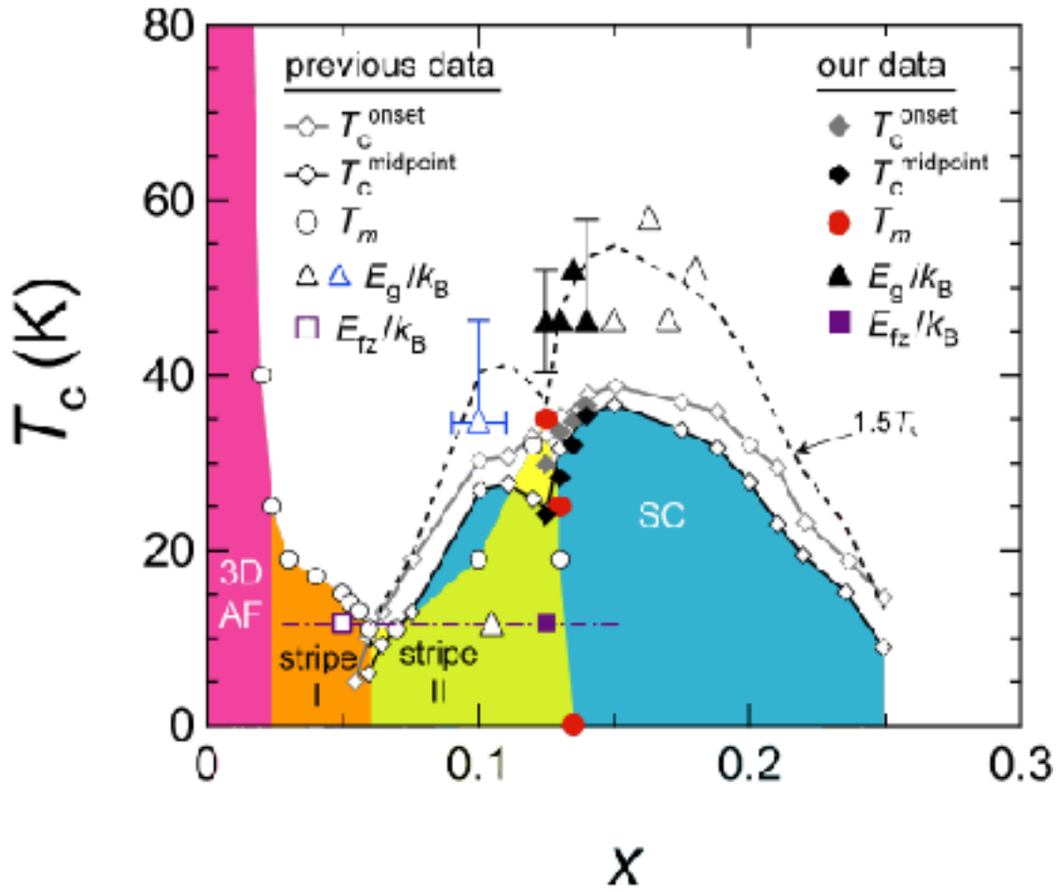
ELECTRON CORRELATION & ITS SIGNATURES

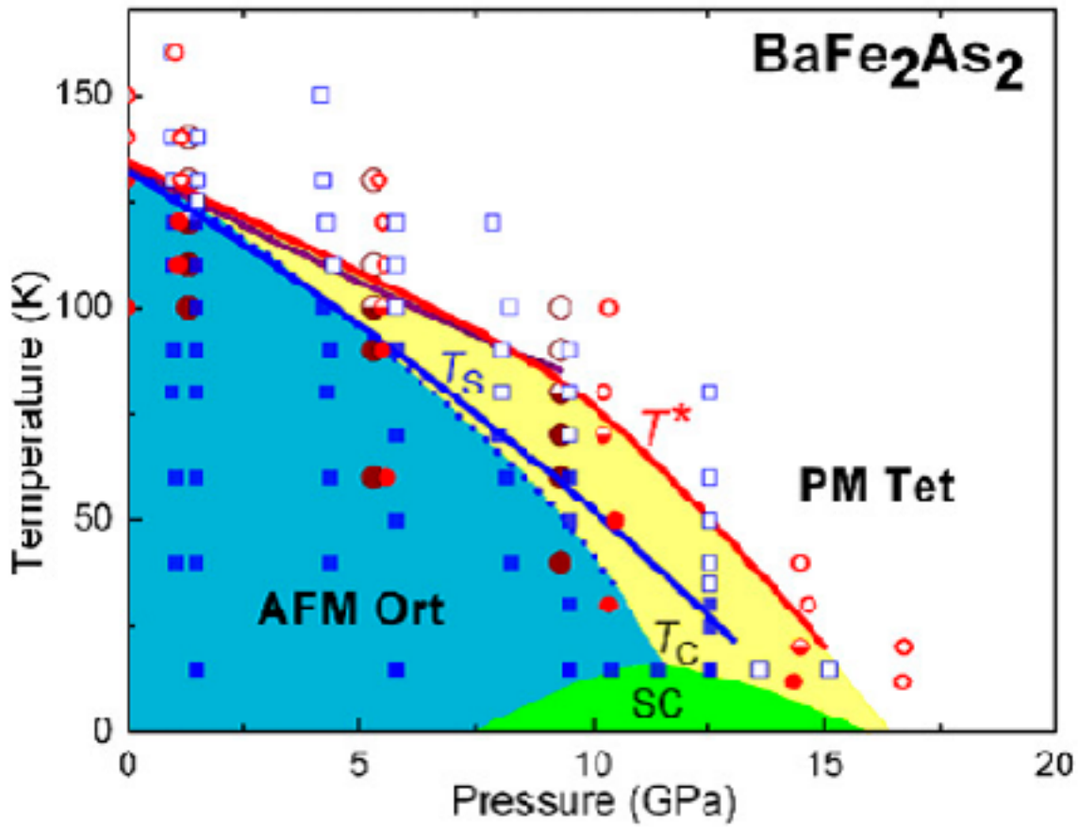
Reza Nourafkan
Institut Quantique & Université de Sherbrooke

Computational Quantum Materials
Jouvence, Quebec (2018)

WITH EACH NEW GENERATION OF MATERIALS SYNTHESIZED COMES A NEW SET OF CHALLENGES TO UNDERSTAND AND EXPLOIT



Cuprate high-Tc superconductors



Iron-based high-Tc superconductors

OUTLINE

- Correlation
- Why is the problem of electronic structure hard?
- Mean field approaches (independent-particle picture):
    1. Hartree-Fock method
    2. Kohn-Sham approach
- What is meant by electron correlation?
- Weak vs strong correlation

CORRELATION IN EVERYDAY LIFE

IN A MANY BODY SYSTEM, THE BEHAVIOUR OF A GIVEN ENTITY IS NOT INDEPENDENT OF THE OTHERS!

CORRELATION IN MATHEMATICS & NATURAL SCIENCES

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

$$C_{AB} = \langle AB \rangle - \langle A \rangle \langle B \rangle$$

- Spatial

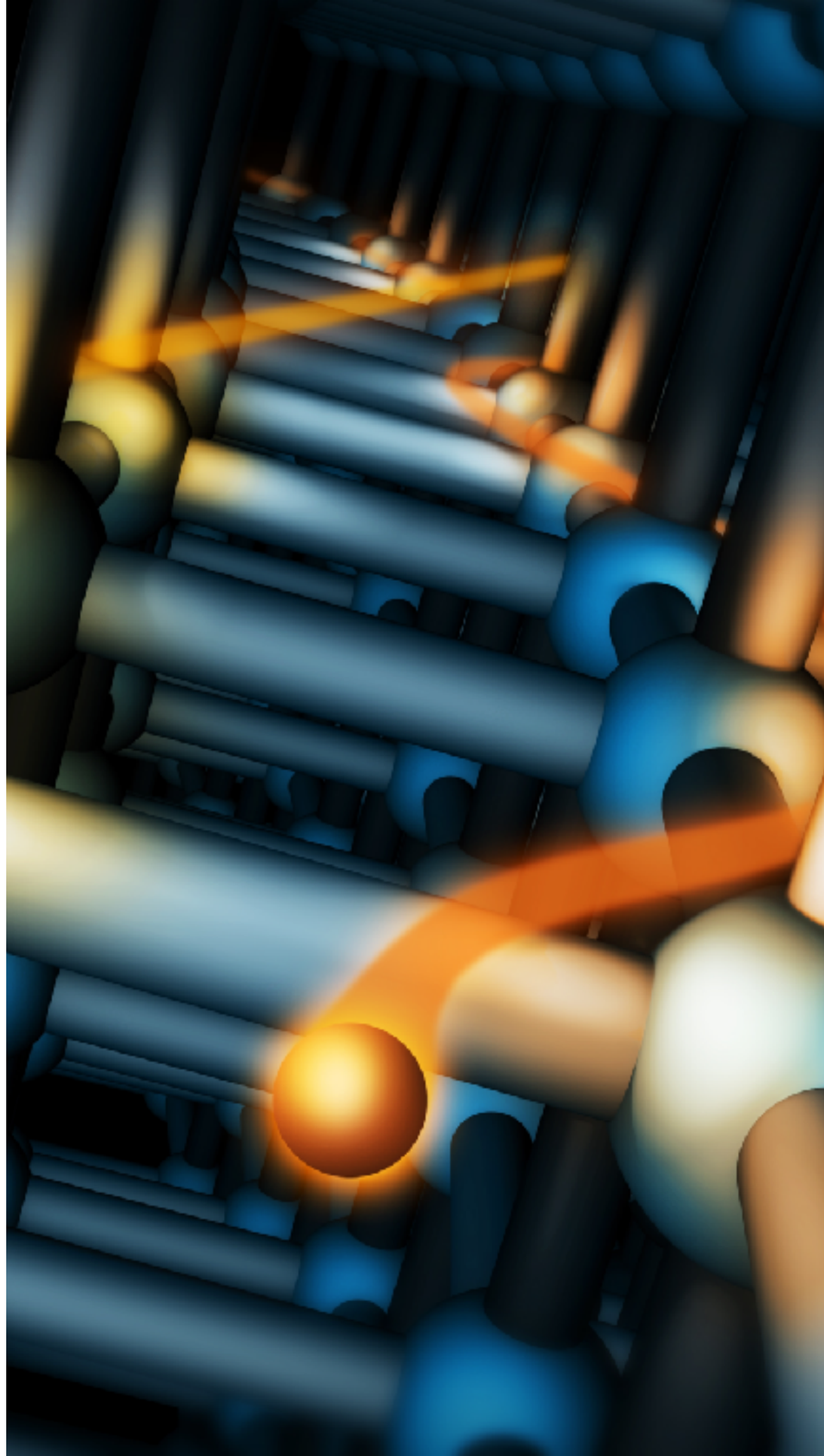
$$\langle n(\mathbf{r}, t) n(\mathbf{r}', t) \rangle \neq \langle n(\mathbf{r}, t) \rangle \langle n(\mathbf{r}', t) \rangle$$

- Temporal

$$\langle n(\mathbf{r}, t) n(\mathbf{r}, t') \rangle \neq \langle n(\mathbf{r}, t) \rangle \langle n(\mathbf{r}, t') \rangle$$

