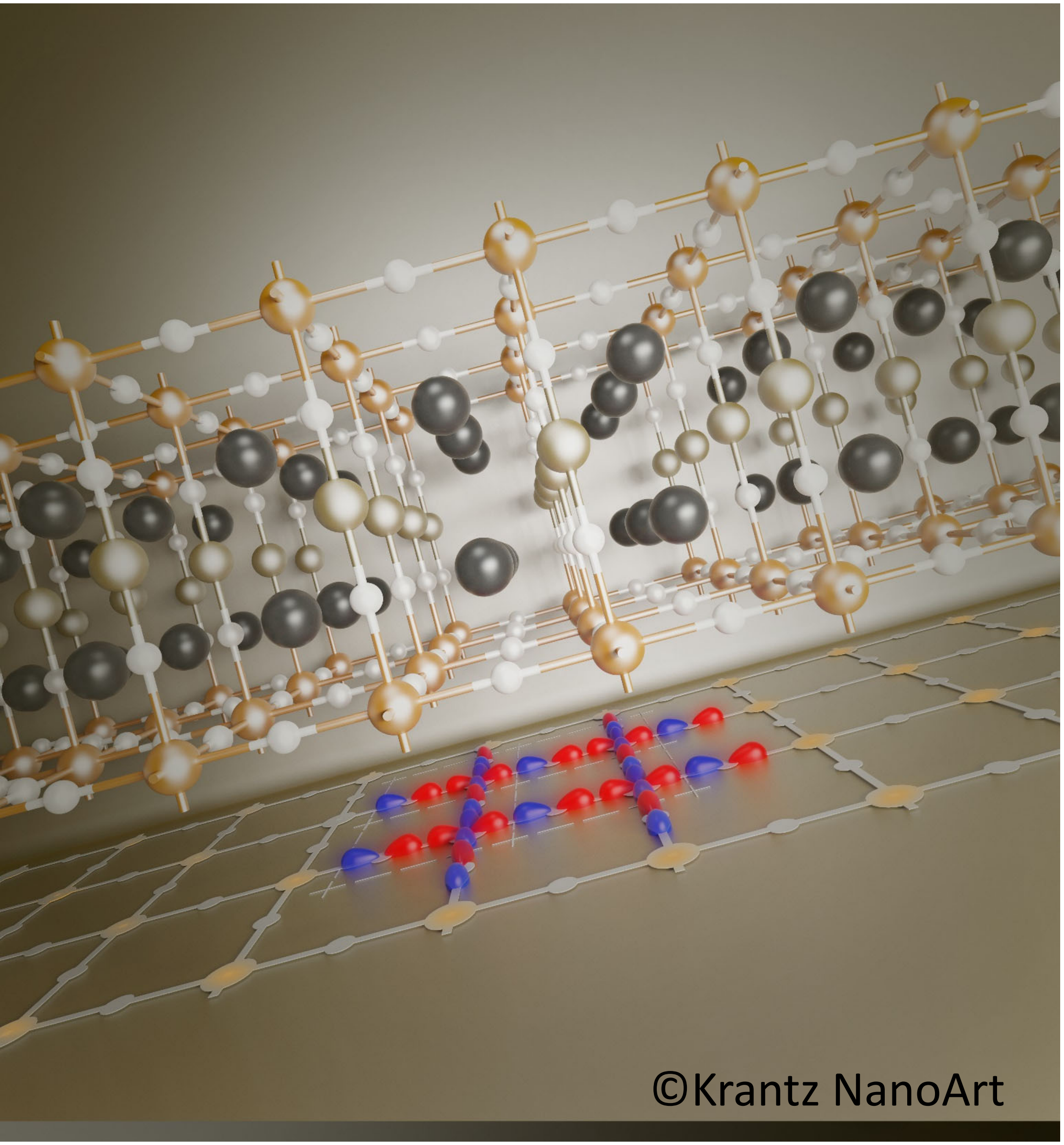

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Fonds de recherche Nature et technologies Québec

Mechanism of Superconductivity in Cuprates : oxygen as a witness

André-Marie Tremblay
Université de Sherbrooke
Institut quantique

Paris, May – June 2023

Institut quantique

Université de Sherbrooke

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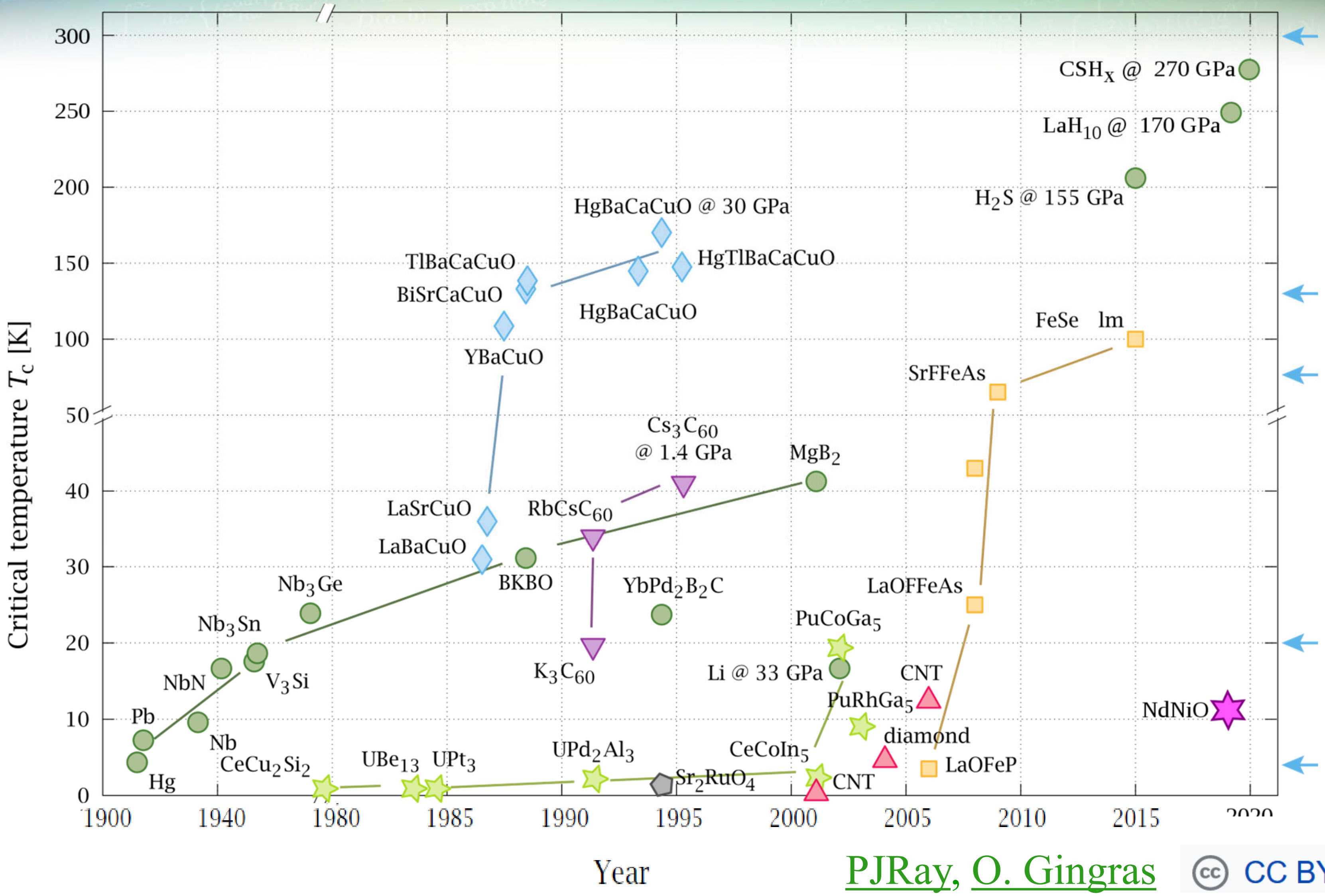
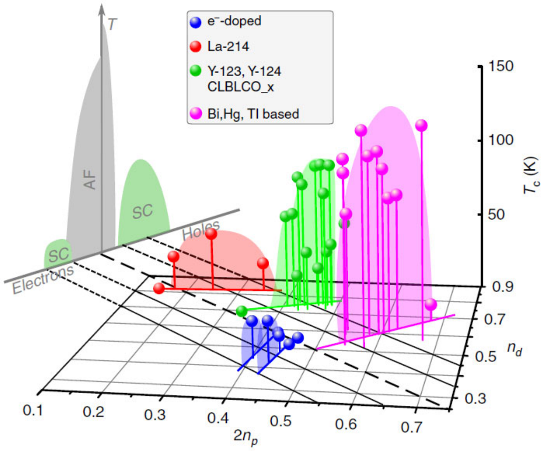
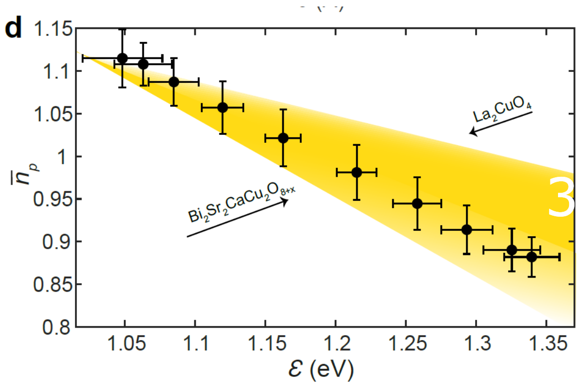


PJRay, O. Gingras

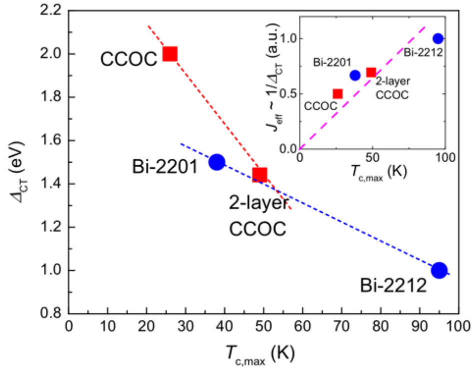
Three experimental observations on optimizing T_c



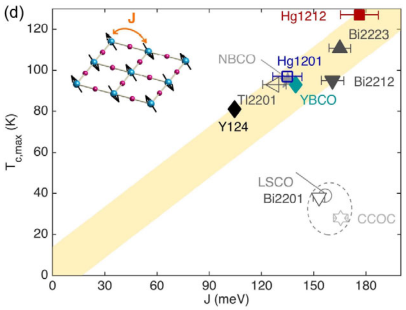
Rybicki, … Haase,
Nat. Comm. 7, 11413
(2016)



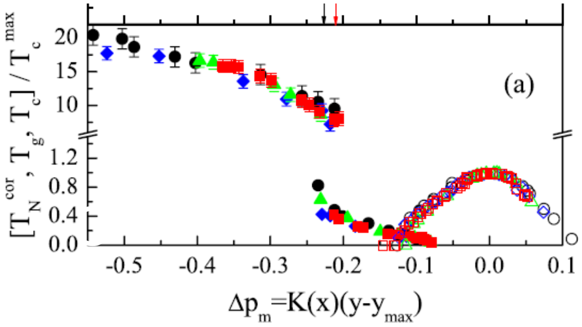
O'Mahony *et al.*
PNAS **119** e2207449119 (2022)



Ruan *et al.*
Sci. Bull. **61** (2016)



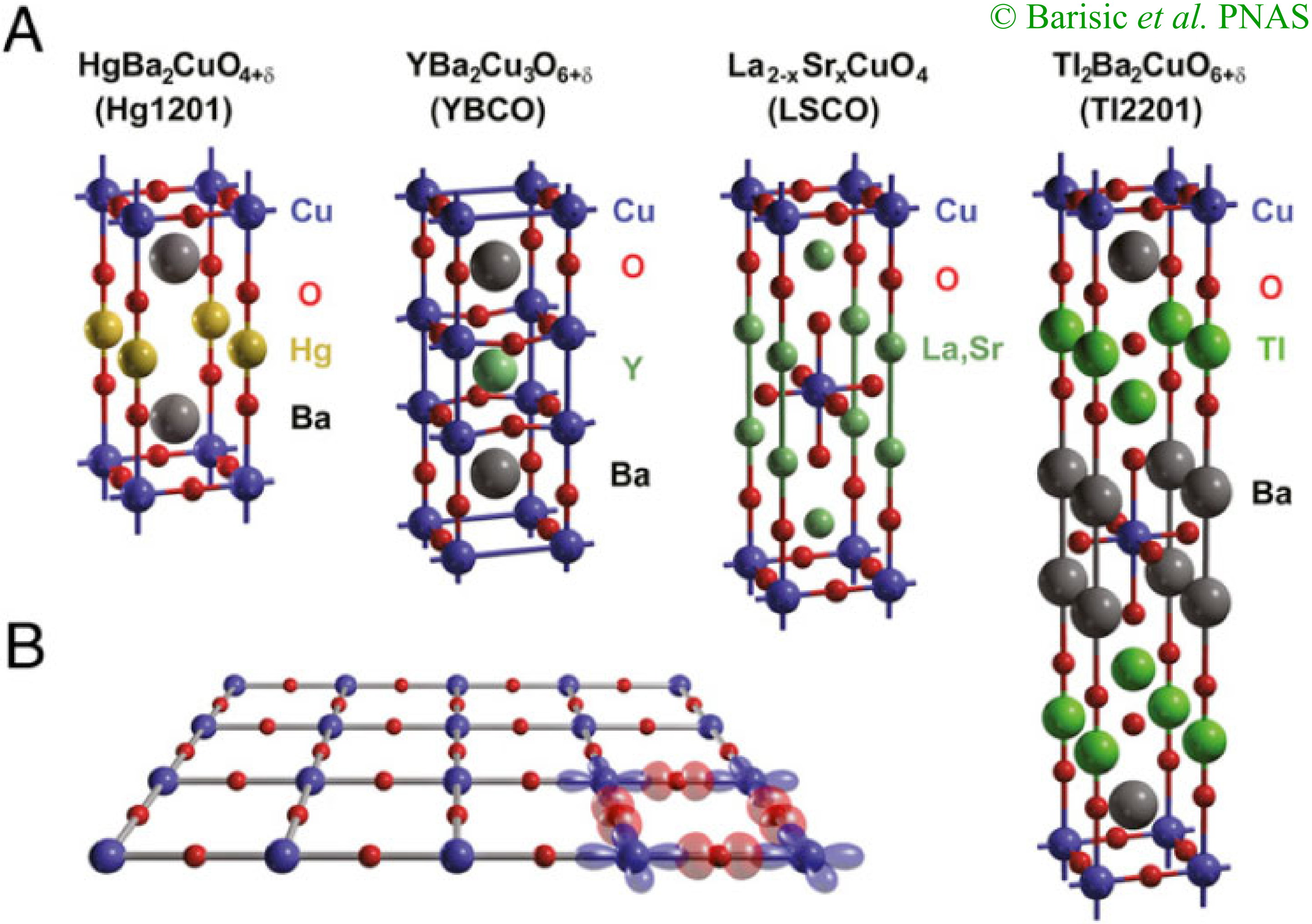
Lichen Wang,
Nat. Comm. **13**, 3163 (2022)



A. Keren
B. New J. Phys. **11** 065006

There are different kinds of cuprates : All with CuO_2 planes

© Barisic *et al.* PNAS **110**, 12235 (2013)



Three-band (Emery VSA) Hubbard model

Sidhartha Dash

Nicolas Kowalski

Patrick Sémon

David Sénéchal

V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987)

C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Communications **62**, 681–685 (1987), ISSN 0038-1098,

PNAS **118** (40) e2106476118 (2021)

Outline

- Method for Hubbard-like models
- 3-band model
- Superconductivity
  - 3-band Model (Two classes)
  - Three experiments that tell us how to optimize Tc.
    - Pairing mechanism
    - Bonus

- Conclusion

Method
Solving the models

Metzner, Vollhardt PRL **62**, 324 (1989)
Georges, Kotliar, PRB **45,** 6479 (1992)
Jarrell PRL **69,** 168 (1992)
Review: Georges, Kotliar, Krauth, Rozenberg, RMP **68**, 13 (1996)

Dynamical Mean-Field Theory : DMFT

Method

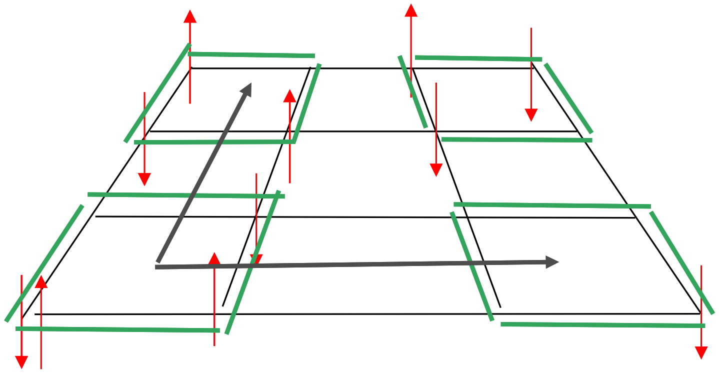
Cluster generalization of
Dynamical Mean-Field Theory : DMFT

REVIEWS
Maier, Jarrell et al., RMP. (2005)
Kotliar *et al.* RMP (2006)
AMST *et al.* LTP (2006)

