Successes and challenges in the electronic structure of correlated materials: towards theoretical spectroscopy and materials design.

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Outline / Take Home Points

- Model Hamiltonians and First Principles Approaches for Correlated Materials: why we need both. Weakly correlated systems DFT, GW which one ? When is a material correlated? Different Types. Correlation Strength. Concept of Locality and its Basis Dependence.

- Quantum Embedding Methods LDA+DMFT , Gutzwiller, RiSB Material design project for f electron systems.

Thursday Morning June 16 (2022)

Nicola Lanata (University of Aahrus) : 8:30 – 10:30 Quantum-embedding formulation of the GA/RISB equations

Break.10:30 - 11

Corey Melnick (Brookhaven National Laboratories) 11:00 – 12:00
Quantum Embedding Methods: GPU Acceleration and Mutual Support

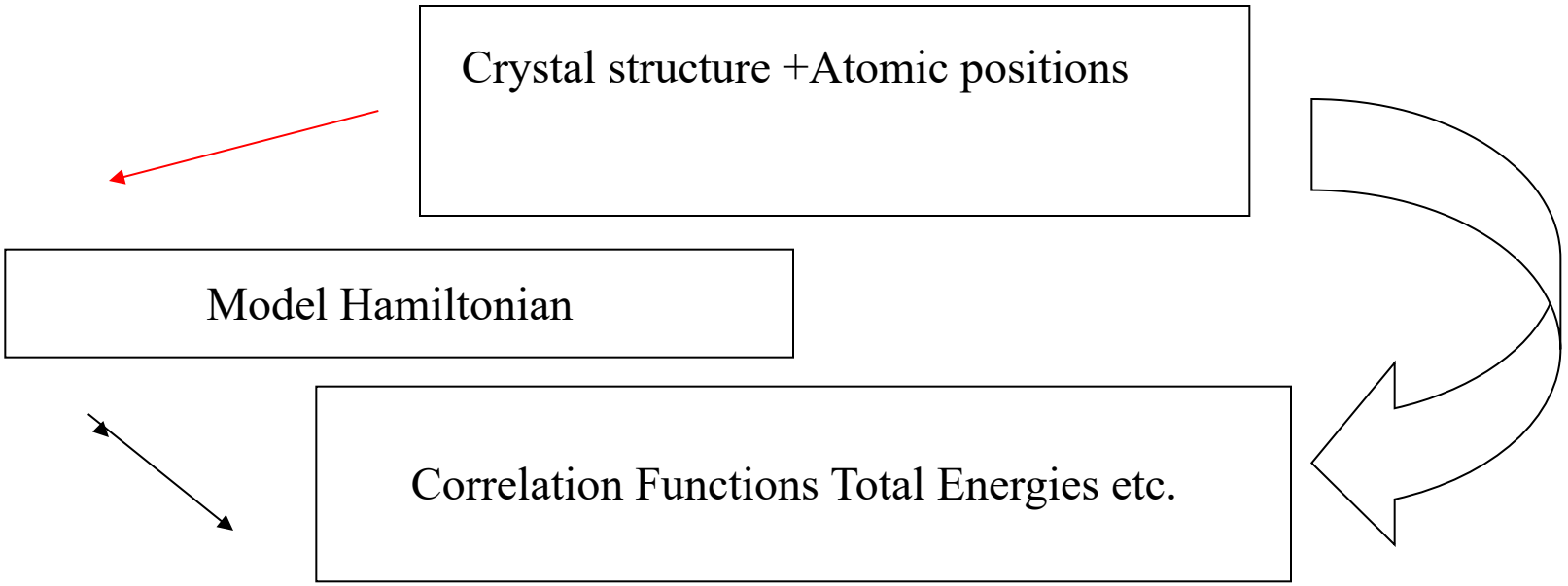
Material Design Project Correlated Semiconductors a la BaBiO3.

Different Roads to Correlated Materials: use models and ab initio Mott, Heavy fermions, Hund metals , actinides , correlated insultaors FeSb2

Thursday Afternoon.

Sangkook Choi 15:30- 17:30
From LDA+DMFT to LQSGW+DMFT and Full GW+DMFT: application to materials

Two paths for ab-initio calculation of electronic structure of strongly correlated materials



We need both. For many systems we have no idea what is the right for model for a given property.

$$H = \sum_i \frac{\nabla_i^2}{2m_e} + \sum_\alpha \frac{\nabla_\alpha^2}{2m_\alpha} - \sum_{\alpha,i} \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{R}_i|} + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\vec{R}_i - \vec{R}_j|} + \frac{1}{2}\sum_{\alpha\neq\beta} \frac{Z_\alpha^2 e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$
$+$relativistic effects.

TOE

Theory of everything vs Hubbard model

$$H = \sum_{i,j} c_\alpha^\dagger(i) t_{ij}^{\alpha\beta} c_\beta(j) + \sum_i U_{\alpha\beta\gamma\delta} c_\alpha^\dagger(i) c_\beta^\dagger(i) c_\gamma(i) c_\delta(i).$$

Tight binding form.

Eliminate the “irrelevant” high energy degrees of freedom

Add effective Coulomb interaction terms

Model Hamiltonians good to learn qualitative lessons common to many materials. TOE is needed to answer what each material does . Model Hamiltonians are useful to understand the results of TOE and to discover new physics, new types of correlated electron behavior.

Simplified coordinate system in the space of all materials.

Correlation strength?

DFT Non interacting electrons as a reference.

Density Functional Theory (Kohn Hohenberg , Kohn Sham 1964)

$$\Gamma\ [\ \rho\ (r)\ ] = \Gamma_{univ}\ [\ \rho\ (r)\ ] + \int dr V_{cryst}(r)\rho\ (r)$$

$$-\nabla^2 + V_{KS}(r)[\rho]\ \psi_{kj} = \varepsilon_{kj}\psi_{kj}$$

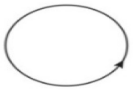
$$\rho(r) = \sum_{\varepsilon_{kj}<0} \psi_{kj}{}^*(r)\psi_{kj}(r)$$

$$V_{KS} = V_{Hartree} + V_{cryst} + V_{xc}$$

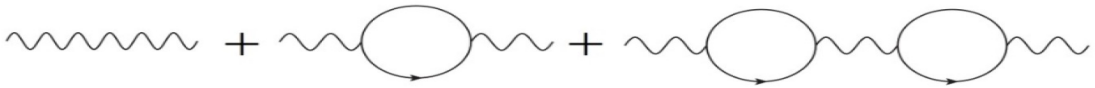
Kohn Sham Greens Function

$$G_0^{-1}{}_{KS} = i\omega_n + \mu + \nabla^2 - V_{KS}(r)[\rho]$$

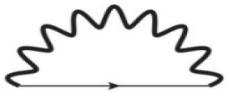
Feynman Diagrams and Their Resummations

$\Pi = G_0 G_0 =$  $v_{Coul} =$ 

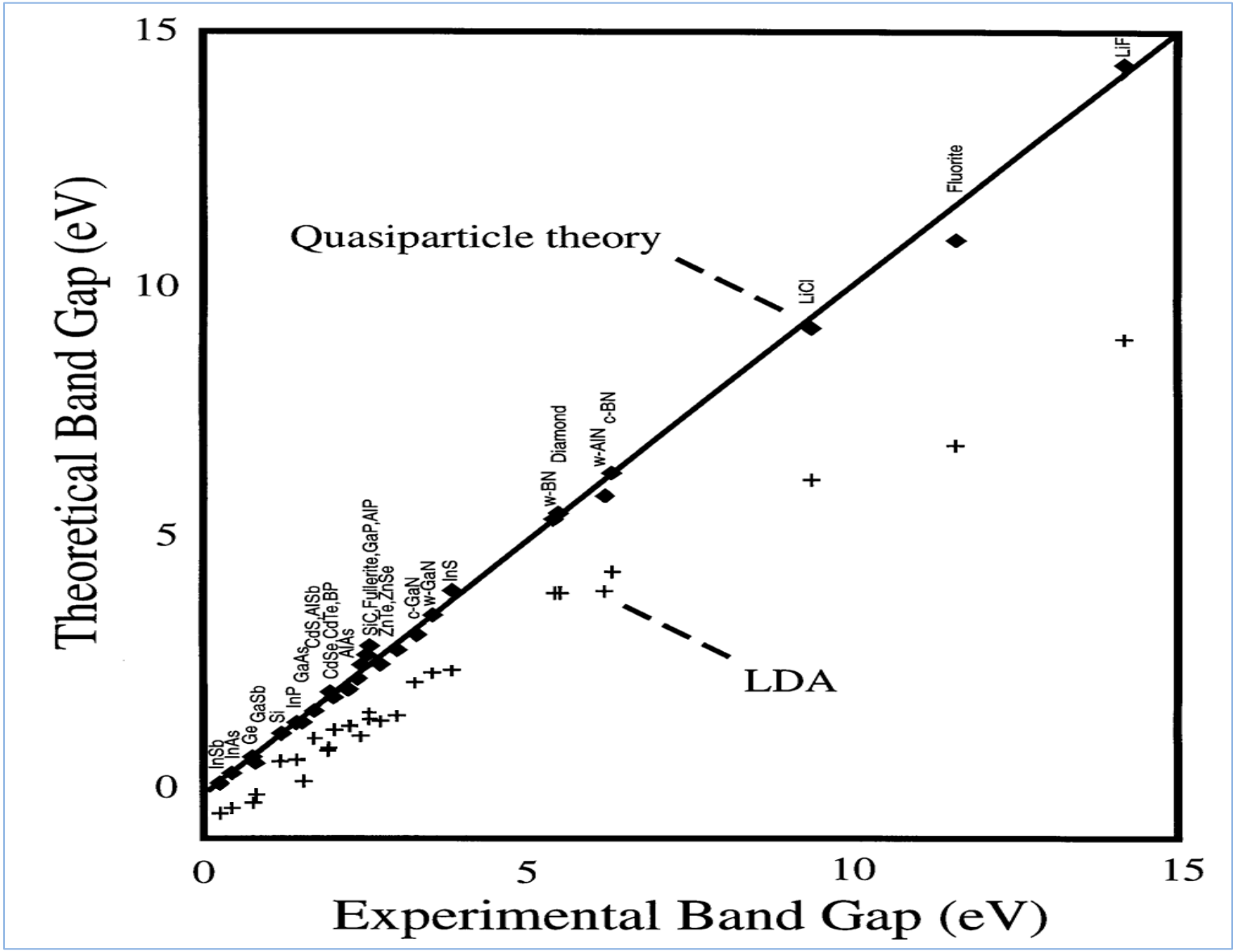
$W =$ 

$=$ 

$+ \ldots$

$\Sigma_{GW} = G_0 W =$ 

- But what to take as G0? Self consistent G, scGW (Hedin), G0 = GLDA (G0W0 Hyberstsen Louie , qpscGW (van Schilfgaarde) . Starting point of Sangkook Choi on Thursday, comparing self consisent GW+DMFT and sc qpGW+DMFT.



