

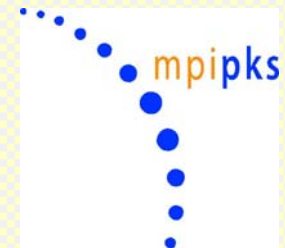
Workshop on
Surface Spin Correlations

28. – 30. September 2006

**Electron correlations:
which changes do we
expect at surfaces?**

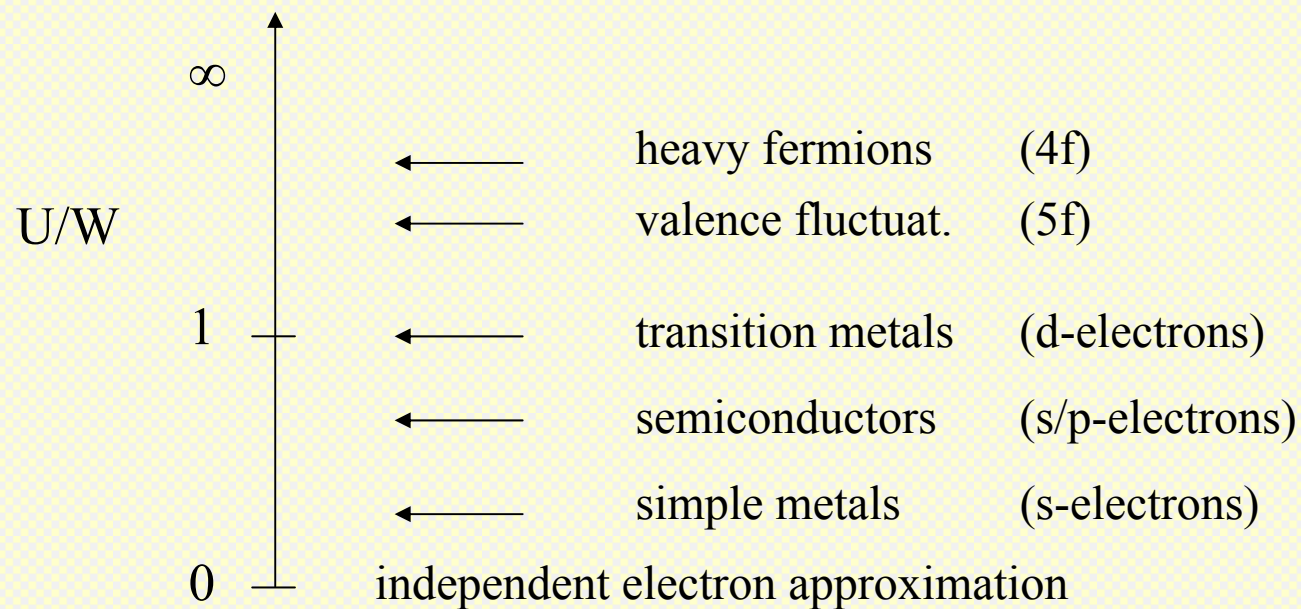


Universität Hamburg



Electronic motion in solids is governed by:

- (a) overlaps of atomic wavefunctions (W) \Rightarrow delocalization
 (b) mutual Coulomb repulsion (U) \Rightarrow localization



also: stretched lattice parameter, e.g, of diamond $a \rightarrow \infty$

Coulomb repulsion of electrons \rightleftarrows electrons avoid each other

\rightleftarrows correlation hole

electron + correlation hole = quasiparticle

Hartree-Fock approximation: electrons move independently

\rightleftarrows wavefunction of the system is product of one-particle wavefunctions

$$\Phi_0(\mathbf{r}_1\sigma_1; \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N) = A[\phi_1(\mathbf{r}_1\sigma_1) \cdots \phi_N(\mathbf{r}_N\sigma_N)]$$

Slater determinant — with correlation hole:

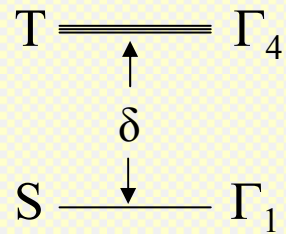
$$\psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_{i < j} f(\mathbf{r}_i, \mathbf{r}_j) \Phi_0(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

$$\text{Jastrow ansatz} = \exp \left[\sum_{i < j} g(\mathbf{r}_i, \mathbf{r}_j) \right] \Phi_0(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

