Correlated Electron Compounds: from real materials to model systems and back again

A. J. Millis
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Boulder 2010

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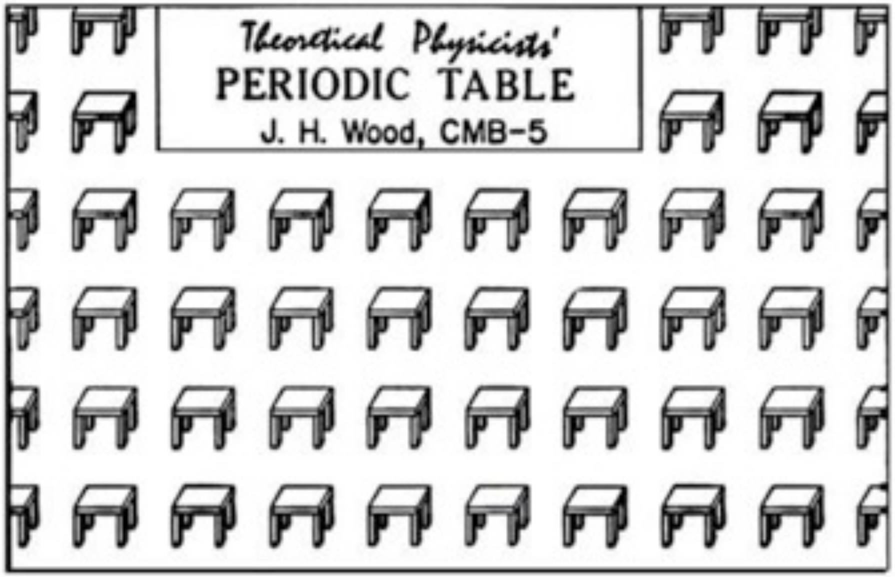
Stereotypical theoretical physicist's view of condensed matter physics

Crystal structure => Quantum Field Theory



$$=> \quad \frac{\kappa}{2}\epsilon^{\mu\nu\lambda}\mathbf{A}_{\mu}\partial_{\nu}\mathbf{A}_{\lambda}+\ldots$$

These lectures--where we are on attempts to do better, connecting material-specificity to behavior.

Periodic table from J H Wood; quoted in Z Fisk 2010 KITP talk

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$YBa_2Cu_3O_7$

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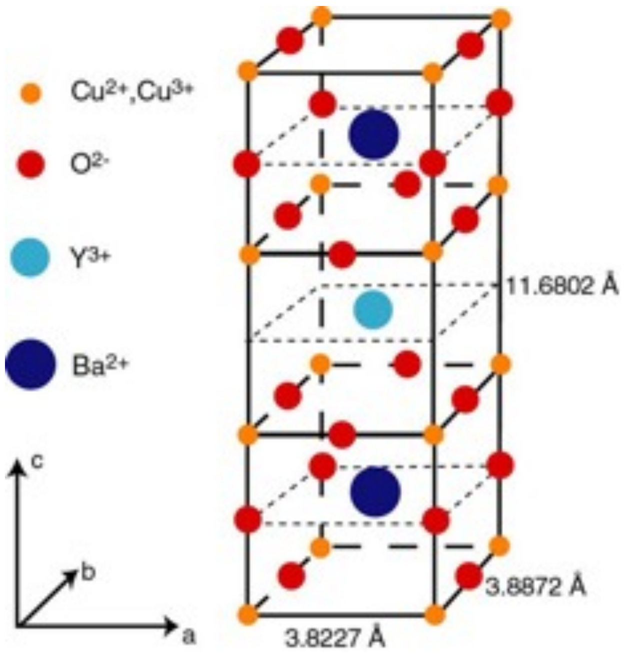