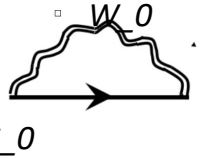
M. Hybersent S. Louie in (1997)

$$G_0^{-1} = \imath\omega_n + \mu - h_0,$$

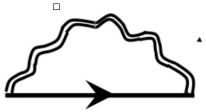
$$h_0 = -\nabla^2 + V_{ext} + V_{Hartree}$$

$$G_{KS}^{-1} = G_0^{-1} - V_{xc}$$

$$G_{G_0W_0}^{-1} = G_0^{-1} -$$



$$G^{-1} = [G_0^{-1} - V_{KS}^{DFT}] - [-V_{KS}^{DFT} -]$$



Landau-Fermi liquid; perform Taylor expansion.

M. VanSchilfgaarde Phys. Rev. Lett. 93, 126406 (2004) lqsGW

$$G \approx \frac{1}{\imath\omega - h_0 - \Sigma(\omega = 0) - \imath\omega \frac{\partial\Sigma}{\partial(\imath\omega)}(\omega = 0)}$$

Linearized or better Landau

$$G \approx \frac{1}{\frac{\imath\omega}{Z} - \left(h_0 - \Sigma(\omega = 0)\right)}, \qquad \frac{1}{Z} = 1 - \frac{\partial\Sigma}{\partial(\imath\omega)}(\omega = 0)$$

Quasiparticle Self-consistent GW

$$G = \sqrt{Z}\frac{1}{\imath\omega - h_{qp}}\sqrt{Z} = \sqrt{Z}G_{qp}\sqrt{Z}, h_{qp} = \sqrt{Z}(h_0 + \Sigma(\omega = 0))\sqrt{Z}$$

Linearized qsGW approximation: use
Works in Matsubara .

G_{qp} G_0

Linearized (or Landau) self consistent quasiparticle GW

$$\hat{G}^{-1}_{QP}(\mathbf{k}, i\omega_n) = i\omega_n \hat{I} - \hat{H}_{QP}(\mathbf{k})$$

$$\hat{\chi}_{QP}(\mathbf{k},' i\omega_n) = 2\sum_{\mathbf{R}} \int d\tau \hat{G}_{QP}(\mathbf{R}, \tau) \circ \hat{G}^{T}_{QP}(-\mathbf{R}, -\tau) e^{-i(\mathbf{k}\cdot\mathbf{R} - \omega_n \tau)}$$

$$\hat{W}^{-1}_{QP}(\mathbf{k}, i\omega_n) = \hat{V}^{-1}(\mathbf{k}) - \hat{\chi}_{QP}(\mathbf{k}, i\omega_n)$$

$$\hat{\Sigma}_{QP}(\mathbf{k}, i\omega_n) = -\sum_{\mathbf{R}} \int d\tau \hat{G}_{QP}(\mathbf{R}, \tau) \circ \hat{W}_{QP}(\mathbf{R}, \tau) e^{-i(\mathbf{k}\cdot\mathbf{R} - \omega_n \tau)}$$

$$\hat{Z}^{-1}(\mathbf{k}) = \hat{I} - \partial\hat{\Sigma}_{QP}(\mathbf{k}, i\omega_n = 0)/\partial(i\omega_n)$$

$$\hat{H}_{QP}(\mathbf{k}) = \hat{Z}^{1/2}(\mathbf{k}) \left(\hat{H}_H(\mathbf{k}) + \hat{\Sigma}_{QP}(\mathbf{k}, i\omega_n = 0)\right) \hat{Z}^{1/2}(\mathbf{k})$$

$$H_H = -\nabla^2 + V_H(r)[\rho] + V_{cryst}$$

A. Kutepov et. al. PR*B* **85**, 155129 (2012).

B. A. Kutepov et. al. Computer Physics Communications 219, 407 (2017)

Comparison of lqsGW with qsgw

[15] M. van Schilfgaarde et. al. PRL **96**, 226402, (2006) [24]Takao Kotani et. al. PRB **76**, 165106 (2007)
[16] M. Shishkin, M. Marsman, and G. Kresse PRL **99**, 246403 (2007)
[17] Wei Chen and Alfredo Pasquarello PRB **92**, 041115(R) (2015)
Table from A Kutepov V Oudovenko G Kotliar (present work) CPC 219, 407, (2017)

	[15], [24]	[16]	[17]	Present work	Exp.
Si	**1.23**	**1.41**	**1.47**	**1.41(14.8%)**	**1.22**
SiC	2.14	2.88	2.90	3.08(22.7%)	2.51
C	6.52	6.18	6.40	6.71(14.1%)	5.88
GaAs	1.93	1.85	1.75	2.08(23.1%)	1.69
ZnO	3.87	3.8	4.61	4.47(24.2%)	3.60
MgO		9.16	9.29	9.42(18.0%)	7.98
ZnS	4.04	4.15		4.19(6.3%)	3.94
ZnSe	3.08			3.17(5.7%)	3.00
LiF		15.9		16.63(14.8%)	14.48
NaCl				9.81(15.4%)	8.5
BN		7.14	7.51	7.06(7.0%)	6.6
AlP		2.90	3.10	2.80(13.4%)	2.47
NiO	4.8		4.97	4.47(3.9%)	4.3
Cu_2O	2.36		2.65	2.42(10.0%)	2.20
TiO_2	3.78		4.22	3.80(22.6%)	3.1
$Sr\ TiO_3$	4.19			4.01(21.5%)	3.3
CeO_2	~5			5.83(70.1%)	3–3.5

correlations locality lattice model

$$\Sigma_{latt}(\omega, k) \sim \Sigma_{imp}(\omega)$$

$$\Sigma(\omega)_{lattij} \sim \Sigma_{imp}(\omega)\delta_{ij}$$

DMFT assumes locality in an irreducible quantity, (a self energy, not the greens function).

DMFT is exact in various limits, atomic limit and band limit.

DMFT is exact in a non trivial large dimensional limit.

DMFT gives the best local approximation

Good when the correlation lengths are short, at high temperatures, strong frustration.

Cluster extensions of DMFT provide systematic improvements.

In multi orbital systems even the DMFT self energy is k dependent

$$H = -\Sigma_{R\acute{R}}\, t^{\alpha\beta}_{R\acute{R}} c^{\dagger}_{R\alpha} c_{\beta\acute{R}} + \Sigma_R\, U_{\alpha\beta\gamma\delta}\, c^{\dagger}_{\alpha R} c^{\dagger}_{\beta R} c_{\gamma R} c_{\delta R}$$

$$\Sigma_{R\acute{R}} = \Sigma(\imath\omega_n)\, \delta_{R\acute{R}}$$

$$G^{-1}_{R\acute{R}} = (\imath\omega + \mu)\, \delta_{R\acute{R}}\, \delta^{\alpha\beta} - t^{\alpha\beta}_{R\acute{R}} - \delta_{R\acute{R}}\, \Sigma^{\alpha\beta}(\imath\omega)$$

$$t^{\alpha\beta}(k) = U_k \begin{pmatrix} \epsilon_{k1} & 0 & \cdots & \cdots \\ 0 & \epsilon_{k2} & \cdots & \cdots \\ \vdots & \vdots & \ddots & \vdots \\ \cdots & \cdots & \cdots & \epsilon_{kn} \end{pmatrix} U^{\dagger}_k$$

$$\Sigma_{j\acute{j}}(k, \imath\omega_n) = \Sigma^{\alpha\beta}(\imath\omega_n)\, \psi^{\alpha\dagger}_{jk}\, \psi^{\beta}_{\acute{j}k}$$

$$G(k)^{-1}_{j\acute{j}} = \imath\omega_n + \mu - \epsilon_k \delta_{R\acute{R}} - \Sigma_{j\acute{j}}(k, \imath\omega_n)$$

Points to notice

- Correlations depend on the reference point (HF, Vxc, hybrid , qsgw, etc)
- Correlations depend on the energy scale that is being probed.
- Locality depends on the basis set used to express the self energy.
- Locality depends on the energy scale.
- Static vs Dynamic Correlation (in chemistry the terms are inverted, k dependent vs omega dependent self energy)
- Many roads to strongly correlated systems. We discover new ones as we study materials.
- DMFT takes us from the atomic multiplets of an open shell at high energies to Fermi liquid theory at low energy (generally speaking.. Sometimes not) . Different crossovers. Different roads to strong correlation: Mott , Hund, Heavy fermions, many still to be discovered.

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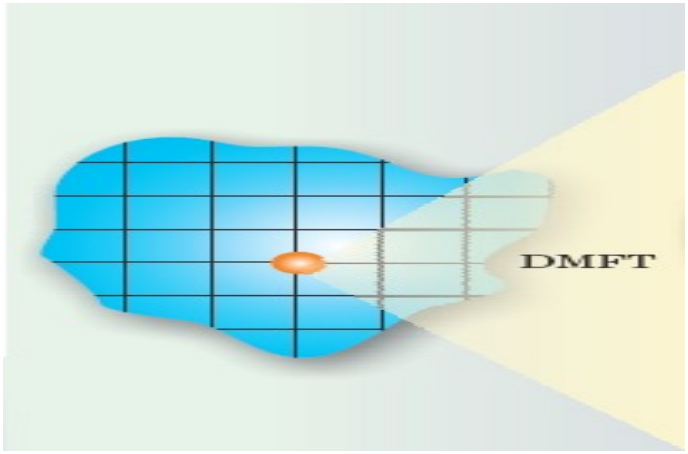
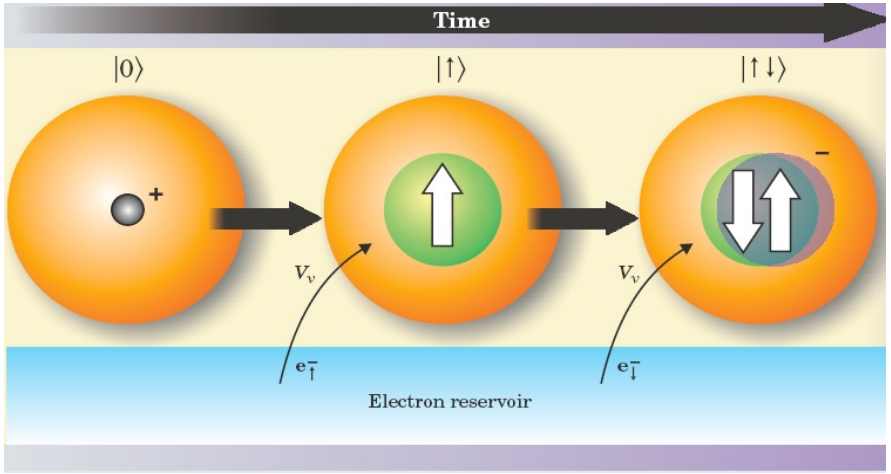
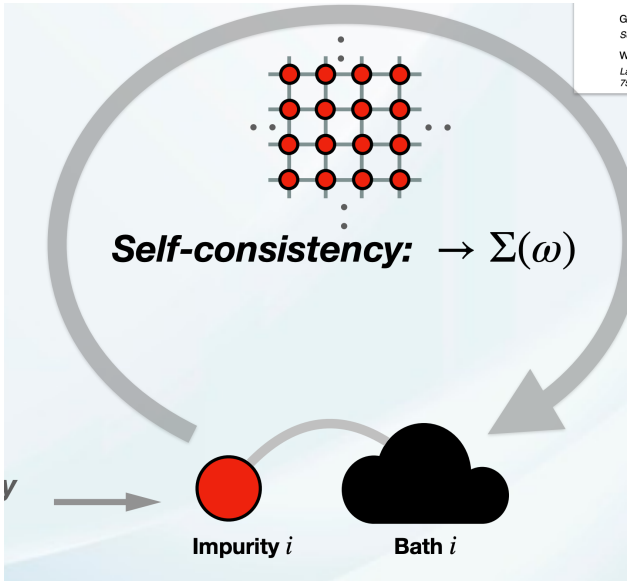
Dynamical Mean Field Theory and Quantum Embeddings