ELECTRON CORRELATION PECULIARITY

QUANTUM MECHANICS, INDISTINGUISHABLE PARTICLES



MANY-BODY PROBLEM IN SOLIDS

- Many-body Hamiltonian of an electronic system

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \hat{\nabla}_i^2 + \frac{1}{2}\sum_{i\neq i'}\frac{e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_{i'}|} - \sum_{i\hat{\alpha}}\frac{Z_\alpha e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{R}}_\alpha|}$$
$$-\sum_\alpha \frac{\hbar^2}{2M_\alpha}\hat{\nabla}_\alpha^2 + \frac{1}{2}\sum_{\alpha\neq\alpha'}\frac{Z_\alpha Z'_\alpha e^2}{|\hat{\mathbf{R}}_\alpha - \hat{\mathbf{R}}_{\alpha'}|}$$

- Many-body wave-function for N electrons

$$\Psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_N\sigma_N)$$

MANY-BODY PROBLEM IN SOLIDS

- Trial many-body wave function for an N electrons system

$$\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N) = \sum_i c_i\psi_i(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)$$

$$\langle\Psi|\hat{H}|\Psi\rangle = \sum_{ij} c_i^* c_j \langle\psi_i|\hat{H}|\psi_j\rangle$$

- Many-body basis set?
  - Product of one-particle wave-functions
    - Choose M (M>N) single particle basis function (spin-orbital)

$$\{\phi_{1\sigma_1}(\mathbf{r}),\phi_{2\sigma_2}(\mathbf{r}),\ldots,\phi_{M\sigma_M}(\mathbf{r})\}$$

    - Electrons are indistinguishable fermions

$$\Psi(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) = -\Psi(\mathbf{r}_2\sigma_2,\mathbf{r}_1\sigma_1)$$

HARTREE-FOCK METHOD

- A wave function composed of a *single* Slater determinant

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1\sigma_1) & \phi_2(\mathbf{r}_1\sigma_1) & \dots & \phi_N(\mathbf{r}_1\sigma_1) \\ \phi_1(\mathbf{r}_2\sigma_2) & \phi_2(\mathbf{r}_2\sigma_2) & \dots & \phi_N(\mathbf{r}_2\sigma_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N\sigma_N) & \phi_2(\mathbf{r}_N\sigma_N) & \dots & \phi_N(\mathbf{r}_N\sigma_N) \end{vmatrix}$$

- The single-electron functions are chosen *cleverly* to produce the best approximation possible $\delta\langle\psi|H|\psi\rangle/\delta\phi_i^* = 0$

$$-\left(\frac{\hbar^2}{2m_e}\nabla^2 + \sum_\alpha \frac{Z_\alpha e^2}{|\mathbf{r}-\mathbf{R}_\alpha|}\right)\phi_i(\mathbf{r}) + \left(\sum_j^{occ} \int d\mathbf{r}'\phi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_j(\mathbf{r}')\right)\phi_i(\mathbf{r})$$

Hatree-potential

$$-\left(\sum_j^{occ} \int d\mathbf{r}'\phi_j^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_i(\mathbf{r}')\right)\phi_j(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

Exchange-potential

WHY IS THE PROBLEM OF ELECTRONIC STRUCTURE HARD?

- N electrons system and M (M>N) single particle basis function

$$\Psi(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)=\sum_i c_i\psi_i(\mathbf{r}_1\sigma_1,\ldots,\mathbf{r}_N\sigma_N)$$

- Number of Slater determinants

$$\binom{M}{N}=\frac{M!}{N!(M-N)!}$$

- Two carbon atoms (N=12). Suppose M=36

more that 10^9 determinants

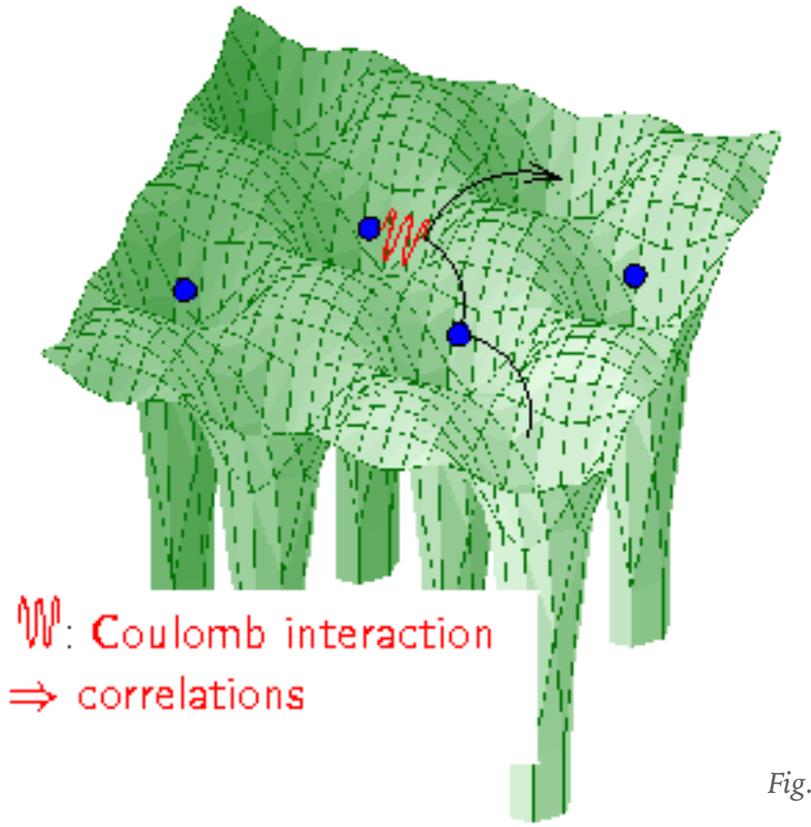
Dimensionality

IT IS HOPELESS TO LOOK FOR AN EXACT SOLUTION OF A MANY-BODY SYSTEM

How we are going to proceed?

MEAN FIELD APPROACHES

spatial and temporal correlation



structureless cloud : particles are uncorrelated

except that they obey the exclusion principle

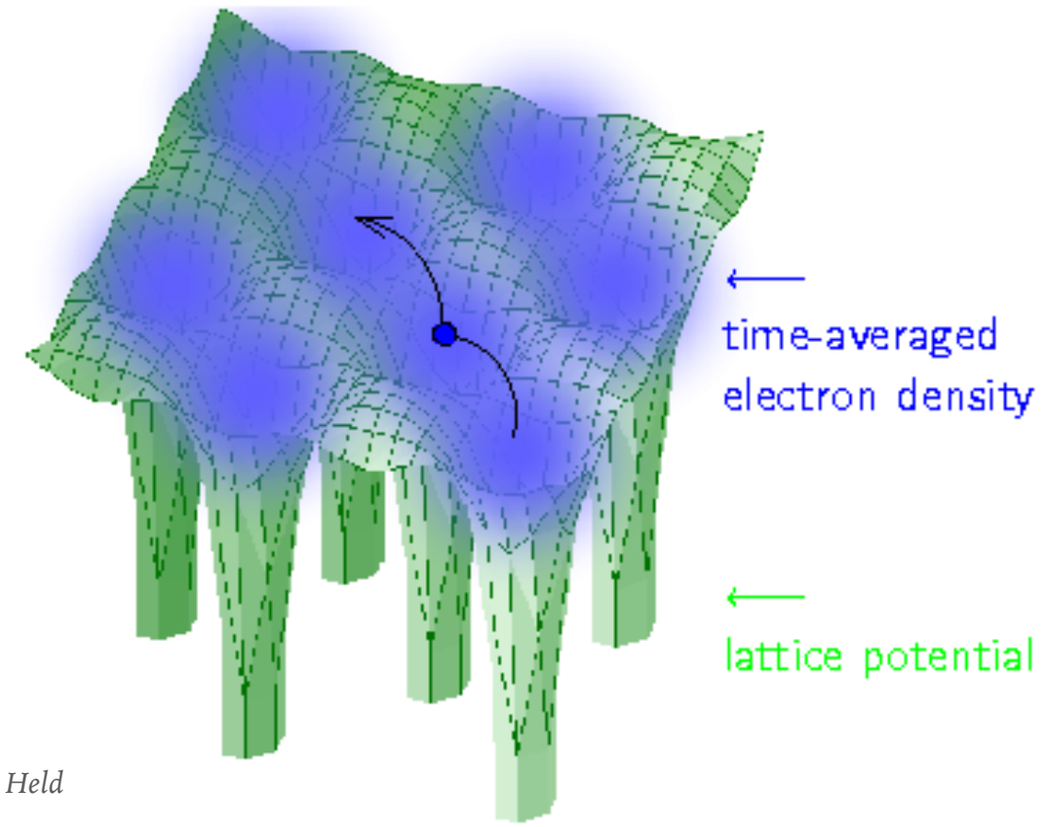


Fig. from K. Held

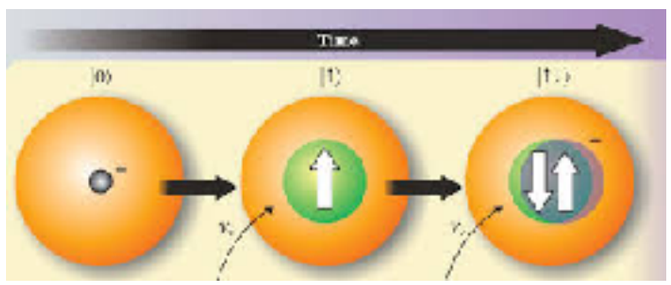


Fig. from G. Kotilar et al

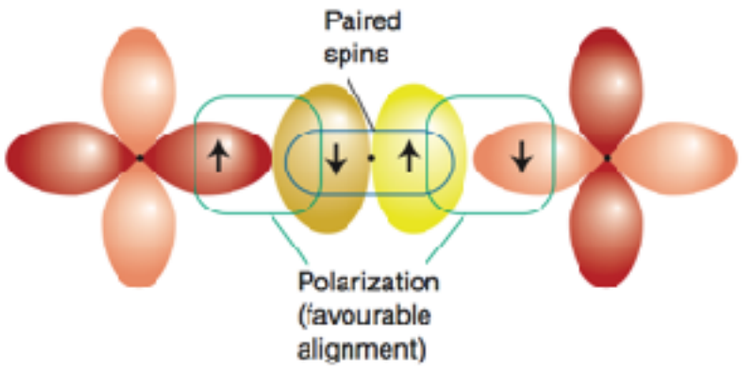


Fig. from ChemTube3D

WHAT IS MEANT BY ELECTRON CORRELATION?

