Towards First Principles Theories of Strongly Correlated Materials :What is Currently Possible and What Needs to be Done to Make it Happen ?

Please Give me Suggestions!!

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K. Haule (Rutgers) S. Savrasov (U.C Davis)

N. Zein (Kurchatov) A. Kutepov (Rutgers/UCDavis)

From Basic Concepts to Real Materials

Towards Material Design Using Strongly Correlated Electron Systems

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Scientific Advisors: Jim W. Allen, Zachary Fisk, Andrew J. Millis, Nicola Spaldin

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Constrained dft
P.Dederichs, S. Blugel, R. Zeller and H. Akai, Phys. Rev. Lett. **53**, 2512 (1984)

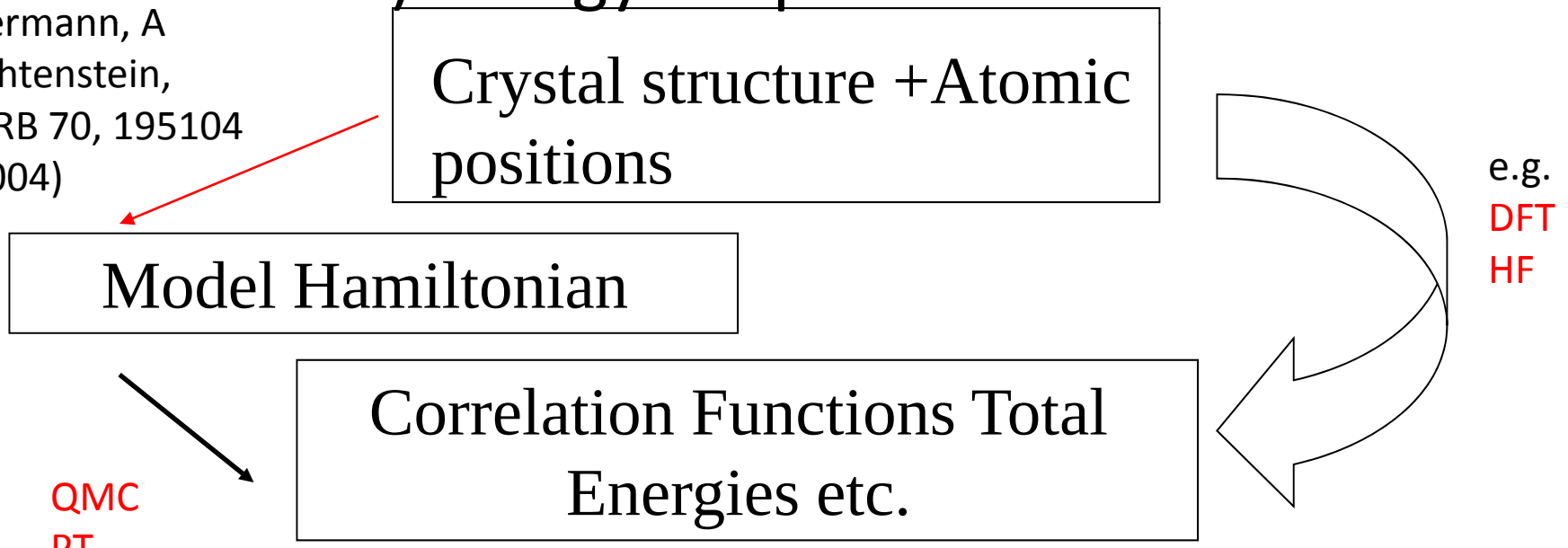
Constrained RPA
Aryasetiawan Imada, A Georges, G Kotliar, S Biermann, A Lichtenstein, PRB 70, 195104 (2004)

Historical PerspectiveTwo roads to the electronicstructure of strongly correlated materials, which one to chose ?

a) direct vs indirect

b) ab initio vs semi-empirical

c) energy vs spectra



e.g. Early work: M. M. Steiner, R. C. Albers, and L. J. Sham. Phys. Rev. B, 45:13272, 1992.
Hybersten et. al. Phys. Rev. B 39, 9028 - 9041 (1989)

DMFT for model Hamiltonians Hubbard model

$$\sum_{<i,j>,\sigma} (t_{ij} - \mu\delta_{ij})(c^{\dagger}_{i\sigma}c_{j\sigma} + c^{\dagger}_{j\sigma}c_{i\sigma}) + U\sum_{i} n_{i\uparrow}n_{i\downarrow}$$

Baym Kadanoff Functional, sum over two particle irreducible graphs.

$$\Gamma[G_{ii}, M] = -TrLn[i\omega + \mu - t_{ij} - M] - Tr[MG] + \Phi[G]$$

$$\Phi_{dmft}[G] \sim \Phi[G_{ii}, G_{ij \neq o}] = \Sigma_i \Phi_{atom}[G_{ii}]$$

Paradigm Shift: partial selection of graphs → sum ALL LOCAL graphs

Summation is done by considering an atom in a bath [Quantum Impurity Model]

$$G_{ii} = \sum_k \frac{1}{[i\omega + \mu - t(k) - M_{ii}]} \qquad M_{ii} = \frac{\delta}{\delta Gii}\Phi_{atom}[Gii]$$

Review : A.Georges, G. Kotliar ., W. Krauth and M. J. Rozenberg, R. M.P. 68, 13 (1996).
Longer Ranges: Cluster Dynamical Mean Field Theories.

