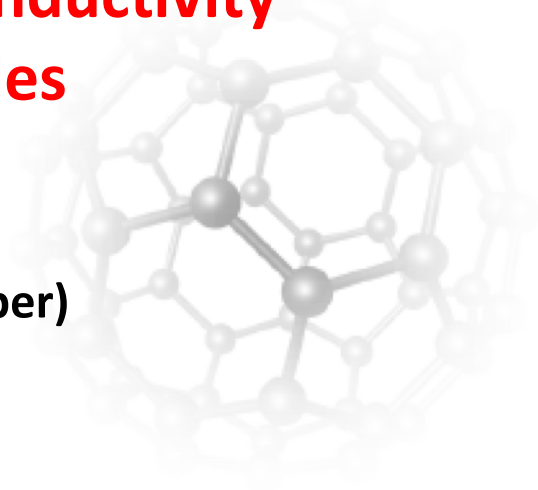
27/09/2016
NGSCES2016

Exotic high-T_c *s*-wave superconductivity in alkali-doped fullerides



Yusuke Nomura

University of Tokyo (from September)
Before: École polytechnique

In collaboration with
S. Sakai, M. Capone, R. Arita,
M. Kim, P. Seth, O. Parcollet, M. Ferrero, A. Georges,
K. Steiner, S. Hoshino, and P. Werner

References:

YN *et al.*, Science Advances 1, e1500568 (2015)
YN *et al.*, J. Phys.: Condens. Matter 28, 153001 (2016)
M. Kim *et al.*, arXiv:1606.05796
K. Steiner *et al.*, Phys. Rev. B 92, 115123 (2015)

Outline

1. understanding of equilibrium phase diagram of fullerides
   → degenerate 3-orbital model (half-filling)

2. understanding of nonequilibrium phase diagram
   → degenerate 3-orbital model (half-filling) + perturbations

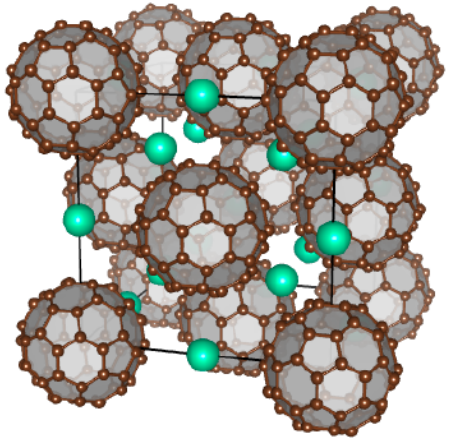
   Minjae's talk (yesterday)

3. Orbital freezing and its relation to SC
   → degenerate 2-orbital model away from half-filling

Some keywords: negative (inverted) Hund's coupling, orbital fluctuation

Alkali-doped fullerides

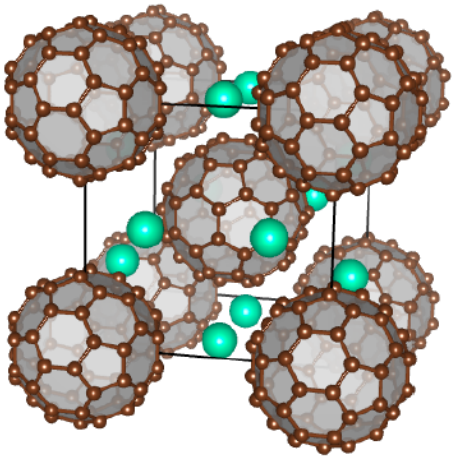
- fcc A_3C_{60} (A=K, Rb, Cs)



K_3C_{60} : T_c = 19 K
Rb_3C_{60} : T_c = 29 K
Cs_3C_{60} : T_c = 35 K

O.Gunnarsson Rev.Mod.Phys. 69, 575 (1997)
Ganin et al, Nature 466,221(2010)

- A15 Cs_3C_{60}



T_c = 38 K

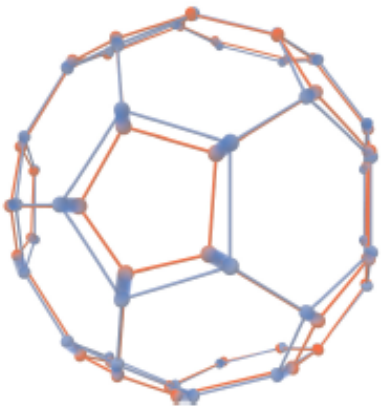
A.Ganin et al Nature Mater. 7,367-371(2008)
Y.Takabayashi et al Science 323,1285-1590(2009)

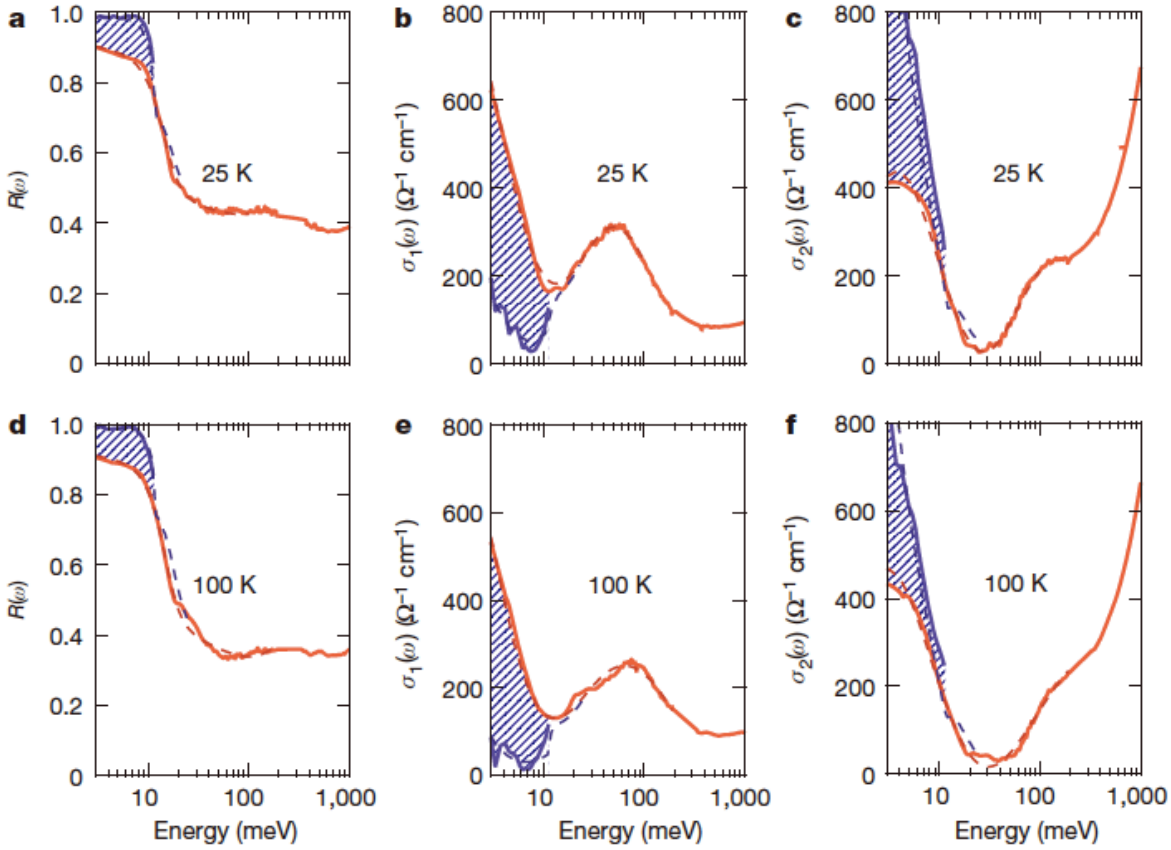
- ✓ Highest T_c among molecular superconductors
- ✓ For a review, see e.g. O. Gunnarsson 1997 (RMP), 2004 (book)

Possible light–induced superconductivity in K_3C_{60} at high temperature

M. Mitrano[1], A. Cantaluppi[1,2], D. Nicoletti[1,2], S. Kaiser[1], A. Perucchi[3], S. Lupi[4], P. Di Pietro[3], D. Pontiroli[5], M. Riccò[5], S. R. Clark[1,6,7], D. Jaksch[7,8] & A. Cavalleri[1,2,7]

Nature 530, 461 (2016)



