First-principles study of the Mott transition and superconductivity in A_3C_{60}

Ryotaro Arita — RIKEN CEMS

Yusuke Nomura — Univ. Tokyo

Shiro Sakai — RIKEN CEMS

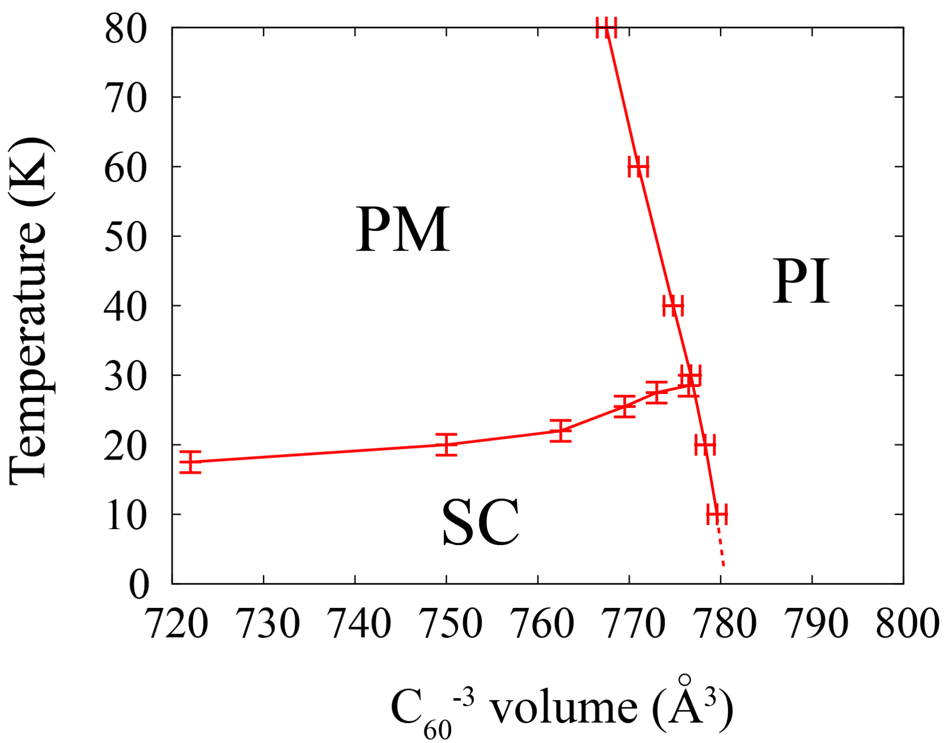
Ryosuke Akashi — Univ. Tokyo

Kazuma Nakamura — Kyushu Inst. Technology

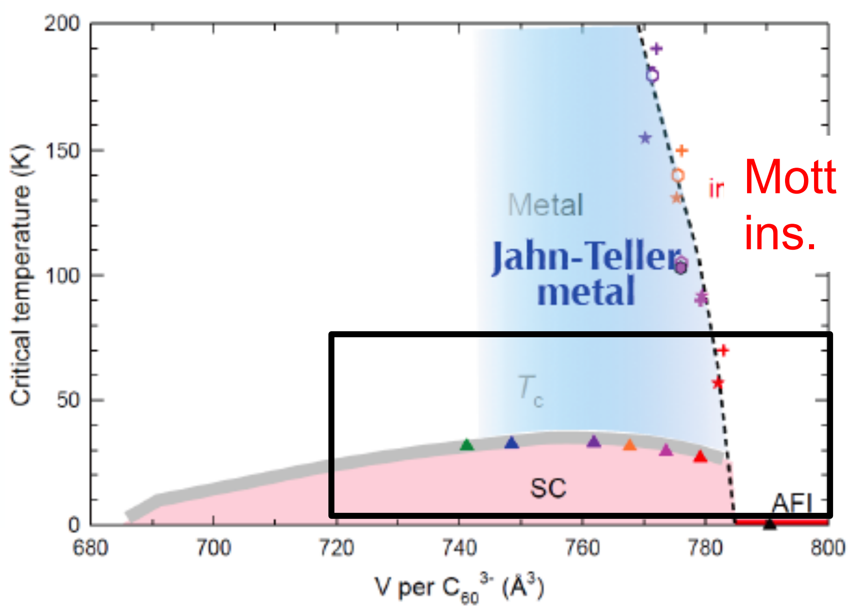
Massimo Capone — SISSA

Phase diagram of A_3C_{60}

Theory



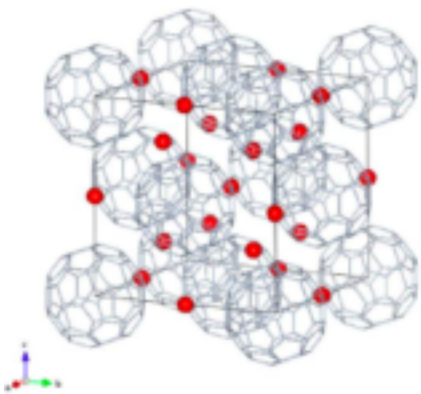
Experiment
(taken from Kasahara et al., 2014)



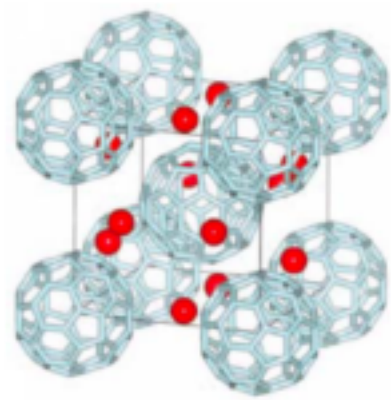
SC phase with T_c~30K close to MI phase
reproduced by <u>fully non-empirical calculation</u>

C_{60} superconductors

Cf) Talk by H. Alloul



fcc A_3C_{60}
K_3C_{60} : Tc=19K
Rb_3C_{60} : Tc=29K
Cs_3C_{60} : Tc=35K

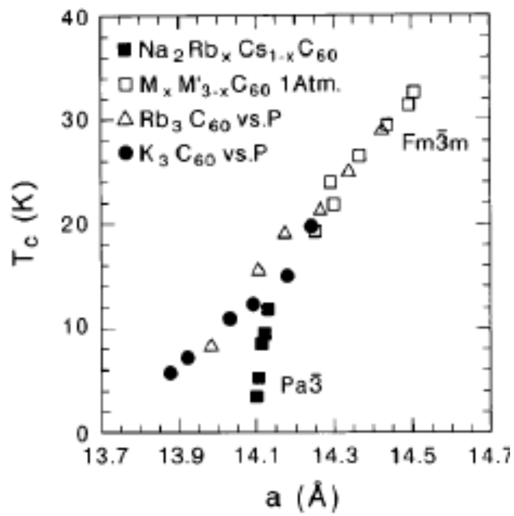


A15 Cs_3C_{60}
Tc = 38K

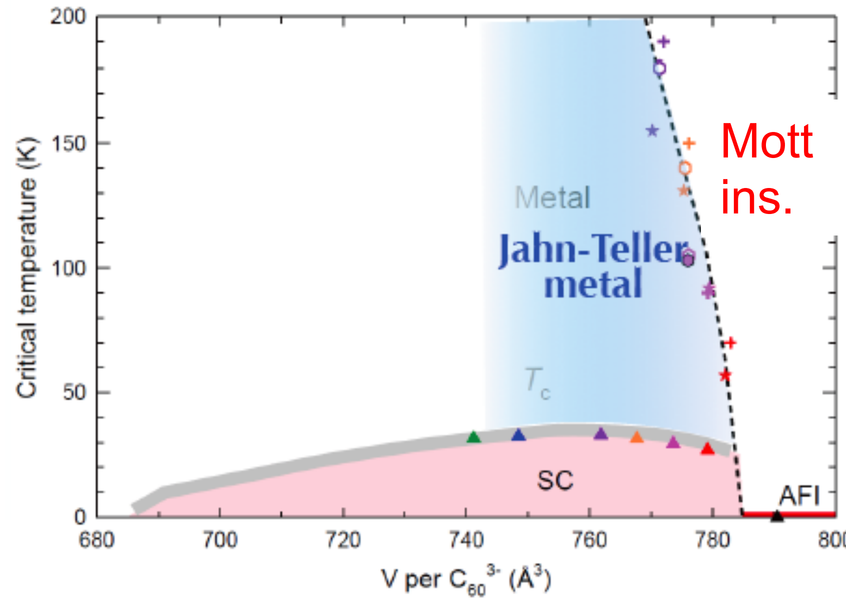
Pairing mechanism ?

Pairing mechanism of doped C_{60}

Cf) Talk by H. Alloul



Taken from
O. Gunnarsson, RMP 69, 575 (1997)



Taken from Y. Kasahara et al., (2014)

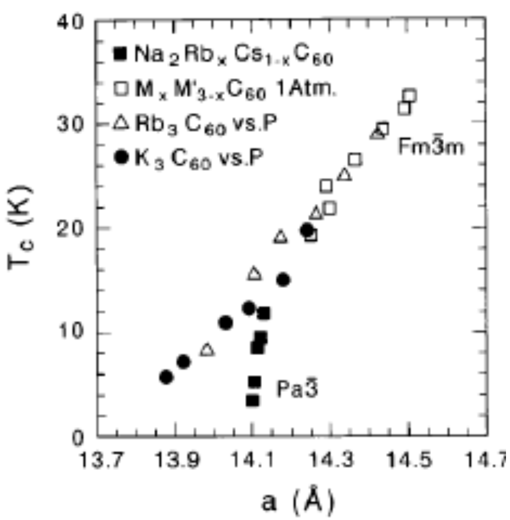
$$k_B T_C = \hbar\omega_D \exp\left(-1/N(E_F)V\right)$$

SC lies next to Mott

ω_D~1000K
conventional SC ?

Strongly correlated
unconventional SC ?

