Strongly correlated electrons: LDA+U in practice

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Outline

- Introduction: why strong correlations ?

  - Failure of one-electron theories
  - Examples of strongly correlated materials
  - Different energy scales and MIT in TMO

- Methods to deal with correlations in realistic ways

  - Concepts (LDA+U)
  - Practical details
  - Example of $CaFeO_3$ and $La_{1/2}Sr_{2/3}FeO_3$

Electronic Structure Calculations:

- Good description of many microscopic properties are obtained in terms of -

Born-Oppenheimer Approximation

Nuclei and the electrons to a good approximation may be treated separately.

One-electron Approximation

Each electron behaves as an independent particle moving in the mean field of the other electrons plus the field of the nuclei.

LDA

Most satisfactory foundation of the one electron picture is provided by the local approximation to the Hohenberg-Kohn-Sham density functional formalism

$$\boxed{\equiv \text{LDA}}$$

$$\Downarrow$$

- LDA leads to an effective one electron potential which is a function of local electron density.
- Leads to Self consistent solution to an one electron Schrödinger Eqn.

Flow-chart for LDA self-consistency

First principles information: atomic no., crystal structure

$$\Downarrow$$

Choose initial electron density $\rho(r)$

Calculate effective potential through LDA:

$$V_{eff}(r) = V_{ion}(r) + \int d^3r' V_{ee}(r-r')\rho(r') + \frac{\delta E_{xc}[\rho]}{\delta r}$$

Solve K-S eqns:

$$[-\Delta + V_{ion}(r) + + \int d^3r' V_{ee}(r-r')\rho(r') + \frac{\delta E_{xc}[\rho]}{\delta r}]\phi_i(r) = \epsilon_i \phi_i(r)$$

Needs to expand K-S wavefunctions in terms of basis, Φ_{ilm}

Calculate charge density: $\rho(r) = \sum |\phi_i(r)|^2$

Iterate to selfconsistency

$$\Downarrow$$

Total energy, inter-atomic forces, stress or pressure, band structure, . . .

Strongly correlated electron materials

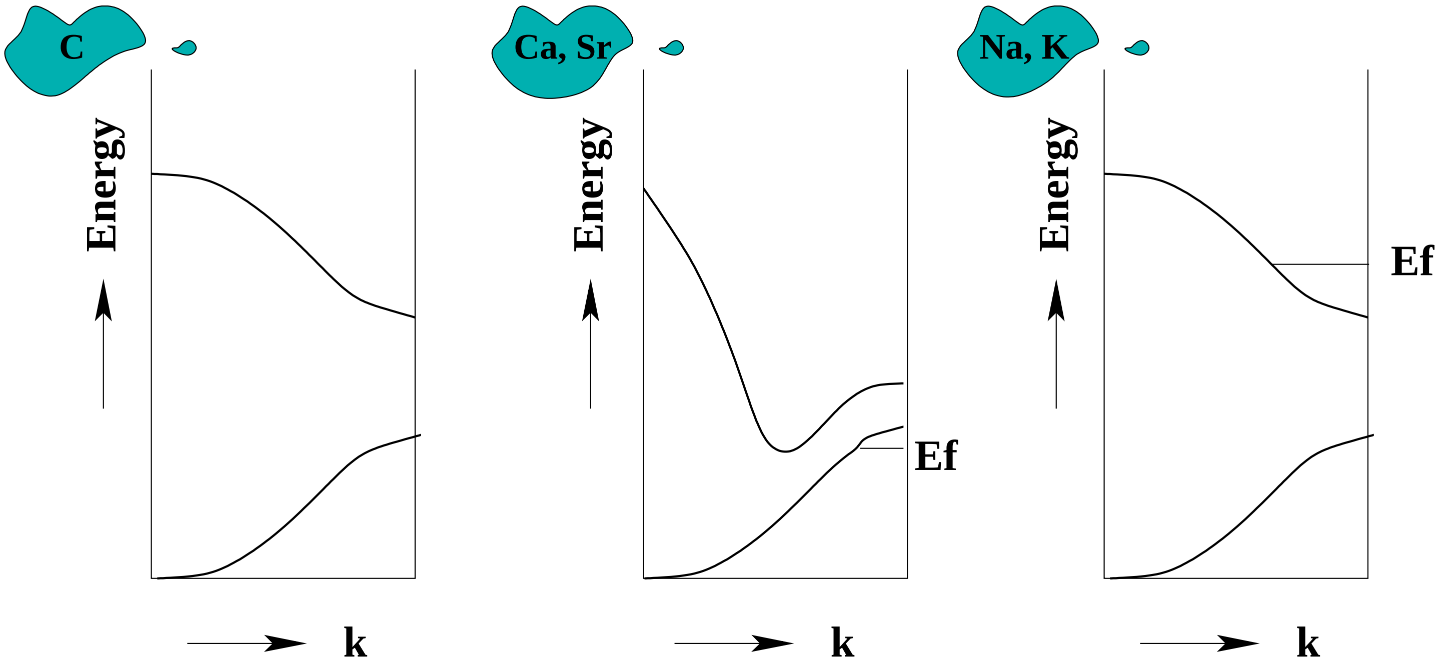
$\ast$ The conventional band-structure calculations within the framework of LDA is surprising successful for many materials.

$\ast$ However, they fail for materials with strong e-e correlation !

- correlation effect necessarily arise, and
- the consideration of electron correlation effects provides the natural way to understand the phenomena like the insulating nature of CoO.

Strongly correlated electron materials

Predictions from LDA (Bandstructure)



Even No. of e's per unitcell

$\rho\ (\varepsilon_F) = 0$

Even No. of e's per unitcell

+ band overlap

$\rho\ (\varepsilon_F) \neq 0$

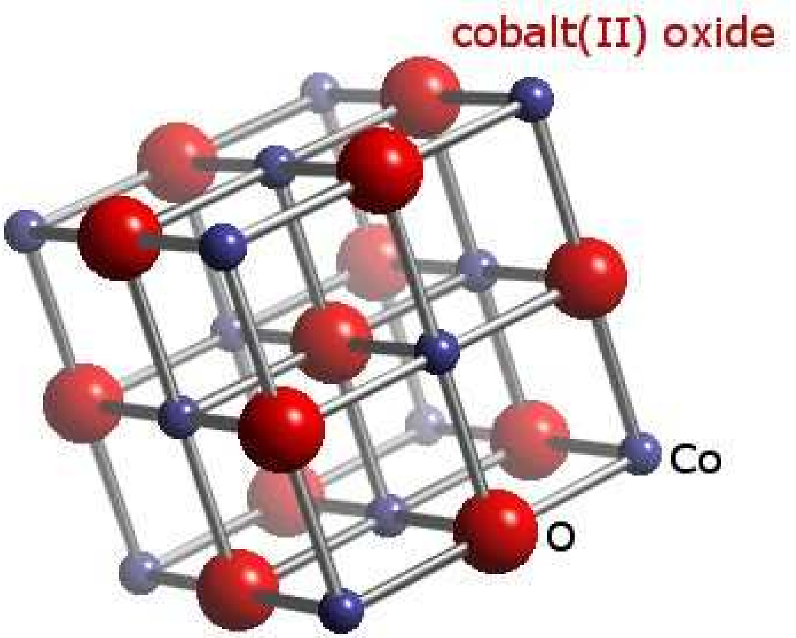
Odd No. of e's per unitcell

$\rho\ (\varepsilon_F) \neq 0$

Accordingly to LDA, odd no. of e's per unit cell always give rise to Metal !

Strongly correlated electron materials

Failure of Band Theory



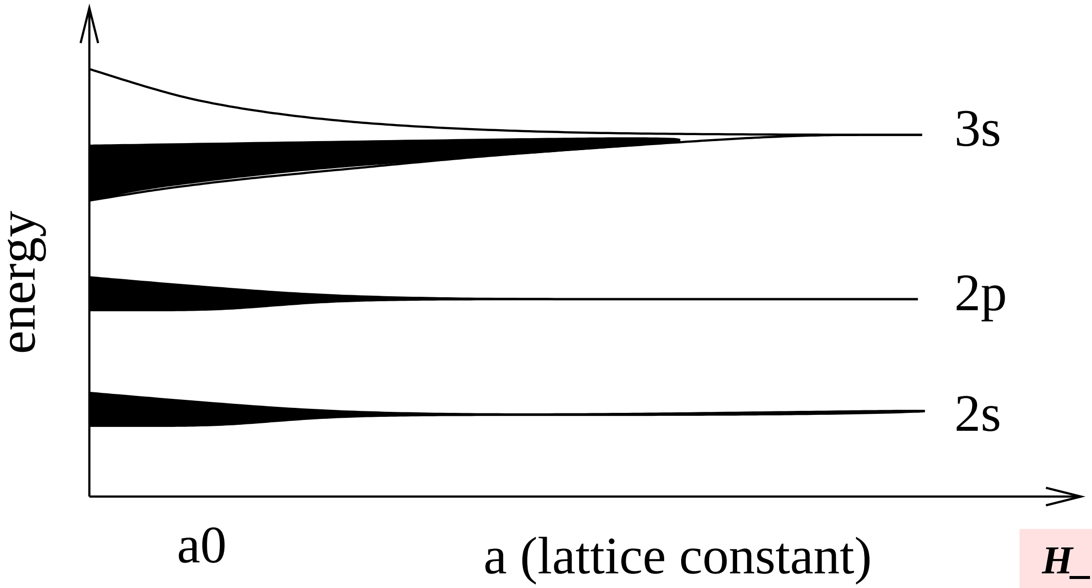
Total No. of electrons = 9 +6 = 15

Band theory predicts CoO to be metal, while it is the toughest insulator known

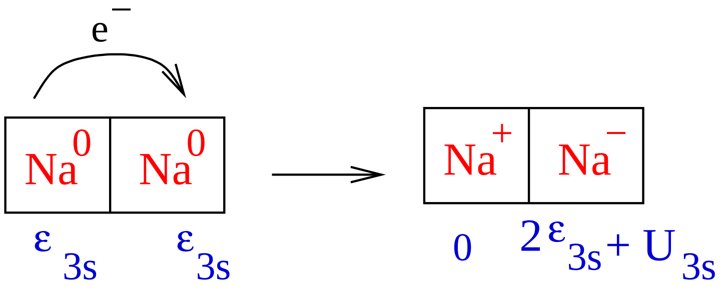
Failure of LDA −) Failure of single particle picture