LDA+DMFT V. Anisimov, A. Poteryaev, M. Korotin, A. Anokhin and G. Kotliar, J. Phys. Cond. Mat. 35, 7359 (1997)

- The light, SP (or SPD) electrons are extended, well described by LDA .The heavy, D (or F) electrons are localized treat by DMFT.
- LDA Kohn Sham Hamiltonian already contains an average interaction of the heavy electrons, subtract this out by shifting the heavy level (double counting term)

❑ The U matrix can be estimated from first principles of viewed as parameters. Solve resulting model using DMFT.

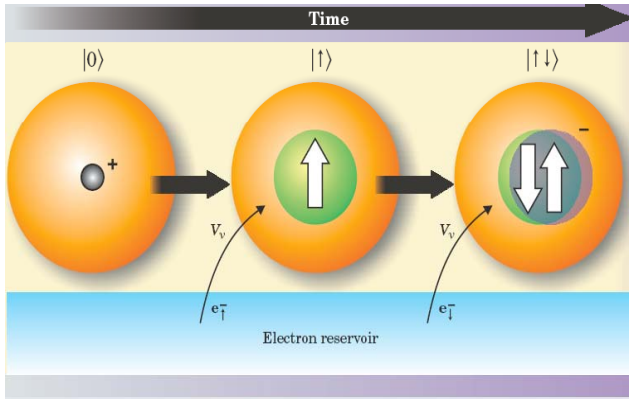
❑ Brings chemistry [Local configuration interaction in a bath] — and Band Physics [Electrons in a frequency dependent potential] together.

See also LDA++. A Lichtenstein and M. Katsnelson PRB 57, 6884 (1988).

LDA+DMFT. V. Anisimov, A. Poteryaev, M. Korotin, A. Anokhin and G. Kotliar, J. Phys. Cond. Mat. 35, 7359 (1997).

$$U \longrightarrow U_{abcd}$$

$$\Sigma \longrightarrow \begin{pmatrix} 0 & 0 \\ 0 & \Sigma_{ff} \end{pmatrix}$$



$$t(k) \longrightarrow \begin{pmatrix} H[k]_{spd,sps} & H[k]_{spd,f} \\ H[k]_{f,spd} & H[k]_{ff} - Edc \end{pmatrix}$$

$$|0>, |\uparrow>, |\downarrow>, |\uparrow\downarrow> \longrightarrow |LSJM_J\gamma...>$$

Pros

- Freed Model Hamiltonian treatments from many parameters.
- Brought DMFT to the attention of the electronic stuture community.
- Serious improvement over LDA+U
- Triggered numerous collaborations between electronic structure groups and many body theorists
- Implementation for Spectra of LaSrTiO3 including Ti and ligands

Remaining Issues

- H[k] is not affected by correlations. No feedback on the density.
- Parameters (i.e. U)

- How to compute total Energies ?
- Better Impurity Solvers (IPT)
- More accurate basis sets H[k] LMTO-ASA
  - Foundation for the method.

Conceptual Underpinning : Chitra and Kotliar Phys. Rev. B 62, 12715 (2000)

and Phys. Rev.B (2001).

$$S = \int dx\psi^{+}(x)[\partial_\tau - \nabla^2 + V_{ext}(x)]\psi(x)$$
$$+\frac{1}{2}\int dxdx'\psi^{+}(x)\psi^{+}(x')v_C(x-x')\psi(x)\psi(x')$$

$$S = \int dx\psi^{+}(x)[\partial_\tau - \nabla^2 + V_{ext}(x)]\psi(x)$$
$$+\frac{1}{2}\int\int \phi(x)V_C^{-1}(x,x')\phi(x') + \int i\phi(x)\psi^{\dagger}(x)\psi(x)$$

$$G = -<\psi(x')\ \psi^{\dagger}(x)>$$

$$<\phi(x')\phi(x)> - <\phi(x')><\phi(x)> = W$$

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

C-.O.Almbladh, U.von Barth and R.vanLeeuwen Int.J.Mod.Phys. B**13**, 535 (1999)

Introduce Notion of Local Greens functions, Wloc, Gloc G=Gloc+Gnonloc .