Image from www.tkk.fi/

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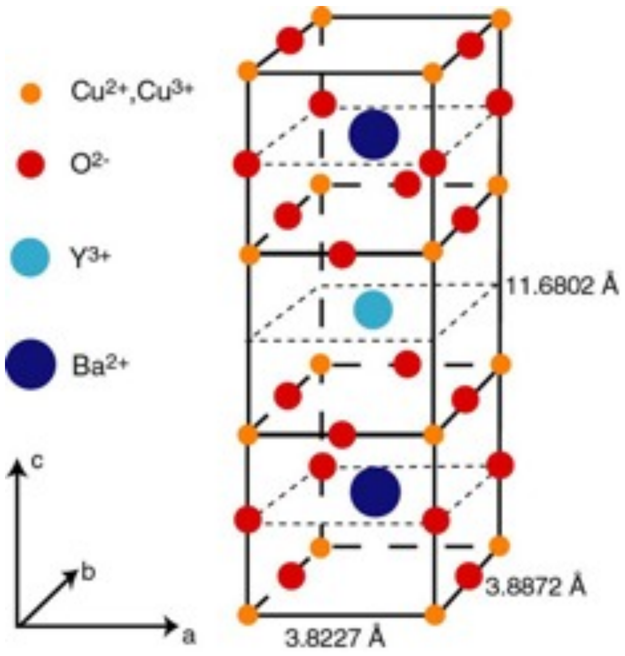

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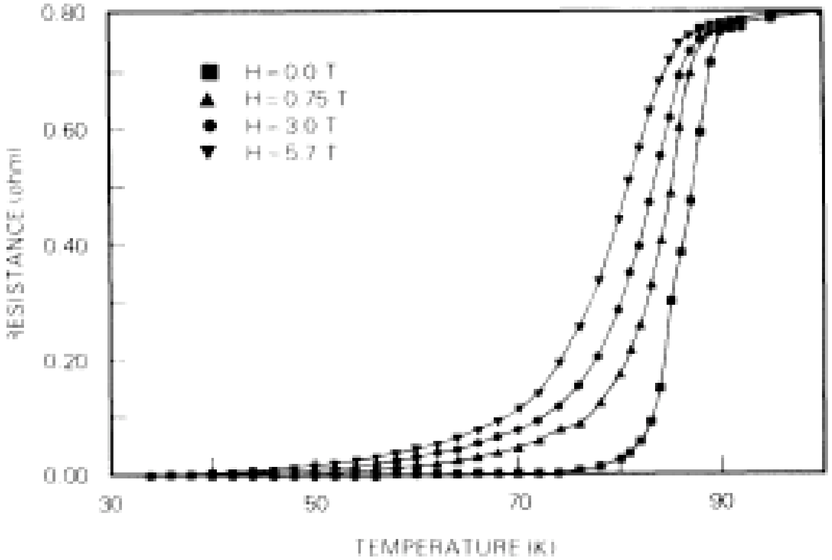
Wu et. al. PRL 58 908 (1987)



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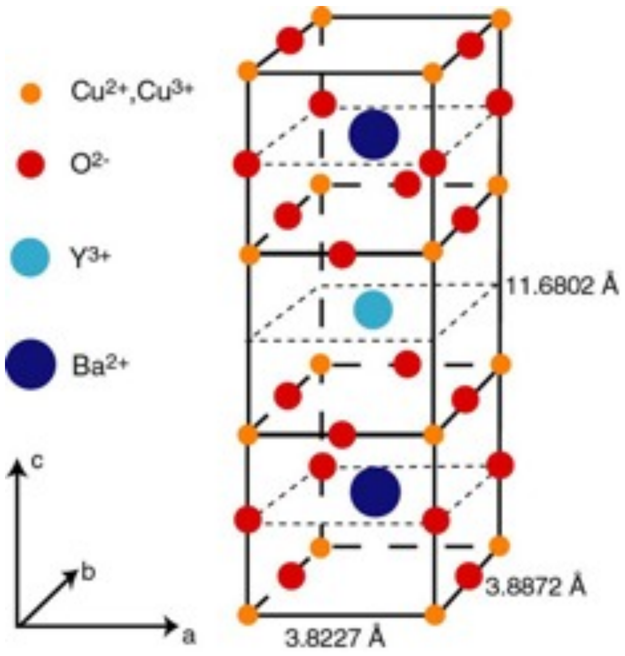

