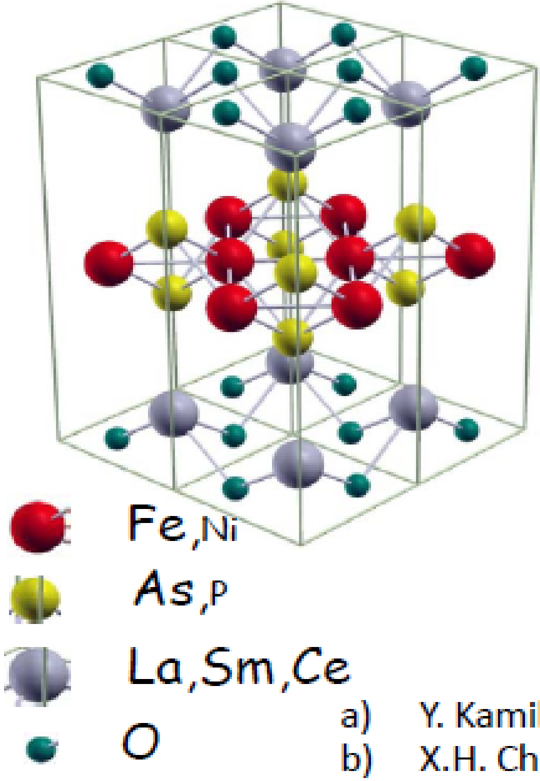
Bangalore, 2014-01-06→17

The constrained RPA method

Ferdi Aryasetiawan
Lund University

Iron-based high-temperature superconductors



a) Y. Kamihara et.al., Tokyo, JACS
b) X.H. Chen, et.al., Beijing, cm/0803.3790
c) G.F. Chen et.al., Beijing, cm/0803.3603
d) Z.A. Ren et.al, Beijing, unpublished

- 2D square lattice of Fe
- Fe - magnetic moment

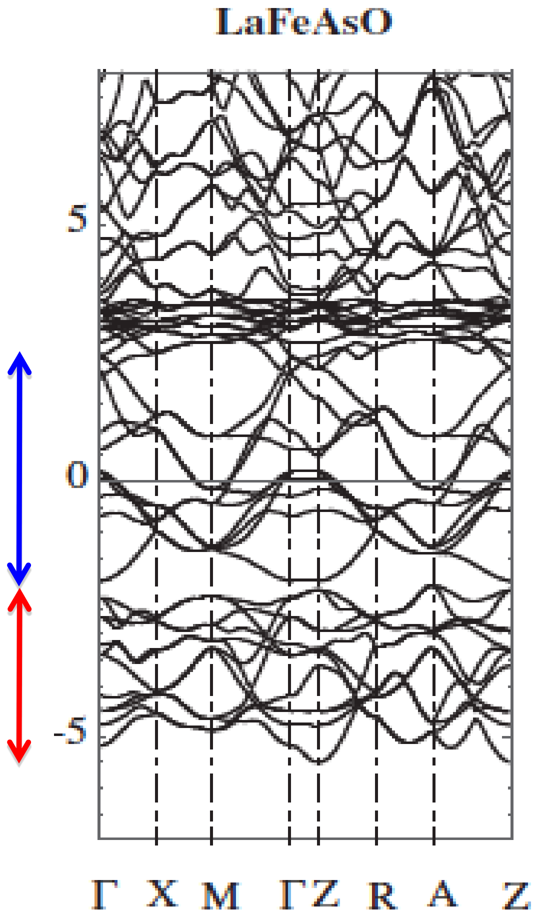
x~5-20%

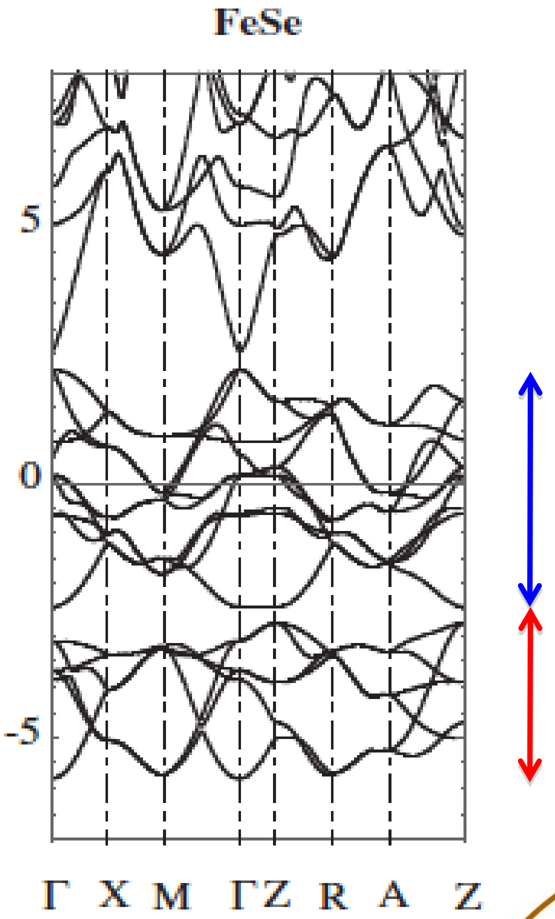
Smaller c
Higher T_c

LaOFeP	3.2K, JACS-2006 a=3.964A, c=8.512A
$\mathrm{SmF_xO_{1-x}FeAs}$ c)	55K, cm/0803.3603 a=3.940A, c=8.496A
$\mathrm{PrF_xO_{1-x}FeAs}$ d)	52K, unpublished a=3.985A, c=8.595A
$\mathrm{CeF_xO_{1-x}FeAs}$ b)	41 K, cm/0803.3790 a=3.996A, c=8.648A
$\mathrm{LaF_xO_{1-x}FeAs}$ a)	26 K, JACS-2008 a=4.036A, c=8.739 A
$\mathrm{La_{1-x}Sr_xOFeAs}$	25K, cm/0803.3021, a=4.035A, c = 8.771A
$\mathrm{LaCa_xO_{1+x}FeAs}$	0 K
$\mathrm{LaF_xO_{1-x}NiAs}$	2.75K, cm/0803.2572a =4.119A , c=8.180A
$\mathrm{La_{1-x}Sr_xONiAs}$	3.7K, cm/0803.3978 a=4.045A, c=8.747A

Fe 3d
(As 4p)

(Fe 3d)
As 4p
O 2p





Fe 3d
(Se 4p)

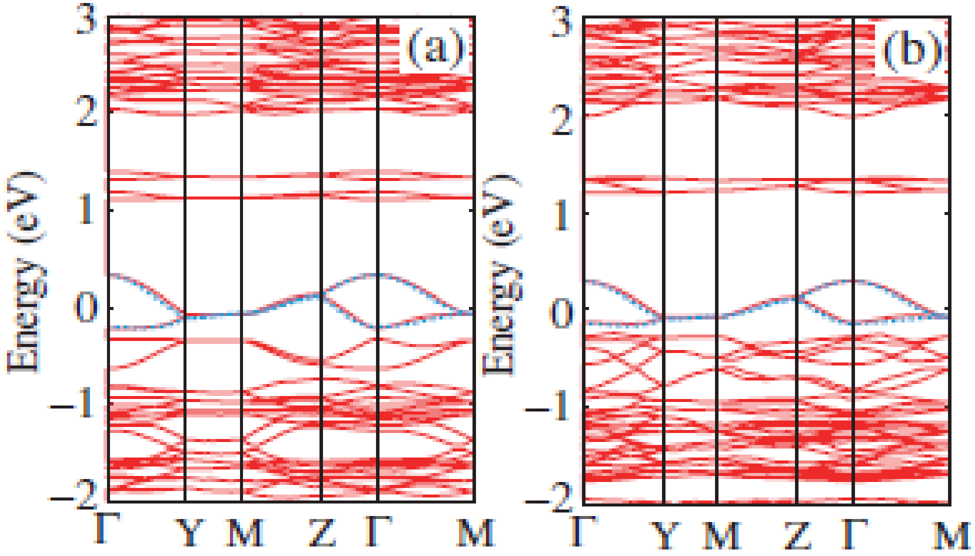
(Fe 3d)
Se 4p

From Takashi Miyake

BEDT-TTF organic conductors

BEDT-TTF=bis(ethylenedithio)tetrathiafulvaene

	$\kappa-(BEDTTF)_2$ $Cu(NCS)_2$	$\kappa-(BEDTTF)_2$ $Cu_2(CN)_3$
Exp:	metal	insulator

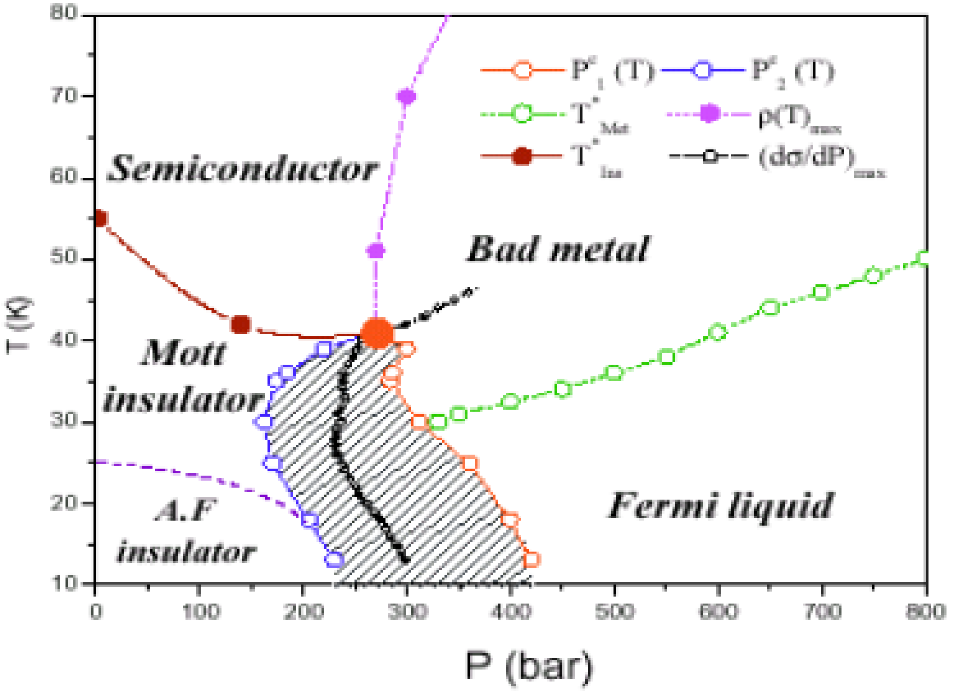


Metallic in LDA!

LDA band structures

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

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl



P. Limelette et al., PRL 91 (2003) 016401

See also:

Kagawa et al. cond-mat/0307304

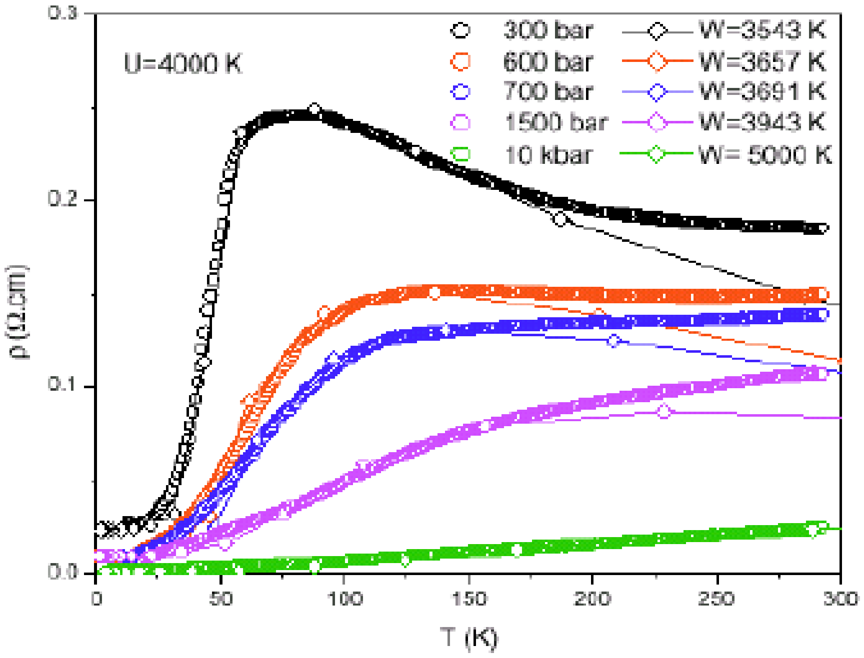
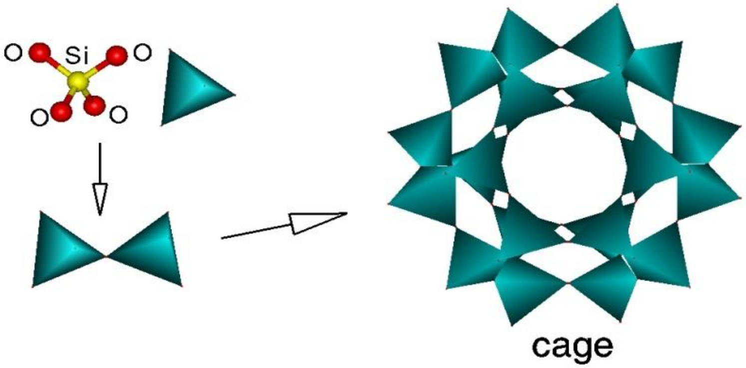
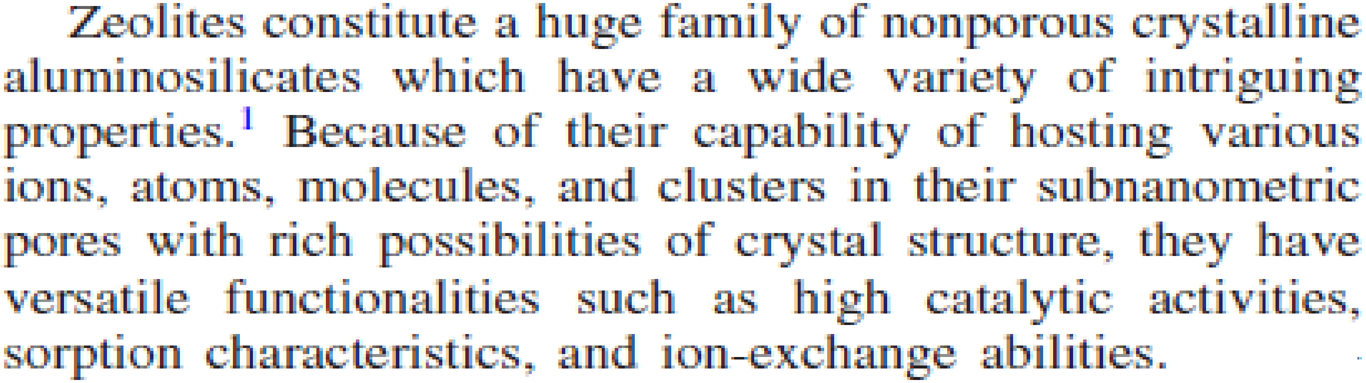


FIG. 6: Temperature-dependence of the resistivity at different pressures. The data (circles) are compared to a DMFT-NRG calculation (diamonds), with a pressure dependence of the bandwidth as indicated. The measured residual resistivity ρ_0 has been added to the theoretical curves.

Zeolites




Zeolites constitute a huge family of nonporous crystalline aluminosilicates which have a wide variety of intriguing properties.[1] Because of their capability of hosting various ions, atoms, molecules, and clusters in their subnanometric pores with rich possibilities of crystal structure, they have versatile functionalities such as high catalytic activities, sorption characteristics, and ion-exchange abilities.

Nakamura, Koretsune, and Arita, PRB80, 174420 (2009)

Alkali-cluster-loaded sodalites

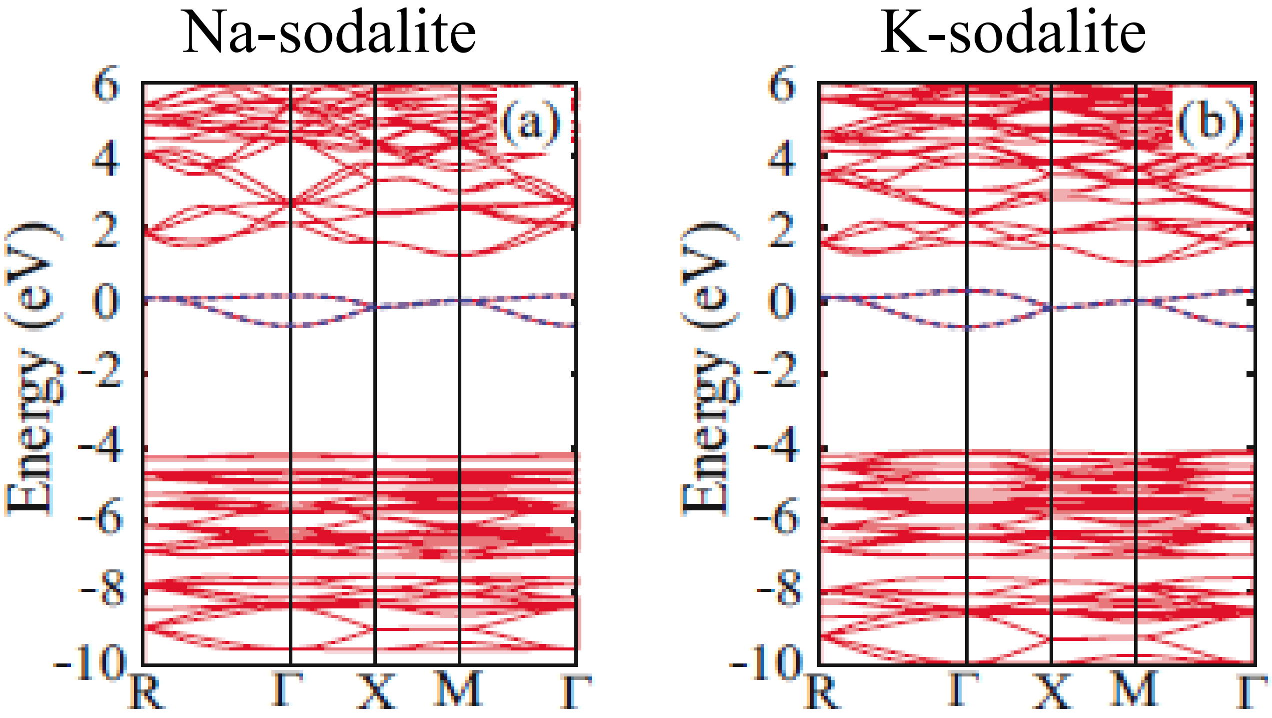
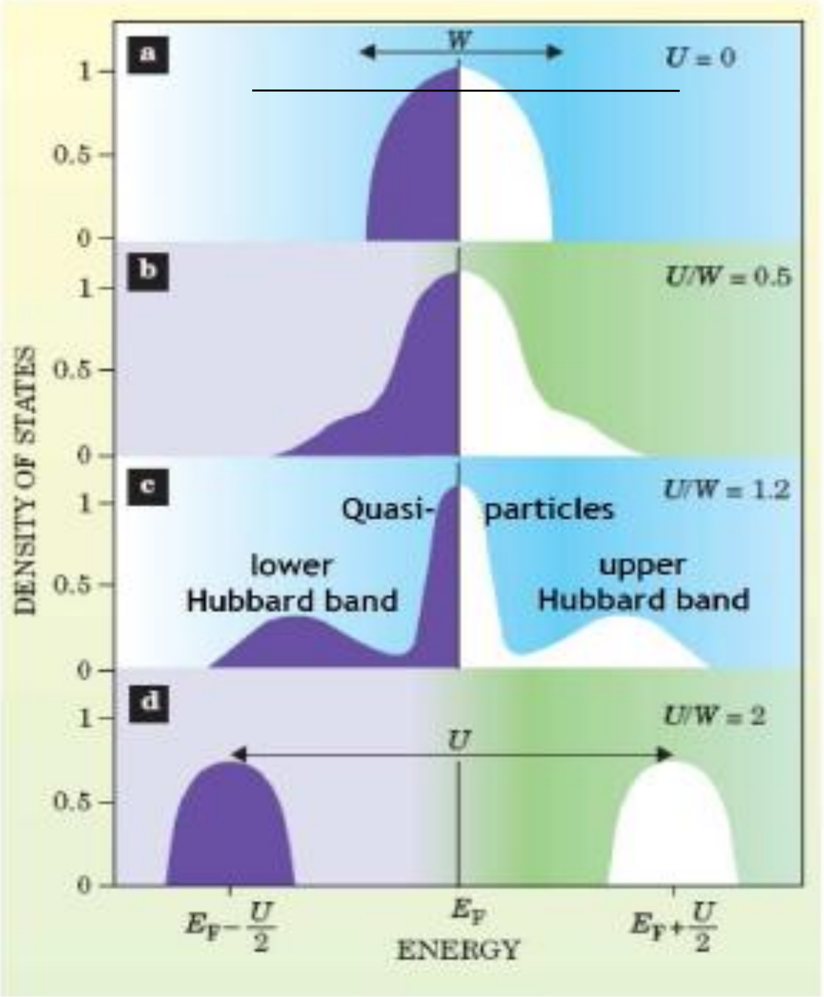


FIG. 3. (Color online) Calculated *ab initio* band structures (red solid lines) of (a) sodium electrosodalite and (b) potassium electrosodalite. The blue dotted dispersions are obtained by the t_1-t_2 model, where t_1 and t_2 are nearest and next-nearest transfers, respectively. For the values, see the text. The zero of energy is the Fermi level.

Nakamura, Koretsune, and Arita, PRB80, 174420 (2009)

The Hubbard model



Kotliar and Vollhardt, Physics Today 2004

The usual approach is
to model the narrow band
by a Hubbard Hamiltonian.

One-band Hubbard model:

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

(A similar Hamiltonian was also
introduced independently
around the same time by
Anderson, Gutzwiller, and Kanamori)

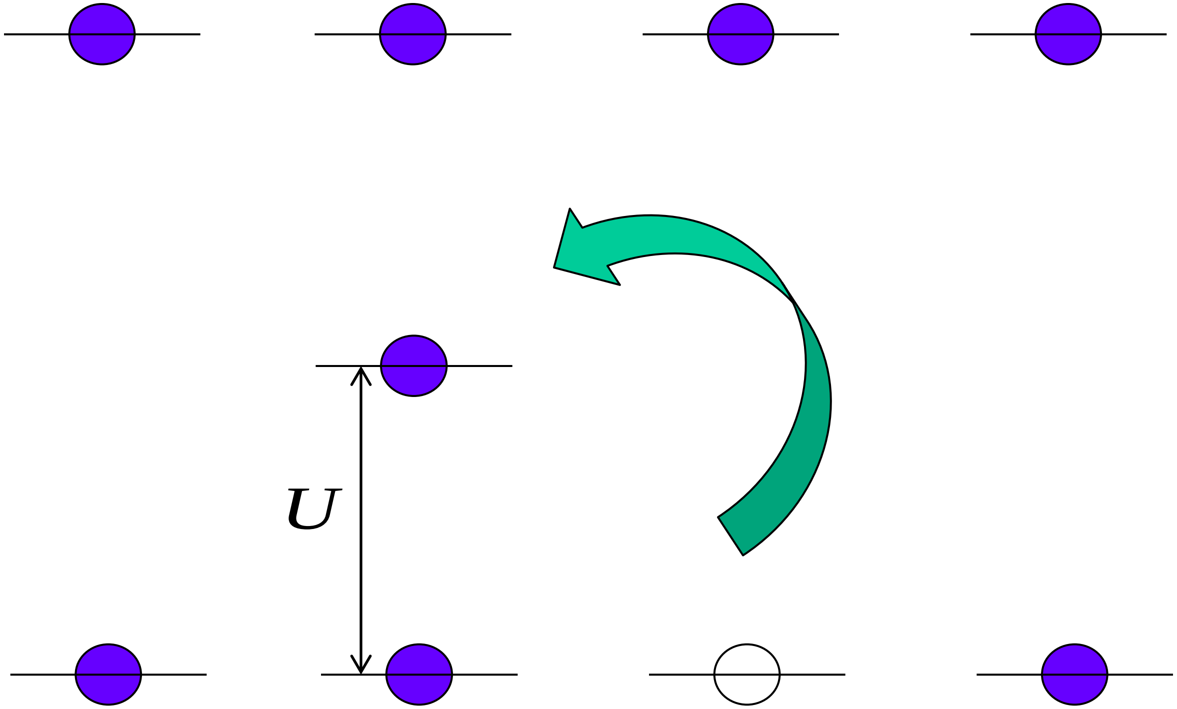
What is *U*?

Herring's definition of *U*

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

U is the energy cost of moving an electron between two atoms.

Half filling



Herring's definition of U

U is the energy cost of moving an electron between two atoms.

Example: $3d$ transition metal with configuration $3d^n 4s^1$

$$U = \underbrace{[E(3d^{n-1}4s^2) - E(3d^n 4s^1)]}_{\text{Ionisation energy}} + \underbrace{[E(3d^{n+1}4s^0) - E(3d^n 4s^1)]}_{\text{Electron affinity}}$$

$$= E(3d^{n-1}4s^2) - 2E(3d^n 4s^1) + E(3d^{n+1}4s^0)$$

The change in the number of localised $3d$ electrons is *fully compensated* by the change in the number of delocalised $4s$ electrons on the same atom.

$$U = \frac{\partial^2 E}{\partial n_d^2} = \frac{\partial \varepsilon_d}{\partial n_d}$$

From Density Functional Theory
(Janak's theorem)

$$\varepsilon_d = \frac{\partial E}{\partial n_d}$$

Works on constrained LDA (cLDA)

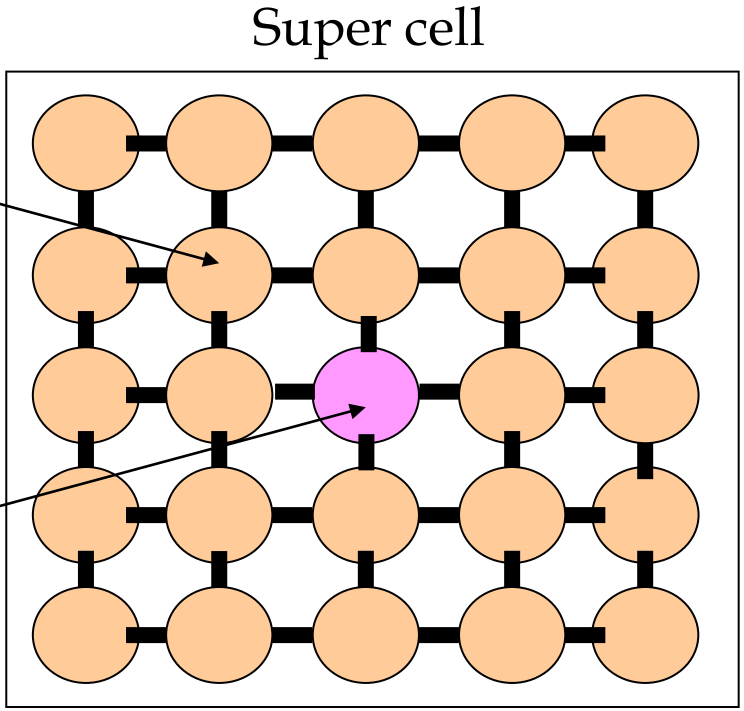
Seminal work:

Dederichs, Blugel, Zeller, and Akai, PRL 53, 2512 (1984)
Gunnarsson, Andersen, Jepsen, and Zaanen, PRB 39, 1708 (1989)
Anisimov and Gunnarsson, PRB 43, 7570 (1991)

Improvement on constrained LDA

McMahan, Martin, and Satpathy, PRB 38, 6650 (1988)
Hybertsen, Schluter, and Christensen, PRB 39, 9028 (1989)
Cococcioni and de Gironcoli, PRB 71, 035105 (2005)

Constrained LDA (cLDA)



Transition metal
or rare earth atom

The occupation
number n_d is
constrained by q
at the chosen site

$$E[q] = \min_{\rho,\alpha}\left\{E_{LDA}[\rho(r)] + \alpha(n_d - q)\right\}$$

α = Lagrange multiplier

$$U = \frac{\partial^2 E[q]}{\partial q^2} - \frac{\partial^2 E^{KS}[q]}{\partial q^2}$$

Non-interacting
Kohn-Sham energy

Cococcioni and de Gironcolo, PRB 71, 035105 (2005)
Hybertsen, Schluter, and Christensen, PRB 39, 9028 (1989)

Kohn-Sham equation in constrained LDA (cLDA)

$$E[q] = \min_{\rho,\alpha} \{ E_{LDA}[\rho(r)] + \alpha(n_d - q \}$$

$$\left(-\frac{1}{2}\nabla^2 + V_{ext} + V_H + V_{xc} + \alpha P_d \right) \psi_{kn} = \varepsilon_{kn} \psi_{kn}$$

Additional *non-local* potential acting on the impurity site

$$P_d = |\varphi_d\rangle\langle\varphi_d|,$$

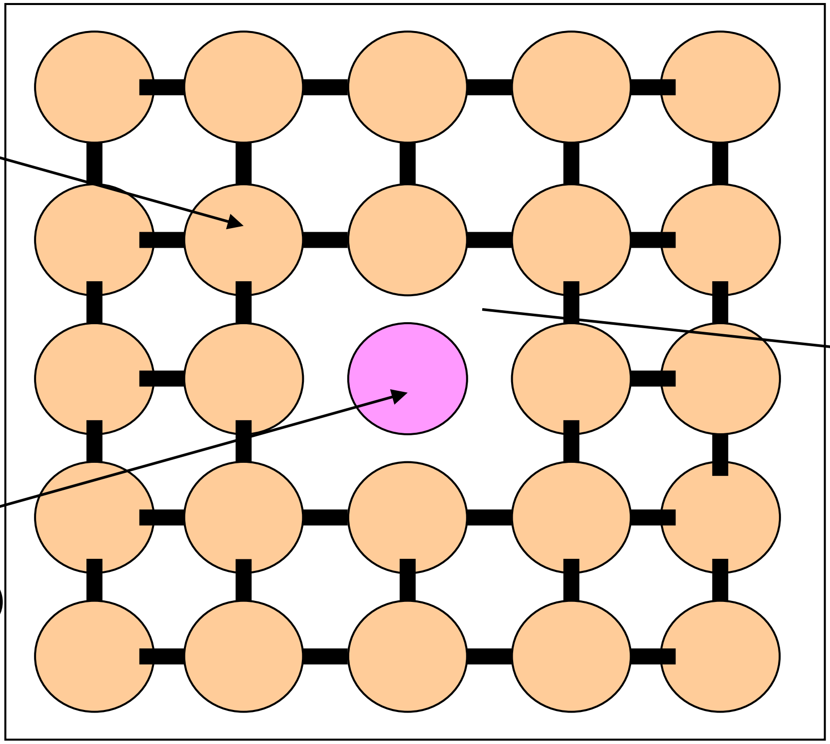
$$n_d = \sum_{kn}^{occ} |\langle\varphi_d|\psi_{kn}\rangle|^2$$

$$= \sum_{kn}^{occ} \langle\psi_{kn}|\varphi_d\rangle\langle\varphi_d|\psi_{kn}\rangle$$

Constrained LDA (cut-off method)

Anisimov and Gunnarsson, PRB 43, 7570 (1991)

Super Cell



Transition metal or
rare earth atom

"impurity"
(3d or 4f atom)

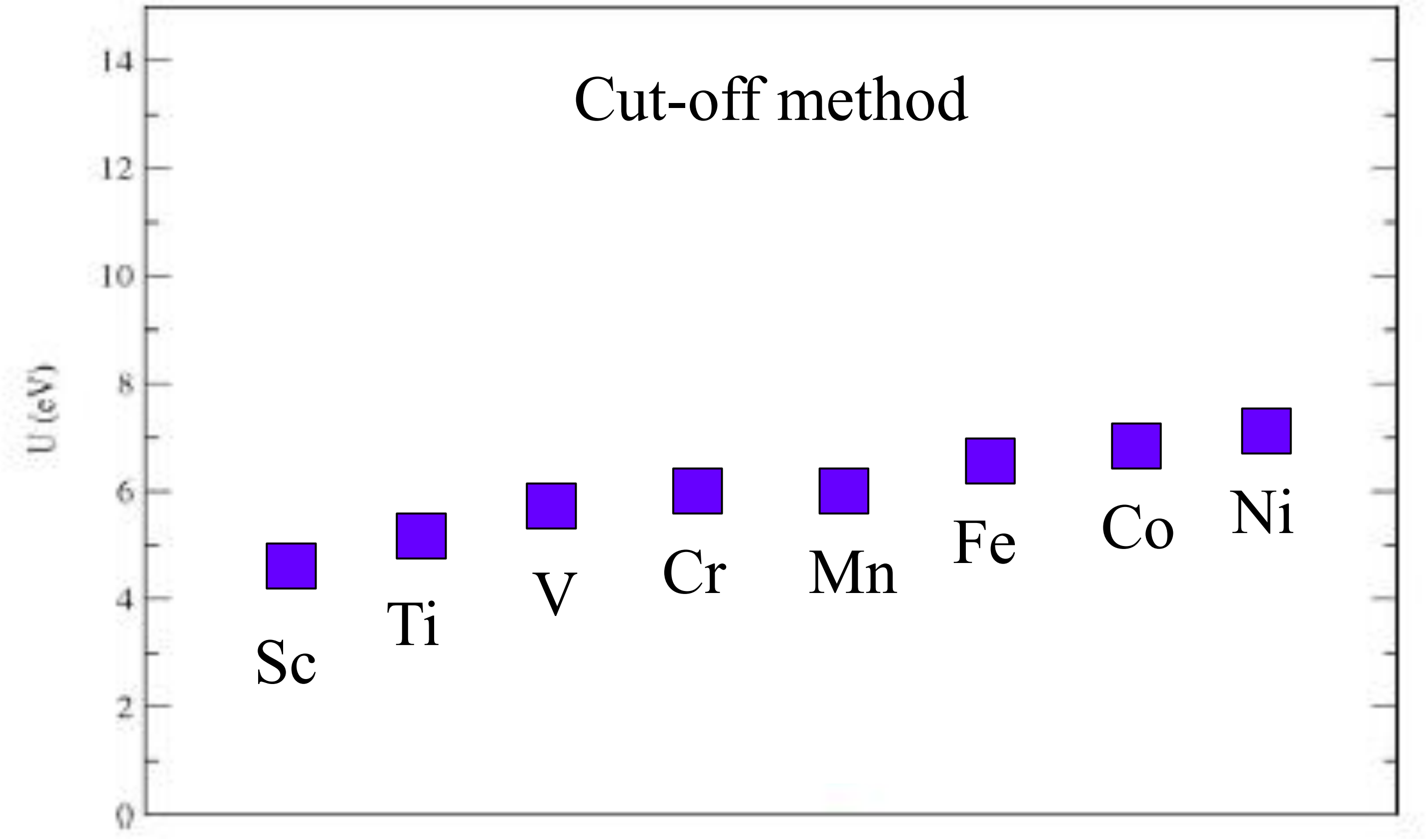
Hopping from and to
the 3d orbitals is cut off:

$$-\frac{\partial^2 E^{KS}[q]}{\partial q^2}$$

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 →

$$U = \frac{\partial^2 E}{\partial n_d^2} = \frac{\partial \varepsilon_d}{\partial n_d}$$

U for 3d transition metals from cLDA



PRB 74, 125106 (2006)

U from cLDA tends to be too large

Some results from cLDA

$$U = \frac{\partial^2 E[q]}{\partial q^2} - \frac{\partial^2 E^{KS}[q]}{\partial q^2}$$

	***U* (eV)**
Fe	**2.2**
Ce	**4.5**
FeO	**4.3**
NiO	**4.6**

Smaller than normally used values

Cococcioni and de Gironcolo, PRB 71, 035105 (2005)

Difficulties with cLDA

cLDA is simple to apply but:

The system is disturbed when we perform constrained calculations
so that the localised orbitals are modified (relaxation, breathing)
→ Unclear whether the *U* so obtained corresponds to the *U* in the model.

$$U_{ij,kl} = \int drdr' \, \varphi_i(r)\varphi_j(r)U(r,r')\varphi_k(r')\varphi_l(r')$$

Attempt to compensate for modification in KS orbitals:

$$U = \frac{\partial^2 E[q]}{\partial q^2} - \frac{\partial^2 E^{KS}[q]}{\partial q^2} \longleftarrow \begin{array}{l}\text{Non-interacting}\\ \text{Kohn-Sham energy}\end{array}$$

But it is not clear that the effects on the Kohn-Sham orbitals can be accounted for by simply subtracting the corresponding noninteracting expression.

