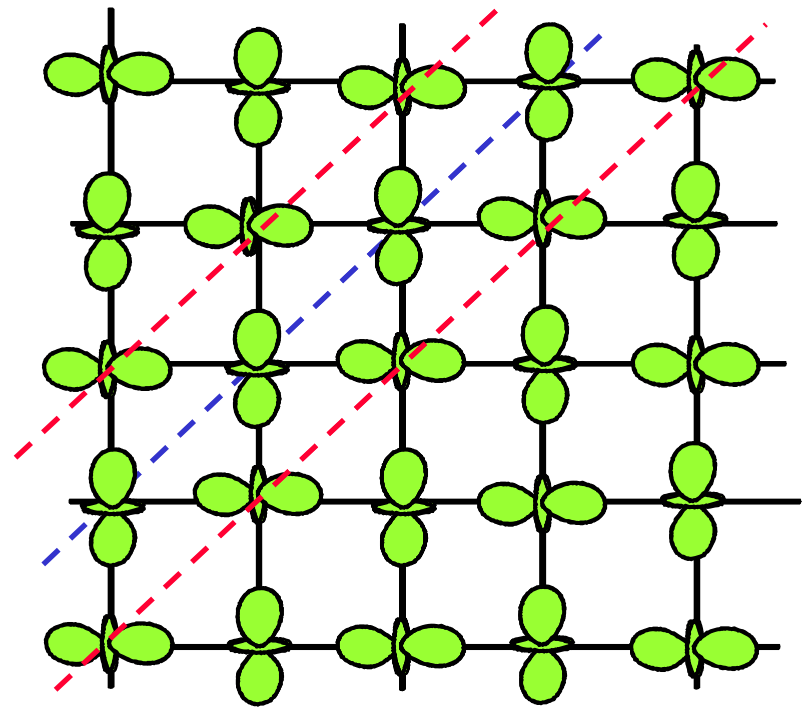
Resonant x-ray scattering

Paolasini et al., Sawa et al., Murakami et al

Resonant x-ray scattering



Sensitive to the anisotropic charge distribution



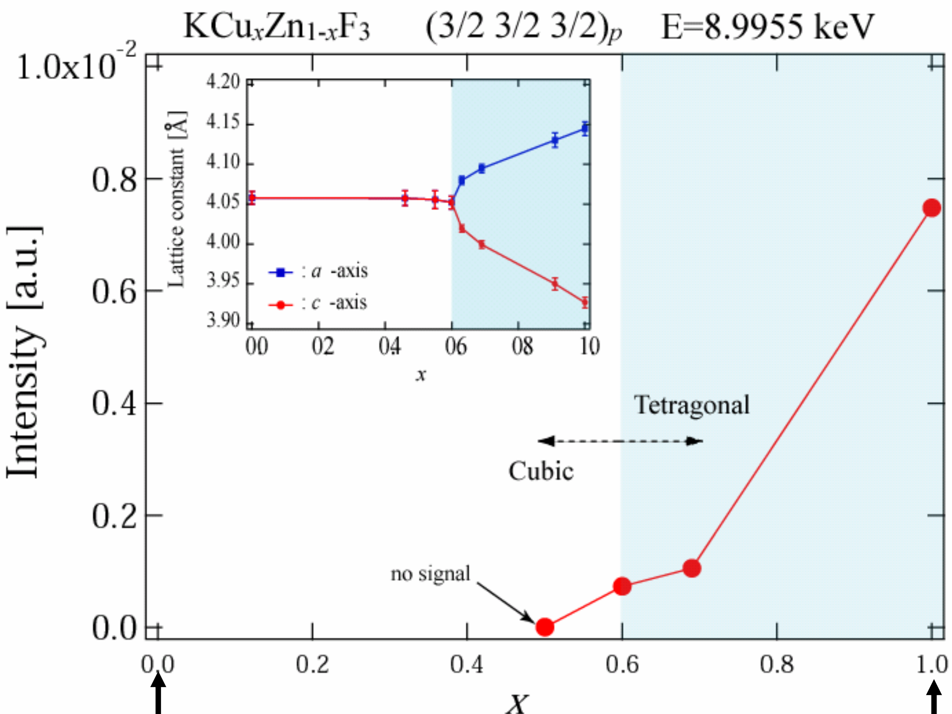
- Element specific (Resonant)
- Polarization (X-ray)
- Diffraction

Zn doping in $KCuF_3$

Resonant x-ray scattering

$KCu_{1-x}Zn_xF_3$

Murakami-G.

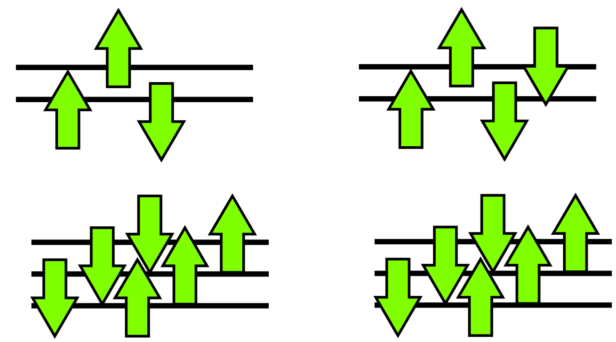


$KZnF_3$

1-x(=p)

$KCuF_3$

Cu (d^9) ⟶ Zn (d^{10})

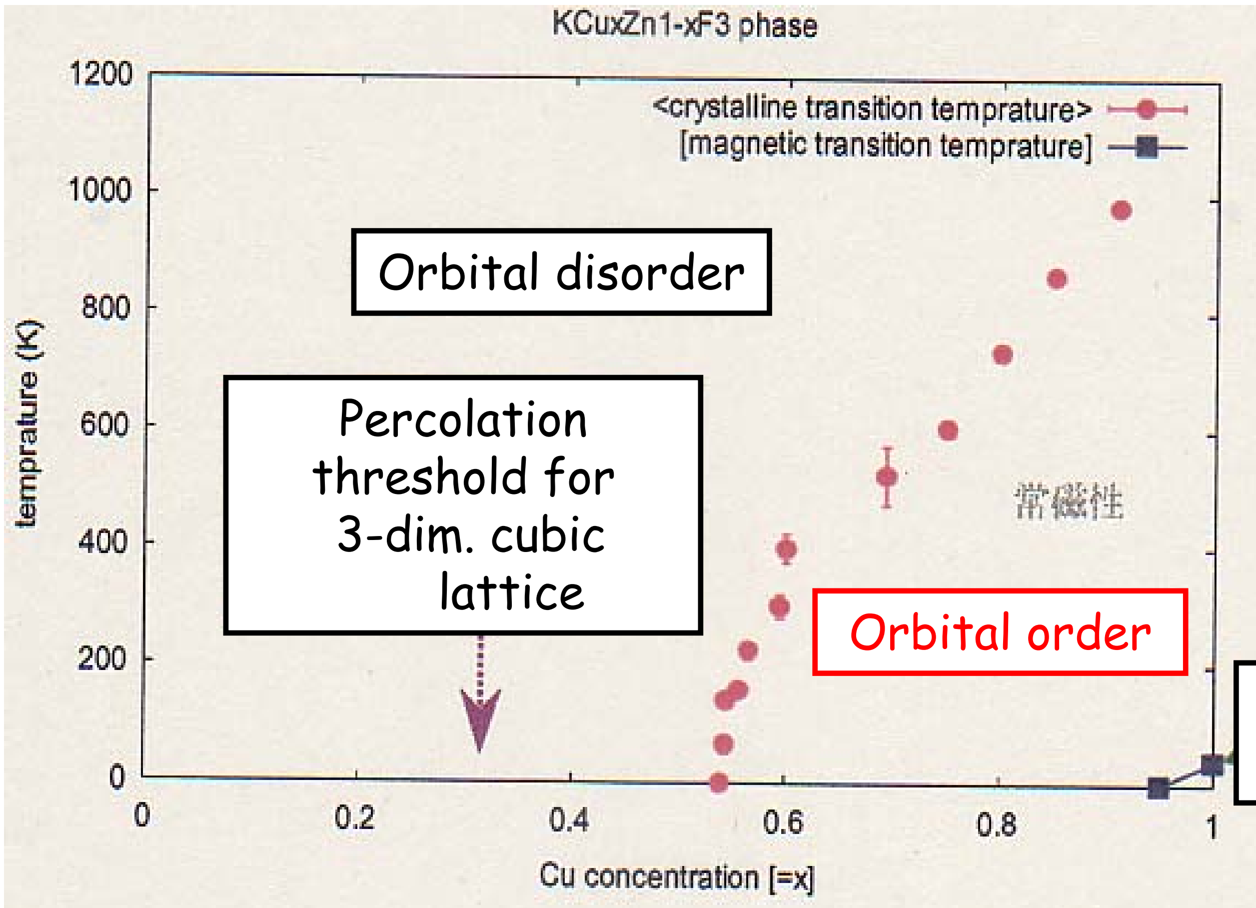


Orbital dilution by Zn

Orbital order disappears around x=0.5

Orbital ordering temperature

(Murakami G.)



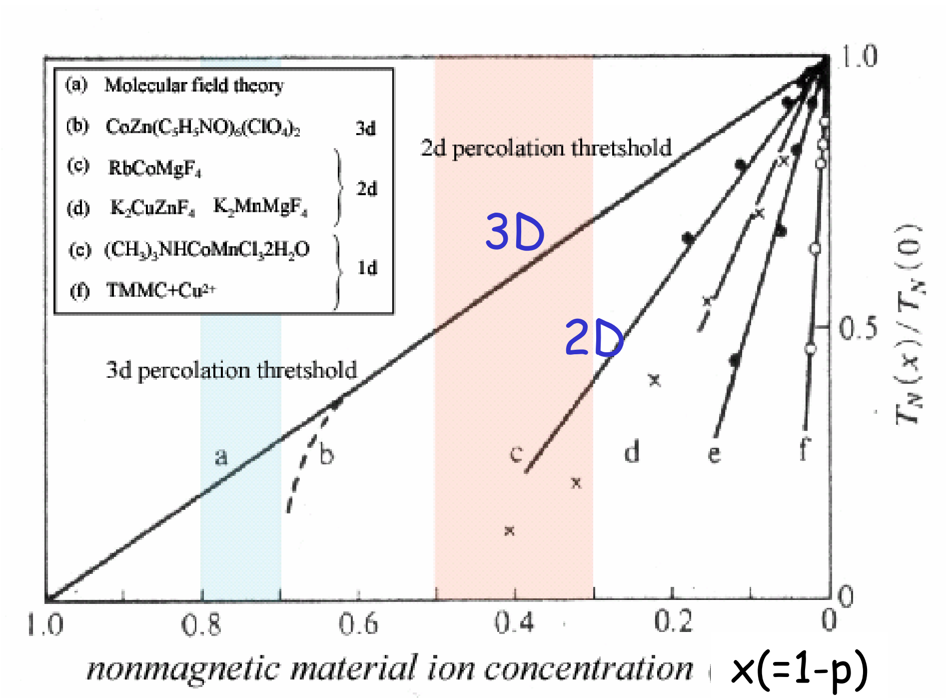
Neel temperature

1-dim. AFM

1-x(=p)

Dilute magnets and percolation

Dilute magnets



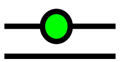
	Dimension	z	η	p_c
Honeycomb	2D	3	0.61	0.70
Cubic	2D	4	0.79	0.59
Triangle	2D	6	0.91	0.50
Diamond	3D	4	0.34	0.43
sc	3D	6	0.52	0.31
bcc	3D	8	0.68	0.24
fcc	3D	12	0.74	0.20

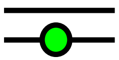
Dilute magnets are well explained by the percolation theory

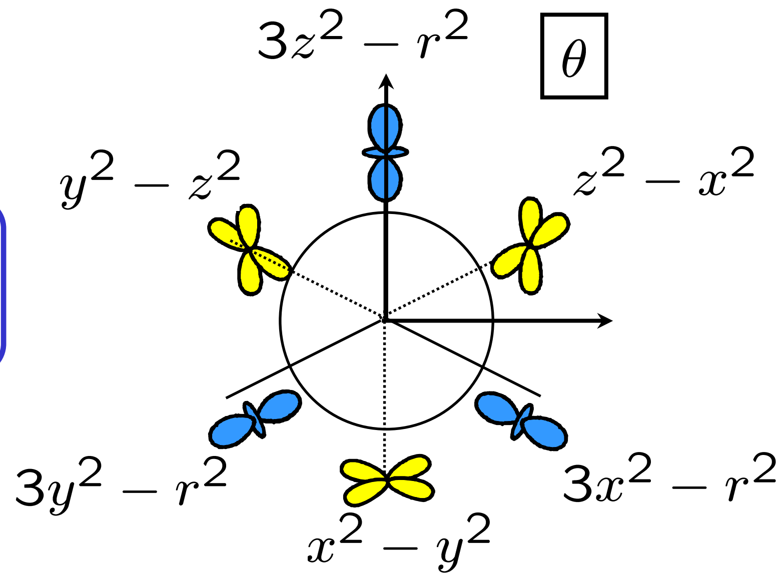
Orbital x_c (=0.5) [illegible] percolation threshold(=0.69)

