KITP 2010.02.8-12
Materials by Design

Downfolding the many-electron problem to a low-energy model

Ferdi Aryasetiawan
Chiba University, Japan

Collaborators:

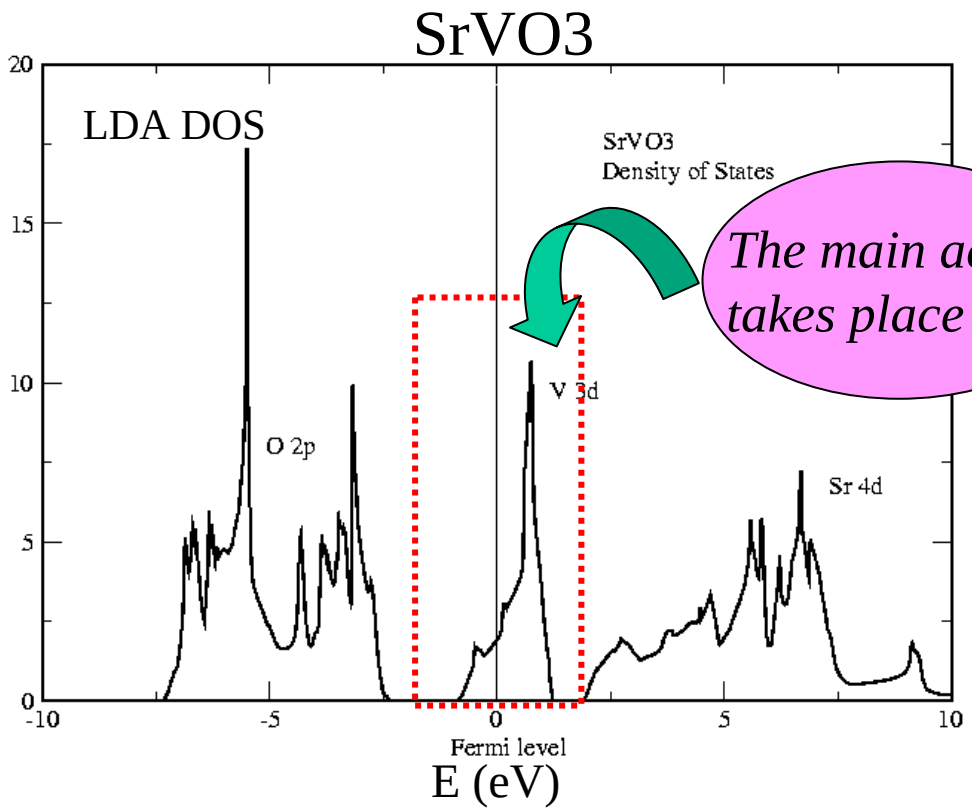
T Miyake (AIST, Japan),

J Tomczak (Rutgers), R Sakuma (Chiba),

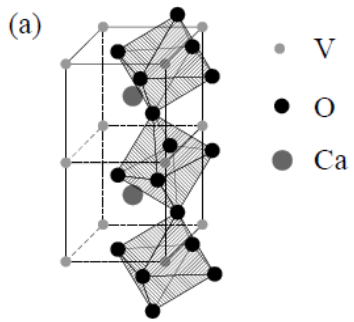
K Karlsson (Skovde, Sweden), O Jepsen (MPI Stuttgart),

S Biermann, A Georges (Ecole Polytechnique, France), M Imada (Tokyo)

Typical electronic structure of correlated materials: Partially filled narrow band (3d or 4f) crossing the Fermi level

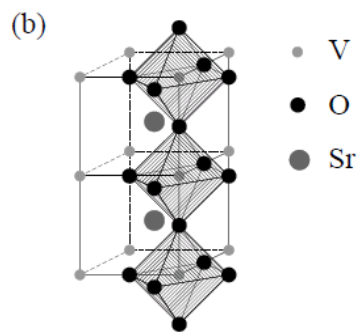


→many configurations close in energy
→strong correlations
→one-particle description can be problematic



$CaVO_3$

La/YTiO3

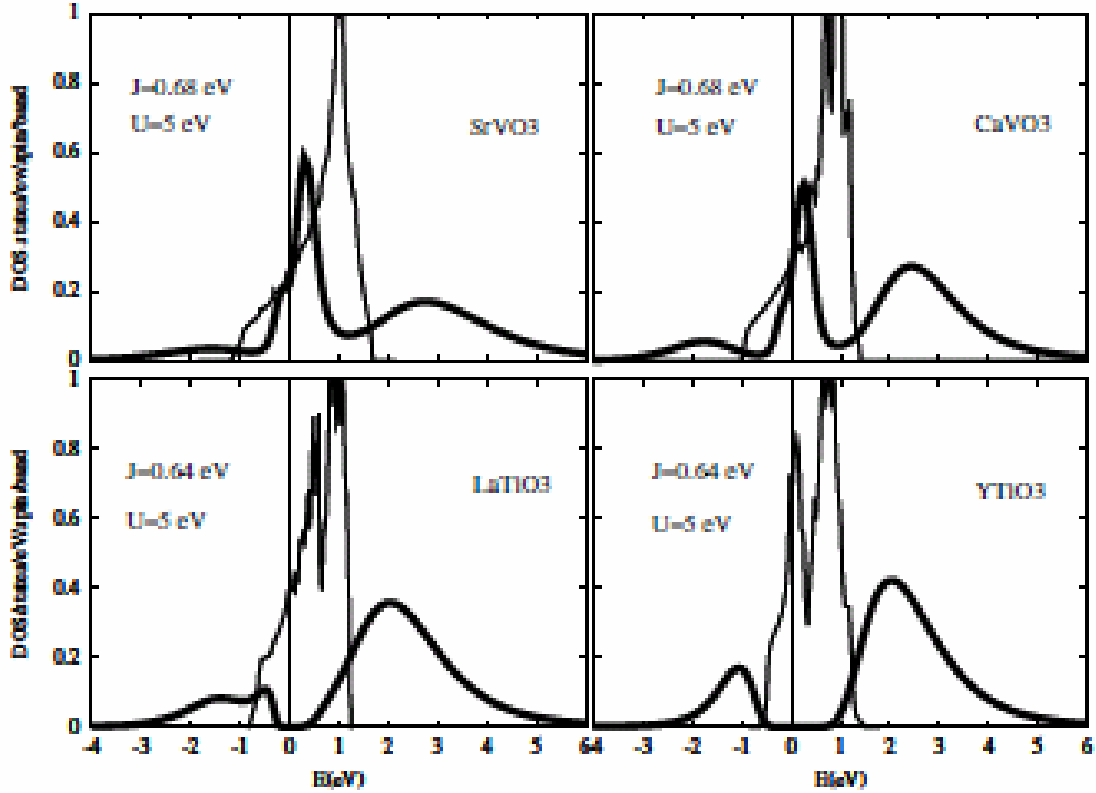


$SrVO_3$

Slight change of parameters can induce large change in materials properties. E.g., by slight distortion or pressure *the ratio of U/bandwidth* changes and the materials can undergo phase transitions (metal-insulator).
→competition between kinetic energy and U.

Experimentally
SrVO3 and CaVO3 are metals
LaTiO3 and YTiO3 are insulators

In LDA
These materials share very similar electronic structure and they are all metals.
LDA+U→all insulators



Correlated metals

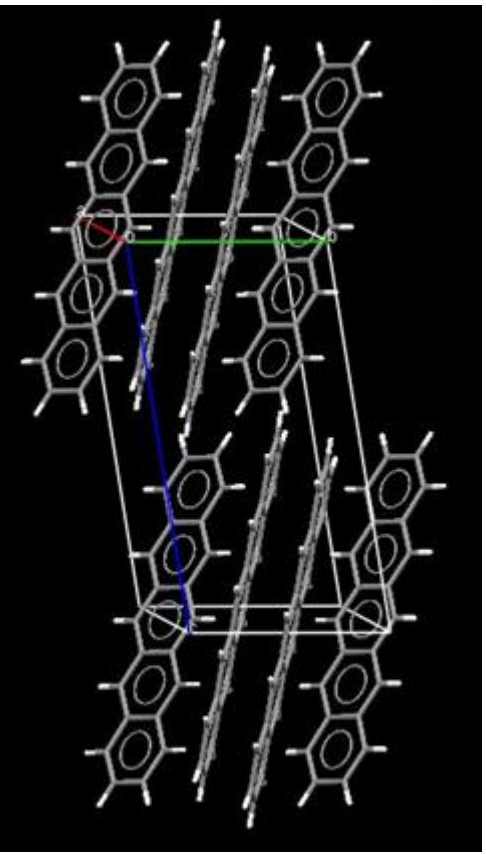
Insulators

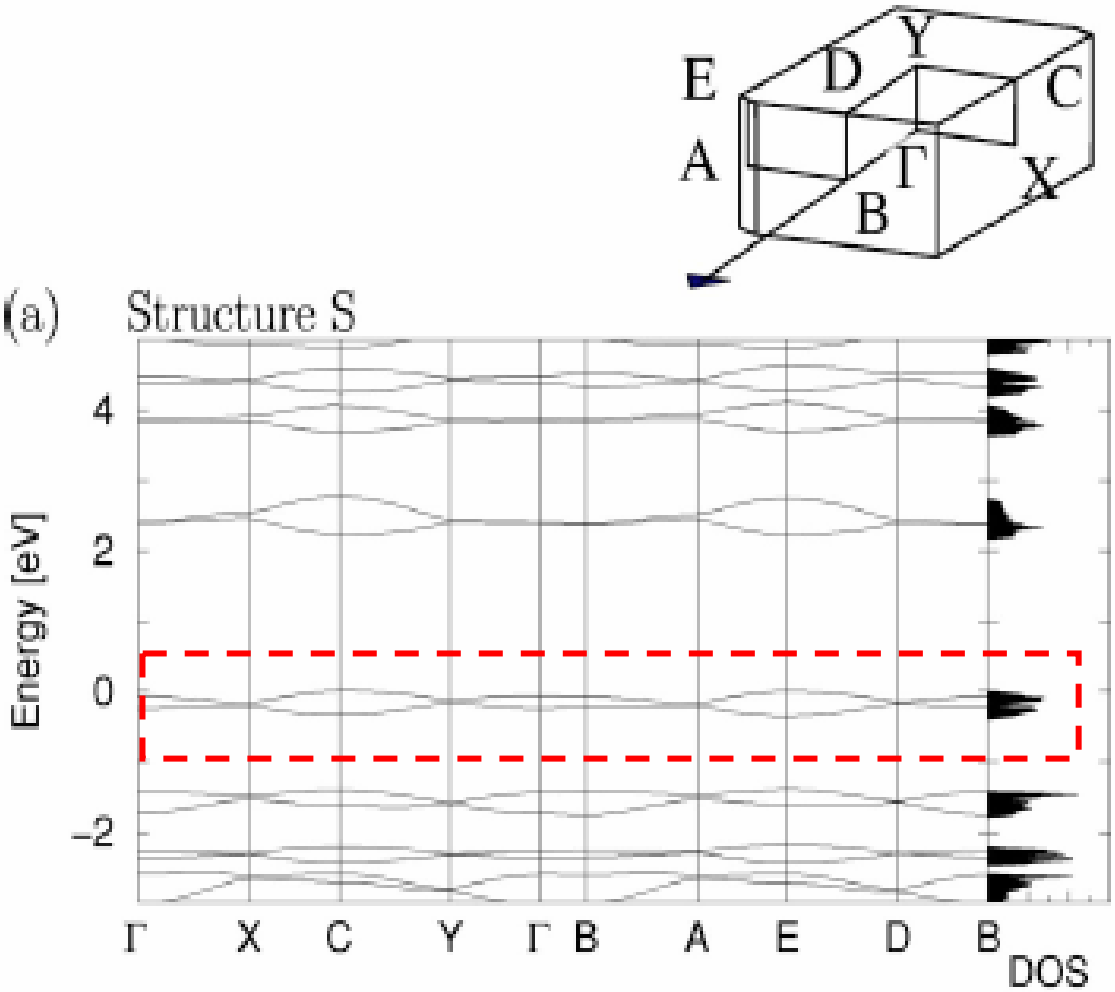
FIG. 3. DMFT spectral function at $T = 770$ K (thick line) and LDA DOS (thin line). $\mu \equiv 0$.