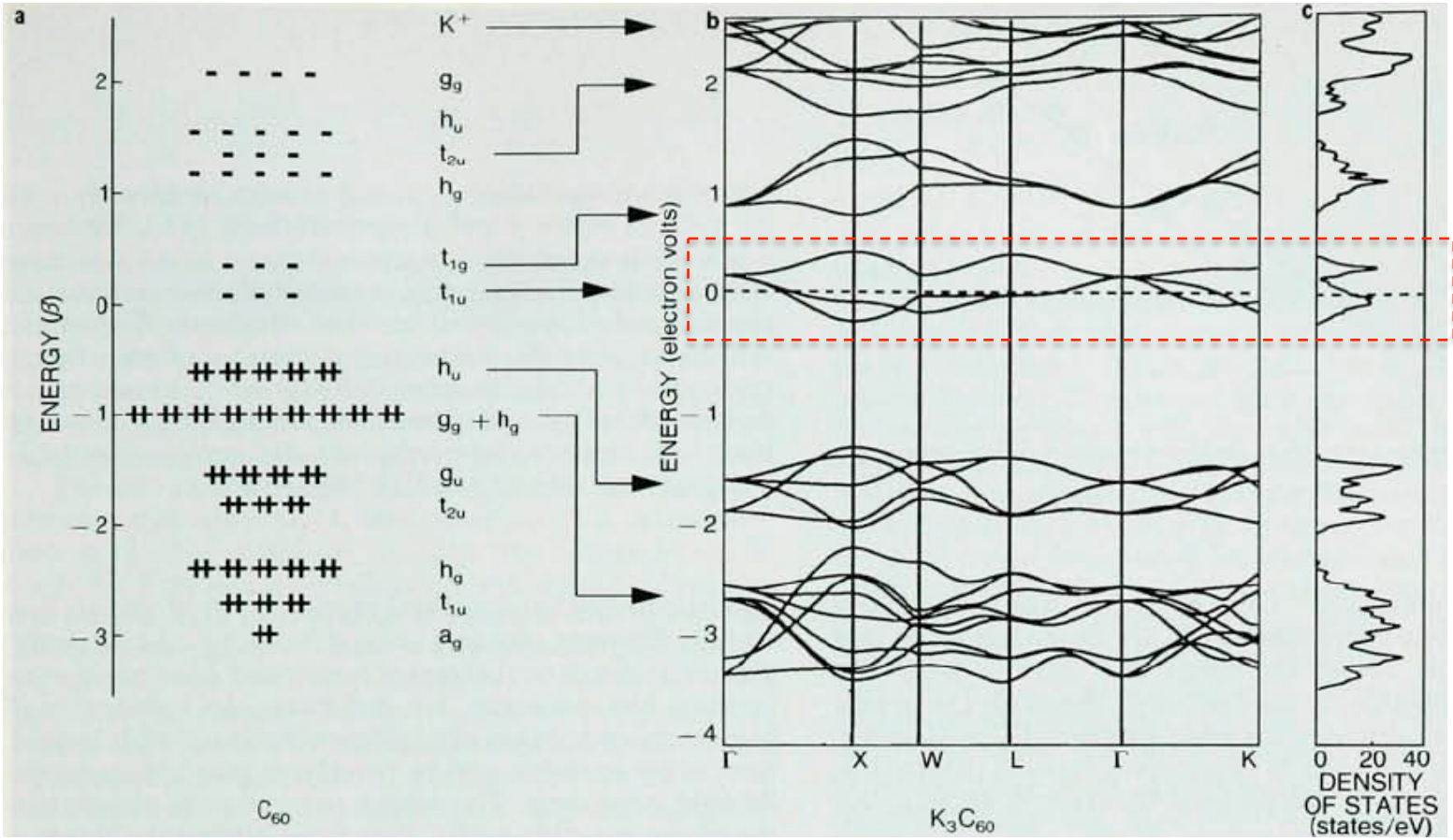


Talks by Stephen, Matteo, and Minjae (yesterday)

Electronic structure

S. C. Erwin, W. E. Pickett, Science 254, 842 (1991); A. F. Hebard, Physics Today 45, 26 (1992)

Band structure (fcc system)



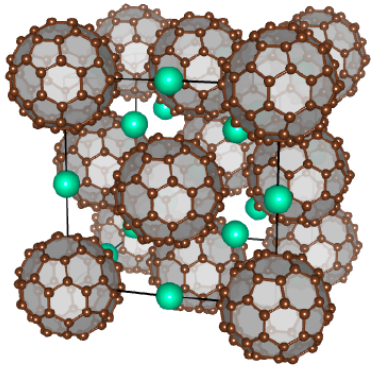
LUMO band
$W \sim 0.5$eV

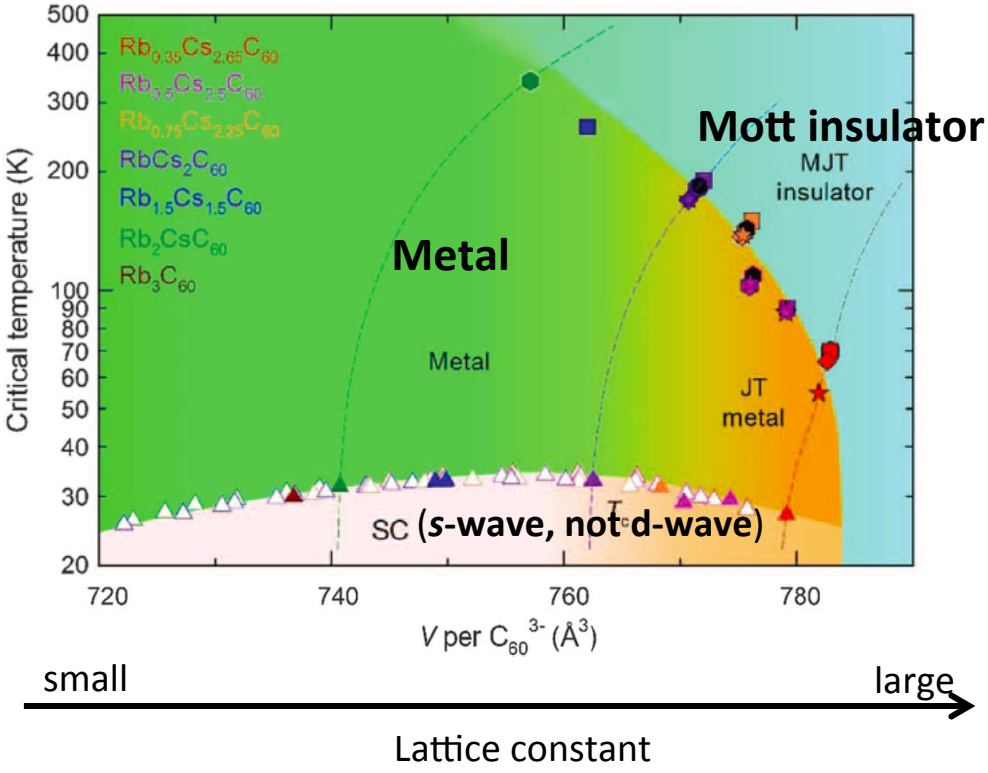
- ✓ 3 orbital, half-filled
- ✓ Molecular orbital + small hopping between them

Phase diagram of fcc A_3C_{60} (A = K, Rb, Cs)

Zadik *et al.*, Sci. Adv. **1**, e1500059 (2015); Ihara *et al.*, PRL **104**, 256402 (2010).
Kawasaki *et al.*, JPSJ **82**, 014709 (2013)

Crystal structure





- Mott insulating phase: induced by repulsive interaction
- *s*-wave superconductivity (T_c ~ 35K, very high for small bandwidth): induced by attractive interaction
- Low-spin state and dynamical Jahn-Teller effect in Mott phase (positive Hund's coupling should favor high-spin state)

Motivation

- Unified description of the phase diagram
  - Pairing mechanism?
  - Why s-wave? (naïvely, strong correlation is incompatible with *s*-wave)
  - Origin of low-spin state?

- Fully *ab initio* calculation of superconducting transition temperature T_c
  - Previous methods have often employed empirical parameters
  - No reliable way to calculate T_c for unconventional superconductors

Understanding of equilibrium SC

→ firm basis for understanding non equilibrium phenomena

Outline

(first part: understanding of equilibrium phase diagram of fullerides)

✓ Method: DFT + DMFT (density-functional theory + dynamical mean-field theory)

→ Construction of realistic Hamiltonian and DMFT analysis

DMFT is particularly powerful in the case of fcc lattice with $z = 12$

A. I. Lichtenstein and M. I. Katsnelson Phys. Rev. B 57, 6884 (1998)
G. Kotliar et al., Rev. Mod. Phys. 78, 865 (2006)
K. Held, Adv. Phys. 56, 829 (2007).

We show that the system has unusual form of intramolecular interaction with strongly repulsive Hubbard and weakly negative exchange interactions

→ unusual cooperation between strong correlations and phonons

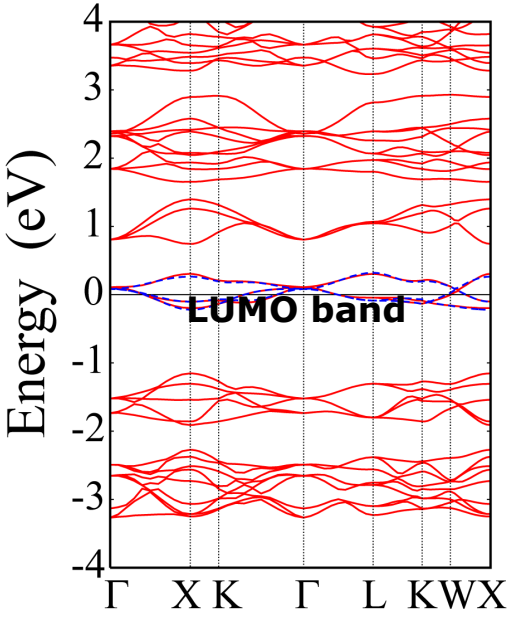
(proposed by Massimo Capone et al.)

Unconventional mechanism !

