Magnetism: Models and Mechanisms

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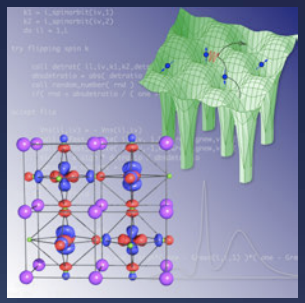


magnetism and emergence

introduction

what are the fundamental laws of the universe?
what are the fundamental particles?

reductionist approach
given those I can explain the universe

electrons and lattice

electronic Hamiltonian

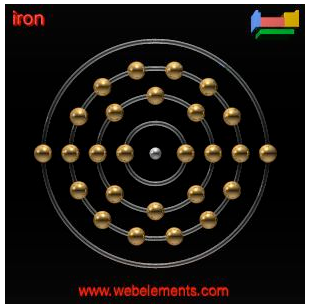
$$\begin{aligned}\hat{H}_e &= -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2}\sum_{\alpha\neq\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \\ &= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}\end{aligned}$$

lattice Hamiltonian

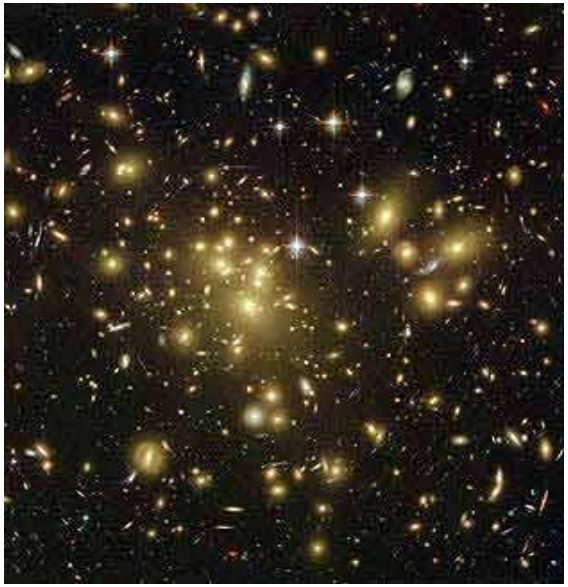
$$\begin{aligned}\hat{H}_n &= -\sum_\alpha \frac{1}{2M_\alpha}\nabla_\alpha^2 + \varepsilon(\{\boldsymbol{R}_\alpha\}) \\ &= \hat{T}_n + \hat{U}_n,\end{aligned}$$

if we crystal structure known
we can concentrate on electrons

a single iron atom



26 electrons, 78 arguments,
10^{78} values
10 X 10 X 10 grid



$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{26})$$

more is different

The effectiveness of this message may be indicated by the fact that I heard it quoted recently by a leader in the field of materials science, who urged the participants at a meeting dedicated to "fundamental problems in condensed matter physics" to accept that there were few or no such problems and that nothing was left but extensive science, which he seemed to equate with device engineering.

The main fallacy in this kind of thinking is that the reductionist hypothesis does not by any means imply a "constructionist" one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe. In fact, the more the ele-

Philp Warren Anderson

Nobel Prize in Physics 1977

4 August 1972, Volume 177, Number 4047

SCIENCE

http://www.emergentuniverse.org/

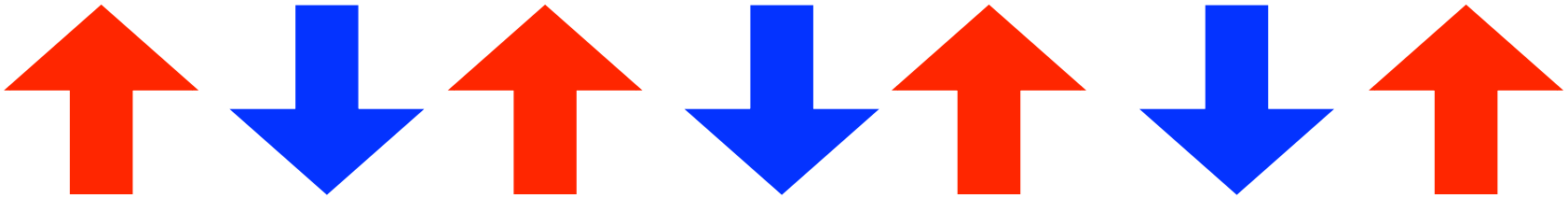
do we want the exact solution?

no.

- too many details
- really we need to understand idealized cases (thermodynamic limit, ideal crystals,...)
- elementary entities depend on energy scale (electron vs spins)
- we want to understand cooperative phenomena (ferromagnetism, antiferromagnetism)
- co-operative phenomena/ effective elementary entities = emergent properties
- prediction is difficult, experiments normally first

anti-ferromagnetism

prediction: Néel (1932)



experiment: Shull and Smart (1949)

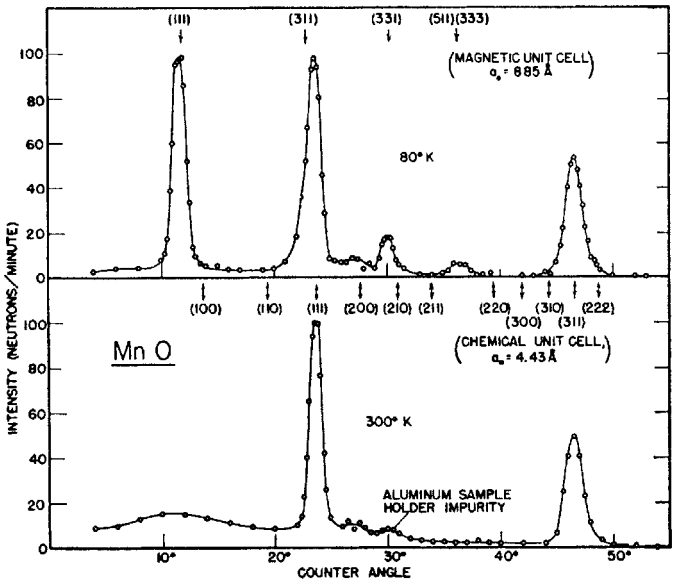
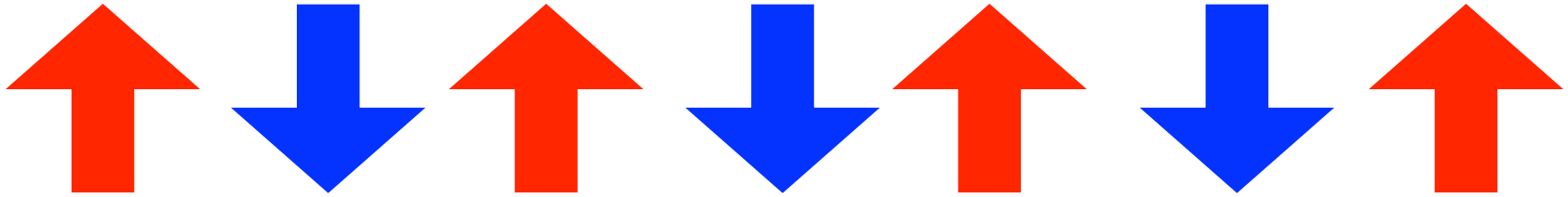


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

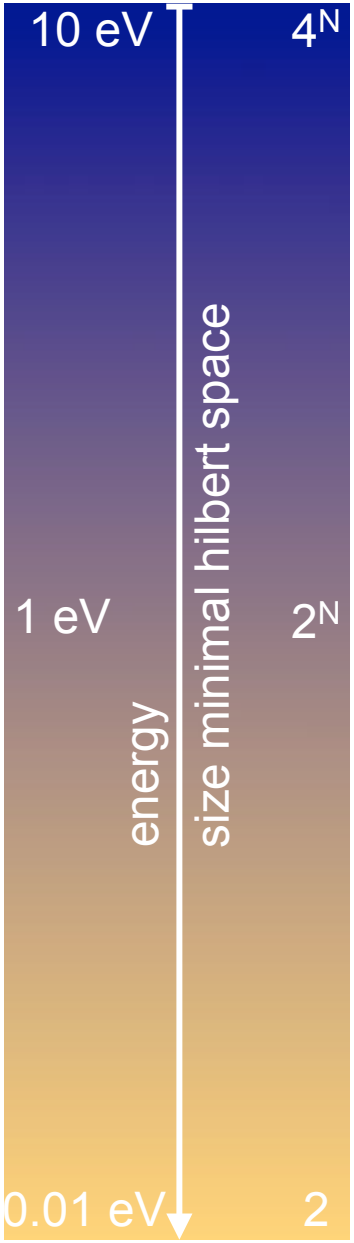
exact solution?

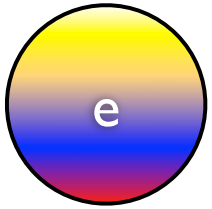
Bethe: ground state of linear Heisenberg chain has S=0



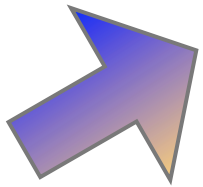
Anderson: broken symmetry & quantum fluctuations

magnetism & emergence



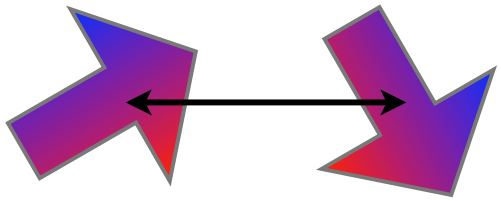


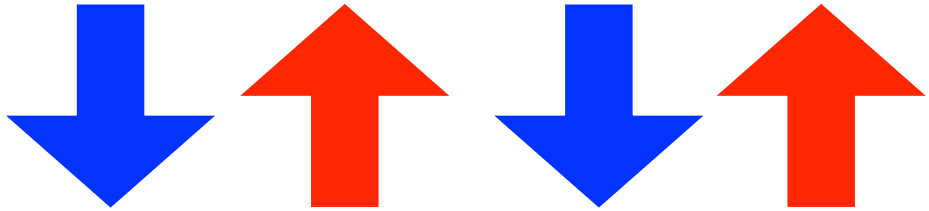
from electrons emerge spins



effective elementary entities

spins interact

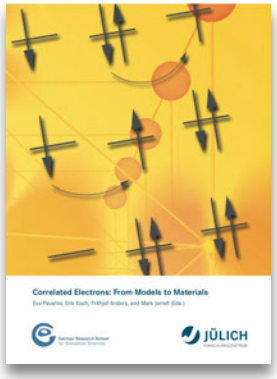


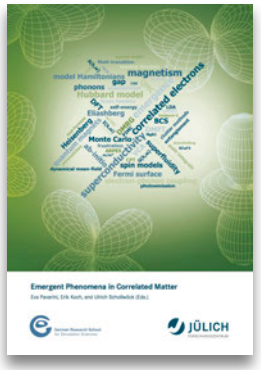


cooperative state

this lecture

- the general electronic Hamiltonian
- isolated atoms and ions
- ions in solids
- the Hubbard model
    - idealized cases: itinerant & atomic limit
    - itinerant limit
        - Pauli paramagnetism
        - Stoner instabilities
    - atomic limit
        - localized moments
        - paramagnetism of isolated magnetic ions
        - interacting magnetic ions
- the Kondo model
- conclusions





the Hamiltonian

electronic Hamiltonian

non relativistic electronic Hamiltonian

$$H_e^{\mathrm{NR}} = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq i'} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_{i'}|} - \sum_{i\alpha} \frac{Z_\alpha}{|\boldsymbol{r}_i - \boldsymbol{R}_\alpha|} + \frac{1}{2}\sum_{\alpha\neq\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_{\alpha'}|}$$

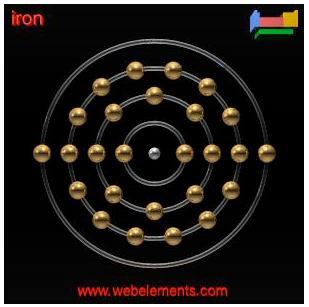
kinetic Coulomb potential constant

magnetism is a quantum mechanical effect

interplay between Coulomb interaction, Pauli principle and hoppings

atoms and ions

atoms and ions



$$H_e^{\mathrm{NR}} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i>j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

self-consistent potential

$$H_e^{\mathrm{NR}} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i>j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

$$H_e^{\mathrm{NR}} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v_R(r_i)$$

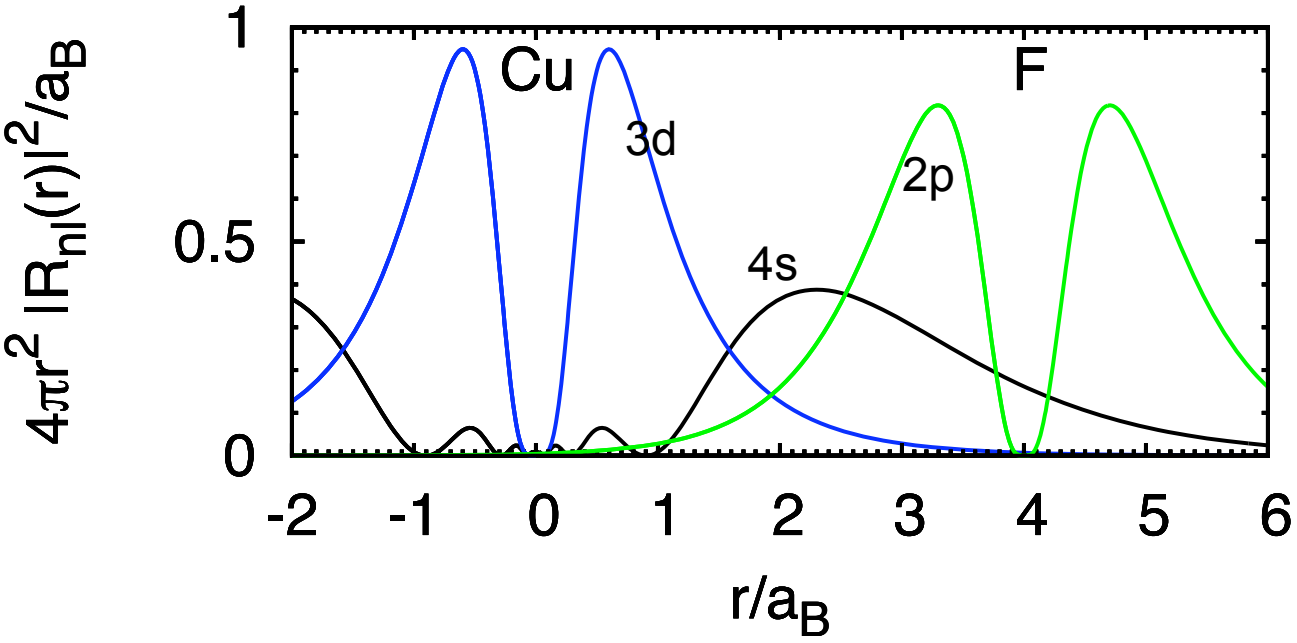
e.g., DFT/LDA

contains e.g. Hartree term

hydrogen-like atom

$$H_e^{\mathrm{NR}} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i Z_{\mathrm{eff}}/r_i$$

atomic functions



$$\psi_{nlm}(\rho,\theta,\phi) = R_{nl}(\rho)Y_l^m(\theta,\phi)$$

(hydrogen-like atom)

$$R_{nl}(\rho) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\rho/n} \left(\frac{2\rho}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2\rho}{n}\right)$$

Laguerre polynomials

real harmonics

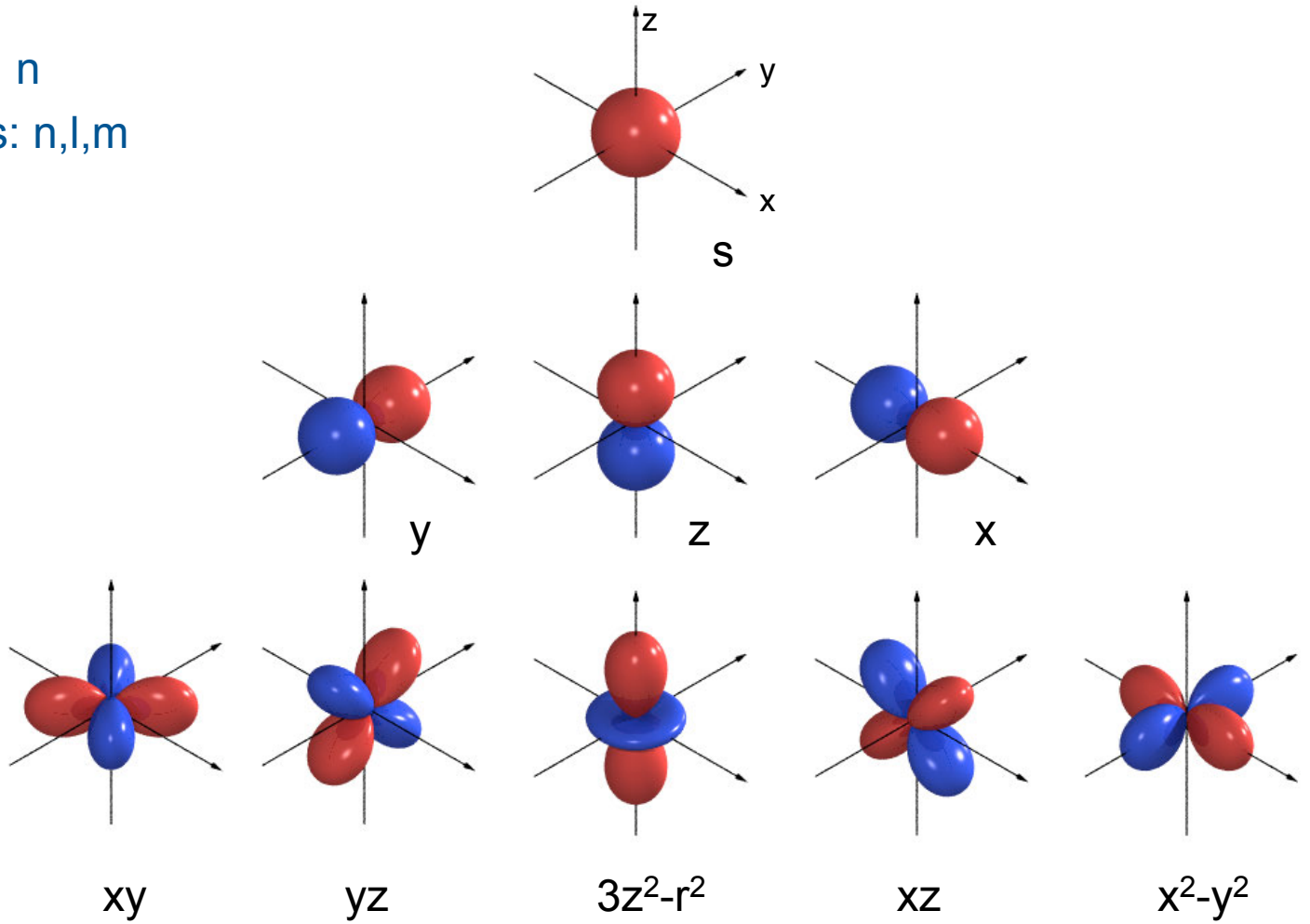
$$
\begin{aligned}
s &= y_{00} &&= Y_0^0 &&= \sqrt{\tfrac{1}{4\pi}} \\
p_y &= y_{1-1} &&= \tfrac{i}{\sqrt{2}}(Y_1^1 + Y_{-1}^1) &&= \sqrt{\tfrac{3}{4\pi}} && y/r \\
p_z &= y_{10} &&= Y_2^0 &&= \sqrt{\tfrac{3}{4\pi}} && z/r \\
p_x &= y_{11} &&= \tfrac{1}{\sqrt{2}}(Y_1^1 - Y_{-1}^1) &&= \sqrt{\tfrac{3}{4\pi}} && x/r \\
d_{xy} &= y_{2-2} &&= \tfrac{i}{\sqrt{2}}(Y_2^2 - Y_{-2}^2) &&= \sqrt{\tfrac{15}{4\pi}} && xy/r^2 \\
d_{yz} &= y_{2-1} &&= \tfrac{i}{\sqrt{2}}(Y_1^2 + Y_{-1}^2) &&= \sqrt{\tfrac{15}{4\pi}} && yz/r^2 \\
d_{3z^2-r^2} &= y_{20} &&= Y_2^0 &&= \sqrt{\tfrac{15}{4\pi}}\tfrac{1}{2\sqrt{3}} && (3z^2 - r^2)/r^2 \\
d_{xz} &= y_{21} &&= \tfrac{1}{\sqrt{2}}(Y_1^2 - Y_{-1}^2) &&= \sqrt{\tfrac{15}{4\pi}} && xz/r^2 \\
d_{x^2-y^2} &= y_{22} &&= \tfrac{1}{\sqrt{2}}(Y_2^2 + Y_{-2}^2) &&= \sqrt{\tfrac{15}{4\pi}}\tfrac{1}{2} && (x^2 - y^2)/r^2
\end{aligned}
$$

atomic functions

spherical potential

eigenvalues: n

eigenvectors: n,l,m

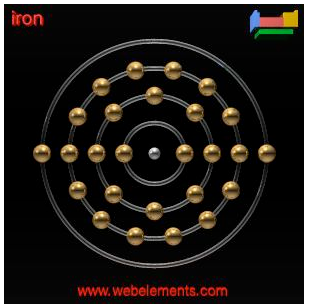


l=0

l=1

l=2

many-electrons



$$H_e^{\mathrm{NR}} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i>j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

one shell, 2nd quantization

$$H_e^{\mathrm{NR}} = \varepsilon_{nl} \sum_{m\sigma} c^\dagger_{m\sigma} c_{m\sigma} + \frac{1}{2} \sum_{\sigma\sigma'} \sum_{m\tilde{m}m'\tilde{m}'} U^l_{mm'\tilde{m}\tilde{m}'} c^\dagger_{m\sigma} c^\dagger_{m'\sigma'} c_{\tilde{m}'\sigma'} c_{\tilde{m}\sigma}$$

kinetic+central potential

Coulomb interaction

$$U^{iji'j'}_{mm'\tilde{m}\tilde{m}'} = \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \, \frac{\overline{\psi_{im\sigma}}(\boldsymbol{r}_1)\overline{\psi_{jm'\sigma'}}(\boldsymbol{r}_2)\psi_{j'\tilde{m}'\sigma'}(\boldsymbol{r}_2)\psi_{i'\tilde{m}\sigma}(\boldsymbol{r}_1)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

many electron atoms

does the atom/ion carry a magnetic moment?

total spin **S** and total angular momentum **L**

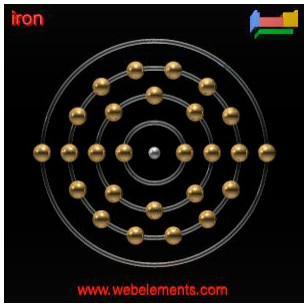
filled shells

S=L=0

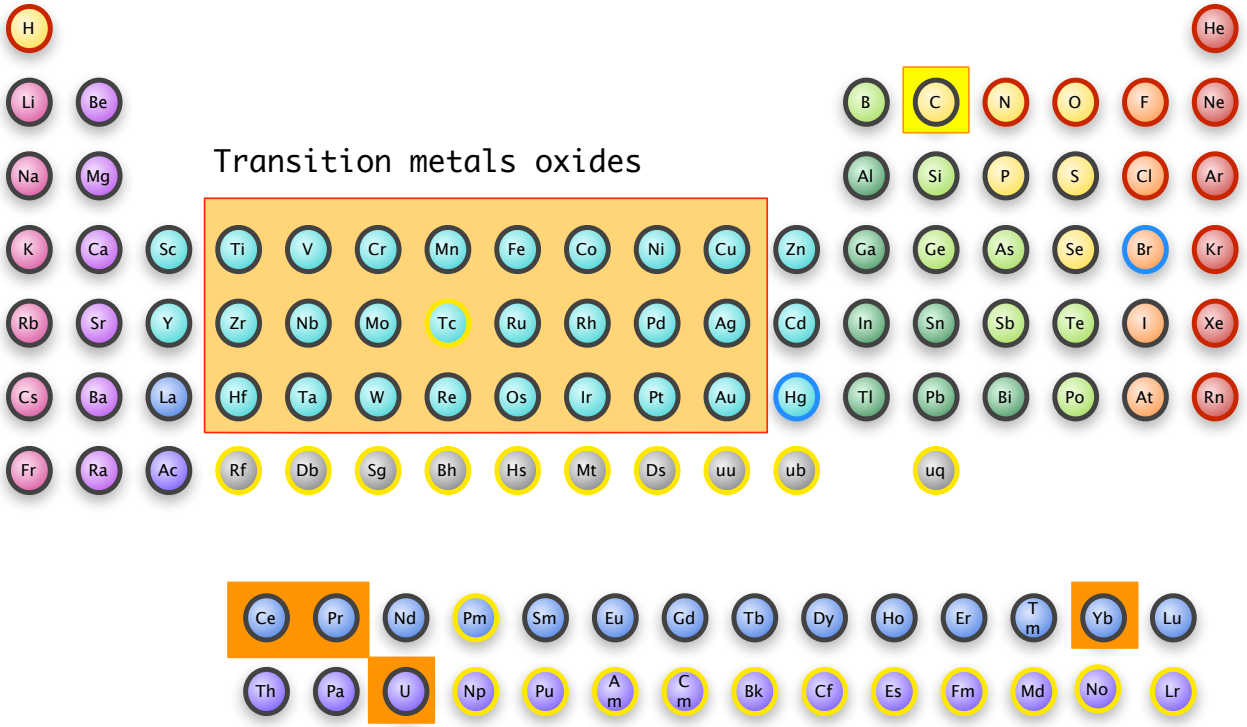
partially filled shell: **magnetic ions**

1. Hund's rule — max S

2. Hund's rule — max L



strongly correlated systems



here in particular transition-metal oxides
and f electron systems

origin: Coulomb repulsion

direct term: the same for all N electron states

$$U_{\mathrm{avg}} = \frac{1}{(2l+1)^2} \sum_{mm'} U^l_{mm'mm'}$$

exchange term: 1. Hund's rule

$$U_{\mathrm{avg}} - J_{\mathrm{avg}} = \frac{1}{2l(2l+1)} \sum_{mm'} \left(U^l_{mm'mm'} - U^l_{mm'm'm} \right)$$

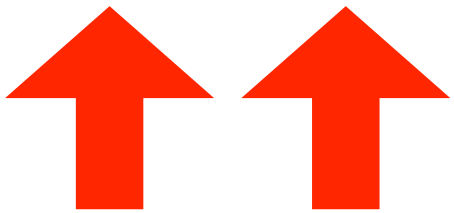
Coulomb exchange

C atom, p shell

$$
\begin{aligned}
J^p_{m,m'} &= U^p_{mm'm'm} \\
&= \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \, \frac{\overline{\psi_{im\sigma}}(\boldsymbol{r}_1)\overline{\psi_{im'\sigma}}(\boldsymbol{r}_2)\psi_{im\sigma}(\boldsymbol{r}_2)\psi_{im'\sigma}(\boldsymbol{r}_1)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \\
&= \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \, \frac{\phi_{imm'\sigma}(\boldsymbol{r}_1)\overline{\phi_{imm'\sigma}}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \frac{1}{V}\sum_{\boldsymbol{k}} \frac{4\pi}{k^2} \left|\phi_{imm'\sigma}(\boldsymbol{k})\right|^2 ,
\end{aligned}
$$

positive, hence ferromagnetic

$$
-\frac{1}{2}\sum_{\sigma}\sum_{m\neq m'} J^p_{m,m'} c^\dagger_{m\sigma} c_{m\sigma} c^\dagger_{m'\sigma} c_{m'\sigma} = -\frac{1}{2}\sum_{m\neq m'} 2J^p_{m,m'} \left[S^m_z S^{m'}_z + \frac{1}{4} n_m n'_m \right]
$$



a C atom

[He] $2s^2 2p^2$

incomplete p shell: l=1
total spin and angular momentum

S $1/2 \otimes 1/2 = 0 \oplus 1$

L $1 \otimes 1 = 0 \oplus 1 \oplus 2$

S P D

S=0 ——— S

S=0 ——— D

2. Hund's rule

1. Hund's rule

^3P S=1 ——— P

spin-orbit interaction

if weak, LS coupling approximation

$$H_e^{\mathrm{SO}} \sim \lambda \, \boldsymbol{L} \cdot \boldsymbol{S} = \frac{1}{2} \lambda \, \left(\boldsymbol{J}^2 - \boldsymbol{S}^2 - \boldsymbol{L}^2 \right),$$

$$\lambda \sim \left[2\Theta(1-2n) - 1 \right] \, g\mu_B^2 \, \frac{1}{2S} \left\langle \frac{1}{r} \frac{d}{dr} v_{\mathrm{R}}(r) \right\rangle$$

3. Hund's rule

- total angular momentum $J = \begin{cases} |L-S| & \text{for filling } n < 1/2 \\ S & \text{for filling } n = 1/2 \\ L+S & \text{for filling } n > 1/2 \end{cases}$

^{3}P S=1 ——— P ^{3}P$_0$ $^{2S+1}$L$_J$

energy scales

local magnetic moment depends on Coulomb & spin orbit
but also on energy scale...