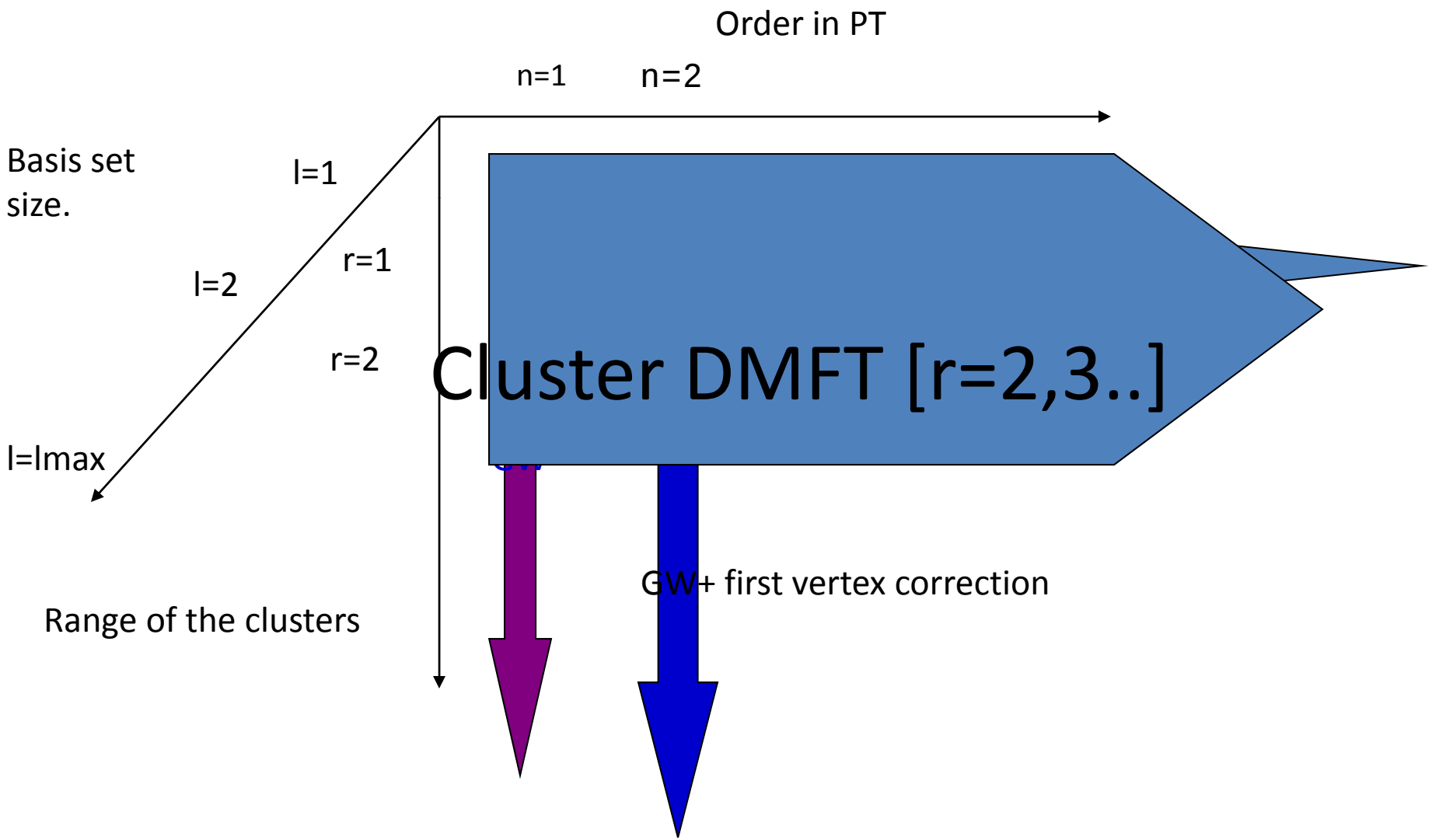
Ex. Ir>=|R, ρ> Gloc=G(R ρ, R ρ') $\delta_{R,R'}$

Φ Sum of 2PI graphs

$$\Phi[G,W] \approx \Phi_{EDMFT}[G_{loc}, W_{loc}, G_{nonloc} = 0, W_{nonloc} = 0]$$

One can also view as an approximation to an exact Spectral Density Functional of Gloc and Wloc . One can do further PT in Gloc Gnonloc by keeping perturbative theory in them. Φ

Space of all dressed diagrams for Sigma and Pi

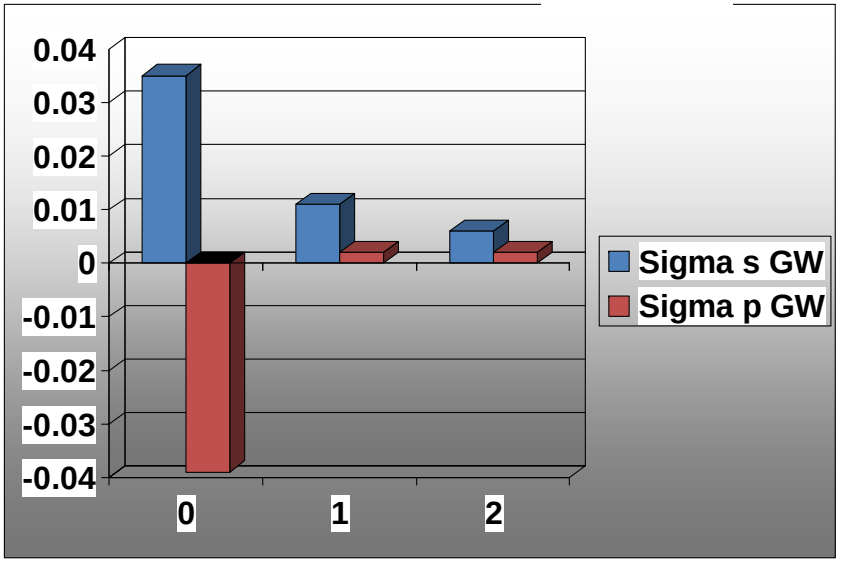


Proof of Principle Implementation

Full implementation in the context of a one orbital lattice model.
P Sun and G. Kotliar Phys. Rev. B 66, 85120 (2002). DMFT+non lovsl GW corrections
P.Sun and GK PRL (2004): Test various levels of self consistency in Gnonloc Pinonloc