A. Georges and G. Kotliar PRB 45, 6479 (1992).

Metzner and Vollhardt Phys. Rev. Lett. **62**, 324 (1989)







View the solid as a collection of atoms. View each atom as surrounded by an effective self consistent medium.

Quantum Embedding: atom = fragment

Enviromement= quantum bath

Impurity= bath +fragment

High level solvers for impurity

Low level solver for the lattice.

Compatibility condition between lattice and fragment= DMFT self consistency condition.

Many examples, DMET, Gtuzwiller, Rotationally Invariant Slave Bosons

See Nicola Lanata's talk Thursday.

Slave boson formalism

$$|n\rangle = (d_1^\dagger)^{n_1} \cdots (d_M^\dagger)^{n_M} |\text{vac}\rangle$$

$$H_{\text{loc}} = \sum_\alpha \varepsilon_\alpha^0 \hat{n}_\alpha + \sum_{\alpha\beta} U_{\alpha\beta} \hat{n}_\alpha \hat{n}_\beta$$

$$|n\rangle_f \equiv (f_1^\dagger)^{n_1} \cdots (f_M^\dagger)^{n_M} |\text{vac}\rangle$$

$$|\underline{n}\rangle \equiv \phi_n^\dagger |\text{vac}\rangle \otimes |n\rangle_f$$

Constraints

$$\sum_n \phi_n^\dagger \phi_n = 1 \qquad \sum_n n_\alpha \phi_n^\dagger \phi_n = f_\alpha^\dagger f_\alpha, \quad \forall \alpha$$

Physical content

Emergence of renormalized QP

$$\underline{d}_\alpha^\dagger = \sum_{nm} \langle n | f_\alpha^\dagger | m \rangle [\hat{\Delta}_\alpha]^{-1/2} \phi_n^\dagger \phi_m [1 - \hat{\Delta}_\alpha]^{-1/2} f_\alpha^\dagger$$

$$\hat{\Delta}_\alpha[\phi] \equiv \sum_n n_\alpha \phi_n^\dagger \phi_n$$

$|\phi_n|^2$:

Probabilty of state n to be occupied

Coupling of fermions to local spin orbital charge modesl

Kinetic Part

$$\underline{H} = \sum_{ij} R_\alpha[\phi] f_\alpha^\dagger(i)\, t_{ij}^{\alpha\beta} R_\beta[\phi] f_\beta(j)\,.$$

Local Part

$$H_{loc} = \sum_n \phi_n{}^\dagger \phi_n \epsilon_n \qquad \epsilon_n = \sum_\alpha (n_\alpha + \sum_\beta U_{\alpha\beta} n_\alpha n_\beta).$$

Interpretation in terms of self energies.

$$\Sigma_\alpha(\omega) = \Sigma_\alpha(0) + \omega\left(1 - \frac{1}{Z_\alpha}\right),$$

$$Z_\alpha = |R_\alpha|^2,$$

$$\Sigma_\alpha(0) = \lambda_\alpha/|r_\alpha|^2 - \epsilon_\alpha^0.$$

Rotationally invariant slave bosons

$$d_\alpha = \hat{R}_{\alpha\beta}[\phi] f_\beta.$$

DFT+DMFT is 25 years old

- The light, sp (or spd) electrons are extended, well described by DFT Kohn Sham hamiltonian.The heavy, d (or f) electrons are more localized treat with DMFT.
- LDA Kohn Sham Hamiltonian already contains an average interaction of the heavy electrons, we subtract this out by shifting the heavy level (double counting term). Multiple prescriptions for its determination. As in LDA+U: around mean field, atomic limit. Or more DMFT specific, nominal double counting, exact double counting K Haule Phys. Rev. Lett. **115**, 196403 (2015)

- ❑ Kinetic energy is provided by the Kohn Sham Hamiltonian (sometimes after downfolding). The U matrix can be estimated from first principles or viewed as parameters (as in constrained DFT or RPA). Solve resulting model using DMFT.
- ❑ The charge can be determined self consistently within LDA+DMFT and the self consistent equations can be derived from a functional. (*R. Chitra PRB 62, 12725 (2000), DFT +DMFT as an exact theory. First implementation of charge self consistency S. Savrasov PRB69 , 245102 (2004). More recent implementations of LDA+DMFT total energy, forces (K Haule S. Savrasov).*

V. Anisimov, A. Poteryaev, M. Korotin, A. Anokhin and G. Kotliar, J. Phys. Cond. Mat. 35, 7359 (1997). A. Lichtenstein and M. Katsenelson PRB 57, 6884 (1998).

DFT+DMFT is a very successful active area.

- Correlations (beyond DFT) that are not captured by LDA+U are present in many materials of interest
- Hundness, Mottness, Kondo physics, heavy fermion behavior
- There are many interesting correlated systems beyond solids. versions of electronic structure + DMFT has been use for molecules, correlated sites in biomolecules, surfaces, correlated atoms in surfaces, even work on correlation effects on excited states with application to catalysis might require quantum embedding approaches
- LDA +DMFT is available in many electronic structure codes.

DMFT has been incorporated into many packages available, a few examples

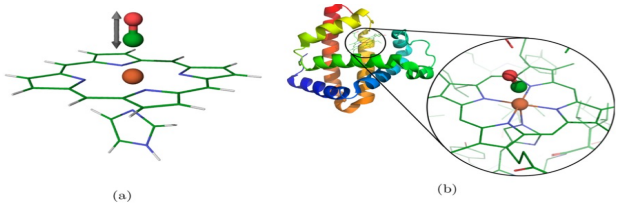
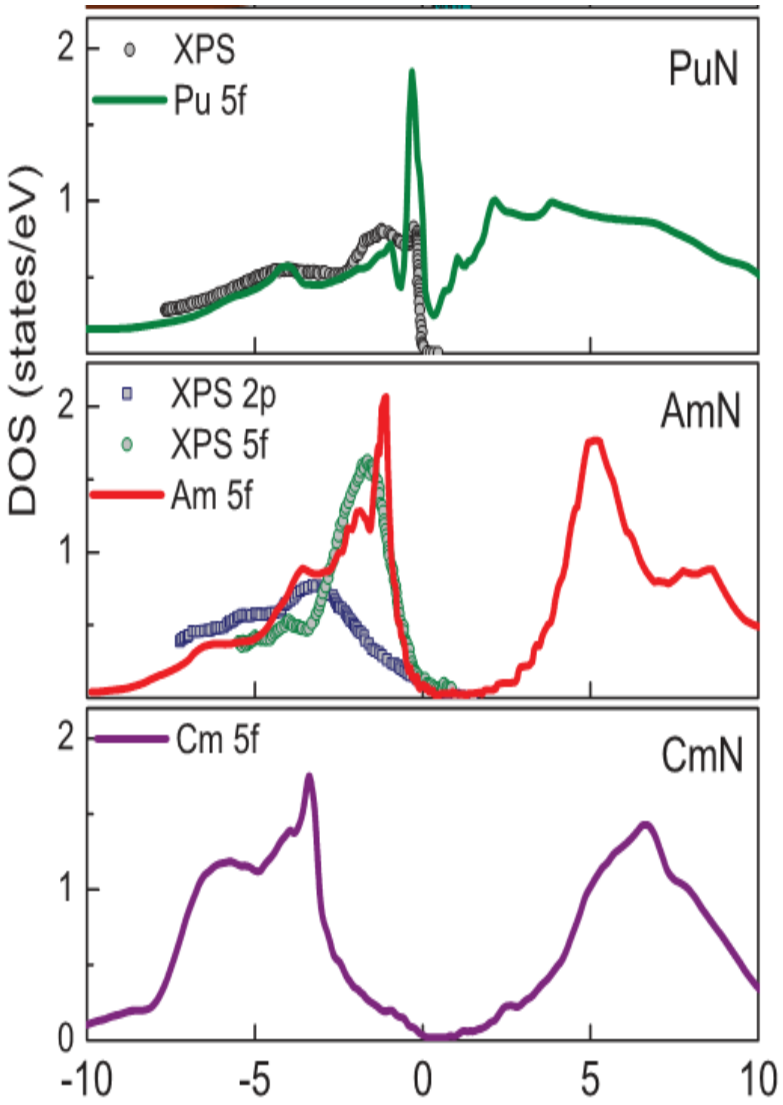


Figure 6. (a) Model complex studied in this work: iron porphyrin with axial imidazole and carbon monoxide ligands. Hydrogen, carbon, nitrogen, oxygen, and iron atoms are shown in white, green, blue, red, and orange, respectively. (b) Carboxymyoglobin, showing the iron binding site.[72]