10 eV	U, v	central potential, direct Coulomb
1 eV	J	Coulomb exchange
0.1 eV	dJ	Coulomb anisotropy
10 meV	λ	spin-orbit

ions in solids

ions in solids

$$H_e^{\mathrm{NR}} = -\sum_{ii'\sigma}\sum_{mm'} t_{m,m'}^{i,i'} c_{im\sigma}^{\dagger} c_{i'm'\sigma} + \frac{1}{2}\sum_{ii'jj'}\sum_{\sigma\sigma'}\sum_{mm'}\sum_{\tilde{m}\tilde{m}'} U_{mm'\tilde{m}\tilde{m}'}^{iji'j'} c_{im\sigma}^{\dagger} c_{jm'\sigma'}^{\dagger} c_{j'\tilde{m}'\sigma'} c_{i'\tilde{m}\sigma}$$

one-electron basis: Wannier functions

crystal field & hopping integrals

$$t_{m,m'}^{i,i'} = -\int d\boldsymbol{r}\, \overline{\psi_{im\sigma}}(\boldsymbol{r}) \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{R}}(\boldsymbol{r})\right] \psi_{i'm'\sigma}(\boldsymbol{r})$$

crystal field

crystal field

i=i’

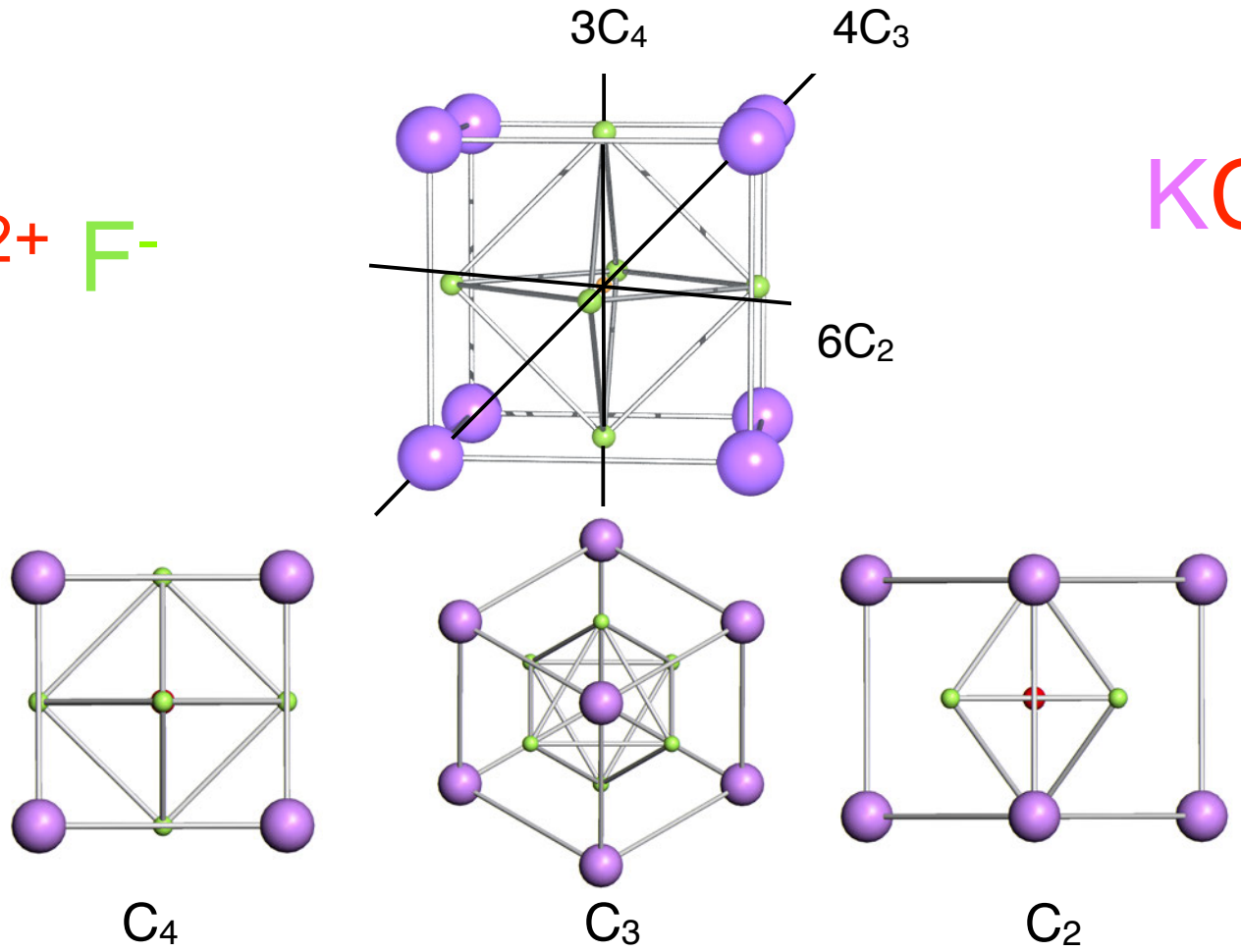
$$\varepsilon^{i,i}_{m,m'} = t^{i,i}_{m,m'} = -\int d\boldsymbol{r}\, \overline{\psi_{im\sigma}}(\boldsymbol{r}) \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{R}}(\boldsymbol{r})\right] \psi_{im'\sigma}(\boldsymbol{r})$$

modifies on-site energies
and thus local magnetic moment

perovskite structure ABC_3

K^+ Cu^{2+} F^-

$KCuF_3$



it is the symmetry group of the cube

crystal-field theory

how do *d* levels split at the Cu site?

point charge model

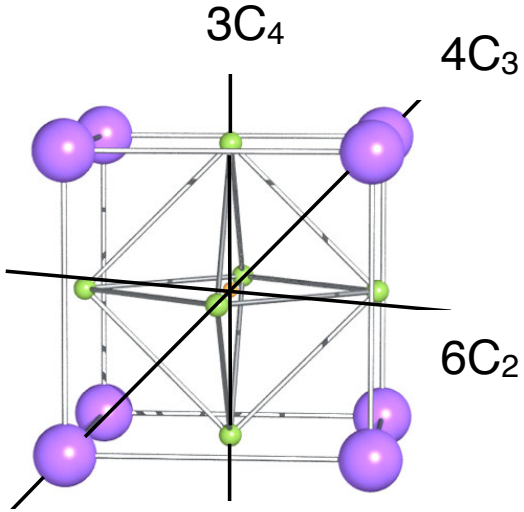
$$v_{\mathrm{R}}(\boldsymbol{r}) = \sum_{\alpha} \frac{q_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|} = v_0(r) + \sum_{\alpha \neq 0} \frac{q_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|} = v_0(r) + v_c(\boldsymbol{r})$$

crystal field

$KCuF_3$

K^+ Cu^{2+} F^-

q_K q_{Cu} q_F



(in real materials, also covalency effects!)

cubic perovskite

point charge model: F_6 octahedron

$$v_{\mathrm{oct}}(\boldsymbol{r}) = \frac{35}{4}\frac{q_C}{a^5}\left(x^4+y^4+z^4-\frac{3}{5}r^4\right) = D\left(x^4+y^4+z^4-\frac{3}{5}r^4\right).$$

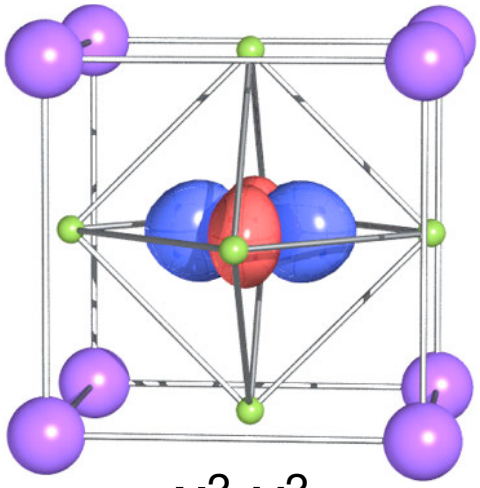
$$H_{\mathrm{CF}} = \begin{array}{c} \begin{array}{ccccc} \text{m=-2} & \text{m=-1} & \text{m=0} & \text{m=1} & \text{m=2} \end{array} \\ \begin{pmatrix} Dq & 0 & 0 & 0 & 5Dq \\ 0 & -4Dq & 0 & 0 & 0 \\ 0 & 0 & 6Dq & 0 & 0 \\ 0 & 0 & 0 & -4Dq & 0 \\ 5Dq & 0 & 0 & 0 & Dq \end{pmatrix} \end{array}.$$

$$\psi_{nlm}(\rho,\theta,\phi) = R_{nl}(\rho)Y_l^m(\theta,\phi)$$

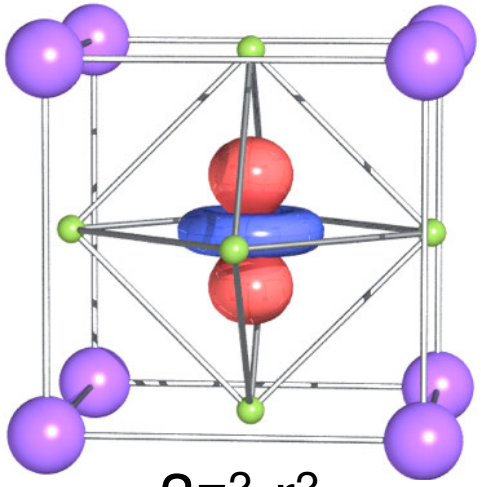
atomic functions

$$Dq = -q_F\langle r^4\rangle/6a^5$$

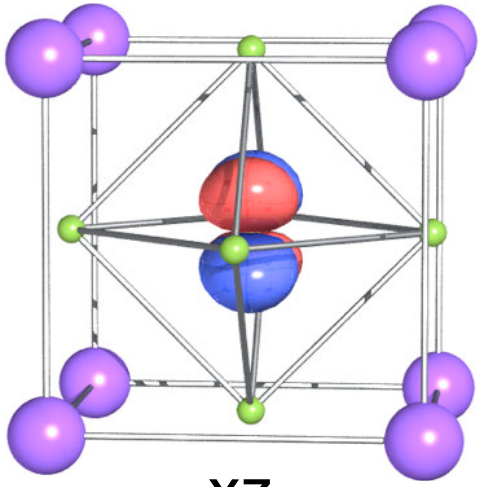
atomic *d* orbitals



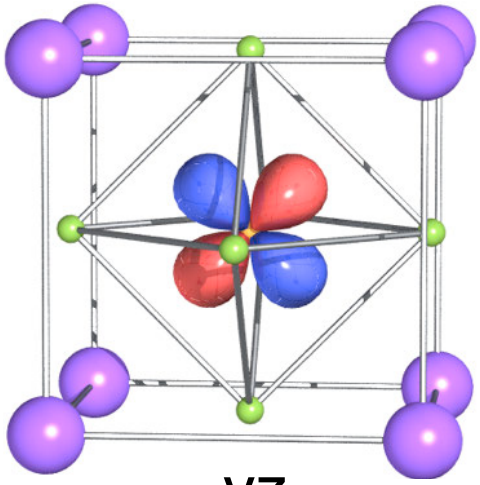
x^2-y^2



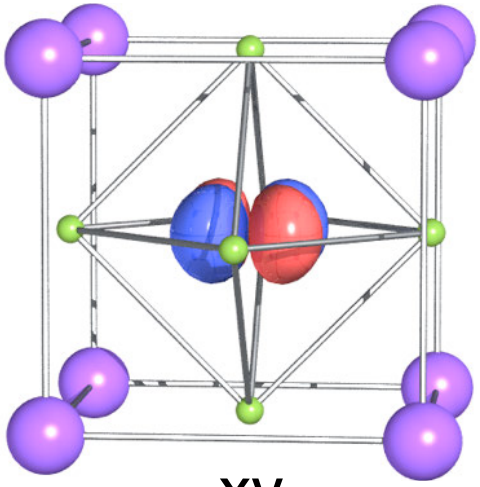
$3z^2-r^2$



xz

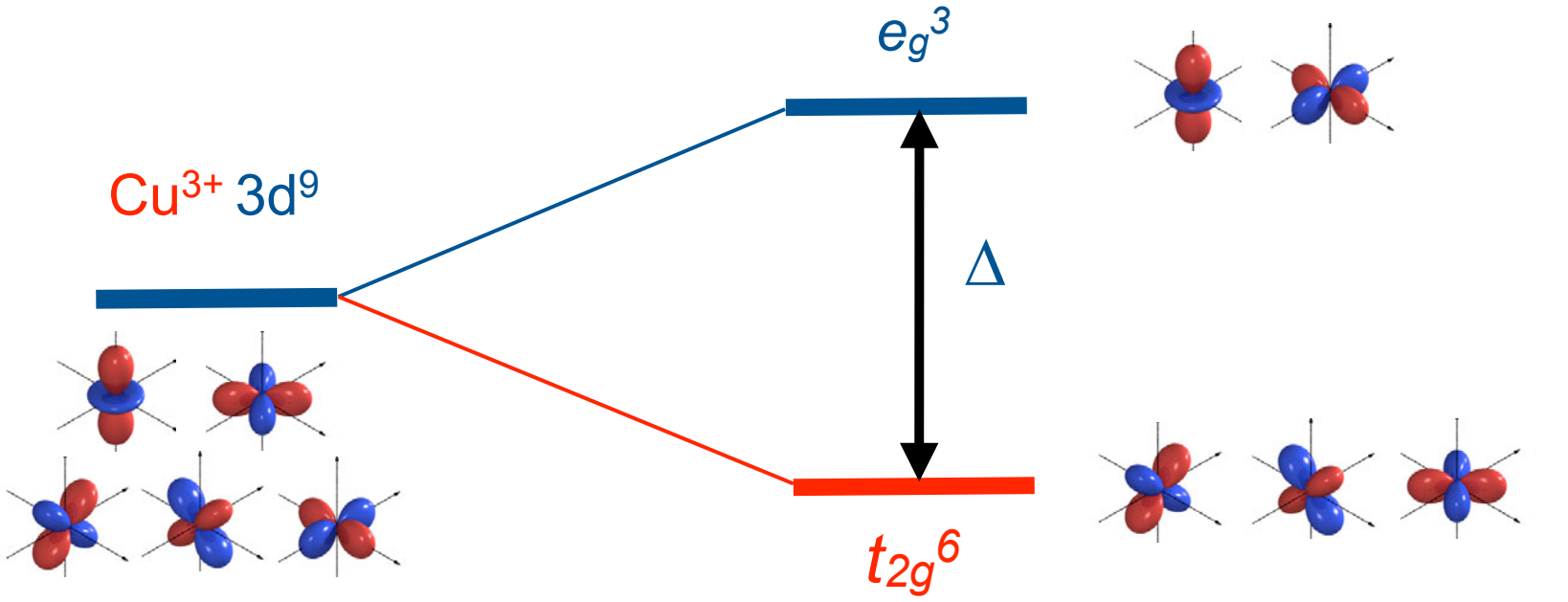


yz



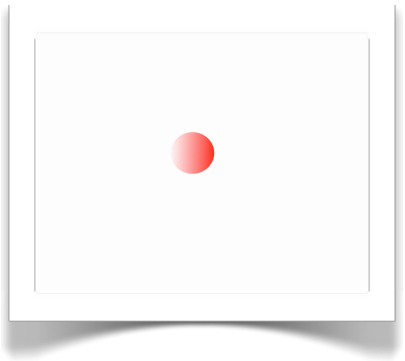
xy

cubic crystal-field

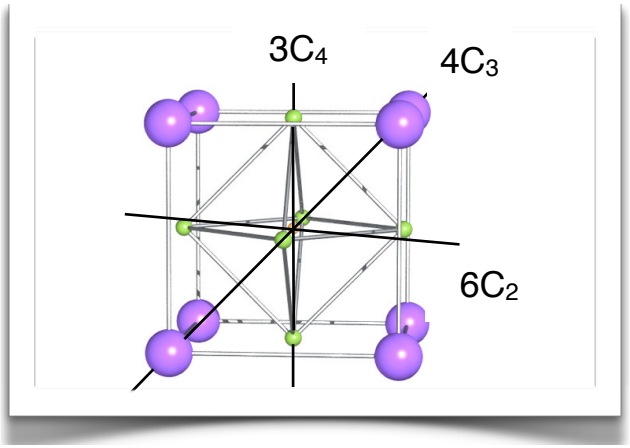


"Wannier functions"

spherical



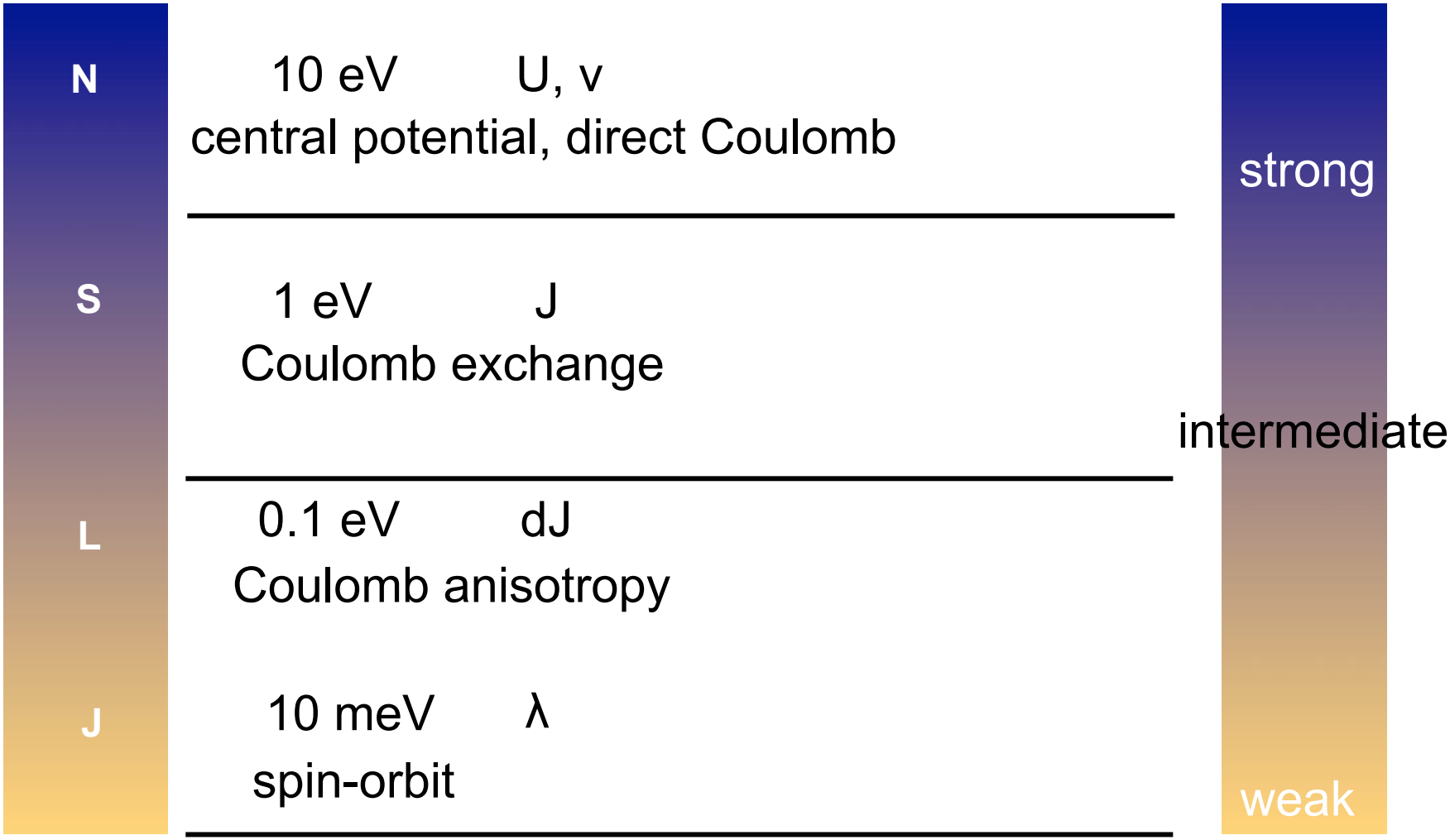
cubic



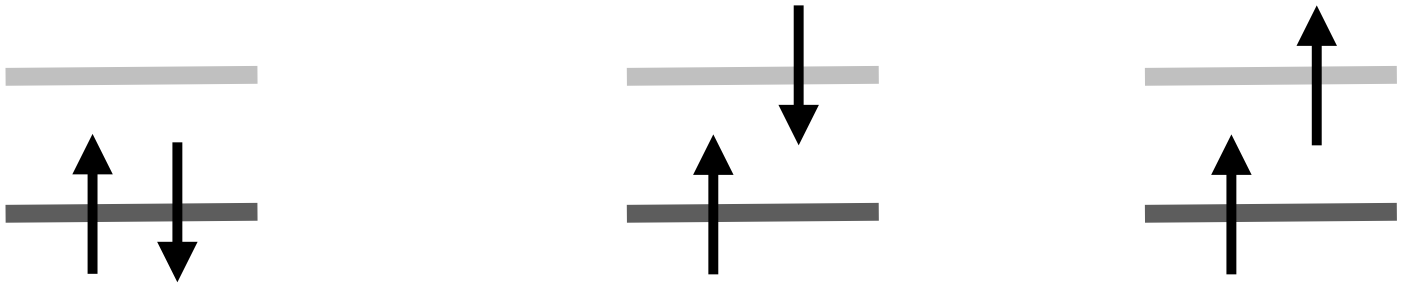
energy scales

Hilbert space

crystal field



density-density Coulomb

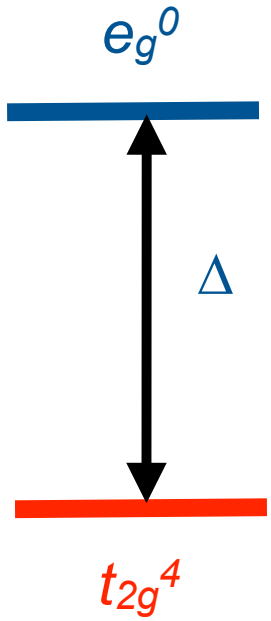


U

U-2J+Δ

U-3J+Δ

strong field

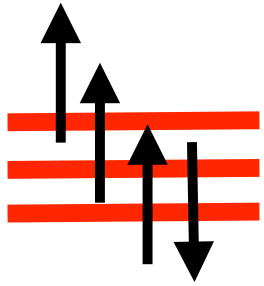


t_{2g}^4

4d, ruthenates

no 1. Hund's rule!

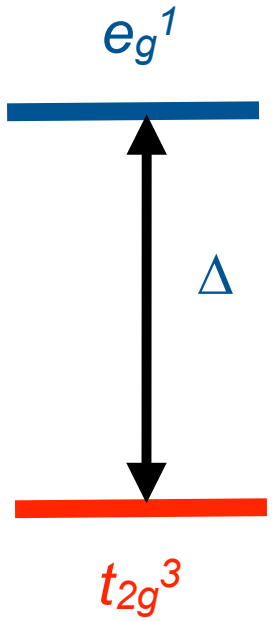
Δ > 3J



S=1

6U-15J

intermediate

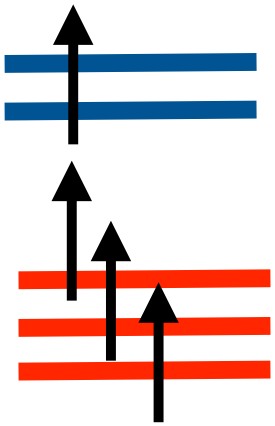


$t_{2g}^3\ e_g^1$

3d, manganites

1. Hund's rule satisfied

however, no 2. Hund's rule!



