

Center for
Electronic Correlations and Magnetism
University of Augsburg

Surprising Effects of Electronic Correlations in Solids

Dieter Vollhardt

Frontiers in Chemical Physics of Solids

Max-Planck-Institute for Chemical Physics of Solids, Dresden
March 19, 2009

Outline:

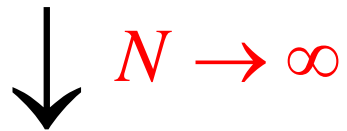
1. Peculiarities of many-particle systems
2. Correlations
3. Electronic correlations in solids
4. Dynamical Mean-Field Theory:
Models vs. materials
5. New Developments & Perspectives

Supported by Deutsche Forschungsgemeinschaft (SFB 484)

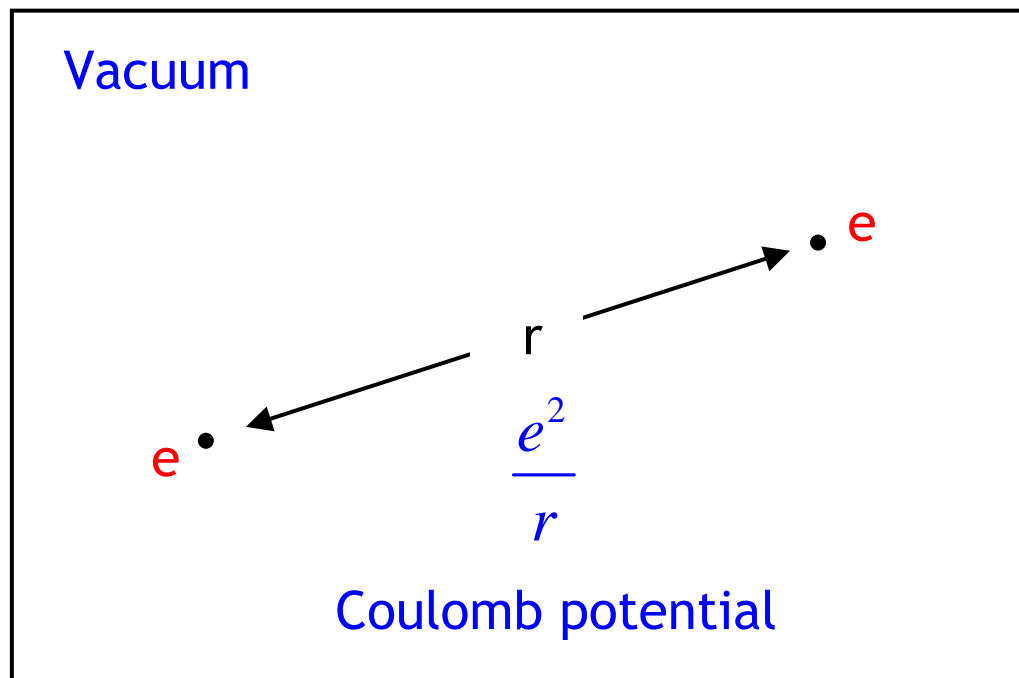
1.
Peculiarities of
Many-Particle Systems

Interacting many-particle systems

Elementary (“bare”) particles + interactions

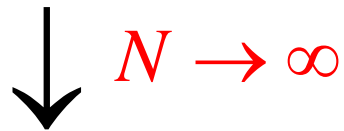


effective (“quasi”) particles + effective interactions



Interacting many-particle systems

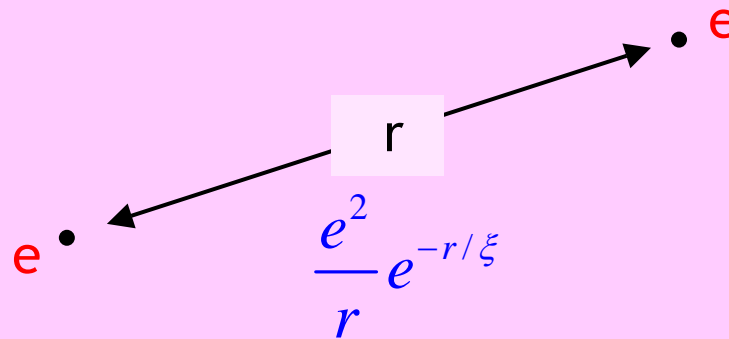
Elementary (“bare”) particles + interactions



effective (“quasi”) particles + effective interactions

Electron gas: **Screening**

Simplest approximation: Thomas-Fermi



Effective Yukawa potential

Interacting many-particle systems

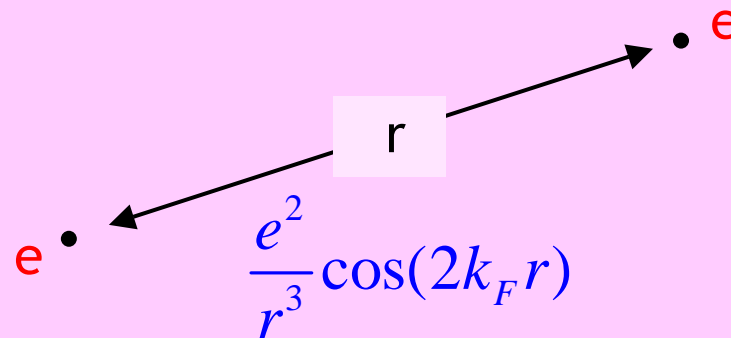
Elementary (“bare”) particles + interactions