- Abinit (2012) : in TRIQS with tutorial in this school 2022. https://pitp.phas.ubc.ca/confs/sherbrooke2012/archives/DFTDMFT_Abinit_Amadon.pdf
- Kristjan Haule's EDMFT code (2009, based on Wien2K): https://www.bnl.gov/comscope/software/EDMFTF.php
- Comsuite: https://www.bnl.gov/comscope/software/comsuite-user-guide.php
- VASP): https://triqs.github.io/dft_tools/unstable/guide/conv_vasp.html
- Quantum Espresso, OpenMX: https://ma.issp.u-tokyo.ac.jp/wp-content/uploads/sites/3/2019/07/20180730_dftdmft.pdf
- Elk: https://github.com/AlynJ/Elk_interface-TRIQS , http://www.amulet-code.org
- Wien2K: https://triqs.github.io/dft_tools/latest/guide/conv_wien2k.html
- Questaal: https://www.questaal.org/tutorial/qsgw_dmft/dmft0/
- Onetep: https://pubs.acs.org/doi/abs/10.1021/acs.jctc.0c00162
- CASTEP: https://journals.aps.org/prb/abstract/10.1103/PhysRevB.98.075129
- RSPT: https://www.physics.uu.se/research/materials-theory/ongoing-research/code-development/rspt-main/
- Siesta: https://github.com/DMFTwDFT-project/DMFTwDFT

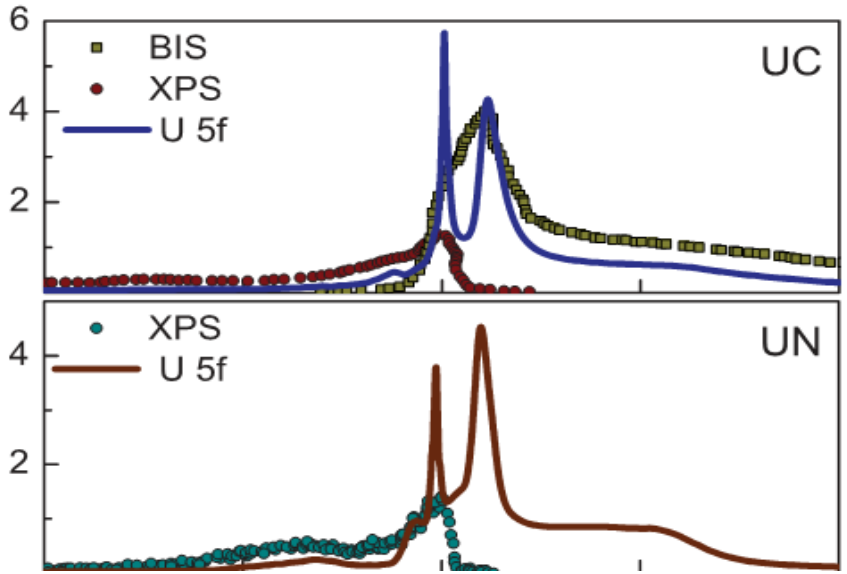
Q. Yin, A. Kutepov, K. Haule, GK S. Savrasov and W. Pickett
PRB B 84, 195111 (2011)

Electronic correlation and transport properties of nuclear fuel materials

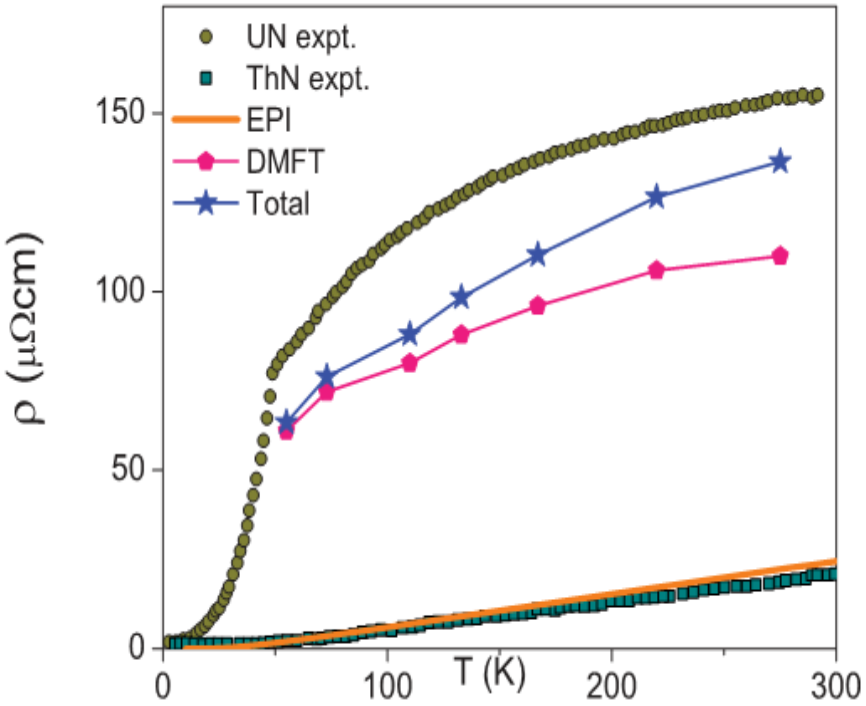


U n_f	U	Np			
C	5.1 2.3	5.3 3.5	5.5 4.7	5.8 5.7	6.2 6.9
N	5.2 2.4	5.5 3.7	5.8 4.8	6.4 5.9	6.6 7.0
itor					
O_2	6.0 2.0	6.3 3.0	6.5 4.0	7.0 5.0	7.4 6.0

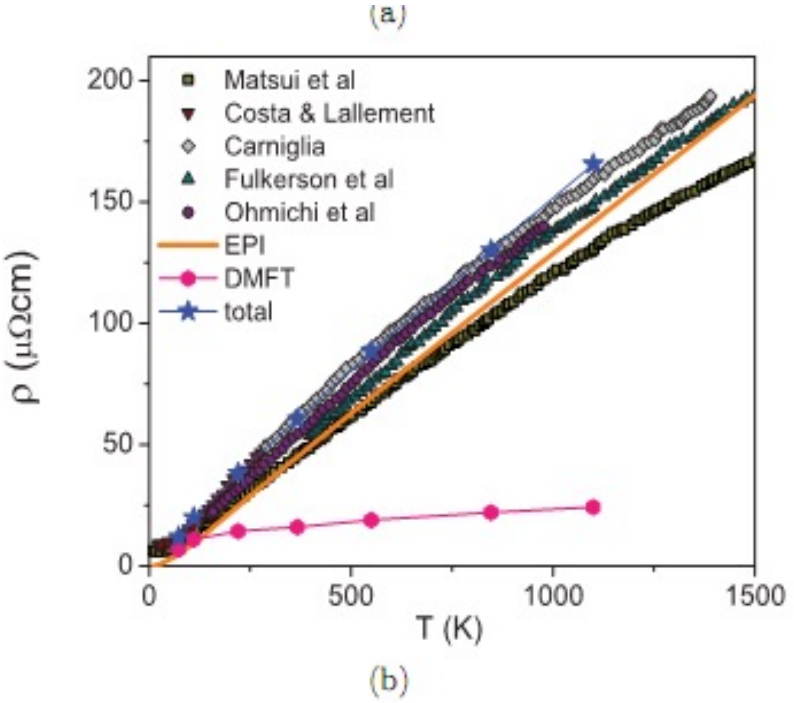
Find the localization delocalization boundary



Evaluate all the transport coefficients.



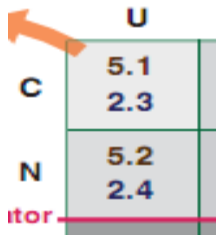
UN



UC

UC and UN are known metallic nuclear fuels with high melting temperatures. Suggestion :$U(C_{.5}N_{.5})$ should have improved thermal conductivity (and not checked similar melting point)!!

All



Material design project perspective

- For the actinide ZSA phase boundary determination, K. Haule CTQMC solver was used for the early actinides and K. Haule NCA and OCA was used for the later actinides.
- Lesson: simpler solvers benchmarked agains accurate calculations (CTQMC for Pu had been carried out and benchmarked against OCA for late actinides) will be essential in material design projects.
- In the school see talks by N. Lanata (tests of the accuracy of RISB and ghost RISB vs DMFT) and C. Melnick (X-fields in Pu) on Thursday, a possible direction for progress in f systems.

Knobs in the DFT +DMFT calculations.

- The type of DFT used, i.e. Vxc
- The type of double counting used. Important advance (exact double counting K. Haule)
- The U matrix. Original proposal (use constrained DFT). More recent suggestions (several types of contrained RPA's Imada et. al. constrained DMFT K. Haule)
- The orbital to which the correlations are applied.
- They are all interrelated, and they have been estimated successefully, making LDA +DMFT a successful first principles method.
- Next step to derive and control the approach diagrammatically? An diagrammatic approach exploiting locality [Sangkook Choi's lectures]

Natural next step GW+DMFT

- P. Sun and G. Kotliar, Phys. Rev. B 66, 085120 (2002).
- S. Biermann, F. Aryasetiawan, and A. Georges,
  Phys. Rev. Lett. 90, 086402 (2003).
- ……
- Sangkook Choi, A. Kutepov, K. Haule, M. van Schilfgaarde, and G. Kotliar, npj Quantum Materials 1, 16001 (2016).
- F. Nilsson L. Boehnke P. Werner and F. Aryasetiawan Phys. Rev. Materials 1, 043803 (2017).
- ……

Similar in structure to LDA+DMFT, but with only one knob left: the choice of correlated shells or orbitals.

Thursday Afternoon.