Cut-off method:

When hopping from the localised orbitals is cut off,
some screening channels are missed → too large *U*

Electron correlations in narrow energy bands

By J. Hubbard

Theoretical Physics Division, A.E.R.E., Harwell, Didcot, Berks

(*Communicated by B. H. Flowers, F.R.S.—Received* 23 *April* 1963)

$$H = \sum_{i,j} \sum_{\sigma} T_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \tfrac{1}{2} I \sum_{i,\sigma} n_{i\sigma} n_{i,-\sigma}$$

The most obvious approximation has been the neglect of all the interaction terms in (6) other than the $(ii|\,1/r\,|ii)$ term. For the sake of comparison one may note that I has the order of magnitude 20 eV for $3d$-electrons in transition metals. The largest of the neglected terms are those of the type $(ij|\,1/r\,|ij)$ where i and j are nearest neighbours. From (9) these integrals can be estimated to have the order of magnitude $(2/R)$ Ry ~ 6 eV ($R =$ interatomic spacing in Bohr units). Actually this figure should be reduced appreciably to allow for the screening of the interactions of electrons on different atoms by the conduction electron gas. This screening effect may be allowed for approximately by multiplying the above estimate by a factor $\mathrm{e}^{-\kappa R}$ where κ is an appropriate screening constant. In the case of $3d$ transition metals $\mathrm{e}^{-\kappa R} \sim \frac{1}{3} - \frac{1}{2}$, reducing the $(ij|\,1/r\,|ij)$ term to the order of magnitude 2 to 3 eV. For the case in which i and j are now nearest neighbours

$$(ij|\,1/r\,|ij) \sim \frac{2\mathrm{e}^{-\kappa|\mathbf{R}_i - \mathbf{R}_j|}}{|\mathbf{R}_i - \mathbf{R}_j|}\,\mathrm{Ry}$$

The Hubbard model

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

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

$$H = \sum_{Rn,R'n'}^{all} c^{+}_{Rn} h_{Rn,R'n'} c_{R'n'} + \frac{1}{2} \sum_{R,nn',mm}^{all} c^{+}_{Rn} c_{Rn'} v_{nn',mm'} c^{+}_{Rm} c_{Rm'}$$

→ *Focus on the correlated subspace (narrow band across the Fermi level)*

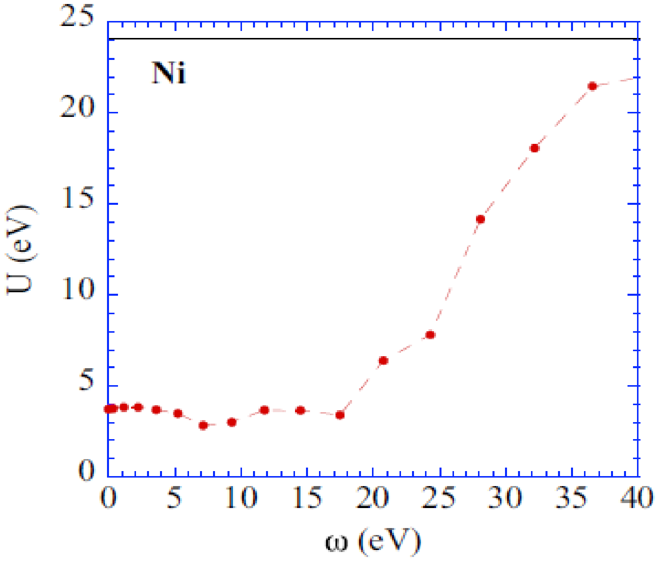
$$H_{Hubbard} = \sum_{Rn,R'n'}^{correl.} c^{+}_{Rn} h_{Rn,R'n'} c_{R'n'} + \frac{1}{2} \sum_{R,nn',mm}^{correl.} c^{+}_{Rn} c_{Rn'} U_{nn',mm'} c^{+}_{Rm} c_{Rm'}$$

How do we map the full Hamiltonian to the Hubbard model?
What is *U* and how do we calculate it?

Key physical idea:

The Hubbard *U* should be obtained as a screened interaction **without screening** from the electrons residing in the subspace that defines the Hubbard model.

Sneak preview



$$v = \int drdr' |\varphi_d(r)|^2\, v(r-r')\, |\varphi_d(r')|^2 \approx 25\,eV$$

$$U = \int drdr' |\varphi_d(r)|^2\, U(r,r';\omega=0)\, |\varphi_d(r')|^2 \approx 3-5\,eV$$

In solids, the bare Coulomb interaction is strongly screened at low energy.

SCREENING

External perturbation

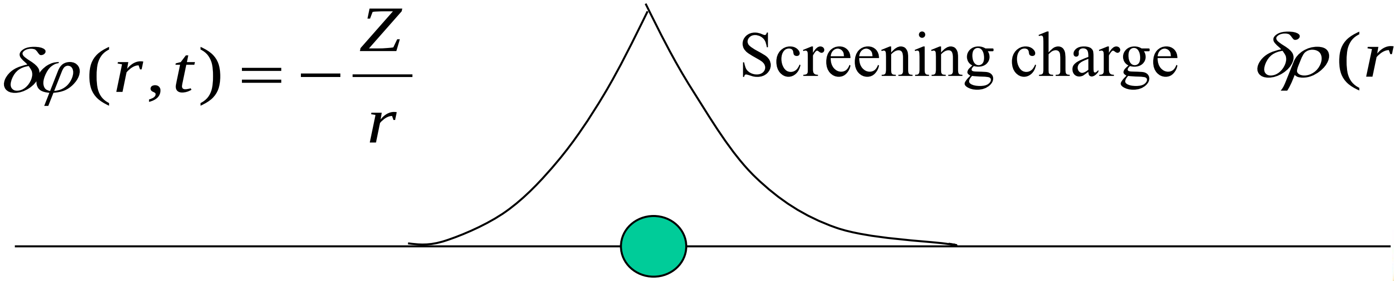
$$\overset{\downarrow}{\delta\varphi}(r,t) \;\rightarrow \delta\rho(r,t) \;\rightarrow \delta V_H(r,t) = \int dr'\, v(r-r')\delta\rho(r',t)$$

$$\delta V_{tot}(r,t) = \delta\varphi(r,t) + \delta V_H(r,t)$$

The external perturbation is *screened* by the electrons.

Example: Proton in an electron gas

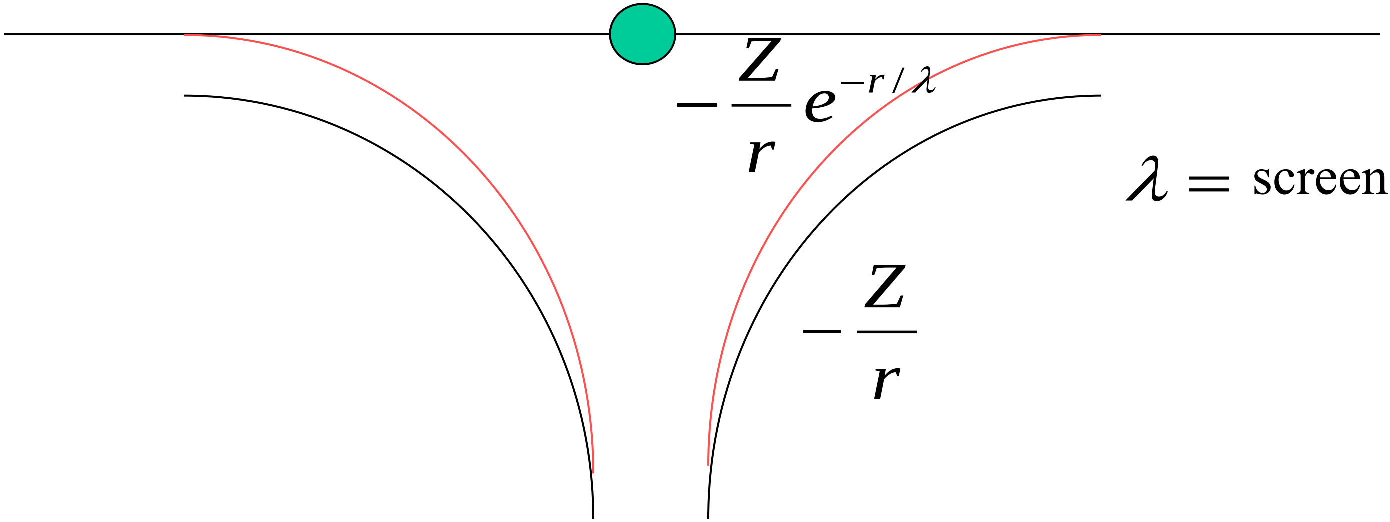
$$\delta\varphi(r,t) = -\frac{Z}{r}$$



Screening charge $\delta\rho(r,t)$

Proton Z

SCREENED POTENTIAL



$$-\frac{Z}{r}e^{-r/\lambda}$$

$$-\frac{Z}{r}$$

$\lambda =$ screening length

In semiconductors or insulators the screening, due to the band gap, is not complete

$$-\frac{Z}{\varepsilon r}$$

SCREENING IN TERMS OF LINEAR RESPONSE FUNCTION

Linear response function

↓

perturbing field

$$\delta\rho(rt) = \int dr'dt'\, \underline{R(rt,r't')}\,\delta\varphi(r't')$$

Key quantity

$$\boxed{\rightarrow R(rt,r't') = \frac{\delta\rho(rt)}{\delta\varphi(r't')}}$$

Total field

$$\delta V_{tot}(rt) = \delta\varphi(rt) + \delta V_H(rt), \quad \delta V_H(rt) = \int dr'\,dt'\, v(r-r')\delta(t-t')\delta\rho(r't')$$

$$\delta V_{tot} = \delta\varphi + v\delta\rho \;= [1+vR]\delta\varphi = \varepsilon^{-1}\delta\varphi$$

$$\varepsilon^{-1} = \frac{\delta V_{tot}}{\delta\varphi} = [1+vR]$$

$$v(1-2) = \frac{1}{|r_1 - r_2|}$$

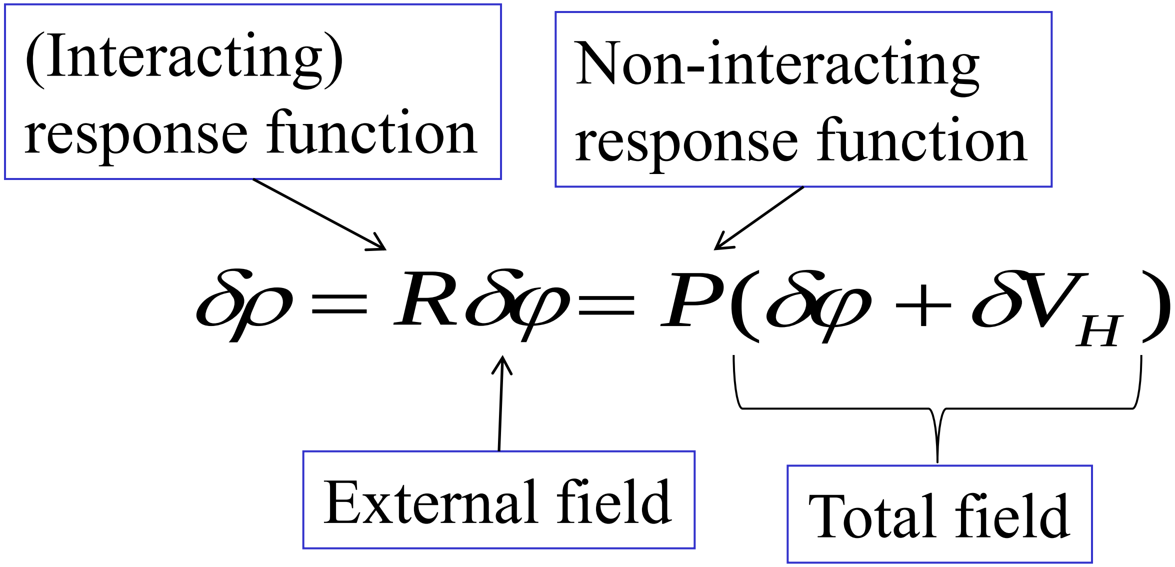
Can think of it as a Coulomb potential at 2 from a point charge at 1

$$\boxed{W = \varepsilon^{-1}v = v + vRv}$$

$W(1,2)$ is the screened Coulomb potential at 2 of a point charge located at 1

TIME-DEPENDENT HARTREE APPROXIMATION or RANDOM-PHASE APPROXIMATION (RPA)

Basic assumption of RPA:
The response of an interacting system to an external perturbation is assumed to be given by the response to the total field as if the system is non-interacting.



(Interacting) response function

Non-interacting response function

$$\delta\rho = R\,\delta\varphi = P\underbrace{(\delta\varphi + \delta V_H)}_{\text{Total field}}$$

External field

$$\delta\rho = R\delta\varphi = P(\delta\varphi + \delta V_H)$$

$$\delta V_H = v\delta\rho = vR\delta\varphi$$

$$R\delta\varphi = P(\delta\varphi + vR\delta\rho) = P(1 + vR)\delta\varphi$$

Since $\delta\varphi$ is arbitrary:

$$R = P(1 + vR) \longrightarrow R = P + PvR$$

$$R = [1 - Pv]^{-1} P = \varepsilon^{-1} P$$

$$W = v + vRv = v + vPv + vPvPv + \ldots$$

$$W = v + vPW$$

To calculate the screened interaction *W* or the response function *R* within the RPA we need the non-interacting response function *P*

TIME-DEPENDENT PERTURBATION THEORY

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = [\hat{H}+\delta\hat{\phi}(t)]|\Psi(t)\rangle$$

Interaction (Dirac) representation: $|\Psi_D(t)\rangle = e^{i\hat{H}t}|\Psi(t)\rangle$

$$i\frac{\partial}{\partial t}|\Psi_D(t)\rangle = \delta\hat{\phi}_D(t)|\Psi_D(t)\rangle, \qquad \delta\hat{\phi}_D(t) = e^{i\hat{H}t}\delta\hat{\phi}(t)e^{-i\hat{H}t}$$

$$|\Psi_D(t)\rangle = |\Psi_D(0)\rangle - i\int_0^t dt'\,\delta\hat{\phi}_D(t')|\Psi_D(0)\rangle$$

To first order in the perturbation

General, also true for interacting systems

INTERACTION PICTURE

$$|\Psi_D(t)\rangle = e^{i\hat{H}t}|\Psi(t)\rangle$$

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle = [\hat{H}+\delta\hat{\phi}(t)]|\Psi(t)\rangle$$

$$i\frac{\partial}{\partial t}\left(e^{-iHt}|\Psi_D(t)\rangle\right) = [\hat{H}+\delta\hat{\phi}(t)]e^{-iHt}|\Psi_D(t)\rangle$$

$$e^{-iHt}\left(H|\Psi_D(t)\rangle + i\frac{\partial}{\partial t}|\Psi_D(t)\rangle\right) = [\hat{H}+\delta\hat{\phi}(t)]e^{-iHt}|\Psi_D(t)\rangle$$

$$i\frac{\partial}{\partial t}|\Psi_D(t)\rangle = e^{iHt}\delta\hat{\phi}(t)e^{-iHt}|\Psi_D(t)\rangle$$

$$i\frac{\partial}{\partial t}|\Psi_D(t)\rangle = \delta\hat{\phi}_D(t)|\Psi_D(t)\rangle, \qquad \delta\hat{\phi}_D(t) = e^{i\hat{H}t}\delta\hat{\phi}(t)e^{-i\hat{H}t}$$

$$i\int_0^t dt'\frac{\partial}{\partial t}|\Psi_D(t')\rangle = \int_0^t dt'\delta\hat{\phi}_D(t')|\Psi_D(t')\rangle,$$

$$|\Psi_D(t)\rangle = |\Psi_D(0)\rangle - i\int_0^t dt'\,\delta\hat{\phi}_D(t')|\Psi_D(0)\rangle$$

To first order in
the perturbation

$$|\Psi_D(t)\rangle = |\Psi_D(0)\rangle - i\int_0^t dt'\,\delta\hat{\phi}_D(t')|\Psi_D(0)\rangle$$

To first order in the perturbation

$$\rho(rt) = \sum_i^N |\varphi_i(rt)|^2$$

Non-interacting system

$$e^{iHt}|\varphi_i(t)\rangle = |\varphi_i\rangle - i\int_0^t dt'\, e^{iHt'}\delta\hat{\phi}(t')e^{-iHt'}|\varphi_i\rangle$$

$$|\varphi_i(t)\rangle = e^{-iHt}|\varphi_i\rangle - i\int_0^t dt'\, e^{iH(t'-t)}\delta\hat{\phi}(t')e^{-iHt'}|\varphi_i\rangle$$

$$= e^{-i\varepsilon_i t}|\varphi_i\rangle - i\int_0^t dt'\sum_n e^{iH(t'-t)}|\varphi_n\rangle\langle\varphi_n|\delta\hat{\phi}(t')e^{-i\varepsilon_i t'}|\varphi_i\rangle$$

$$e^{i\varepsilon_i t}\varphi_i(rt) = \varphi_i(r) - i\int_0^\infty dt'\sum_n \varphi_n(r)\langle\varphi_n|\delta\phi(t')|\varphi_i\rangle e^{-i(\varepsilon_n-\varepsilon_i)(t-t')}\theta(t-t')$$

$$\delta\rho(rt) = \int_0^\infty dt'\int dr'\underbrace{\left\{-i\sum_{i=1}^{occ}\sum_n \varphi_i^*(r)\varphi_n(r)\varphi_i(r')\varphi_n^*(r')e^{-i(\varepsilon_n-\varepsilon_i)(t-t')}\theta(t-t') + c.c.\right\}}_{P(rt,r't')}\delta\phi(r't')$$

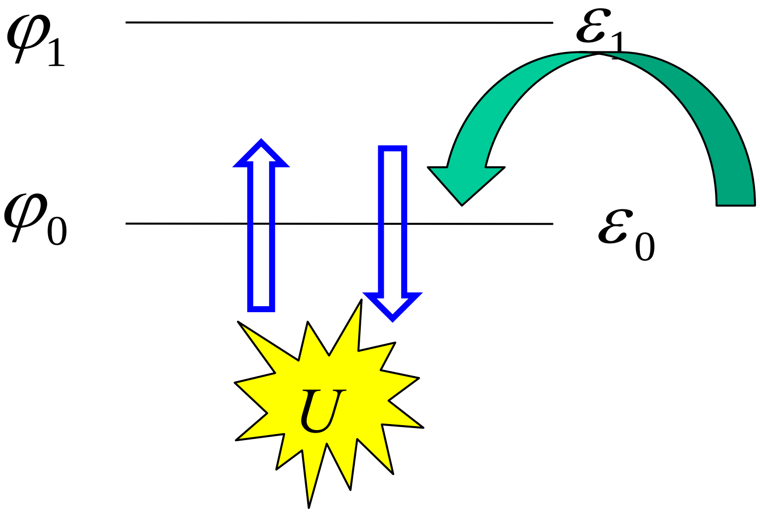
THE NON-INTERACTING LINEAR RESPONSE FUNCTION (RETARDED)

$$P(rt,r't') = -i\sum_{i}^{occ}\sum_{n}\varphi_i^*(r)\varphi_n(r)\varphi_i(r')\varphi_n^*(r')e^{-i(\varepsilon_n-\varepsilon_i)(t-t')}\theta(t-t') + c.c.$$

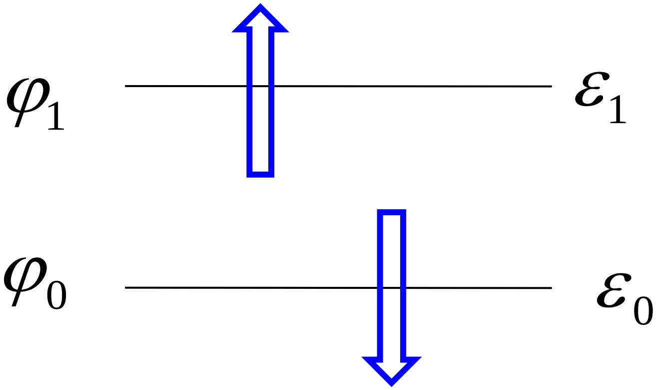
Fourier transform

$$P(r,r';\omega) = \sum_{i}^{occ}\sum_{n}^{unocc}\left[\frac{\varphi_i^*(r)\varphi_n(r)\varphi_i(r')\varphi_n^*(r')}{\omega-(\varepsilon_n-\varepsilon_i)+i\delta} - \frac{\varphi_i(r)\varphi_n^*(r)\varphi_i^*(r')\varphi_n(r')}{\omega+(\varepsilon_n-\varepsilon_i)+i\delta}\right]$$

SCREENING PROCESS



Coulomb repulsion *U*



To reduce the Coulomb interaction the spin-up electron moves to the excited state → polarisation.

Screening or correlation amounts to lowering interaction energy

The Kubo formula for the linear response R

$$i\frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = [\hat{H}+\delta\hat{\phi}(t)]\left|\Psi(t)\right\rangle$$

H = many-electron Hamiltonian

$$\delta\hat{\phi}(t) = \int dr\,\delta\varphi(rt)\hat{\rho}(rt)$$

Interaction (Dirac) representation $\left|\Psi_D(t)\right\rangle = e^{i\hat{H}t}\left|\Psi(t)\right\rangle$

$$i\frac{\partial}{\partial t}\left|\Psi_D(t)\right\rangle = \delta\hat{\phi}_D(t)\left|\Psi_D(t)\right\rangle, \qquad \delta\hat{\phi}_D(t) = e^{-i\hat{H}t}\delta\hat{\phi}(t)e^{i\hat{H}t}$$

$$\left|\Psi_D(t)\right\rangle = \left|\Psi_D(0)\right\rangle - i\int_0^t dt'\,\delta\hat{\phi}(t')\left|\Psi_D(t')\right\rangle$$

$$\delta\rho(rt) = \left\langle\Psi_D(t)\right|\hat{\rho}_D(rt)\left|\Psi_D(t)\right\rangle - \left\langle\Psi_D(0)\right|\hat{\rho}_D(r,0)\left|\Psi_D(0)\right\rangle$$

$$= i\int_0^t dt'\left\langle\Psi_D(0)\right|[\delta\hat{\phi}_D(t'),\hat{\rho}_D(rt)]\left|\Psi_D(0)\right\rangle$$

$$= \int_0^t dt'\int dr'\,(-i)\left\langle\Psi_D(0)\right|[\hat{\rho}_D(rt),\hat{\rho}_D(r't')]\left|\Psi_D(0)\right\rangle\,\delta\varphi(r't')$$

$$\delta\rho(rt) = \int_0^\infty dt' \int dr' \, (-i)\langle \Psi_D(0) \,|\, [\hat{\rho}_D(rt), \hat{\rho}_D(r't')] \,|\, \Psi_D(0) \rangle \, \theta(t-t') \, \delta\varphi(r't')$$

Compare with $\delta\rho(rt) = \int dr'dt' \, R(rt, r't')\delta\varphi(r't')$

Retarded linear response function
(density-density correlation function)

$$R(rt, r't') = -i\langle \Psi_D(0) \,|\, [\hat{\rho}_D(rt), \hat{\rho}_D(r't')] \,|\, \Psi_D(0) \rangle \theta(t-t')$$

GREEN FUNCTION

$$iG(rt,r't')=\left\langle \Psi_0 \,|\, T[\hat{\psi}(rt)\hat{\psi}^+(r't')] \,|\, \Psi_0 \right\rangle \quad =\left\langle \Psi_0 \,|\, \hat{\psi}(rt)\hat{\psi}^+(r't') \,|\, \Psi_0 \right\rangle \theta(t-t')$$

$$-\left\langle \Psi_0 \,|\, \hat{\psi}^+(r't')\hat{\psi}(rt) \,|\, \Psi_0 \right\rangle \theta(t'-t)$$

Ψ_0 is the exact *N*-electron ground state : $\hat{H}\Psi_0 = E_0\Psi_0$

The field operator is defined in the Heisenberg picture: $\hat{\psi}(rt)=e^{i\hat{H}t}\hat{\psi}(r)e^{-i\hat{H}t}$

Consider the case $t > t'$

$$\hat{\psi}(r)=\sum_n \varphi_n(r)\hat{c}_n$$

$$iG(rt,r't')=\left\langle \Psi_0 \,|\, e^{iHt}\hat{\psi}(r)e^{-iHt} \underset{\Uparrow}{\;} e^{iHt'}\hat{\psi}^+(r')e^{-iHt'} \,|\, \Psi_0 \right\rangle$$

Insert a complete set of eigenstates of *H:* $\sum_n |n\rangle\langle n|$

Fourier transformation yields the Lehmann or spectral representation of the Green function:

$$G(r,r';\omega)=\sum_n \left\{ \frac{f_n(r)f_n^*(r')}{\omega - E_n(N+1)+E_0+i\delta} - \frac{h_n(r)h_n^*(r')}{\omega + E_n(N-1)-E_0-i\delta} \right\}$$

$$f_n(r)=\left\langle \Psi_0 \,|\, \hat{\psi}(r) \,|\, \Psi_n(N+1) \right\rangle, \quad h_n(r)=\left\langle \Psi_0 \,|\, \hat{\psi}^+(r) \,|\, \Psi_n(N-1) \right\rangle$$

$$iG(rt, r't') = \left\langle \Psi_0 \,|\, T[\hat{\psi}(rt)\hat{\psi}^+(r't')] \,|\, \Psi_0 \right\rangle$$

From the Green function we can obtain the expectation value of any one-particle operator in the ground state.