Pairing mechanism of doped C_{60}



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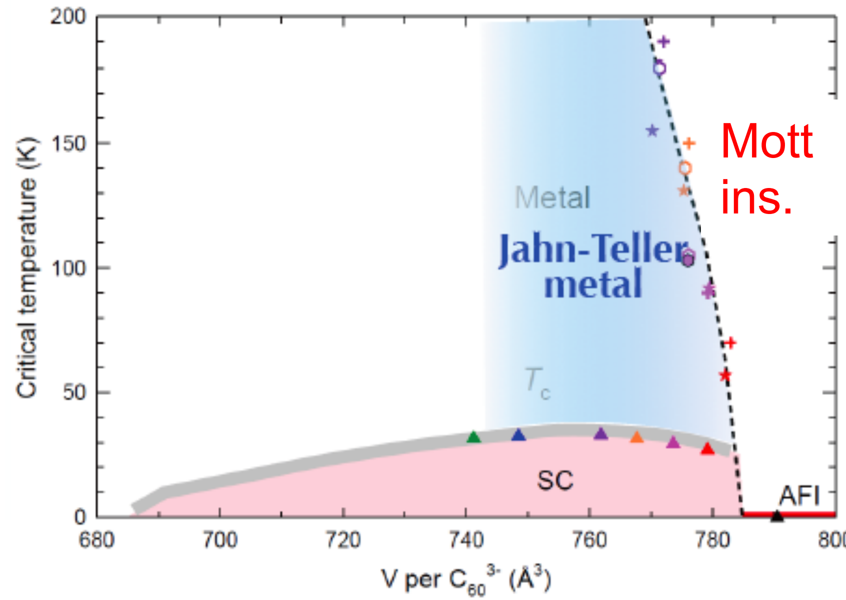

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ω_D~1000K
conventional SC ?

SCDFT: R. Akashi & RA, PRB88 054510 (2013)

SC lies next to Mott

Strongly correlated
unconventional SC ?

DFT for superconductors

SCDFT= Extension of DFT

Oliveira et al., PRL 60, 2430 (1988)
Kreibich & Gross PRL 86, 2984 (2001)

$$\hat{H}_e = \hat{T}_e + \hat{W}_{ee} + \int \hat{\rho} v(r) \mathrm{d}^3 r - \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \left(\hat{\chi}(r,r') \Delta^*(r,r') + \mathrm{H.c.} \right)$$

$$\rho(r) = \left\langle \sum_{\sigma=\uparrow\downarrow} \hat{\psi}_\sigma^+(r) \hat{\psi}_\sigma(r) \right\rangle$$ electron density

$$\chi(r,r') = \left\langle \hat{\psi}_\uparrow(r) \hat{\psi}_\downarrow(r') \right\rangle$$ anomalous density

For $T < T_c$, $\Delta, \chi \neq 0$

DFT for superconductors

M. Lüders et al, PRB 72, 024545 (2005)
M. Marques et al, PRB 72, 024546 (2005)

Kohn-Sham BdG equation

↓

Linearized gap equation

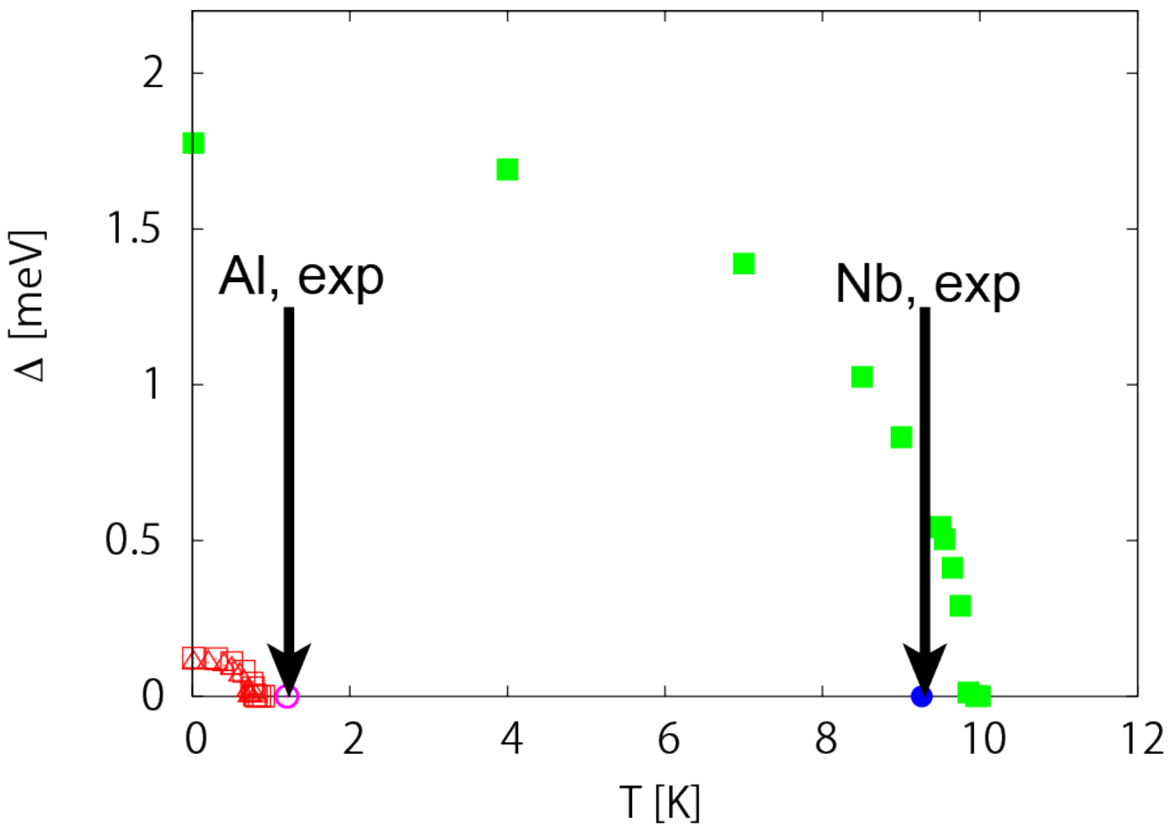
$$\Delta_i = \frac{-1}{2}\sum_j F_{ij}^{\mathrm{Hxc}} \frac{\tanh[\beta\xi_j/2]}{\xi_j}\Delta_j$$

$$F_{ij}^{\mathrm{Hxc}} = \frac{\delta^2(E_H + F_{xc})}{\delta\chi_i^*\delta\chi_j}$$

$$E_H = \frac{1}{2}\int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d^3r \int d^3r' \frac{|\chi(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