- Chemist: what is not captured in Hartree-Fock method
  - Correlation energy

$$E_{\text{corr}} = \langle \Psi | H | \Psi \rangle - E_{\text{HF}}$$

$$|\Sigma(\omega) - \Sigma_{HF}|$$

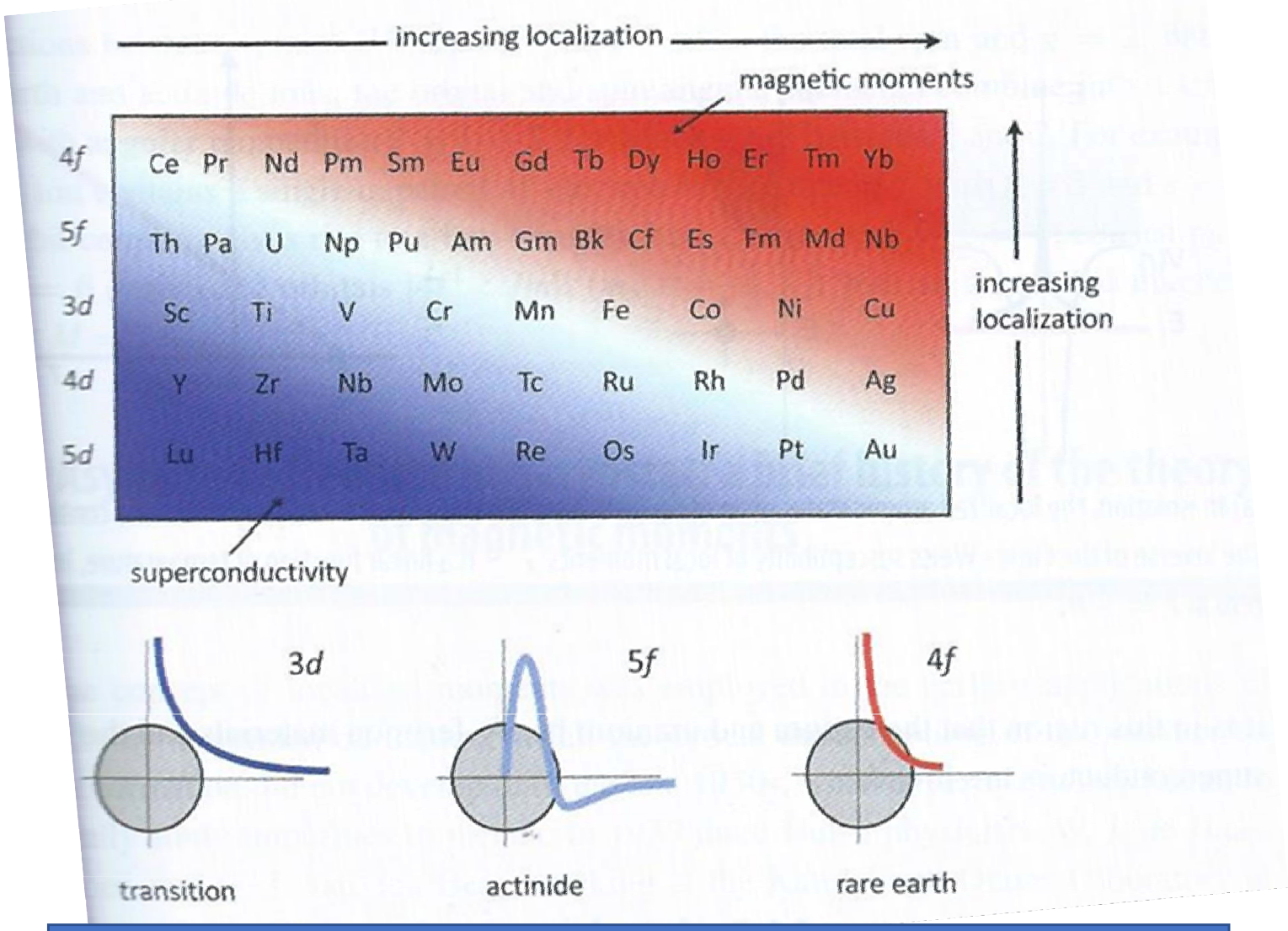
- Physicist: what is not captured in Khon-Sham approach in LDA/GGA approximation
  - Correlation energy

$$E_{\text{corr}} = \langle \Psi | H | \Psi \rangle - E_{\text{LDA/GGA}}$$

$$|\Sigma(\omega) - v_{xc}^{LDA/GGA}|$$

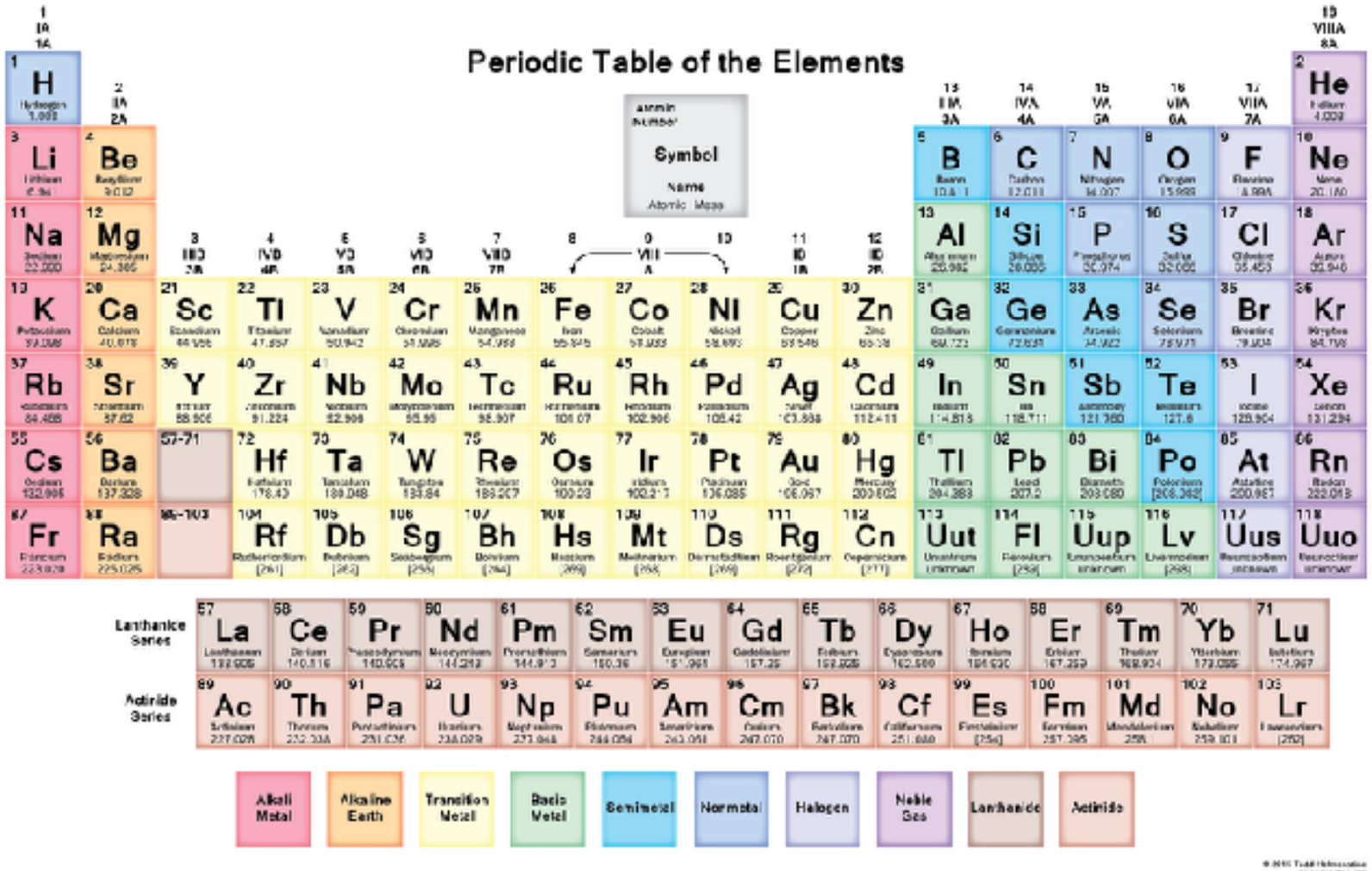
J.L. Smith, E.A. Kmetko *

Journal of the Less Common Metals
Volume 90, Issue 1, March 1983, Pages 83-88



WEAK VS STRONG CORRELATIONS

- A weakly-correlated system is one for which a mean-field approximation or a low-order perturbation expansion around it suffices

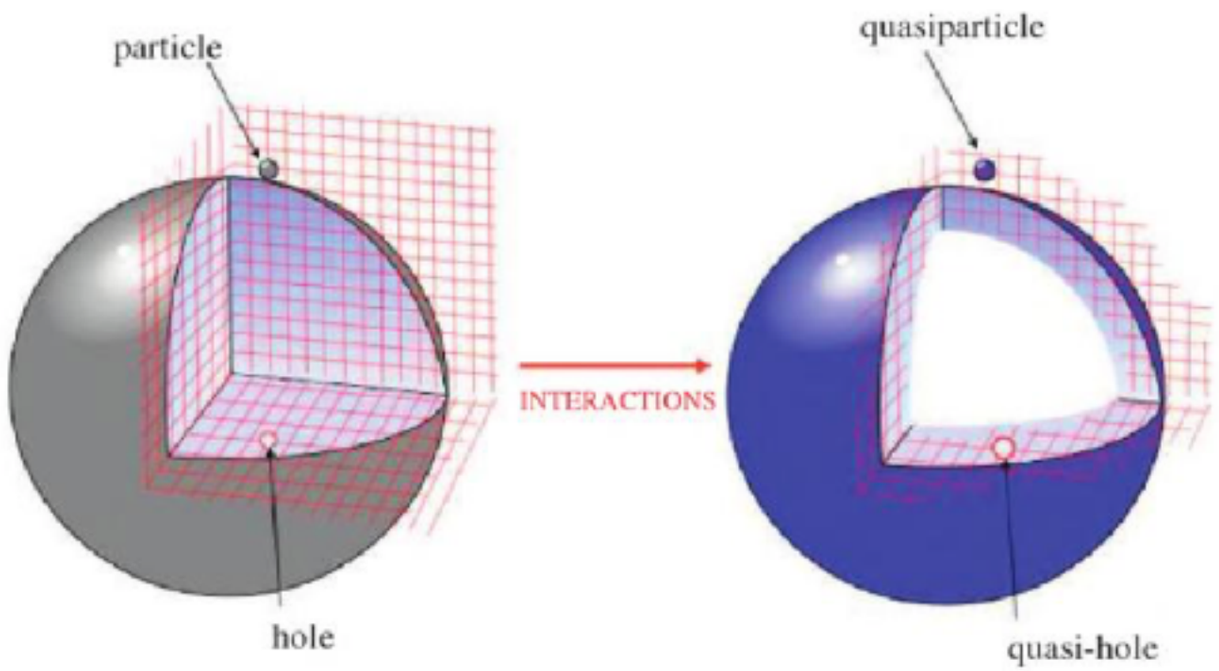


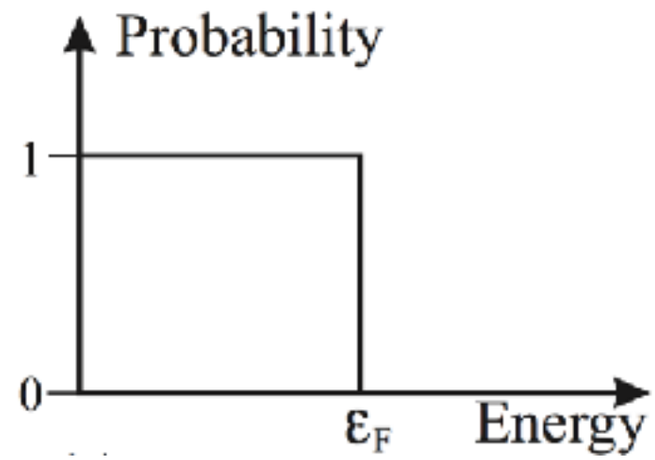
ELECTRON CORRELATION SIGNATURES

Thermodynamic and transport properties which are fundamentally different from mean-field theory or Landau Fermi-liquid theory predictions

LANDAU FERMI LIQUID

- Landau argued that the ground state of a non-interacting system (Fermi sea) adiabatically evolves into the ground state of the interacting system
- Conserved quantum numbers: spin, charge and momentum





