'Botany' of correlated fermion physics

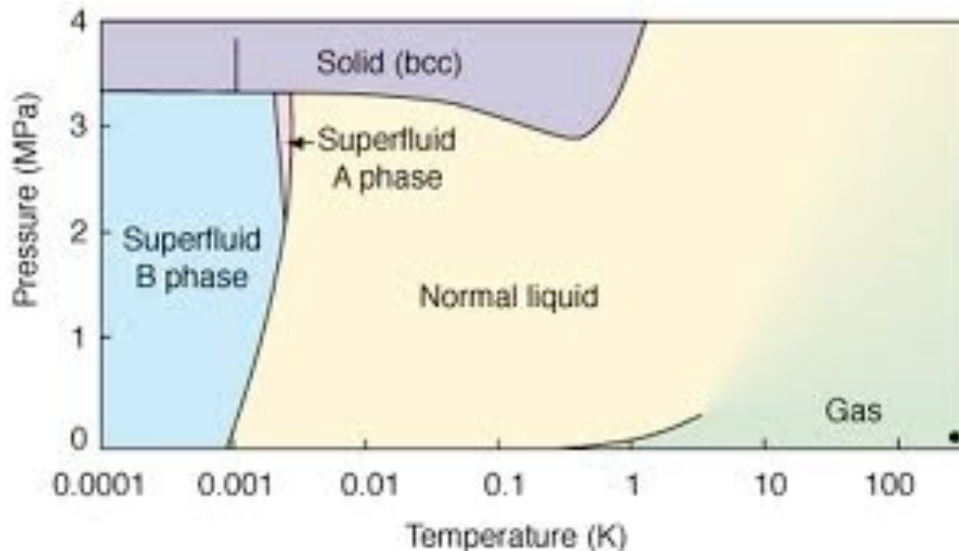Department of Physics
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Example: ^{3}He

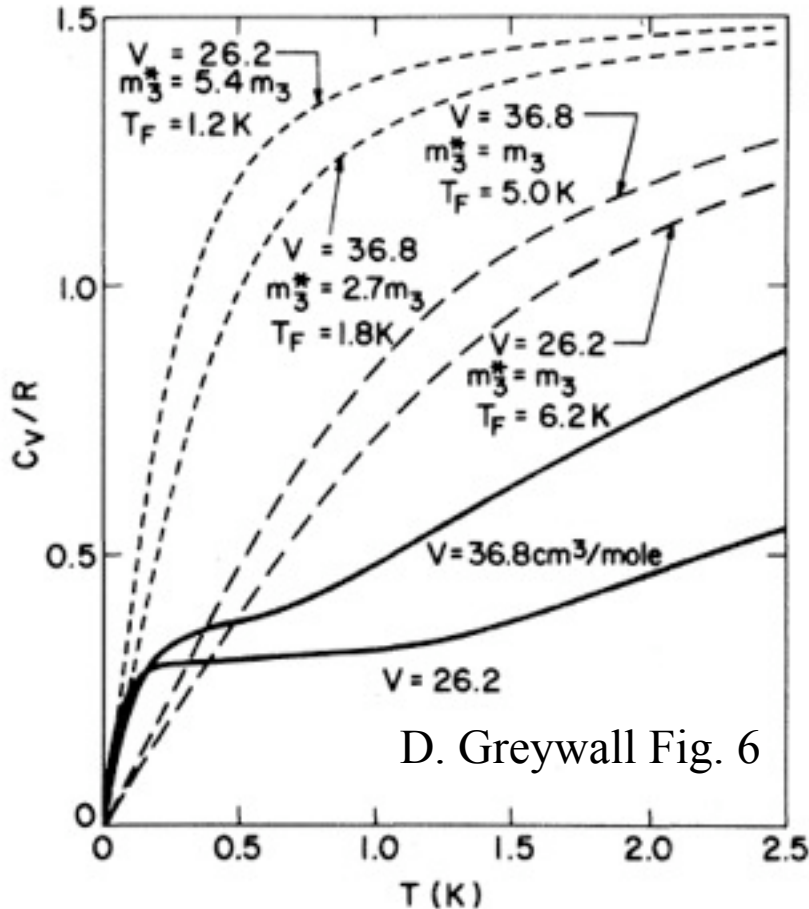**Fermions: short ranged interaction**

Phase diagram

ltl.tkk.fi

Low temperatures: quantum liquid phase, unstable to localized (solid) phase and to other phases with interesting quantum orders (superfluid)

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Normal liquid

D. Greywall PRB **27** 2747 (1983)

D. Greywall Fig. 6

Low T: specific heat linear in T but coefficient enhanced. Higher T; saturation

$$\frac{C}{T} \sim m^* k_F$$

$$P \approx 0 \ (\textbf{vol=36.8})$$

$$m^* = 2.7 m_{bare}$$

$$P \approx 29\textbf{bar} \ (\textbf{vol=26.2})$$
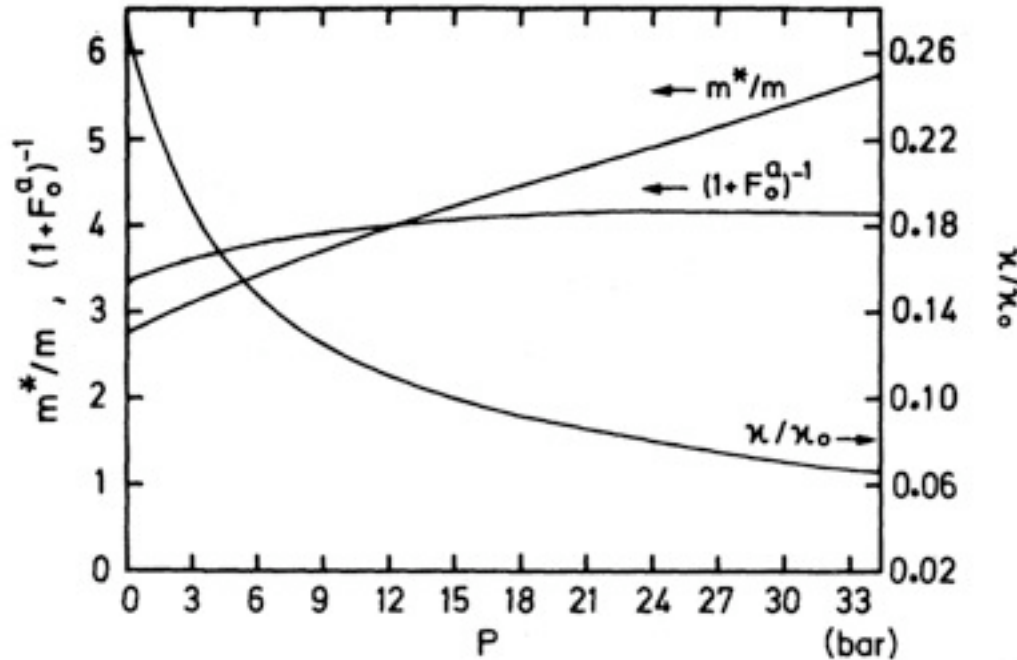
$$m^* = 5.4 m_{bare}$$

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Other quantities

charge susceptibility κ

spin susceptibility $\chi_{spin} = \frac{\chi_0}{1+F_0^a}$

Vollhardt RMP 56 p. 99 (1984) from Greywall data

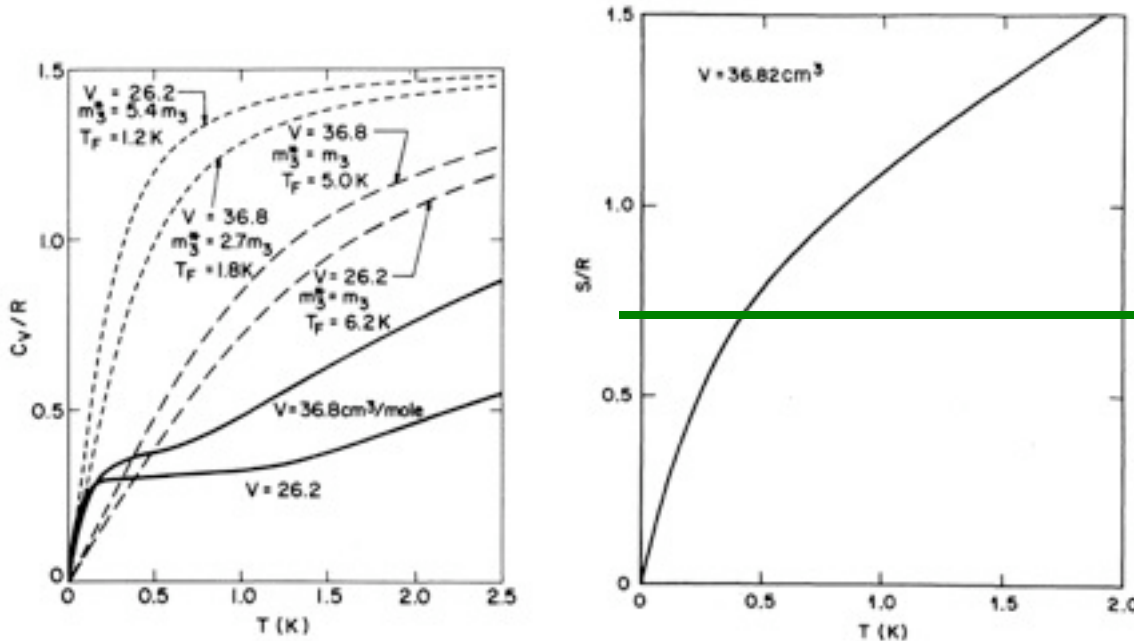Department of Physics
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Values of renormalization