The importance of going beyond the one-particle theory

Pavarini, Biermann, Poteryaev, Lichtenstein, Georges, and Andersen, PRL 92, 176403 (2004)

Another example: Pentacene molecular crystal



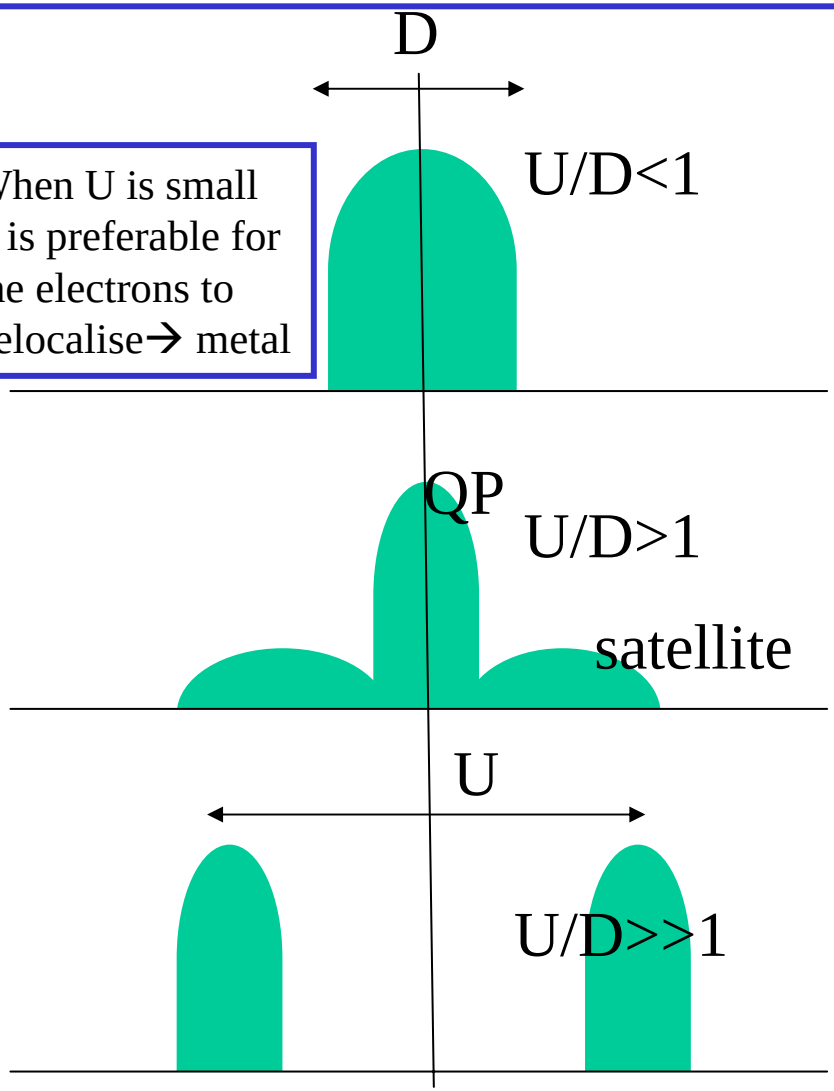


Narrow bands

5 benzene C_6H_6 rings

Tiago, Northrup, and Louie, PRB67, 115212 (2003)

Focus on the correlated bands → Mappping to a Hubbard model: Competition between kinetic energy and U (itineracy and localisation)

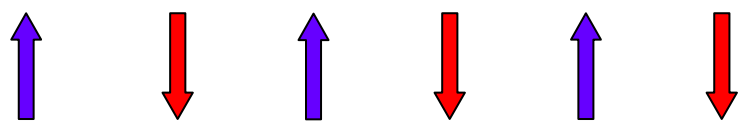


When U is small it is preferable for the electrons to delocalise→ metal

$$H = \frac{D}{4}\sum_{<ij>} c_j^{+} c_i + U\sum_i n_{i\uparrow} n_{i\downarrow}$$

For intermediate U it is a mixture of localised and delocalised electrons (correlated metals) Difficult to treat within one-particle theory

When U is large it is costly for the electrons to hop → insulator



The Hubbard model

J. Hubbard, Proc. Roy. Soc. A276, 238 (1963)

Many-electron Hamiltonian is too complicated to be solved directly.

$$H = -\frac{1}{2}\int d^3r\,\hat{\psi}^+(\vec{r})\nabla^2\hat{\psi}(\vec{r}) + \frac{1}{2}\int d^3r d^3r'\,\hat{\psi}^+(\vec{r})\frac{\hat{\rho}(\vec{r}')}{|\vec{r}-\vec{r}'|}\hat{\psi}(\vec{r})$$

→ *Focus on the correlated bands*

$$H_{Hubbard} = \sum_{Rn,R'n'} c^+_{Rn} h_{Rn,R'n'} c_{R'n'} + \frac{1}{2}\sum_{R,nn',mm'} c^+_{Rn} c_{Rn'} U_{nn',mm'} c^+_{Rm} c_{Rm'}$$

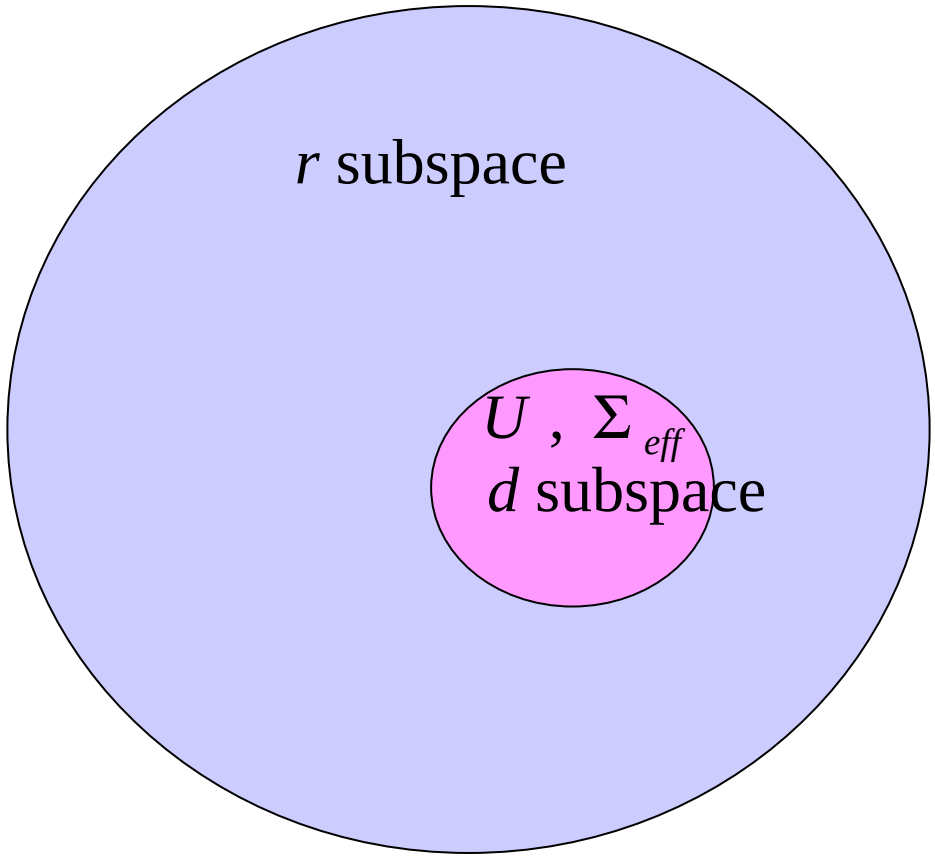
Is there any formal way of deriving the Hubbard *model* from the many-electron Hamiltonian?

What is the Hubbard U?

How do we calculate the Hubbard U?

Downfolded self-energy

Full one-particle Hilbert space



What are U , Σ_{eff} ?

$$(\omega - h^{dd} - \Sigma^{eff})G^{d} = 1$$

$$G^{d} = g^{d} + g^{d}\Sigma^{eff} G^{d}$$

Step 1: The Green Functions

$$\hat{\psi} = \sum_d \chi_d \hat{c}_d + \sum_r \chi_r \hat{c}_r = \hat{\psi}_d + \hat{\psi}_r$$

$$iG^{\,d}(1,2) = \frac{\left\langle T\left[\hat{S}\,\hat{\psi}_d(1)\hat{\psi}_d^{+}(2)\right]\right\rangle}{\left\langle \hat{S} \right\rangle}$$

$$iG^{\,rd}(1,2) = \frac{\left\langle T\left[\hat{S}\,\hat{\psi}_r(1)\hat{\psi}_d^{+}(2)\right]\right\rangle}{\left\langle \hat{S} \right\rangle}$$

Describes the coupling between the d and r subspaces

$$\hat{S} = T\,\exp\left[-i\int d3\,\varphi(3)\hat{\rho}(3)\right]$$

Step 2: The Equations of Motion for G^d and G^{rd}

$$[\hat{H}, \hat{\psi}(1)] = i\partial_{t_1}\hat{\psi}(1)$$

$$i\partial_{t_1} G^d - \Delta_d h[G^{rd} + G^d] - \Delta_d \tilde{\Sigma} G^d = \Delta_d$$

$$i\partial_{t_1} G^{rd} - \Delta_r h[G^{rd} + G^d] - \Delta_r \tilde{\Sigma} G^d = 0$$

$$\Delta_d(1,2) = \sum_{i=d} \chi_i(r_1)\chi_i(r_2)\delta(t_1 - t_2), \quad \Delta_d(1,2) + \Delta_r(1,2) = \delta(1-2)$$

$$\tilde{\Sigma} G^d = \Sigma G \Delta_d \qquad \text{Definition of } \tilde{\Sigma}$$