Once F_{xc} is given, we can calculate T_c without adjustable parameters

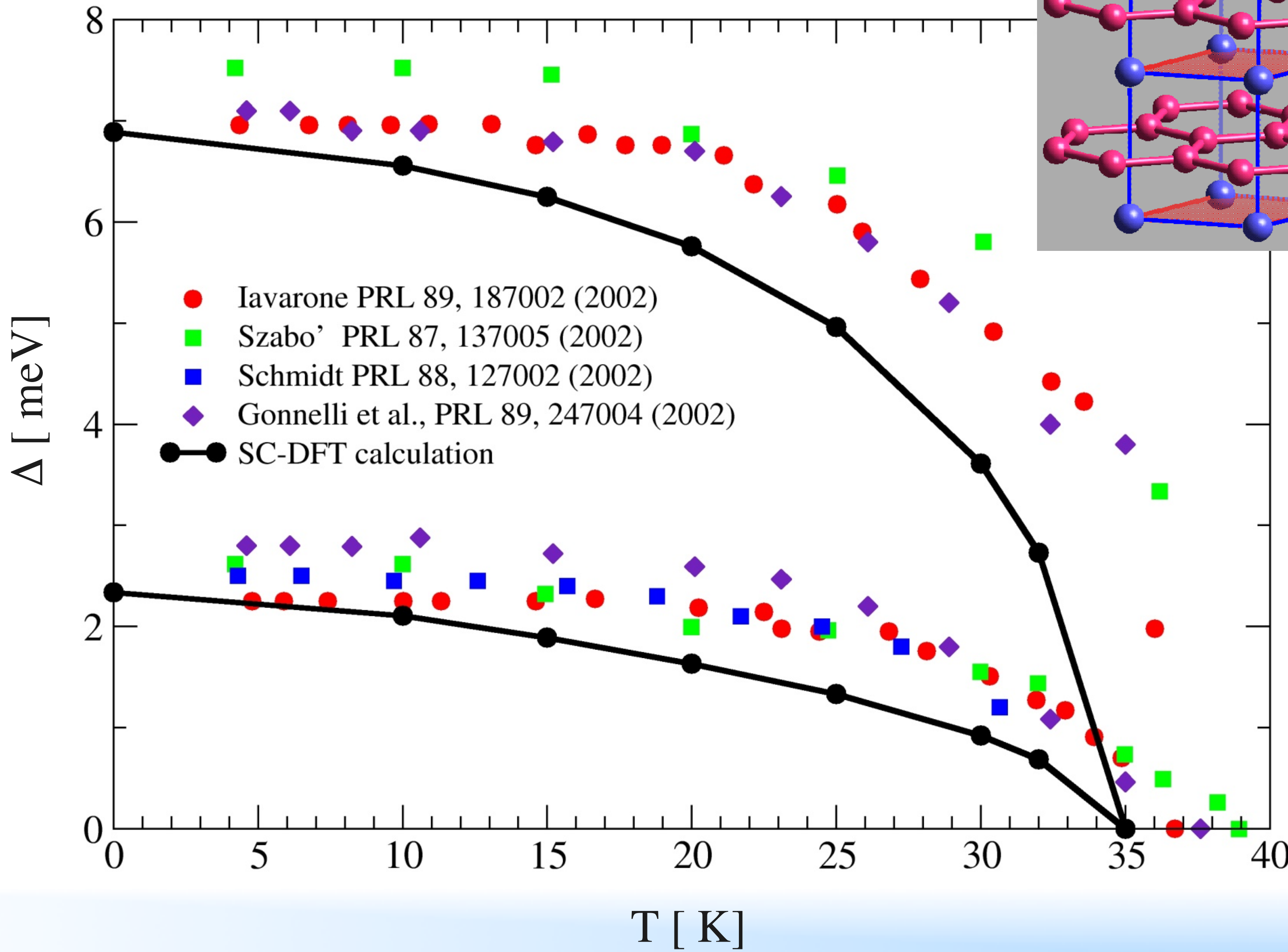
SCDFT calculation for simple metals

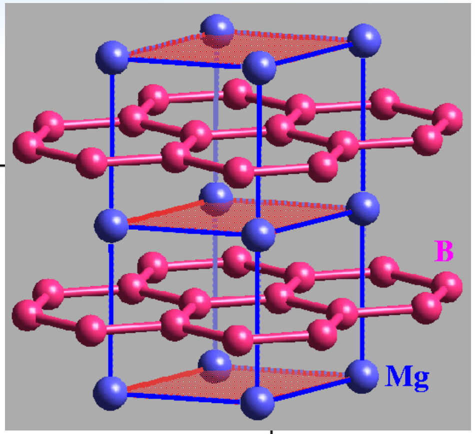


SCDFT accurately reproduces T_c^{exp} of conventional SC

SCDFT calculation for MgB_2

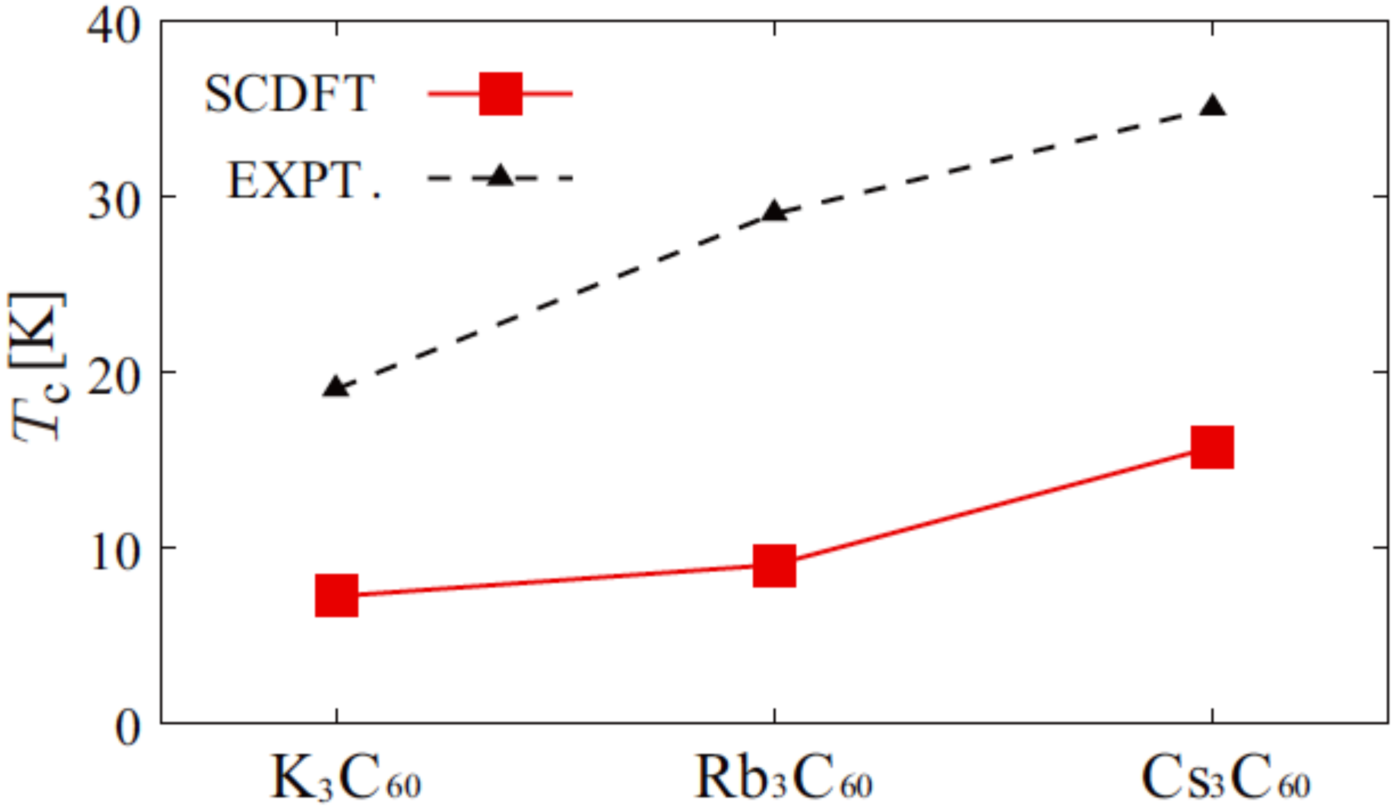
A. Floris et al, Phys. Rev. Lett. 94, 037004 (2005)





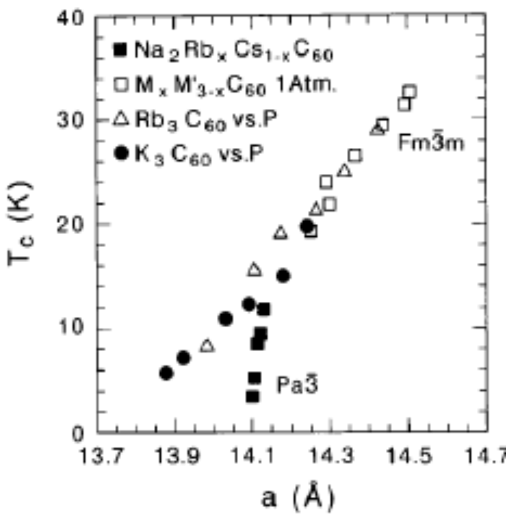
SCDFT calculation for A_3C_{60}

R. Akashi & RA, PRB88 054510 (2013)



T_c is significantly underestimated:
Conventional scenario does not explain high T_c in C_{60}

Pairing mechanism of doped C_{60}



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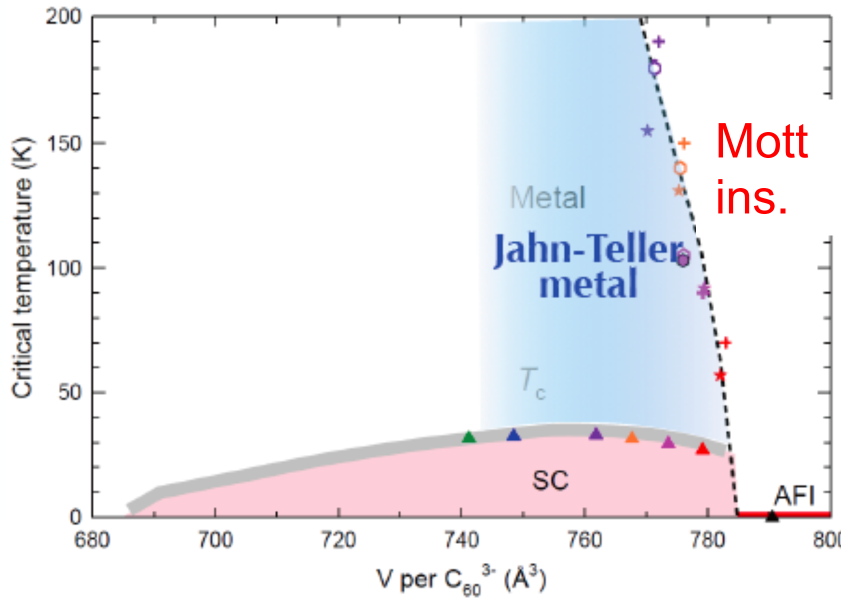

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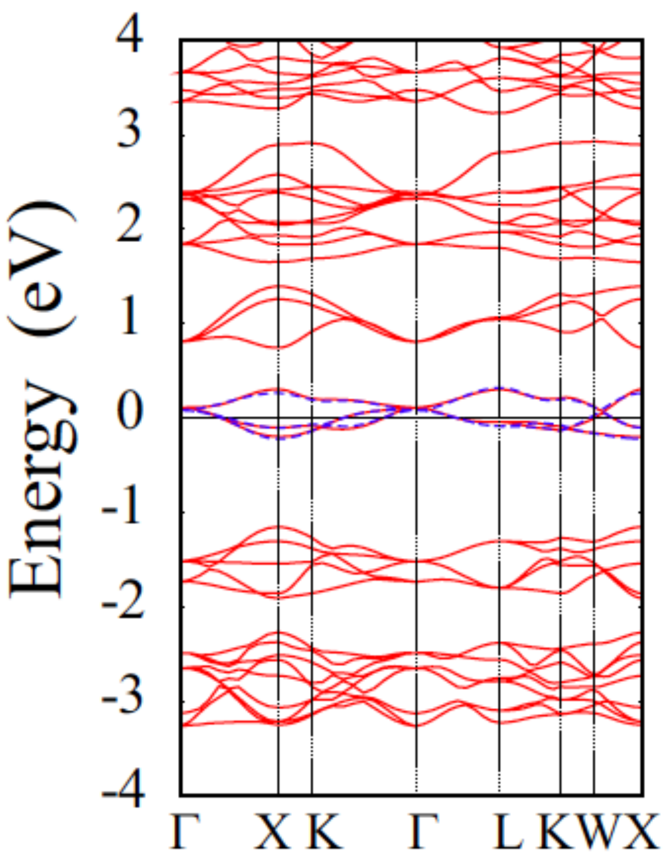
Low-energy effective model for A_3C_{60}



$$-t \sum_{<ija>} c^{+}_{ia\sigma} c_{ja\sigma}$$

Kinetic Term t_{1u} 3bands **W ~ 0.6 eV**

$$+\frac{U}{2} \sum_{i} n_i^2$$

Coulomb Repulsion **U > W**

$$+J(2S_i^2 + \frac{1}{2} L_i^2)$$

Ele-ph (Jahn-Teller) interaction > 0
Hund's rule coupling < 0

J > 0 favors **minimum S & L** (inverted Hund's rule)

Unconventional mechanism

M. Capone, M. Fabrizio, C. Castellani, and E. Tosatti, Science 296, 2364 (2002)

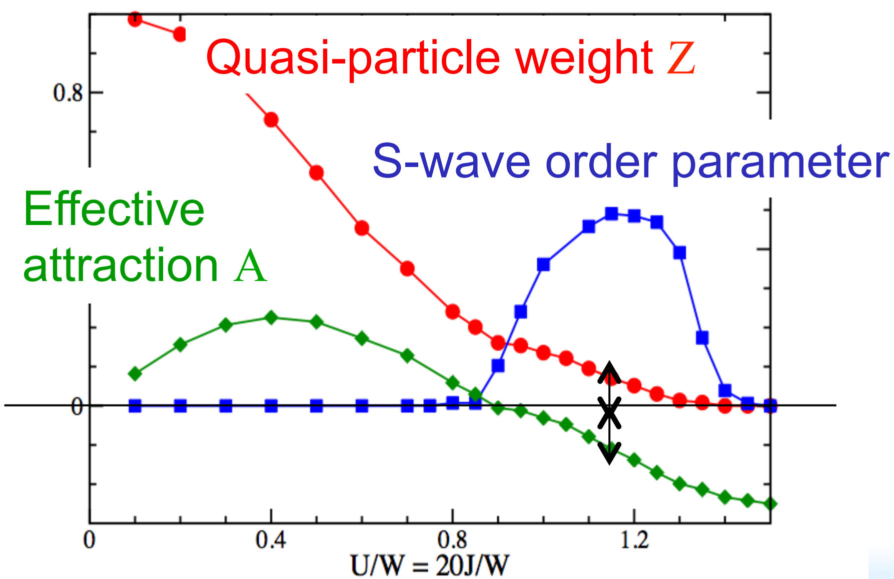
"heavy" quasiparticles experience the bare attraction and reduced repulsion