While fermi liquid theory tells you what kind of renormalizations to expect, the values of the mass enhancement, landau parameters etc are

beyond the scope of FLT

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At higher T specific heat 'flattens off'

S=R ln(2)/particle

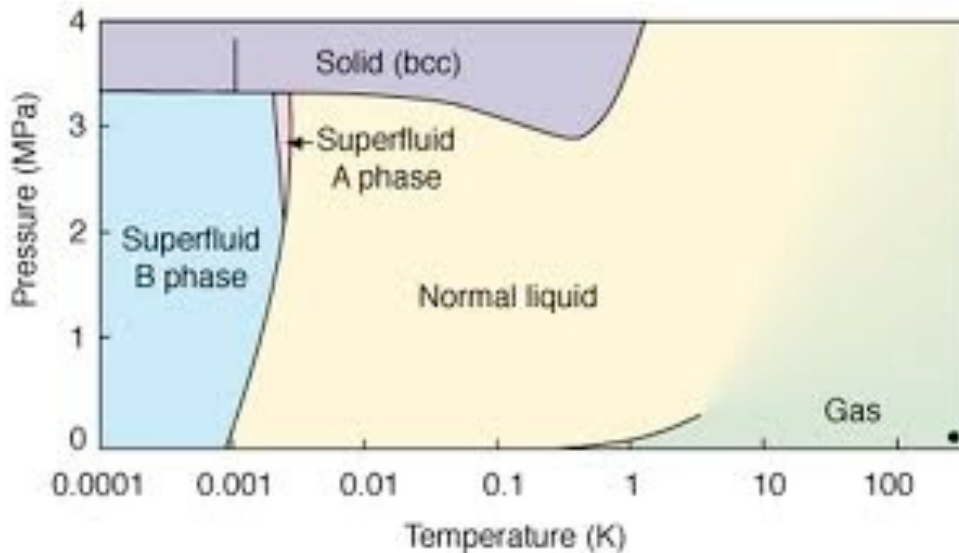**=> 'free spin' like behavior T>0.4K + positional entropy of classical liquid**

Qualitative idea: particle motion quenches spin entropy. Interaction-induced 'blocking' of particle motion=>quenching scale low, C/T high

This is beyond the scope of FLT

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Transitions to other states

While some idea of which states are favored and a rough order of magnitude of the transitions can be found from fermi liquid theory, a detailed understanding

is beyond the scope of FLT

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Digression: consequences of long ranged order (not discussed here)

Spontaneously broken symmetry (superconductivity, antiferromagnetism, ...) => order parameter (e.g. gap magnitude and phase; neel vector amplitude and direction). Many properties associated with the order parameter and its fluctuations are 'universal' (depending only on a few properties of host material) and can be studied from a relatively general field-theoretic point of view. Fermi liquid theory itself can be formulated in this language

P. W. Anderson, *Basic Notions in Condensed Matter Physics*
D. Forster, *Hydrodynamics, Broken Symmetry and Correlation Functions*

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Questions beyond the scope of fermi liquid theory

- **Higher T behavior**
- **Instability to other phases**
- **Value of m* and other fermi liquid parameters**

Modern (correlated fermion) 'materials theory':

2 themes:

--New (esp. non-classical) orders+fluctuations
--beyond fermi liquid theory in above sense

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Summary

- **Fermi liquid theory: successful description of low T properties of strongly coupled fermion system**

- **Simple physics: fermions+short range repulsion (basically 'hard core' contact interaction) => nontrivial behavior**

- **Electron Green function (esp coherent ('quasiparticle') part is a good thing to look at**

These insights are the basis of our understanding of the physics of 'correlated electron' materials

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Basic Solid State Physics:

Fermi liquid approach: start from non-interacting electrons then add interaction-driven renormalizations
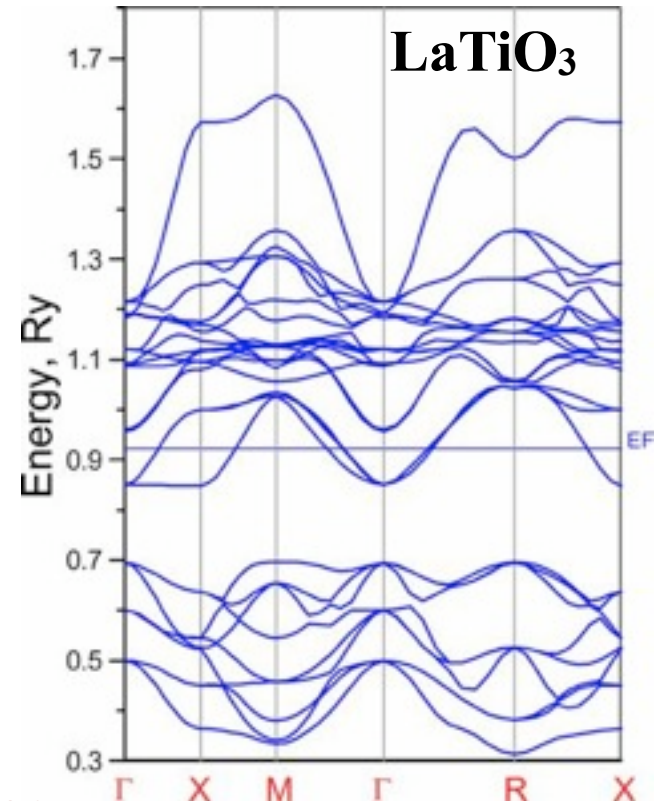
New feature: periodic potential

$$H = -\sum_i \frac{\nabla_i^2}{2m} + V_{lattice}(r_i)$$

=>Energy bands

all bands full or empty: insulator
some partly filled bands: metal

If number of electrons/cell not even: insulator impossible (in band theory)

LaTiO₃

http://dmft.rutgers.edu/
LDA/lmto/lmto_run.htm

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'Band' classification doesnt always work

LaTiO$_3$

LaTiO$_3$:
- **# electrons/unit cell is odd**
- **material is insulating!**
- **YTiO$_3$ even more insulating**
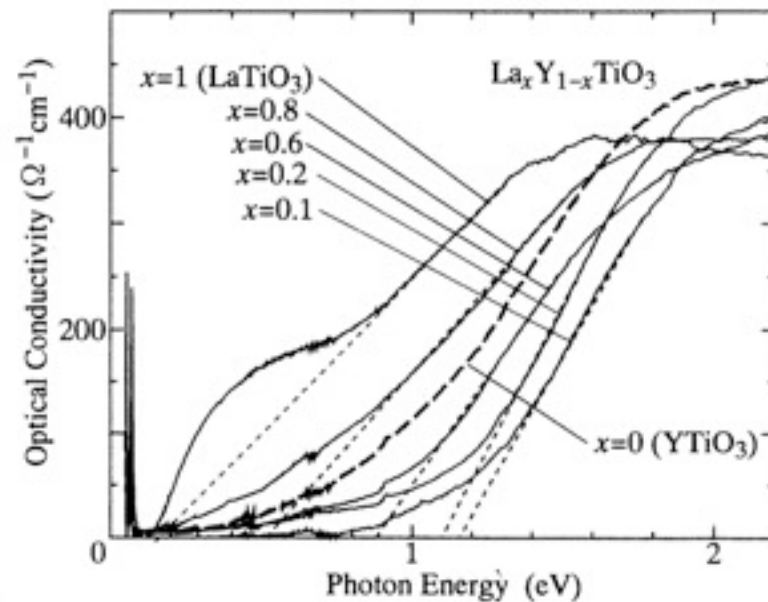
Okimoto et al. PRB51 9581 (1995)
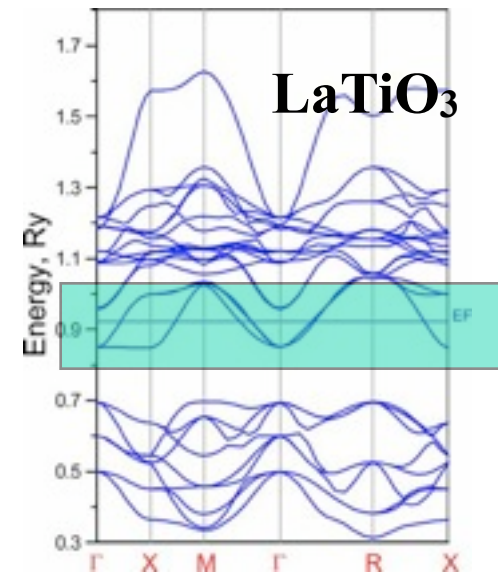
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'Mott' insulating behavior