Step 3: Eliminate G^{rd} to obtain an effective equation for G^{d}

$$[\omega - h - \Sigma^{eff}(\omega)]G^{d} = 1$$

$$\Sigma^{eff} = \tilde{\Sigma} + hg^{r}[h + \tilde{\Sigma}]$$

Step 4: Construct the equation for $\tilde{\Sigma}$

$$\Sigma G = iW\frac{\delta G}{\delta V} \quad \rightarrow \quad \tilde{\Sigma}G^{d} = iW\frac{\delta \tilde{G}}{\delta V} \qquad V = \varphi_{ext} + V_{H}$$

$$\tilde{\Sigma}G^{d} = iW\left(\frac{\delta G^{rd}}{\delta V} + \frac{\delta G^{d}}{\delta V}\right) = (\Sigma^{d} + \Sigma^{rd})G^{d}$$

$$\tilde{\Sigma} = \Sigma^{gW}\tilde{G}(G^{d})^{-1} + iWg\frac{\delta \tilde{\Sigma}}{\delta V} + iWg\tilde{\Sigma}G^{d}\Gamma^{d}$$

After some algebra …

A closed set of equations for the downfolded self-energy. "Energy-dependent Hubbard model"

Decouple the d and r subspaces →

Conventional Hubbard model

$$\Sigma^{eff} = \Sigma^{d} + \Sigma^{rd} + \Sigma^{drd} \quad \Rightarrow \quad \Sigma^{eff} = \Sigma^{d}$$

$$P_d = -iG^d \Gamma^d G^d \qquad P_d = -iG^d \Gamma^d G^d$$

$$\Gamma^d = 1 + \frac{\delta \Sigma^{eff}}{\delta G^d} G^d \Gamma^d G^d \qquad \Gamma^d = 1 + \frac{\delta \Sigma^{eff}}{\delta G^d} G^d \Gamma^d G^d$$

$$W = v + vPW = W_r + W_r P_d W \qquad W = U + UP_d W$$

$$\boxed{W_r = v + vP_r W_r,} \quad P_r = P - P_d \quad \Rightarrow \quad \boxed{U = W_r(0)}$$

$$G^d = G_0^d + G_0^d \Sigma^{eff} G^d \qquad G^d = G_0^d + G_0^d \Sigma^{eff} G^d$$

v = bare Coulomb interaction

Furnishes a formal definition of *U*.

PRL **102**, 176402 (2009)

Possible applications

- A starting point for construction of models and
  a general procedure for combining first-principles and model approaches.

- Inclusion of vertex corrections (beyond GW) for the chosen subspace only.

- A possible route for simplifying GW calculations by treating the chosen subspace accurately and the rest of the Hilbert space in an approximate way.

Related works on the Hubbard U

Seminal work on U (constrained LDA):

O Gunnarsson, OK Andersen, O Jepsen, J Zaanen, PRB 39, 1708 (1989)

VI Anisimov and O Gunnarsson, PRB 43, 7570 (1991)

Improvement on constrained LDA

M Cococcioni and S de Gironcoli, PRB 71, 035105 (2005)

Nakamura et al (PRB 2005)

Random-Phase Approximation (RPA):

M Springer and FA, PRB 57, 4364 (1998)

T Kotani, J. Phys.: Condens. Matter 12, 2413 (2000)

Constrained RPA (cRPA)

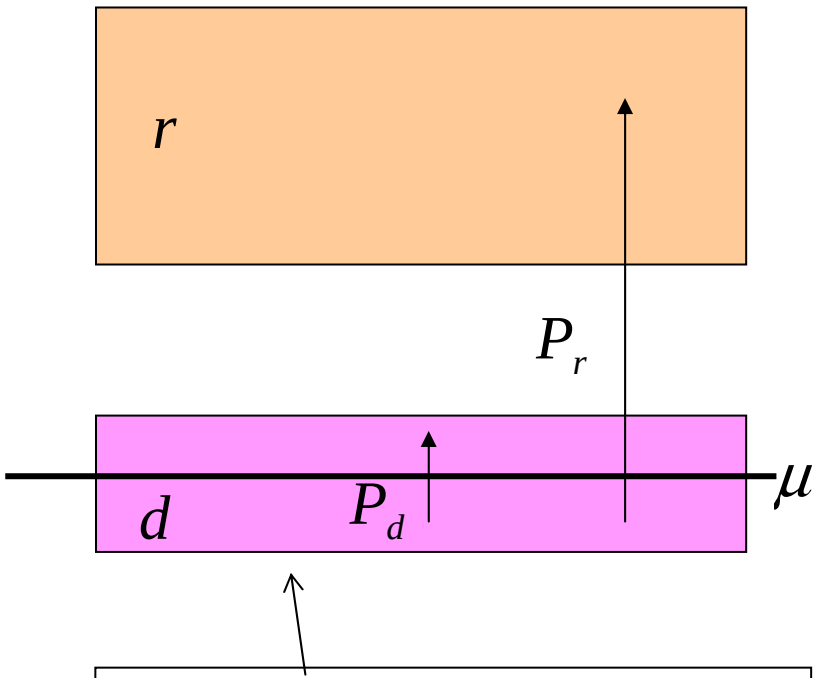
→PRB 70, 195104 (2004)

→PRB 80, 155134 (2009) for entangled bands

Constrained RPA (cRPA): A method for calculating the Hubbard U

Polarisation:

$$P = P_d + P_r$$



Calculate U of the narrow band (the d subspace)

Fully screened interaction

$$W = \frac{v}{1 - v(P_d + P_r)} = \frac{U}{1 - UP_d}$$

$$U = \frac{v}{1 - vP_r}$$

Advantages:

- Full matrix *U*
- Energy-dependent *U*
- Onsite and offsite *U*
- *U(r,r';ω)* is *basis-independent:* *Can use any band-structure method*

P_r is <u>not</u> the same as the polarisation of the r-subspace only. It includes transitions between the d- and r-subspaces.

Phys. Rev. B 70, 195104 (2004)

Polarisation function

Full system

$$P(r,r';\omega) = \sum_{i}^{occ} \sum_{j}^{unocc} \frac{\psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r')}{\omega - \varepsilon_j + \varepsilon_i \pm i\delta}$$

Correlated bands

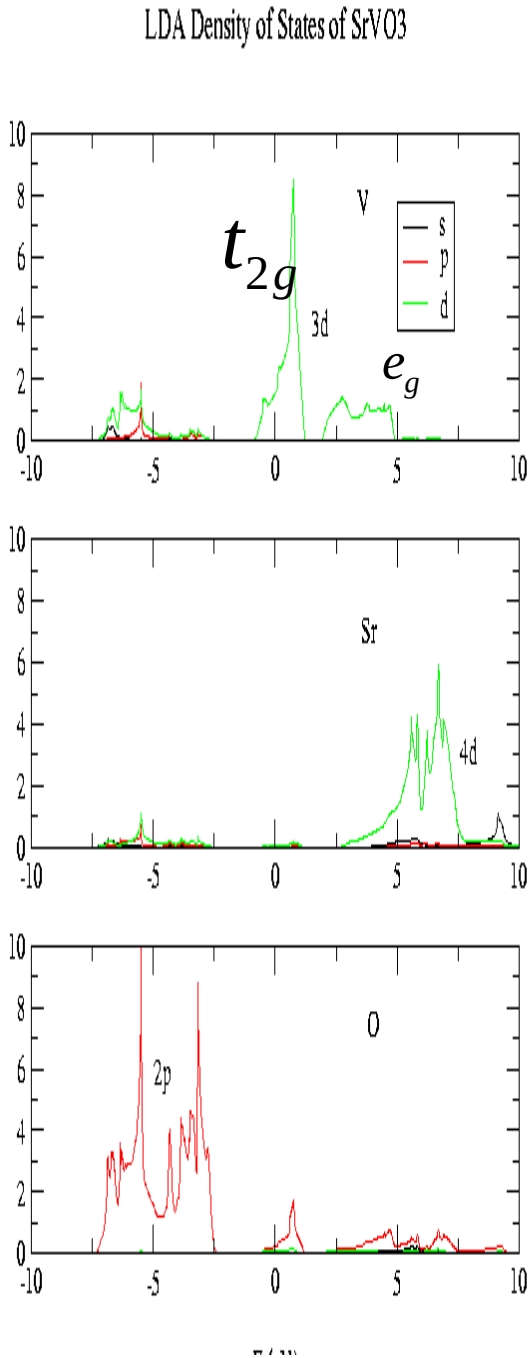
$$P_d(r,r';\omega) = \sum_{i\in d}^{occ} \sum_{j\in d}^{unocc} \frac{\psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r')}{\omega - \varepsilon_j + \varepsilon_i \pm i\delta}$$