In position representation $\hat{A} = \sum_i A(\hat{r}_i)$

In occupation number rep. (second quantisation) $\hat{A} = \int dr\, \hat{\psi}^+(r) A(r) \hat{\psi}(r)$

$$\hat{\psi}(r) = \sum_n \varphi_n(r)\hat{c}_n$$

Density

$$\hat{\rho}(r) = \sum_i \rho(r - \hat{r}_i)$$

$$\hat{\rho}(r) = \int dr' \hat{\psi}^+(r')\delta(r - r')\hat{\psi}(r') = \hat{\psi}^+(r)\hat{\psi}(r)$$

$$\hat{\rho}(r) = \hat{\psi}^+(r)\hat{\psi}(r) = -iG(rt, rt^+)$$

Kinetic energy

$$\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2$$

$$\hat{T} = -\frac{1}{2}\int dr\,\hat{\psi}^{+}(r)\nabla^2\hat{\psi}(r)$$

$$\hat{T} = \frac{i}{2}\lim_{r'\to r}\int dr\nabla^2 G(rt, r't^{+})$$

Total energy (special case)

$$E = T - \frac{i}{2}\lim_{r'\to r, t'\to t^{+}}\int dr\left(i\frac{\partial}{\partial t} - h_0(r)\right)G(rt, r't')$$

GREEN FUNCTION IN THE INTERACTION PICTURE

$$iG(1,2)=\frac{\left\langle \Psi_0 \,|\, T[\hat{S}\hat{\psi}(1)\hat{\psi}^{+}(2)] \,|\, \Psi_0 \right\rangle}{\left\langle \Psi_0 \,|\, \hat{S} \,|\, \Psi_0 \right\rangle}$$

$$\hat{S}=T\exp\left[-i\int d3\,\varphi(3)\hat{\rho}(3)\right] \qquad 1=r_1 t_1$$

φ is an external perturbation

Ψ_0 is the exact ground state *without* the perturbation: $\hat{H}\Psi_0=E_0\Psi_0$

The field operator in the interaction picture is *independent* of φ

$$\hat{\psi}(rt)=e^{i\hat{H}t}\hat{\psi}(r)e^{-i\hat{H}t}$$

$$R(1,2)=\frac{\delta\rho(1)}{\delta\varphi(2)}=-i\left.\frac{\delta G(1,1^{+})}{\delta\varphi(2)}\right|_{\varphi=0}=\left.\frac{\delta}{\delta\varphi(2)}\frac{\left\langle \Psi_0 \,|\, T[\hat{S}\hat{\rho}(1)] \,|\, \Psi_0 \right\rangle}{\left\langle \Psi_0 \,|\, \hat{S} \,|\, \Psi_0 \right\rangle}\right|_{\varphi=0}$$

$$\left.\frac{\delta\hat{S}}{\delta\varphi(2)}\right|_{\varphi=0}=-iT\left[\hat{S}\hat{\rho}(2)\right]_{\varphi=0}=-i\hat{\rho}(2) \qquad \hat{S}(\varphi=0)=1$$

The Kubo formula

$$R(1,2)=-i\left[\left\langle \Psi_0 \,|\, T[\hat{\rho}(1)\hat{\rho}(2)] \,|\, \Psi_0 \right\rangle-\rho(1)\rho(2)\right]$$

$$=-i\left\langle \Psi_0 \,|\, T[\Delta\hat{\rho}(1)\Delta\hat{\rho}(2)] \,|\, \Psi_0 \right\rangle \qquad \Delta\hat{\rho}=\hat{\rho}-\rho$$

$$\hat{\psi}_H(t)=\hat{U}_D(0,t)\hat{\psi}_D(t)\hat{U}_D(t,0) \qquad \left|\psi_D(t)\right\rangle = U(t,0)\left|\psi_D(0)\right\rangle$$

$$\hat{U}(t_1,t_2) = T\exp\left[-i\int_{t_1}^{t_2} dt_3 \int dr_3\; \varphi(3)\hat{\rho}(3)\right] \qquad \hat{S} = \hat{U}(-\infty,\infty)$$

$$\begin{aligned} & iG_{\sigma\sigma'}(1,2) \\ &= \frac{\left\langle 0|T[\hat{U}(\infty,0)\hat{U}(0,t_1)\hat{\psi}_D(1)\hat{U}(t_1,0)\hat{U}(0,t_2)\hat{\psi}_D^{+}(2)\hat{U}(t_2,0)\hat{U}(0,-\infty)|0\right\rangle}{\left\langle 0|\hat{U}(\infty,0)\hat{U}(0,-\infty)|0\right\rangle} \\ &= \frac{\left\langle\Psi_D(0)|T[\psi_H(1)\psi_H^{+}(2)]|\Psi_D(0)\right\rangle}{\langle\Psi_D(0)|\Psi_D(0)\rangle} \\ &= \frac{\left\langle\Psi_0|T[\psi_H(1)\psi_H^{+}(2)]|\Psi_0\right\rangle}{\langle\Psi_H|\Psi_H\rangle}. \end{aligned}$$

To obtain the third line we have utilised the condition that the state at $t = \pm\infty$ is the interacting state without the perturbing field φ so that

$$|\Psi_D(0)\rangle = \hat{U}(0,-\infty)\,|0\rangle\,, \quad \langle\Psi_D(0)| = \langle 0|\,\hat{U}(\infty,0).$$

Using $\Delta\hat{\rho}(rt) = e^{i\hat{H}t}\Delta\hat{\rho}(r)e^{-i\hat{H}t}$

and inserting a complete set of eigenstates of *H* in between the density fluctuation operators and Fourier transforming yields the Lehmann or spectral representation of the response function:

$$R(r,r';\omega) = \sum_n \left\{ \frac{\langle \Psi_0 | \Delta\hat{\rho}(r') | n \rangle \langle n | \Delta\hat{\rho}(r) | \Psi_0 \rangle}{\omega - E_n + E_0 + i\delta} - \frac{\langle \Psi_0 | \Delta\hat{\rho}(r) | n \rangle \langle n | \Delta\hat{\rho}(r') | \Psi_0 \rangle}{\omega + E_n - E_0 - i\delta} \right\}$$

The poles of *R* give the exact excitation energies of the interacting *N*-electron system.

TIME-DEPENDENT HARTREE APPROXIMATION (RANDOM-PHASE APPROXIMATION)

$$R(1,2) = \frac{\delta\rho(1)}{\delta\varphi(2)} = -i\,\frac{\delta G(1,1^{+})}{\delta\varphi(2)}$$

$$GG^{-1} = 1 \rightarrow \frac{\delta G}{\delta\varphi}G^{-1} + G\frac{\delta G^{-1}}{\delta\varphi} = 0 \rightarrow \frac{\delta G}{\delta\varphi} = -G\frac{\delta G^{-1}}{\delta\varphi}G$$

From the equation of motion

$$\left[i\frac{\partial}{\partial t} - h_0 - \varphi - V_H - \Sigma\right]G = 1 \rightarrow G^{-1} = -\left[-i\frac{\partial}{\partial t} + h_0 + \varphi + V_H + \Sigma\right]1$$

$$\rightarrow \frac{\delta G^{-1}}{\delta\varphi} = -\left[1 + \frac{\delta V_H}{\delta\varphi} + \frac{\delta\Sigma}{\delta\varphi}\right]$$

$$R = -i\frac{\delta G}{\delta\varphi} = iG\frac{\delta G^{-1}}{\delta\varphi}G = -iG\left[1 + \frac{\delta V_H}{\delta\varphi} + \frac{\delta\Sigma}{\delta\varphi}\right]G$$

Time-dependent Hartree
(Random-Phase Approximation)

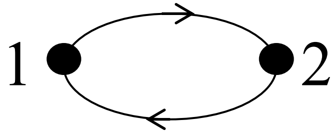
$$\frac{\delta\Sigma}{\delta\varphi} = 0 \rightarrow \quad R = -iG\left[1 + \frac{\delta V_H}{\delta\varphi}\right]G$$

$$R(1,2) = -iG(1,2)G(2,1^+) - i\int d3\, G(1,3)\frac{\delta V_H(3)}{\delta\varphi(2)}G(3,1^+)$$

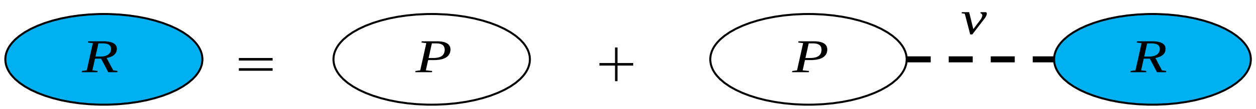
$$\frac{\delta V_H(3)}{\delta\varphi(2)} = \int d4\, v(3-4)\frac{\delta\rho(4)}{\delta\varphi(2)} = \int d4\, v(3-4)R(4,2)$$

$$P(1,2) = -iG(1,2)G(2,1^+)$$

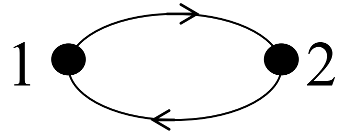
Polarisation function



$$R(1,2) = P(1,2) + \int d3\, d4\, P(1,3)v(3-4)R(4,2)$$



$$P(r,r';\omega) = -i\int d\omega\, G(r,r';\omega+\omega')G(r',r;\omega')$$



$$G^0(r,r';\omega) = \sum_n^{occ} \frac{\varphi_n(r)\varphi_n^*(r')}{\omega-\varepsilon_n-i\delta} + \sum_m^{unocc} \frac{\varphi_n(r)\varphi_n^*(r')}{\omega-\varepsilon_m+i\delta}$$

$$P^0(r,r';\omega) = \sum_n^{occ}\sum_m^{unocc}\left\{ \frac{\varphi_n^*(r)\varphi_m(r)\varphi_n(r')\varphi_m^*(r')}{\omega-\varepsilon_m+\varepsilon_n+i\delta} - \frac{\varphi_n(r)\varphi_m^*(r)\varphi_n^*(r')\varphi_m(r')}{\omega+\varepsilon_m-\varepsilon_n-i\delta} \right\}$$

$$P^0(r,r';\omega) = \sum_\alpha \left[\frac{b_\alpha(r)b_\alpha^*(r')}{\omega-\Delta_\alpha} - \frac{b_\alpha^*(r)b_\alpha(r')}{\omega+\Delta_\alpha} \right]$$

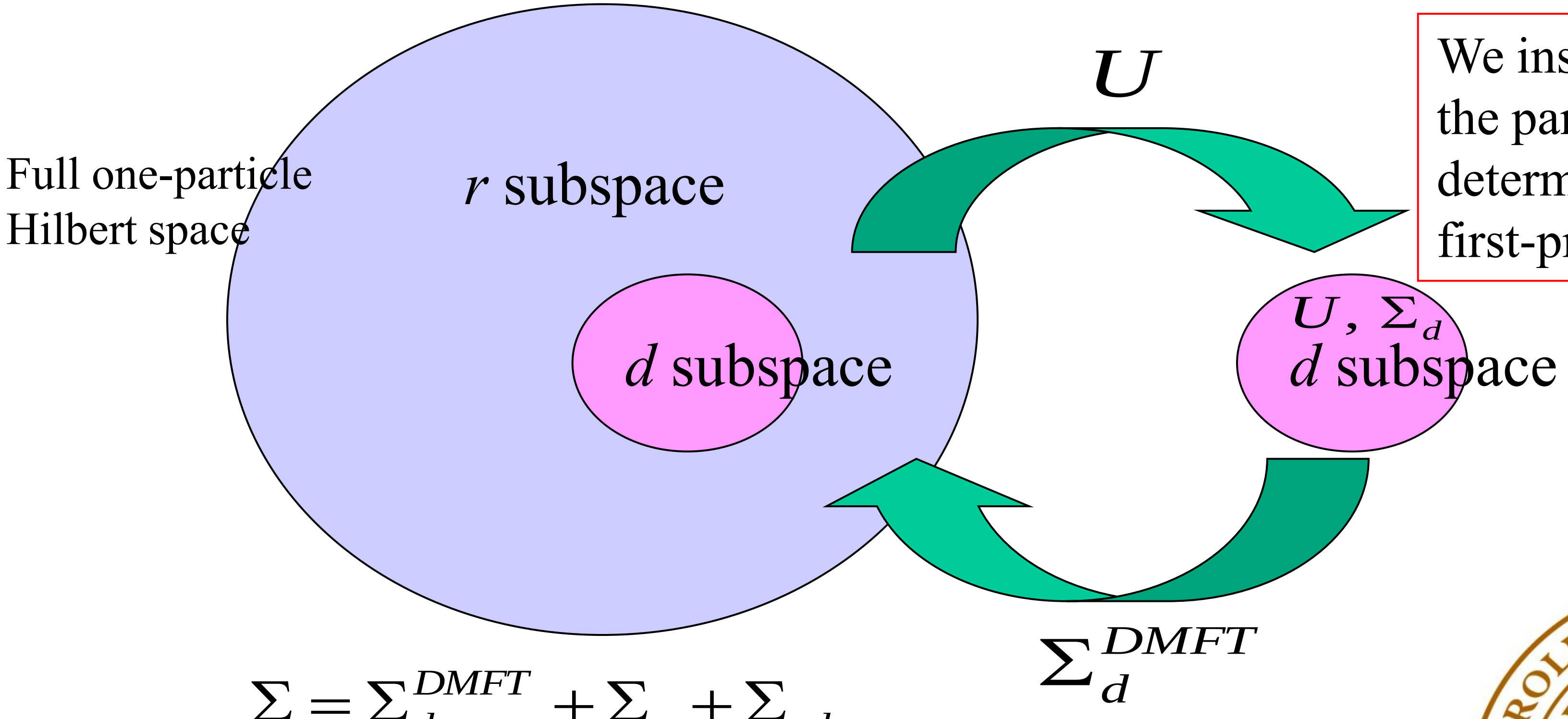
$$b_\alpha = \varphi_n^*\varphi_m, \quad \Delta_\alpha = \varepsilon_m-\varepsilon_n-i\eta, \quad \varepsilon_m>\mu, \;\; \varepsilon_n<\mu$$

First-Principles Methods:
Parameter-free but insufficient
for strongly correlated systems

- Local Density Approximation (LDA)
- GW method

Model Approaches:
Good for strongly correlated systems
but need parameters

- Dynamical Mean-Field Theory(DMFT)



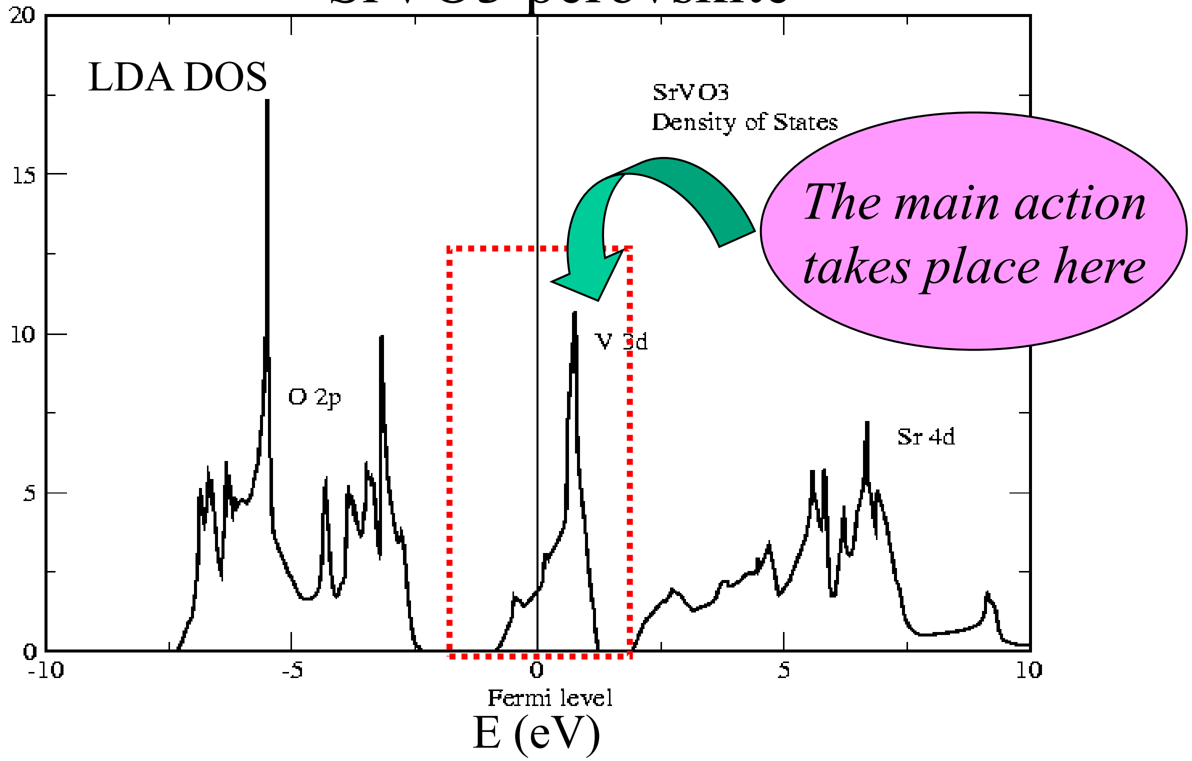
We insist that
the parameters are
determined from
first-principles

$$\Sigma = \Sigma_d^{DMFT} + \underbrace{\Sigma_r + \Sigma_{rd}}_{\text{e.g., GW approximation}}$$

PRL **102**, 176402 (2009)

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

SrVO3 perovskite



The main action takes place here

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

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

Related works on constrained RPA

Random-Phase Approximation (RPA):

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

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

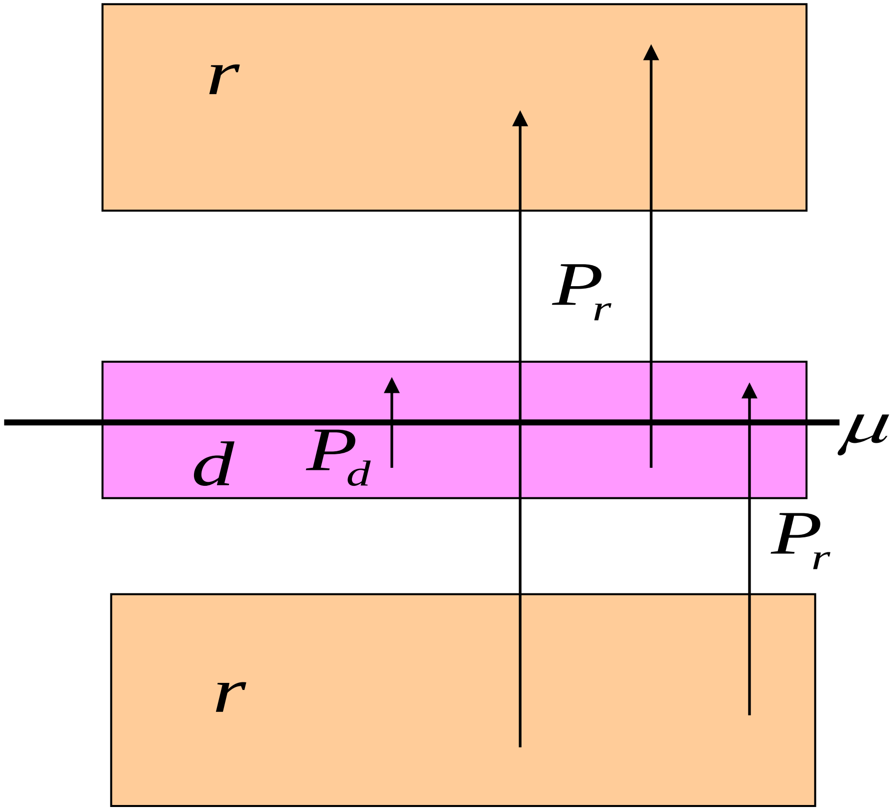
Constrained RPA (cRPA)

→PRB 70, 195104 (2004)

→PRB 80, 155134 (2009) for entangled bands

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

Polarisation: $P = P_d + P_r$



PRB 70, 195104 (2004)

Derivation of cRPA formula for *U*

Fully screened interaction

$$W = v + vPW \;\longrightarrow W = (1 - vP)^{-1} v$$

$$W = (1 - vP)^{-1}(1 - vP_r)(1 - vP_r)^{-1} v$$

$$= [(1 - vP_r)^{-1}(1 - vP)]^{-1}(1 - vP_r)^{-1} v \qquad (AB)^{-1} = B^{-1}A^{-1}$$

$$= [(1 - vP_r)^{-1}(1 - vP_r - vP_d)]^{-1}(1 - vP_r)^{-1} v$$

$$= [1 - \underbrace{(1 - vP_r)^{-1} v}_{W_r} P_d]^{-1} \underbrace{(1 - vP_r)^{-1} v}_{W_r}$$

$$W = (1 - W_r P_d)^{-1} W_r$$

$W_r = (1 - vP_r)^{-1} v$ is interpreted as the Hubbard *U*

$$U = v + vP_r U$$

Polarisation function in RPA: vertex $\Gamma = 1 \rightarrow P=-iGG$

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

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

$$P_r = P - P_d$$

$$U(r,r';\omega)=v(r-r')+\int dr_1 dr_2 v(r-r_1)P_r(r_1,r_2;\omega)U(r_2,r';\omega)$$

Basis independent, can use any bandstructure method.

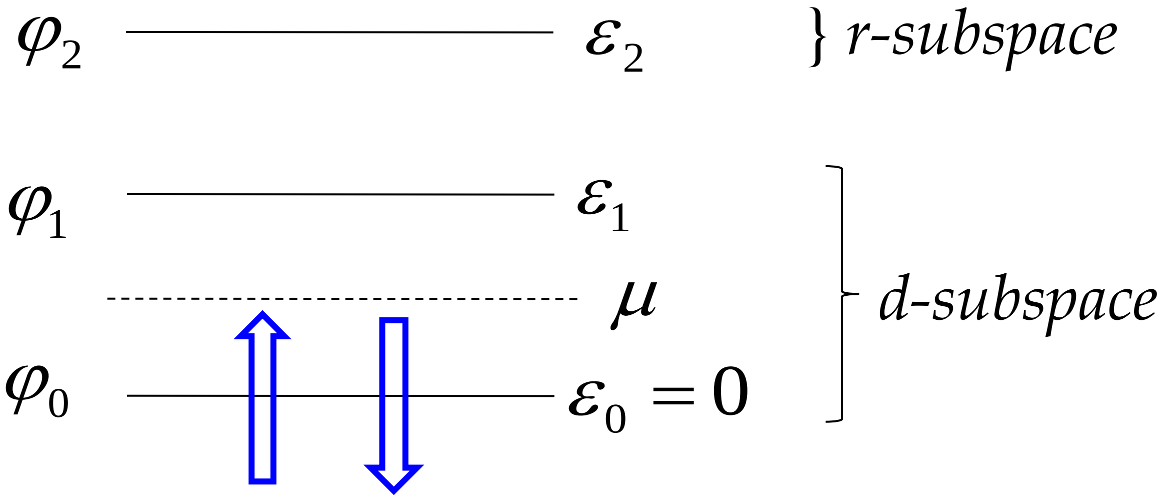
$$U_{ij,kl}(\omega)=\int drdr'\,\varphi_i(r)\varphi_j(r)U(r,r';\omega)\varphi_k(r')\varphi_l(r')$$

The *matrix elements* of *U* evidently depend on the choice of the orbitals

The Hubbard *U* is determined by two factors:

- Screening
- The choice of the orbitals

A simple model



φ_2 ε_2 } *r-subspace*

φ_1 ε_1

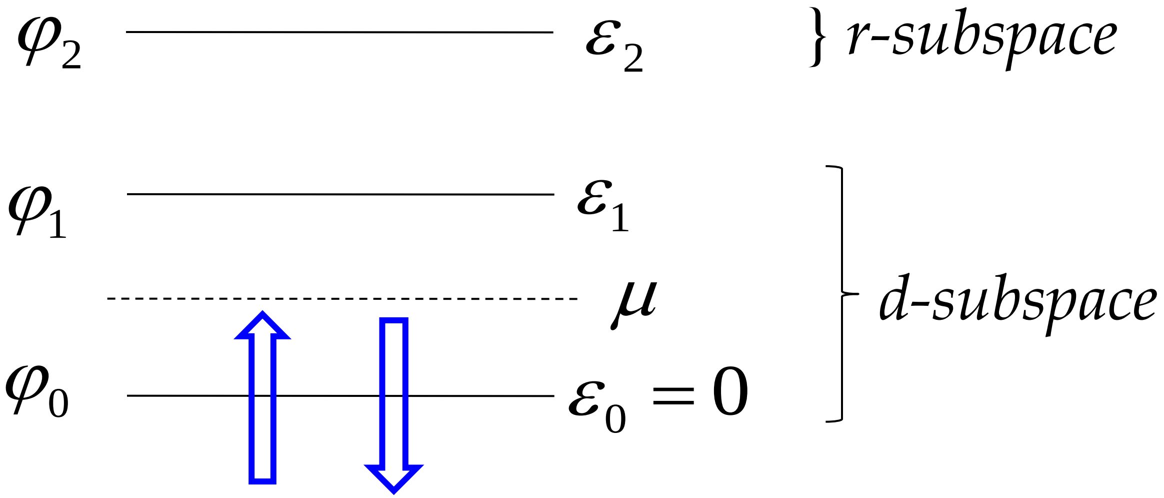
μ *d-subspace*

φ_0 $\varepsilon_0 = 0$

The bare interaction is *v*.
Our aim is to calculate the effective interaction *U* in the *d*-subspace

Define $\boxed{b_{ij} = \varphi_i \varphi_j}$

A simple model



φ_2 ε_2 } *r-subspace*

φ_1 ε_1

μ *d-subspace*

φ_0 $\varepsilon_0 = 0$

$$b_{ij} = \varphi_i \varphi_j$$

$$P(1,2;\omega) = 2\left(\frac{b_{01}(1)b_{01}(2)}{\omega - \varepsilon_1 + i\delta} - \frac{b_{01}(1)b_{01}(2)}{\omega + \varepsilon_1 - i\delta} \right) + 2\left(\frac{b_{02}(1)b_{02}(2)}{\omega - \varepsilon_2 + i\delta} - \frac{b_{02}(1)b_{02}(2)}{\omega + \varepsilon_2 - i\delta} \right)$$

$$P_d(1,2;\omega) = 2\left(\frac{b_{01}(1)b_{01}(2)}{\omega - \varepsilon_1 + i\delta} - \frac{b_{01}(1)b_{01}(2)}{\omega + \varepsilon_1 - i\delta} \right)$$

$$P_r(1,2;\omega) = 2\left(\frac{b_{02}(1)b_{02}(2)}{\omega - \varepsilon_2 + i\delta} - \frac{b_{02}(1)b_{02}(2)}{\omega + \varepsilon_2 - i\delta} \right)$$

The Hubbard *U*

$$P_r(1,2;\omega) = 2\left(\frac{b_{02}(1)b_{02}(2)}{\omega-\varepsilon_2+i\delta} - \frac{b_{02}(1)b_{02}(2)}{\omega+\varepsilon_2-i\delta}\right) \quad = \quad b_{02}(1)P_r(\omega)b_{02}(2)$$

$$P_r(\omega) = 2\left(\frac{1}{\omega-\varepsilon_2+i\delta} - \frac{1}{\omega+\varepsilon_2-i\delta}\right)$$

$$U(1,2) = v(1,2) + \int d3d4\, v(1,3)P_r(3,4;\omega)U(4,2)$$

$$= v(1,2) + \int d3d4\, v(1,3)b_{02}(3)P_r(\omega)b_{02}(4)U(4,2)$$

Let us calculate $\langle \varphi_0\varphi_0 | U | \varphi_0\varphi_0 \rangle = \langle b_{00} | U | b_{00} \rangle = U_{00,00}$ “Onsite *U*”

“Onsite U”

$$U(1,2) = v(1,2) + \int d3d4\, v(1,3) b_{02}(3) P_r(\omega) b_{02}(4) U(4,2)$$

Take expectation value $\langle b_{00} |$ $| b_{00} \rangle$ on both sides

$$U_{00,00} = v_{00,00} + v_{00,02} P_r(\omega) U_{02,00}$$

Take expectation value $\langle b_{02} |$ $| b_{00} \rangle$ on both sides

$$U_{02,00} = v_{02,00} + v_{02,02} P_r(\omega) U_{02,00}$$

$$U_{02,00} = \frac{v_{02,00}}{1 - v_{02,02} P_r(\omega)}$$

$$U_{00,00}(\omega) = v_{00,00} + \frac{v_{00,02} P_r(\omega) v_{02,00}}{1 - v_{02,02} P_r(\omega)}$$

“Hund’s exchange *J*”

$$U(1,2) = v(1,2) + \int d3d4\, v(1,3) b_{02}(3) P_r(\omega) b_{02}(4) U(4,2)$$

Take expectation value $\langle b_{01}| \qquad |b_{01}\rangle$ on both sides

$$J = U_{01,01} = v_{01,01} + v_{01,02} P_r(\omega) U_{02,01}$$

Take expectation value $\langle b_{02}| \qquad |b_{01}\rangle$ on both sides

$$U_{02,01} = v_{02,01} + v_{02,02} P_r(\omega) U_{02,01}$$

$$U_{02,01} = \frac{v_{02,01}}{1 - v_{02,02} P_r(\omega)}$$

$$J(\omega) = U_{01,01}(\omega) = v_{01,01} + \frac{v_{01,02} P_r(\omega) v_{02,01}}{1 - v_{02,02} P_r(\omega)}$$

U and J

$$U_{00,00}(\omega) = v_{00,00} + \frac{v_{00,02}P_r(\omega)v_{02,00}}{1 - v_{02,02}P_r(\omega)}$$

$$U_{11,11}(\omega) = v_{11,11} + \frac{v_{11,02}P_r(\omega)v_{02,11}}{1 - v_{02,02}P_r(\omega)}$$

$$J(\omega) = U_{01,01}(\omega) = v_{01,01} + \frac{v_{01,02}P_r(\omega)v_{02,01}}{1 - v_{02,02}P_r(\omega)}$$

$$v_{01,02} << v_{00,02}, \quad v_{01,02} << v_{11,02}$$

→ In contrast to *U*, J is much less screened

J is close to its atomic value

Advantages of cRPA:

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

Justification of RPA:

U is determined mainly by long-range screening.
Short-range screening is taken care of by the Hubbard model.
cRPA is general, can go beyond RPA .

