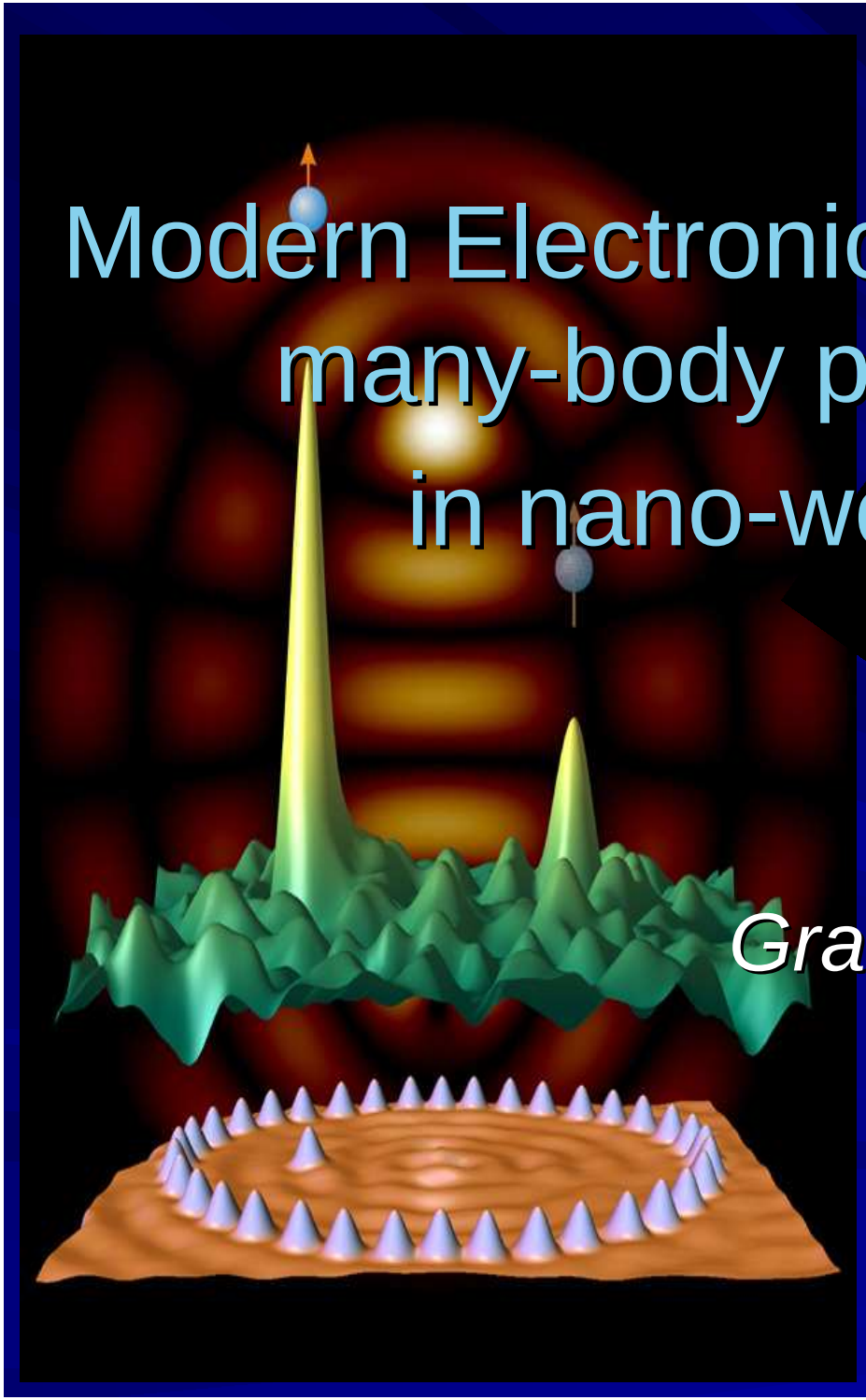
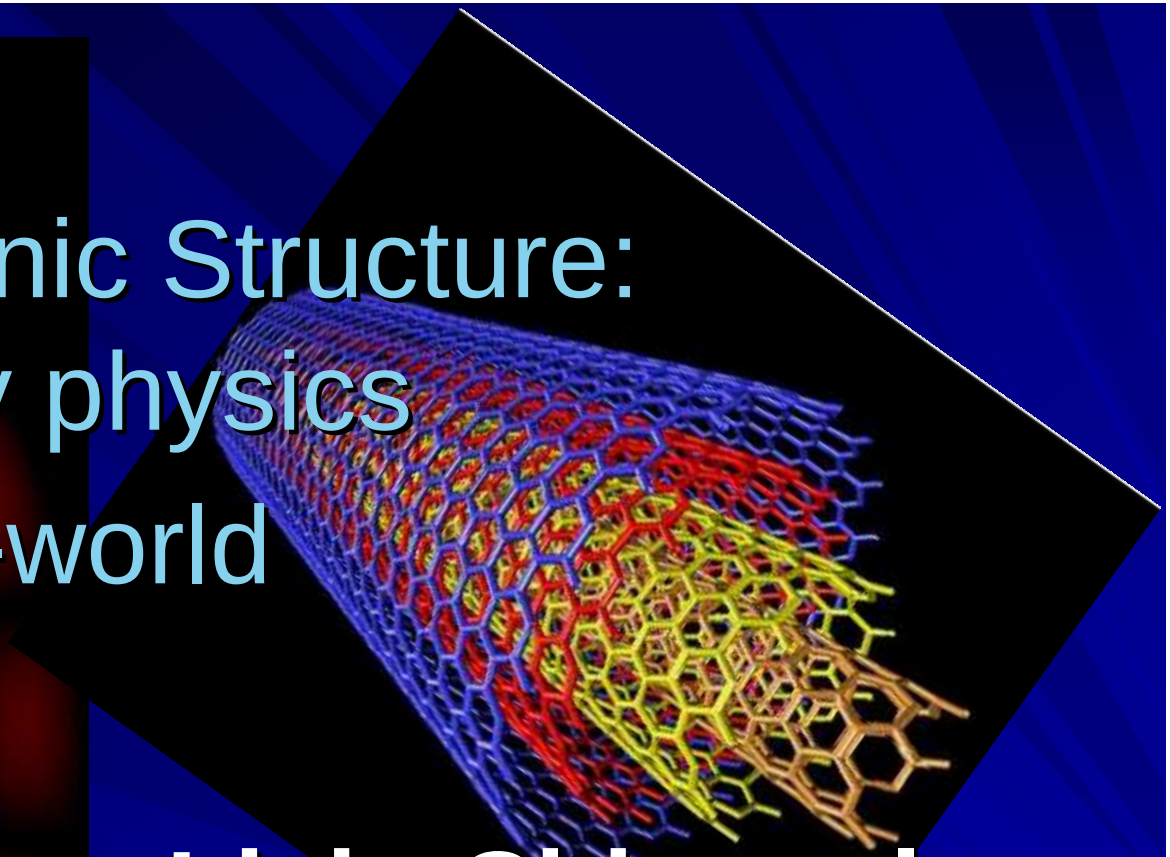
# Modern Electronic Structure: many-body physics in nano-world





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*Graz University of Technology*

Austria

*Universitatea din Oradea*

*Romania*

# Content

- NANO  scale
  - More than just length and size
- Electronic structure,
  - Density Functional Theory, implementations
- Many-body physics and electronic structure
  - Dynamical Mean Field Theory (DMFT)
- Magnetism in nanosystems
  - Molecular magnets
  - Surface states vs. Kondo effect
  - Correlated adatom on a metal surface