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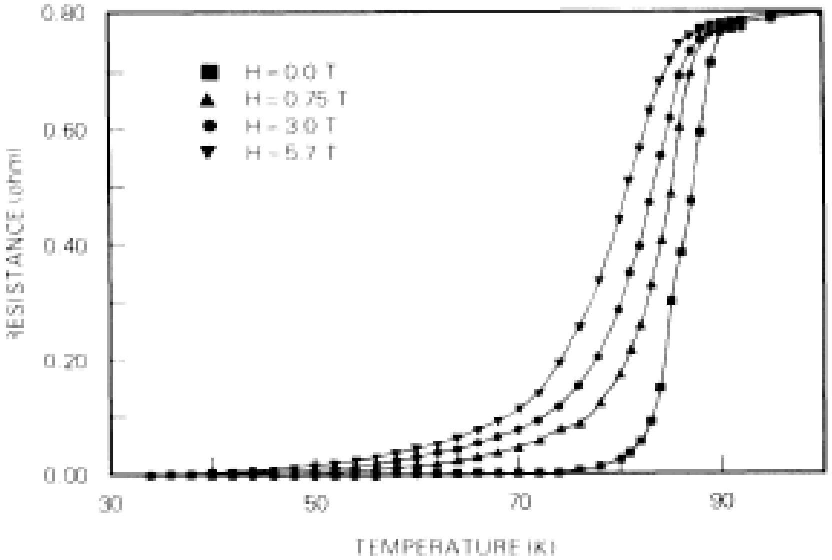
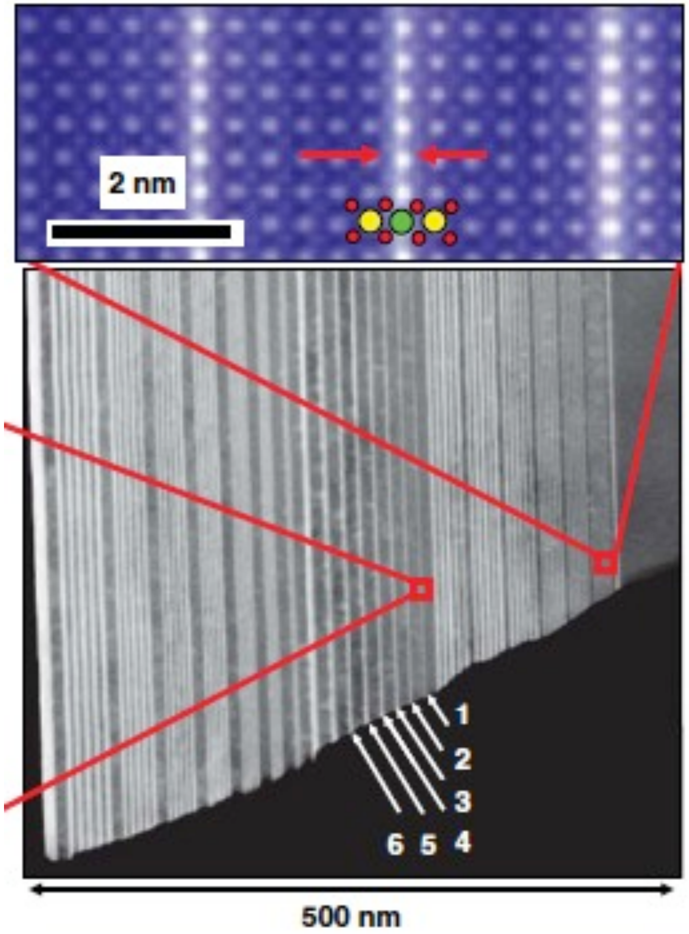


??What is special about this material??