For isolated d subspace

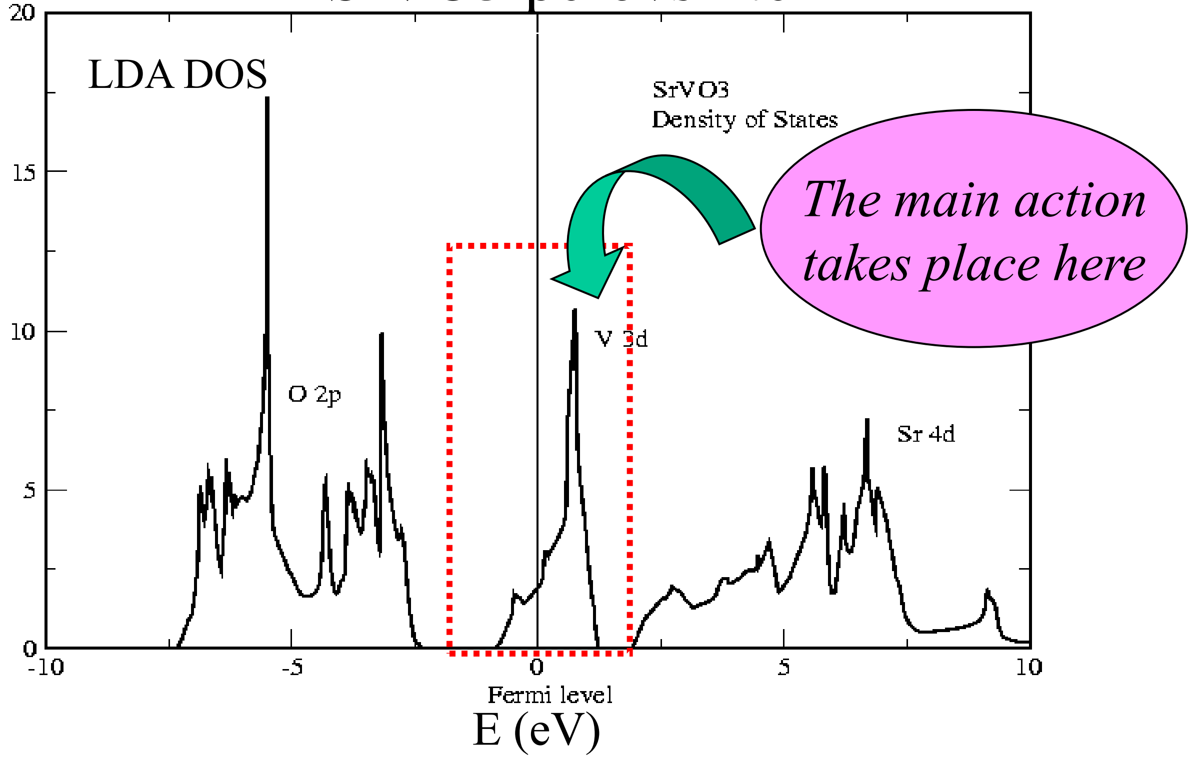
$$U \sim \frac{1}{\alpha r}$$

is *long range*,
because metallic screening is absent when calculating *U*.

$$\alpha > 1$$

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

SrVO3 perovskite



The main action takes place here

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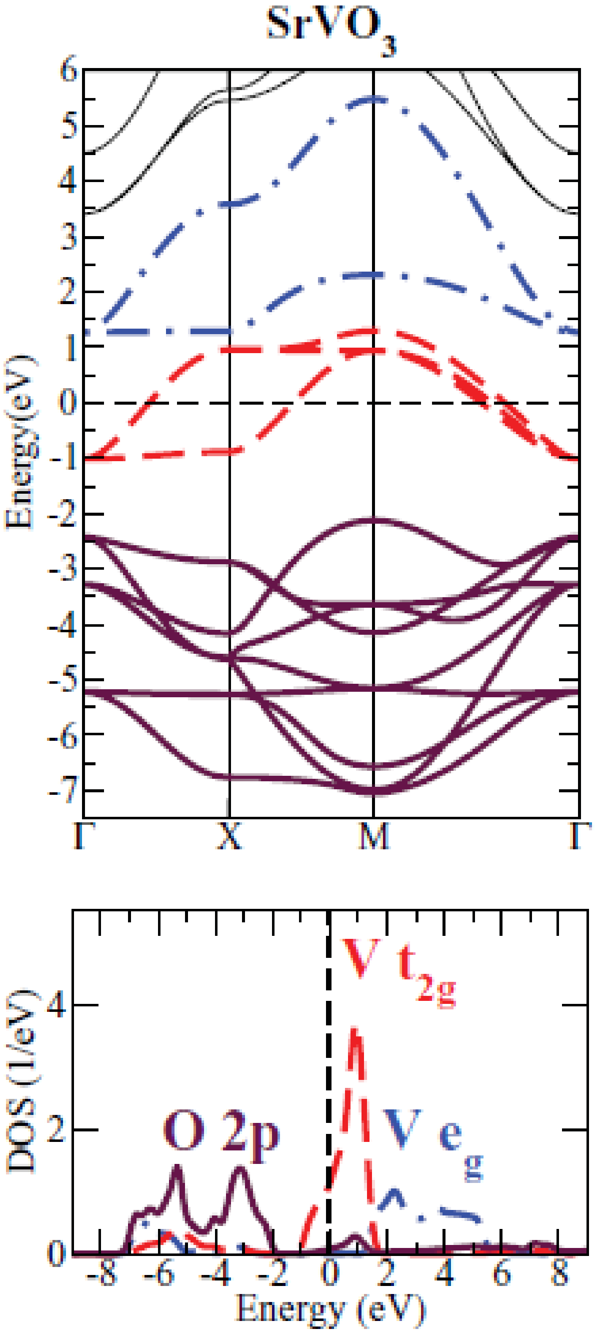


Vaugier, Jiang, and Biermann, PHYSICAL REVIEW B **86**, 165105 (2012)

Maximally localised Wannier orbitals

$$|\varphi_{n\mathbf{R}}\rangle = \frac{V}{(2\pi)^3}\int d^3k\, e^{-i\mathbf{k}\cdot\mathbf{R}}|\psi^{(\mathrm{w})}_{\mathbf{k}n}\rangle,$$

$$\left|\psi_{kn}^{(w)}\right\rangle = \sum \left|\psi_{km}\right\rangle S_{mn}(k)$$

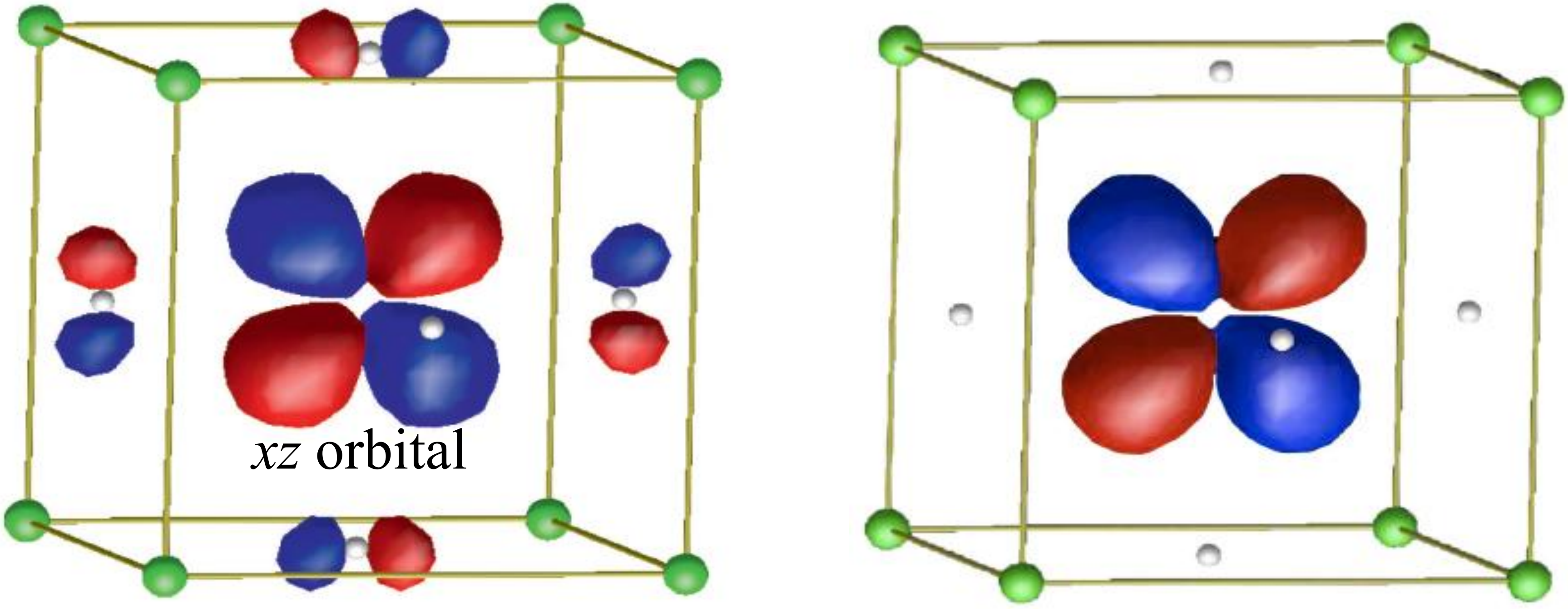
LDA wave functions

By varying *S,* minimise the extent of the orbitals

$$\Omega = \sum_n \left(\langle\varphi_{n\mathbf{0}}|r^2|\varphi_{n\mathbf{0}}\rangle - |\langle\varphi_{n\mathbf{0}}|\mathbf{r}|\varphi_{n\mathbf{0}}\rangle|^2\right)$$

Marzari and Vanderbilt, PRB 56, 12847 (1997)

Wannier orbitals of SrVO3



t_{2g} model

$(t_{2g}+e_g)+O_p$ model

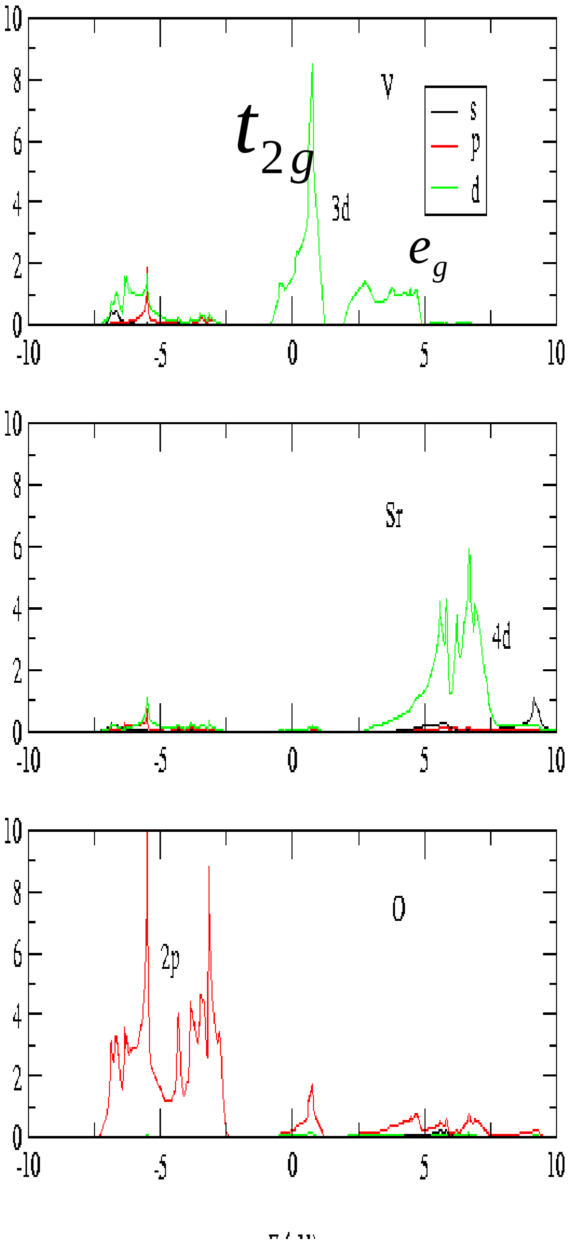
Fig. 4: *Contour plot of the maximally localized Wannier function (MLWF) of* $SrVO_3$*. If we take the x axis to be the horizontal direction and the z axis to be the vertical direction, the Wannier function corresponds to xz. The red (blue) represents the positive (negative) contour. The Wannier function is centered at the vanadium site, which is located at the center of the cube. The green spheres at the corners are strontium atoms, and white spheres at the centers of the faces are oxygen atoms. The MLWF is optimized in the* t_{2g} *model which consists of three* t_{2g}*-like states. We note that the Wannier function has tails on the oxygen sites.*

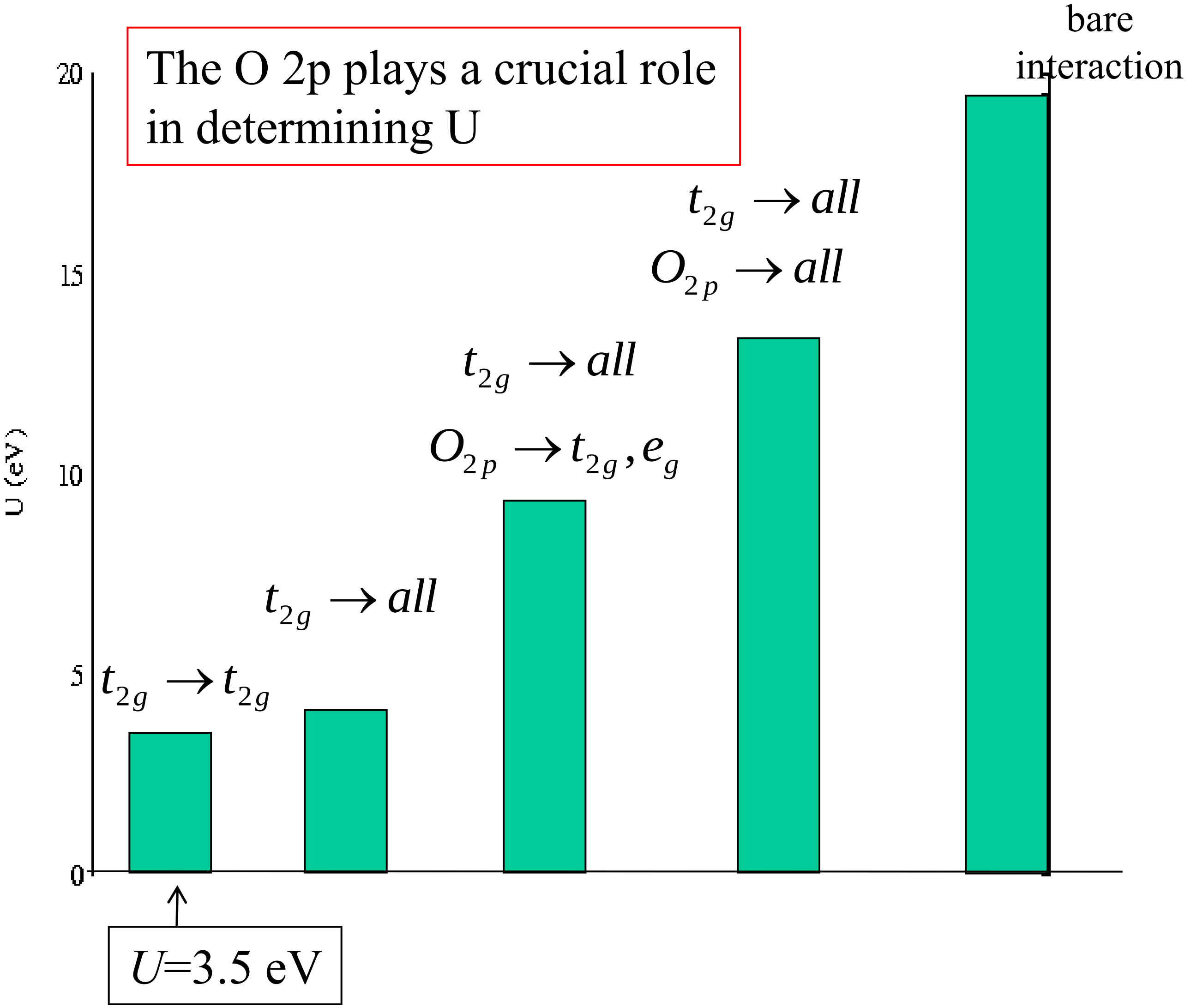
SrVO3

Controlling the screening channels:

U as a function of P_d (*eliminated* transitions)

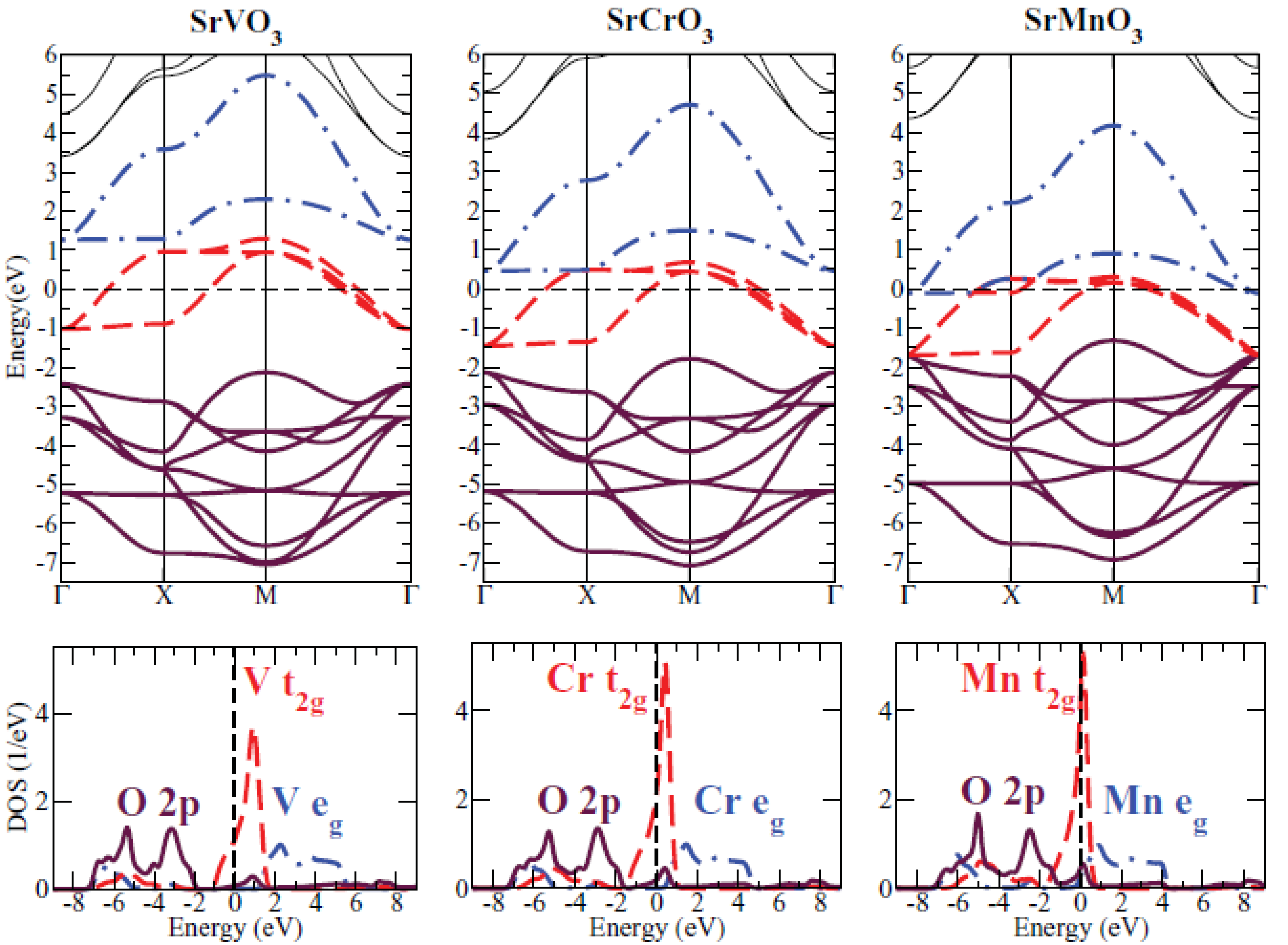
LDA Density of States of SrVO3




The O 2p plays a crucial role in determining U

PRB 74, 125106 (2006)

c.f. Solovyev PRB 2007



Well separated
from other bands

Vaugier, Jiang, and Biermann, PHYSICAL REVIEW B **86**, 165105 (2012)

LOÏG VAUGIER, HONG JIANG, AND SILKE BIERMANN

PHYSICAL REVIEW B **86**, 165105 (2012)

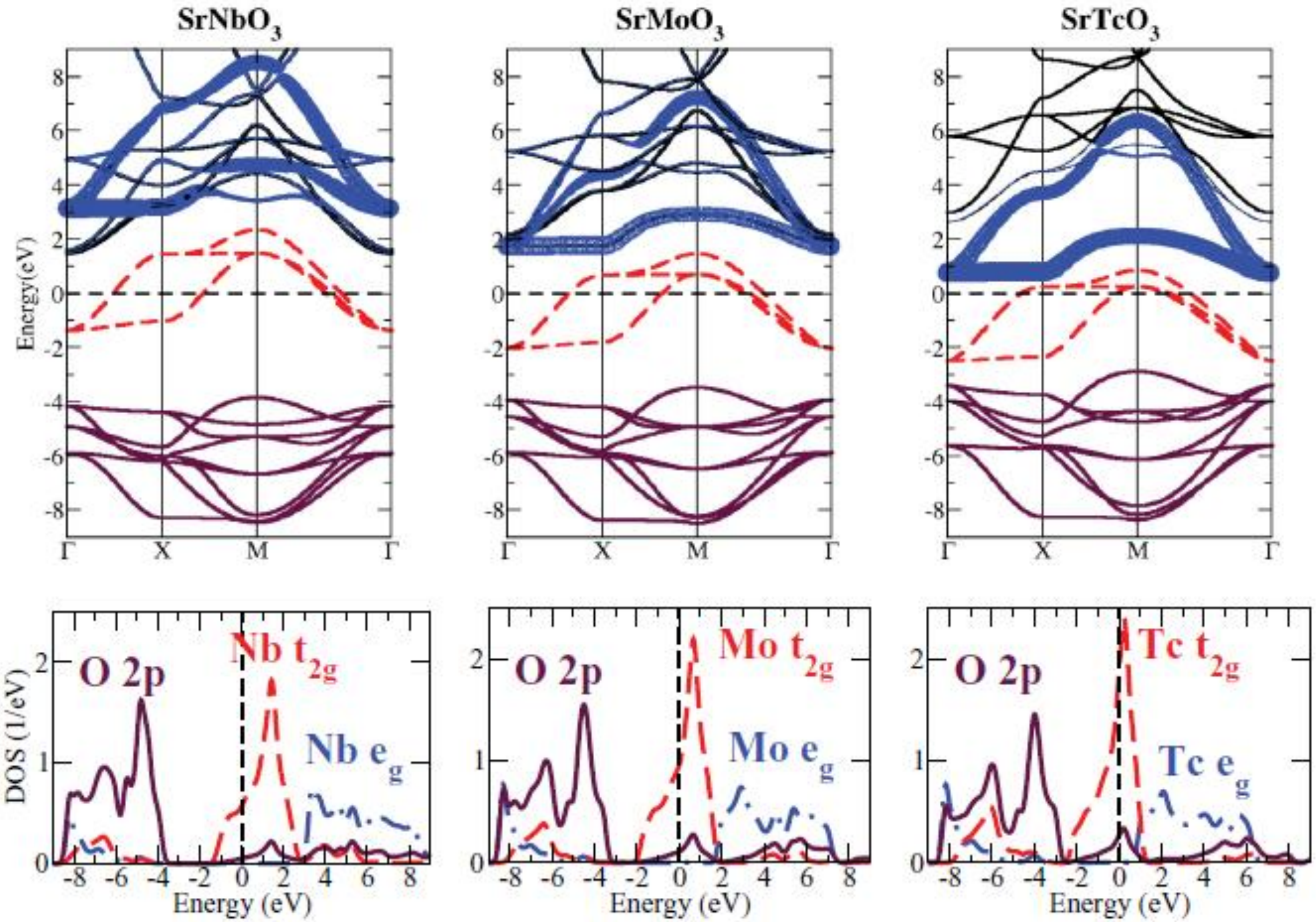
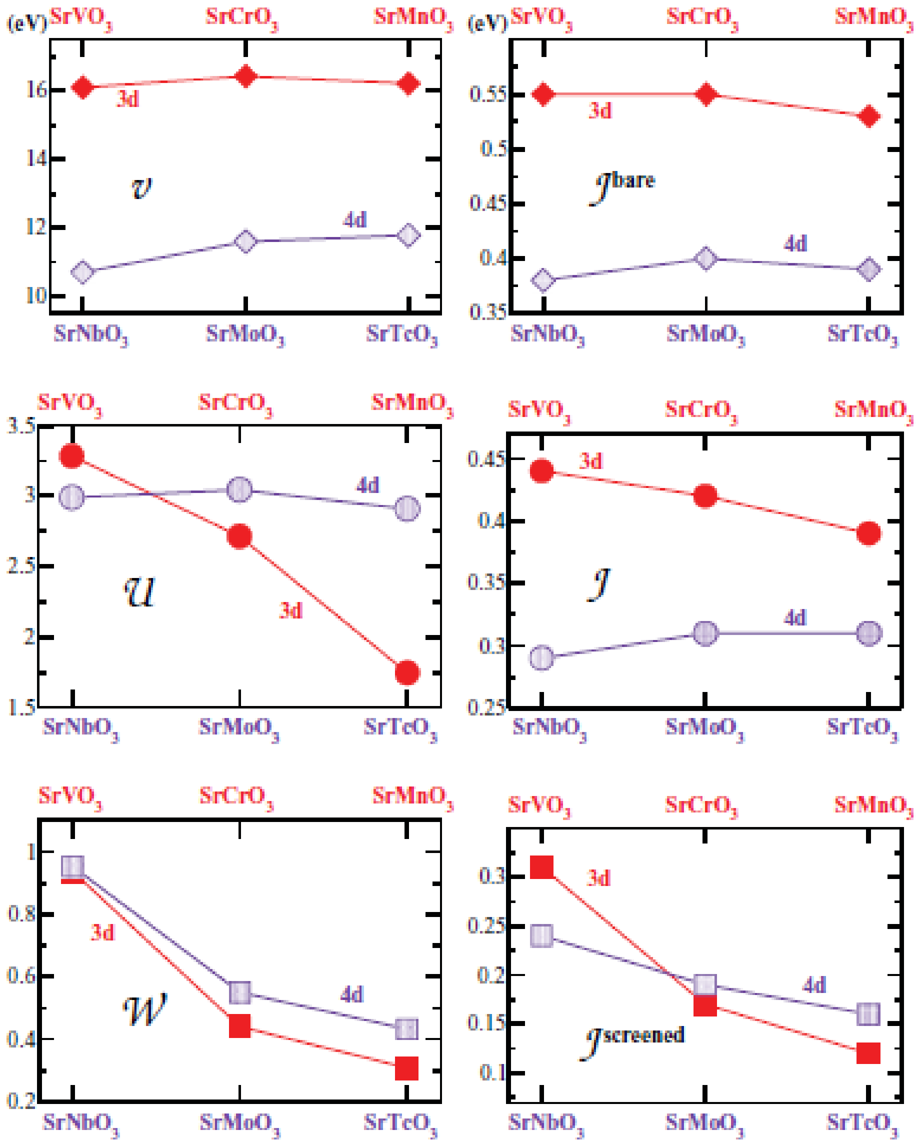


FIG. 2. (Color online) Electronic band structures (top) and projected density of states (bottom) of SrMO$_3$ (M = Nb, Mo, Tc from left to right), obtained from DFT-LDA paramagnetic calculations. The 4d t_{2g} states are highlighted in red (dashed line), the 4d e_g states in blue (dashed-dotted line), and the oxygen p states in maroon (solid line).

Vaugier, Jiang, and Biermann, PHYSICAL REVIEW B 86, 165105 (2012)

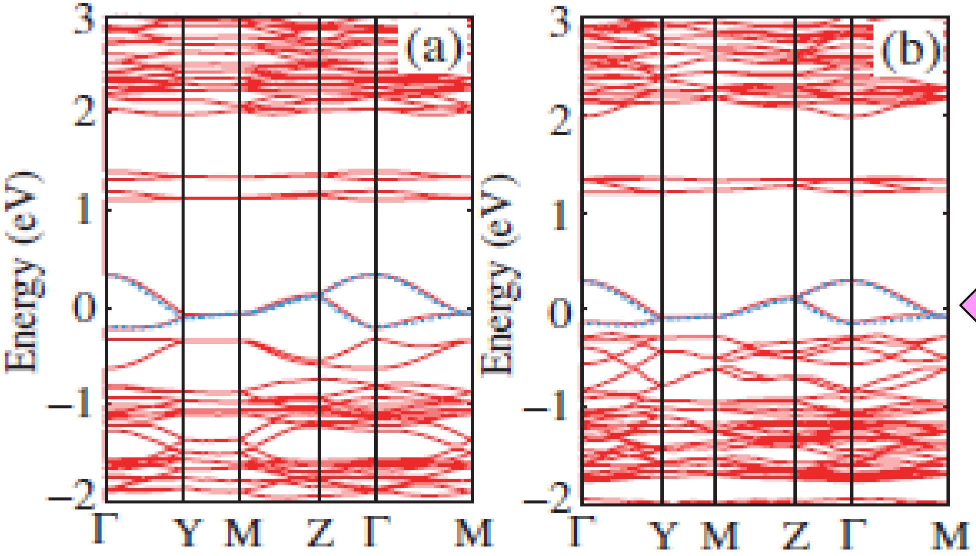


Competition between localisation of orbitals and polarisation.

BEDT-TTF organic conductors

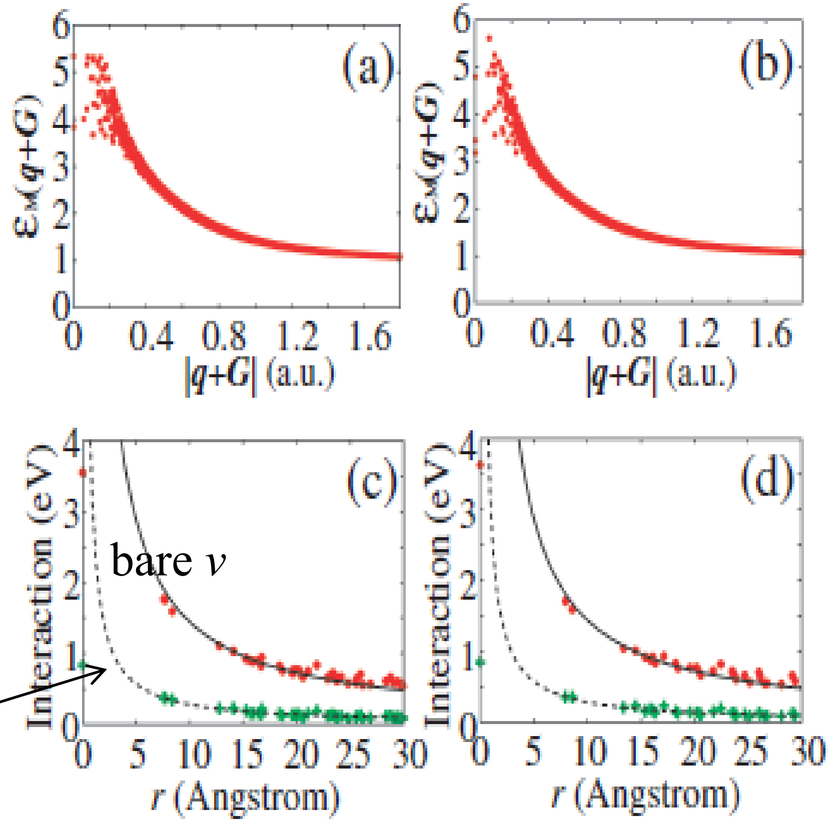
$\kappa-(BEDTTF)_2$ $Cu(NCS)_2$ Exp: metal

$\kappa-(BEDTTF)_2$ $Cu_2(CN)_3$ insulator

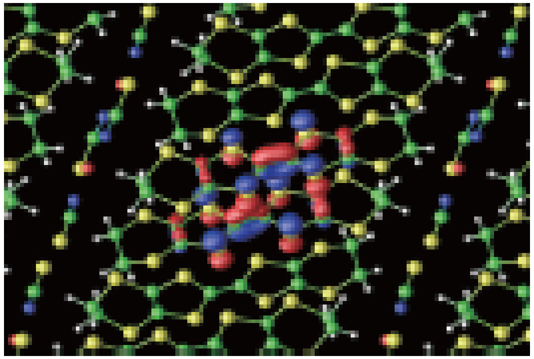


$\kappa-(BEDTTF)_2$ $Cu(NCS)_2$

$\kappa-(BEDTTF)_2$ $Cu_2(CN)_3$



$U \sim 1/(5r)$

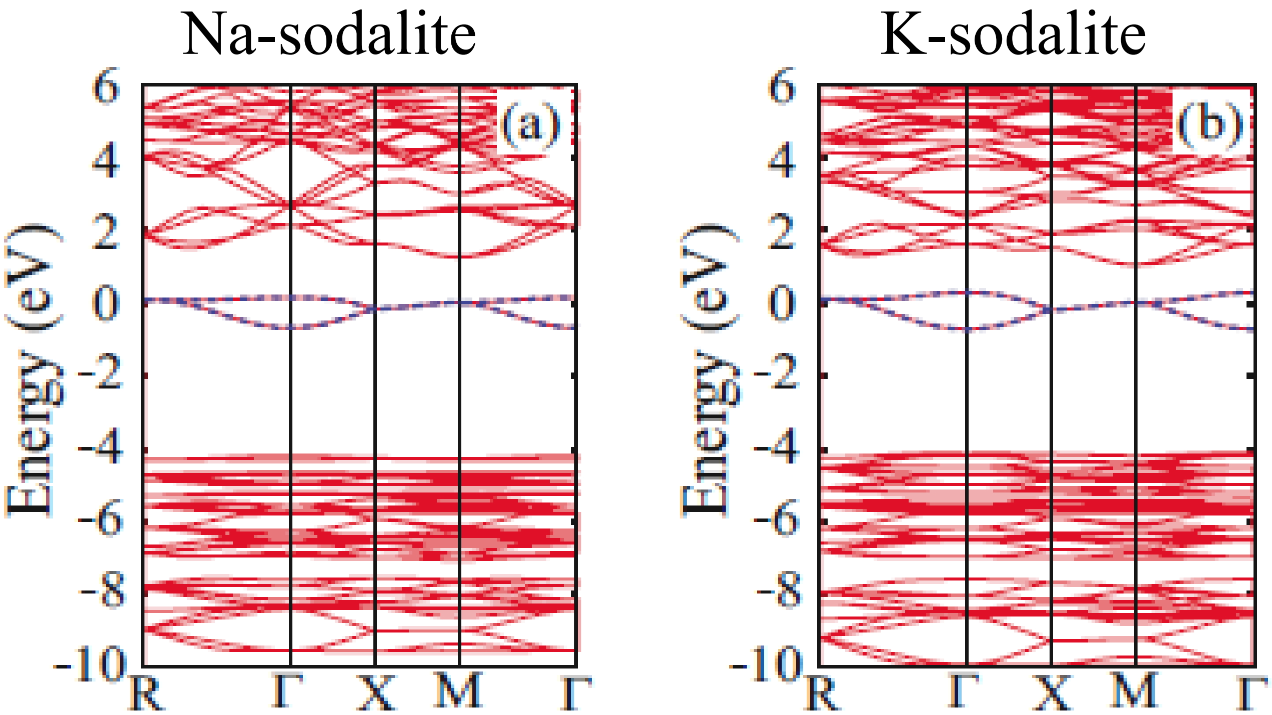


Maximally localised Wannier orbitals of $\kappa-(BEDTTF)_2Cu(NCS)_2$

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)

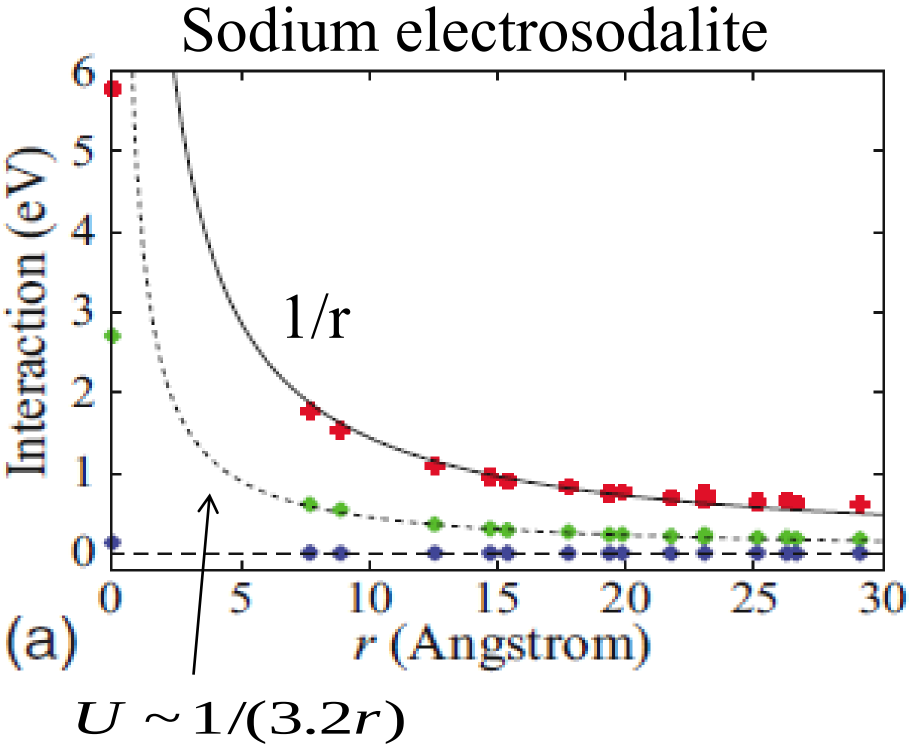
Alkali-cluster-loaded sodalites


Na-sodalite

K-sodalite

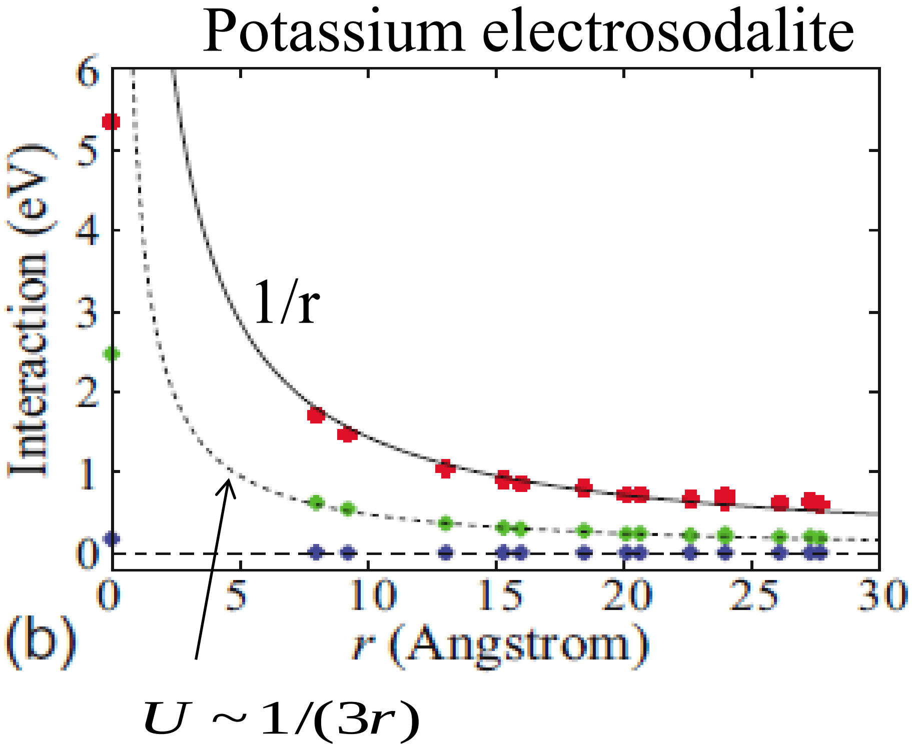
FIG. 3. (Color online) Calculated *ab initio* band structures (red solid lines) of (a) sodium electrosodalite and (b) potassium electrosodalite. The blue dotted dispersions are obtained by the t_1-t_2 model, where t_1 and t_2 are nearest and next-nearest transfers, respectively. For the values, see the text. The zero of energy is the Fermi level.

