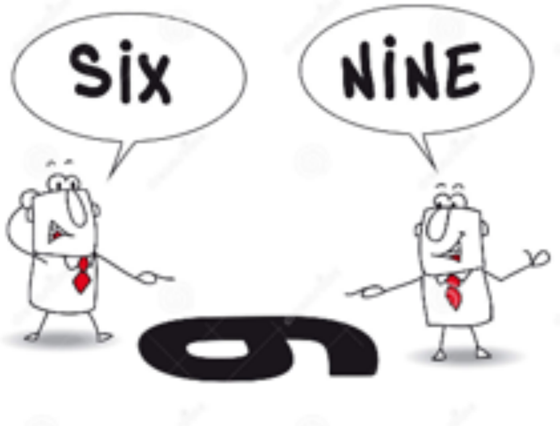
# Magnetic interaction in the Density Functional Theory: Learn from successes and learn from failures

**Igor Mazin, Naval Research Laboratory, Washington D. C.**

*And I wiped my mouth and said, "It is well that they are dead,*
***For I know my work is right and theirs was wrong**."*

*But my Totem saw the shame; from his ridgepole-shrine he came,*
*And he told me in a vision of the night: —*
***"There are nine and sixty ways of constructing tribal lays*, ***
***And every single one of them is right!"***



*R. Kipling, In the Neolithic Age*

*[*]tribal lays: tribal songs or ballads*

# Outline

1. Spin-density functional theory

2. Two main deficiency of LDA: local correlations and (often nonlocal) fluctuations

3. How do typical magnetic interactions appear in LDA and why they are usually overestimated?
    - AF direct exchange
    - FM kinetic exchange (≈double xc≈RKKY)
    - “Extended Stoner theory”
    - AF superexchange
    - FM 90$^o$ superexchange
    - Direct FM (Heisenberg) exchange

# 1. Spin-density functional theory

LSDA

$$E = \frac{1}{2}\int n(r)V_C(r,r')n(r') - \frac{1}{2}\int m(r)I_{xc}(r\,)m(r) + E_{xc}$$

$$n(r) = \sum\nolimits_{i,l} n_l(r-R_i);\ m = \sum\nolimits_{i,l} m_l(r-R_i)$$

$$m = n_\uparrow - n_\downarrow;\ n = n_\uparrow + n_\downarrow$$

Hubbard

$$E = \frac{1}{2}Un^2 - \frac{1}{2}Jm^2 - (U-J)\sum_{i,l} n_{l\sigma}n_{l\sigma}$$

LSDA: more accurate account of spatial variations

Hubbard: avoids self-interaction (more important for localized systems, less so for itinerant ones)

*Corollary: LDA+U, DMFT etc are not always better, they are simply different.*

# local correlations (more specific)

The exact LDA+U (or DMFT) Hamiltonian depends on the double counting (we do not want to throw away our good DFT treatment of Coulomb energy)

The general concept of double-counting corrections:

$H=H_{LDA}+\Delta H-\langle\Delta H\rangle_{LDA}$

where $\langle\rangle_{\mathrm{LDA}}$ means $\Delta H$ reduced to a local density functional.

$$E = \frac{1}{2}\cancel{Un^2} - \cancel{\frac{1}{2}J}m^2 - (U-J)\sum_{i,l,\sigma} n_{l\sigma}n_{l\sigma}$$

Substitute $n_{l\sigma}n_{l\sigma}$ with a function of $x_\sigma = x(n_\sigma)$ – function of $n_\sigma$ only.

# Double counting

$$E = \frac{1}{2}\cancel{Un^2} - \frac{1}{2}\cancel{Jm^2} - (U - J)\sum_{i,l,\sigma} n_{l\sigma} n_{l\sigma}$$

Two most common schemes:

**1. Around-mean field (AMF):**

$n_{l\sigma} \rightarrow \langle n_\sigma \rangle$ and $x_\sigma = (2l + 1)\langle n_\sigma \rangle^2$, thus $\Delta V \propto n_{l\sigma} - \langle n_\sigma \rangle$

This scheme assumes that all orbitals are ≈ equally occupied

**2. Fully Localized Limit (FLL):**

$n_{l\sigma} = 0\ or\ 1$ and $x_\sigma = (2l + 1)\langle n_\sigma \rangle$, thus $\Delta V \propto n_{l\sigma} - 1/2$

*A common misconception is that they are roughly the same.*

$$\Delta I = \frac{U - J}{N^2}\left(\sum N_l^2 - a\frac{N^2}{2l + 1}\right); \quad if \quad N_l = N/(2l + 1)$$

$$FLL \rightarrow a = 0 \rightarrow \Delta I \approx \frac{U - J}{2l + 1}; \quad AMF \rightarrow a = 1 \rightarrow \Delta I \approx 0$$

# Two main deficiency of LDA: local correlations and (often nonlocal) fluctuations

Fluctuations:
DFT is, by construction, a mean field theory.

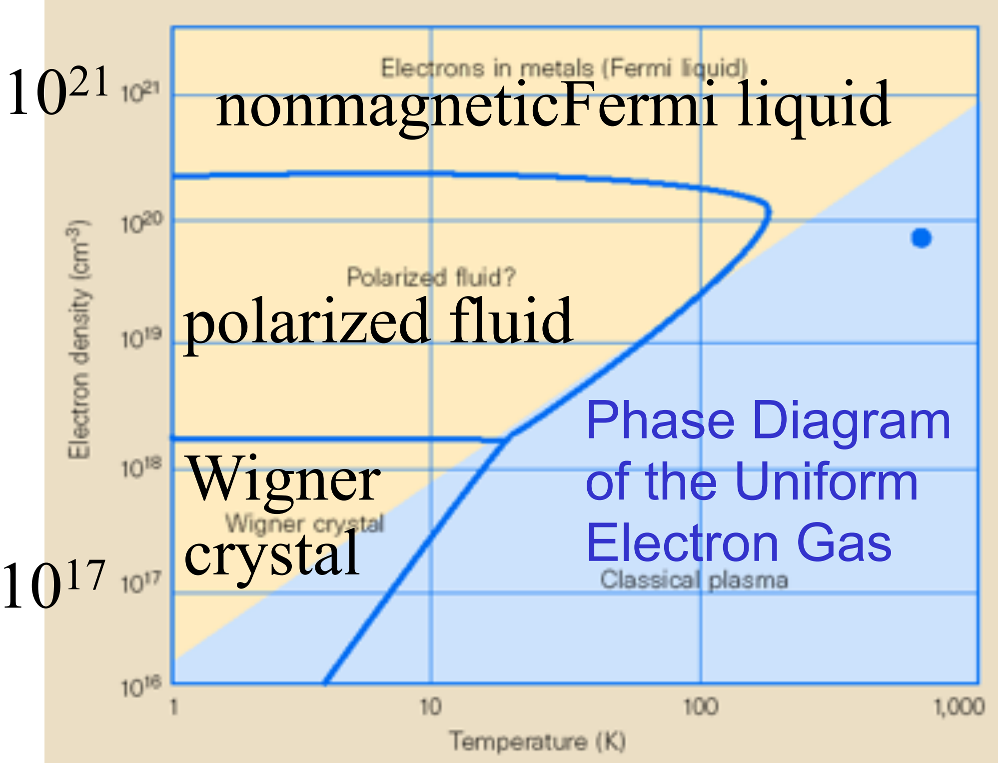
- Local quantum fluctuations reduce a local spin by δS~0.1-0.3 (depending on the lattice)
- Itinerant fluctuations, in principle, can be anything, but they are accounted for as long as they are included in the reference system.

**bcc Fe:**

$n_{av}$ =2.2x$10^{24}$ e/cm$^3$ (total)

$n_{av}$= 6.8x$10^{23}$ e/cm$^3$ (valence)

***Nothing Interesting Happens in the Uniform Electron Gas for Densities Relevant to Solids***



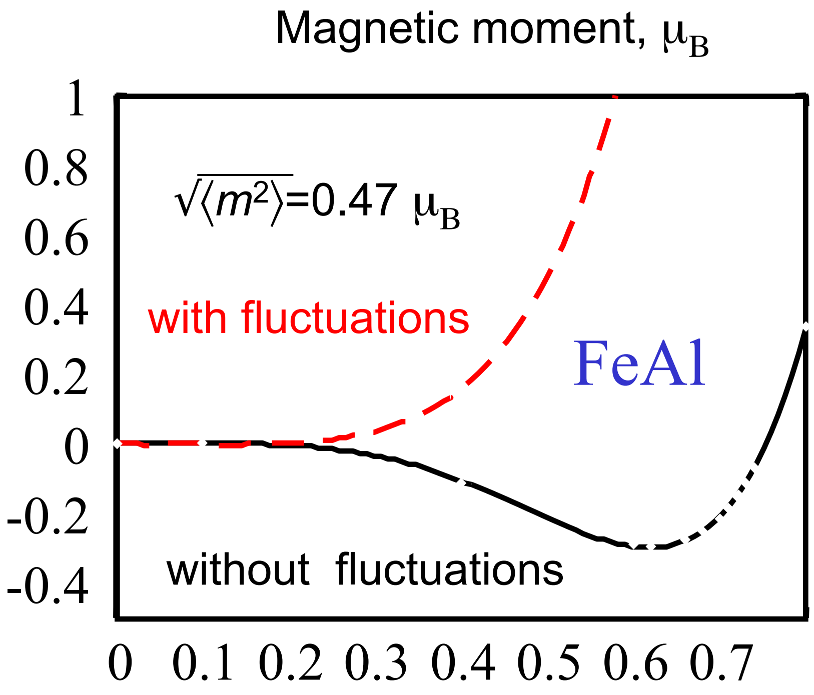
Phase Diagram of the Uniform Electron Gas