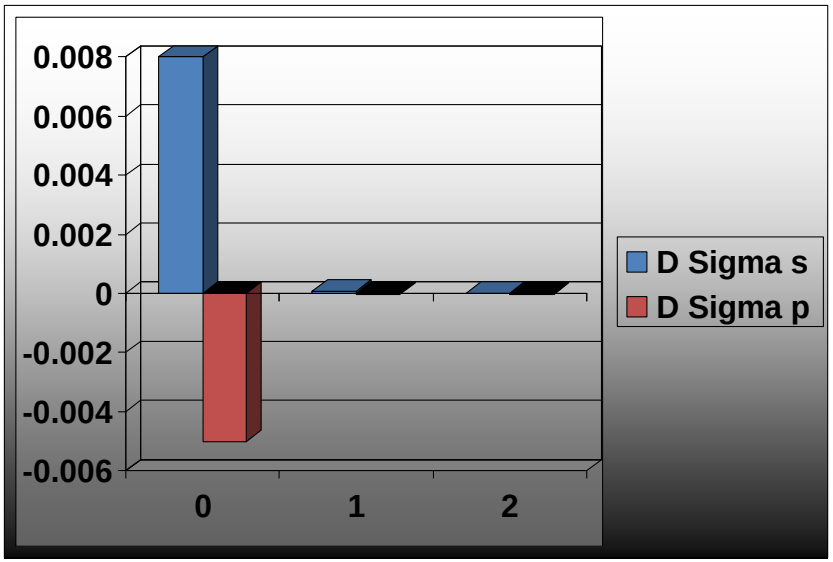
Test notion of locality (in LMTO basis) set in various materials.
N. Zeyn S. Savrasov and G. Kotliar PRL 96, 226403, (2006)

GW self energy for Si



Coordination Sphere

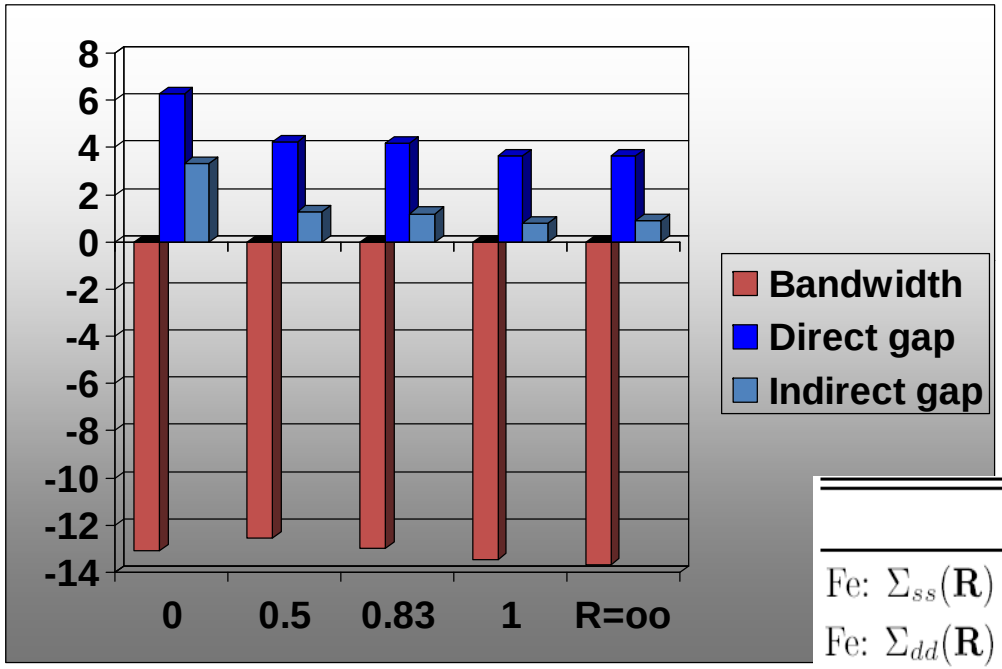
Beyond GW



Coordination Sphere

Zeyn and Antropov (local GW) Phys. Rev. Lett. **89, 126402 (2002)**

N Zeyn S. Savrasov and G. K PRL 96, 226403 (2006)



	$\mathbf{R}=0$	$\mathbf{R}_1$	$\mathbf{R}_2$	$\mathbf{R}_3$
Fe: $\Sigma_{ss}(\mathbf{R})$	0.70	0.35	0.16	
Fe: $\Sigma_{dd}(\mathbf{R})$	6.53	0.05	0.08	
Ni: $\Sigma_{ss}(\mathbf{R})$	-0.54	0.05	0.03	
Ni: $\Sigma_{dd}(\mathbf{R})$	7.34	0.38	-0.03	
Na: $\Sigma_{ss}(\mathbf{R})$	-1.36	0.52	0.30	0.05
Al: $\Sigma_{pp}(\mathbf{R})$	0.46	0.16	-0.08	
Si: $\Sigma_{ss}(\mathbf{R})$	0.95	0.30	0.14	0.03
Si: $\Sigma_{pp}(\mathbf{R})$	-1.06	0.05	-0.27	-0.03