Sangkook Choi 15:30- 17:30
From LDA+DMFT to LQSGW+DMFT and Full GW+DMFT: application to materials

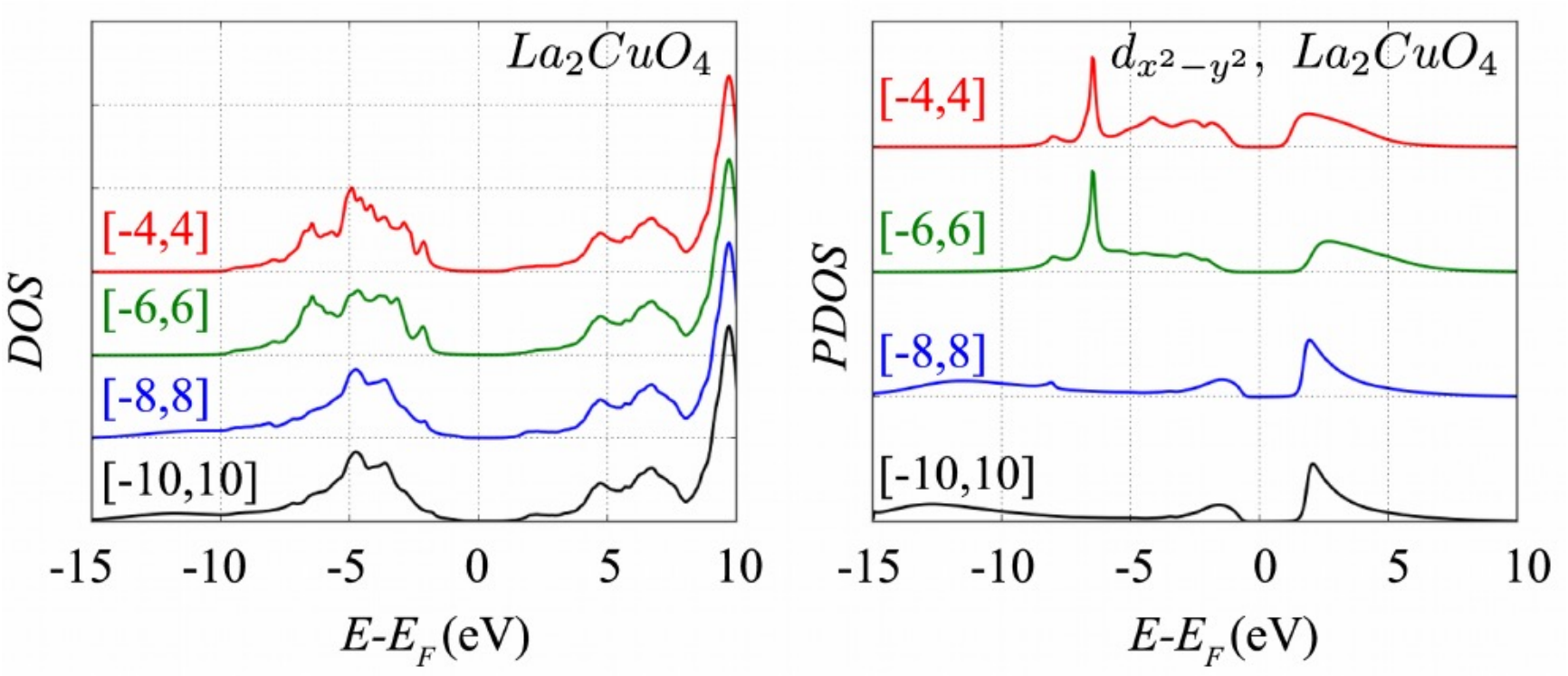
Break 17:30 -18:00

Sangkook Choi 18:00 – 19:00 1 Hands on Session on COMSUITE

Sensitivity in the choice of projector should be reasonable to trust the results.

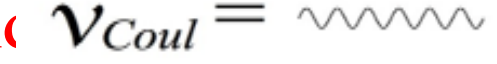
Explore Window (Orbital Choice)Dependence of the results

Sangkook Choi, A. Kutepov, K. Haule, M. van Schilfgaarde, and G. Kotliar, npj Quantum Materials 1, 16001 (2016).



Many Body Theory . Baym Kadanoff functional Green's function G.

$$\Gamma_{BK}[G] = -TrLn[G^{-1}] - Tr[(G_0{}^{-1} - G^{-1})G] + \Phi[G]$$

$\Phi[G]$ = Sum 2PI graphs with G lines and v_{Coul} = 

$$\Gamma[G,\Sigma] = -TrLn[G_0{}^{-1} - \Sigma] - Tr[\Sigma G] + \Phi[G]$$

Phi is the sum of two particle irreducible graphs. The version in terms of G and W

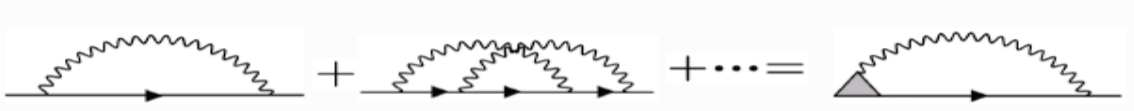
$$\Gamma[G,W,\Sigma,\Pi] = -\mathrm{Tr}\ln[G_0^{-1} - \Sigma] - \mathrm{Tr}[\Sigma G]$$
$$+ \frac{1}{2}\mathrm{Tr}\ln[v_{Coul}^{-1} - \Pi] - \frac{1}{2}\mathrm{Tr}[\Pi W] + E_H + \Phi[G,W],$$

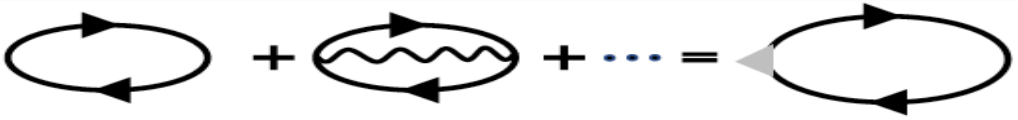
Almbladh et. al. Int. J. Mod. Phys. B **13**, 535 (1999)

R. Chitra, and G. Kotliar arXiv:cond-mat/99112
Phys. Rev. B **63**, 115110 (2001).

The Hedin Program L. Hedin, Phys. Rev. 139, A796 (1965).

$$\Phi(G,W)=$$ 

$$\Sigma=\frac{\delta\Phi}{\delta G}=$$ 

$$\Pi=2\frac{\delta\Phi}{\delta W}=$$ 

$$\Gamma[G,W,M,P]=-TrLn[G_0^{-1}-M]-Tr[\mathrm{M}G]+\frac{1}{2}TrLn[V_C^{-1}-P]-\frac{1}{2}Tr[P]W+E_{hartree}+\Phi[G,W]$$

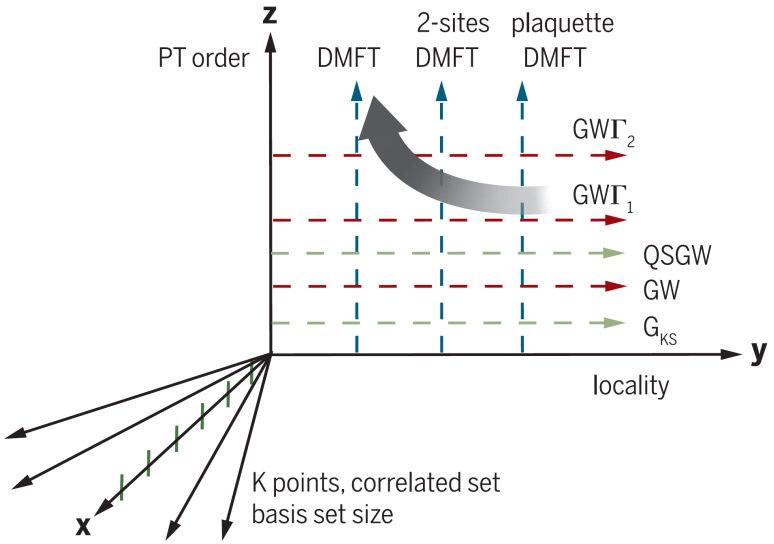
Starting Point for Derivation Combinations of GW+DMFT, Sangkook Choi Thursday afternoon.

R. Chitra, and G. Kotliar arXiv:cond-mat/9911223
Phys. Rev. B **63**, 115110 (2001).

Why not stop at the LDA+DMFT Level ? In many classes of materials where important systematic failures of LDA+DMFT were noticed

- Size of electron and hole pockets in iron based semiconductors, i.e. Fermi surfaces are much smaller in experiment than in theory.
- Small gap correlated semiconductors with the marcasite structure

DFT cannot get the correct gap, GW gives too large of a gap and fails to describe many anomalous physical properties.

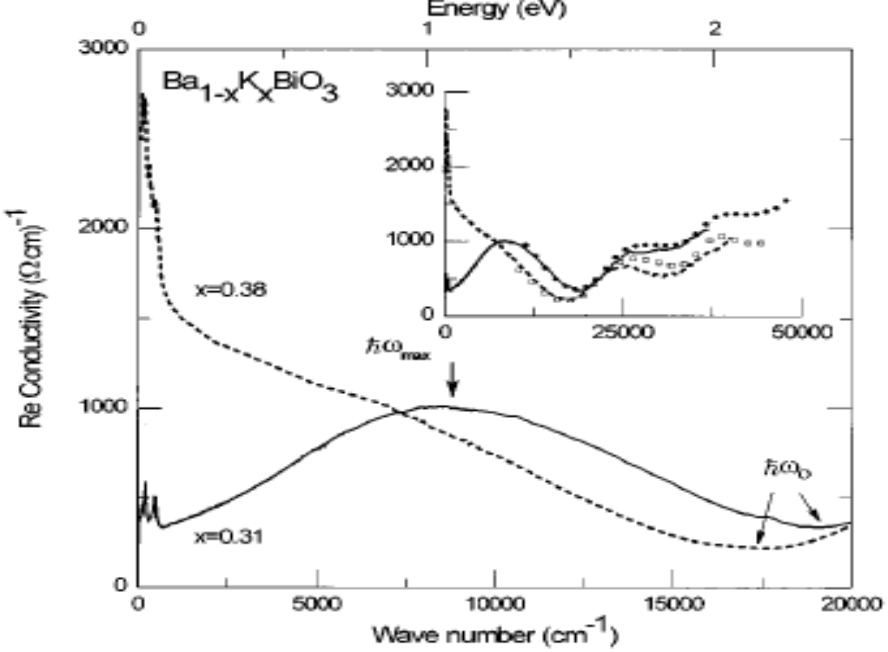


Kent and Kotliar Science 361, 348 (2018)

- Ligand p (and also f states) are substantially off (~1 ev) from the d states in LDA+DMFT
- We want to treat simultaneously static and dynamic correlations, important in BaBiO3 like sytems. Designing Materials.
- Conceptual reasons, we would like to understand better LDA+DMFT and its versions (double counting corrections, choice of U's , choice of orbitals etc.) from a more fundamental perspective.

- Vision: a controlled approach to Materials along the Hedin axis and the DMFT axis. A multidimensional version of Jacob's ladder in DFT's.

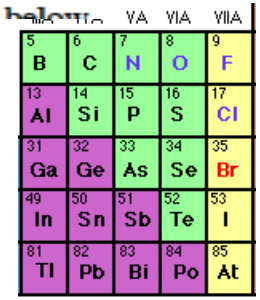
- Multiple embedding methods and multiple solvers for trade offs of speed and accuracy.