‘Oxide Superlattices’

Ohtomo, Muller, Grazul and Hwang, Nature 419 p. 378 (2002)

$(LaSrO_3)_m(LaTiO_3)_n$



$SrTiO_3$:
d^0 “band” insulator

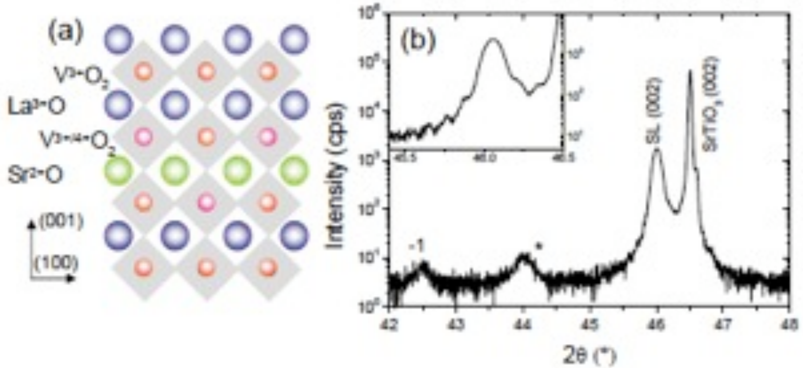
$LaTiO_3$:
d^1 “Mott” insulator

‘any’ desired (n,m)
can be synthesized

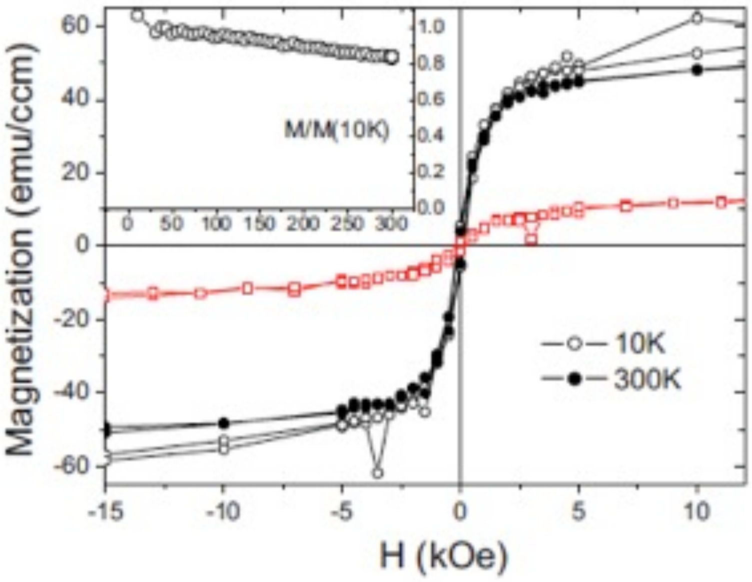
Many systems now being made: many effects can be produced

Luders et al

‘Room temperature magnetism in $LaVO_3$/ $SrVO_3$ superlattices--but not in bulk alloy

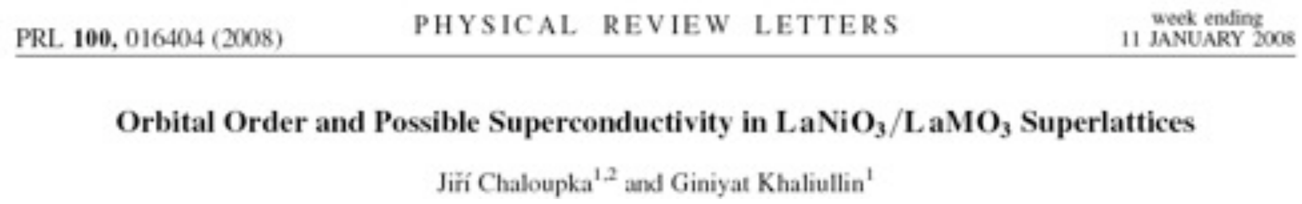


PHYSICAL REVIEW B **80**, 241102 (2009)



??Why room T magnetism in superlattice??