Capone *el al*., RMP 81, 943 (2009); Capone *et al*., Science 296, 2364 (2002).
Capone *et al*,. PRL 86, 5361-5364 (2001); YN *et al*, Sci. Adv. 1, e1500568 (2015).

Ab initio derivation of realistic low-energy Hamiltonian

- Low-energy Hamiltonians for C_{60} superconductors (3 orbital, half-filled)



$$\mathcal{H} = \sum_{\mathbf{k}} \sum_{ij} \left[\mathcal{H}_0^{(\mathrm{w})}(\mathbf{k})\right]_{ij} c_{i\mathbf{k}}^{\sigma\dagger} c_{j\mathbf{k}}^{\sigma} + \sum_{\mathbf{q}} \sum_{\mathbf{k}\mathbf{k}'} \sum_{ij,i'j'} \sum_{\sigma\sigma'} U_{ij,i'j'}^{(p)}(\mathbf{q}) c_{i\mathbf{k}+\mathbf{q}}^{\sigma\dagger} c_{i'\mathbf{k}'}^{\sigma'\dagger} c_{j'\mathbf{k}'+\mathbf{q}}^{\sigma'} c_{j\mathbf{k}}^{\sigma}$$
$$+ \sum_{\mathbf{q}\nu} \sum_{\mathbf{k}} \sum_{ij} \sum_{\sigma} g_{ij}^{(p)\nu}(\mathbf{k},\mathbf{q}) c_{i\mathbf{k}+\mathbf{q}}^{\sigma\dagger} c_{j\mathbf{k}}^{\sigma} \left(b_{\mathbf{q}\nu} + b_{-\mathbf{q}\nu}^{\dagger}\right) + \sum_{\mathbf{q}\nu} \omega_{\mathbf{q}\nu}^{(p)} b_{\mathbf{q}\nu}^{\dagger} b_{\mathbf{q}\nu}$$

- Electronic one-body part (red): realistic hopping from DFT
- Coulomb interaction part (green): cRPA method

  Lewin's talk (yesterday)
- Phonon (lattice vibration) part (blue): cDFPT method

All the parameters are calculated by *ab initio* methods, not determined by hand

YN et al,, PRB **85**, 155452 (2012); **YN** et al., PRL **112**, 027002 (2014); **YN** and R. Arita PRB **92**, 245108 (2015)

Comparison between cRPA and cDFPT

YN et al., PRL **112**, 027002 (2014); YN and R. Arita PRB 92, 245108 (2015)

- Constrained random phase approximation (cRPA)

$$W^{(f)} = \left(1 - v\chi^0\right)^{-1} v \quad \xrightarrow{\chi^0 = \chi_t^0 + \chi_r^0} \quad \begin{cases} W^{(p)} = \left(1 - v\chi_r^0\right)^{-1} v \\ W^{(f)} = \left(1 - W^{(p)}\chi_t^0\right)^{-1} W^{(p)} \end{cases}$$

- Constrained density-functional perturbation theory (cDFPT)

  - Electron-phonon coupling

$$g^{(f)} = \left(1 - \tilde{v}\chi^0\right)^{-1} g^{(b)} \quad \xrightarrow{\chi^0 = \chi_t^0 + \chi_r^0} \quad \begin{cases} g^{(p)} = \left(1 - \tilde{v}\chi_r^0\right)^{-1} g^{(b)} \\ g^{(f)} = \left(1 - \tilde{W}^{(p)}\chi_t^0\right)^{-1} g^{(p)} \end{cases}$$

$$\tilde{v} = v + K_{\mathrm{xc}} \quad \tilde{W}^{(p)} = \left(1 - \tilde{v}\chi_r^0\right)^{-1} \tilde{v}$$

  - Phonon frequency (given by pole of *D*)

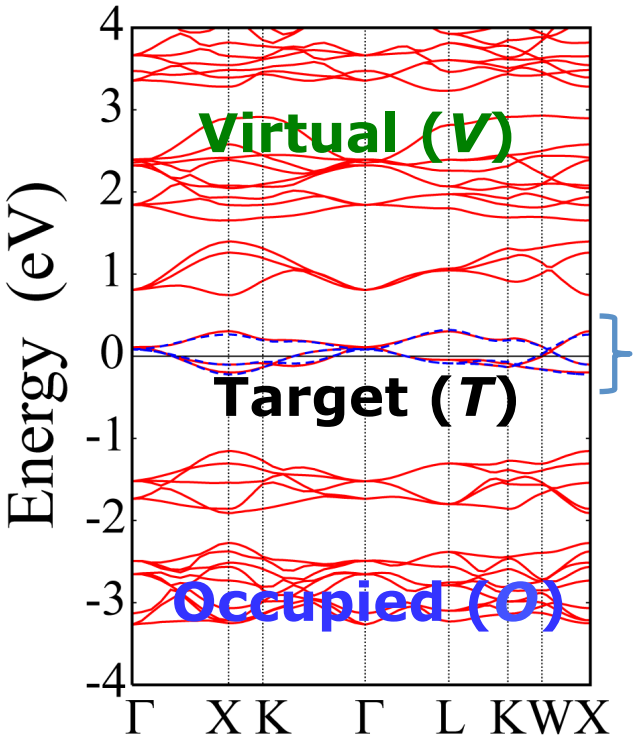
$$\left[D^{(f)}\right]^{-1} = \left[D^{(b)}\right]^{-1} - \Sigma \quad \xrightarrow{\Sigma = \Sigma_t + \Sigma_r} \quad \begin{cases} \left[D^{(p)}\right]^{-1} = \left[D^{(b)}\right]^{-1} - \Sigma_r \\ \left[D^{(f)}\right]^{-1} = \left[D^{(p)}\right]^{-1} - \Sigma_t \end{cases}$$

$$\Sigma = \frac{{}^{\mathrm{ren.}}C}{2M\omega^{(b)}} = |g^{(b)}|^2 \chi_{\mathrm{DFT}}$$

One body part of the Hamiltonian

N. Marzari and D. Vanderbilt, Phys. Rev. B. 56 12847 (1997)
I. Souza et al., ibid. 65, 035109 (2001)

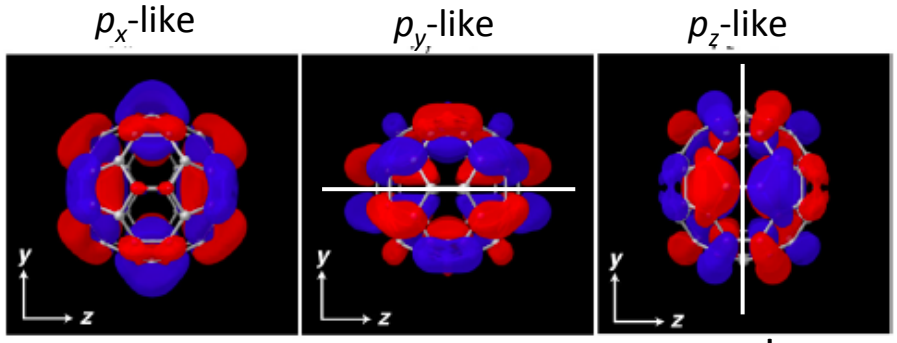
Band structure of fcc K_3C_{60}

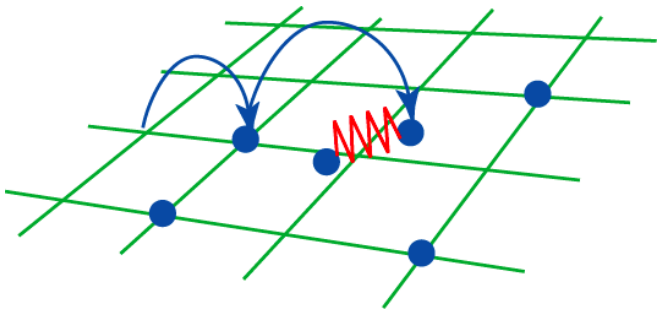


LUMO band
$W \sim 0.5$ eV

Wannier orbitals

molecular-orbital like, 3-fold degenerate





Hopping between molecular orbital

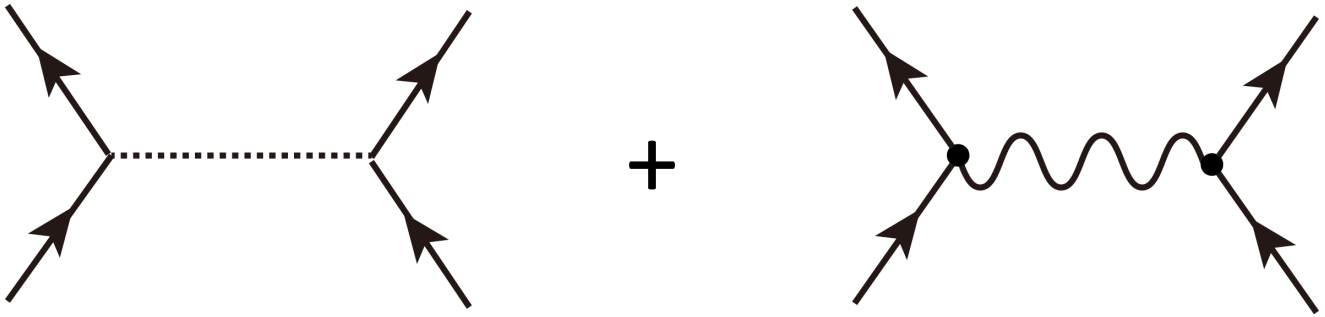
$$t_{m\mathbf{R}n\mathbf{R}'} = \langle w_{m\mathbf{R}} | \mathcal{H}_{KS} | w_{n\mathbf{R}'} \rangle$$