Imada et al. Rev. Mod. Phys., 70, 1039,1998

•**Many materials (transition metal oxides, low-d organic materials, C-60 variants...) are insulating when band theory says they should be metallic**

•**Common feature: narrow bands, spatially confined orbitals, separated from other bands**
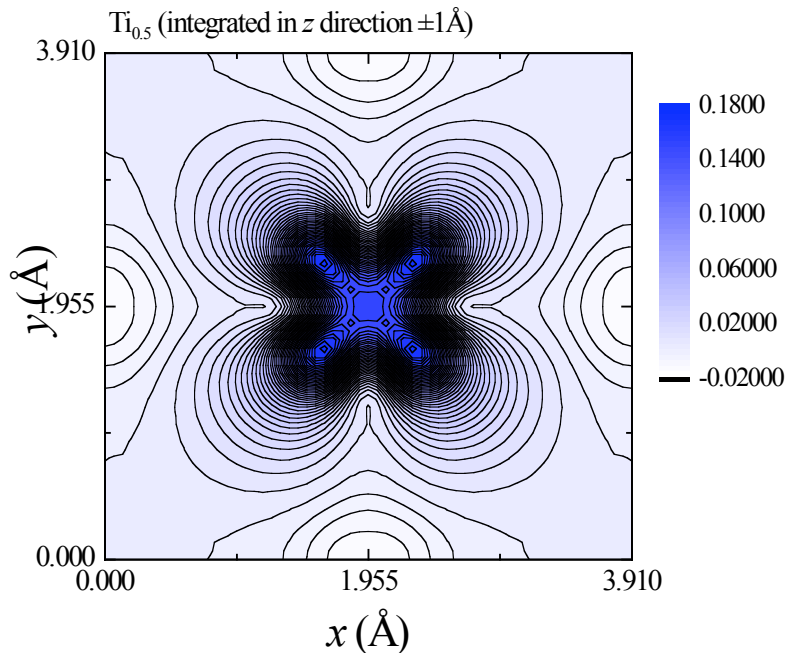
$LaTiO_3$

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Spatial extent of charge in important orbitals is small relative to lattice constant

LaTiO₃ Lattice constant 3.91A Important orbital Ti 3d

Ti$_{0.5}$ (integrated in z direction ± 1Å)

Here: Ti 3d charge density, integrated over z and plotted using false color (for LTO-STO superlattice).

S. Okamoto, N, Spaldin and
AJM PRL 97 056802 (2006)

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Implications of nearly localized wave function

- **Bandwidth ('bare mass' or kinetic energy) arises from overlap of orbitals: => small and controllable by changes in crystal structure**
- **e^2/r =>expensive to put 2 electrons into same orbital=>strong local repulsion is dominant interaction**

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=>Model Hamiltonian:
'Hubbard model'

http://www.engr.utexas.edu/news/
6544-goodenough-royal-society

One (spin degenerate) orbital per lattice site.
hopping t short ranged.

$$\mathbf{H} = -\sum_{ij} t_{i-j} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

Important parameters:
--relative interaction strength U/t
--electron density n

?Where do parameters come from?

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Qualitative view of physics
of Hubbard Model

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Conventional (band) Insulator: physics of filled shells

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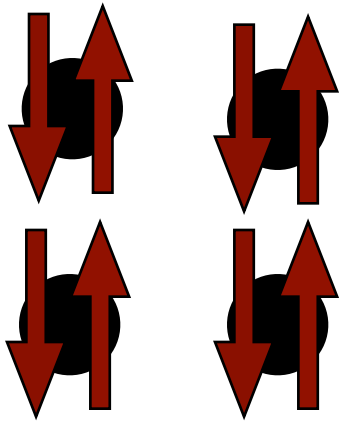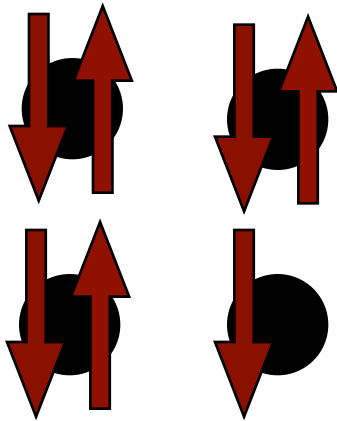# Conventional (band) Insulator: physics of filled shells

●

Conventional (band) Insulator: physics of filled shells

Conventional (band) Insulator: physics of filled shells
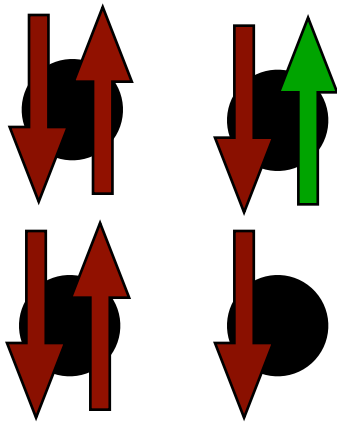
Pauli principle: no motion
possible=>insulator

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Conventional (band) Insulator: physics of filled shells

Add a "hole":

Conventional (band) Insulator: physics of filled shells

Add a "hole":
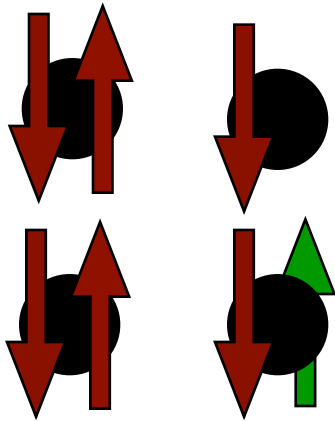
Conventional (band) Insulator: physics of filled shells

Add a "hole": motion possible

Conventional (band) Insulator: physics of filled shells

in k-space: filled and empty bands, with gap
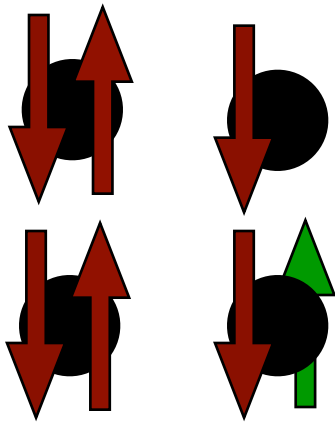
Add a "hole": motion possible
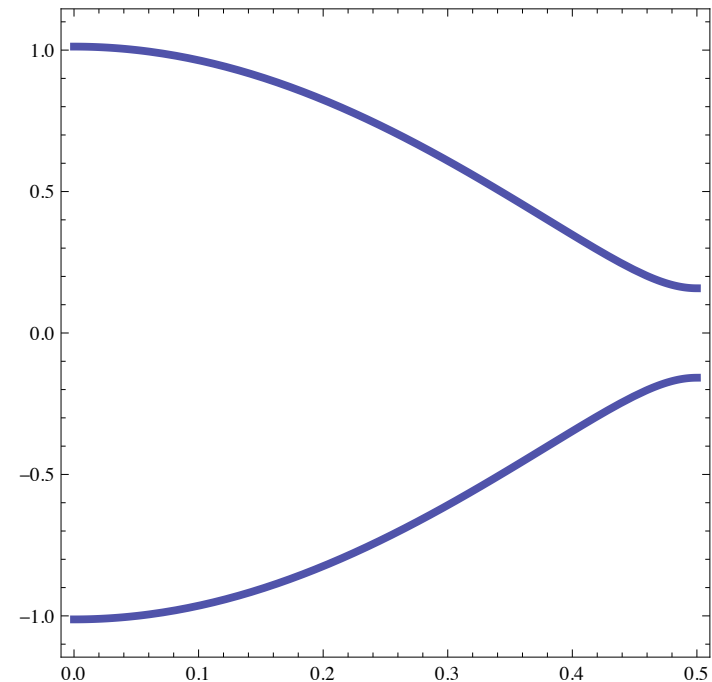
Unconventional ('Mott') Insulator: physics of "Coulomb blockade"

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Unconventional ('Mott') Insulator: physics of "Coulomb blockade"
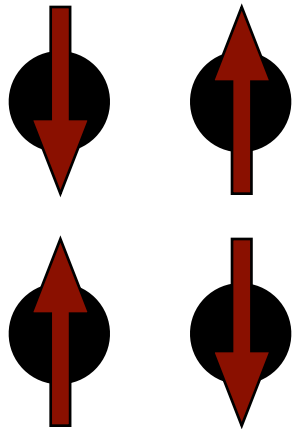
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Unconventional ('Mott') Insulator: physics of "Coulomb blockade"

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Unconventional ('Mott') Insulator: physics of "Coulomb blockade"

strong repulsion: no charge
motion possible=>insulator

Unconventional ('Mott') Insulator: physics of "Coulomb blockade"