Magnetism in 4f systems

Surfaces of Van Vleck ferro- and paramagnets

e.g., Pr : $4f^2$ non-Kramers ion , CEF splitting of $J = 4$ multiplet



$$H = \sum_i H_{\text{CEF}} - \sum_{\langle ij \rangle} K_{ij} \mathbf{J}_i \cdot \mathbf{J}_j \quad \text{cubic environm.: } \Gamma_1, \Gamma_3, \Gamma_4, \Gamma_5$$

single site suscept:
$$u(T) = \frac{20}{3} \frac{2}{\delta} \frac{1 - e^{-\delta/T}}{1 + 3e^{-\delta/T}} + \frac{1}{2T} \frac{e^{-\delta/T}}{1 + 3e^{-\delta/T}}$$

bulk suscept:
$$\chi(\mathbf{q}, T) = \frac{u(T)}{1 - K(\mathbf{q})u(T)}$$

induced magnetism:
$$K(\mathbf{q}_0)u(T_c) = 1$$

$\mathbf{q}_0 = 0$ ferromagn.

$\mathbf{q}_0 = \mathbf{Q}$ antiferromagn.

at **surface**: CEF quite different from bulk ,

cubic:
$$H_{\text{CEF,b}} = B_4^0 (O_4^0 + 5O_4^4) + B_6^0 (O_6^0 - 21O_6^4)$$

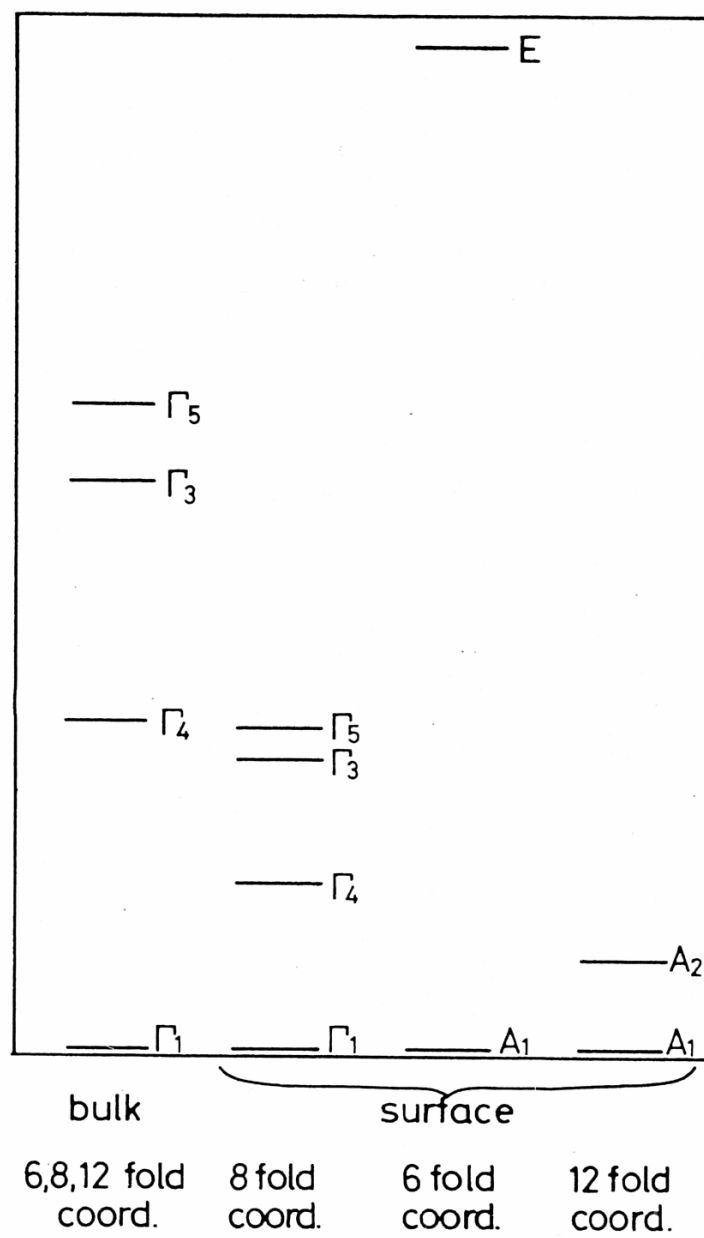
$$H_{\text{CEF,s}} = B_2 O_2^0 + B_4' O_4^0 + B_4'' 5O_4^4 + B_6' O_6^0 - B_6'' 21O_6^4$$