YN-Nakamura-Arita, Phys. Rev. B 85, 155452 (2012)

Interaction between electrons

Coulomb interaction

Interaction mediated by phonons (lattice vibration)



U : intra-orbital (Hubbard int.)
U' : inter-orbital
J_H : exchange (Hund's coupling)

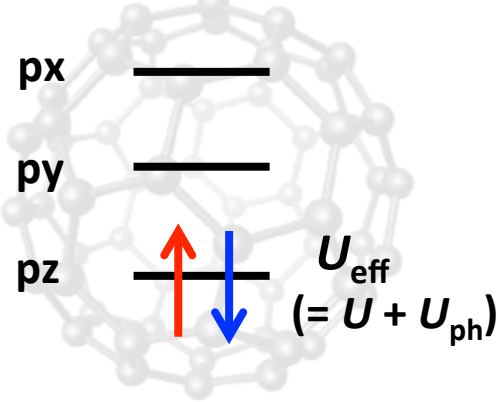
repulsive

U_{ph} : intra-orbital
U'_{ph} : inter-orbital
J_{ph} : exchange

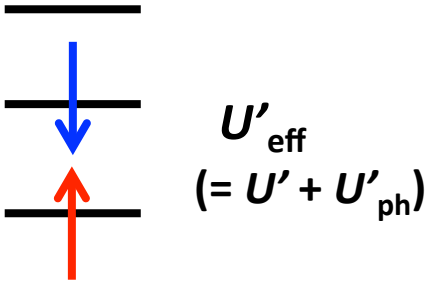
attractive

Types of intramolecular interaction

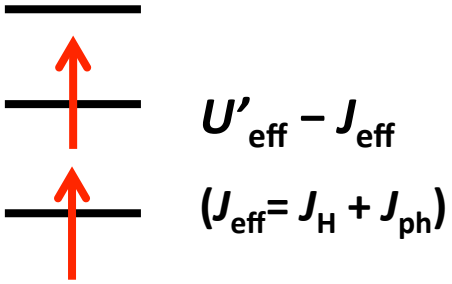
- Intraorbital



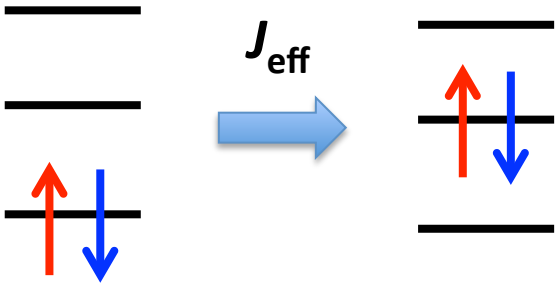
- Interorbital (opposite spin)



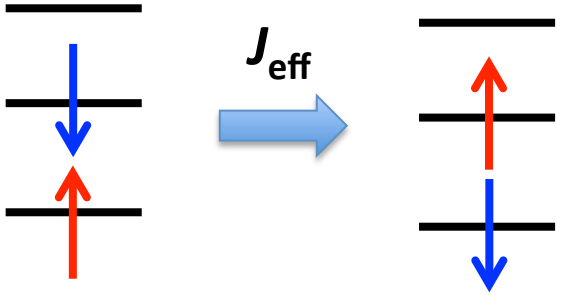
- Interorbital (same spin)



- Pair hopping

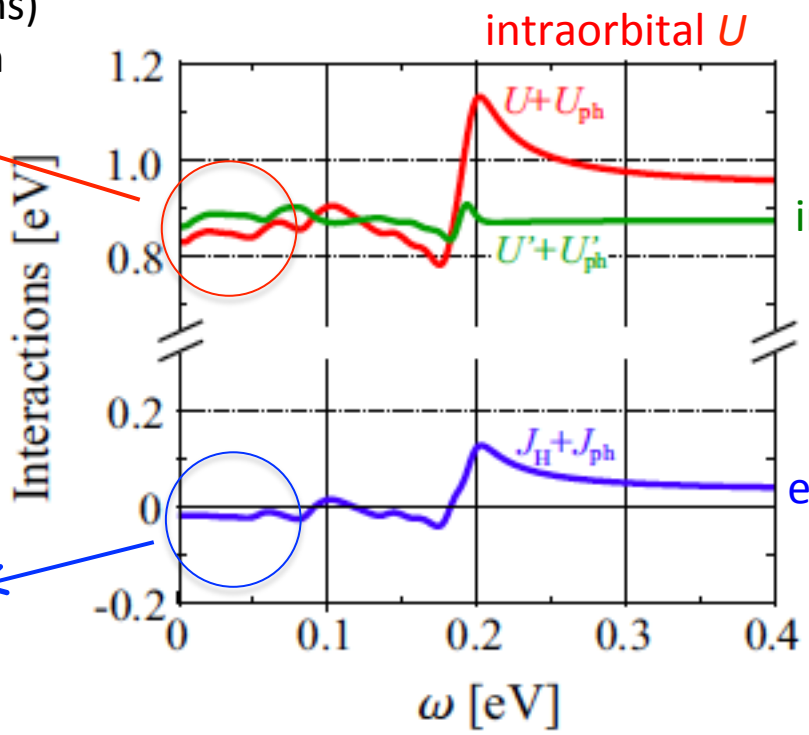


- Spin flip



Effective intramolecular interaction

- ✓ Repulsive interaction (Coulomb wins)
- ✓ U > bandwidth → strong correlation
- ✓ Effectively, $U' > U$



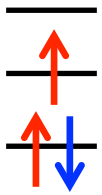
- ✓ Effectively, $J < 0$ (phonon wins)
- ✓ Attractive interaction

snap shot

$U > U', J > 0$

(111) configuration

$U < U', J < 0$

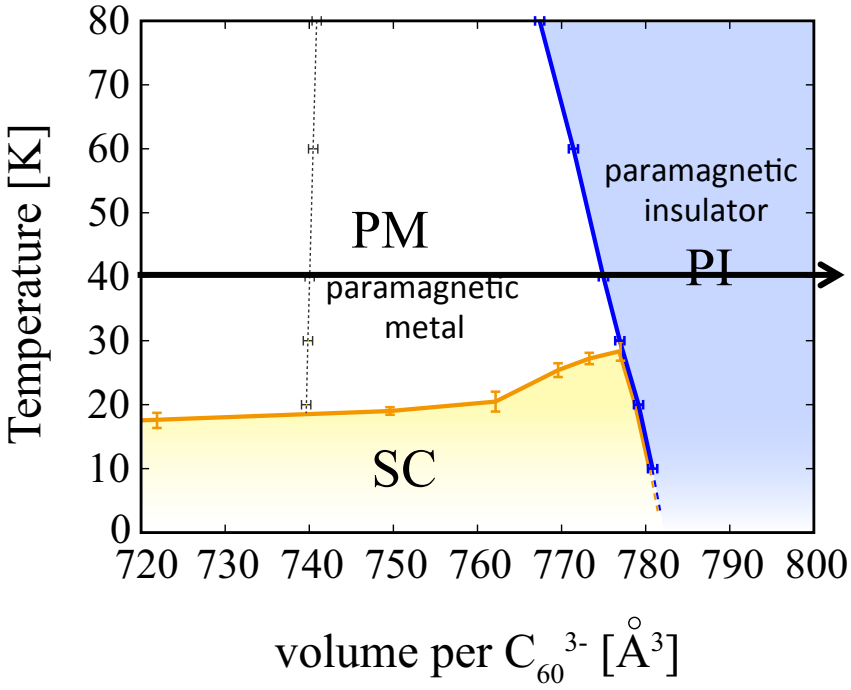


(210) configuration

Phase diagram

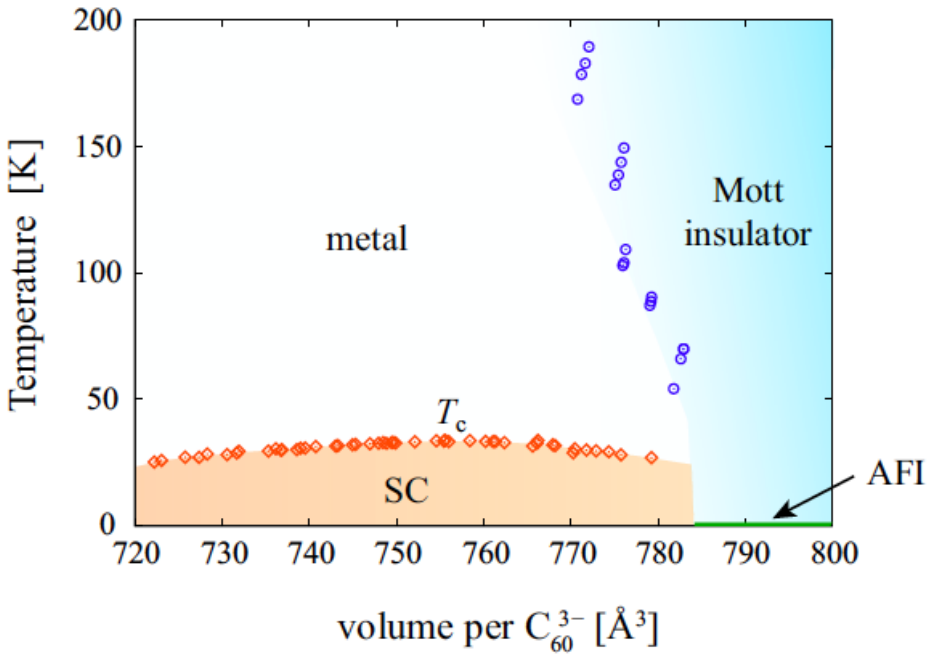
Theoretical (fcc)

DMFT analysis using realistic Hamiltonian



YN *et al.*, Science Advances **1**, e1500568 (2015).