J is related to Spin and Orbital Degrees of Freedom
Still active when charge fluctuations are frozen by correlations
Even in the Mott state the singlet energy gain is J

$W \longrightarrow ZW$

$A = ZU - 10/3\, J$

$Z \ll 1$



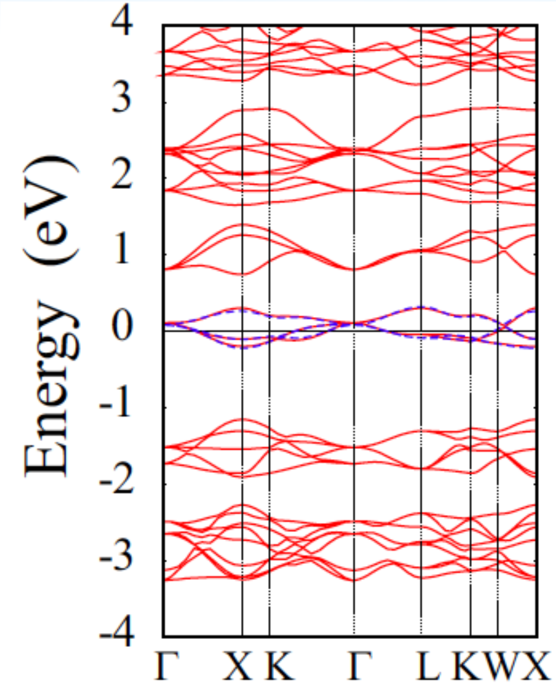
$U \longrightarrow ZU$

Coulomb Repulsion

$J \longrightarrow J$

$J = J_{ph} - J_{Hund}$

Ab initio downfolding



Let us consider to derive a low-energy Hamiltonian from first principles and solve it by means of a non-perturbative method (extended DMFT)

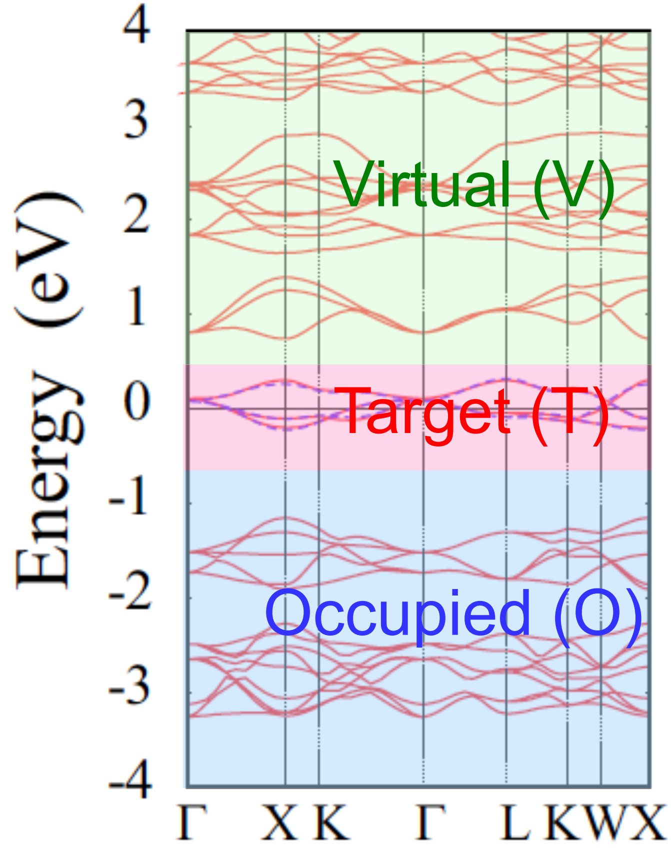
Correlation part

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

Nomura, Nakamura & RA, PRB 85, 155452 (2012)

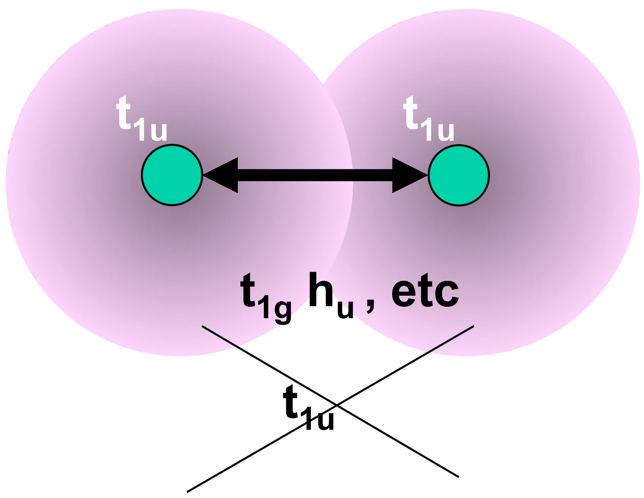
Constrained RPA

$$W = (1 - v\chi)^{-1} v$$



Full RPA polarizability:

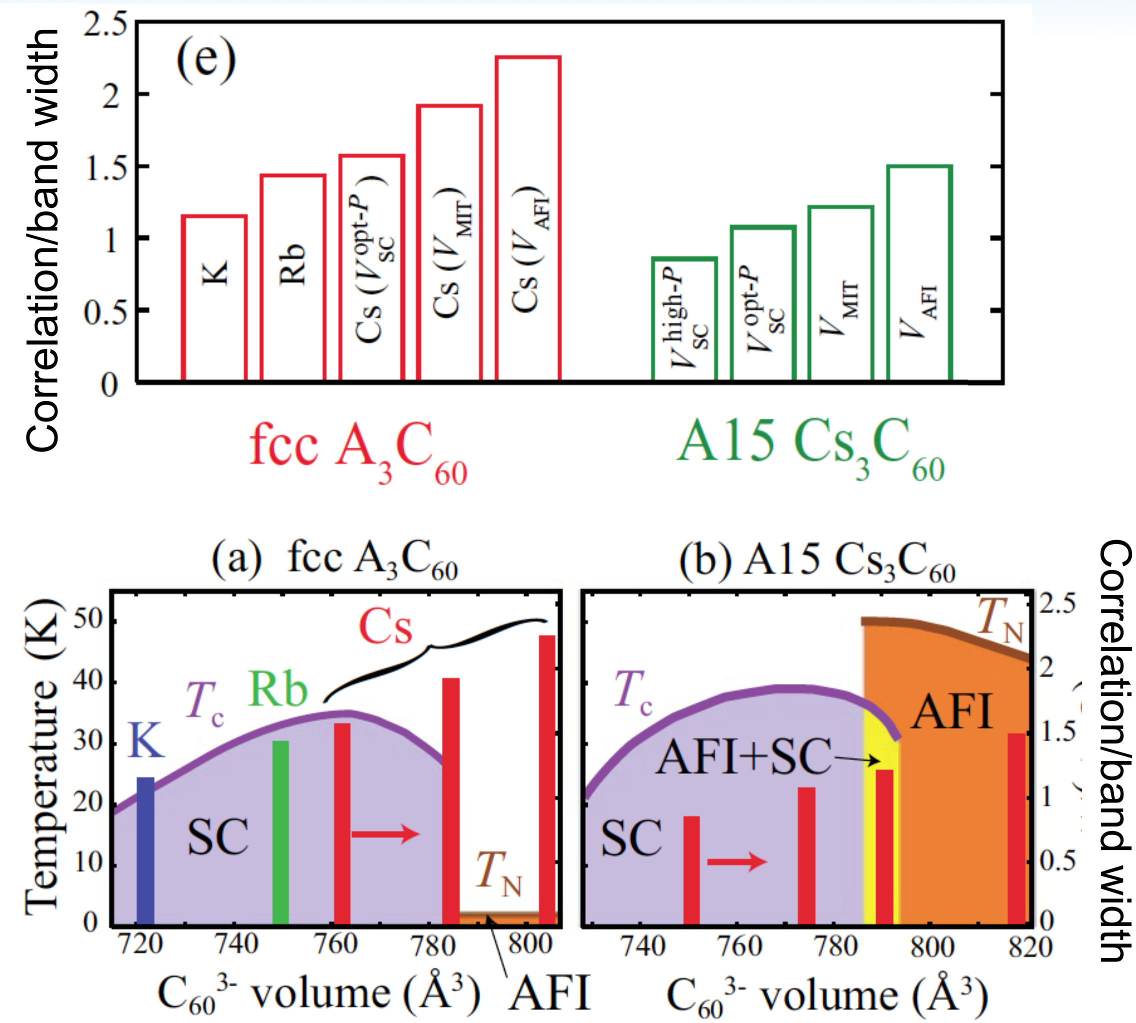
$$\chi = \sum_i^{occ} \sum_j^{unocc} \frac{\psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r')}{\omega - \varepsilon_j + \varepsilon_i \pm i\delta}$$



Constrained RPA method

Aryasetiawan et al, PRB 70, 195104 (2004)
Solovyev-Imada, PRB 71, 045103 (2005)