Nakamura, Koretsune, and Arita, PRB80, 174420 (2009)



Sodium electrosodalite

$U \sim 1/(3.2r)$



Potassium electrosodalite

$U \sim 1/(3r)$

Nakamura, Koretsune, and Arita, PRB80, 174420 (2009)

What happens when the bands are entangled?

Cerium

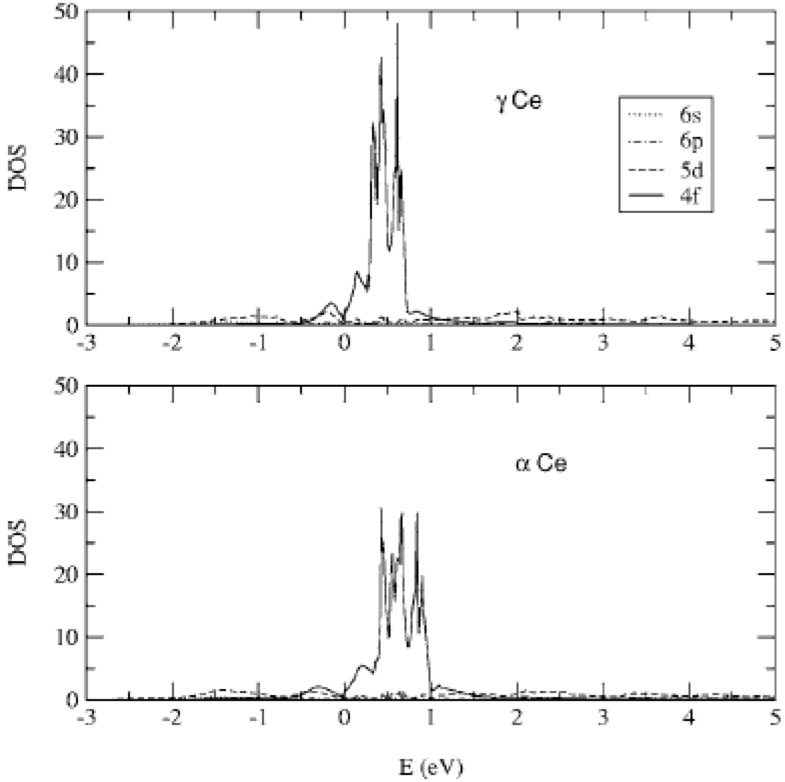
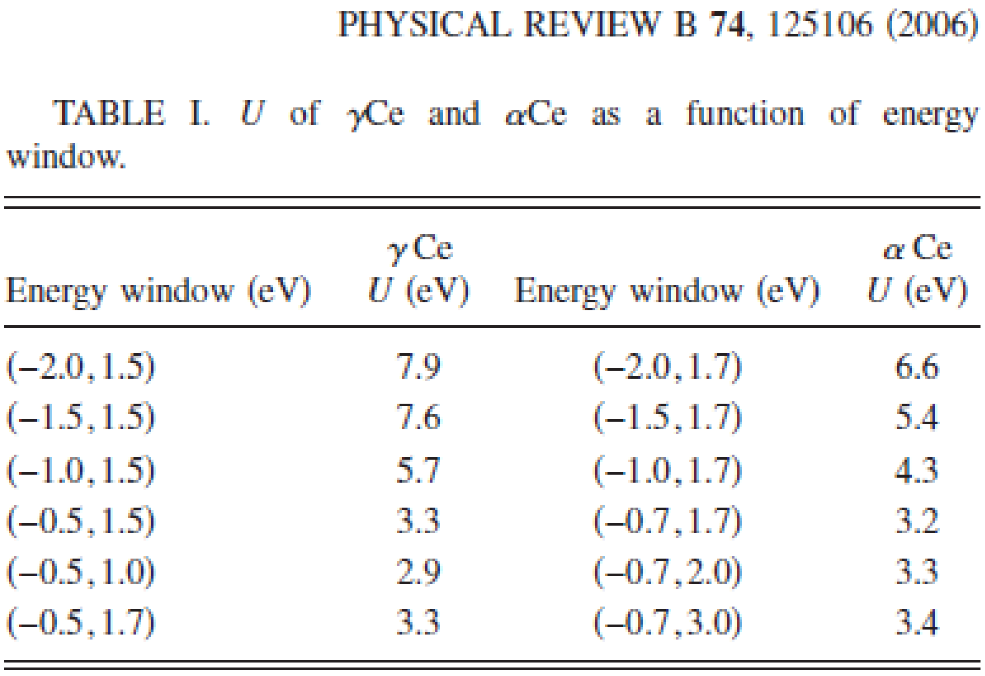


FIG. 4. Partial density of states of αCe and γCe.



PHYSICAL REVIEW B **74**, 125106 (2006)

TABLE I. U of γCe and αCe as a function of energy window.

Energy window (eV)	γ Ce U (eV)	Energy window (eV)	α Ce U (eV)
(−2.0, 1.5)	7.9	(−2.0, 1.7)	6.6
(−1.5, 1.5)	7.6	(−1.5, 1.7)	5.4
(−1.0, 1.5)	5.7	(−1.0, 1.7)	4.3
(−0.5, 1.5)	3.3	(−0.7, 1.7)	3.2
(−0.5, 1.0)	2.9	(−0.7, 2.0)	3.3
(−0.5, 1.7)	3.3	(−0.7, 3.0)	3.4

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

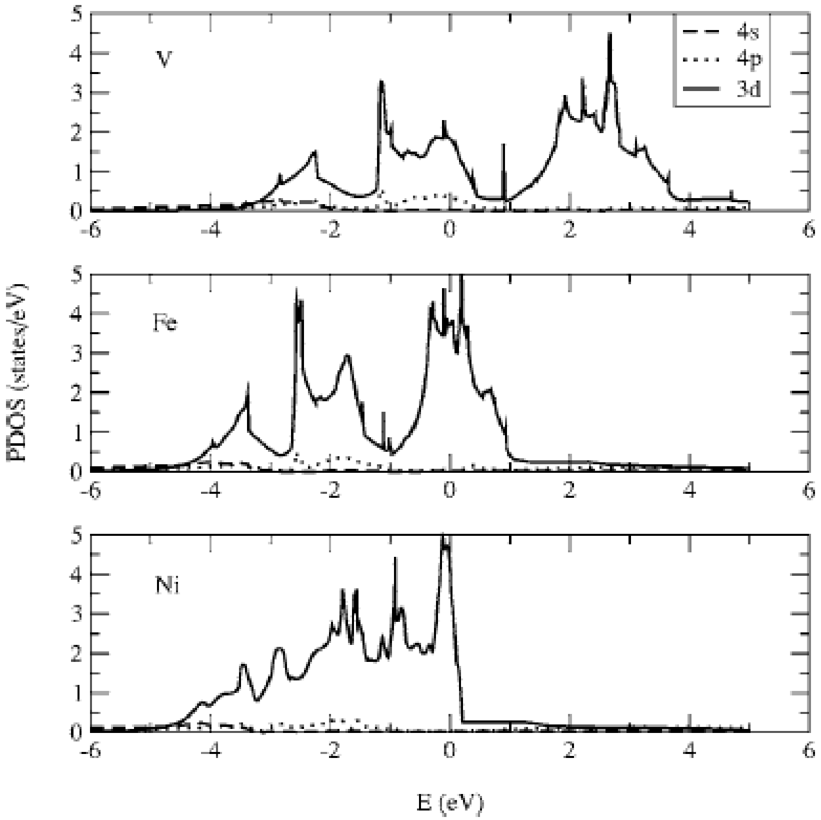
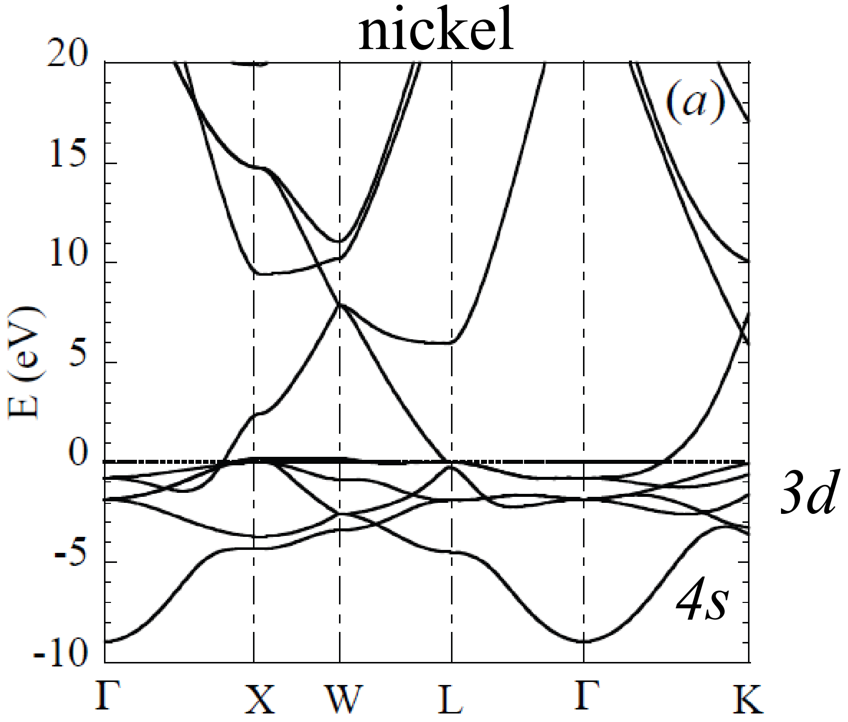


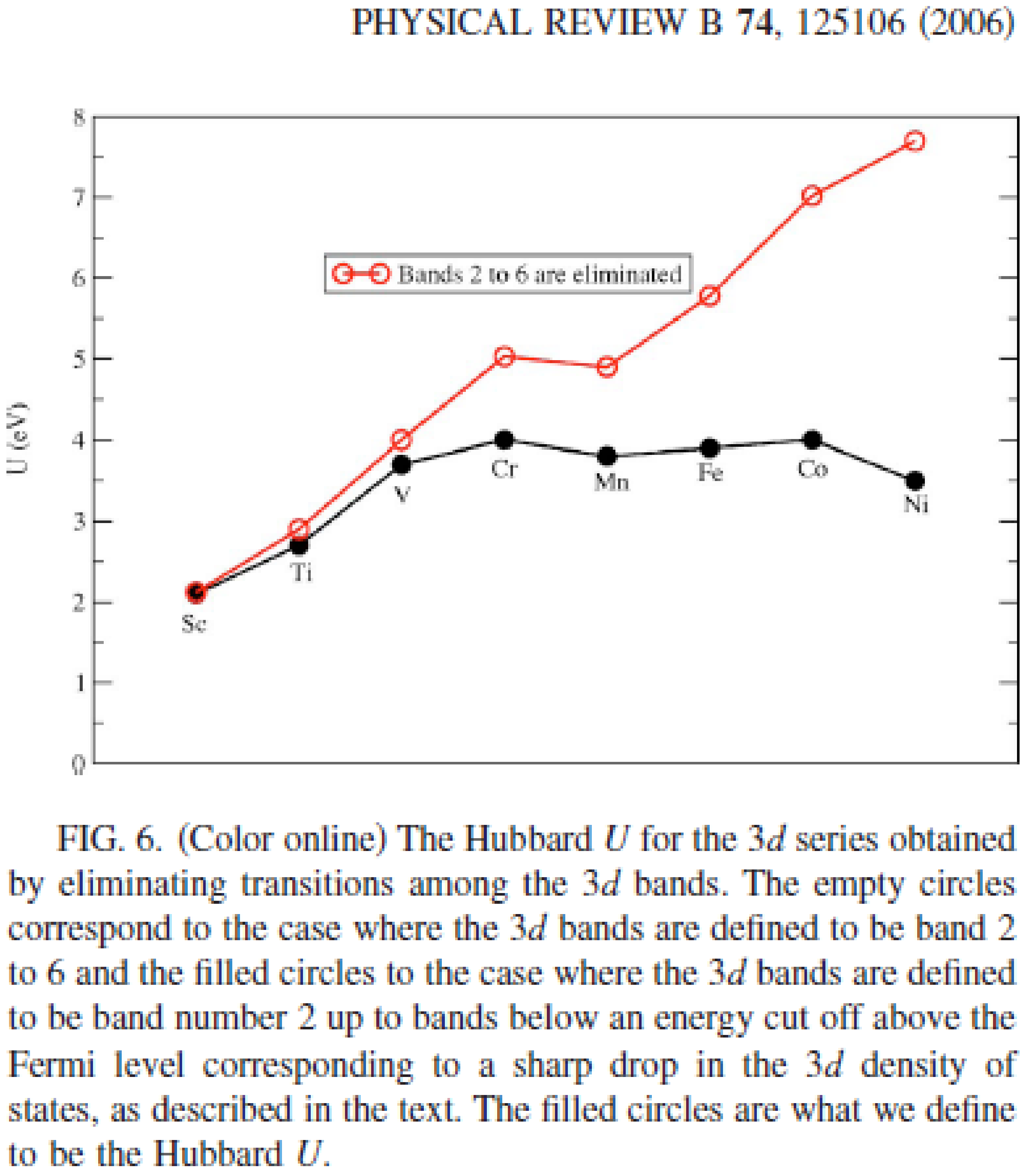
FIG. 5. Partial density of states of vanadium, paramagnetic iron, and nickel.



Clearly, energy window is not a good choice for determining U.

TABLE II. U of V, paramagnetic Fe and Ni as a function of energy window.

	V		Fe		Ni
Energy window (eV)	U (eV)	Energy window (eV)	U (eV)	Energy window (eV)	U (eV)
(−2.0,4.0)	3.7	(−3.0,1.2)	4.0	(−5.0,0.5)	3.7
(−3.0,4.0)	6.3	(−4.0,1.2)	4.8	(−5.0,1.0)	3.7
(−4.0,4.0)	7.0	(−5.0,1.2)	5.0	(−5.0,2.0)	6.3
(−2.0,5.0)	3.8	(−3.0,2.0)	4.3	(−6.0,0.5)	3.7



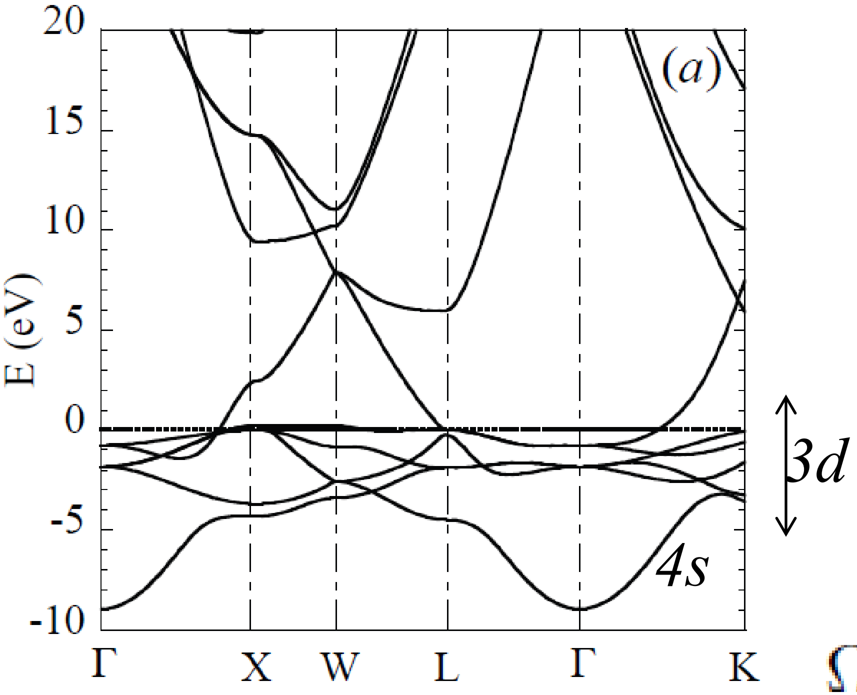
PHYSICAL REVIEW B 74, 125106 (2006)

FIG. 6. (Color online) The Hubbard *U* for the 3*d* series obtained by eliminating transitions among the 3*d* bands. The empty circles correspond to the case where the 3*d* bands are defined to be band 2 to 6 and the filled circles to the case where the 3*d* bands are defined to be band number 2 up to bands below an energy cut off above the Fermi level corresponding to a sharp drop in the 3*d* density of states, as described in the text. The filled circles are what we define to be the Hubbard *U*.

Choosing band indices
is not a good choice either

cRPA for entangled bands

We first choose an energy window covering the 3d band and construct maximally localised Wannier orbitals



$$|\varphi_{n\mathbf{R}}\rangle = \frac{V}{(2\pi)^3}\int d^3k\, e^{-i\mathbf{k}\cdot\mathbf{R}}|\psi^{(\mathrm{w})}_{\mathbf{k}n}\rangle,$$

$$\left|\psi_{kn}^{(w)}\right\rangle = \sum \left|\psi_{km}\right\rangle S_{mn}(k)$$

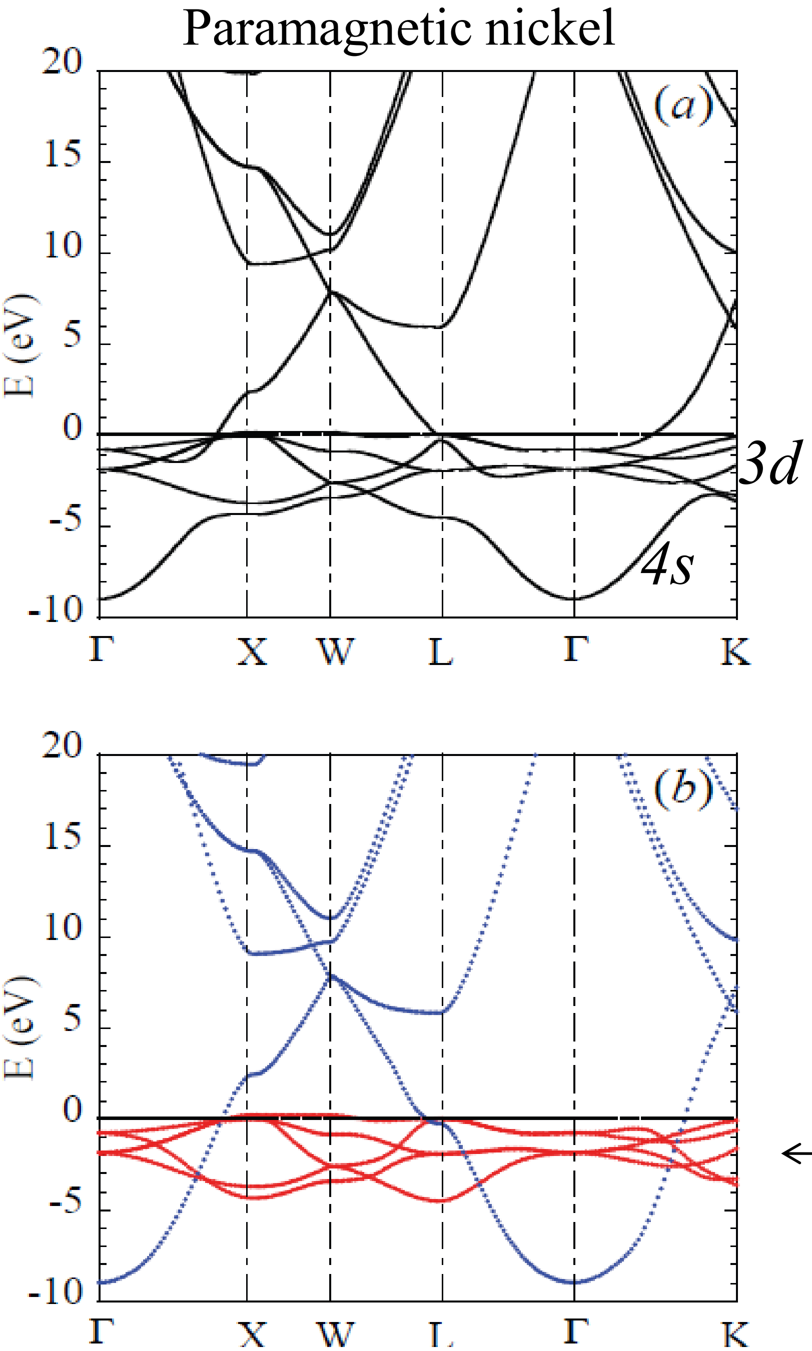
LDA wave functions

Minimise the extent of the orbitals

$$\Omega = \sum_n \left(\langle\varphi_{n\mathbf{0}}|r^2|\varphi_{n\mathbf{0}}\rangle - |\langle\varphi_{n\mathbf{0}}|\mathbf{r}|\varphi_{n\mathbf{0}}\rangle|^2\right)$$

Marzari and Vanderbilt, PRB 56, 12847 (1997)

cRPA for entangled bands



Construct projection operator for the *d* subspace:

$$P = \sum_{m \in d} \left| \varphi_{mR} \right\rangle \left\langle \varphi_{mR} \right|$$

Define the *r* subspace:

$$\left| \psi^{r}_{kn} \right\rangle = (1-P) \left| \psi_{kn} \right\rangle$$

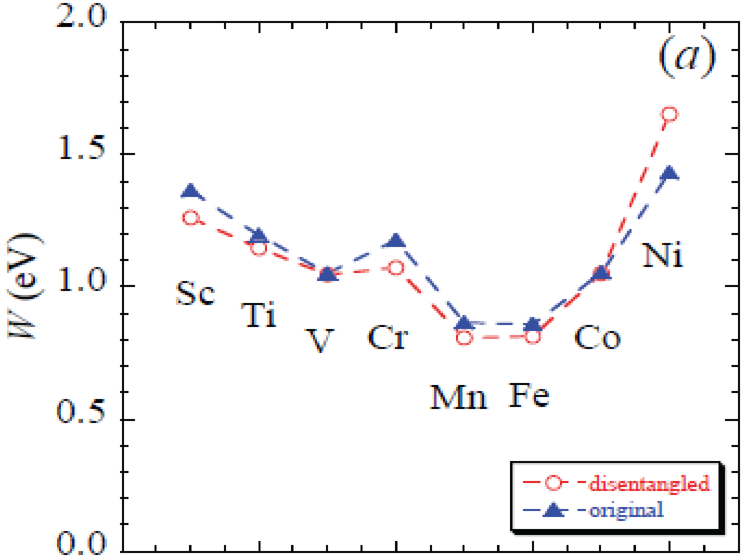
$$H = \begin{pmatrix} d\ space & 0 \\ 0 & r\ space \end{pmatrix}$$

$\uparrow$

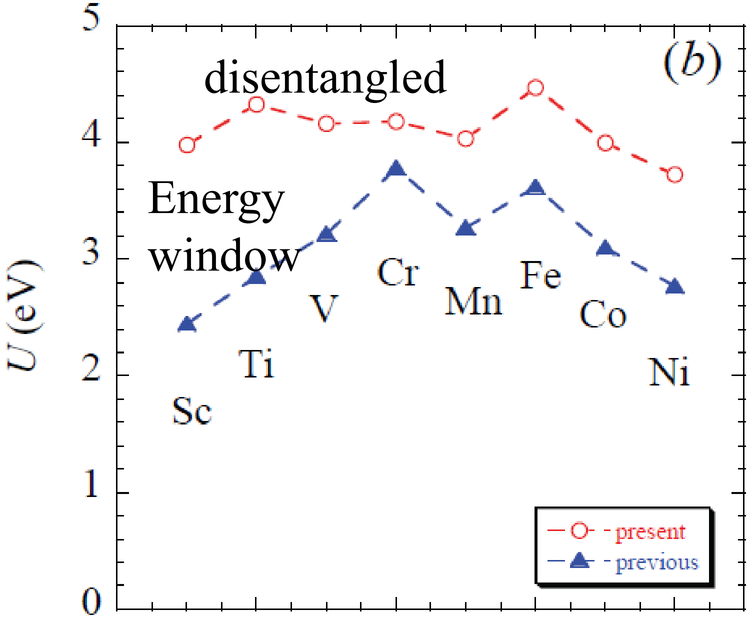
Approximation: The off-diagonal elements are set to zero

← Disentangled 3d band structure from maximally localised Wannier orbitals

Miyake *et al* PRB 80, 155134 (2009), also Sasioglu, Friedrich, and Bluegel PRB 2011



Fully screened interaction W of the 3d series



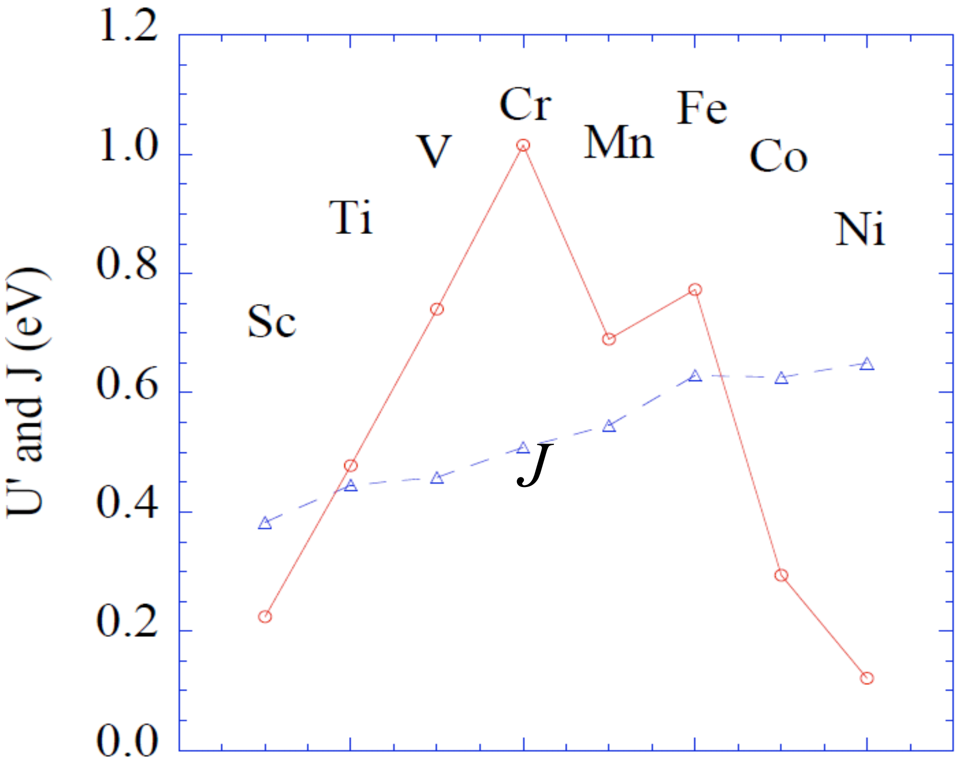
Hubbard U for the 3d series

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 *J*



Other methods dealing with entangled bands

Projection approach:

$$P_d(r,r';\omega)=\sum_{i\in d}^{occ}\sum_{j\in d}^{unocc}\frac{\tilde{\psi}_i(r)\tilde{\psi}_j^*(r)\tilde{\psi}_i^*(r')\tilde{\psi}_j(r')}{\omega\pm\Delta_{ij}}$$

$$\tilde{\psi}_i=\sum_d|\varphi_d\rangle\langle\varphi_d|\psi_i\rangle$$

Weighting approach:

$$P_d(r,r';\omega)=\sum_{i}^{occ}\sum_{j}^{unocc}\frac{\psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r')}{\omega\pm\Delta_{ij}}w_{ij}$$

$w_{ij}=p_i p_j$ Product of probabilities of the electron residing in the d-subspace before and after the transition.