Practical Route to Total Energies LDA+DMFT functional

$$\Gamma_{LDA+DMFT}[\rho(r)\ G_{ab}\ V_{KS}(r)\ \Sigma_{ab}]$$

$$-Tr\log[i\omega_n + \nabla^2/2 - V_{KS} - \chi^*_{\alpha R}(r)\Sigma_{\alpha\beta R}\chi_{\beta R}(r)] -$$

$$\int V_{KS}(r)\rho(r)dr - \sum_{i\omega_n} Tr\Sigma(i\omega_n)G(i\omega_n) +$$

$$\int V_{ext}(r)\rho(r)dr + \frac{1}{2}\int \frac{\rho(r)\rho(r')}{|r-r'|}drdr' + E_{xc}^{LDA}[\rho] +$$

$$\sum_R \Phi[G_{\alpha\beta R}] - \Phi_{DC}$$

Φ Sum of local 2PI graphs with local U matrix and local G

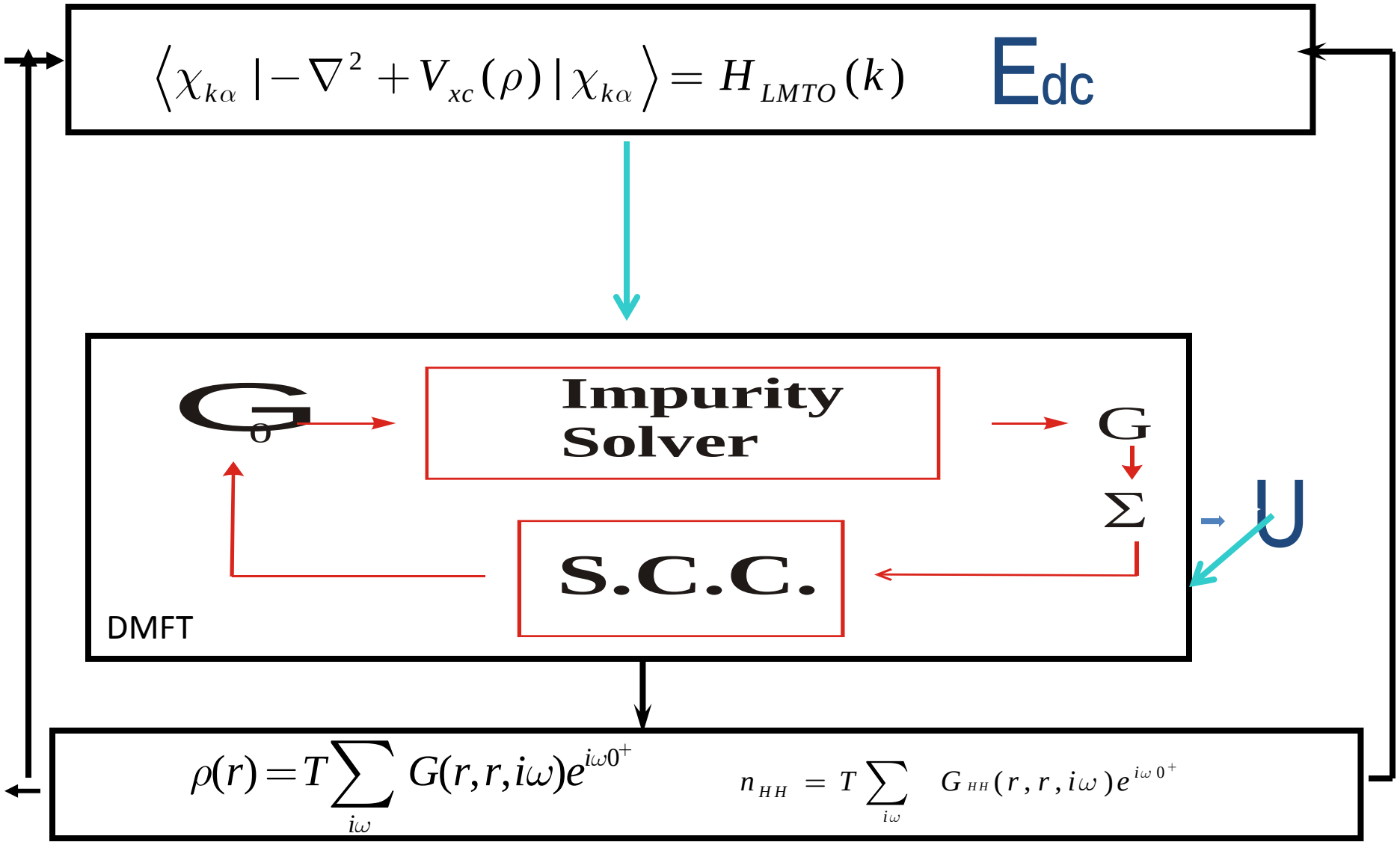
$$\Phi_{DC}[G] = Un(n-1)\frac{1}{2}$$

$$n = T\sum_{ai\omega}\left(G_{aa}(i\omega)e^{i0^+}\right)$$

Notice Explicit Dependence on : U , DC, and Projectors [Orbitals], and Independence of basis set.