effective (“quasi”) particles + effective interactions

Electron gas: **Screening**

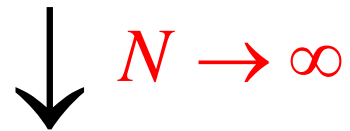
Better approximation: Lindhard



Friedel oscillations

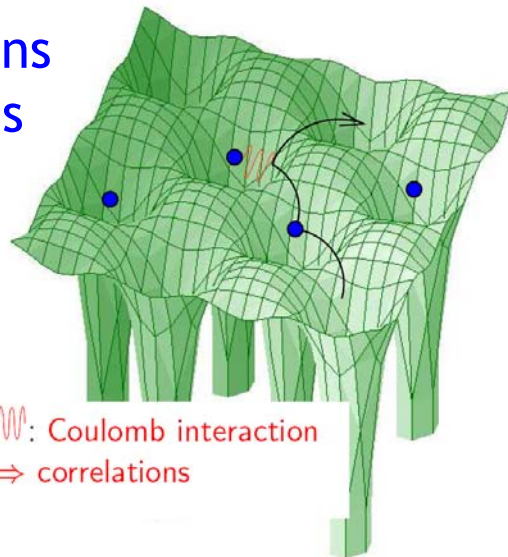
Interacting many-particle systems

Elementary (“bare”) particles + interactions

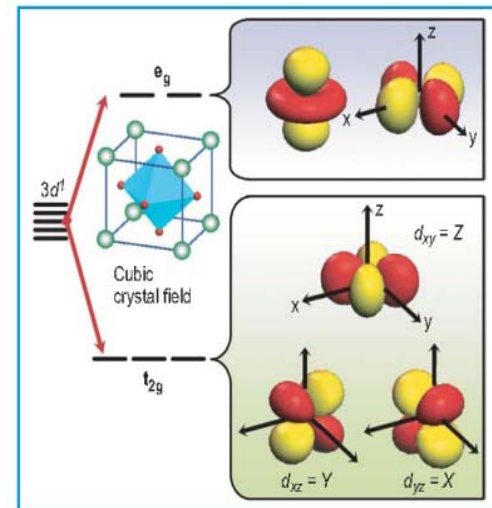


effective (“quasi”) particles + effective interactions

Electrons
in solids



: Coulomb interaction
=> correlations



“Strong interaction” of
electrons in localized orbitals

Quasiparticles

Electrons

$$\text{Spin} = \frac{1}{2}\hbar \quad \text{Fermion}$$



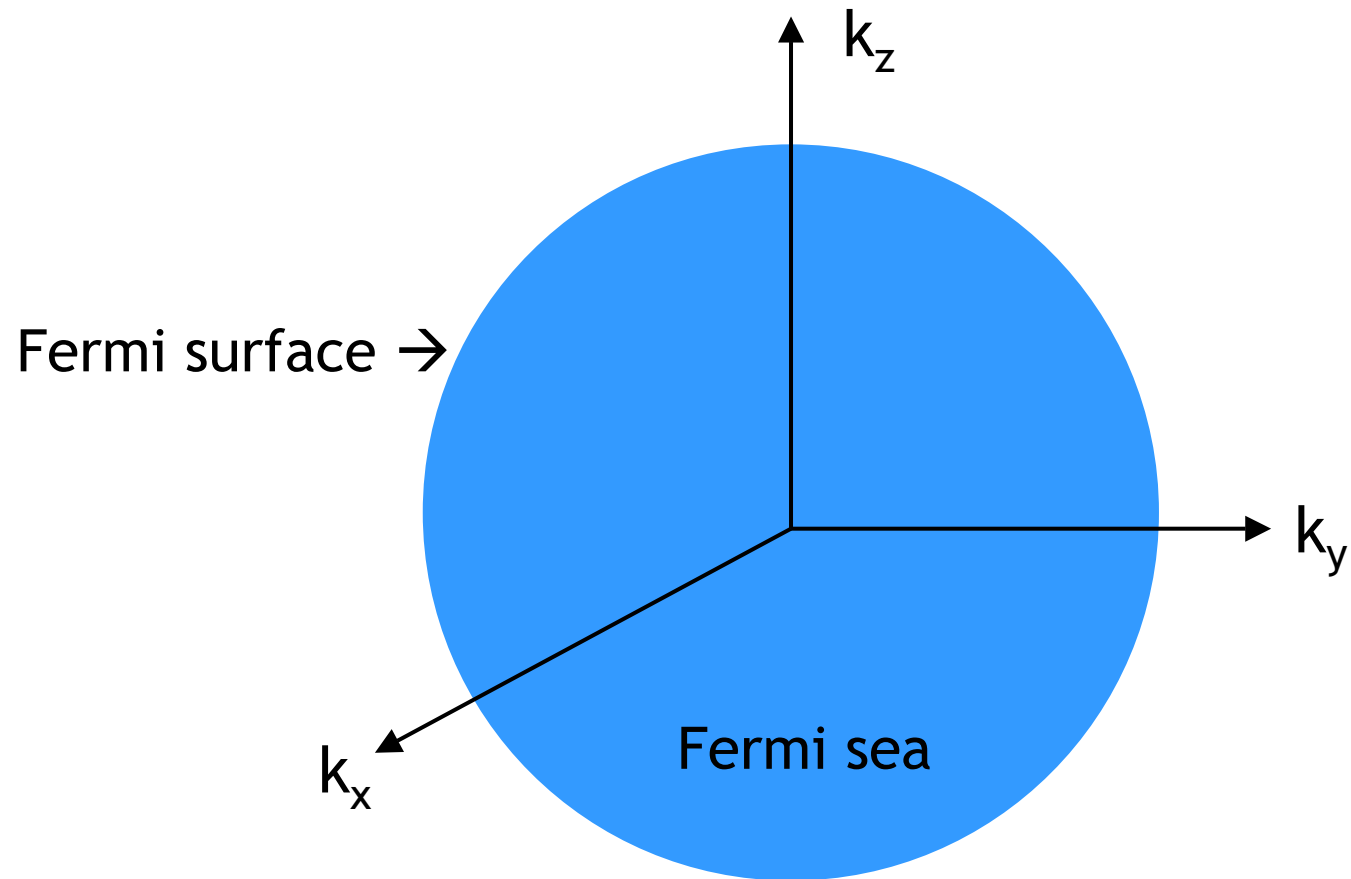
Fermi-Dirac statistics



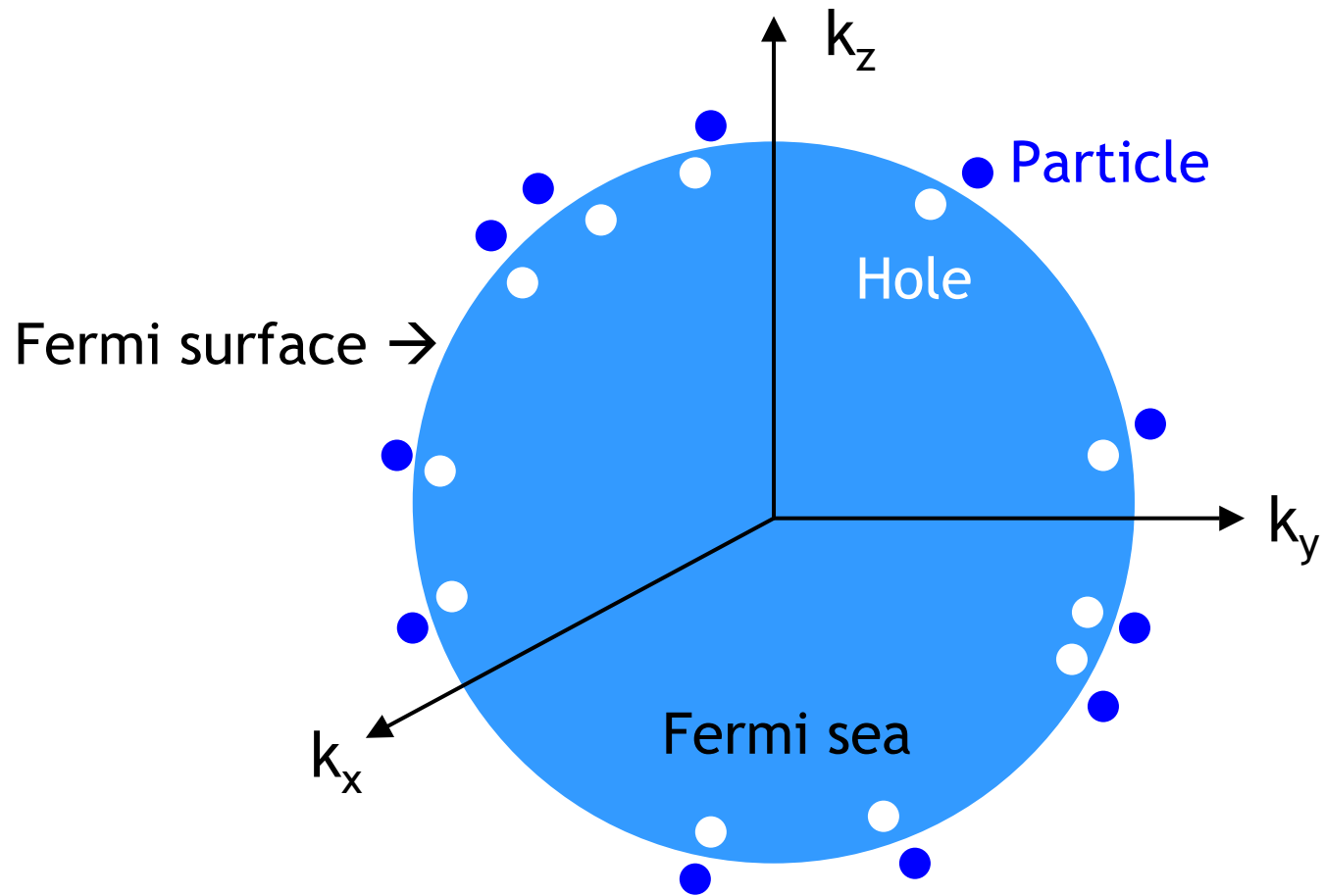
Pauli exclusion principle
of many fermions

Fermi body/surface

Fermi gas: Ground state



Fermi gas: Excited states ($T > 0$)



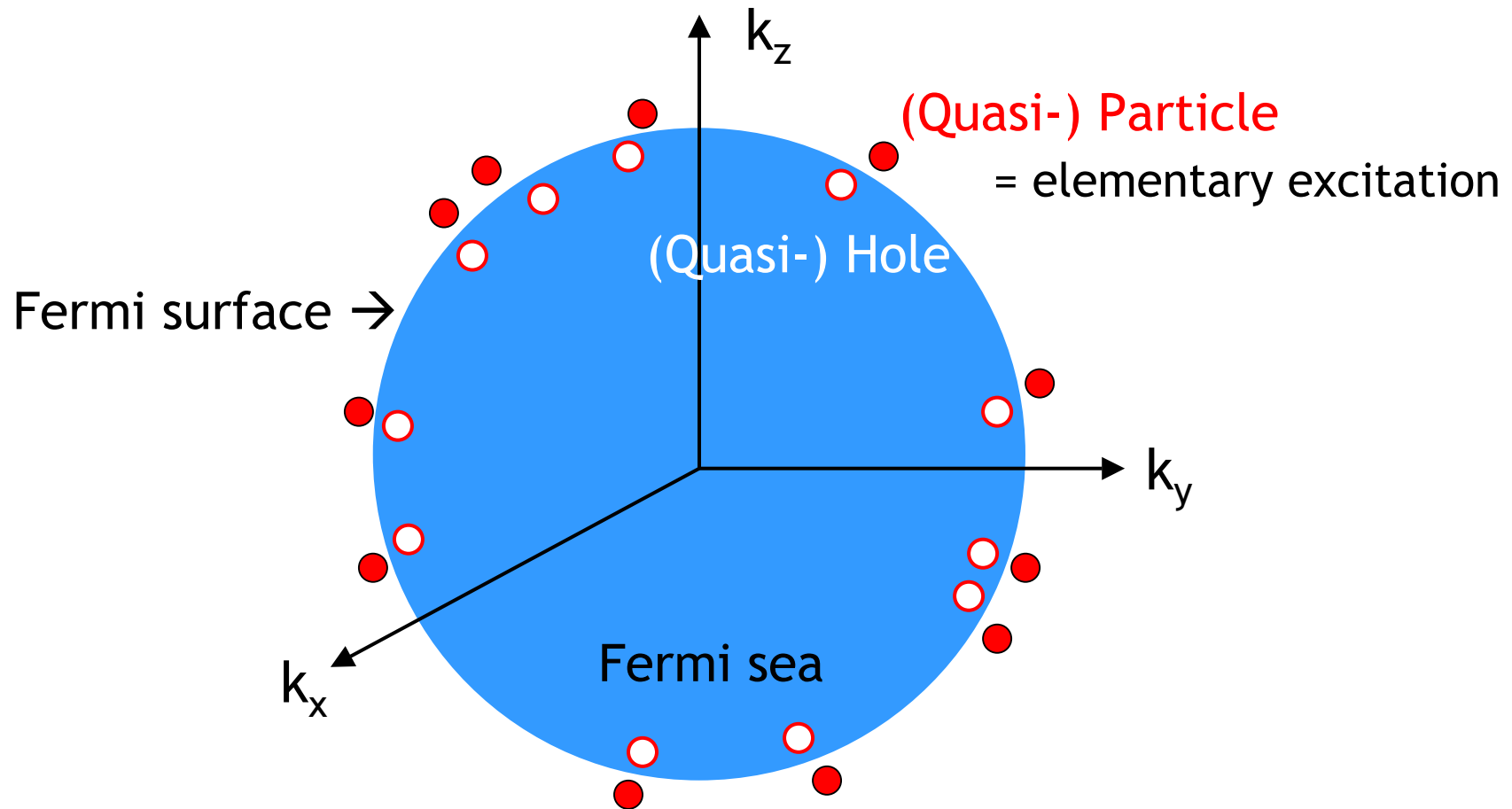
Exact k-states ("particles"): **infinite** life time

Switch on interaction adiabatically ($d=3$)

Landau Fermi liquid

Landau (1956/58)

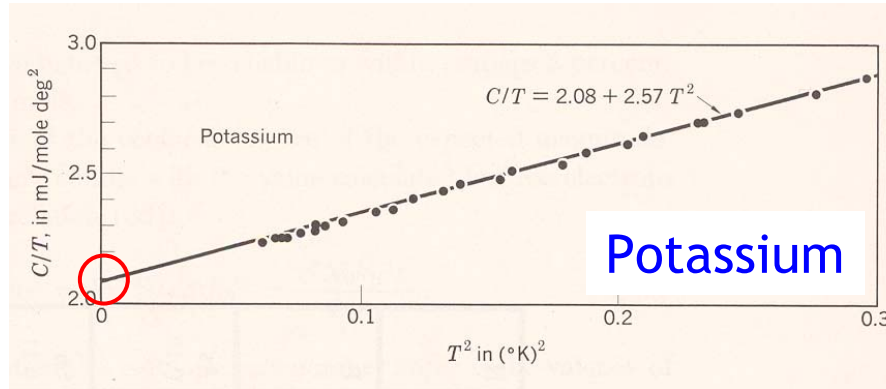
1-1 correspondence between k-states



Well-defined k-states ("quasiparticles") with

- finite life time
- effective mass
- effective interaction

Simple metals

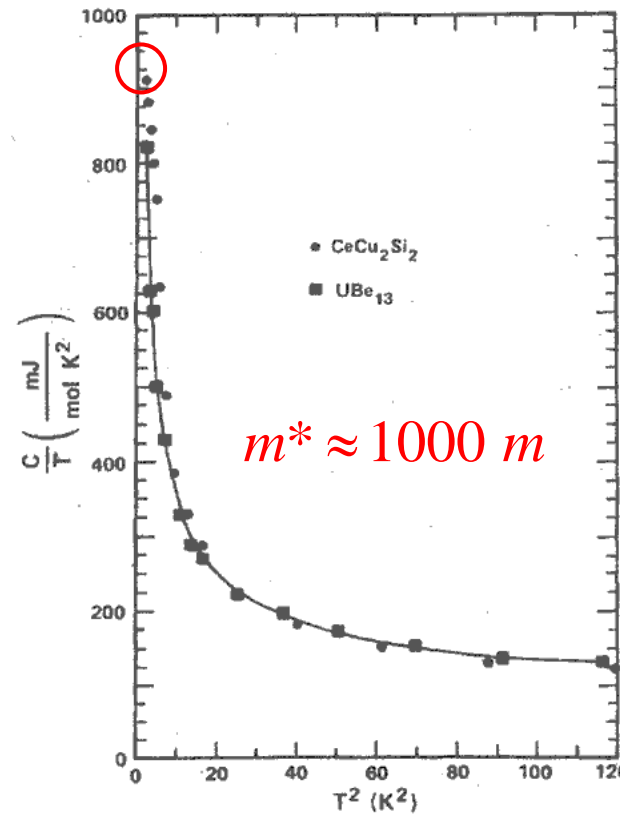


Consequence of elementary excitations (quasiparticles)

$$\lim_{T \rightarrow 0} \frac{C_V}{T} \approx \gamma_0 \Rightarrow m^* \approx m$$

"Heavy Fermions"

Steglich *et al.* (1979)



CeCu_2Si_2 , UBe_{13} :
strongly interacting electrons

$$\lim_{T \rightarrow 0} \frac{C_V}{T} = \gamma \propto \frac{m^*}{m}, \quad v_F = \frac{\hbar k_F}{m^*}$$

Interacting many-particle systems

↓ $N \rightarrow \infty$

Entirely new phenomena, e.g., **phase transitions**

↓

Unpredicted **“emergent”** behavior

We used to think that if we knew one, we knew two,
because one and one are two.

We are finding out that we must learn a great deal more about 'and'.

Arthur Eddington (1882-1944)

“More is different”

Anderson (1972)

Interacting many-particle systems

↓ $N \rightarrow \infty$

Emergence

Examples:

Superconductivity
Magnetism
Galaxy formation

Traffic
Weather
Stock market

Ants
Human body
Consciousness

→ The Institute for Complex Adaptive matter (ICAM)

2. Correlations

Correlation [lat.]: *con + relatio* ("with relation")

Grammar: *either ... or*

Mathematics, natural sciences:

$$\langle AB \rangle \neq \langle A \rangle \langle B \rangle$$

e.g., densities:

$$\langle \rho(\mathbf{r})\rho(\mathbf{r}') \rangle \neq \langle \rho(\mathbf{r}) \rangle \langle \rho(\mathbf{r}') \rangle$$

Temporal/spatial correlations in everyday life



Time/space average
insufficient

3. Electronic Correlations in Solids

Periodic Table of the Elements

1 IA New Original	2 IIA	3	4	5	6	7	8	9	10	11	12	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H Hydrogen 1.00794	2 He Helium 4.002602	3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797	11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.921595	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (99)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.3675	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 to 71 Lanthanide series	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 to 103 Actinide series	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 Uun Ununium (269)	111 Uuu Ununium (272)	112 Uub Ununium (277)	113 Uuq Ununquadium (285)	114 Uuh Ununhexium (289)	115 Uuq Ununquadium (285)	116 Uuh Ununhexium (289)	117 Uue Ununseptium (289)	118 Uuo Ununoctium (293)

Partially filled d-orbitals

Atomic masses in parentheses are those of the most stable or common isotope.

Web Page Design Copyright © 1997-1999 Michael Davah. <http://www.davah.com/periodic/>

Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 110-118 are the Latin equivalents of those numbers.