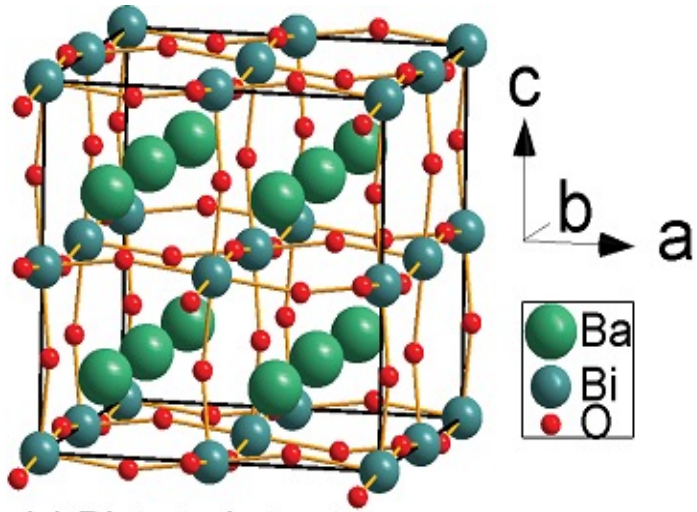
site.

, Pb

"Pb4+ =Bi 5+"



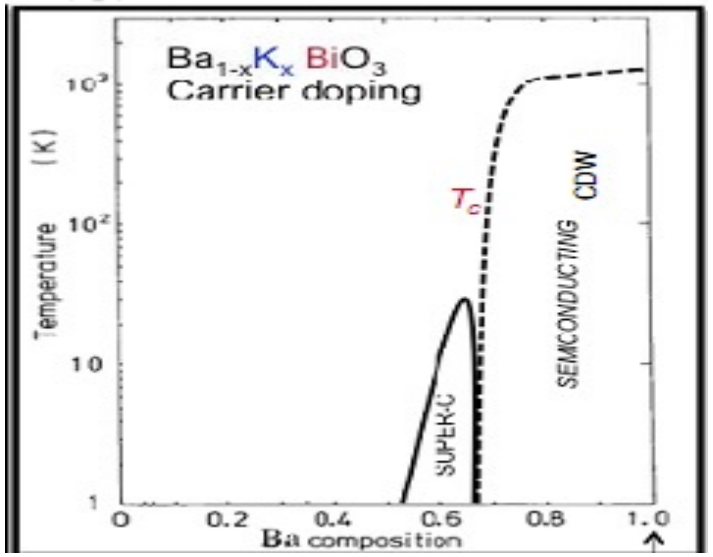
5 B	6 C	7 N	8 O	9 F
13 Al	14 Si	15 P	16 S	17 Cl
31 Ga	32 Ge	33 As	34 Se	35 Br
49 In	50 Sn	51 Sb	52 Te	53 I
81 Tl	82 Pb	83 Bi	84 Po	85 At

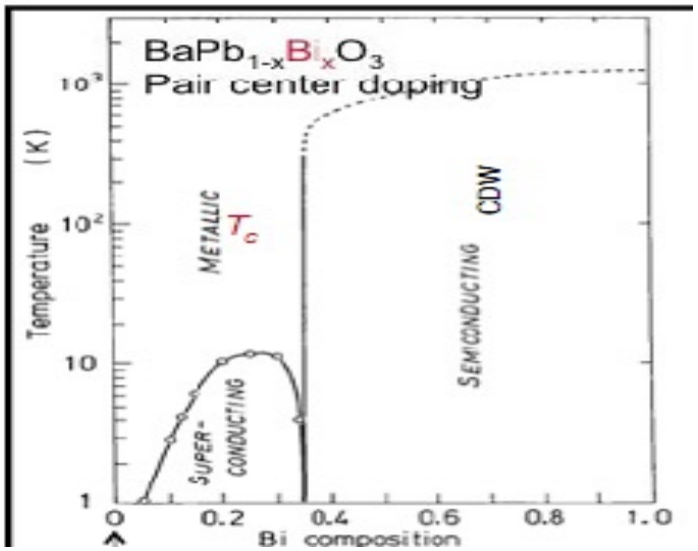


(c) Distorted structure

$(sp)^0$ Bi5+

$Bi4+(sp)^1$





$(sp)^0$

$(sp)^1$

ELSEVIER
Current Applied Physics 2 (2002) 425–430
www.elsevier.com/locate/cap

The superconducting bismuth-based mixed oxides ☆

E.V. Antipov [a,*], N.R. Khasanova [a], J.S. Pshirkov [a], S.N. Putilin [a], C. Bougerol [b], O.I. Lebedev [c], G. Van Tendeloo [c], A.N. Baranov [d], Y.W. Park [d]

Correlation-Enhanced Electron-Phonon Coupling: Applications of *GW* and Screened Hybrid Functional to Bismuthates, Chloronitrides, and Other High-T_c Superconductors

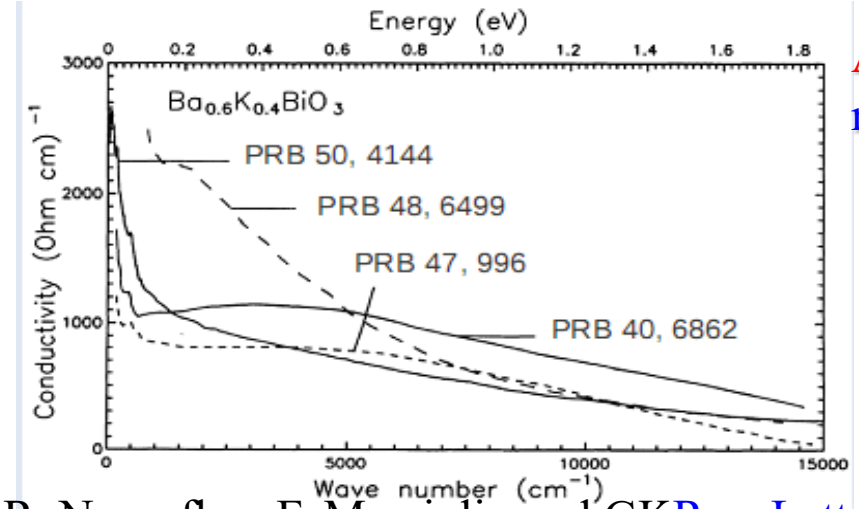
Z. P. Yin,* A. Kutepov, and G. Kotliar

Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, United States

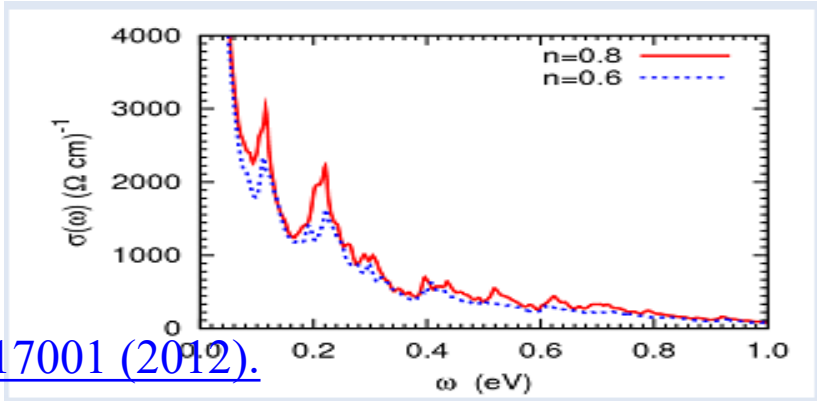
(Received 26 September 2012; revised manuscript received 7 March 2013; published 30 May 2013)

We show that the electron-phonon coupling (EPC) in many materials can be significantly underestimated by the standard density-functional theory (DFT) in the local-density approximation (LDA) due to large nonlocal correlation effects. We present a simple yet efficient methodology to evaluate the realistic EPC, going beyond the LDA by using more advanced and accurate *GW* and screened-hybrid-functional DFT approaches. The corrections that we propose explain the extraordinarily high superconducting temperatures that are observed in two distinct classes of compounds—the bismuthates and the transition-metal chloronitrides—thus solving a 30-year-old puzzle. Our work calls for the critical reevaluation of the EPC of certain phonon modes in many other materials, such as cuprates and iron-based superconductors. The proposed methodology can be used to design new correlation-enhanced high-temperature superconductors and other functional materials that involve electron-phonon interaction.

Our proposal: the correlation enhancement of λ relative to its LDA estimate is responsible for superconductvity in BaKBiO3 (λ ~ .1) , Occurs in many other systems close to an insulating state. This is what charcaterizes the "Other High Temperature superconductors". HfNCl, Borocarbides, Bucky Balls.

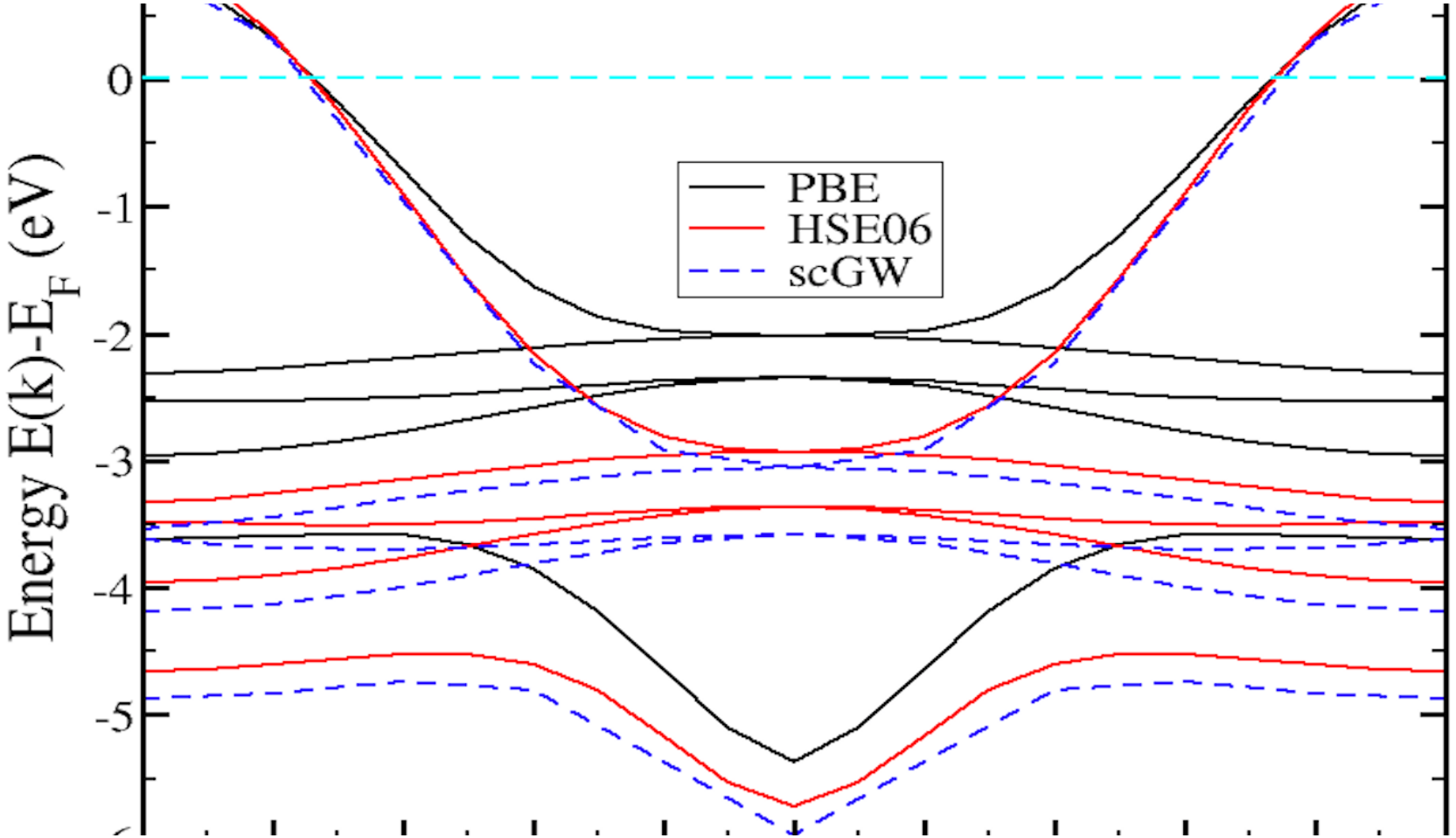


Anomalous optical conductivity in the metallic region can be understood within DMFT λ ~ .1 .