example: 8-fold coordination $\Rightarrow B_2 = 0 \quad B_4' = B_4'' = \frac{1}{2} B_4^0 \quad , \quad B_6' = B_6'' = \frac{1}{2} B_6^0$

\Rightarrow CF splitting at surface half as large

$\Rightarrow T_{\text{cs}} > T_{\text{cb}} \quad \text{or} \quad T_{\text{cs}} \neq 0 \quad \text{while} \quad T_{\text{cb}} = 0$

(I. Peschel, P. F., Z. Phys. 1973)



Transition Metals: correlation effects

Hamiltonian: $H = \sum_{\nu\sigma\mathbf{k}} \varepsilon_{\nu}(\mathbf{k}) n_{\nu\sigma}(\mathbf{k}) + \sum_{\ell} H_1(\ell)$ extended Hubbard

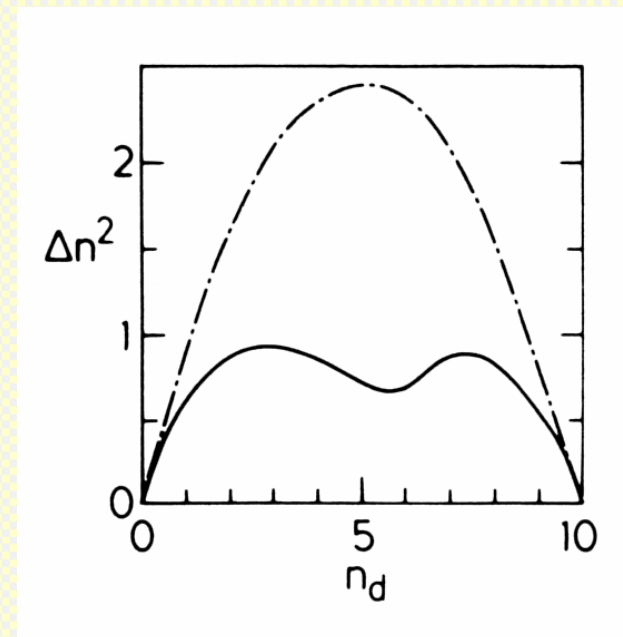
$$H_1(\ell): \begin{array}{lll} U + 2J & i = j & (\sigma = -\sigma') \\ U - J & i \neq j & \sigma = \sigma' \\ U & i \neq j & \sigma = -\sigma' \end{array}$$

reduction of **charge fluctuations**

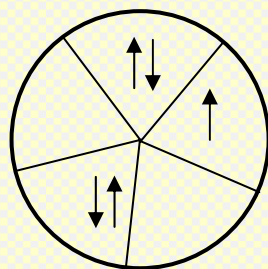
(interatomic correl.)

$$U/W = 0.5 \quad J/W = 0.1$$

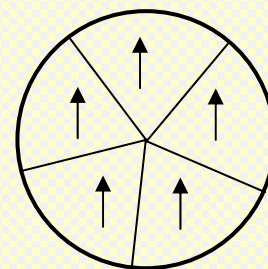
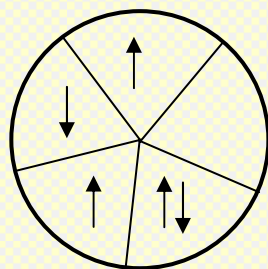
$$\Delta n^2 = \langle n^2(i) \rangle - \langle n(i) \rangle^2$$