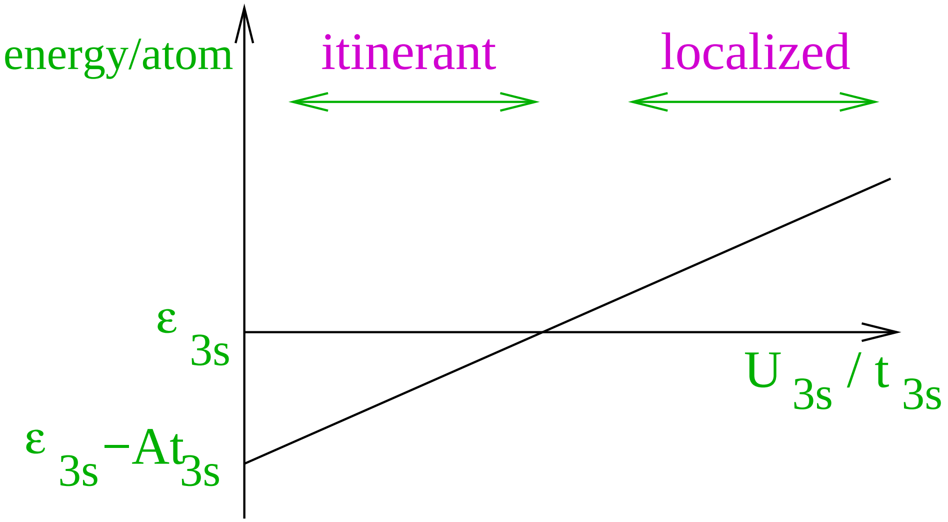
−−) Importance of e−e interaction effects (Correlation)

Strongly correlated electron materials



H_3s = H_band + H_columb





Examples of strongly correlated materials

Transition metals:

- d-orbitals extend much further from the nucleus than the *core* electrons.

- throughout the 3d series (and even more in 4d series), d-electrons do have an itinerant character, giving rise to quasiparticle bands!

- electron correlations do have important physical effects, but not extreme ones like localization.

Examples of strongly correlated materials

f-electrons: rare earths, actinides and their compounds:

- rare-earth 4f-electrons tend to be localized than itinerant, contribute little to cohesive energy, other e- bands cross E$_F$, hence the metallic character.

- actinide (5f) display behavior intermediate between TM and rare earths

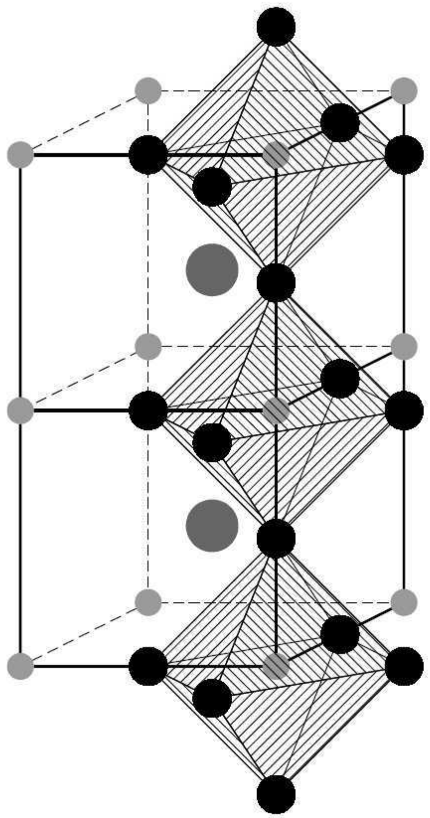
- e- correln becomes more apparent in compounds involving rare-earth or actinides.

- extremely large effective mass → *heavy fermion behavior*.

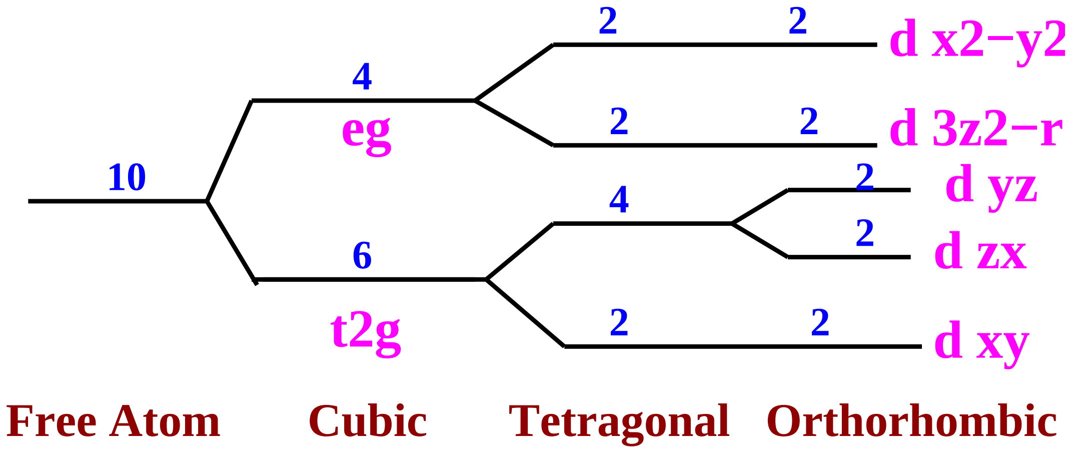
- At high temp local mag. mom and Curie law, low-temp screening of the local moment and Pauli form → *Kondo effect*

Examples of strongly correlated materials - TMO

- direct overlap between d-orbitals small, can only move through hybridization!

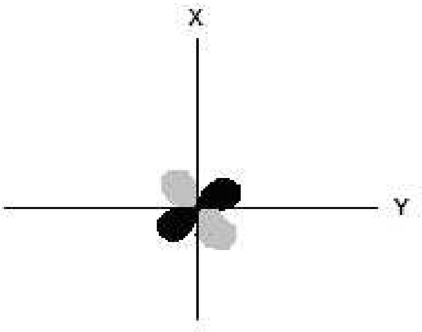


Crystal Field Splitting

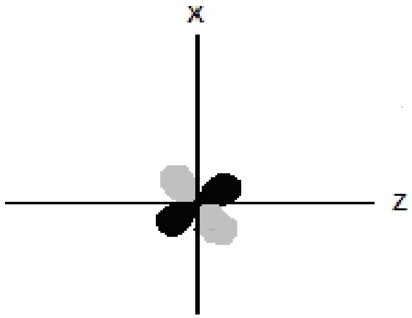


Examples of strongly correlated materials- TMO

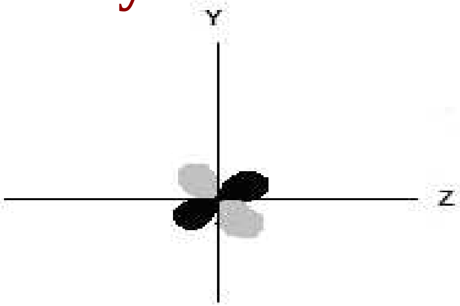
d xy



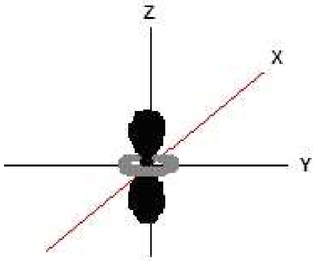
d xz



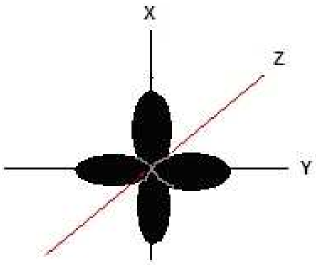
d yz



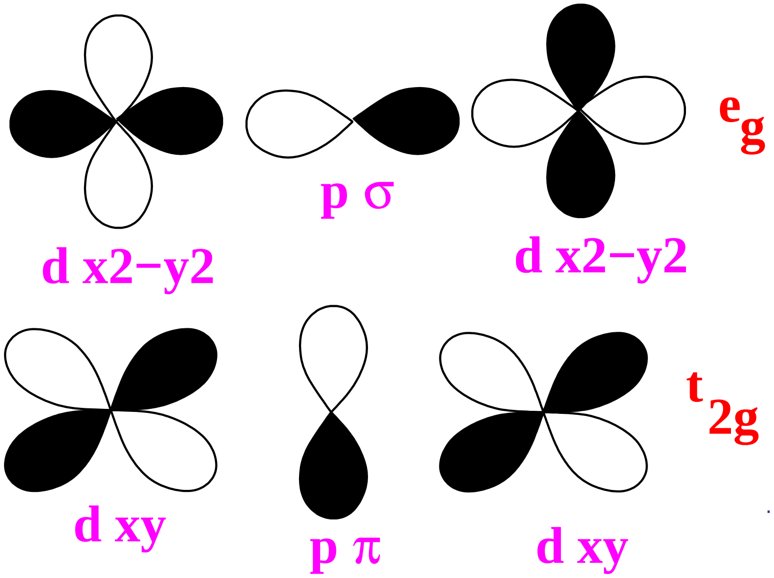
d 3z2−r2



d x2−y2



Hybridization via the Ligands (orbitals p/O)