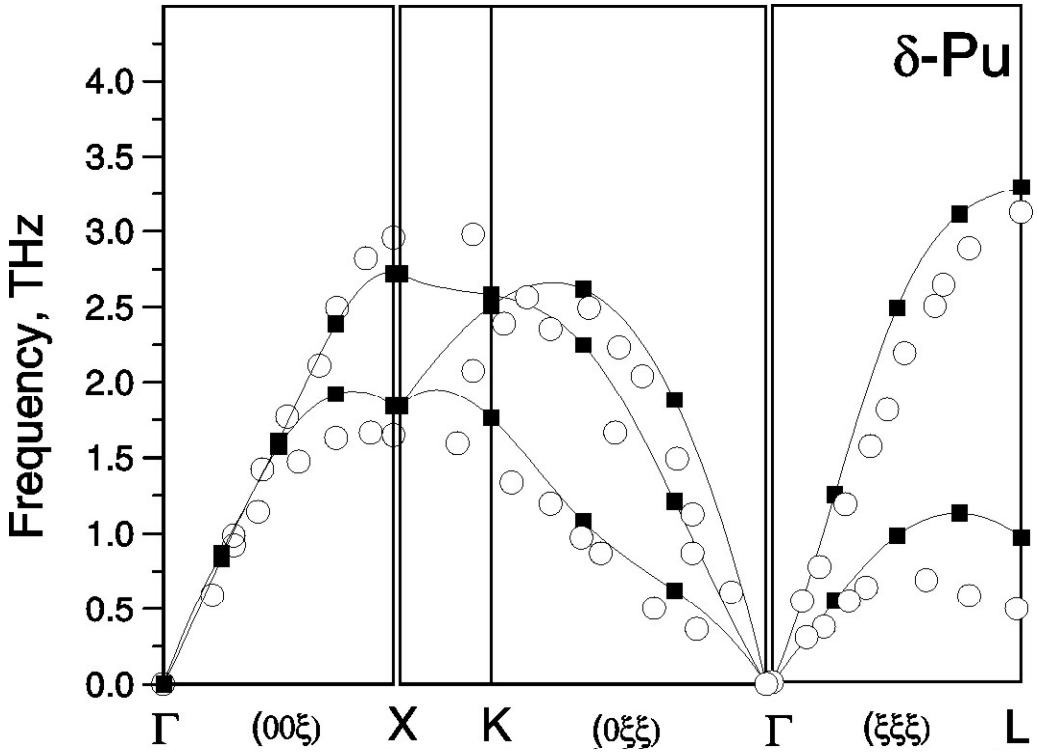
R. Chitra and G Kotliar Phys.Rev.B62:12715 (2000). S. Savrasov and G. Kotliar PRB Phys. Rev. B 69, 245101 (2004).

LDA+DMFT Self-Consistency loop



REVIEW : G. Kotliar S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, C.A. Marianetti, RMP 78, 865 (2006)

DMFT Phonons in fcc δ-Pu



	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)	C'(GPa)
Theory	34.56	33.03	26.81	3.88
Experiment	36.28	33.59	26.73	4.78

(Dai, Savrasov, Kotliar,Ledbetter, Migliori, Abrahams, Science, 9 May 2003)

(experiments from Wong et.al, Science, 22 August 2003)

Physical Picture of Plutonium : Non Magnetic Strongly Correlated Mixed Valent Metal.
Different Phases : Redistribution of Spectral Weight.
Total Energy and Spectra within the framework!

Remaining Issues

- Spectra: no multiplet structure due to solver limitations.
- Test quality and role of projectors / U's