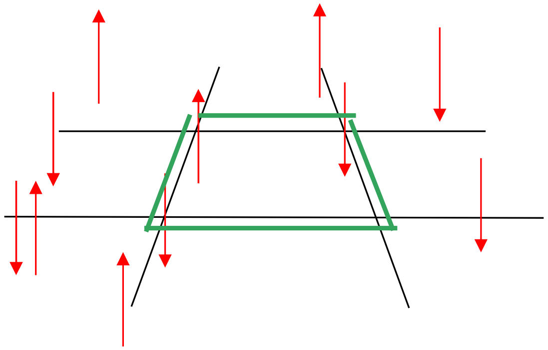
Lichtenstein *et al.*,PRB 2000
Kotliar *et al.*, PRB 2000
M. Potthoff, EJP 2003

Localized and delocalized pictures C-DMFT

Delocalized



Localized



$$\mathbf{R} \longrightarrow \widetilde{k}$$

$$G_{ij} = \int \frac{d^d\widetilde{k}}{(2\pi)^d}\left(\frac{1}{(i\omega_n+\mu)I-\varepsilon\left(\widetilde{k}\right)-\Gamma_O(i\omega_n)-\Sigma(i\omega_n)}\right)_{ij} \qquad \left(G^{-1}\right)_{ij} = \left(G_0^{-1}\right)_{ij} - \Sigma_{ij}$$

REVIEWS

Maier, Jarrell et al., RMP. (2005)

Kotliar *et al.* RMP (2006)

AMST *et al.* LTP (2006)

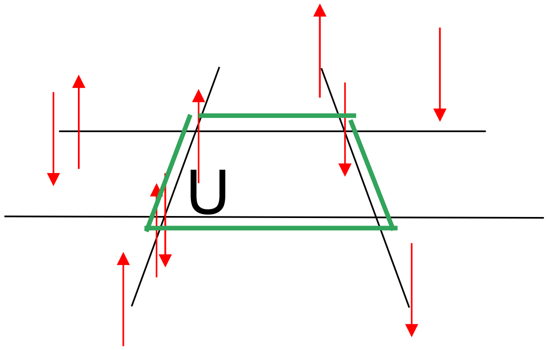
Lichtenstein *et al.*,PRB 2000

Kotliar *et al.*, PRB 2000

M. Potthoff, EJP 2003

Impurity solvers

Impurity solver (Exact diagonalisation)



Caffarel, Krauth, PRL **72** 1545 (1994)

QCM David Sénéchal
ArXiV: 2305.18643 (and Bitbucket)

Some groups using these methods for cuprates

- Europe:
  - Georges, Parcollet, Ferrero, Civelli, Fratino (Paris)
  - Sordi (London), Lichtenstein, Potthoff, (Hamburg) Aichhorn (Graz), Liebsch (Jülich) de Medici (Grenoble) Capone (Italy)
- USA:
  - Gull (Michigan) Millis (Columbia)
  - Kotliar, Haule (Rutgers)
  - Jarrell (Louisiana)
  - Maier, Okamoto (Oakridge)
- Japan
  - Imada (Tokyo) Sakai, Tsunetsugu, Motome
- China
  - Wei Wu …

Critique of the method: advantages and limitations

UNIVERSITÉ DE SHERBROOKE

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+ and -

- Long range order:
  - No mean-field factorization on the cluster
  - Symmetry breaking allowed in the bath
  - Pairing dynamically through the bath
- Included exactly:
  - Short-range dynamical and spatial correlations

- Missing:
  - Long wavelength p-h and p-p fluctuations
  - Hence good when the corresponding correlation lengths are small
  - Exact as cluster size increases

Three-band (Emery VSA) Hubbard model

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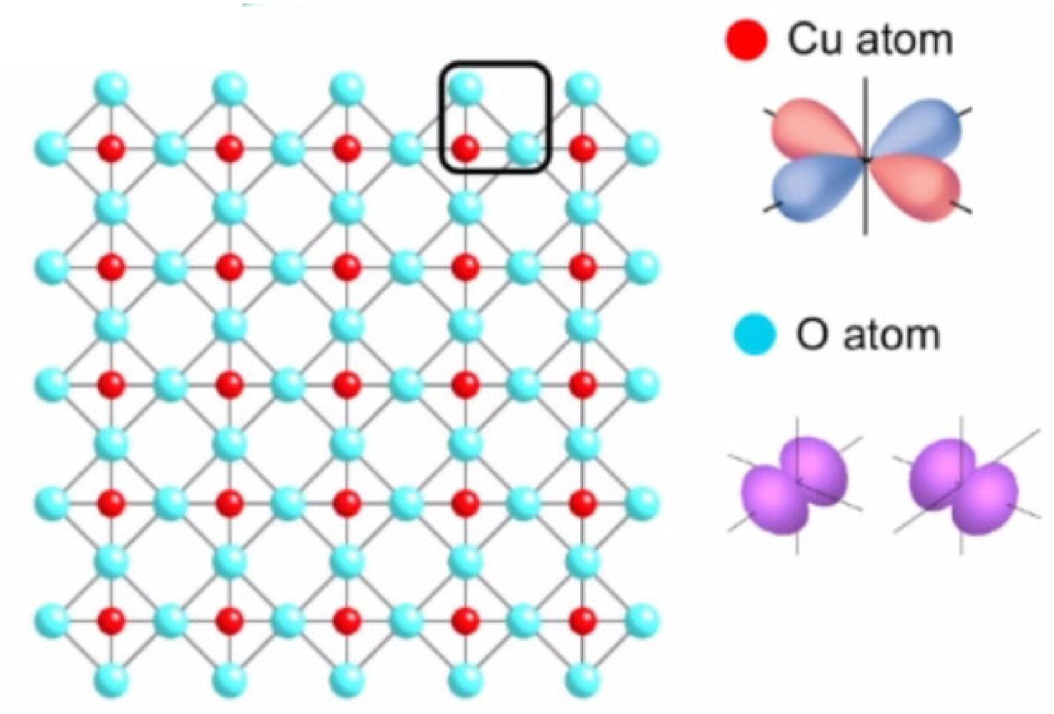
V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987)

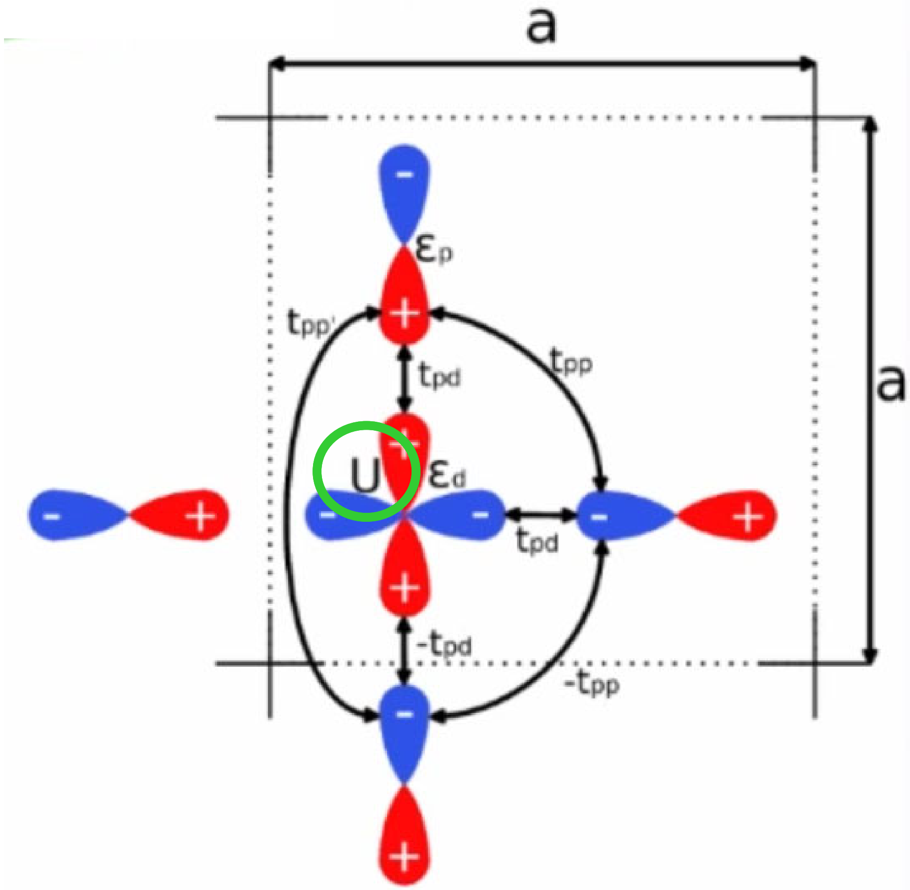
C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Communications **62**, 681–685 (1987), ISSN 0038-1098,

PNAS **118** (40) e2106476118 (2021)

Copper and oxygen planes



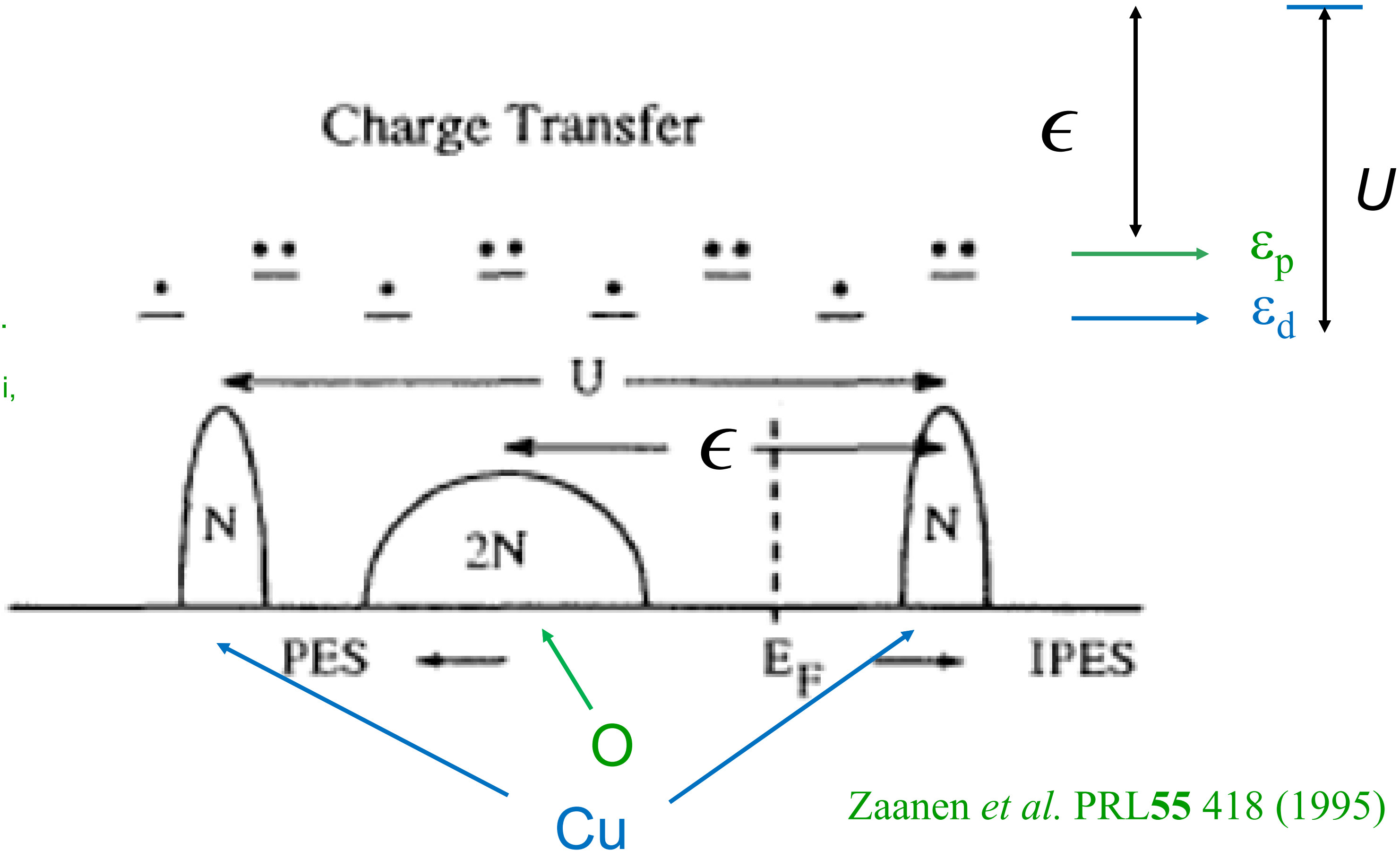
© Nicolas Kowalski



© Nicolas Kowalski

Cartoon of the charge transfer insulator

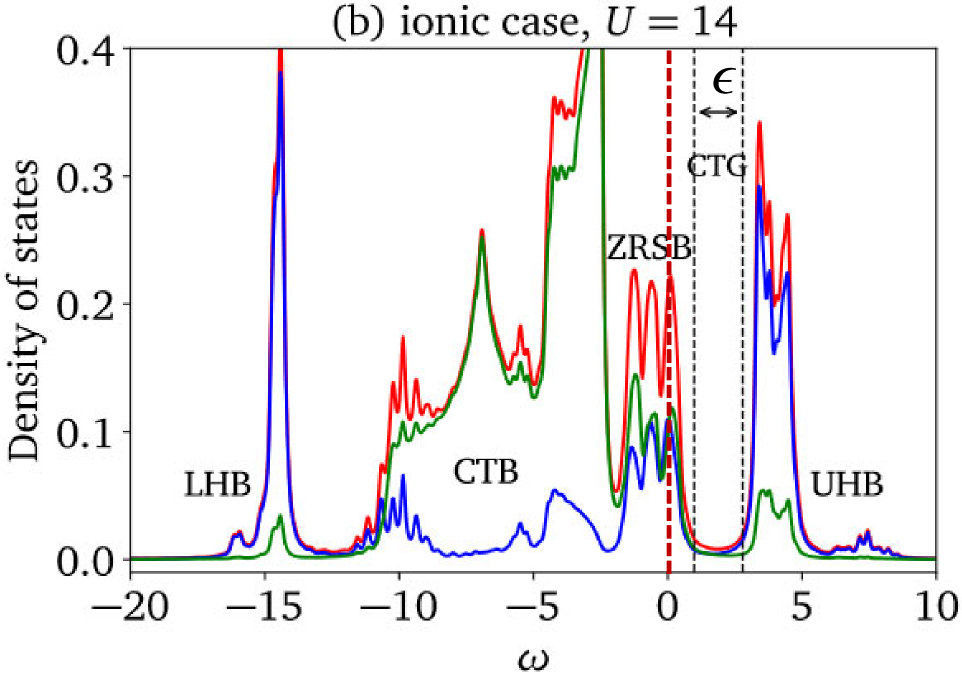
C. Weber, T. Giamarchi, C. M. Varma, PRL **112**, 117001
L. Fratino, P. Sémon, G. Sordi, A.-M. S. T
PRB **93**, 245147 (2016)
Z.-H. Cui PRR **2**, 043259
M. Zegrodnik, *et al.* J. Phys. Cond Mat **33**, 415601
P. Mai,*et al.*. NPJ Quantum Mater. **6**, 1–5
P. Mai *et al.*,
PRB **103**, 144514 (2021).