Pseudo-spin operator for e_g orbital

Wave function

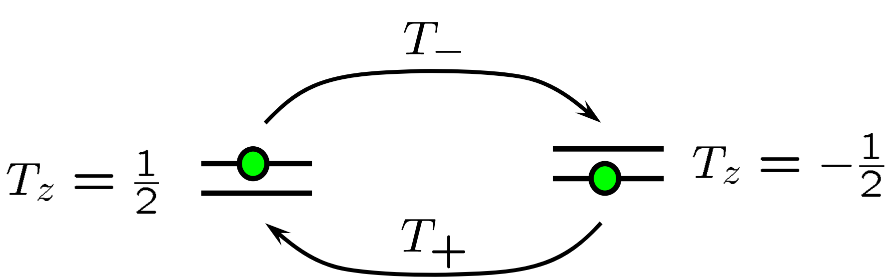

$|d_{3z^2-r^2}\rangle$


$|d_{x^2-y^2}\rangle$



$$|\theta\rangle = \cos\left(\frac{\theta}{2}\right)|d_{3z^2-r^2}\rangle + \sin\left(\frac{\theta}{2}\right)|d_{x^2-y^2}\rangle$$

Pseudo-spin operator: $\vec{T}$



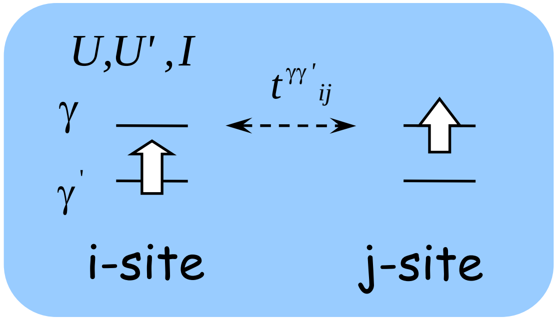
$$T_z|d_{3z^2-r^2}\rangle = \frac{1}{2}|d_{3z^2-r^2}\rangle$$

$$T_z|d_{x^2-y^2}\rangle = -\frac{1}{2}|d_{x^2-y^2}\rangle$$

$$T_z(\theta) = \cos\theta T_z + \sin\theta T_x$$

Superexchange-type interaction

$$\mathcal{H} = \sum_{<ij>\sigma\gamma\gamma'} \left(t_{ij}^{\gamma\gamma'} d_{i\gamma\sigma}^{\dagger} d_{j\gamma'\sigma} + H.c. \right)$$
$$+ U \sum_{i\gamma} n_{i\gamma\uparrow} n_{i\gamma\downarrow} + U' \sum_{i} n_{ia} n_{ib}$$
$$+ J \sum_{i\sigma\sigma'} d_{ia\sigma}^{\dagger} d_{ib\sigma'}^{\dagger} d_{ia\sigma'} d_{ib\sigma}$$



Multi-orbital Hubbard model

⇓

Spin part — Orbital part

$$\mathcal{H}_{SE} = - J_1 \sum_{\langle ij \rangle} \left(\frac{3}{4} + \vec{S}_i \cdot \vec{S}_j \right) \left(\frac{1}{4} - \tau_i^l \tau_j^l \right)$$
$$- J_2 \sum_{\langle ij \rangle} \left(\frac{1}{4} - \vec{S}_i \cdot \vec{S}_j \right) \left(\frac{3}{4} + \tau_i^l \tau_j^l + \tau_i^l + \tau_j^l \right)$$

Spin-orbital model

$J_1 = \frac{t^2}{(U-3J)}$ $J_2 = \frac{t^2}{U}$

$l (= x, y, z)$: bond direction

$$\tau_i^l = \cos\left(\frac{2\pi}{3} n_l\right) T_{iz} + \sin\left(\frac{2\pi}{3} n_l\right) T_{ix}, \qquad (n_x, n_y, n_z) = (1, 2, 3)$$

Paramagnetic spin
(T_N << T_{OO})

$$\mathcal{H} = 2J \sum_{\langle ij \rangle} \tau_i^l \tau_j^l$$

Orbital model

$$\mathcal{H} = 2J \sum_{\langle ij \rangle} \tau_i^l \tau_j^l \varepsilon_i \varepsilon_j$$

$$\varepsilon_i = \begin{cases} 1 & Cu \\ 0 & Zn \end{cases}$$

$$J > 0$$

Orbital model with impurity

Cooperative Jahn-Teller coupling

$$\mathcal{H} = \mathcal{H}_{JT} + \mathcal{H}_{ph} + \mathcal{H}_{str} + \mathcal{H}_{el-str}$$

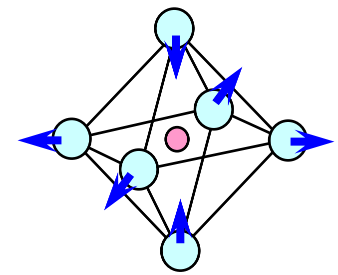
Jahn-Teller Hamiltonian

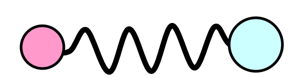
$$\mathcal{H}_{JT} = g \sum_{i,l=(x,z)} T_l(i) Q_l(i)$$ Jahn-Teller

$$\mathcal{H}_{ph} = \sum_{km} \frac{\hbar\omega_{km}}{2} \left[p^*_m(k) p_m(k) + q^*_m(k) q_m(k) \right]$$ Phonon

$$\mathcal{H}_{el-str} = g_o \sum_{l=(x,z)} u_l T_l(k=0)$$ Orbital-strain

$$\mathcal{H}_{str} = c_0 \sum_{l=(x,z)} u_l^2$$ strain





Canonical transformation

$$\tilde{q}_m(k) = q_m(k) - \frac{1}{\sqrt{\hbar\omega_{mk}}} \sum_l g_m(k) T_l(k)$$

⇓

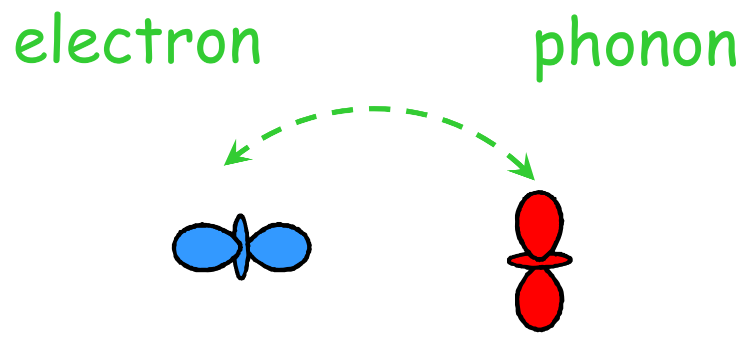
$$\mathcal{H}_{JT} + \mathcal{H}_{ph} = \boxed{\frac{g^2}{K} \sum_{\langle ij \rangle} \tau_i^l \tau_j^l} + \sum_{km} \frac{\hbar\omega_{km}}{2} \left[\tilde{p}^*_m(k) \tilde{p}_m(k) + \tilde{q}^*_m(k) \tilde{q}_m(k) \right]$$

Orbital model
(virtual exchange of phonon)

Interactions between orbitals

$$\mathcal{H} = (J_{SE} + J_{JT}) \sum_{\langle ij \rangle} \tau_i^l \tau_j^l \varepsilon_i \varepsilon_j \qquad \varepsilon_i = \begin{cases} 1 & Cu \\ 0 & Zn \end{cases}$$

$$\tau_i^l = \cos\left(\frac{2\pi}{3} n_l\right) T_{iz} + \sin\left(\frac{2\pi}{3} n_l\right) T_{ix},$$



Same form of the interaction

e_g Orbital Model

$$\mathcal{H} = 2J \sum_{\langle ij \rangle} \tau_i^l \tau_j^l$$

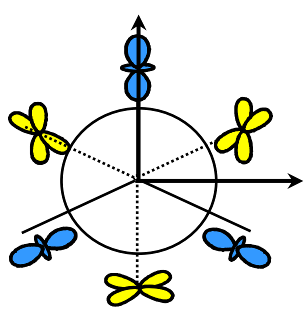
$$\tau_i^l = \cos\left(\frac{2\pi}{3} n_l\right) T_{iz} + \sin\left(\frac{2\pi}{3} n_l\right) T_{ix},$$

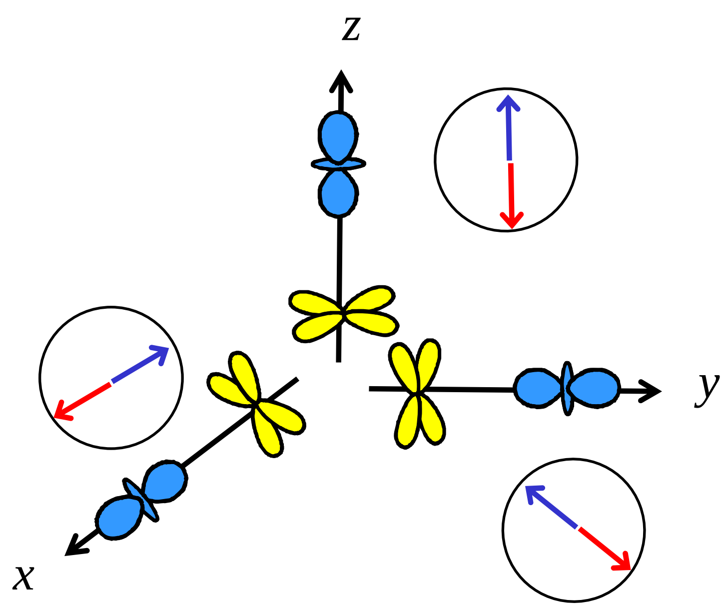
$l(= x, y, z)$: bond direction

$$(n_x, n_y, n_z) = (1, 2, 3)$$

- Interaction depends on bond direction
- No continuous symmetry
- $\langle T_{iz} \rangle$ not conserved

$$\begin{cases} T_{iz}T_{jz} & l = z \\ \left[-\frac{1}{2}T_{iz} + \frac{\sqrt{3}}{2}T_{ix}\right]\left[-\frac{1}{2}T_{jz} + \frac{\sqrt{3}}{2}T_{jx}\right] & l = x \\ \left[-\frac{1}{2}T_{iz} - \frac{\sqrt{3}}{2}T_{ix}\right]\left[-\frac{1}{2}T_{jz} - \frac{\sqrt{3}}{2}T_{jx}\right] & l = y \end{cases}$$





A kind of frustration
Impurity in a frustrated system

Classical orbital state at x=0

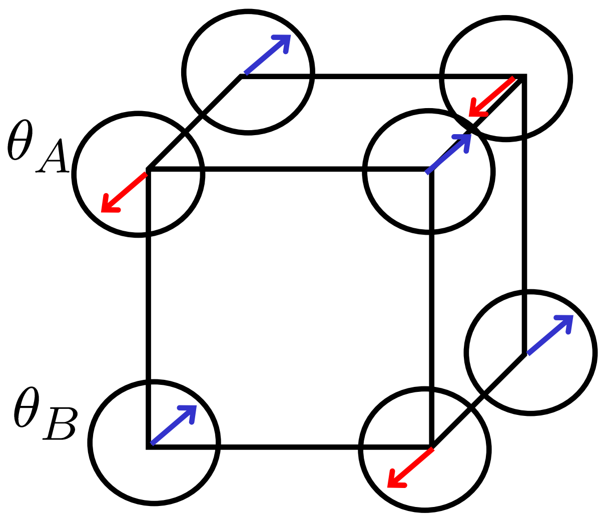
<u>Classical ground state</u>:

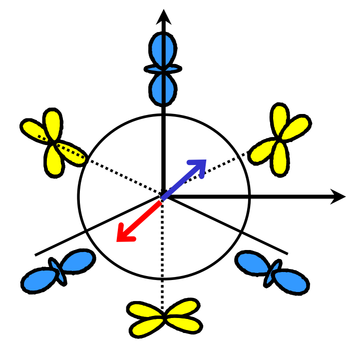
AF-type orbital configuration, but

Largely degenerate continuous solutions

Feiner et al PRL(97)
Khaliullin et al. PRB(97)
SI et al. PRB (00)
Kubo et al. JPSJ (02)
Nussinov et al. EPL(04)