1 **2** **3**

**BUT:
virtual
hopping**

**=>'superexchange':
magnetic scale $J \sim t^2/U$**
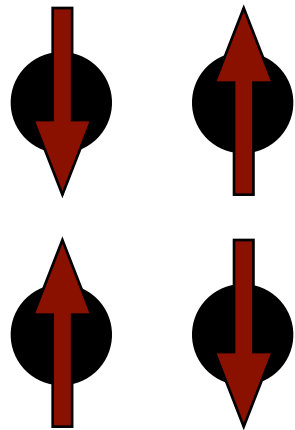
strong repulsion: no
motion possible=>insulator

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Unconventional ('Mott') Insulator: physics of "Coulomb blockade"

add a hole

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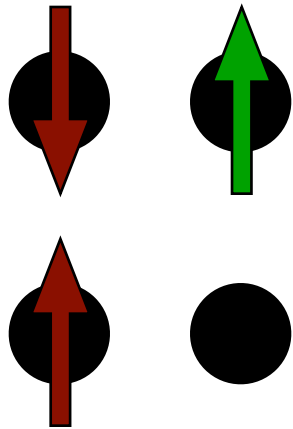
Unconventional ('Mott') Insulator: physics of "Coulomb blockade"

add a hole
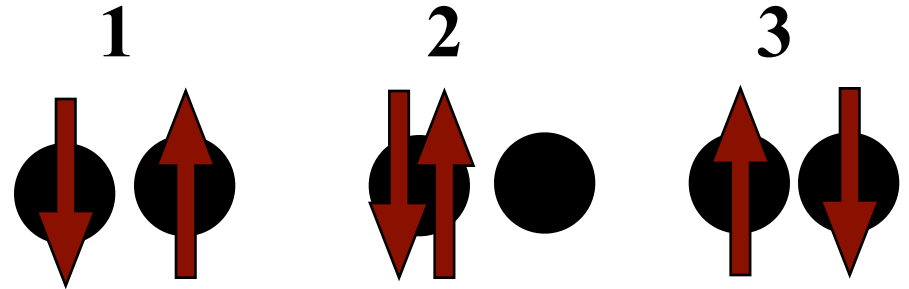
Department of Physics
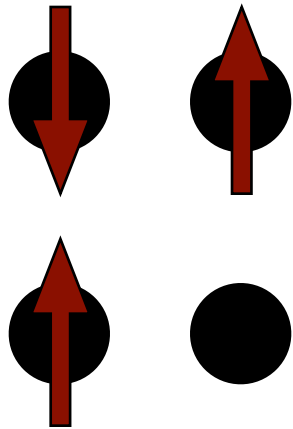Columbia University
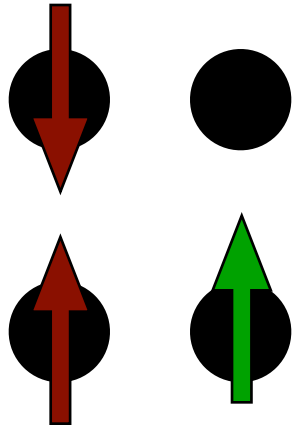
Unconventional ('Mott') Insulator:
physics of "Coulomb blockade"

add a hole: charge
motion possible

Unconventional ('Mott') Insulator: physics of "Coulomb blockade"
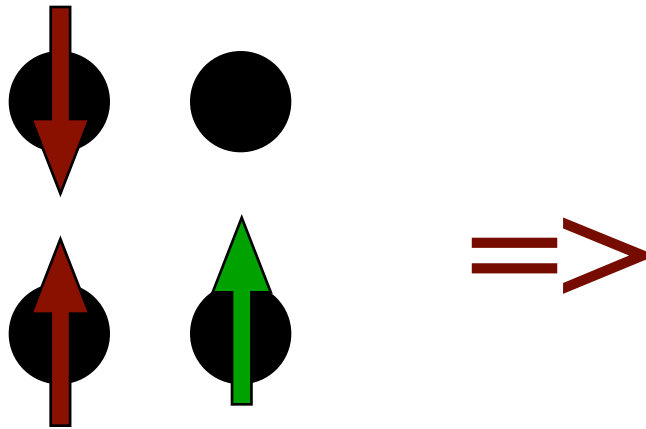
add a hole: charge motion possible. Properties scale with hole density

Deep theoretical questions:

- **Metal-insulator transition as vary U/t and n**
- **role of long and short ranged order**
- **nature of hole motion in background of correlated spins**
- **consequences for other physical properties**

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Data: LaTiO3 reveal divergent effective mass (specific heat) associated with approach to insulating phase

Fig 104 Imada et al Rev Mod Phys
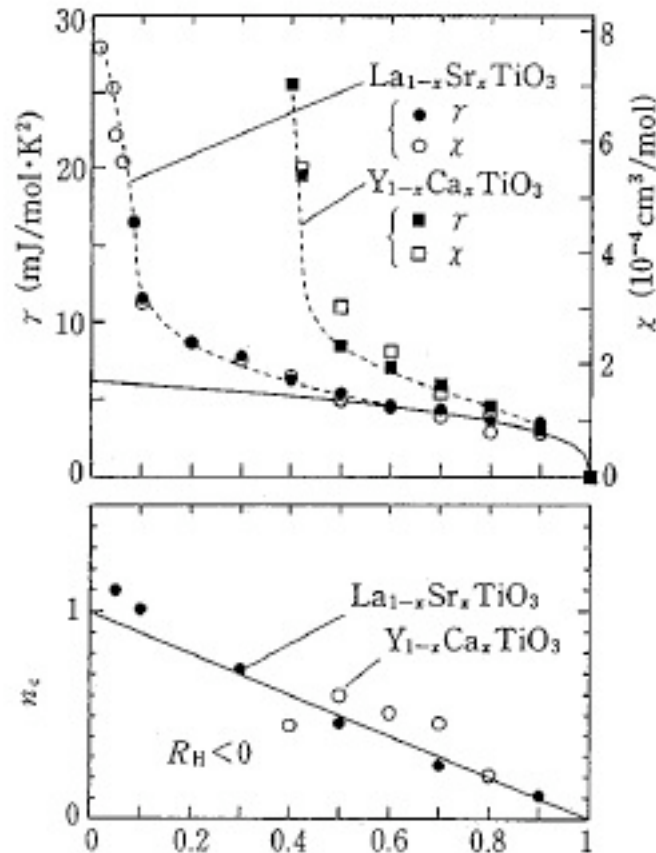
Consistent with idea: entropy comes from spins, which are correlated by hole motion

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But there is more to life than the 1 orbital Hubbard model

Orbital degeneracy:

in free space: d-level is 5 fold degenerate
in solid state, O(3) rotation symmetry broken
  =>degeneracy lifted (mainly by `ligand field' i.e.
  hybridization to neighboring atoms)

Cubic ligand field: 5->2+3

t_{2g}: xy, xz, yz

e_g: $3z^2 - r^2$, $x^2 - y^2$

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digression: in transition metal oxides hybridization of transition metal (Tm) to oxygen is crucial

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digression: in transition metal oxides hybridization of transition metal (Tm) to oxygen is crucial

Tm   O   Tm   O

O   O

Tm   O   Tm   O

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digression: in transition metal oxides hybridization of transition metal (Tm) to oxygen is crucial

Tm   O   Tm   O

O   O

Tm   O   Tm   O

LaNiO$_3$ LDA

J. Rondinelli ANL prvt comm

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digression: in transition metal oxides hybridization of transition metal (Tm) to oxygen is crucial

Tm   O   Tm   O

O   O

Tm   O   Tm   O

LaNiO$_3$

LDA

e_g anti-bonding

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digression: in transition metal oxides hybridization of transition metal (Tm) to oxygen is crucial

Tm   O   Tm   O

O   O

Tm   O   Tm   O

LaNiO$_3$

LDA

e_g anti-bonding

e_g bond-ing

J. Rondinelli ANL prvt comm

digression: in transition metal oxides hybridization of transition metal (Tm) to oxygen is crucial