$$P_r = P - P_d$$

$$U = \frac{v}{1 - vP_r}$$

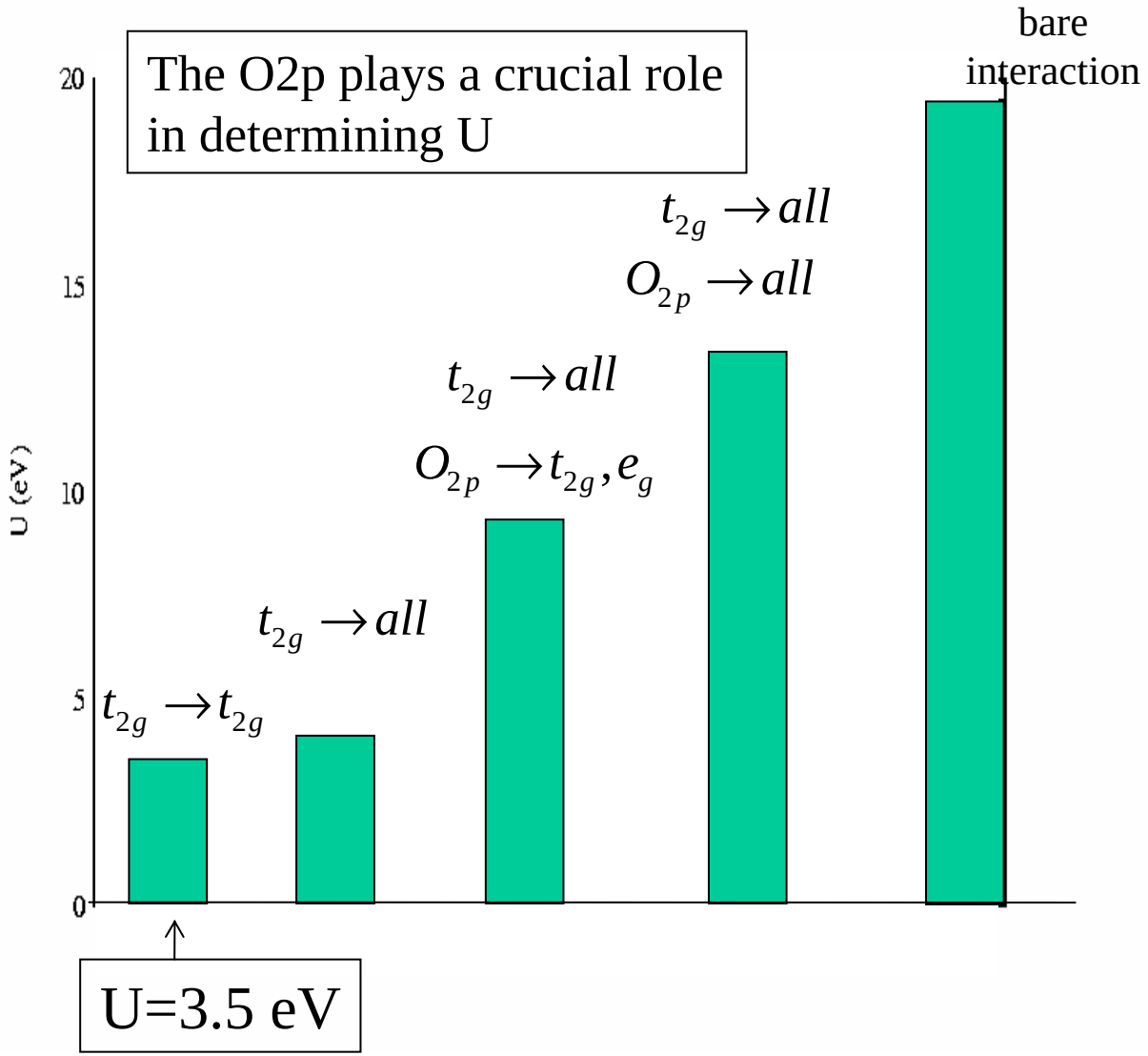
P_r is <u>not</u> the same as
the polarisation of the r-subspace only.
It includes transitions between
the d- and r-subspaces.

SrVO3



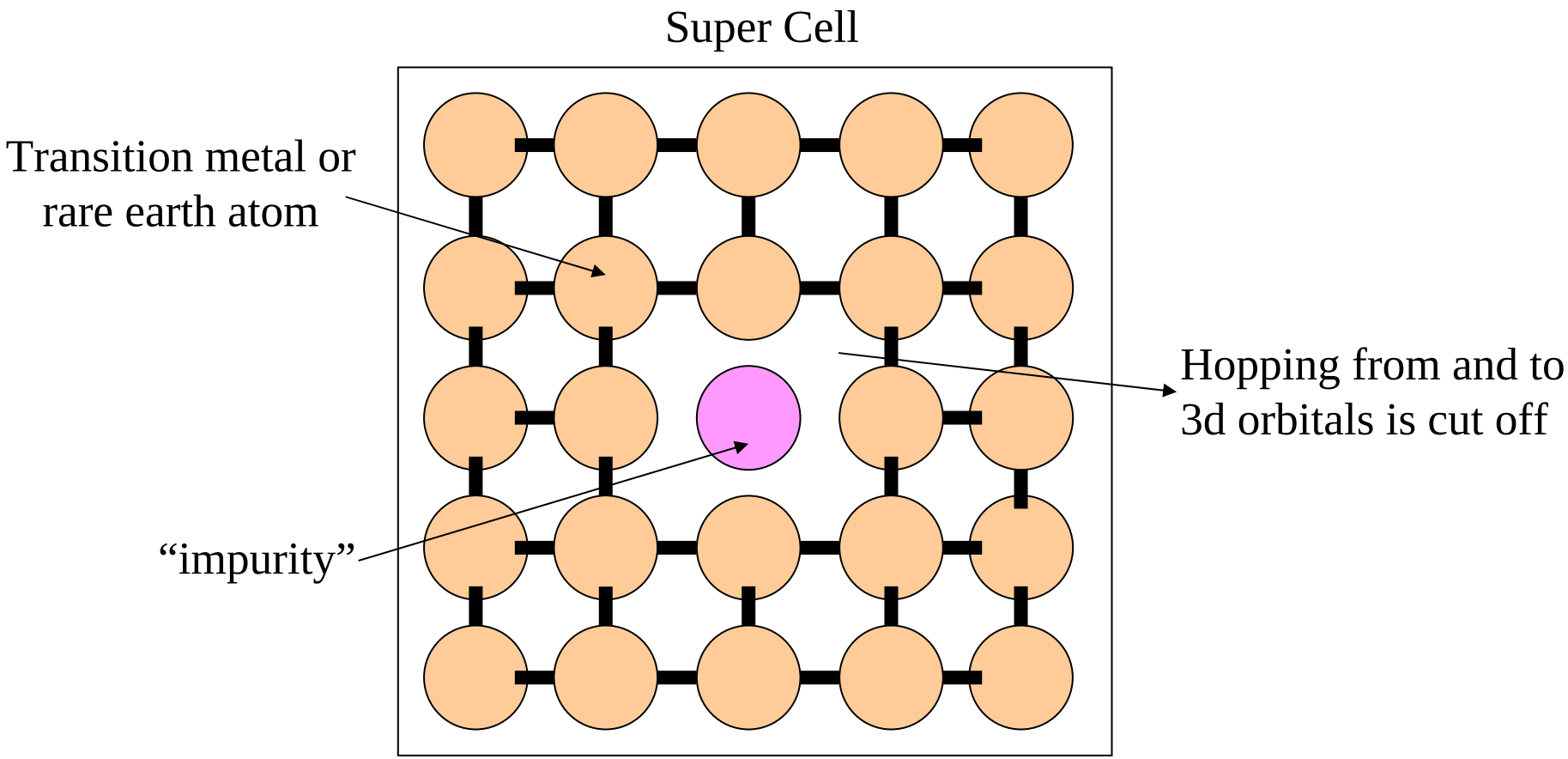
Controlling the screening channels:
U as a function of *eliminated* transitions

The O2p plays a crucial role in determining U



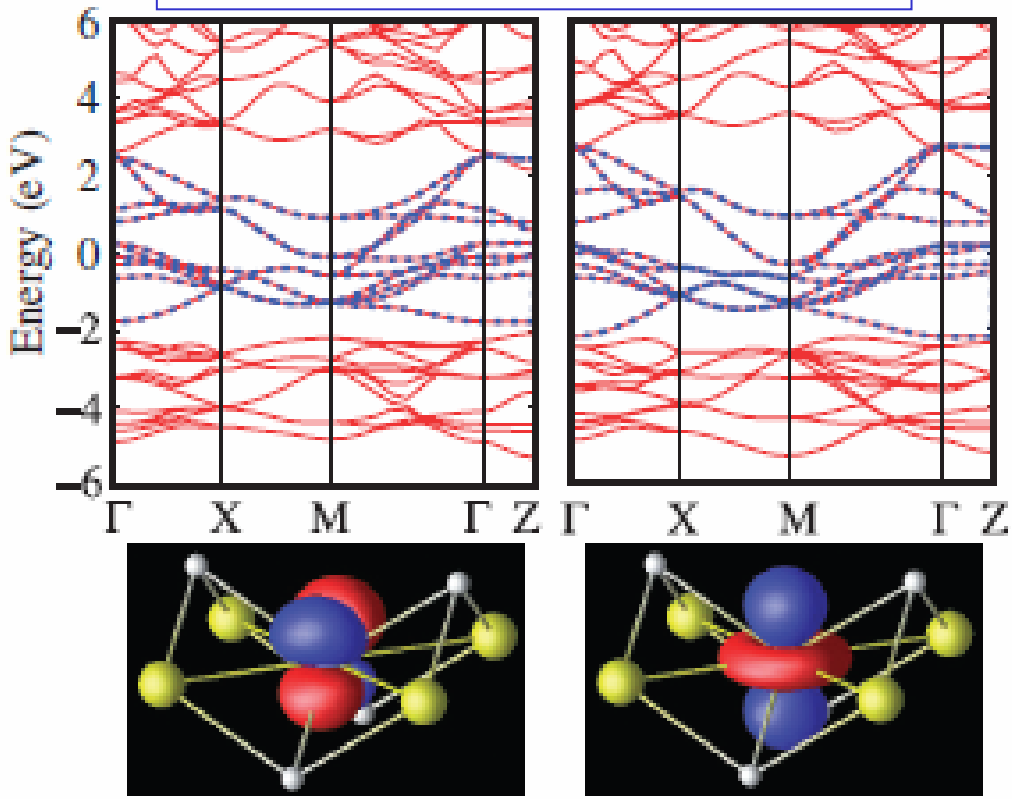
PRB 74, 125106 (2006)

Constrained LDA



Change the 3d charge on the impurity, keeping the system neutral,
do a self-consistent calculation
and calculate the change in the 3d energy level → U(3d).

Iron-based superconductors



Fe 3d bands

Fig. 1. Upper panels: *Ab initio* band structures of LaFeAsO (left) and LaFePO (right). Red line and Blue dots are original-GGA and Wannier-interpolated bands, respectively. The zero of energy is the Fermi level. Lower panels: Isosurface contours of yz- (left) and z^2- (right) MLWOs in LaFeAsO. The amplitudes of the contour surface are $+1.5/\sqrt{v}$ (blue) and $-1.5/\sqrt{v}$ (red), where v is the volume of the primitive cell. Fe and As nuclei are illustrated by yellow and silver spheres, respectively.