Fermi gas *Fermi liquid*

Fig. from P. Coleman

QUASI-PARTICLES

- Each quasiparticle contributes additively to the total *entropy* of the system but not to the *energy*
- A quasiparticle's energy also depends on the distribution of other quasiparticles
- The inertial mass of the quasiparticle is modified by the back-flow m → m*

$$m^* = m(1 + F_1^s)$$

$$\mathbf{v}_F = \frac{\mathbf{P}_F}{m^*} = \frac{\mathbf{P}_F}{m} - \frac{\mathbf{P}_F}{m}\left(\frac{F_1^s}{1 + F_1^s}\right)$$

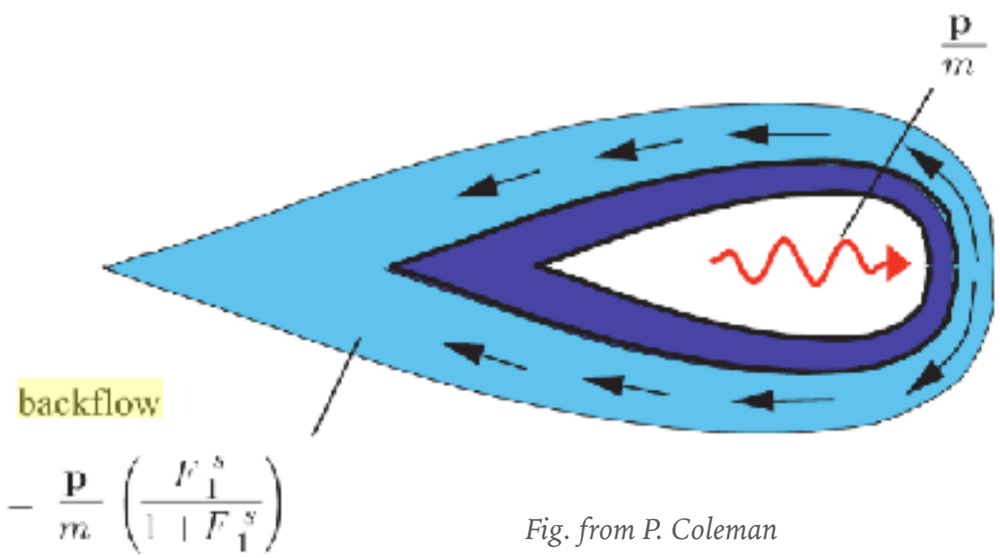


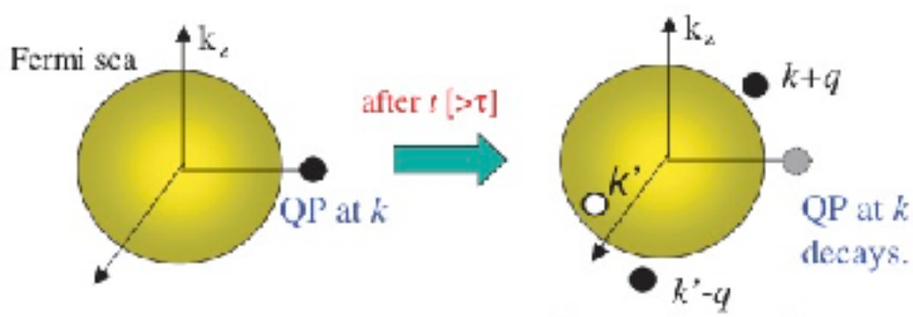
Fig. from P. Coleman

QUASI-PARTICLE LIFE TIME

- Quasiparticles and holes are only approximate eigenstates of the system
- Decay rate of a quasiparticle with energy ε above the Fermi surface at T=0

$$\frac{1}{\tau_\epsilon} \propto \epsilon^2$$

- Quasiparticle is well defined close to the Fermi level
- At T>0, the scattering rate goes like T^2



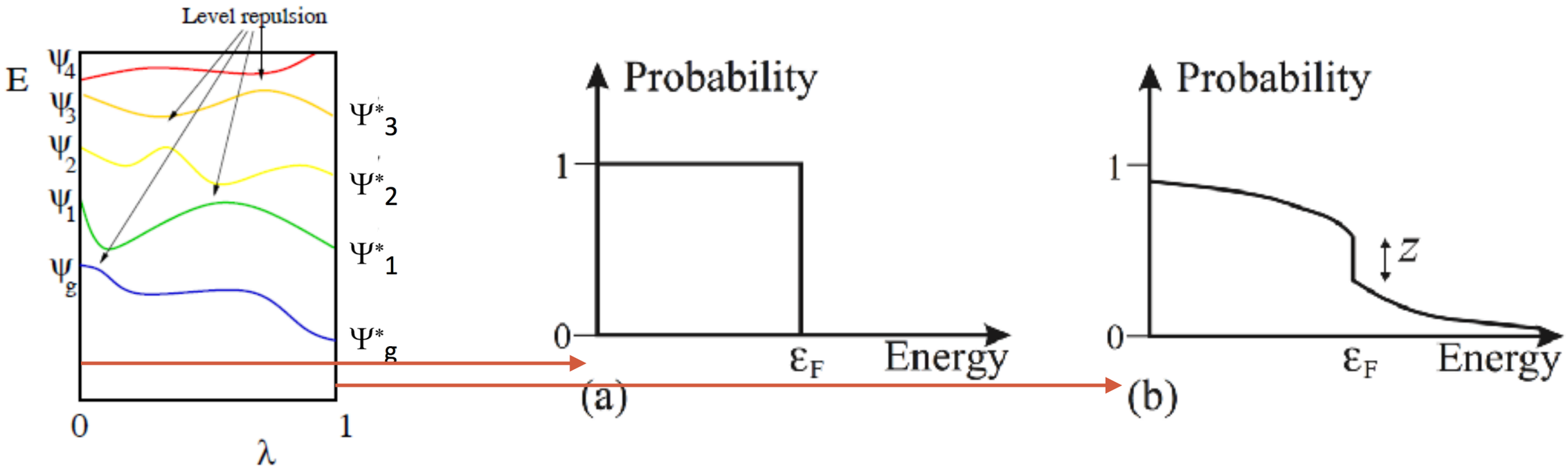
QP scattering process

WHAT ABOUT ELECTRON THEMSELVES?

- There must remain a fraction of the original non-interacting excited state wave function in the quasiparticle wave function

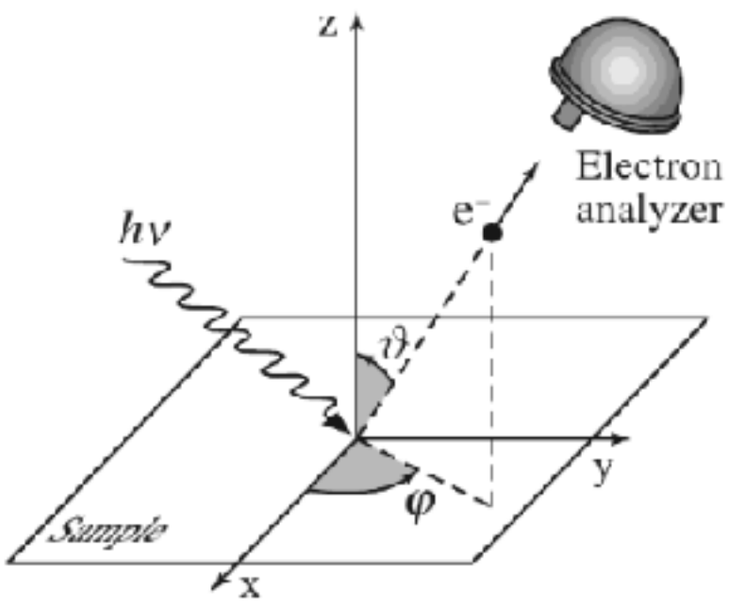
$$\tilde{\phi}_{QP}(\mathbf{k}\sigma) = \sqrt{z}\phi_{el}(\mathbf{k}\sigma) + \text{particle} - \text{hole excitations etc.}$$

- The fraction, z<1, plays the role of the order parameter of the zero temperature Fermi liquid state

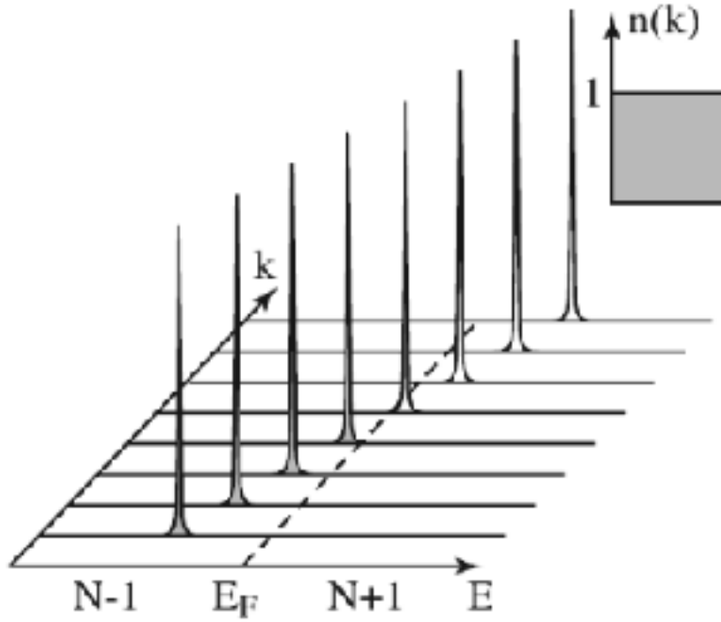


PHOTOEMISSION SPECTROSCOPY

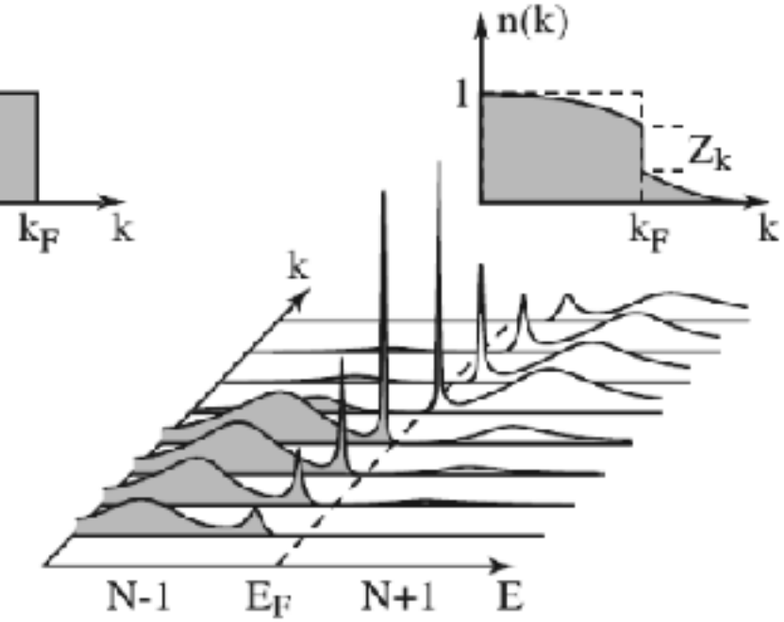
- Spectral function: A tool for following the fate of the original electrons



Photoemission geometry



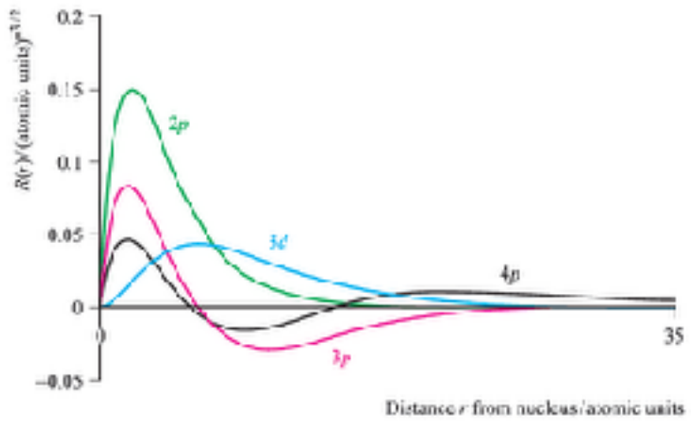
Non-interacting electron system

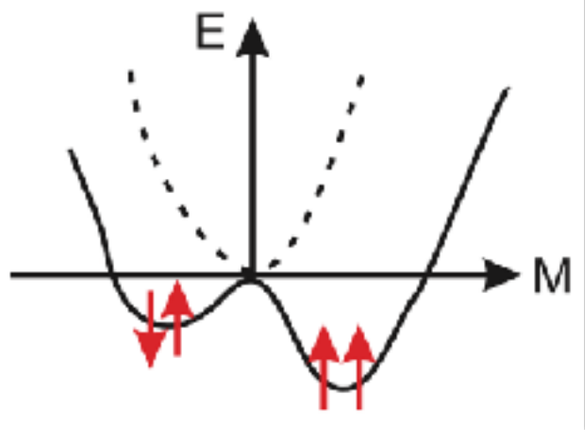


Fermi liquid system

WHEN IS THE INDEPENDENT-PARTICLE PICTURE NOT SUFFICIENT?