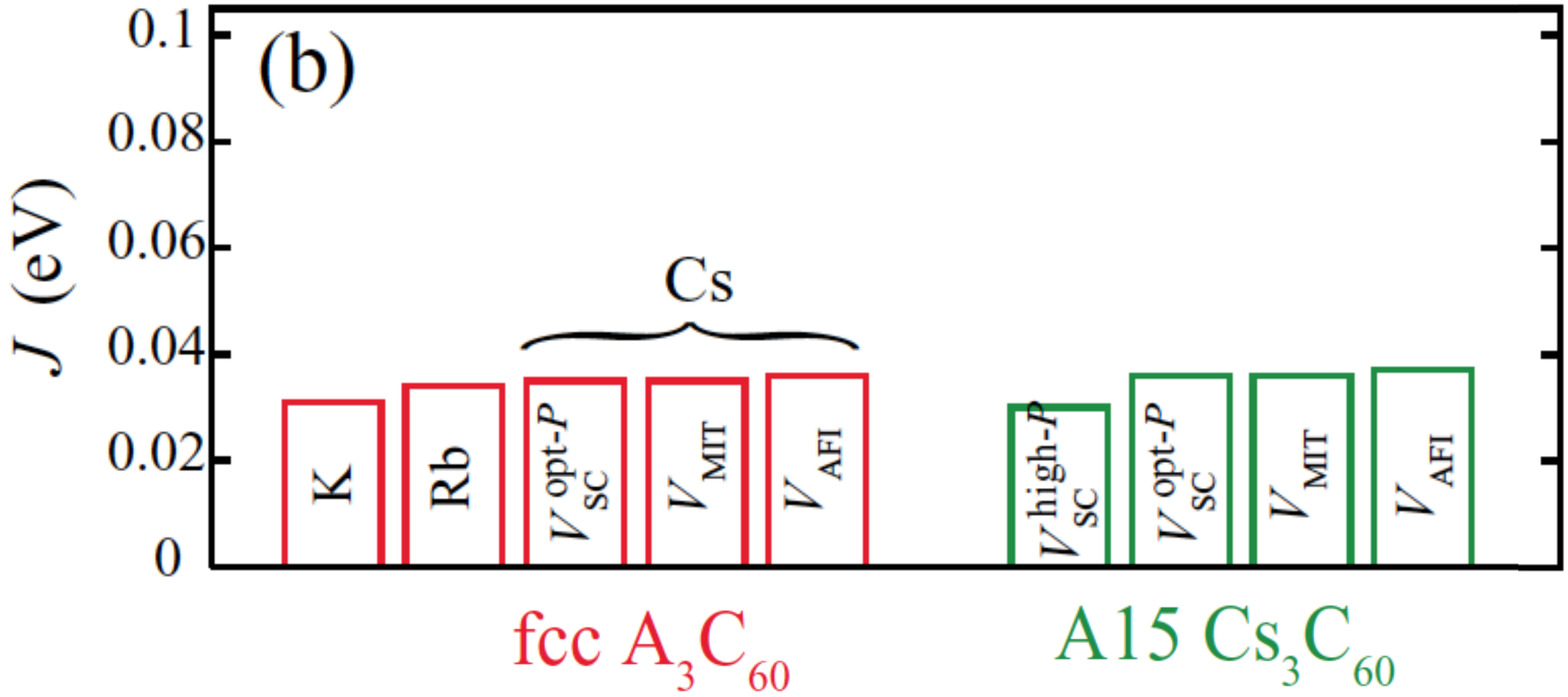
Hubbard U of C_{60} superconductors



Larger U → higher T_c

Nomura, Nakamura, RA, PRB85 155452(2012)

Hund J of C_{60} superconductors



J_{Hund}~0.035 eV (much smaller than 10% of U)

Ab initio derivation of low-energy Hamiltonian

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

$$+ \sum_{\mathbf{q}\nu} \sum_{\mathbf{k}} \sum_{ij} \sum_{\sigma} g_{ij}^{(p)\nu}(\mathbf{k},\mathbf{q}) c_{i\mathbf{k}+\mathbf{q}}^{\sigma\dagger} c_{j\mathbf{k}}^{\sigma} \left(b_{\mathbf{q}\nu} + b_{-\mathbf{q}\nu}^{\dagger}\right) + \sum_{\mathbf{q}\nu} \omega_{\mathbf{q}\nu}^{(p)} b_{\mathbf{q}\nu}^{\dagger} b_{\mathbf{q}\nu}$$

How to evaluate $g_{ij}^{(p)\nu}(\mathbf{k},\mathbf{q})$ and $\omega_{\mathbf{q}\nu}^{(p)}$?

We have to exclude the effect of low-energy screening
(we need to estimate partially screened values)

⇩

cDFPT method

Y. Nomura, K. Nakamura and RA, PRL112 027002 (2014)

cf) Talk by M. Casula

Density functional perturbation theory

Electron-phonon coupling g $\quad \langle \psi_{k+q} | \frac{\partial V}{\partial u} | \psi_k \rangle$

Phonon frequency ω $\quad \frac{\partial^2 E}{\partial u \partial u}$

In DFT, physical quantities are represented in terms of ρ

$$E[\rho] \qquad V[\rho]$$

$$\frac{\partial}{\partial u} = \boxed{\frac{\partial \rho}{\partial u}} \frac{\partial}{\partial \rho}$$

from $\frac{\partial \rho}{\partial u}$, we can estimate g and ω

Constrained DFPT

$$\Delta\rho = 2\sum_n \psi_n^* \Delta\psi_n$$

$$\Delta\psi_n(\mathbf{r}) = \sum_{m\neq n} \psi_m(\mathbf{r}) \frac{\langle\psi_m|\Delta V_{SCF}|\psi_n\rangle}{\epsilon_n - \epsilon_m}$$

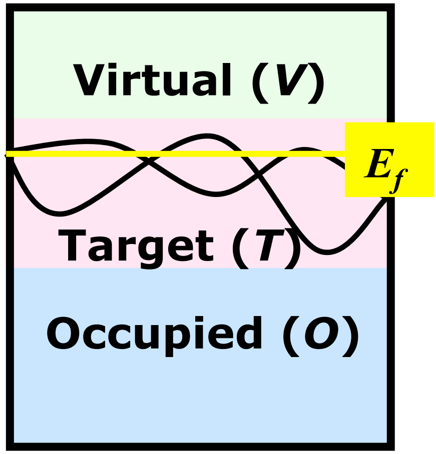
If ψ_n belongs to the target subspace, we modify the sum over *m* as

$$\sum_m \longrightarrow \sum_{m\in occ.,vir.}$$

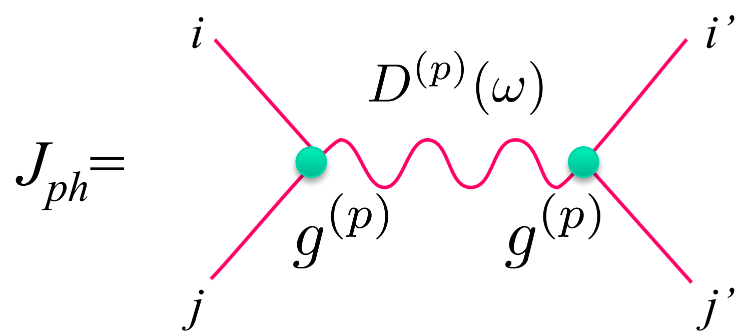
exclude the target-target processes

We can obtain $\Delta\rho^{(p)}$ and then

$\omega^{(p)}$ and $g^{(p)}$



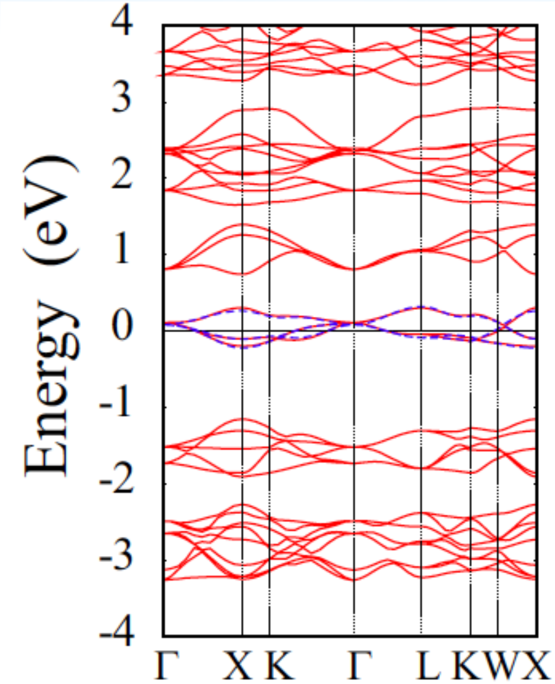
Phonon-mediated J vs Hund's J



	K_3C_{60}	Rb_3C_{60}	Cs_3C_{60}
J_{Hund} (eV)	-0.031	-0.034	-0.035
J_{ph} (eV)	0.050	0.051	0.051

$J_{eff}=J_{ph}+J_{hund}>0$ (inverted Hund's coupling)

Ab initio downfolding



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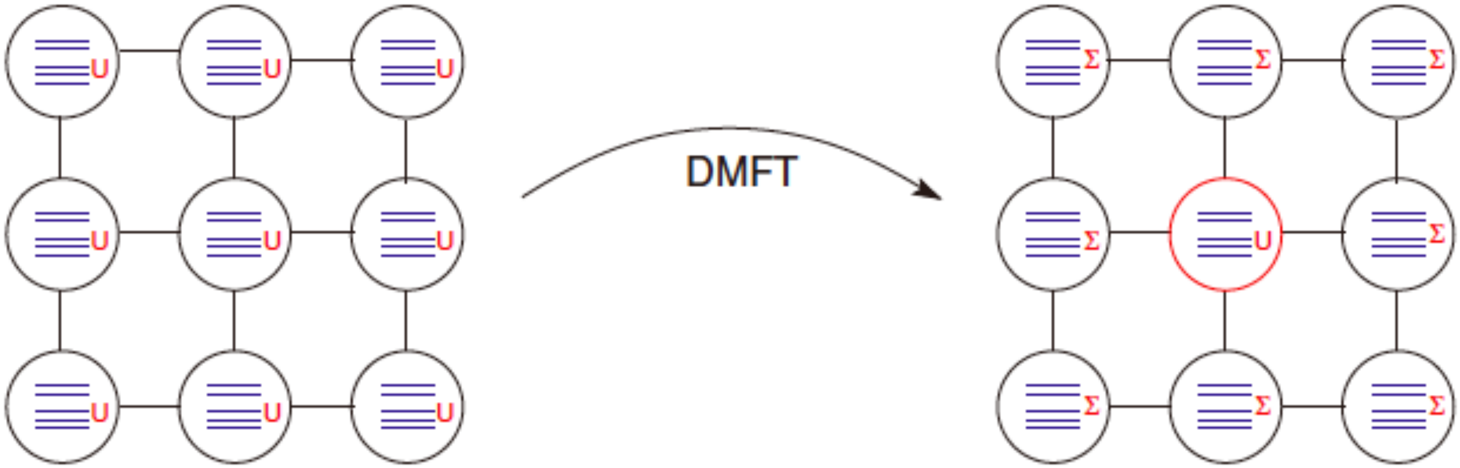
Model Analysis: Dynamical Mean Field theory



DMFT maps the lattice many-body problem with interactions U on every site onto a single-site problem where the interaction has been replaced by the self-energy Σ except for a single site.