Experimental (fcc)

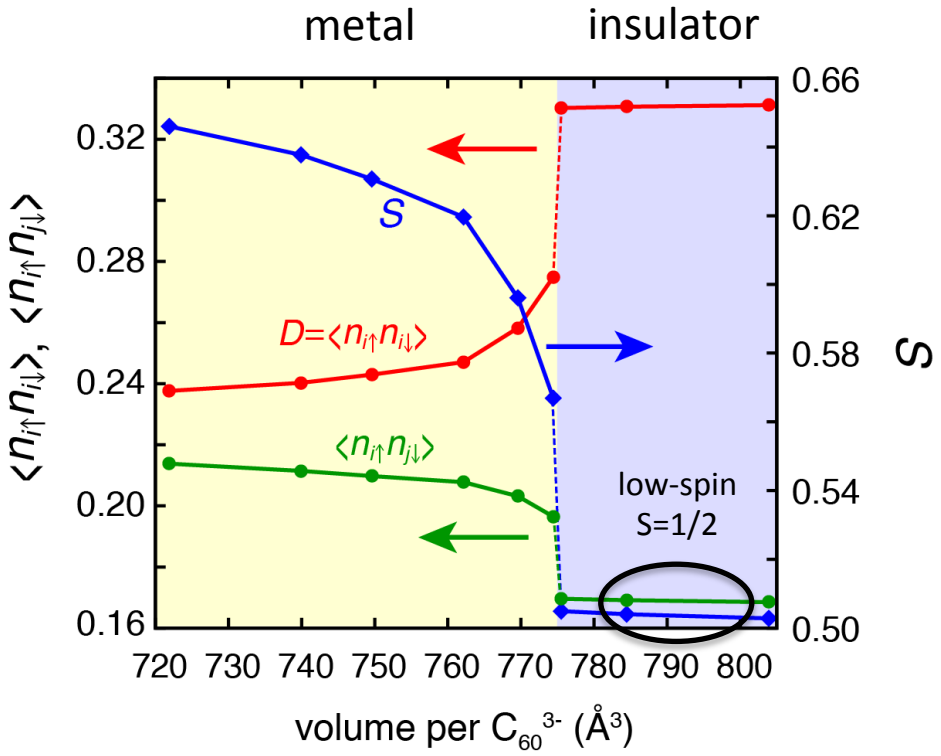


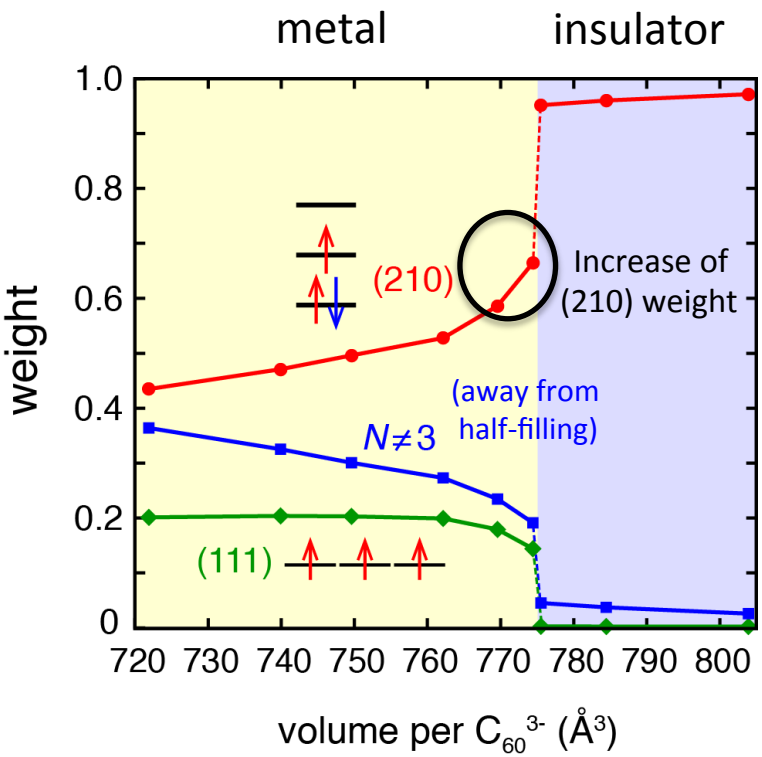
Zadik *et al.*, Sci. Adv. **1**, e1500059 (2015).
Ihara *et al.*, PRL **104**, 256402 (2010).
Kawasaki *et al.*, JPSJ **82**, 014709 (2013)

- ✓ *s*-wave SC next to Mott phase with T_c ~ 30 K
- ✓ Critical volume
- ✓ Slope between PM and PI

Property of metal-insulator transition at 40 K (above T_c)

YN *et al.*, Science Advances **1**, e1500568 (2015).
YN *et al.*, J. Phys.: Condens. Matter 28, 153001 (2016)





Haule PRB (2007)

- (210) configurations dominate (because of $U' > U$)
- Mott physics: filling is (nearly) fixed at half-filling in the insulating phase

no ferro-orbital order, i.e., six types of (210) configurations
($\{n_1,n_2,n_3\}$ ={2,1,0}, {0,2,1}, {1,0,2}, {2,0,1}, {1,2,0}, {0,1,2}) are degenerate

Superconducting mechanism: Is it BCS?

$$\mathcal{H}_{\rm int} = \sum_i U_{\rm eff}\,\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} + \sum_{i<j,\sigma} U'_{\rm eff}\,\hat{n}_{i\sigma}\hat{n}_{j\bar{\sigma}} + \sum_{i<j,\sigma} (U'_{\rm eff} - J_{\rm eff})\,\hat{n}_{i\sigma}\hat{n}_{j\sigma}$$
$$+ \sum_{i\neq j} J_{\rm eff}\,\hat{c}^\dagger_{i\uparrow}\hat{c}_{j\uparrow}\hat{c}^\dagger_{j\downarrow}\hat{c}_{i\downarrow} + \sum_{i\neq j} J_{\rm eff}\,\hat{c}^\dagger_{i\uparrow}\hat{c}_{j\uparrow}\hat{c}^\dagger_{i\downarrow}\hat{c}_{j\downarrow}$$

Effective interaction = Coulomb + phonon contributions

- mean-field decoupling (assuming intraorbital pairing)

$$\hat{c}^\dagger_{i\uparrow}\hat{c}_{j\uparrow}\hat{c}^\dagger_{i\downarrow}\hat{c}_{j\downarrow} \longrightarrow \hat{c}^\dagger_{i\uparrow}\hat{c}^\dagger_{i\downarrow}\langle\hat{c}_{j\downarrow}\hat{c}_{j\uparrow}\rangle$$
$$\Delta = \langle\hat{c}_{1\downarrow}\hat{c}_{1\uparrow}\rangle = \langle\hat{c}_{2\downarrow}\hat{c}_{2\uparrow}\rangle = \langle\hat{c}_{3\downarrow}\hat{c}_{3\uparrow}\rangle$$

$$\mathcal{H}_{\rm BCS} = \sum_i (U_{\rm eff} + 2J_{\rm eff})\Delta\,\hat{c}^\dagger_{i\uparrow}\hat{c}^\dagger_{i\downarrow}$$

repulsive attractive (pair-hopping int.)

- ✓ $U_{\rm eff}$ + 2$J_{\rm eff}$ = intra-orbital + 2 inter-orbital scattering (we have 3 orbital)
- ✓ If $U_{\rm eff}$ + 2$J_{\rm eff}$ < 0, we can have BCS-type SC, but it's not the case because of strongly repulsive $U_{\rm eff}$

Superconducting mechanism

YN *et al.*, Science Advances **1**, e1500568 (2015).