- Electrons hesitate between being localized on short time scales and itinerant on long time scales
- Some phase transitions and ordered states: ordered magnetic states
- Screening
- Strange metals (Non-Fermi liquid behaviour)
- Strong fluctuations between different low-energy fermionic configurations





SIGNATURES OF ELECTRON CORRELATION

- Correlation-induced phase transition
- Differences between LDA band masses and measured masses
- Satellites in photoemission
- Non-linear T dependance of the electronic contribution in specific heat
- Small Drude weights
- .....

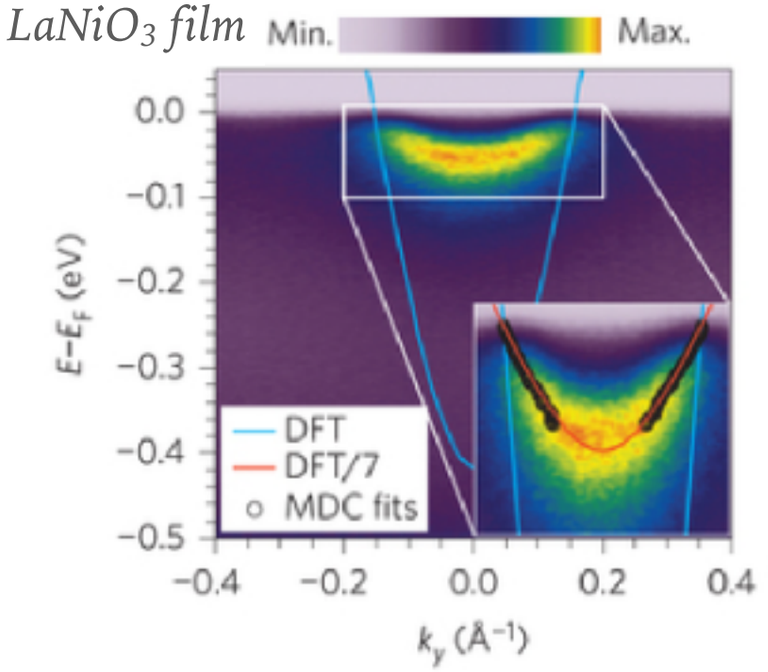
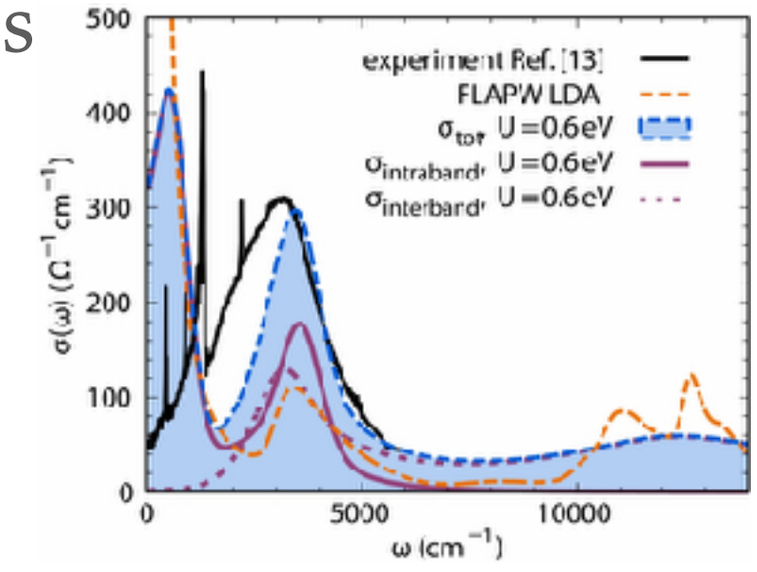
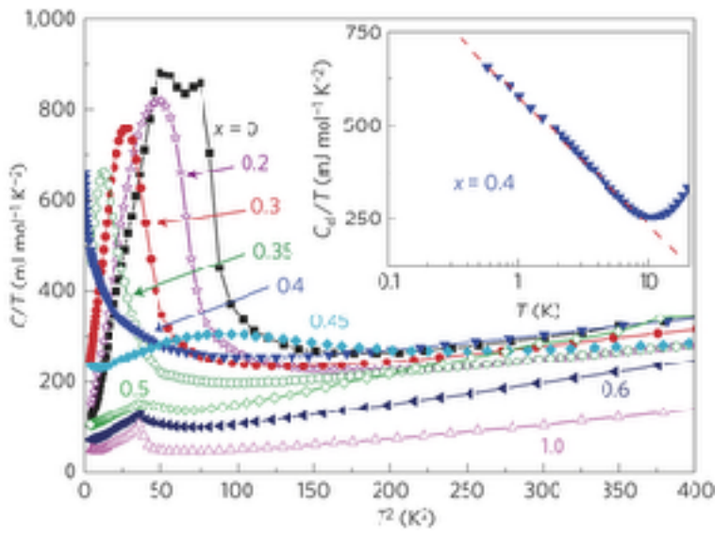


Fig. from P. D. C. King et al





$CeNiAs_{1-x}P_xO$ (Fig. from Y. Luo et al)

A. Georges http://arxiv.org/abs/cond-mat/0403123

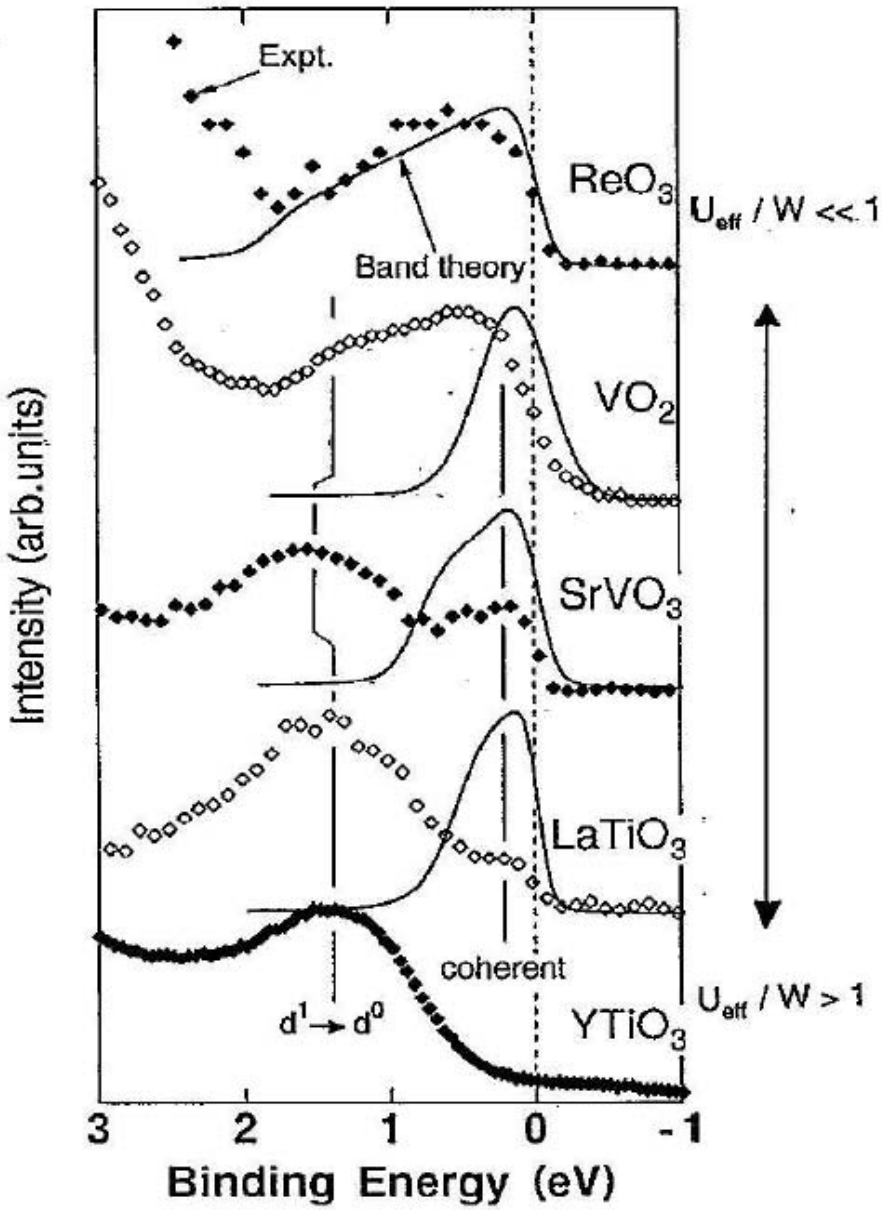


FIGURE 10. Photoemission spectra of several d^1 transition metal oxides, reproduced from Ref. [88]. The effects of correlations increases from ReO_3 (a weakly correlated metal) to $YTiO_3$ (a Mott insulator). The plain lines are the d.o.s obtained from band structure calculations. A lower Hubbard band around -1.5 eV is clearly visible in the most correlated materials, both in the metallic and insulating case.