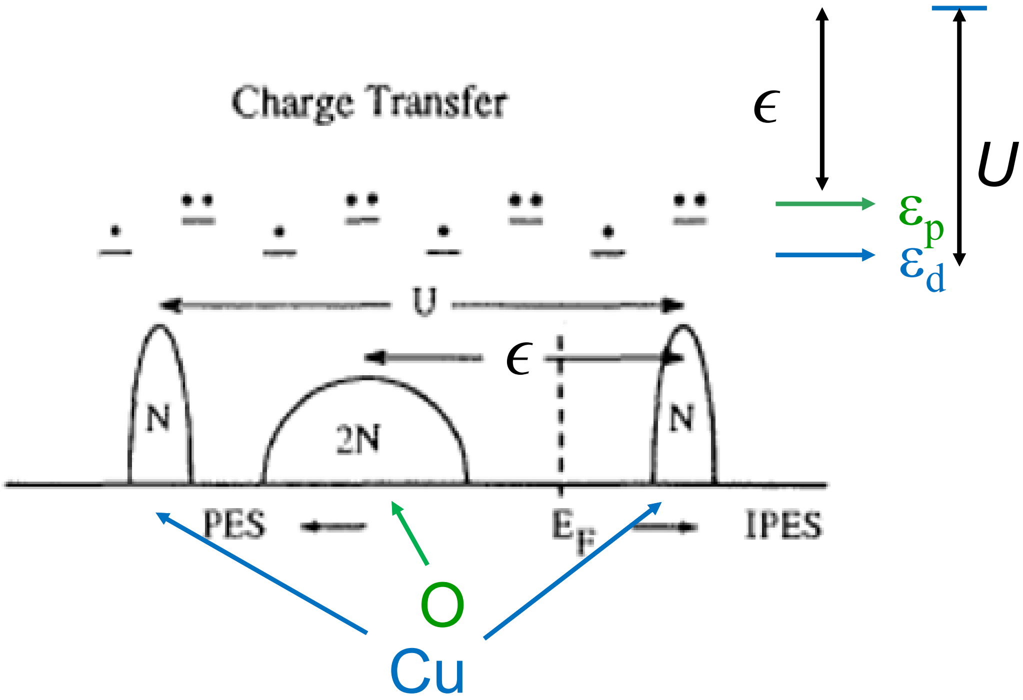


Zaanen *et al.* PRL**55** 418 (1995)

From Meinders *et al.* PRB **48**, 3916 (1993)

"Ionic" limiting case





Meinders *et al.* PRB **48**, 3916 (1993)

Zaanen *et al.* PRL**55** 418 (1995)

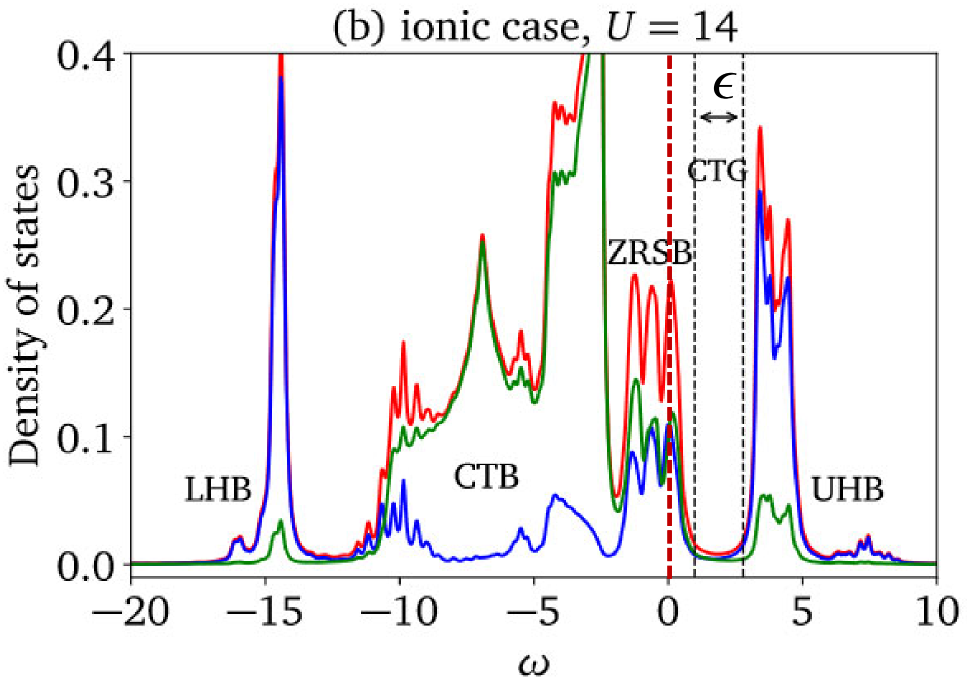
The strategy

The strategy

- Variations in microscopic parameters in Hamiltonian
  - "Ionic" class of models
    - Large value of $\varepsilon_p - \varepsilon_d$
  - "Covalent" class of models
    - Smaller and more realistic value of $\varepsilon_p - \varepsilon_d$

Ionic limiting case

"Ionic" limiting cases



- $\boxed{\varepsilon_p - \varepsilon_d = 7.0,}$ $t_{pd} = 1.5,$ $\boxed{t_{pp} = 1.0,}$ $t'_{pp} = 1.0$

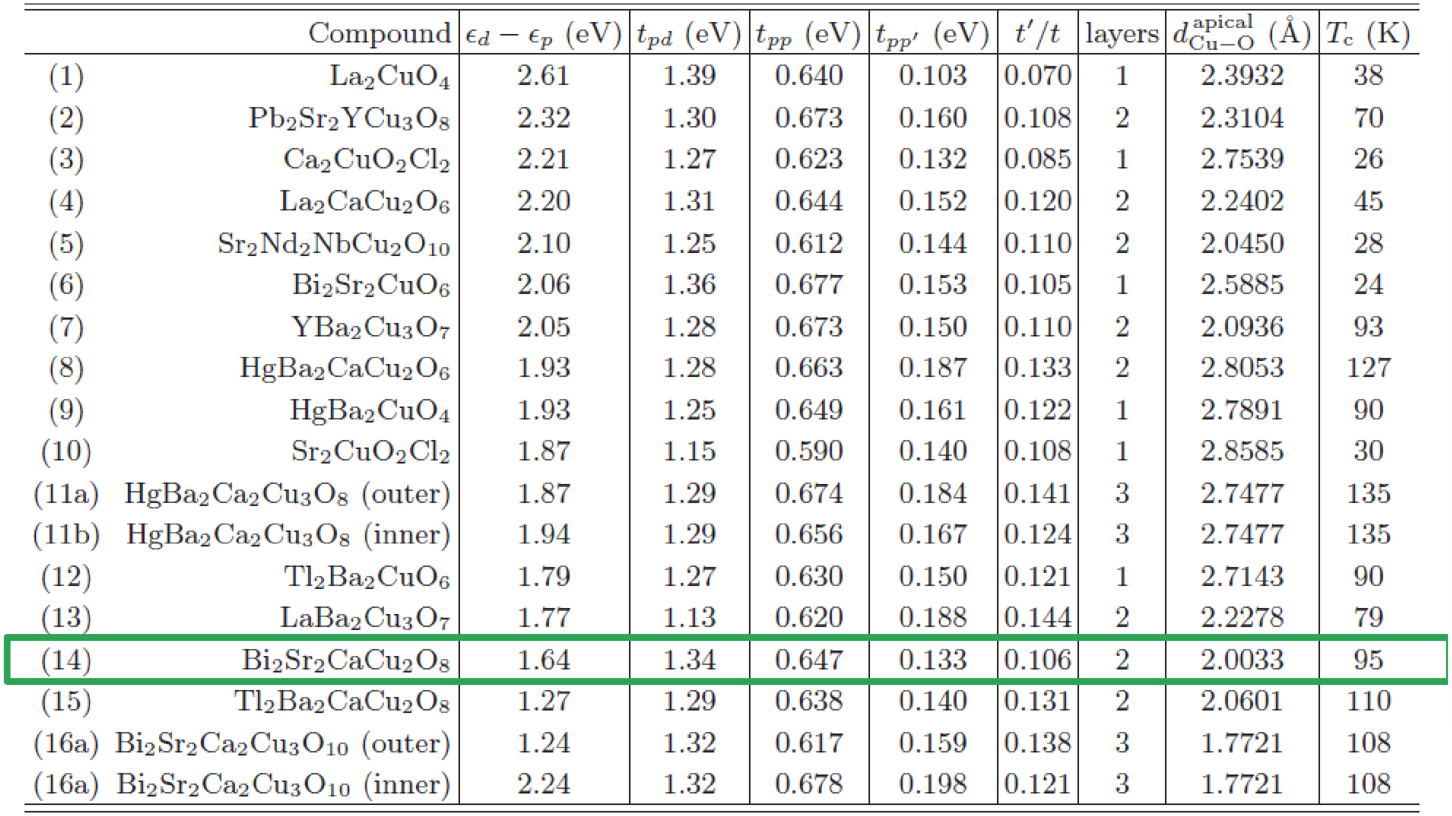
Also, Fratino, Sémon, Sordi, AMT, PRB **93**, 245147 (2016)

Covalent limiting case
" Realistic model"

Hohenberg-Kohn : Exchange correlation
Kohn-Sham : Basis set

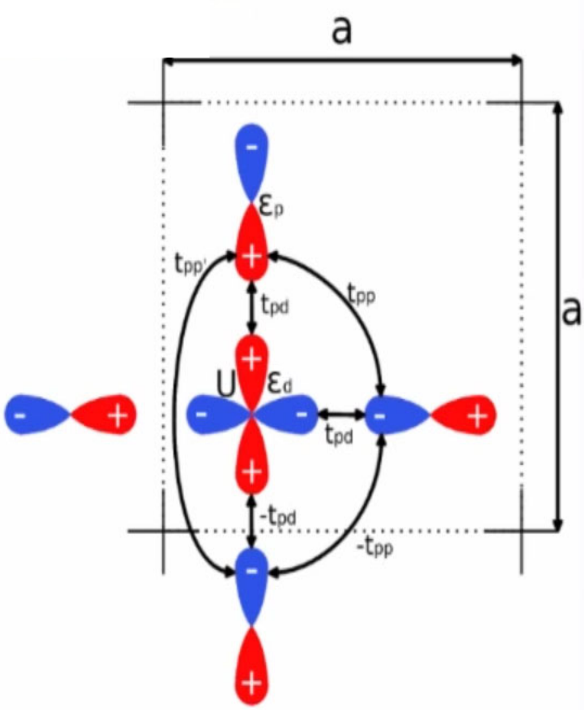
Density Functional Theory

Electronic structure



	Compound	$\epsilon_d - \epsilon_p$ (eV)	t_{pd} (eV)	t_{pp} (eV)	$t_{pp'}$ (eV)	t'/t	layers	$d^{\mathrm{apical}}_{\mathrm{Cu-O}}$ (Å)	T_c (K)
(1)	La_2CuO_4	2.61	1.39	0.640	0.103	0.070	1	2.3932	38
(2)	$Pb_2Sr_2YCu_3O_8$	2.32	1.30	0.673	0.160	0.108	2	2.3104	70
(3)	$Ca_2CuO_2Cl_2$	2.21	1.27	0.623	0.132	0.085	1	2.7539	26
(4)	$La_2CaCu_2O_6$	2.20	1.31	0.644	0.152	0.120	2	2.2402	45
(5)	$Sr_2Nd_2NbCu_2O_{10}$	2.10	1.25	0.612	0.144	0.110	2	2.0450	28
(6)	$Bi_2Sr_2CuO_6$	2.06	1.36	0.677	0.153	0.105	1	2.5885	24
(7)	$YBa_2Cu_3O_7$	2.05	1.28	0.673	0.150	0.110	2	2.0936	93
(8)	$HgBa_2CaCu_2O_6$	1.93	1.28	0.663	0.187	0.133	2	2.8053	127
(9)	$HgBa_2CuO_4$	1.93	1.25	0.649	0.161	0.122	1	2.7891	90
(10)	$Sr_2CuO_2Cl_2$	1.87	1.15	0.590	0.140	0.108	1	2.8585	30
(11a)	$HgBa_2Ca_2Cu_3O_8$ (outer)	1.87	1.29	0.674	0.184	0.141	3	2.7477	135
(11b)	$HgBa_2Ca_2Cu_3O_8$ (inner)	1.94	1.29	0.656	0.167	0.124	3	2.7477	135
(12)	$Tl_2Ba_2CuO_6$	1.79	1.27	0.630	0.150	0.121	1	2.7143	90
(13)	$LaBa_2Cu_3O_7$	1.77	1.13	0.620	0.188	0.144	2	2.2278	79
(14)	$Bi_2Sr_2CaCu_2O_8$	1.64	1.34	0.647	0.133	0.106	2	2.0033	95
(15)	$Tl_2Ba_2CaCu_2O_8$	1.27	1.29	0.638	0.140	0.131	2	2.0601	110
(16a)	$Bi_2Sr_2Ca_2Cu_3O_{10}$ (outer)	1.24	1.32	0.617	0.159	0.138	3	1.7721	108
(16a)	$Bi_2Sr_2Ca_2Cu_3O_{10}$ (inner)	2.24	1.32	0.678	0.198	0.121	3	1.7721	108

Weber, Yee, Haule, Kotliar, EPL 100, 2012



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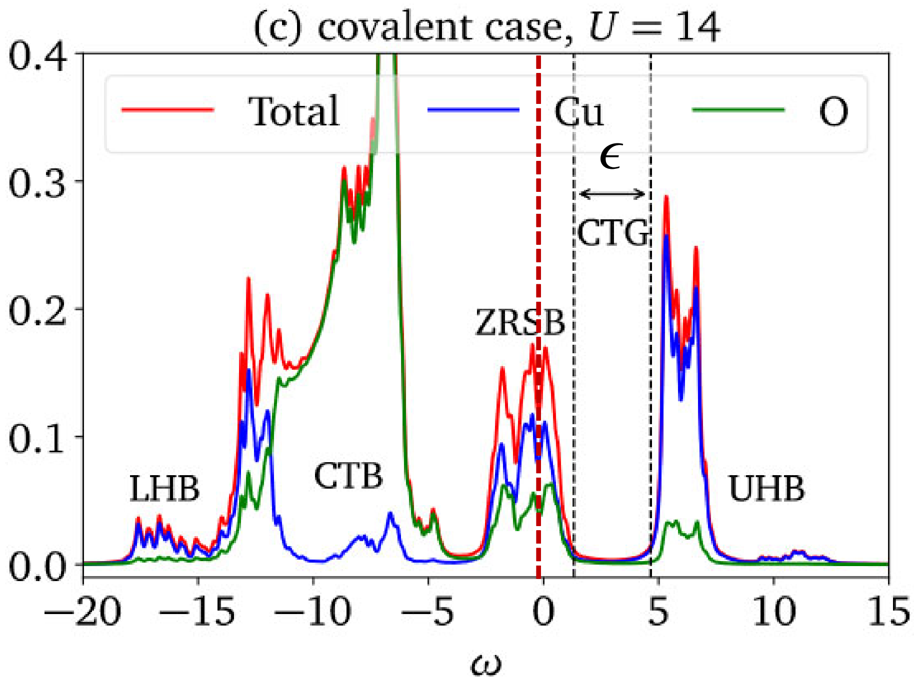
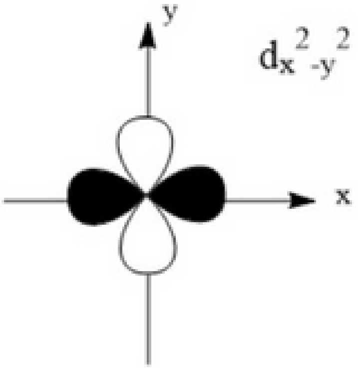
"Covalent" models (*T = 0)*

"Realistic"



○ $\boxed{\varepsilon_p - \varepsilon_d = 2.3}$, $t_{pd} = 2.1$, $\boxed{t_{pp} = 1.0}$, $t'_{pp} = 0.2$



d-wave Superconductivity

Order parameter

$$2\hat{\Delta} = \sum_{\langle ij \rangle_x} (d_{i,\uparrow} d_{j,\downarrow} - d_{i,\downarrow} d_{j,\uparrow}) - \sum_{\langle ij \rangle_y} (d_{i,\uparrow} d_{j,\downarrow} - d_{i,\downarrow} d_{j,\uparrow}) + \text{H.c.},$$

Reduced wave vector

$$\langle\hat{\Delta}\rangle = \oint \frac{d\omega}{2\pi} \frac{d^2\tilde{\mathbf{k}}}{(2\pi)^2}\, tr\left[\boldsymbol{\Delta}(\tilde{\mathbf{k}})\mathbf{G}(\tilde{\mathbf{k}}, \omega)\right]$$

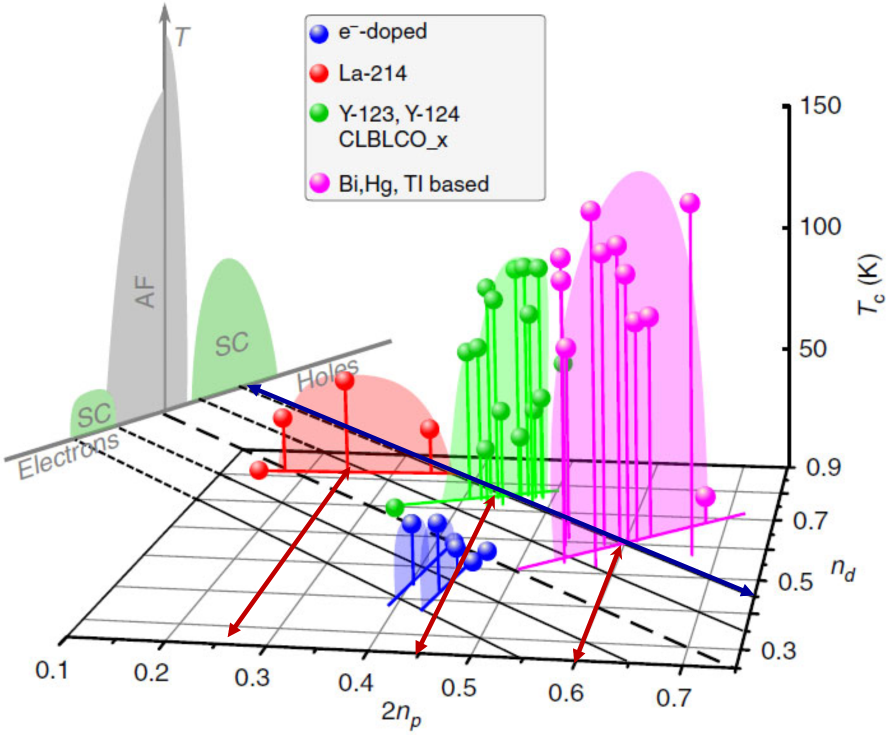
Average per site

Green function from CDMFT

#1 Optimizing T_c with oxygen hole content

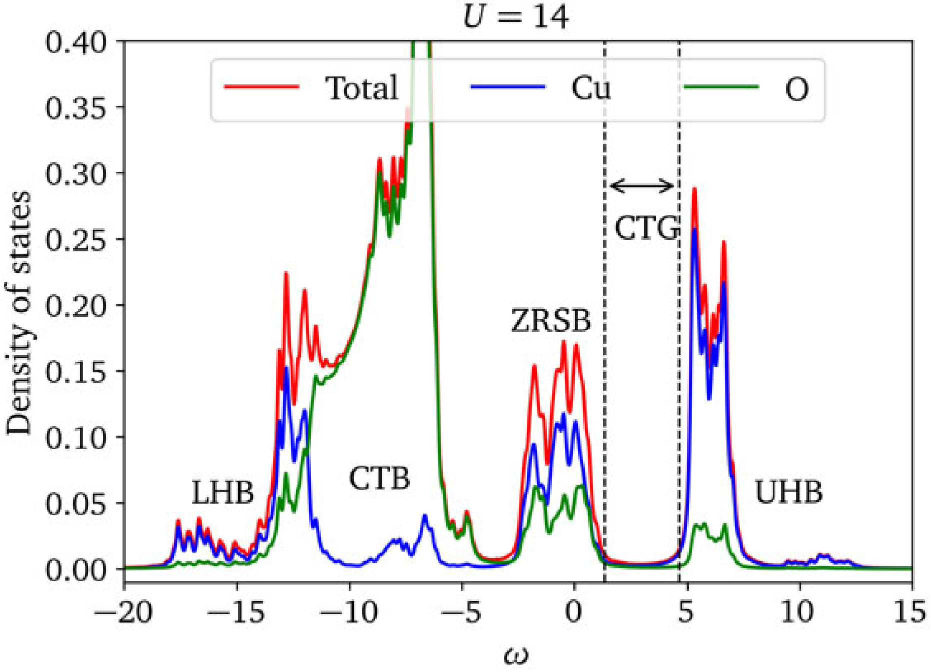
#1 Optimizing T_c with oxygen hole content