Partially filled f-orbitals

Narrow d,f-orbitals/bands → strong electronic correlations

Correlated electron materials

Fascinating topics for fundamental research

- large resistivity changes
- huge volume changes
- high T_c superconductivity
- strong thermoelectric response
- colossal magnetoresistance
- gigantic non-linear optical effects

} Large susceptibilities

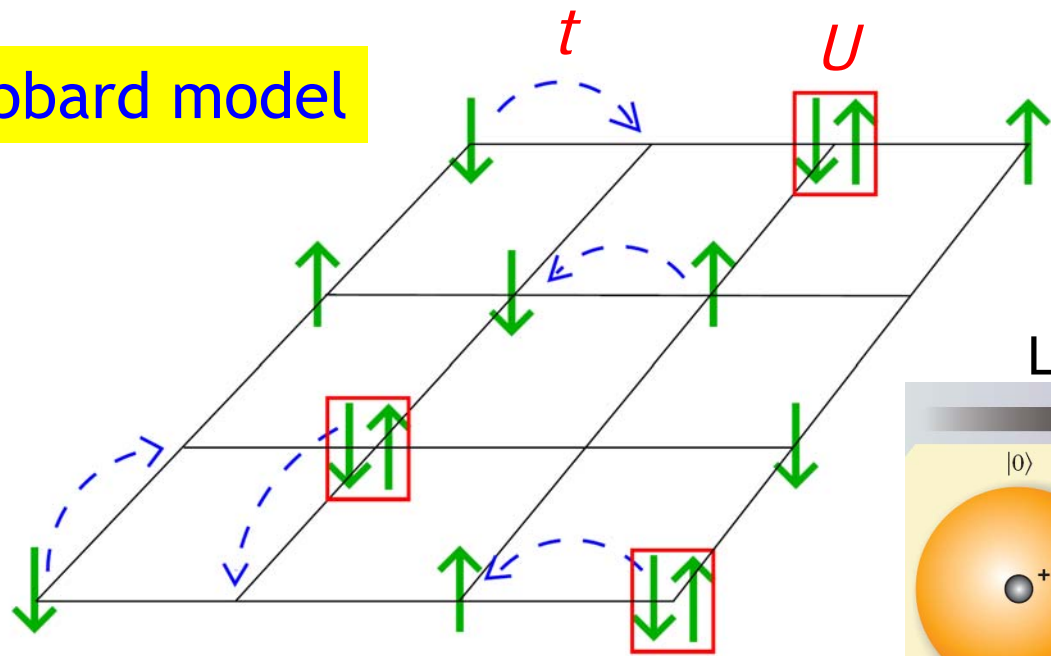
with

Technological applications:

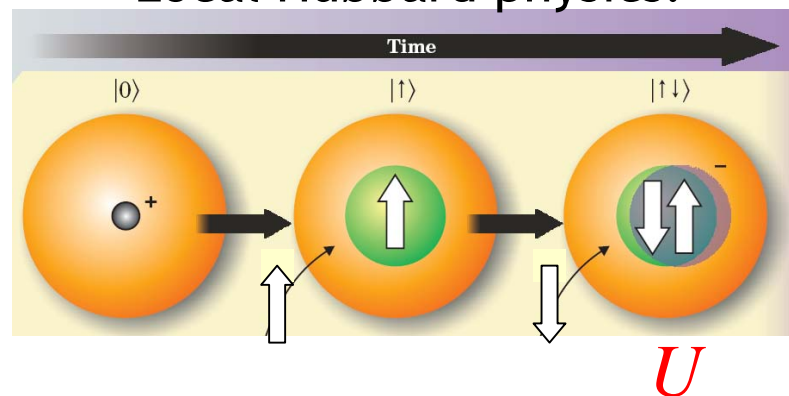
- sensors, switches
- magnetic storage
- refrigerators
- functional materials, ...

Electronic Correlations: Models

Hubbard model



Local Hubbard physics:

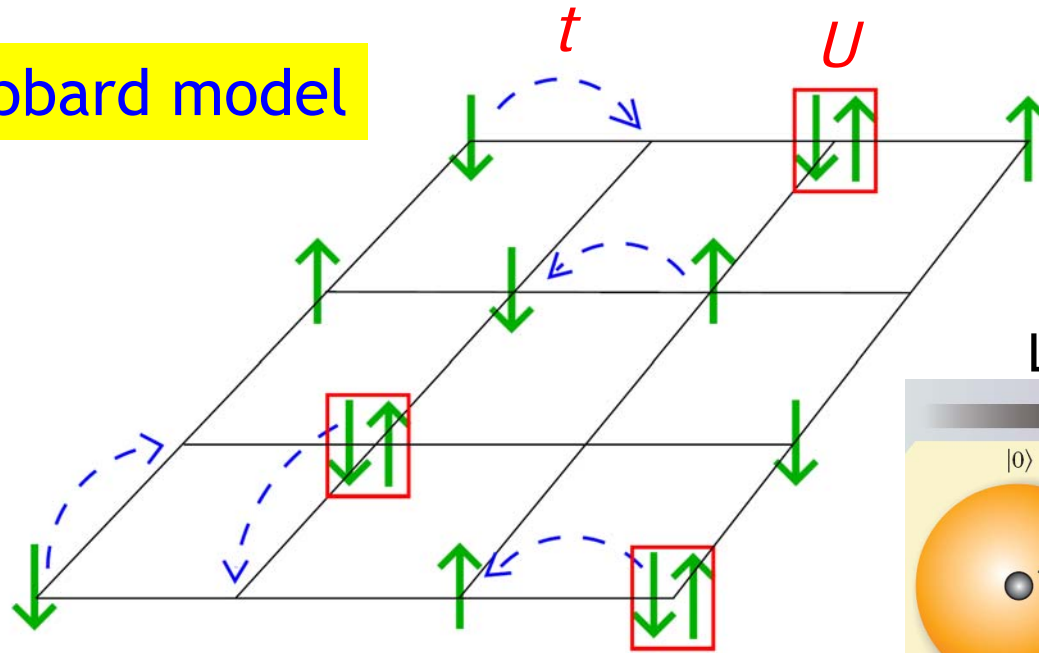


$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

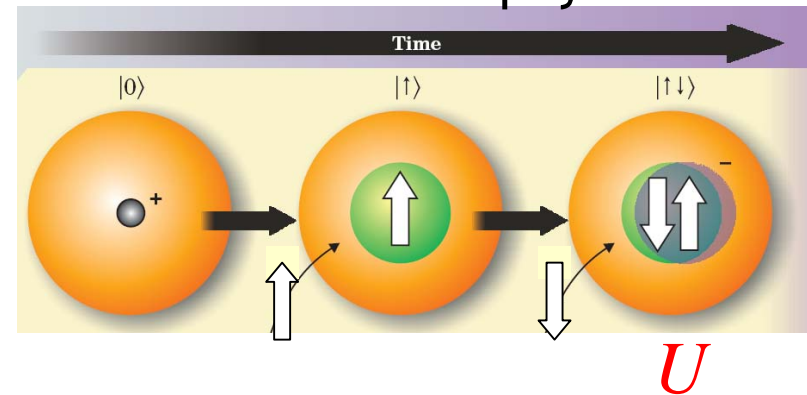


time

Hubbard model



Local Hubbard physics:



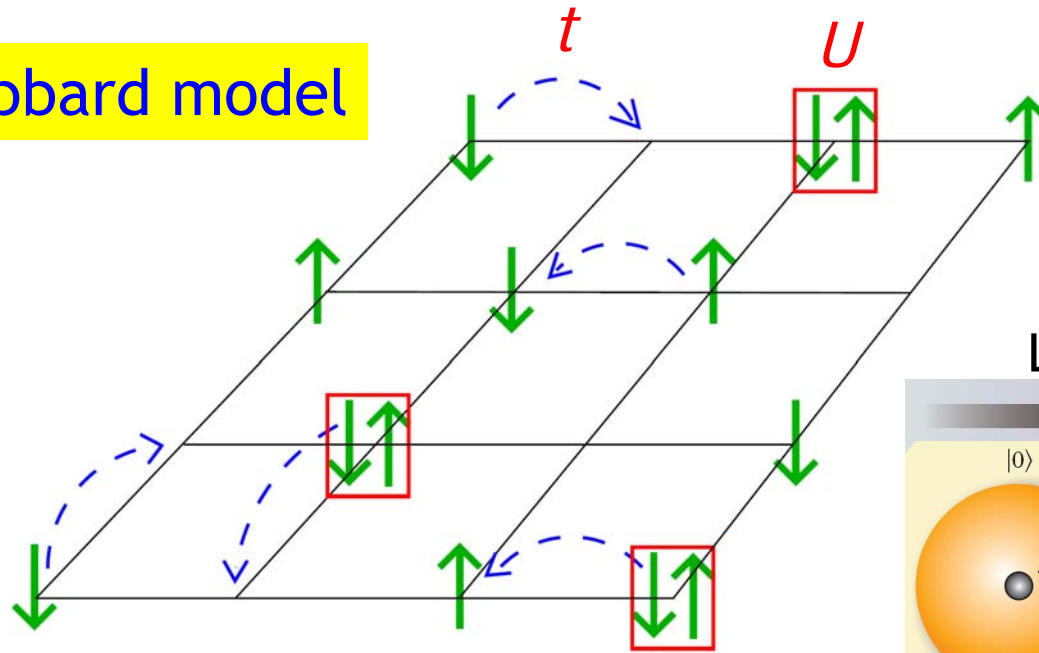
$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$\langle n_{i\uparrow} n_{i\downarrow} \rangle \neq \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$$

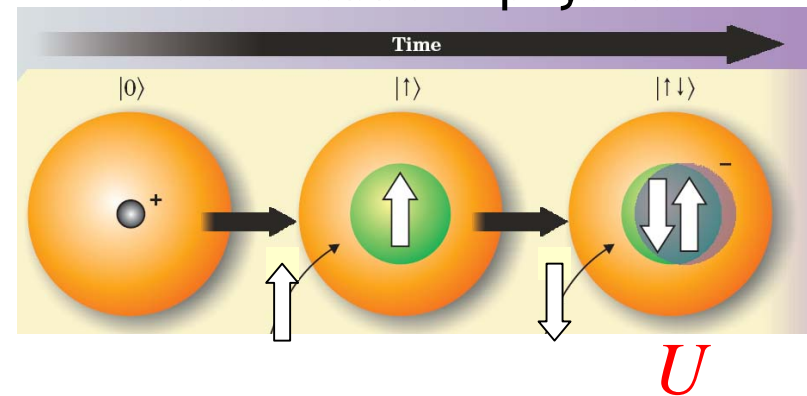
Correlation phenomena:
e.g., metal-insulator transition, ...

Static (Hartree-Fock)
mean-field theories
generally insufficient

Hubbard model



Local Hubbard physics:



$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$\langle n_{i\uparrow} n_{i\downarrow} \rangle \neq \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle$$

Main theoretical challenge:
Construct reliable, comprehensive approximation schemes

Static (Hartree-Fock) mean-field theories generally insufficient

4.

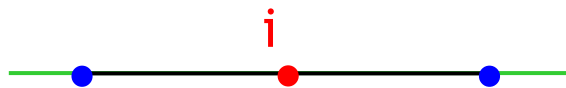
Dynamical Mean-Field Theory (DMFT)
of Correlated Electrons

Theory of strongly correlated electrons

$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{\mathbf{i}} n_{i\uparrow} n_{i\downarrow} \quad \text{Hubbard model}$$

Hypercubic lattices: Coordination number $Z=2d$

Dimension $d=1$



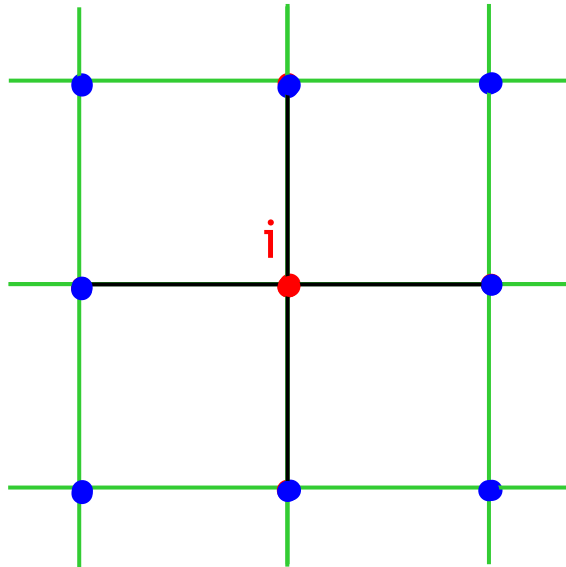
$$Z=2$$

Theory of strongly correlated electrons

$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{\mathbf{i}} n_{i\uparrow} n_{i\downarrow} \quad \text{Hubbard model}$$

Hypercubic lattices: Coordination number $Z=2d$

Dimension $d=2$



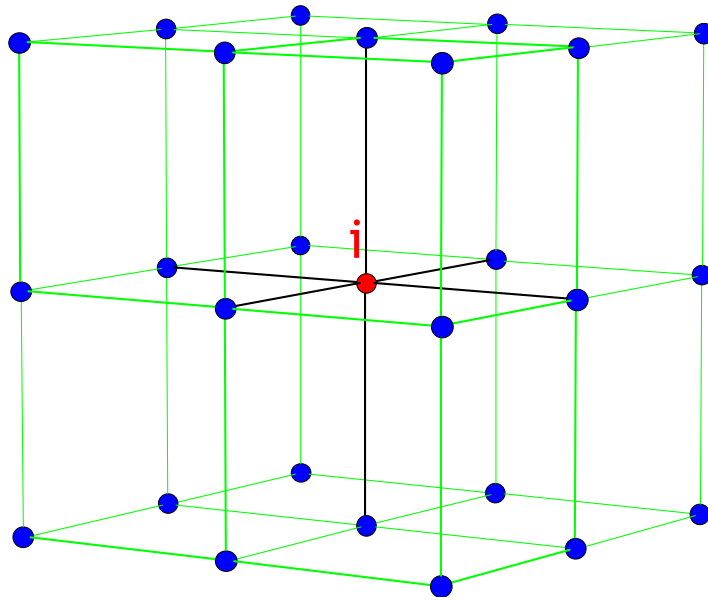
$Z=4$

Theory of strongly correlated electrons

$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{\mathbf{i}} n_{i\uparrow} n_{i\downarrow} \quad \text{Hubbard model}$$