Nakamura, Arita, Imada, J. Phys. Soc. Jpn. 77, 093711 (2008)

t (LaFeAsO)	xy	yz	z^2	zx	x^2-y^2
xy	−0.32	−0.25	−0.30	−0.25	0.00
yz	−0.25	−0.21	−0.08	−0.13	0.18
z^2	−0.30	−0.08	0.08	−0.08	0.00
zx	−0.25	−0.13	−0.08	−0.21	−0.18
x^2-y^2	0.00	0.18	0.00	−0.18	−0.18
U (LaFeAsO)	xy	yz	z^2	zx	x^2-y^2
xy	3.31	1.95	1.89	1.95	2.09
yz	1.95	2.77	2.20	1.78	1.67
z^2	1.89	2.20	3.27	2.20	1.65
zx	1.95	1.78	2.20	2.77	1.67
x^2-y^2	2.09	1.67	1.65	1.67	2.20
J (LaFeAsO)	xy	yz	z^2	zx	x^2-y^2
xy	—	0.54	0.64	0.54	0.27
yz	0.54	—	0.41	0.45	0.43
z^2	0.64	0.41	—	0.41	0.50
zx	0.54	0.45	0.41	—	0.43
x^2-y^2	0.27	0.43	0.50	0.43	—

Nakamura, Arita, Imada, J. Phys. Soc. Jpn. 77, 093711 (2008)

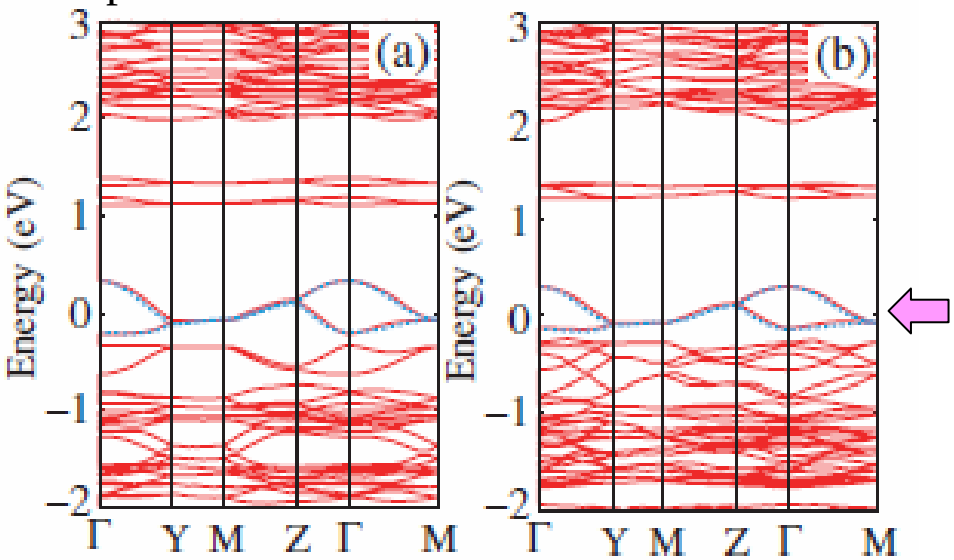
- Large orbital dependence of U.
- U is considerably smaller than the values (~4 eV) used in some model studies.

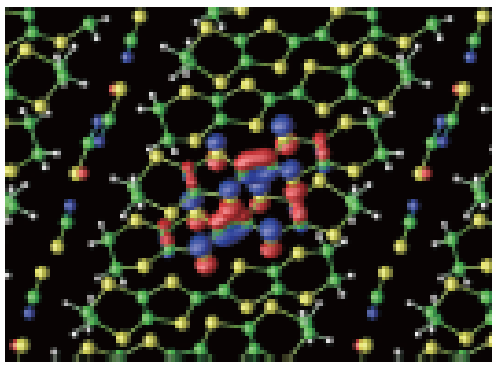
Recent comprehensive calculations by Miyake et al

BEDT-TTF organic conductors

$\kappa-(BEDTTF)_2Cu(NCS)_2$ $\kappa-(BEDTTF)_2Cu_2(CN)_3$

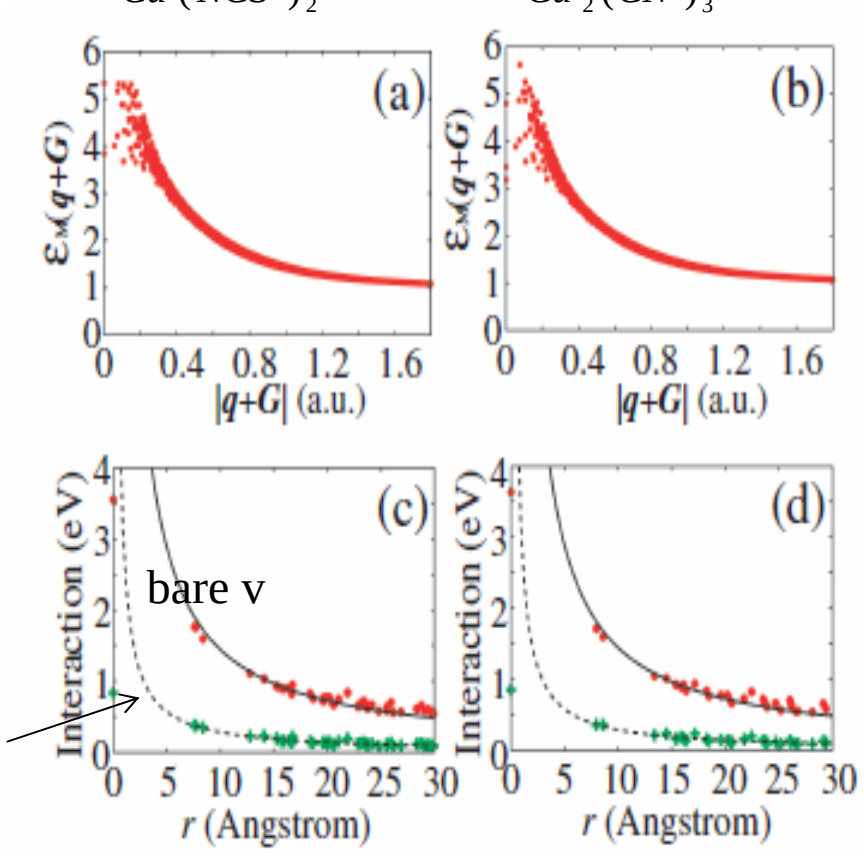
Exp: metal insulator





Maximally localised Wannier orbitals of $\kappa-(BEDTTF)_2Cu(NCS)_2$

$\kappa-(BEDTTF)_2Cu(NCS)_2$ $\kappa-(BEDTTF)_2Cu_2(CN)_3$



$U \sim 1/r^5$

The dielectric constant is anisotropic.
U is almost isotropic and long ranged.
Nearest-neighbour U/onsite U ~0.45

Nakamura et al, J. Phys. Soc. Jpn. 78, 083710 (2009)

MnO

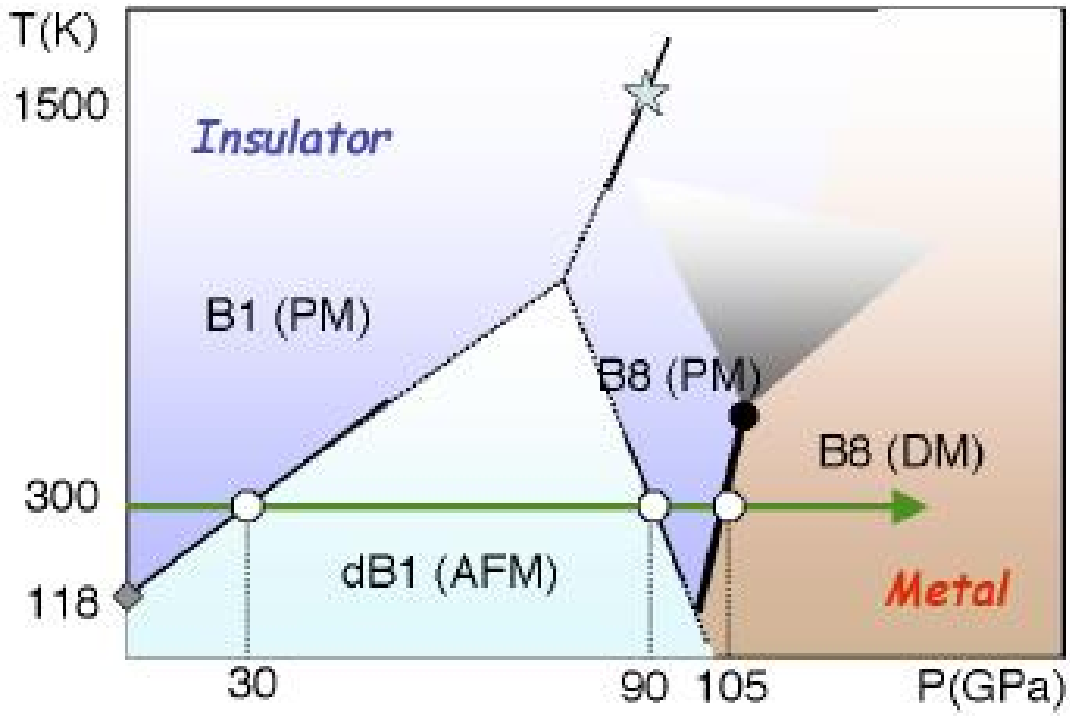
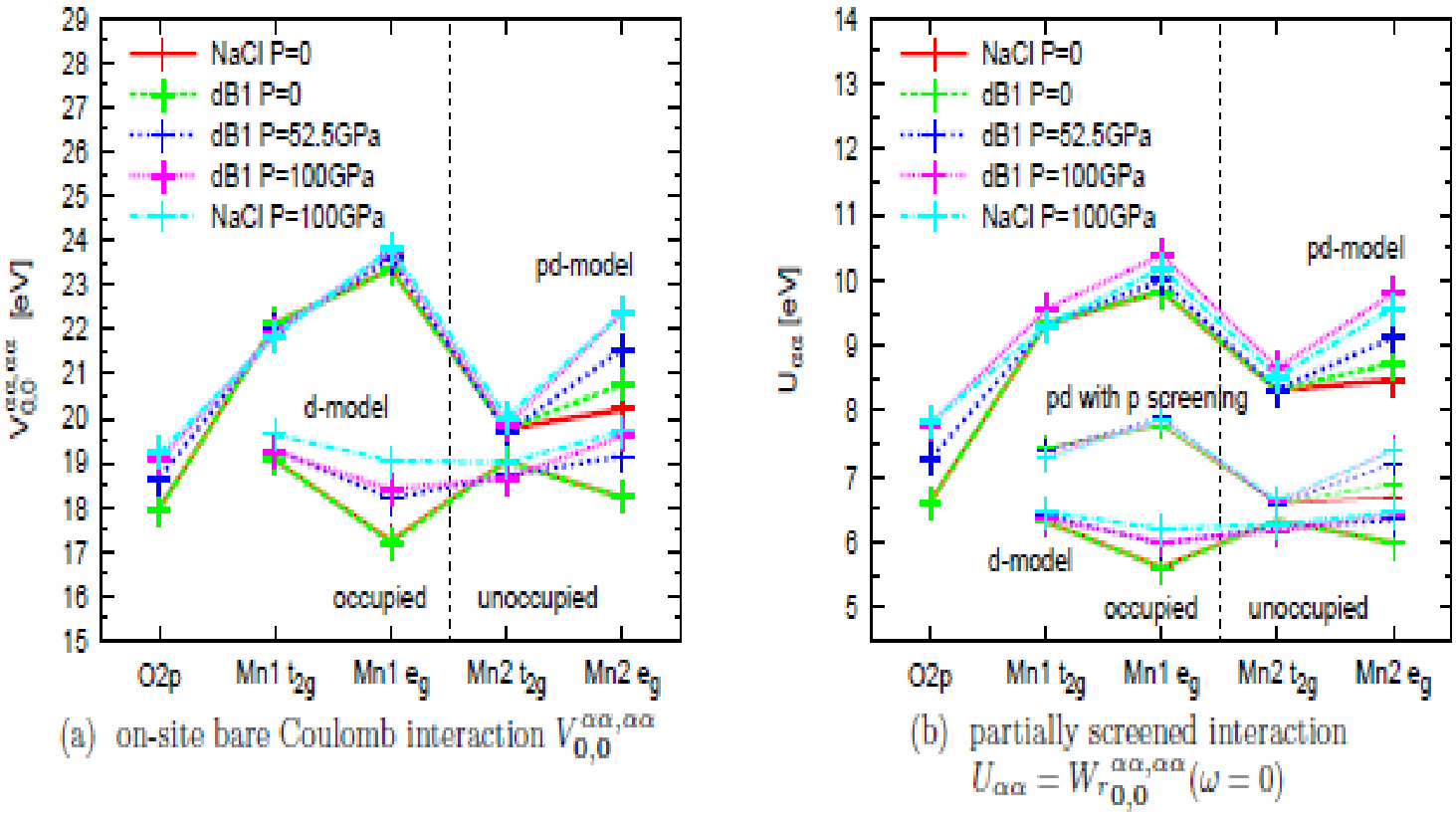


FIG. 1 (color online). The conceptual phase diagram of MnO based on the present static high-pressure data (open circles), the previous shock data (star) [7], and the ambient-pressure Néel temperature (diamond) [6]. The thick phase line signifies the first-order isostructural Mott transition which simultaneously accompanies with loss of magnetic moment, a large volume collapse and metallization, and should end at the critical point (solid circle). The gray fan above the critical point represents a smooth crossover to metallic behavior at high temperature.