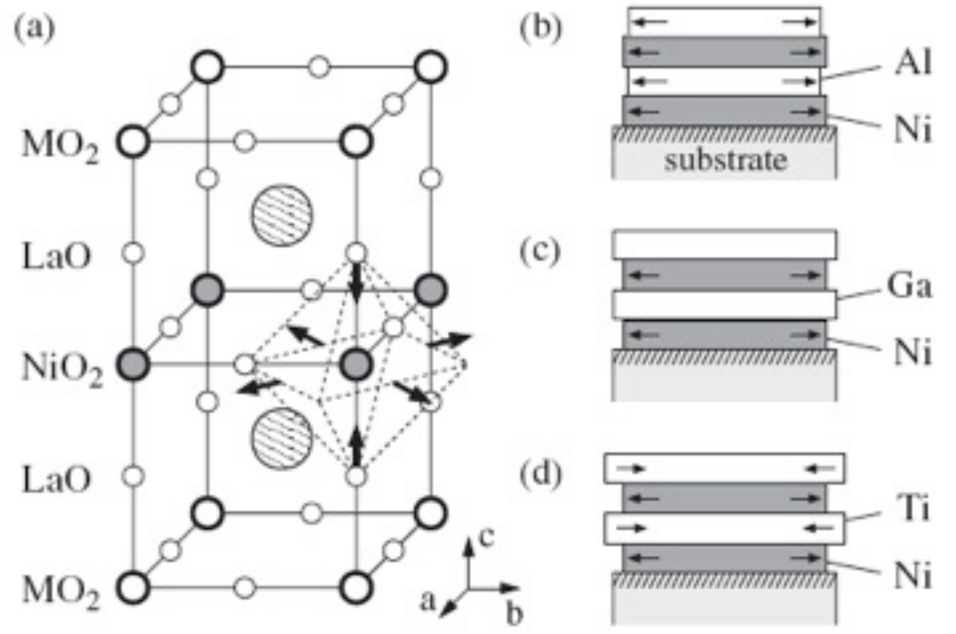
Chaloupka/Khaliullin: ?superlattices allow us to design a new high-T_c superconductor?



PRL **100**, 016404 (2008) PHYSICAL REVIEW LETTERS week ending 11 JANUARY 2008

Orbital Order and Possible Superconductivity in $LaNiO_3/LaMO_3$ Superlattices

Jiří Chaloupka[1,2] and Giniyat Khaliullin[1]



Idea:

Bulk $LaNiO_3$ Ni $[d]^7$ (1 electron in two degenerate e_g bands).

In correctly chosen structure, split e_g bands, get 1 electron in 1 band--"like" high-Tc

Chaloupka and Khalliulin argue

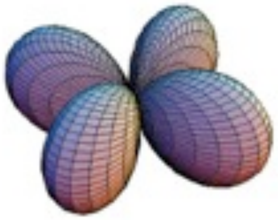
(1) Pseudocubic $LaNiO_3$

Relevant orbitals: e_g symmetry
Ni-O antibonding combinations

$3z^2$-r^2

Hybridizes strongly along z
Hybridizes weakly in x-y

x^2-y^2



Hybridizes strongly along x-y
Hybridizes very weakly in z

2 orbitals transform as doublet in cubic symmetry

Heterostructuring breaks the symmetry

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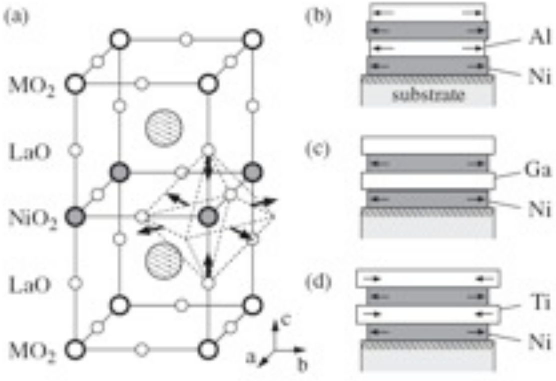