S=2

6U-18J+Δ

quenching of angular momentum

perfect quenching

$$\langle \boldsymbol{L} \rangle = 0$$

partial quenching: L smaller than expected from 2. Hund's rule

magnetic ions

if no hopping integrals....

magnetic ions=isolated localized moments

insulating behavior

Coulomb interaction

$$H_e^{\mathrm{NR}} = -\sum_{ii'\sigma}\sum_{mm'} t_{m,m'}^{i,i'} c_{im\sigma}^{\dagger} c_{i'm'\sigma} + \frac{1}{2}\sum_{ii'jj'}\sum_{\sigma\sigma'}\sum_{mm'}\sum_{\tilde{m}\tilde{m}'} U_{mm'\tilde{m}\tilde{m}'}^{iji'j'} c_{im\sigma}^{\dagger} c_{jm'\sigma'}^{\dagger} c_{j'\tilde{m}'\sigma'} c_{i'\tilde{m}\sigma}$$

inter-site Coulomb exchange

$$J^{i,i'} = U_{mmmm}^{ii'i'i} = \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \, \frac{\overline{\psi_{im\sigma}}(\boldsymbol{r}_1)\overline{\psi_{i'm\sigma}}(\boldsymbol{r}_2)\psi_{im\sigma}(\boldsymbol{r}_2)\psi_{i'm\sigma}(\boldsymbol{r}_1)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|},$$

ferromagnetic!

ions in solid: conclusion

itinerant vs local moments

local moment regime

t << U

local moments survive in crystal

integer filling: Mott insulator

local moment determined by Coulomb & crystal field

Heisenberg-like model

ferromagnetic Coulomb exchange

AFM kinetic exchange

itinerant regime

t >> U

local moments *melt*

integer filling: metal

hoppings, bands

Stoner instabilities

hopping integrals

hopping integrals

$$H_e^{\mathrm{NR}} = -\sum_{ii'\sigma}\sum_{mm'} t_{m,m'}^{i,i'} c_{im\sigma}^{\dagger} c_{i'm'\sigma} + \frac{1}{2}\sum_{ii'jj'}\sum_{\sigma\sigma'}\sum_{mm'}\sum_{\tilde{m}\tilde{m}'} U_{mm'\tilde{m}\tilde{m}'}^{iji'j'} c_{im\sigma}^{\dagger} c_{jm'\sigma'}^{\dagger} c_{j'\tilde{m}'\sigma'} c_{i'\tilde{m}\sigma}$$

one-electron basis: Wannier functions

crystal field & hopping integrals

$$t_{m,m'}^{i,i'} = -\int d\boldsymbol{r}\, \overline{\psi_{im\sigma}}(\boldsymbol{r}) \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{R}}(\boldsymbol{r})\right] \psi_{i'm'\sigma}(\boldsymbol{r})$$

hopping integrals

i≠i′

$$t_{m,m'}^{i,i'} = -\int d\boldsymbol{r}\, \overline{\psi_{im\sigma}}(\boldsymbol{r}) \left[-\frac{1}{2}\nabla^2 + v_{\mathrm{R}}(\boldsymbol{r})\right] \psi_{i'm'\sigma}(\boldsymbol{r})$$

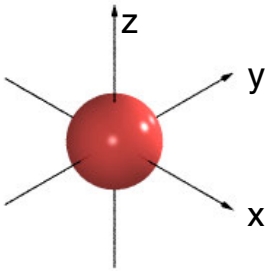
generates band structure

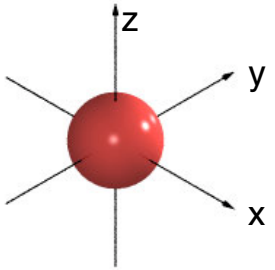
delocalizes electrons, **suppresses local moment**

hydrogen molecular ion

$$\hat{h}_e(\boldsymbol{r}) = -\frac{1}{2}\nabla^2 - \frac{1}{|\boldsymbol{r}-\boldsymbol{R}_1|} - \frac{1}{|\boldsymbol{r}-\boldsymbol{R}_2|} = -\frac{1}{2}\nabla^2 + v(\boldsymbol{r}-\boldsymbol{R}_1) + v(\boldsymbol{r}-\boldsymbol{R}_2) = -\frac{1}{2}\nabla^2 + v_R(\boldsymbol{r}).$$

basis: atomic s functions



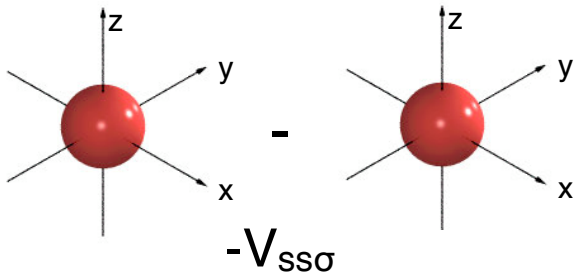


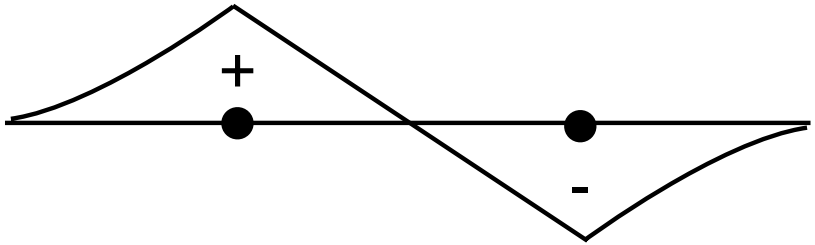
hydrogen molecular ion

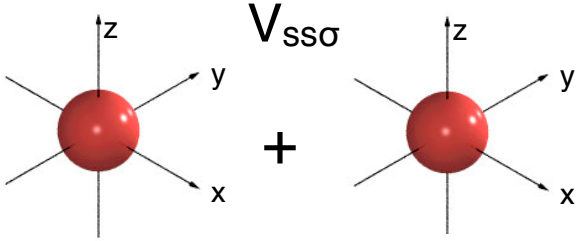
$$H = \varepsilon_{1s}^{0}\, O + \begin{pmatrix} \Delta\varepsilon_{1s} & V_{ss\sigma} \\ V_{ss\sigma} & \Delta\varepsilon_{1s} \end{pmatrix} \qquad O = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}$$

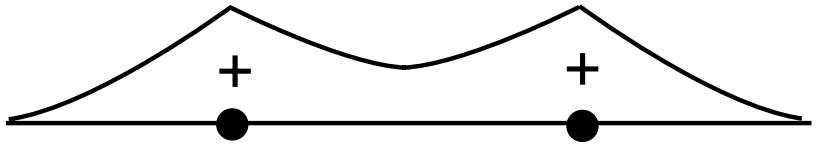
$$\begin{aligned}
\Delta\varepsilon_{1s} &= \int d\boldsymbol{r}\, \psi_{1s}(\boldsymbol{r}-\boldsymbol{R}_\alpha)\left[v_R(\boldsymbol{r}) - v(\boldsymbol{r}-\boldsymbol{R}_\alpha)\right]\psi_{1s}(\boldsymbol{r}-\boldsymbol{R}_\alpha), \quad \alpha = 1,2 \\
V_{ss\sigma} &= \int d\boldsymbol{r}\, \psi_{1s}(\boldsymbol{r}-\boldsymbol{R}_\alpha) v(\boldsymbol{r}-\boldsymbol{R}_\alpha)\psi_{1s}(\boldsymbol{r}-\boldsymbol{R}_{\alpha'}), \quad \alpha \neq \alpha' \\
S &= \int d\boldsymbol{r}\, \psi_{1s}(\boldsymbol{r}-\boldsymbol{R}_\alpha)\psi_{1s}(\boldsymbol{r}-\boldsymbol{R}_{\alpha'}), \quad \alpha \neq \alpha'.
\end{aligned}$$

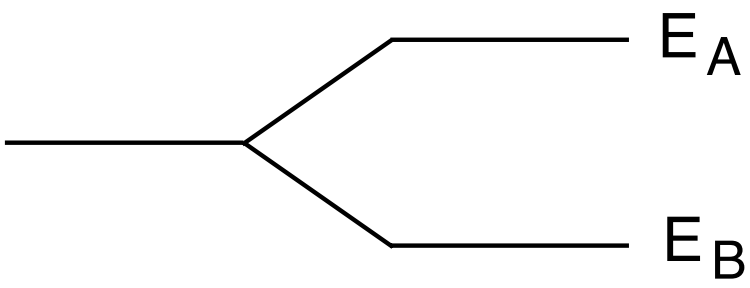
hydrogen molecular ion











$$E_A = \varepsilon_{1s}^0 + \frac{\Delta\varepsilon_{1s} - V_{ss\sigma}}{1 - S}$$

$$E_B = \varepsilon_{1s}^0 + \frac{\Delta\varepsilon_{1s} + V_{ss\sigma}}{1 + S}.$$

crystal

$$\hat{h}_e(\boldsymbol{r}) = -\frac{1}{2}\nabla^2 - \sum_{i,\alpha} \frac{Z_{i,\alpha}}{|\boldsymbol{r} - \boldsymbol{T}_i - \boldsymbol{R}_\alpha|} = -\frac{1}{2}\nabla^2 + \sum_{i,\alpha} v(\boldsymbol{r} - \boldsymbol{T}_i - \boldsymbol{R}_\alpha) = -\frac{1}{2}\nabla^2 + v_R(\boldsymbol{r}),$$

Bloch functions

$$\psi^\alpha_{lm}(\boldsymbol{k}, \boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_i e^{i\boldsymbol{T}_i \cdot \boldsymbol{k}}\, \psi_{lm}(\boldsymbol{r} - \boldsymbol{T}_i - \boldsymbol{R}_\alpha).$$

Wannier functions

$$\begin{aligned} H^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) &= \langle \psi^\alpha_{lm}(\boldsymbol{k}) | \hat{h}_e | \psi^{\alpha'}_{l'm'}(\boldsymbol{k}) \rangle, \\ O^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) &= \langle \psi^\alpha_{lm}(\boldsymbol{k}) | \psi^{\alpha'}_{l'm'}(\boldsymbol{k}) \rangle. \end{aligned}$$

Hamiltonian

Overlap

crystal

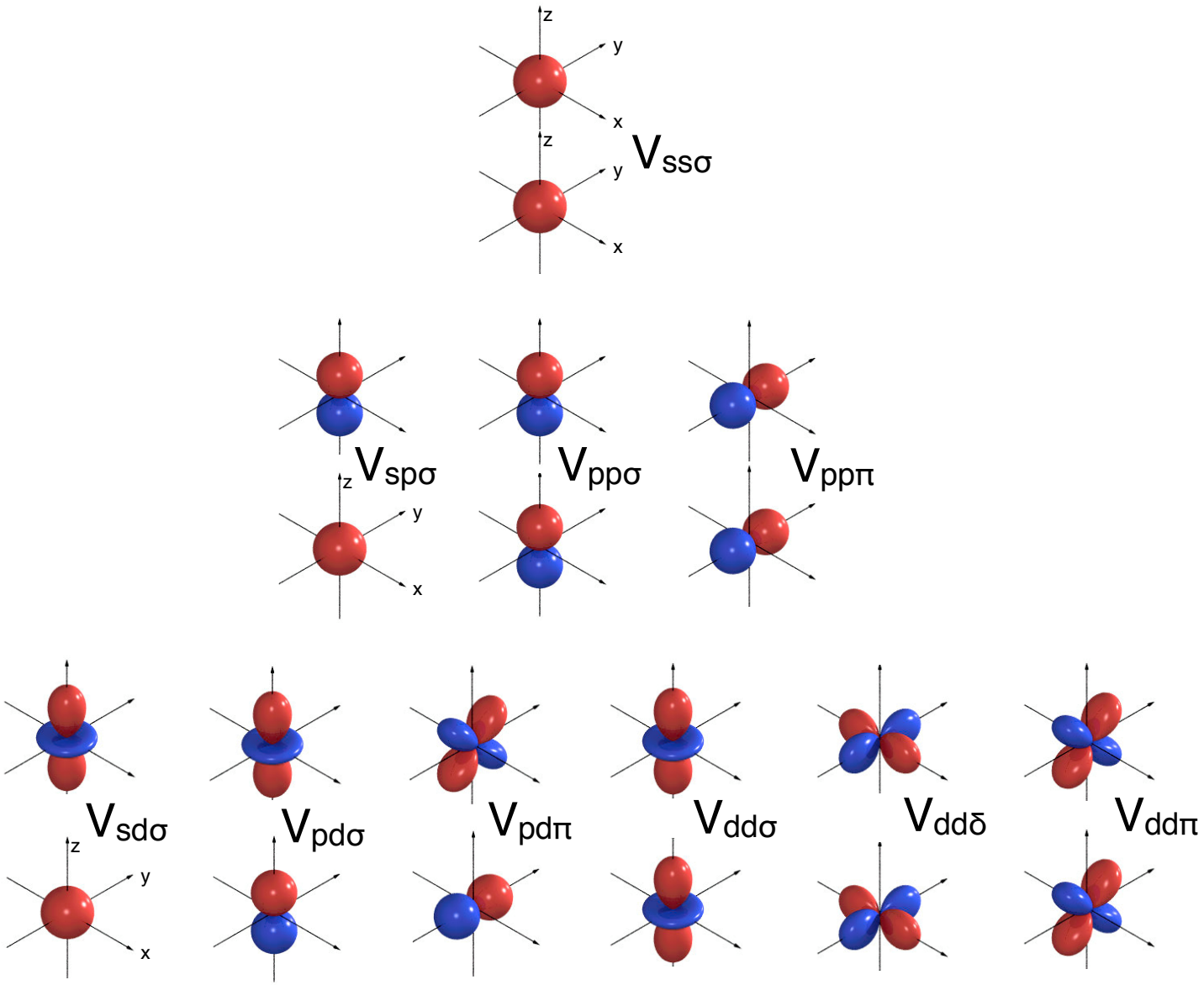
$$H^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) = \varepsilon^{0}_{l'\alpha'} O^{\alpha,\alpha'}_{lm,l'm'}(\boldsymbol{k}) + \Delta\varepsilon^{\alpha}_{lm,l'm'}\delta_{\alpha,\alpha'} - \frac{1}{N}\sum_{i\alpha\neq i'\alpha'} e^{i(\boldsymbol{T}_{i'}-\boldsymbol{T}_i)\cdot\boldsymbol{k}}\, t^{i\alpha,i'\alpha'}_{lm,l'm'}.$$

$$\Delta\varepsilon^{\alpha}_{lm,l'm'} = \int d\boldsymbol{r}\, \overline{\psi}_{lm}(\boldsymbol{r}-\boldsymbol{R}_\alpha)[v_R(\boldsymbol{r}) - v(\boldsymbol{r}-\boldsymbol{R}_\alpha)]\psi_{l'm'}(\boldsymbol{r}-\boldsymbol{R}_\alpha),$$

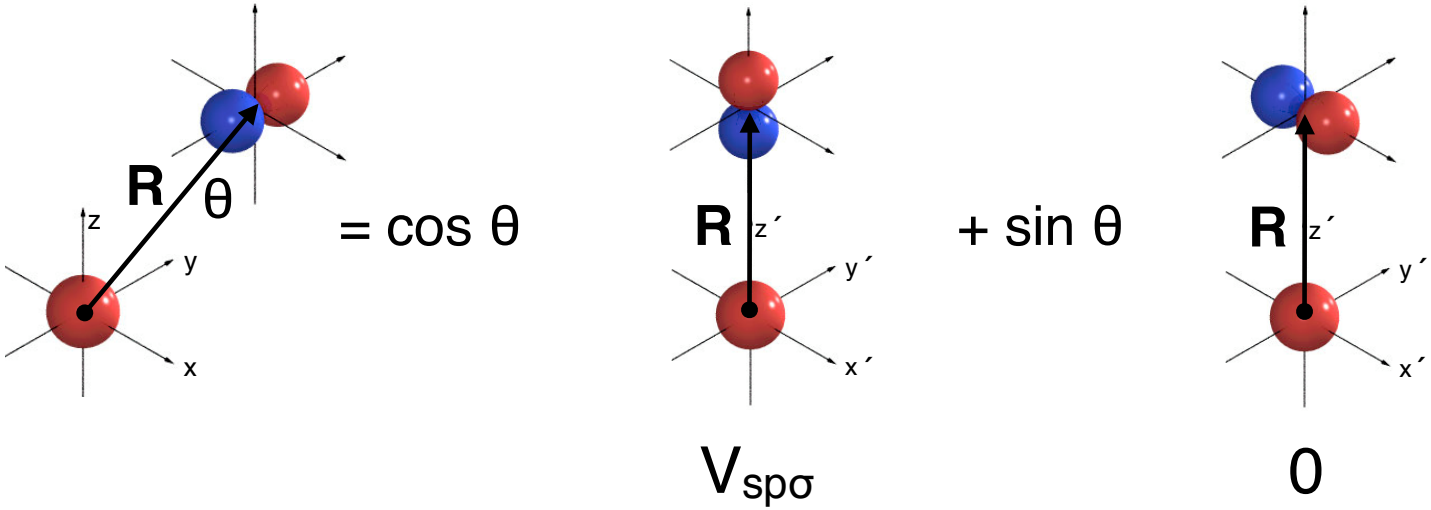
$$t^{i\alpha,i'\alpha'}_{lm,l'm'} = -\int d\boldsymbol{r}\, \overline{\psi}_{lm}(\boldsymbol{r}-\boldsymbol{R}_\alpha-\boldsymbol{T}_i)[v_R(\boldsymbol{r}) - v(\boldsymbol{r}-\boldsymbol{R}_{\alpha'}-\boldsymbol{T}_{i'})]\psi_{l'm'}(\boldsymbol{r}-\boldsymbol{R}_{\alpha'}-\boldsymbol{T}_{i'}).$$

$$V^{i\alpha,i'\alpha'}_{lm,l'm'} = \int d\boldsymbol{r}\, \overline{\psi}_{lm}(\boldsymbol{r}-\boldsymbol{R}_\alpha-\boldsymbol{T}_i) v(\boldsymbol{r}-\boldsymbol{R}_\alpha-\boldsymbol{T}_i)\psi_{l'm'}(\boldsymbol{r}-\boldsymbol{R}_{\alpha'}-\boldsymbol{T}_{i'})$$

two-center integrals

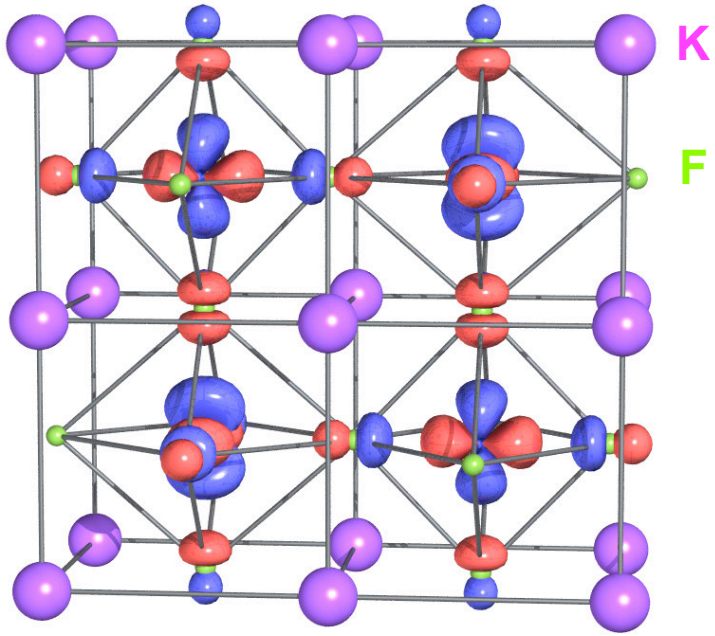


two-center integrals



an example: $KCuF_3$

atomic orbitals replaced by localized LDA Wannier functions



$K^+ Cu^{2+} F^-$

$K\ 4s^0\ Cu\ 3d^9\ F\ 2p^6$

an example: $KCuF_3$

$$H_e^{\mathrm{NR}} = -\sum_{ii'\sigma}\sum_{mm'} t_{m,m'}^{i,i'} c_{im\sigma}^{\dagger} c_{i'm'\sigma} + \frac{1}{2}\sum_{ii'jj'}\sum_{\sigma\sigma'}\sum_{mm'}\sum_{\tilde{m}\tilde{m}'} U_{mm'\tilde{m}\tilde{m}'}^{iji'j'} c_{im\sigma}^{\dagger} c_{jm'\sigma'}^{\dagger} c_{j'\tilde{m}'\sigma'} c_{i'\tilde{m}\sigma}$$

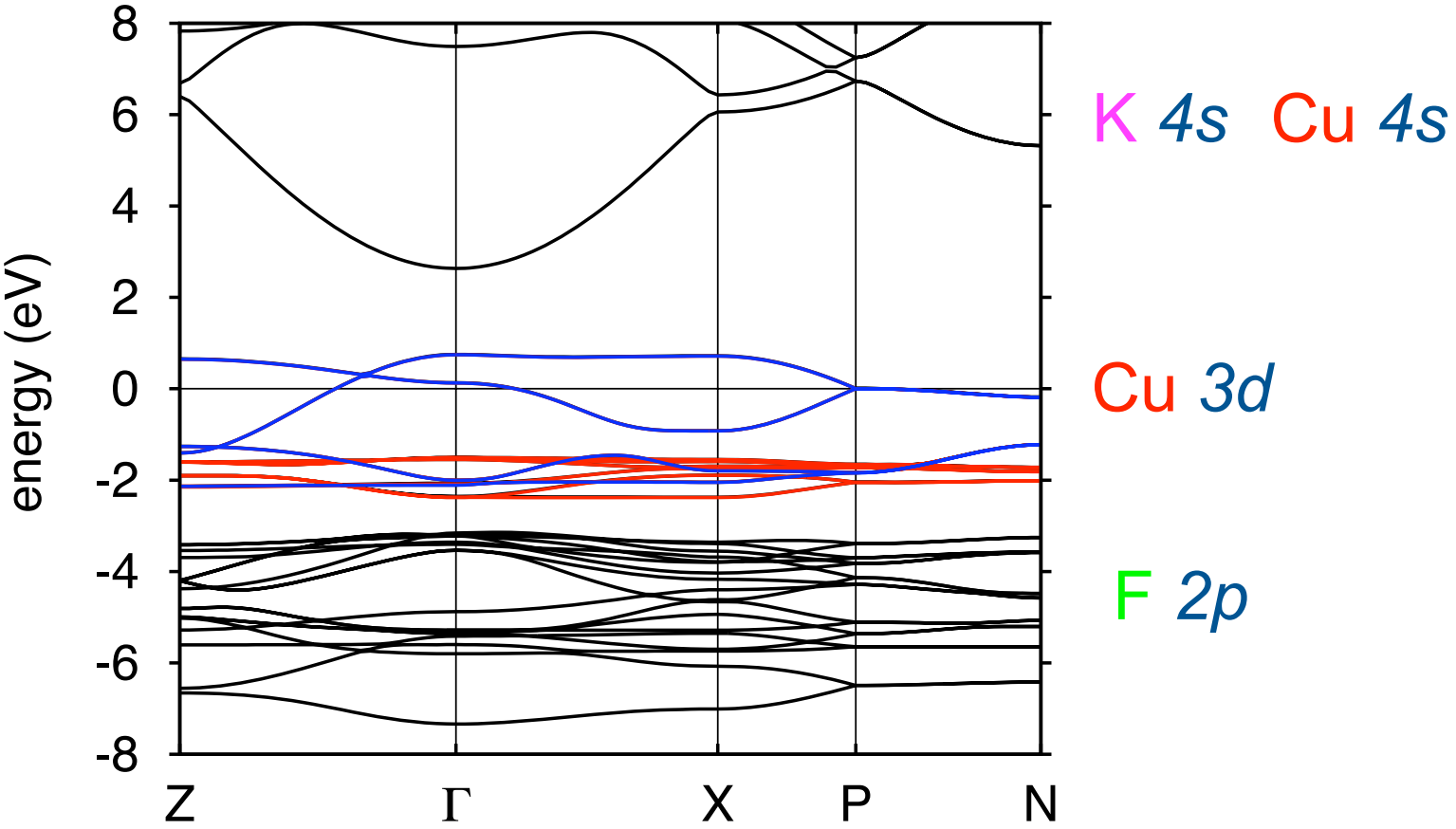
one-electron basis: localized LDA Wannier functions

only Coulomb effects contained in LDA

LDA band structure

partially filled d-like bands, metallic

non-magnetic & no local moments



(in reality: Mott insulator, local moment, paramagnetic for T>40 K)

the Hubbard model

the Hubbard model

$$H = \varepsilon_d \sum_i \sum_\sigma c^\dagger_{i\sigma} c_{i\sigma} - t \sum_{\langle ii' \rangle} \sum_\sigma c^\dagger_{i\sigma} c_{i'\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} = H_d + H_T + H_U$$

$$\begin{cases} \varepsilon_d &= -t^{i,i}_{1,1} \\ t &= t^{\langle i,i' \rangle}_{1,1} \\ U &= U^{iiii}_{1111} \end{cases}$$

half filling

t=0: N_s atoms, insulator

U=0: half-filled band, metal

the *t=0* limit

atomic limit (*t=0*) & half filling

$\lvert N,S,S_z\rangle$			N	S	$E(N)$
$\lvert 0,0,0\rangle$	$=$	$\lvert 0\rangle$	0	0	0
$\lvert 1,\frac{1}{2},\uparrow\rangle$	$=$	$c^\dagger_{i\uparrow}\lvert 0\rangle$	1	$1/2$	ε_d
$\lvert 1,\frac{1}{2},\downarrow\rangle$	$=$	$c^\dagger_{i\downarrow}\lvert 0\rangle$	1	$1/2$	ε_d
$\lvert 2,0,0\rangle$	$=$	$c^\dagger_{i\uparrow}c^\dagger_{i\downarrow}\lvert 0\rangle$	2	0	$2\varepsilon_d+U$

S=1/2

$$H_d + H_U = \varepsilon_d \sum_i n_i + U \sum_i \left[-\left(S^i_z\right)^2 + \frac{n_i^2}{4} \right]$$

emergence of the spin!

half filling: highly degenerate states, 2^{Ns} degrees of freedom

insulating behavior

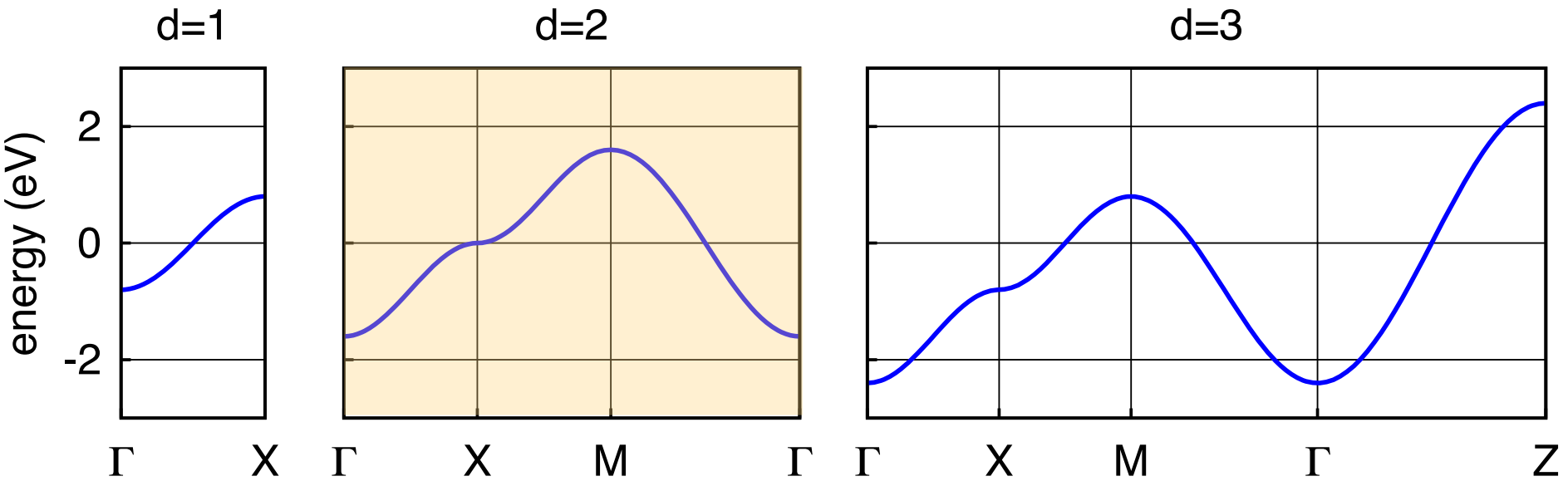
the $U=0$ limit

the *U=0* limit

$$H_d + H_T = \sum_{\boldsymbol{k}} \sum_{\sigma} [\varepsilon_d + \varepsilon_{\boldsymbol{k}}] c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}$$