Examples of strongly correlated materials - TMO

Three crucial Energies

$\boxed{t_{pd}}$ Metal-ligand Hybridization

$\boxed{\Delta = \epsilon_d - \epsilon_p}$ Charge Transfer Energy

$\boxed{\mathrm{U}}$ On-site Coulomb Repulsion

Band-width is controlled by: $\boxed{t_{eff} = t_{pd}^2/\Delta}$

Examples of strongly correlated materials - TMO

The infamous Hubbard U

Naively: $\boxed{\int \phi^*_{i\uparrow}\phi_{i\uparrow}\frac{1}{|r-r'|}\phi^*_{i\downarrow}\phi_{i\downarrow}}$

But this is HUGE (10 -20 eV)!

SCREENING plays a key role, in particular by 4s electrons

- *Light* TMOs (left of V): p-level much below d-level; 4s close by : U not so big $\boxed{U < \Delta}$

- *Heavy* TMOs (right of V): p-level much closer; 4s much above d-level : U is very big $\boxed{U > \Delta}$

Examples of strongly correlated materials - TMO

The Mott phenomenon: turning a half-filled band into an insulator

Consider the simpler case first: $\boxed{U < \Delta}$

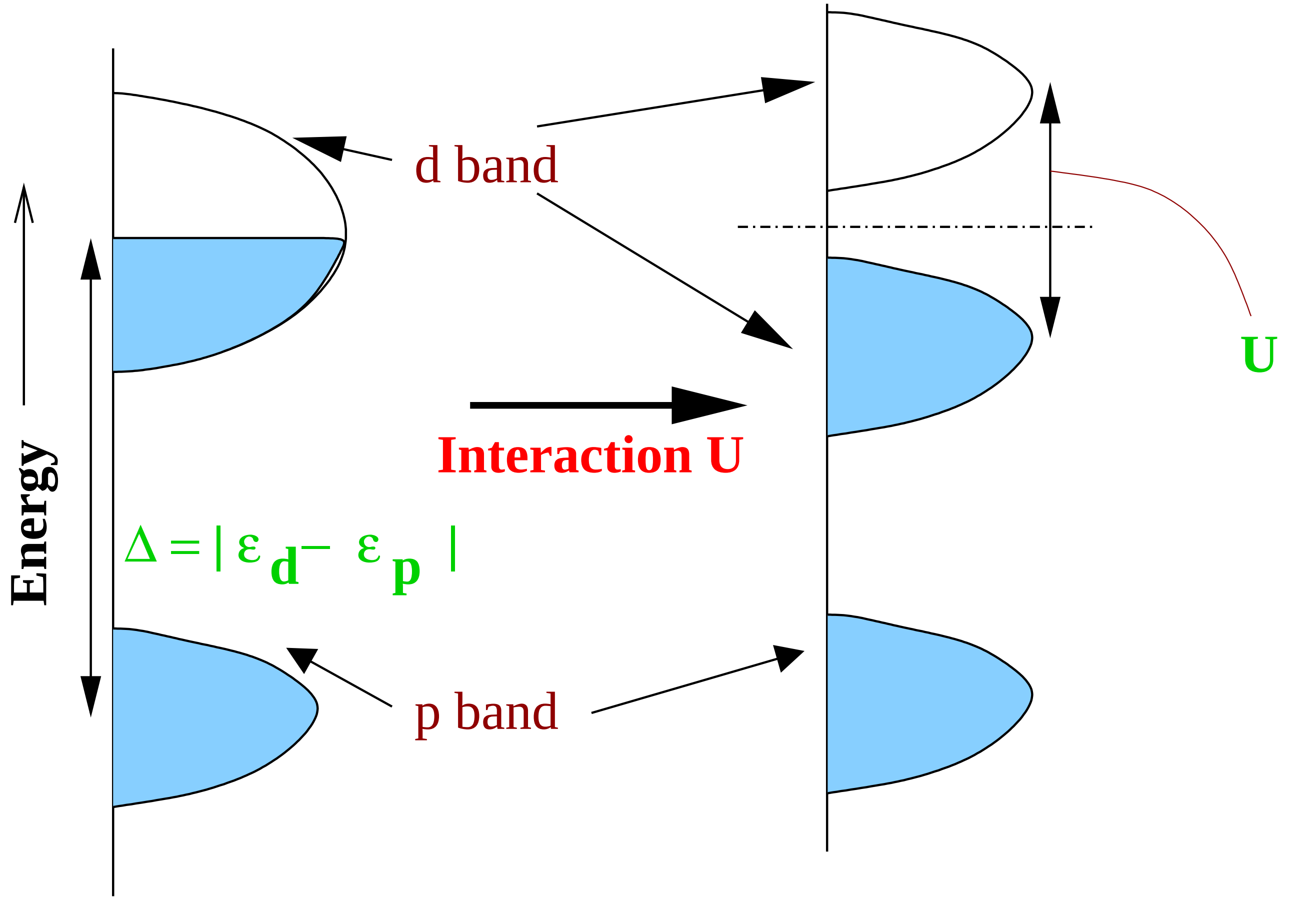
Moving an electron requires creating a hole and a double occupancy: ENERGY COST U

This object, once created, can move with a kinetic energy of order of the bandwidth **W**!

U < W: A METALLIC STATE IS POSSIBLE

U > W: AN INSULATING STATE IS PREFERRED

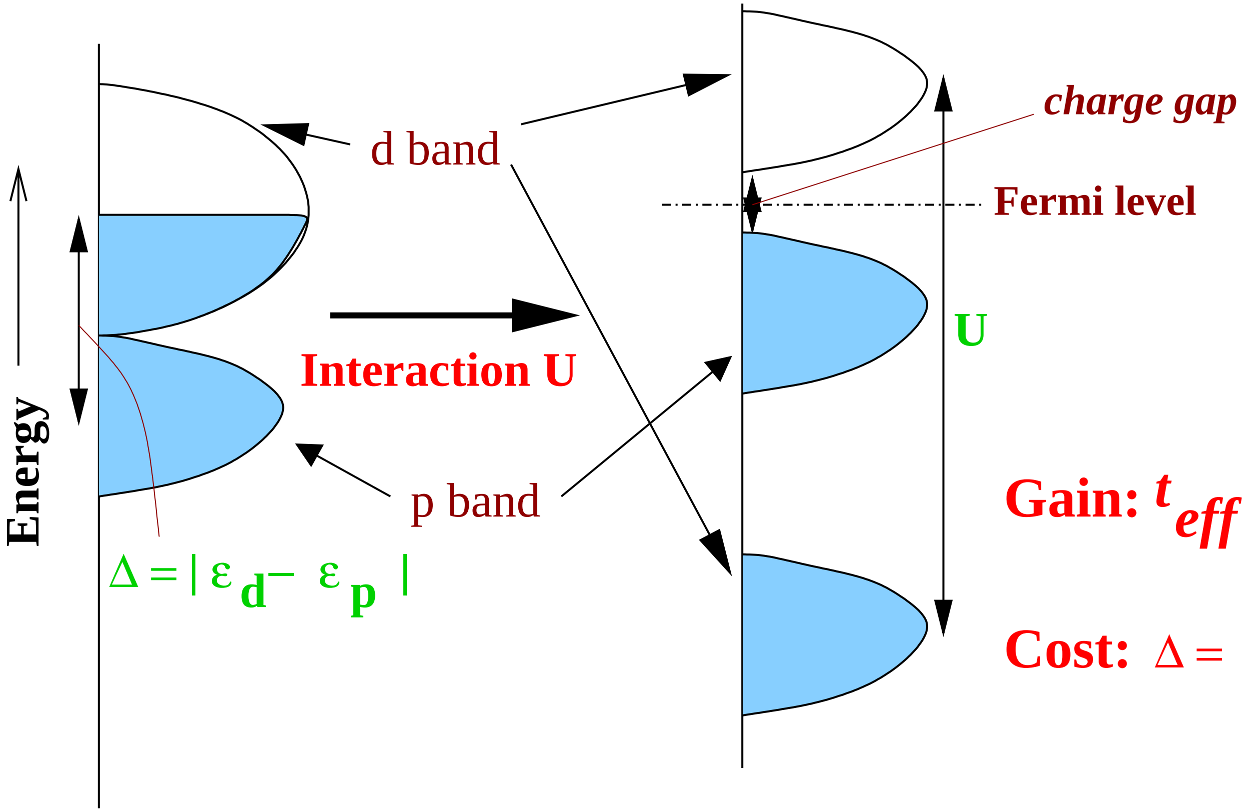
Hubbard bands



The composite excitation hole+double occupancy forms a *band* (cf excitonic band)