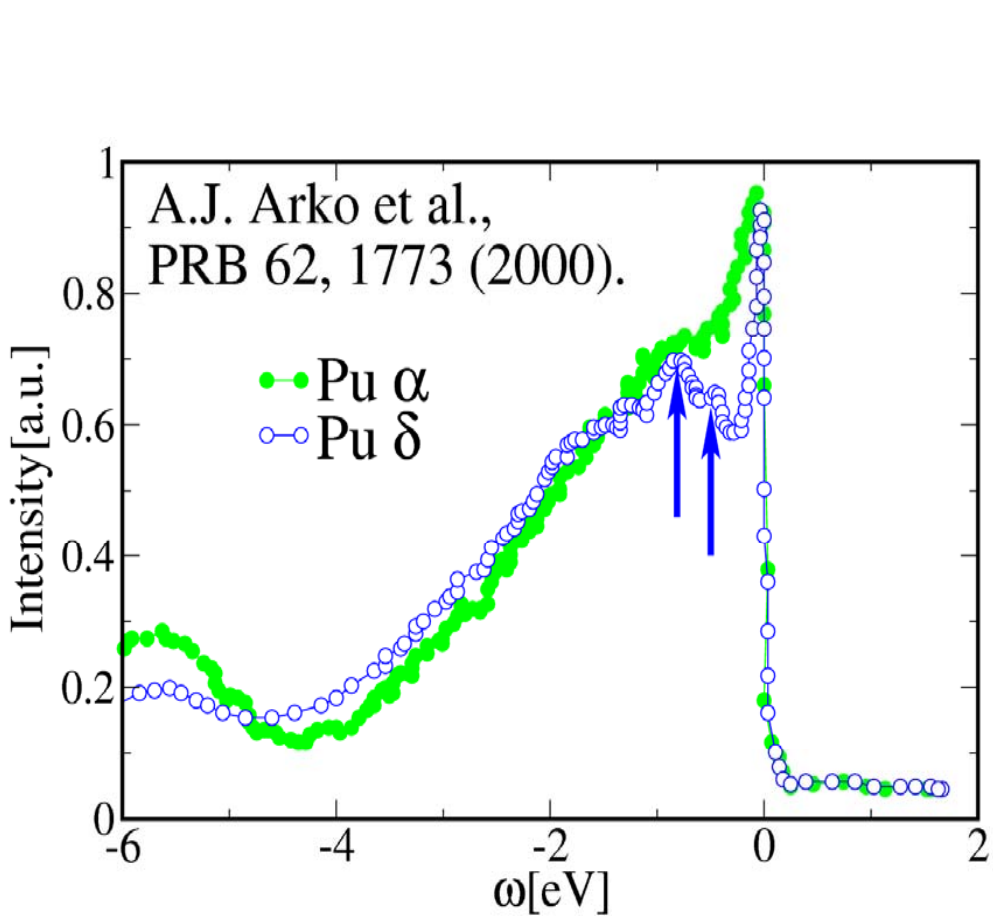
Issues Largely Resolved in the past few years.
Introduction of methods starting from the atomic limit CTQMC and vertex corrected NCA's
P. Werner et. al. PRL (2006) K.Haule Phys. Rev. B **75**, 155113 (2007)

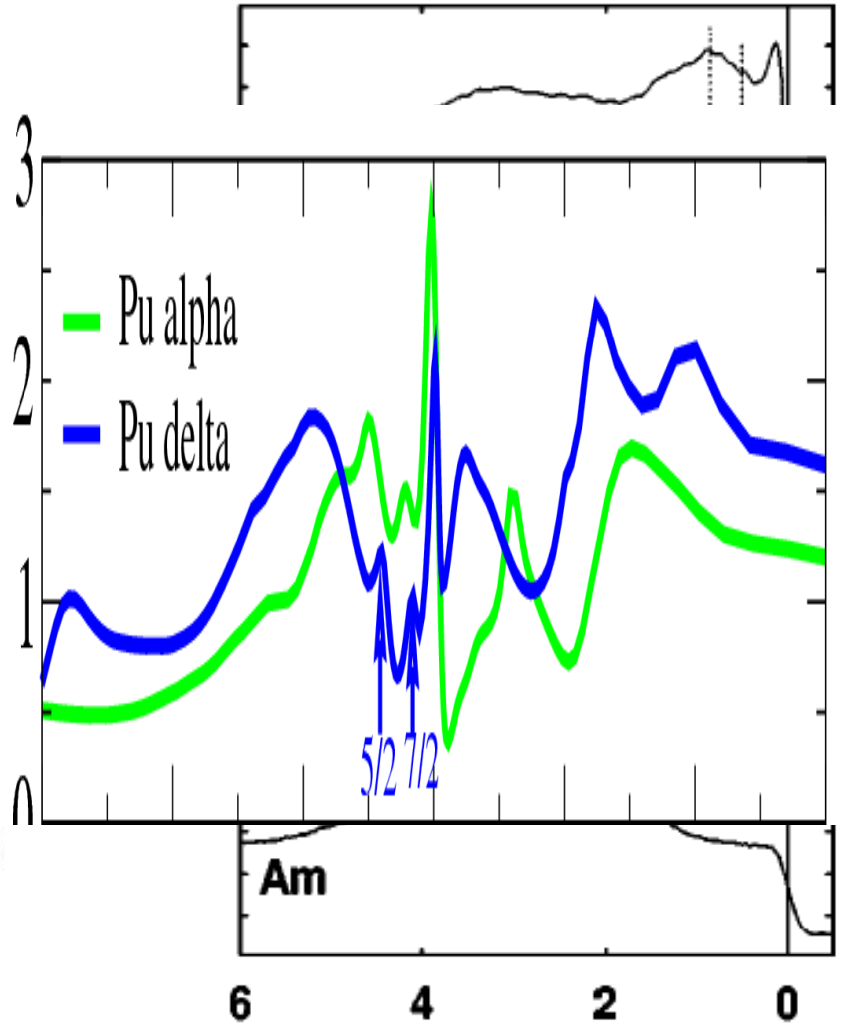
K. Haule, J. Kroha, and P. Wölfle, Phys. Rev. B **64**, 155111 (2001)

Tests orbital-sensitive LDA+DMFT results against experiments.