[1] : Continuous orbital AF configuration



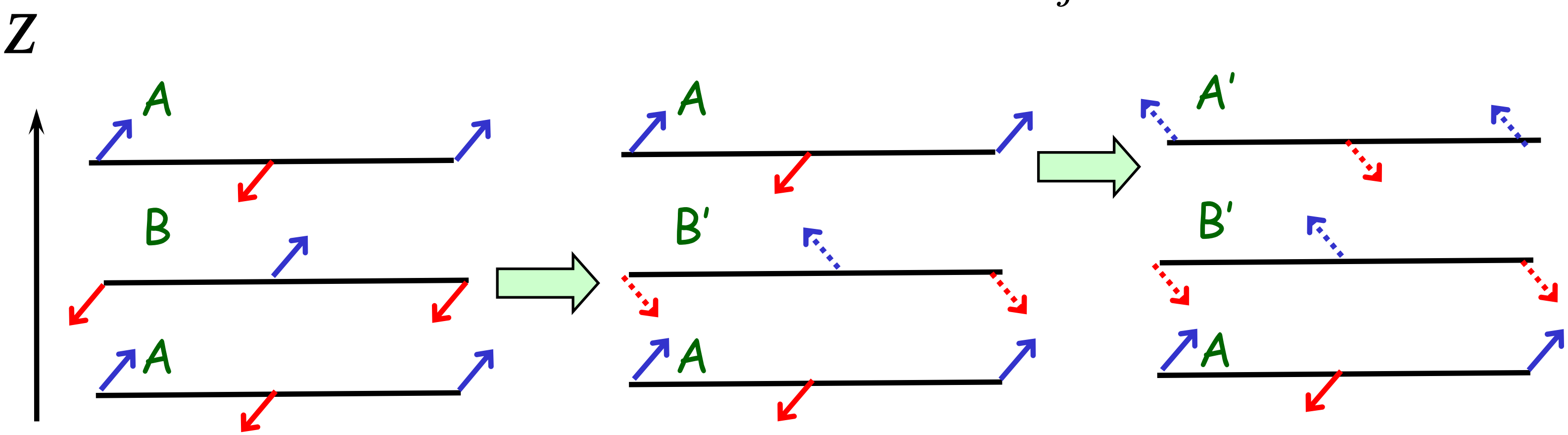


$$(\theta_A/\theta_B) \;=\; (\theta/\theta+\pi)$$
$$\forall\theta$$

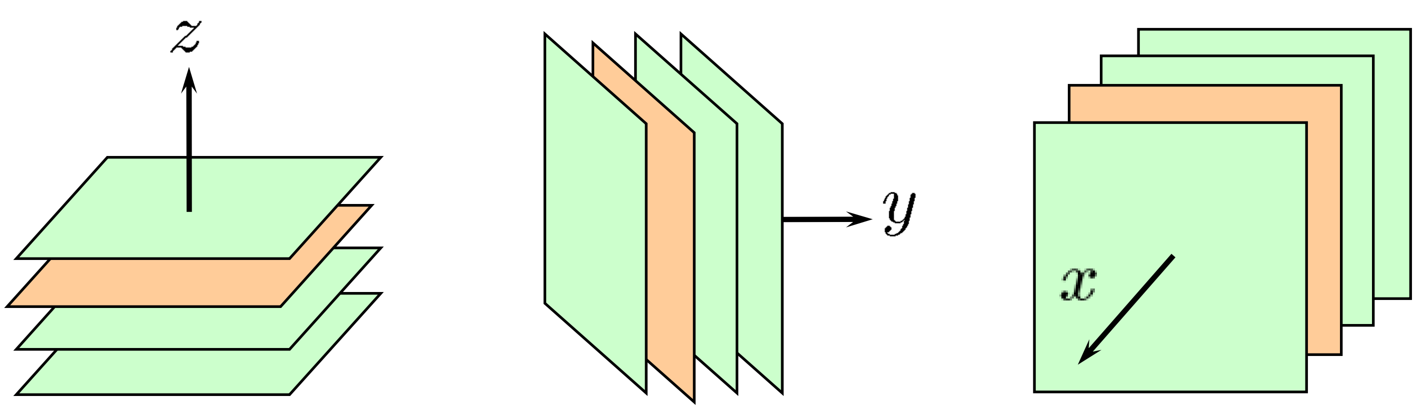
Classical orbital state at x=0

[2] : Stacking degeneracy

$$\mathcal{H}(\mathrm{z-direction}) \sim 2JT_i^zT_j^z$$



$T^x \to -T^x$ $T^x \to -T^x$

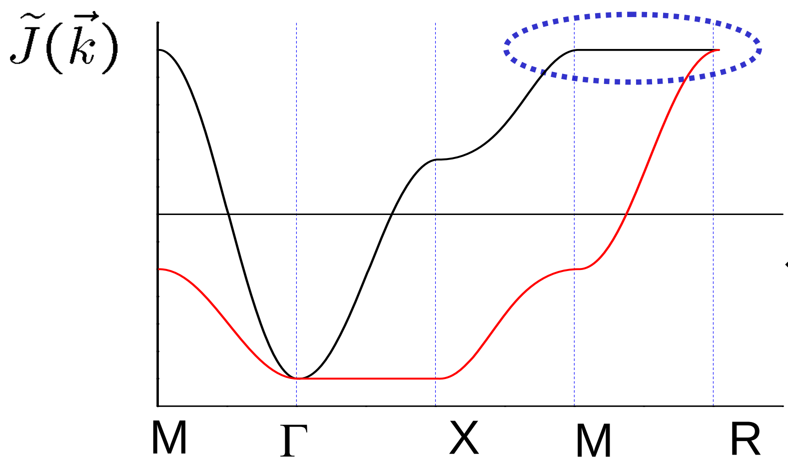


Momentum dependence of orbital interaction

Orbital Model

$$\mathcal{H} = \sum_k \begin{pmatrix} T_z(k) & T_x(k) \end{pmatrix} \hat{J}(k) \begin{pmatrix} T_z(k) \\ T_x(k) \end{pmatrix}$$

Heisenberg Model



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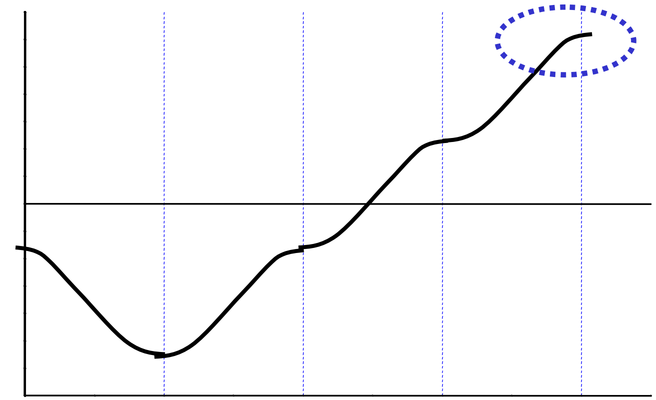


$$\begin{aligned} \tilde{J}(\vec{k}) &= J\Big[-c_x - c_y - c_z \\ &\pm \sqrt{c_x^2 + c_y^2 + c_z^2 - c_x c_y - c_y c_z - c_z c_x}\ \Big] \end{aligned}$$

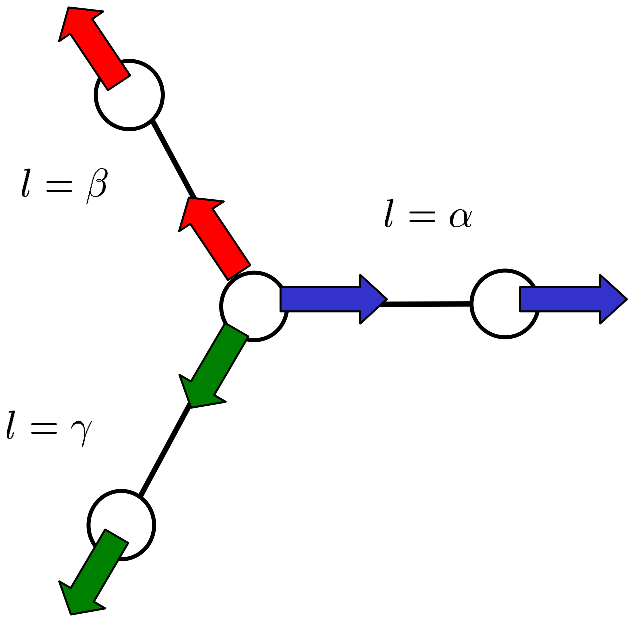
$$J(\vec{k}) = J\{c_x + c_y + c_z\}$$

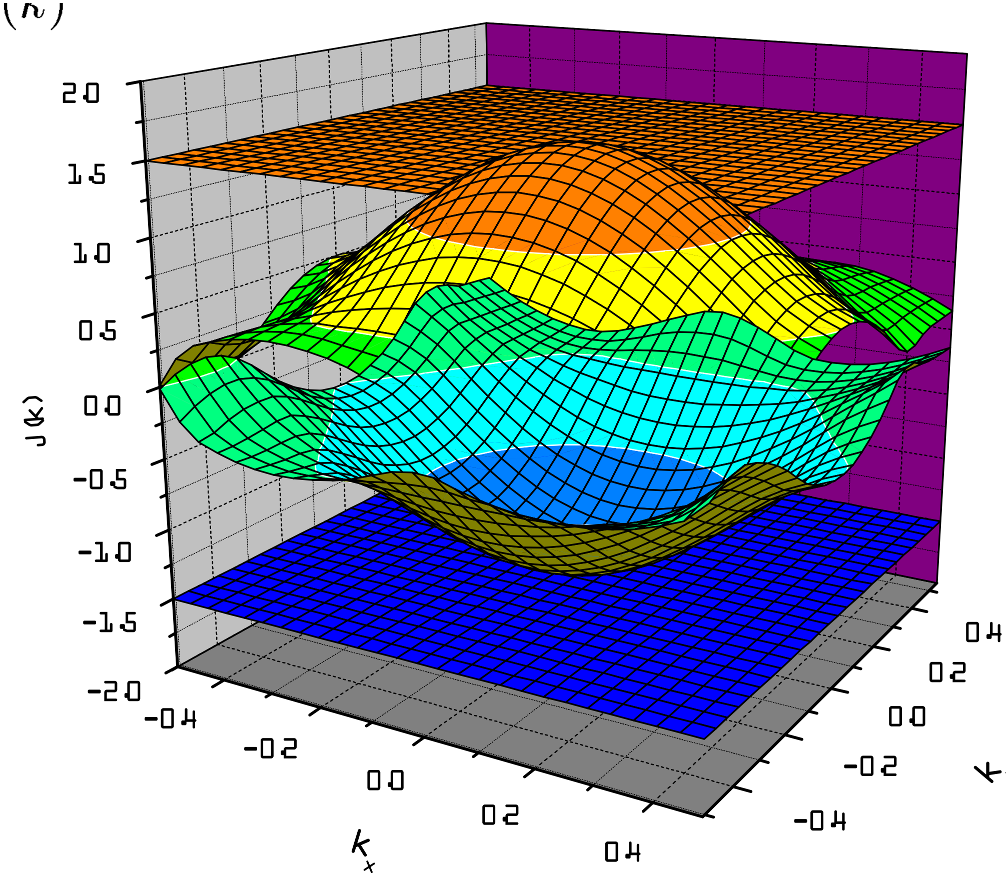
$$c_l = \cos(ak_l)$$

Orbital configuration is not determined uniquely by mean field (like frustrated spin systems)

Doubly-degenerate orbital model on a honeycomb lattice

$$\mathcal{H}_{orbital} = \frac{1}{2} J \sum_i \left(\frac{3}{4} + \tau_i^{\alpha} \tau_{i+\delta_\alpha}^{\alpha} + \tau_i^{\beta} \tau_{i+\delta_\beta}^{\beta} + \tau_i^{\gamma} \tau_{i+\delta_\gamma}^{\gamma} \right)$$





Flat dispersion for
orbital interaction

Nagano-Naka-Nasu-SI PRL 99, 217202 (2007)
c.f. Balents & coworkers, Kitaev et al.

Monte Carlo simulation

Classical Monte Carlo method

L*L*L cubic lattice (L<40)

Periodic boundary condition

T: 2-dimensional classical vector

Wang-Landau method

Cluster expansion method

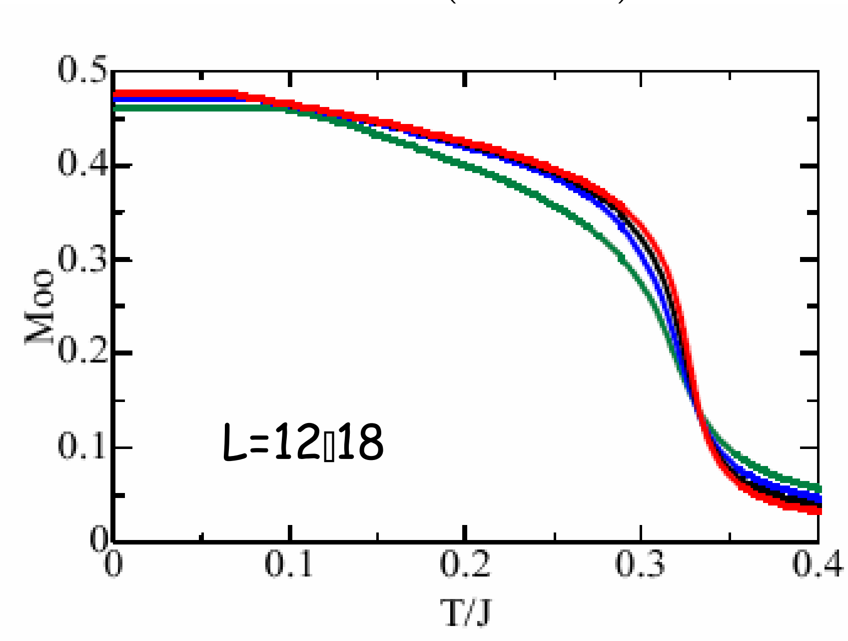
Orbital order by fluctuation

Classical Monte Carlo

c.f. Kubo et al. JPSJ (02)
Nussinov et al. EPL(04)