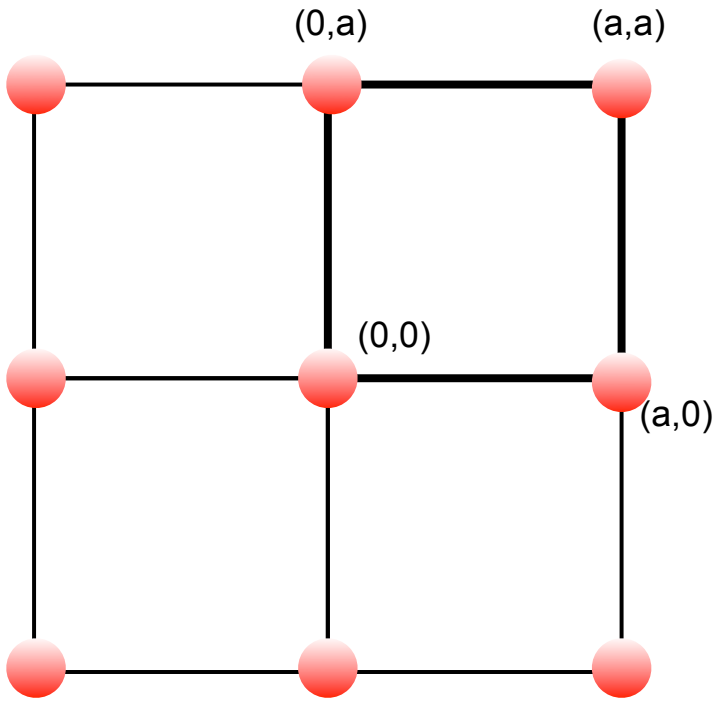
hypercubic lattice

$$\varepsilon_{\boldsymbol{k}} = -2t \sum_{\nu=1}^{d} \cos(k_{r_\nu} a)$$

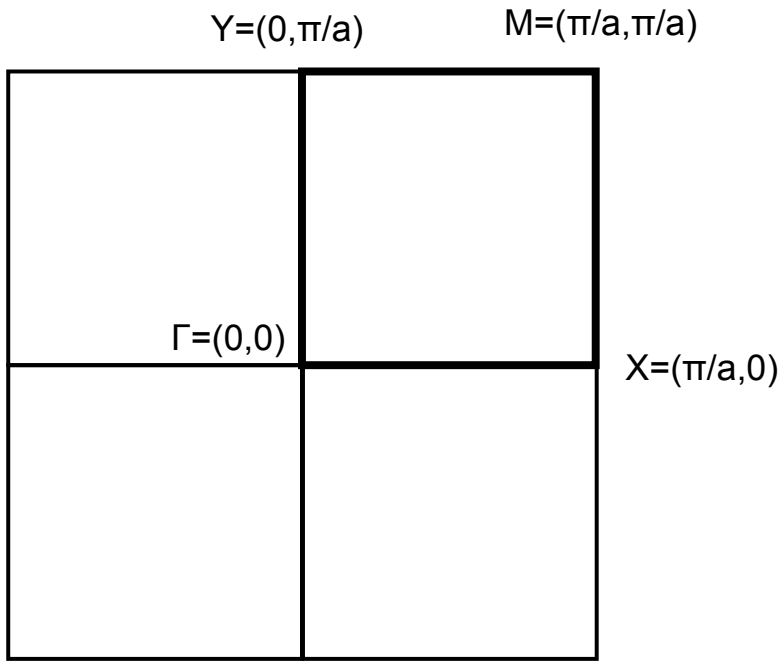


unit cell and Brillouin zone

unit cell



Brillouin zone

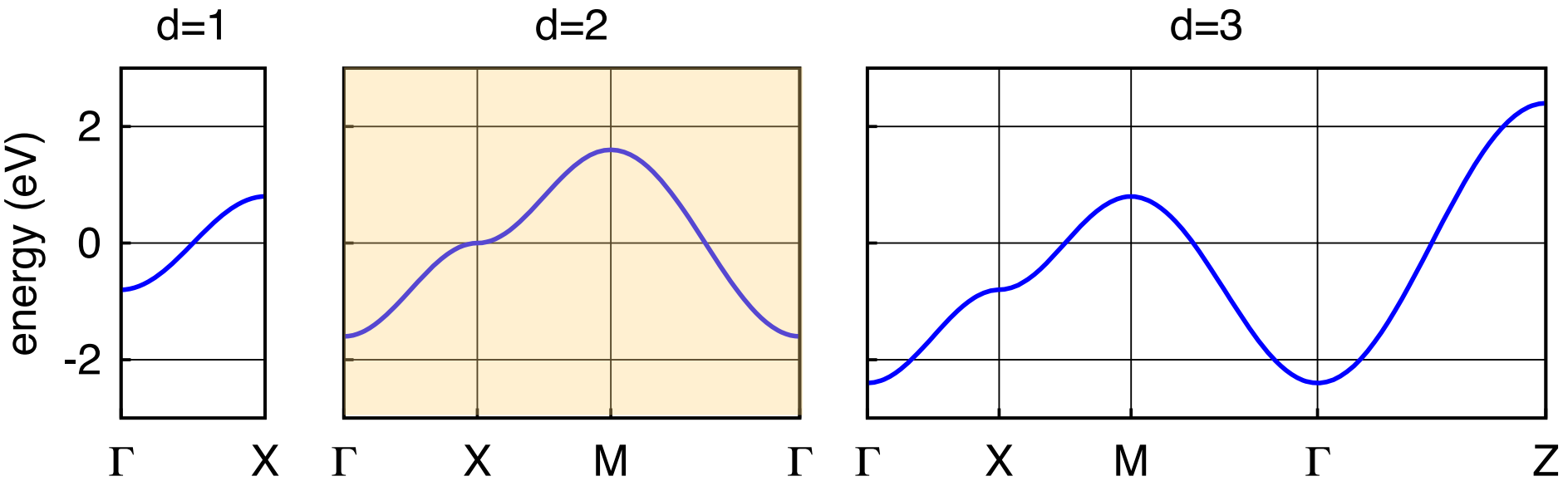


the *U=0* limit

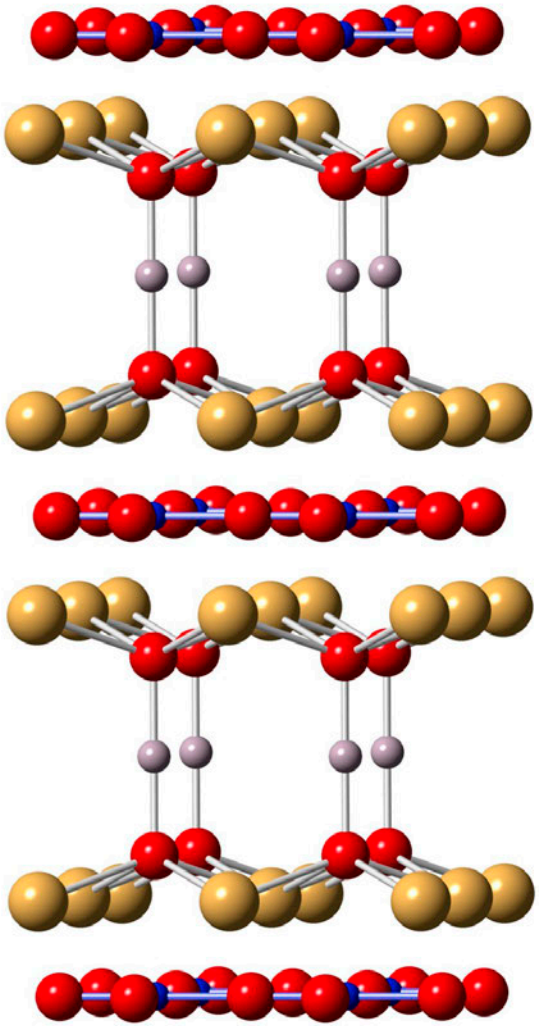
$$H_d + H_T = \sum_{\boldsymbol{k}} \sum_{\sigma} [\varepsilon_d + \varepsilon_{\boldsymbol{k}}] c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}$$

hypercubic lattice

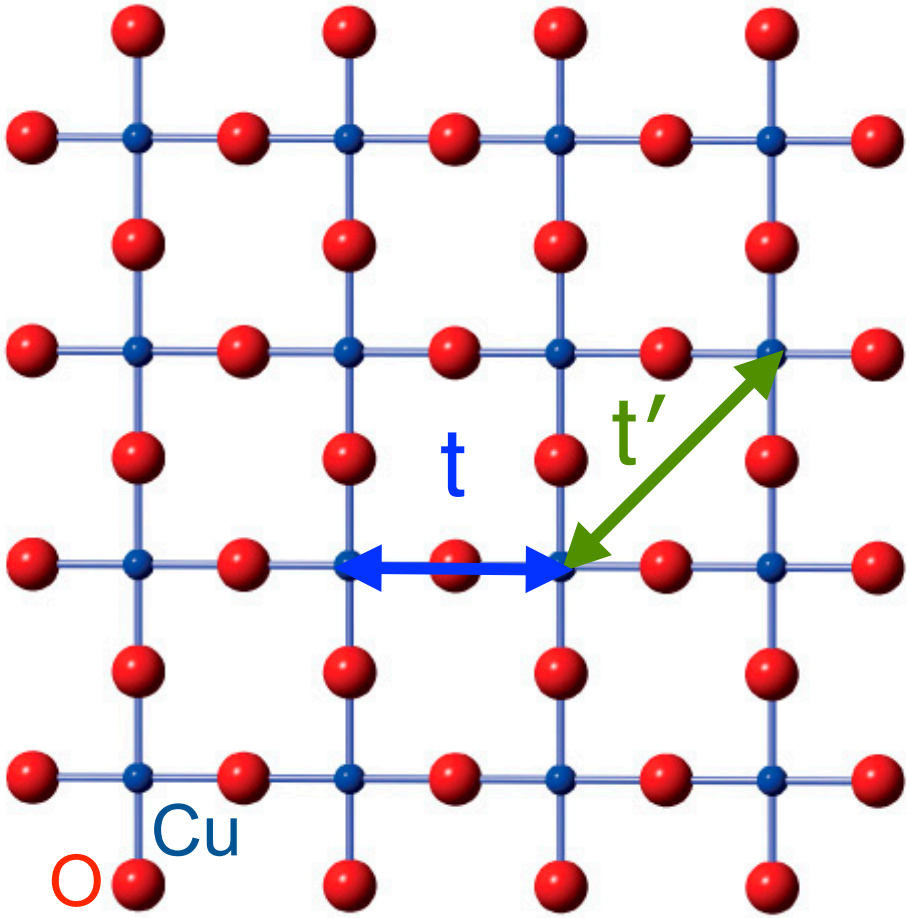
$$\varepsilon_{\boldsymbol{k}} = -2t \sum_{\nu=1}^{d} \cos(k_{r_\nu} a)$$



high-T_c superconducting cuprates



$HgBa_2CuO_4$



CuO_2 planes

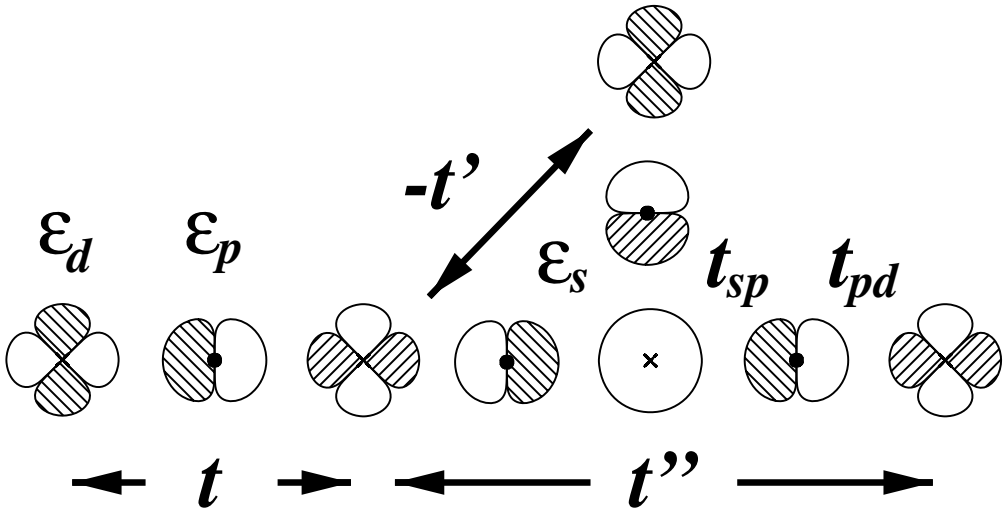
high-T_c superconducting cuprates

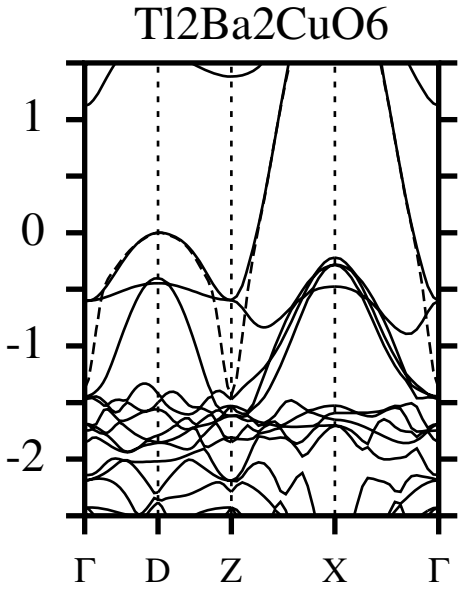
VOLUME 87, NUMBER 4 PHYSICAL REVIEW LETTERS 23 JULY 2001

Band-Structure Trend in Hole-Doped Cuprates and Correlation with $T_{c\,\max}$

E. Pavarini, I. Dasgupta,* T. Saha-Dasgupta,† O. Jepsen, and O. K. Andersen
Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany
(Received 4 December 2000; published 10 July 2001)

By calculation and analysis of the bare conduction bands in a large number of hole-doped high-temperature superconductors, we have identified the range of the intralayer hopping as the essential, material-dependent parameter. It is controlled by the energy of the axial orbital, a hybrid between Cu $4s$, apical-oxygen $2p_z$, and farther orbitals. Materials with higher $T_{c\,\max}$ have larger hopping ranges and axial orbitals more localized in the CuO_2 layers.



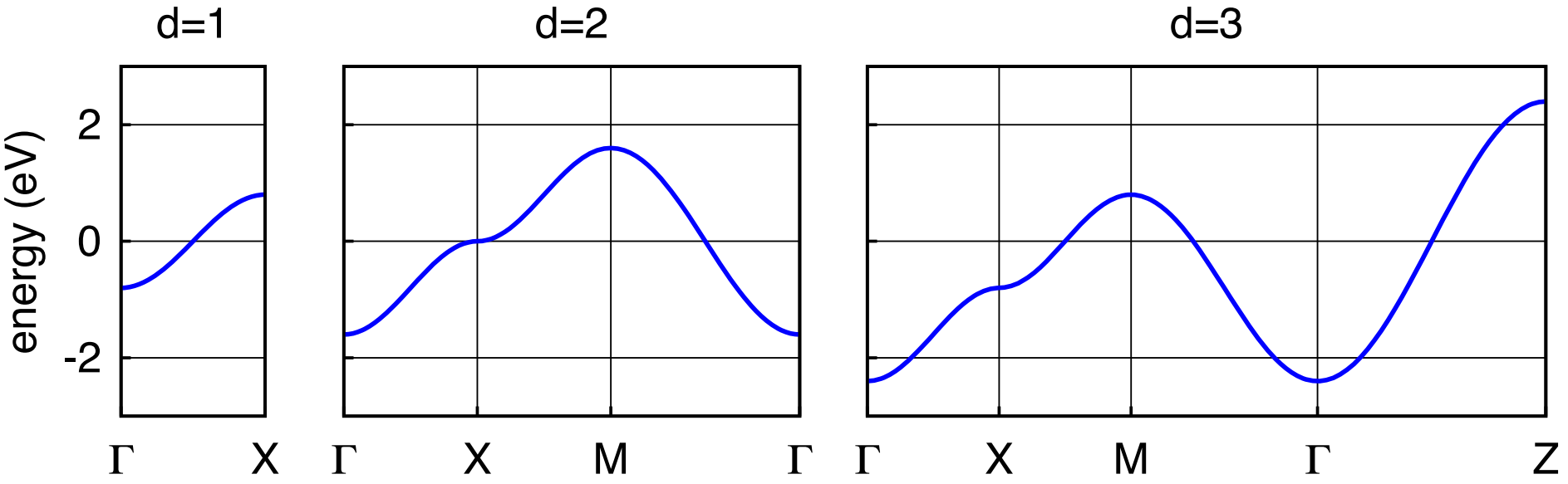


itinerant limit

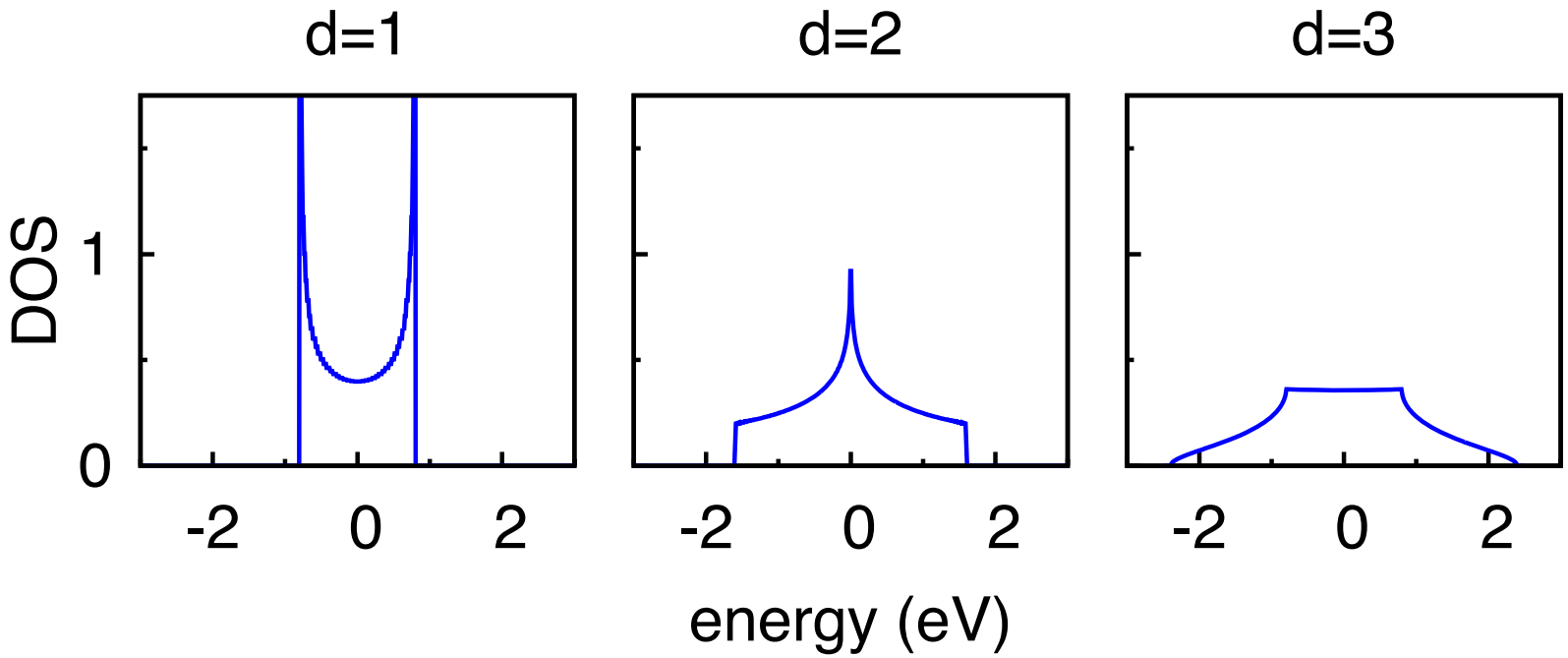
$$H_d + H_T = \sum_{\boldsymbol{k}} \sum_{\sigma} [\varepsilon_d + \varepsilon_{\boldsymbol{k}}] c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma}$$

hypercubic lattice

$$\varepsilon_{\boldsymbol{k}} = -2t \sum_{\nu=1}^{d} \cos(k_{r_\nu} a)$$



density of states



parameters for high-T_c superconductors

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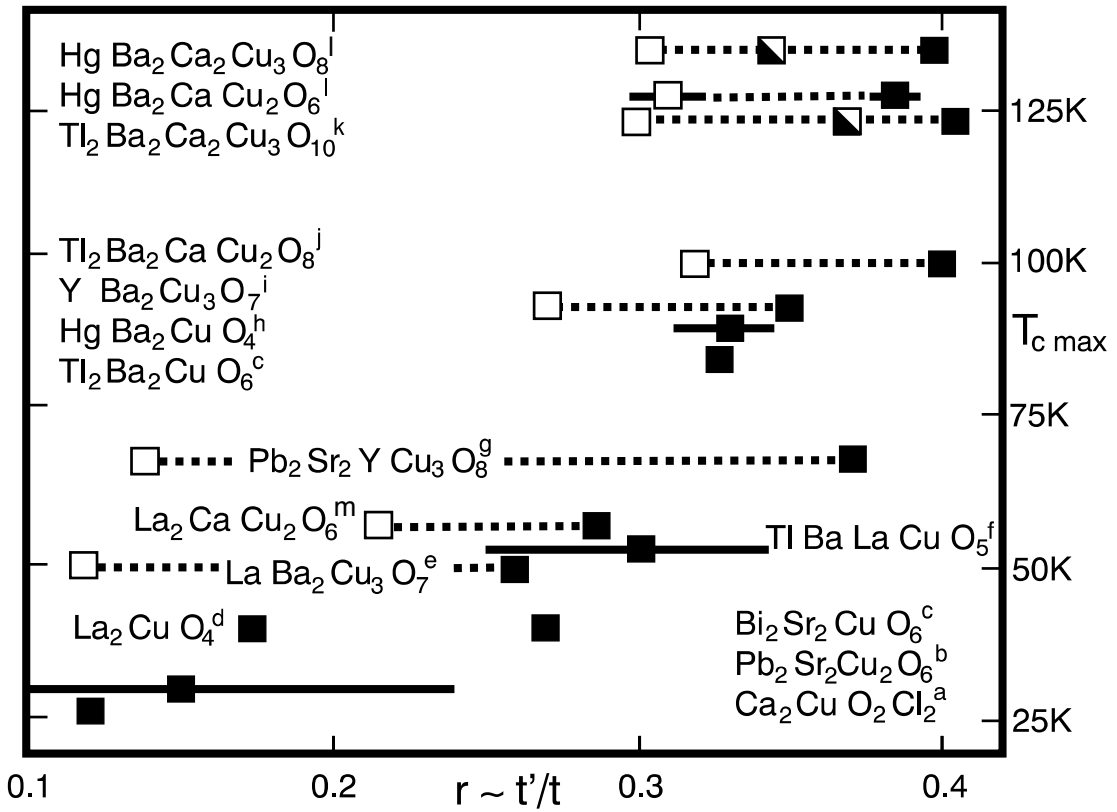
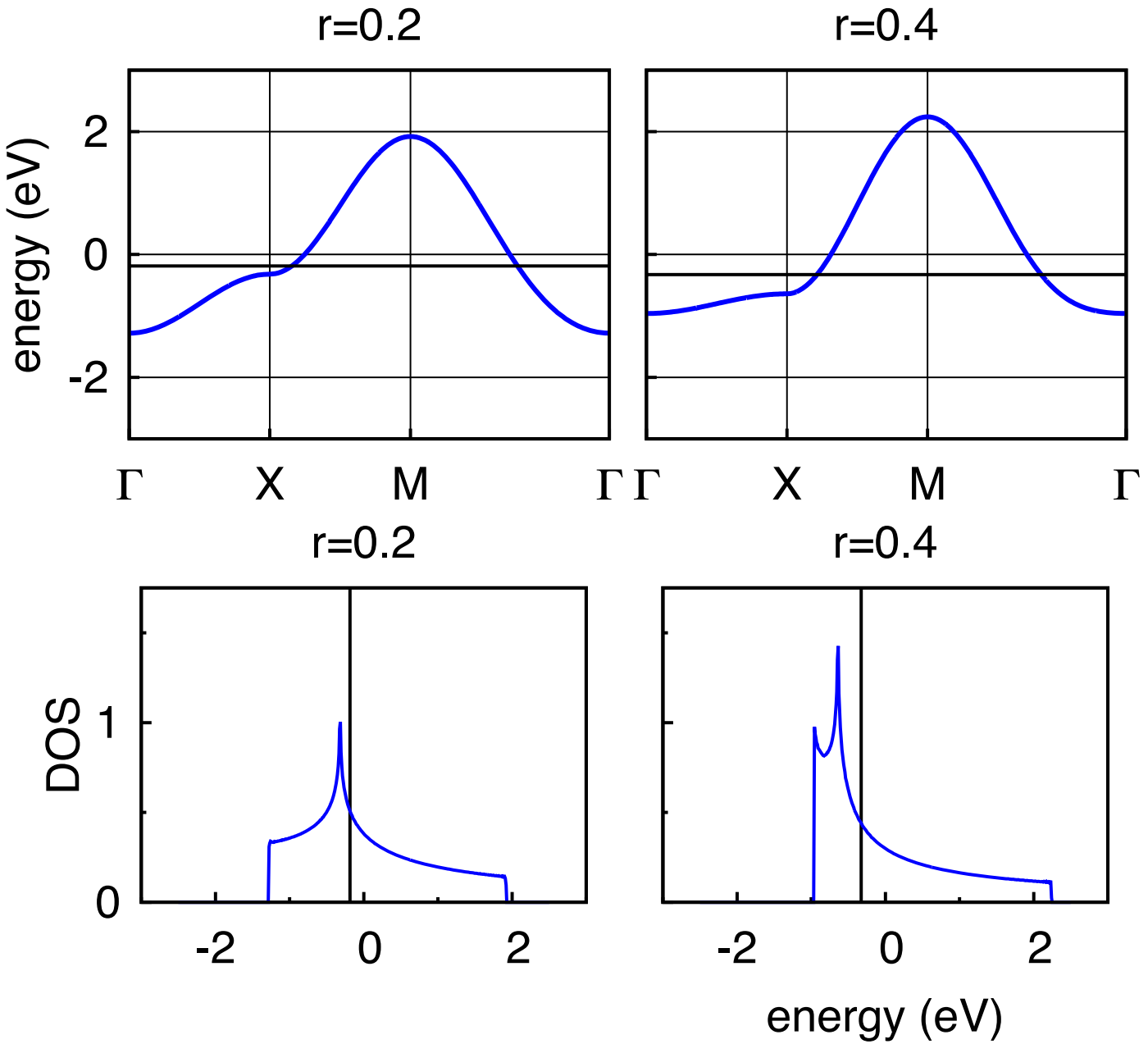


band and density of states



the small *t/U* limit

perturbation theory

Hubbard model

$$H = \varepsilon_d \sum_i \sum_\sigma c^\dagger_{i\sigma} c_{i\sigma} - t \sum_{\langle ii' \rangle} \sum_\sigma c^\dagger_{i\sigma} c_{i'\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} = H_d + H_T + H_U$$

half filling: N=1 electrons per site

n_D = number of doubly occupied sites

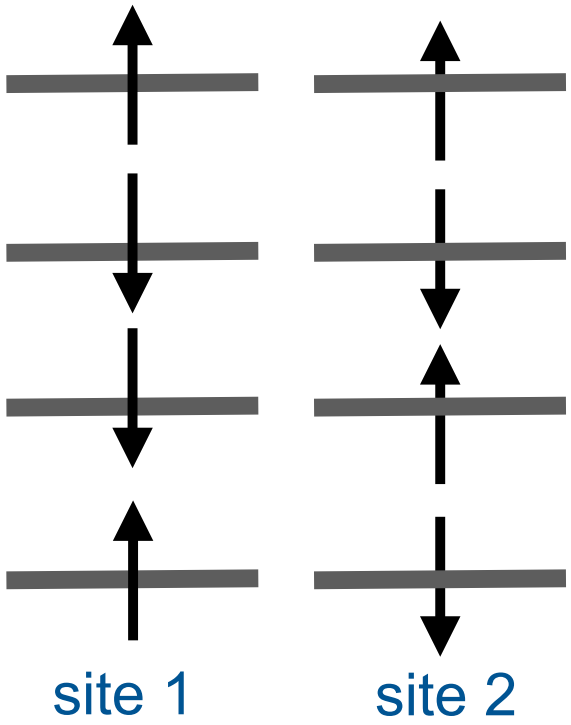
idea: divide Hilbert space into $n_D=0$ and $n_D>0$ sector