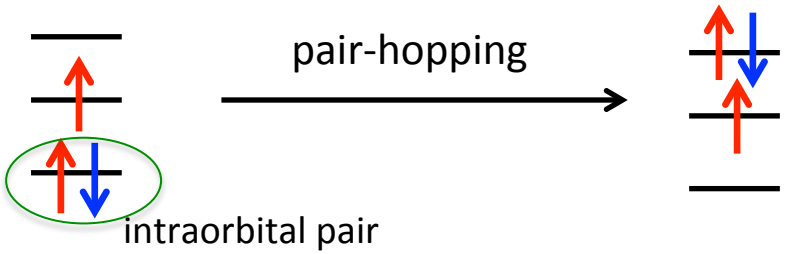
- Stability of superconductivity at 10 K

realistic	(pair hopping)=0	(spin flip)=0	$U'_{eff} < U_{eff}$ (U'_{ph}(new) = U_{ph})
SC	Non SC	SC	Non SC

- The crucial factors for *s*-wave superconductivity are

1. Generation of intraorbital pair by $U'_{eff} > U_{eff}$
   strong correlation helps it by suppressing kinetic energy
2. Tunneling of the pairs due to pair-hopping term (Suhl-Kondo mechanism)

H. Suhl et al. (1959); J. Kondo (1963)



strong electron correlations and phonons cooperatively work for SC (unconventional)

Short Summary

Unusual form of intramolecular interaction
with strongly repulsive U and weakly negative J

Unusual cooperation between phonons and strong correlations
in stark contrast with BCS mechanism

Unconventional superconducting mechanism

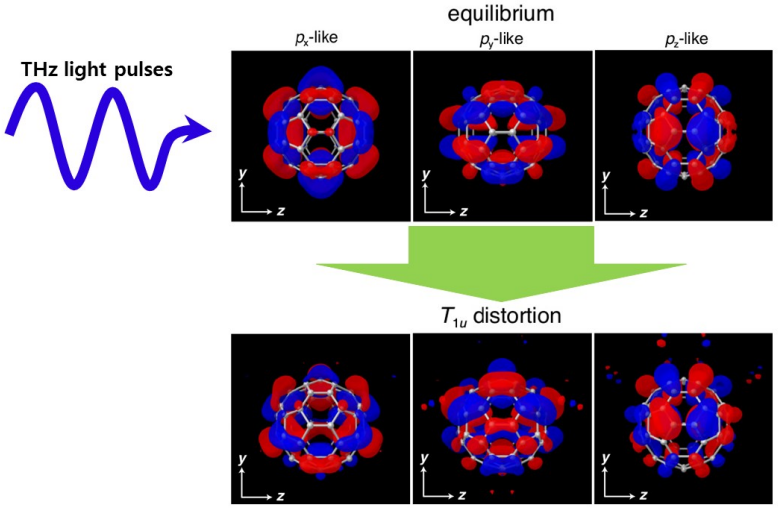
YN *et al*., Science Advances 1, e1500568 (2015).
YN *et al*., J. Phys.: Condens. Matter 28, 153001 (2016)

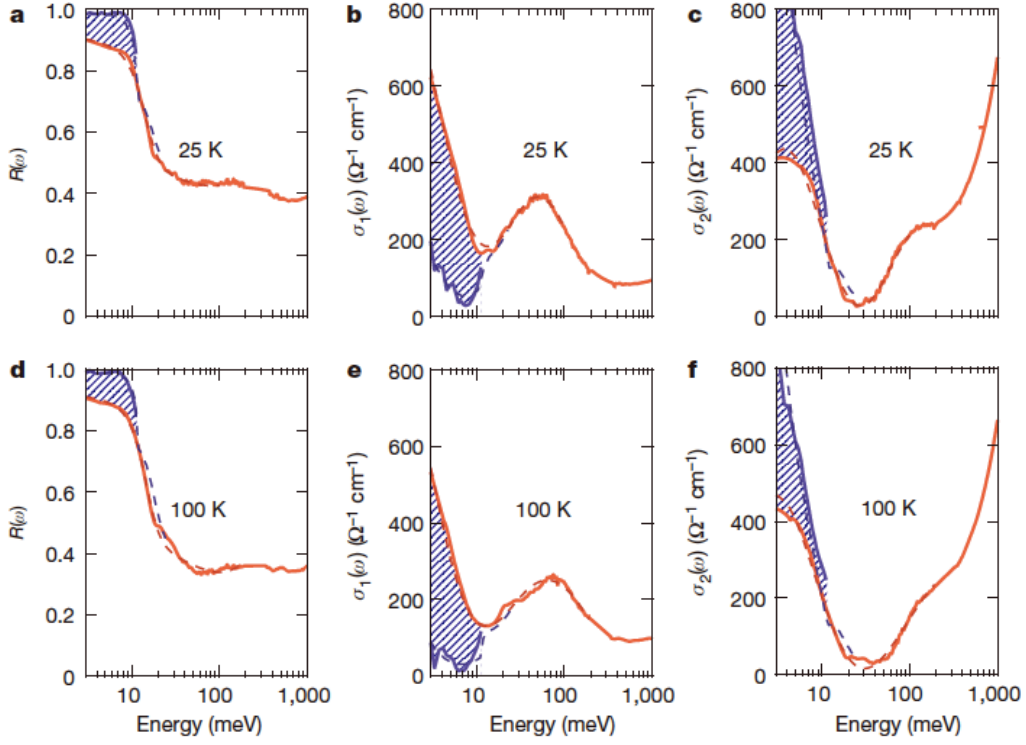
see also Han et al. 2003, Jiang and Kivelson 2016, Chakravarty et al 1991,
Varma et al. 1991, Schluter et al. 1992, Zhang et al. 19991, Mazin et al. 1992, …

Second part

Enhancing superconductivity of A_3C_{60} fullerides by asymmetric perturbation

M. Kim et al., arXiv:1606.05796





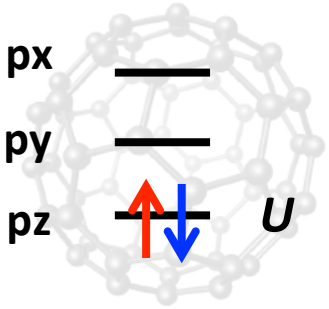
In collaboration with

Minjae Kim, P. Seth, O. Parcollet, M. Ferrero, and A. Georges

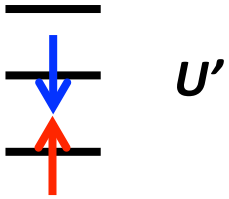
Negative-*J* 3orbital Hubbard model

$$H_{\text{int}} = (U - 3J)\frac{\hat{N}(\hat{N}-1)}{2} + \frac{5}{2}J\hat{N} - 2J\vec{S}^2 - \frac{1}{2}J\vec{T}^2$$

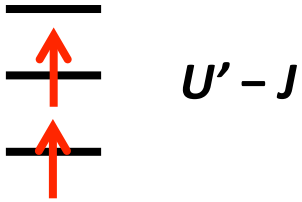
- Intraorbital



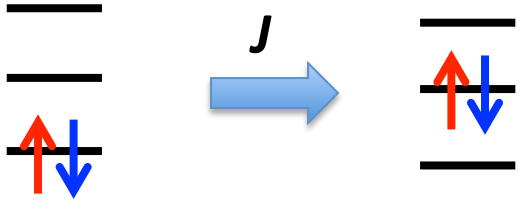
- Interorbital (opposite spin)



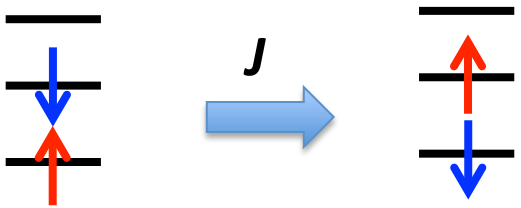
- Interorbital (same spin)



- Pair hopping



- Spin flip

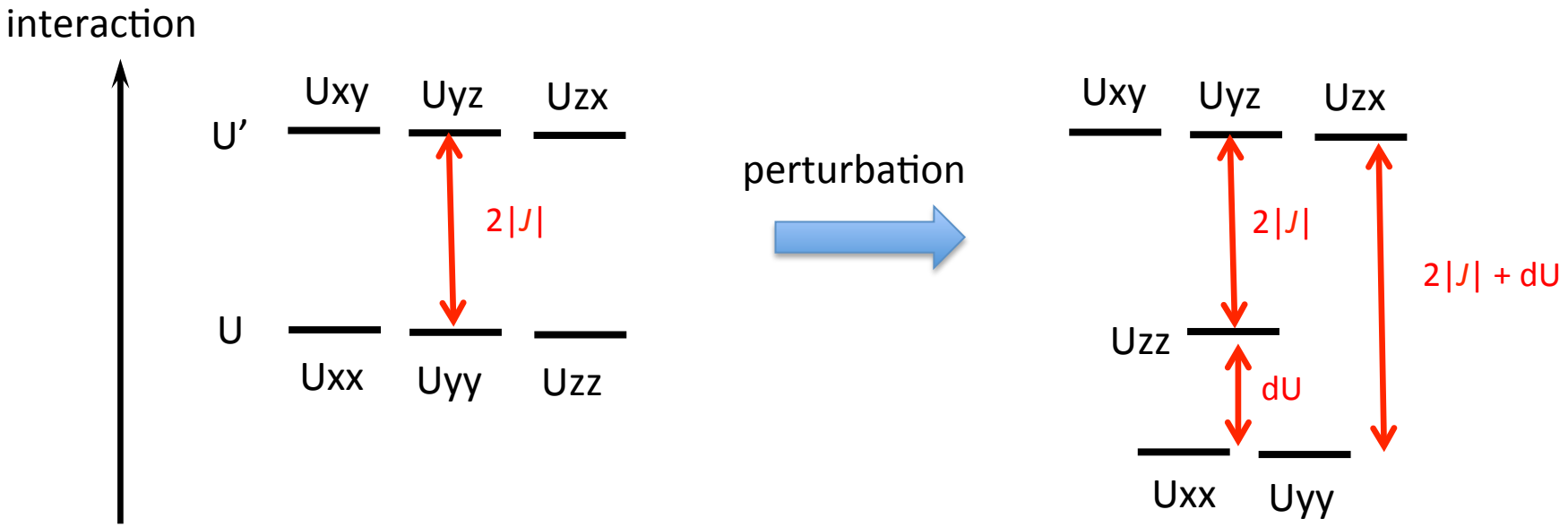


Perturbations:

Interaction imbalance: $H_{dU} = -dU(n_{x,\uparrow}n_{x,\downarrow} + n_{y,\uparrow}n_{y,\downarrow})$

onsite level splitting: $H_{CF} = h_{CF}(n_x + n_y)$

Enhancement of SC by dU > 0 (*U*-imbalance)



- ✓ Effective difference between *U'* and *U* increases from 2|*J*| to 2|*J*|+d*U*
  → stabilization of intraorbital electron-pair in *x* and *y* orbitals
- ✓ Orbital fluctuation within *x* and *y* orbitals

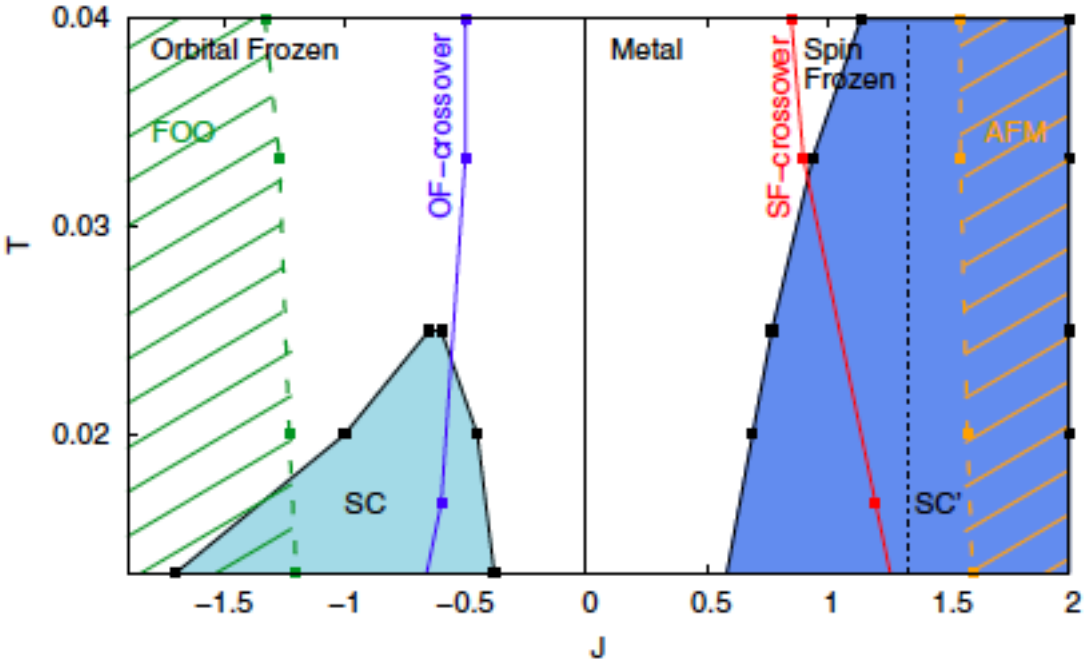
→ Enhancement of superconductivity

Future perspective : nonequilibrium calculation (Giacomo)

Final part

Long-range orders and spin/orbital freezing in two-orbital Hubbard model

K. Steiner *et al*., Phys. Rev. B 92, 115123 (2015)



In collaboration with

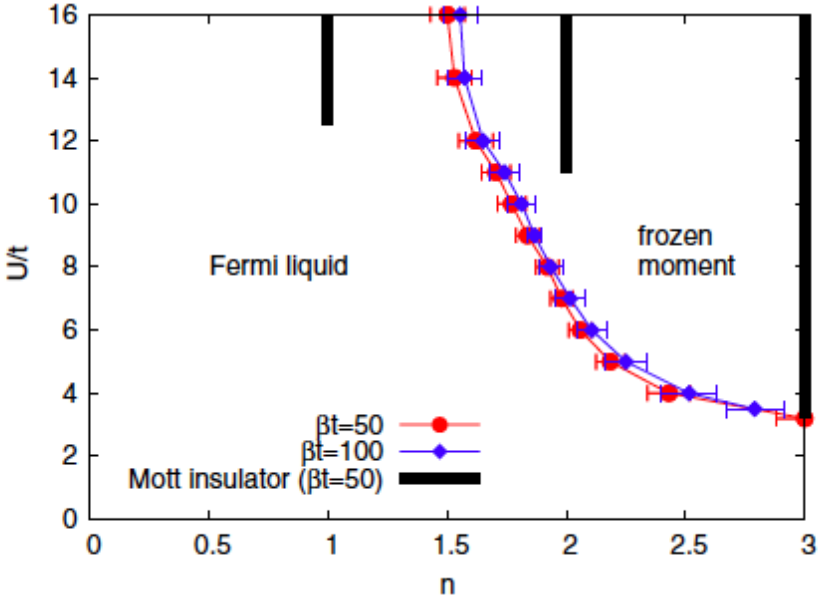
Karim Steiner, Shintaro Hoshino, and Philipp Werner

Spin freezing behavior (J > 0)

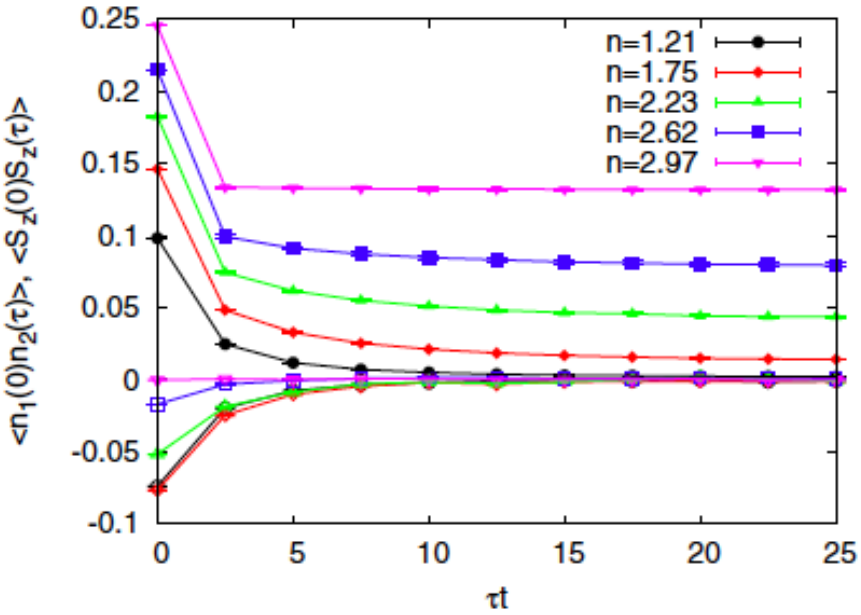
P. Werner *et al.*, Phys. Rev. Lett. **101**, 166405 (2008)

Phase diagram

3 orbital Hubbard model, bethe lattice, J=U/6



Correlation functions



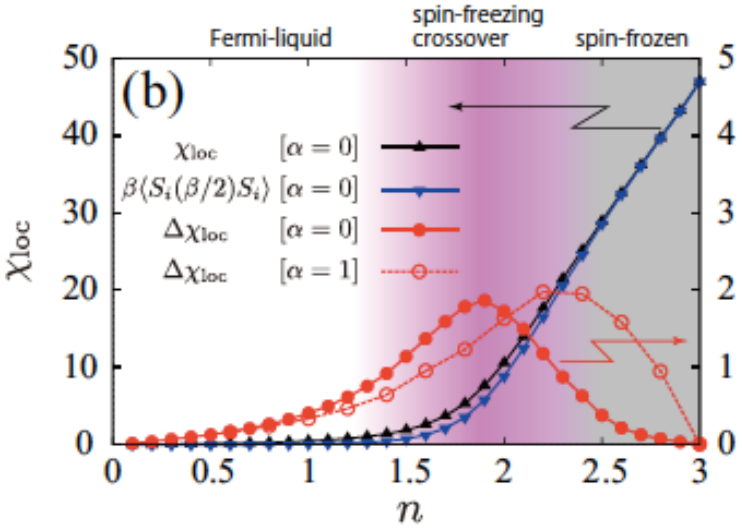
✓ Existence of frozen spin moment → non-Fermi liquid behavior

Hund's Physics

Related talk by Laura Fanfarillo (Friday)

Spin freezing and triplet superconductivity (J > 0)