A. Georges http://arxiv.org/abs/cond-mat/0403123

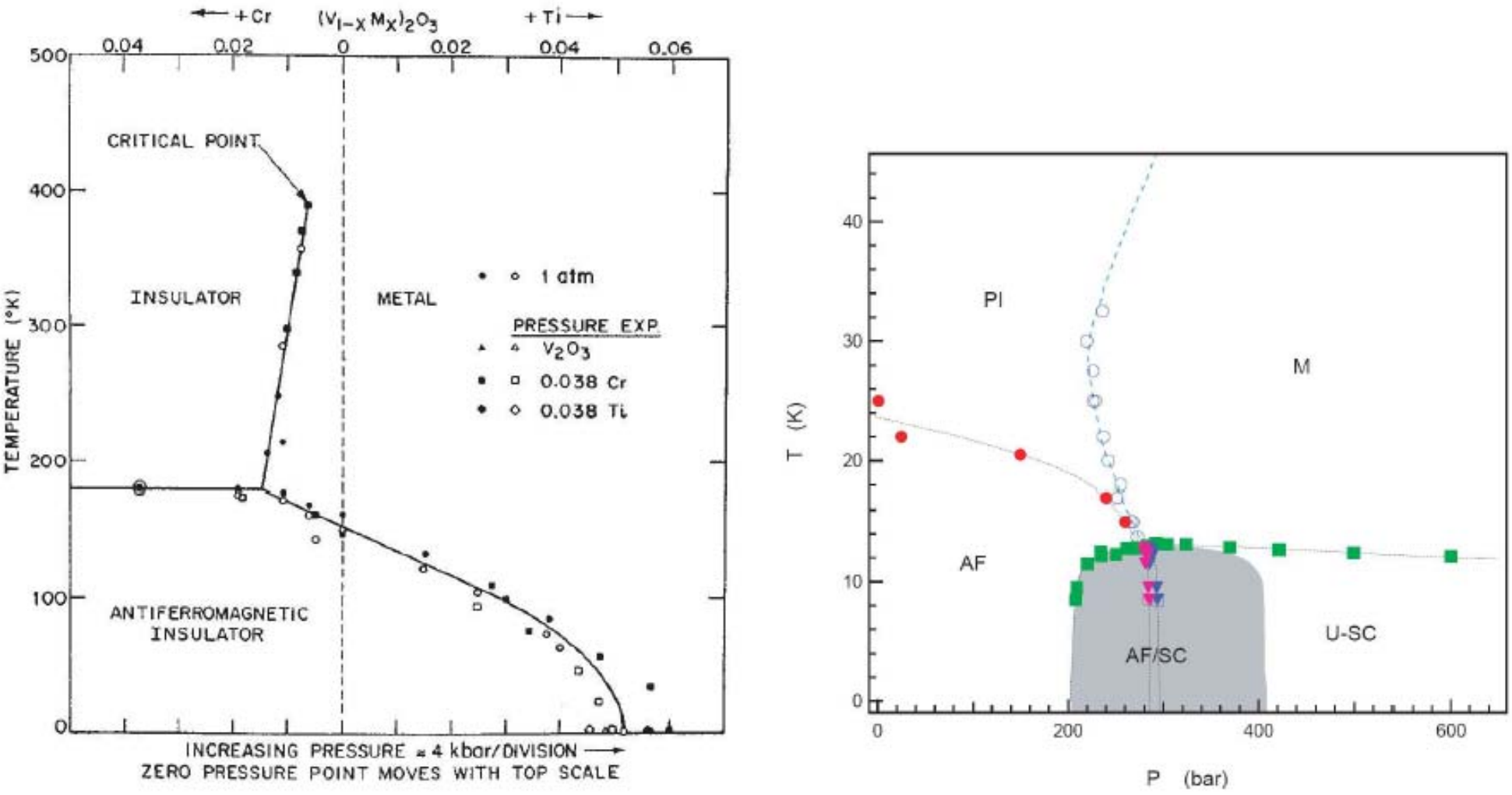
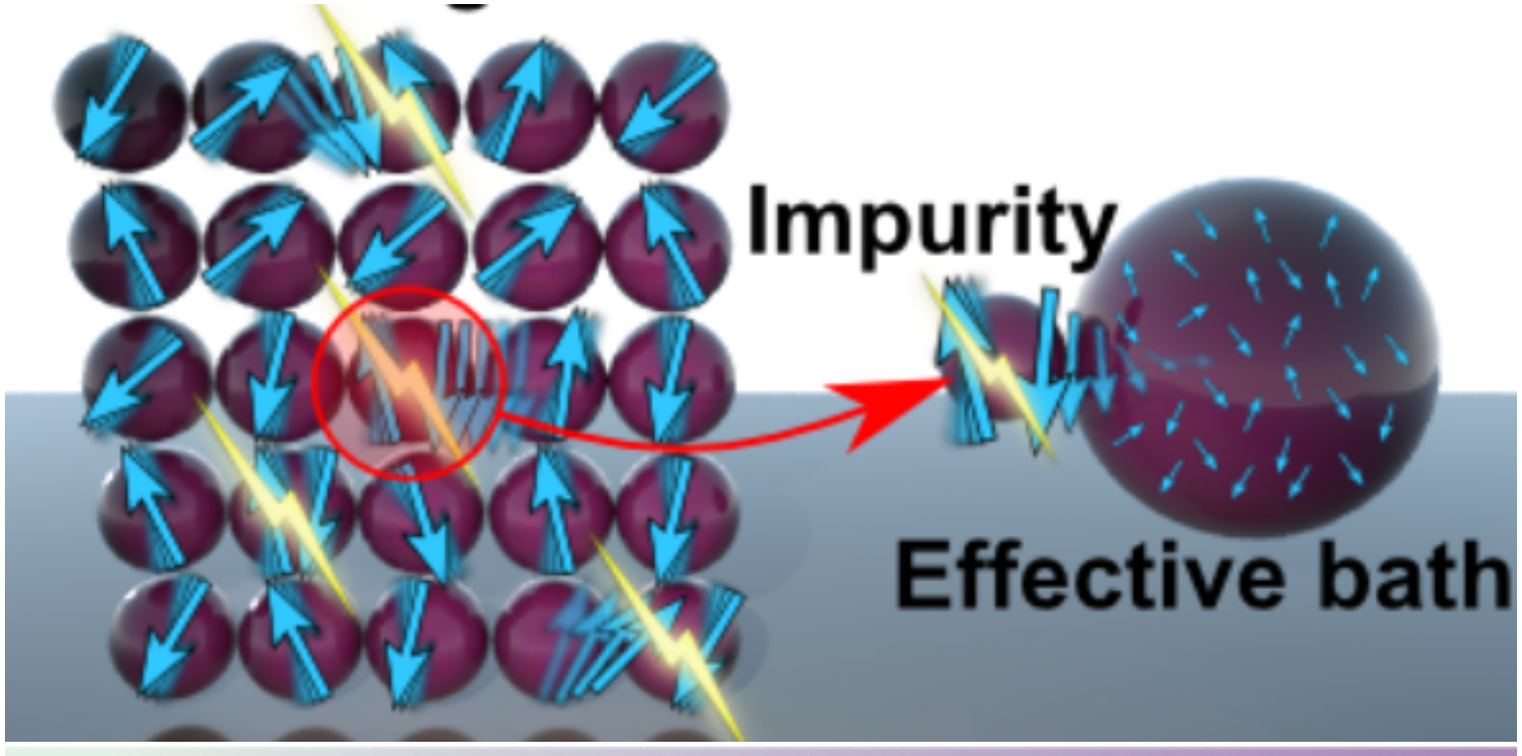
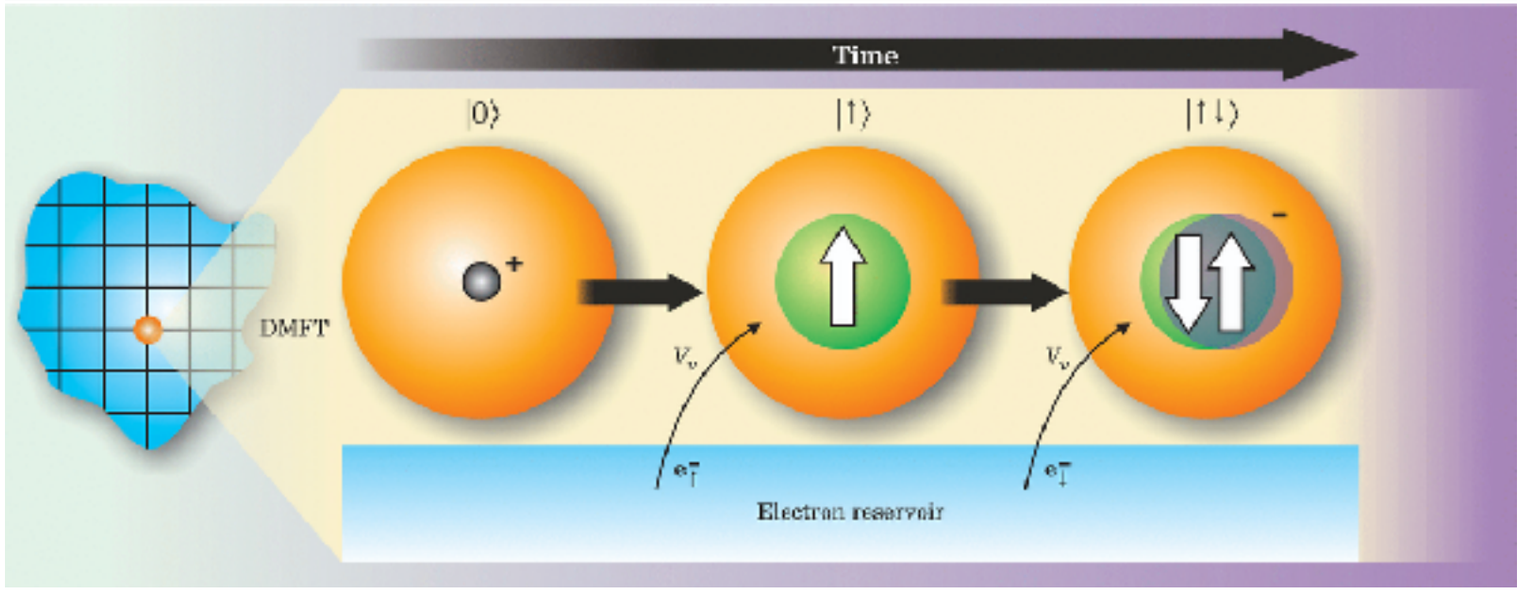


FIGURE 7. Left: Phase diagram of $(V_{1-x}\,Cr_x)_2O_3$ as a function of either Cr-concentration x or pressure (after[75]). Increasing x by 1% produces similar effects than *decreasing* pressure by $\sim$ 4kbar, for this material. Right: Phase diagram of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl as a function of pressure (after [76]).