Charge transfer insulators

Heavy TMOs



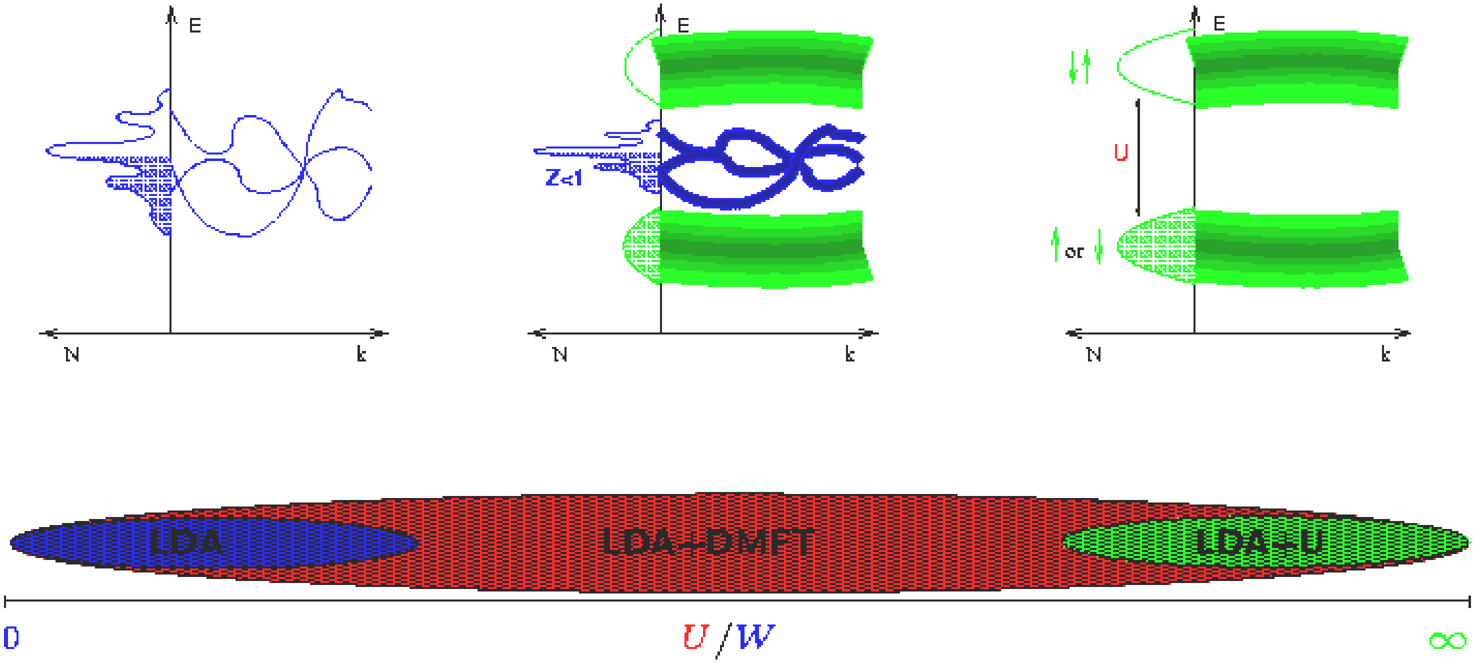
Gain: $t_{eff} \sim t_{pd}^2 / \Delta$

Cost: $\Delta = \varepsilon_d - \varepsilon_p$

Transition for $\boxed{\Delta > t_{pd}}$

Zaanen, Sawatzky, Allen; Fujimori and Minami

Methods



Weakly correlated Metal

U < W

LDA gives correct answer

Strongly correlated Metal

Intermediate regime − Hubbard bands + QS peak (reminder of LDA metal)

?

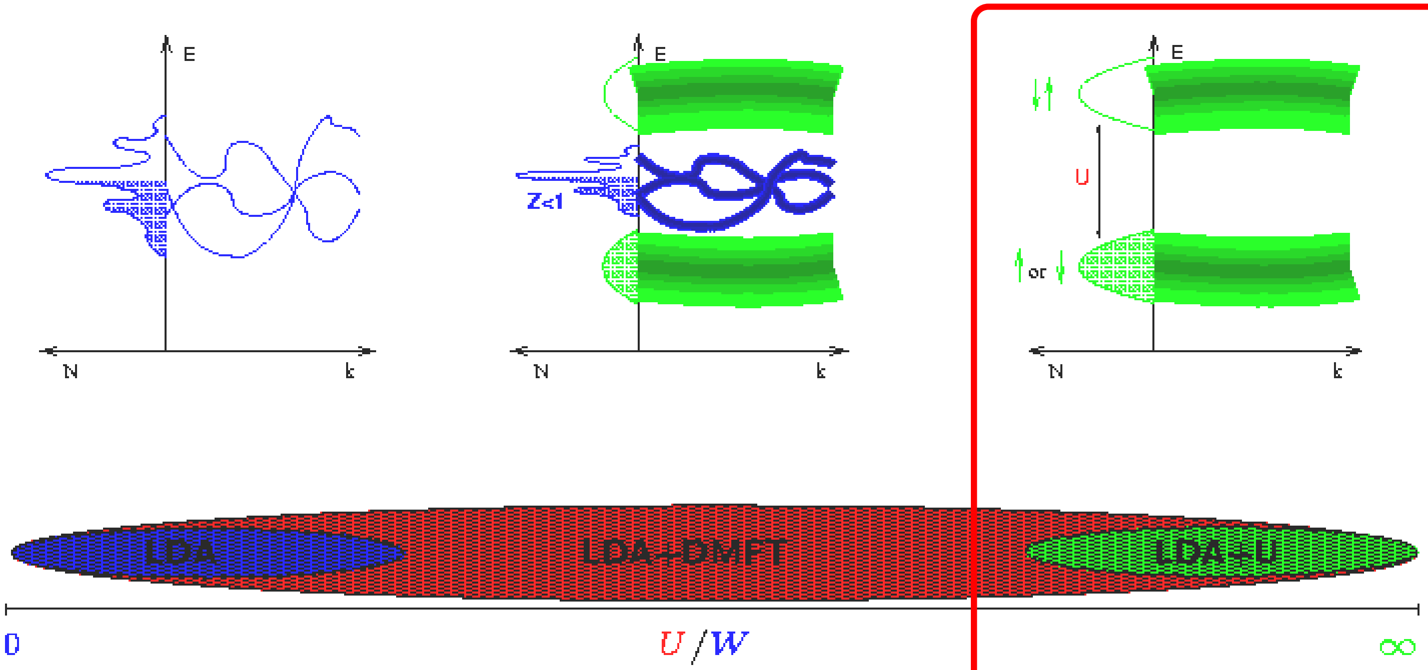
Mott insulator

U >> W

Can be described by "LDA+U" method

courtesy: K. Held

Methods



Weakly correlated Metal

U < W

LDA gives correct answer

Mott insulator

U >> W

Can be described by "LDA+U" method

Basic Idea of LDA+U

PRB 44 (1991) 943, PRB 48 (1993) 169

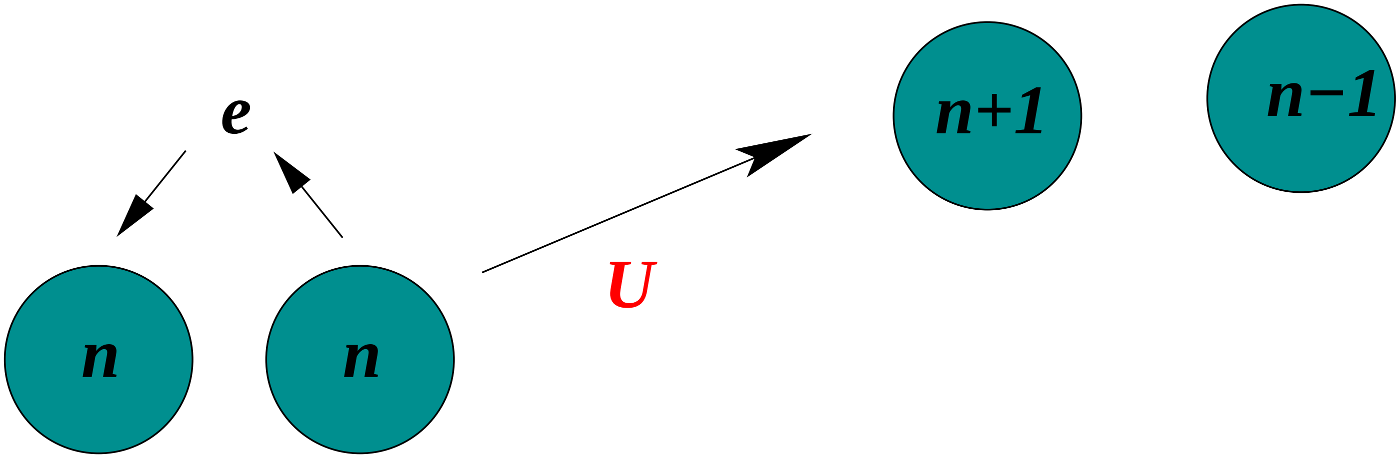
- Delocalized s and p electrons: LDA

- Localized d or f-electrons: + U

using on-site d-d Coulomb interaction (Hubbard-like term)
$U \sum_{i \neq j} n_i n_j$
instead of averaged Coulomb energy
U N(N-1)/2