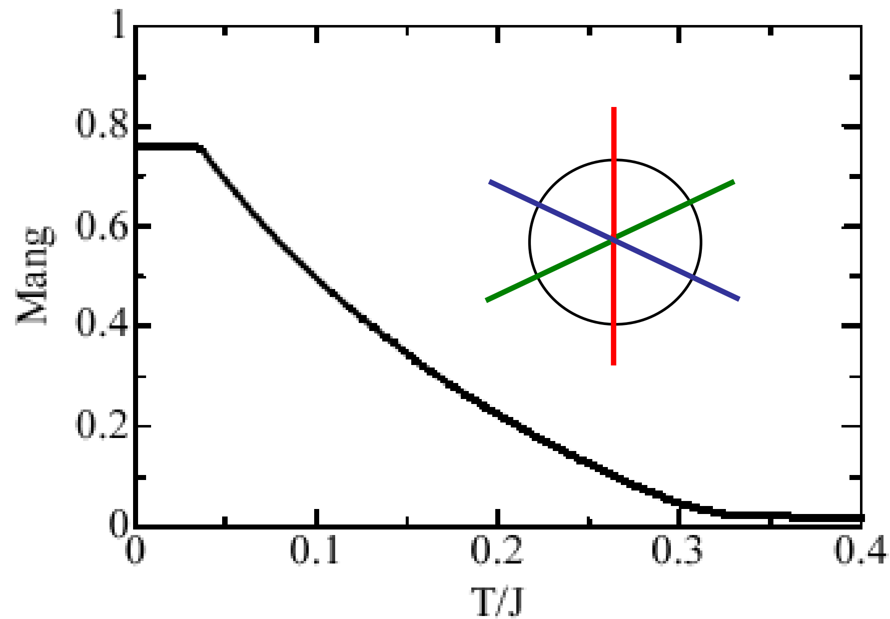
Orbital order parameter

$$M_{\rm OO} = \langle \left((-1)^i T_i \right)^2 \rangle^{1/2}$$



Orbital angle

$$M_{\rm ang} = \langle \left((-1)^i \cos 3\theta_i \right)^2 \rangle^{1/2}$$

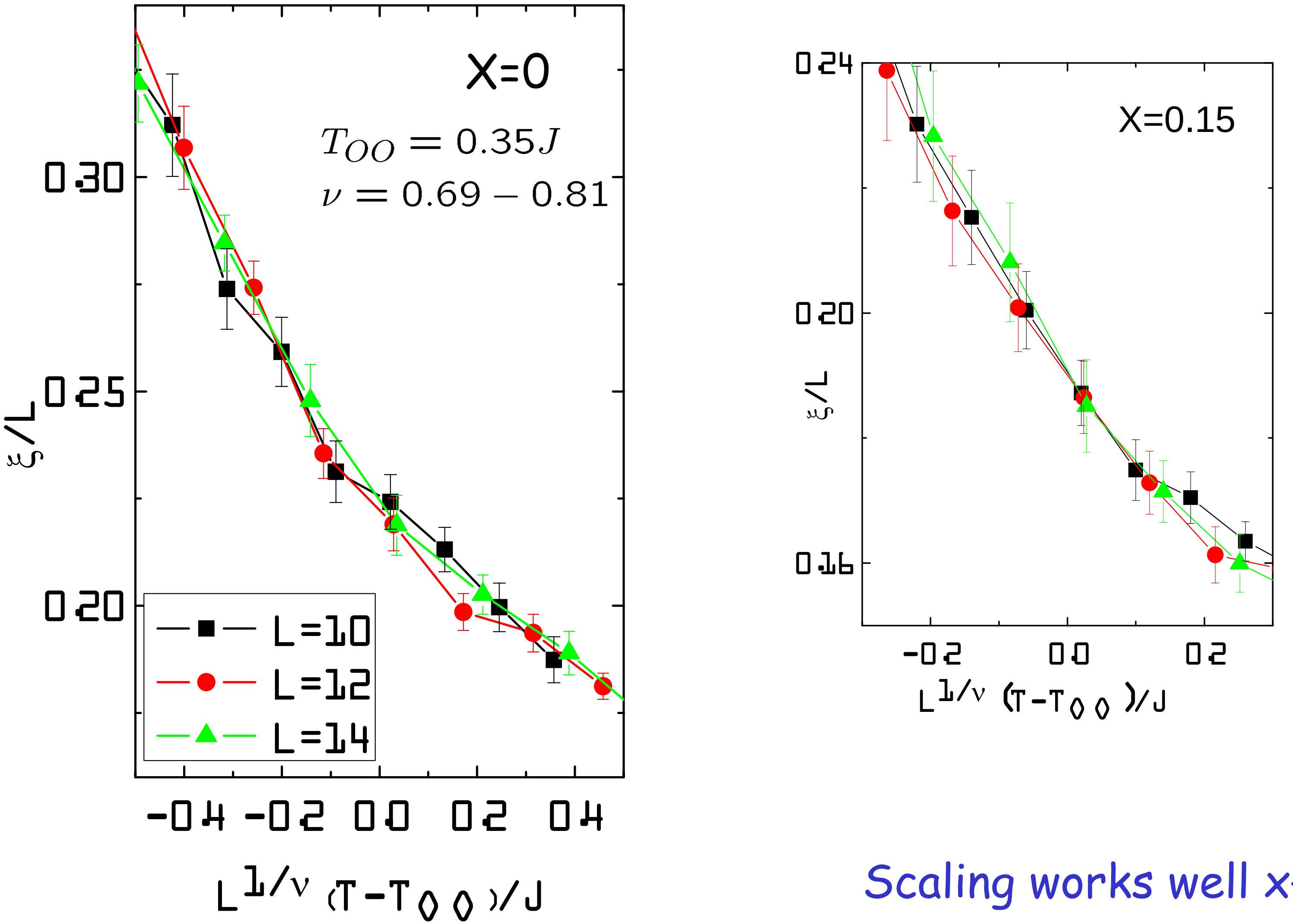


Degeneracy is lifted by fluctuation

$$(\theta_A/\theta_B) = \left(\frac{2\pi n}{3} / \frac{2\pi n}{3} + \pi \right) \quad \vec{Q} = (\pi, \pi, \pi)$$

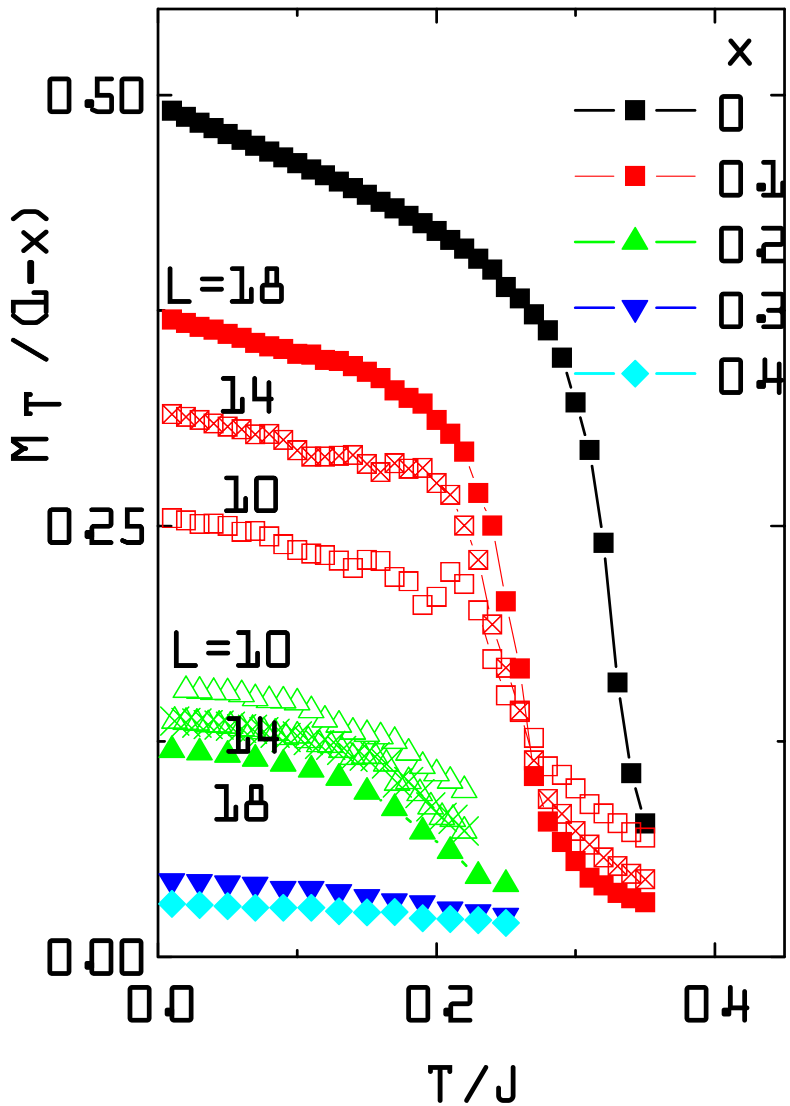
Finite size scaling analyses

Correlation length



Scaling works well x<0.15

Orbital order parameter



$$M_T^2 = \frac{1}{N^2} \sum_{l=x,z} \sum_{i,j} e^{i\vec{Q}\cdot(\vec{r}_i - \vec{r}_j)} \langle T_{il} T_{jl} \rangle$$

- $\frac{M_T}{1-x}$ does not reach to 0.5

x>0.15

$\frac{M_T}{1-x}$ decreases with increasing L

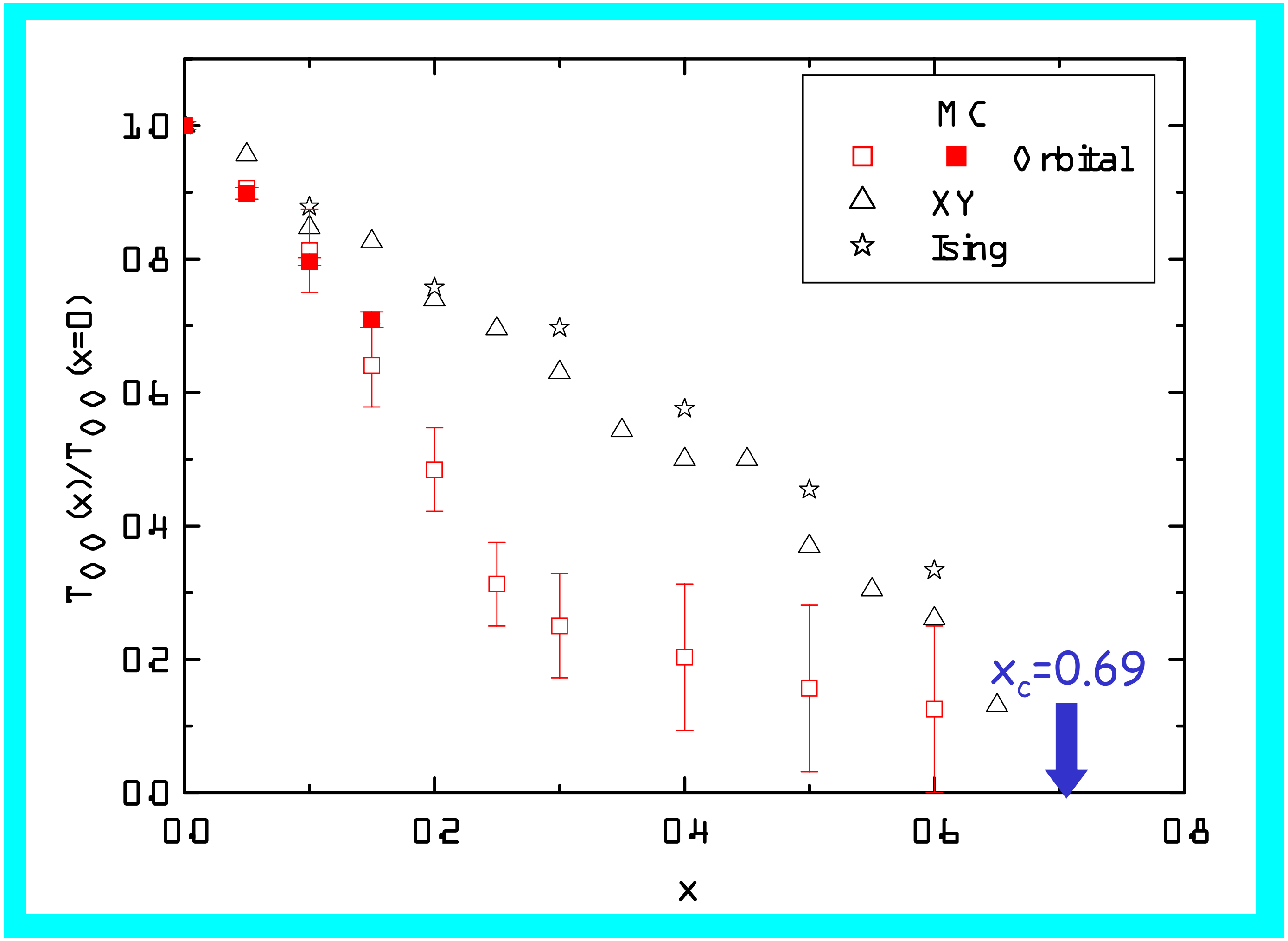
Transition becomes broad

Orbital glass state ?
Short range relaxor ?

c.f. Quadrupole glass by Binder et al.