Maddox *et al*
PRL (2005)

U of MnO as a function of pressure

Jan Tomczak et al (to appear in PRB)



(a) on-site bare Coulomb interaction $V_{0,0}^{\alpha\alpha,\alpha\alpha}$

(b) partially screened interaction $U_{\alpha\alpha} = W_{r_{0,0}}^{\alpha\alpha,\alpha\alpha}(\omega = 0)$

FIG. 3: (Color online) local Coulomb interaction of the antiferromagnetic dB1 phase of MnO for different pressures. (a) diagonal elements of the local, bare interaction V for the pd and d-only model, and resolved for the different orbitals α. (b) zero frequency limit of the RPA partially screened local interaction $U_{\alpha\alpha} = W_{r_{0,0}}^{\alpha\alpha,\alpha\alpha}(\omega = 0)$ for the pd model (with and without p screening), and the d-only model. For comparison are shown also the results of undistorted, B1 (NaCl) structured MnO.

U tends to *increase* with pressure.

1D chain model: U as a function of pressure

$$\psi_0(x) = \sum_n A_n \chi(x - na),$$

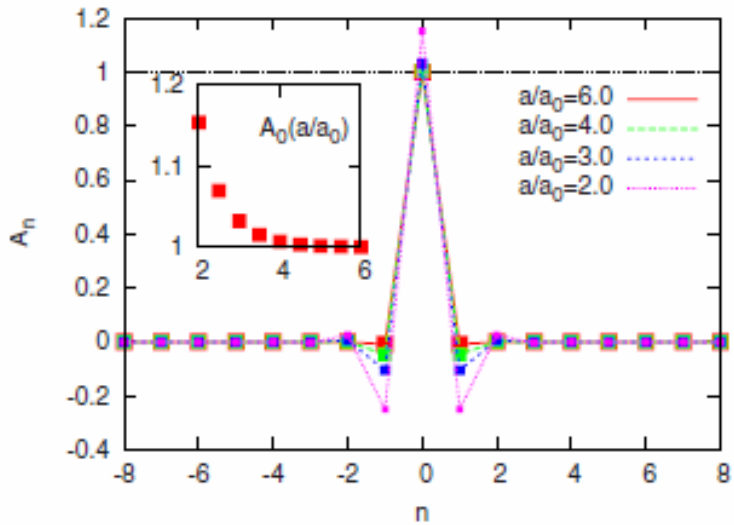


FIG. 1. (Color online) The discrete distribution A_n for different lattice constants, a/a_0, as a function of the atomic "distance," n, in real space. The inset shows the dependence of A_0, i.e., the weight of the atomic function at the origin on the lattice constant.

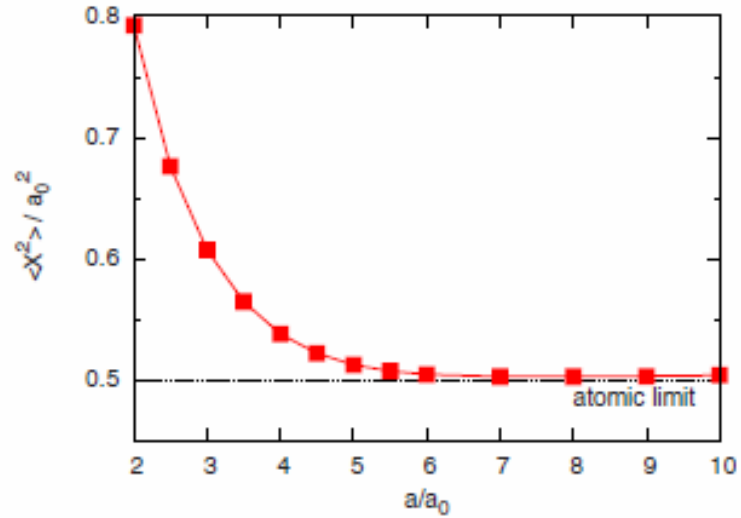


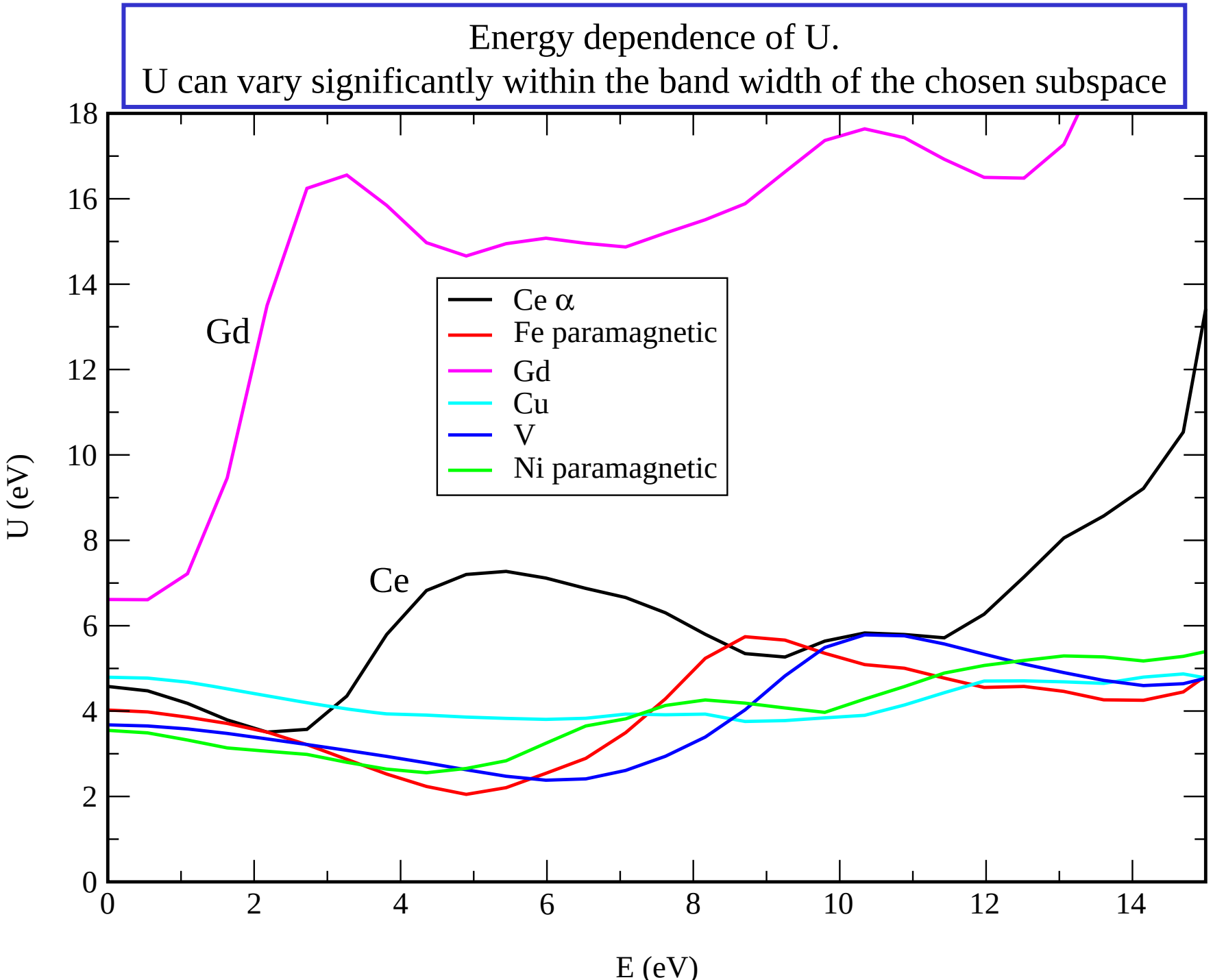
FIG. 3. (Color online) Spread of the model as a function of lattice constant a/a_0. The dotted line indicates the atomic limit $\langle X^2 \rangle = a_0^2/2$.

Hund's coupling *J* of AF dB1 MnO (d-only model)