# Nano-scales in every day life

Aircraft Carrier

Boeing 747

Car

**Humans**

1 m

Laptop

**Butterfly**

← Microprocessor

1 mm

← Resolving power of the eye ~ 0.2 mm

Micromachines

**Biological cell**
**Nucleus of a cell**

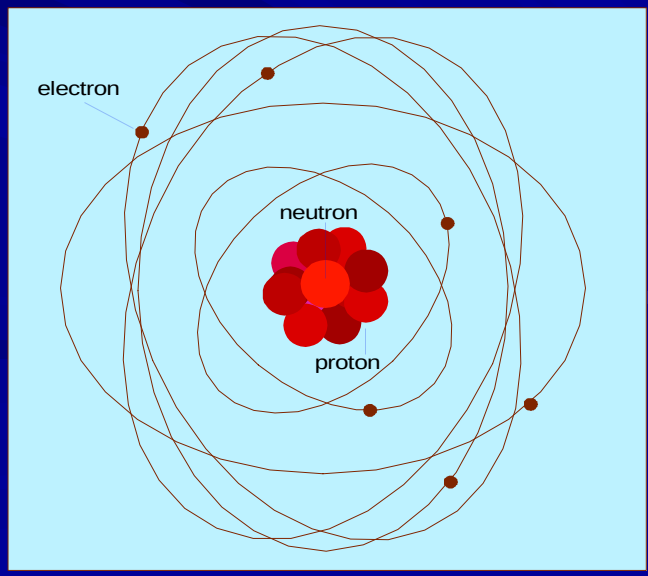
1 µm Visible Light

Microelectronic chips

**Proteins**
**Width of DNA**

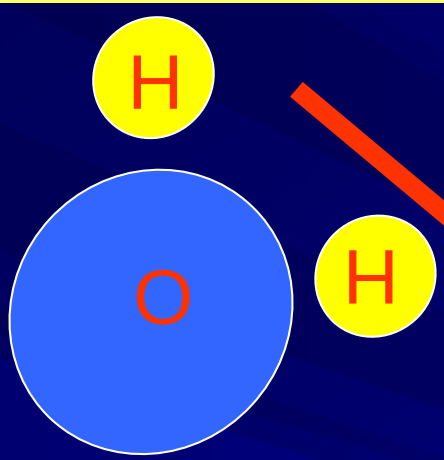
Nanostr. & Quantum Devices

1 nm Size of an atom

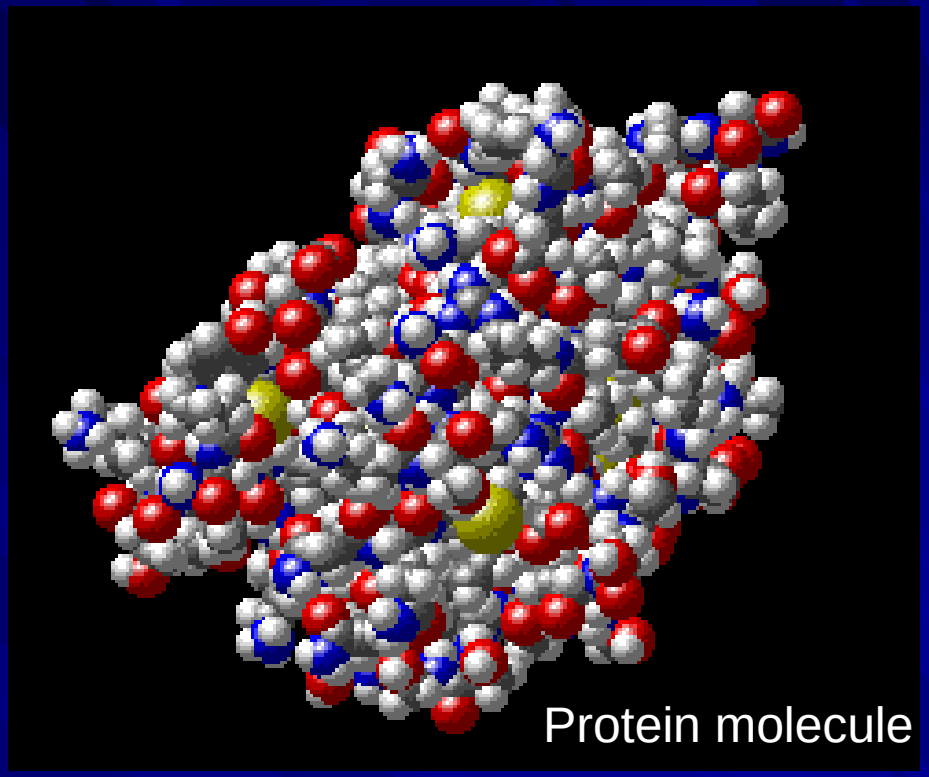


# Nano-scale in numbers

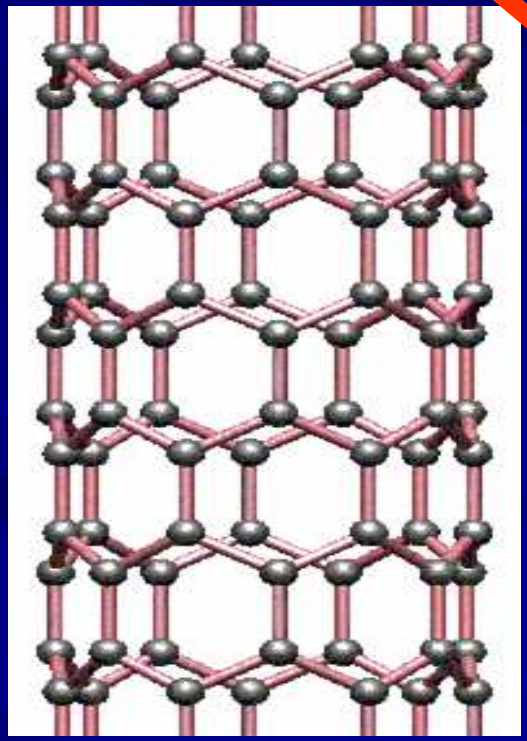
Water molecules – 3 atoms



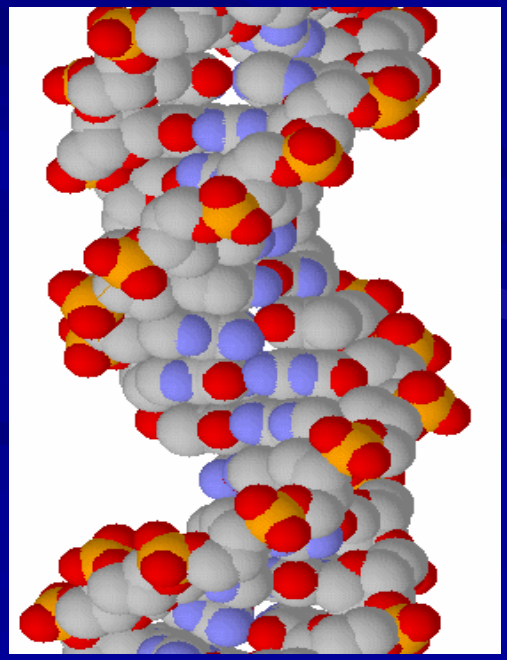

thousands




Carbon nanotube

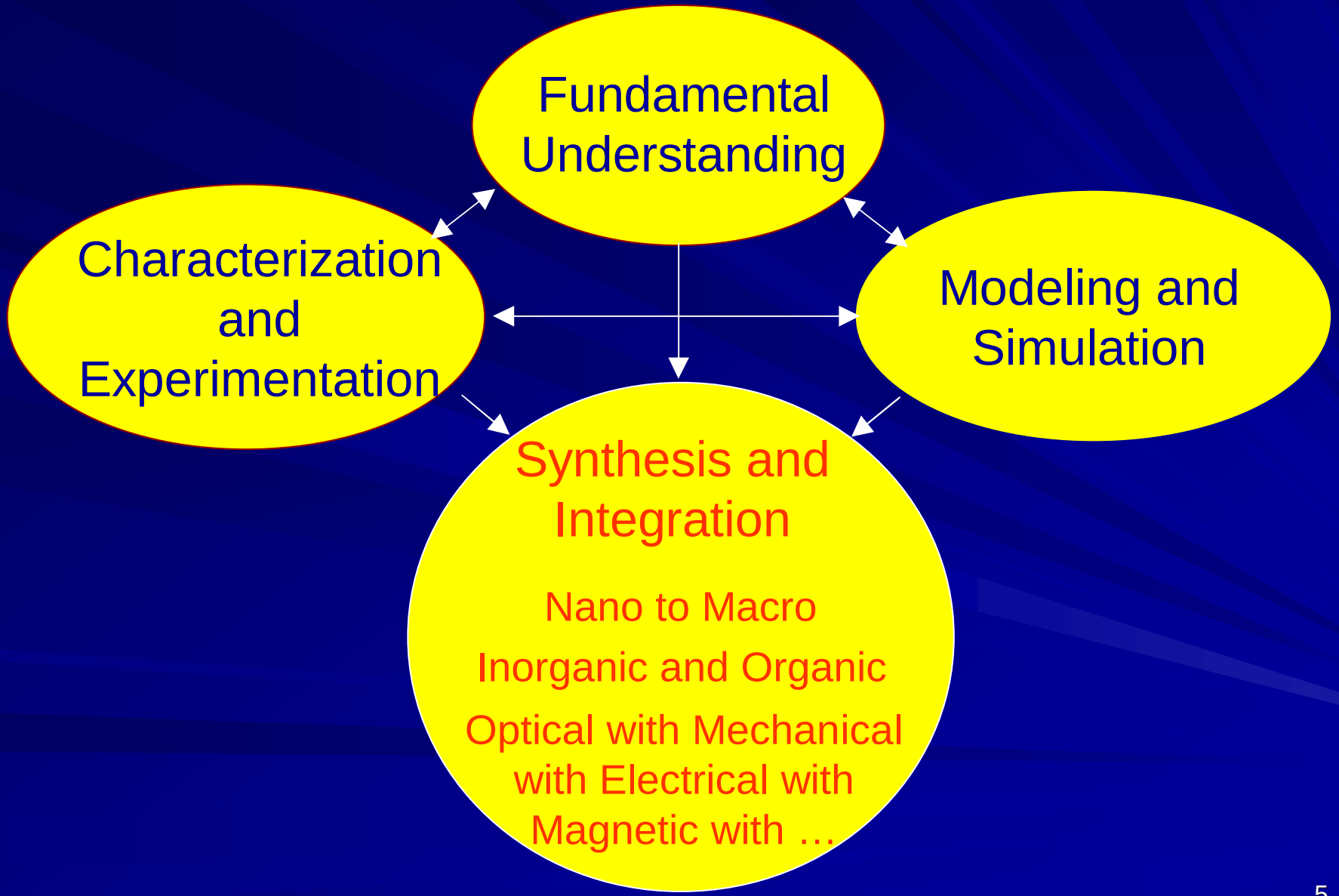


milions



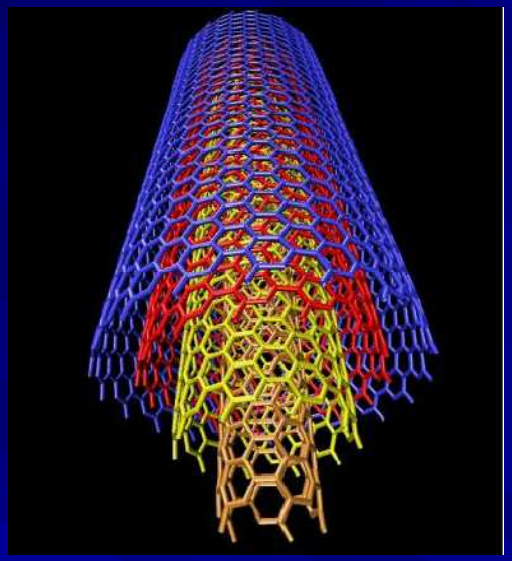
Molecule of DNA

# Development of Nanotechnology

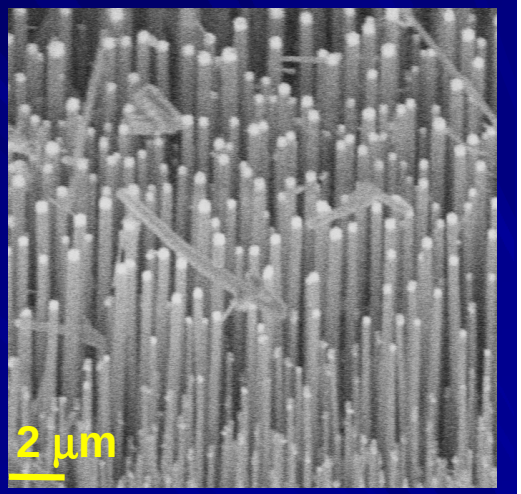


# Nanostructures
# (At least one dimension is between 1 - 100 nm)

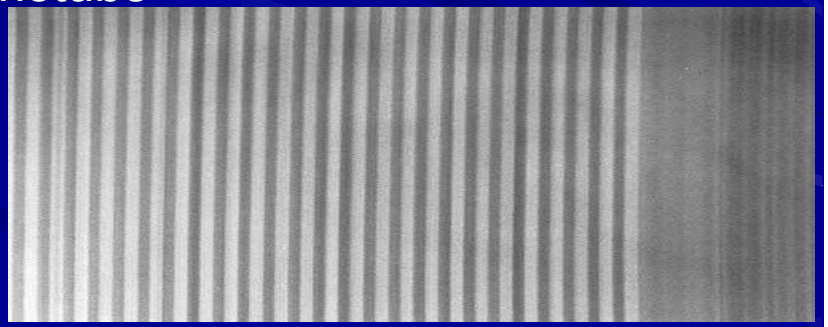
- 2-D structures (1-D confinement):
  - Thin films
  - Planar quantum wells
  - Superlattices
- 1-D structures (2-D confinement):
  - Nanowires
  - Quantum wires
  - Nanorods
  - Nanotubes
- 0-D structures (3-D confinement):
  - Nanoparticles
  - Quantum dots



Multi-wall carbon nanotube




Si Nanowire Array



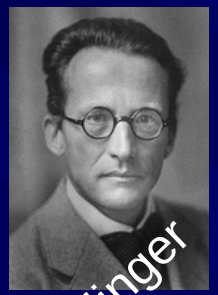
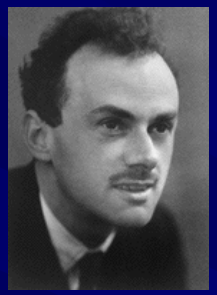
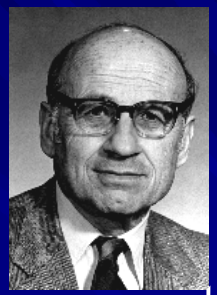
$Si_{0.76}Ge_{0.24}$ / $Si_{0.84}Ge_{0.16}$ superlattice

# NaNo....

- “The art of understanding / developing materials on an atomic or molecular scale with the aim of building devices.”

# Condensed matter physics

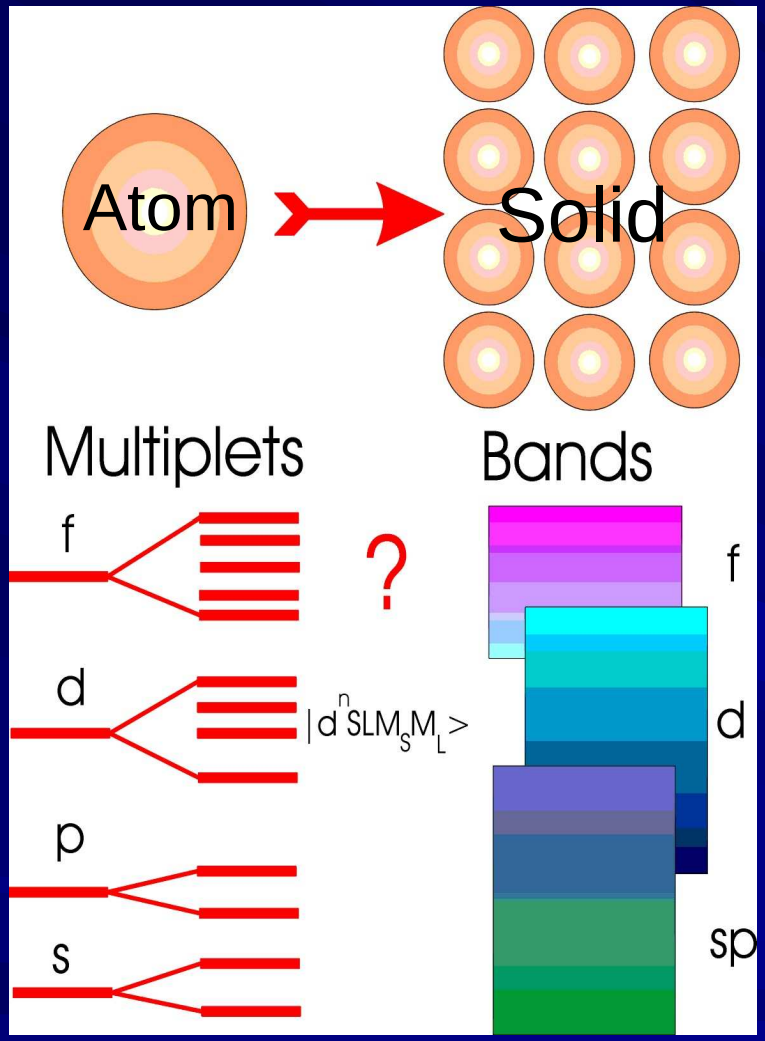
## Quantum theory & Electronic structure

1900 Planck
'26 Schrodinger
'28 Dirac
'37 APW
'59 Pseudopotential
'64 DFT
'75 LMTO, LAPW
'85 Car-Parrinello
1998 Nobel Prize Kohn
2007
1900
'27 Fermi
'30 Hartree
'51 Slater X
'72 LSDA
'86 GGA
'91 LDA+U
'96 DMFT



# Electrons in solids




- Effective potential
- Bloch states
- Pauli principle

} FERMI sea

1964

**Density Functional Theory (DFT)**

- Effective one-particle states
- Local Density Approximation (LDA)

**?** Behaviour at different dimensions

# Density Functional Theory (DFT)

many-particle interacting system → non-interacting reference system

$$F[\rho(r)] = F_H[\rho(r)] + F_{xc}[\rho(r)]$$

$$F_H[\rho(r)] = \frac{1}{2}\int dr dr' \, \rho(r) V_{e-e} \rho(r')$$

$$F_{xc}[\rho(r)] = \frac{1}{2}\int dr dr' V_{e-e} \int_0^1 d\alpha g_\alpha[\rho, r, r']$$

Hohenberg-Kohn theorems:

1. Existence of the single particle density of a non-degenerate ground state of an interacting electron system

2. Variational principle The total energy of the N-electron system is minimized by the ground state electron density

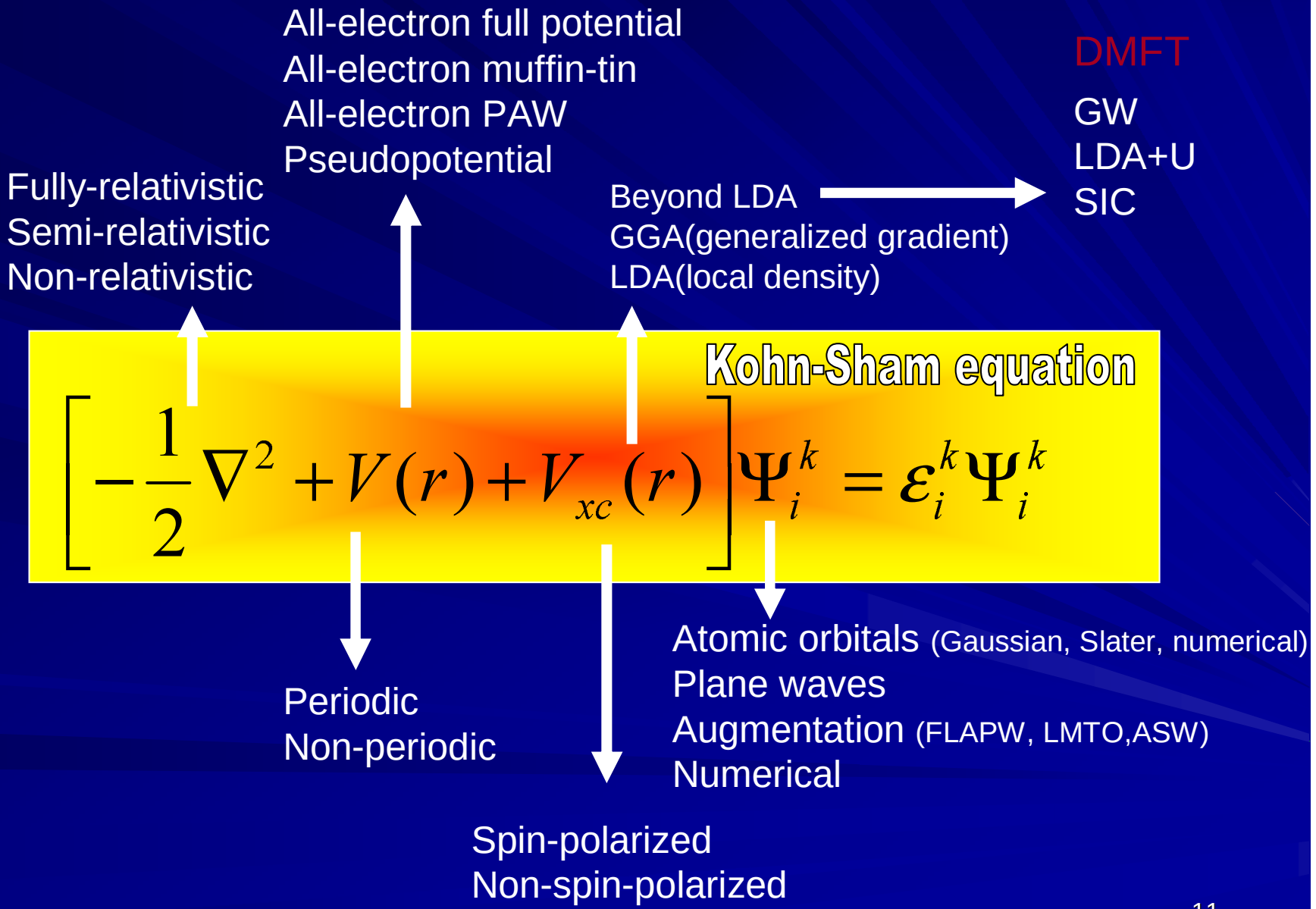
Local density approximation

$$g_\alpha[\rho, r, r'] = \langle (n(r) - \rho(r))(n(r') - \rho(r')) \rangle$$

$$g_\alpha[\rho, r, r'] = \left[ \frac{\delta F_\alpha}{\delta\rho\delta\rho'} \right]_{rr'}$$

$$F_{xc}^{LDA}[\rho(r)] = \frac{1}{2}\int dr \rho(r) \varepsilon_{xc}^{LDA}[\rho(r)]$$

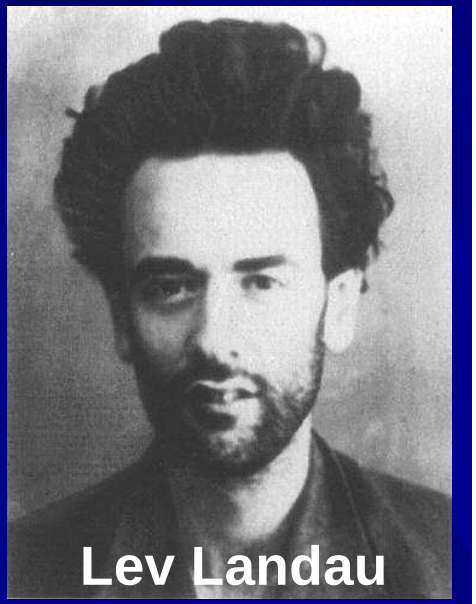
# DFT implementations: choices of the methods



# How well performs the DFT-LSDA

- **The Fermi Liquid Theory (1957-59):**
  - Quasiparticles - weak interactions
  - Interactions - slowly switched on
  - Energy levels - modified
  - Eigenstate - given by occupation number

$$E = \sum_{\sigma,k} n_\sigma(k)\varepsilon(k) + \frac{1}{2}\sum_{\sigma,\sigma',k,k'} f_{\sigma,\sigma'}(k,k')n_\sigma(k)n_{\sigma'}(k')$$