$$p_i=\sum_d|\langle\varphi_d|\psi_i\rangle|^2$$

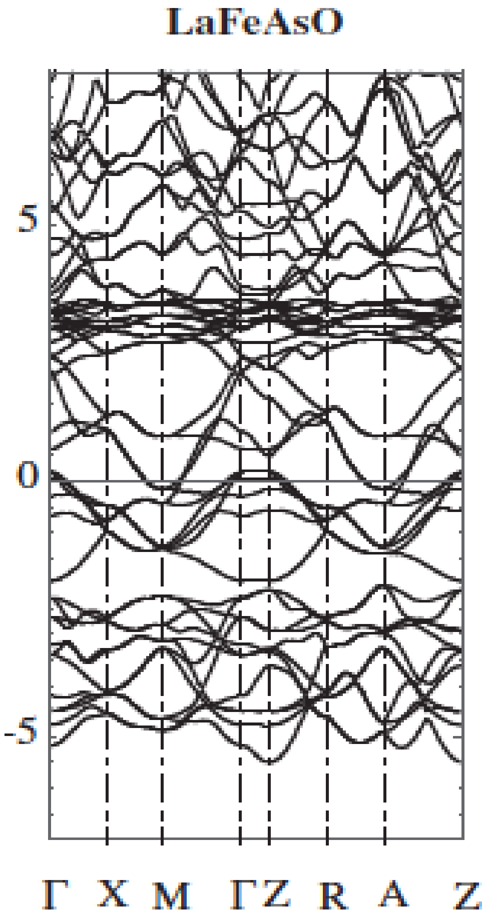
Sasioglu, Friedrich, and Bluegel PHYSICAL REVIEW B 83, 121101(R) (2011)

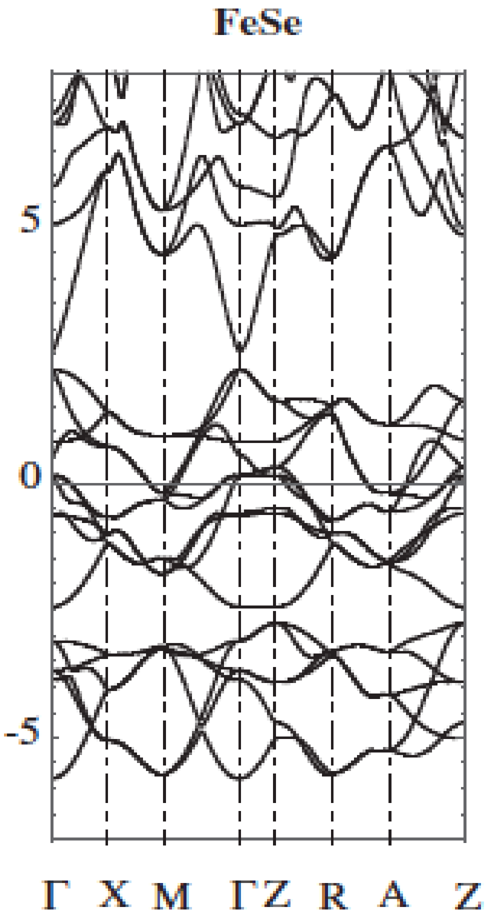
Application of disentanglement method to LaFeAsO and FeSe

1111: LaFePO, LaFeAsO, …
122: $BaFe_2As_2$, …
111: LiFeAs, …
11: FeSe, FeTe
…

Fe 3*d*
(As 4*p*)

(Fe 3*d*)
As 4*p*
O 2*p*


LaFeAsO


FeSe

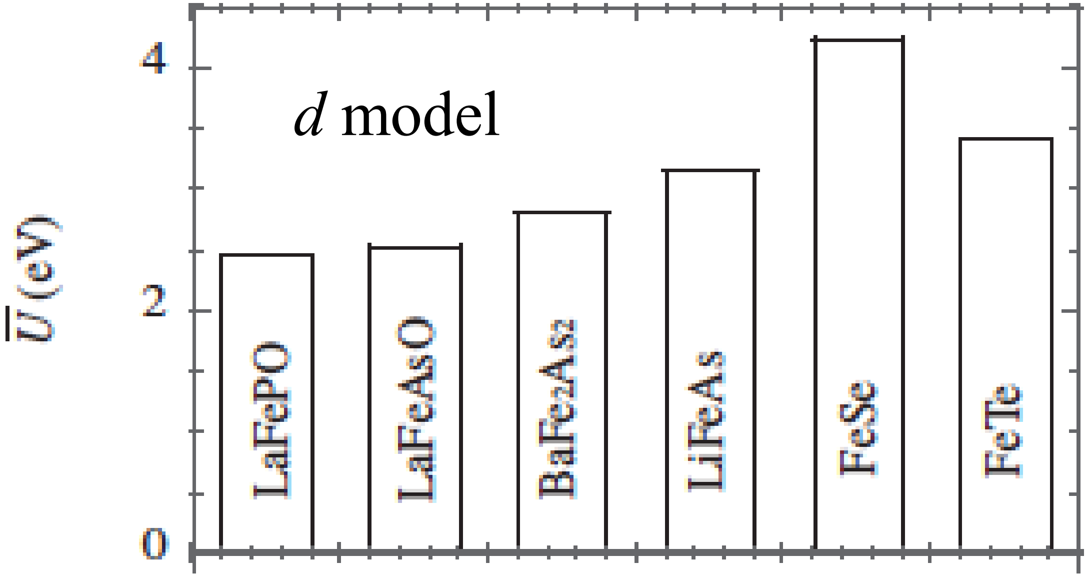
Fe 3*d*
(Se 4*p*)

(Fe 3*d*)
Se 4*p*

Effective interaction in the cRPA

T.Miyake, K.Nakamura, R.Arita and M.Imada, JPSJ (2010)

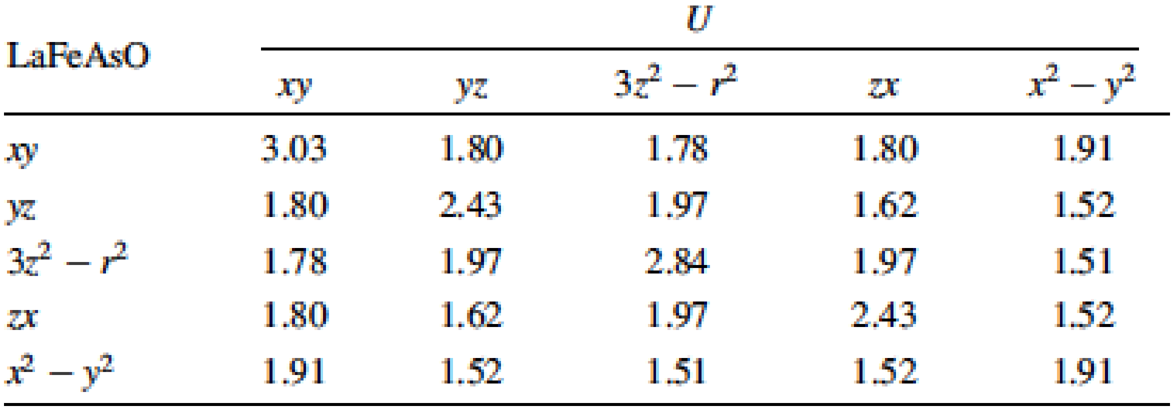
- strong family dependence in *U*
  (the 11 family is substantially more correlated)
- *t* = 0.3-0.4 eV in the *d* model
- strongly orbital dependent in the *d* model,
  due to the different extents of the Wannier orbitals



FeSe is probably
the most correlated

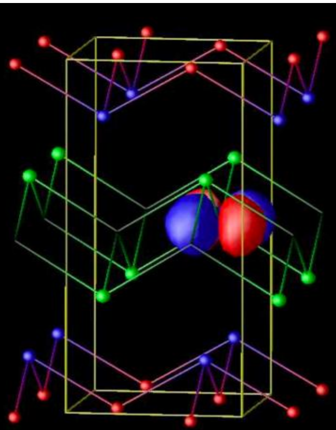
U matrix in the *d* model (in eV)

c.f. K.Nakamura, R.Arita and M.Imada, J.Pys.Soc.Jpn.**77**, 093711(2008).
T.Miyake et al., J.Phys.Soc.Jpn.**77** Suppl.C99(2008).

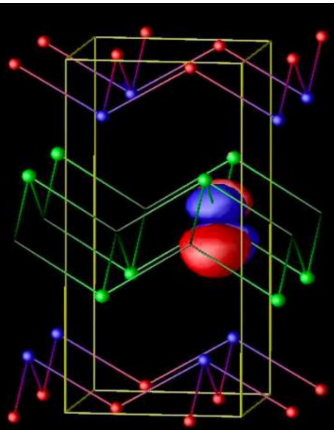


LaFeAsO	U				
	xy	yz	$3z^2-r^2$	zx	x^2-y^2
xy	3.03	1.80	1.78	1.80	1.91
yz	1.80	2.43	1.97	1.62	1.52
$3z^2-r^2$	1.78	1.97	2.84	1.97	1.51
zx	1.80	1.62	1.97	2.43	1.52
x^2-y^2	1.91	1.52	1.51	1.52	1.91

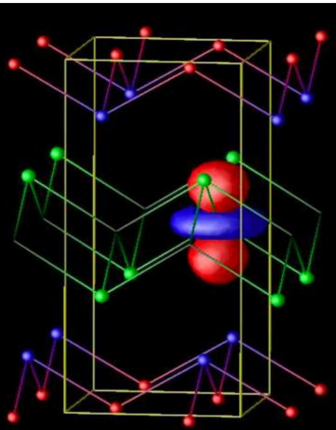
xy



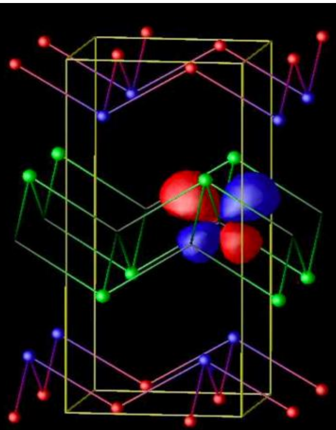
yz



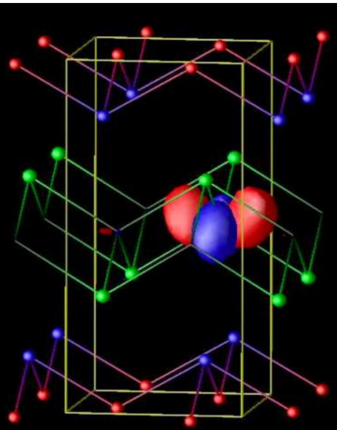
$3z^2-r^2$



xz



x^2-y^2



PRL 109, 146401 (2012) PHYSICAL REVIEW LETTERS week ending 5 OCTOBER 2012

Strength of the Effective Coulomb Interaction at Metal and Insulator Surfaces

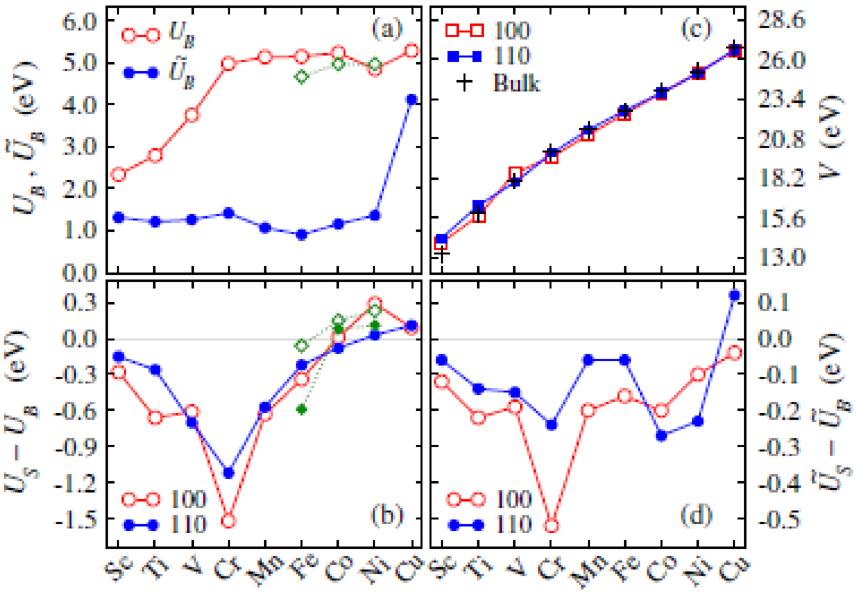
Ersoy Şaşıoğlu,* Christoph Friedrich, and Stefan Blügel
Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

(Received 29 May 2012; published 1 October 2012)

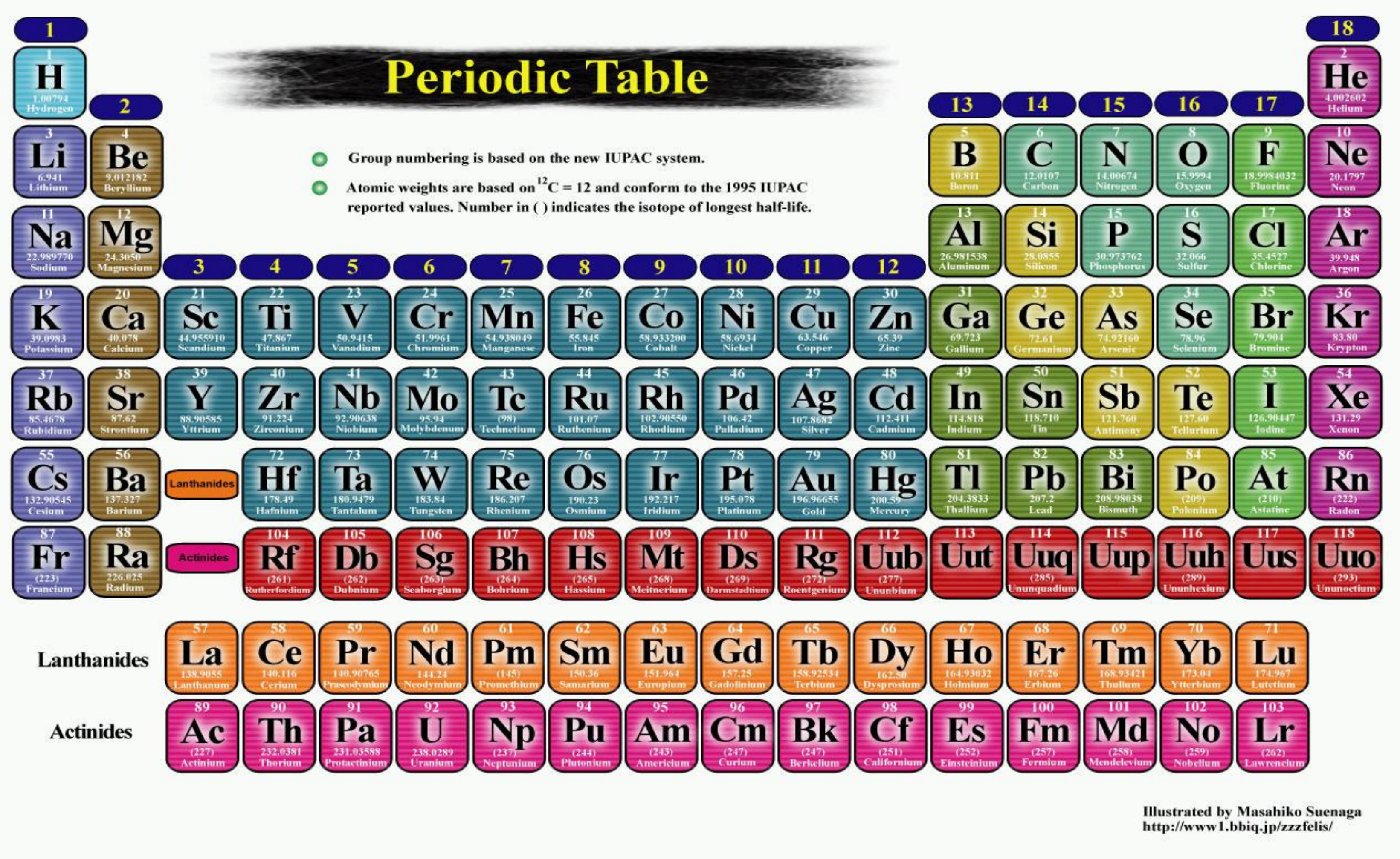
The effective on-site Coulomb interaction (Hubbard *U*) between localized electrons at crystal surfaces is expected to be enhanced due to the reduced coordination number and reduced subsequent screening. By means of first principles calculations employing the constrained random-phase approximation we show that this is indeed the case for simple metals and insulators but not necessarily for transition metals and insulators that exhibit pronounced surface states. In the latter case, the screening contribution from surface states as well as the influence of the band narrowing increases the electron polarization to such an extent as to overcompensate the decrease resulting from the reduced effective screening volume. The Hubbard *U* parameter is thus substantially reduced in some cases, e.g., by around 30% for the (100) surface of bcc Cr.

TABLE I. Bulk and surface Hubbard *U* and *J* values for simple metals and insulators. The corresponding orbitals for which the *U* and *J* are calculated are given in parentheses.

	Bulk		100 Surface		110 Surface	
	U_B	J_B	U_S	J_S	U_S	J_S
Na [3*s*]	1.39		1.50		1.47	
Al [3*p*]	2.18	0.36	2.46	0.39	2.36	0.38
MgO [O-2*p*]	7.10	0.63	7.23	0.62	6.38	0.59
NaCl [Cl-3*p*]	7.13	0.55	7.60	0.54	7.53	0.55
$SrTiO_3$ [Ti-3*d*]	3.34	0.37	3.62	0.39		
$SrTiO_3$ [O-2*p*]	4.42	0.56	4.79	0.55		



U and J for the early lanthanides



Periodic Table

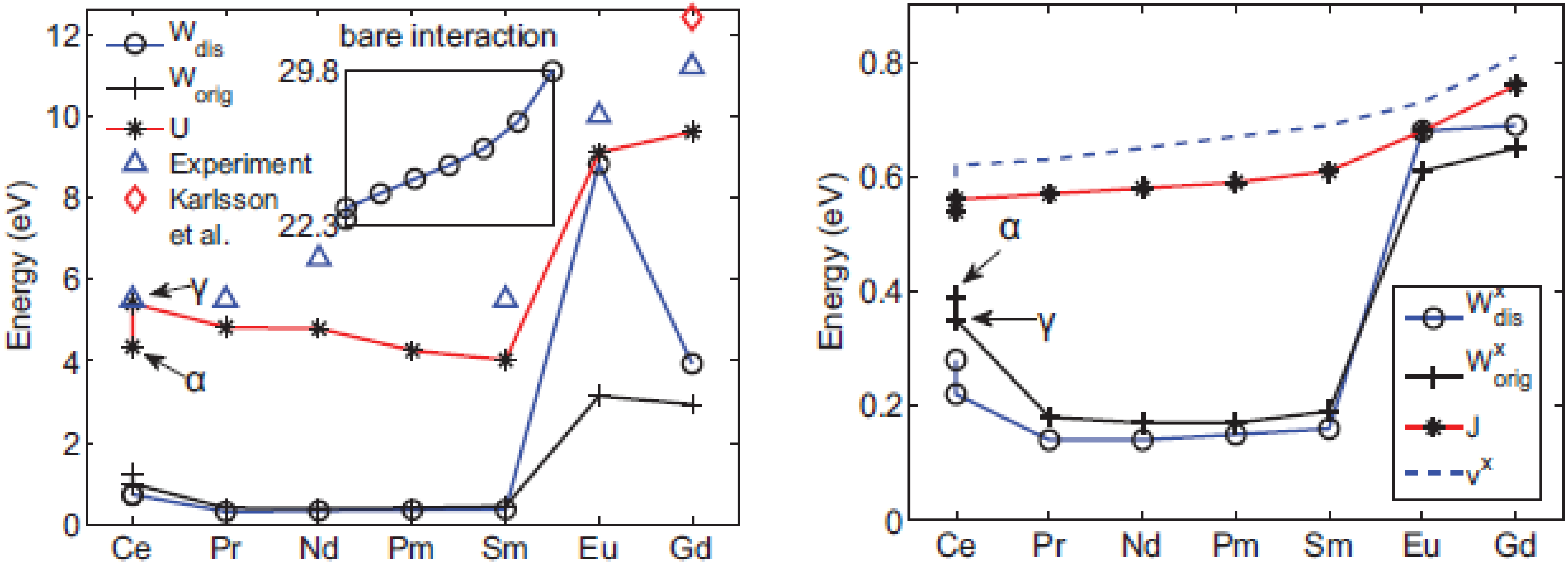
- Group numbering is based on the new IUPAC system.
- Atomic weights are based on ^{12}C = 12 and conform to the 1995 IUPAC reported values. Number in ( ) indicates the isotope of longest half-life.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.00794 Hydrogen																	2 He 4.002602 Helium
3 Li 6.941 Lithium	4 Be 9.012182 Beryllium											5 B 10.811 Boron	6 C 12.0107 Carbon	7 N 14.00674 Nitrogen	8 O 15.9994 Oxygen	9 F 18.9984032 Fluorine	10 Ne 20.1797 Neon
11 Na 22.989770 Sodium	12 Mg 24.3050 Magnesium											13 Al 26.981538 Aluminum	14 Si 28.0855 Silicon	15 P 30.973762 Phosphorus	16 S 32.066 Sulfur	17 Cl 35.4527 Chlorine	18 Ar 39.948 Argon
19 K 39.0983 Potassium	20 Ca 40.078 Calcium	21 Sc 44.955910 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938049 Manganese	26 Fe 55.845 Iron	27 Co 58.933200 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.39 Zinc	31 Ga 69.723 Gallium	32 Ge 72.61 Germanium	33 As 74.92160 Arsenic	34 Se 78.96 Selenium	35 Br 79.904 Bromine	36 Kr 83.80 Krypton
37 Rb 85.4678 Rubidium	38 Sr 87.62 Strontium	39 Y 88.90585 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.90638 Niobium	42 Mo 95.94 Molybdenum	43 Tc (98) Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.90550 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.411 Cadmium	49 In 114.818 Indium	50 Sn 118.710 Tin	51 Sb 121.760 Antimony	52 Te 127.60 Tellurium	53 I 126.90447 Iodine	54 Xe 131.29 Xenon
55 Cs 132.90545 Cesium	56 Ba 137.327 Barium	Lanthanides	72 Hf 178.49 Hafnium	73 Ta 180.9479 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.217 Iridium	78 Pt 195.078 Platinum	79 Au 196.96655 Gold	80 Hg 200.59 Mercury	81 Tl 204.3833 Thallium	82 Pb 207.2 Lead	83 Bi 208.98038 Bismuth	84 Po (209) Polonium	85 At (210) Astatine	86 Rn (222) Radon
87 Fr (223) Francium	88 Ra 226.025 Radium	Actinides	104 Rf (261) Rutherfordium	105 Db (262) Dubnium	106 Sg (263) Seaborgium	107 Bh (264) Bohrium	108 Hs (265) Hassium	109 Mt (268) Meitnerium	110 Ds (269) Darmstadtium	111 Rg (272) Roentgenium	112 Uub (277) Ununbium	113 Uut	114 Uuq (285) Ununquadium	115 Uup	116 Uuh (289) Ununhexium	117 Uus	118 Uuo (293) Ununoctium

Lanthanides	57 La 138.9055 Lanthanum	58 Ce 140.116 Cerium	59 Pr 140.90765 Praseodymium	60 Nd 144.24 Neodymium	61 Pm (145) Promethium	62 Sm 150.36 Samarium	63 Eu 151.964 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.92534 Terbium	66 Dy 162.50 Dysprosium	67 Ho 164.93032 Holmium	68 Er 167.26 Erbium	69 Tm 168.93421 Thulium	70 Yb 173.04 Ytterbium	71 Lu 174.967 Lutetium
Actinides	89 Ac (227) Actinium	90 Th 232.0381 Thorium	91 Pa 231.03588 Protactinium	92 U 238.0289 Uranium	93 Np (237) Neptunium	94 Pu (244) Plutonium	95 Am (243) Americium	96 Cm (247) Curium	97 Bk (247) Berkelium	98 Cf (251) Californium	99 Es (252) Einsteinium	100 Fm (257) Fermium	101 Md (258) Mendelevium	102 No (259) Nobelium	103 Lr (262) Lawrencium

Illustrated by Masahiko Suenaga
http://www1.bbiq.jp/zzzfelis/

U and J for the early lanthanides



Nilsson *et al* PRB 88, 125123 (2013)

Band structures of Eu and Gd

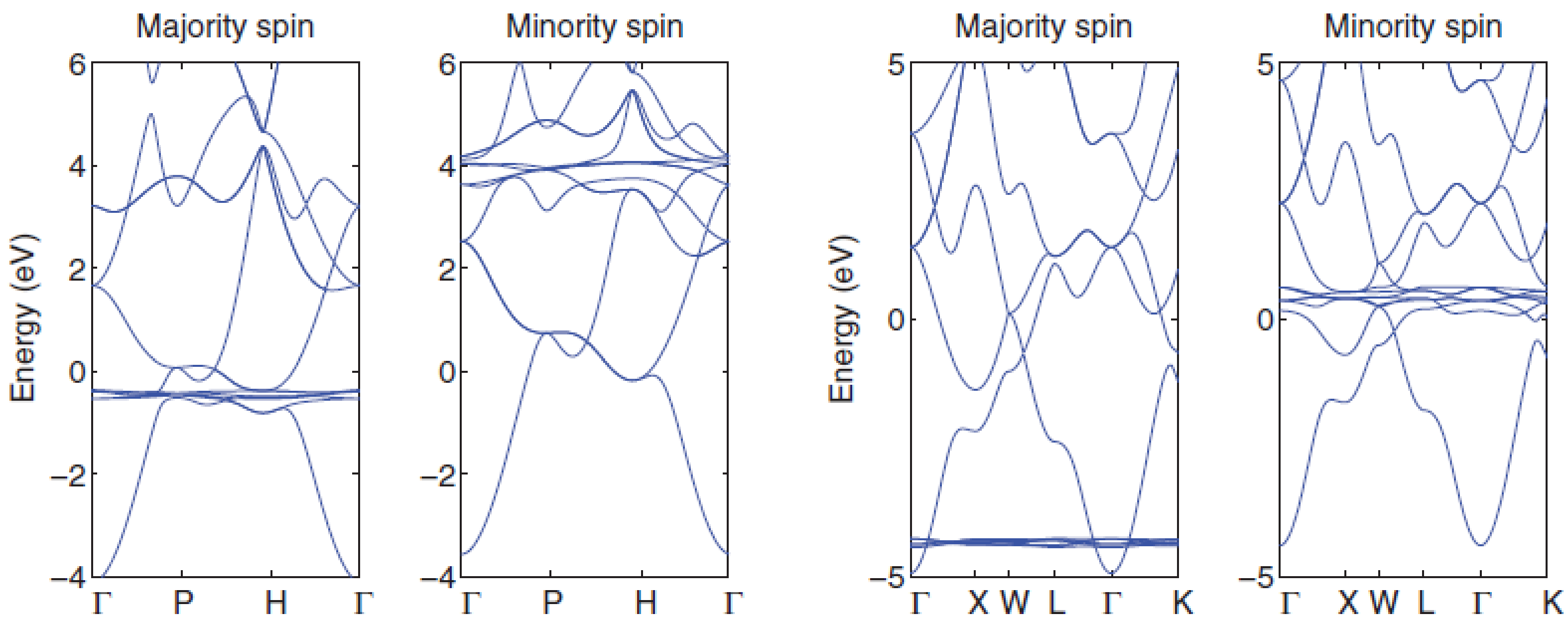
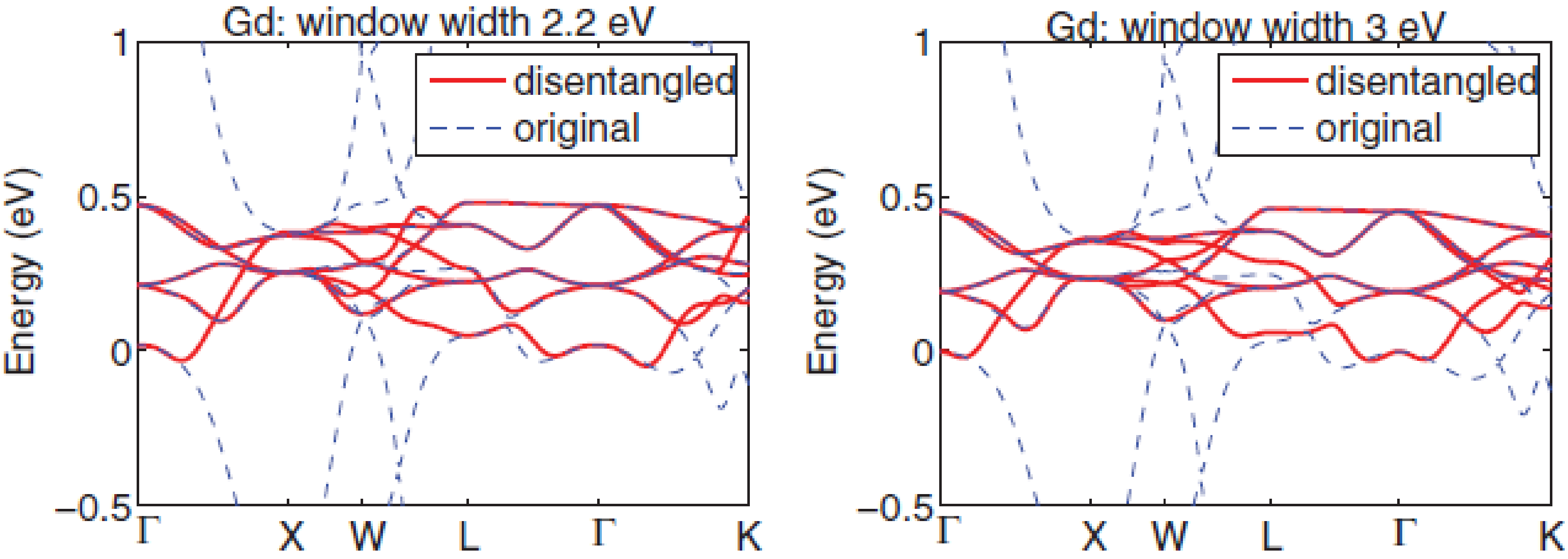


FIG. 2. (Color online) LDA band structure of Eu (left) and Gd (right).

Disentangled band structures of Gd

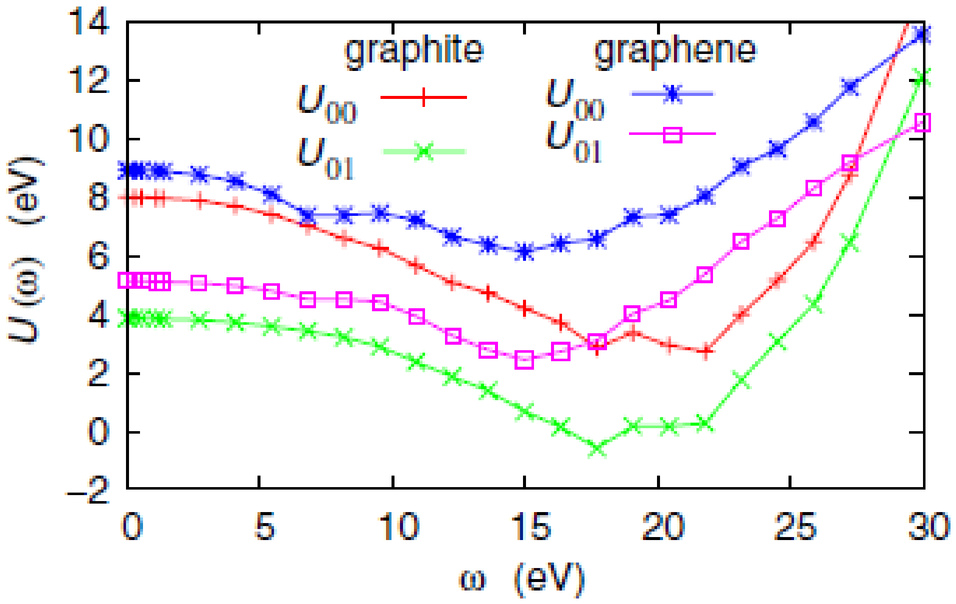


Frequency-dependent onsite and nearest-neighbour U of graphene and graphite

PRL **106,** 236805 (2011) PHYSICAL REVIEW LETTERS week ending 10 JUNE 2011

Strength of Effective Coulomb Interactions in Graphene and Graphite

T. O. Wehling,[1] E. Şaşıoğlu,[2] C. Friedrich,[2] A. I. Lichtenstein,[1] M. I. Katsnelson,[3] and S. Blügel[2]



Large nearest-neighbour *U*

FIG. 3 (color online). Frequency dependence of the on-site and nearest-neighbor interaction obtained from cRPA for graphene ($h = 21.2$ Å) and graphite. For graphite $U_{00}(\omega) = U^A_{00}(\omega)$ is shown, which is virtually the same as $U^B_{00}(\omega)$. $|U^A_{00}(\omega) - U^B_{00}(\omega)| < 0.15$ eV for $\omega < 20$ eV.