Photoemission

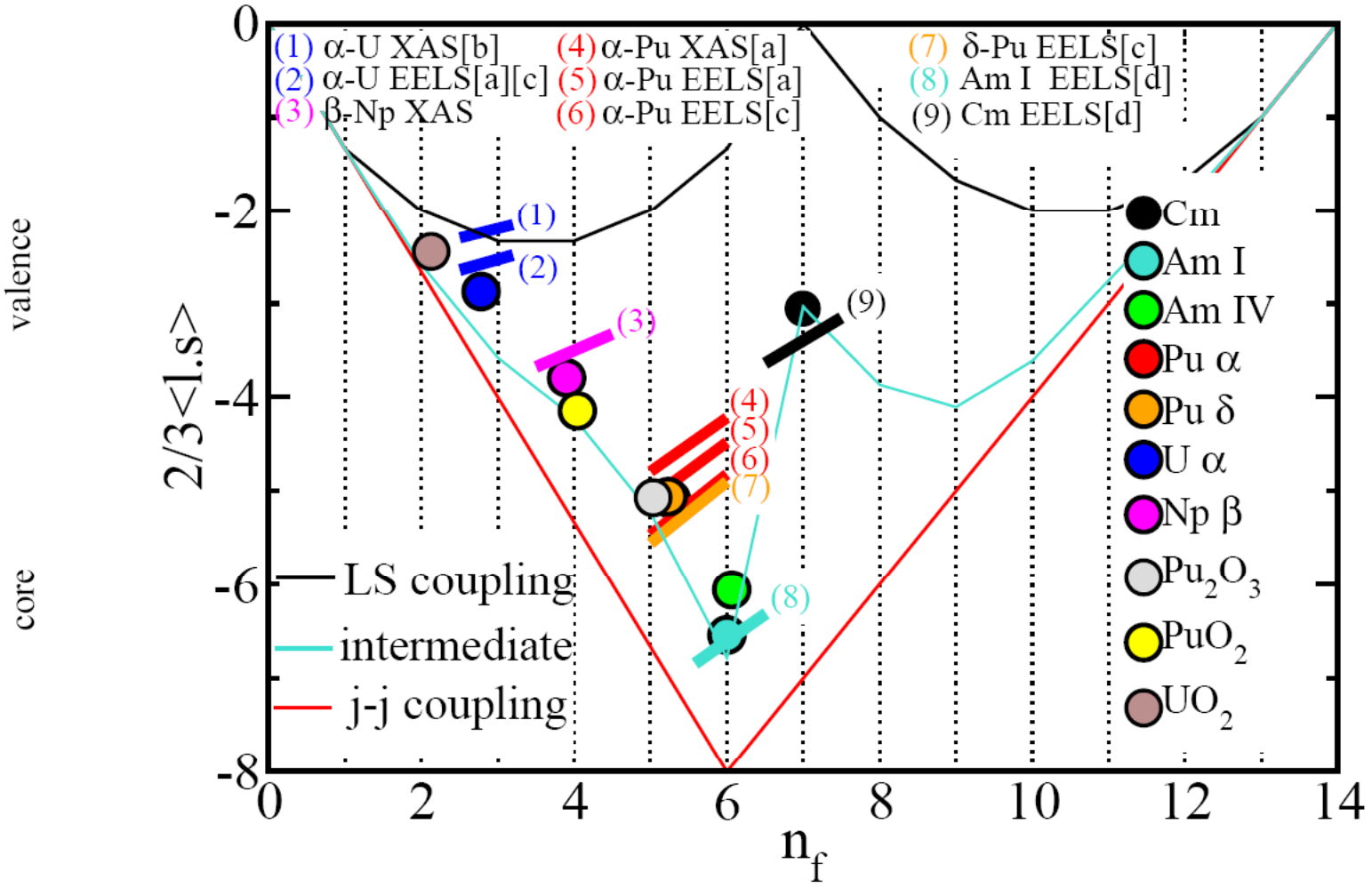
Havela et. al. Phys. Rev. B 68, 085101 (2003)

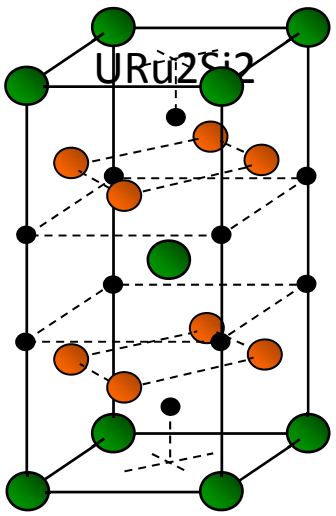




Finding the f occupancyTobin et. al. PRB 72, 085109 2005 K. Moore and G. VanDerLaan RMP (2009). Shim Haule and Kotliar Europhysics Lett (2009)

$$B = \frac{3}{5} - \frac{4}{15}\frac{1}{\langle n^h \rangle}\sum_{i \in 5f}\langle \mathbf{l}_i \cdot \mathbf{s}_i \rangle. \qquad B = \frac{I_{5/2}}{I_{5/2} + I_{3/2}}$$





A challenge to the electronic structure community ?

- U
- Ru
- Si