R. Nourafkan F. Marsiglio and GK Rev. Lett. 109, 017001 (2012).

BaKBiO3 qscGW vs HSE with tuned hybrid parameters to fit the qscGW

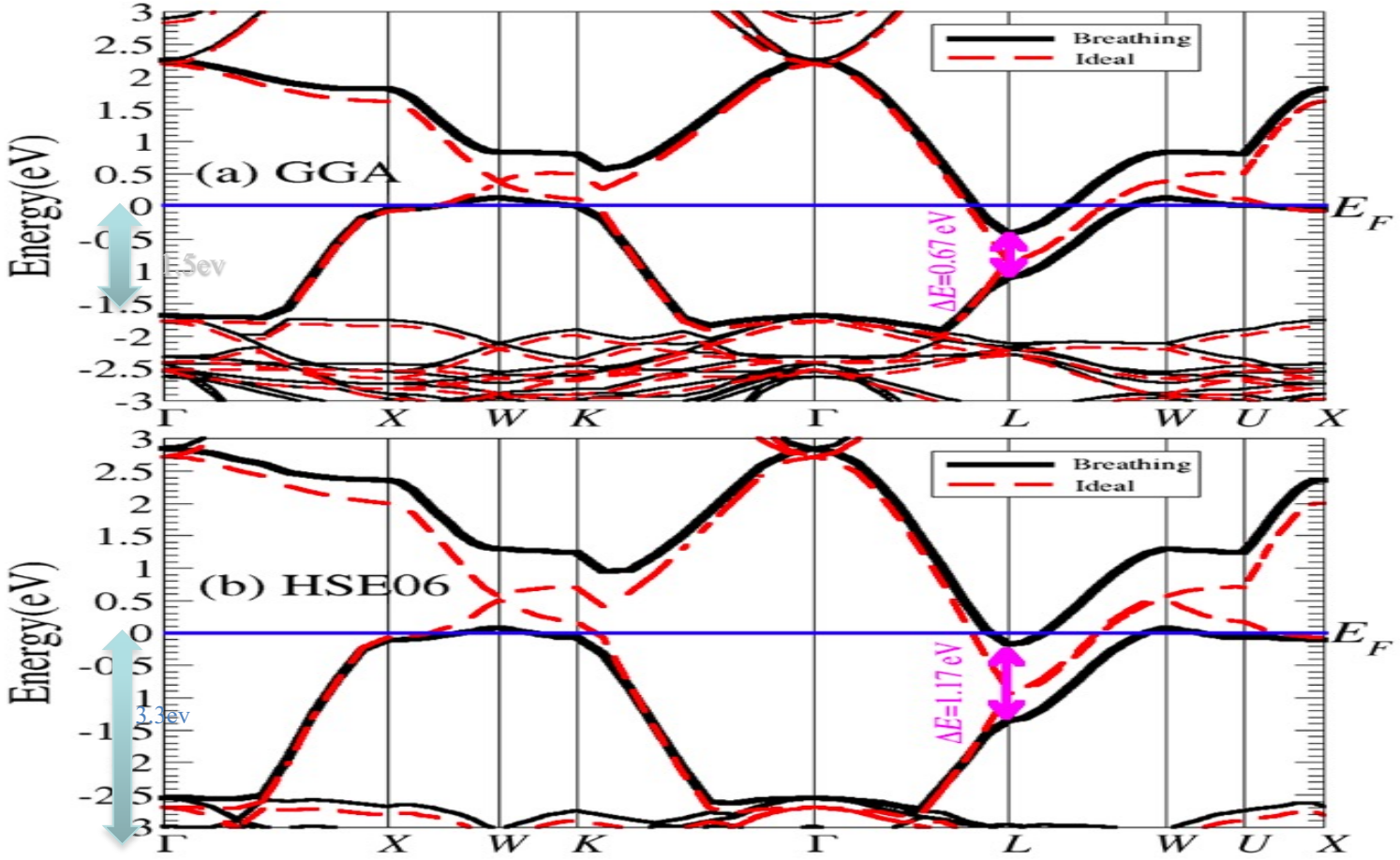


PHYSICAL REVIEW X 3, 021011 (2013)

Correlation-Enhanced Electron-Phonon Coupling: Applications of *GW* and Screened Hybrid Functional to Bismuthates, Chloronitrides, and Other High-T_c Superconductors

Z. P. Yin,* A. Kutepov, and G. Kotliar

Obsrvation of dynamic correlation enhanced bandwidth and electron phonon coupling



epl A Letters Journal Exploring the Frontiers of Physics

January 2013

EPL, **101** (2013) 27002
doi: 10.1209/0295-5075/101/27002

www.epljournal.org

Rational material design of mixed-valent high-T_c superconductors

Z. P. Yin and G. Kotliar

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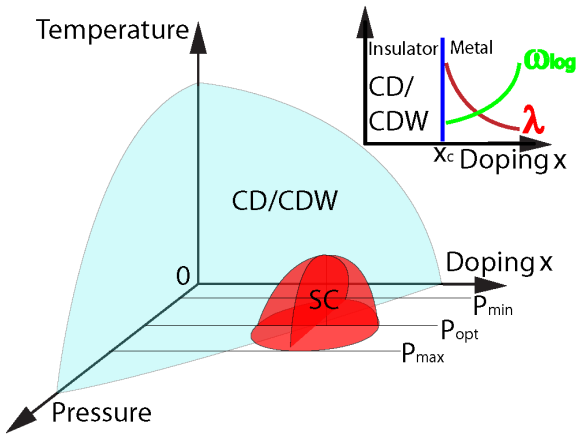
Abstract – We design, from first principles calculations, a novel family of thallium halide-based compounds as candidates for new high temperature superconductors, whose superconductivity is mediated by the recently proposed mechanism of non-local correlation-enhanced strong electron-phonon coupling. Two prototype compounds namely $CsTlF_3$ and $CsTlCl_3$ are studied with various hole doping levels and volumes. The critical superconducting temperature T_c are predicted to be about 30 K and 20 K with ∼0.35/f.u. hole doping and require only modest pressures (∼5 and ∼2 GPa), respectively. Our procedure of designing this class of superconductors is quite general and can be used to search for other "other high temperature superconductors".

To check the energetic stability, we consider here

The materials are not in the ICSD database
The parent compound should be easy to make
It should be hard to dope



currently existing compound Cs_3TlF_6 and a
thesis reaction: $3CsF+TlF_3 \rightarrow Cs_3TlF_6+Q$.
actually absorbs about 1.7 eV energy per
(164 kJ/mol) according to our DFT-GGA
Therefore, $CsTlF_3$ is more energetically favored than the existing Cs_3TlF_6 compound.

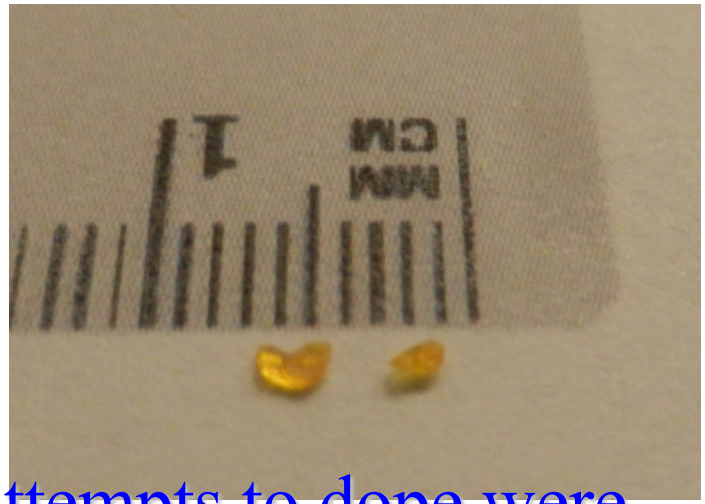
Synthesis and properties of charge-ordered thallium halide perovskites, CsTl1+0.5Tl3+0.5X3 (X = F, Cl)- theoretical precursors for superconductivity?

Maria Retuerto , Thomas J Emge , Joke Hadermann , Peter W. Stephens , Man-Rong Li , Zhiping P. Yin , Mark C. Croft , Alexander Ignatov , Si-Jia Zhang , Zhen Yuan , Changqing Jin , Jack W. Simonson , Meigan C. Aronson , Athena Pan , Dimitri N. Basov , Gabriel Kotliar , and Martha Greenblatt

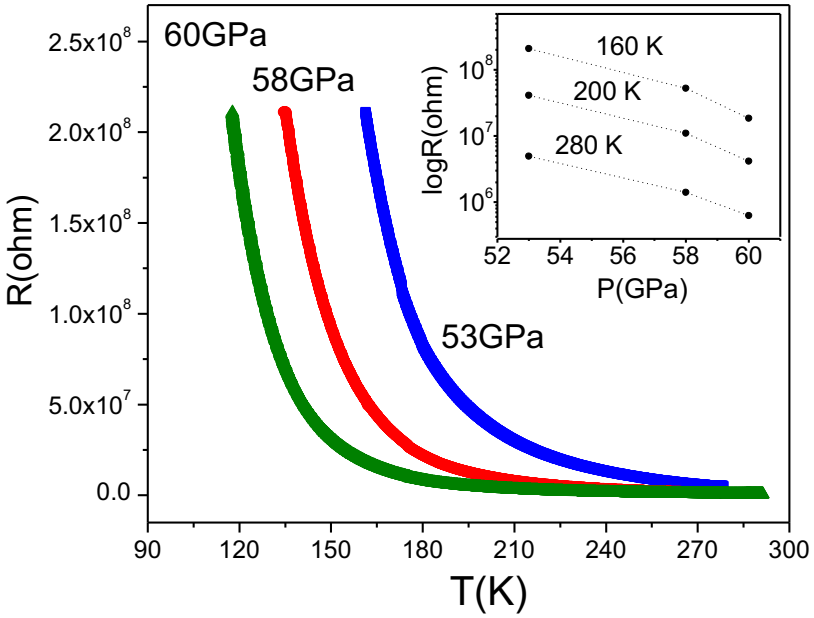
***Chemistry of Materials* 25** (20), 4071 (2013).