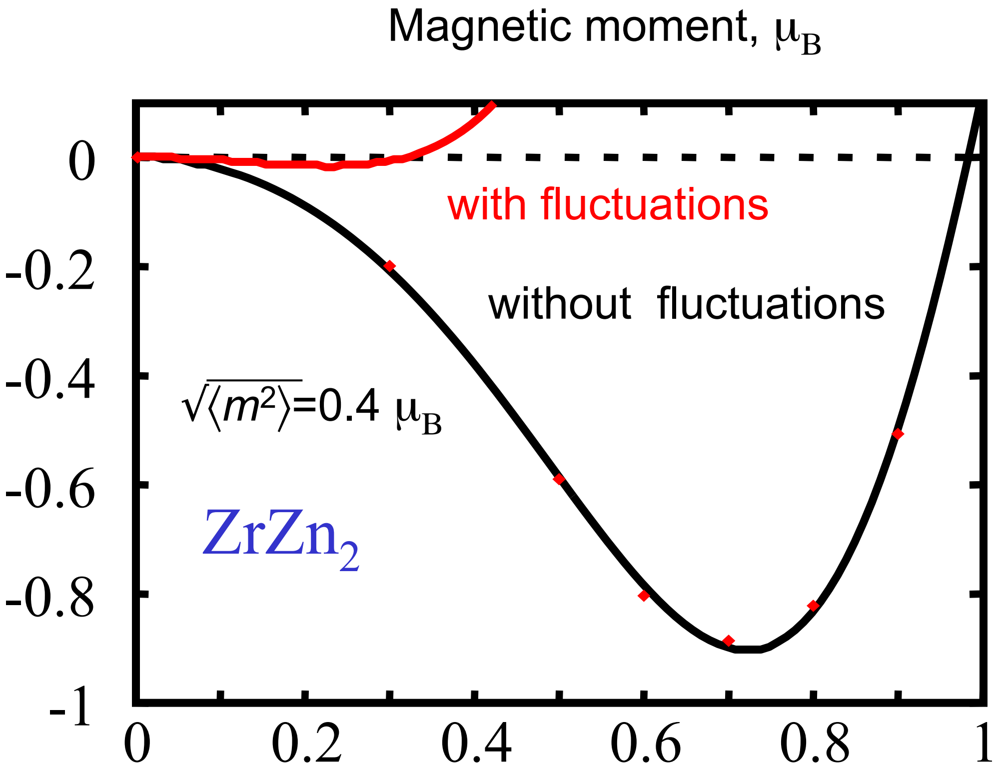
# Some examples

Ferromagnets where the LDA overestimates the magnetization: $ZrZn_2$, $Ni_3Al$, $Sc_3In$, MnSi

Paramagnets where the LDA predicts ferromagnetism: FeAl, $Ni_3Ga$, $Sr_3Ru_2O_7$, $Na_{0.5}CoO_2$, ε-Fe, $LiV_2O_4$, $Ni_3In$, $SrRhO_3$, $(Sr,Ca)RuO_3$

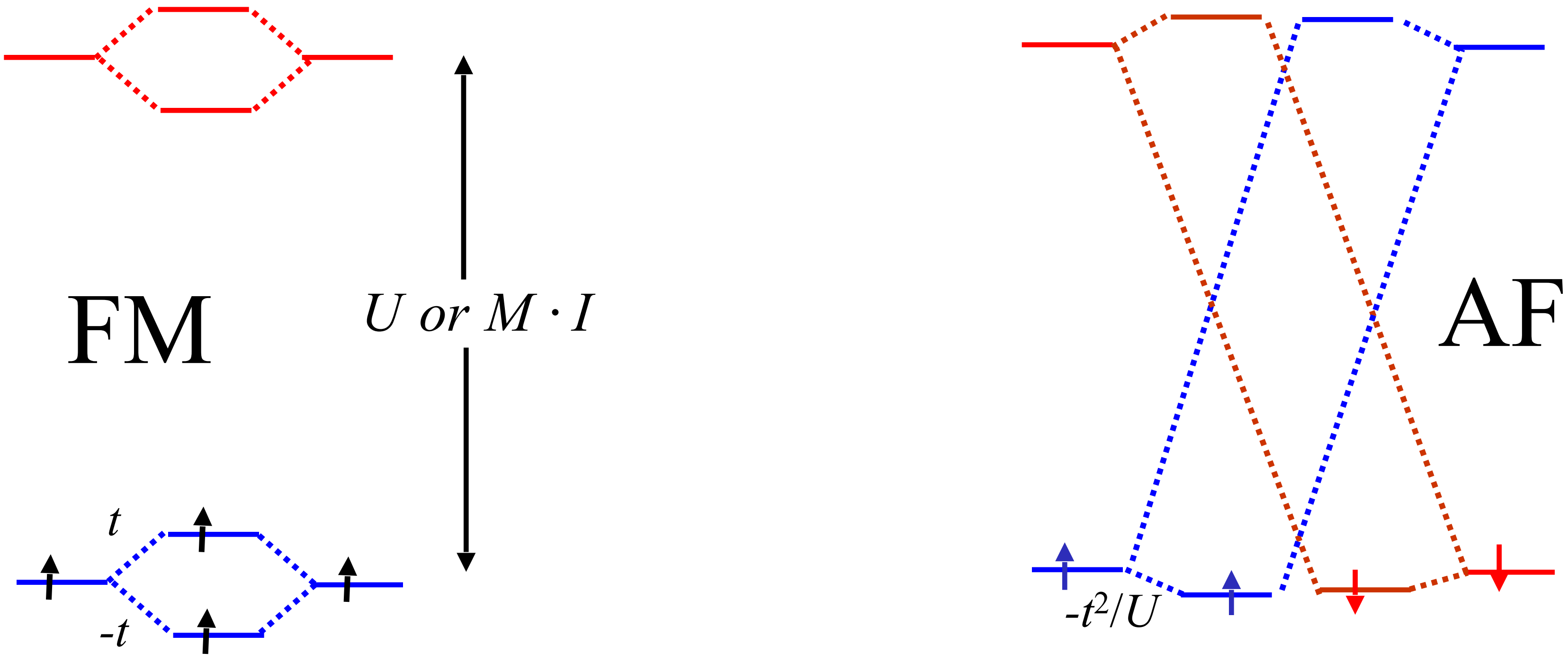
Paramagnets where the LDA overestimates the susceptibility: Pd, $Sr_2RuO_4$





# How do typical magnetic interaction appear in LDA?

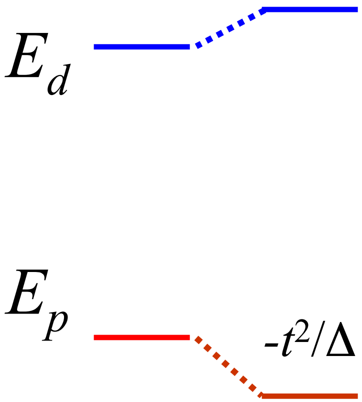
## AF direct exchange

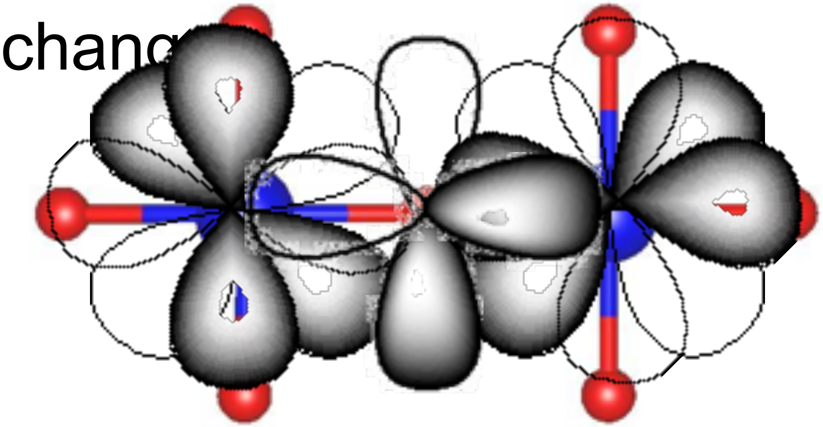


Energy gain of $J \sim 2t^2/U$
Short range

# How do typical magnetic interaction appear in LDA?

AF superexchang





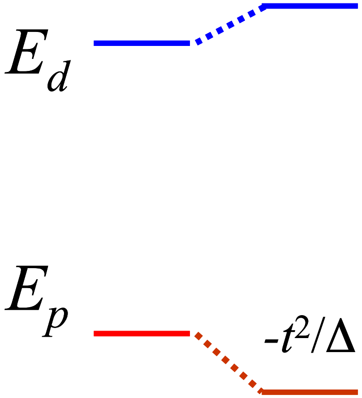
Effective hopping of $-2t^2/U$

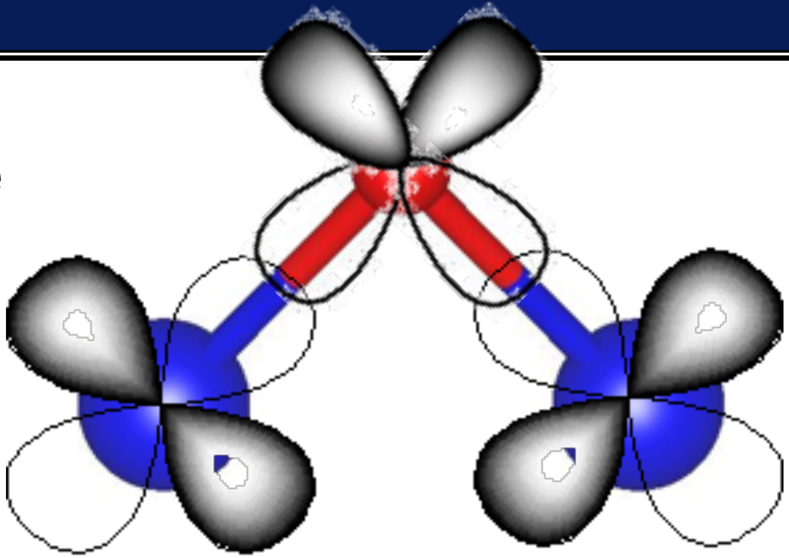
Effective AF exchange

$$\begin{pmatrix} E_d & 0 & t \\ 0 & E_d & t \\ t & t & E_p \end{pmatrix} \xrightarrow{\text{yields}} \begin{pmatrix} E_d + \frac{t^2}{\Delta} & -\frac{t^2}{\Delta} \\ -\frac{t^2}{\Delta} & E_d + \frac{t^2}{\Delta} \end{pmatrix}$$