Hypercubic lattices: Coordination number $Z=2d$

Dimension $d=3$



$Z=6$

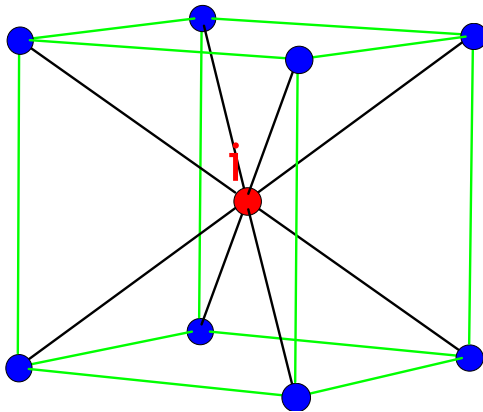
Theory of strongly correlated electrons

$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{\mathbf{i}} n_{i\uparrow} n_{i\downarrow}$$

Hubbard model

Body-centered cubic lattice

Dimension $d=3$



$Z=8$

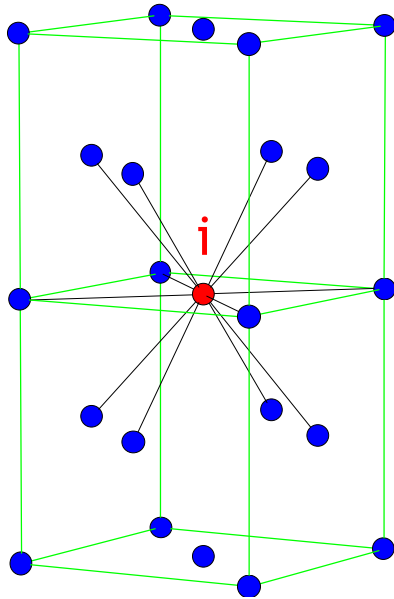
Theory of strongly correlated electrons

$$H = -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Hubbard model

Face-centered cubic lattice

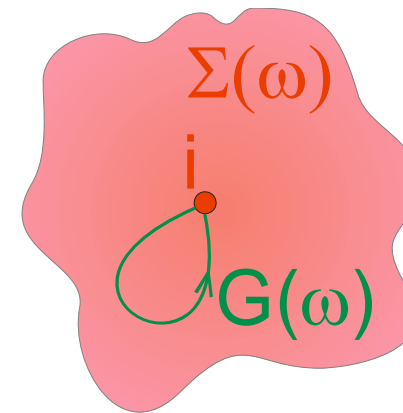
Dimension $d=3$



$Z=12$

Metzner, DV (1989)

$d \rightarrow \infty$
 $Z \rightarrow \infty$

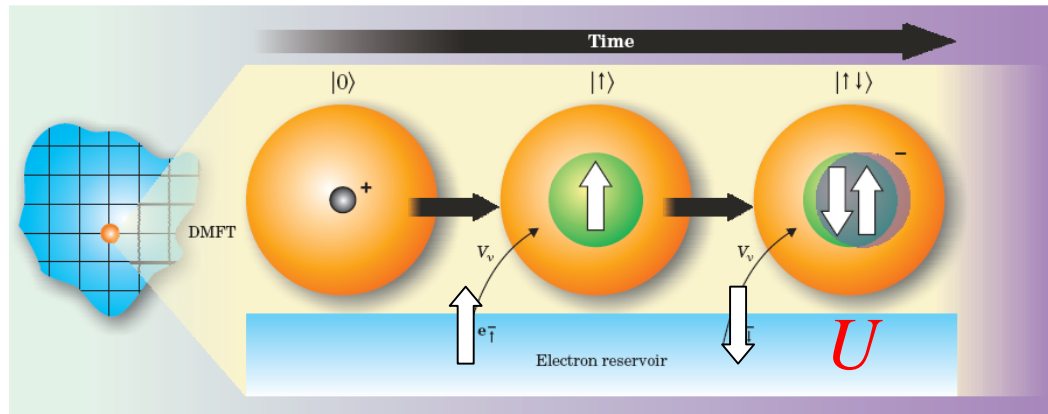


“Dynamical mean-field theory“ (DMFT)

Müller-Hartmann (1989), Janis (1991)
Georges and Kotliar (1992)

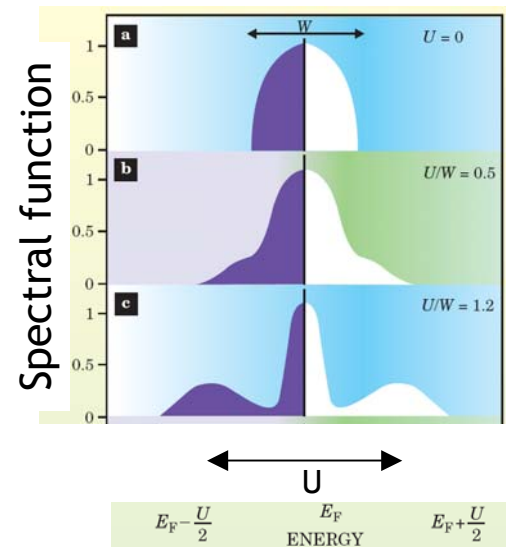
Dynamical mean-field theory (DMFT) of correlated electrons

Proper **time** resolved treatment of **local** electronic interactions:



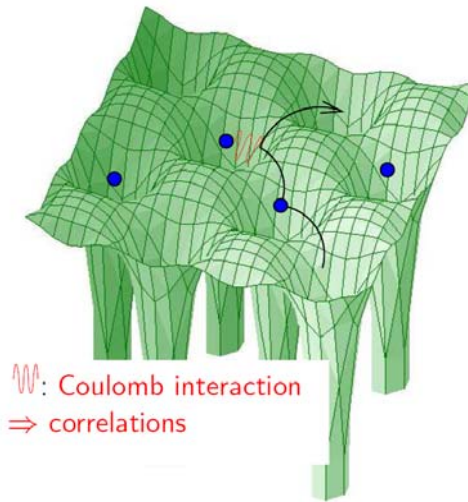
Physics Today
Kotliar, DV (2004)

Electronic correlations
→ Transfer of spectral weight



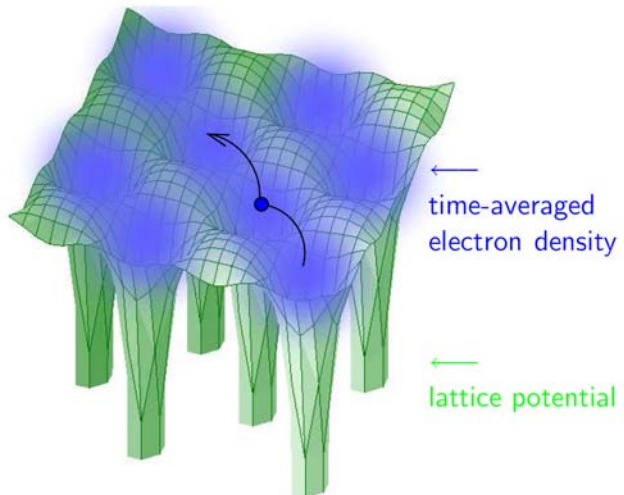
Experimentally
measurable ?

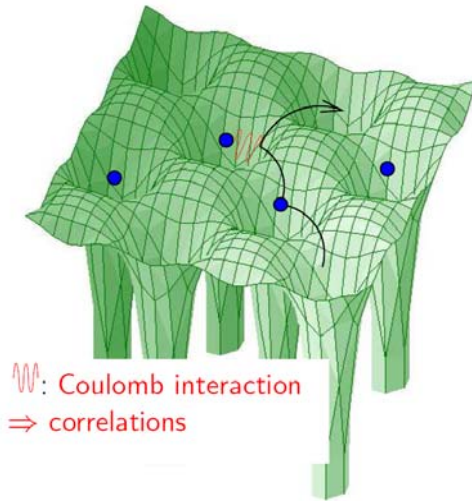
Correlated Electron: Materials



DFT/LDA

- + material specific: “ab initio”
- fails for strong correlations
- + fast code packages



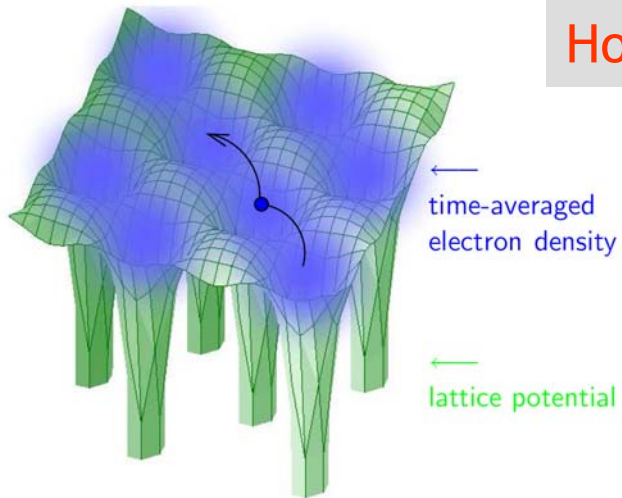


DFT/LDA

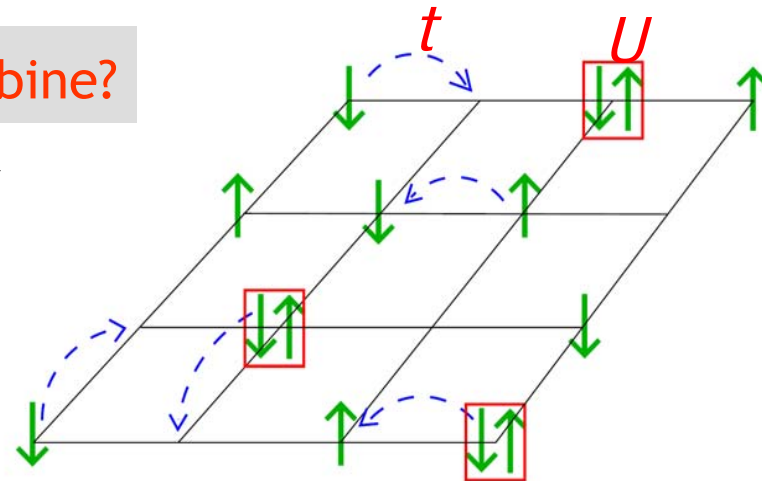
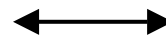
Model Hamiltonians

- + material specific: "ab initio"
- fails for strong correlations
- + fast code packages

- input parameters unknown
- + systematic many-body approach
- computationally expensive



How to combine?



Computational scheme for correlated electron materials:

Material specific electronic structure
(Density functional theory: LDA, GGA, KKR, ...)