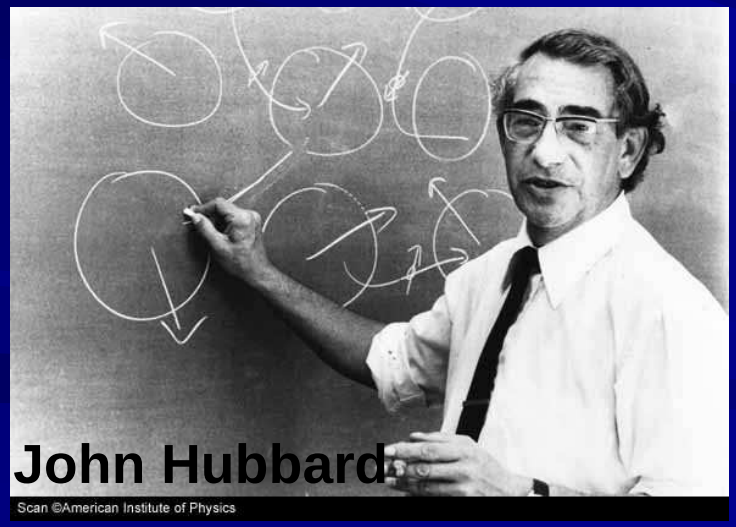

Lev Landau

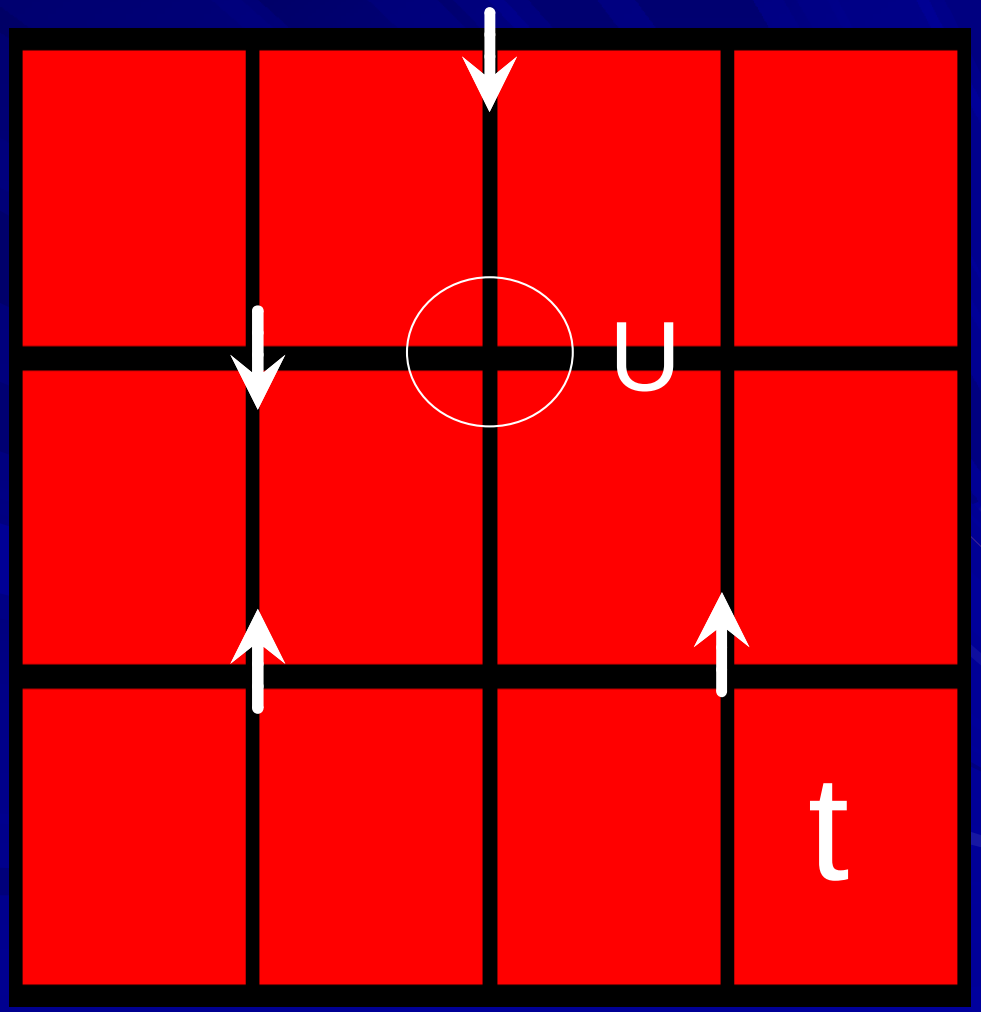
- **DFT-LSDA - fails for correlated electrons…**
  - Mott insulators (long range order) V2O3
  - High Tc superconductors (quasi 2D)
  - Organic conductors (quasi 1D)
  - Quantumdots (0D)

# Correlated electrons on lattices

$$H = \sum_{ij} \left( t_{ij} + \mu \delta_{ij} \right) \cdot c_{i\sigma}^{+} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

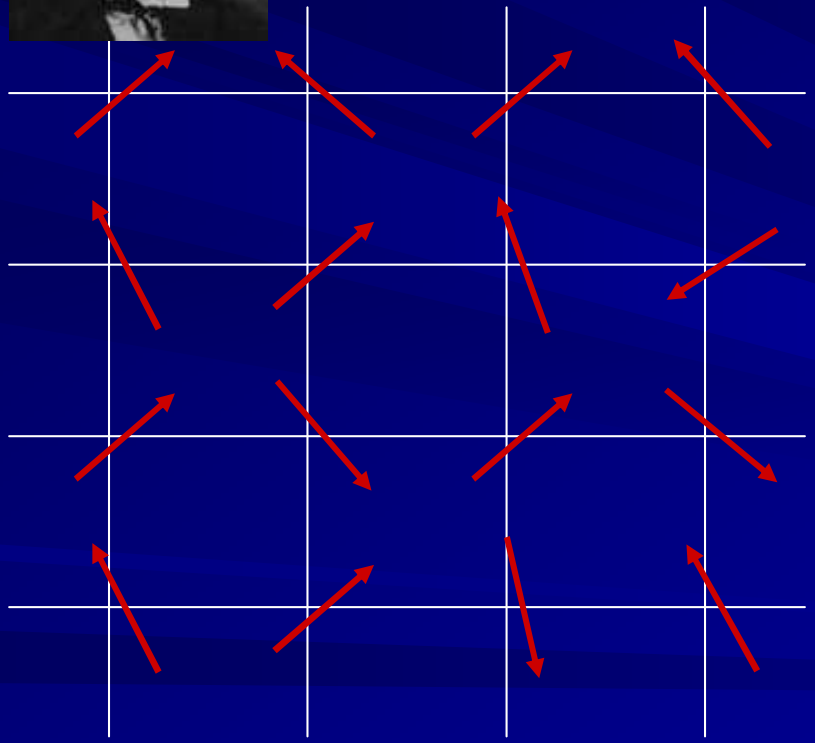
- U/t
- Chemical potential



# Solving the correlated electrons problem

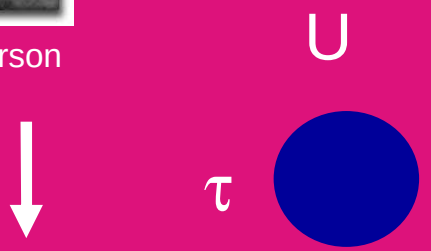
**P. Weiss**



**Mean Field Theory**

Impurity embedded
in a fermionic bath

P.W.Anderson




G.Kotliar

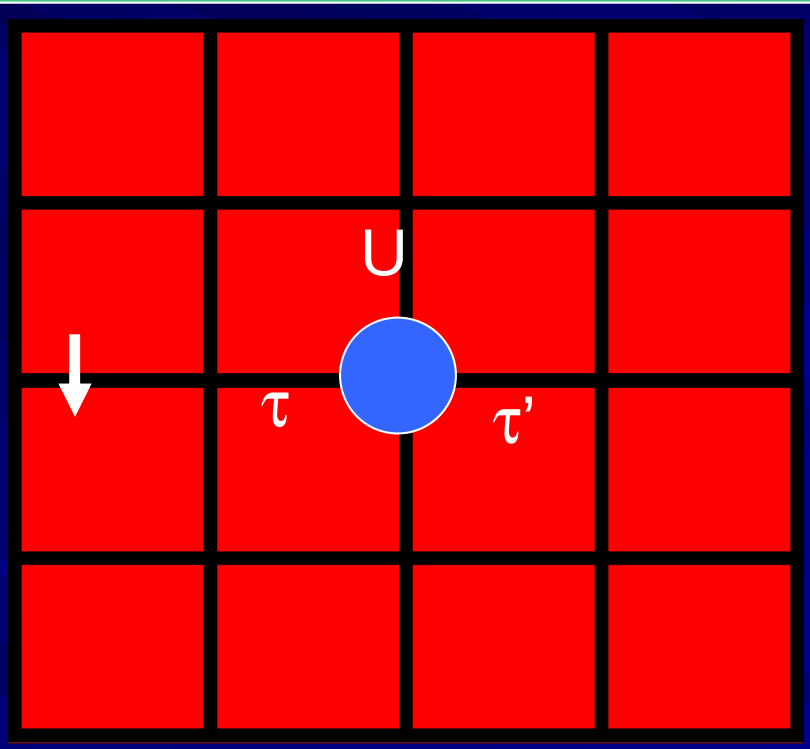
Local quantum
fluctuations = dynamics

**Dynamical Mean Field Theory**

# Dynamical Mean-Field: Cavity construction

Effective medium characterized by the action:

$$S_{eff} = -\int_0^\beta d\tau \int_0^\beta d\tau' c_\sigma^+(\tau) G^{-1}_{bath,\sigma}(\tau-\tau') c_\sigma(\tau') + U\int_0^\beta d\tau n_\uparrow(\tau) n_\downarrow(\tau)$$




Single impurity in the effective medium:

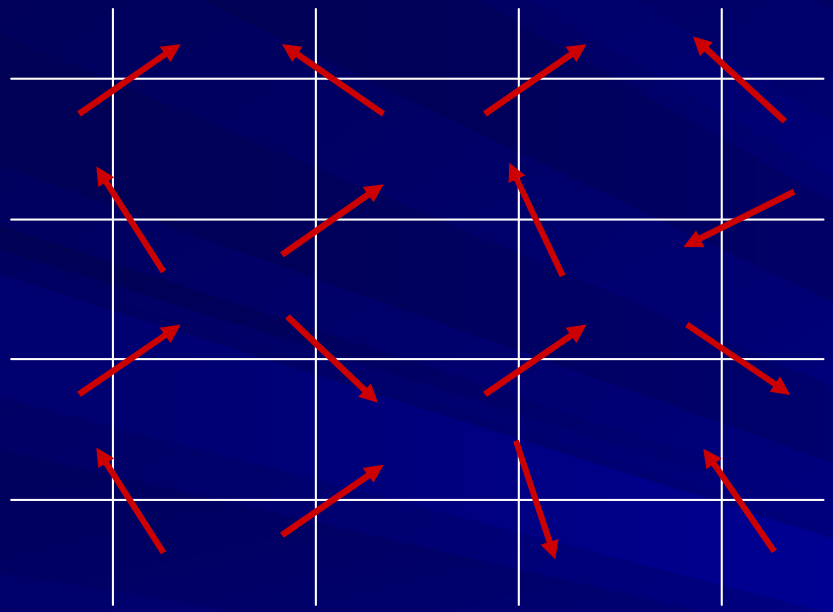
$$G_\sigma(\tau-\tau') = -\left\langle T_\tau c_\sigma(\tau) c_\sigma^+(\tau') \right\rangle_{S_{eff}}$$

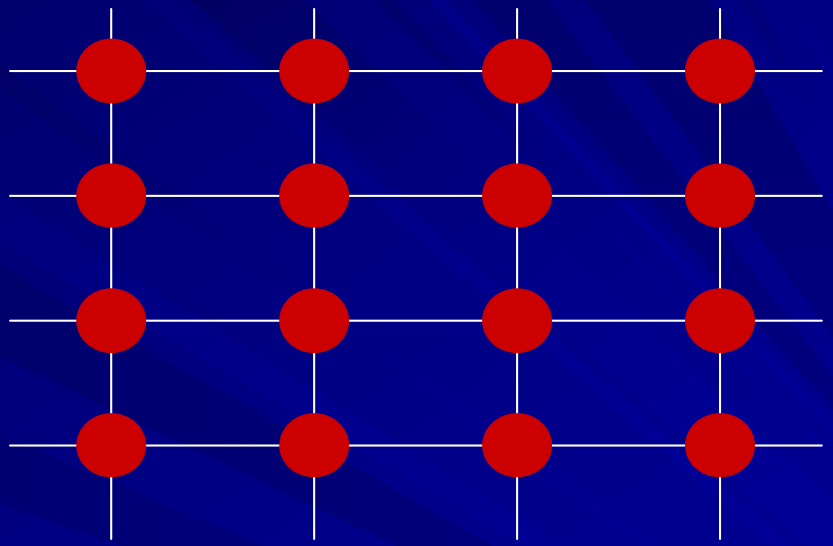
SCF condition connect the impurity solution with the effective medium

$$G^{-1}_{bath,\sigma} = i\omega + \mu - t^2 G_\sigma - \sigma H$$

W.Metzner, D. Vollhardt, PRL 62, ….(1989)
A.Georges et.al. Rev. Mod. Phys 68,13 (1996)

# Analogy with conventional MF





$$H = \sum_{ij} J_{ij} S_i S_j$$

$$H_{eff} = (\sum_i J_{0i} S_i) S_0 = zJmS_0 = h_{eff} S_0$$

$$m = \langle S_0 \rangle = tanh(\beta z J m)$$

$$J_{ij} \sim 1/z$$

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

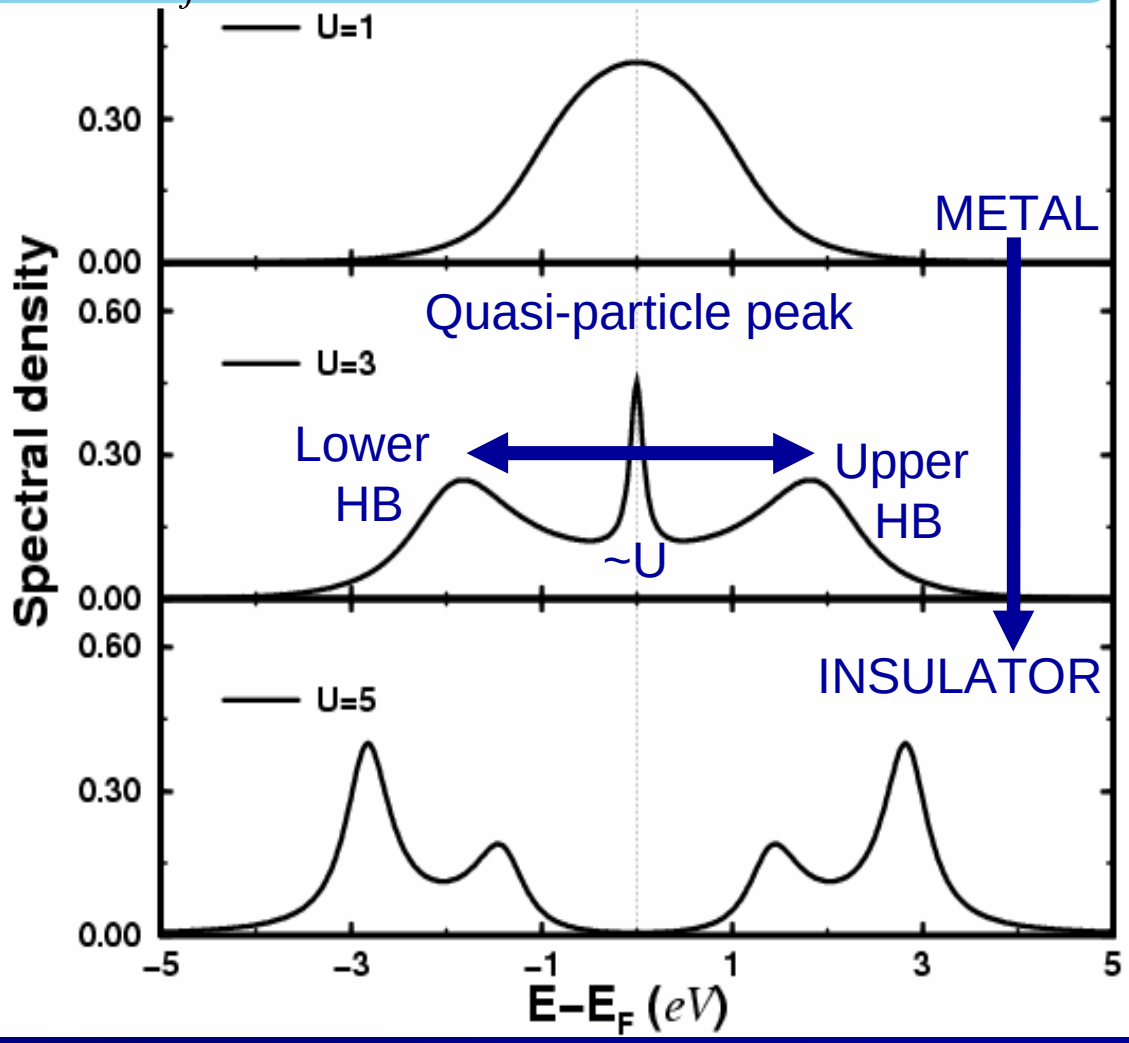
$$S_{eff}[G_0] = -\int\int d\tau d\tau \; c^+_{0\sigma} \; G_0^{-1} \; c_{0\sigma} + U \int d\tau' \; n_{0\uparrow} n_{0\downarrow}$$