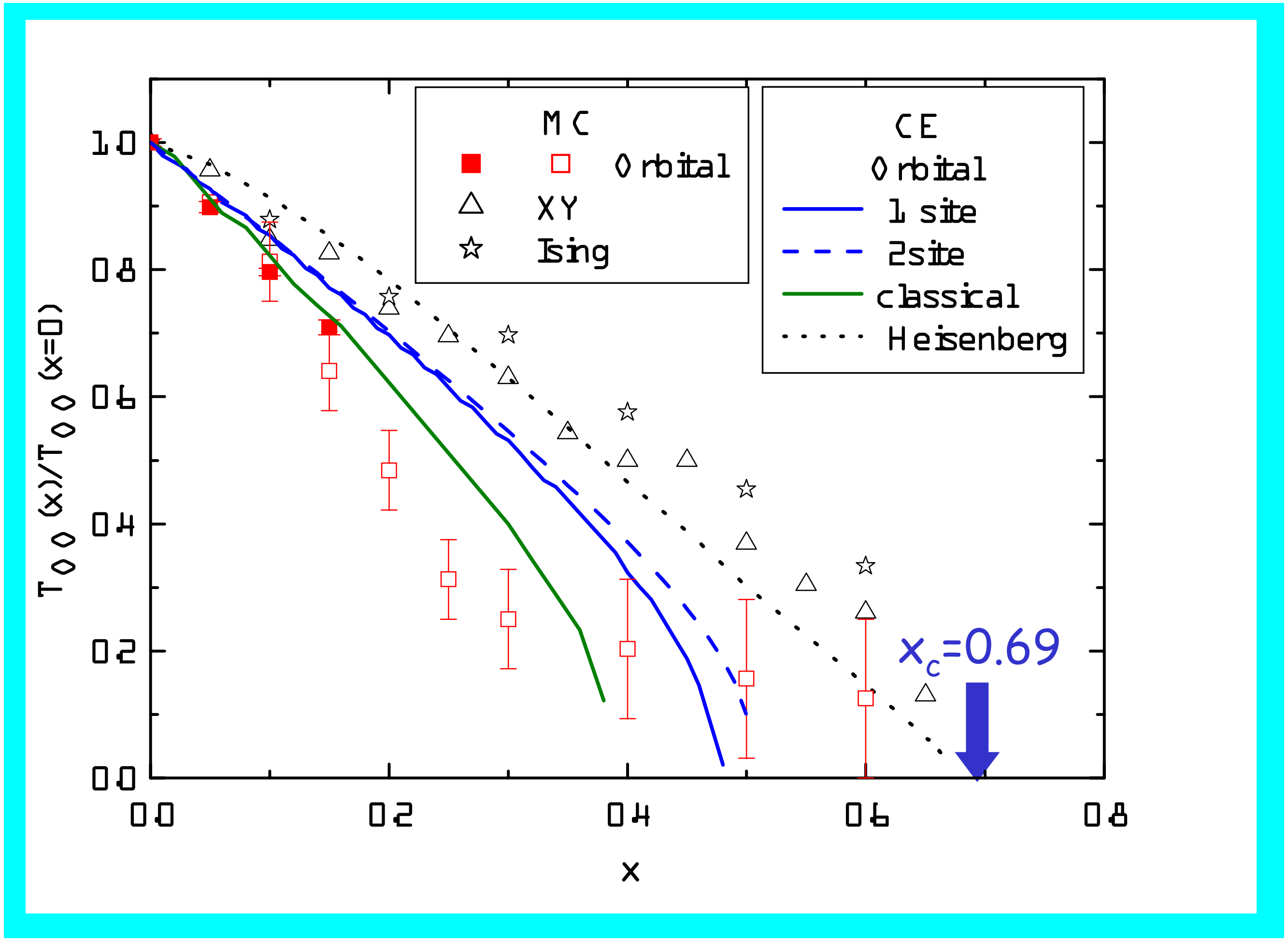
Orbital ordering temperature

Monte Carlo



T_{OO} reduction is more remarkable than that in the spin models

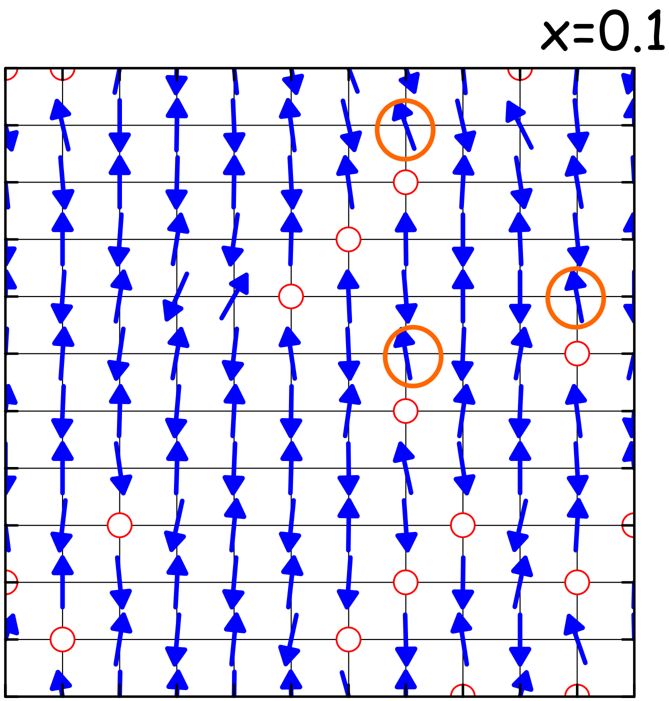
Cluster expansion method

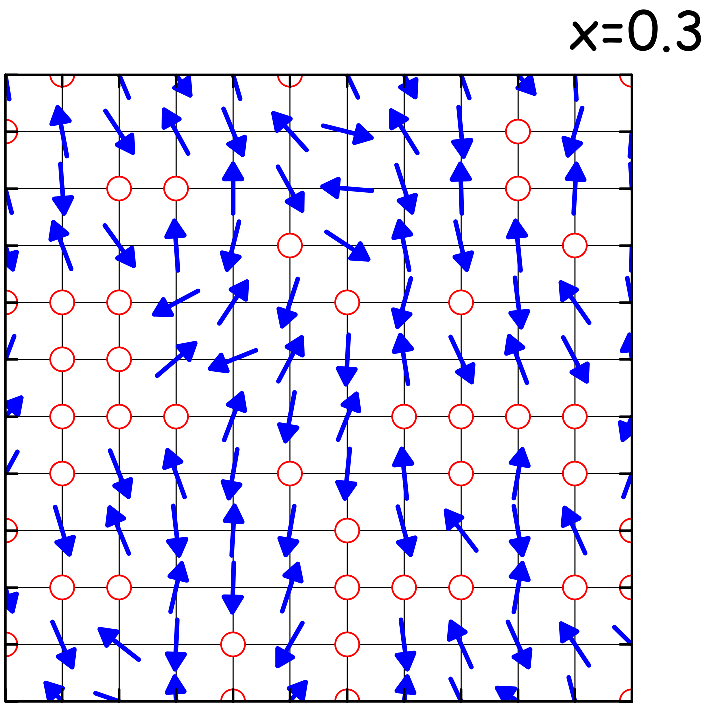


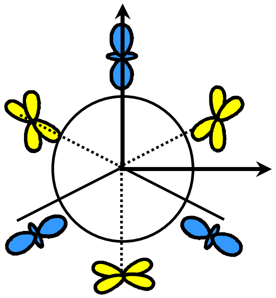
Critical concentration is smaller than the percolation threshold