+

Local electronic correlations
(Many-body theory: DMFT)



LDA+DMFT

Anisimov *et al.* (1997)
Lichtenstein, Katsnelson (1998)
Nekrasov *et al.* (2000)

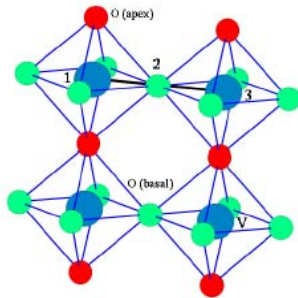
Kotliar, DV (Physics Today, March 2004)
Kotliar *et al.* (RMP, 2006)

Application of LDA+DMFT:
(Sr,Ca)VO₃

Electronic structure

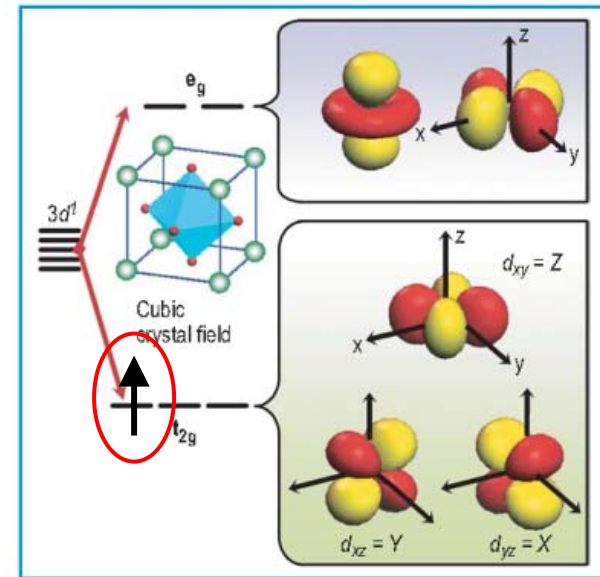
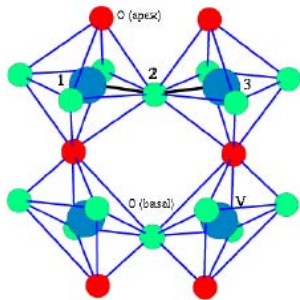
Crystal structure

SrVO_3 : $\angle V-O-V = 180^\circ$

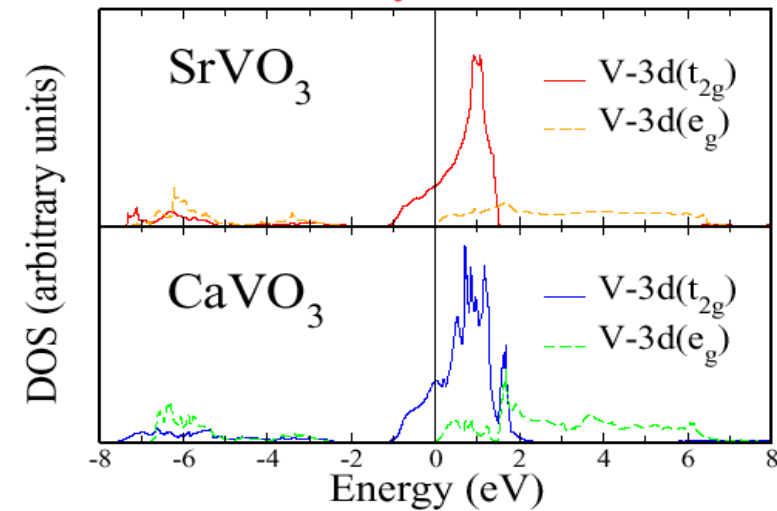


orthorhombic distortion

CaVO_3 : $\angle V-O-V \approx 162^\circ$

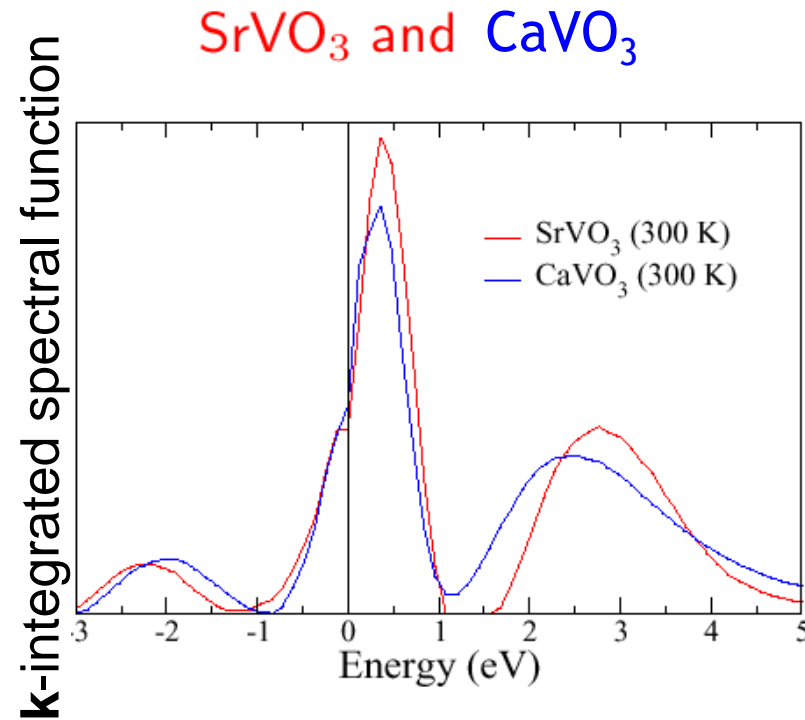


LDA density of states



No correlation effects/spectral transfer

LDA+DMFT results



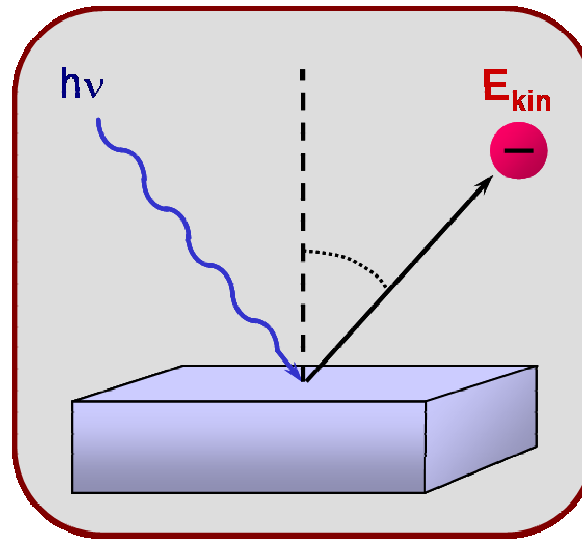
constrained LDA:
U=5.55 eV, J=1.0 eV

Osaka - Augsburg - Ekaterinburg collaboration: Sekiyama *et al.* (2004)

How to measure ?

Excursion: Spectroscopy

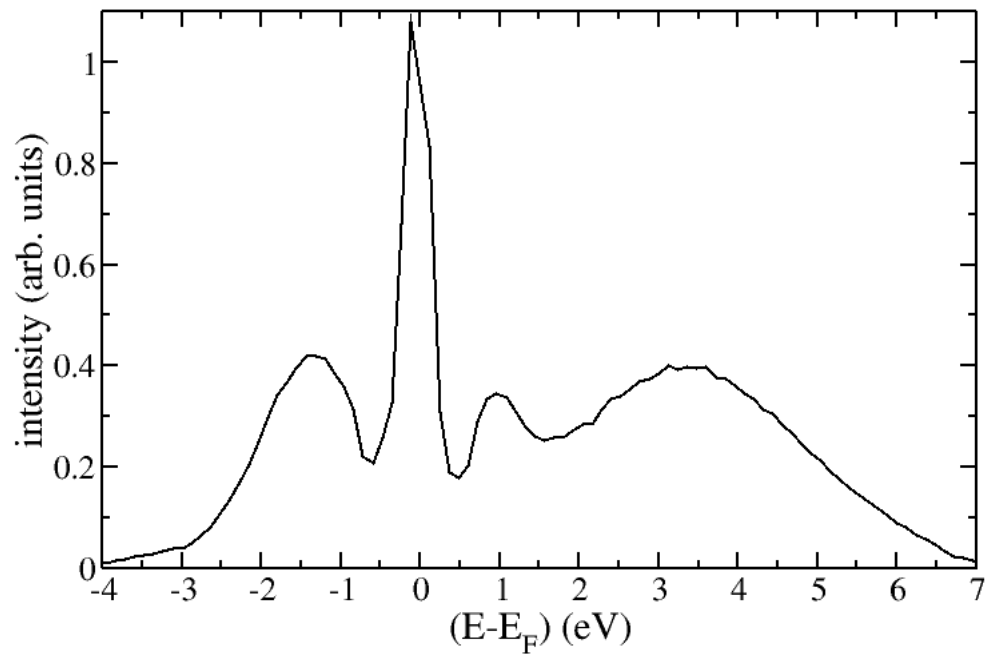
1. Photoemission Spectroscopy (PES)



Angular Resolved PES = ARPES

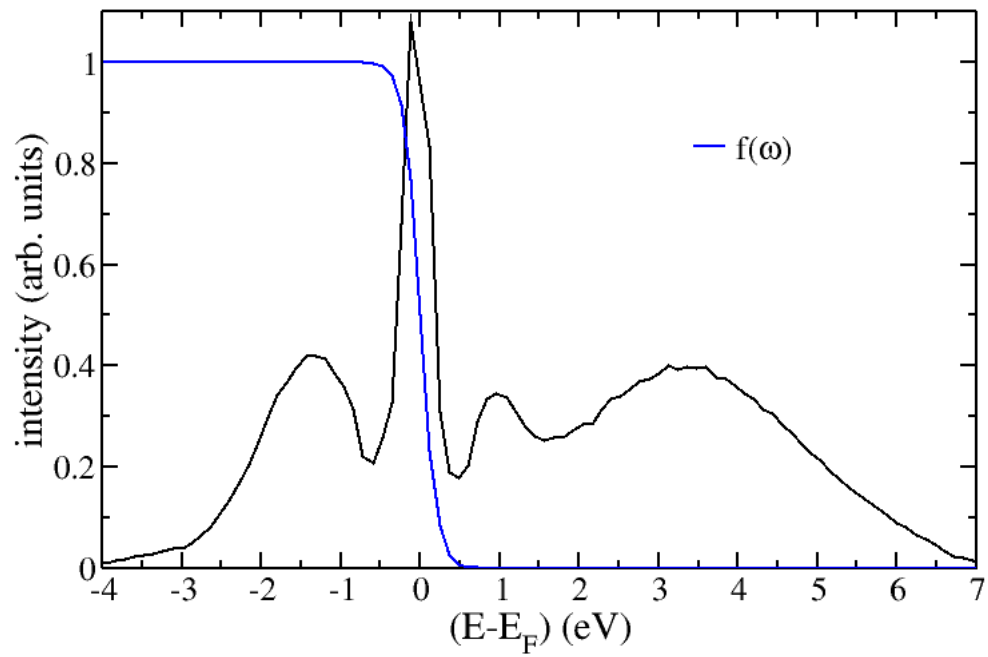
Measures **occupied** states of electronic spectral function

PES



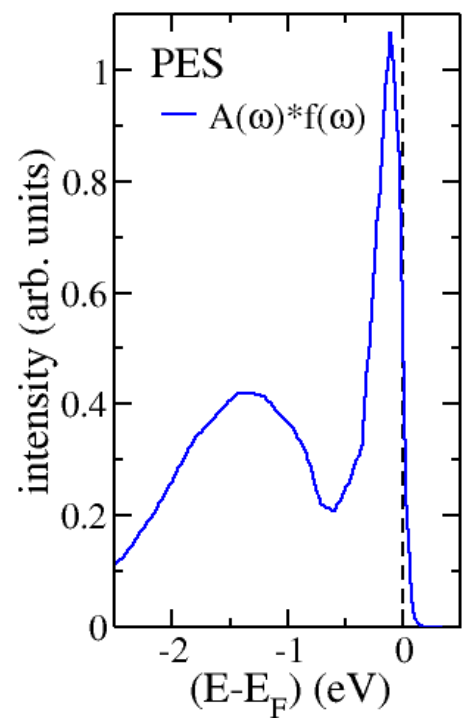
Ideal spectral function of a material

PES



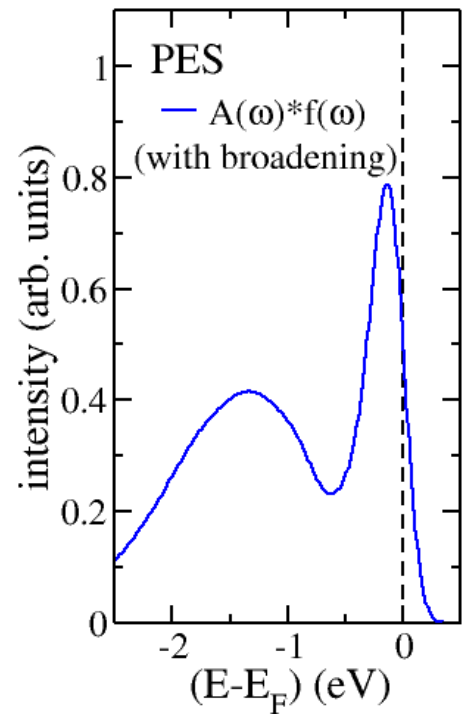
Ideal spectral function of a material

PES



Occupied states
(ideal)