# How do typical magnetic interaction appear in LDA?

FM 90° superexchange





$M_O$~$(t/\Delta)^2$; FM energy gain of $J_{FM}=IM_O^2$~$It^4/\Delta^4$

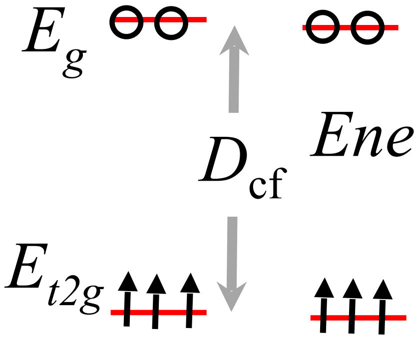
$J_{AF}=2t^4/\Delta^2U$

$J_{FM}/J_{AF}$~$IU/\Delta^2 << 1$

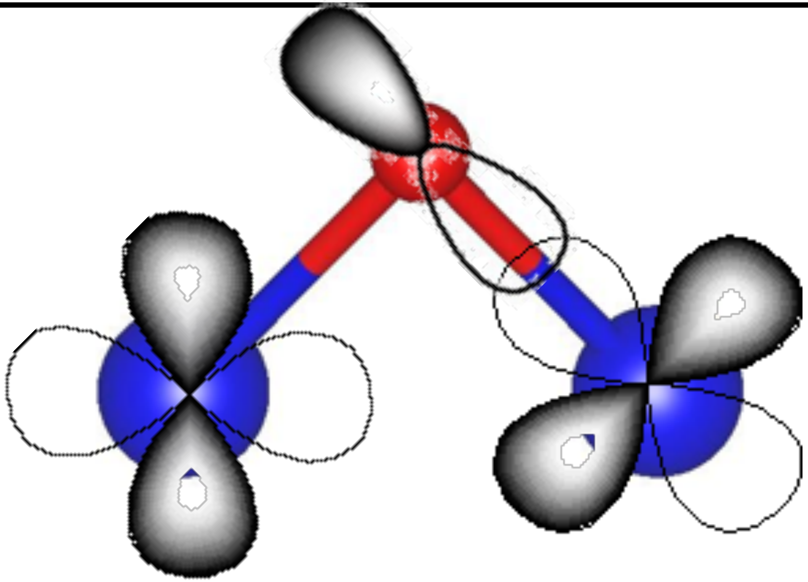
*Note: in LDA FM superexchange does not depend on the bond angle. But, this is usually a minor error*

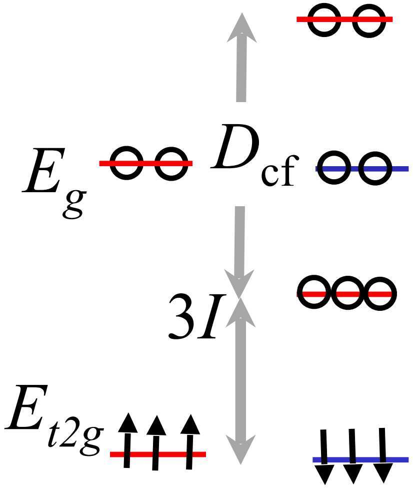
# How do typical magnetic interaction appear in LDA?

## FM multiorbital superexchange



*Energy gain*: $3t^2/D_{cf}$





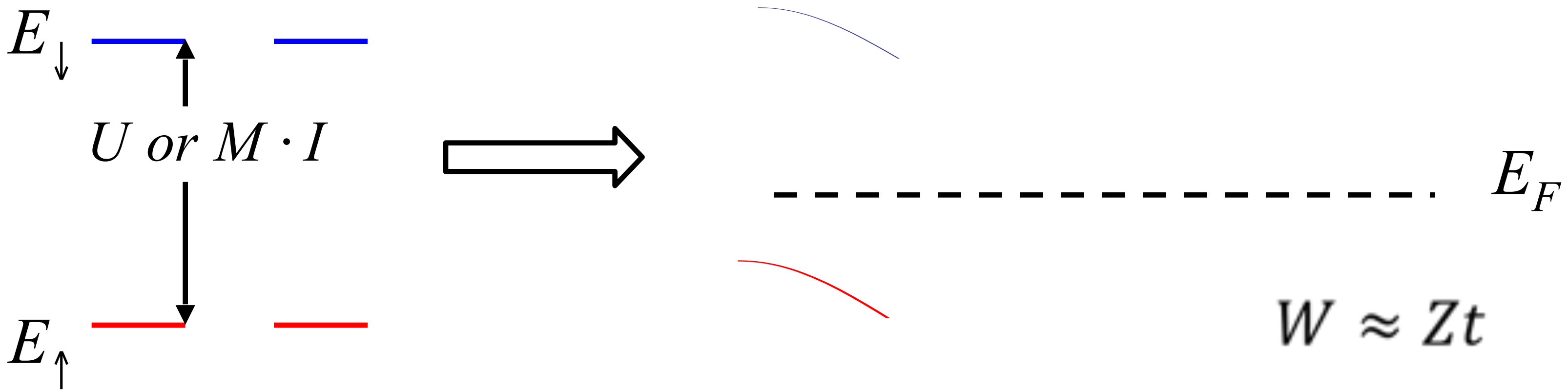
*Energy gain*:
$3t^2/(3I+D_{cf})$

$$J_{FM} \approx \frac{9It^2}{D_{cf}^2}$$

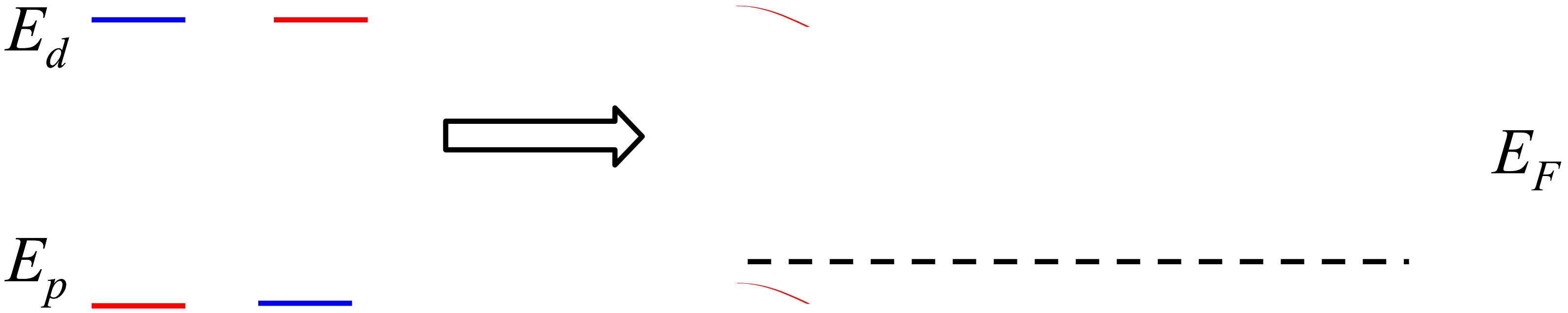
The same result may be obtained in the Hund-Hubbard model using perturbation theory – but DFT accounts for all interactions simultaneously and on the same footing.

# How do typical magnetic interaction appear in LDA?

FM kinetic exchange (≈double xc≈RKKY)



$W \approx Zt$



$W \approx Zt^2/U$

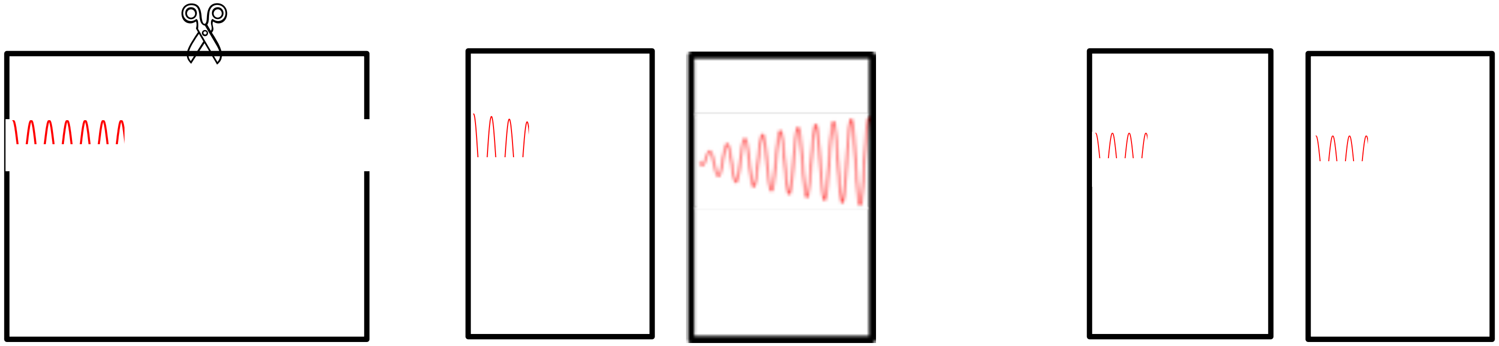
# How do typical magnetic interaction appear in LDA?

FM kinetic exchange (≈double xc≈RKKY)

FM energy gain ~ *tn (max for half-filling)*

Several incarnations of the same physics:
1. Extended Stoner theory (O.K. Andersen)

Andersen’s force theorem: Difference of one-electron energies calculated with the same charge density is equal, in the lowest order, to the difference of the self-consistent total energies



# Why does it work?

$$E = W_{ee}[\rho] + \int \rho V_{ext} + T[\rho]$$

where

$$\begin{aligned} T[\rho] &= \sum_{occ} \left\langle i \right| -\frac{\nabla^2}{2m} + V_{ee}[\rho] + V_{ext} \left| i \right\rangle - \int \rho V_{ext} - \int \rho V_{ee}[\rho] \\ V_{ee}[\rho] &= \delta W_{ee}[\rho]/\delta\rho \end{aligned}$$

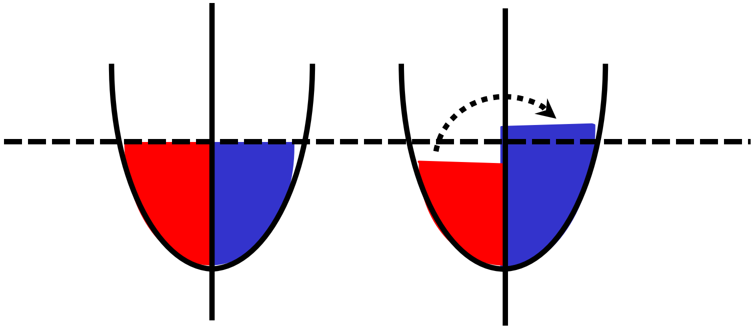
And therefore

$$E = W_{ee}[\rho] - \int \rho V_{ee}[\rho] + \sum_{occ} \left\langle i \right| -\frac{\nabla^2}{2m} + V_{ee}[\rho] + V_{ext} \left| i \right\rangle$$

Suppose the external potential changes by $\Delta V_{ext}$, which *self-consistently* generates $\Delta\rho$ and $\Delta V_{ee}$. Then, to the second order,

$$\begin{aligned} \Delta E &= \cancel{\int \frac{\delta W_{ee}[\rho]}{\delta\rho} \Delta\rho} - \cancel{\int \Delta\rho V_{ee}[\rho]} - \cancel{\int \rho \Delta V_{ee}[\rho]} \\ &\quad + \sum_{occ} \langle i | \cancel{\Delta V_{ee}[\rho]} + \Delta V_{ext} | i \rangle \\ &= \sum_{occ} \langle i | \Delta V_{ext} | i \rangle \end{aligned}$$