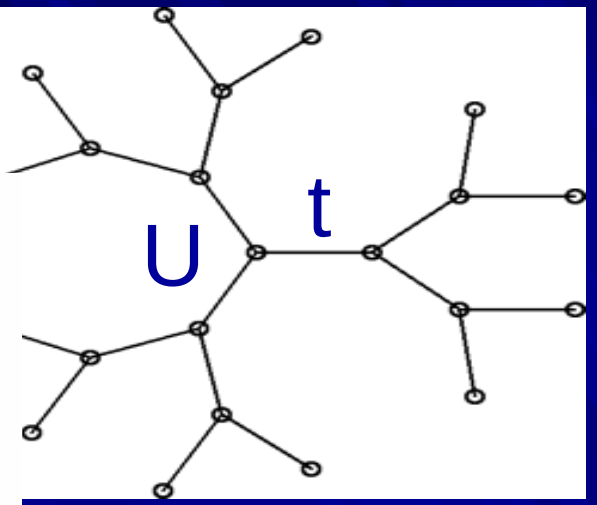
$$G_0^{-1} = i\omega_n + \mu - t^2 G(i\omega_n)$$

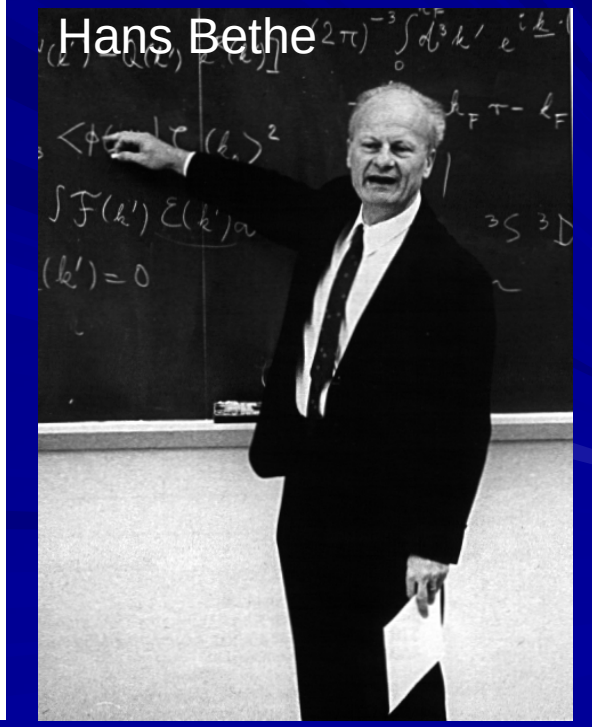
$$t_{ij} \sim 1/\sqrt{z}$$

# DMFT solution for the Hubbard model

$$H = \sum_{ij} \left( t_{ij} + \mu \delta_{ij} \right) \cdot c_{i\sigma}^{+} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$



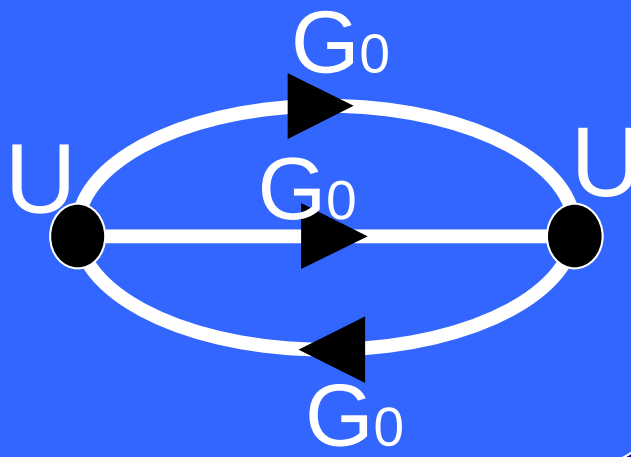
# Diagrammatic: Iterated Perturbation Theory

Yoshida & Yamada
Prog. Theor. Phys. 46, 244, 1970

$$H_I = U(n_\uparrow - 1/2)(n_\downarrow - 1/2)$$

Compute Self-energy in the second order perturbation theory

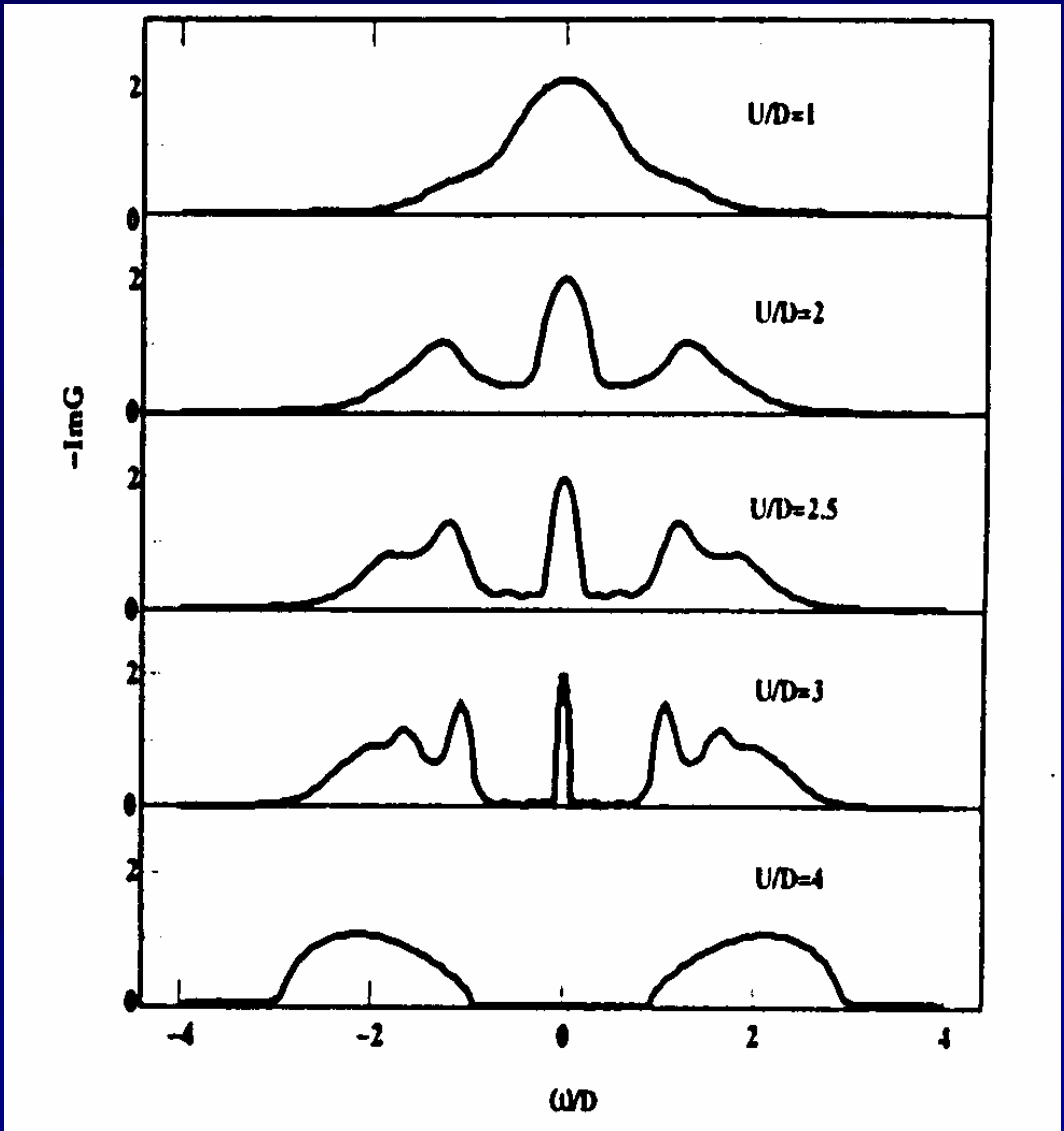
$$\Sigma^{(2)} =$$




$$G_0(\omega) \rightarrow \Sigma(\omega) = FT\left(U^2 G_0^3(\tau)\right) \rightarrow G = \int \frac{\rho^0(\varepsilon)d\varepsilon}{i\omega - U/2 - \Sigma(\omega)}$$

$$G_0^{-1} = G^{-1} + \Sigma$$

# Metal to Insulator transition
# IPT-solution




Georges & Kotliar
PRB 45, 6479, 1992

Zhang, Rozemberg, Kotliar
PRL 70, 1666, 1993

# Exact Diagonalization

$$H_{AM} = \sum_k \varepsilon_k c_k^+ c_k + \sum_k V_k f^+ c_k + hc. + U n_{f\uparrow} n_{f\downarrow}$$

Mapping to the Anderson impurity model

$$G_0^{-1}(i\omega_n) = i\omega_n + \mu - \int d\omega' \frac{\Delta(\omega')}{i\omega_n - \omega'}$$

$$G_0^{-1}(i\omega_n)^{n_s} = i\omega_n + \mu - \sum_{p=2}^{n_s} \frac{V_p^2}{i\omega_n - \varepsilon_p}$$

Solution corresponding the Anderson Hamiltonian for a finite number orbitals ns

$$H = H_0(V, \varepsilon) + U n_{f\uparrow} n_{f\downarrow} \xrightarrow{E.D} G$$

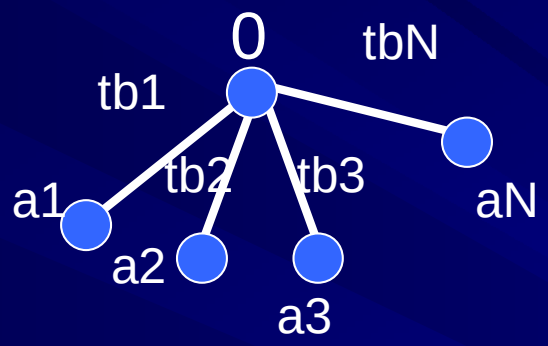
$$G_0^{-1} = i\omega - t^2 G$$

Modified Lanczos (Dagotto & Moreo '85) Recursion Method

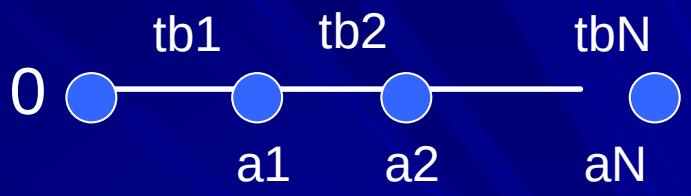
Get new set of parameters $\{V, \varepsilon\}$

# Algorithm:

Parameterization (2N parameters, ai, bi, i=1,N)




$$G_0^{-1} = i\omega - t^2 G^p$$




$$G_0 = \cfrac{1}{i\omega - t^2 \cfrac{b_1^2}{i\omega - a_1 - t^2 \cfrac{b_2^2}{i\omega - a_2 - t^2 \cfrac{b_3^2}{i\omega - a_3 - \ldots}}}}$$

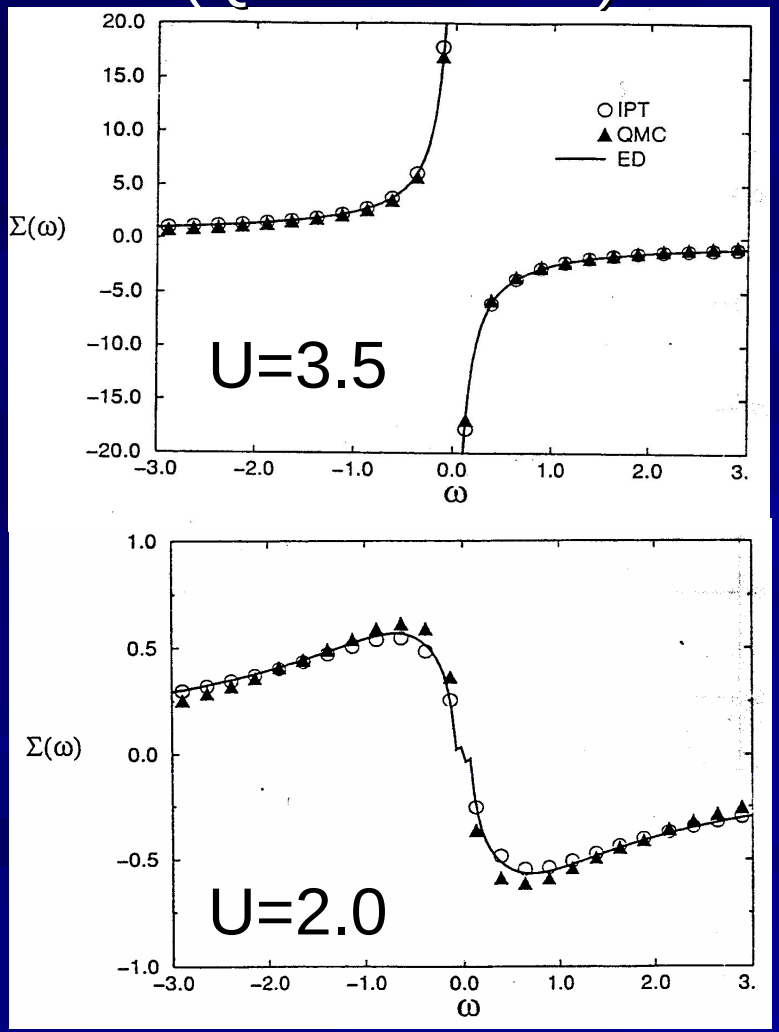
$$G_0 = \cfrac{1}{i\omega - \sum_{i=1}^{N} t^2 \cfrac{b_i^2}{i\omega - a_i}}$$

$$H = H_0(a_i, b_i) + U n_{0\uparrow} n_{0\downarrow} \xrightarrow{E.D} G$$

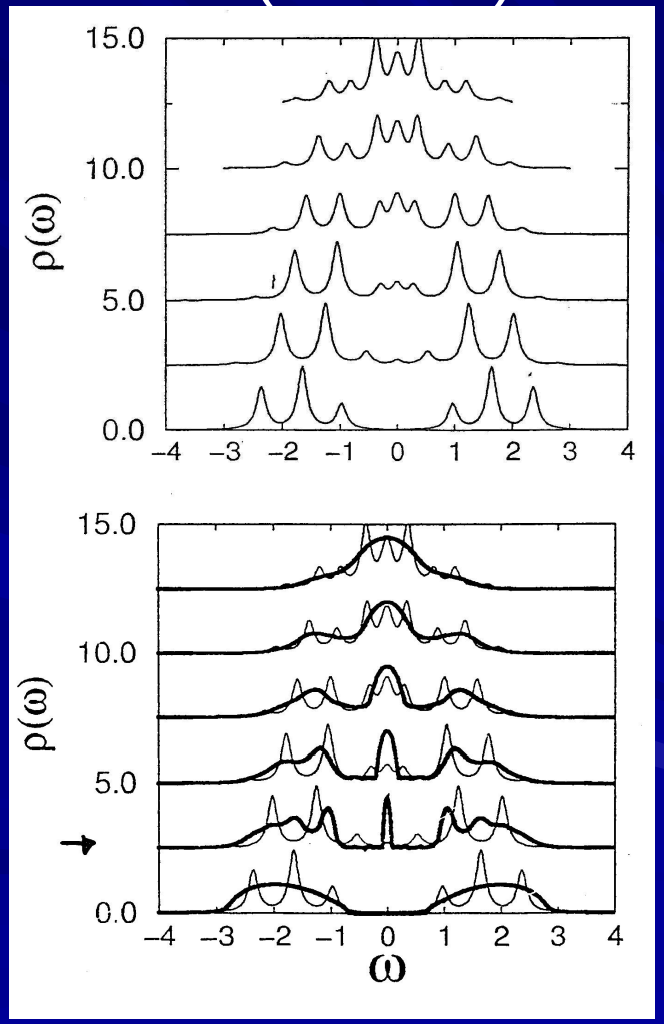
New set of parameters $G^p \cong G$

# Metal-Insulator transition

Self-energy
(QMC-ED-IPT)




Spectral function
DOS (ED-IPT)




U=1
1.5
2.0
2.5
3.0
3.5

U=1
1.5
2.0
2.5
3.0
3.5

# Realistic description of correlations in solids

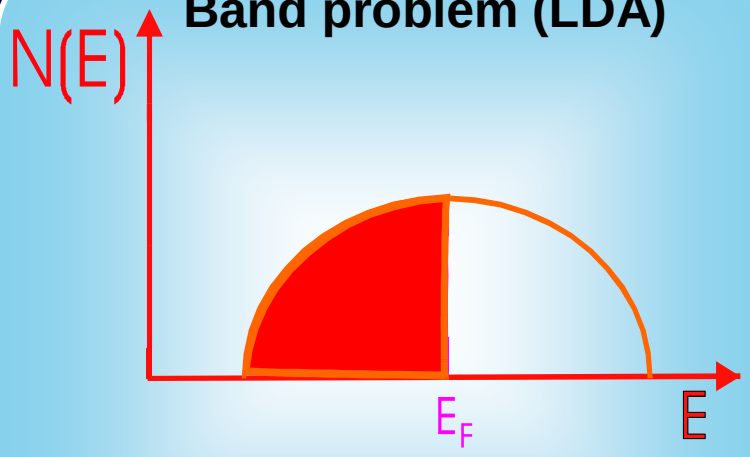
- DFT(LDA+U) = LDA + on-site Coulomb interaction between localized electrons on the same ion; mean field approach for strongly correlated materials; no dynamics