PES

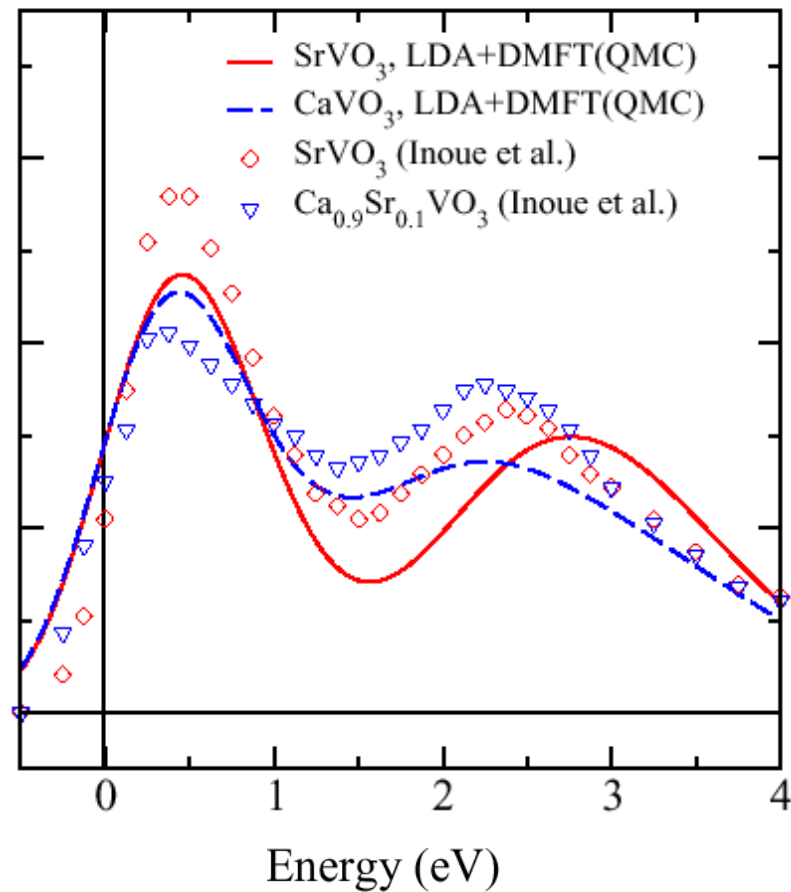
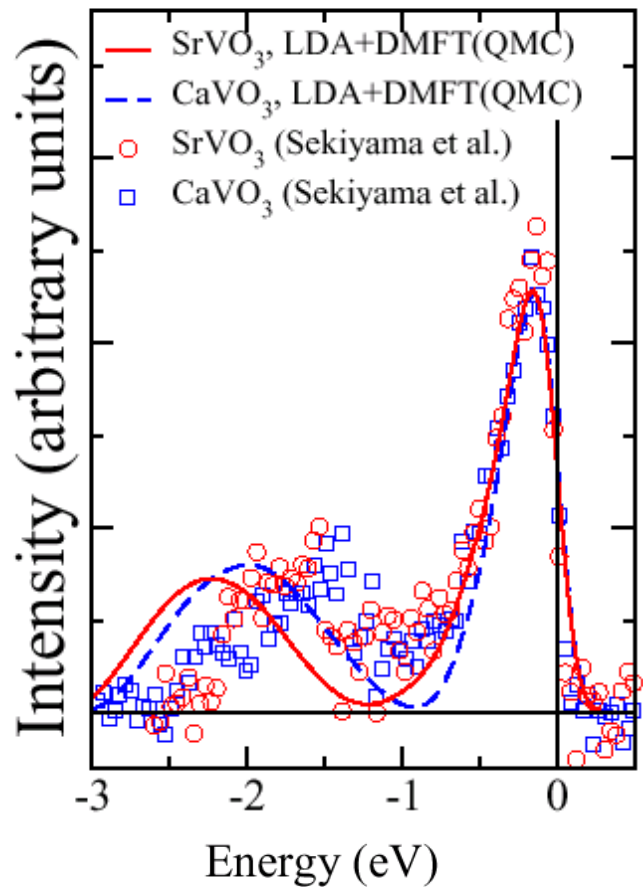


Occupied states
(experiment)

Comparison with experiment

Osaka - Augsburg -
Ekaterinburg collaboration,
(2004, 2005)

- (i) bulk-sensitive high-resolution photoemission spectra (PES)
- (ii) $1s$ x-ray absorption spectra (XAS) → **unoccupied states**



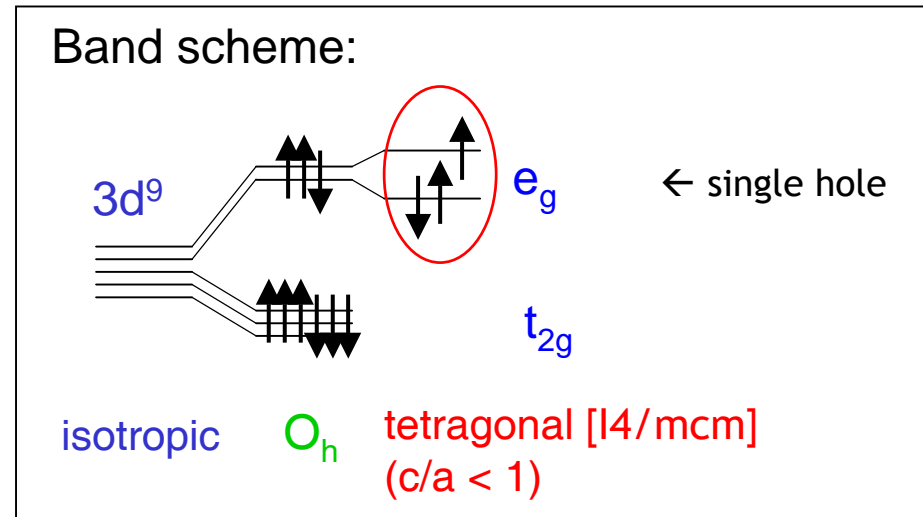
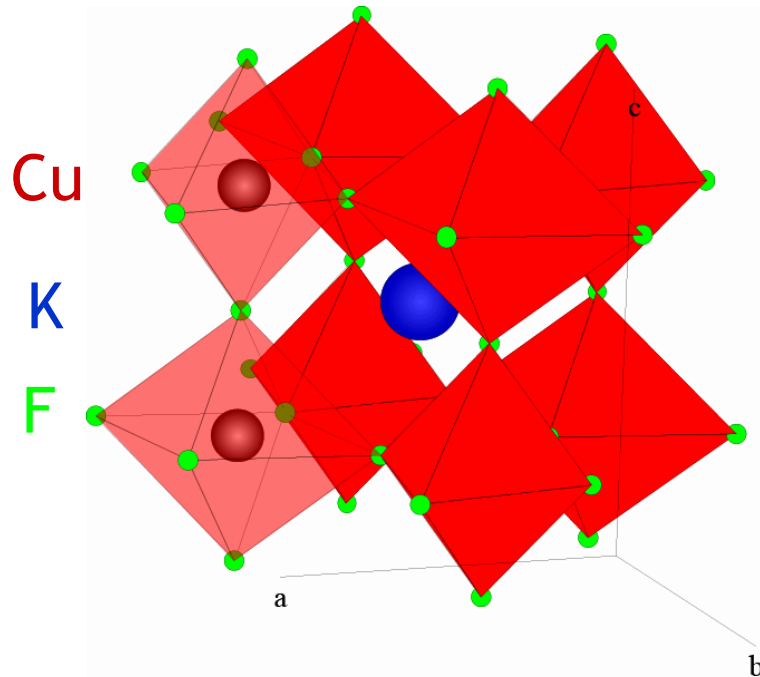
Application of LDA+DMFT:
Electronic correlations & structural transformation

KCuF₃: Prototypical Jahn-Teller system

Room temperature crystal structure:

Kugel, Khomskii (1982)

Lichtenstein, Anisimov, Zaanen (1995)

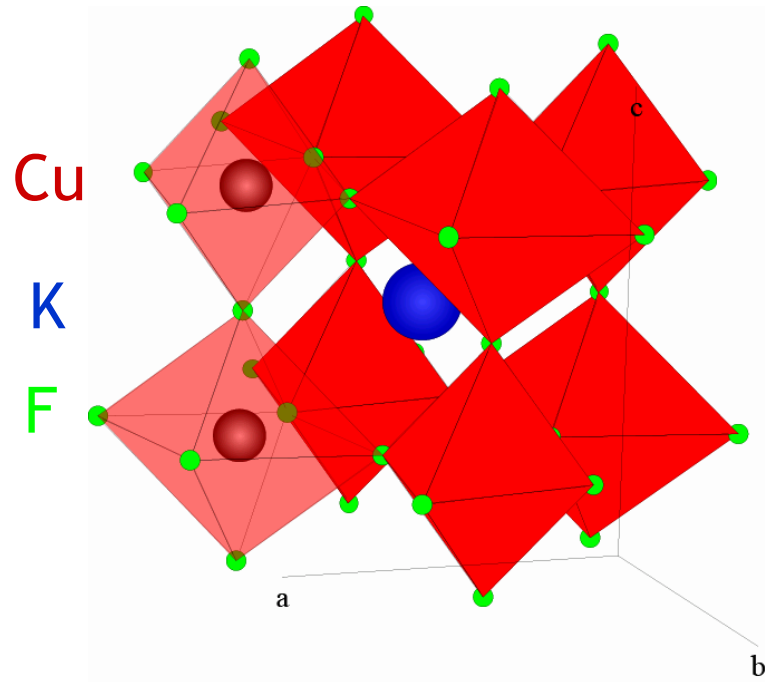


- insulating, pseudo-cubic perovskite
- $T_{\text{Neel}} \sim 38$ K

- cooperative JT distortion = spontaneous lifting of orbital degeneracy
→ orbital order → structural relaxation with symmetry reduction

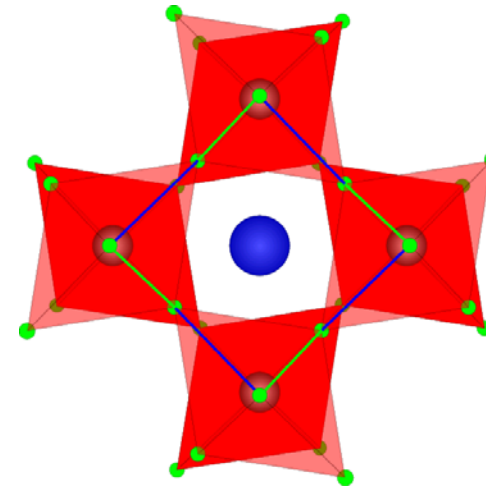
KCuF₃: Prototypical Jahn-Teller system

Room temperature crystal structure:



Kugel, Khomskii (1982)

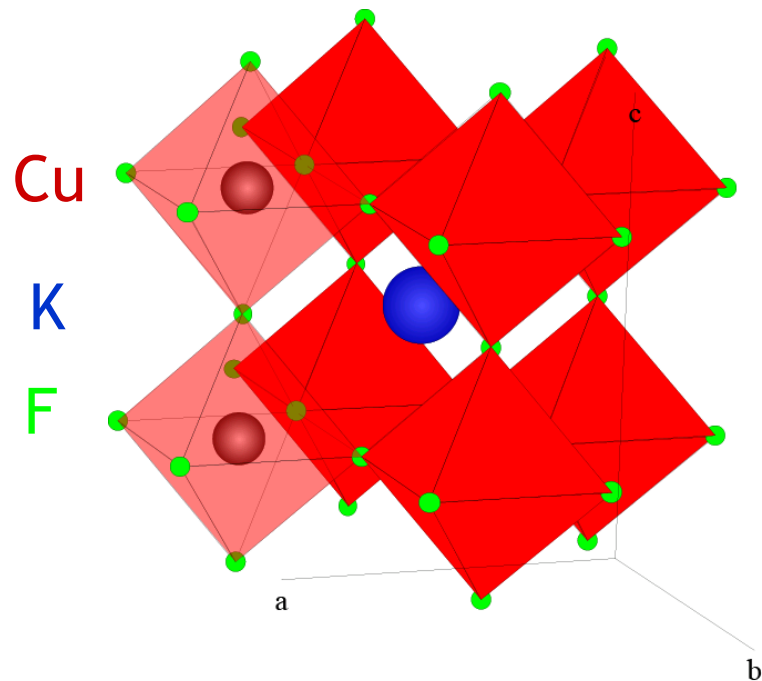
Liechtenstein, Anisimov, Zaanen (1995)



Cooperative JT distortion

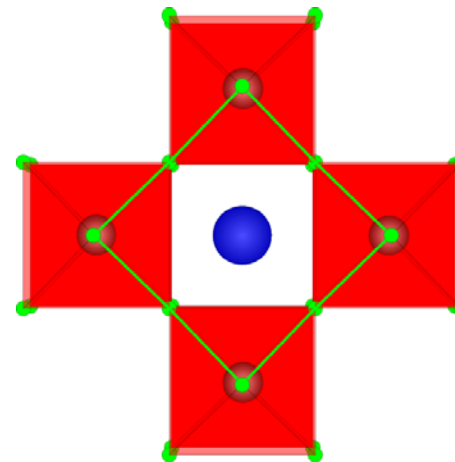
KCuF₃: Prototypical Jahn-Teller system

Room temperature crystal structure:



Kugel, Khomskii (1982)