# Application: Extended Stoner theory



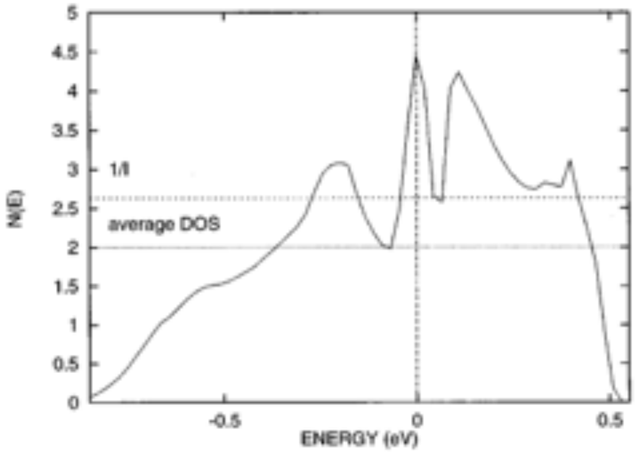
Exchange splitting: $M/N_\uparrow$

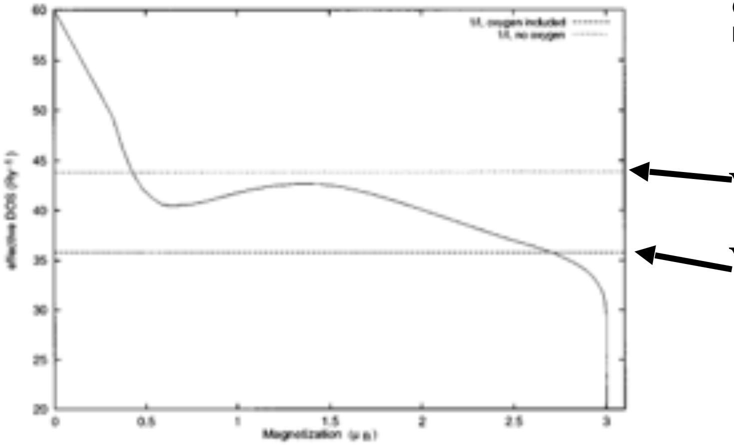
Energy gain: $-IM^2/4$

Energy loss: $M^2/4N_\uparrow$

Stoner criterion: $IN_\uparrow>1$

$$E(m)=\frac{1}{2}\int_0^m \frac{m'dm'}{\overline{N}(m')}-\frac{Im^2}{4} \qquad \Delta=m/\overline{N}(m)$$





SrYRu$_2$O$_3$

without O

with O

# Stoner theory for compounds

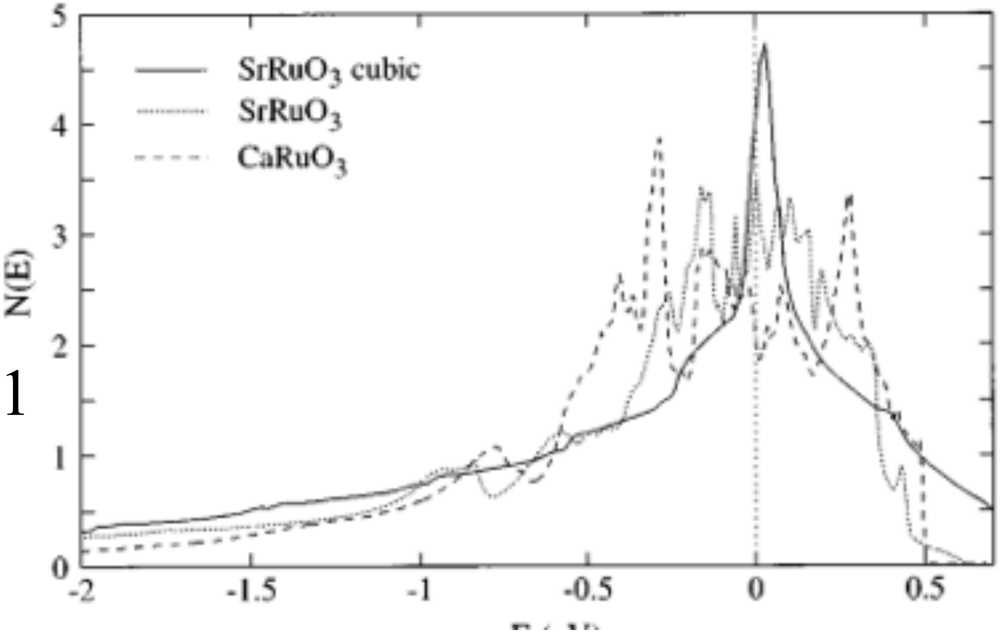
$$E = -IM^2/4; \quad M = \Delta N = M_{Ru} + 3\ \ _O; \quad \ \ _a = \Delta\ \ _a$$

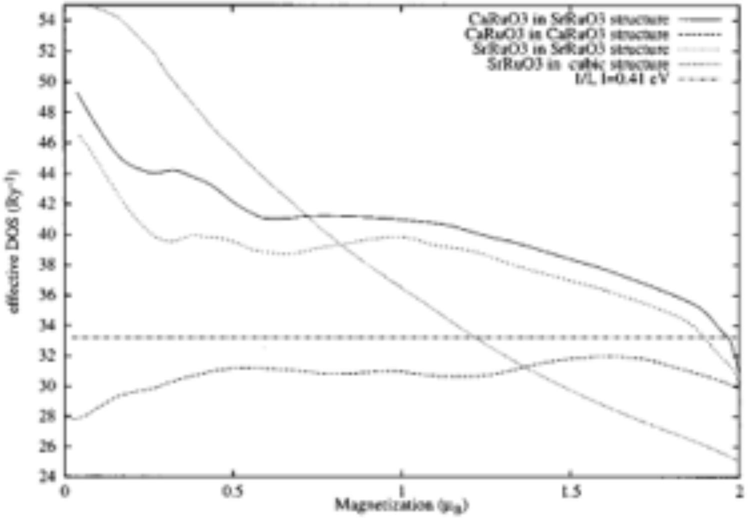
$$E = -(I_{Ru}M_{Ru}^2 + 3I_O M_O^2)/4 = -(I_{Ru}N_{Ru}^2 + 3I_O N_O^2)\Delta^2/4$$

$$I = I_{Ru}\left(\frac{N_{Ru}}{N}\right)^2 + 3I_O\left(\frac{N_O}{N}\right)^2$$

$$I_{Ru} \approx 0.7\text{ eV}; I_O \approx 1.6\text{ eV}$$

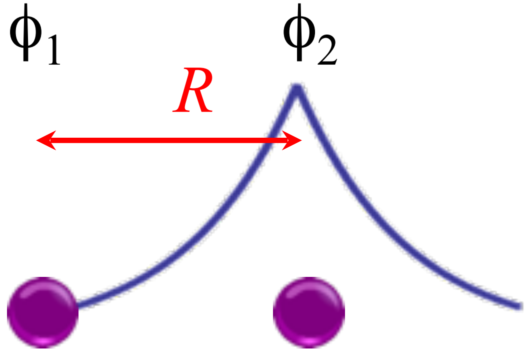
$$I_{Ru}\left(\frac{N_{Ru}}{N}\right)^2 = 0.35\text{ eV}; I = 0.41$$





This is a multi-atom analogue of the classic Heisenberg ferromagnetic exchange ⇒

# Ferromagnetic (Heisenberg) exchange



$$\phi \sim \exp(-r/r_d)$$

$$J_{FM} \sim I\exp(-R/r_d)$$

$$J_{AF} \sim t^2/I$$

FM $t \sim \langle\phi_1|-\nabla^2|\phi_2\rangle$

$$\sim\langle\phi_1|\phi_2\rangle/r_d^2 \sim \exp(-R/2r_d)/r_d^2$$

$$m(\mathbf{r})=\phi_1^2+\phi_2^2,\ E_{\mathrm{St}}=-\int I(\phi_1^2+\phi_2^2)^2/4$$

$$-$$

$$\underline{m(\mathbf{r})=\phi_1^2-\phi_2^2,\ E_{\mathrm{St}}=-\int I(\phi_1^2-\phi_2^2)^2/4}$$

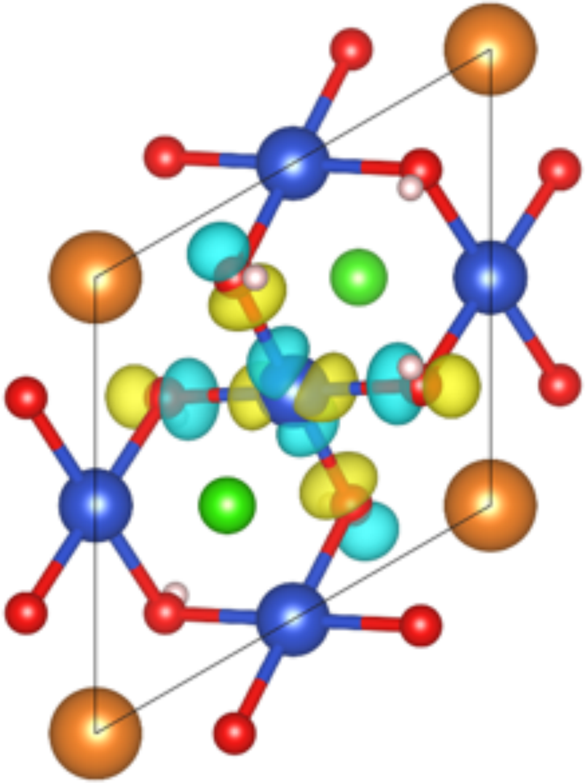
$$= I\langle\phi_1^2|\phi_2^2\rangle$$

How large is direct FM exchange compared to direct AFM exchange?

$$J_{\mathrm{FM}}/J_{\mathrm{AFM}} \sim I^2\exp(-R/r_d)/[\exp(-R/2r_d)/r_d^2]^2 = I^2 r_d^4$$

$$\sim 10^{-3}$$

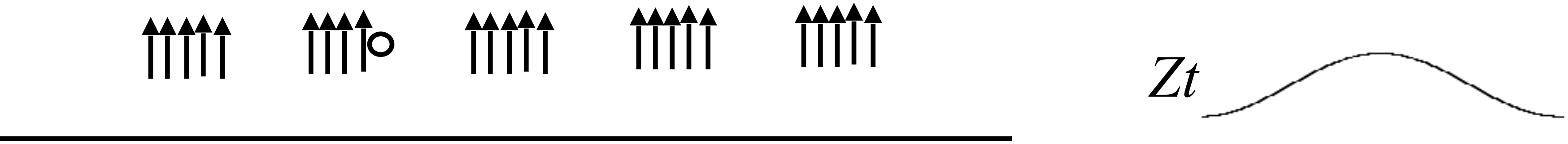
So direct FM exchange is negligible (and fully accounted for). Then why do we see papers claiming to see this effect in their calculations?