Hubbard U for localized d orbital:

$$U = E(d^{n+1}) + E(d^{n-1}) - 2\,E(d^{n})$$



LDA+U energy functional (Static Mean Field Theory):

$$\begin{aligned} E^{LDA+U}_{local} &= E^{LDA} \\ & -UN(N-1)/2 + \frac{1}{2}U\sum_{i\neq j} n_i n_j \end{aligned}$$

LDA+U potential :

$$V_i(\hat{r}) = \frac{\delta E}{\delta n_i(\hat{r})} = V^{LDA}(\hat{r}) + U(\frac{1}{2} - n_i)$$

LDA+U eigenvalue :

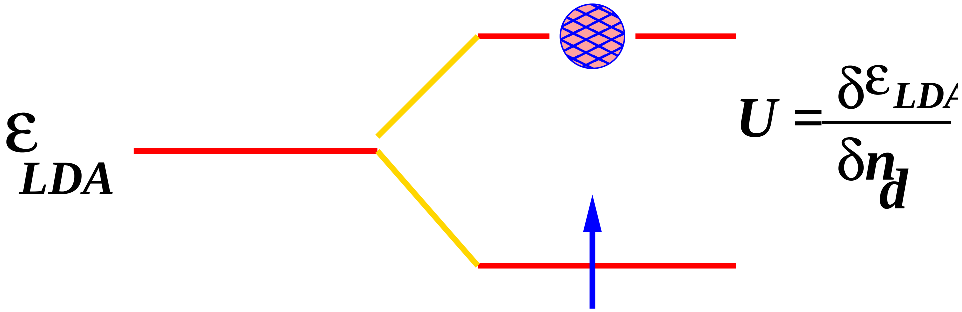
$$\epsilon_i = \frac{\delta E}{\delta n_i} = \epsilon_i^{LDA} + U(\frac{1}{2} - n_i)$$

For occupied state n_i = 1 $\rightarrow \epsilon_i = \epsilon^{LDA} - U/2$

For unoccupied state n_i = 0 $\rightarrow \epsilon_i = \epsilon^{LDA} + U/2$

$$\Downarrow$$

$\Delta\epsilon_i = U$ MOTT-HUBBARD GAP



Issues of Double Counting

Original LDA+U(HMF)：PRB 44 (1991) 943

$$E = E^{LDA} + \frac{1}{2}\sum_{m,m',\sigma} U(n_{m\sigma} - n^0)(n_{m'-\sigma} - n^0)$$

$$+\frac{1}{2}\sum_{m,m',m\neq m',\sigma} (U - J)(n_{m\sigma} - n^0)(n_{m'\sigma} - n^0)$$

$$V_{m\sigma} = V^{LDA} + U\sum_{m'}(n_{m'-\sigma} - n^0)$$

$$+(U - J)\sum_{m'(\neq m)}(n_{m'\sigma} - n^0)$$

Issues of Double Counting

LDA+U(SIC): PRB 48 (1993) 16929

$$E = E_{LDA} - [UN(N-1)/2 - JN(N-2)/4]$$

$$\frac{1}{2}\sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2}\sum_{m\neq m',m',\sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}$$

$$V_{m\sigma} = V_{LDA} + \sum_{m'} (U_{mm'} - U_{eff}) n_{m-\sigma}$$

$$- \sum_{m'\neq m} (U_{mm'} - J_{mm'} - U_{eff}) n_{m\sigma} + U_{eff}\left(\frac{1}{2} - n_{m\sigma}\right) - \frac{1}{4} J$$

$$U_{eff} = U - \frac{1}{2} J$$

Issues of Double Counting

LDA+U(AMF) : PRB 49 (1994) 14211

$$E = E^{LDA} + \frac{1}{2}\sum_{m,m',\sigma} U_{mm'}(n_{m\sigma} - n_{\sigma}{}^{0})(n_{m'-\sigma} - n_{-\sigma}{}^{0})$$

$$+ \frac{1}{2}\sum_{m,m',m\neq m',\sigma} (U_{mm'} - J_{mm'})(n_{m\sigma} - n_{\sigma}{}^{0})(n_{m'\sigma} - n_{\sigma}{}^{0})$$

$$V_{m\sigma} = V_{\sigma}{}^{LDA} + \sum_{m'} U_{mm'}(n_{m'-\sigma} - n_{-\sigma}{}^{0})$$

$$+ \sum_{m'(\neq m)} (U_{mm'} - J_{mm'})(n_{m'\sigma} - n_{\sigma}{}^{0})$$

Rotationally Invariant LDA+U

LDA+U functional:

$$E^{LSDA+U}[\rho^\sigma(r), \{n^\sigma\}] = E^{LSDA}[\rho^\sigma(r)] + E^U[\{n^\sigma\}] - E_{dc}[\{n^\sigma\}]$$

Screened Coulomb Correlations:

$$\begin{aligned} E^U[\{n^\sigma\}] \quad = \quad & \frac{1}{2}\sum_{\{m\},\sigma}\{\langle m, m^{''}|V_{e,e}|m^{'}, m^{'''}\rangle n^\sigma_{mm'} n^{-\sigma}_{m''m''''} + \\ & (\langle m, m^{''}|V_{e,e}|m^{'}, m^{'''}\rangle - \langle m, m^{''}|V_{e,e}|m^{'''}, m^{'}\rangle) n^\sigma_{mm'} n^\sigma_{m''m''''} \end{aligned}$$

LDA-double counting term:

$$E_{dc}[\{n^\sigma\}] = \frac{1}{2}Un(n-1) - \frac{1}{2}J[n^\uparrow(n^\uparrow - 1) + n^\downarrow(n^\downarrow - 1)]$$

Slater parametrization of U

Multipole expansion:

$$\frac{1}{|r - r^{'}|} = \sum_{kq} \frac{4\pi}{2k+1} \frac{r_<^k}{r_>^{k+1}} Y_{kq}^*(\hat{r}) Y_{kq}(\hat{r}^{'})$$

Coulomb Matrix Elements in Y$_{lm}$ basis:

$$\langle mm^{'} || m^{''} m^{'''} \rangle = \sum_k a_k(m, m^{''}, m^{'}, m^{'''}) F^k$$

F^k $\longrightarrow$ Slater integrals

Average interaction: U and J

U = F^0; J (for d electrons) = $\frac{1}{14}(F^2 + F^4)$

Issues of Double Counting

Simplified rotationally invariant
LDA+U : PRB 57 (1998) 1505

$$E = E_{LDA} + \frac{(\bar{U} - \bar{J})}{2} \sum_{\sigma} [(\sum_{j} n_{jj}^{\sigma}) - (\sum_{jl} n_{jl}^{\sigma} n_{lj}^{\sigma})]$$

$$V_{jl}^{\sigma} = \frac{\delta E_{LDA}}{\delta n_{lj}^{\sigma}} + (\bar{U} - \bar{J})[\frac{1}{2}\delta_{jl} - \delta_{jl}^{\sigma}]$$

Issues of Double Counting

Various LDA+U methods

- Hubbard model in mean field approx. (HMF) LDA+U : PRB 44 (1991) 943 (WIEN2K, LMTO)
- Approximate self-interaction correction (SIC) LDA+U : PRB 48 (1993) 16929 (WIEN2K)
- Around the mean field (AMF) LDA+U : PRB 49 (1994) 14211 (WIEN2K)
- Rotationally invariant LDA+U : PRB 52 (1995) R5468 (VASP4.6, LMTO)
- Simplified rotationally invariant LDA+U : PRB 57 (1998) 1505 (VASP4.6, LMTO)

How to calculate U and J

PRB 39 (1989) 9028

- Constrained DFT + Super-cell calculation
- Calculate the energy surface as a function of local charge fluctuations.
- Mapped onto a self-consistent mean-filed solution of the Hubbard model.
- Extract U and J from band structure results.

Notes on calculation of U

- Constrained DFT works in the fully localized limit. Therefore often overestimates the magnitude of U.
- For the same element, U depends also on the ionicity in different compounds → higher the ionicity, larger the U.
- One thus varies U in the reasonable range (Comparison with photoemission..).

Better or more recent approach: **Constrained RPA method**
See *e.g.*
http://icts.res.in/media/uploads/Talk/Document/AryasetiawancRPA.pdf
for details.