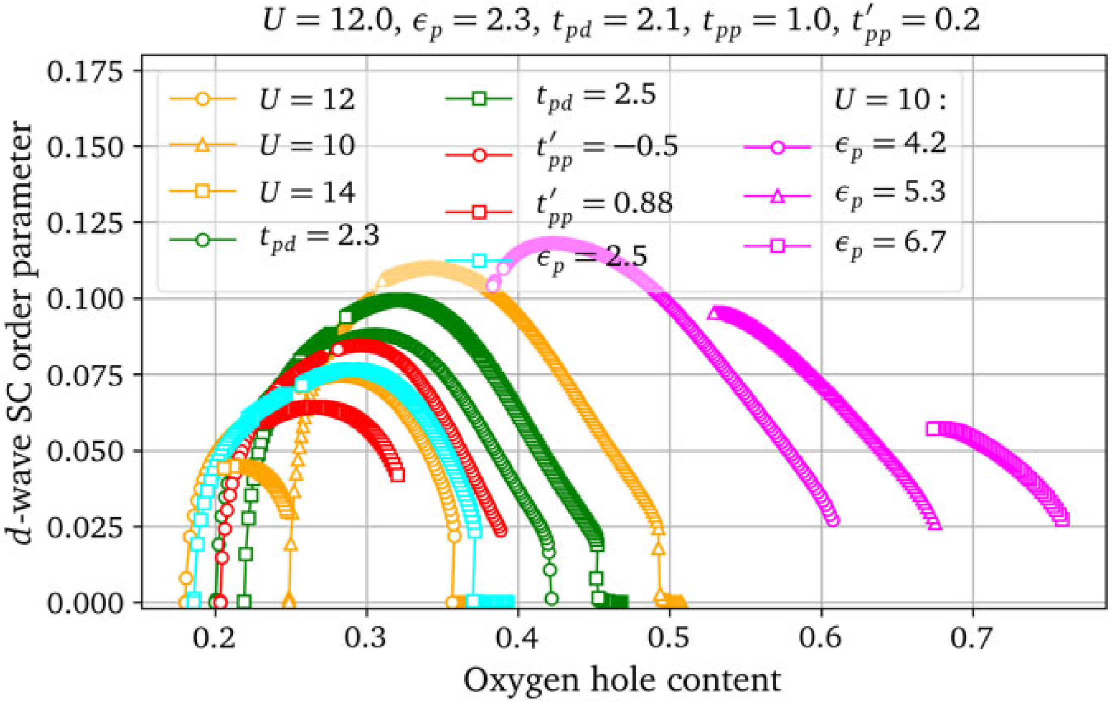
$$n = n_d + 2n_p$$



Rybicki,,, Haase, Nat. Comm. 7, 11413 (2016)

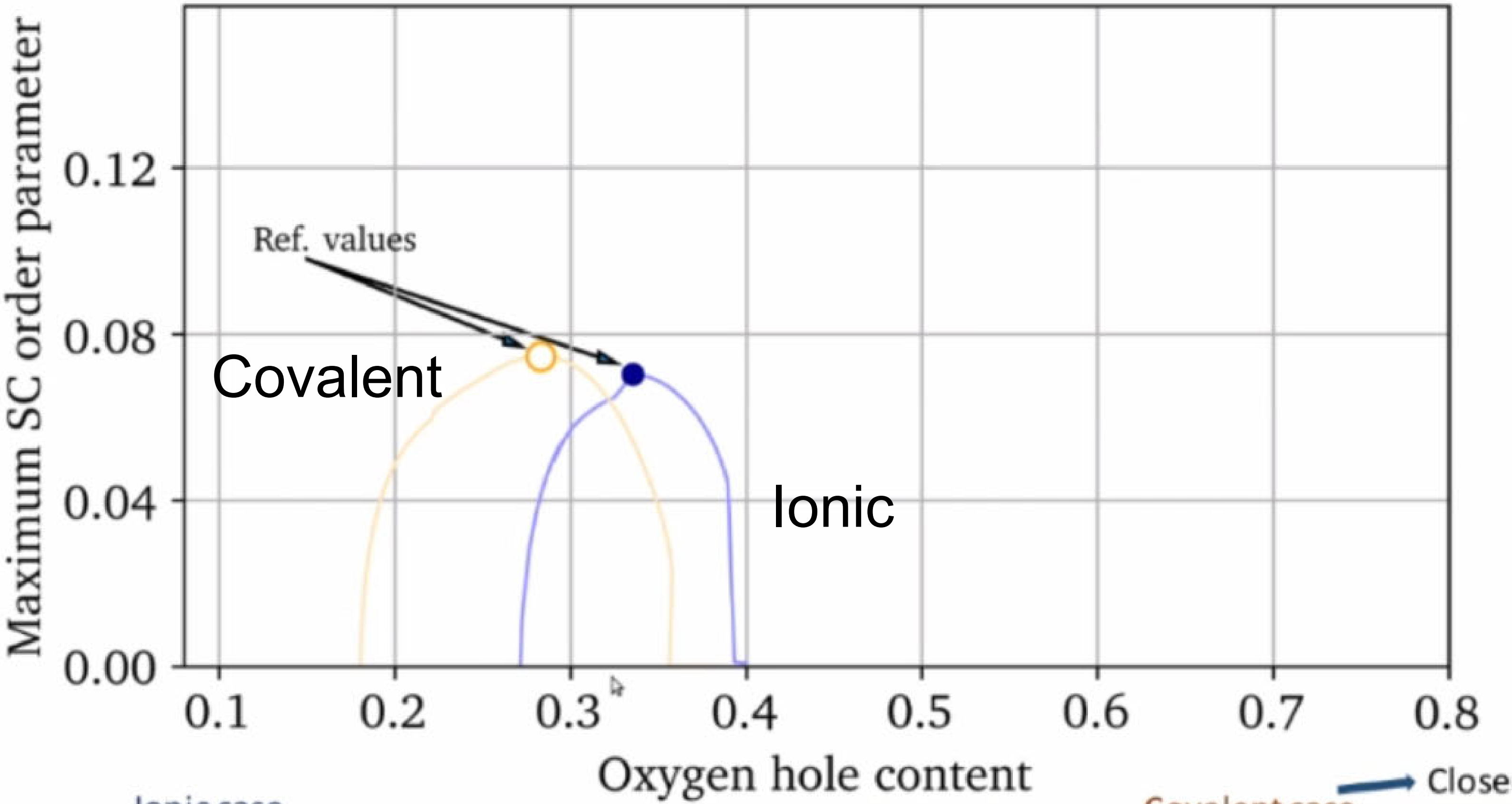
T = *0* superconducting domes for the covalent models





Kowalski, Dash, Sémon, Sénéchal, A-M.T.
PNAS **118** (40) e2106476118 (2021)

T = *0* superconducting domes for the reference models



Ionic case

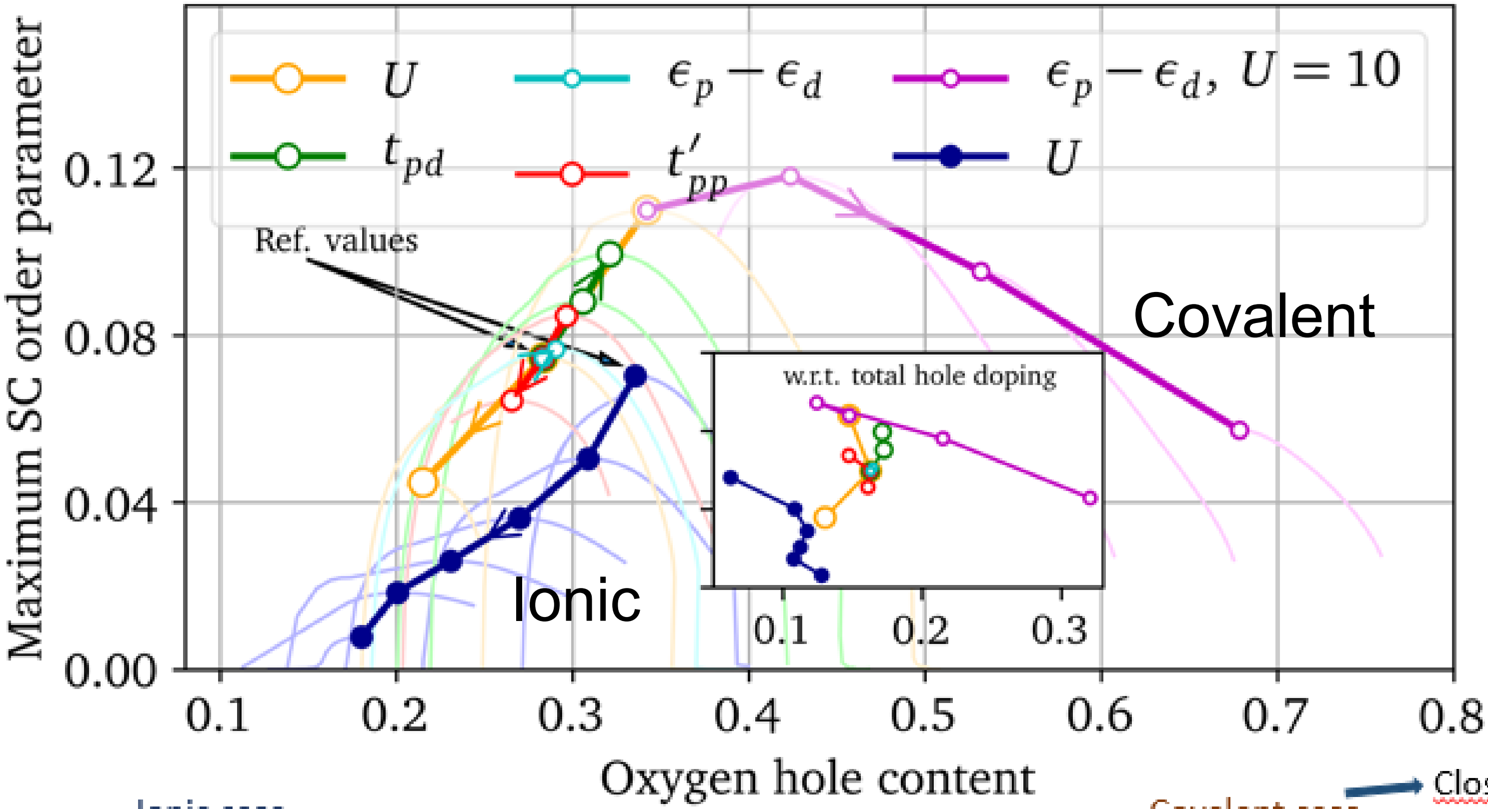
Covalent case

Closer to cuprates

● $U = 12, \boxed{\epsilon_p - \epsilon_d = 7.0}, \ t_{pd} = 1.5, \ t_{pp} = 1.0, \ t'_{pp} = 1.0$ ○ $U = 12, \boxed{\epsilon_p - \epsilon_d = 2.3}, \ t_{pd} = 2.1, \ t_{pp} = 1.0, \ t'_{pp} = 0.2$

Kowalski, Dash, Sémon, Sénéchal, A-M.T.
PNAS **118** (40) e2106476118 (2021)

T = 0 max order parameter for the two models



→ Closer to cuprates

Ionic case

Covalent case

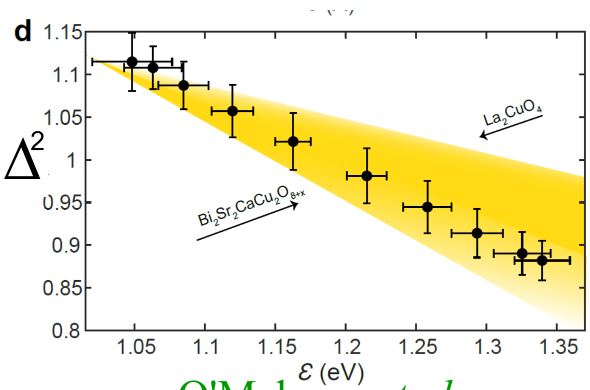
● $U = 12$, $\boxed{\epsilon_p - \epsilon_d = 7.0}$, $t_{pd} = 1.5$, $t_{pp} = 1.0$, $t'_{pp} = 1.0$ ○ $U = 12$, $\boxed{\epsilon_p - \epsilon_d = 2.3}$, $t_{pd} = 2.1$, $t_{pp} = 1.0$, $t'_{pp} = 0.2$

Kowalski, Dash, Sémon, Sénéchal, A-M.T. PNAS **118** (40) e2106476118 (2021)

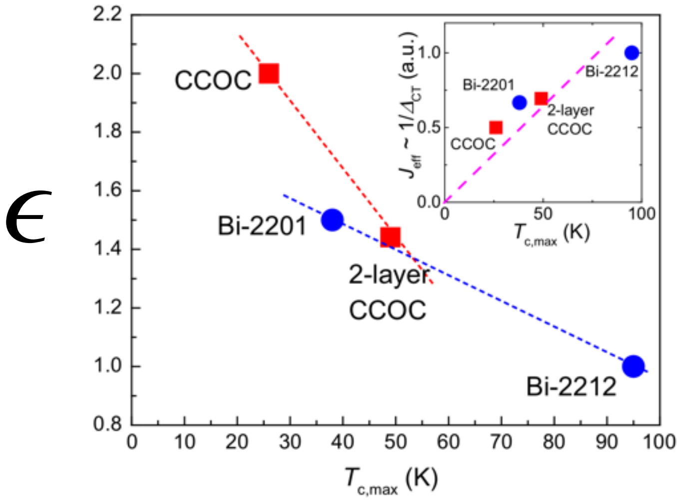
#2 Optimizing T_c with Charge Transfer gap ϵ

(Oxygen as a witness)

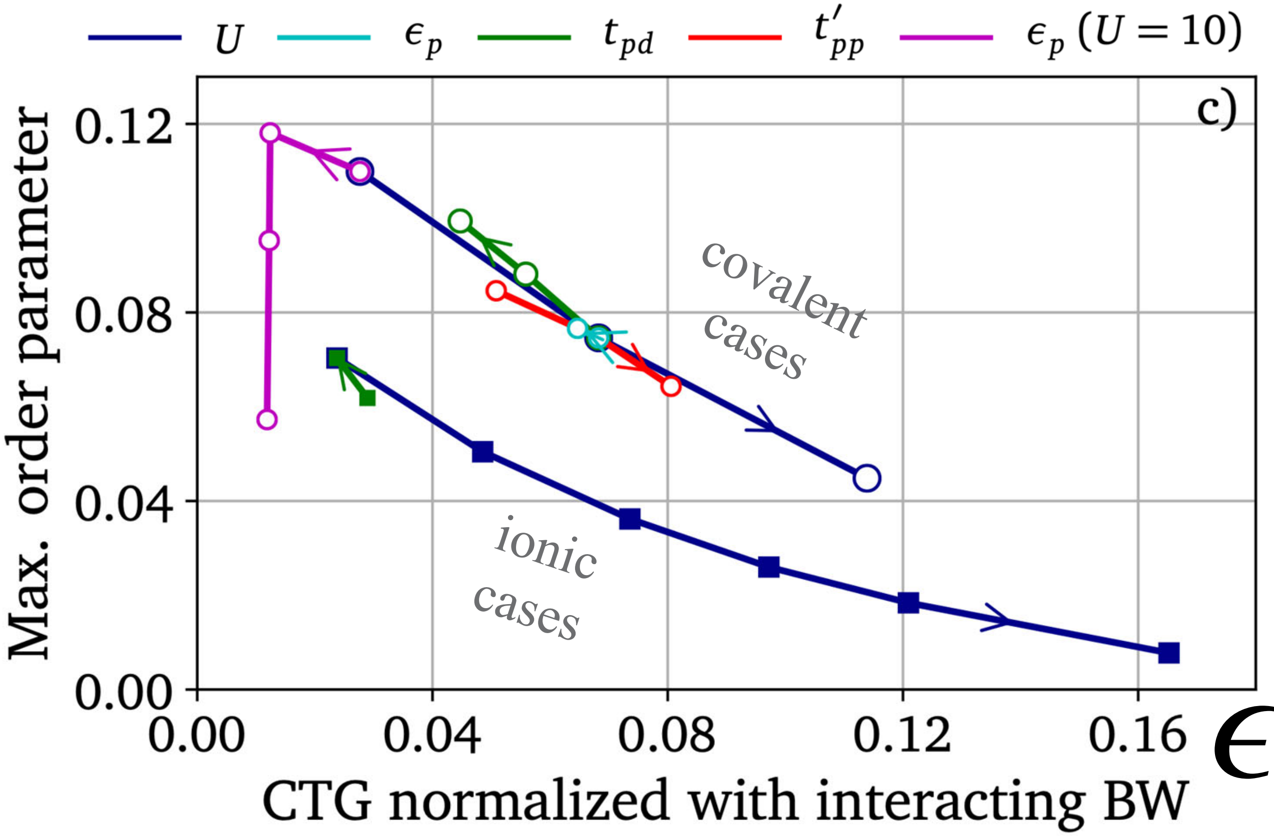
#2 Optimizing T_c with CT gap ε (Oxygen as a witness)