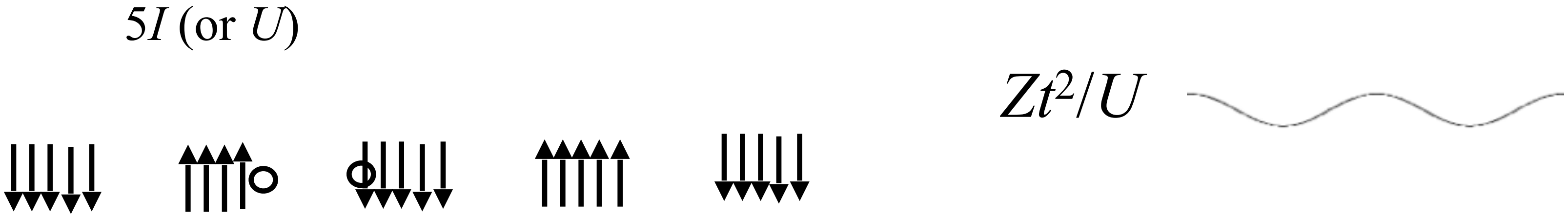


Answer: Misleading Wannier functions aka Alternative Facts).

Wannier functions overlap can be as huge as Trump's inauguration crowds,  but in reality it is not Cu-d (in this example), but O-p *on the same site* that overlap.

# Duplicity of double exchange





Energy gain of $J \sim t$
Long range

# Duplicity of double exchange

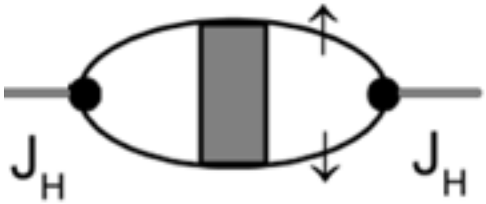
Let us formalize the model. Assume we have some electrons forming local moments and some itinerant (in reality these are the same electrons, just "piling up" their moments)

$$H = t\sum c_{i\sigma}^{\dagger} c_{j\sigma} - J_H \sum c_{i\sigma}^{\dagger} \boldsymbol{\sigma} c_{i\sigma\, H} \cdot \mathbf{S}$$

For small $J_H$, after integrating out the itinerant electrons,

$$H \approx \sum J_{RKKY}(\mathbf{R}_i - \mathbf{R}_j)\mathbf{S}_i \cdot \mathbf{S}_j$$

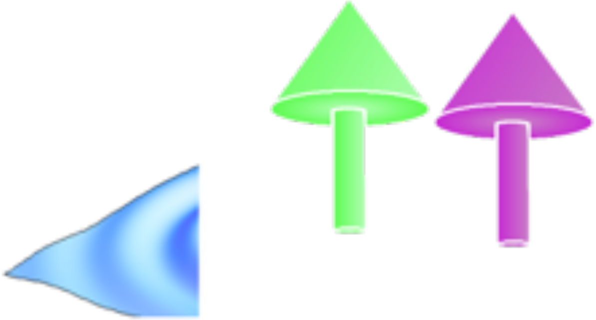
$$J_{RKKY}(R) \sim N(0) J_H^2 (\sin 2k_F R - 2k_F R \cos 2k_F R) / (2k_F R)^3$$

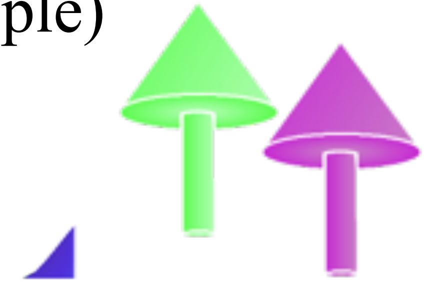


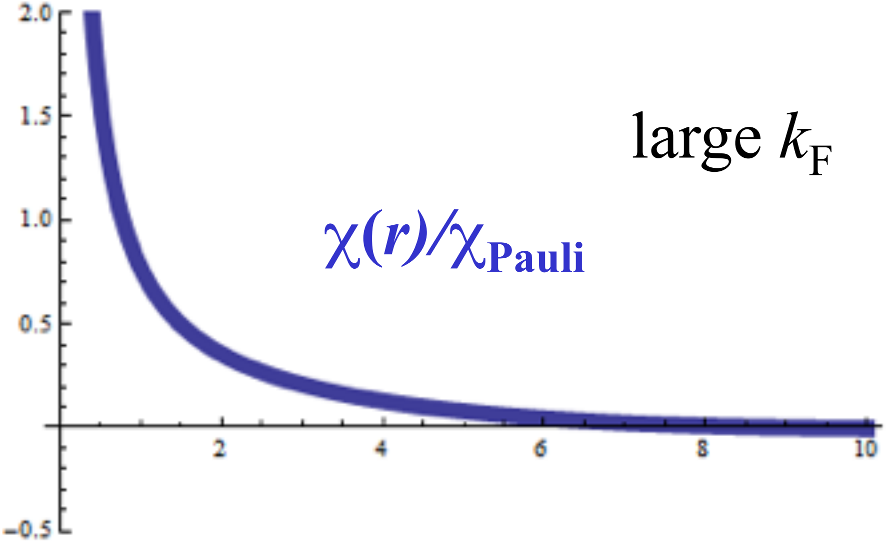
# Duplicity of double exchange

For large $k_F$ (large occupancy) it is a complicated, sign changing function.

For small $k_F$ (few free carriers) it is just ferromagnetic (manifestation of the uncertainty principle)





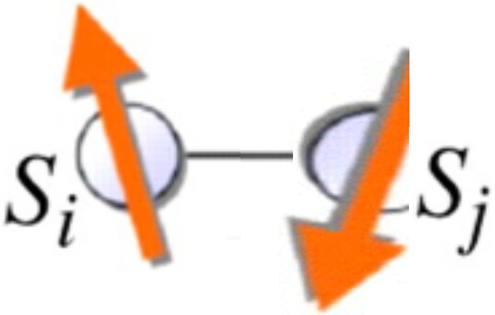


large $k_F$

small $k_F$

$2k_F=0.50$

# Solving the double exchange model



$$t_{eff} = t\cos(\theta/2)$$

$$J_{SEX} \propto t^2; \quad J_{DEX} \propto -t$$

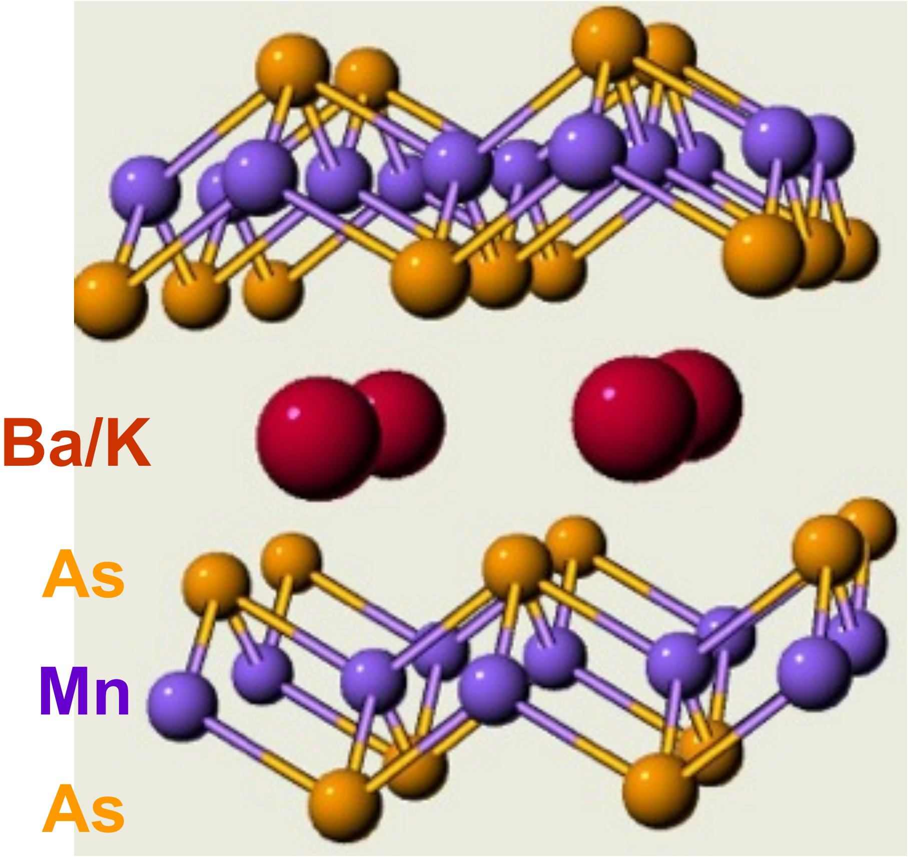
$$E = J_0\cos\theta - nt\cos(\theta/2)$$

$$\cos(\theta/2) = tx/4J_0$$

Spins cant (or spiral) with an angle defined
by hopping and carrier concentration

# A misconception about double exchange

Double exchange does NOT require that itinerant and localized electrons belong to the same atom and are coupled by Hund.