Where to find U and J

PRB 44 (1991) 943 : 3d atoms

PRB 50 (1994) 16861 : 3d, 4d, 5d atoms

PRB 58 (1998) 1201 : 3d atoms

PRB 44 (1991) 13319 : Fe(3d)

PRB 54 (1996) 4387 : Fe(3d)

PRL 80 (1998) 4305 : Cr(3d)

PRB 58 (1998) 9752 : Yb(4f)

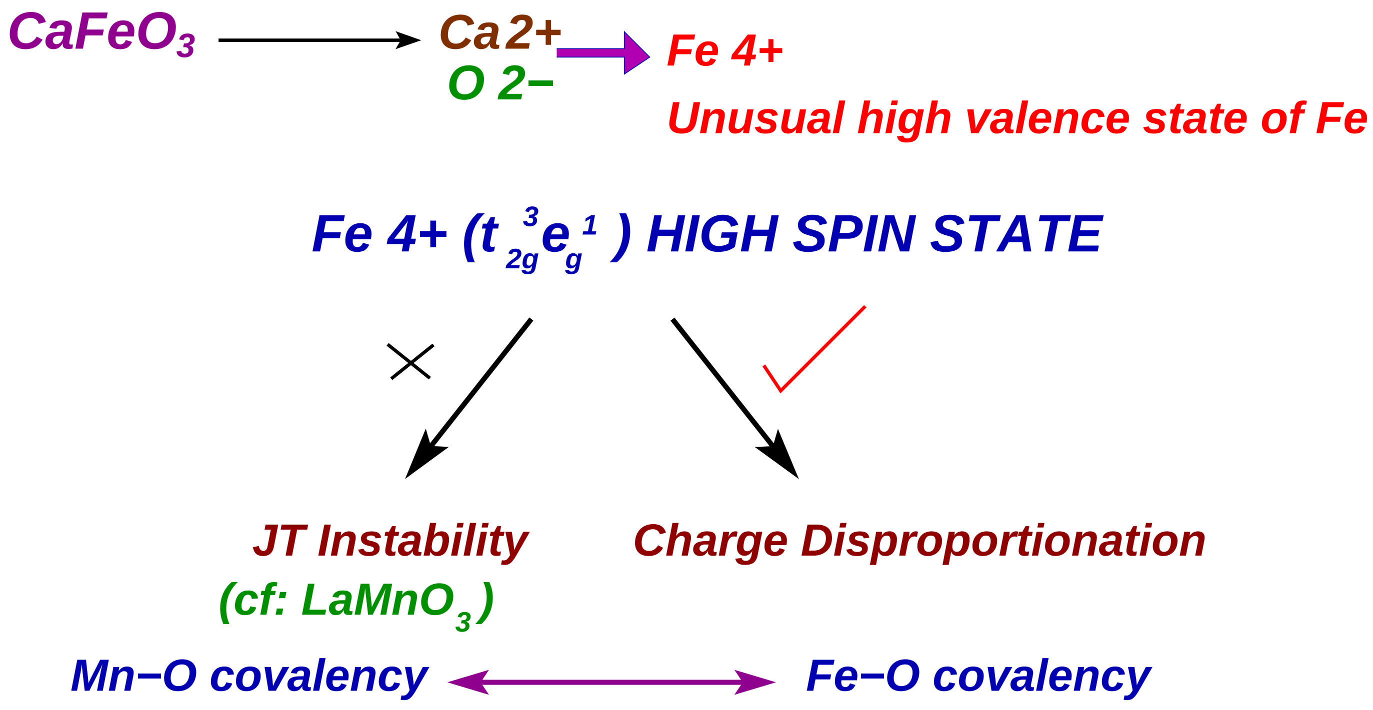
CO and Insulating state in $CaFeO_3$, $La_{1/3}Sr_{2/3}FeO_3$

TSD, Z. S. Popovic, S. Satpathy

Phys. Rev. B 72, 045143

$CaFeO_3$

NOMINAL VALENCE CONSIDERATION:



$CaFeO_3$ → *$Ca\,2+$* *$O\,2-$* → *Fe 4+*

Unusual high valence state of Fe

Fe 4+ ($t_{2g}^{3}e_{g}^{1}$) HIGH SPIN STATE

× ↙ ↘ ✓

JT Instability
(cf: $LaMnO_3$)

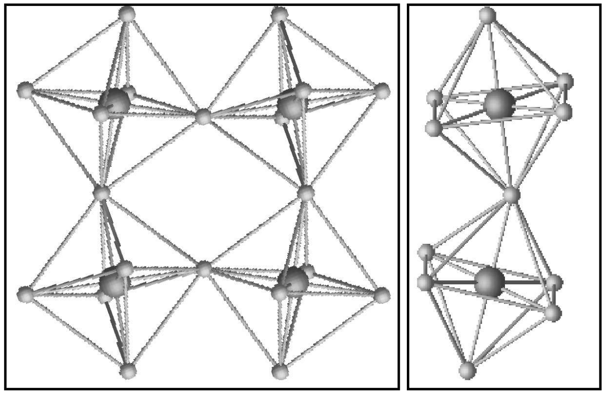
Charge Disproportionation

Mn−O covalency ↔ ***Fe−O covalency***

Whangbo et al, Inorg Chem (2002)