O'Mahony *et al.*
PNAS **119** e2207449119 (2022)

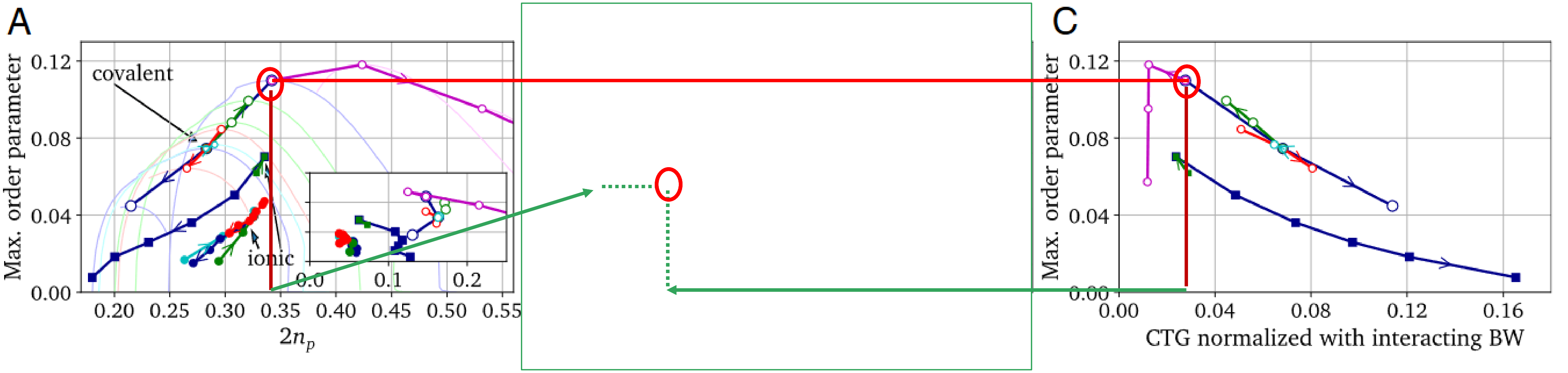


Ruan *et al.* Sci. Bull. **61** (2016)

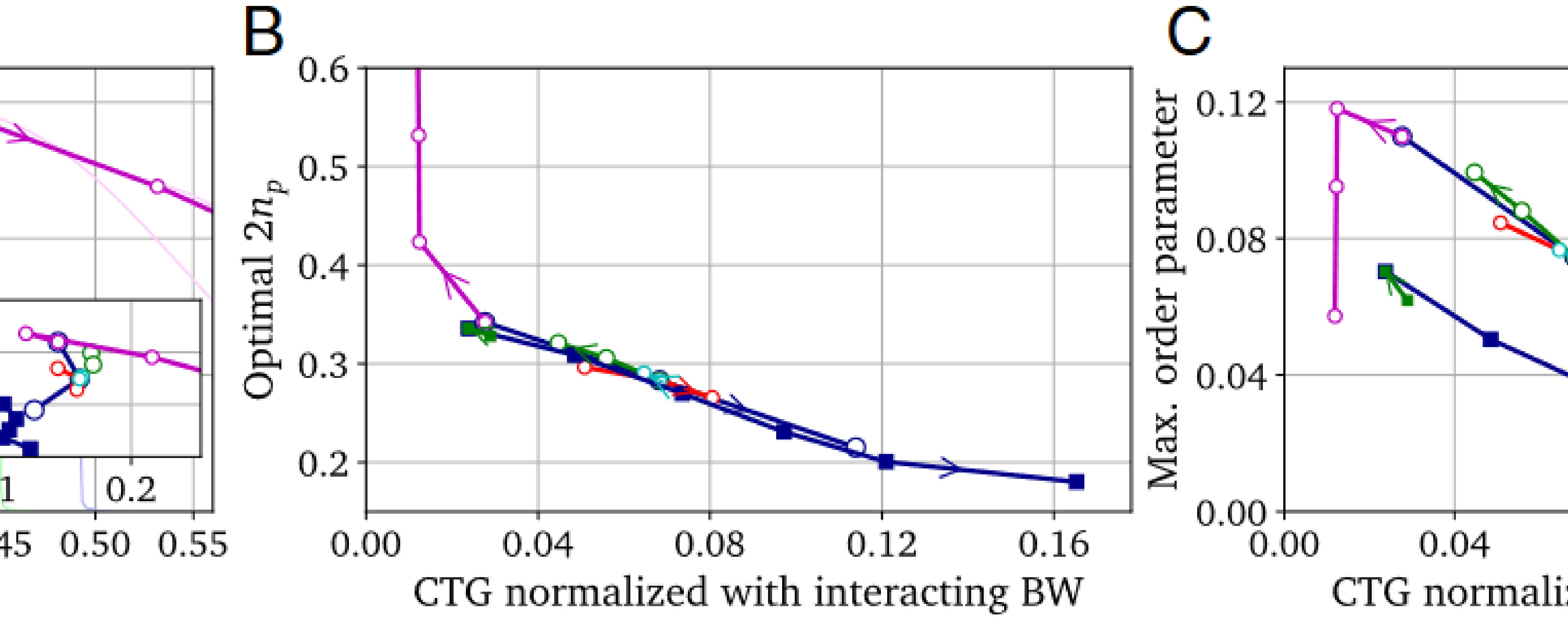


Kowalski, Dash, Sémon, Sénéchal, A-M.T.
PNAS **118** (40) e2106476118 (2021)

¸Oxygen hole content OR charge transfer gap?

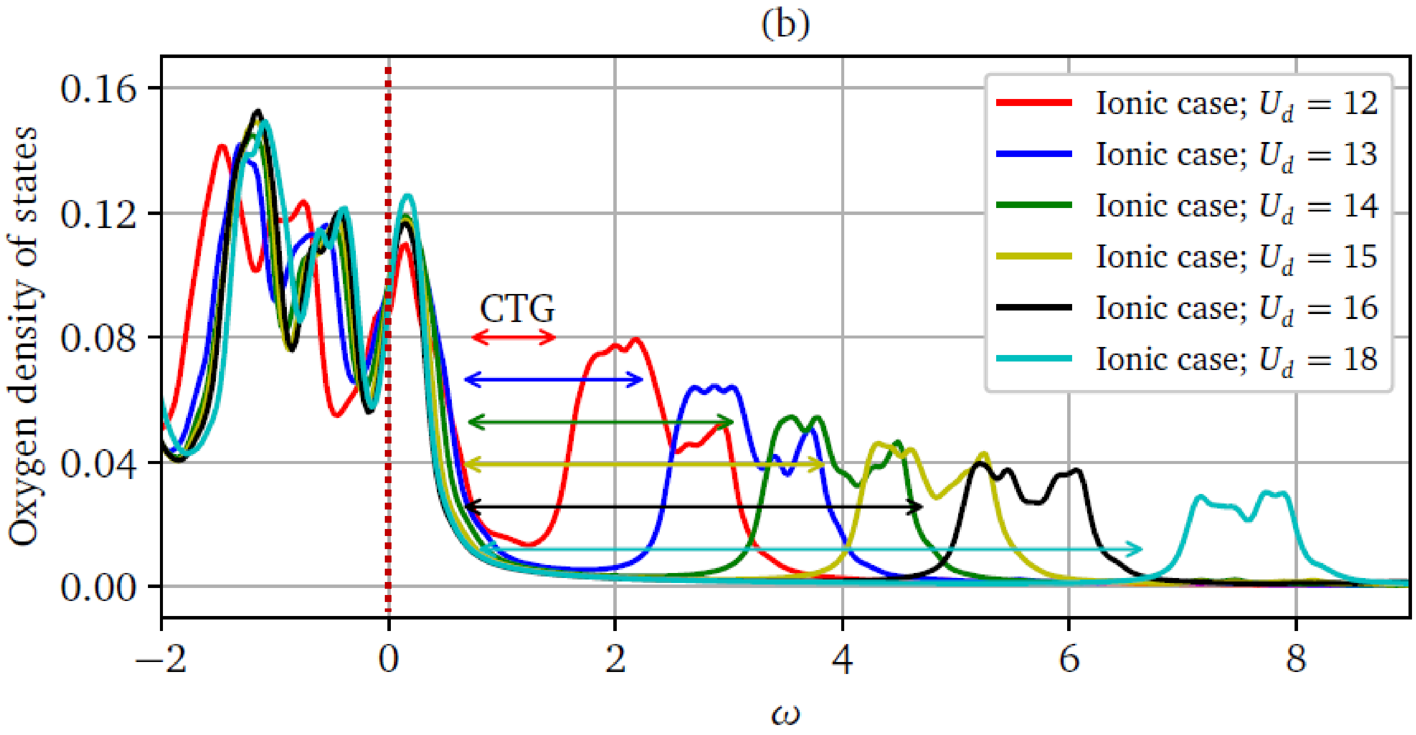


Charge-transfer gap, oxygen hole content



Kowalski, Dash, Sémon, Sénéchal, A-M.T.
PNAS **118** (40) e2106476118 (2021)

Charge transfer gap and oxygen hole content : Oxygen as a witness



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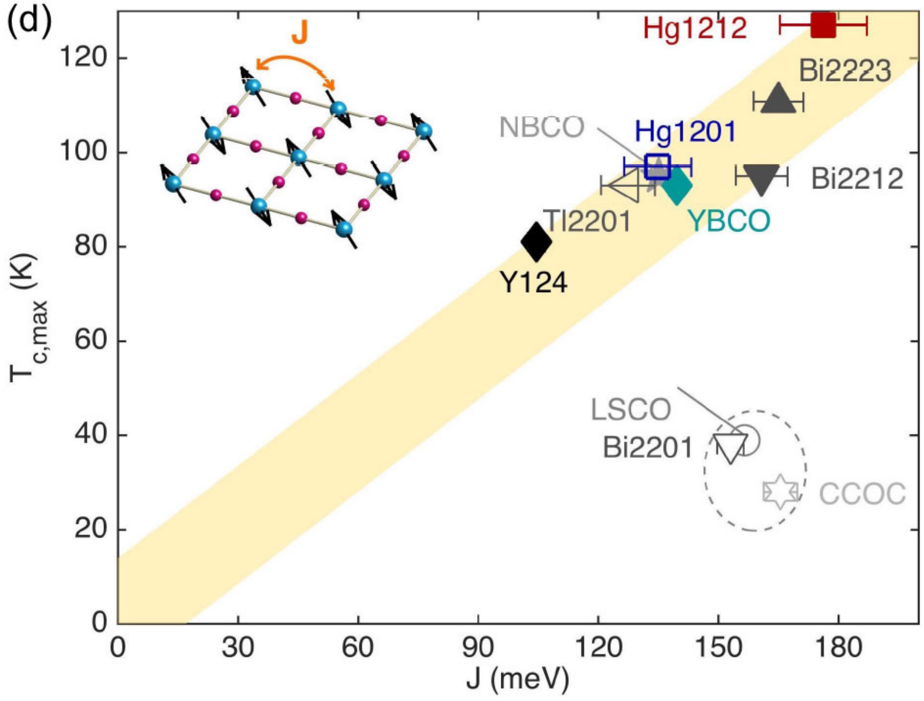
#3 Optimizing T_c with superexchange

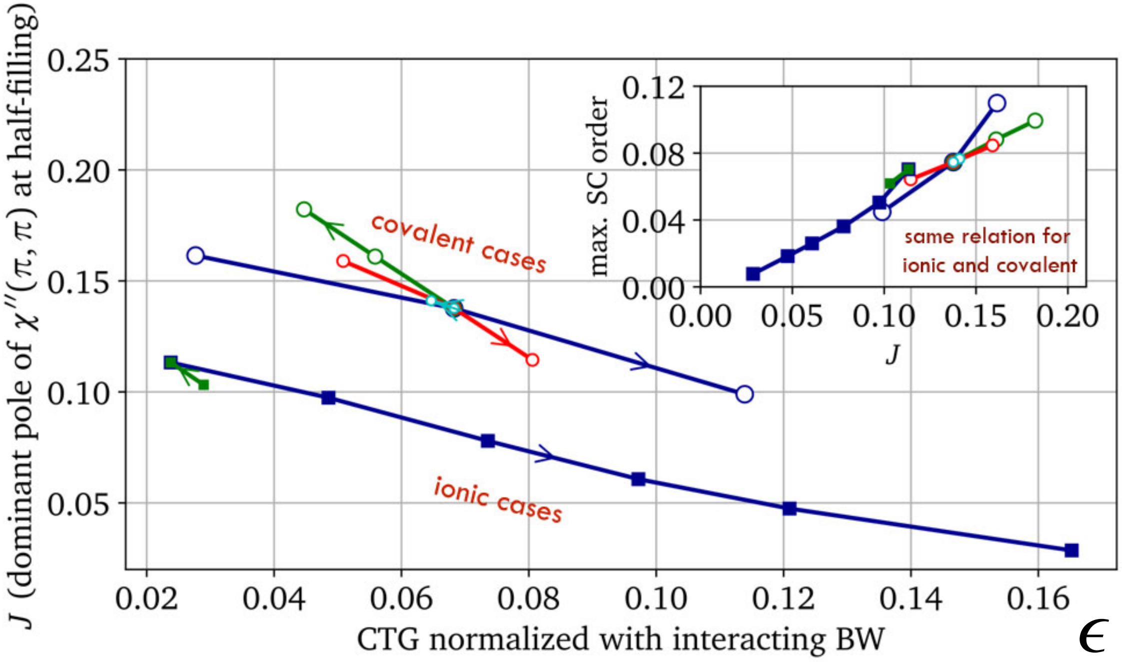
#3 Optimizing T_c with superexchange

E. Müller-Hartmann *et al*. Eur. Phys. J. B **28**, 173 (2002)

$$J = \frac{4t_{pd}^4(U+\epsilon)}{U\epsilon^3} \xrightarrow[U\to\infty]{} \frac{4t_{pd}^4}{\epsilon^3}$$



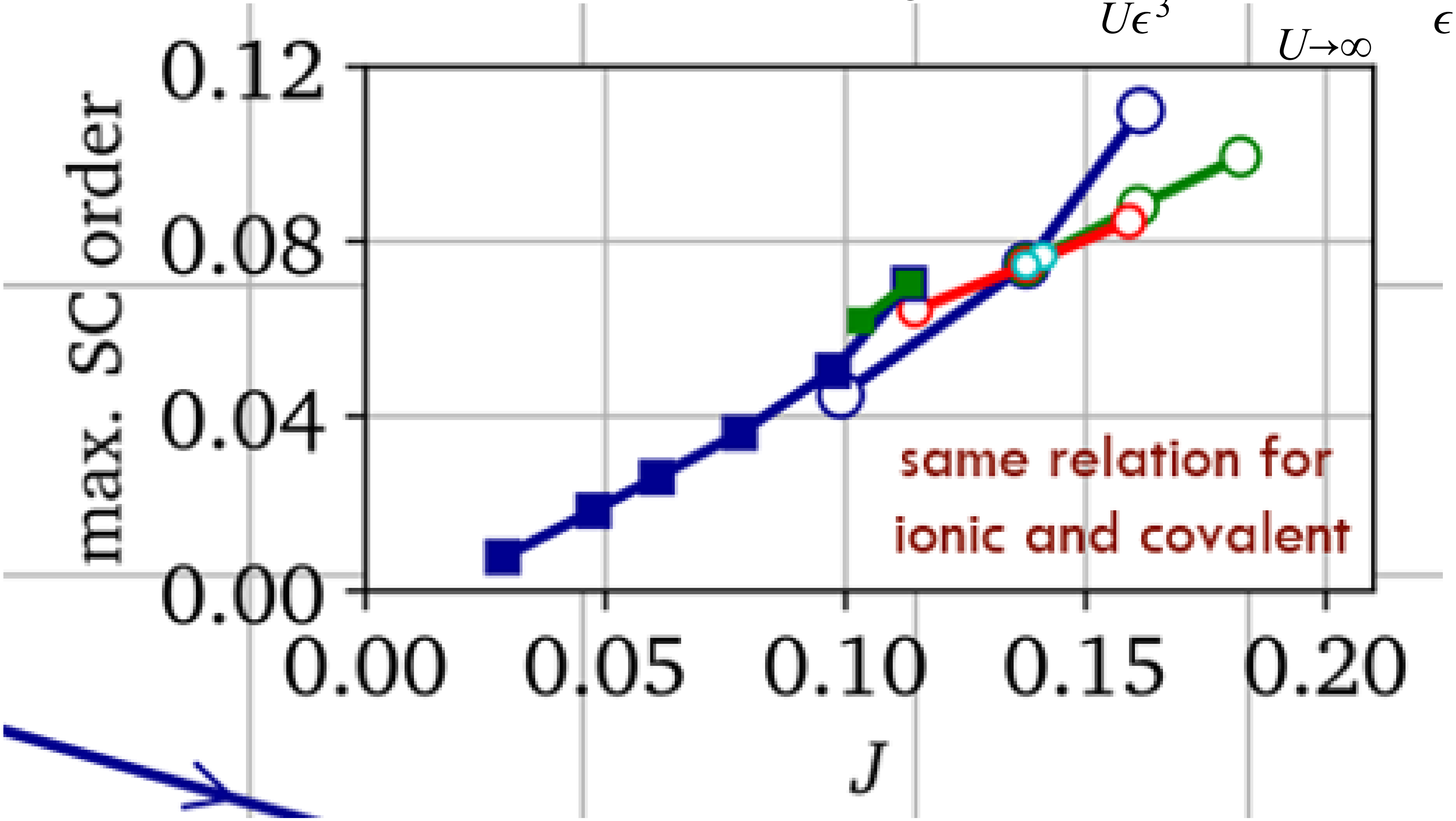
Lichen Wang et al.
Nat. Comm. **13**, 3163 (2022)



Super exchange

E. Müller-Hartmann *et al.* Eur. Phys. J. B **28**, 173 (2002)

$$J = \frac{4t_{pd}^4(U+\epsilon)}{U\epsilon^3} \xrightarrow[U\to\infty]{} \frac{4t_{pd}^4}{\epsilon^3}$$



same relation for ionic and covalent

Other references on the three-band model

C. Weber, T. Giamarchi, C. M. Varma,
Phase diagram of a three-orbital model for high-Tc cuprate superconductors. Phys. Rev. Lett. 112, 117001 (2014).