- DFT(LDA+DMFT) = Treats Hubbard band and QP's on the same footing; many energy scales=many competing forms of interactions

# Flow diagram for the LDA+DMFT approach

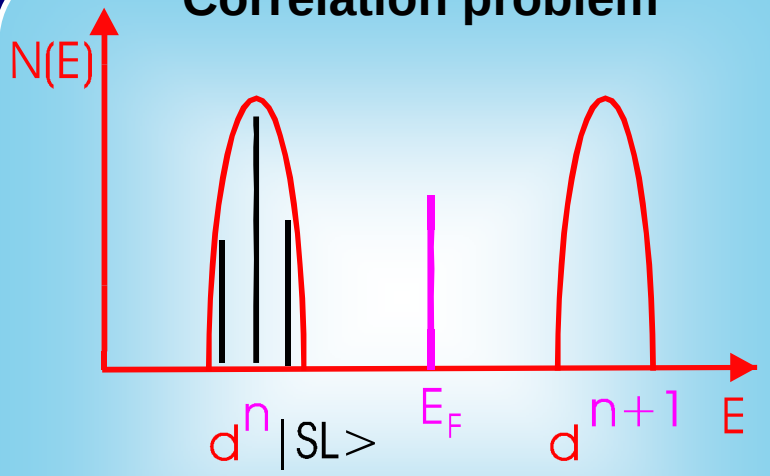
$\Sigma$

**Band problem (LDA)**




$$\sum_{\kappa}\left[G^{-1}_{LDA}-\Sigma\right]^{-1}=G_{loc}$$

**Correlation problem**

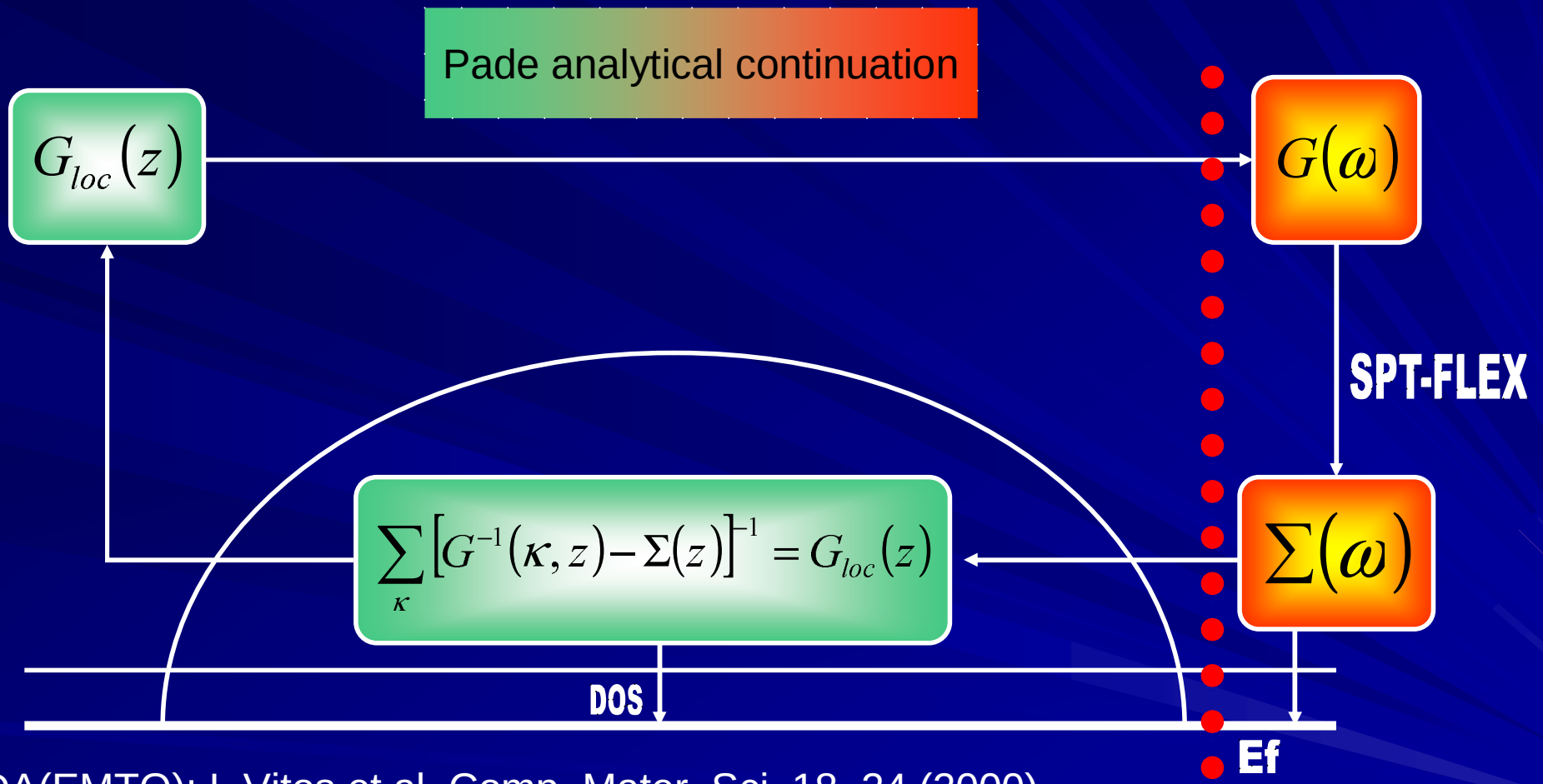



$$\Sigma\left[G_{bath}\right]$$

**DMFT self-consistency**

$$G^{-1}_{loc}+\Sigma=G^{-1}_{bath}$$

# SCF scheme- LDA+DMFT





LDA(EMTO): L.Vitos et al. Comp. Mater. Sci. 18, 24 (2000)

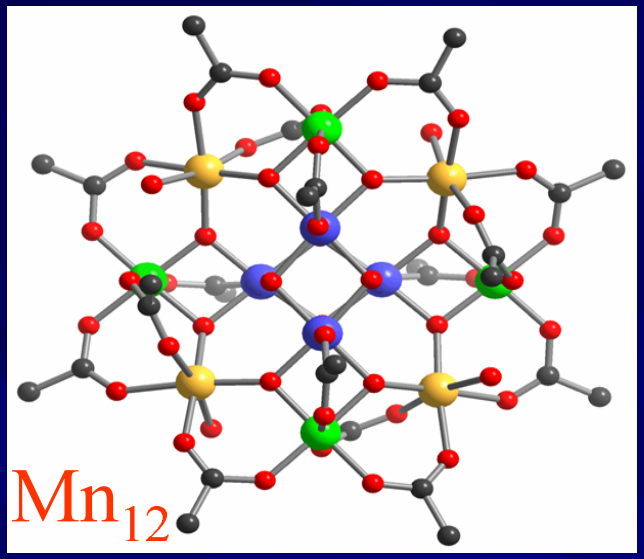
DMFT(SPT-FLEX): M.I.Katsnelson et al. J.Phys.Cond.Matter. 11, 1037 (1999)
A.I.Lichtenstein et al. PRB 57, 6884 (1998)

LDA+DMFT: L. C., L.Vitos, I.Abrikosov, J.Kollar, M.I. Katsnelson and
A.I. Lichtenstein, PRB 67, 235106 (2003)

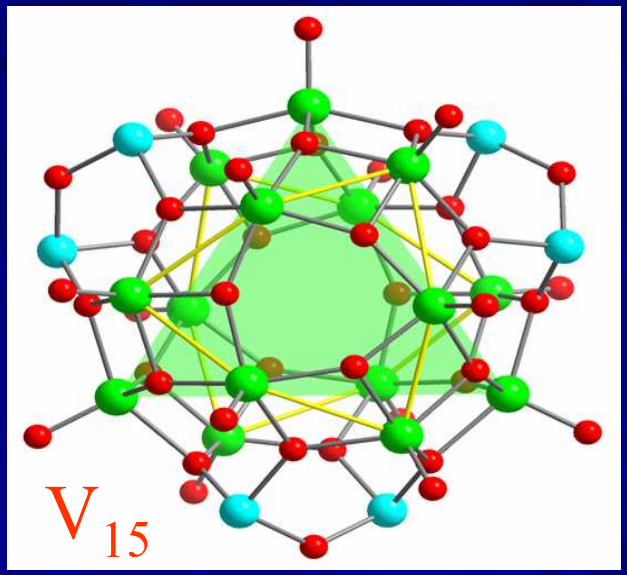
# Applications: Magnetism in nano-systems

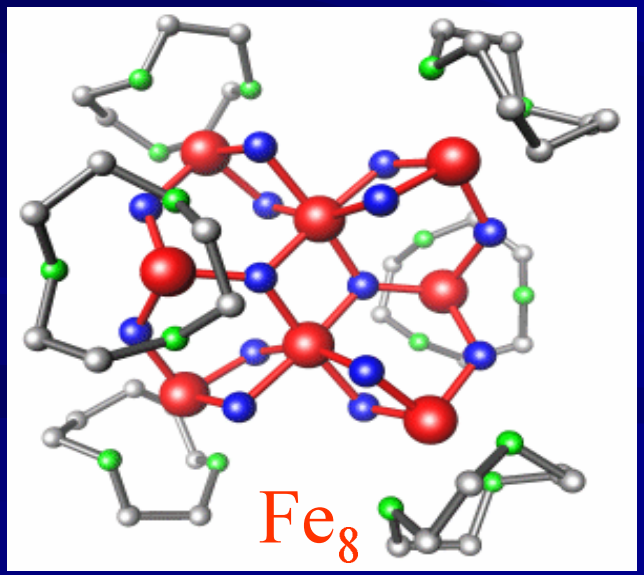
- Molecular magnetism - Nano-magnets
- Correlated surface magnetism
  - Surface states and the Kondo effect
- Dimensional crossover - 1D systems
  - From Fermi to Luttinger liquid
- Correlated adatom trimer on a metal surface

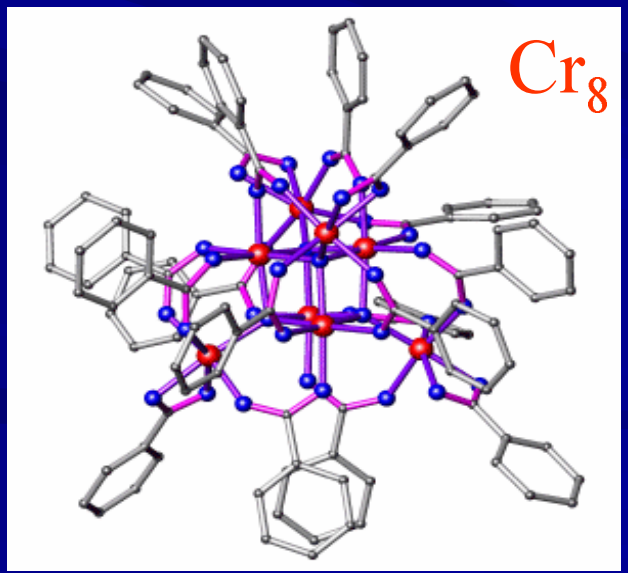
# Molecular architecture: new nanomagnets




B. Barbara,
J. Friedman,
D. Gatteschi,
R. Sessoli,
W. Wernsdorfer
1994




Computing properties:

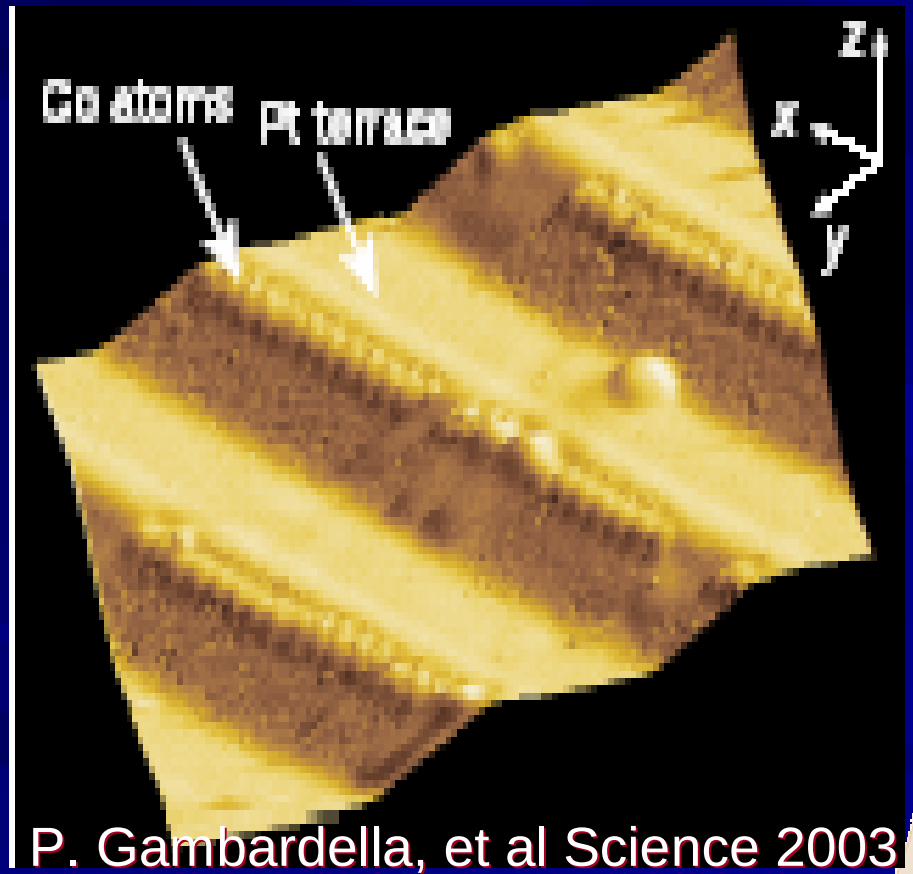
-Exchange Interactions (LDA,LDA+U, LDA+DMFT)