next downfold high energy $n_D>0$ sector

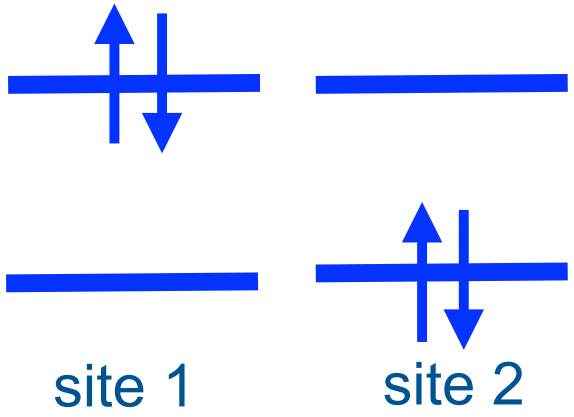
two sites

N=1 per site; $N_{tot}=2$

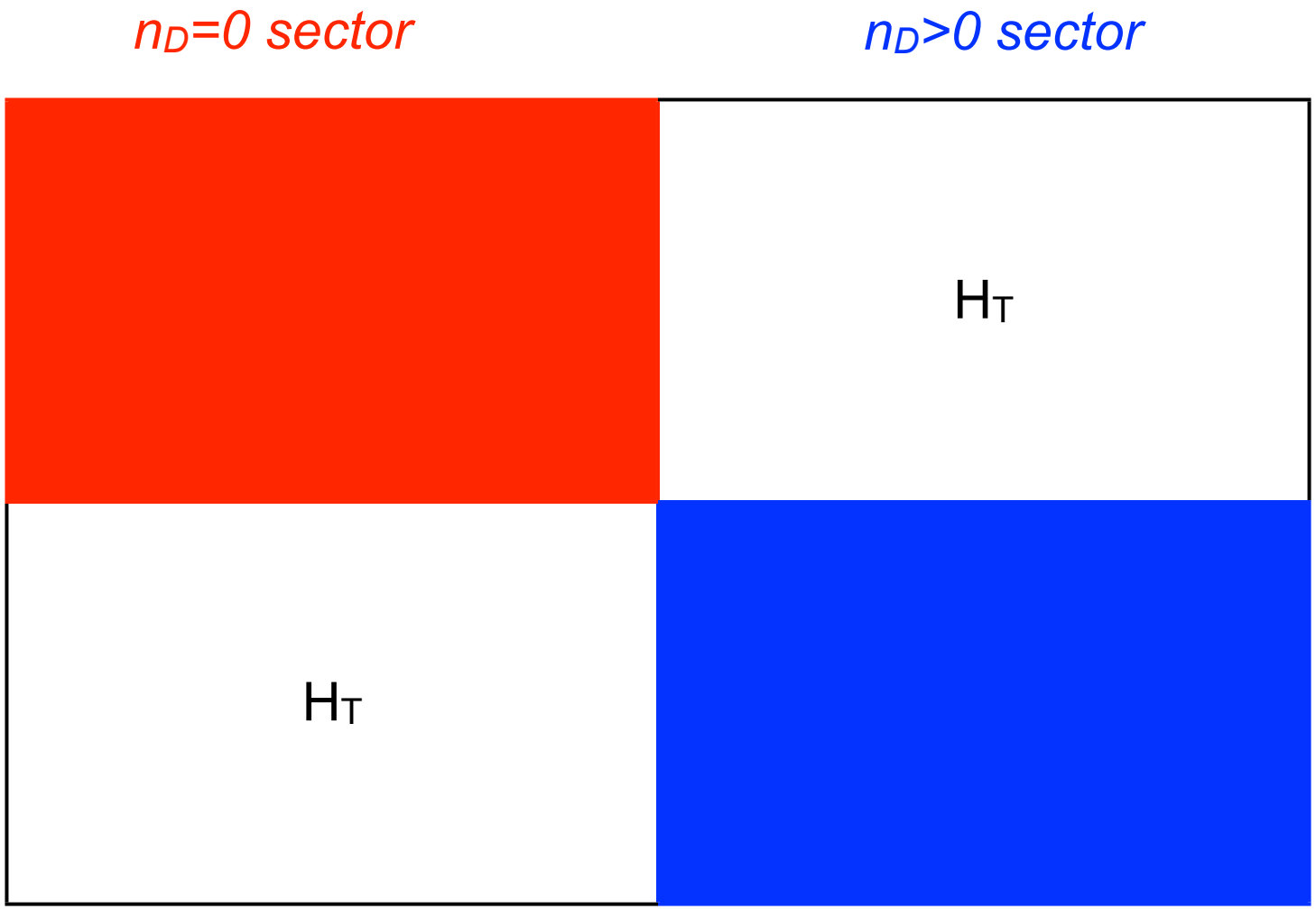
n_D=0 sector



n_D=1 sector



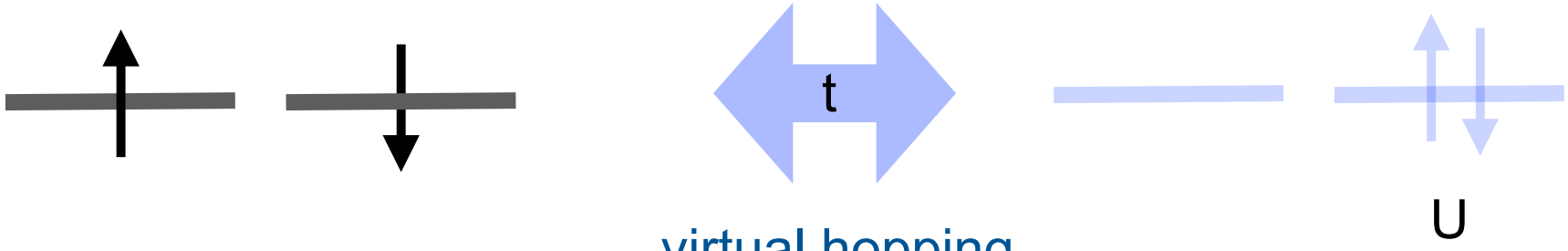
Hilbert space



next downfold high energy $n_D>0$ sector

low energy model

eliminate states with a doubly occupied site



virtual hopping

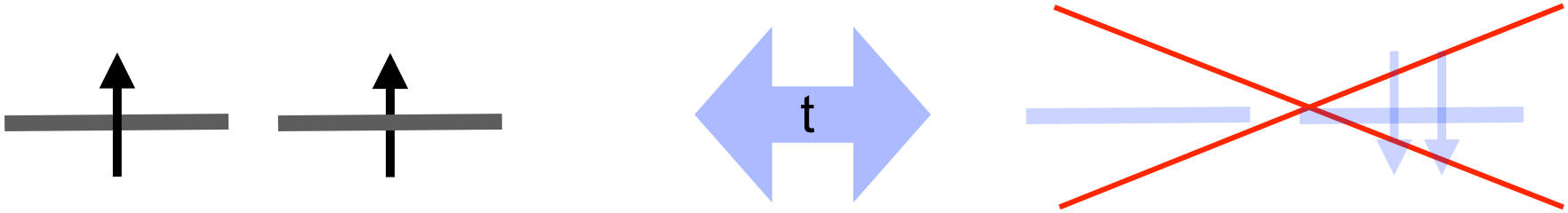
energy gain

$$\Delta E_{\uparrow\downarrow} \sim -\sum_I \langle\uparrow,\downarrow|H_T|I\rangle\langle I\left|\frac{1}{E(2)+E(0)-2E(1)}\right|I\rangle\langle I|H_T|\uparrow,\downarrow\rangle \sim -\frac{2t^2}{U}.$$

=t =1/U =t

low energy model

energy gain only for antiferromagnetic arrangement



$$\frac{1}{2}\Gamma \sim (\Delta E_{\uparrow\uparrow} - \Delta E_{\uparrow\downarrow}) = \frac{1}{2}\frac{4t^2}{U}$$

Pauli principle

$$H_S = \frac{1}{2}\Gamma \sum_{\langle ii' \rangle} \left[\boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} - \frac{1}{4} n_i n_{i'} \right]$$

a canonical transformation

Hubbard model

$$H = -t \sum_{\langle ii' \rangle} \sum_{\sigma} c^{\dagger}_{i\sigma} c_{i'\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} = H_T + H_U$$

here for simplicity $\varepsilon_d = 0$

half filling: N=1 per site

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t/U expansion for the Hubbard model

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(Received 8 January 1988)

a canonical transformation

$$H_T = -t \sum_{\langle ii' \rangle} \sum_{\sigma} c^{\dagger}_{i\sigma} c_{i'\sigma} = H_T^0 + H_T^+ + H_T^-$$

$$H_T^0 = -t \sum_{\langle ii' \rangle} \sum_{\sigma} n_{i-\sigma} c^{\dagger}_{i\sigma} c_{i'\sigma} n_{i'-\sigma} - t \sum_{\langle ii' \rangle} \sum_{\sigma} (1 - n_{i-\sigma}) c^{\dagger}_{i\sigma} c_{i'\sigma} (1 - n_{i'-\sigma}),$$

no change in n_D

$$H_T^+ = -t \sum_{\langle ii' \rangle} \sum_{\sigma} n_{i-\sigma} c^{\dagger}_{i\sigma} c_{i'\sigma} (1 - n_{i'-\sigma}),$$

from n_D to n_D+1

$$H_T^- = \left(H_T^+\right)^{\dagger}$$

from n_D to n_D-1

n_D = number of doubly occupied states

a canonical transformation

$$H = -t \sum_{\langle ii' \rangle} \sum_{\sigma} c^{\dagger}_{i\sigma} c_{i'\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} = H_T + H_U$$

$$S = -\frac{i}{U} \left(H_T^+ - H_T^- \right)$$

$$H_S = e^{iS} H e^{-iS} = H + [iS, H] + \frac{1}{2} [iS, [iS, H]] + \ldots .$$

$[H_T^{\pm}, H_U] = \mp U H_T^{\pm}$ cancels $H_T^+ + H_T^-$

in $$H_T = -t \sum_{\langle ii' \rangle} \sum_{\sigma} c^{\dagger}_{i\sigma} c_{i'\sigma} = H_T^0 + H_T^+ + H_T^- ,$$

half filling

thus

$$H_S = H_U + H_T^0 + \frac{1}{U}\left\{\left[H_T^+, H_T^-\right] + \left[H_T^0, H_T^-\right] + \left[H_T^+, H_T^0\right]\right\} + O(U^{-2})$$

these are zero at half filling

(no hopping possible without changing n_D)

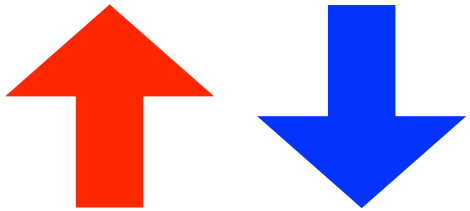
the remaining term is

$$H_S^{(2)} = \frac{1}{2}\frac{4t^2}{U}\sum_{ii'}\left[\boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} - \frac{1}{4}n_i n_{i'}\right].$$

example of kinetic exchange

interacting spins

$$H_S = \frac{1}{2}\Gamma \sum_{\langle ii' \rangle} \left[\boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} - \frac{1}{4} n_i n_{i'} \right]$$



from Hubbard model

to **antiferromagnetic** Heisenberg model

(remember, Coulomb exchange ferromagnetic)

magnetic properties

linear response theory

linear response

$$M_z(\boldsymbol{q};\omega) = \chi_{zz}(\boldsymbol{q};\omega) h_z(\boldsymbol{q};\omega)$$

magnetization　　magnetic field

response function

thermodynamic sum rule

$$\chi_{zz}(\mathbf{0};0) = \lim_{h_z \to 0} \frac{\partial M_z}{\partial h_z}$$

interaction with magnetic field

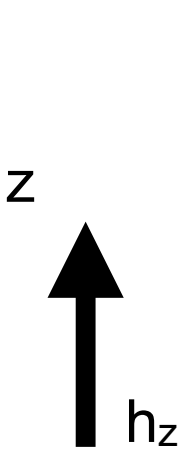
Zeeman term

$$H_{\mathrm{Z}} = g\mu_B h_z S_z$$

.. plus second oder corrections (van Vleck & Larmor)

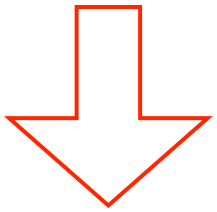
Zeeman term

$$H_Z = g\mu_B h_z S_z$$

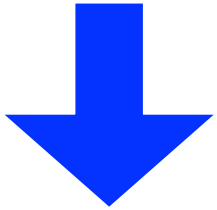


S_z=1/2

M_z=-gμ_B/2

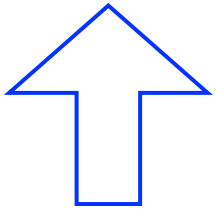


M_z=-g$\mu_B S_z$



S_z=-1/2

M_z=+gμ_B/2



the itinerant limit

U=0 case

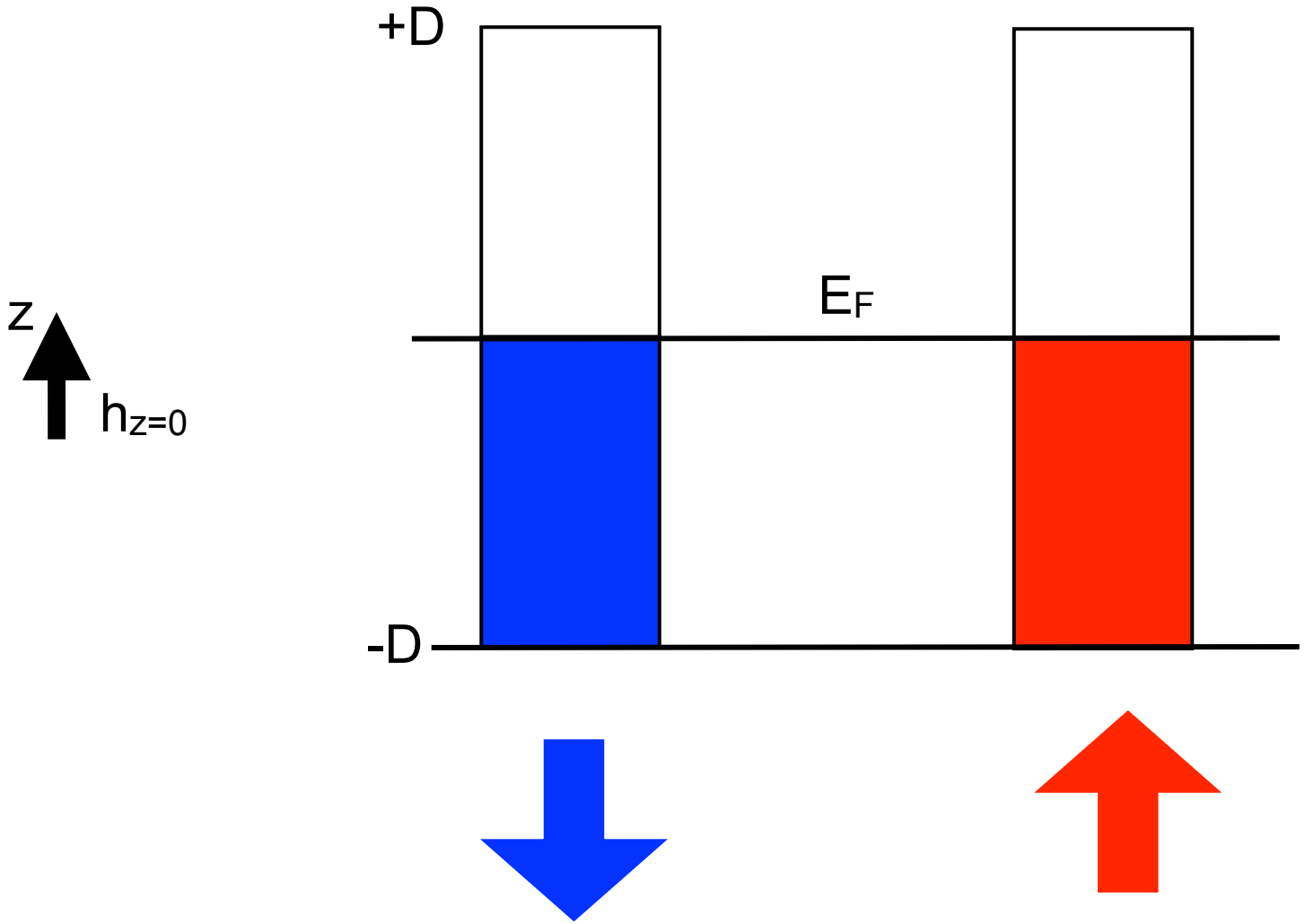
Pauli paramagnetism

$$\varepsilon_{\boldsymbol{k}} \to \varepsilon_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + \frac{1}{2}\sigma g \mu_B h_z$$

Zeeman term

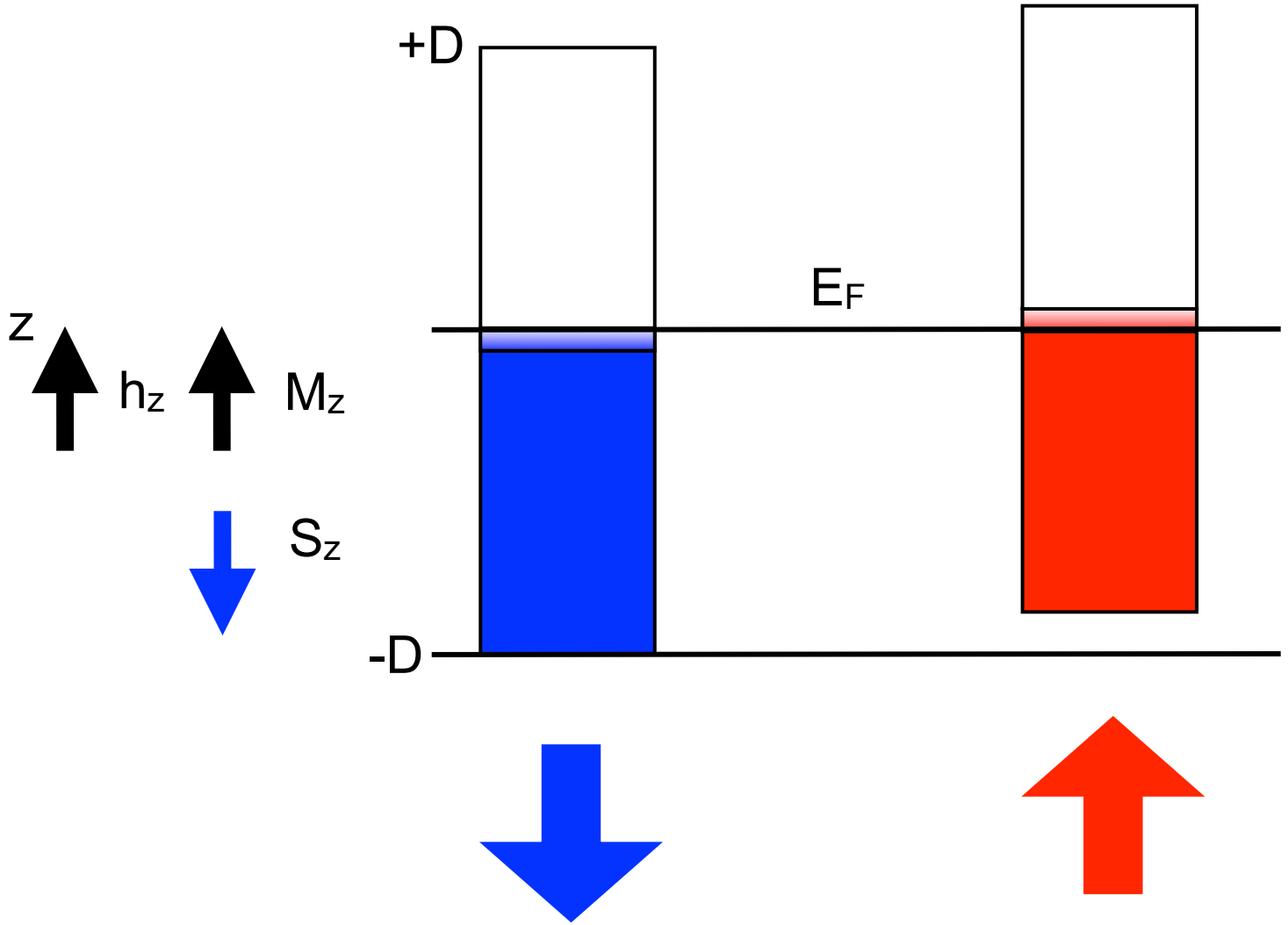
Pauli paramagnetism

$$\varepsilon_{\boldsymbol{k}\uparrow} = \varepsilon_{\boldsymbol{k}\downarrow}$$



Pauli paramagnetism

$$\varepsilon_{\boldsymbol{k}} \rightarrow \varepsilon_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + \frac{1}{2}\sigma g \mu_B h_z$$



Pauli paramagnetism

$$M_z = -\frac{1}{2}(g\mu_B)\frac{1}{N_{\boldsymbol{k}}}\sum_{\boldsymbol{k}}\left[n_{\boldsymbol{k}\uparrow} - n_{\boldsymbol{k}\downarrow}\right] \sim \frac{1}{4}\left(g\mu_B\right)^2 \rho(\varepsilon_F) h_z$$

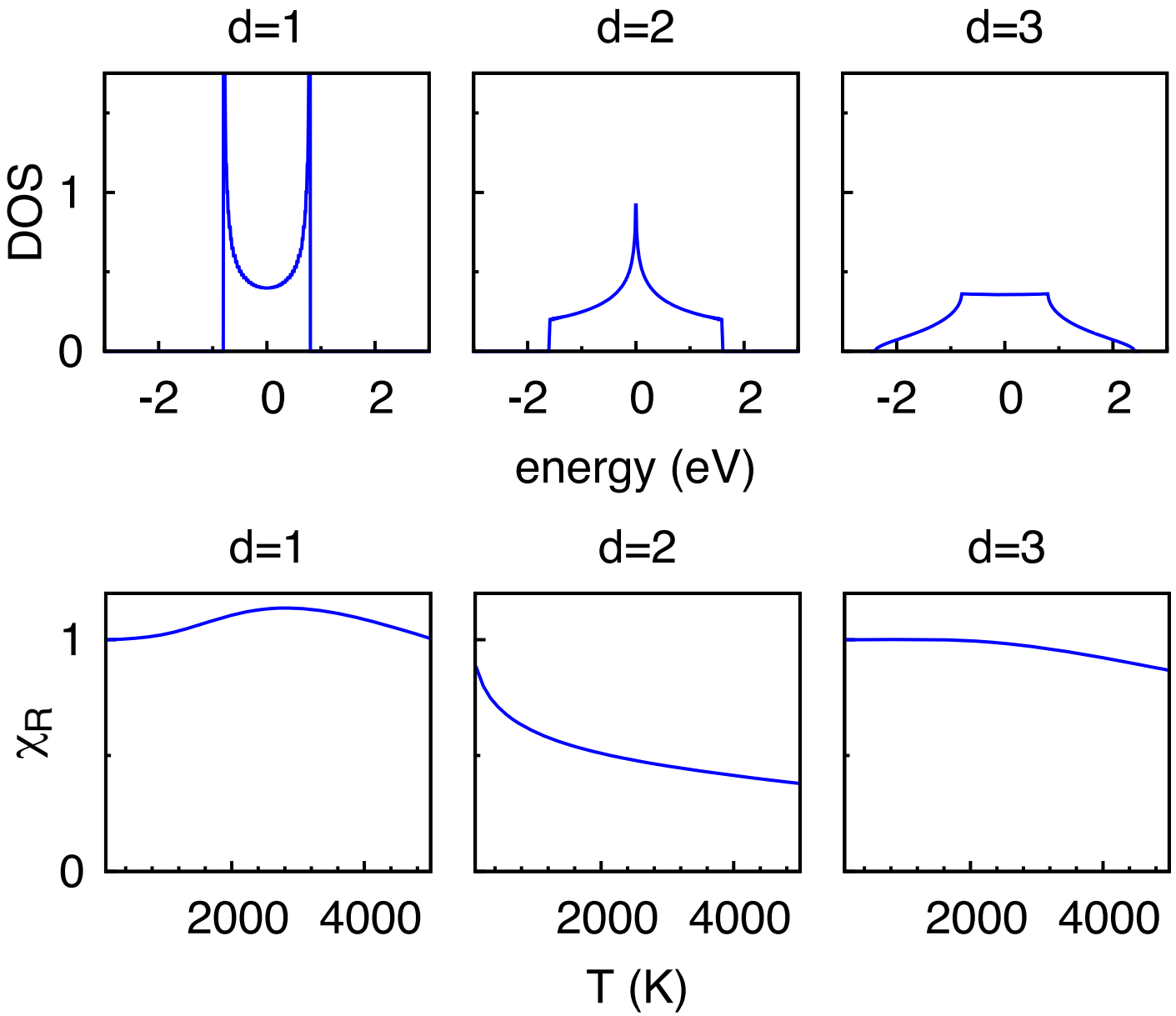
zero temperature

$$\chi^P(0) = \frac{1}{4}\left(g\mu_B\right)^2 \rho(\varepsilon_F)$$

finite temperature

$$\chi^P(T) = \frac{1}{4}\left(g\mu_B\right)^2 \int d\varepsilon \rho(\varepsilon) \left(-\frac{dn(\varepsilon)}{d\varepsilon}\right)$$

finite temperature



linear response theory

Pauli susceptibility: uniform and static

$$M_z(\boldsymbol{q};\omega) = \chi_{zz}(\boldsymbol{q};\omega) h_z(\boldsymbol{q};\omega)$$

small *U/t* case

Fermi liquid

in *some* limit an interacting electron system can be described via independent quasi-electrons

weakly interacting: small U/t ratio

one-to-one correspondence between electrons & quasiparticles

$$\frac{m^*}{m} = 1 + \frac{1}{3}F_1^s > 1, \qquad F_1^s > 0$$

enhanced masses

$$\frac{\chi}{\chi^P} = \frac{1}{1+F_0^a} > 1, \qquad F_0^a < 0$$

enhanced Pauli susceptibility

F_0^a and F_1^s: Landau parameters

Stoner instabilities: Hartree Fock

$$
\begin{aligned}
H_U &= U \sum_i n_{i\uparrow} n_{i\downarrow} \rightarrow H_U^{\mathrm{HF}} \\
H_U^{\mathrm{HF}} &= U \sum_i \left[n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\uparrow} \rangle n_{i\downarrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right] .
\end{aligned}
$$

ferromagnetic instability?

$$
\langle n_{i\sigma} \rangle = n_\sigma = \frac{n}{2} + \sigma m
$$

$$
\varepsilon^U_{\boldsymbol{k}\sigma} = \varepsilon_{\boldsymbol{k}} + n_{-\sigma} U = \varepsilon_{\boldsymbol{k}} + \frac{n}{2} U - \sigma m U
$$

effective total magnetic field

$$\varepsilon_{\boldsymbol{k}\sigma} = \varepsilon^{U}_{\boldsymbol{k}\sigma} + \frac{1}{2} g \mu_B h_z \sigma$$