L. Fratino, P. Sémon, G. Sordi, A.-M. S. Tremblay,
Pseudogap and superconductivity in two-dimensional doped charge-transfer insulators. Phys. Rev. B 93, 245147 (2016)

Z.-H. Cui et al.,
Ground-state phase diagram of the three-band Hubbard model from density matrix embedding theory.
Phys. Rev. Res. 2, 043259 (2020).

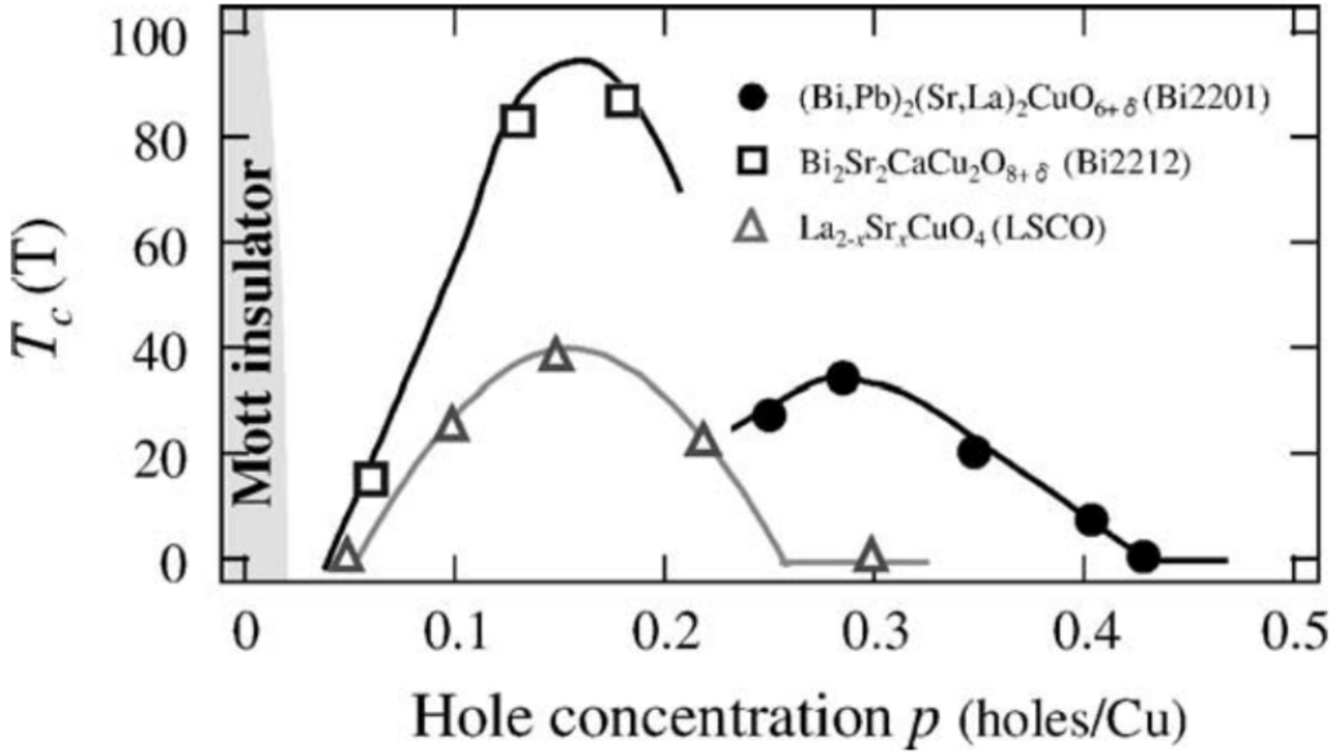
M. Zegrodnik, A. Biborski, M. Fidrysiak, J. Spalek,
Superconductivity in the three band model of cuprates: Nodal direction characteristics and influence of intersite interactions.
J. Phys. Condens. Matter 33, 415601 (2021).

P. Mai, G. Balduzzi, S. Johnston, T. A. Maier,
Orbital structure of the effective pairing interaction in the high-temperature superconducting cuprates.
NPJ Quantum Mater. 6, 1–5 (2021).

P. Mai et al.,
Pairing correlations in the cuprates: A numerical study of the three-band Hubbard model. Phys. Rev. B 103, 144514 (2021).

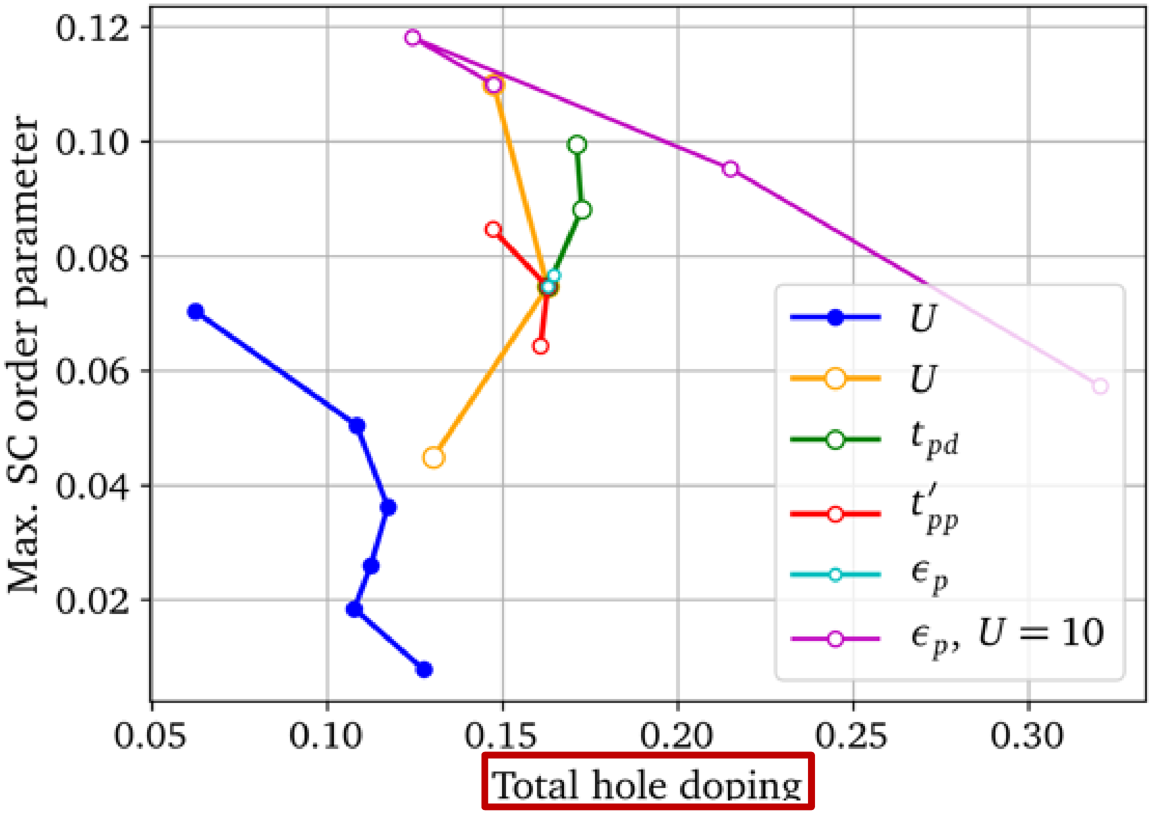
Bonus

T_c and total hole concentration are not well correlated



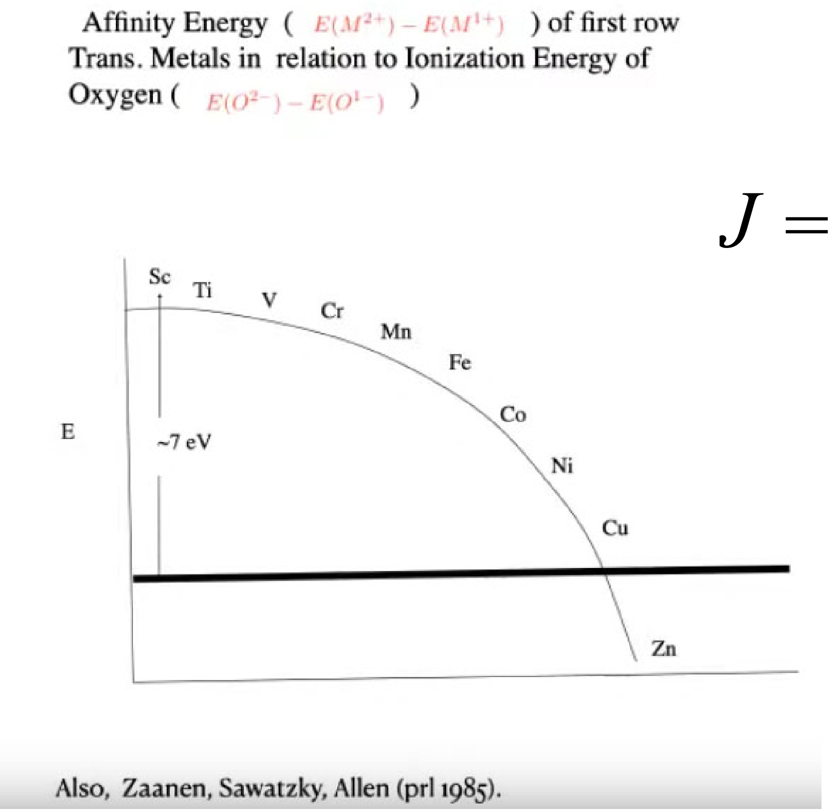
T. Kondo *et al.*
Journal of Electron Spectroscopy and Related Phenomena **137-140**, 663 (2004)

Bonus: total hole doping does not explain max order parameter for the two classes of models



Kowalski, Dash, Sémon, Sénéchal, A-M.T.
PNAS **118** (40) e2106476118 (2021)

Bonus : Importance of covalency



Affinity Energy ($E(M^{2+}) - E(M^{1+})$) of first row Trans. Metals in relation to Ionization Energy of Oxygen ($E(O^{2-}) - E(O^{1-})$)

Also, Zaanen, Sawatzky, Allen (prl 1985).

$$J = \frac{4t_{pd}^4(U+\epsilon)}{U\epsilon^3} \xrightarrow[U\to\infty]{} \frac{4t_{pd}^4}{\epsilon^3}$$

C. M. Varma and T. Giamarchi, *Model for copper oxide metals and superconductors* (Elsevier Science B.V., 1995).

Copper pairing mechanism : superexchange and retardation

D. Sénéchal

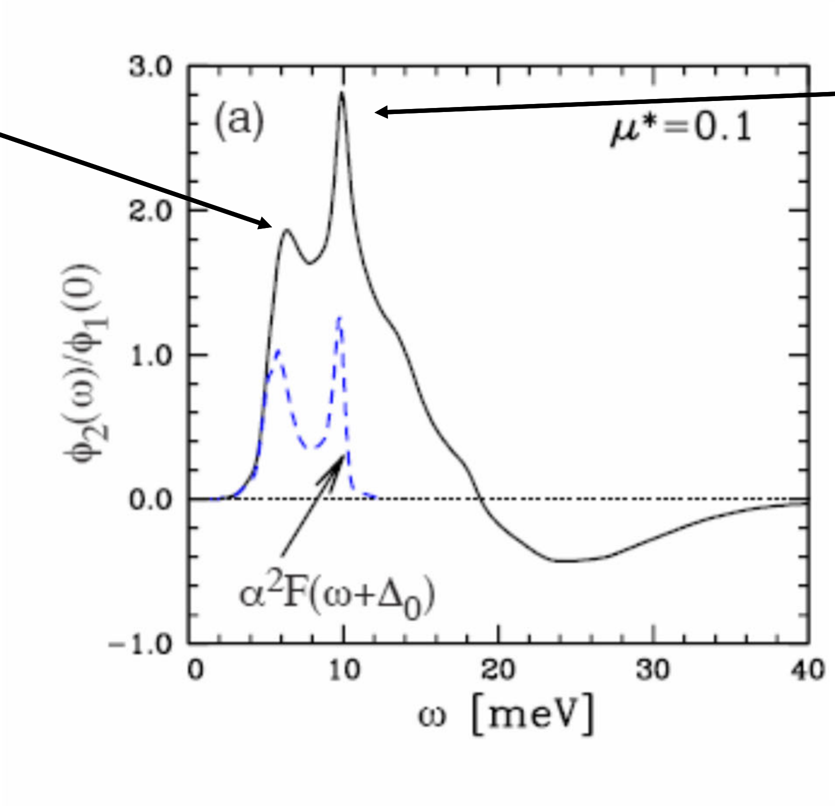
Bumsoo Kyung

The glue

Kyung, Sénéchal, Tremblay, Phys. Rev. B **80,** 205109 (2009)
Sénéchal, Day, Bouliane, AMST, Phys. Rev. B **87**, 075123 (2013)
A. Reymbaut *et al.* PRB **94** 155146 (2016)

Im Σ_{an} and electron-phonon in Pb

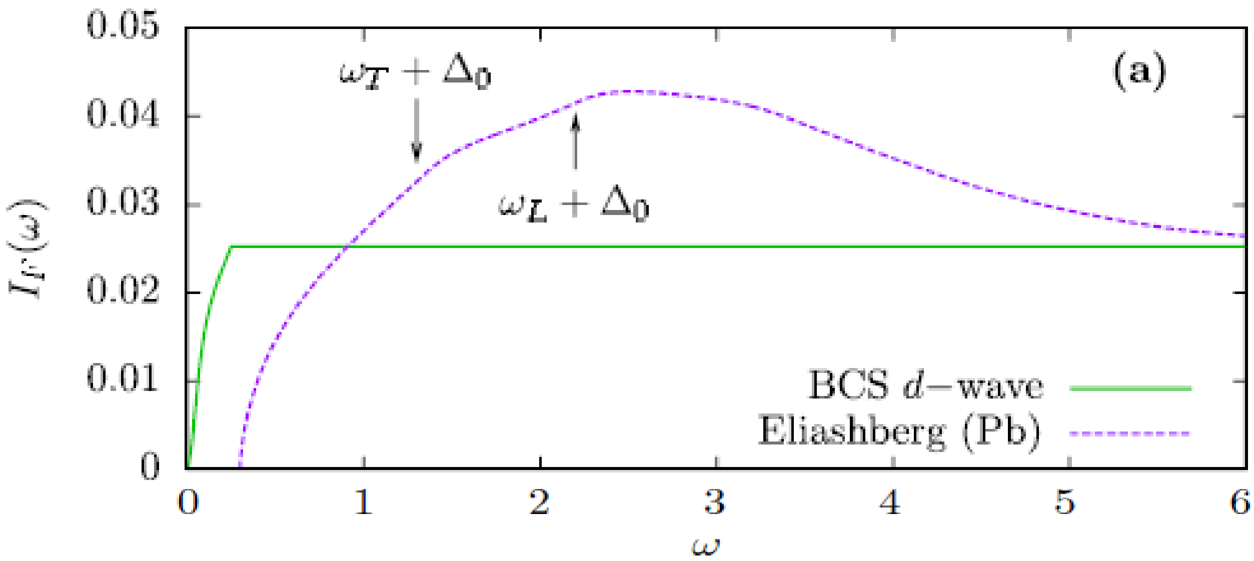
Maier, Poilblanc, Scalapino, PRL (2008)