Psudo-spins around impurity

Snapshot of orbital pseudo-spin



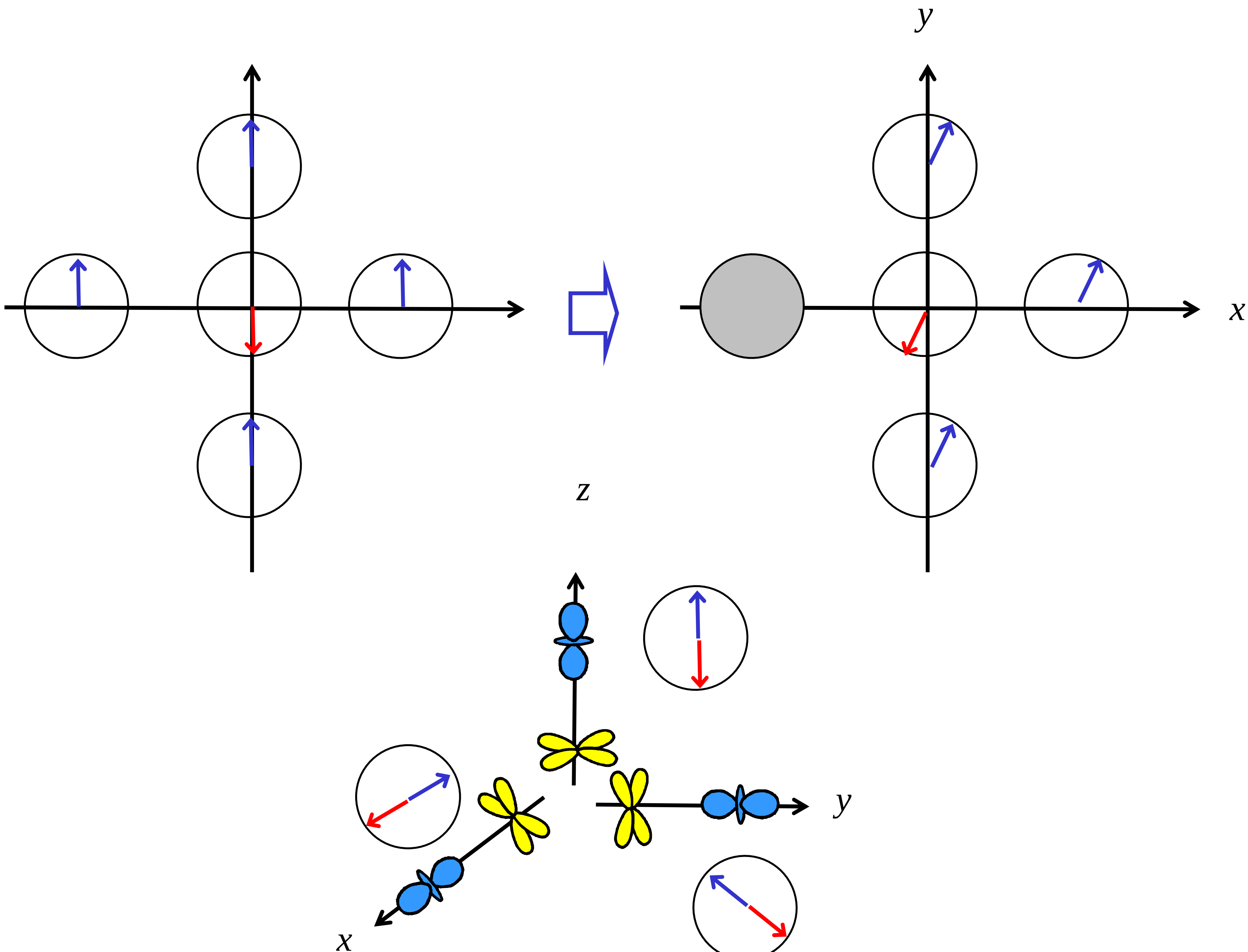




Disturbance of orbitals around impurity sites

⇧

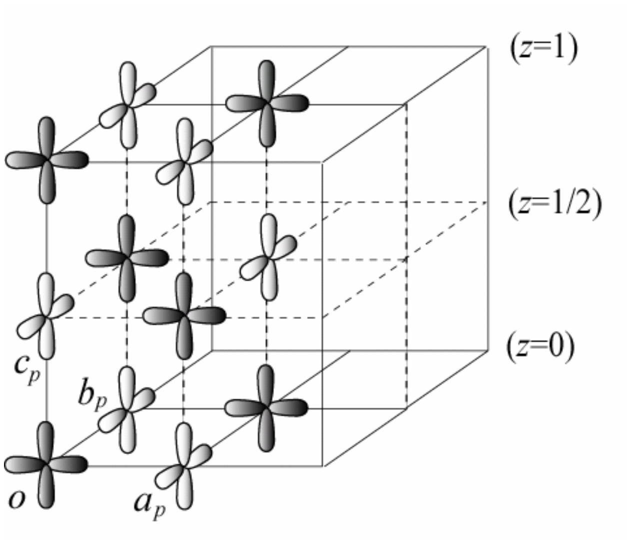
local symmetry breaking



y
x
z
y
x

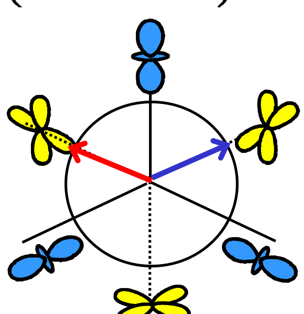
Higher order Jahn-Teller coupling

- Orbital order in $KCuF_3$



$$Q = (\pi, \pi, \pi)$$

$$d(y^2 - z^2)/d(z^2 - x^2)$$



Orbital cant

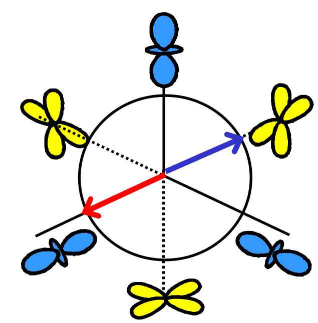
- Orbital model

$$\mathcal{H} = 2J \sum_{\langle ij \rangle} \tau_i^l \tau_j^l$$

$$Q = (\pi, \pi, \pi)$$

$$(\theta_A/\theta_B) = \left(\frac{2\pi n}{3} / \frac{2\pi n}{3} + \pi\right)$$

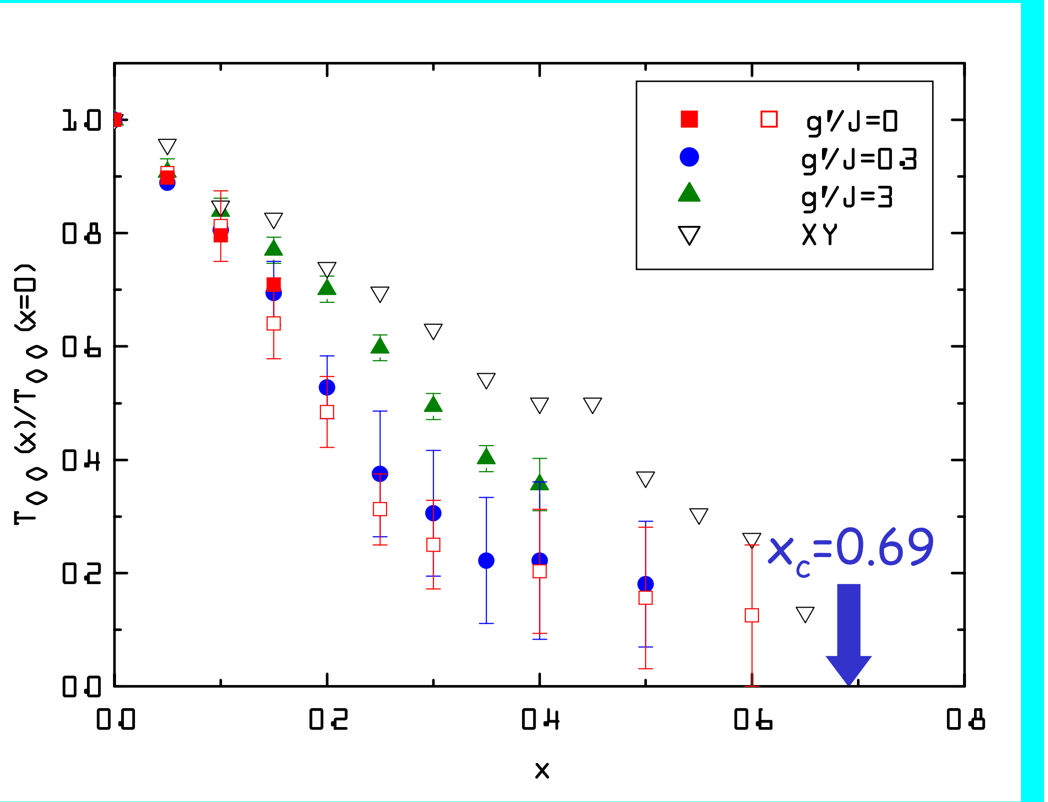
Orbital AF



⇩

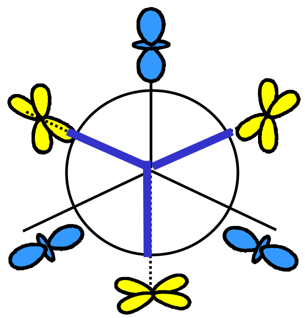
Higher order JT coupling

Higher order Jahn-Teller coupling



$$\mathcal{H}_{HJT} = g_H \sum_i \{ \left(Q_{iz}^2 - Q_{ix}^2 \right) T_{iz} - 2Q_{iz}Q_{ix}T_{ix} \}$$

Anisotropy in orbital space



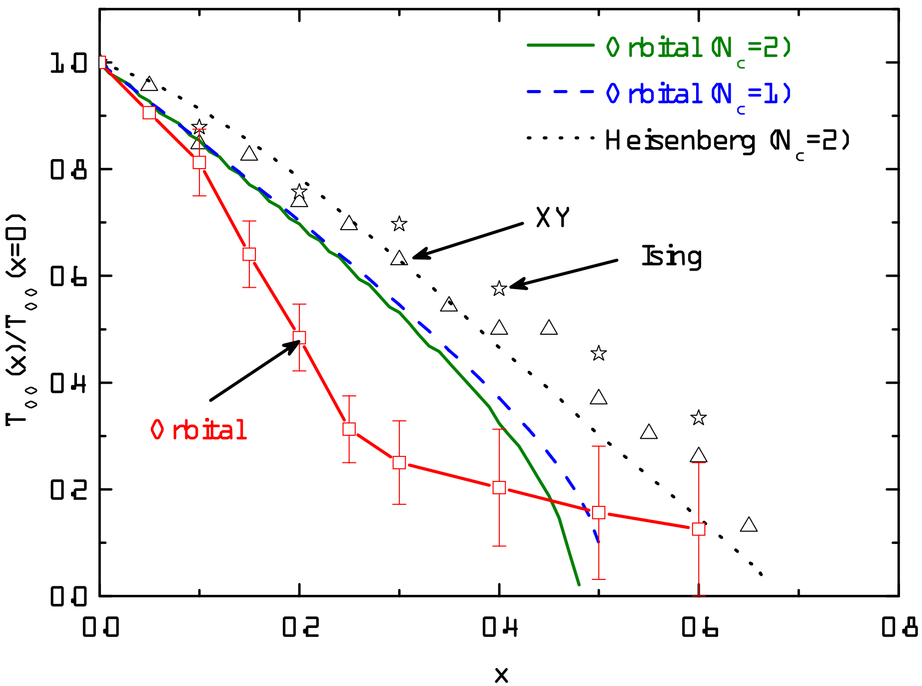
$g'/J \sim 0.3$ in $KCuF_3$

Suppression of the orbital tilting by impurity

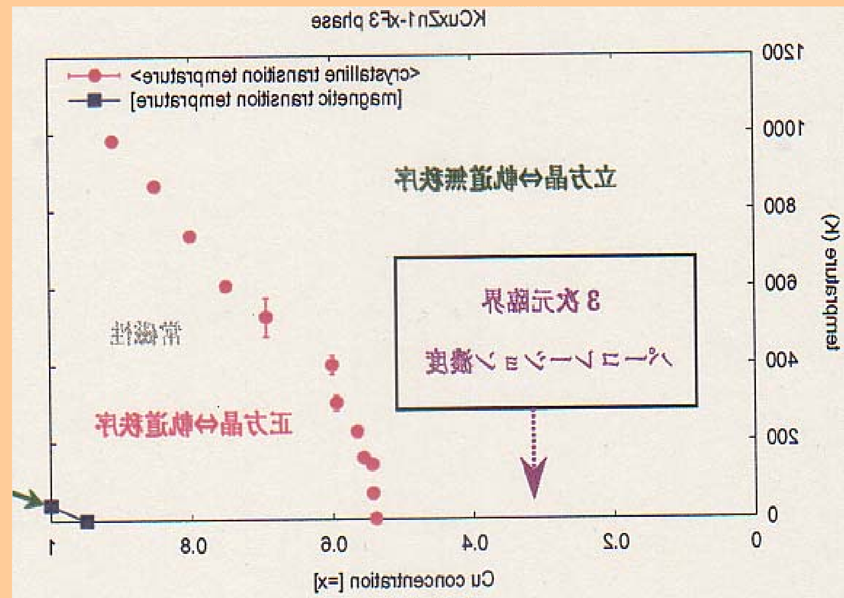
Rapid reduction of $T_{OO}(x)$ survives under higher-order JT.

Comparison with experiments

Theory



Experiments (Murakami G)



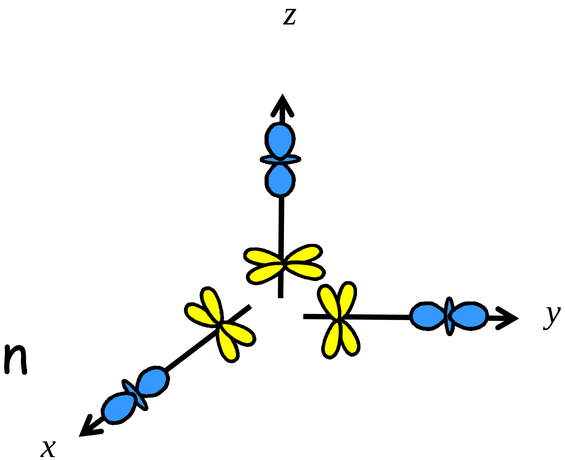
Qualitatively consistent with experiments

3. Quantum effects in dilute orbital system

"e_g Orbital model" in a 3-dim. cubic lattice

$$\mathcal{H} = J \sum_i \left(\tau_i^x \tau_{i+\hat{x}}^x + \tau_i^y \tau_{i+\hat{y}}^y + \tau_i^z \tau_{i+\hat{z}}^z \right)$$

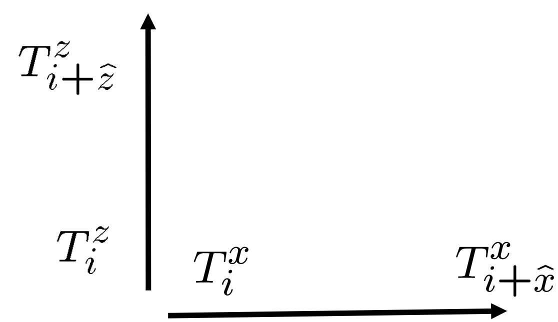
$$\tau_i^l = \cos\left(\frac{2\pi}{3} n_l\right) T_{iz} + \sin\left(\frac{2\pi}{3} n_l\right) T_{ix},$$



Classical treatment for pseudo-spin

"Orbital compass model" in a 2-dim. square lattice

$$\mathcal{H} = J \sum_i \left(T_i^x T_{i+\hat{x}}^x + T_i^z T_{i+\hat{z}}^z \right)$$



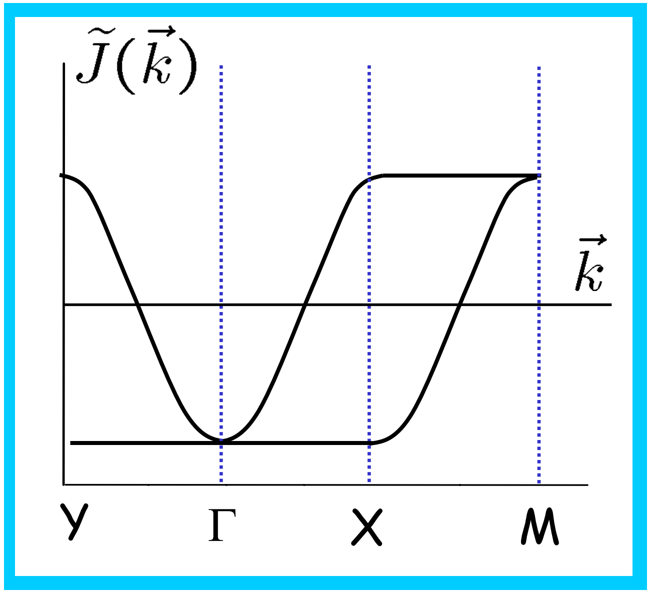
Quantum effects in orbital dilution

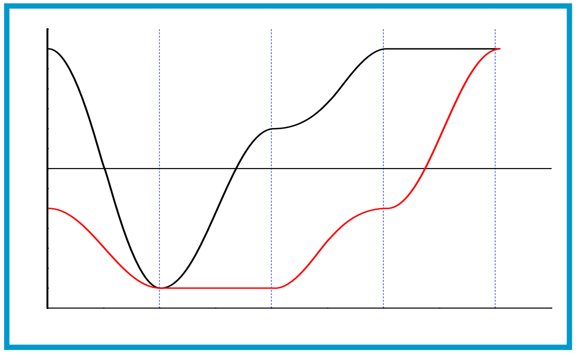
Kugel-Khomskii JETP (73), Khomskii-Mostovoy J. Phys (03)