To study SC, we explicitly consider the anomalous Green's function:

$$F(\mathbf{k},\tau) \equiv -\langle T c_{\mathbf{k}\uparrow}(\tau) c_{-\mathbf{k}\downarrow}(0) \rangle$$

$$\hat{G}(\mathbf{k},\tau) \equiv -\langle T \Psi_{\mathbf{k}}(\tau) \Psi_{\mathbf{k}}^{+}(0) \rangle = \begin{pmatrix} G(\mathbf{k},\tau) & F(\mathbf{k},\tau) \\ F(\mathbf{k},\tau)^* & -G(-\mathbf{k},-\tau) \end{pmatrix}$$

Effective impurity model is solved by CTQMC (CT-HYB) E. Gull et al., RMP 2011

Phonon Contribution

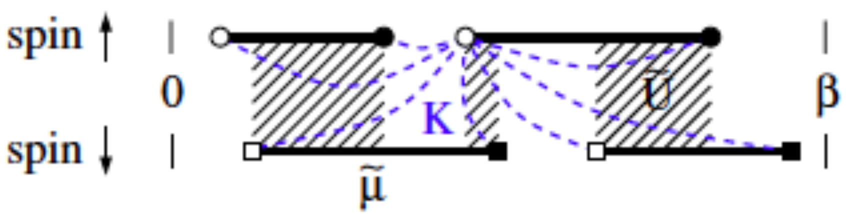
Lang-Firsov transformation (1962)

$$H_{\mathrm{loc}} = -\mu(n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow + \sqrt{2}\lambda(n_\uparrow + n_\downarrow - 1)X + \frac{\omega_0}{2}(X^2 + P^2)$$

$$X = (b^\dagger + b)/\sqrt{2} \qquad P = (b^\dagger - b)/i\sqrt{2},$$

$$\tilde{H}_{\mathrm{loc}} = e^{iPX_0} H_{\mathrm{loc}} e^{-iPX_0} \Rightarrow \tilde{H}_{\mathrm{loc}} = -\tilde{\mu}(\tilde{n}_\uparrow + \tilde{n}_\downarrow) + \tilde{U}\tilde{n}_\uparrow \tilde{n}_\downarrow + \frac{\omega_0}{2}(X^2 + P^2).$$

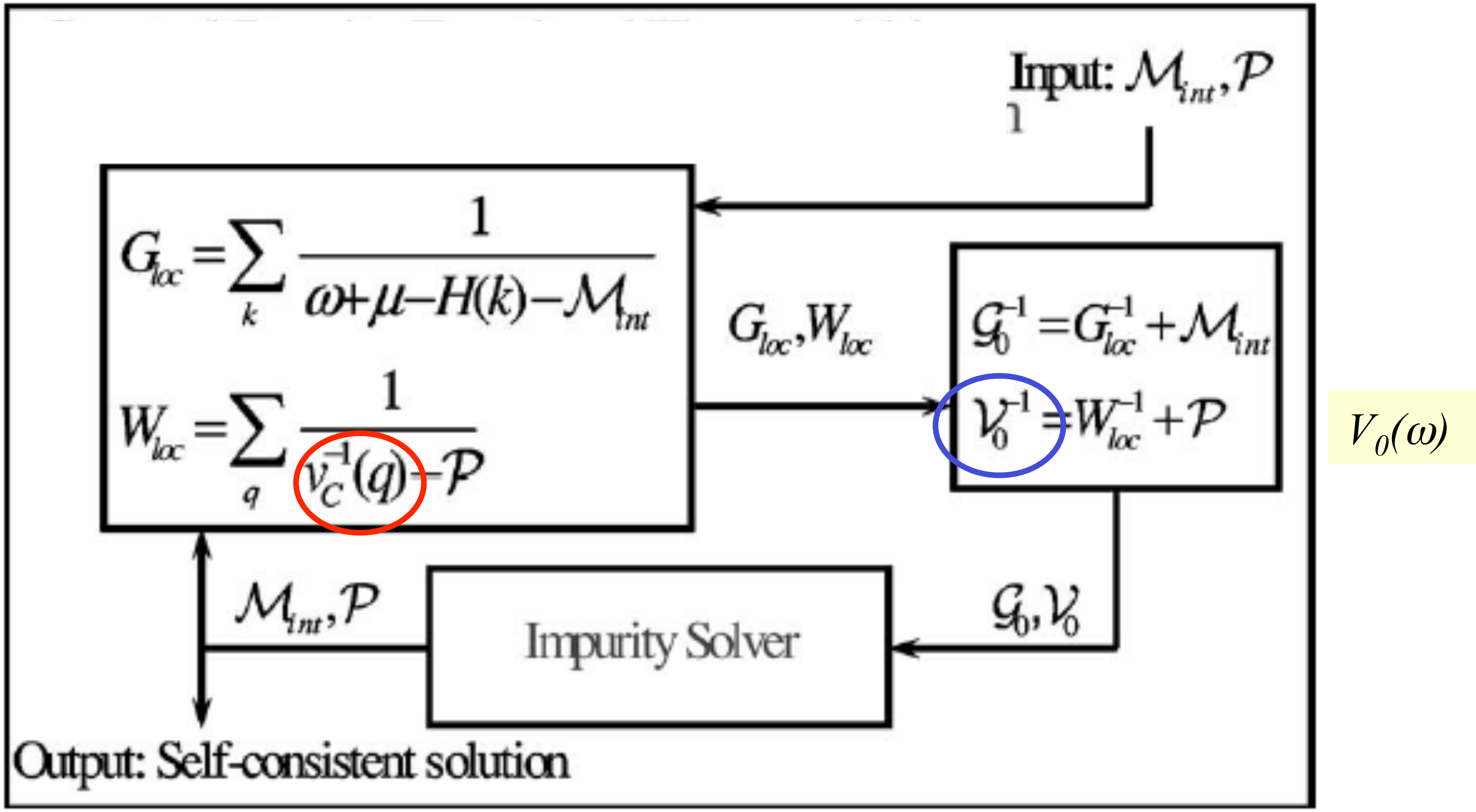
$$\tilde{\mu} = \mu - \lambda^2/\omega_0 \qquad \tilde{U} = U - 2\lambda^2/\omega_0$$



The phonon contribution can be interpreted as an interaction K(τ−τ')

(Werner & Millis PRL2010)

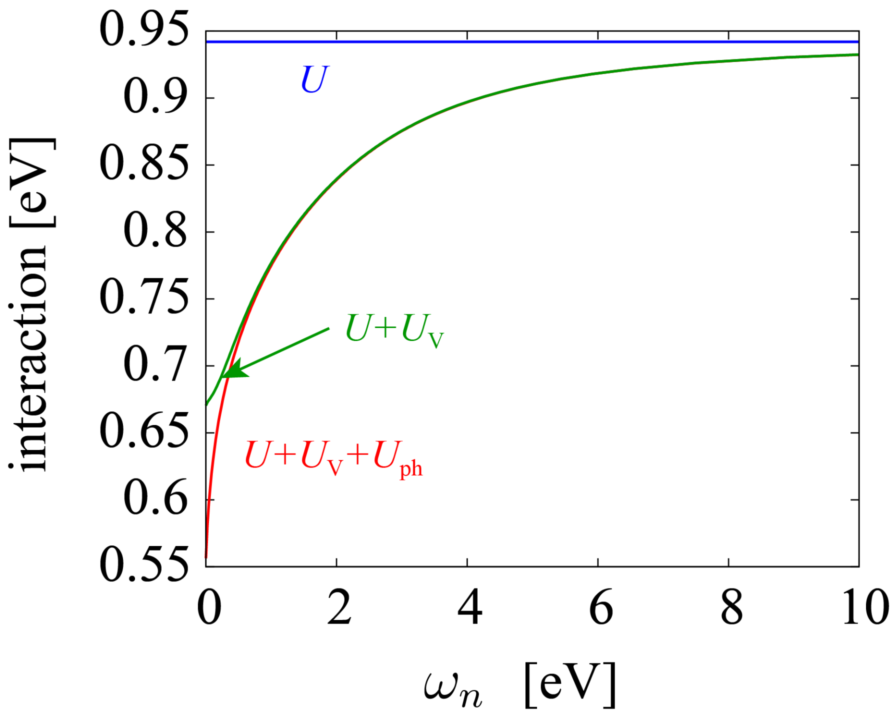
Off-site Coulomb interaction: Extended DMFT



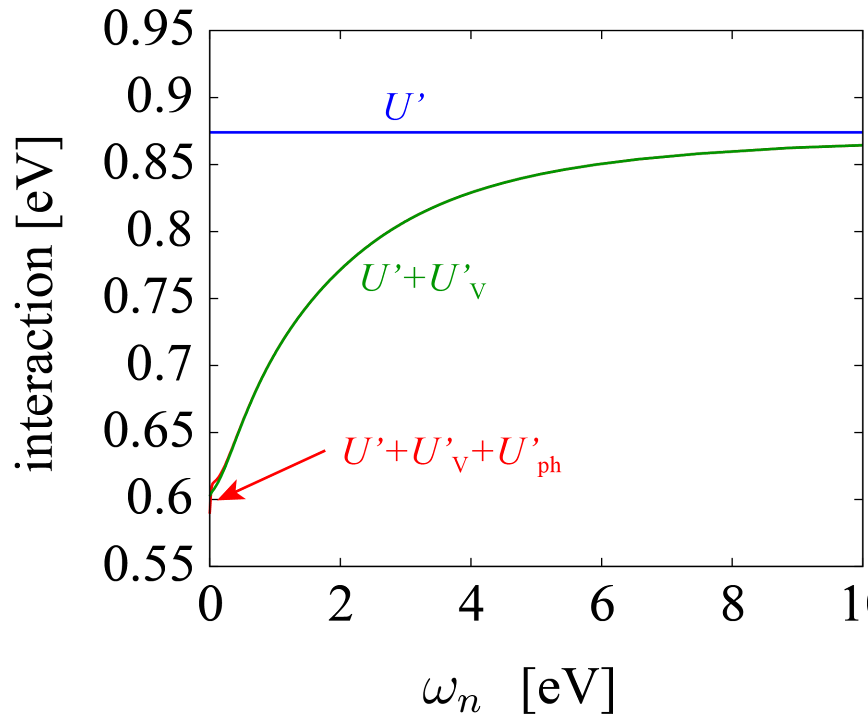
A.M. Senguputa and A. Georges, PRB 1995
Q. Si and J.L. Smith, PRL 1996
P. Sun and G. Kotliar, PRB 2002, PRL 2004, …

Interaction parameters in the effective impurity model

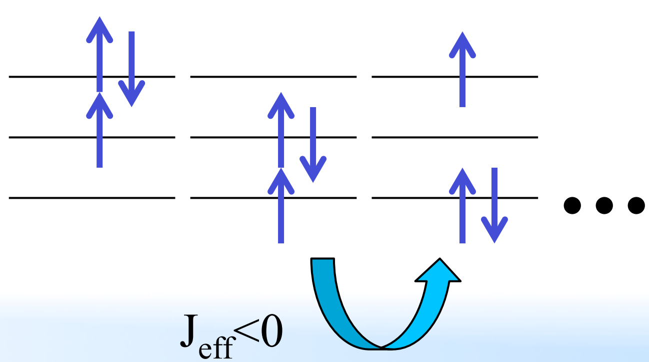
Intra-orbital Hubbard U



Inter-orbital Hubbard U'