$\omega_T + \Delta_0$

$\omega_L + \Delta_0$

Another way to look at this

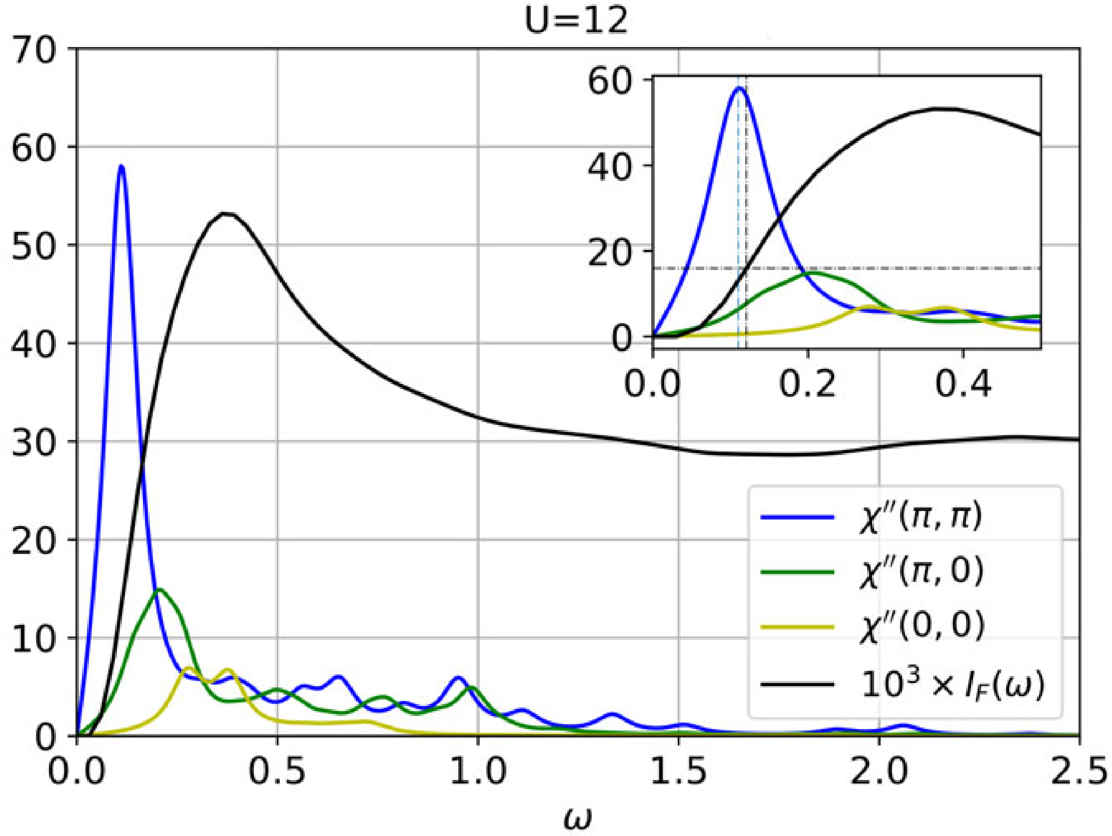


$$I_F(\omega) \equiv -\int_0^\omega \frac{d\omega'}{\pi} \mathrm{Im}\, F_{ij}^R(\omega')$$

$$F_{ij} \equiv -\langle T c_{i\uparrow}(\tau) c_{j\downarrow}(0) \rangle$$

Kyung, Sénéchal, Tremblay, Phys. Rev. B **80,** 205109 (2009)
Sénéchal, Day, Bouliane, AMST, Phys. Rev. B **87**, 075123 (2013)
A. Reymbaut *et al.* PRB **94** 155146 (2016)

Spin fluctuations on copper in the three-band model



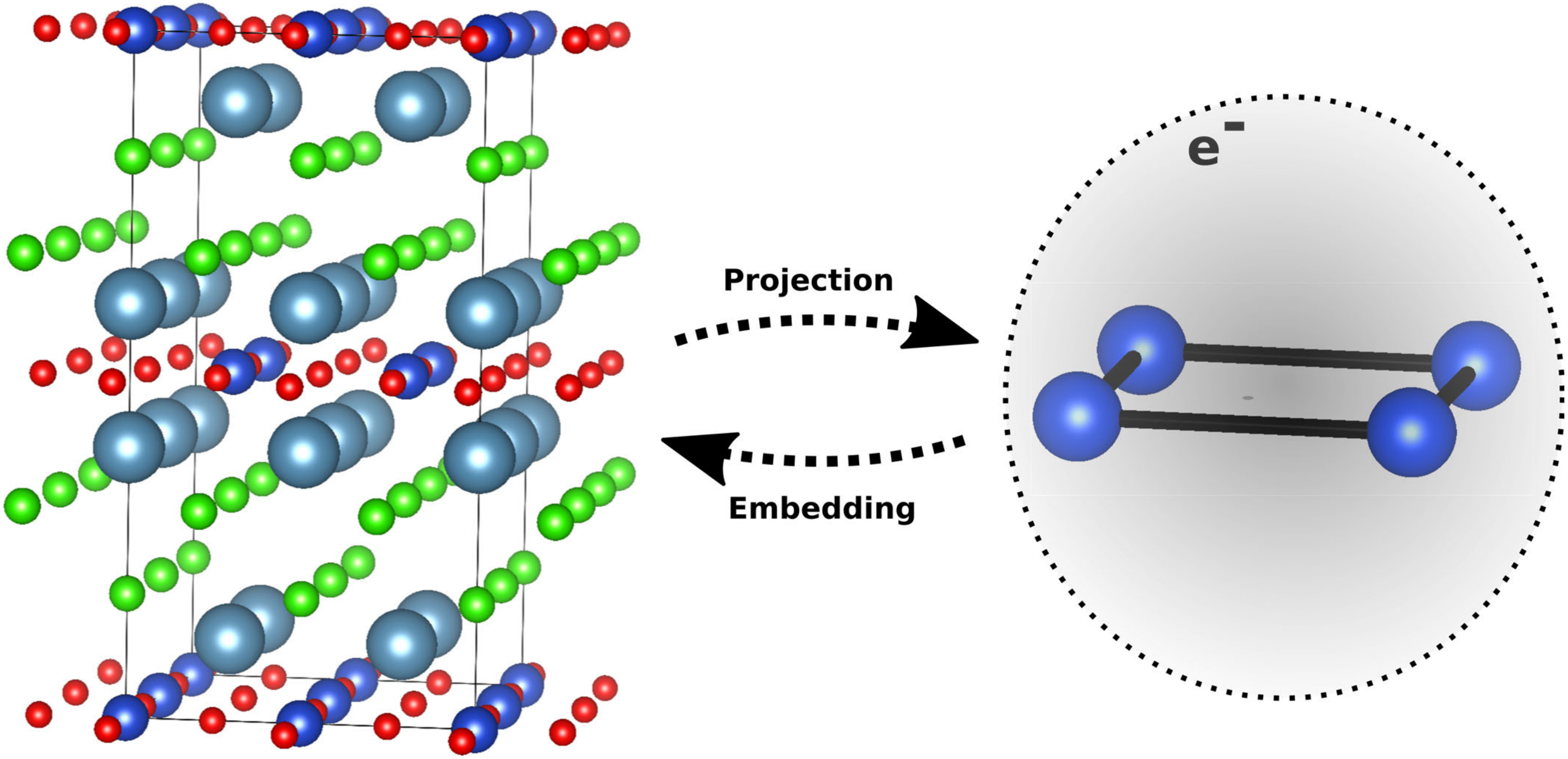
$$I_F(\omega) \equiv -\int_0^\omega \frac{d\omega'}{\pi} \mathrm{Im}\, F^R_{ij}(\omega')$$

$$F_{ij} \equiv -\langle T c_{i\uparrow}(\tau) c_{j\downarrow}(0) \rangle$$

Kowalski, Dash, Sémon, Sénéchal, A-M.T.
PNAS **118** (40) e2106476118 (2021)

Next step : Realistic

DFT + CDMFT



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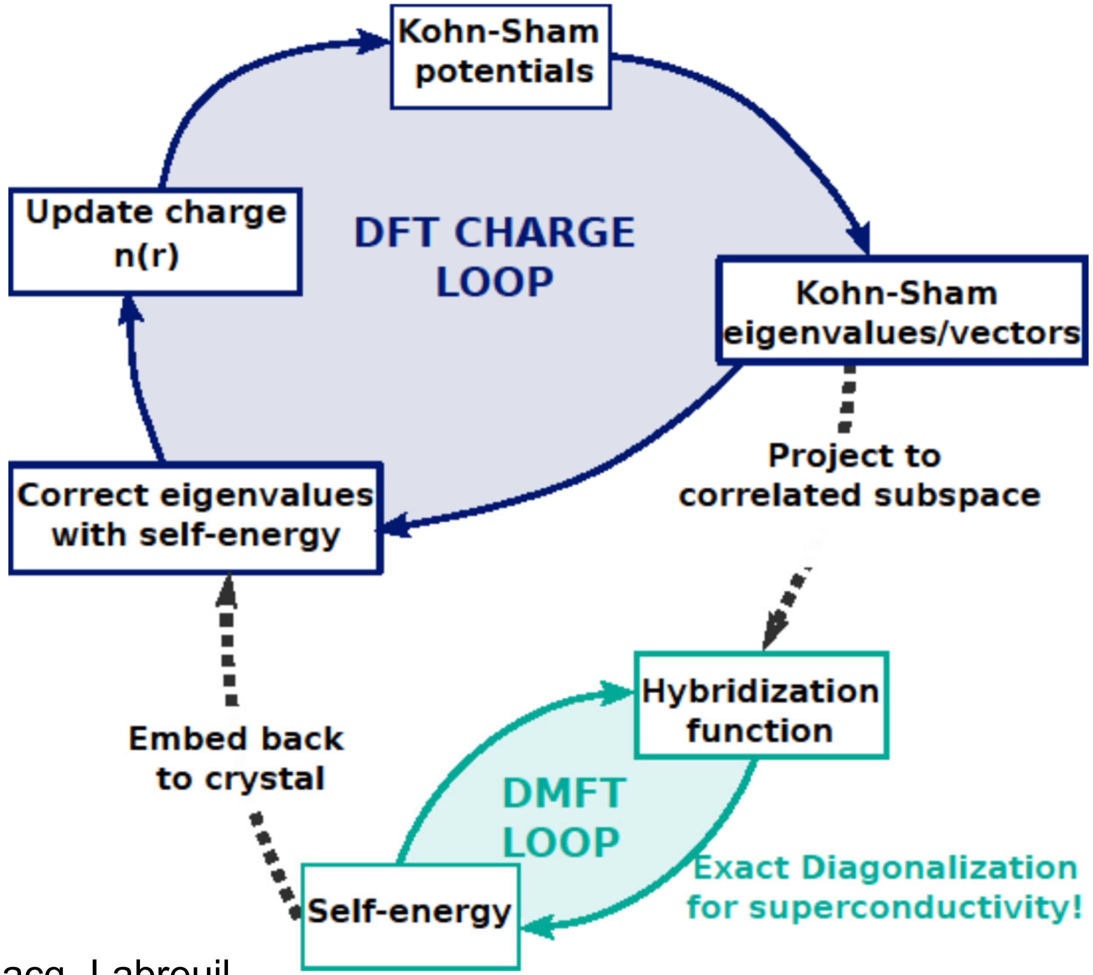
Realistic materials simulations



Kohn-Sham potentials

Update charge n(r)

DFT CHARGE LOOP

Kohn-Sham eigenvalues/vectors

Project to correlated subspace

Correct eigenvalues with self-energy

Hybridization function

Embed back to crystal

DMFT LOOP

Exact Diagonalization for superconductivity!

Self-energy

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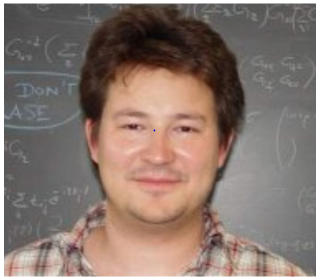
Benjamin Bacq Labreuil