TABLE I. On-site (U_{00}^{A}, U_{00}^{B}), nearest-neighbor (U_{01}), next-nearest-neighbor (U_{02}^{A}, U_{02}^{B}), and third-nearest-neighbor (U_{03}) (intralayer) Coulomb interaction parameters for freestanding graphene and graphite. In graphene $U_{00}^{A} = U_{00}^{B}$ and $U_{02}^{A} = U_{02}^{B}$ due to the sublattice symmetry. The bare and partially screened (cRPA) parameters are given. The cRPA parameters should be used in the effective Hamiltonian (1).

	Graphene		Graphite	
	Bare	cRPA	Bare	cRPA
$U_{00}^{A\text{ or }B}$ (eV)	17.0	9.3	17.5, 17.7	8.0, 8.1
U_{01} (eV)	8.5	5.5	8.6	3.9
$U_{02}^{A\text{ or }B}$ (eV)	5.4	4.1	5.4, 5.4	2.4, 2.4
U_{03} (eV)	4.7	3.6	4.7	1.9

Heisenberg exchange parameters

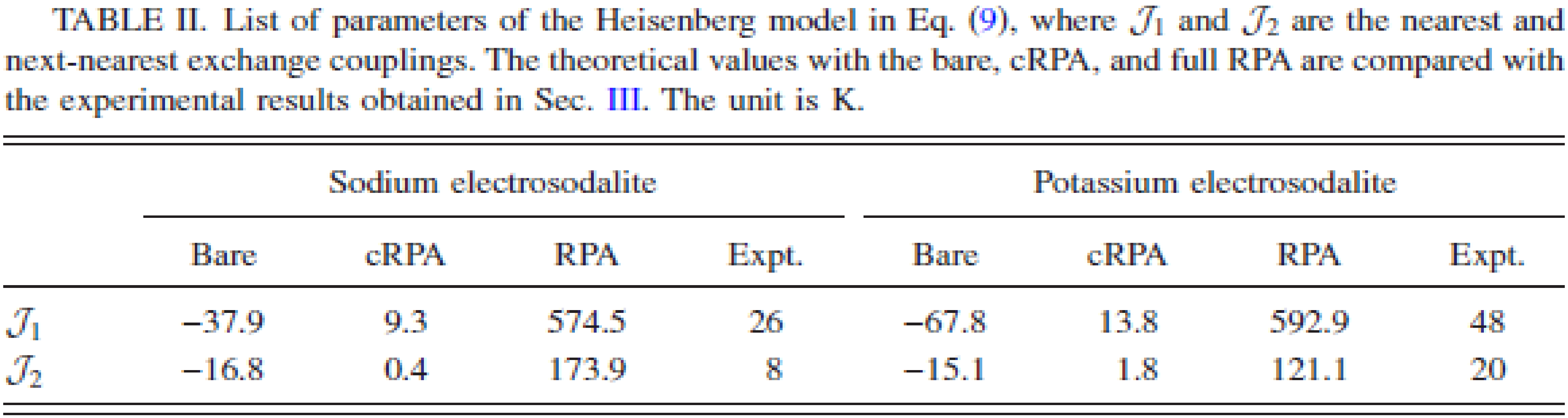


TABLE II. List of parameters of the Heisenberg model in Eq. (9), where $\mathcal{J}_1$ and $\mathcal{J}_2$ are the nearest and next-nearest exchange couplings. The theoretical values with the bare, cRPA, and full RPA are compared with the experimental results obtained in Sec. III. The unit is K.

	Sodium electrosodalite				Potassium electrosodalite			
	Bare	cRPA	RPA	Expt.	Bare	cRPA	RPA	Expt.
$\mathcal{J}_1$	−37.9	9.3	574.5	26	−67.8	13.8	592.9	48
$\mathcal{J}_2$	−16.8	0.4	173.9	8	−15.1	1.8	121.1	20

$\mathcal{J}_{ij} = K_{ij} - J_{ij}$ → Exchange integral

$$\mathcal{H}_{\rm eff} = 2\sum_{i>j} \mathcal{J}_{ij} S_i \cdot S_j,$$

$K_{ij} = \dfrac{2|t_{ij}|^2}{U - V_{ij}}.$ → Intersite Coulomb interaction

Nakamura, Koretsune, and Arita, PRB80, 174420 (2009)

Dynamic (frequency-dependent) U

Major progress in solving the impurity problem with a dynamic *U*

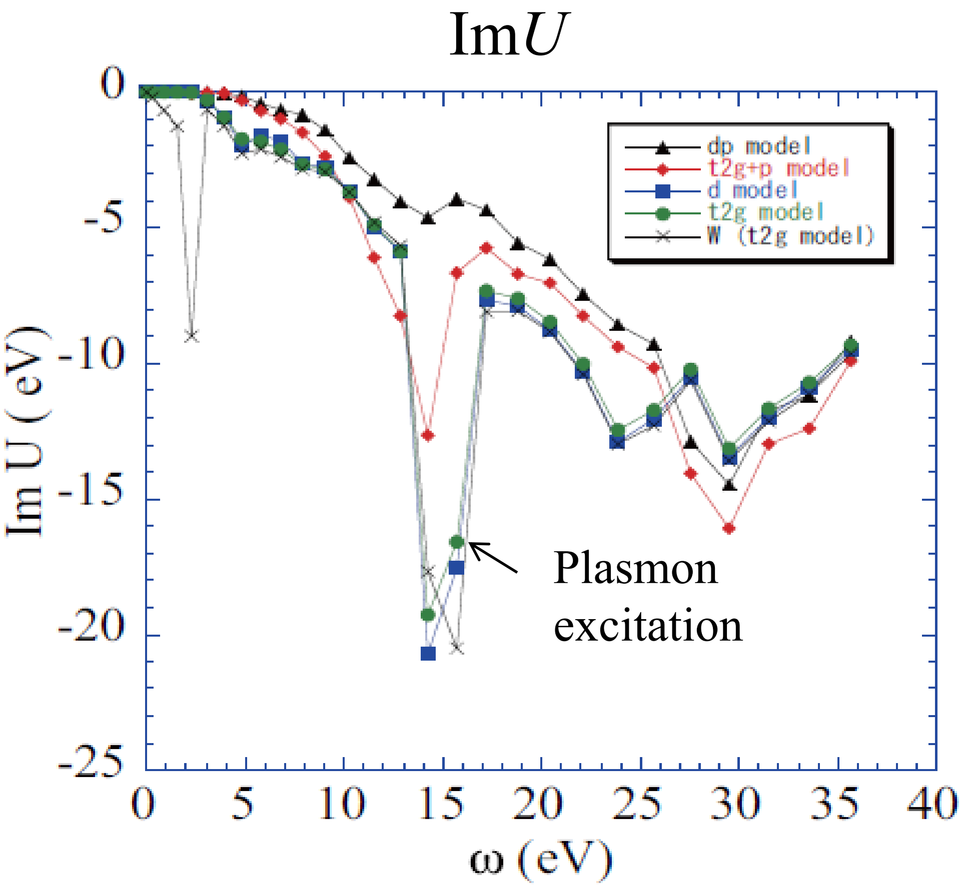
Continuous time Quantum Monte Carlo (CTQMC) algorithm:

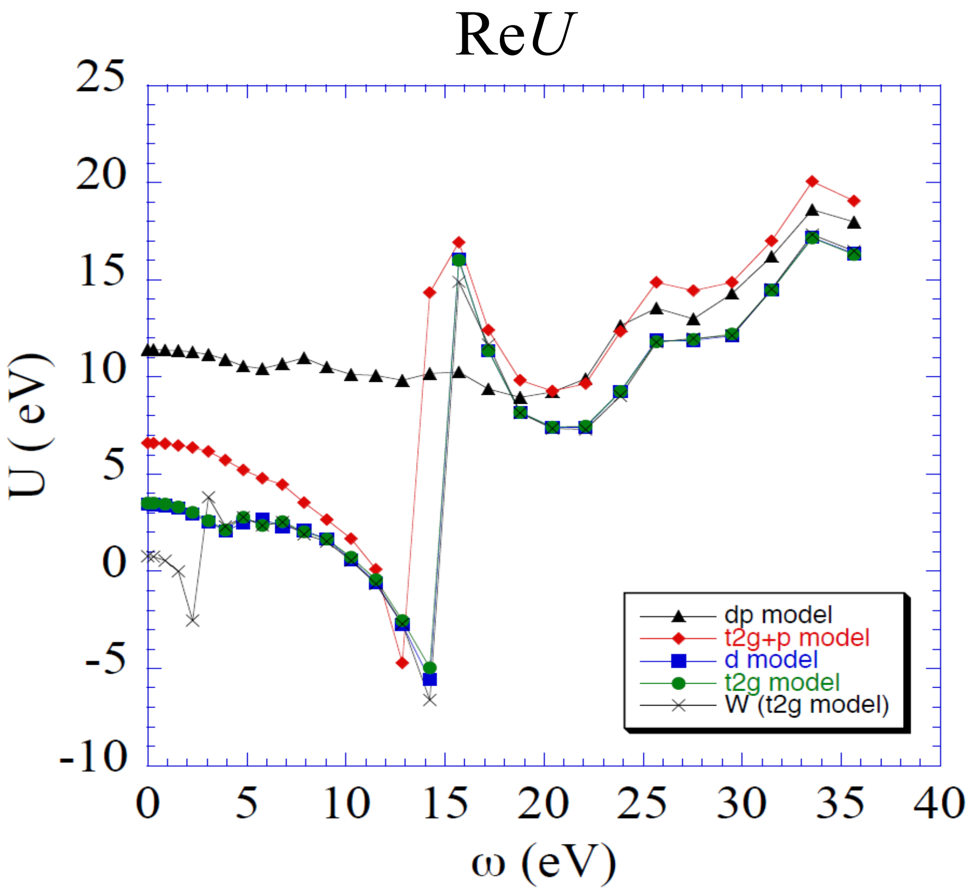
Werner and Millis (PRL 2007, 2010)
Hybridisation expansion: strong-coupling approach

Rubtsov (JETP 2004, PRB2005)
Perturbation expansion: weak-coupling limit

Approximate method:
Casula, Rubtsov, Biermann PRB (2012)
Bose Factor Ansatz (BFA),
Dynamic Atomic Limit Approximation (DALA)

SrVO3

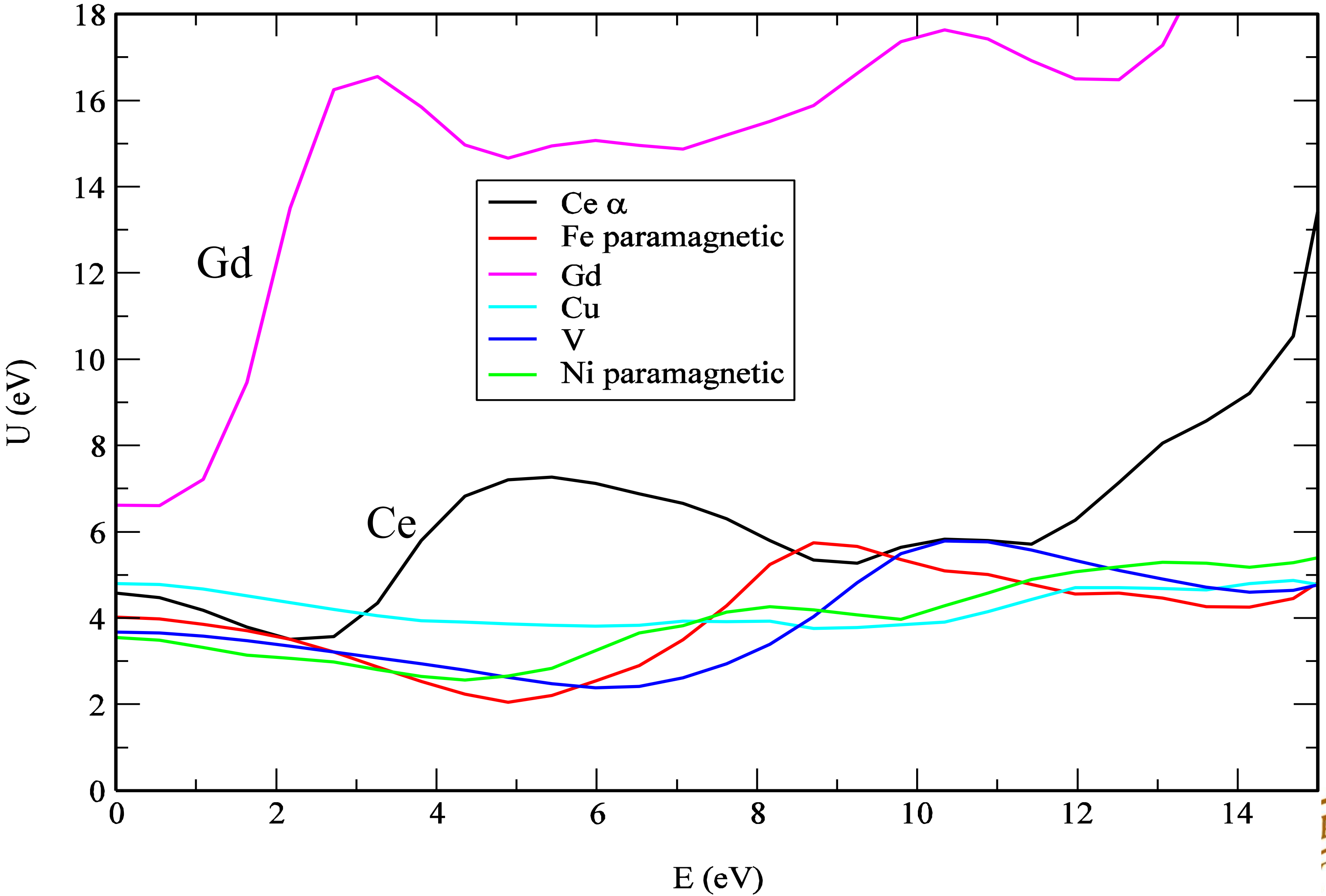




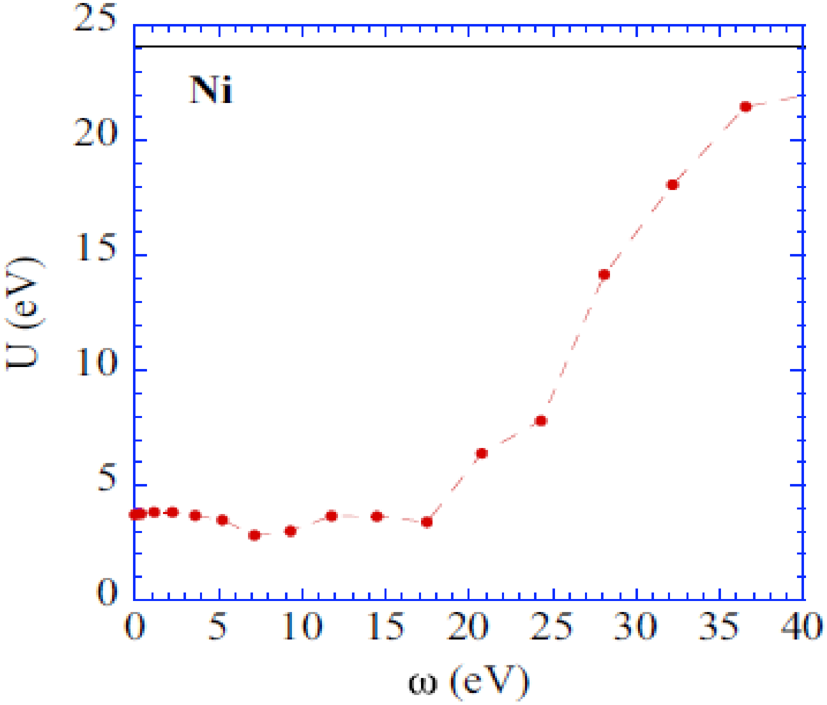
$$\mathrm{Re}\,U(\omega) = v - \frac{2}{\pi}\int_0^\infty d\omega' \frac{\omega' \,\mathrm{Im}\,U(\omega')}{\omega^2 - \omega'^2}$$

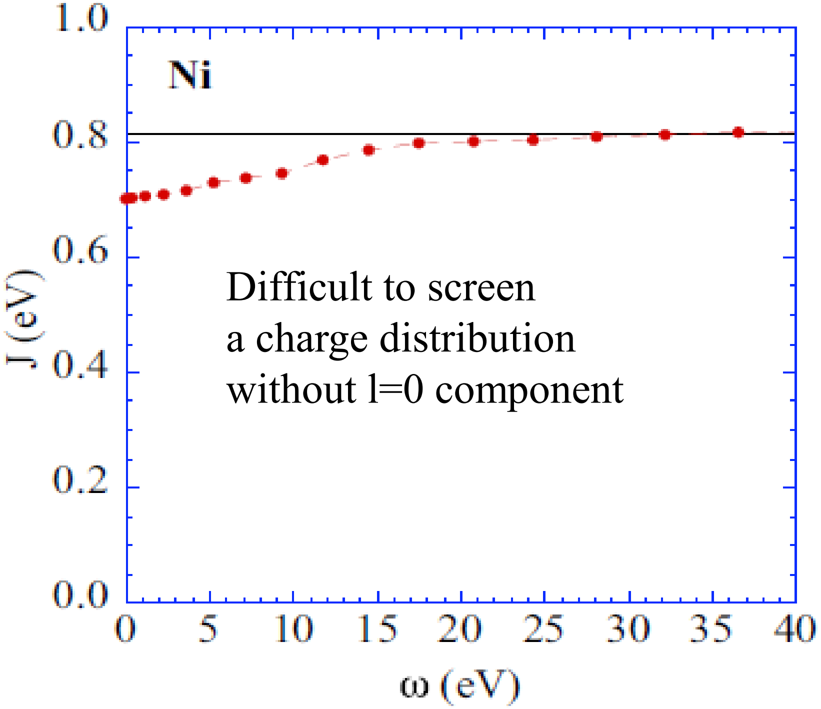
Miyake *et al*, unpublished

Energy dependence of U.
U can vary significantly within the band width of the chosen subspace



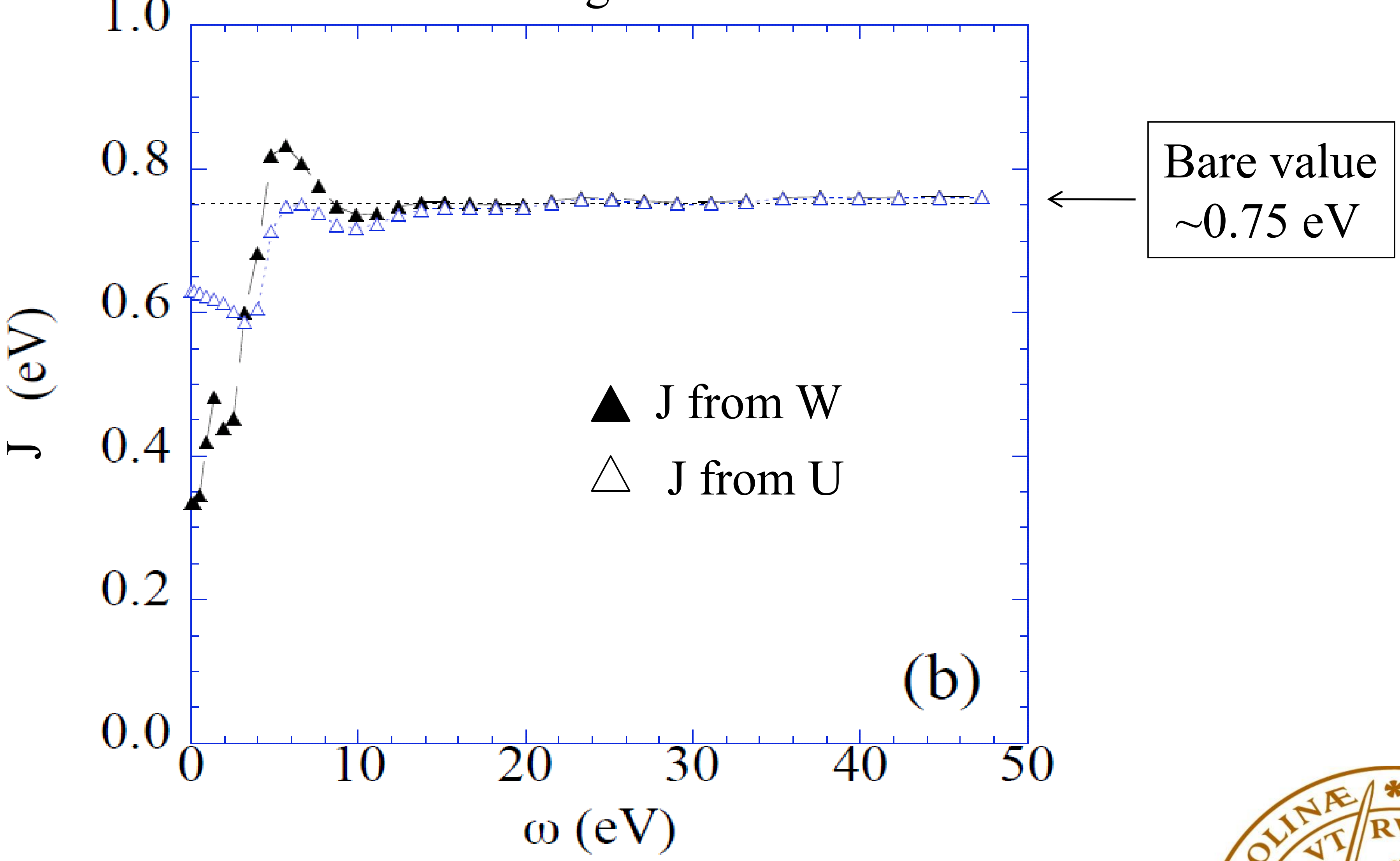
U and *J* of Ni as a function of frequency





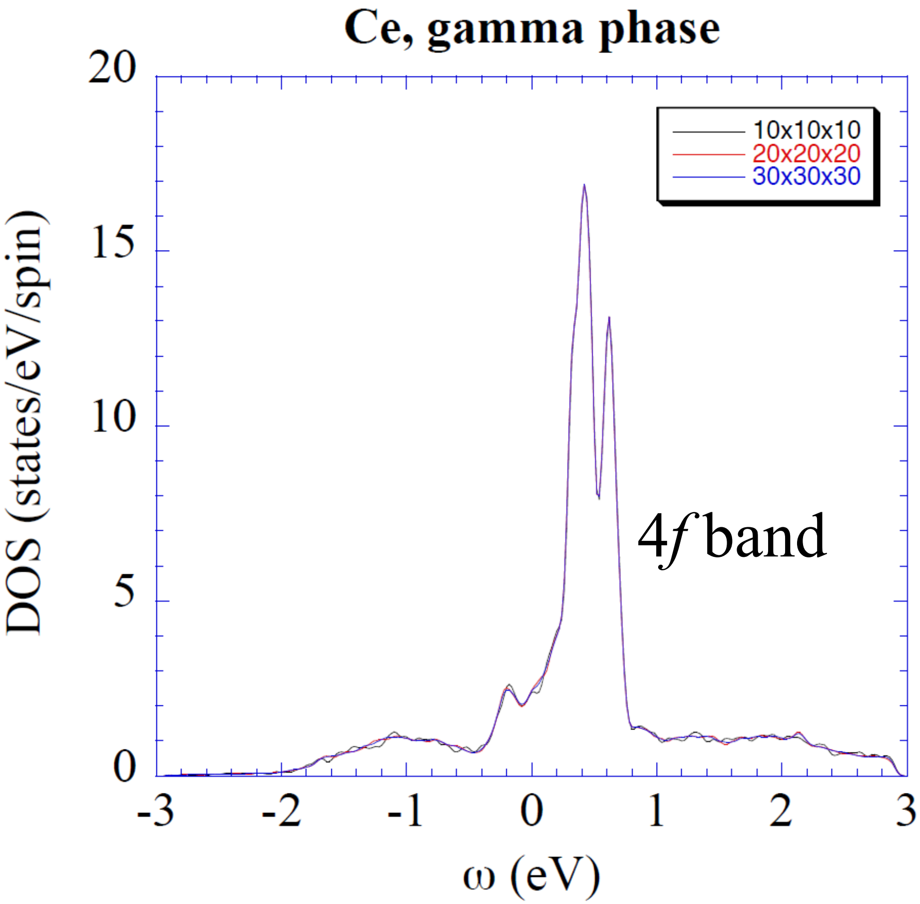
Difficult to screen
a charge distribution
without l=0 component

Onsite exchange J of Fe

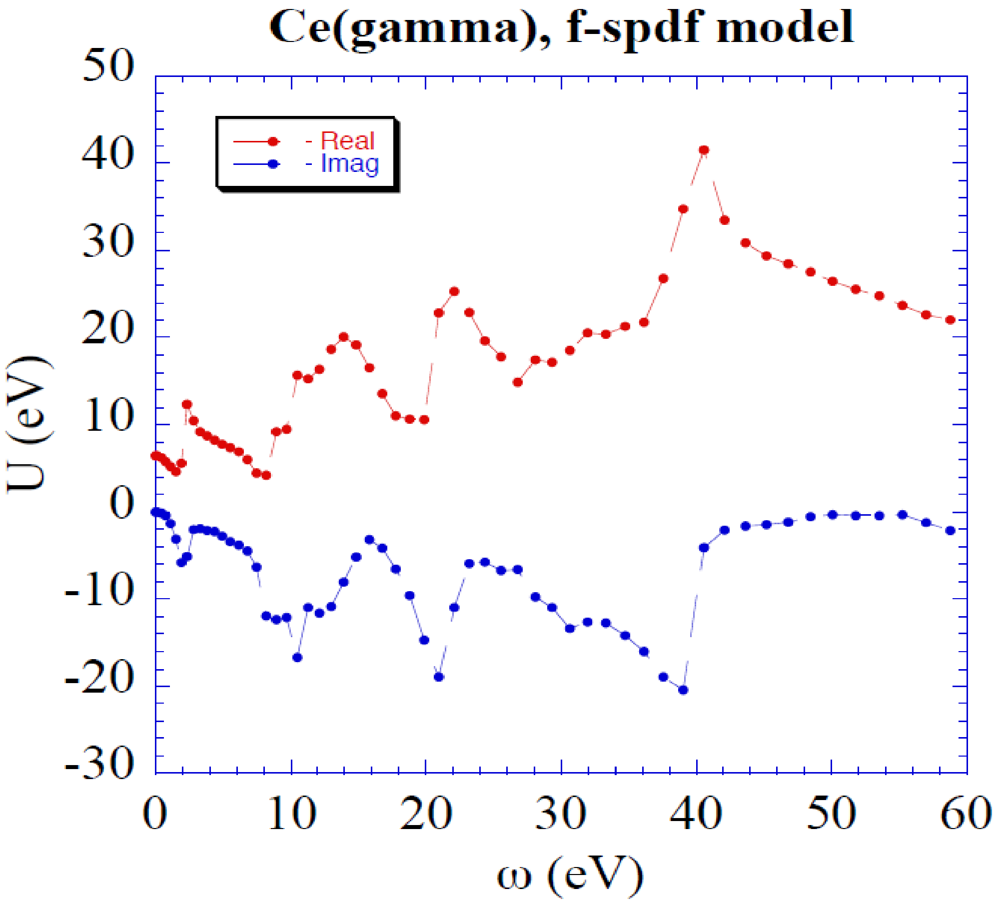


Bare value
~0.75 eV

Screening effects on J are not negligible
(About 15 %)



Ce, gamma phase



Ce(gamma), f-spdf model

PRL 109, 146401 (2012) PHYSICAL REVIEW LETTERS week ending
5 OCTOBER 2012

Strength of the Effective Coulomb Interaction at Metal and Insulator Surfaces

Ersoy Şaşıoğlu,* Christoph Friedrich, and Stefan Blügel
Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany
(Received 29 May 2012; published 1 October 2012)

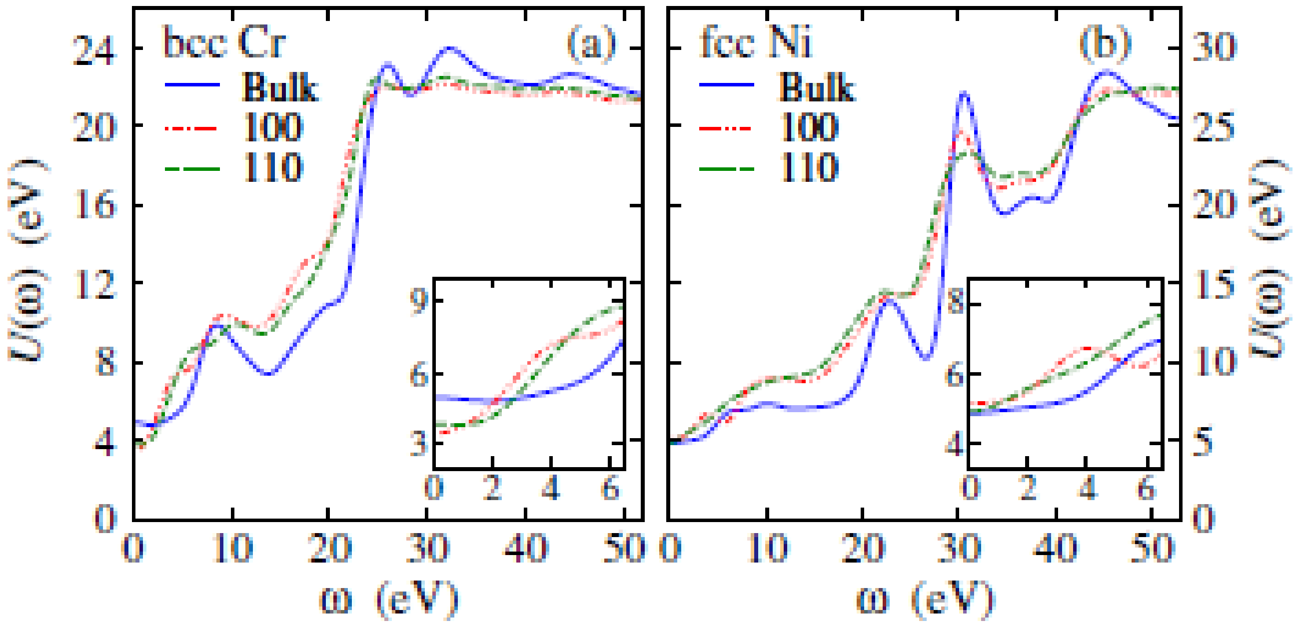
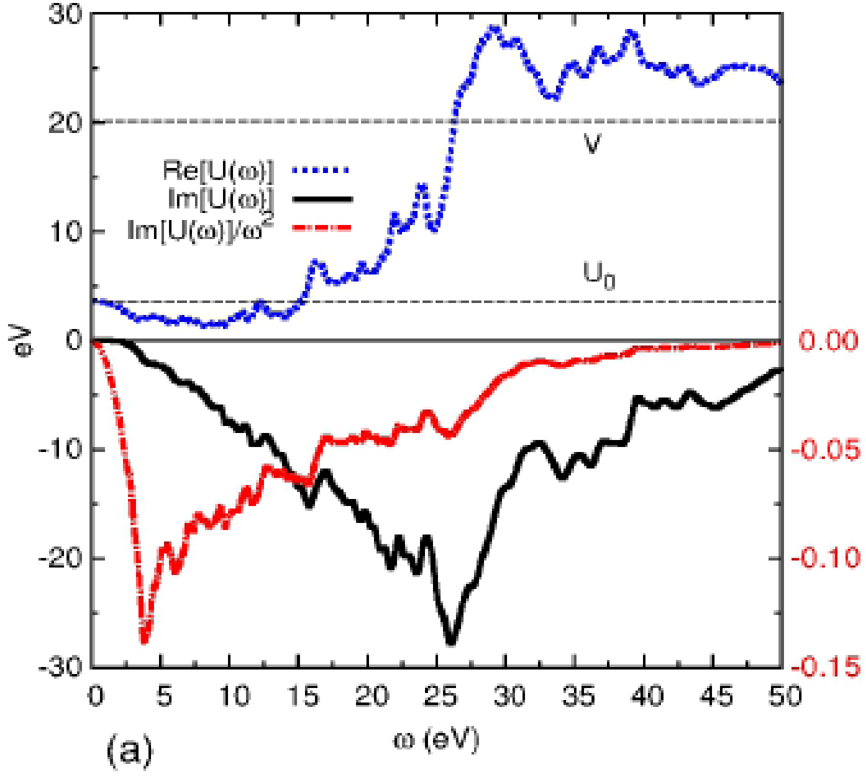
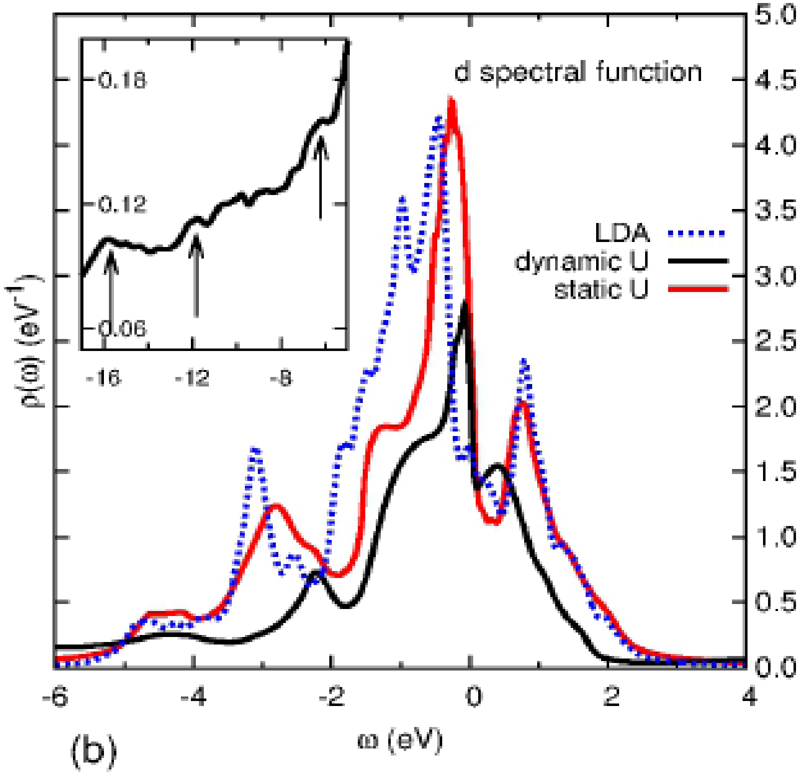


FIG. 3 (color online). (a) Frequency dependence of the bulk and surface Hubbard U parameter for bcc Cr. In the inset we expand the low frequency region. (b) The same for fcc Ni.