-Excitation energies

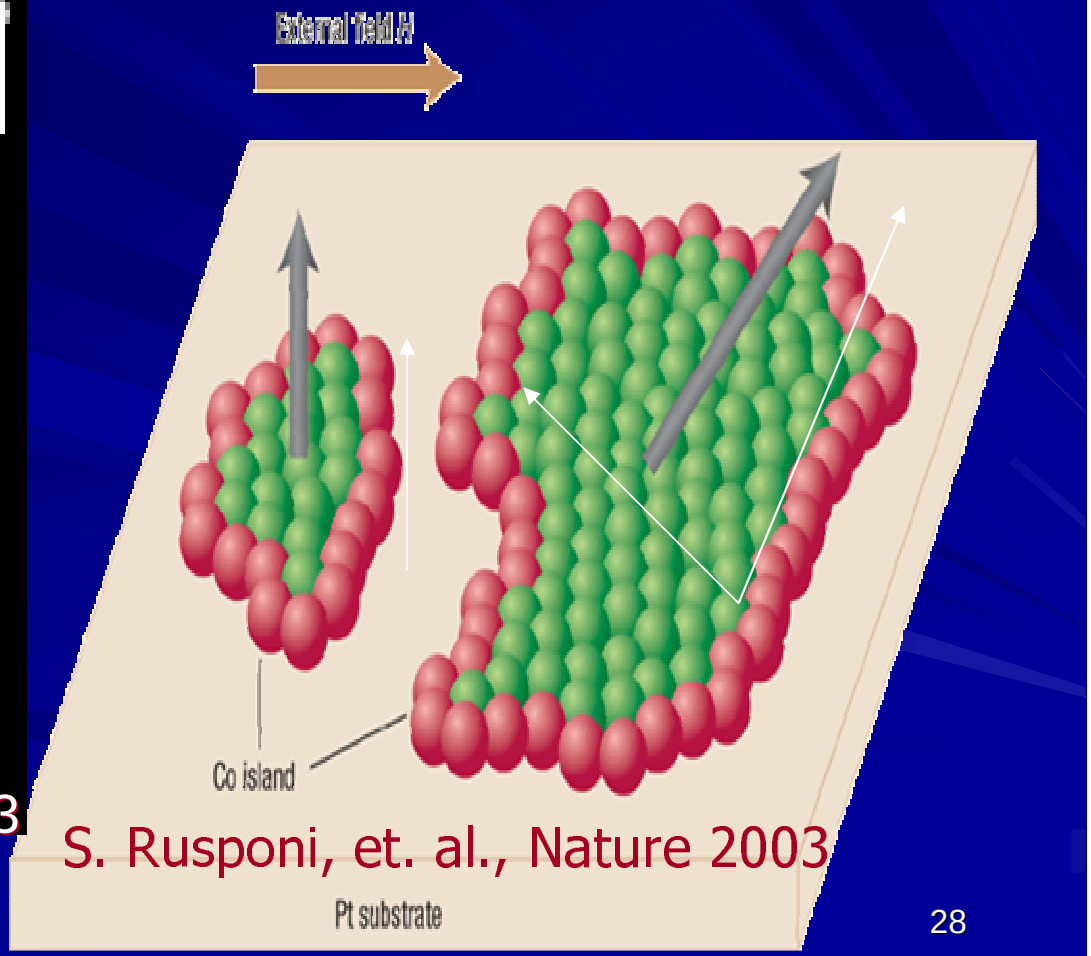
-anisotropy

# Magnetic Co-nanoparticles at Pt-surface

Magnetism vs. Kondo screening:
Huge magnetic anisotropy for Co on Pt



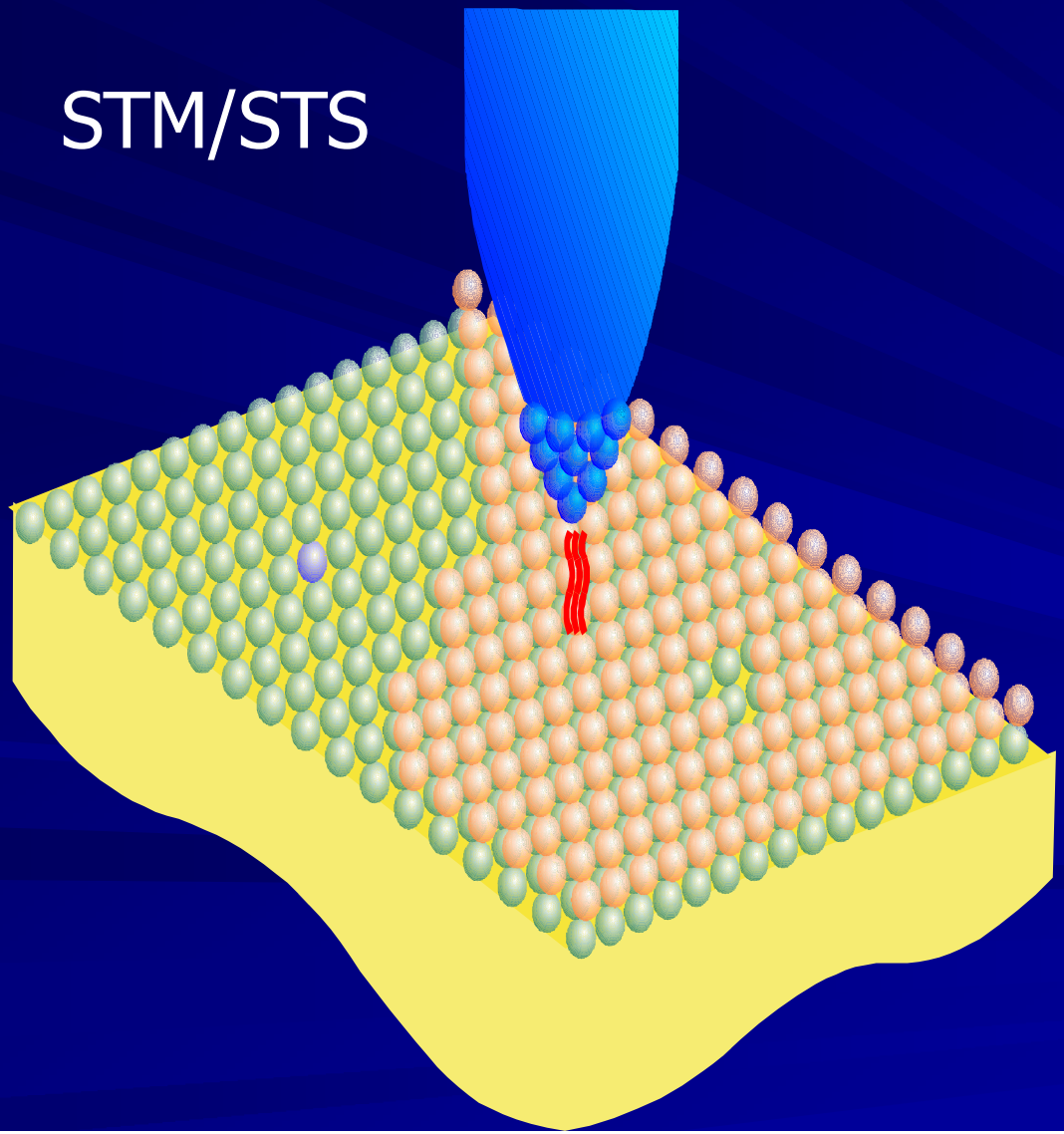

P. Gambardella, et al Science 2003




S. Rusponi, et. al., Nature 2003

# Scanning Tunneling Microscopy and Spectroscopy

STM/STS



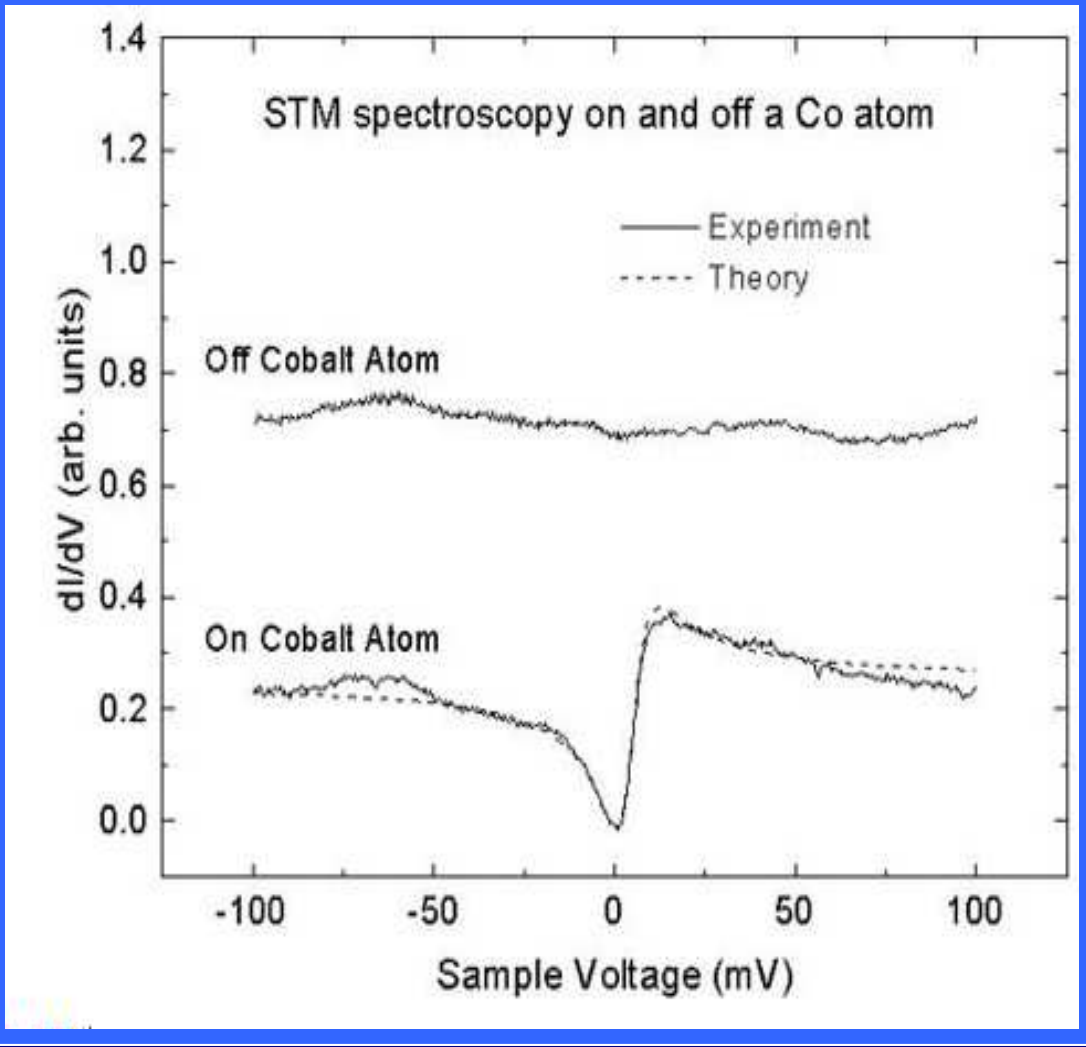
Allows to

Obtain information about the surface topography via
I ~ V LDOS exp(-2kz)

Investigate the surface electronic structure on the atomic scale via
dI/dV ~ LDOS exp(-2kz)

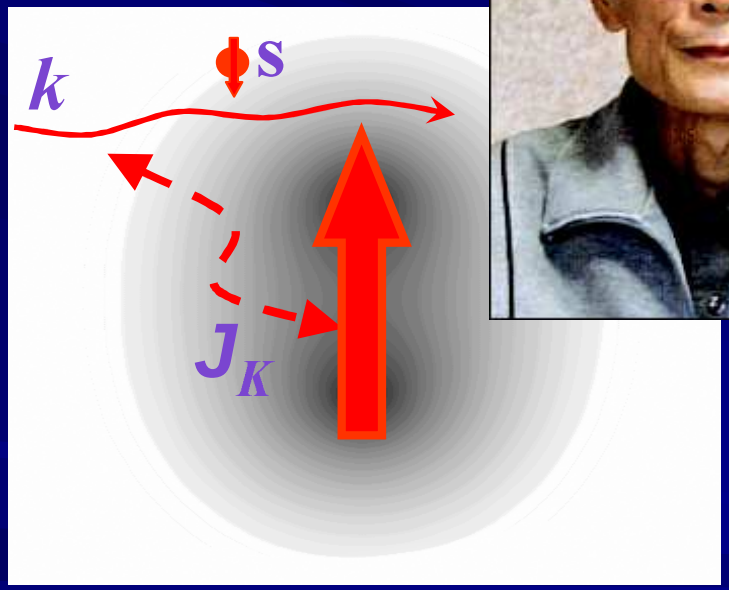
# STM and Kondo

H.C. Manoharan et.al., Nature 403, 512, 2000

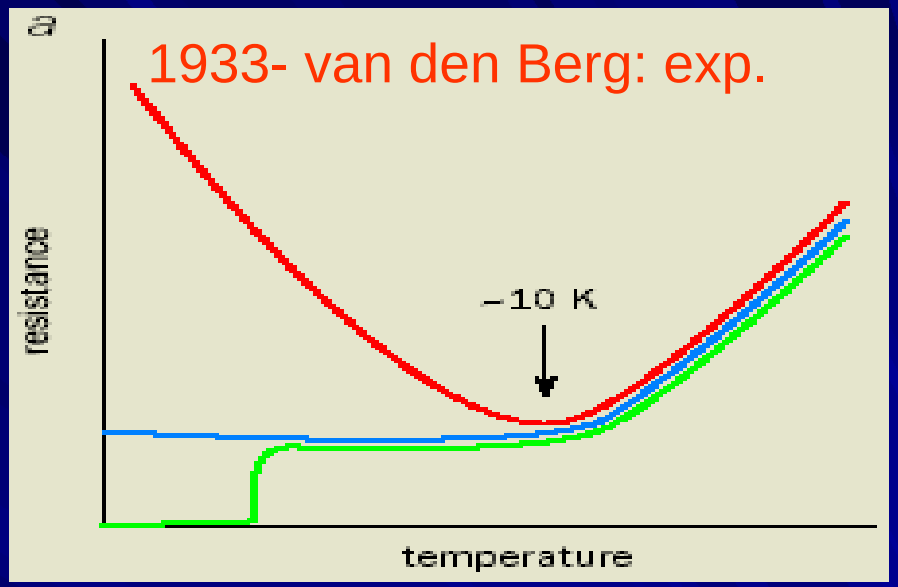


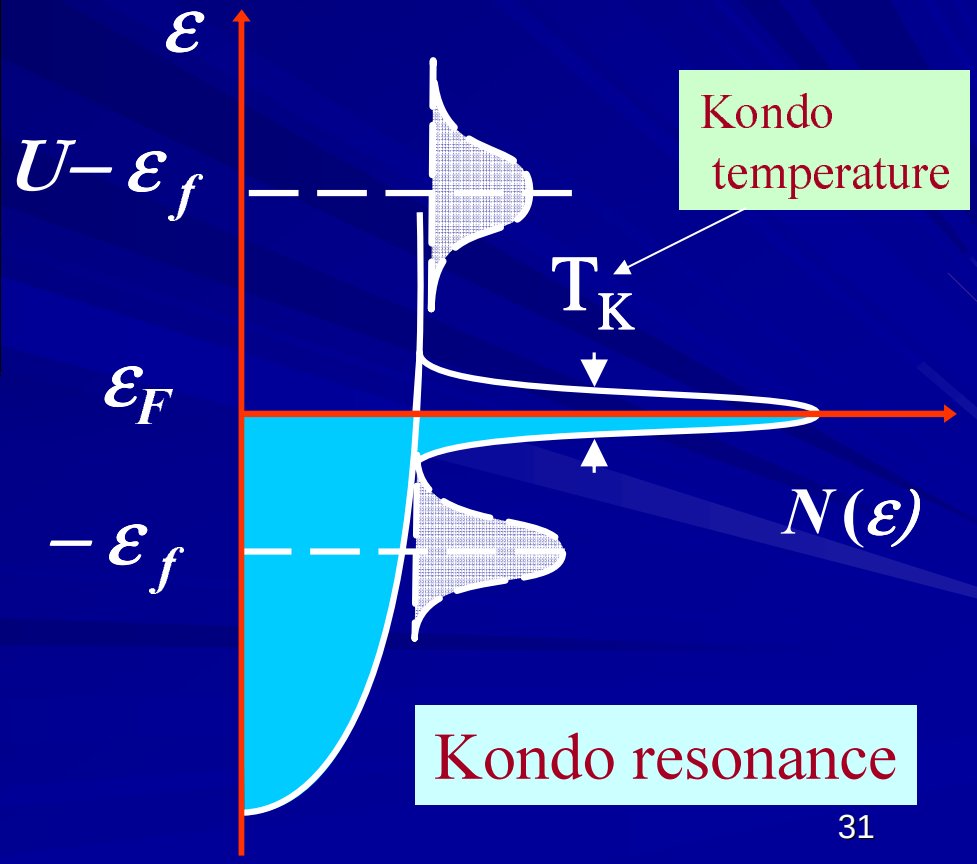
The magnetic moment of the "*4f* "electron is screened by the conduction electrons spins (Kondo effect). As a consequence, a replica of the local orbital arises at the Fermi level called Kondo-Suhl resonance.