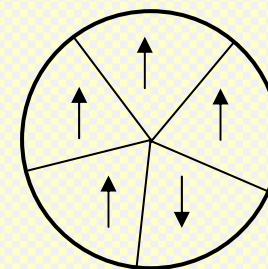
Intra-atomic correlations



unfavourable

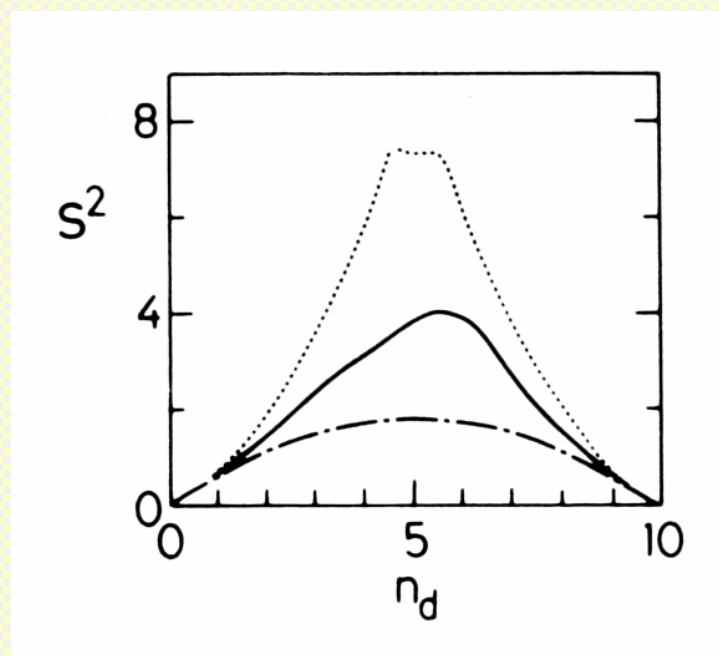


favourable

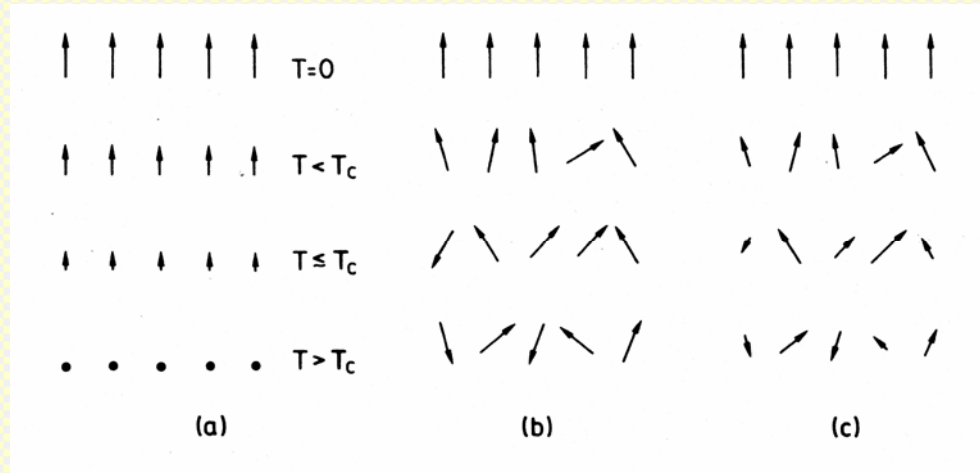


build-up of **Hund's rule correlat.**

$$\Delta S^2 = \frac{\langle S^2 \rangle - S_{\text{HF}}^2}{S_{\text{loc}}^2 - S_{\text{HF}}^2}$$



Finite temperatures

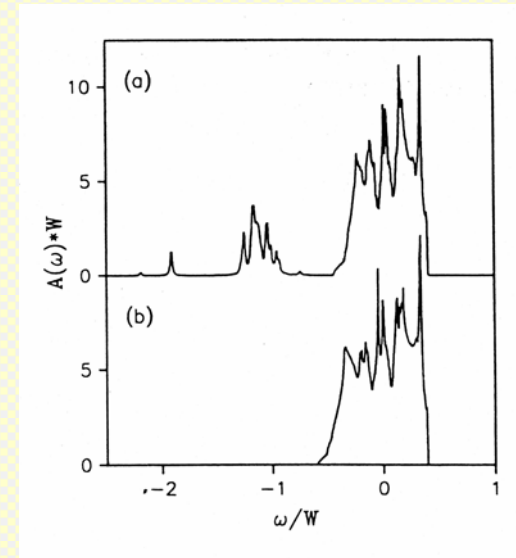


(a) convent. band theory (itiner. electr.)