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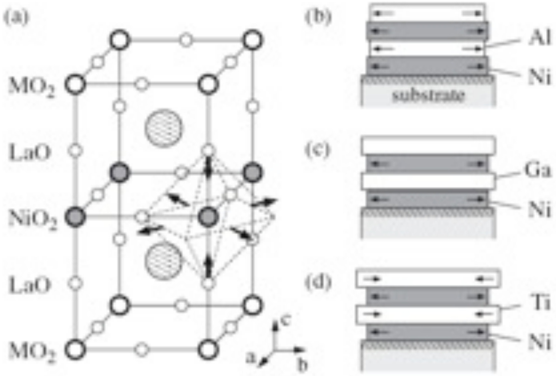
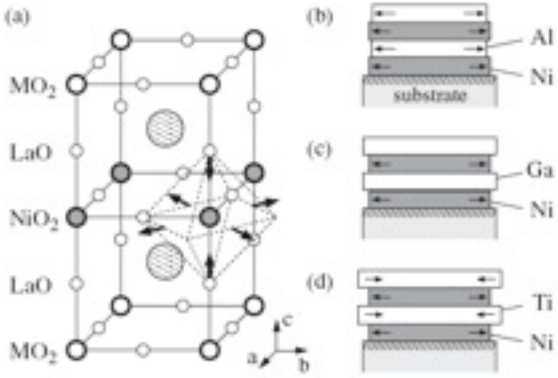


$3z^2$-r^2 orbital goes up in energy

Heterostructuring breaks the symmetry



$3z^2-r^2$ orbital goes up in energy

Result: planar array of x^2-y^2 orbitals
'just like CuO_2 high Tc superconductors'

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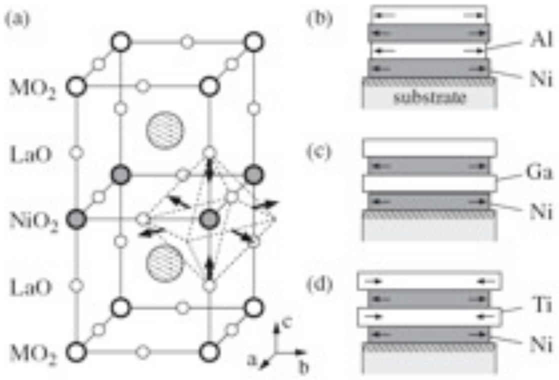

$3z^2$-r^2 orbital goes up in energy

Result: planar array of x^2-y^2 orbitals
‘just like CuO_2 high Tc superconductors’

Query: How do we know if this is right?

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More generally:

If experimentalists can make ‘anything’ --what would one want to make?

How do we connect crystal structure/atomic properties to interesting electronic behavior?

Why is it hard?

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We know the Hamiltonian

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We know the Hamiltonian

$$\mathbf{H} = \sum_i \frac{-\nabla_i^2}{2m_e} + \sum_i V_{ext}(r_i) + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|r_i - r_j|}$$

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$$\mathbf{H}\Psi_n = -i\partial_t\Psi_n$$

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So stop complaining and solve it (?!)

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Not so fast:

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Typical lattice constant: 4 Angstrom

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Interesting length ~100 Angstrom

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$$\Psi(\vec{r}_1, ...\vec{r}_{1000}...)$$

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$\Psi(\vec{r}_1, ...\vec{r}_{1000}...)$ **Intractable**

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Not so fast:

Typical lattice constant: 4 Angstrom

Interesting length ~100 Angstrom

=> ~1000 electrons with 3 (x,y,z) coordinates.
Interaction 'entangles' coordinates=>