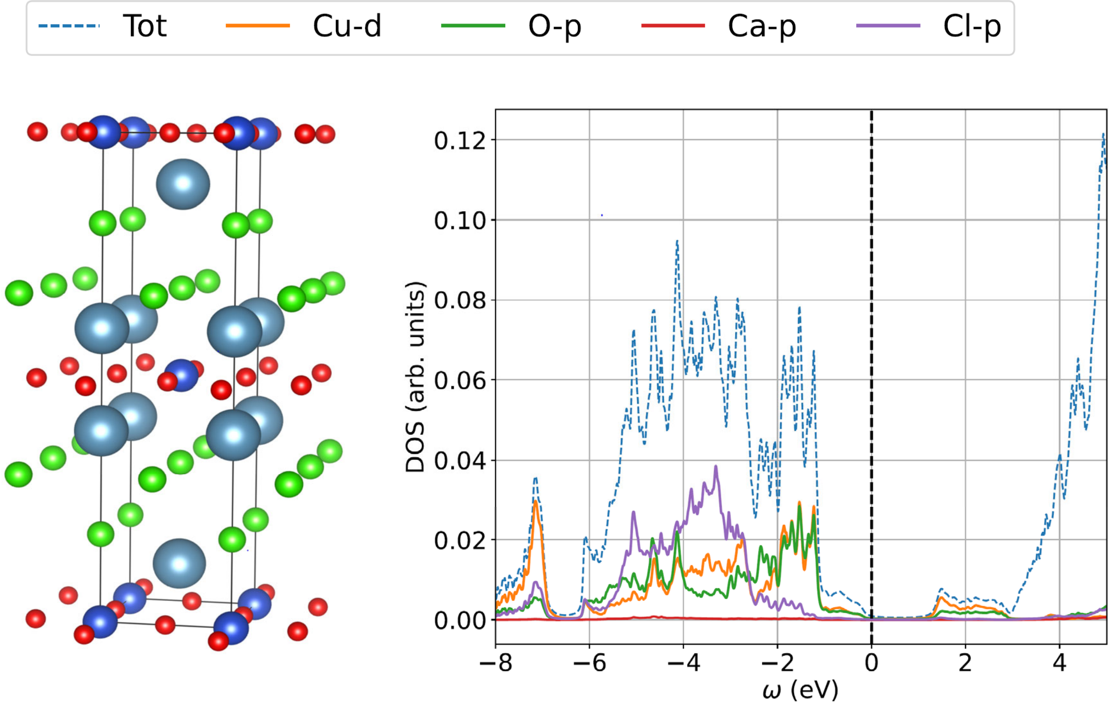
David Sénéchal

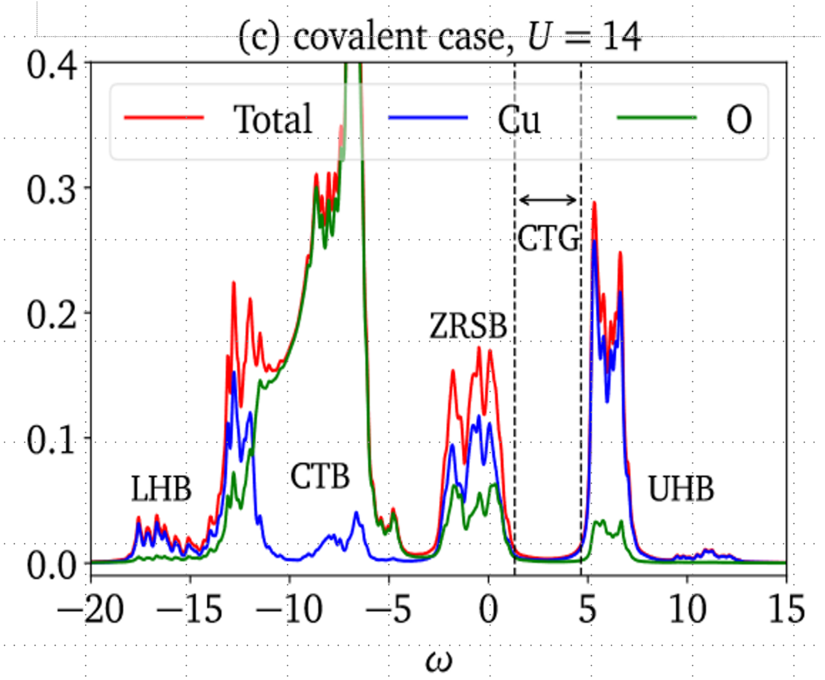


Kristjan Haule

Realistic vs model

$Ca_2CuO_2Cl_2$





Summary Conclusion

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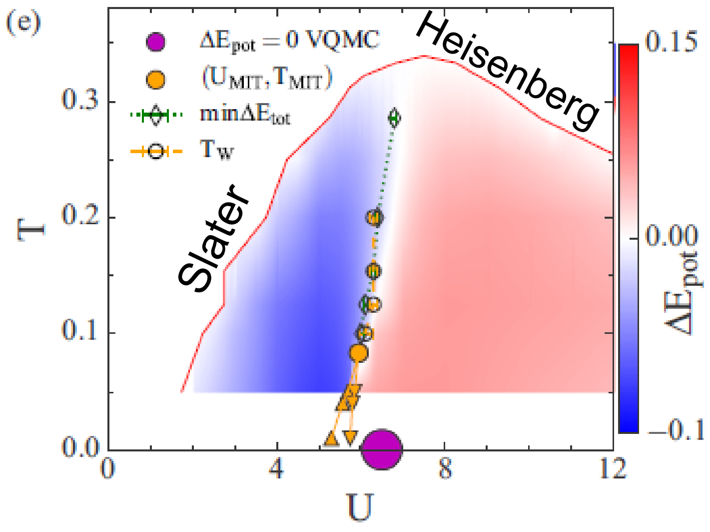
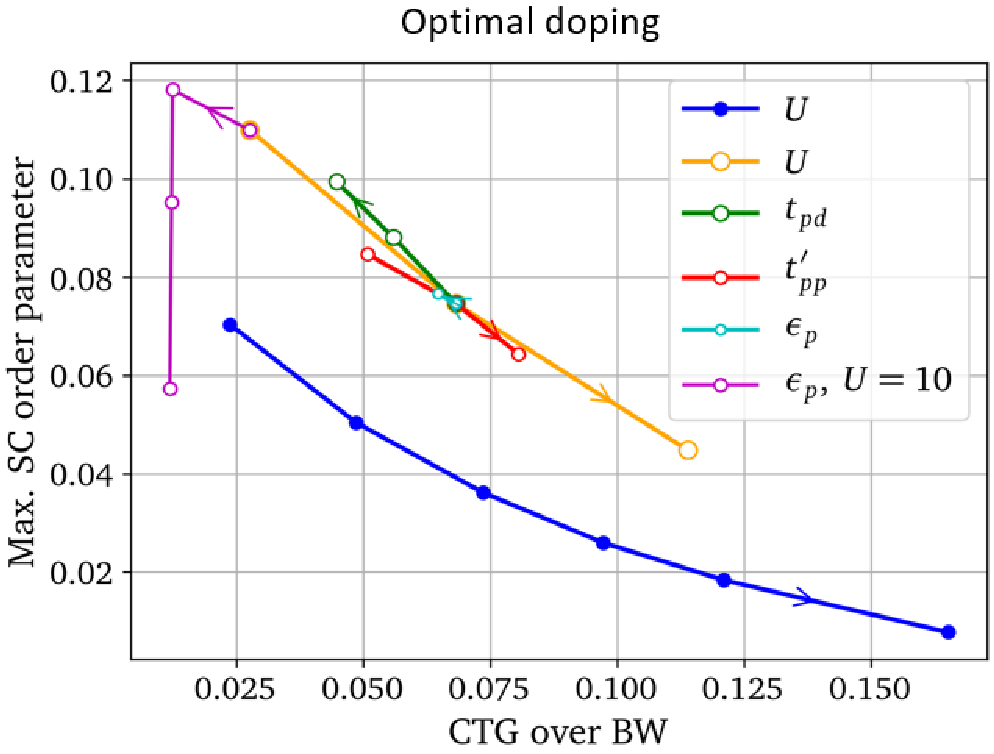
Pairing at small and large *U* : An analogy



Fratino et al. PRB **95**, 235109 (2017)



Kowalski, Dash, Sémon, Sénéchal, A-M.T.
PNAS **118** (40) e2106476118 (2021)
Weber et al Europhys. Lett. 100, 37001 (2012)
Yee et al Phys. Rev. B 89, 094517 (2014)
Acharya et al Phys. Rev. X 8, 021038 (2018)

Optimizing T*c*

- Spin ½
- One band
- Two-dimensions
- Strong covalency between chalcogen and transition metal.
  - Chalcogen screens U
- Charge-transfer gap just opening (intermediate interactions).
- Large *J* at half-filling
- … and more

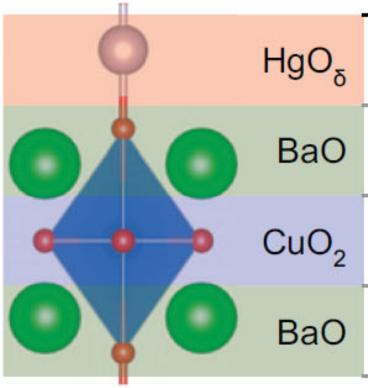
C. Weber, PNAS 2021 Vol. **118** No. 46 e2115874118

Chuck-Hou Yee *et al EPL* **111** 17002 (2015)

Stanev *et al.*, npj Computational Materials **4**, 29 (2018)

Liu *et al.* APL Materials **8**, 061104 (2020)

Optimizing T_c



	charge	dopants	structure	hamiltonian
HgO_δ	balances -2 charge	supplies	harbors dopants	tunes chemical potential
BaO	neutral	inert	protects CuO_2 from disorder	tunes in-plane *t*, *t'*, *U*
CuO_2	-2 charge/u.c.	accepts	roughly sets lattice const.	superconducts
BaO	(same as other CaS layer)			

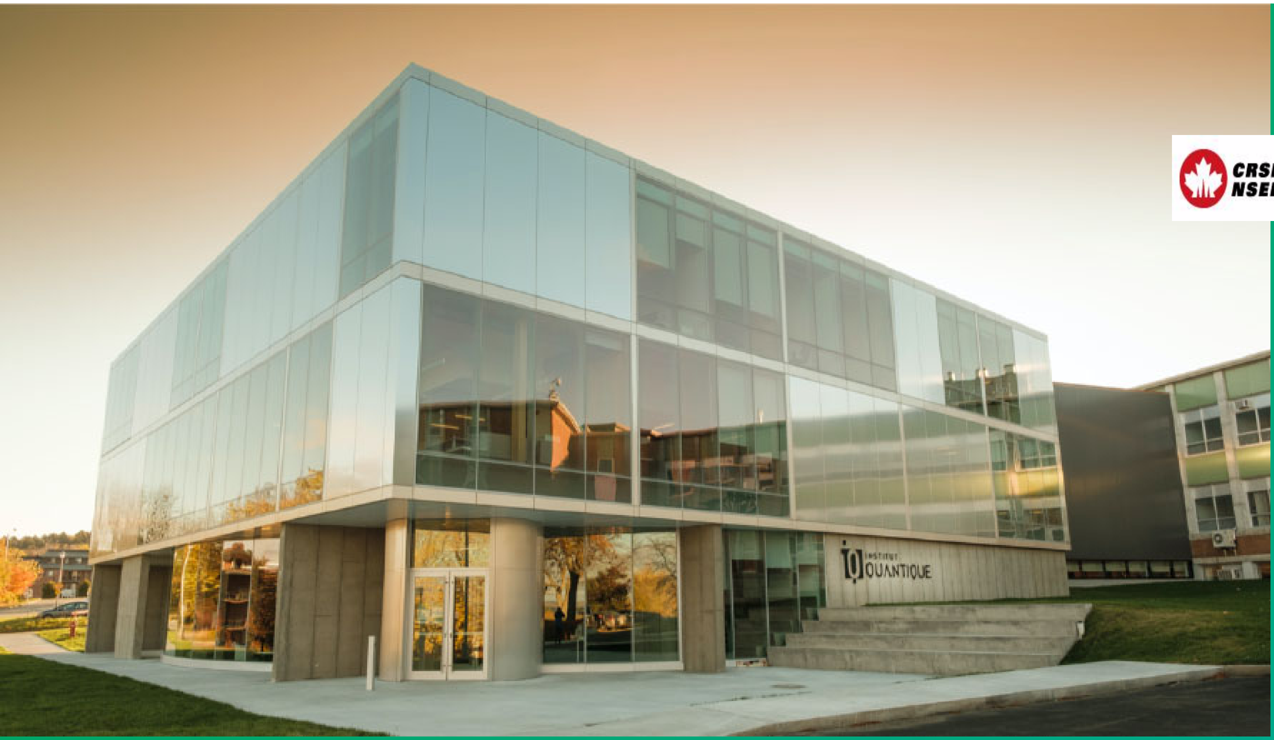
$$\mathrm{Hg(CaS)_2CuO_2}$$

Chuck-Hou Yee *et al EPL* **111** 17002 (2015)

Take home messages

- A detailed picture of the origin of superconductivity in cuprates follows from a model that takes into account Cu, O, kinetic energy and repulsion

- We need to look beyond traditional tools of solid state physics to work this out.



Fondation canadienne pour l'innovation

Fonds de recherche
Nature et
technologies
Québec

Merci
Thank you

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CDMFT

hybridization

bath energy

$$H_{\mathrm{AIM}} = \sum_{\alpha,\beta} t_{c,\alpha\beta} c_\alpha^\dagger c_\beta + \sum_{\alpha,r} \left(\theta_{\alpha r} c_\alpha^\dagger a_r + \mathrm{H.c.} \right) + \sum_{r}^{N_b} \varepsilon_r a_r^\dagger a_r + H_1$$

bath annihilation operator

$$\boldsymbol{G}_{0\,c}^{-1} = z - \boldsymbol{t}_c - \boldsymbol{\Gamma}(z)$$

$$\boldsymbol{\Gamma}(z) = \boldsymbol{\theta} \frac{1}{z - \boldsymbol{\varepsilon}} \boldsymbol{\theta}^\dagger$$

hybridization function

$$\begin{aligned} \boldsymbol{G}_c^{-1}(z) &= z - \boldsymbol{t}_c - \boldsymbol{\Gamma}(z) - \boldsymbol{\Sigma}(z) \\ &= \boldsymbol{\mathscr{G}}_0^{-1}(z) - \boldsymbol{\Sigma}(z) \end{aligned}$$

CDMFT (cont.)

The local, cluster Green function $\boldsymbol{G}_c$ must be consistent with the projection $\bar{\boldsymbol{G}}$ to the cluster of the lattice Green function:

$$\bar{\boldsymbol{G}}(z) = \frac{L}{N}\sum_{\tilde{\boldsymbol{k}}}\left[z - \boldsymbol{t}(\tilde{\boldsymbol{k}}) - \boldsymbol{\Sigma}(z)\right]^{-1}$$

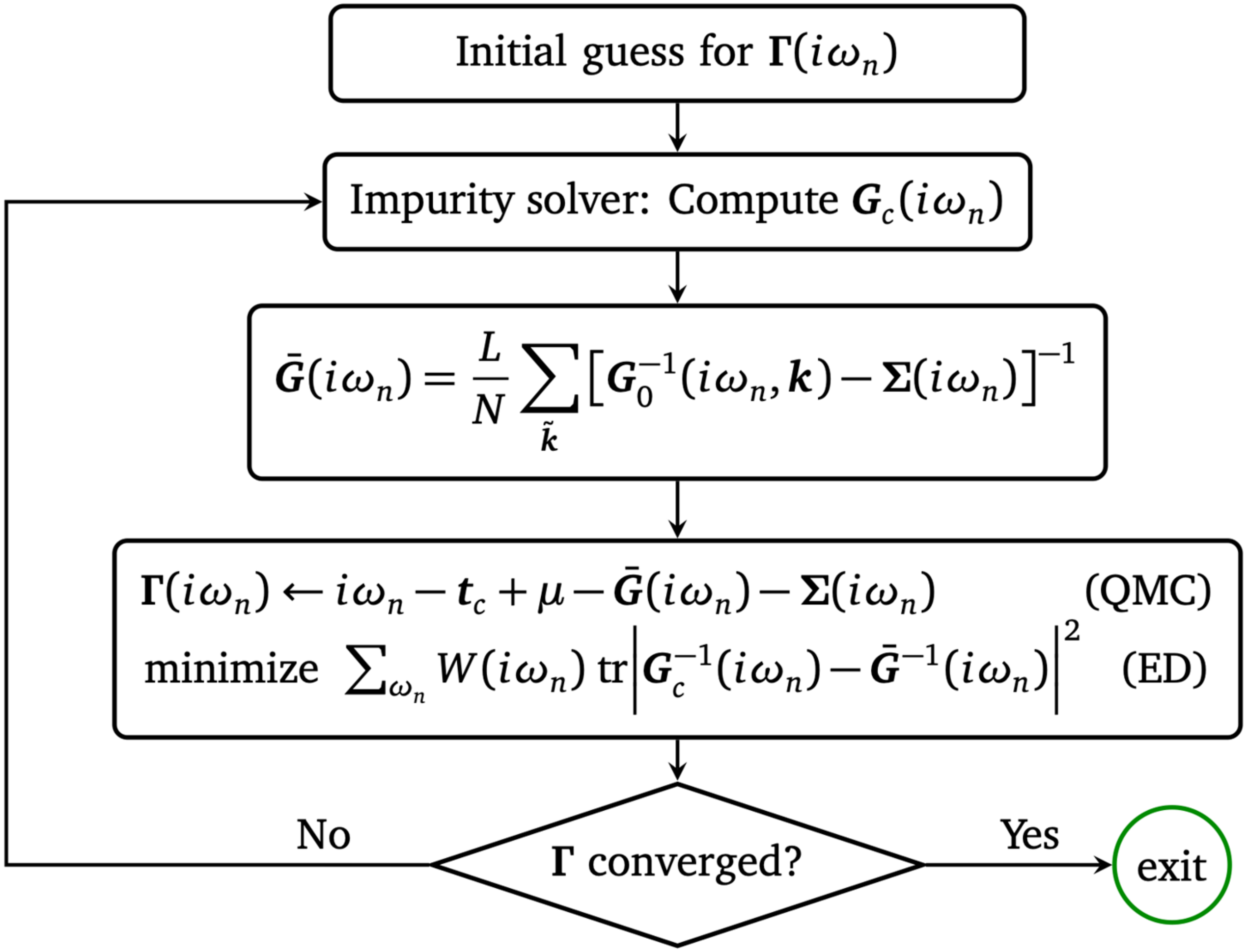
This condition may be statisfied (up to statistical errors) in QMC.
It can only be satisfied approximately in ED (i.e. with a finite bath).
Instead, one minimizes the distance function:

→ weight

$$d(\boldsymbol{\theta},\boldsymbol{\varepsilon}) = \sum_{i\omega_n} W(i\omega_n)\,\mathrm{Tr}\left|\boldsymbol{G}_c^{-1}(i\omega_n) - \bar{\boldsymbol{G}}^{-1}(i\omega_n)\right|^2$$

→ Matsubara freqs from a fictitious temperature β^{-1}

CDMFT (cont.)



Initial guess for $\boldsymbol{\Gamma}(i\omega_n)$

Impurity solver: Compute $\boldsymbol{G}_c(i\omega_n)$

$$\bar{\boldsymbol{G}}(i\omega_n) = \frac{L}{N}\sum_{\tilde{\boldsymbol{k}}}\left[\boldsymbol{G}_0^{-1}(i\omega_n,\boldsymbol{k}) - \boldsymbol{\Sigma}(i\omega_n)\right]^{-1}$$

$$\boldsymbol{\Gamma}(i\omega_n) \leftarrow i\omega_n - \boldsymbol{t}_c + \mu - \bar{\boldsymbol{G}}(i\omega_n) - \boldsymbol{\Sigma}(i\omega_n) \qquad \text{(QMC)}$$

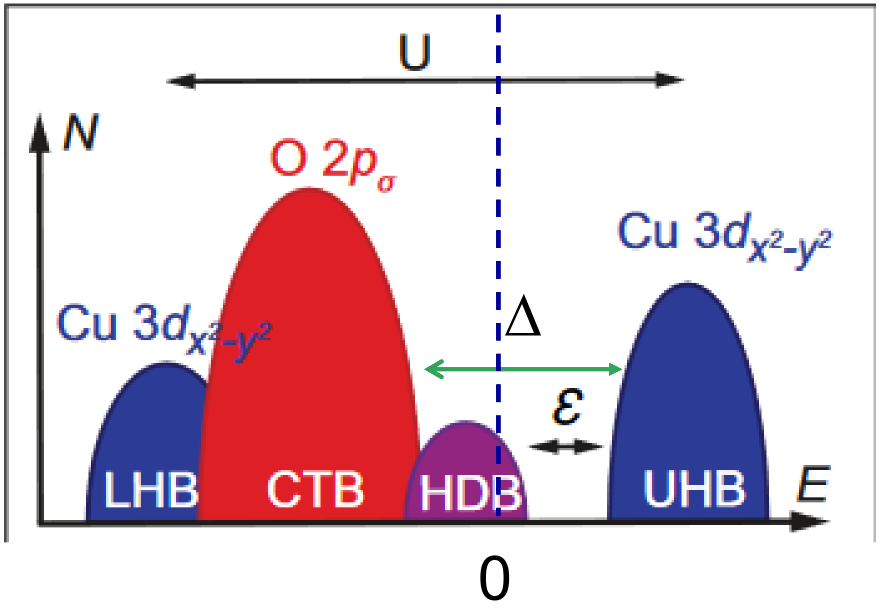
$$\text{minimize} \ \sum\nolimits_{\omega_n} W(i\omega_n)\,\mathrm{tr}\left|\boldsymbol{G}_c^{-1}(i\omega_n) - \bar{\boldsymbol{G}}^{-1}(i\omega_n)\right|^2 \qquad \text{(ED)}$$

$\boldsymbol{\Gamma}$ converged?

No

Yes

exit


U
N
O $2p_\sigma$
Cu $3d_{x^2-y^2}$
Cu $3d_{x^2-y^2}$
Δ
ε
LHB
CTB
HDB
UHB
E
0