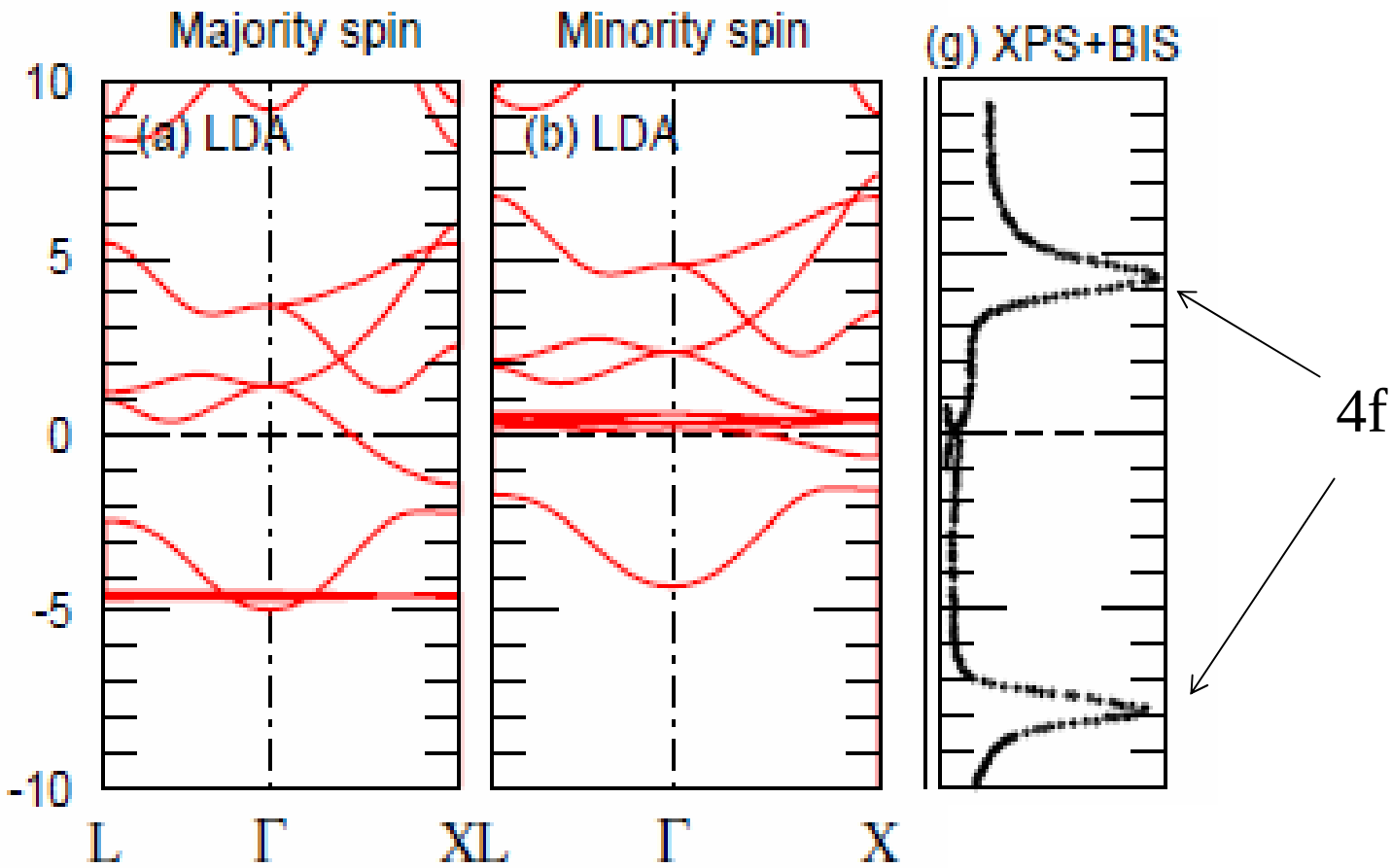
0 (100) GPa	d_{xy}	d_{xz}	d_{z^2}	d_{yz}	$d_{x^2-y^2}$
d_{xy}	–	0.61 (0.62)	0.66 (0.68)	0.61 (0.62)	0.38 (0.37)
d_{xz}	0.61 (0.62)	–	0.46 (0.45)	0.61 (0.62)	0.59 (0.60)
d_{z^2}	0.66 (0.68)	0.46 (0.45)	–	0.45 (0.45)	0.58 (0.65)
d_{yz}	0.61 (0.62)	0.61 (0.62)	0.45 (0.45)	–	0.59 (0.60)
$d_{x^2-y^2}$	0.38 (0.37)	0.59 (0.60)	0.58 (0.65)	0.59 (0.60)	–

Energy in eV

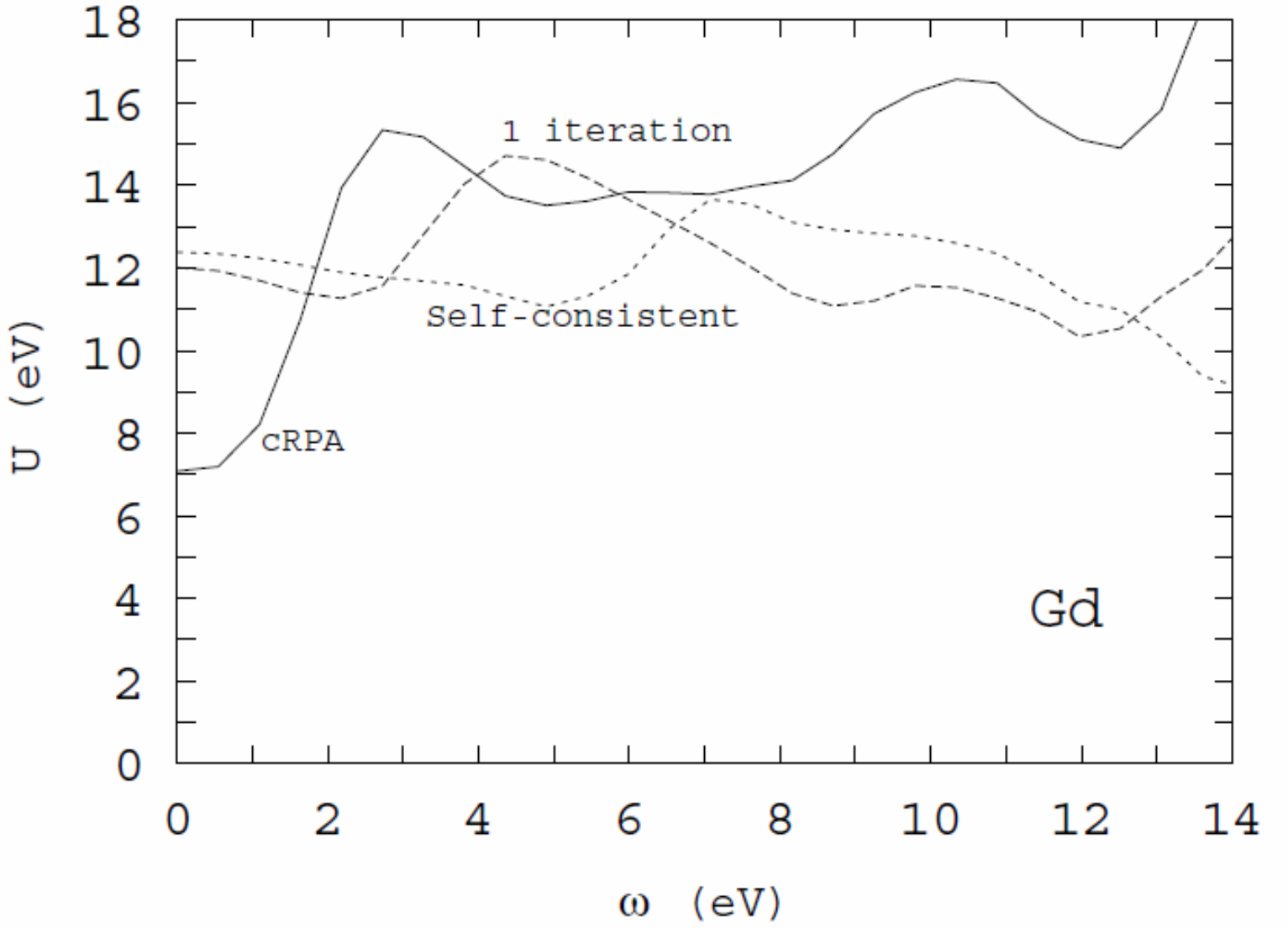
In contrast to *U*, *J* changes little with pressure


Energy dependence of U.
U can vary significantly within the band width of the chosen subspace
Gd
Ce
Ce α
Fe paramagnetic
Gd
Cu
V
Ni paramagnetic
U (eV)
E (eV)
0
2
4
6
8
10
12
14
16
18

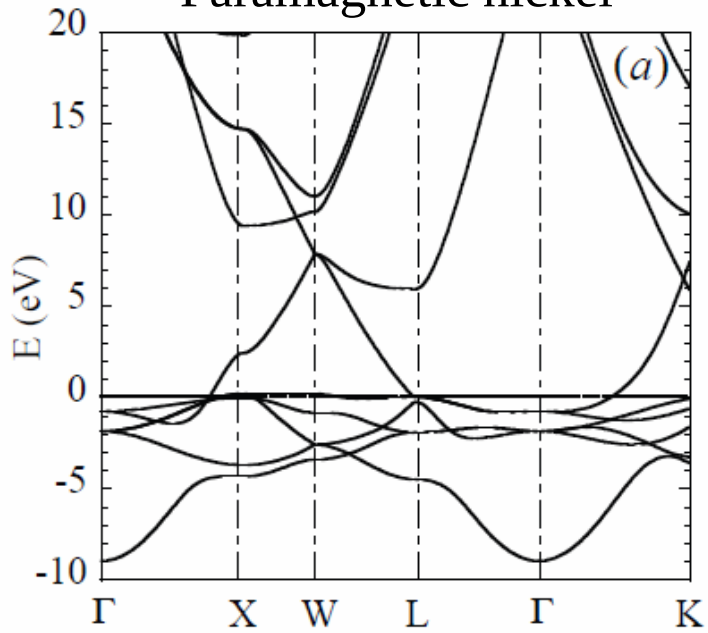
Gd

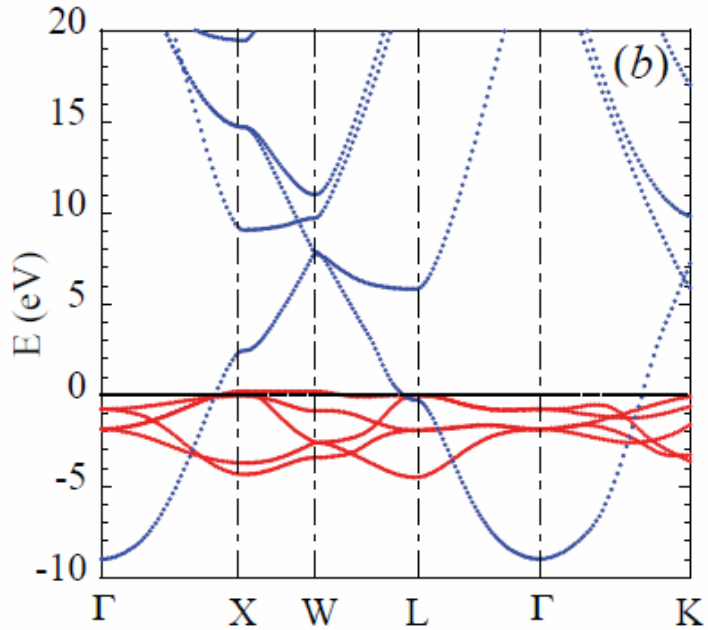

Majority spin
Minority spin
(g) XPS+BIS
(a) LDA
(b) LDA
10
5
0
-5
-10
L
Γ
XL
Γ
X
4f

Self-consistent LDA+U:
U is updated using constrained RPA (cRPA)