$CaFeO_3$

HT

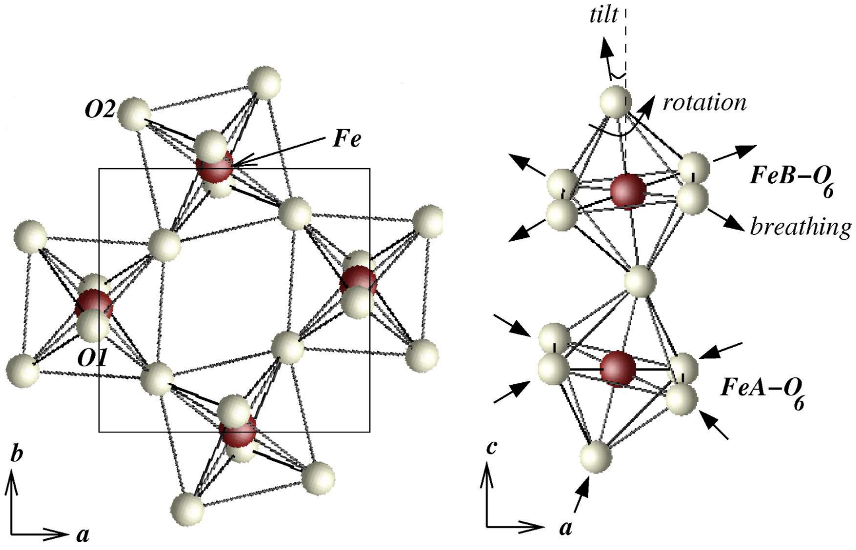


METALLIC

Pbnm

290 K

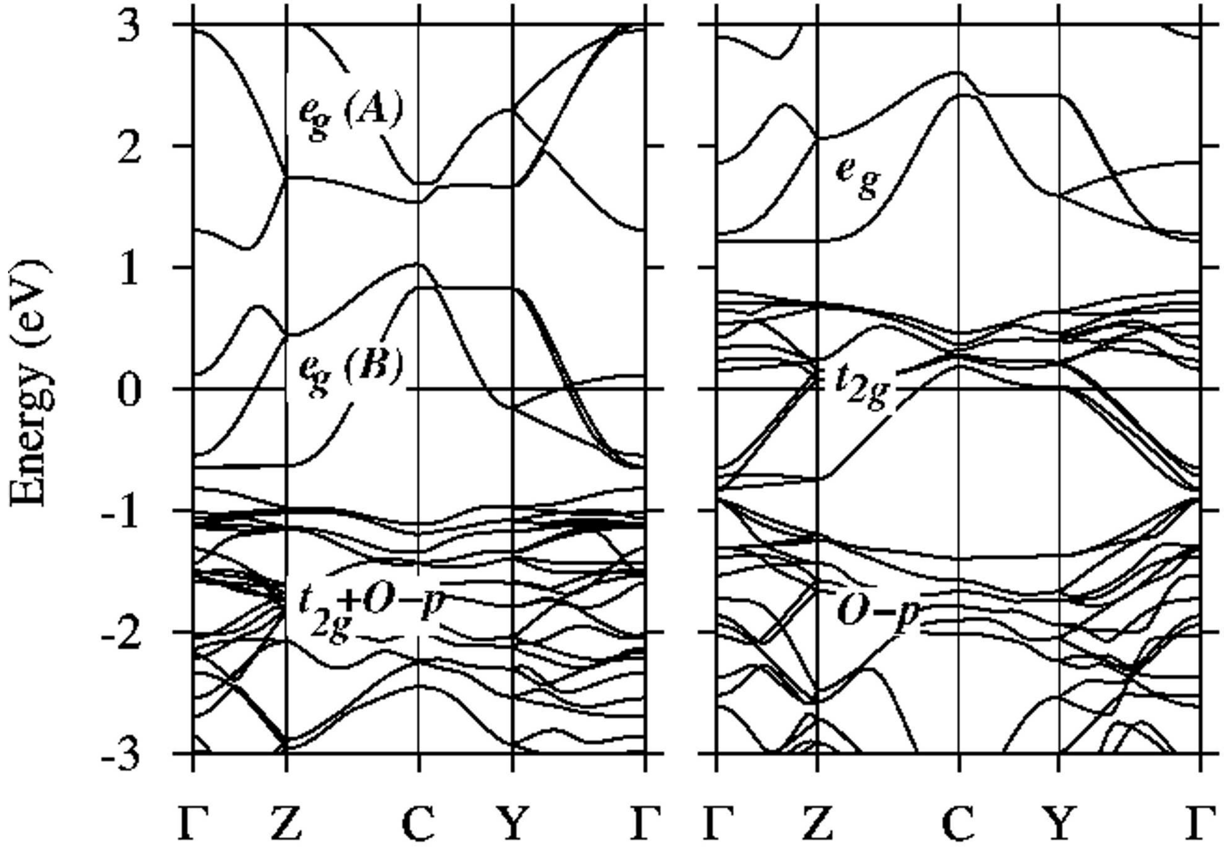
LT



SEMICONDUCTING

P2_1/n

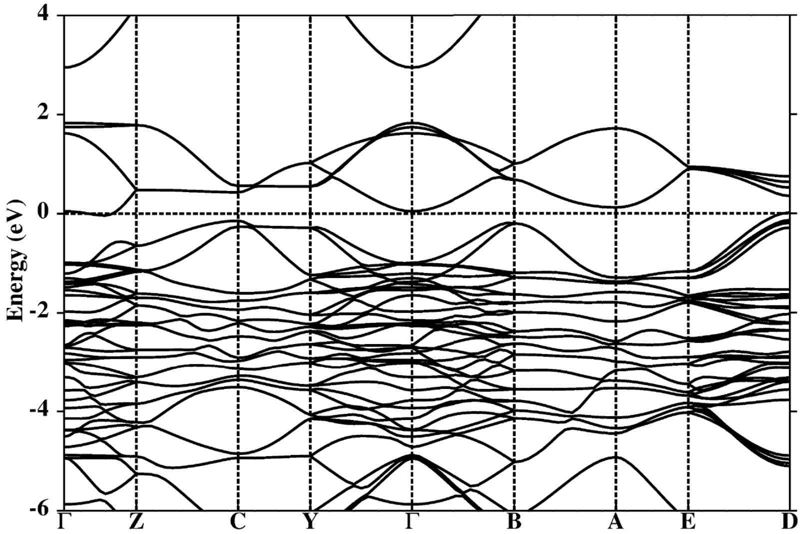
LDA Band structure at LT



Metallic!

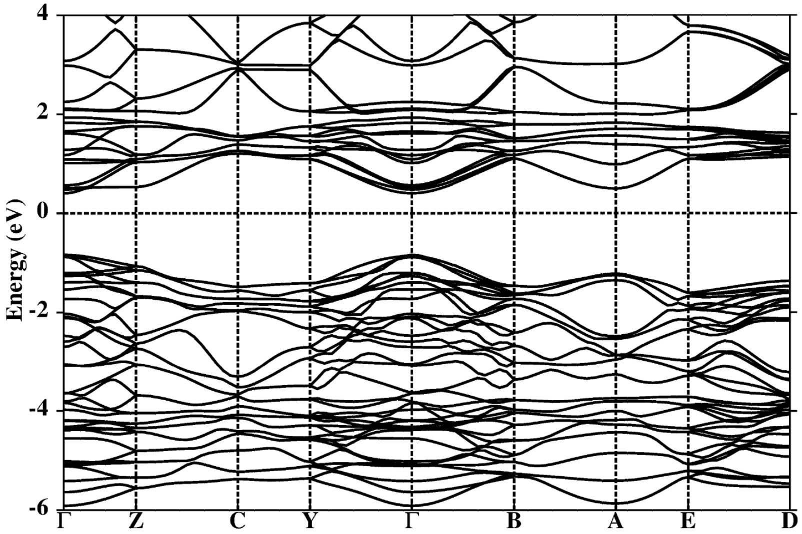
LDA+U band structure

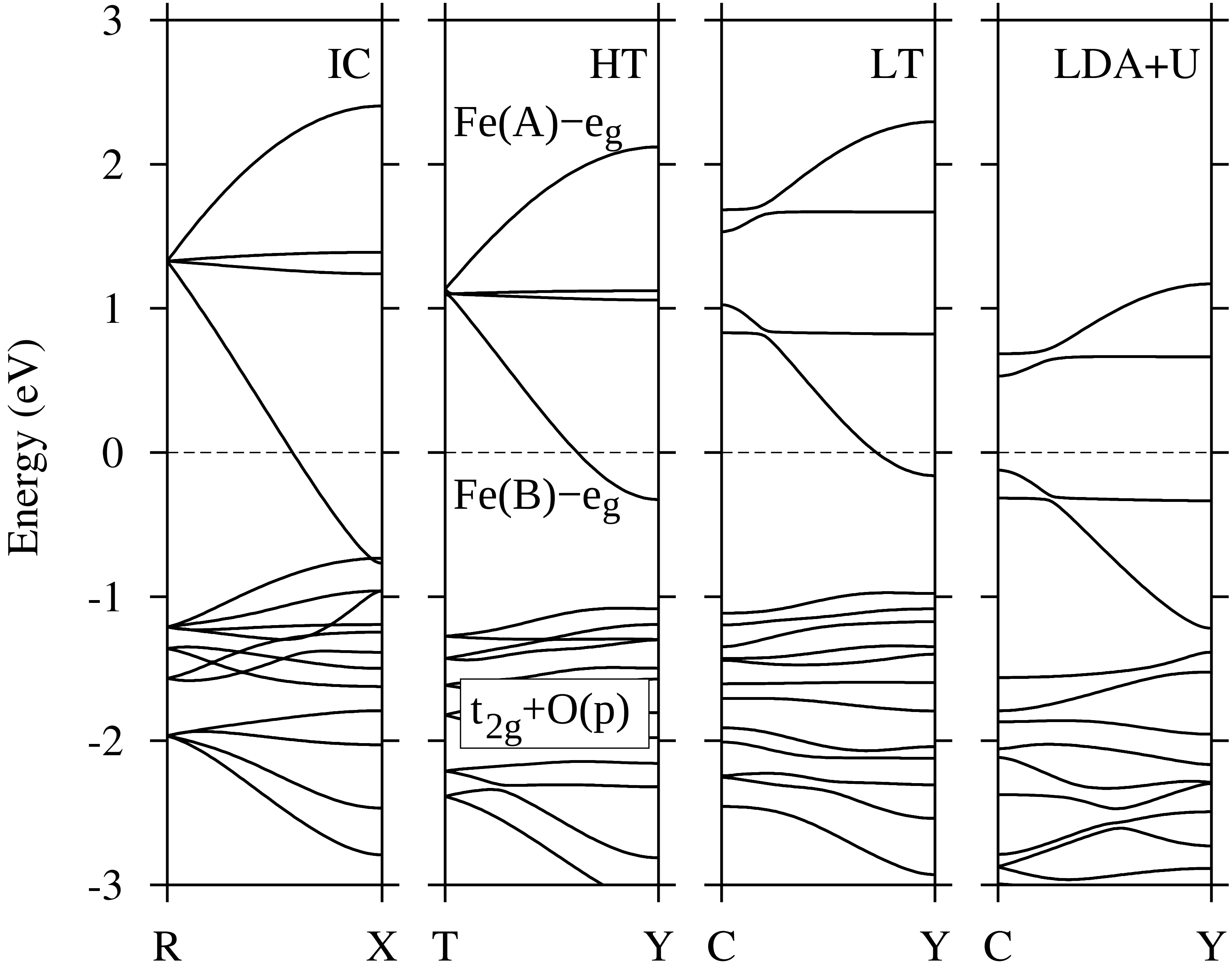
UP



INSULATING!

DN



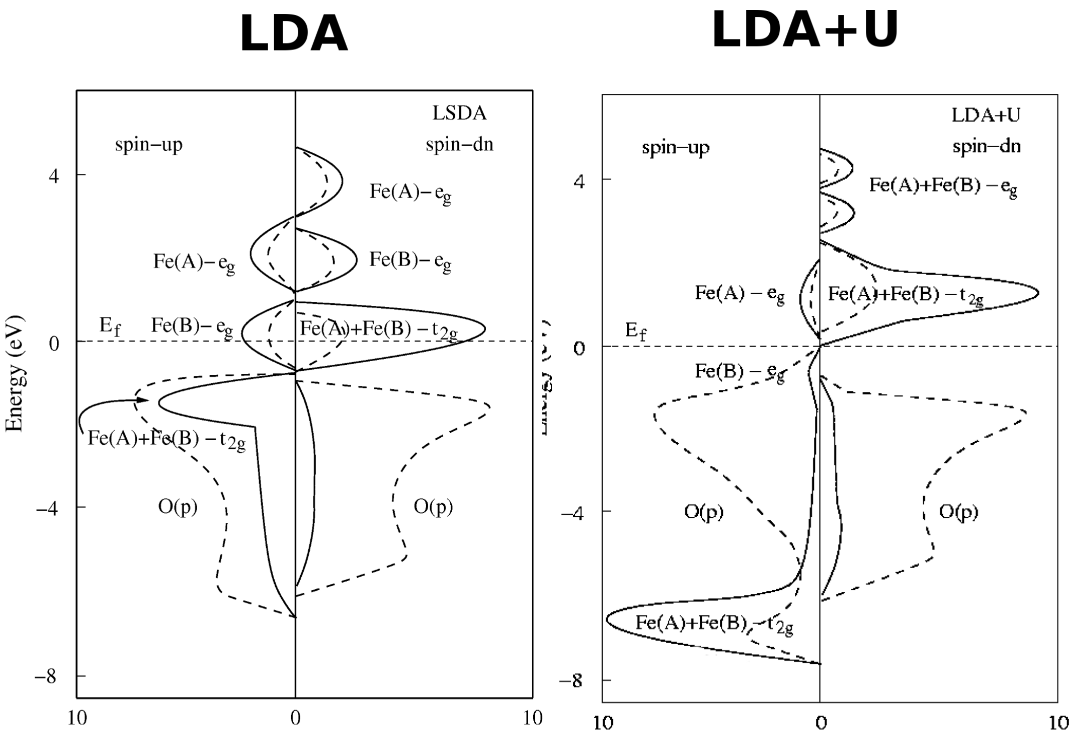

Energy (eV)
3
2
1
0
-1
-2
-3
IC
HT
LT
LDA+U
Fe(A)−e_g
Fe(B)−e_g
t_{2g}+O(p)
R
X
T
Y
C
Y
C
Y