Tm   O   Tm   O

O   O

Tm   O   Tm   O

LaNiO$_3$

LDA

e_g anti-bonding

t_{2g} anti-bonding

e_g bond-ing

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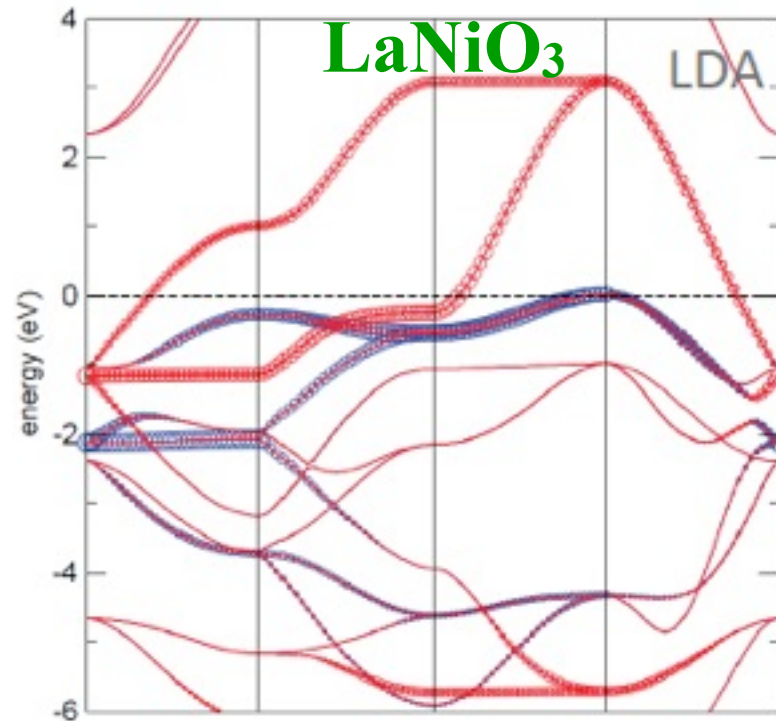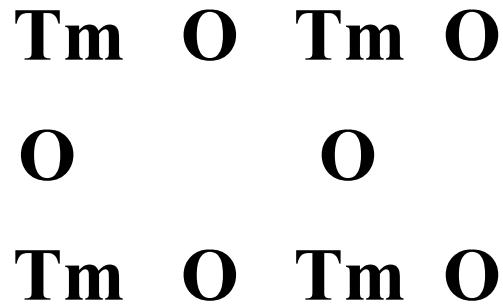# digression: in transition metal oxides hybridization of transition metal (Tm) to oxygen is crucial

Tm O Tm O

O   O

Tm O Tm O

LaNiO$_3$

LDA

e$_g$ anti-bonding

t$_{2g}$ anti-bonding
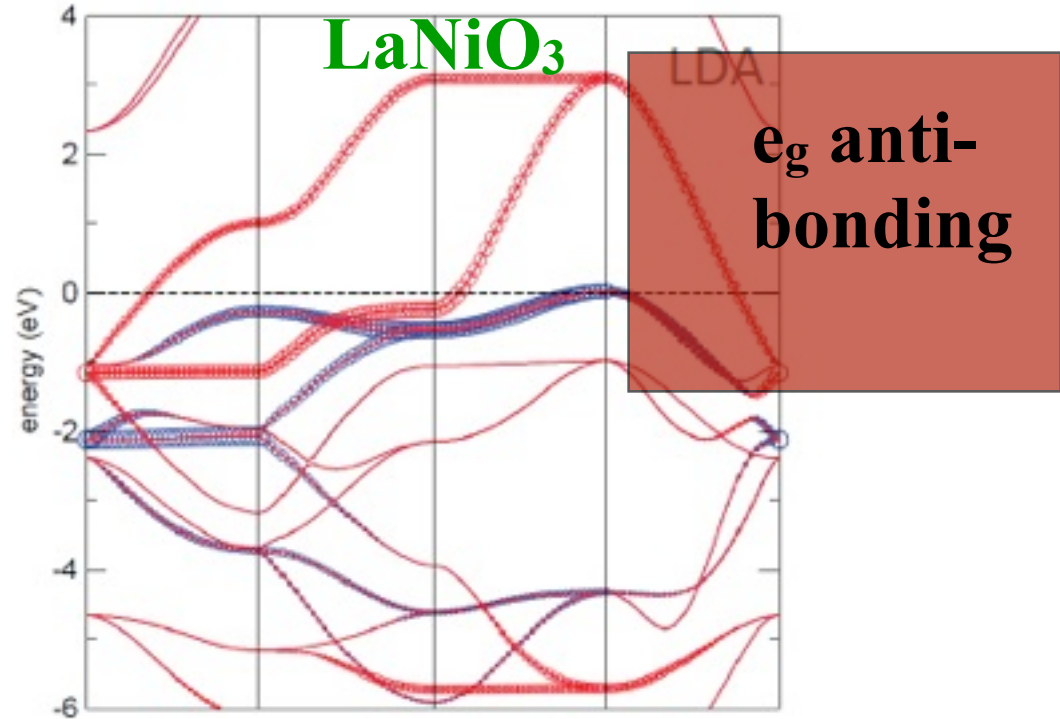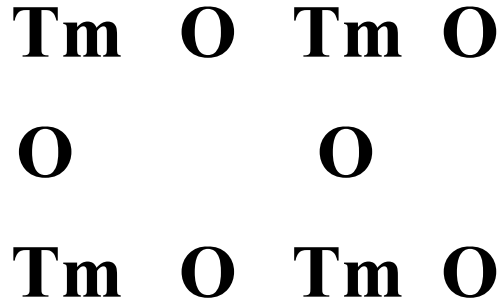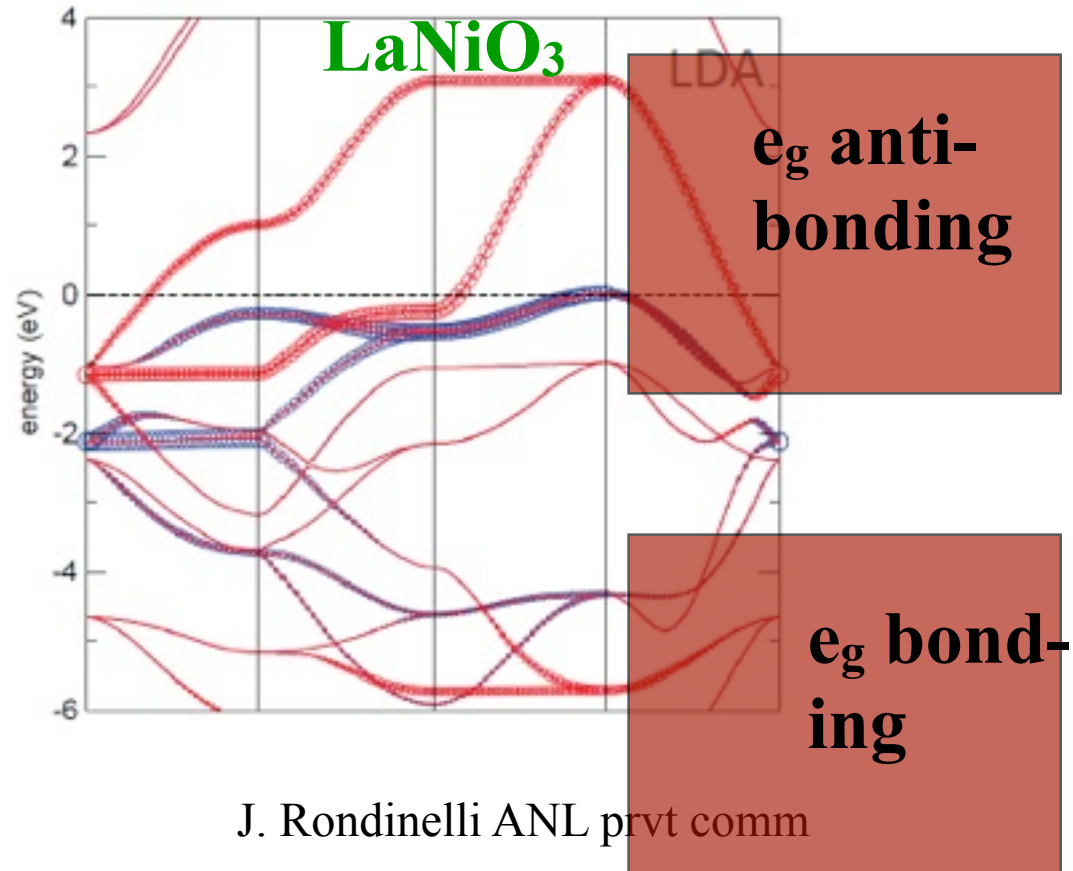
t$_{2g}$ bonding
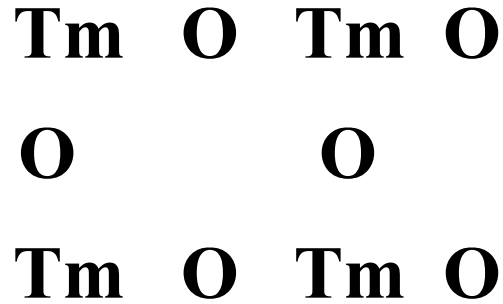
e$_g$ bond-ing

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digression: in transition metal oxides hybridization of transition metal (Tm) to oxygen is crucial

Tm   O   Tm   O

O   O

Tm   O   Tm   O

LaNiO$_3$

LDA

e_g anti-bonding

t_{2g} anti-bonding

t_{2g} bonding

e_g bond-ing

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Rule of thumb: e_g has wider bands, bigger bonding/ antibonding split than t_{2g}

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Back to orbital degeneracy

Transition metal ion in free space

(For simplicity neglect spin orbit coupling here)