Zeeman

$$H_U^{\mathrm{HF}} = U \sum_i \left[-2 m S_z^i + m^2 + \frac{n^2}{4} \right]$$

HF

Stoner instabilities

linear response

$$M_z \sim \chi^P(0)\left[h_z - \frac{2}{g\mu_B}Um\right] = \chi^P(0)\left[h_z + 2(g\mu_B)^{-2}UM_z\right]$$

self-consistent solution for M_z

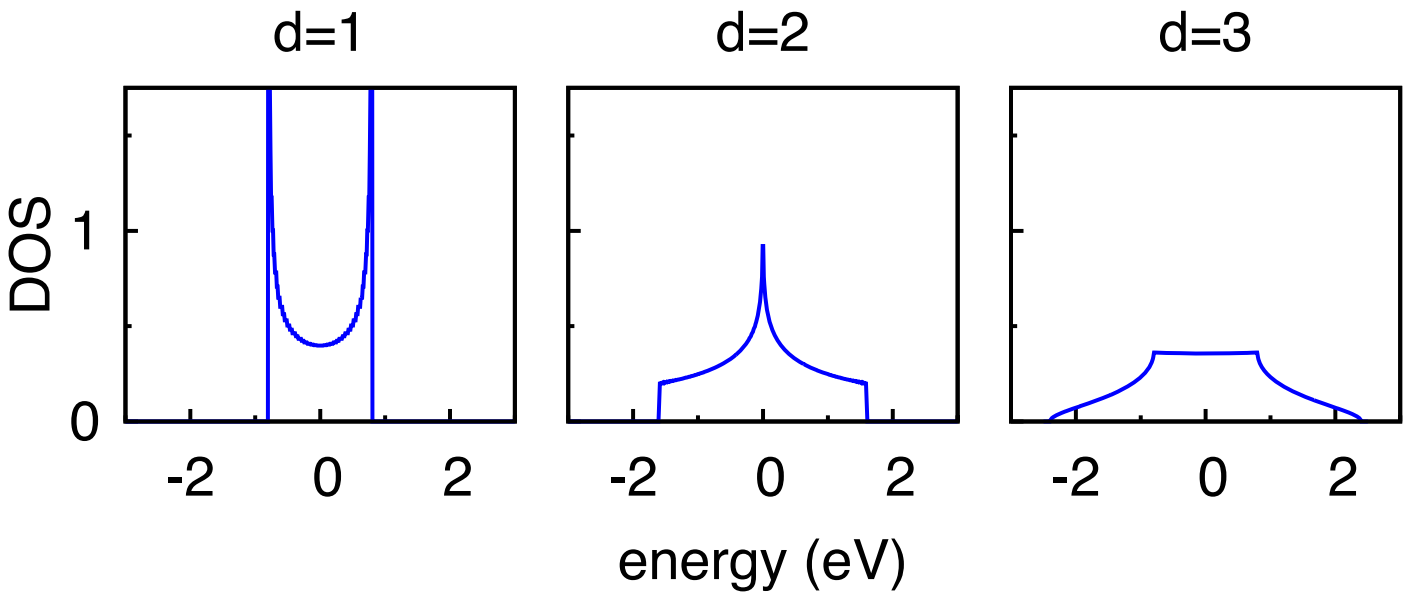
$$\chi^S(\mathbf{0};0) = \frac{\chi^P(0)}{1 - 2\left(g\mu_B\right)^{-2}U\chi^P(0)}$$

RPA susceptibility

$$U_c = 2/\rho(\varepsilon_F)$$

critical U

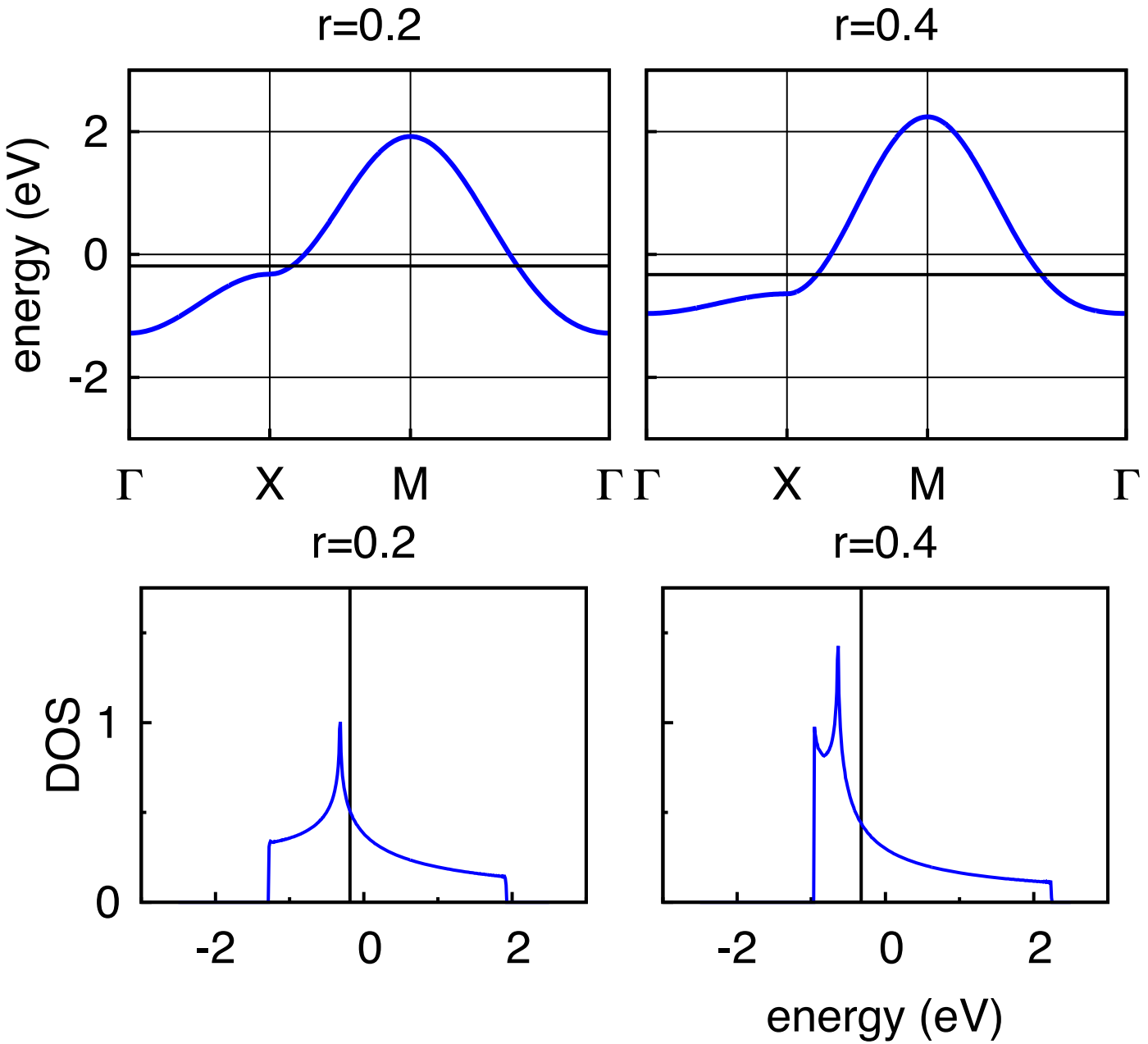
2-dimensional case



logarithmic singularity

any U>0 triggers the instability

band and density of states

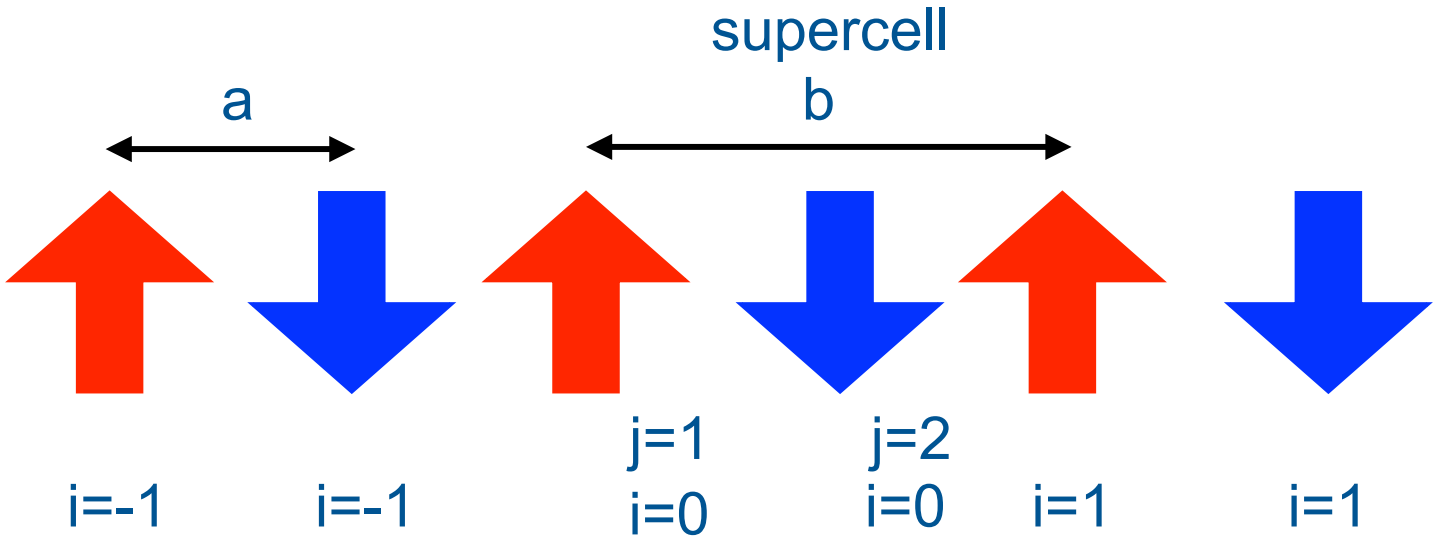


Stoner instabilities with finite q

oscillating magnetic
field and spin polarization

$$S_z^i(\boldsymbol{q}) = \sum_j e^{i\boldsymbol{q}\cdot\boldsymbol{R}_j} S_z^{ji}$$

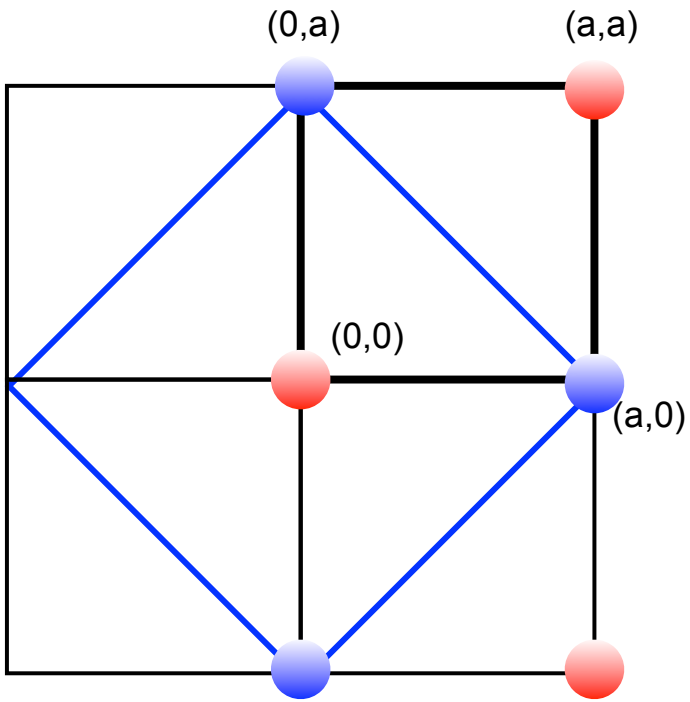
$$\langle S_z^{ji} \rangle = m\cos(\boldsymbol{q}\cdot\boldsymbol{R}_j)$$

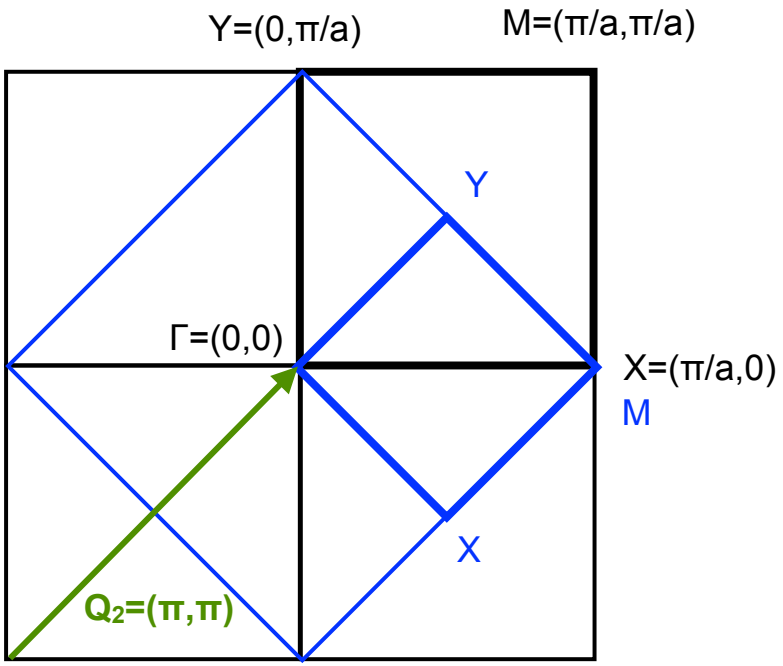


linear chain, **q**=(π/a,0,0)

antiferromagnetism

two dimensional case





Stoner instabilities with finite q

$$H_U^{\mathrm{HF}} + H_Z = \sum_i \left[\frac{g\mu_B}{2} \left(h_z - \frac{2}{g\mu_B} mU \right) \left[S_z^i(\boldsymbol{q}) + S_z^i(-\boldsymbol{q}) \right] + m^2 + \frac{n^2}{4} \right]$$

sums over supercell sites!

$$\chi^S(\boldsymbol{q};0) = \frac{1}{2}(g\mu_B)^2 \frac{\chi_0(\boldsymbol{q};0)}{[1 - U\chi_0(\boldsymbol{q};0)]},$$

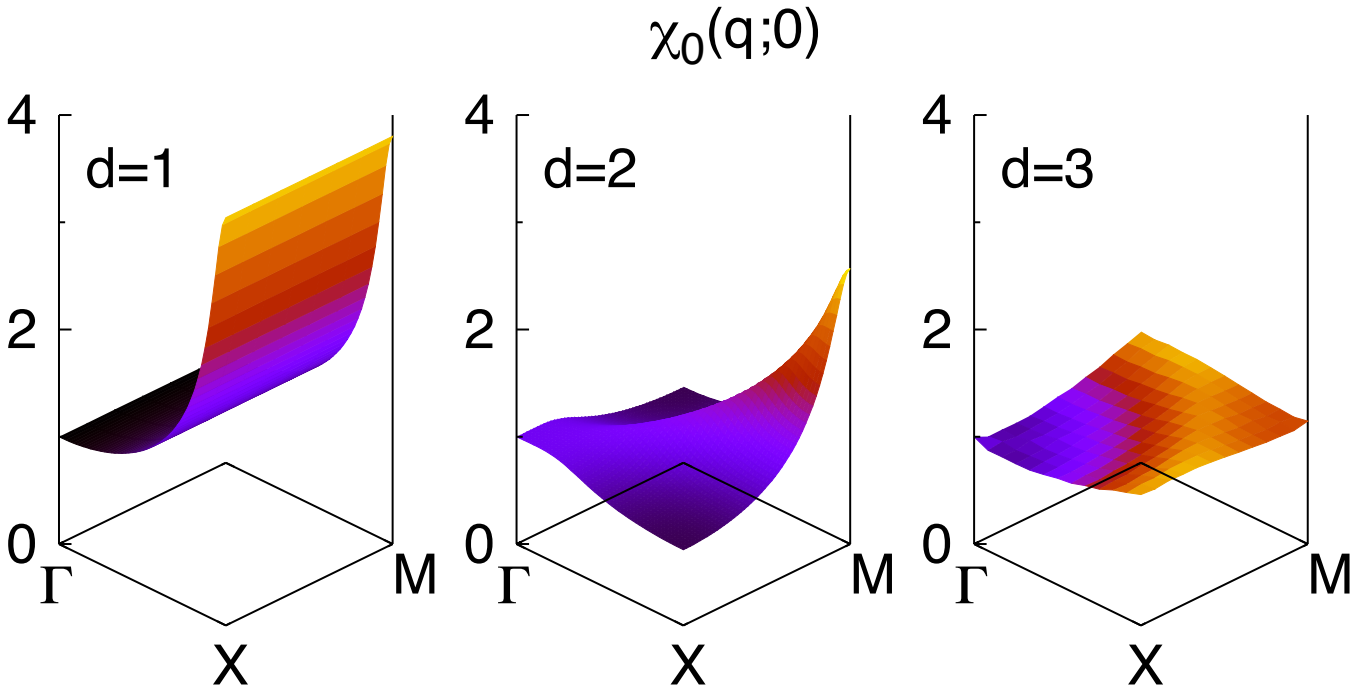
$$\chi_0(\boldsymbol{q};0) = -\frac{1}{N_{\boldsymbol{k}}} \sum_{\boldsymbol{k}} \frac{n_{\boldsymbol{k}+\boldsymbol{q}} - n_{\boldsymbol{k}}}{\varepsilon_{\boldsymbol{k}+\boldsymbol{q}} - \varepsilon_{\boldsymbol{k}}}$$

$$\chi_0(\mathbf{0};0) = 2\,(g\mu_B)^{-2}\,\chi^P(0) \sim \frac{1}{2}\rho(\varepsilon_F)$$

Stoner instabilities with finite q

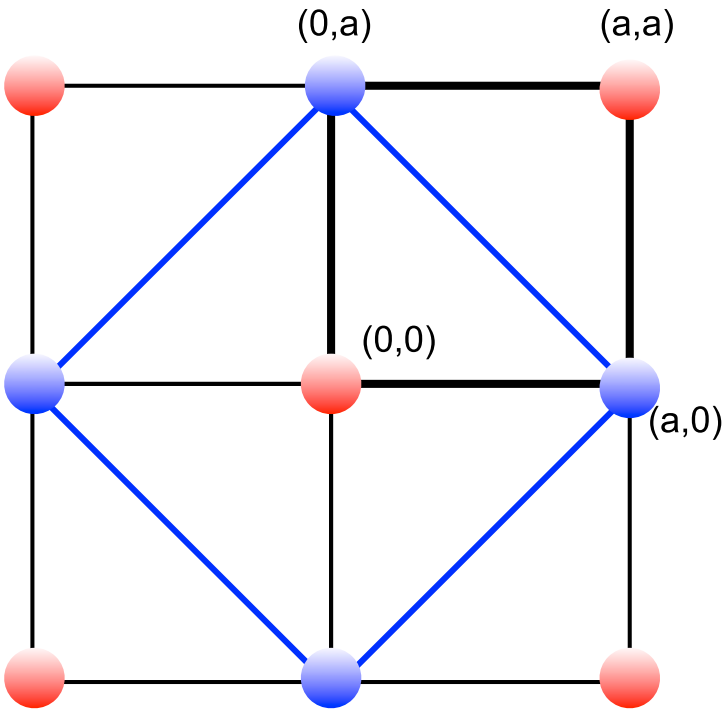
$$\varepsilon_{\boldsymbol{k}} = -2t[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)]$$

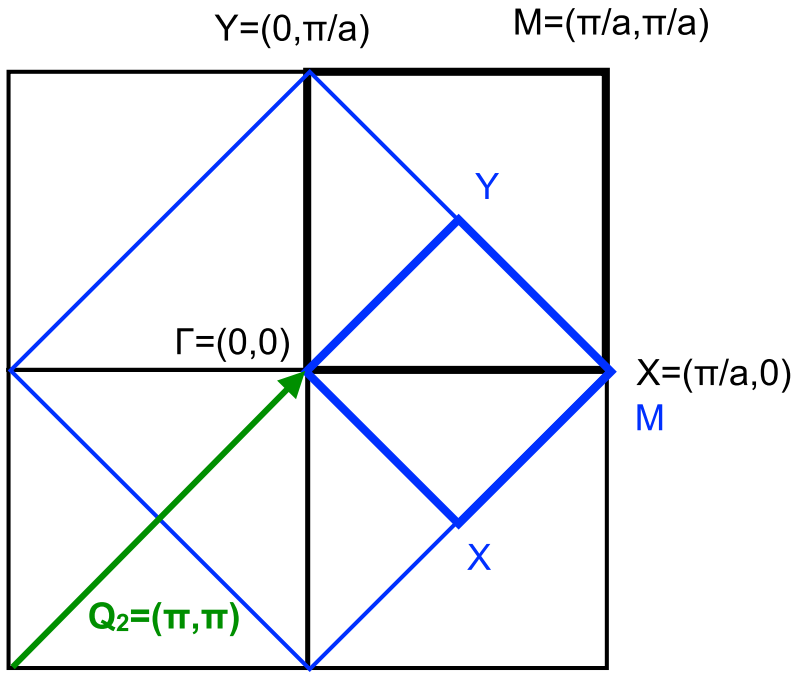
finite temperature ~ 350 K



2-dimensional case: M point!

two-dimensional case





perfect nesting

$$\varepsilon_{\boldsymbol{k}+\boldsymbol{Q}_i} = -\varepsilon_{\boldsymbol{k}}$$

$$\chi_0(\boldsymbol{Q}_i;0) \propto \frac{1}{4}\int_{-\infty}^{\varepsilon_F=0} d\varepsilon \rho(\varepsilon)\frac{1}{\varepsilon} \to \infty.$$

2-dimensional case: Q_2=M point

2-dimensional case: divergence also at Γ point

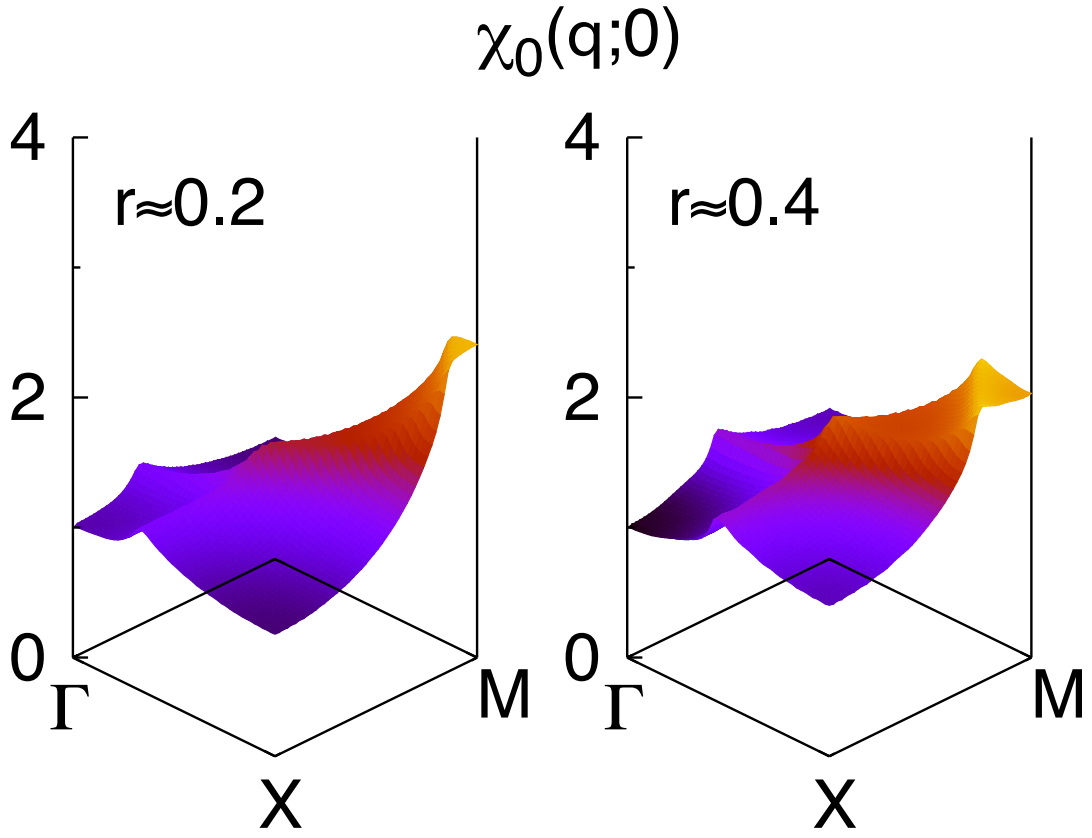
however, finite T: Q_2 singularity most important one

what about t' ?

$$\varepsilon_{\boldsymbol{k}+\boldsymbol{Q}_2} = -\varepsilon_{\boldsymbol{k}} + 8t' \cos(k_x a)\ \cos(k_y a)$$

two-dimensional case

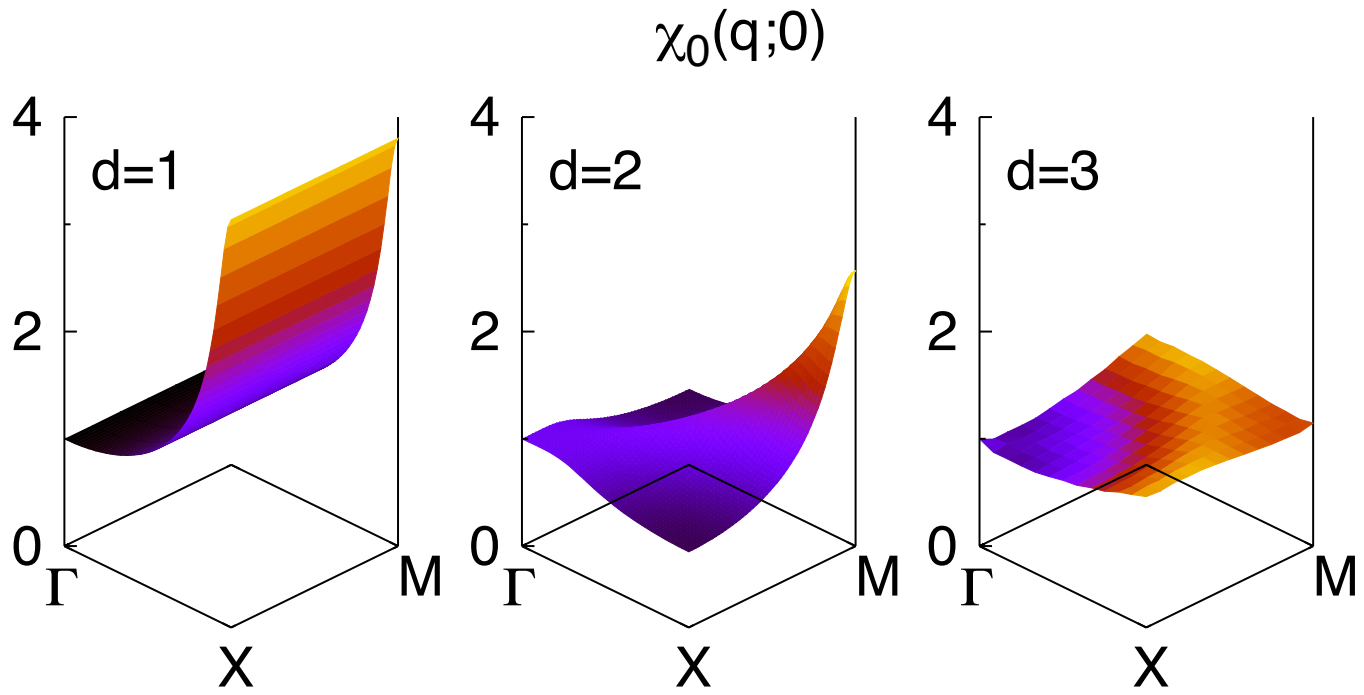
$r \sim t'/t$



$$\varepsilon_{\boldsymbol{k}} = -2t[\cos(k_x a) + \cos(k_y a)] + 4t' \cos(k_x a)\ \cos(k_y a)$$

remarks

- in general several instabilities possible (different **q**)
- which one dominates: check finite temperature susceptibility!
- instabilities possible at any doping
- **q** can also be incommensurate with lattice



non-interacting magnetic ions

magnetization

non interacting ions

uniform magnetic field h_z, Zeeman term

$$M_z = \langle M_z^i \rangle = -g\mu_B \frac{\mathrm{Tr}\left[e^{-g\mu_B h_z \beta S_z^i} S_z^i\right]}{\mathrm{Tr}\left[e^{-g\mu_B h_z \beta S_z^i}\right]} = g\mu_B S \tanh\left(g\mu_B h_z \beta S\right)$$

derivative with respect to h_z

$$\frac{\partial M_z}{\partial h_z} = \left(g\mu_B S\right)^2 \frac{1}{k_B T} \left[1 - \tanh^2\left(g\mu_B h_z \beta S\right)\right]$$