1964- J.Kondo: theory

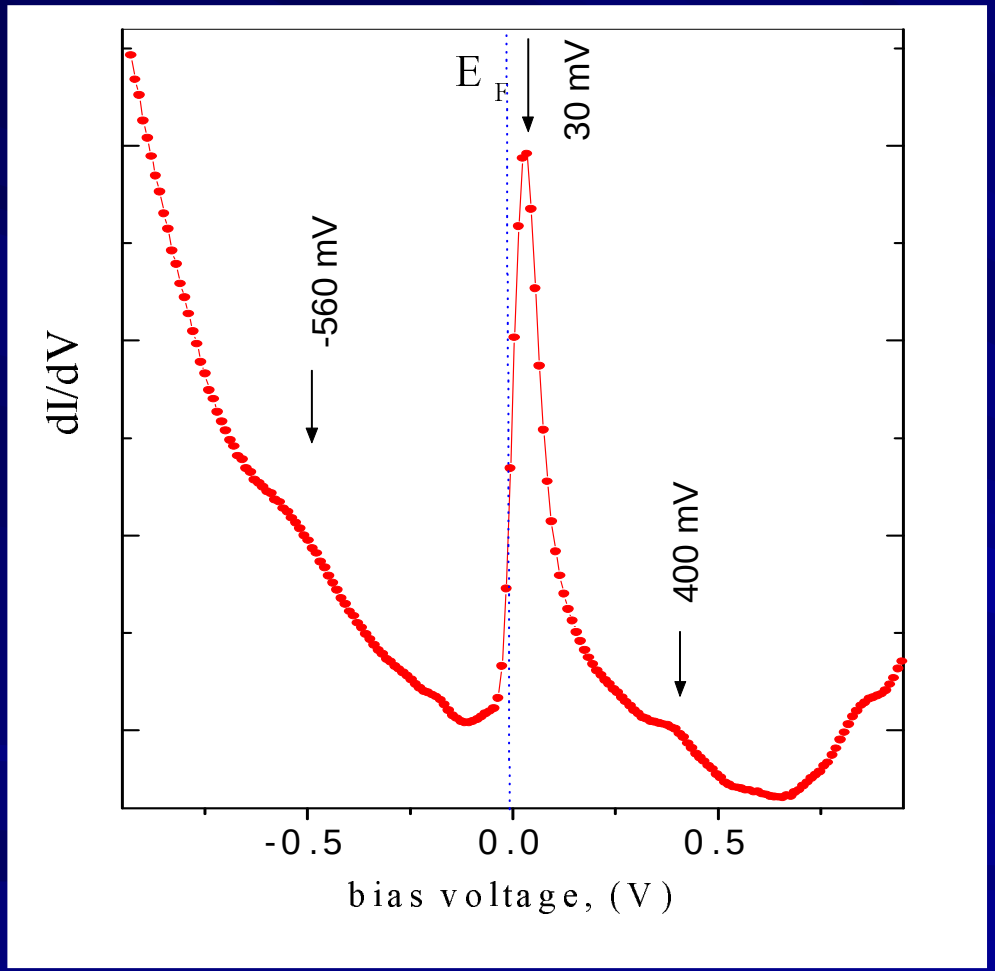


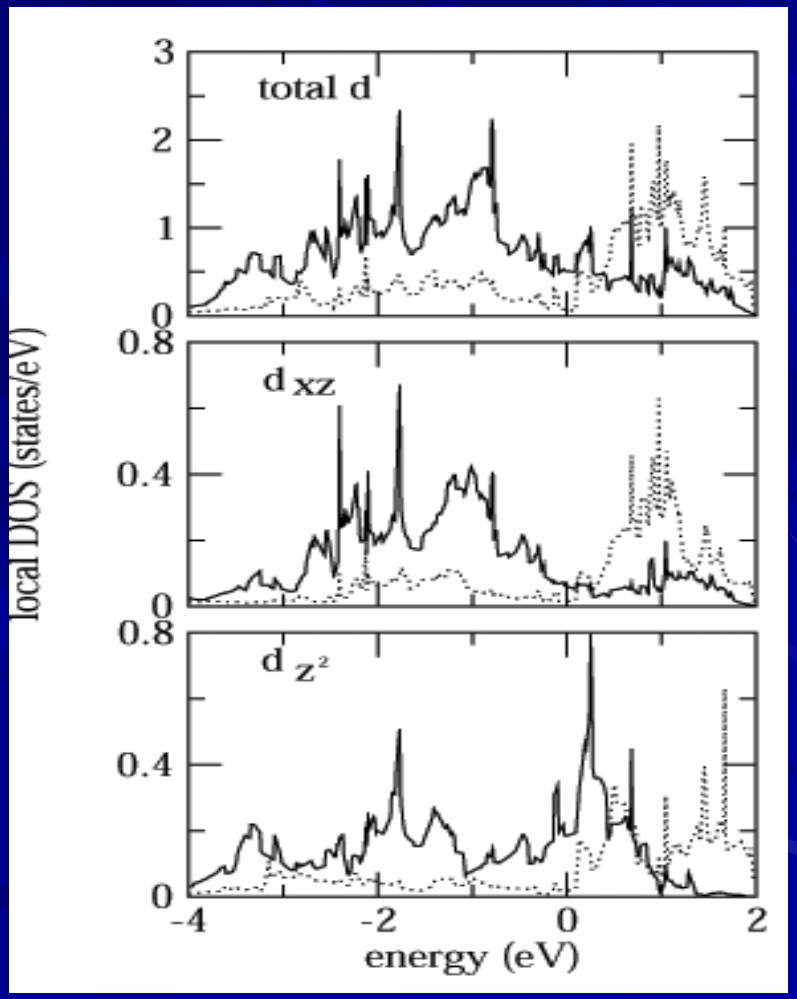

4f (local) moments screening by conduction electrons spins "Kondo screening"



# STS investigations of the Cr(001) electronic structure

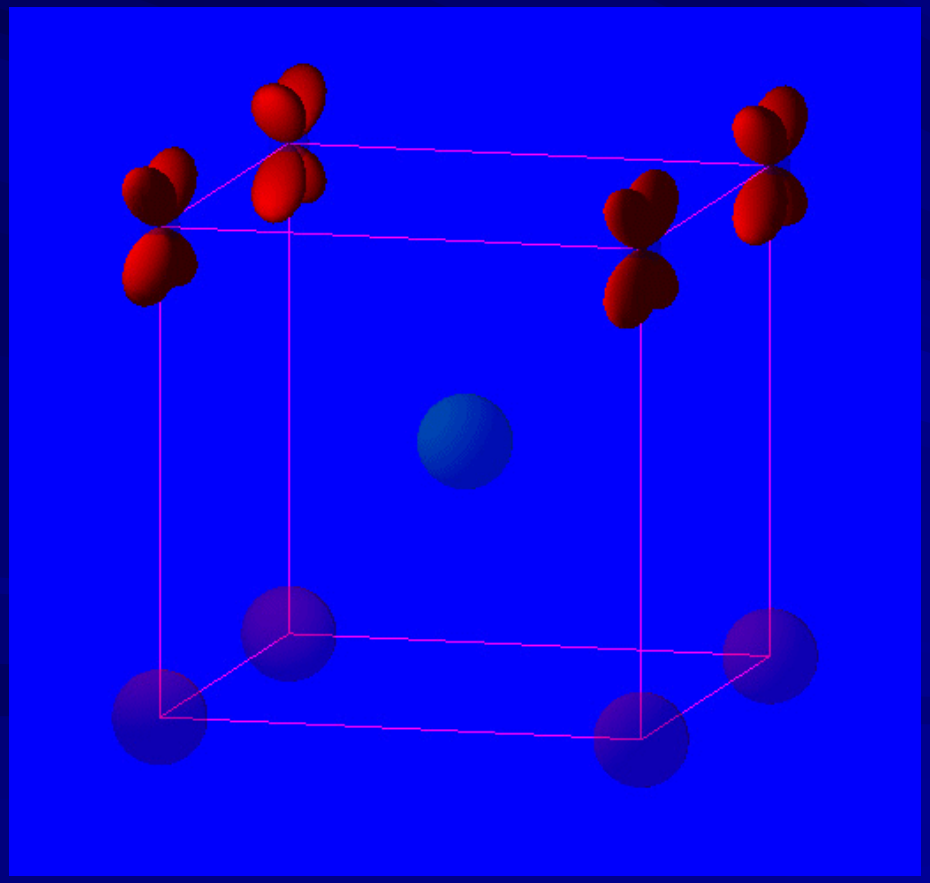


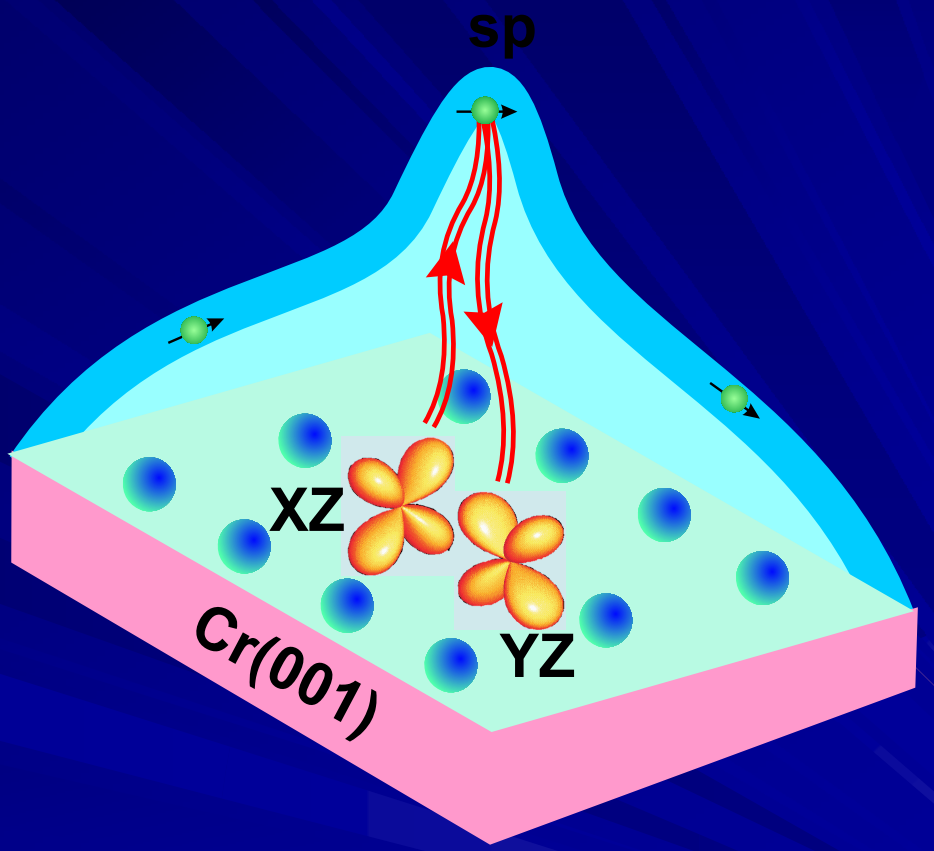




O. Kolesnychenko et. al. Nature (2002)

# Orbital Kondo resonance on Cr(001)

Cr(001) has not only $d_{z^2}$, but also two degenerated $d_{xz}$, $d_{yz}$ surface states






The interaction of these states with the conduction electrons can lead to the formation of a many-body Kondo resonance near the Fermi level

# Dimensional crossover: Chain-DMFT

Crossover between the Luttinger-liquid and coherent Fermi liquid, difficulty: breakdown of perturbation expansion in $t_\perp$

E. Arrigoni, PRL 83, 128 (1999); PRB 61, 7909 (2000)

Generalization of DMFT = limit of infinite transverse dimensionality

$$z_\perp \to \infty$$

$$t_\perp = \frac{\tilde{t}_\perp}{\sqrt{z_\perp}}$$

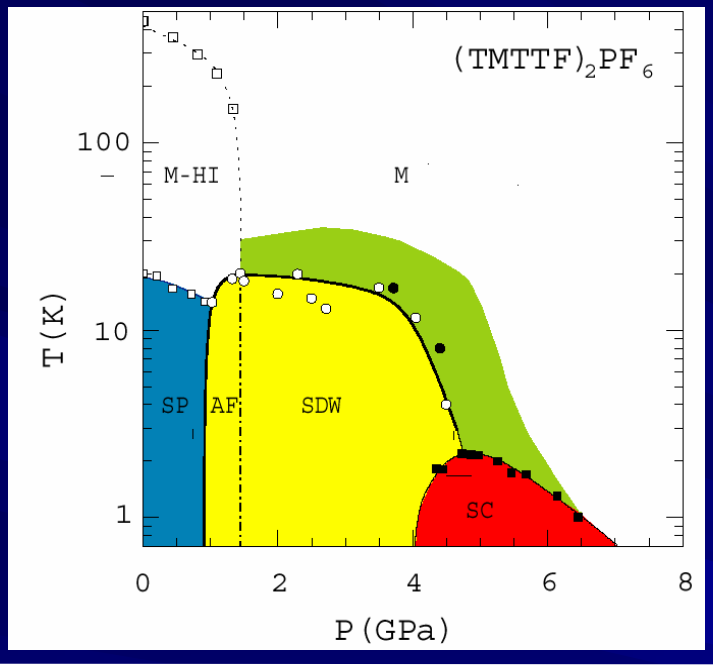
$$D(\varepsilon_\perp) = \sum_{k_\perp} \delta[\varepsilon_\perp - \varepsilon(k_\perp)]$$

Self-energy independent of transverse momentum

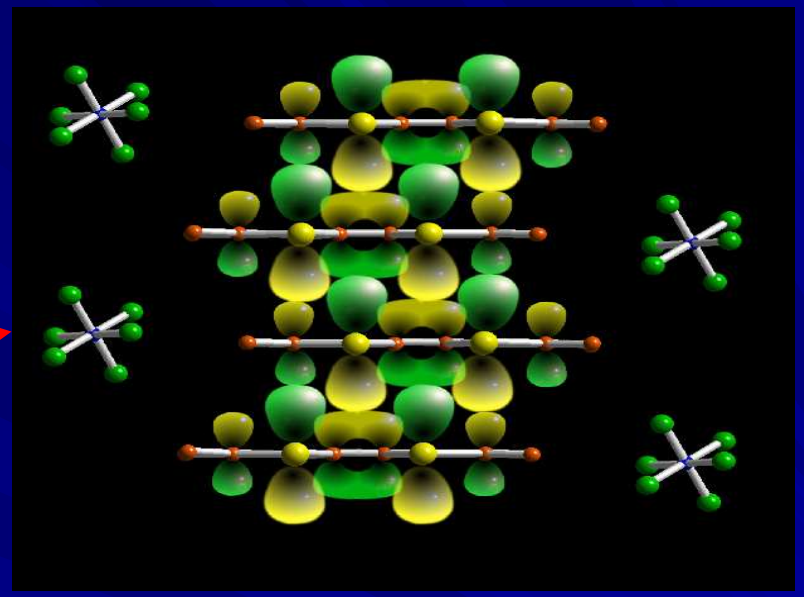
$$\kappa = (k, k_\perp)$$

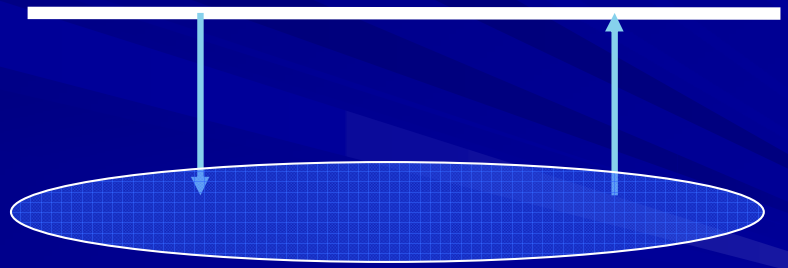
$$\Sigma = \Sigma(k, i\omega)$$

# Quasi-one-dimensional organic conductor: weakly coupled chains




TMTTF2(X)





**Effective 1d-**problem in the bath (QMC) with self-consistency condition

# Chain-DMFT for quasi-1D system

Effective one-dimensional problem:

$$H = \sum_m H_{1D}^m - \sum_{<m,m'>} t_\perp \sum_{i,\sigma} (c_{im\sigma}^+ c_{im'\sigma} + h.c.)$$

A. Georges et al.
PRB, 61,16393 (2000)

$$S_{eff} = \int_0^\beta d\tau \int_0^\beta d\tau' \sum_{i,j,\sigma} c_{i\sigma}^+(\tau) G_{bath}^{-1}(i-j,\tau-\tau') c_{j\sigma}(\tau') + \int_0^\beta d\tau H_{\text{int}}^{1D}\left[\{c_{i\sigma}, c_{i\sigma}^+\}\right]$$

$$G(i-j,\tau-\tau') = -<T_\tau c_i(\tau') c_j^+(\tau')>_{eff}$$

$$G(k,i\omega) = \int d\varepsilon_\perp \frac{D(\varepsilon_\perp)}{i\omega + \mu - \varepsilon_k - \Sigma(k,i\omega) - \varepsilon_\perp}$$

$$G_{bath}^{-1} = \Sigma + G^{-1}$$

# Luttinger to Fermi Liquid crossover

$$H_{1D} = -t\sum_{i,\sigma}(c^{+}_{i\sigma}c_{i+1'\sigma} + h.c.) + U\sum_{i} n_{i\uparrow}n_{i\downarrow}$$

$$\varepsilon_{\perp}(k_{\perp}) = -2t_{\perp}\cos k_{\perp}$$

S. Biermann et. al
PRL, 87, 276405 (2001)

On-chain spin/charge response function

$$\chi_s(\tau) = \left\langle S^z(j,0)S^z(j,\tau)\right\rangle = \sum_{k,k_{\perp}}\chi_s(k,k_{\perp}\tau)$$

$$\chi_s(\tau) = \chi_s(\beta/2)\left(\sin\pi\tau/\beta\right)^{-(1+K_\rho)}$$

Fermi surface

$$\varepsilon_{\perp}(k^F_{\perp}) = \mu - \mathrm{Re}\sum(k, i\omega_{n=1}) - \varepsilon_k$$

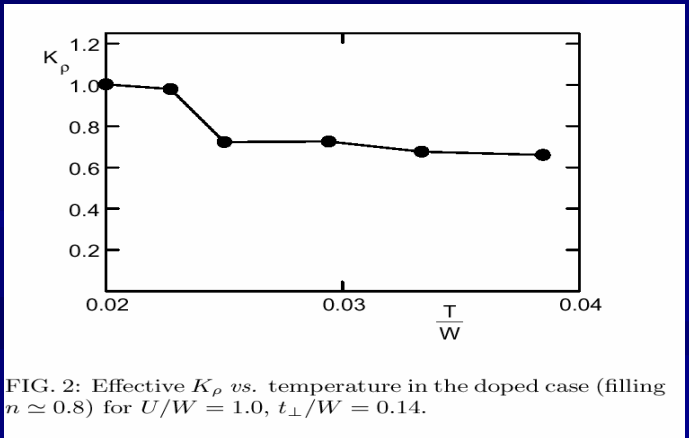



FIG. 2: Effective $K_\rho$ *vs.* temperature in the doped case (filling $n \simeq 0.8$) for $U/W = 1.0$, $t_\perp/W = 0.14$.