J. C. Slater: *Quantum Theory of Atomic Structure*

Fundamental perspective: atom as fully entangled multielectron system. Eigenstates A characterized by quantum numbers

Electron number N

Spin Angular momentum $S,\ S_z$

Orbital Angular momentum $L,\ L_z$

$\Rightarrow$ $\boxed{\text{Energy } E_A(N, S, L)}$

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Needed: a representation in terms of single-particle orbitals (for intuition, and to discuss band formation)

Idea (Slater):

choose basis (e.g. d-symmetry atomic orbitals+...)
devise Hamiltonian whose eigenstates are $E_A(N,S,L)$
(for relevant range of energies)

Example: $$\psi_{2,m,\sigma} = Y_{2,m}(\theta,\phi) f_d(r)$$

$$H = \sum_{(m\sigma)_{i=1\ldots4}} U^{\sigma_1\sigma_2\sigma_3\sigma_4}_{m_1 m_2 m_3 m_4} d^\dagger_{m_1\sigma_1} d^\dagger_{m_2\sigma_2} d_{m_3\sigma_3} d_{m_4\sigma_4}$$

Choose Us to fit $E_A(N,S,L)$--or compute them

Slater, J. C. (1960). Quantum Theory of **Atomic Structure**

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Parametrizing the interaction: Coulomb integrals

$$U^{\sigma_1 \sigma_2 \sigma_3 \sigma_4}_{m_1 m_2 m_3 m_4} =$$

$$e^2 \int d^3 r \, d^3 r' \frac{\psi^\dagger_{m_1 \sigma_1}(r) \psi_{m_3 \sigma_3}(r) \psi^\dagger_{m_2 \sigma_2}(r') \psi_{m_4 \sigma_4}(r')}{|\vec{r} - \vec{r}'|}$$

Spherical symmetry+spin rotation: express all U in terms of interactions between multipoles of charge density

Crucial parameter:

$$\mathbf{F_0 = e^2 \int d^3 r \, d^3 r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\tilde{\mathbf{r}} - \tilde{\mathbf{r}}'|}} \quad \textbf{charge-charge}$$
(monopole) interaction

F_2, F_4, ..: interaction between higher multipoles
Spin-orbit--also need 'G' parameters

d-orbitals
weak spin-orbit coupling

- **Need only F_0, F_2, F_4**
- ***In free space*: definite relation between F2, F4**

 => **Only 2 parameters: Conventional notation: U, J**

Conventional (Slater-Kanamori) representation

$$H \;=\; U \sum_a n_{a\uparrow} n_{a\downarrow} + (U - 2J) \sum_{a>b, \sigma=\uparrow,\downarrow} n_{a\sigma} n_{b\sigma}$$

$$+(U - 3J) \sum_{a \neq b\sigma} n_{a\sigma} n_{b\bar{\sigma}} - J \sum_{a \neq b} c_{a\uparrow}^{\dagger} c_{a\downarrow}^{\dagger} c_{b\uparrow} c_{b\downarrow} + c_{a\uparrow}^{\dagger} c_{b\downarrow}^{\dagger} c_{b\uparrow} c_{a\downarrow}$$

85 interaction terms, determined by 2 parameters

Lower symmetry: more parameters, more complicated form--but generically: charging energy +smaller terms

Orbital degeneracy, interactions make a difference

3 orbital model   **Insulating phase inside lobes**

Critical U for 1 orbital model

J=0
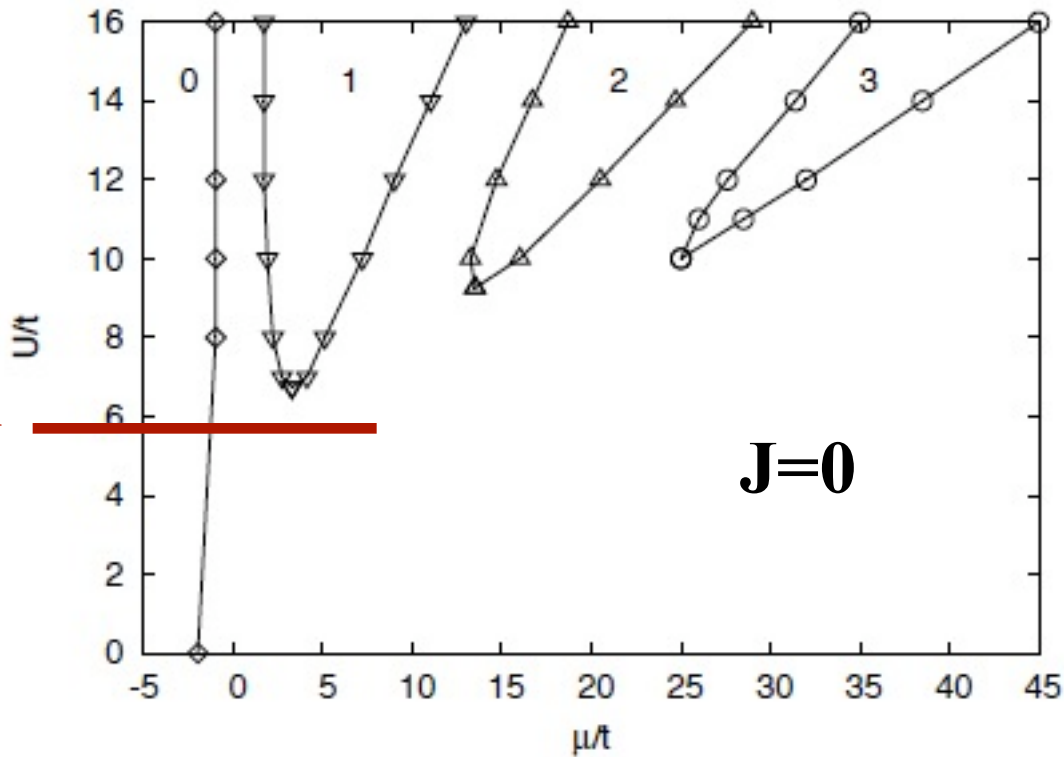
Werner, Gull, AJM, Phys. Rev. B 79, 115119 (2009)

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Effect of J

3 orbital model   **Insulating phase inside lobes**

Phase boundaries move sustantially if J>0
Note also effect of lifting orbital degeneracy slightly

Werner, Gull, AJM, Phys. Rev. B 79, 115119 (2009)

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The case of LaTiO₃

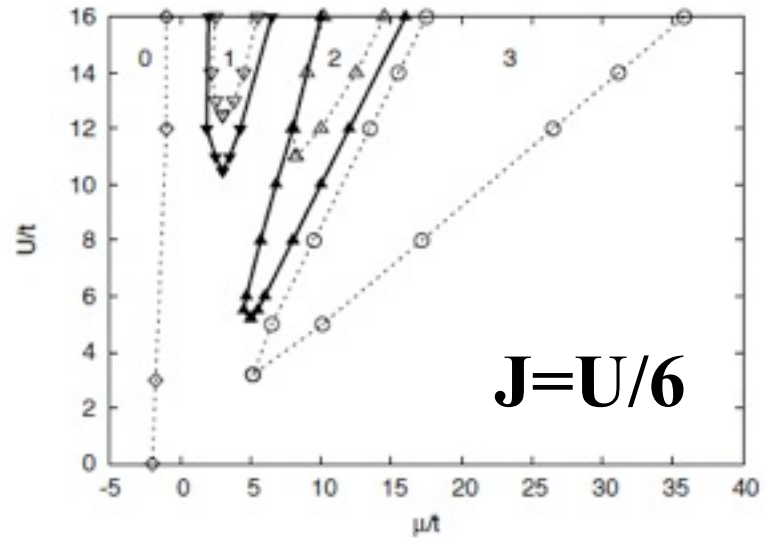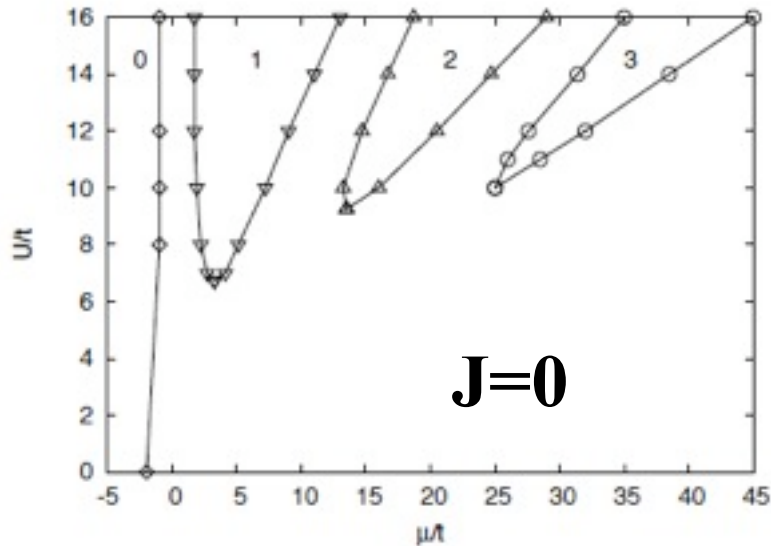## Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini,[1] S. Biermann,[2] A. Poteryaev,[3] A. I. Lichtenstein,[3] A. Georges,[2] and O. K. Andersen[4]

[1]INFM and Dipartimento di Fisica "A. Volta," Università di Pavia, Via Bassi 6, I-27100 Pavia, Italy
[2]Centre de Physique Théorique, Ecole Polytechnique, 91128 Palaiseau Cedex, France
[3]NSRIM, University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands
[4]Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany
(Received 4 September 2003; published 30 April 2004)

Using t_{2g} Wannier functions, a low-energy Hamiltonian is derived for orthorhombic $3d^1$ transition-metal oxides. Electronic correlations are treated with a new implementation of dynamical mean-field theory for noncubic systems. Good agreement with photoemission data is obtained. The interplay of correlation effects and cation covalency (GdFeO₃-type distortions) is found to suppress orbital fluctuations in LaTiO₃ and even more in YTiO₃, and to favor the transition to the insulating state.