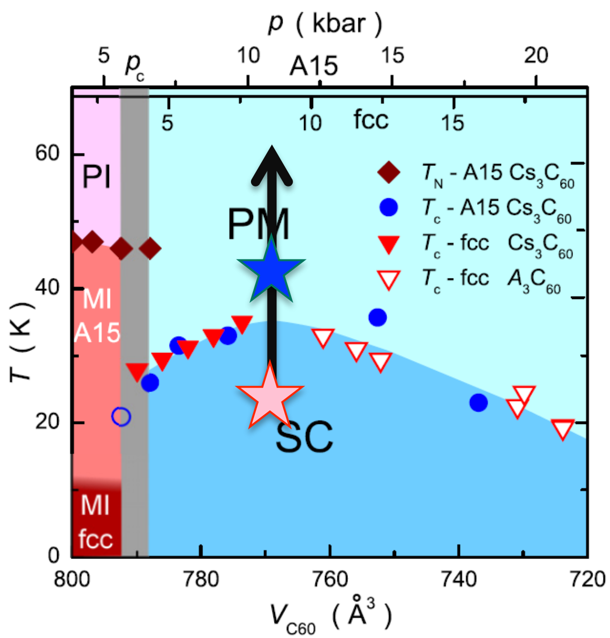
$$U_{eff}(0) < U'_{eff}(0)$$



(2,1,0) configurations favored

Result: Superconductivity

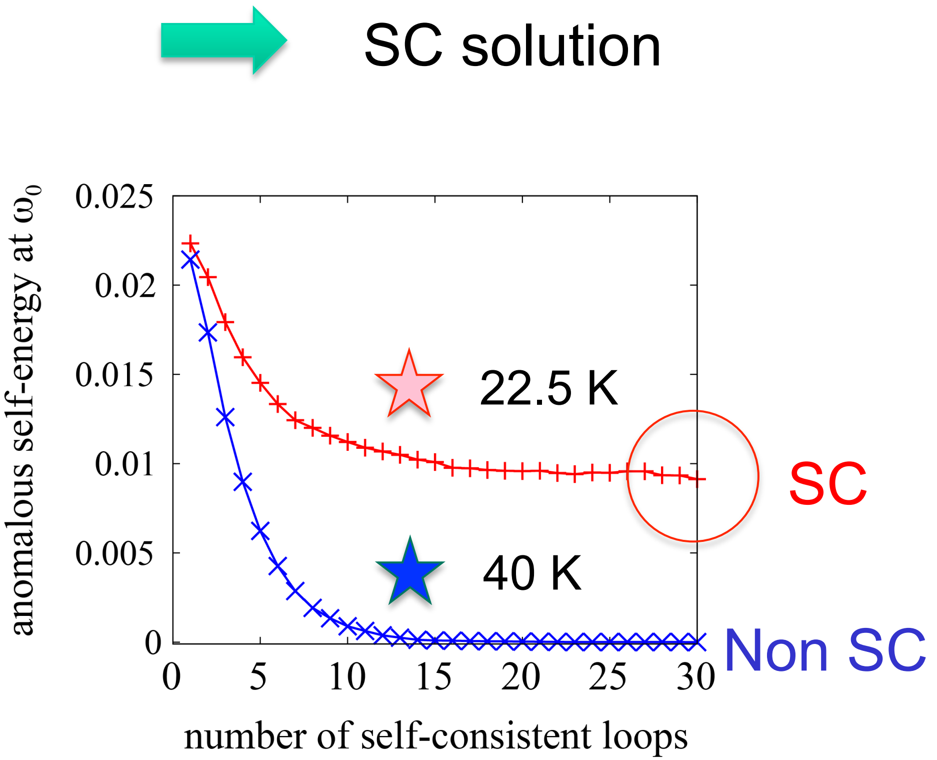
Temperature dependence



Taken from
Y. Ihara et al., EPL 94, 37007 (2011)

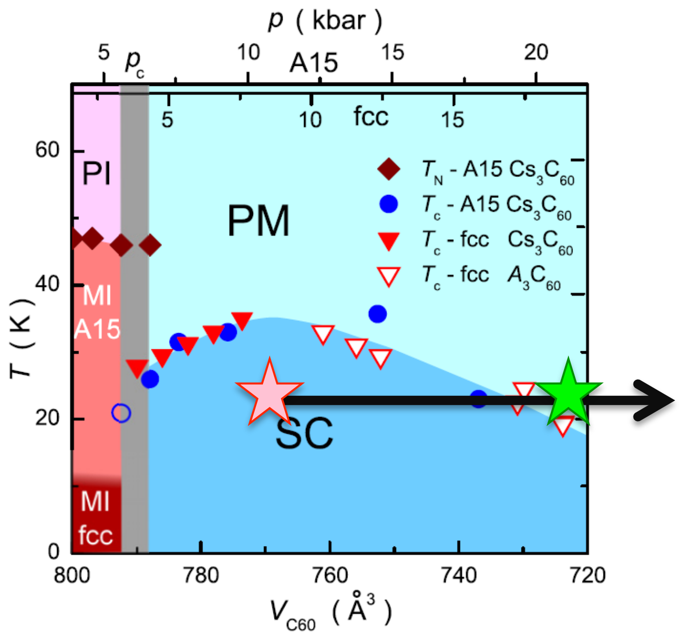
Finite anomalous self-energy

SC solution



Result: Superconductivity

Volume dependence



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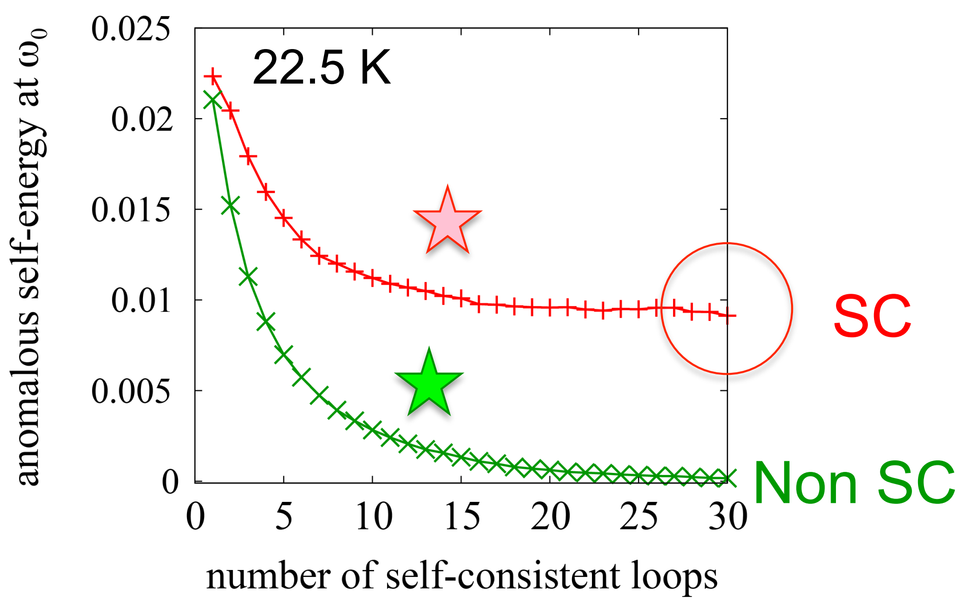
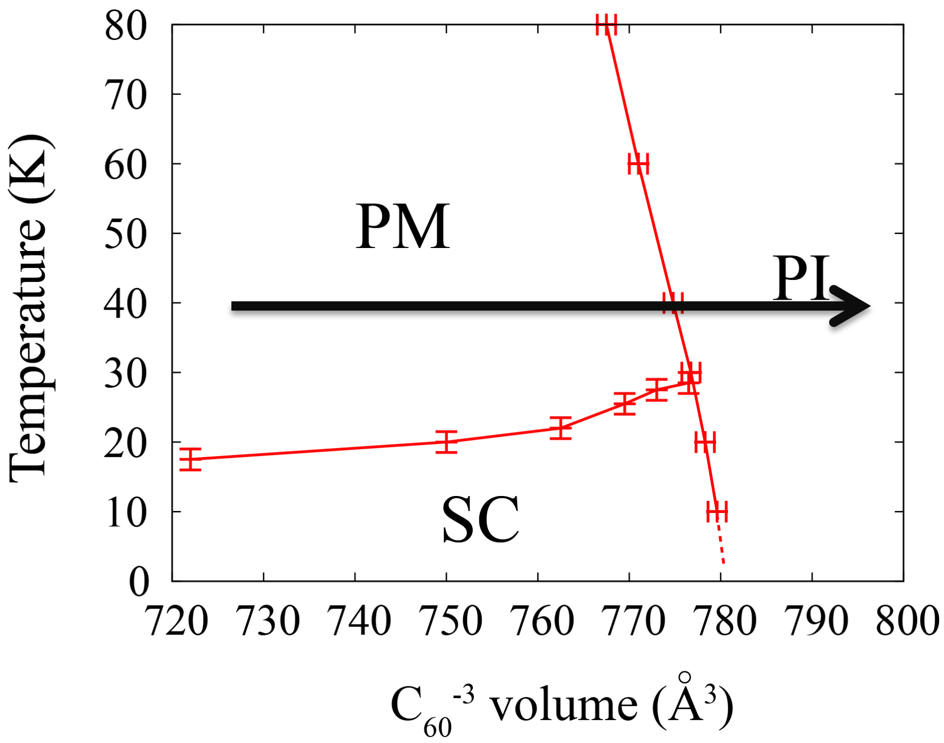
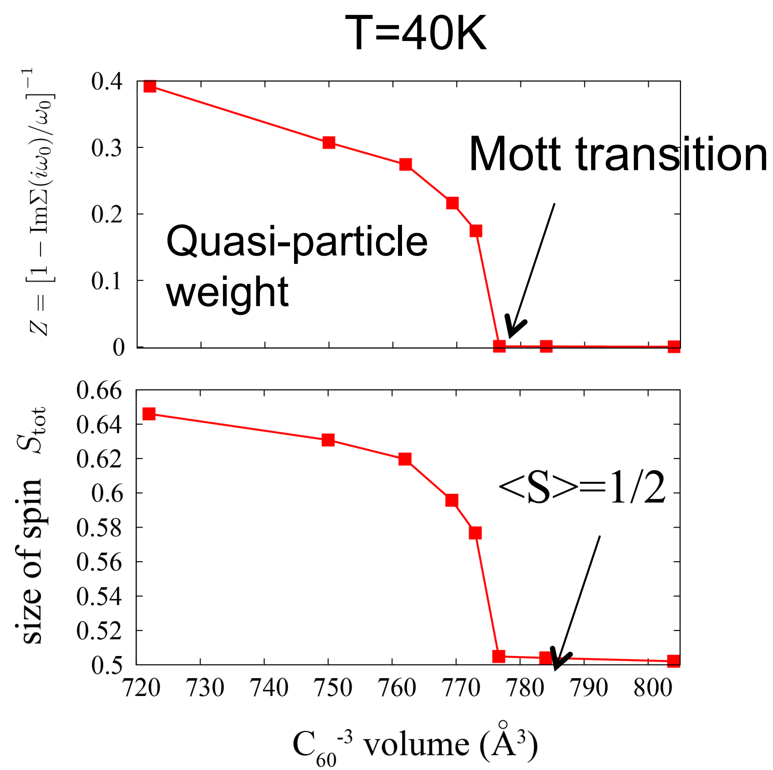