Schroedinger equation for $\Psi(\vec{r}_1, ...\vec{r}_{1000} ...)$

Intractable

Even worse: Ψ is fully antisymmetric function of spins and coordinates

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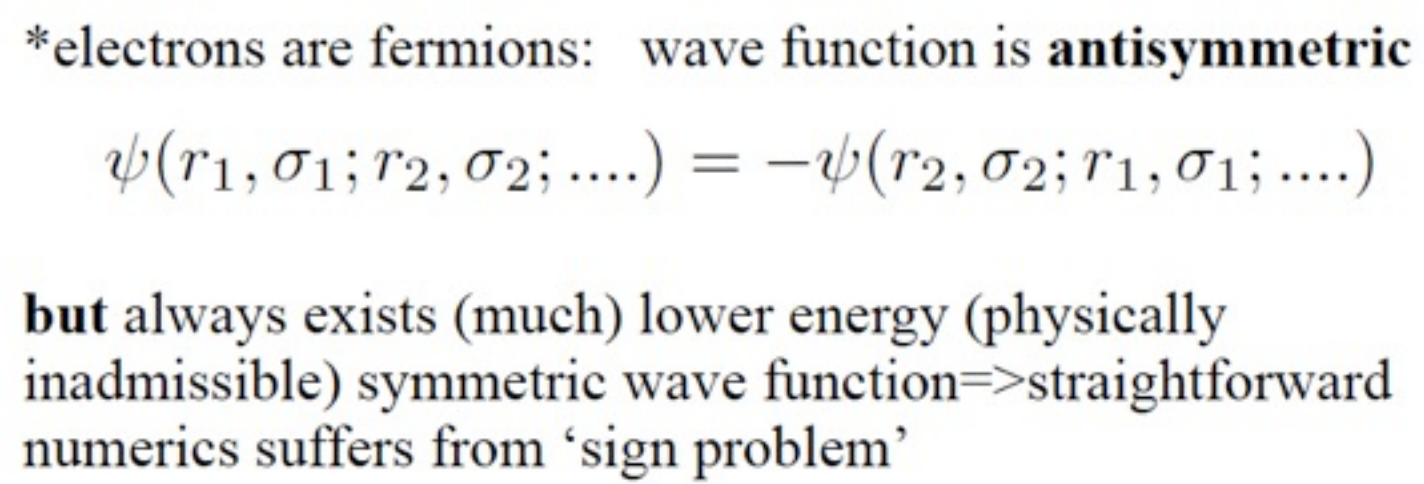
Sign problem:



*electrons are fermions: wave function is **antisymmetric**

$$\psi(r_1,\sigma_1;r_2,\sigma_2;....) = -\psi(r_2,\sigma_2;r_1,\sigma_1;....)$$

but always exists (much) lower energy (physically inadmissible) symmetric wave function=>straightforward numerics suffers from ‘sign problem’

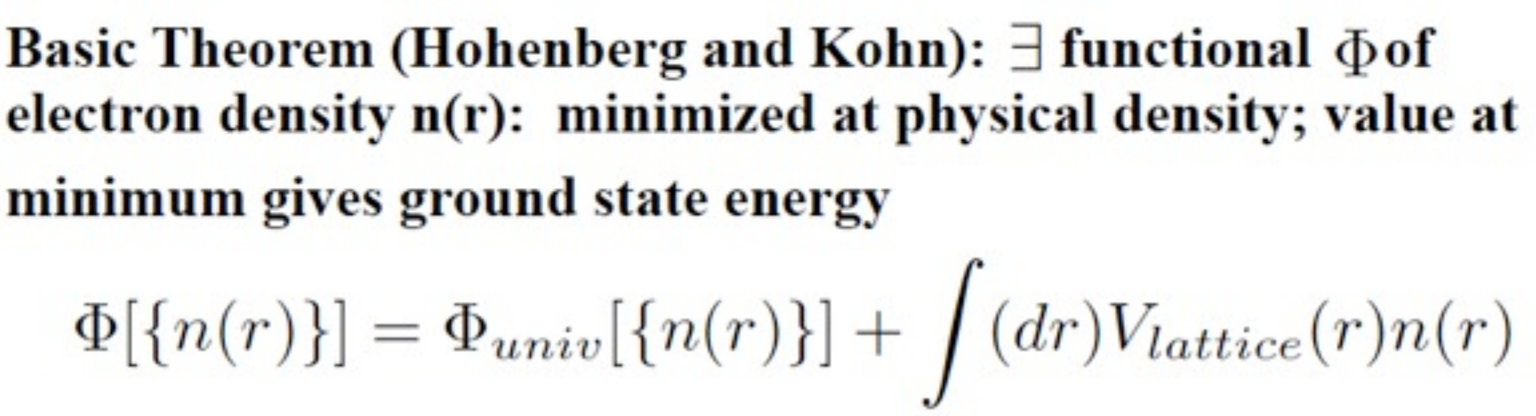
Need some other approach!