BEYOND MEAN-FIELD APPROACHES

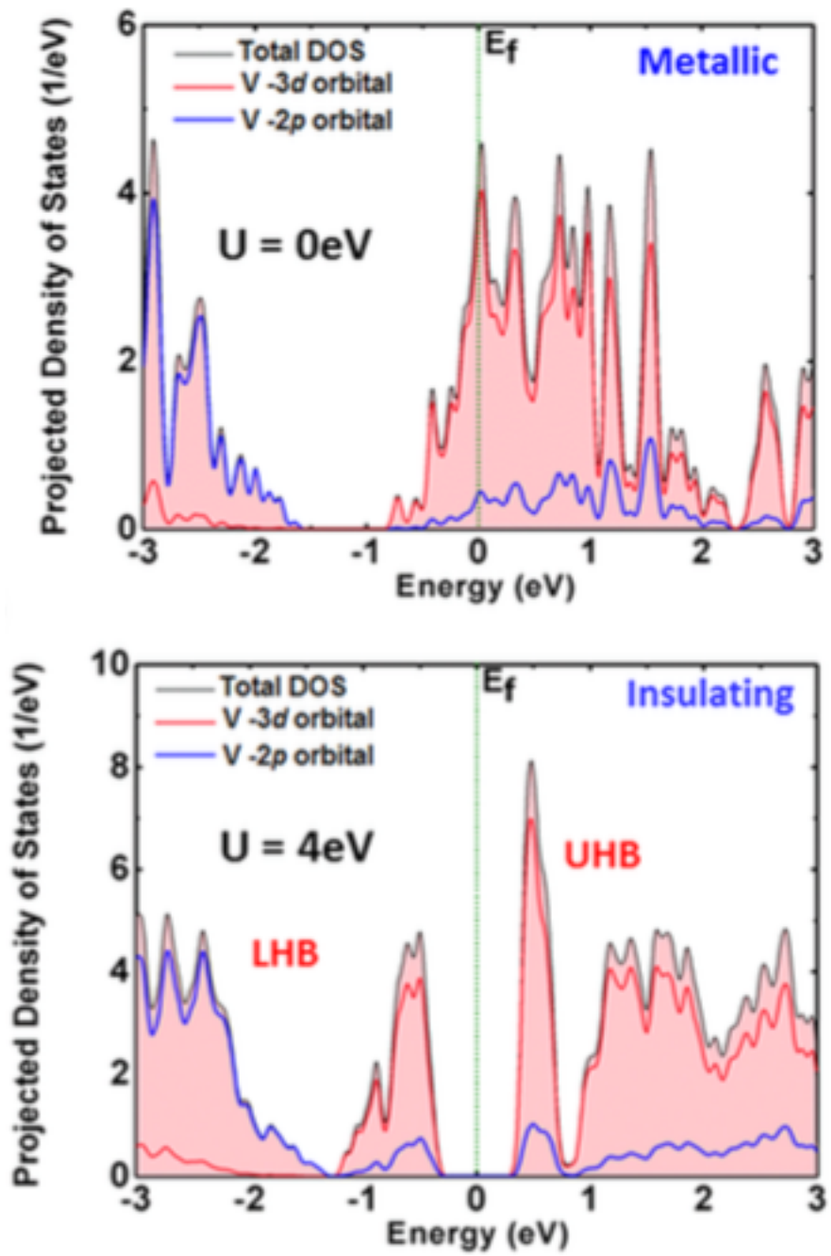
- Dynamical mean-field theory

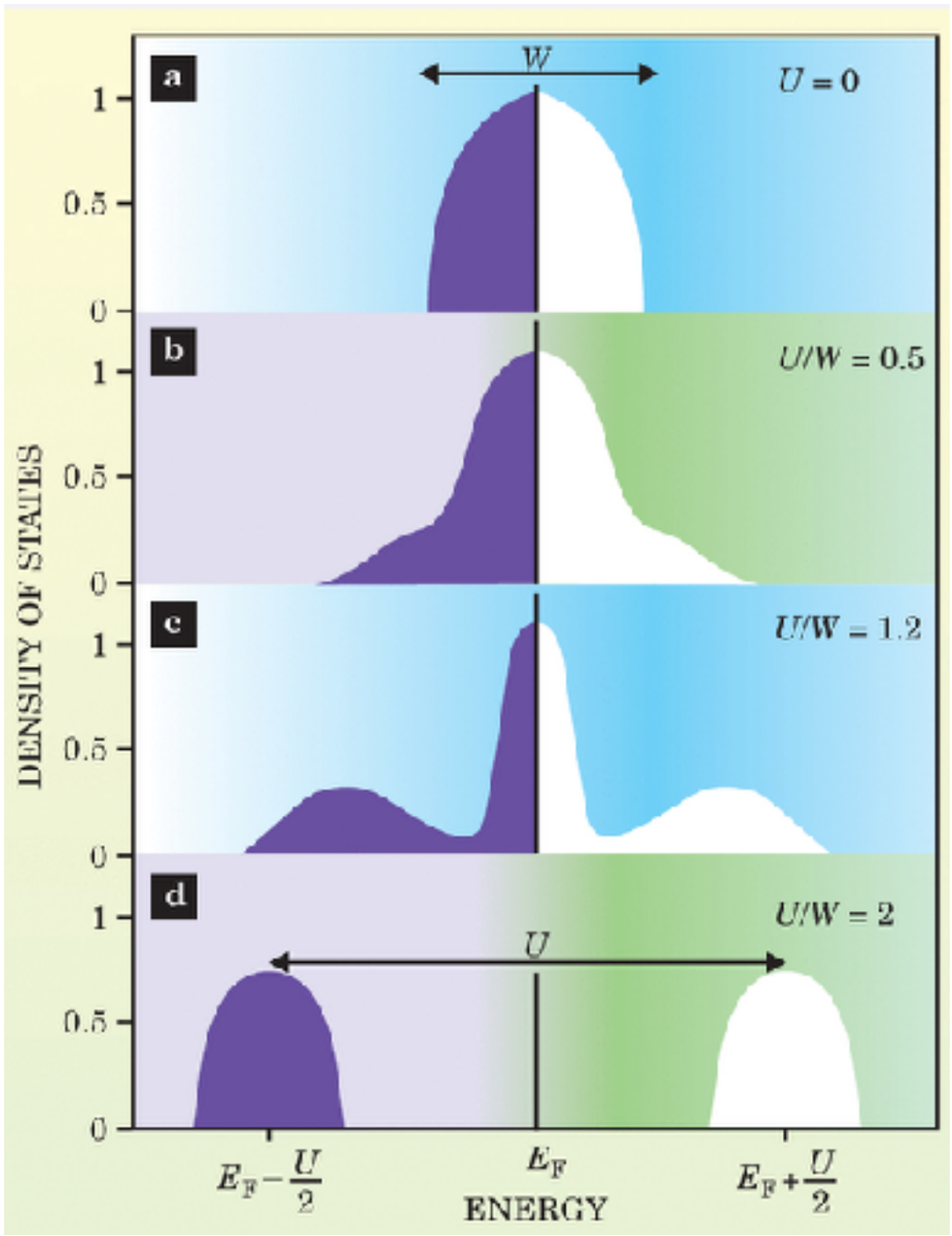




CORRELATION DRIVEN METAL-INSULATOR TRANSITION

- VO_2





SUMMARY

- Most materials with interesting properties such as heavy fermion, high T_c superconductor, giant magnetoresistance, multiferroic etc. are strongly correlated
- Ordered states are usually weakly correlated
- Methods such as QMC (model Hamiltonian) or LDA+DMFT take into account some correlation effects

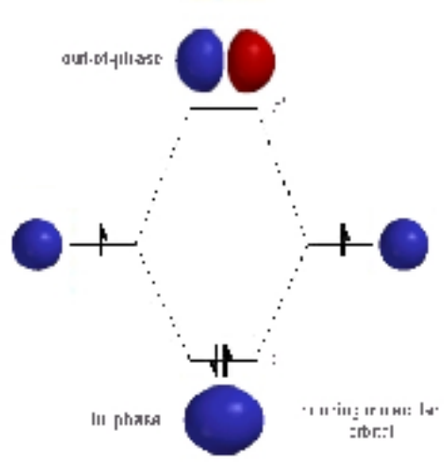
FERMI LIQUID PREDICTIONS

	Low T, ($T << T_D$) Debye temperature : T_D	High T, ($T << T_D$)
Resistivity	$A_{imp} + B_{e\text{-}e} T^2 + C_{e\text{-}ph} T^{d+2}$	$C'_{e\text{-}ph} T$
Seebeck coefficient	$DT + E_{phd} T^d$	$D'_{e\text{-}ph} T + E'_{phd} T^{-1}$
Thermal conductivity	$H_{e\text{-}e} T^{-1} + L_{imp} T + G_{e\text{-}ph} T^{d-1}$	$G'_{e\text{-}ph}$
Specific heat	\gamma T	

HYDROGEN MOLECULE

- A two electrons example

$$\hat{H} = -\frac{\hbar^2}{2m_e}\hat{\nabla}^2 - \sum_{\alpha=1}^{2}\frac{Z_\alpha e^2}{|\hat{\mathbf{r}} - \mathbf{R}_\alpha|}$$



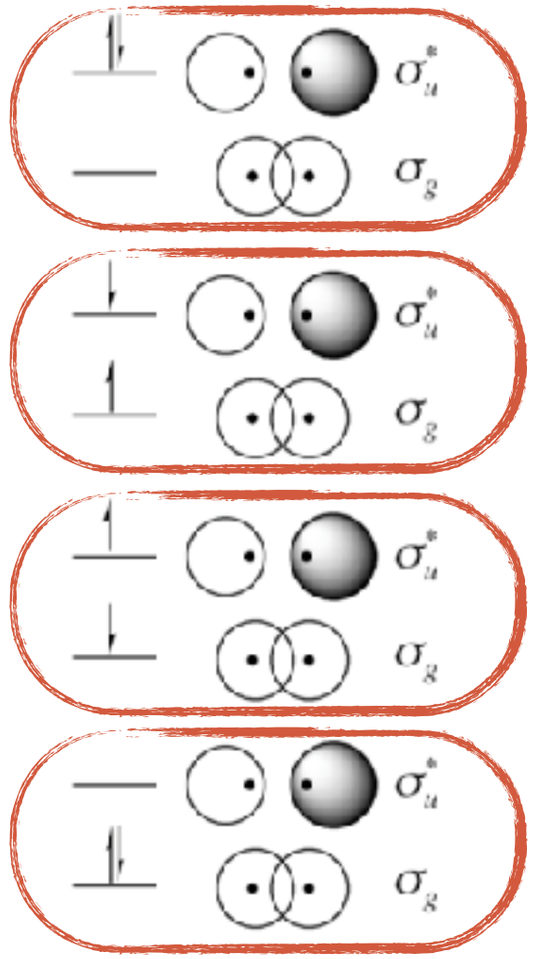
- Basis set for singlet configuration

$$\psi_4 = \frac{1}{\sqrt{2}}[\phi_u(1)\chi_\uparrow(1)\phi_u(2)\chi_\downarrow(2) - \phi_u(1)\chi_\downarrow(1)\phi_u(2)\chi_\uparrow(2)]$$

$$\psi_3 = \frac{1}{\sqrt{2}}[\phi_g(1)\chi_\uparrow(1)\phi_u(2)\chi_\downarrow(2) - \phi_u(1)\chi_\downarrow(1)\phi_g(2)\chi_\uparrow(2)]$$

$$\psi_2 = \frac{1}{\sqrt{2}}[\phi_u(1)\chi_\uparrow(1)\phi_g(2)\chi_\downarrow(2) - \phi_g(1)\chi_\downarrow(1)\phi_u(2)\chi_\uparrow(2)]$$

$$\psi_1 = \frac{1}{\sqrt{2}}[\phi_g(1)\chi_\uparrow(1)\phi_g(2)\chi_\downarrow(2) - \phi_g(1)\chi_\downarrow(1)\phi_g(2)\chi_\uparrow(2)]$$



$$\Psi \simeq c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4$$

SLATER DETERMINANTS ARE UNCORRELATED

- The repulsion energy between two electrons is calculated between an electron and the average electron density for the other electrons

It doesn't take into account the fact that the electron will push away the other electrons as it moves around

- Probability density of finding two electrons

$$\rho(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \sum_{\sigma_3 \ldots \sigma_N} \int d\mathbf{r}_3 \ldots d\mathbf{r}_N |\psi(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_N\sigma_N)|^2$$

$$= \frac{1}{N(N-1)} \sum_{kl} \left[|\phi_k(\mathbf{r}_1\sigma_1)|^2 |\phi_l(\mathbf{r}_2\sigma_2)|^2 - \phi_k^*(\mathbf{r}_1\sigma_1)\phi_k(\mathbf{r}_2\sigma_2)\phi_l^*(\mathbf{r}_2\sigma_2)\phi_l(\mathbf{r}_1\sigma_1) \right]$$

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\sigma_1\sigma_2} \rho(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)$$

Opposite spin orbitals are uncorrelated!