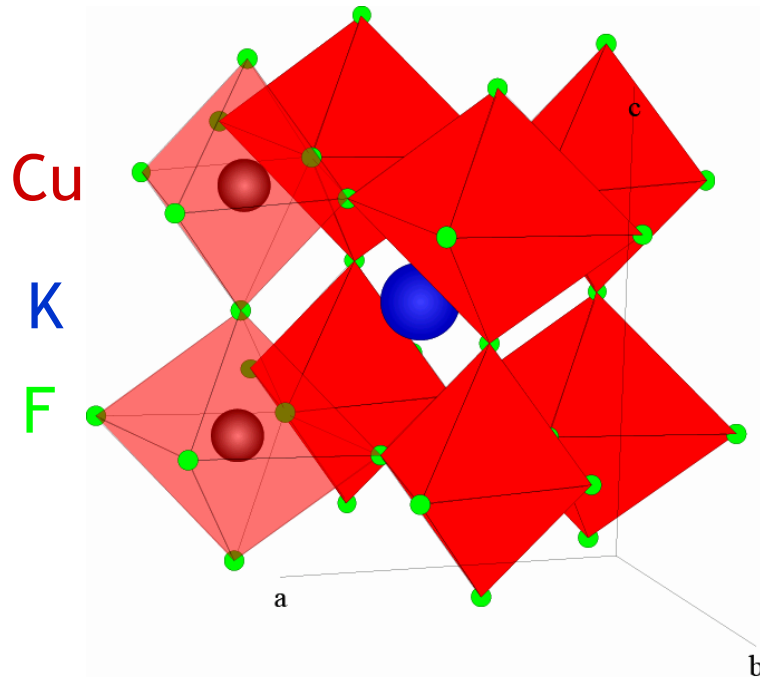
Lichtenstein, Anisimov, Zaanen (1995)



Undistorted structure

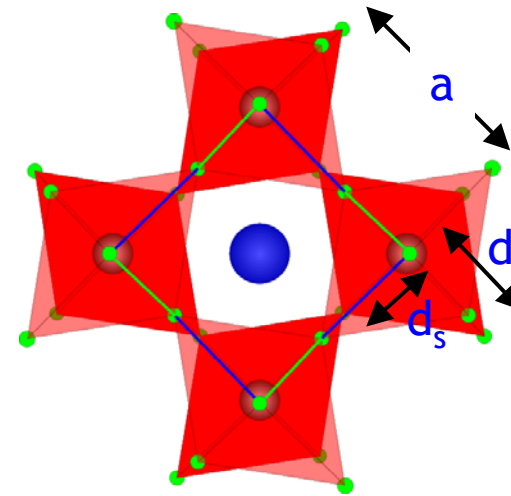
KCuF₃: Prototypical Jahn-Teller system

Room temperature crystal structure:



Kugel, Khomskii (1982)

Liechtenstein, Anisimov, Zaanen (1995)



$$\text{JT-distortion } \delta_{\text{JT}} = (d_l - d_s) / a$$

$T > T_N \sim 38 \text{ K}$: Correlated paramagnetic insulator with strong JT distortion

LDA/GGA+U predicts magnetic LRO

How to determine - cooperative JT-distortion ?
- correct orbital order ?

KCuF₃: GGA+DMFT results

Leonov, Bingelli, Korotin, Anisimov,
Stojic, DV; PRL (2008)

Implementation with plane-wave pseudo-potentials

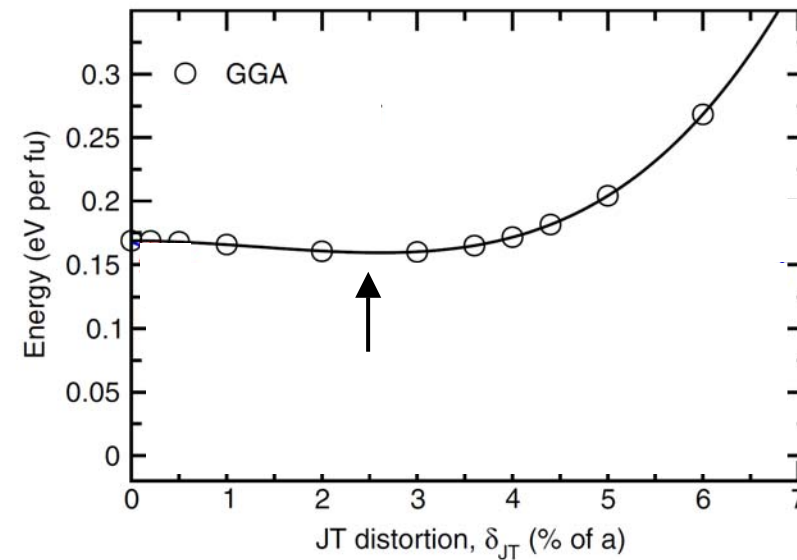
GGA:

- **metallic** solution
- very shallow minimum of energy at $\delta_{JT} = 2.5\%$
→ $\delta_{JT} = 0$ for $T > 100$ K
(no orbital order)

Inconsistent with experiment

$$U = 7.0 \text{ eV}, J = 0.9 \text{ eV}$$

Total energy



KCuF₃: GGA+DMFT results

Leonov, Bingelli, Korotin, Anisimov,
Stojic, DV; PRL (2008)

Implementation with plane-wave pseudo-potentials

$$U = 7.0 \text{ eV}, J = 0.9 \text{ eV}$$

GGA:

- **metallic** solution
- very shallow minimum of energy at $\delta_{JT} = 2.5\%$
→ $\delta_{JT} = 0$ for $T > 100 \text{ K}$
(no orbital order)

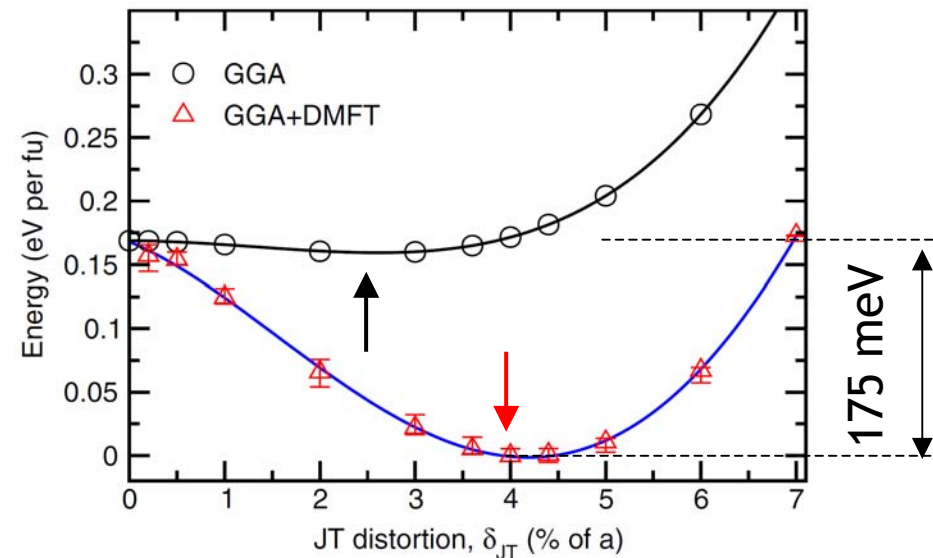
Inconsistent with experiment

GGA+DMFT:

- **paramagnetic** insulator
- $\delta_{JT}^{\text{opt}} = 4.1\%$ → JT distortion **persists** up to **1000 K** (melting)
- **AF orbital order**

Good agreement with experiment at 300 K

Total energy

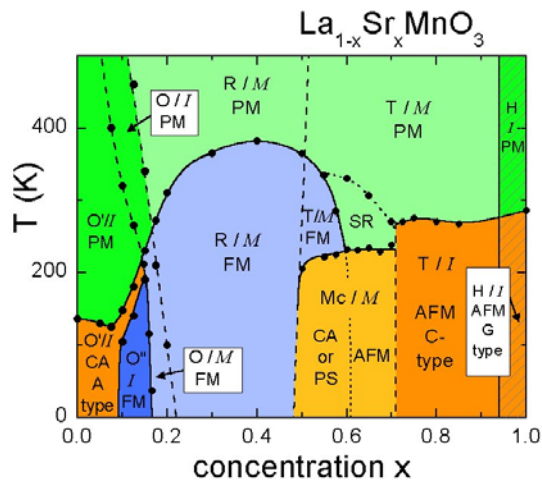


→ Structural transformation caused by electronic correlations

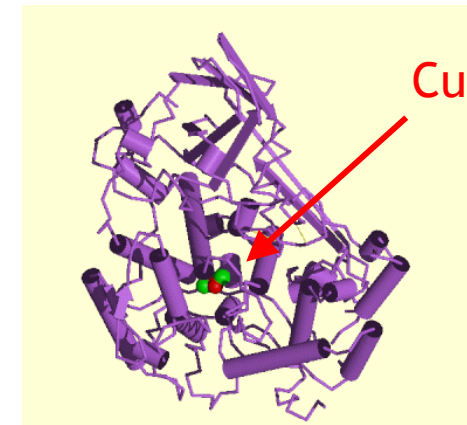
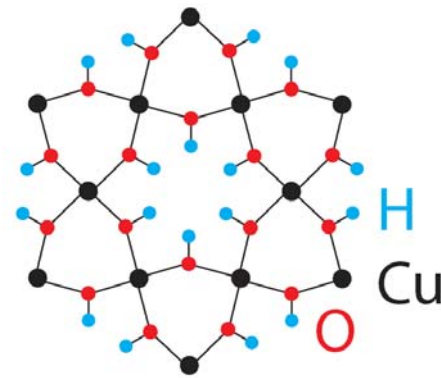
5. New Developments & Perspectives

(i) Complex correlated electron materials

Explanation & prediction of properties of complex materials

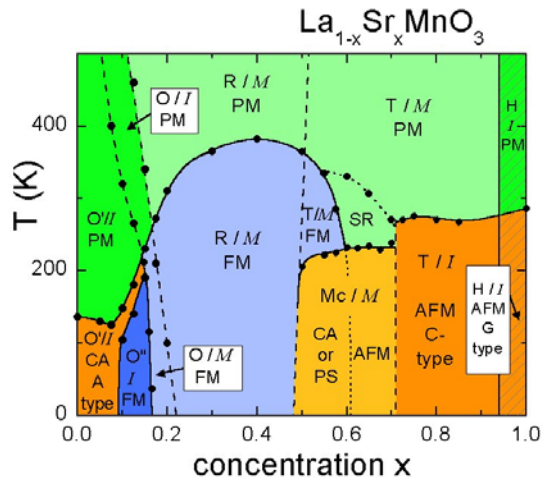


Phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$
Hemberger *et al.* (2002)

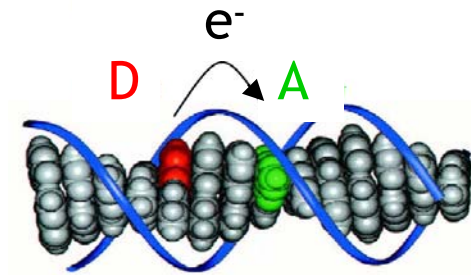
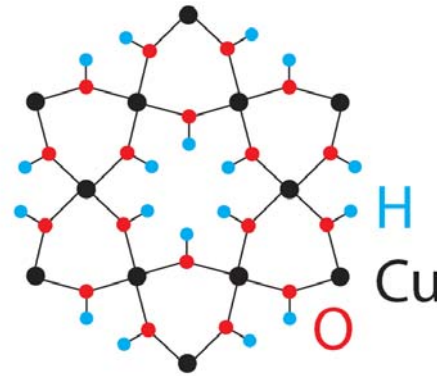


(i) Complex correlated electron materials

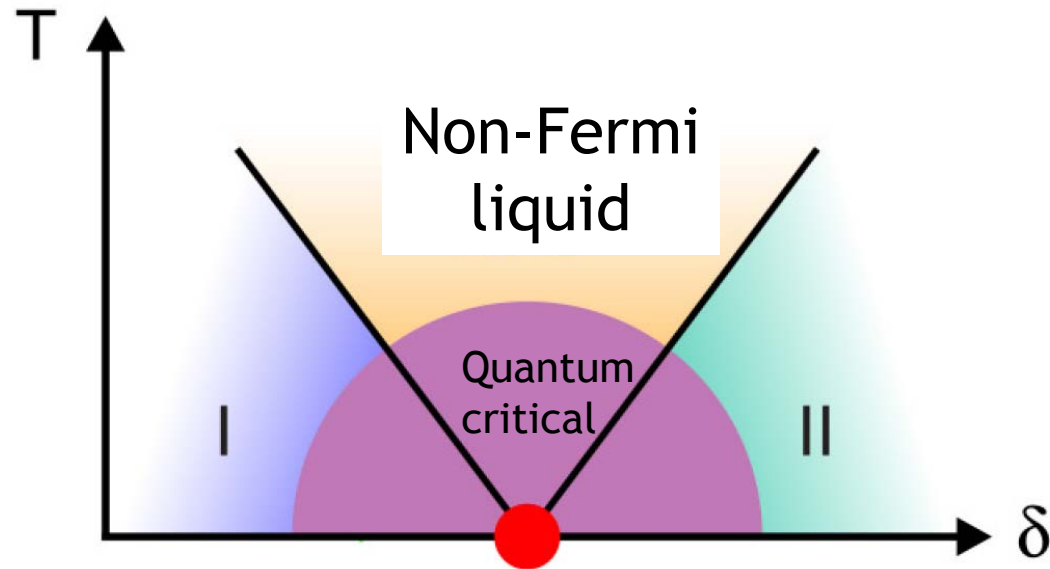
Explanation & prediction of properties of complex materials



Phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$
 Hemberger *et al.* (2002)



(ii) Quantum phase transitions



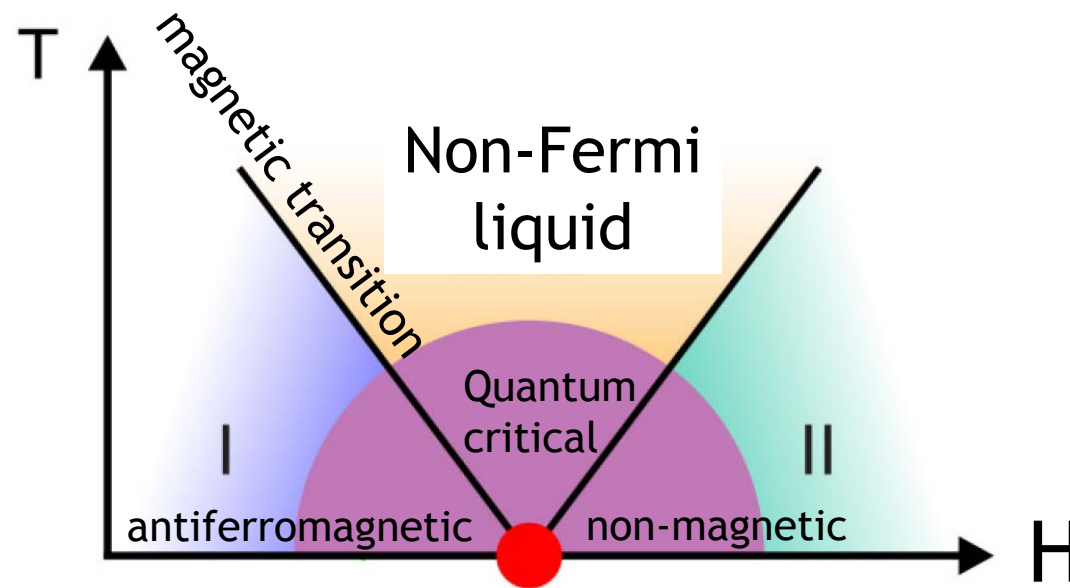
Quantum critical point

© DFG Research Unit
(Augsburg-Dresden-Göttingen-
Karlsruhe-Köln-München, 2007)

Driven by quantum fluctuations

- Non-Fermi liquid behavior
- Emergence of novel degrees of freedom
- New phases of matter

(ii) Quantum phase transitions



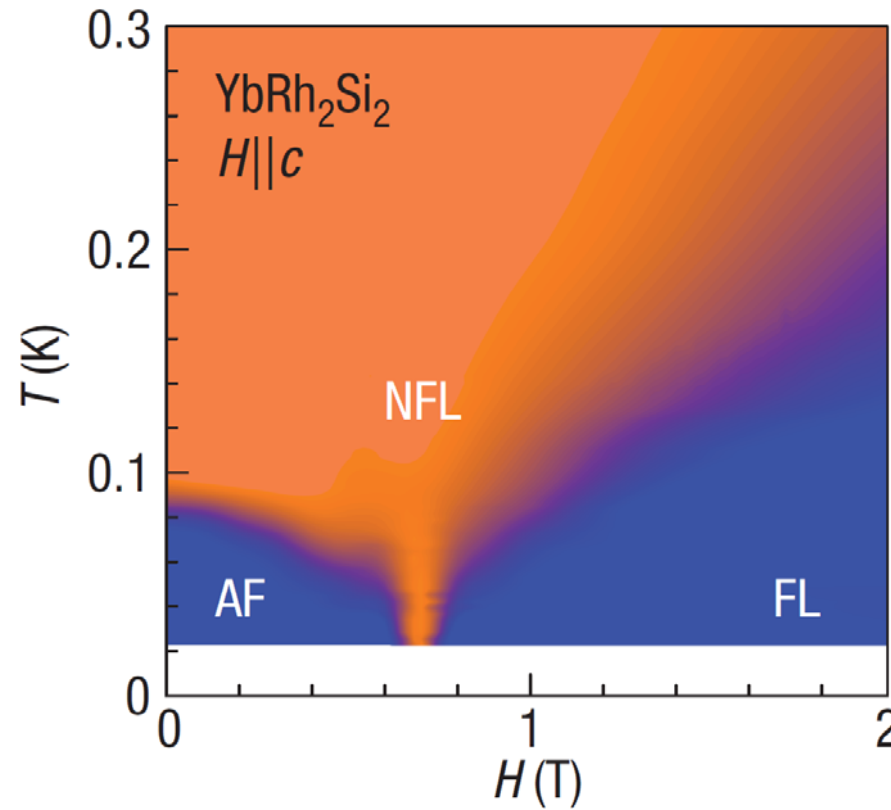
Quantum critical point

© DFG Research Unit
(Augsburg-Dresden-Göttingen-
Karlsruhe-Köln-München, 2007)

Driven by quantum fluctuations

- Non-Fermi liquid behavior
- Emergence of novel degrees of freedom
- New phases of matter

(ii) Quantum phase transitions



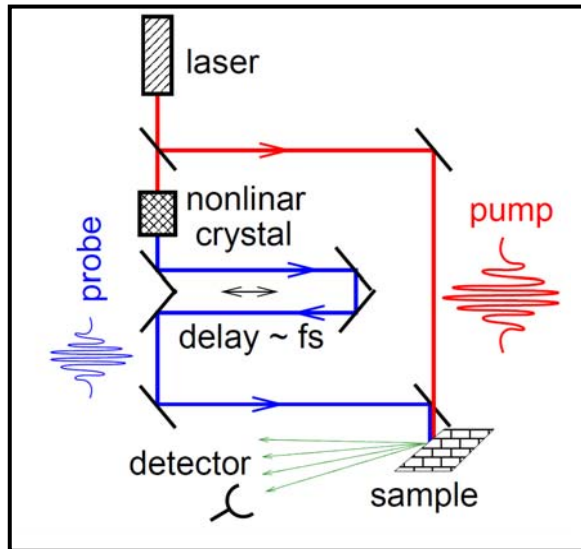
Custers *et al.* (2003)

Driven by quantum fluctuations

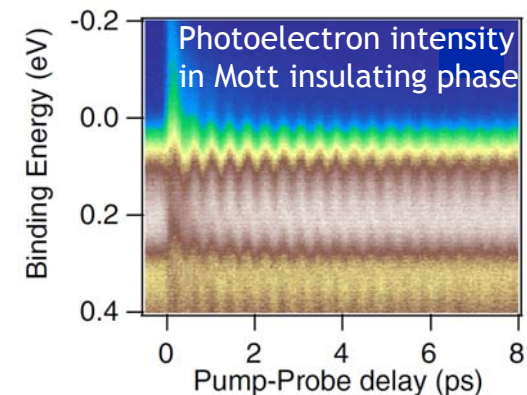
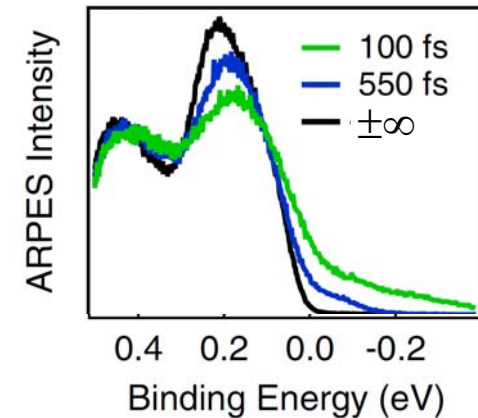
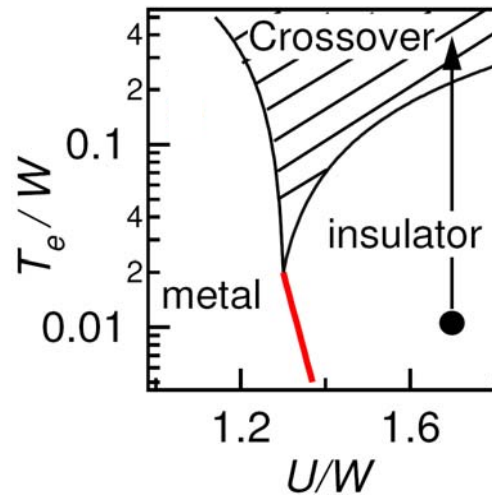
- Non-Fermi liquid behavior
- Emergence of novel degrees of freedom
- New phases of matter

(iii) Correlated electrons in non-equilibrium

Real time evolution of correlation phenomena, e.g.,
time-resolved optical photoemission

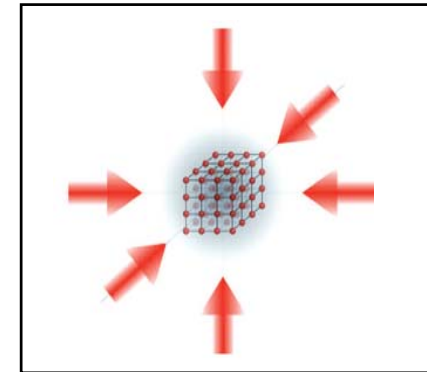
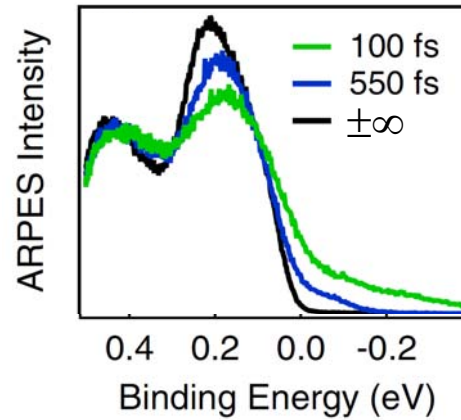
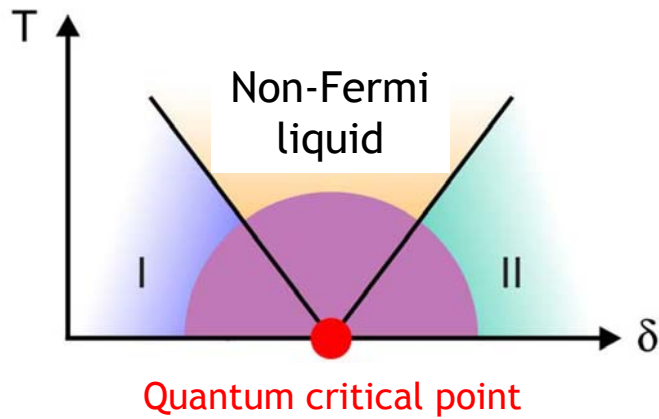
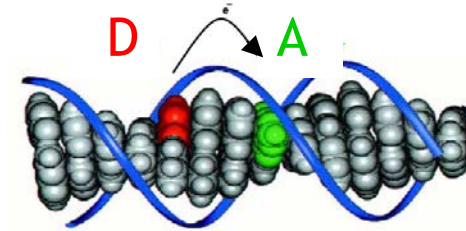
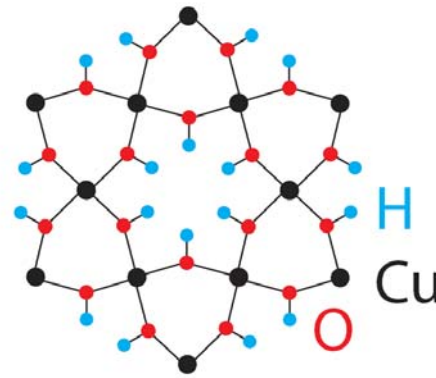
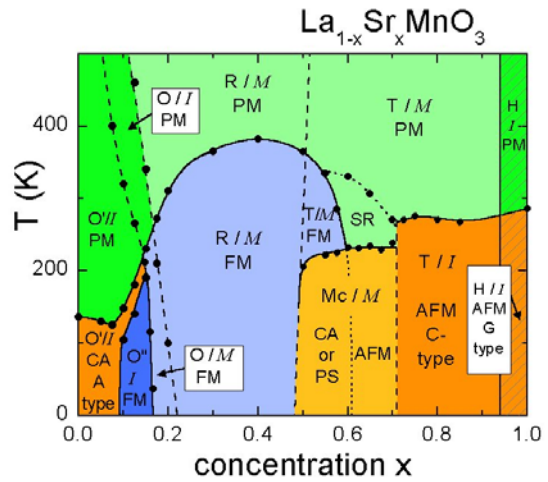


Pump-probe experiment



Perfetti *et al.* (2006)

Required: Theory of non-equilibrium beyond
linear response in correlated **bulk** materials



Correlated many-particle systems:
More manifold and fascinating than ever