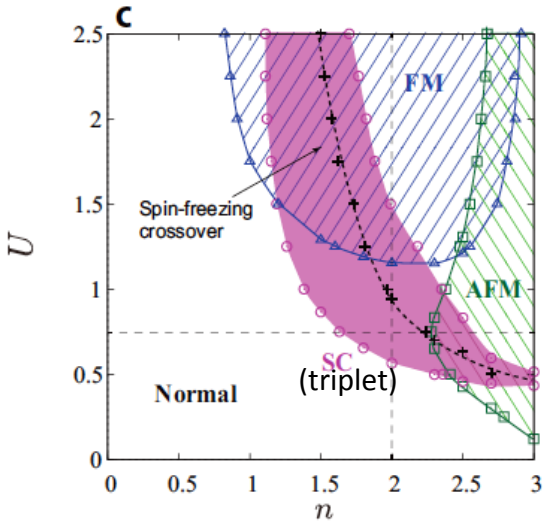
Hoshino and Werner, Phys. Rev. Lett. **115**, 247001 (2015)



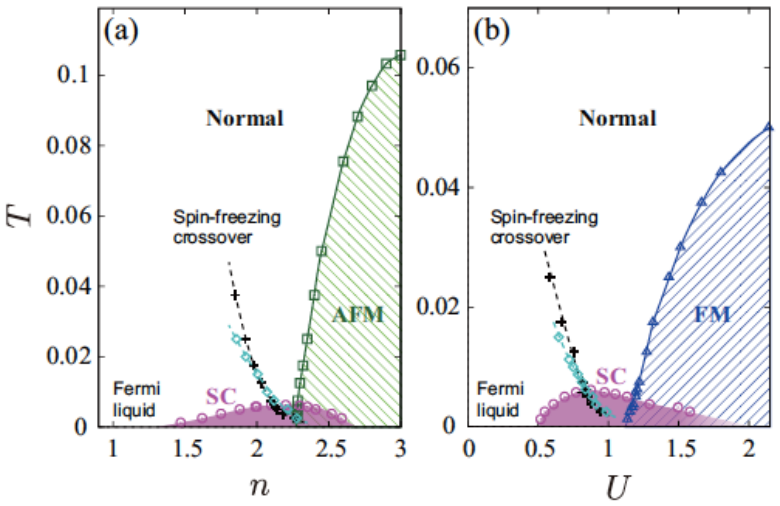
$$\Delta\chi_{\rm loc} = \int_0^\beta d\tau \left(\langle S_i(\tau)S_i\rangle - \langle S_i(\beta/2)S_i\rangle\right)$$

✓ Spin freezing crossover characterized by maximum of $\Delta\chi_{loc}$ (maximum of spin-fluctuation)

Phase diagram at T = 0.0025,U=U/4



Phase diagram along two cuts in left figure

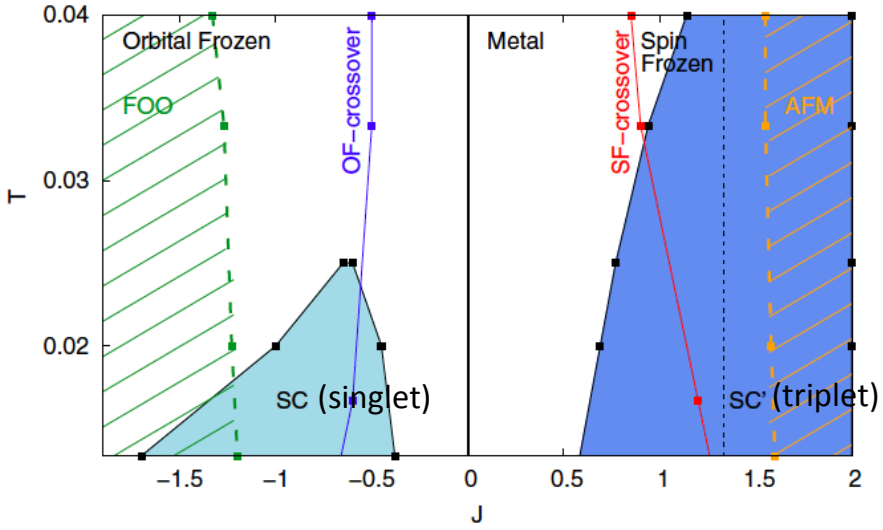


✓ Triplet superconductivity induced by local spin fluctuation, not by quantum critical point

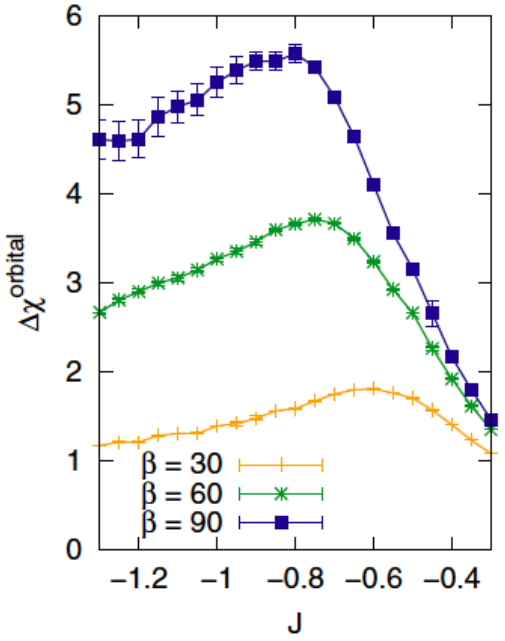
Spin/orbital freezing and their relations with superconductivity

degenerate 2orb, bethe lattice, W = 4, U=W, density-density int., 3/8 filling

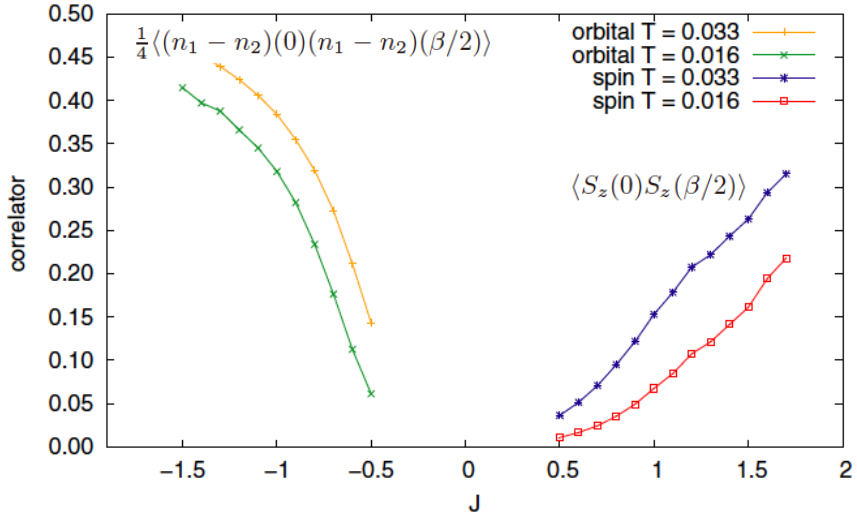
Phase diagram



maximum of orbital fluctuation



Existence of spin/orbital fluctuation



$$\Delta\chi^{\text{orbital}}_{\text{loc}} = \frac{1}{4}\int_0^\beta d\tau(\langle(n_1-n_2)(\tau)(n_1-n_2)(0)\rangle - \langle(n_1-n_2)(\beta/2)(n_1-n_2)(0)\rangle).$$

K. Steiner *et al.*, Phys. Rev. B 92, 115123 (2015)

Mapping from J > 0 to J < 0

K. Steiner *et al*., Phys. Rev. B 92, 115123 (2015)

- Transformation:

$$d_{i,1\downarrow} \longleftrightarrow d_{i,2\uparrow}$$ (orb-1, down-spin → orb-2 up spin)

- Density-density-type interaction after the transformation

$$H_{\rm int}^{\rm dens} \longrightarrow \sum_{\alpha} \tilde{U} n_{\alpha\uparrow} n_{\alpha\downarrow} + \sum_{\sigma} \tilde{U}' n_{1\sigma} n_{2\bar{\sigma}} + \sum_{\sigma} \tilde{U}'' n_{1\sigma} n_{2\sigma}.$$

with $\tilde{U}' = \tilde{U} + J$ ($\tilde{U}' = U - 2J$ and $\tilde{U} = U - 3J$)

✓ Originally, (interorbital int. *U'* = *U*-2*J*) < (intraorbital int. *U*), but, now effectively *U'* > *U*, i.e., negative *J* is realized

- With this transformation:

$$\begin{cases} d_{i,1\uparrow}^{\dagger} d_{i,1\downarrow}^{\dagger} \longleftrightarrow d_{i,1\uparrow}^{\dagger} d_{i,2\uparrow}^{\dagger} & \text{Intraorb. singlet pair} \longleftrightarrow \text{Interorb. triplet pair} \\ \sum_{\sigma} (n_{i,1\sigma} - n_{i,2\sigma}) \longleftrightarrow \sum_{\alpha} (n_{i,\alpha\uparrow} - n_{i,\alpha\downarrow}) & \text{Orbital moment} \longleftrightarrow \text{Spin moment} \end{cases}$$

✓ Roles of spin and orbital are interchanged !

Summary (final part)

- ✓ Positive J case: spin-freezing and triplet superconductivity
- ✓ Negative J case: orbital-freezing and singlet superconductivity
- ✓ They are related by mapping (roles of orbital and spins are interchanged)
- ✓ In Both cases, T_c maximum of SC is related with the maximum of fluctuation

- ✓ Confirm the importance of orbital fluctuation in realizing superconductivity
- ✓ Consistent with first and second parts of the talk (3orb model)

K. Steiner *et al*., Phys. Rev. B 92, 115123 (2015)