Curie susceptibility

$$\chi_{zz}(\mathbf{0};0) = (g\mu_B S)^2 \frac{1}{k_B T} = \frac{C_{1/2}}{T}$$

Curie constant

$$C_{1/2} = \frac{(g\mu_B)^2 S(S+1)}{3k_B}$$

generalization

J=S+L

$$g_J = \frac{\langle JJ_zLS|(g\boldsymbol{S}+\boldsymbol{L})\cdot\boldsymbol{J}|JJ_zLS\rangle}{\langle JJ_zLS|\boldsymbol{J}\cdot\boldsymbol{J}|JJ_zLS\rangle}$$

$$\sim \frac{3}{2}+\frac{S(S+1)-L(L+1)}{2J(J+1)}$$

j=|s-l|,...|s+l|

ground state:third Hund's rule

$$\boldsymbol{M} = -g_J\mu_B\boldsymbol{J}$$

$$M_z = \langle M_z^i\rangle = g_J\mu_B J\ B_J\left(g_J\mu_B h_z\beta J\right)$$

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{1}{2J}x\right)$$

Brillouin function

transition-metal ions

Ion			n	S	L	J	$^{2S+1}L_J$
V^{4+}	Ti^{3+}		$3d^1$	1/2	2	3/2	$^2D_{3/2}$
	V^{3+}		$3d^2$	1	3	2	$^2F_2$
	Cr^{3+}	V^{2+}	$3d^3$	3/2	3	3/2	$^4F_{3/2}$
	Mn^{3+}	Cr^{2+}	$3d^4$	2	2	0	$^5D_0$
	Fe^{3+}	Mn^{2+}	$3d^5$	5/2	0	5/2	$^6S_{5/2}$
		Fe^{2+}	$3d^6$	2	2	4	$^5D_4$
		Co^{2+}	$3d^7$	3/2	3	9/2	$^4F_{9/2}$
		Ni^{2+}	$3d^8$	1	3	4	$^3F_4$
		Cu^{2+}	$3d^9$	1/2	2	5/2	$^2D_{5/2}$

J=S

lanthanides

Ion	n	S	L	J	$^{2S+1}L_J$	g_J
Ce^{3+}	$4f^1$	1/2	3	5/2	$^2F_{5/2}$	6/7
Pr^{3+}	$4f^2$	1	5	4	$^3H_4$	4/5
Nd^{3+}	$4f^3$	3/2	6	9/2	$^4I_{9/2}$	8/11
Pm^{3+}	$4f^4$	2	6	4	$^5I_4$	3/5
Sm^{3+}	$4f^5$	5/2	5	5/2	$^6H_{5/2}$	2/7
Eu^{3+}	$4f^6$	3	3	0	$^7F_0$	0
Gd^{3+}	$4f^7$	7/2	0	7/2	$^8S_{7/2}$	2
Tb^{3+}	$4f^8$	3	3	6	$^7F_6$	3/2
Dy^{3+}	$4f^9$	5/2	5	15/2	$^6H_{15/2}$	4/3
Ho^{3+}	$4f^{10}$	2	6	8	$^5I_8$	5/4
Er^{3+}	$4f^{11}$	3/2	6	15/2	$^4I_{15/2}$	6/5
Tm^{3+}	$4f^{12}$	1	5	6	$^3H_6$	7/6
Yb^{3+}	$4f^{13}$	1/2	3	7/2	$^2F_{7/2}$	8/7

generalization

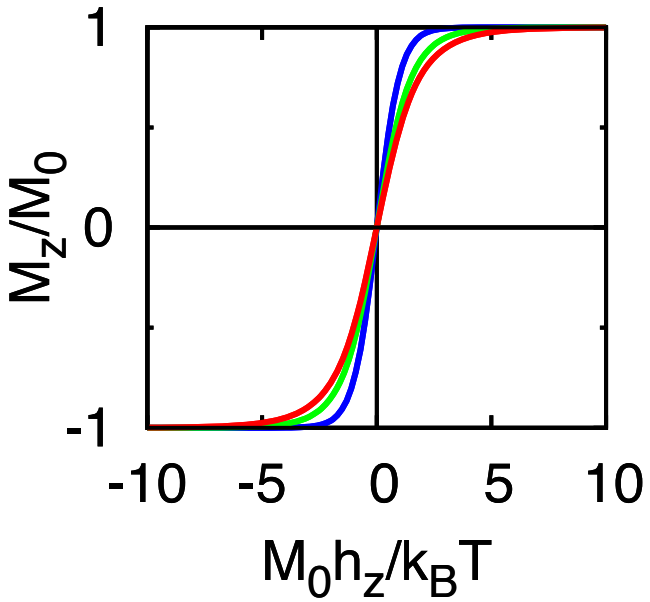
$$C_J = \frac{(g_J \mu_B)^2 J(J+1)}{3k_B}$$

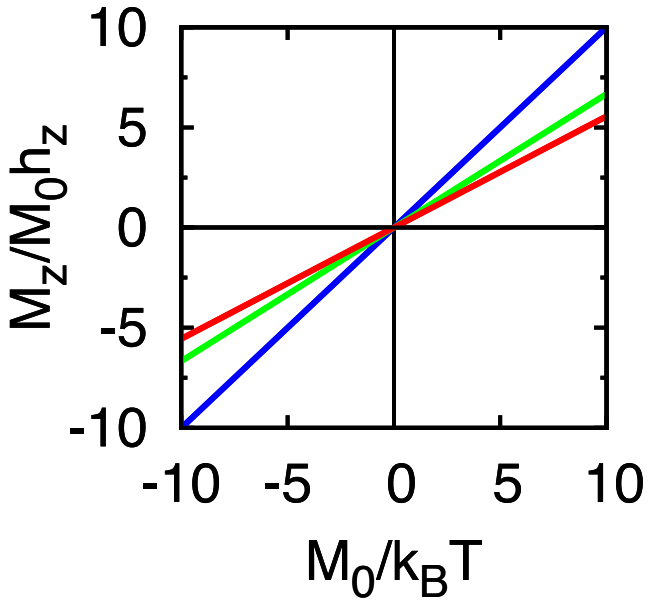
$$\chi_{zz}(\mathbf{0};0) \sim \begin{cases} 0 & k_B T/|M_0|h_z \to 0 \\ C_J/T & |M_0|h_z/k_B T \to 0 \\ C_J/T & h_z \to 0 \end{cases}$$

Curie susceptibility

$$M_z \sim g_J \mu_B J \equiv M_0$$

magnetization





correlation function

$$\mathcal{S}_{i,i'} = \langle (\boldsymbol{S}_i - \langle \boldsymbol{S}_i \rangle) \cdot (\boldsymbol{S}_{i'} - \langle \boldsymbol{S}_{i'} \rangle) \rangle = \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} \rangle - \langle \boldsymbol{S}_i \rangle \cdot \langle \boldsymbol{S}_{i'} \rangle$$

paramagnet

$$\mathcal{S}_{i,i'} = \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} \rangle \sim \begin{cases} \langle \boldsymbol{S}_i \rangle \cdot \langle \boldsymbol{S}_{i'} \rangle & \sim 0 \quad i \neq i' \\ \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_i \rangle & = 3/4 \quad i = i' \end{cases}$$

uncorrelated spins

paramagnet vs disordered system

$$\mathcal{S}_{i,i'} = \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} \rangle \sim \begin{cases} \langle \boldsymbol{S}_i \rangle \cdot \langle \boldsymbol{S}_{i'} \rangle & \sim 0 \quad i \neq i' \\ \langle \boldsymbol{S}_i \cdot \boldsymbol{S}_i \rangle & = 3/4 \quad i = i' \end{cases}$$

paramagnet

Curie susceptibility

different from

$$\sum_{i' \neq i} \langle S_z^i \cdot S_z^{i'} \rangle \sim 0$$

spin disorder

e.g. spin glass behavior

fluctuation-dissipation theorem

(at high-temperature)

$$\chi_{zz}(\boldsymbol{q};0) \sim \frac{(g\mu_B)^2}{k_B T}\sum_{i'}\mathcal{S}^{i,i'}_{zz}\, e^{i\boldsymbol{q}\cdot(\boldsymbol{R}_i-\boldsymbol{R}_{i'})} = \chi^i_{zz}(T)$$

$$= \frac{M_0^2}{k_B T} = \frac{C_{1/2}}{T}$$

$$\chi_{zz}(\mathbf{0};0) = \lim_{h_z\to 0}\frac{\partial M_z}{\partial h_z} = \chi^i_{zz}(T)$$

local susceptibility

spin as emergent entity

one-site Hubbard model

$$\chi_{zz}(\mathbf{0};0) \sim \frac{(g\mu_B)^2}{k_B T}\left\{\frac{\mathrm{Tr}\left[e^{-\beta(H_i-\mu N_i)}\ \left(S_z^i\right)^2\right]}{\mathrm{Tr}\left[e^{-\beta(H_i-\mu N_i)}\right]} - \left[\frac{\mathrm{Tr}\left[e^{-\beta(H_i-\mu N_i)}\ S_z^i\right]}{\mathrm{Tr}\left[e^{-\beta(H_i-\mu N_i)}\right]}\right]^2\right\}$$

$$= \frac{C_{1/2}}{T}\frac{e^{\beta U/2}}{1+e^{\beta U/2}}$$

$$U = E(N_i+1) + E(N_i-1) - 2E(N_i)$$

infinite U limit: the spin S=1/2

only S=1/2 part of Hilbert space remains

Van Vleck paramagnetism

second order correction (i.e., beyond Zeeman)

$$M_z^{\mathrm{VV}} = 2h_z\mu_B^2 \sum_I \frac{|\langle 0|(L_z + gS_z)|I\rangle|^2}{E_I - E_0}$$

relevant if J=0

J=0: non degenerate state, linear correction (Zeeman) is zero

Larmor diamagnetism

$$M_z^{\mathrm{L}} = -\frac{1}{4} h_z \langle 0| \sum_i (x_i^2 + y_i^2) |0\rangle$$

diamagnetic contribution, same order of Van Vleck term

interacting local moments

$$H = \frac{1}{2}\Gamma \sum_{ii'} \left[\boldsymbol{S}_i \cdot \boldsymbol{S}_{i'} - \frac{1}{4} n_i n_{i'} \right]$$

mean-field approach

$$H = g\mu_B \sum_i \left[\boldsymbol{S}_i \cdot (\boldsymbol{h} + \boldsymbol{h}_i^m) + \text{const} \right]$$

$$\boldsymbol{h}_i^m = n_{\langle ii' \rangle} \Gamma \langle \boldsymbol{S}_{i'} \rangle / g\mu_B$$

antiferromagnetic case

bipartite lattice

sublattice A and sublattice B

& Zeeman term

$$\begin{cases} M_z^A/M_0 &= B_{1/2}\left[M_0(h_z+\Delta h_z^A)\beta\right] \\ M_z^B/M_0 &= B_{1/2}\left[M_0(h_z+\Delta h_z^B)\beta\right] \end{cases}$$

$$\begin{cases} \Delta h_z^A = & -(M_z^B/M_0)\, S^2 \Gamma n_{\langle ii'\rangle}/M_0 \\ \Delta h_z^B = & -(M_z^A/M_0)\, S^2 \Gamma n_{\langle ii'\rangle}/M_0 \end{cases}$$

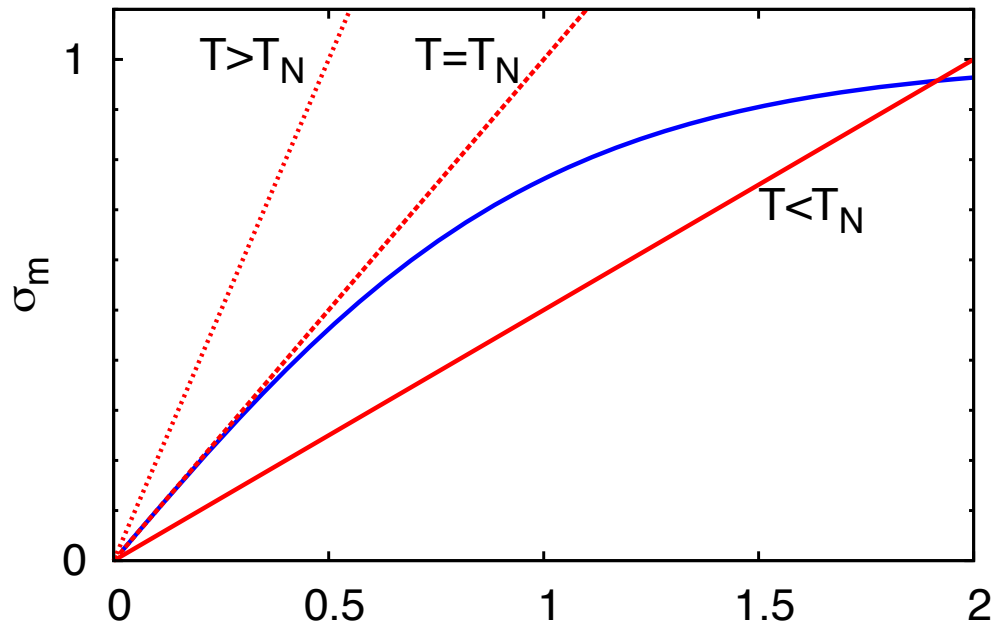
self-consistent equation

order parameter

$$\sigma_m = (M_z^B - M_z^A)/2M_0 = B_{1/2}\left[\sigma_m S^2 \Gamma n_{\langle ii' \rangle} \beta\right]$$

$$\sigma_m = B_{1/2}\left[\frac{T_{\mathrm{N}}}{T}\sigma_m\right]$$

T_N: Neel temperature



around T_N

order parameter small

$$\frac{T}{T_{\rm N}} = \frac{\sigma_m}{B_{1/2}^{-1}\left[\sigma_m\right]}$$

$$\frac{\sigma_m}{B_{1/2}^{-1}(\sigma_m)} \sim \frac{\sigma_m}{\sigma_m + \sigma_m^3/3 + \ldots} \sim 1 - \sigma_m^2/3 + \ldots$$

$$\sigma_m = \sqrt{3}\left(1 - \frac{T}{T_{\rm N}}\right)^{1/2}$$

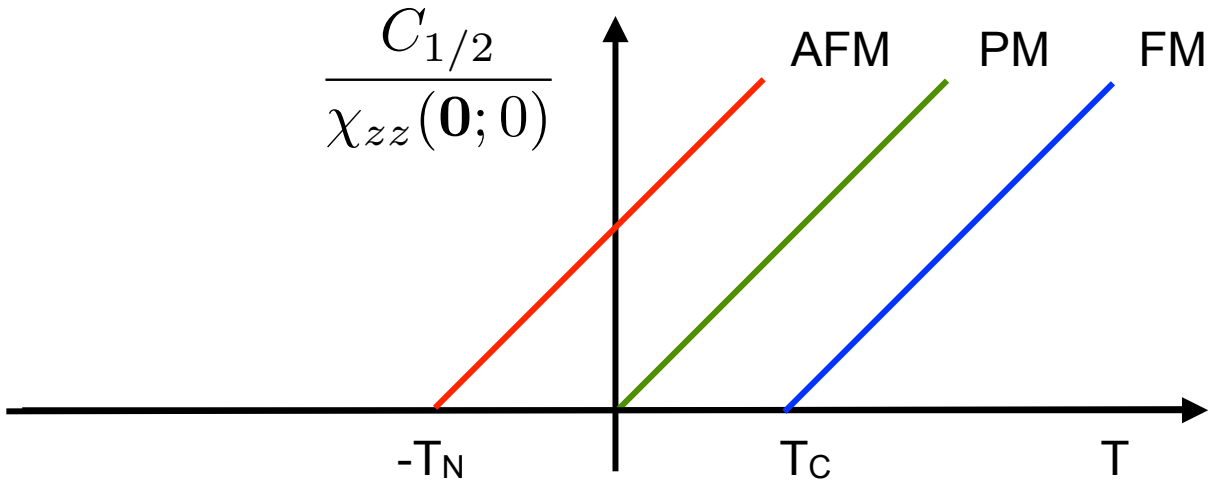
uniform response function

$$\chi_{zz}(\mathbf{0};0) = \frac{C_{1/2}(1-\sigma_m^2)}{T + (1-\sigma_m^2)T_{\mathrm{N}}}$$

Curie-Weiss high-temperature behavior

$$\chi_{zz}(\mathbf{0};0) \sim \frac{C_{1/2}}{T + T_{\mathrm{N}}}$$

no divergence!



finite q

$$\langle M_z^{ji} \rangle \quad = \quad -\sigma_m M_0 \cos(\boldsymbol{q} \cdot \boldsymbol{R}_j) = -g\mu_B \, m \, \cos(\boldsymbol{q} \cdot \boldsymbol{R}_j)$$

relation between critical temperature and couplings

$$k_B T_{\boldsymbol{q}} = \frac{S(S+1)}{3} \Gamma_{\boldsymbol{q}}, \quad \Gamma_{\boldsymbol{q}} = -\sum_{ij \neq 0} \Gamma^{00,ij} e^{i\boldsymbol{q} \cdot (\boldsymbol{T}_i + \boldsymbol{R}_j)}$$

$$\chi_{zz}(\boldsymbol{q}; 0) = \frac{C_{1/2}(1-\sigma_m^2)}{T - (1-\sigma_m^2) T_{\boldsymbol{q}}}$$

divergence at critical temperature

correlation length

q*=*Q instability

fluctuation-dissipation theorem + Fourier transform

$$\chi_{zz}^{00,ji} \propto e^{-r/\xi}/r$$

$$\xi \propto [T_{\boldsymbol{Q}}/(T - T_{\boldsymbol{Q}})]^{1/2}$$

diverges at critical temperature $T_{\boldsymbol{Q}}$!

effective magnetic moment

generalization to materials

$$C_{1/2} \to C_{\rm eff} = \mu_{\rm eff}^2/3k_B$$

depends on: Hund's rules, crystal field etc..

effective moment

$$3k_B T \chi_{zz}(\boldsymbol{q};0) \to \mu_{\rm eff}$$

very large temperature limit

local moment regime and HF

$$H_U = U \sum_i n_{i\uparrow} n_{i\downarrow} \to H_U^{\mathrm{HF}}$$

$$H_U^{\mathrm{HF}} = U \sum_i \left[n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\uparrow} \rangle n_{i\downarrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right].$$

$$\langle n_{i\sigma} \rangle = n_\sigma = \frac{n}{2} + \sigma m$$

$$H_U^{\mathrm{HF}} = U \sum_i \left[-2 m S_z^i + m^2 + \frac{n^2}{4} \right]$$

local moment regime and HF

paramagnetic & ferromagnetic case

Bloch function

$$\Psi_{\boldsymbol{k}\sigma}(\boldsymbol{r}) = \frac{1}{\sqrt{N_s}} \sum_i e^{i\boldsymbol{k}\cdot\boldsymbol{T}_i} \; \Psi_{i\sigma}(\boldsymbol{r})$$

spin scattering function

$$S_z(\boldsymbol{k}, \boldsymbol{k}') = \frac{1}{N_s} \sum_i e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{T}_i} \; \frac{1}{2} \sum_\sigma \sigma c^\dagger_{i\sigma} c_{i\sigma}$$

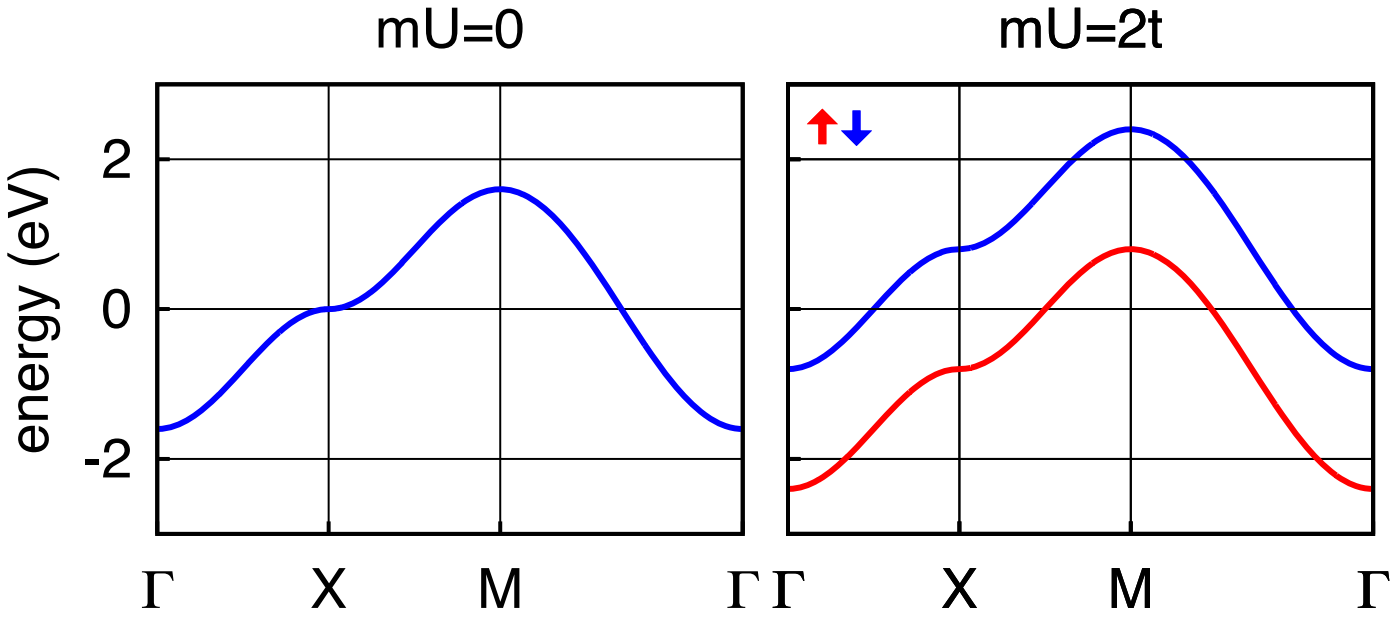
S^i_z

ferromagnetic case

Hartree-Fock Hamiltonian and bands

$$H = \sum_{\sigma} \sum_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma} + U \sum_{\boldsymbol{k}} \left[-2m\, S_z(\boldsymbol{k}, \boldsymbol{k}) + m^2 + \frac{n^2}{4} \right]$$

diagonal in ***k***



Hartree-Fock bands

very large mU case, half filling

spin down band empty, m=1/2

total energy

$$E_{\mathrm{F}} = \frac{1}{N_{\boldsymbol{k}}} \sum_{\boldsymbol{k}} \left[\varepsilon_{\boldsymbol{k}\sigma} - \mu \right] = \frac{1}{N_{\boldsymbol{k}}} \sum_{\boldsymbol{k}} \left[\varepsilon_{\boldsymbol{k}} - \frac{1}{2} U \right] = -\frac{1}{2} U$$

no t^2/U term!

antiferromagnetic case

two sublattices with opposite magnetization +m and -m

$$H_U^{\mathrm{HF}} = \sum_{i\in A}\left[-2mS_z^i + m^2 + \frac{n^2}{4}\right] + \sum_{i\in B}\left[+2mS_z^i + m^2 + \frac{n^2}{4}\right]$$