Two dimensional compass model

Momentum dependence of orbital interaction

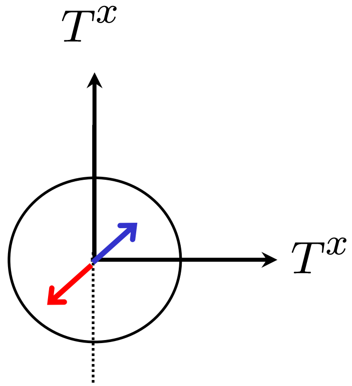
e_g-orbital model in a cubic lattice





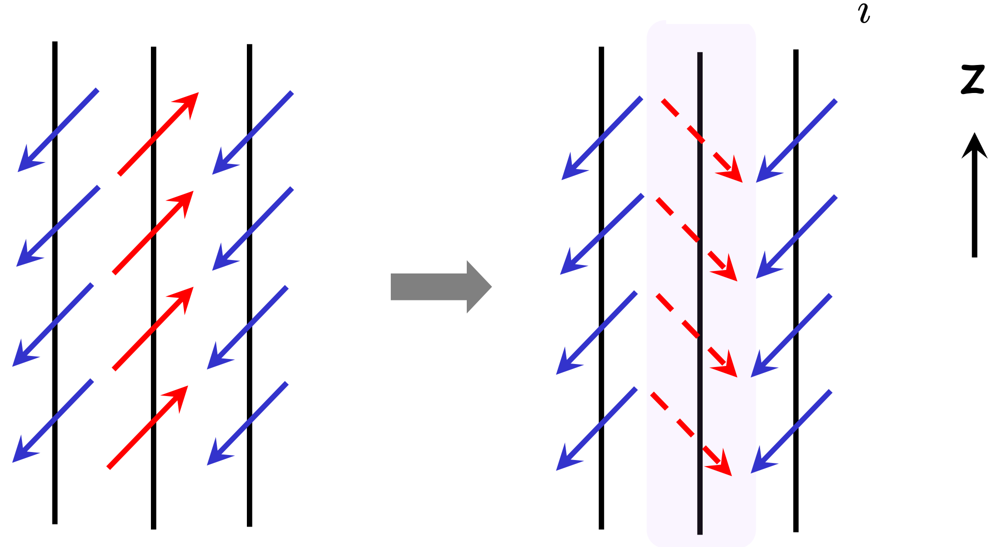
<u>Classical ground state</u>:

continuous rotational symmetry



Symmetry in "Hamiltonian"

$$\mathcal{H} = J\sum_i \left(T_i^x T_{i+\hat{x}}^x + T_i^z T_{i+\hat{z}}^z\right)$$

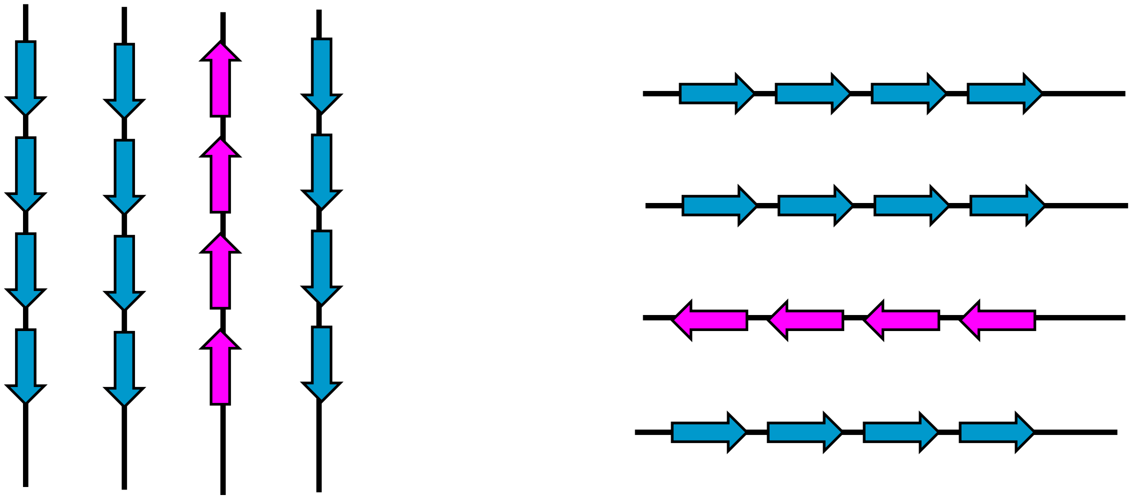


Hamiltonian is invariant
under the transformation of $T^z \to -T^z$ at each column

Mishra et al PRL(04), Nussinov et al. EPL(04),
Dorier et al. PRB('05), Doucot et al. PRB(05)

Conventional orbital order does not appear
(Elitzur's theorem)

Directional order



Directional order

: T^x (T^z) correlation along x (z) direction

$$D = N^{-1} \sum_i \left(T_i^x T_{i+\hat{x}}^x - T_i^z T_{i+\hat{z}}^z \right)$$

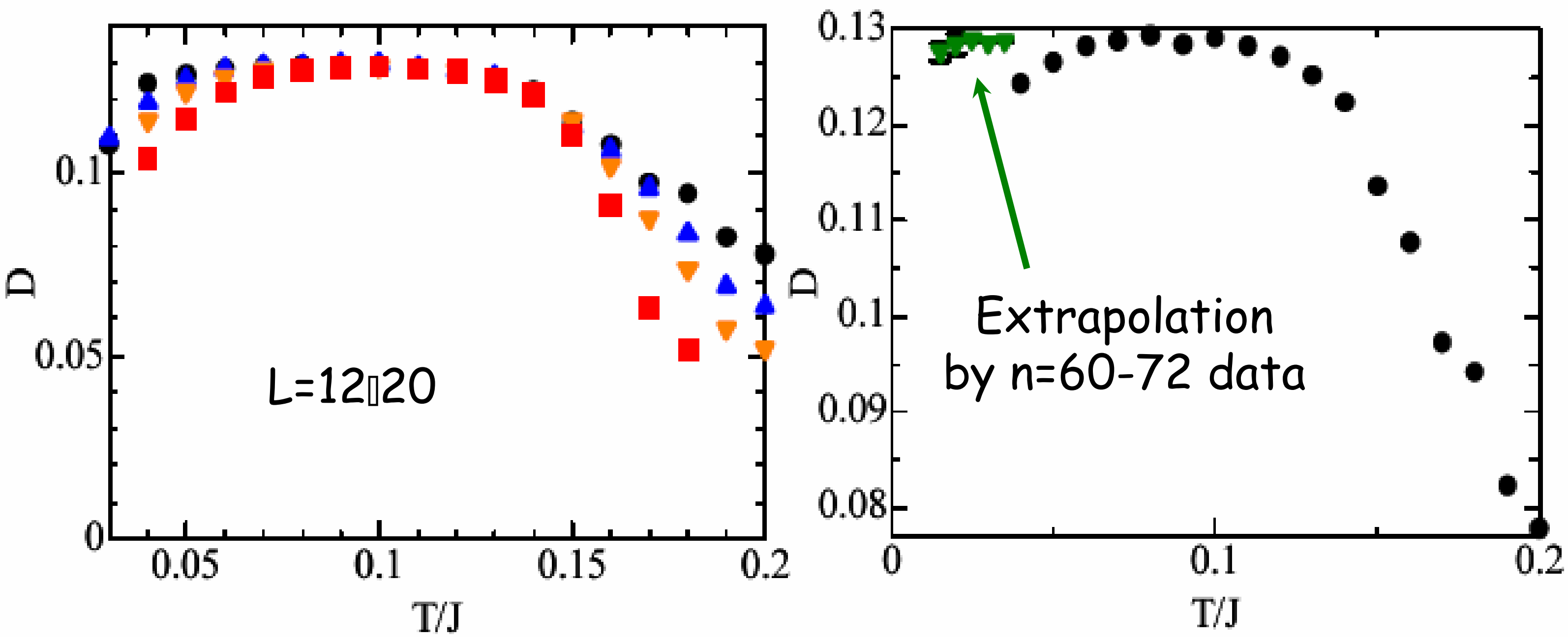
Mishra et al PRL(04) Classical
Dorier et al. PRB('05) T=0
Doucot et al. PRB(05) T=0

Quantum Monte Carlo

X=0

N=L×L sites (L=14-18)
Periodic boundary
Trotter number n=12-22 & 66-72

Directional order parameter



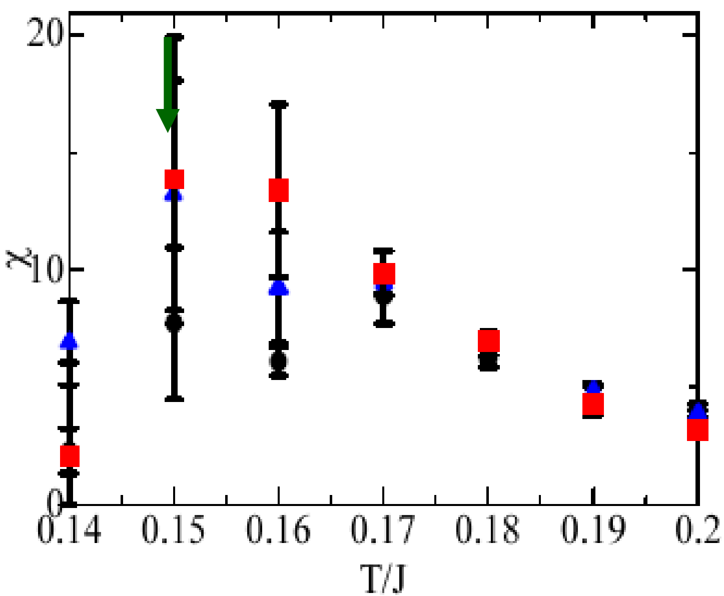
Saturated value $D(T \to 0) \sim 0.13 << 0.25$