(b) localized electrons

(c) electrons in transition metals

Satellite structure



e.g., Ni from $d^9 \rightarrow d^8$


$n_d=9.4$ $U/W=0.56$ $J/W=0.22$

(project. technique)

Ni : expected changes at surface

- smaller number of **neighbors**: fcc bulk: 12 [001]:8 ; [110]:7 ; [111]:9


$$W_s \approx \frac{2}{3} W_{\text{bulk}} \quad ; \quad \text{d electrons more localized, increase in Hund's correlat.}$$

 lowering of T_c

- **lower symmetry** of CEF: t_{2g} splits into d_{xy} and $d_{xz} + d_{yz}$ (filled)

at [001] surface

- **flow of charge**: estimate 0.1 el./surf. atom

- **redistribution** of s and d electrons: Ni atom  $[\text{Ar}] 3d^8 4s^2$

increase of d-holes from 0.6 to ≈ 1.0

like 2D **impurity layer**

possible appearance of broadened **surface resonance** states

several MF surface solution: **ferro- or antiferromagn.** coupling to bulk
(paramagn. solution is much higher in energy)

small energy differences between F and AF solutions

flips of surface magnetization with T ?

H. Takayama et al., Phys. Rev. B **10**, 2022 (1974)

$M_s \rightarrow 0$ at $T_{cs} < T_{c_{bulk}}$?

Satellite structure :

at surface **more d^9** configurat. than in bulk \Rightarrow **larger** intensity expected

Metal-Insulator Transition

Mott-Hubbard
$$H = -t \sum_{\langle ij \rangle_{\sigma}} (c_{i\sigma}^{\dagger} c_{j\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

M-I transition at **half-filling** if $U/t > (U/t)_{\text{crit}}$, **CPA** equations

sc-lattice: $9 \lesssim (U/t)_{\text{crit}} \lesssim 11$

VO₂  **bulk**: MIT $T_{\text{MI}} = 340\text{K}$ (rutile \rightarrow monoclinic struct. change)

surface: $T_{\text{MI,S}} > T_{\text{MI}}$

„impurity sheet“ , **AF** coupling of surface sites

paramagnet. bulk \rightarrow Kondo coupling to „impurities“

interplay between the two

Charged surfaces

NiO \Rightarrow NaCl structure

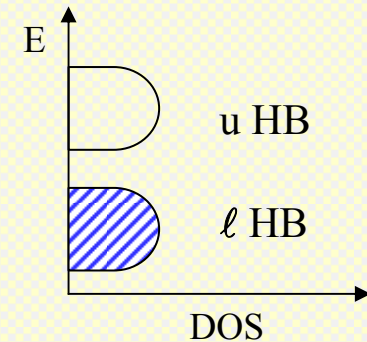
bulk: Ni²⁺ O²⁻ Ni²⁺: 8 valence el., e_g holes

lower + upper Hubbard band \Rightarrow insulator

[111] surface: one type of atoms only

\Rightarrow dipoles

Ni surface: Ni⁺ \Rightarrow surface might be metallic



5f electrons of surface layer

dual model for 5f electrons of U intermetallic systems:

electrons in some of the 5f orbitals remain localized while they delocalize in others

(G. Zwicknagl, P. F.)

physical reason: assume $n_{5f} \approx 2.5$ \Rightarrow 50 % of atoms with $5f^3$
 50 % of atoms with $5f^2$
 (strong intra-atomic correl.)

when $5f^3 \rightarrow 5f^2$ \Rightarrow remaining two electrons should be able to form **Hund's rule** ground state ($J = 4$)

UPd₂Al₃: $n_f \approx 2.6$ $5f^2$: localized in $j = 5/2, |j_z| = 5/2, 1/2$ orbitals
 delocalized in $|j_z| = 3/2$ orbitals