$$T^* \approx 0.5\frac{t_\perp}{\pi}$$

Quasiparticle residue

$$Z = Z(k^F_{\perp})$$

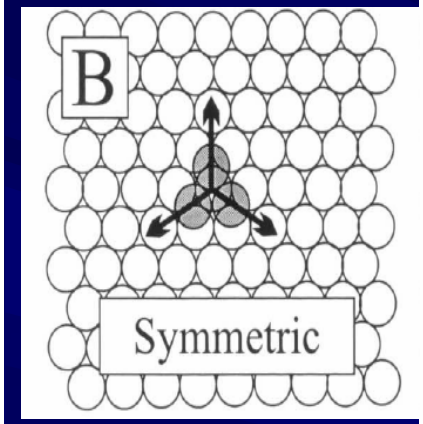
# Magnetic nanoclusters on surface

Experiment:STM: *dI/dV* spectra

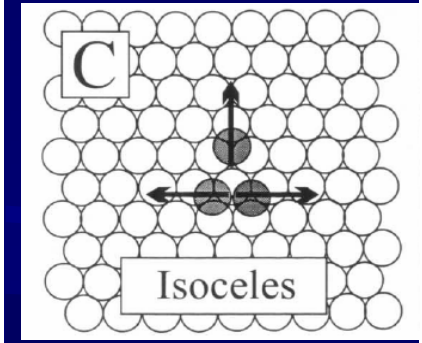
A single antiferromagnetic chromium trimer on gold surface:

M. Crommie Phys. Rev. Lett. **87**, 256804 (2001)

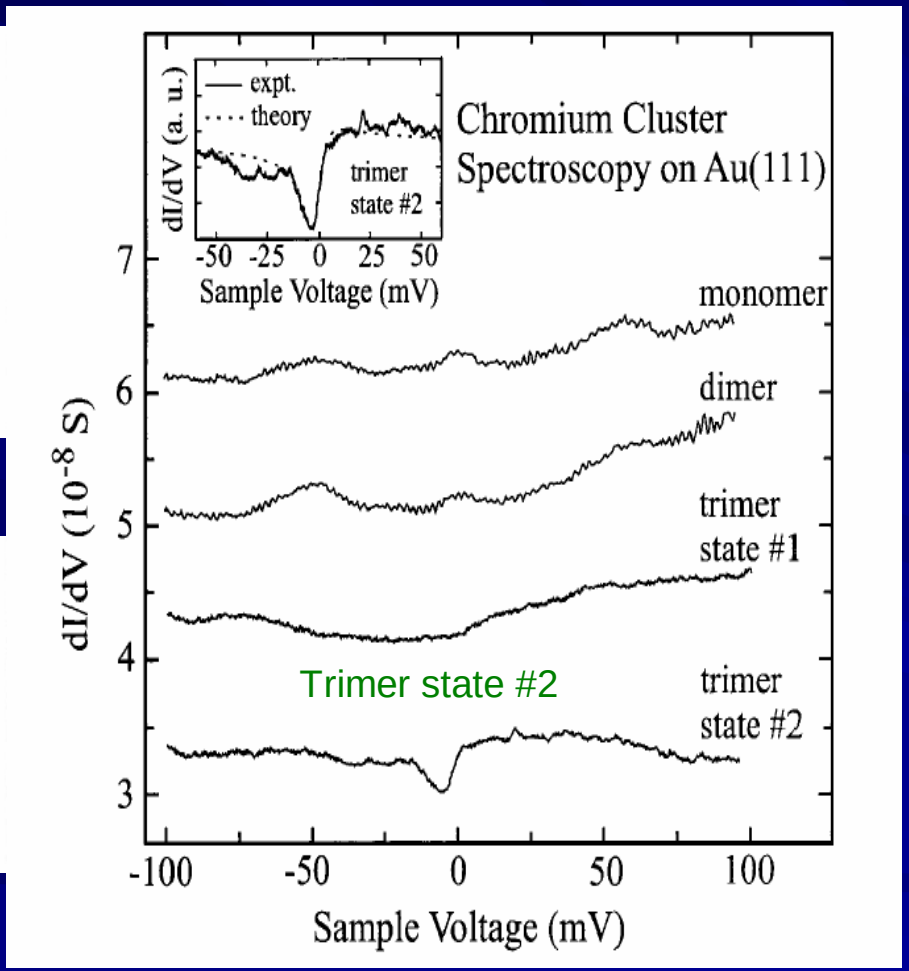
Interplay between single-impurity Kondo effect and RKKY exchange




Trimer state #1




Kondo resonance is observed for isosceles trimer (state #2)




Complicated

phase diagram

Quantum critical points

Heavy fermions

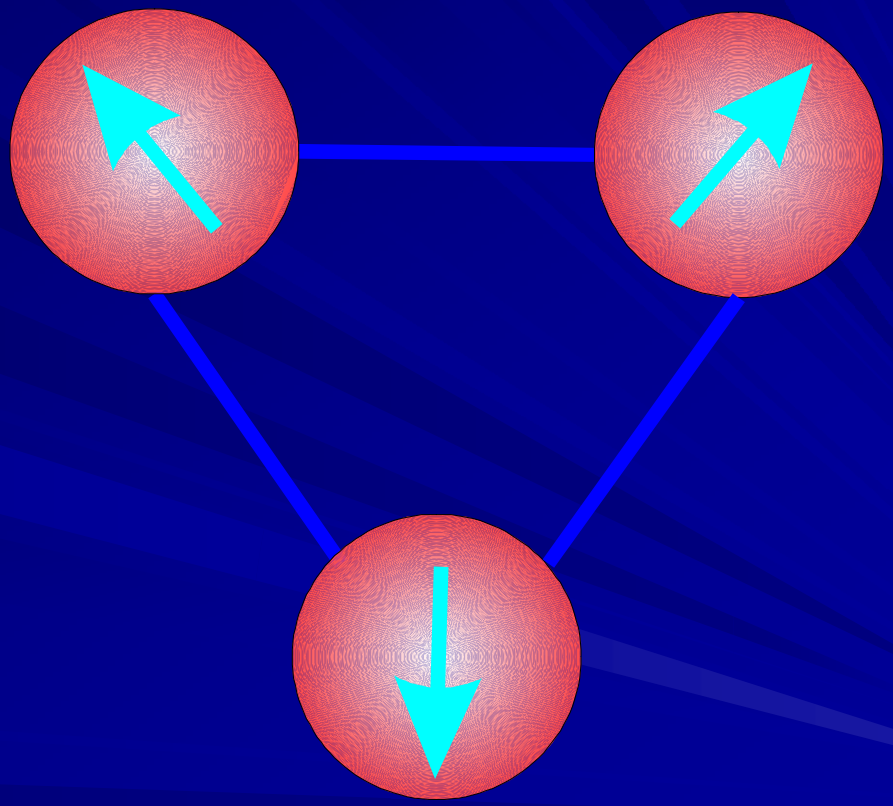
Non-Fermi-liquid behavior

Uncontrollable approximations:

Replacement of Heisenberg exchange by Ising one

# Correlated adatom on surface

- Questions:
  - Is the difference between the Heisemberg and Ising types of exchange interaction essential?
  - How does the geometry of the problem affect the Kondo effect

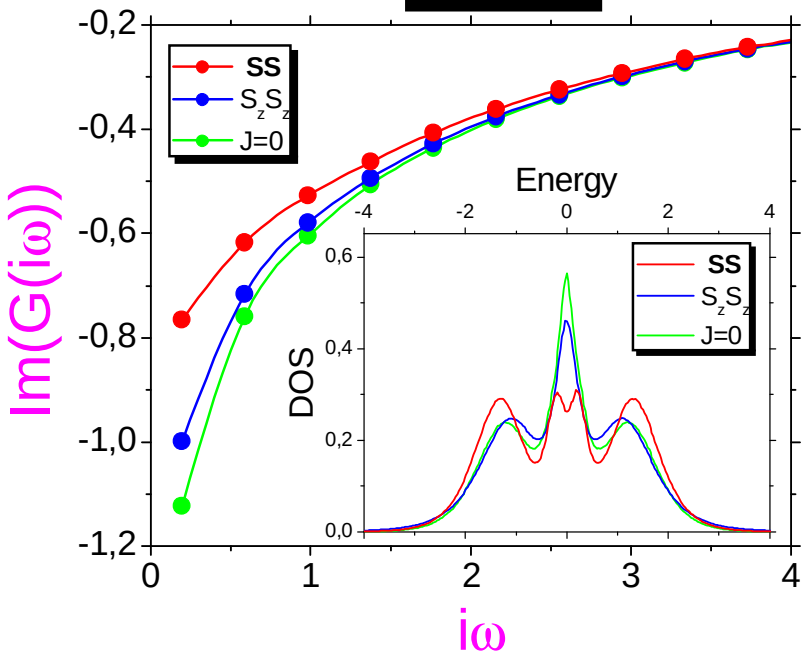


# Heisenberg vs.Ising exchange

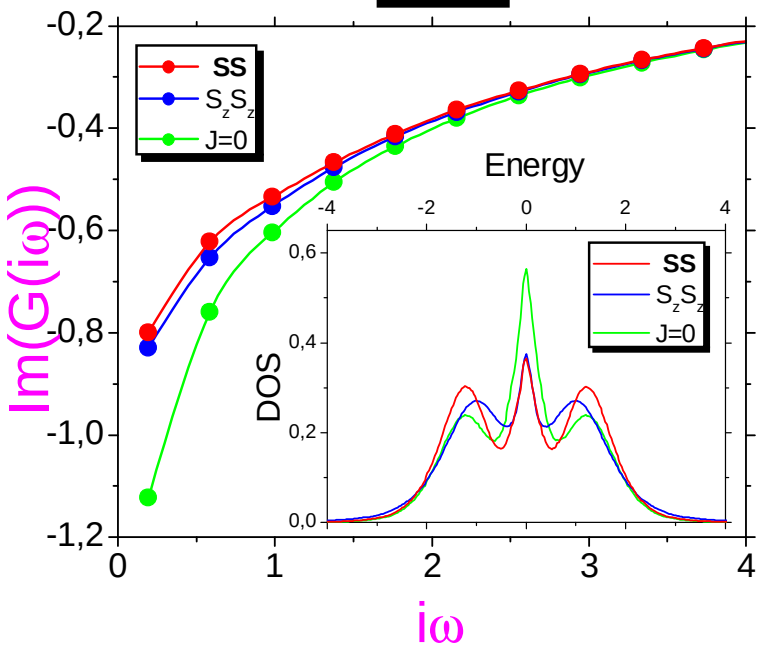
Intersite exchange term can have Heisenberg (**SS**) or Ising (SzSz) form

Exchange integral *J* antiferromagnetic (AFM, *J*>0) or ferromagnetic (FM, *J*<0)

AFM




FM



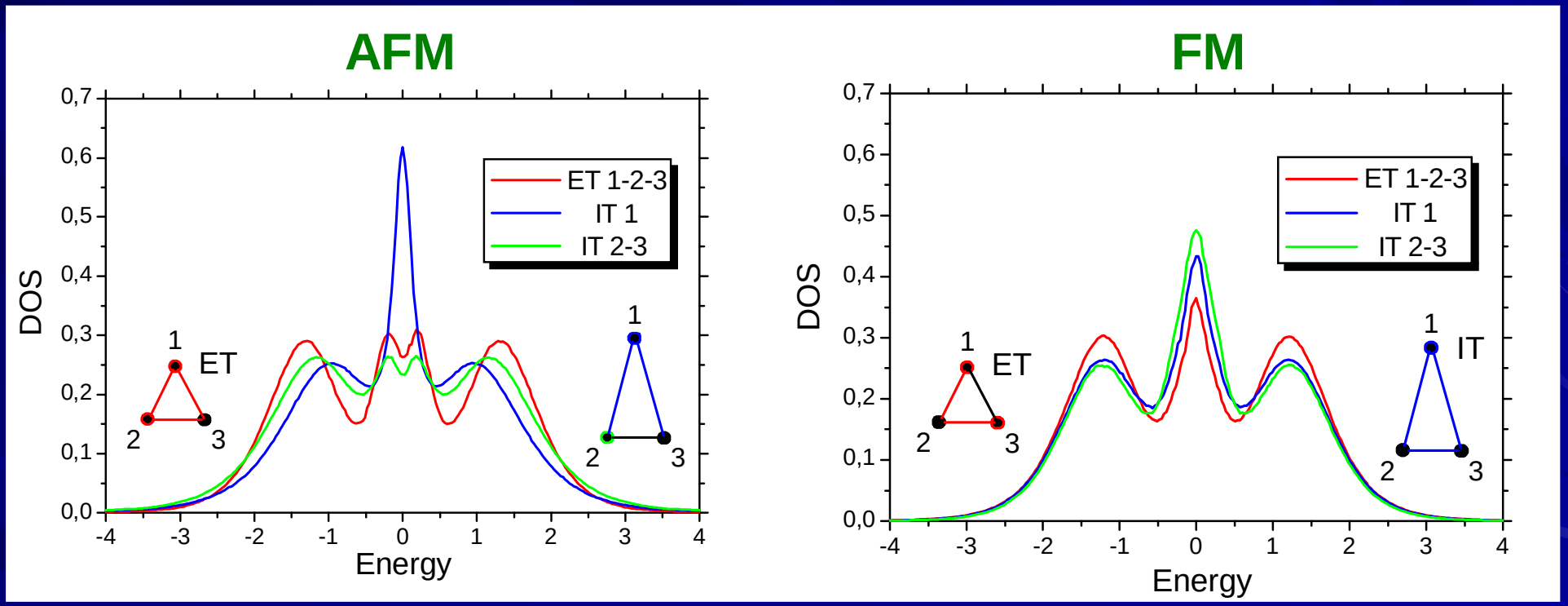

One can see drastic difference between Heisenberg and Ising types of interaction for antiferromagnetic case

# Equilateral and Isoscel Trimers

Density of states at geometry modification of the trimer

Equilateral (ET) and isosceles (IT) trimers

$J_{23}=J,\ J_{12}=J_{13}=J/3$




One can see a reconstruction of the Kondo resonance for isosceles trimer at antiferromagnetic exchange interaction

# Conclusions and perspectives

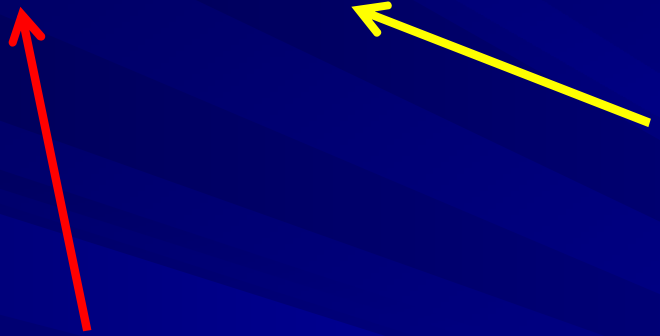
Summary for applications

- Molecular magnets:
- Surface states vs. Kondo physics
  - STS measurements on Cr(001) surface reveal a very narrow resonance near the Fermi level and visualized its orbital character
  - Within Dynamical Mean-Field Theory, the observed peak is explained as an Orbital Kondo resonance from the two dxz and dyz degenerated surface states
  - This is a first evidence that the surface orbital degrees of freedom can lead to the Kondo effect
- Correlated adatom
  - Study of multi-center Kondo systems (Cr-trimer on Au) can open a new research field of quantum coherence effects in nanosystems
- Reducing dimensionality -> Nanoscopy
  - Correlated electron materials
  - Explore more and higher quality materilas
  - Dynamics
  - Potential correlated elctrons devices

# Quantum dots - 0 dimensions

"artificial atoms"

"A mesoscopic island containing conduction electrons"



isolated regime, droplet,…

microscopic < mesoscopic <macroscopic

- electrons move coherently (QM at work) and experience system-specific properties
- correlation effects are important
- large compared to atomic physics ~
- fluctuations are important…

- energy of adding an electron

$$E_C \sim \frac{e^2}{\varepsilon\, d} \sim \frac{1}{13}\frac{a_0}{d}\frac{e^2}{a_0} \sim 10\ K$$

- wavelength $\lambda_F \sim 10\ nm$
- electrons

$$N = \left(d / \lambda_F\right)^2 \sim 100$$

- Fermi energy

$$E_F \sim \hbar^2 /(\lambda_F^2 m^*) \sim 100K$$

- Level spacing

$$\Delta \sim E_F / N \sim 1K$$