Quantum Monte Carlo

X=0

Susceptibility

$$\chi = \frac{1}{NT}\left(\langle D^2\rangle - \langle D\rangle^2\right)$$

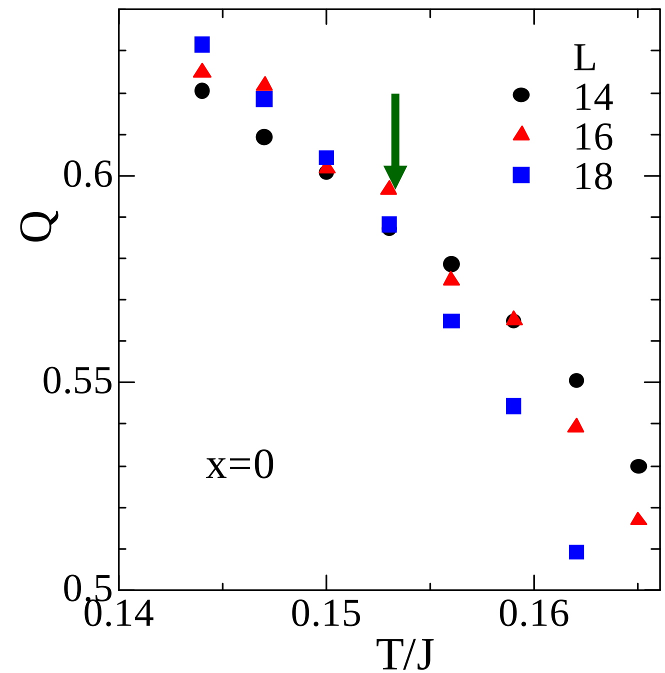


Binder cumulant

$$Q = 1 - \frac{\langle D^4\rangle}{3\langle D^2\rangle^2}$$

0 $T >> T_c$

2/3 $T << T_c$

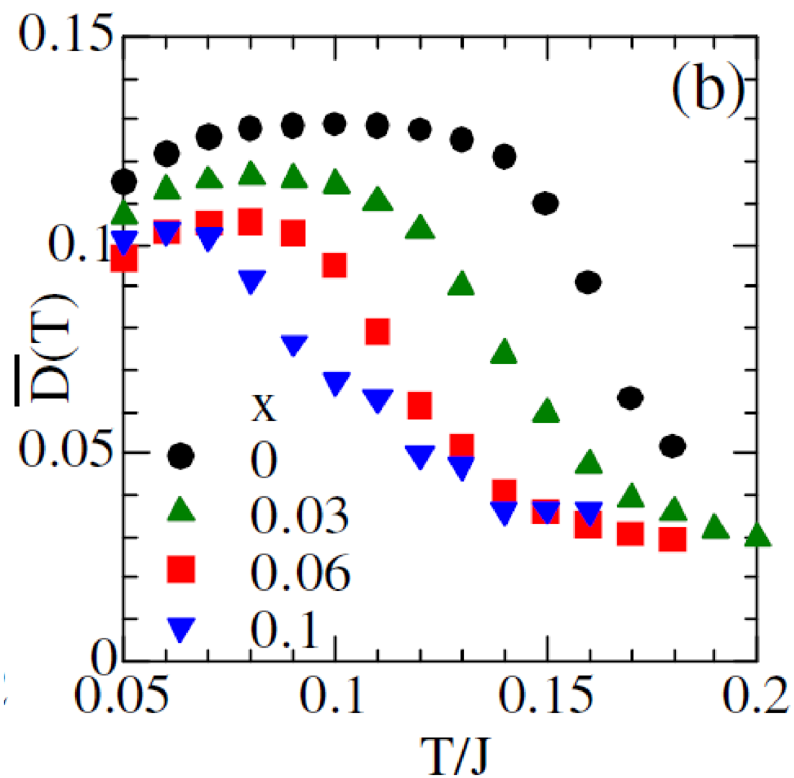


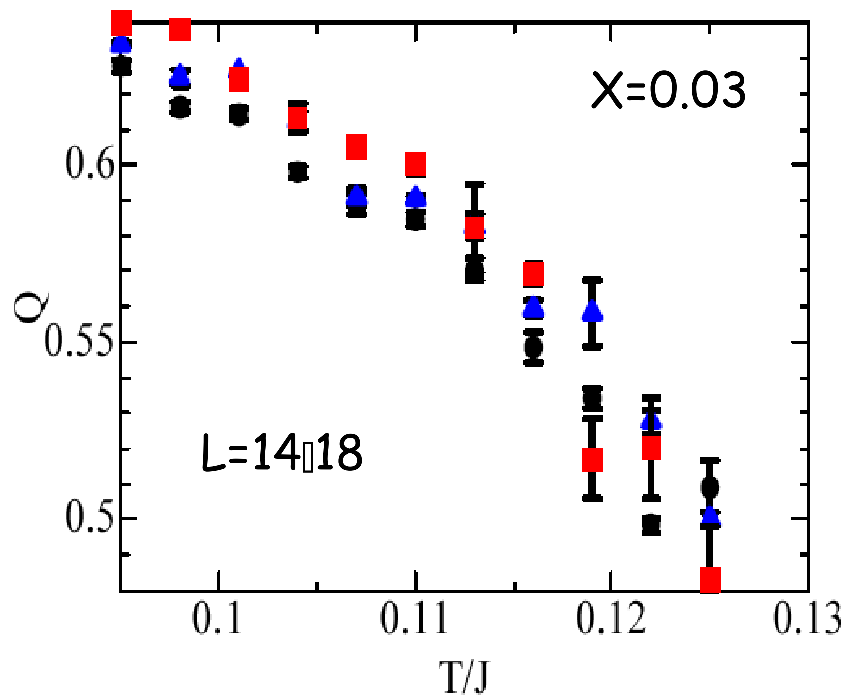
$T_c(\text{directional order}) = 0.15J$

Doping of impurity in directional order

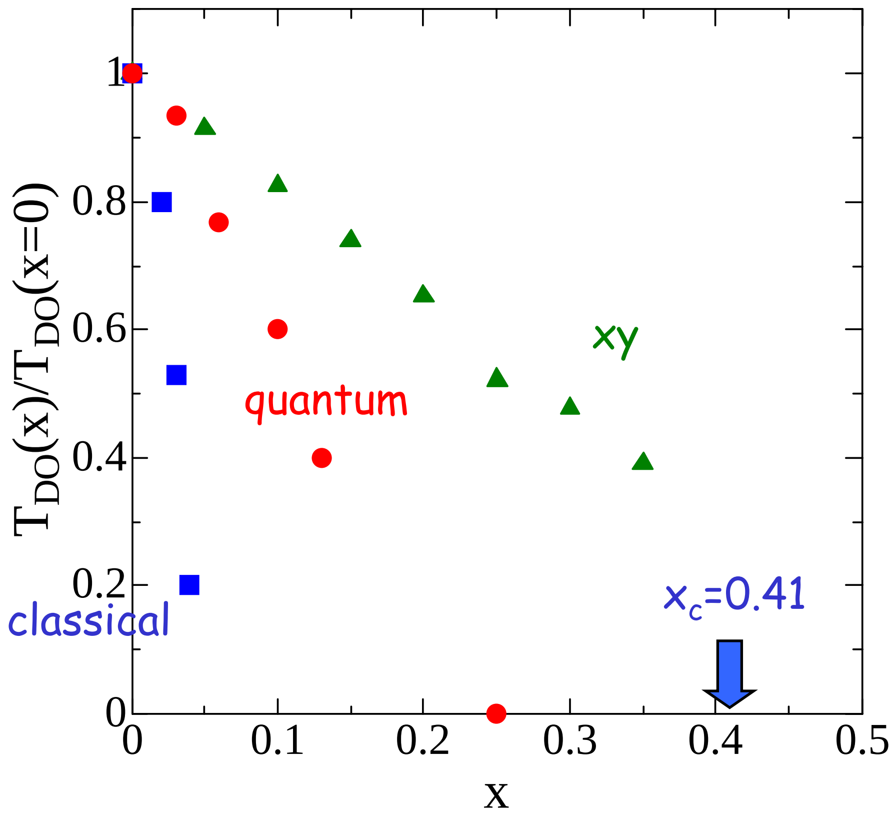
Directional order parameter

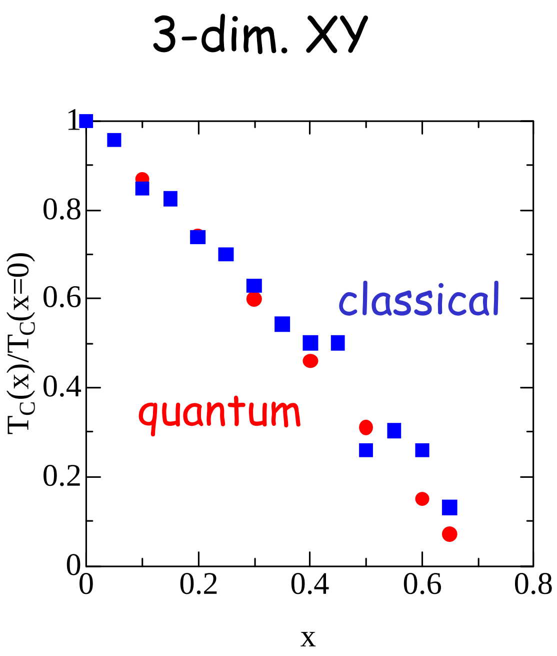
Binder cumulant $Q = 1 - \frac{\langle D^4 \rangle}{3\langle D^2 \rangle^2}$



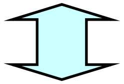


Impurity effects in directional order





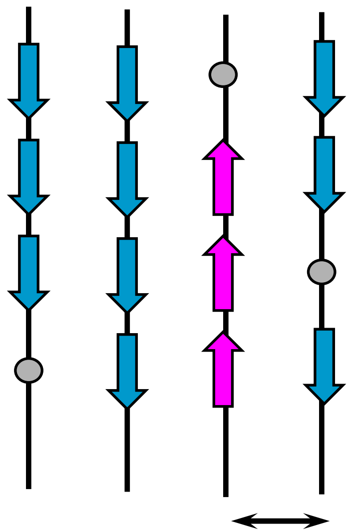
Quantum ordered state is more robust against dilution



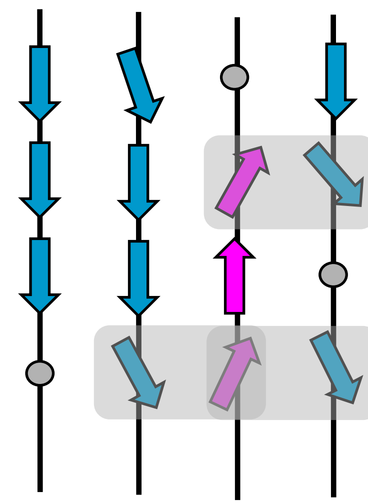
Quantum fluctuation destroys long range order

Directional order

Directional order $D = N^{-1} \sum_i \left(T_i^x T_{i+\hat{x}}^x - T_i^z T_{i+\hat{z}}^z \right)$



$\langle T_i^x T_{i+\hat{x}}^x \rangle \sim 0$



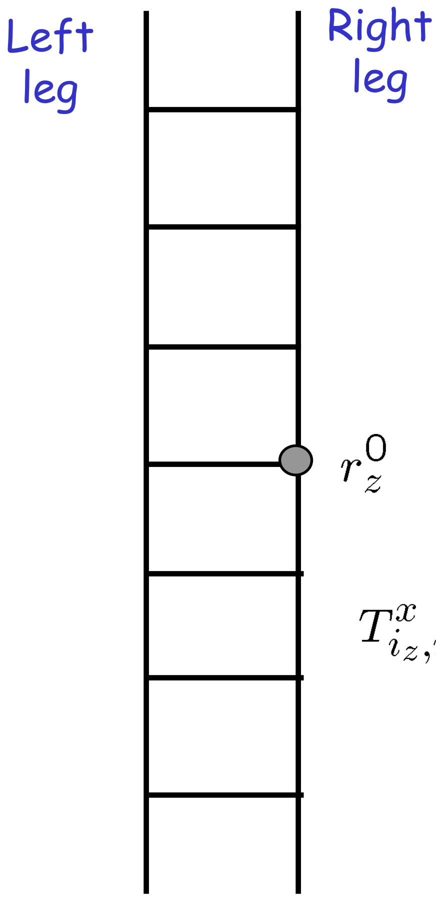
Classical Directional order

Almost 1-dim. in low T

Quantum fluctuation

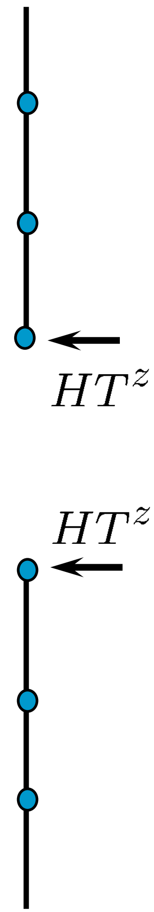
Effective dimensionality increases

Compass model in two leg ladder



$$T^x_{i_z,right}T^x_{i_z,left} \to \frac{1}{2}S^z_{i_z}$$

$$T^z_{i_z} \to S^x_{i_z}$$



Transverse Ising-model
in a chain
with Tz magnetic filed

$$\begin{aligned} \mathcal{H}_{eff} &= -4J\sum_{r_z}{}' S^x_{r_z}S^x_{r_z+1} \\ &- J\sum_{r_z\neq r_z^0} S^z_{r_z} \\ &\pm J(S^x_{r_z^0+1}+S^x_{r_z^0-1}), \end{aligned}$$

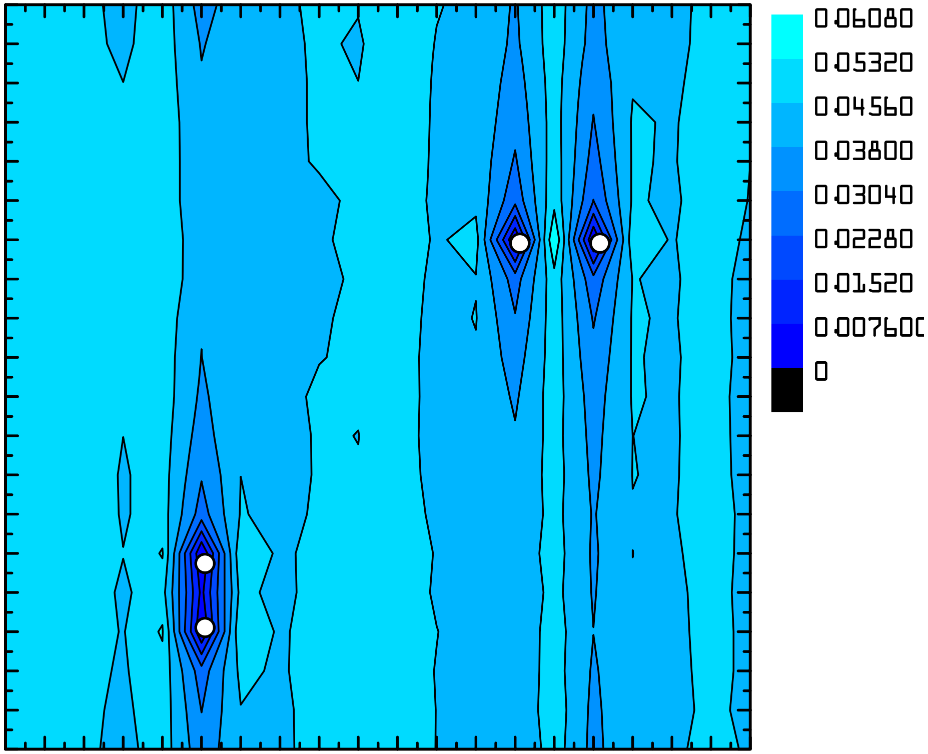
Compass model
in a two-leg ladder
with vacancy

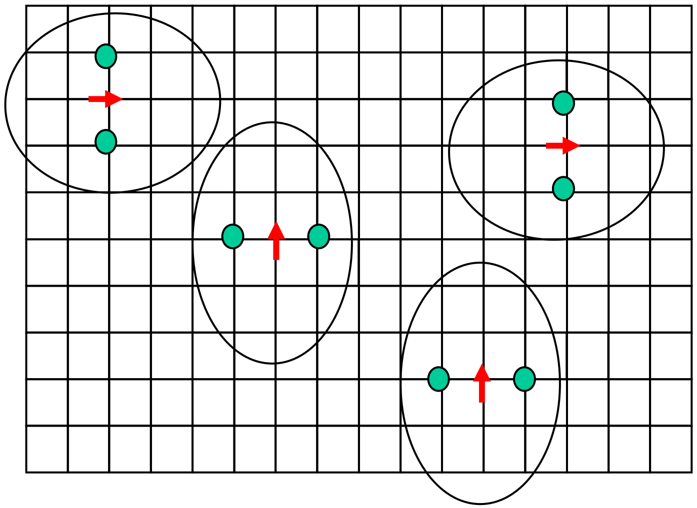
Tz correlation
increases

Local orbital state around impurity

Local static correlation function for pseudo-spin

$$C^{zz}(\vec{r}_i) = \frac{1}{N(1-x)} \sum_j \langle T_i^z T_j^z \rangle$$





Summary

Dilution effects in the orbital systems

1. Orbital order is collapsed rapidly in comparison with dilute magnets/percolation theory
   PRL 95, 2672048 (2005)

2. Spin structure is changed from A-AFM to FM by orbital dilution

3. Quantum effects make order robust against dilution
   PRL 98, 256402 (2007)

Impurity in orbital system is “not” a simple vacancy