Paramagnetic nickel





PRB 80, 155134 (2009)

cRPA for entangled bands

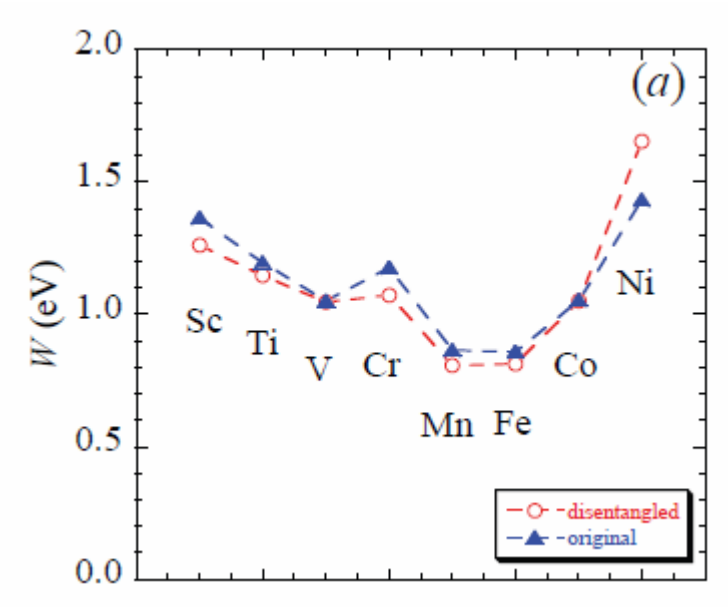
In many materials the correlated bands of interest are entangled with other more extended bands.

$$H = \begin{pmatrix} d \text{ space} & 0 \\ 0 & r \text{ space} \end{pmatrix}$$

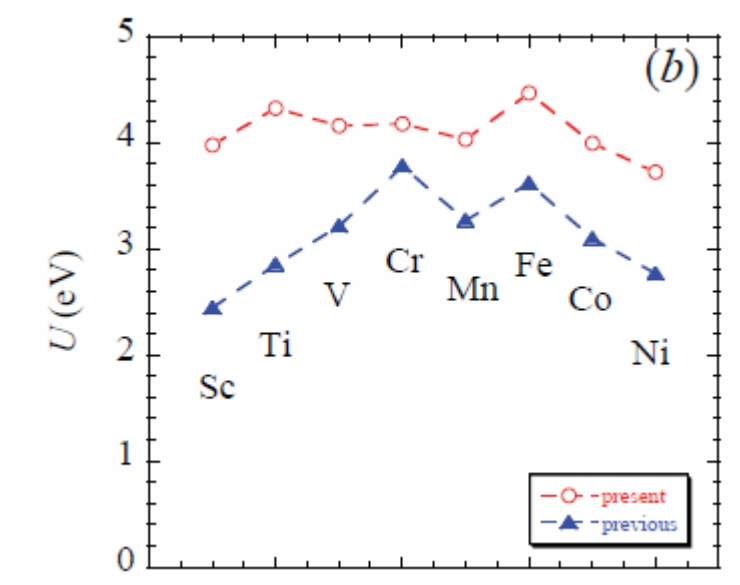
Approximation: The off-diagonal elements are set to zero

←

Disentangled 3d band structure from maximally localised Wannier orbitals (using the procedure of Souza, Marzari and Vanderbilt)



Fully screened interaction W of the 3d series



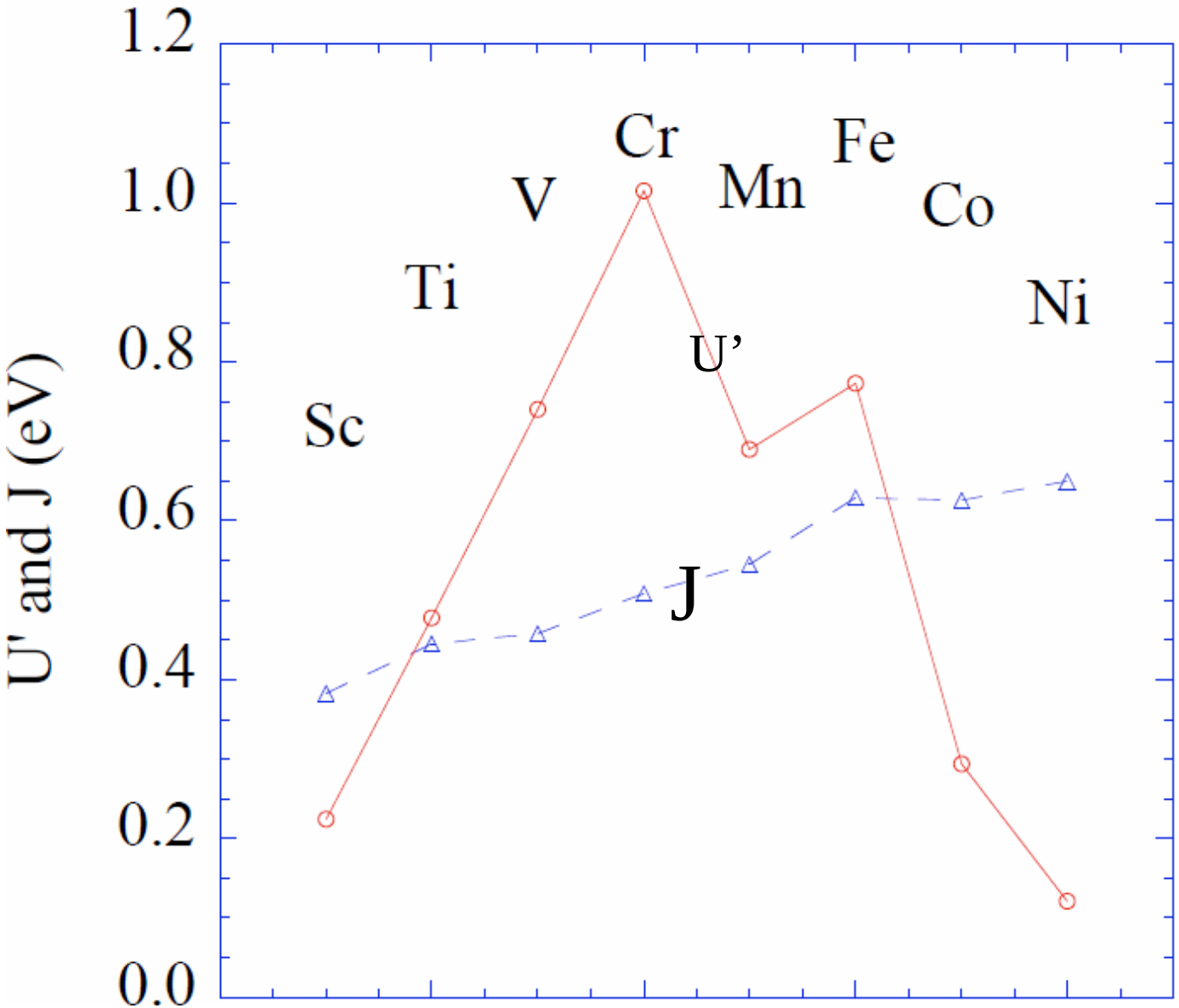
Hubbard U for the 3d series

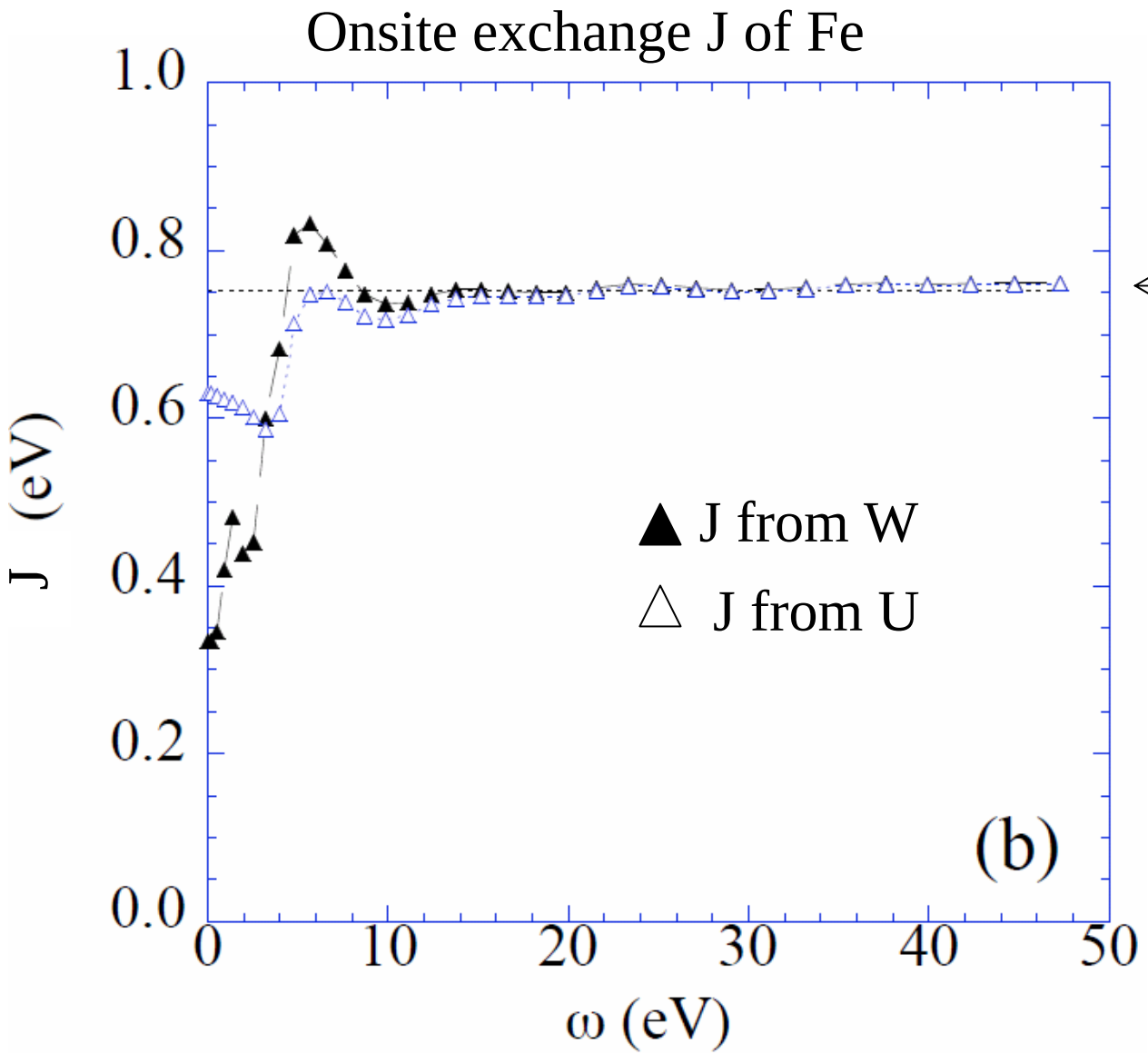
The difference arises from the choice of the d-subspace forming the Hubbard model and the criteria for P_d.

Previous: Phys. Rev. B 77, 085122 (2008)

Present: PRB 80, 155134 (2009)

Nearest-neighbour U and exchange J





Bare atomic value ~0.75 eV

Screening effects on J are not negligible

Summary

Downfolded self-energy of many-electron systems:
Formal expression for the Hubbard *U*

Constrained RPA (cRPA):

-Allows for systematic determination of the Hubbard U
-$U(r,r';\omega)$ is basis independent