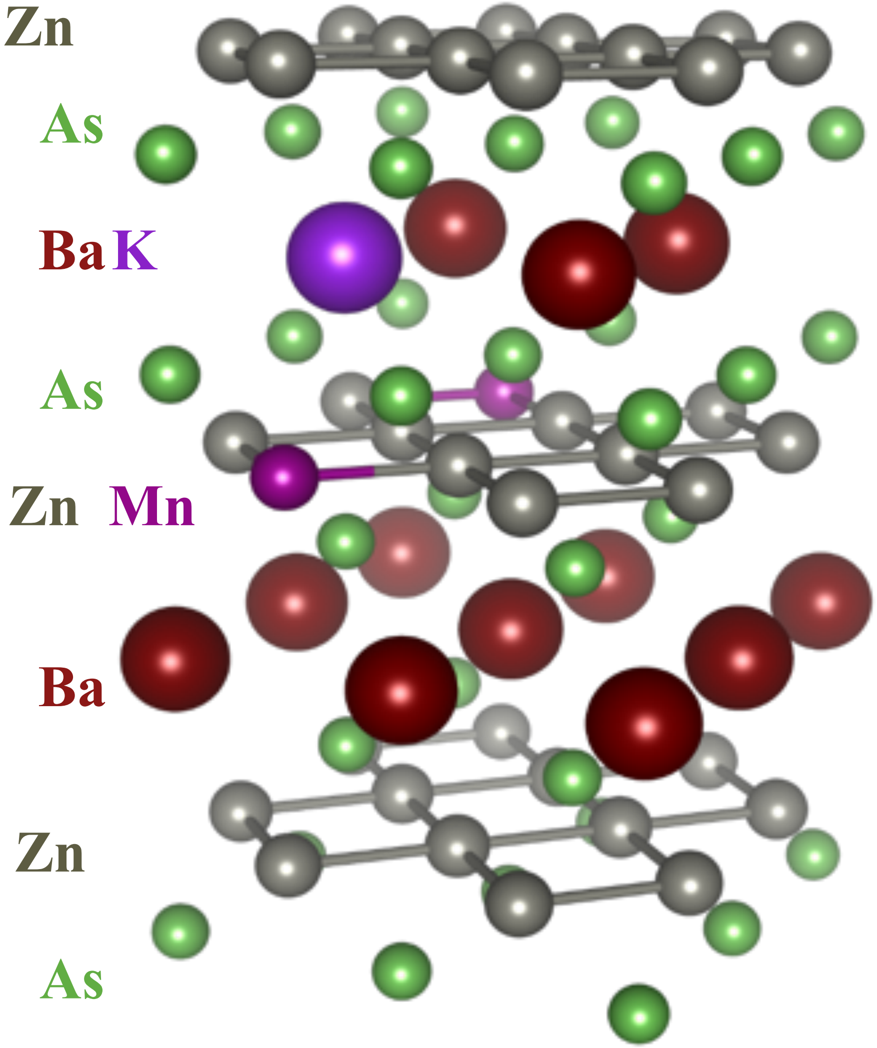


Mn moments appear canted. Why?

**free carriers**

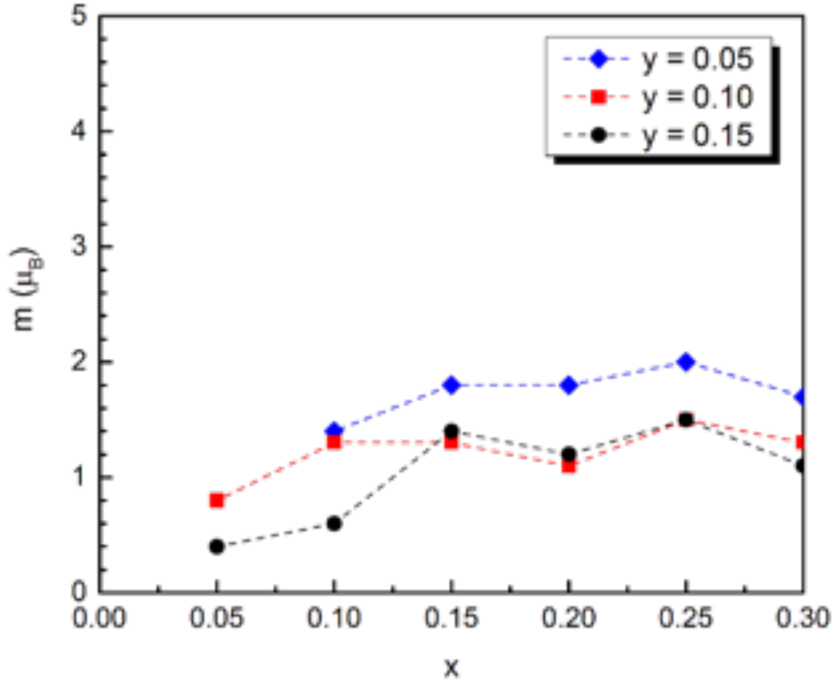
**local moments**

# $Ba_{1-x}K_x(Zn_{1-y}Mn_y)_2As_2$: Experiment

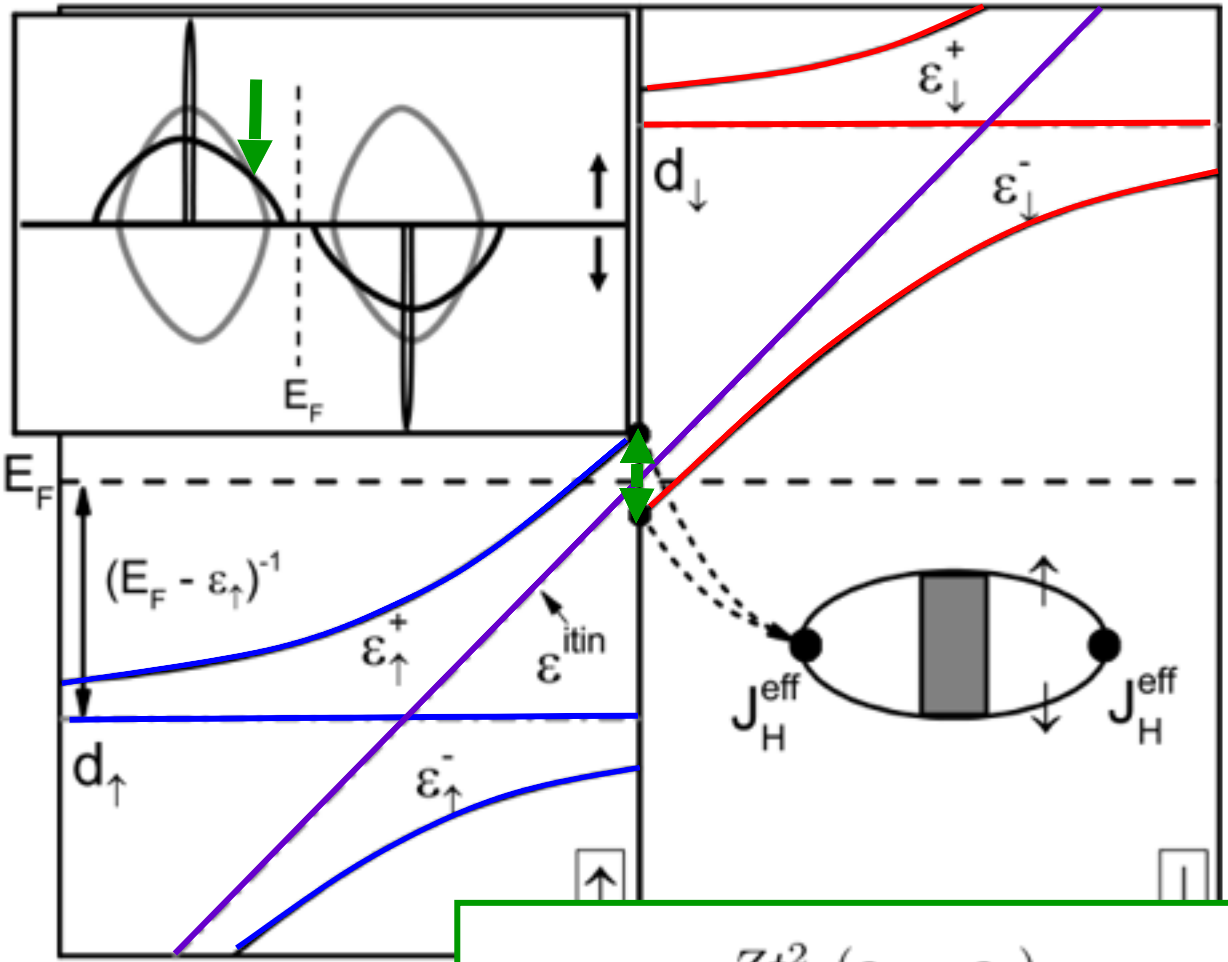


K. Zhao et al, Nature Comm, 2013

Mn moments order ferromagnetically ($T_c \sim 230\ K$). Why?



# Holes are NOT on Mn!



Hybridization effects:

1. As band broadens, gap gets smaller (spin-flip)
2. As states at the Fermi acquire exchange splitting → effective Hund's coupling

$$J_H^{\mathrm{eff}} = \frac{-Zt_{pd}^2(\varepsilon_\uparrow - \varepsilon_\downarrow)}{(E_F - \varepsilon_\uparrow)(\varepsilon_\downarrow - E_F)} = \frac{-Zt_{pd}^2 U}{(E_F - \varepsilon_\uparrow)(\varepsilon_\uparrow + U - E_F)}.$$

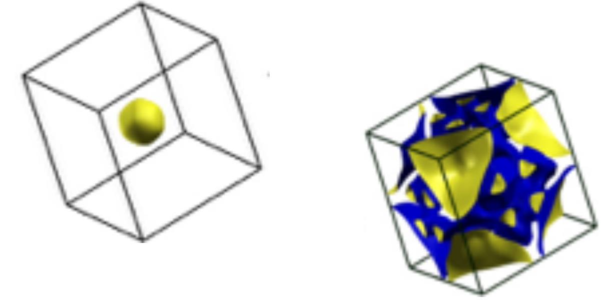
# …rose by any other name…

- Local moments: double exchange
- Itinerant moments: kinetic exchange

- Small FS: double exchange
- Large FS: RKKY

- Same atom: Hund’s rule (>0)
- Different atoms: Schrieffer-Wolff (<0) (also called *p-d* model)

<Squared anyway!>



*In fact, the RKKY+Schrieffer-Wolff is arguably the most common case of double exchange*

*Always the same physics: ferromagnetism facilitates electron motion*

# Why magnetic interaction in LDA are usually overestimated?

Superexchange:

$J_{\mathrm{FM}} \propto It^4/\Delta^4$

$J_{\mathrm{AF}} \propto t^4/\Delta^2 U$

$J_{\mathrm{DEX}} \propto t$

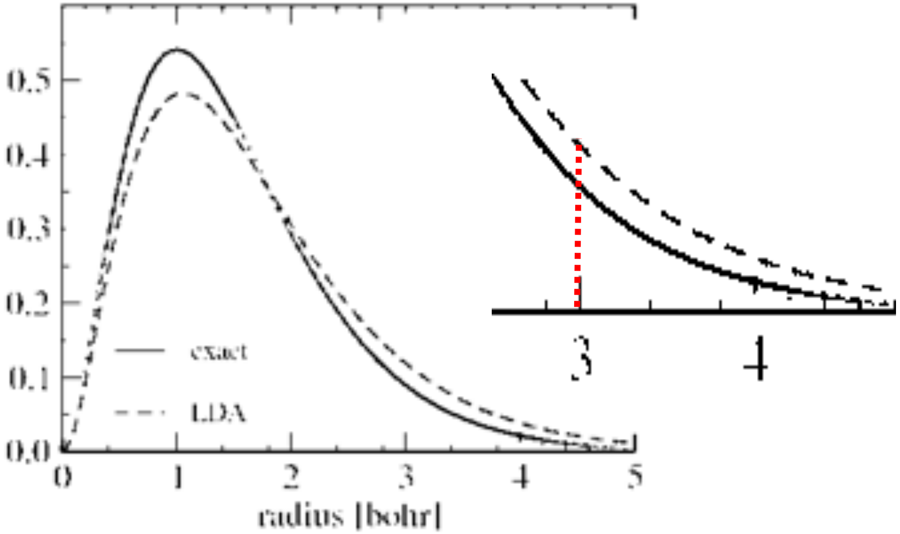
$J_{SW} \propto (t^2_{pd}/U)^2 N$

$U \Rightarrow MI$ usually underestimated

$t$ usually overestimated

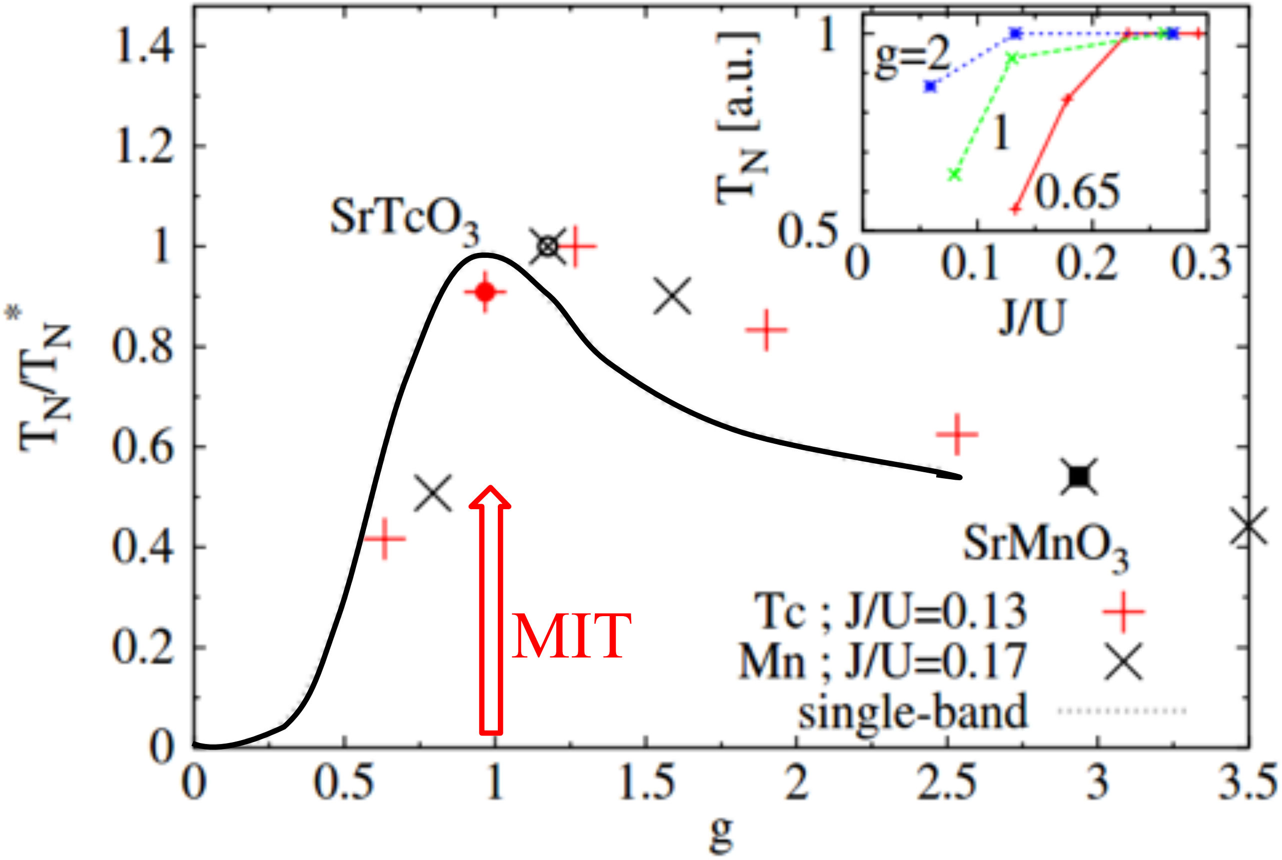
$V_{\mathrm{exact}} \propto 1/\mathrm{r}$; $V_{\mathrm{LDA}} \propto \exp(-ar)$

*(self-interaction)*



# Corollary: the strongest magnetism

…occurs not where the moment is the largest, but on the borderline between localization (strong correlations) and itinerancy (weak correlations).



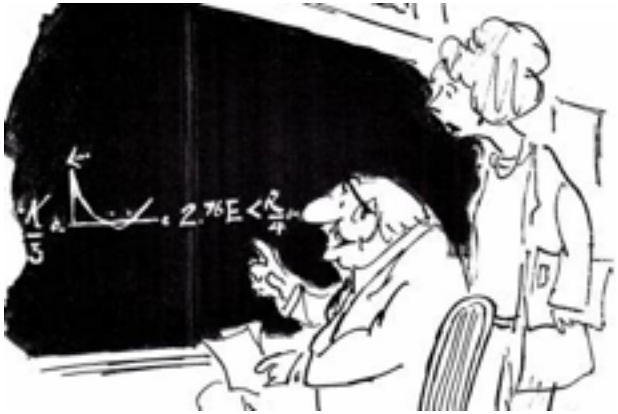
From: Mravlje et al

$SrTcO_3$: 1100 K

$SrMnO_3$: 550 K

# Learn from successes and learn from failures

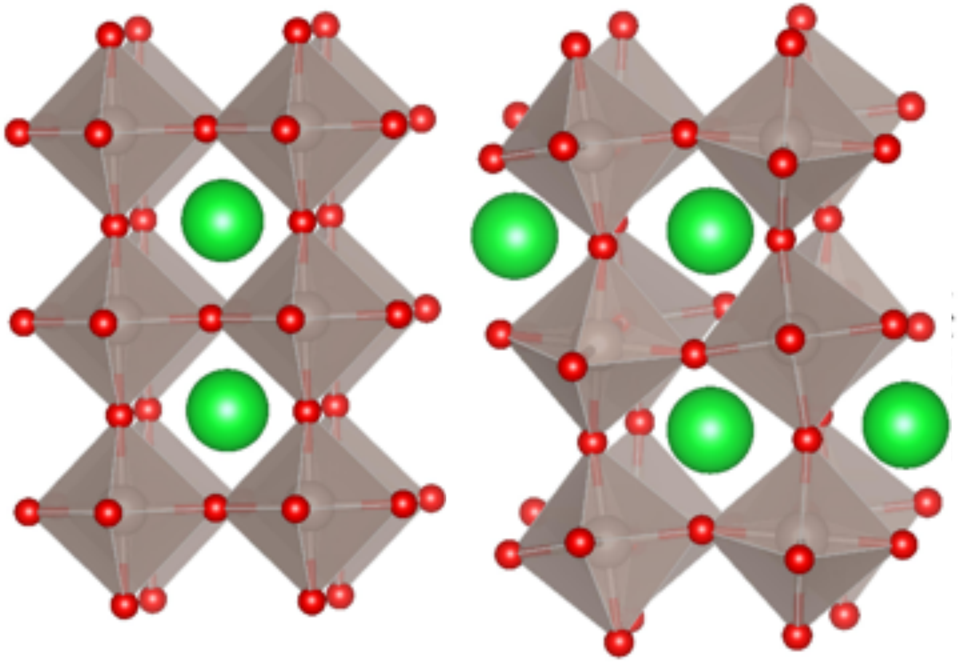
If calculations agree with the experiment, it only proves that the theorist, the experimentalist, and the Lord all believe in the same Schrodinger equation --- Volker Heine, 1982

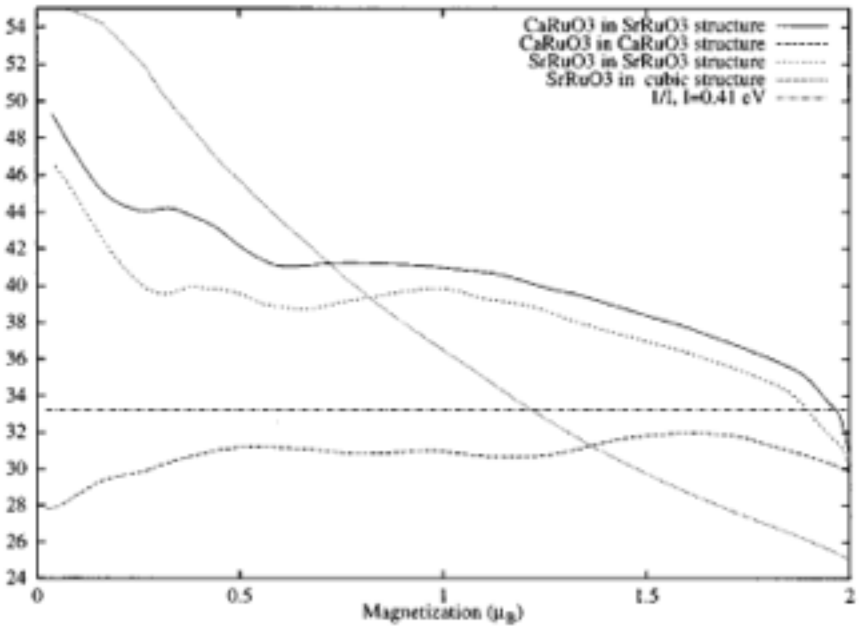


Experimentalists would have given their back teeth to be able to follow step by step what is happening in their experiments
--- Volker Heine, 1982

# Learn from successes …

*If calculations agree with the experiment, the next step is to dive inside and dissect the calculations step by step. What mechanism (as we discussed today) is operative? What role plays the structure and what chemistry? How do results depend on the correlation strength?*