Bloch function

original lattice

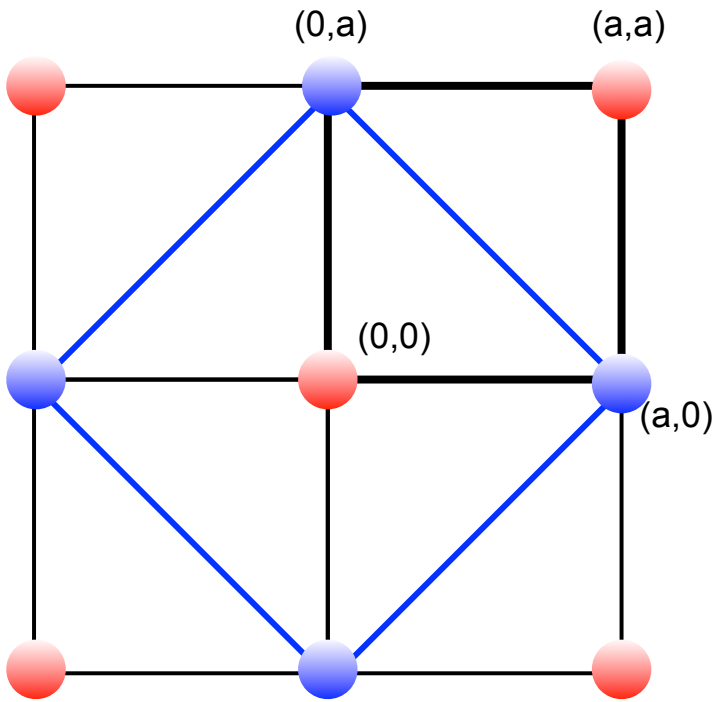
Bloch functions

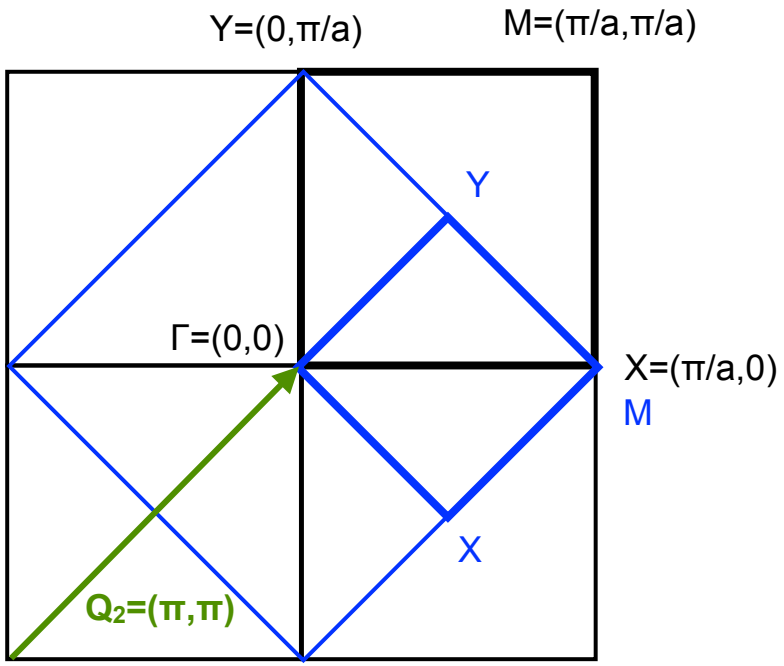
two sublattices A and B

$$\Psi_{\boldsymbol{k}\sigma}(\boldsymbol{r}) = \frac{1}{\sqrt{2}}\left[\Psi^A_{\boldsymbol{k}\sigma}(\boldsymbol{r}) + \Psi^B_{\boldsymbol{k}\sigma}(\boldsymbol{r})\right]$$

$$\Psi^\alpha_{\boldsymbol{k}\sigma}(\boldsymbol{r}) = \frac{1}{\sqrt{N_{s_\alpha}}}\sum_{i_\alpha} e^{i\boldsymbol{T}_i^\alpha\cdot\boldsymbol{k}}\,\Psi_{i_\alpha\sigma}(\boldsymbol{r})$$

two-dimensional case





antiferromagnetic case

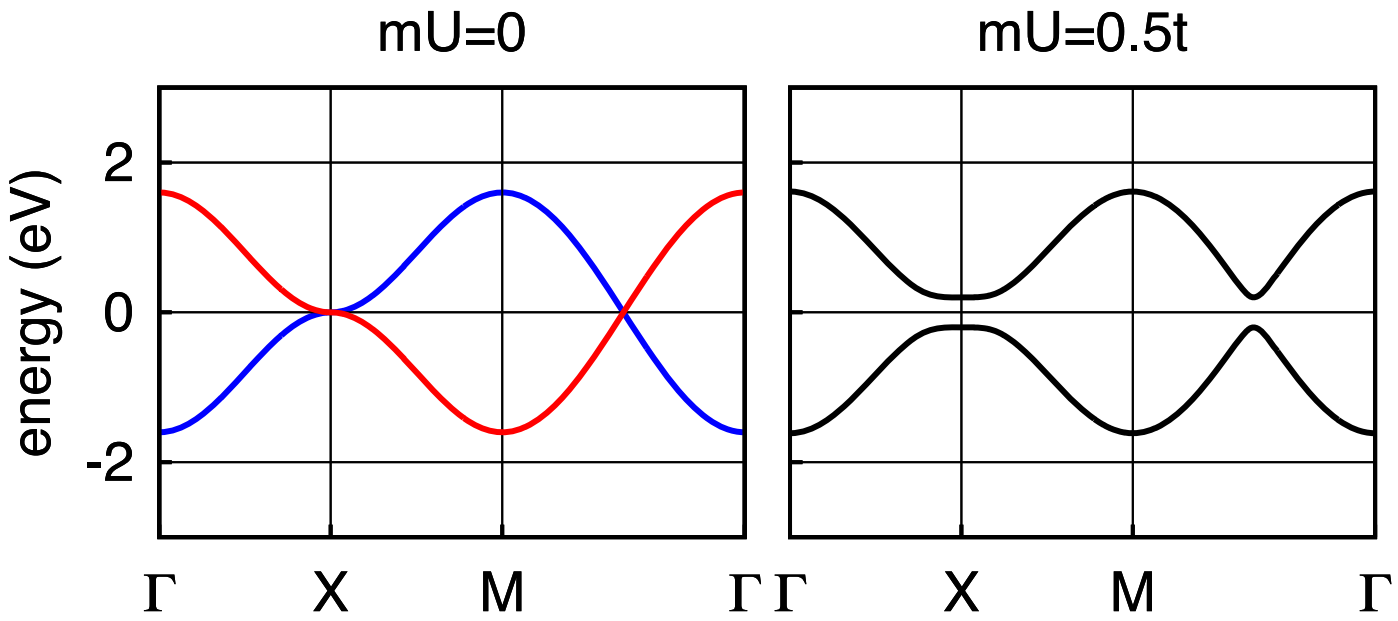
$$
\begin{aligned}
H &= \sum_{\boldsymbol{k}} \sum_{\sigma} \varepsilon_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{k}} \sum_{\sigma} \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}_2} n_{\boldsymbol{k}+\boldsymbol{Q}_2\sigma} \\
&+ U \sum_{\boldsymbol{k}} \left[-2m\, S_z(\boldsymbol{k}, \boldsymbol{k}+\boldsymbol{Q}_2) + 2m^2 + 2\frac{n^2}{4} \right]
\end{aligned}
$$

scattering function couples ***k*** and ***k*+*Q*$_2$**

$$
\varepsilon_{\boldsymbol{k}\pm} - \mu = \frac{1}{2}(\varepsilon_{\boldsymbol{k}} + \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}_2}) \pm \frac{1}{2}\sqrt{(\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}_2})^2 + 4(mU)^2}
$$

HF bands

antiferromagnetic case



gap: mU

$$\varepsilon_{\boldsymbol{k}\pm} - \mu = \frac{1}{2}(\varepsilon_{\boldsymbol{k}} + \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}_2}) \pm \frac{1}{2}\sqrt{(\varepsilon_{\boldsymbol{k}} - \varepsilon_{\boldsymbol{k}+\boldsymbol{Q}_2})^2 + 4(mU)^2}$$

HF bands

antiferromagnetic case

very large U case

half-filling, m=1/2

$$\varepsilon_{\boldsymbol{k}-} - \mu \sim -\frac{1}{2}U - \frac{\varepsilon_{\boldsymbol{k}}^2}{U} = -\frac{1}{2}U - \frac{4t^2}{U}\left(\frac{\varepsilon_{\boldsymbol{k}}}{2t}\right)^2$$

total energy

$$E_{\mathrm{AF}} = -\frac{1}{2}U - \frac{4t^2}{U}\frac{1}{N_{\boldsymbol{k}}}\sum_{\boldsymbol{k}}\left(\frac{\varepsilon_{\boldsymbol{k}}}{2t}\right)^2 \sim -\frac{1}{2}U - \frac{4t^2}{U}$$

energy difference

$$\Delta E^{\mathrm{HF}} = E^{\mathrm{HF}}_{\uparrow\uparrow} - E^{\mathrm{HF}}_{\uparrow\downarrow} = \frac{2}{n_{\langle ii' \rangle}} \left[E_{\mathrm{F}} - E_{\mathrm{AF}} \right] \sim \frac{1}{2} \frac{4t^2}{U} \sim \frac{1}{2} \Gamma$$

in this example for this quantity we obtain
the same result as in exact solution!

however, this is not the triplet-singlet splitting

$$\Delta E = E_{S=1} - E_{S=0} = \Gamma$$

Hartree-Fock problems

Slater vs Mott insulator

insulator with much smaller U than exact solution

gap in single HF calculation ~U

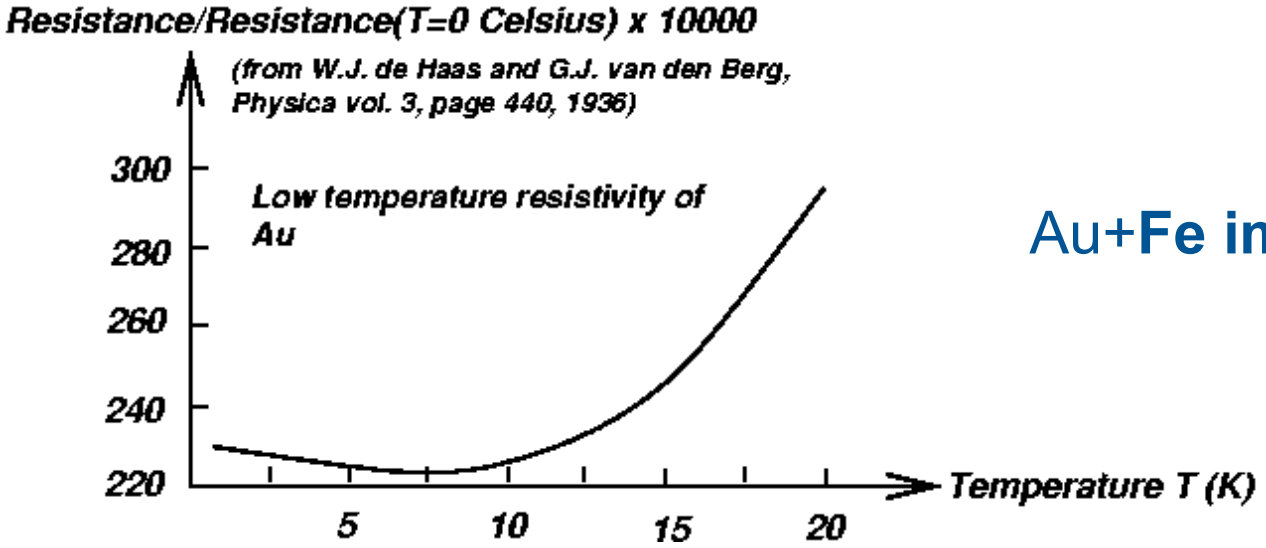
HF does not give correct spin excitation spectrum

NB. HF is used in the LDA+*U* approach

the Kondo effect

the Kondo effect

diluted magnetic alloys: metal+**magnetic** impurities



Au+**Fe impurities**

minimum in resistivity

high-temperature: impurity local moments, Curie susceptibility

low temperature: effective magnetic moment disappears
(Fermi-liquid susceptibility)

characteristic temperature: Kondo temperature T_K

Anderson model

metal impurity

$$H_{\mathrm{A}} = \sum_{\sigma}\sum_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma} + \sum_{\sigma} \varepsilon_f n_{f\sigma} + U n_{f\uparrow} n_{f\downarrow}$$

$$+ \sum_{\sigma}\sum_{\boldsymbol{k}} \left[V_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{f\sigma} + h.c. \right]$$

hybridization

Kondo regime: $n_f \sim 1$

canonical transformation (Schrieffer-Wolff) to Kondo model

$$H_{\mathrm{K}} = \sum_{\sigma}\sum_{\boldsymbol{k}} \varepsilon_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma} + \Gamma \boldsymbol{S}_f \cdot \boldsymbol{s}_c(\boldsymbol{0}) = H_0 + H_{\Gamma}$$

$$\Gamma \sim -2|V_{k_F}|^2 \left[\frac{1}{\varepsilon_f} - \frac{1}{\varepsilon_f + U} \right] > 0$$

antiferromagnetic coupling

susceptibility

high-temperature impurity susceptibility

$$\chi^f_{zz}(T) \sim \frac{(g\mu_B)^2 S_f(S_f+1)}{3k_BT}\left\{1-\frac{1}{\ln\left(T/T_{\rm K}\right)}\right\}$$

Kondo temperature

$$k_BT_{\rm K} \sim De^{-2/\rho(\varepsilon_F)J}$$

low-temperature impurity susceptibility

$$\chi^f_{zz}(T) \sim \frac{C_{1/2}}{\mathcal{W}T_{\rm K}}\left\{1-\alpha T^2+\dots\right\}$$

Fermi liquid!

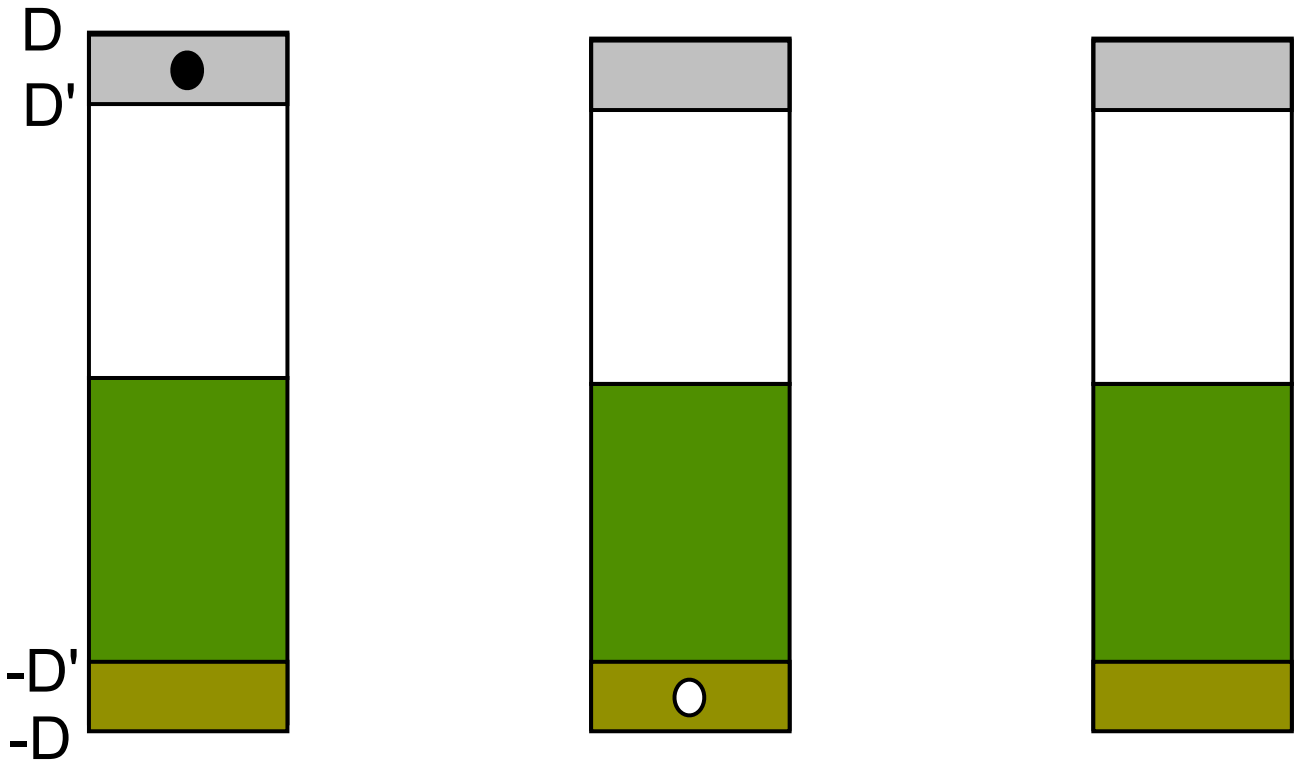
$$\mu^2_{\rm eff}(T) \equiv 3k_BT\chi^f_{zz}(T) \propto \langle S^f_z S^f_z\rangle + \langle S^f_z s^c_z\rangle$$

magnetic moment screened, S=0

poor's man scaling

eliminate high-energy states, i.e., the states with

- at least one electron in high-energy region ●
- at least one hole in high-energy region ○



- one electron
- one hole
- low-energy state

downfolding

electron case: projectors

$$P_H \sim \sum_\sigma \sum_{\boldsymbol{q}} c^\dagger_{\boldsymbol{q}\sigma} |FS\rangle\langle FS| c_{\boldsymbol{q}\sigma}$$ high-energy sector

$$P_L \sim \sum_\sigma \sum_{\boldsymbol{k}} c^\dagger_{\boldsymbol{k}\sigma} |FS\rangle\langle FS| c_{\boldsymbol{k}\sigma}$$ low-energy sector

effect of downfolding high sector at second order

$$\delta H_L^{(2)} \sim P_L H_\Gamma P_H (\omega - P_H H_0 P_H)^{-1} P_H H_\Gamma P_L$$

electron contribution

$$\begin{aligned} \delta H_L^{(2)} &= -\frac{1}{2}\Gamma^2 \sum_{\boldsymbol{q}} \frac{1}{\omega - \varepsilon_{\boldsymbol{q}}} \boldsymbol{S}_f \cdot \boldsymbol{s}_c(\boldsymbol{0}) + \ldots \\ &\sim \frac{1}{4}\rho(\varepsilon_F)\Gamma^2 \frac{\delta D}{D} \boldsymbol{S}_f \cdot \boldsymbol{s}_c(\boldsymbol{0}) + \ldots \end{aligned}$$

scaling equations

thus the Kondo Hamiltonian is modified as follows

$$\begin{aligned} \Gamma &\rightarrow \Gamma' = \Gamma + \delta\Gamma, \\ \frac{\delta\Gamma}{\delta \ln D} &= \frac{1}{2}\rho(\varepsilon_F)\Gamma^2 \end{aligned}$$

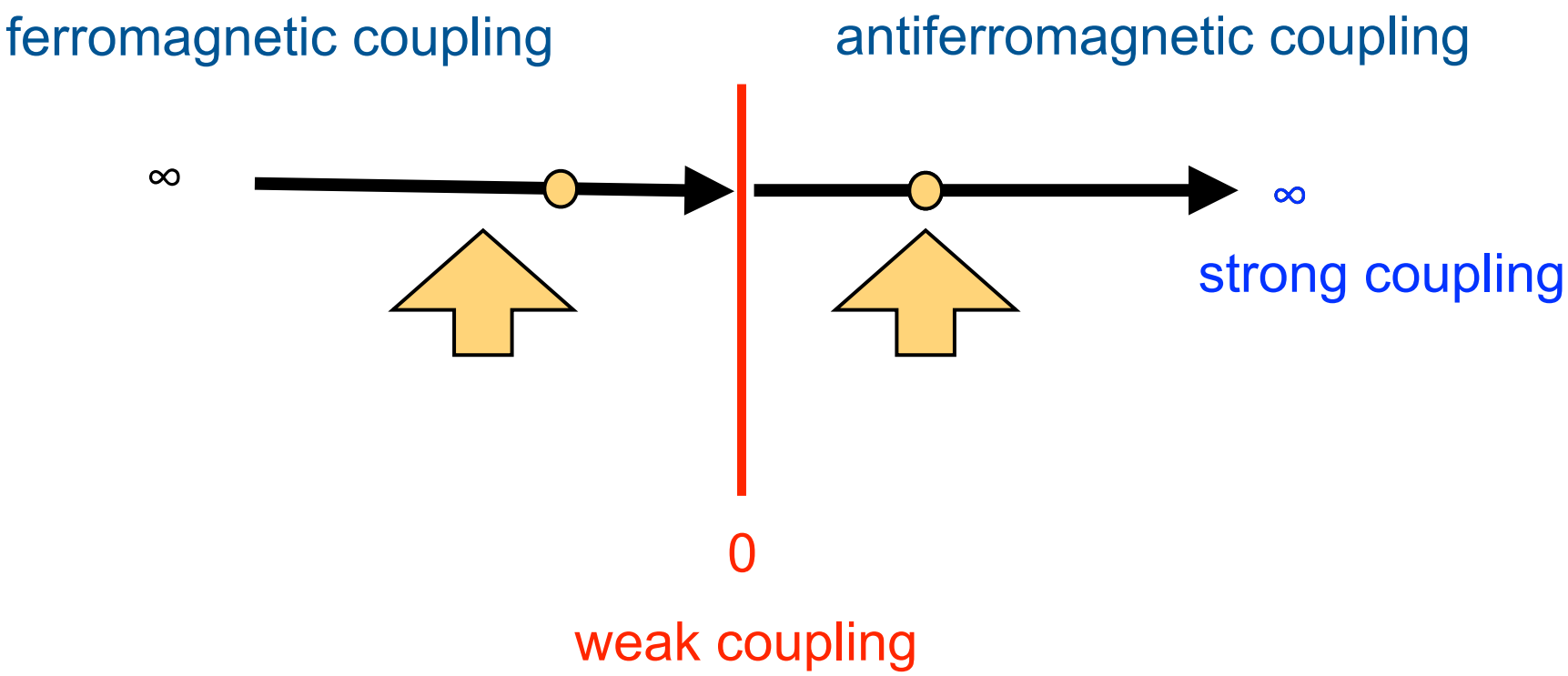
scaling equations

$$\Gamma' = \frac{\Gamma}{1 + \frac{1}{2}\rho(\varepsilon_F)\Gamma \ln \frac{D'}{D}}.$$

scaling equations

$$\Gamma \rightarrow \Gamma' = \Gamma + \delta\Gamma,$$

$$\frac{\delta\Gamma}{\delta \ln D} = \frac{1}{2}\rho(\varepsilon_F)\Gamma^2$$



strong coupling case

one electron screens local moment

spin zero system!

starting point for perturbation theory

nearby electrons polarize moment via virtual excitations

effective repulsive on-site Coulomb interaction

Nozières Fermi liquid

weak coupling case

asymptotic freedom

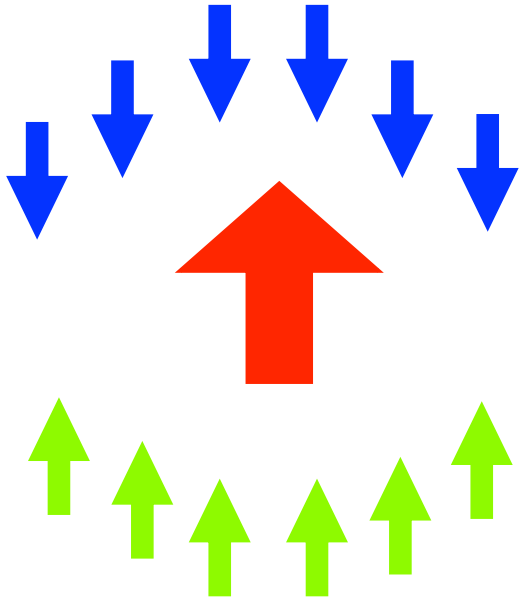
non-interacting local moment

Curie susceptibility

magnetic interaction as perturbation

scaling: two-channel case

conduction band A



kinetic exchange: AFM

conduction band B

Coulomb exchange: FM

situation realized in some Ce and Yb alloys

Kondo or Curie?

scaling: two-channel case

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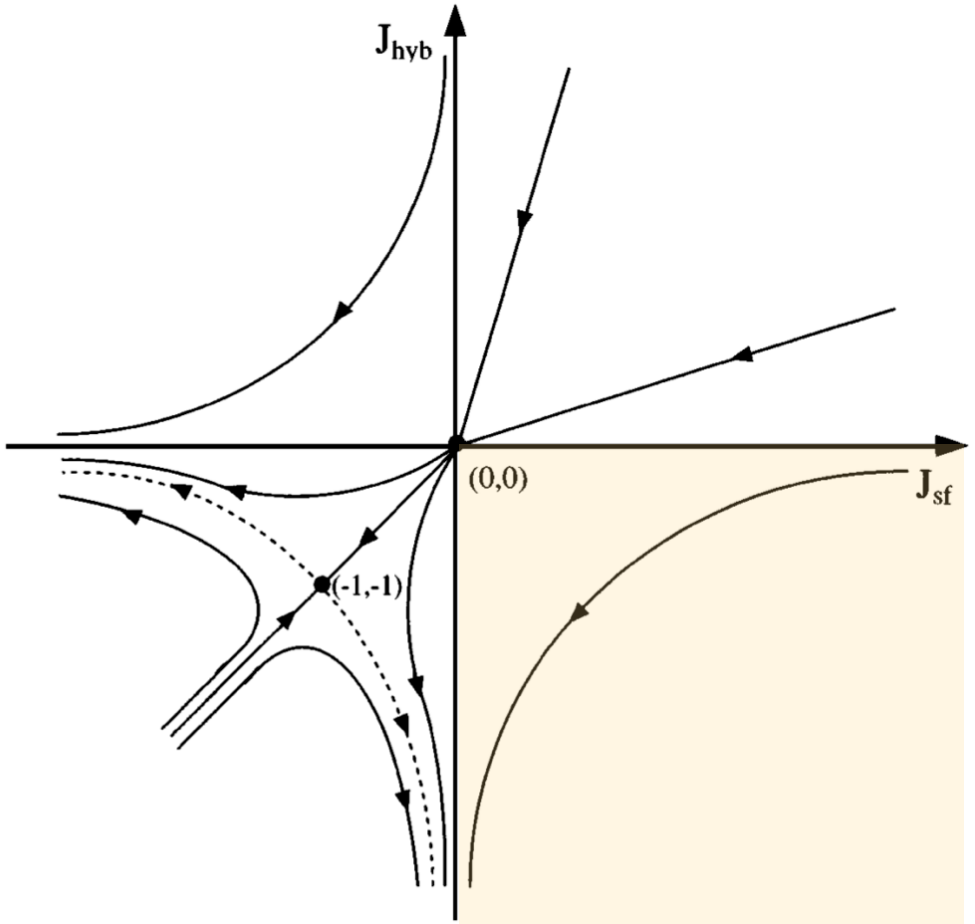
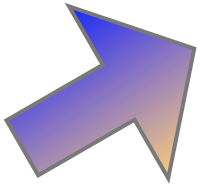
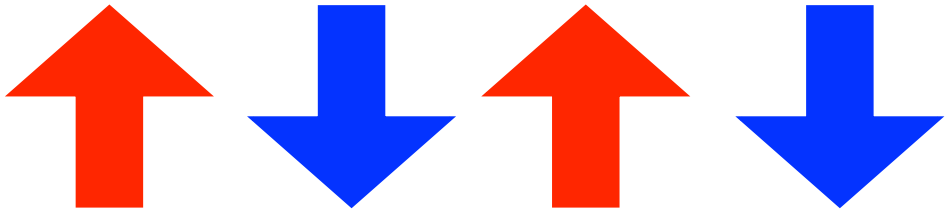
Hybridization versus Local Exchange Interaction in the Kondo Problem: A Two-Band Model

Eva Pavarini and Lucio Claudio Andreani

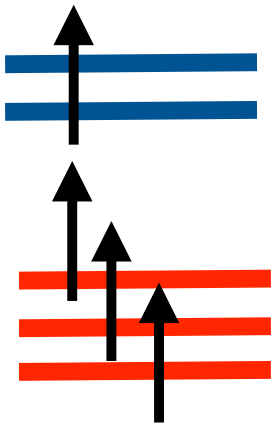


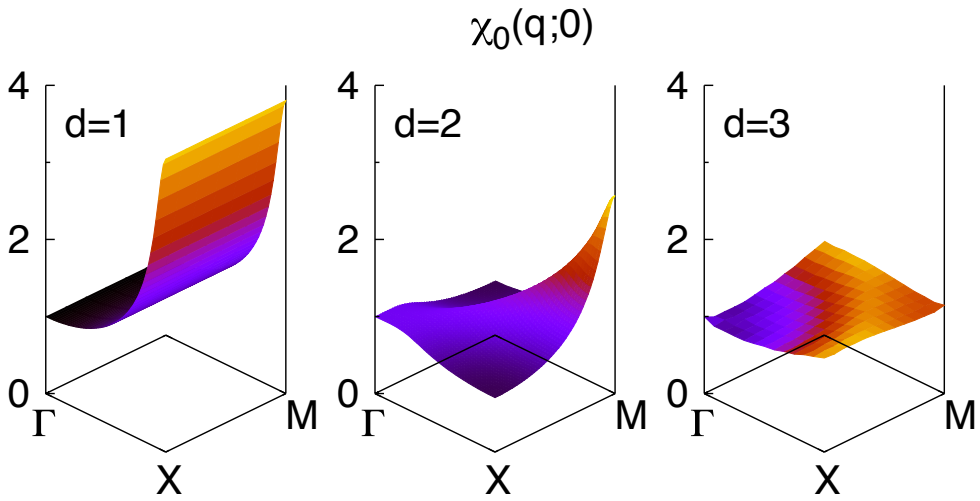
conclusion





- emergence of spin
- emergence of long-range order





- local moment regime
  Curie and Curie-Weiss susceptibility
  Heisenberg model
- itinerant regime
  Pauli susceptibility
  Stoner instabilities

in strongly correlated system both local and delocalized features present

thank you!