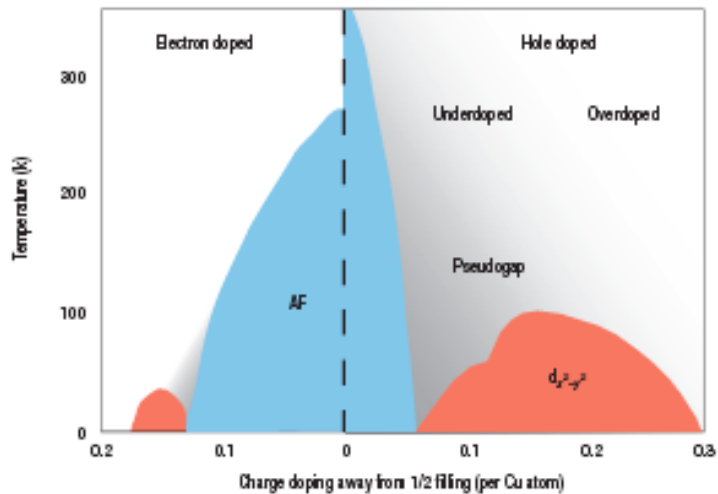## Argument: LaTiO3 is insulating only because crystal structure lifts orbital degeneracy

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Second example:
High Tc (Cu-O₂) superconductors
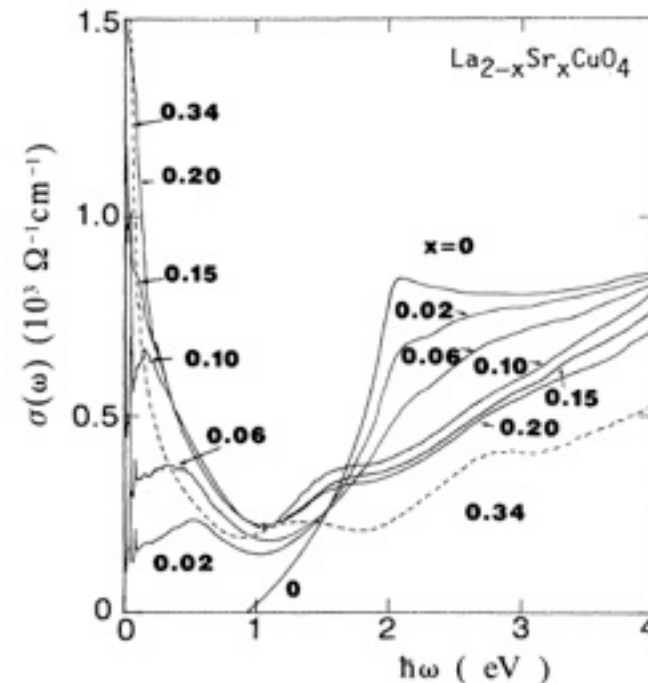
Phase diagram

Data:

A.Zimmers Ph.D. thesis

Uchida, S., T. Ido, H. Takagi, T. Arima, Y. Tokura, and S. Tajima, 1991, Phys. Rev. B **43**, 7942

Electron counting: 1 el/ unit cell at 0 doping

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High T_c CuO$_2$ superconductors are not quite Mott Insulators

O: very electronegative: p-shell almost full

Cu: 'late' transition metal oxide. d-shell almost full.

Ti: 'early transition metal oxide: d-shell almost empty

Electronic configuration:

La$_2$CuO$_4$: Cu d^9 O2p^6

LaTiO$_3$:   Ti d^1 O2p^6

Hole dope: in late TMO 'holes go on the O

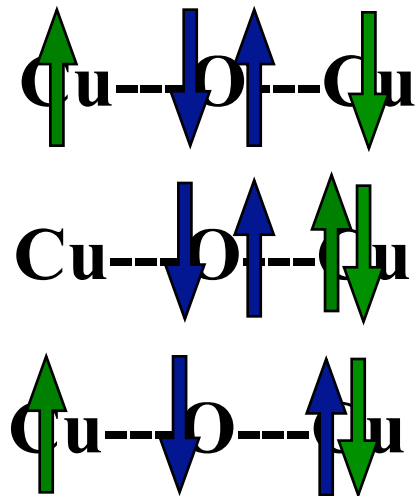**Cu d^9 O2p^5**

Ti d^0 O2p^6
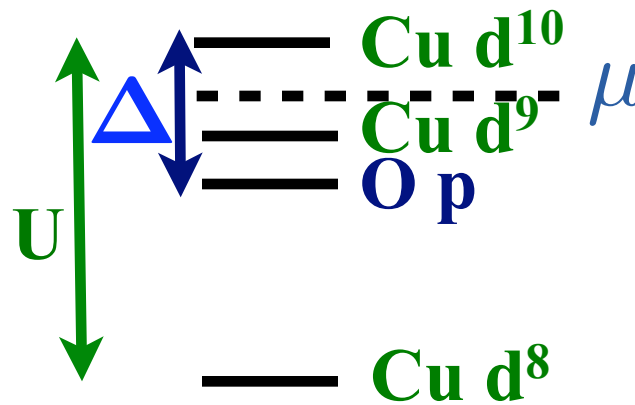
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Mott vs Charge Transfer Insulators

$2d^n => d^{n-1}d^{n+1}$ not the only process

Fragment of CuO$_2$ plane

Energies

$$\Delta > U$$

Cu---O---Cu

Cu---O---Cu

Cu---O---Cu

Cu d^{10}

μ

Cu d^9

O p

Cu d^8

Δ

U

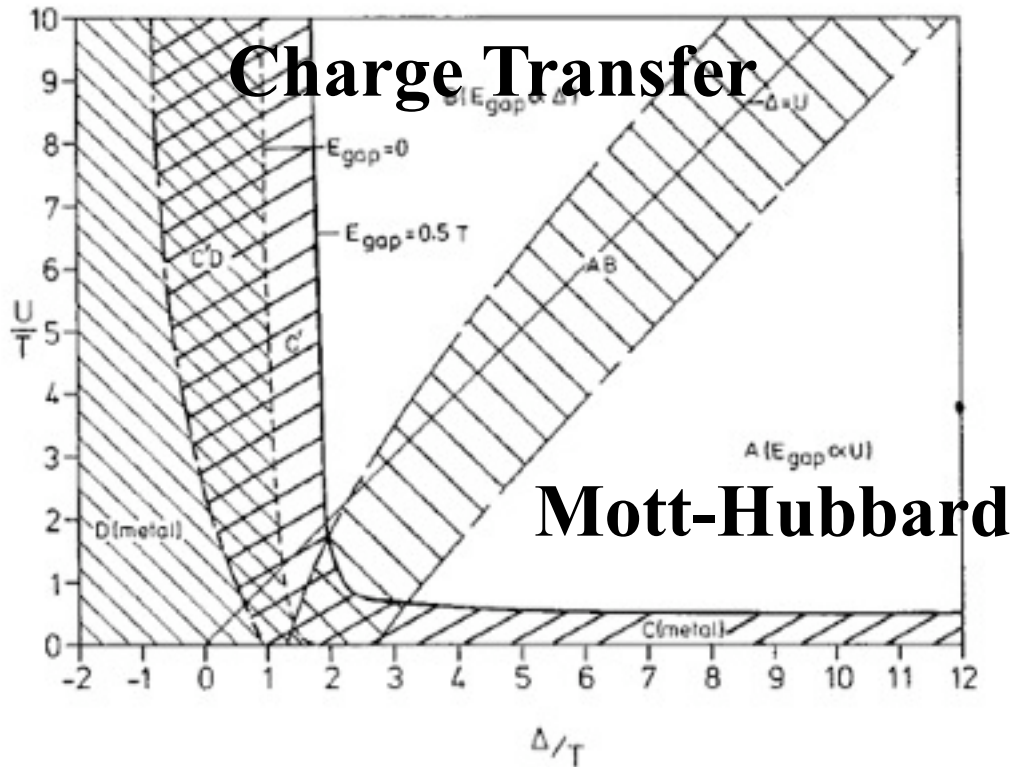**Charge transfer insulator**

Cuprates:

$2d^9 => d^8d^{10}$ **8eV**

$2d^9 => d^9Op^5d^{10}$ **2eV**

Zaanen, Sawatzky, Allen, Phys. Rev. Lett. **55**, 418 (1985)

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Zaanen-Sawatzky-Allen Classification

Charge Transfer

Mott-Hubbard

Questions:
- **Where do you place different materials in this scheme**
- **More generally, what is the role of covalency with other orbitals**
- **what difference does it make?**

Zaanen, Sawatzky, Allen, Phys. Rev. Lett. **55**, 418 (1985)

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Charge transfer insulators: important of other (non-d) orbitals

More extreme example: heavy fermion compounds

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Low T: constant specific heat coefficient; magnitude =>m ~ 1000m$_e$

CeCu$_2$Si$_2$
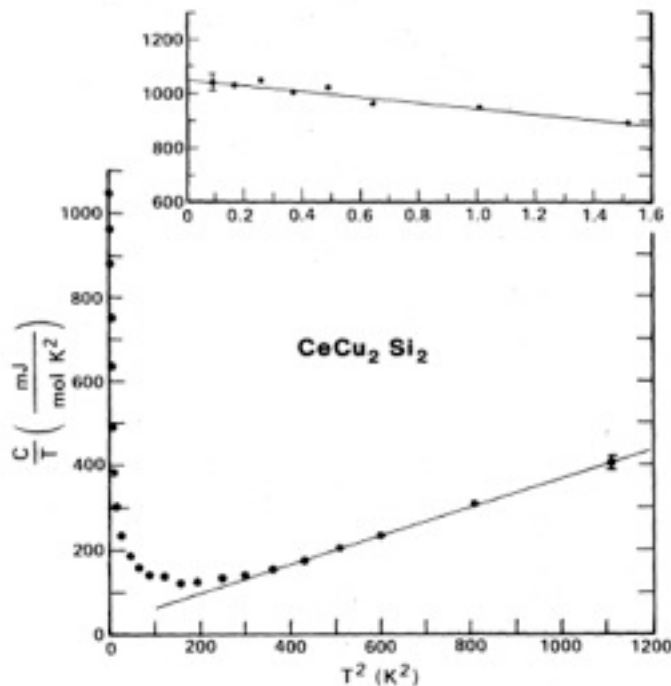
Fig 2 G R Stewart RMP

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Charge transfer insulators=> importance of other (non-d) orbitals

More extreme example: heavy fermion compounds

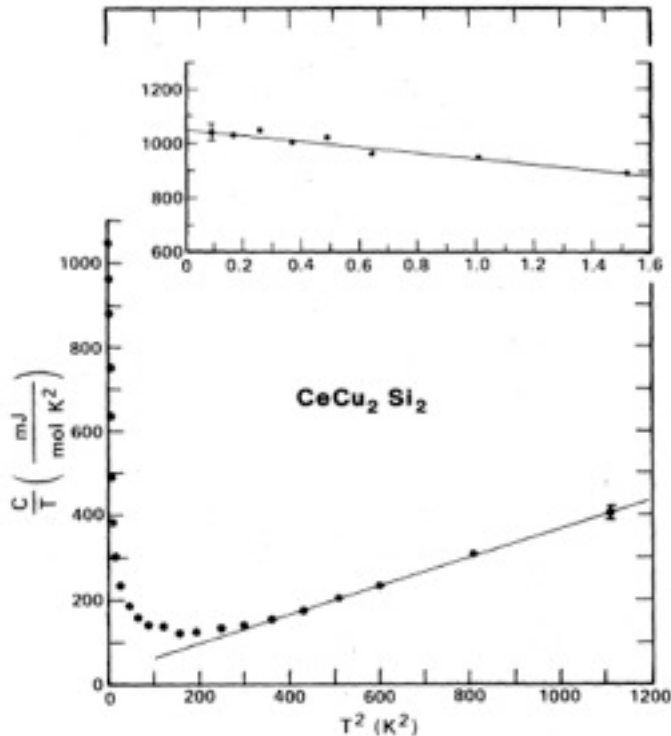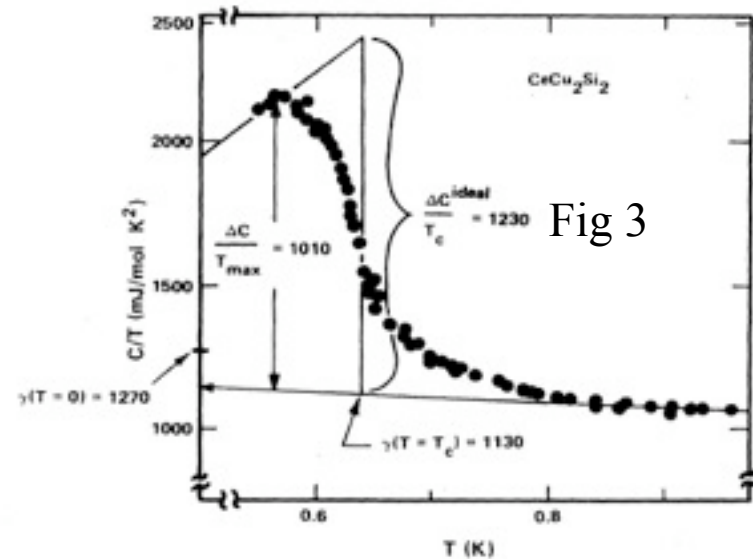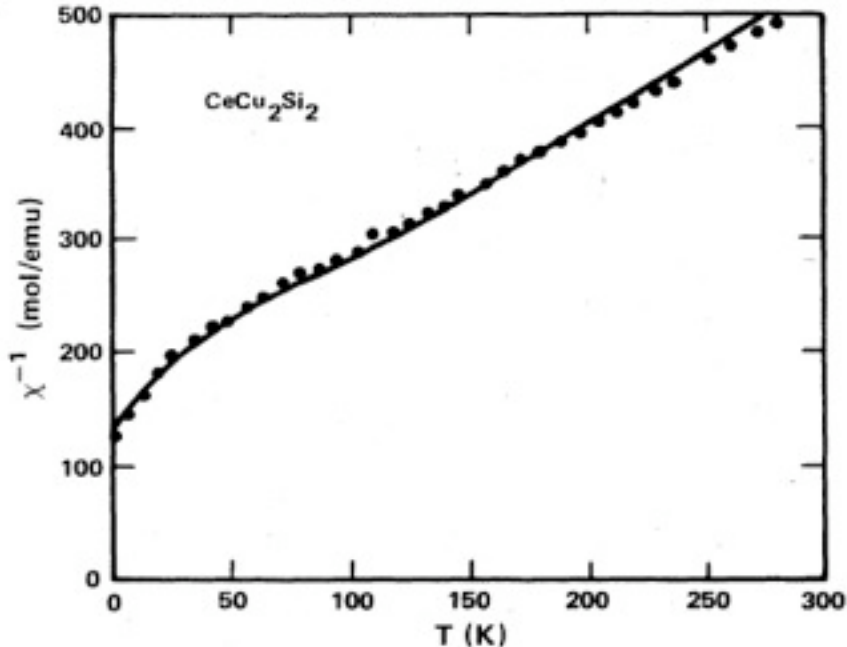**Low T: constant specific heat coefficient; magnitude =>m ~ 1000m$_e$**

Fig 2 G R Stewart RMP 56 755 1984

Fig 3

Large specific heat is due to degrees of freedom that can superconduct

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What is going on?

CeCu₂Si₂

Cu, Si (also Ce): wide spd bands => metallic state

Ce f: small orbital, weakly hybridized. Large U. Holds ~1 electron.

High T: 'free spin' like behavior

Low T: 'heavy fermi liquid'

Anderson Lattice Model

$$\mathbf{H} = \sum_{im\sigma} E_f^m f_{im}^\dagger f_{im} + \frac{1}{2} U \left(N_F^i (N_f^i - 1) \right) + .$$

$$+ \sum_{ikam\sigma} e^{ik \cdot R_i} V_{km\sigma} f_m^\dagger c_{ka\sigma} + H.c. + \sum_{ka\sigma} \varepsilon_k^a c_{ka\sigma}^\dagger c_{ka\sigma}$$

Lattice version of 'Kondo resonance'

Summary:
'botany' of correlated materials

- **Want to understand**
  - **Physics at scales above fermi liquid**
  - **Nature of instabilities to other phases**
  - **Metal-insulator transitions**

- **Wish to relate novel behavior to crystal structure**

- **Need to deal with strong local interactions involving multiple quantum numbes**

Issues

- **Derivation of model parameters (Hubbard of Anderson lattice) from underlying chemistry**

- **Solution of models**

More ambitious goal: fully 'ab initio' theory