$J = 4, J_z = \pm 3$ \Rightarrow splitting in CEF

\Rightarrow explains large **anisotropic effective m^*** (**de Haas – van Alphen**)

layered structure : U-Pd planes separated by Al layers

at surface :

if Al layers at surface \Rightarrow screening \Rightarrow U does not see much of surface

if U-Pd layer at surface \Rightarrow sensitivity to oxygen, CEF changes

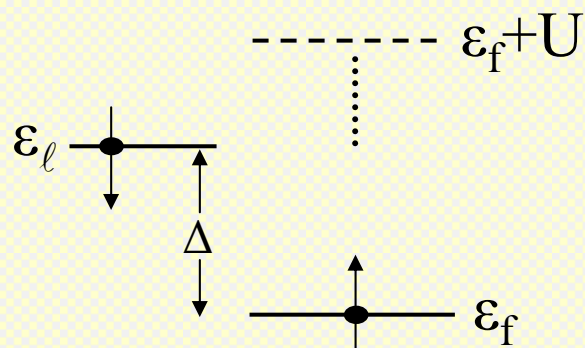
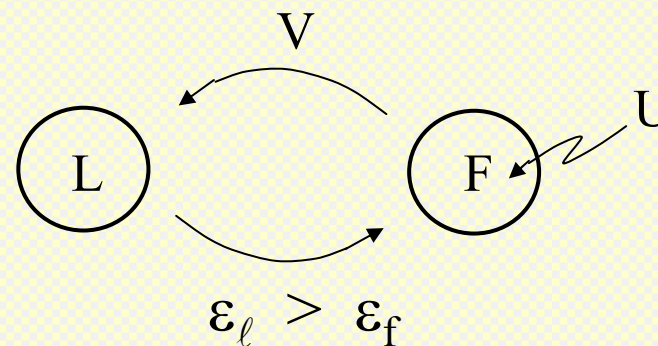
$J_z = \pm 3$ splitting changes and m^* changes

Kondo effect

simplest model:

2 electrons

2 orbitals

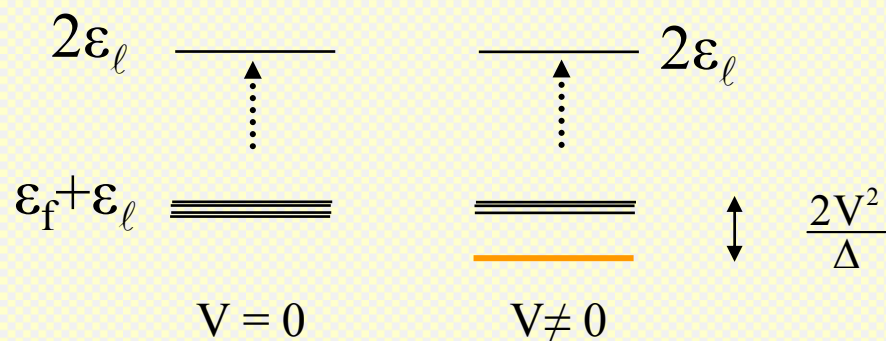


$V = 0$

ground state = four fold degenerate
singlet + triplet

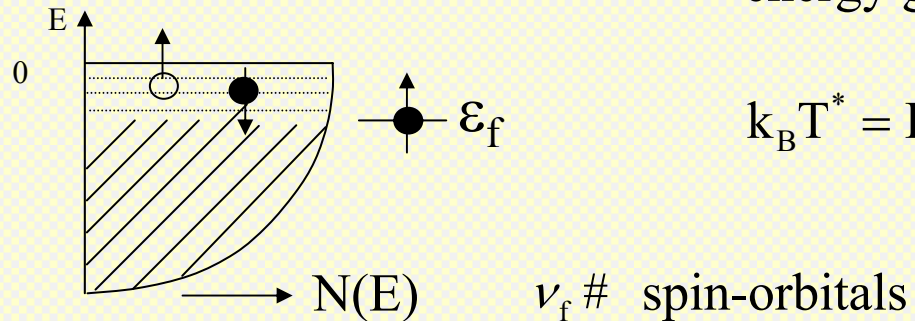
$V \neq 0$

singlet has lower energy



energy gain $k_B T^* = \frac{2V^2}{\Delta}$

bulk metallic system



Kondo effect at a surface

Cu (111)

adatom at surface , e.g., Co on Cu (111) plane

V is changed (less hybridization)

$N(0)$ is changed surface states

ϵ_d is changed (decreased) at surface

several Kondo ions: when T_K is decreased RKKY may win