Hubbard U instead of Stoner I

FeA: 2.3 mB

FeB: 2.5 mB

I ~ 1 eV


LDA

LDA+U

FeA : 3.2 mB

FeB: 4.0 mB

U ~ 4 -8 eV

$La_{1/3}Sr_{2/3}FeO_3$

NOMINAL VALENCE CONSIDERATION:

$La_{1/3}\ Sr_{2/3}\ FeO_3 \longrightarrow$ Sr 2+, La 3+, O 2− $\Rightarrow$ Fe 3.67+

$\boxed{3 \times Fe\ 3.67+}$ $\xrightarrow{T}$

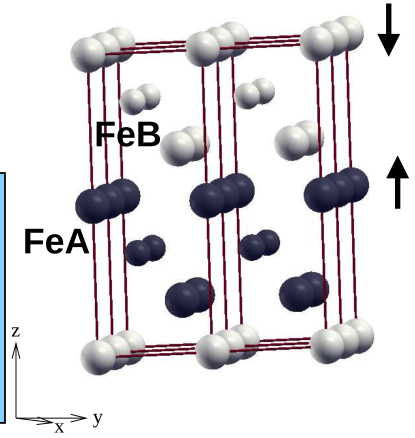
$\boxed{2 \times Fe\ 4+ \oplus 1 \times Fe\ 3+}$ ✗

$\boxed{2 \times Fe\ 3+ \oplus 1 \times Fe\ 5+}$ ✓

(PM Metallic)

(AFM Insulating) [Mossbauer data, Takano et. al.]

CDW of 3−fold periodicity
+ SDW of 6−fold periodicity

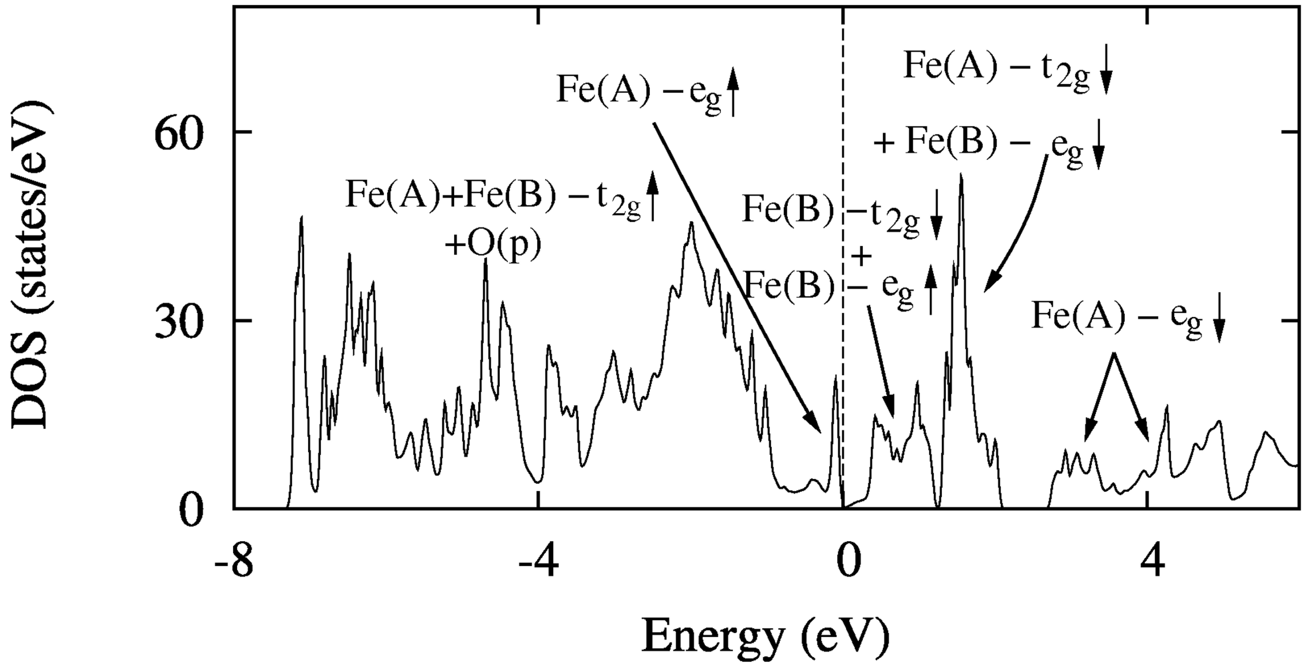


[111] pseudo−cubic direction

> *Neutron Diffraction (Battle et a.'90):*
> *No sign of structural modulation*
>
> *Electron Diffraction (Li et al, '97):*
> *Evidence of structural modulation*

$La_{1/3}Sr_{2/3}FeO_3$

LDA+U LT DENSITY OF STATES

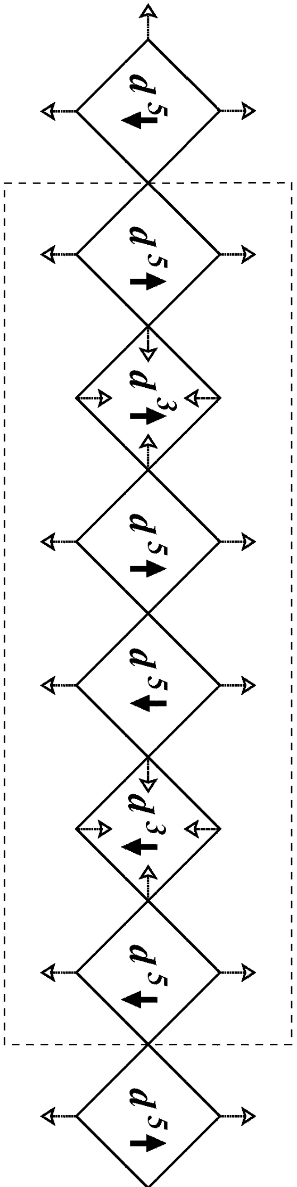


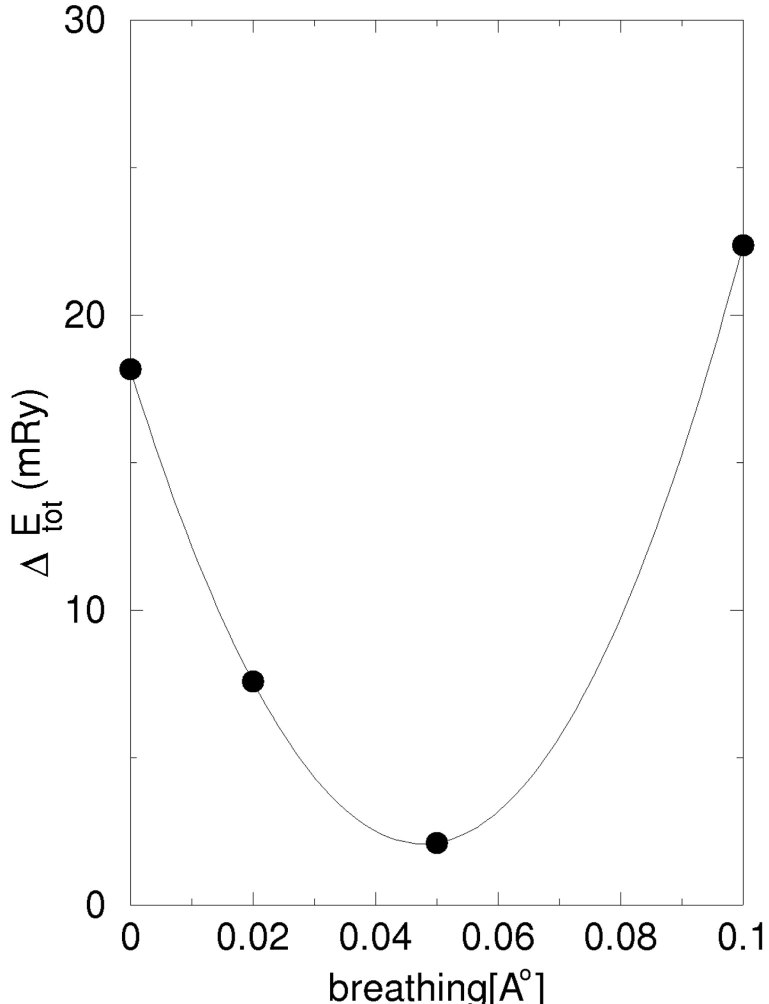
- **Nearly insulating**
- **FeA : 3.7 mB;**
  FeB : 3.4 mB

CD driven by corrln & Disorder

$La_{1/3}Sr_{2/3}FeO_3$

Lattice Response to Charge Disproportionation





Summary

- $*$ Charge disproportionation in CaFeO_3, driven by lattice distortion. Insulating property needs the assistence from correlation.
- $*$ Charge disproportionation and insulating state in $La_{1/2}Sr_{2/3}FeO_3$ driven by correlation, magnetism and disorder.
- $*$ Lattice of $La_{1/2}Sr_{2/3}FeO_3$ reacts to the charge modulation.