# … and learn from failures

*It is much more interesting if calculations do NOT agree with the experiment!*

*Exhibit 1: High-Tc cuprates.*

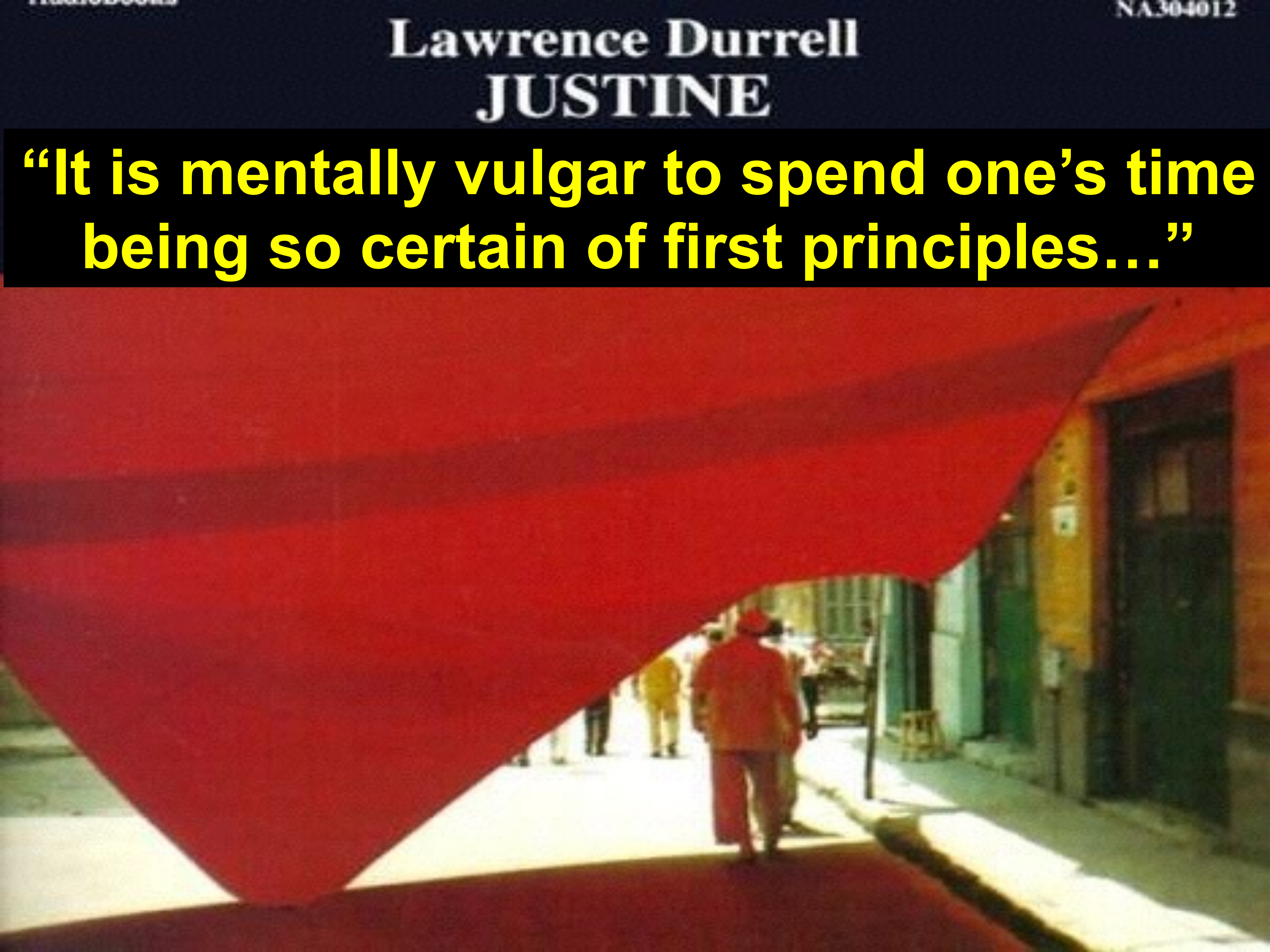
*the first indication of strong correlations: LDA failure to reproduce the magnetic moment*

*Exhibit 2: High-Tc pnictides*

*the first indication of the rampant spin fluctuation: LDA failure to reproduce the paramagnetic state*

*Exhibit 3: High-Tc pnictides*

*the first indication of nematicity: failure of LDA to reproduce the orthorhombic distortion AND the Fe-As bond length without magnetism.*



**“It is mentally vulgar to spend one’s time being so certain of first principles…”**

# Following papers were used in preparing this lecture:

1. *The Seven Seas*, Rudyard Kipling (1896)
2. *Correlated metals and the LDA+U method.* A.G. Petukhov, I.I.Mazin, L. Chioncel and A. I. Lichtenstein, PRB, **67**, 153106 (2003)
3. *Why $Ni_3Al$ is an itinerant ferromagnet but $Ni_3Ga$ is not*. A. Aguayo, I. I. Mazin and D.J. Singh, PRL **92**, 147201 (2004).
4. *Density Functional Calculations near Ferromagnetic Quantum Critical Points,* I. I. Mazin, D.J. Singh, and A. Aguayo, *in Proceedings of the NATO ARW on Physics of Spin in Solids: Materials, Methods and Applications, ed. S. Halilov*, Kluwer, 2003
5. *Electronic structure and magnetism in Ru based perovskites,* I. I. Mazin and D. J. Singh, PRB **56**, 2556(1997)
6. *Electronic structure and magnetism in the frustrated antiferromagnet $LiCrO_2$*: First-principles calculations, I.I. Mazin, PRB 75, 094407 (2007)
7. *Theory of Mn-doped I-II-V Semiconductors,* J. K. Glasbrenner, I. Zutic, and I. I. Mazin. PRB **90**, 140403 (2014)

All but the first item are available on the arxiv.

# Fact or alt-fact (what do you know about Russian scientists?)

The Origin of Chemical Elements

R. A. ALPHER*

cs Laboratory, The Johns Hopkins University,
Silver Spring, Maryland

AND

H. BETHE

rnell University, Ithaca, New York

AND

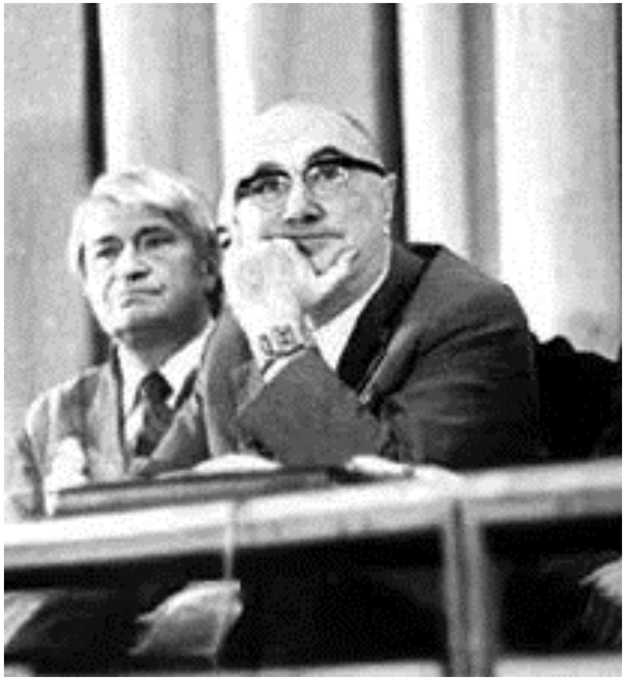
G. GAMOW

Washington University, Washington, D. C.

Gamow once published a paper where he added as the first an second authors Alpher and Bethe, so that the author line looked like Alpher, Bethe, Gamow, which bothering to inform about that the other two scientists.

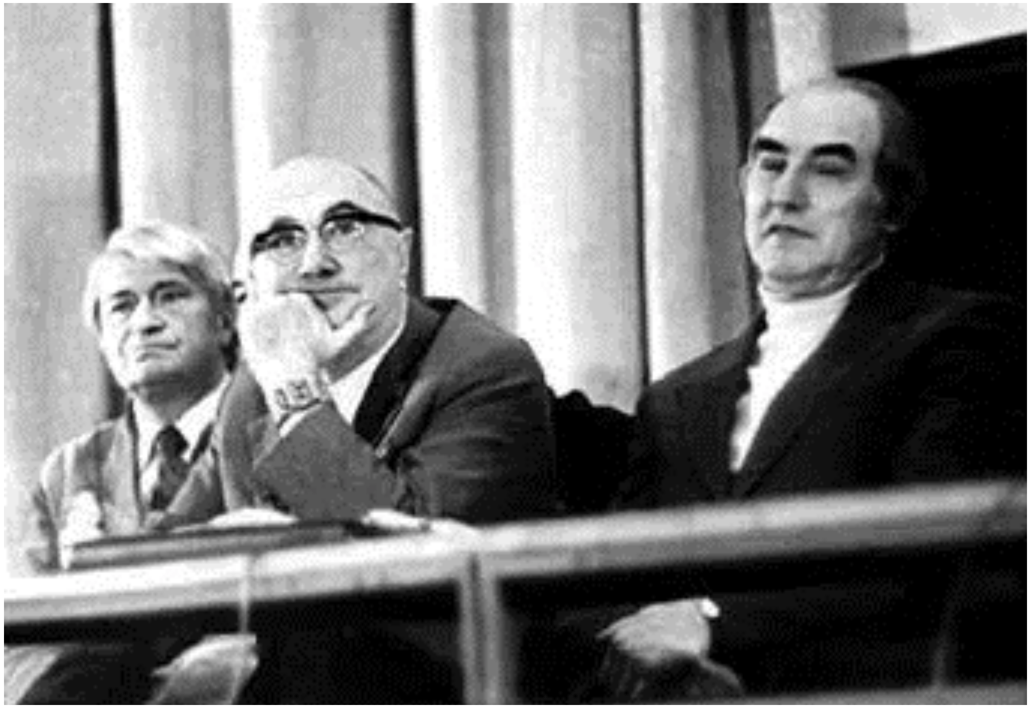
rium corresponding to a certain temperature and density.

# Fact or alt-fact?



Migdal and Zeldovich had a complicated relationship: Migdal illustrated one of his popular science books with cartoons showing a silly bold characters reminiscent of Zeldovich, while Zeldovich published a review on astrophysics, where the first letters of the last words spell out MIGDAL IS AN ASS.

# Fact or alt-fact?



The third person in this photograph is Ginzburg.

While Ginzburg was working on the Russian hydrogen bomb, his future wife was in Gulag, accused of plotting Stalin’s assassination.

# Fact or alt-fact?

Nobel did not establish a prize on mathematics because when he was living in St. Petersburg, the love of his life rejected his proposal and married a Russian mathematician.

*This house on 24 Petrogradskaya Embankment was where the Nobel family lived until 1859.*