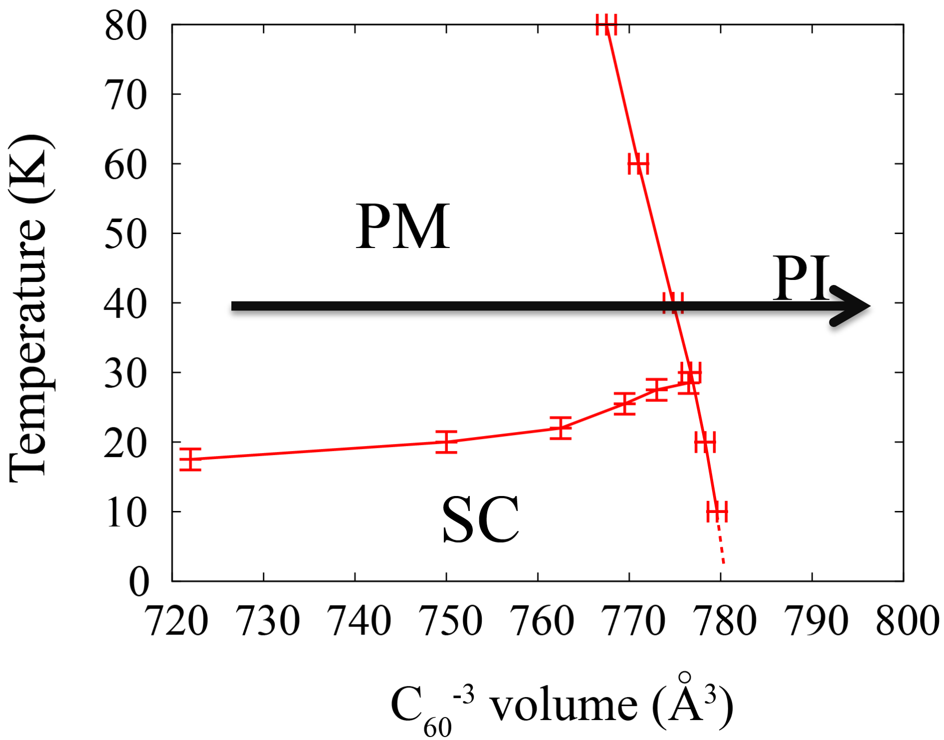
Result: Mott transition

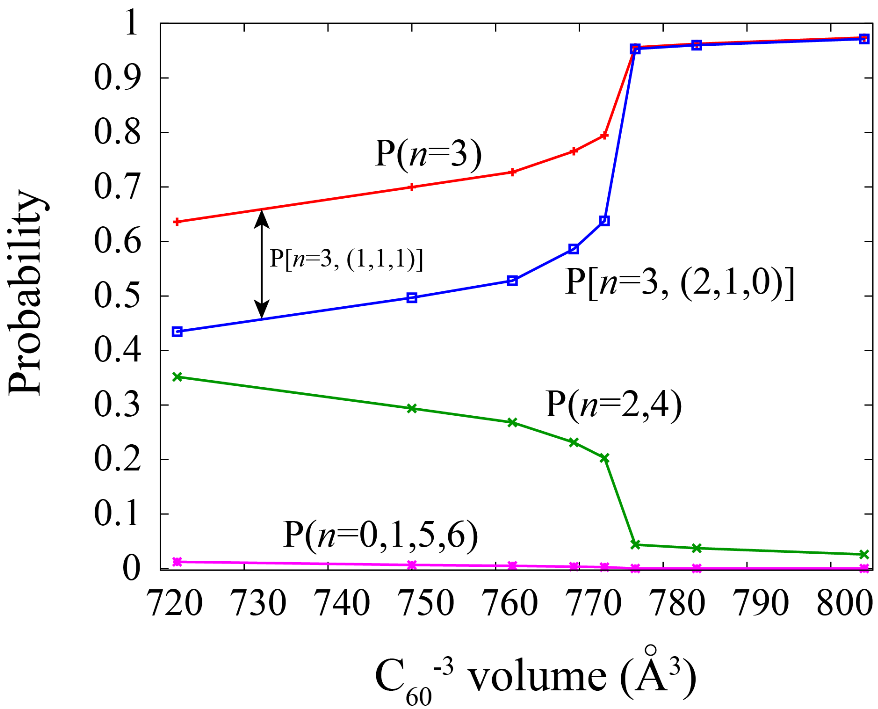


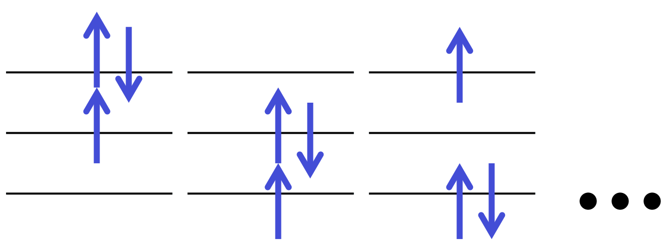


Low-spin state favored

Result: Mott transition





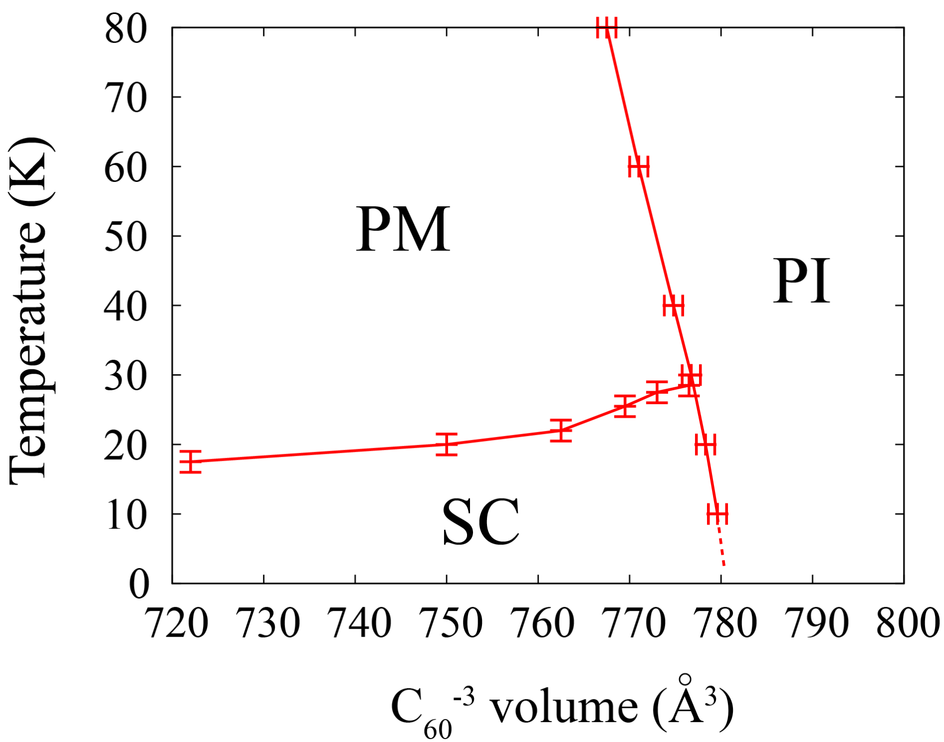


(2,1,0) configurations favored

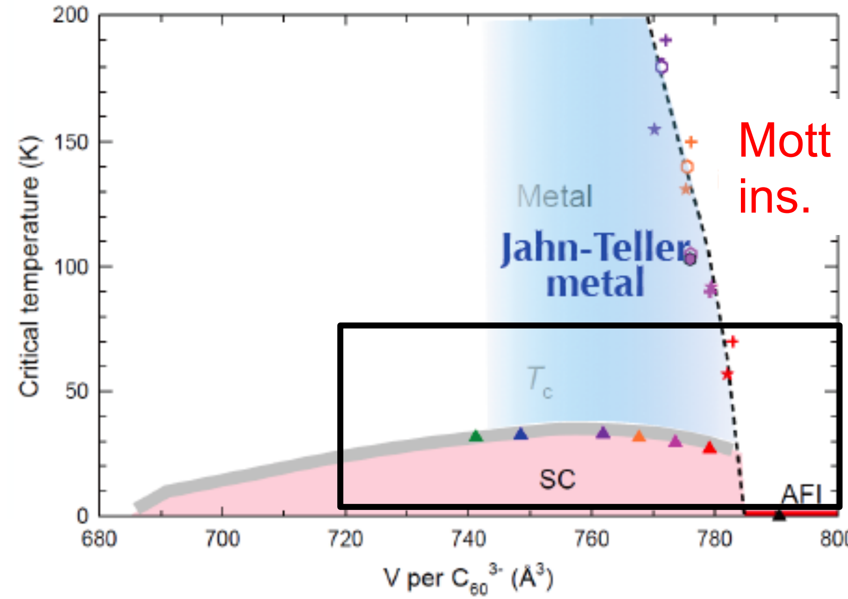
(dynamical JT effect)

Phase diagram

Theory



Experiment
(taken from Kasahara et al., 2014)



SC phase with T_c~30K close to MI phase
reproduced by <u>fully non-empirical calculation</u>

Conclusion: Mechanism of SC in A_3C_{60}

- Conventional scenario
  - SCDFT does not reproduce high T_c

R. Akashi & RA, PRB 2013

- Unconventional scenario
  - *Ab initio* derivation of low-energy Hamiltonian

Y. Nomura, K. Nakamura & RA, PRB2012, PRL2014

- EDMFT analysis:

SC phase with T_c~30K
close to MI phase
reproduced by
<u>fully non-empirical calculation</u>