Re and Im *U* of BaFe2As2



Spectral functions of BaFe2As2



Werner *et al*, Nature Physics 8, 331 (2012)

La_2CuO_4

Kozhevnikov, Eguiluz, Shulthess

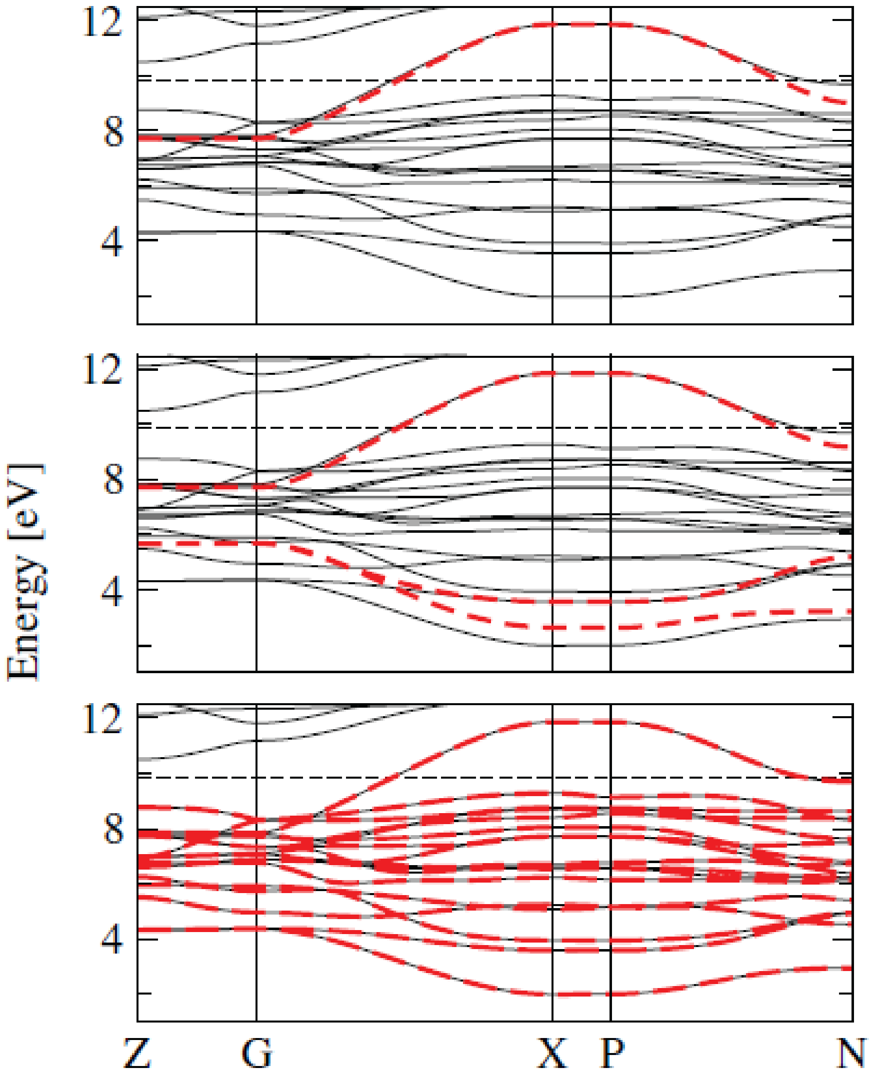


Fig. 1. (color online) Eigen-values of the "downfolded" Hamiltonian in Wannier functions basis (dashed red) plotted on top of the original band structure (solid black) for La_2CuO_4 for three different sets of Wannier functions: one Wannier function of $d_{x^2-y^2}$ character (top panel), three Wannier functions of $d_{x^2-y^2}$, p_x and p_y character (middle panel) and 17 Wannier functions of Cu-d, O-p character (bottom panel). Fermi level is denoted by dashed horizontal line.

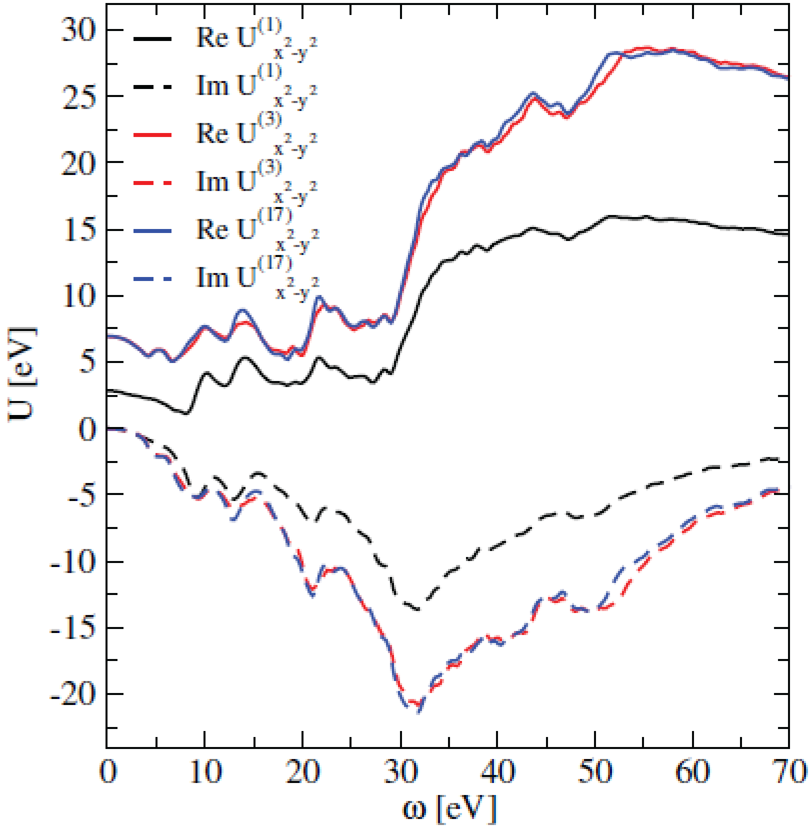
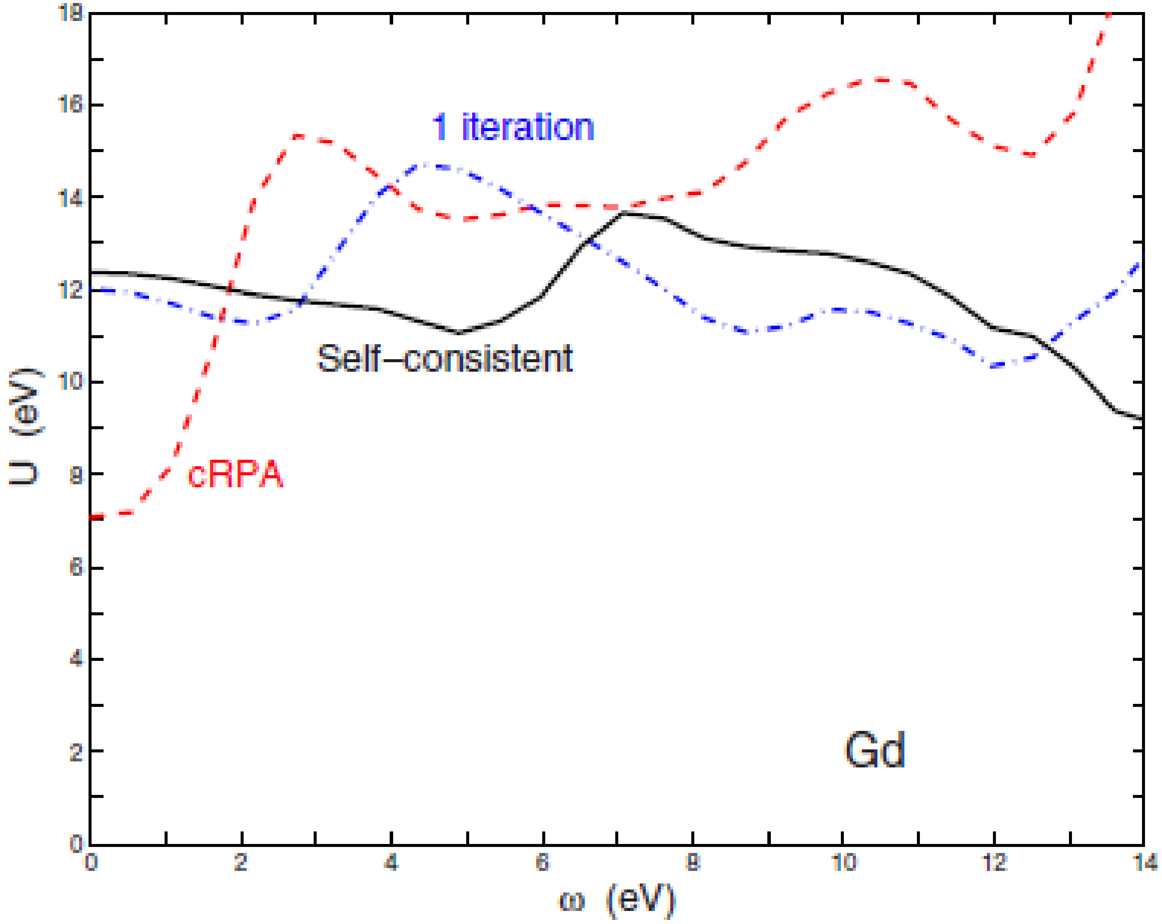


Fig. 2. (color online) Real and imaginary part of the screened frequency-dependent U parameter for the $x^2 - y^2$ orbital for three different basis sets: one-band (black), three-band (red) and seventeen-band (blue).

LDA+U with U determined by cRPA self-consistently



Karlsson *et al* PRB 81, 245113 (2010)

PHYSICAL REVIEW B **81**, 245113 (2010)

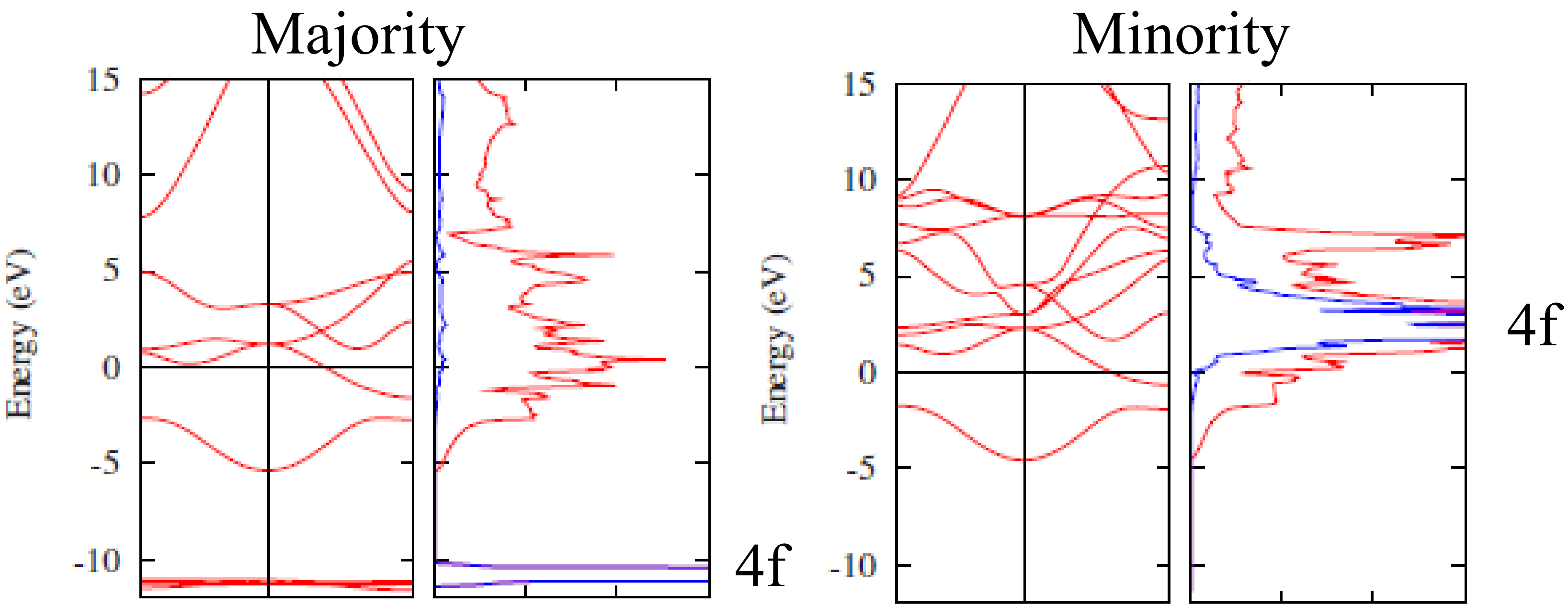


FIG. 1. (Color online) Gadolinium spin-up bands using the self-consistent determined parameters: $U=12.4$ eV and $J=1.0$ eV. Fermi energy at 0 eV and the directions displayed are $1/2(1,1,1) \rightarrow \Gamma \rightarrow (1,0,0)$. The corresponding total density of states (DOS) and f partial DOS are also displayed.

Connection between cLDA and cRPA

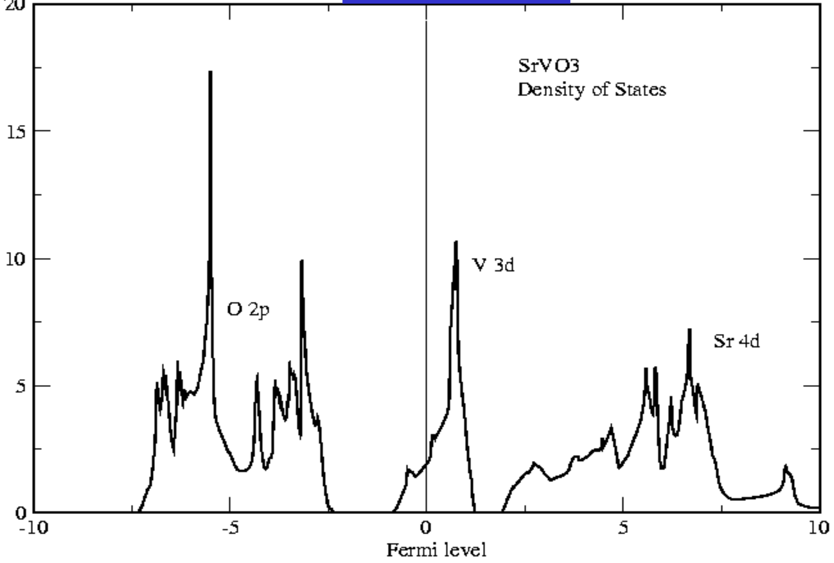
$$\frac{\partial^2 E}{\partial n_i \partial n_j} = \frac{\partial \varepsilon_i}{\partial n_j} = \left\langle \varphi_i \varphi_i \,|\, \varepsilon^{-1}(v + f_{xc}) \,|\, \varphi_j \varphi_j \right\rangle \qquad f_{xc} = \frac{\delta^2 E_{xc}}{\delta \rho^2}$$

In cLDA, calculate $U = \frac{\partial \varepsilon_i}{\partial n_i}$ with constrained hopping

In cRPA, calculate ε^{-1} with constrained screening, i.e., removing screening channels already included in the model.

U. von Barth,
The electronic structure of complex systems, *Advanced Study Institute (1982)*
M. Springer and FA, PRB 57, 4364 (1998).

SrVO3



cLDA (cut-off method):

When hopping from the localised orbitals is cut off, some screening channels are missed → too large *U*

To simulate cLDA, remove

$$t_{2g} \rightarrow all \quad O_{2p} \rightarrow t_{2g}, e_g \qquad \rightarrow U = 9.5 \text{ eV}$$

Compare with cLDA $U = 8.8$ eV

PRB 74, 125106 (2006)   c.f. Solovyev PRB 2007

Modified cLDA
(for comparison with cRPA)

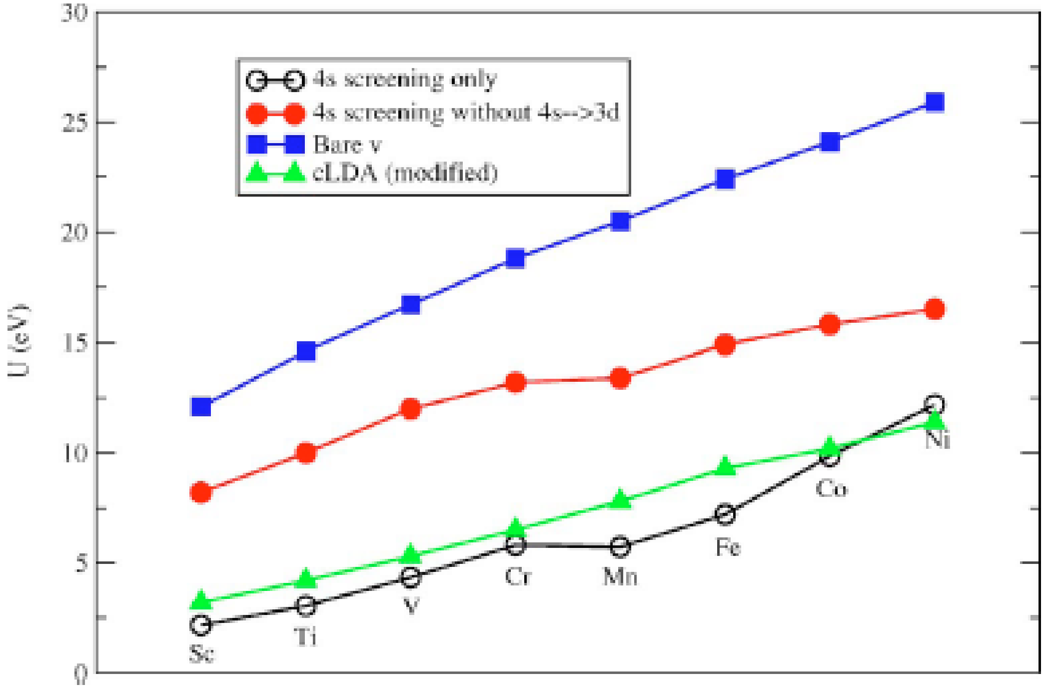


FIG. 8. (Color online) The effect of orbital contraction across the 3*d* series. Since the 3*d* orbital in nickel is most localized the bare Coulomb integral (filled square) is the largest. The bare Coulomb interaction is substantially reduced by the 4*s* screening (empty circle, the same as the empty circles in Fig. 7). The effect of 4*s* to 3*d* screening is illustrated by the filled circles. The effect, represented by the difference between the filled circles and the empty circles, is slightly more important in the early than in the late elements, due to the decreasing number of empty 3*d* states as we go from early to late elements.

$$U = \frac{\Delta \varepsilon_d}{\Delta n_d} \approx \frac{\langle \varphi_d \mid \Delta V \mid \varphi_d \rangle}{\Delta n_d}$$

Fix the orbitals φ_d

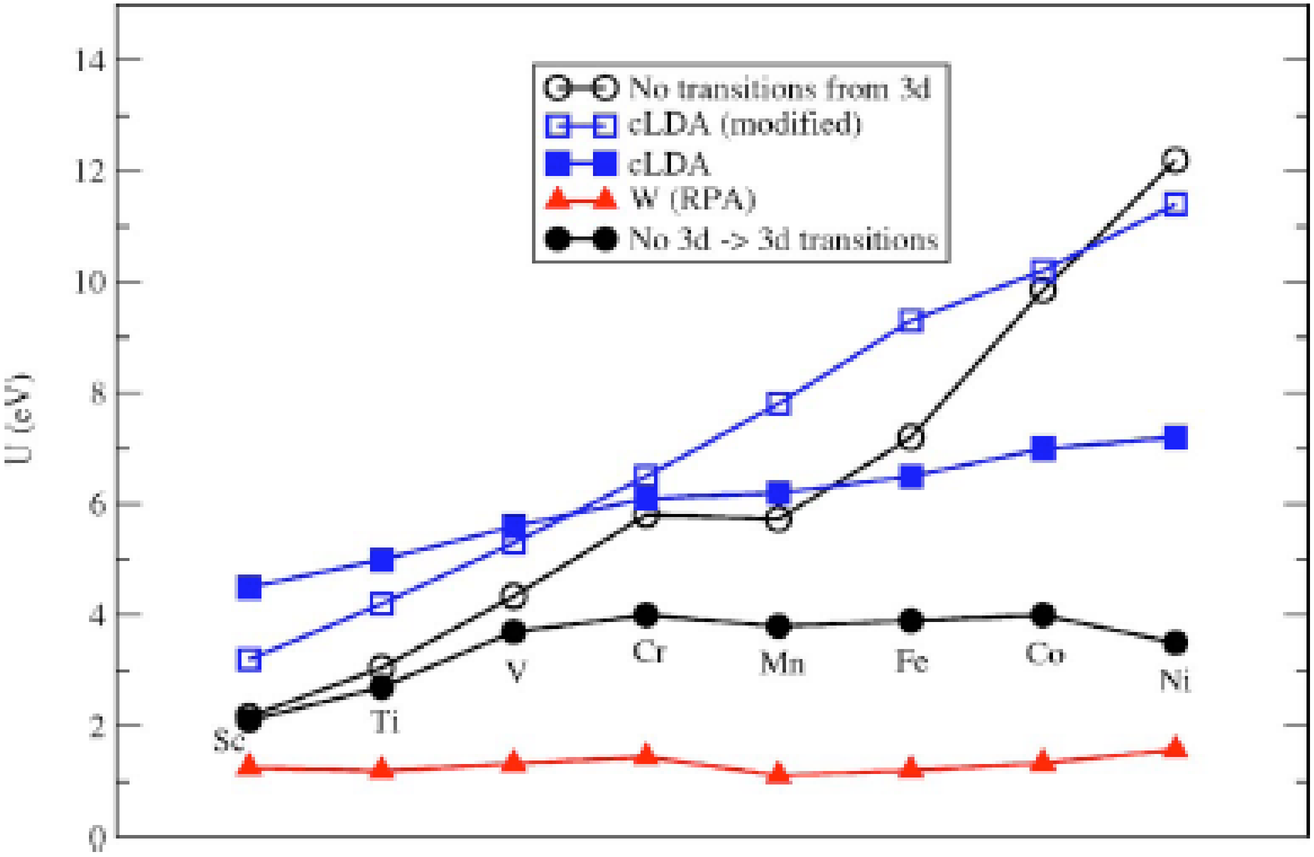
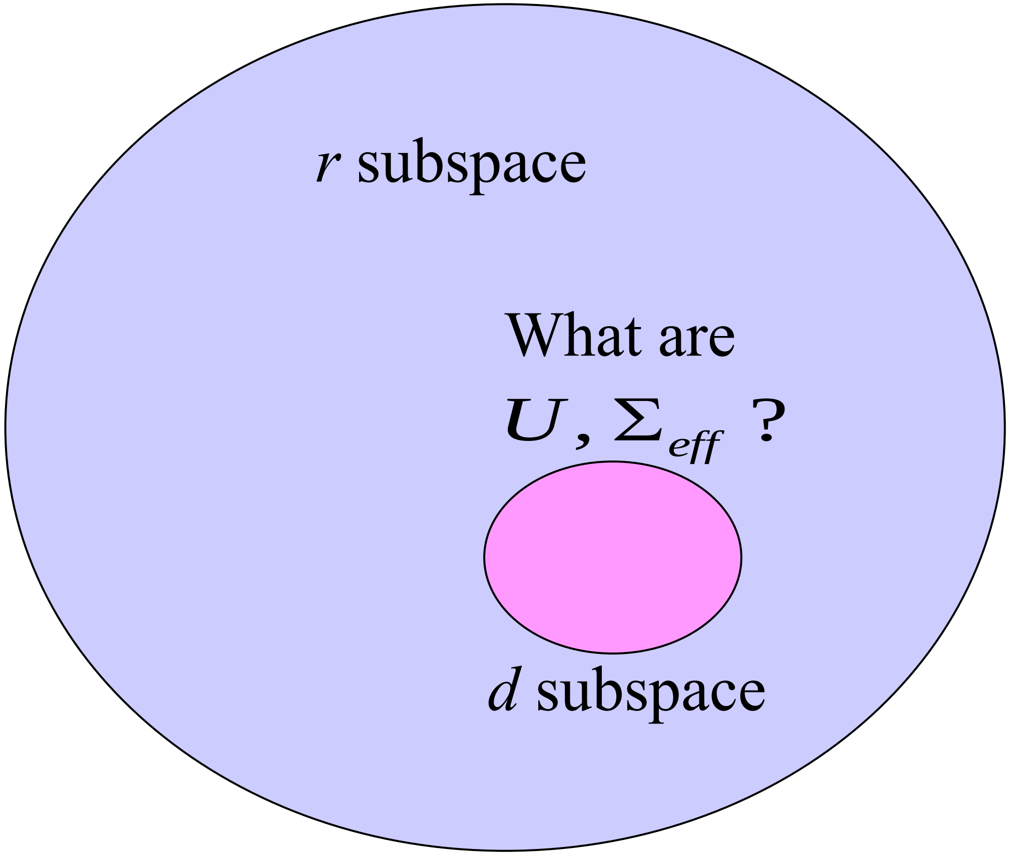


FIG. 7. (Color online) The Hubbard U for the $3d$ transition metal series calculated using the CRPA (filled circle, the same as the filled circles in Fig. 6) and CLDA (filled square). Empty circles correspond to the CRPA result excluding all transitions from the $3d$, i.e., only transitions from the $4s$ band are allowed. This should be compared with the modified CLDA result (empty square), as described in the text. For comparison, the fully screened interaction W is also plotted.

Downfolded self-energy

Full one-particle
Hilbert space



r subspace

What are
U, Σ_{eff} ?

d subspace

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

One-particle
hamiltonian

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

Step 1: The Green Functions

$$\hat{\psi} = \sum_{d} \chi_d \hat{c}_d + \sum_{r} \chi_r \hat{c}_r = \hat{\psi}_d + \hat{\psi}_r$$

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

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

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}

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

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

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

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

Definition of $\tilde{\Sigma}$

$$\tilde{\Sigma}G^d = \Sigma G\Delta_d$$

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 $\tilde{\Sigma}$:The non-trivial part

$$\Sigma G = iW\frac{\delta G}{\delta V} \quad \rightarrow \quad \tilde{\Sigma}G^{d} = iW\frac{\delta \tilde{G}}{\delta V}$$

$$V = \varphi_{ext} + V_{H}$$

$$\tilde{G} = G\Delta_{d}$$

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

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

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

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

➤ $$\Sigma^{eff} = \Sigma^{d}$$

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

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

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

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

$$W = W_r + W_r P_d W$$

$$W = U + UP_d W$$

$$\boxed{W_r = v + vP_r W_r,} \qquad P_r = P - P_d$$

➤ identify $\boxed{U \leftrightarrow W_r}$

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

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

The equations are valid for a *given* W_r

Furnishes a formal expression for *U*.

PRL **102**, 176402 (2009)

Summary

cRPA provides a systematic and precise first-principles scheme for determining U from realistic band structures.

Open problems:

- Entangled bands: not clear how to define the model.

-What is the best way of downfolding the energy-dependence of U?
(How to construct a model with a static U)

Previous works: LDA+U and LDA+DMFT
Can treat systems with strong on-site correlations

$$
\begin{aligned}
H = & \sum_{im\sigma}^{all} H^{LDA}_{im,i'm'}\, c^{+}_{im\sigma} c_{i'm'\sigma} \\
& + \frac{1}{2} \sum_{imm'\sigma}^{correl.} U^{i}_{mm'} n_{im\sigma} n_{im'-\sigma} \\
& + \frac{1}{2} \sum_{im\neq m'\sigma}^{correl.} \left(U^{i}_{mm'} - J^{i}_{mm'}\right) n_{im\sigma} n_{im'\sigma} \\
& - \sum_{im\sigma}^{correl.} H^{doublecounting}_{im,i'm'}\, c^{+}_{im\sigma} c_{i'm'\sigma}
\end{aligned}
$$

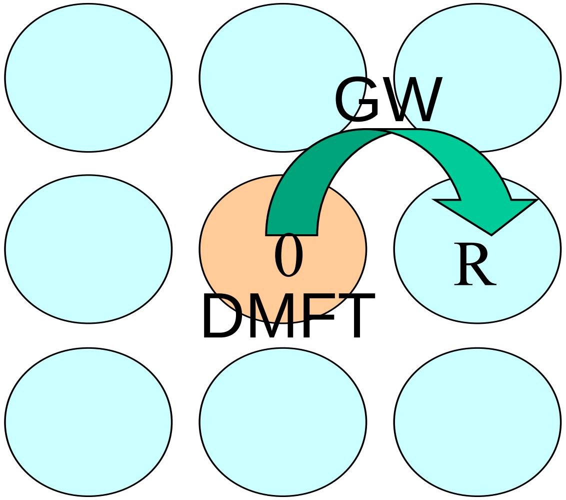
Adjustable U

Ad-hoc double-counting term

Anisimov *et al,* J. Phys. Condens. Matter 9, 7359 (1997) (LDA+U)
Lichtenstein and Kastnelson, PRB 57, 6884 (1998) (LDA+DMFT)

Proposed solution: GW+DMFT

Biermann, FA, and Georges, PRL **90**, 86402 (2003)
Sun and Kotliar, PRB **66**, 085120 (2002).



$$\Sigma_{00}(\omega) = \Sigma_{00}^{DMFT}(\omega)$$

$$\Sigma_{0R}(\omega) = \Sigma_{0R}^{GW}(\omega)$$

DMFT describes short-range local correlations.
GW describes long-range correlations (electron-gas)

Can be rigorously formulated by treating G and W as variables in the Luttinger-Ward functional

(Almbladh, von Barth and van Leeuwen, *Int. J. Mod. Phys. B* **13**, 535 (1999)
R. Chitra and G.Kotliar, PRB 63, 115110 (2001))

$$\Gamma[G,W] = tr\ln G - tr[G/G_0 - 1] - \frac{1}{2} tr\ln W + \frac{1}{2} tr[W/V - 1] + \Psi[G,W]$$