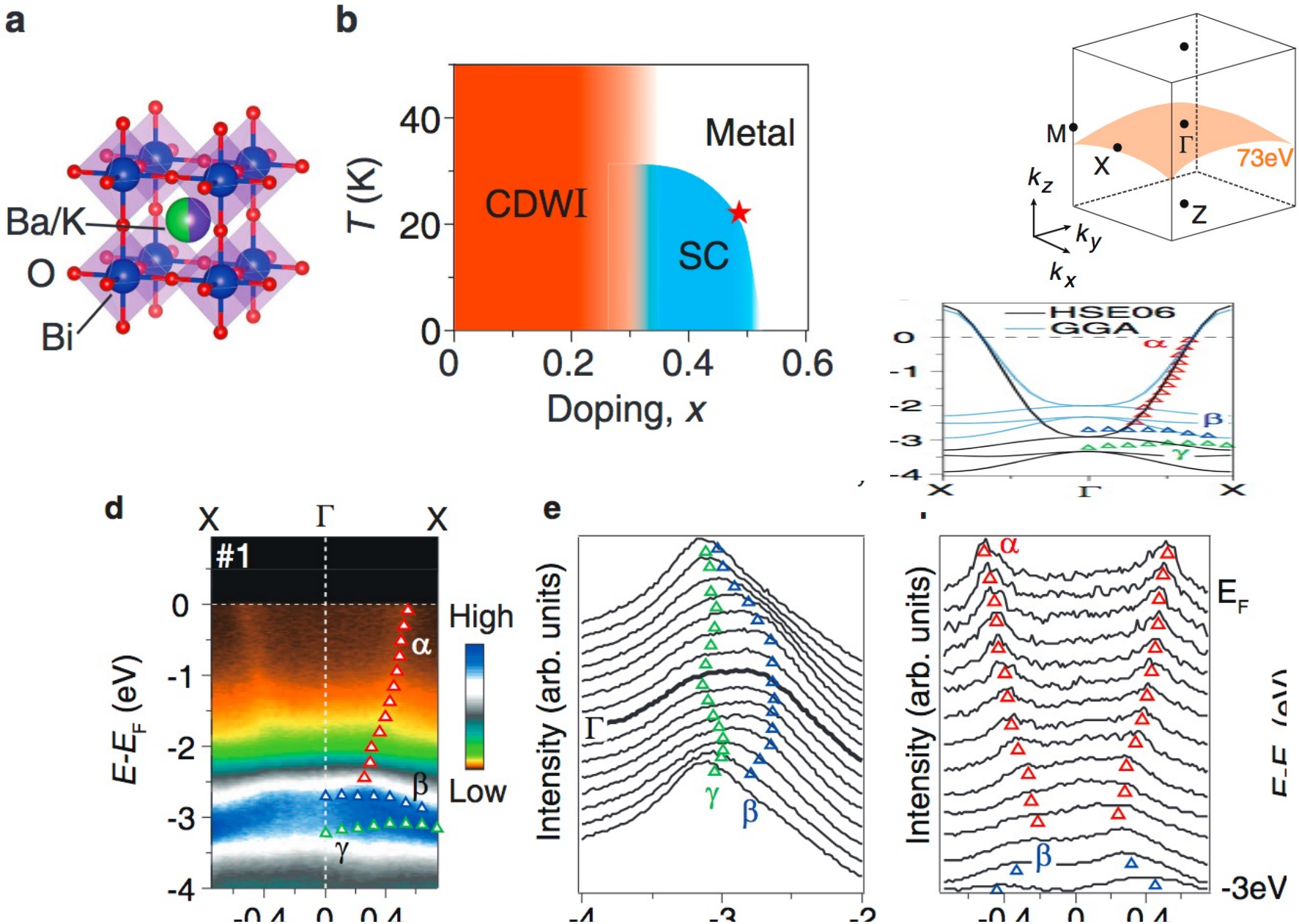
Two phases
One tetragonal the other cubic

Charge ordered mixed valent
Insulator, value of gap~ 2 ev
correctly predicted
by the theory.



Attempts to dope were unsuccessful so far…
Good topic for discussion!





Unveiling the superconducting mechanism of $Ba_{0.51}K_{0.49}BiO_3$

C. H. P. Wen,[1] H. C. Xu,[1,*] Q. Yao,[1] R. Peng,[1] X. H. Niu,[1] Q. Y. Chen,[2] Z. T. Liu,[3,4] D. W. Shen,[3,4] Q. Song,[1] X. Lou,[1] Y. F. Fang,[1] X. S. Liu,[1] Y. H. Song,[1] Y. J. Jiao,[5,6] T. F. Duan,[5,6] H. H. Wen,[5,6] P. Dudin,[7] G. Kotliar,[8] Z. P. Yin,[9,*] and D. L. Feng[1,6,*]

How can theory help find new materials and why correlations matter.

- Workflow. Step 1. Set up the question. An idea we want to test. Heuristics. Intuition. Simple model calculations.
- Step 1. Connecting structure to property. What would an hypothetical compound do. Requires methods that go beyond LDA. Static correlation, GW++. Dynamic correlations LDA+DMFT. Decide how interesting target is.
- Step 2. Finding the structure for an hypothetical composition. DFT main tool. Use correlation methods as a post-processing tool.
- Evaluating the probability for the compound to form. Build on existing material databases. Materials Project. AFLOWlib OQMD Open Quantum Materials Database. Mostly DFT Incorporate empirical corrections. Apply correlations in post proccessing.

We estimate the error of existing methods (GGA, GGA+corrections using a statistical approach. Several examples

- R. Adler C.J. Kang C.H Yee and GK 2019 *Rep. Prog. Phys.* **82** 012504

KEY ISSUES REVIEW

Correlated materials design: prospects and challenges

Ran Adler[1], Chang-Jong Kang[1], Chuck-Hou Yee[1] and Gabriel Kotliar[1,2]

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Reports on Progress in Physics, Volume 82, Number 1

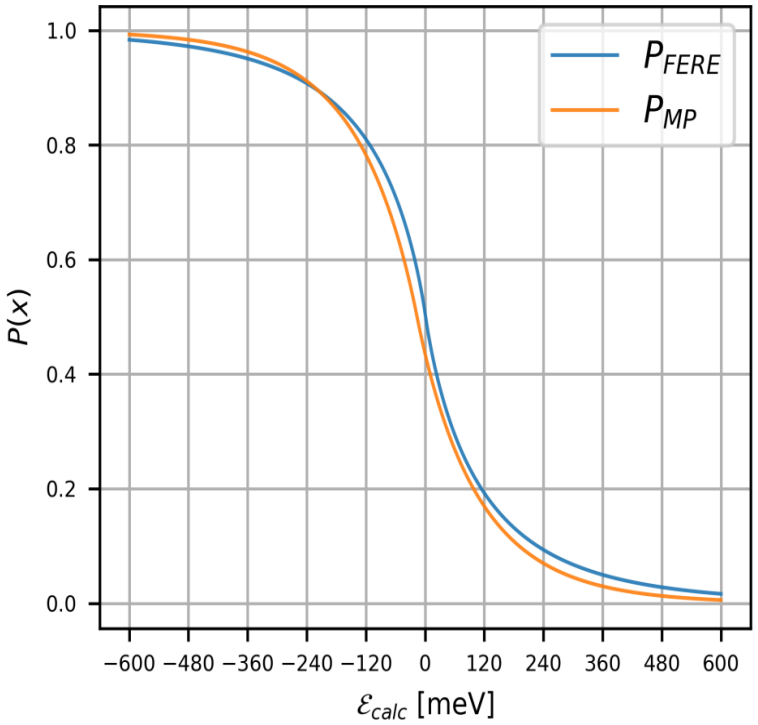

FIG. 14. $\mathcal{P}(\mathcal{E}_{calc})$, probability for a compound to exist, given the computed formation energy $\mathcal{E}_{calc}$ with the two correction schemes summarized in Table III.

Material	Determinant reaction	$\Delta H_{\text{Materials proj.}}$ (eV/atom)	$\mathcal{P}(x)$
$La_2CuS_2O_2$	$La_2SO_2 + CuS \rightarrow La_2CuS_2O_2$	0.232	0.06
La_2CuSO_3	$3\,La_2SO_2 + 4\,Cu + La_2SO_6 \rightarrow 4\,La_2CuSO_3$	0.324	0.02
$Hg(CaS)_2CuO_2$	$HgO + 2\,CaS + CuO \rightarrow Hg(CaS)_2CuO_2$	0.170	0.09
$CsTlCl_3$	$TlCl + Cs_2TlCl_5 \rightarrow 2\,CsTlCl_3$	0.003	0.41
$CaFeAs_2$	$CaAs + FeAs \rightarrow CaFeAs_2$	0.013	0.37
BaCoSO	$4\,Co + 3\,BaS + BaSO_4 \rightarrow 4\,BaCoSO$	0.102	0.17

BROOKHAVEN NATIONAL LABORATORY

Recent Progress

Correlation-Enhanced Electron-Phonon Coupling: Applications of GW and Screened Hybrid Functional to Bismuthates, Chloronitrides, and Other High-T_c Superconductors

Z. P. Yin, A. Kutepov, and G. Kotliar
Phys. Rev. X **3**, 021011 – Published 30 May 2013

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Phys. Rev. Lett. **121**, 117002 – Published 13 September 2018

Electron-Phonon Coupling from *Ab Initio* Linear-Response Theory within the GW Method: Correlation-Enhanced Interactions and Superconductivity in $Ba_{1-x}K_xBiO_3$

Zhenglu Li, Gabriel Antonius, Meng Wu, Felipe H. da Jornada, and Steven G. Louie
Phys. Rev. Lett. **122**, 186402 – Published 10 May 2019