KOHN–SHAM APPROACH

- It is not essential to tabulate the complete many-body wave function
- The Kohn-Sham approach to DFT defines *an auxiliary system of independent fermions* that is chosen to reproduce the ground state *electron density* but not all properties
- DFT guarantees us that such an auxiliary system exist end even more provides us a generator for its external potential

$$(-\frac{\hbar^2}{2m_e}\nabla^2 + v_{eff}(\mathbf{r}))\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i f_i|\phi_i(\mathbf{r})|^2$$

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H([n], \mathbf{r}) + v_{xc}([n], \mathbf{r})$$

Universal exchange-correlation functional

OUTLINE

- Adiabaticity
- Landau Fermi liquid
- Quasi-particles vs original electrons
- When is the independent-particle picture not sufficient?
- Electron correlation signatures
- Beyond mean field approaches
    1. Dynamical mean field theory
    2. Quantum Monte Carlo
- Correlation induced metal-insulator transition

ADIABATIC CONTINUITY

- Labels associated with eigenstates are more robust against perturbations than the eigenstates themselves

$$-\frac{1}{2}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \qquad V(x) = \begin{cases} \frac{1}{2}\lambda x^2 & |x| < \pi, \\ \infty & |x| \geq \pi. \end{cases}$$

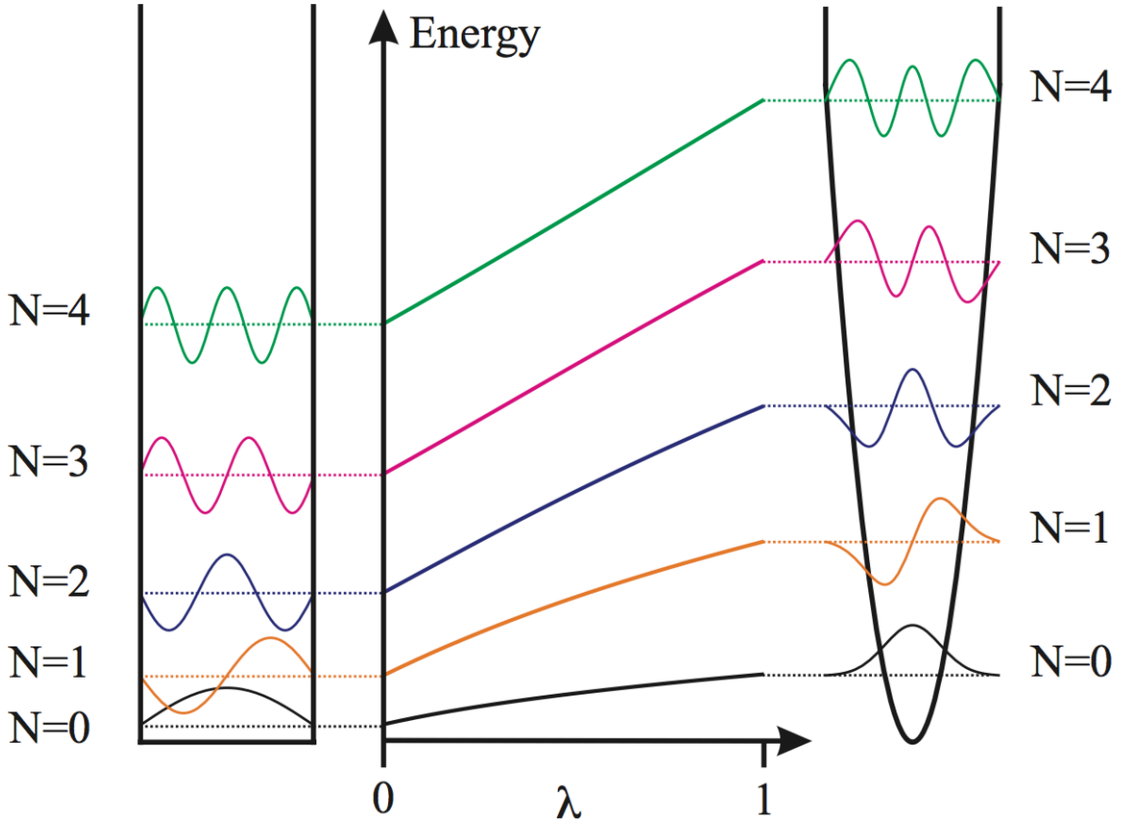
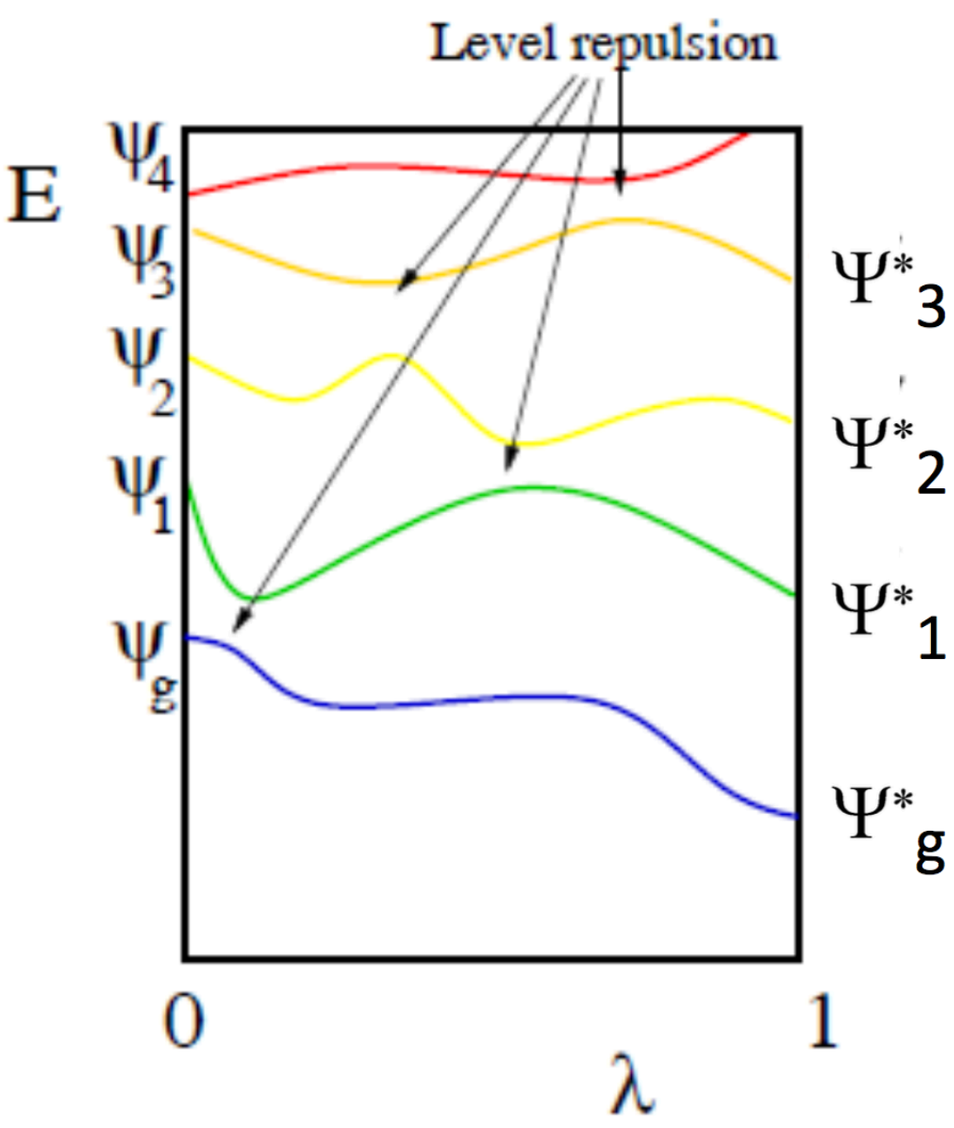
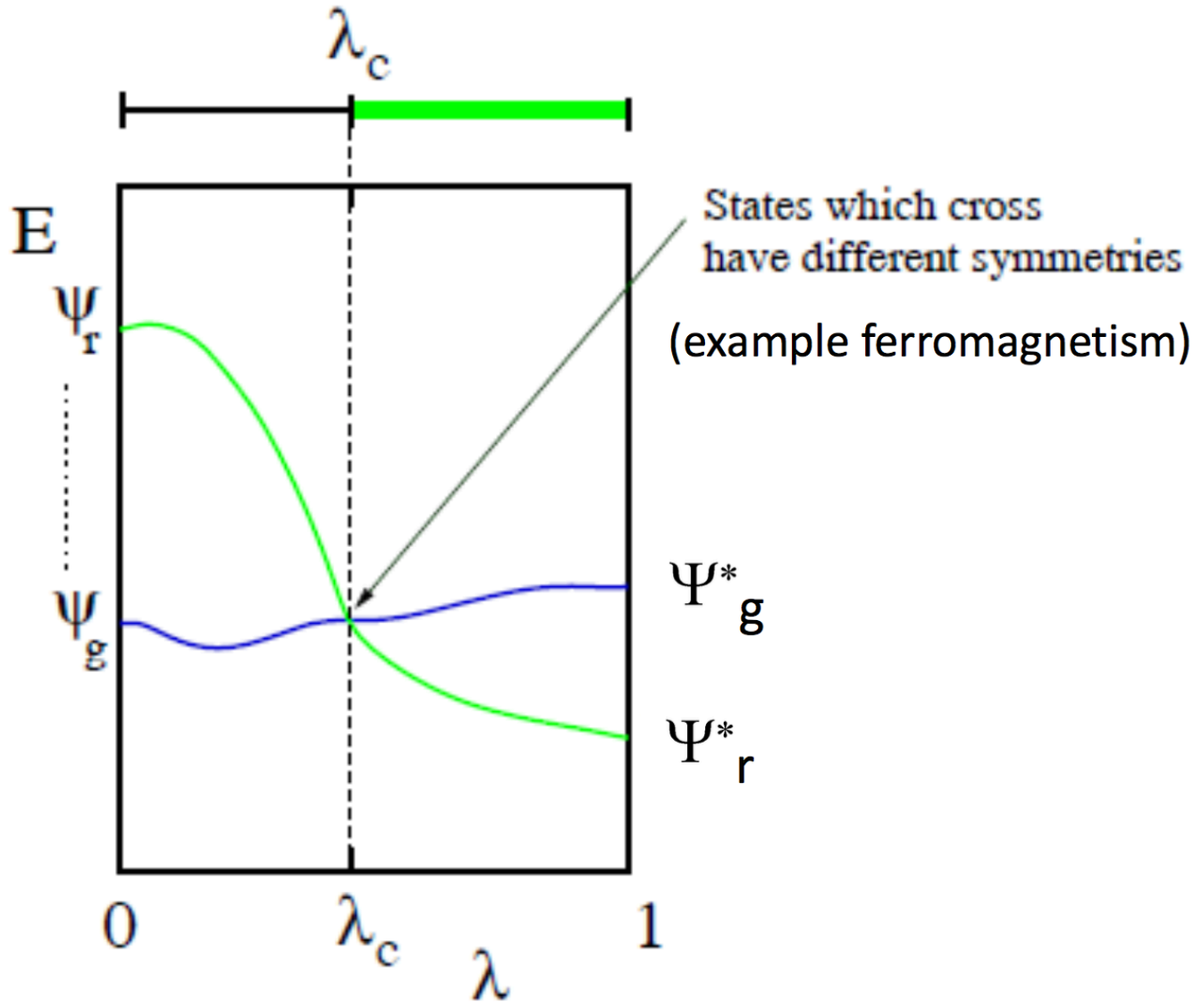


Fig. from A. J. Schofield

ADIABATIC EVOLUTION





$$H(t) = H_0 + \lambda(t)(H - H_0)$$
$$\lambda(t) = e^{-|t|\delta}$$

Fig. from P. Coleman