Work-horse of materials theory: density functional theory

Key idea: dont solve problem directly. Use solution of auxiliary problem to obtain (limited class of) information about problem of interest

Density Functional theory I

Phys. Rev. **136**, B864 (1964)



Basic Theorem (Hohenberg and Kohn): ∃ functional Φ of electron density n(r): minimized at physical density; value at minimum gives ground state energy

$$\Phi[\{n(r)\}] = \Phi_{univ}[\{n(r)\}] + \int (dr) V_{lattice}(r) n(r)$$

Φ_{univ} **is universal: only material dependence is in 2^{nd} term**

Sketch of Proof

$$\mathbf{H} = \sum_i \frac{-\nabla_i^2}{2m_e} + \sum_i V_{ext}(r_i) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|}$$

(1) Ground state energy E is functional of V_{ext}

solution of $H\Psi = (H_0 + V_{ext})\Psi = E\Psi$

gives mapping $V_{ext} \rightarrow E$

Note $E = <\Psi|H_0|\Psi> + \int d^3r V_{ext}(r) n(r)$

(2) Ground state density n(r) is functional of V_{ext}

Ψ **from solution of** $H\Psi = E\Psi \rightarrow n(r)$

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Key statement

****V_{ext} is unique functional of density n(r)**
(up to constant)**

Suppose not.

Then 2 potentials, $V_1 \neq V_2 + const \rightarrow$ **n(r)**

$\rightarrow$ **2 Hamiltonians,** $H_{1,2}$, **energies** $E_{1,2}$ **and** $\Psi_{1,2}$

Thus $E_1 =<\Psi_1|H_1|\Psi_1> \quad < \quad <\Psi_2|H_1|\Psi_2>$

But $H_1 = H_2 + V_1 - V_2$

So $E_1 < E_2 + \int d^3r n(r) \left(V_1(r) - V_2(r)\right)$

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Thus

$$E_1 < E_2 + \int d^3r n(r) \left(V_1(r) - V_2(r)\right)$$

$$E_2 < E_1 + \int d^3r n(r) \left(V_2(r) - V_1(r)\right)$$

Add. Get

$$E_1 + E_2 < E_2 + E_1$$

!!contradiction!!

Thus mapping $n(r) \rightarrow V_{ext}(r) \rightarrow E$

Ground state energy is unique functional of density. Can go on to show that functional is minimal at density corresponding to given V_{ext}

So to get energy

1. Put $V_{ext}(r)$ into universal functional
2. Minimize

Unfortunately

- Dont know universal functional
- Dont know how to perform minimization

W. Kohn and L Sham, Phys. Rev. **140**, A1133 (1965)

To minimize functional: solve auxiliary single-particle problem + self-consistency condition

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ions}(r) + V_{hartree}(r)\right)\psi_n(r)$$
$$+V_{XC}(\{n(r)\}) * \psi_n = E_n\psi_n(r)$$

V_{XC}: exchange correlation potential' (possibly non-local) determined by electron density. Not known.

Wave function (in principle) no meaning except

Self-consistency:

$$\mathbf{n}(\mathbf{r}) = \sum_{\mathbf{E_n}<\mu} \psi^{\dagger}_{\mathbf{n}}(\mathbf{r})\psi_{\mathbf{n}}(\mathbf{r})$$

DFT 2

(2) Uncontrolled (but apparently decent) approximation (recipe) for $V_{ext}[\{n(r)\}]$.

--‘Local density approximation’
for uniform electron gas n(r)->n.
numerics gives $V_{el-gas}(n)$.
Replace Vext[{n(r)}] by $V_{el-gas}(n=n(r))$

--Host of other approximations (GGA, B3LYP, ...) (all uncontrolled; tested by comparison to experiment...)

Result: procedure that works for many purposes. Essential computational task: solve 1 particle schroedinger eq in some V(n(r)); self-consist

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Density functional band theory

Believed good for:

- Total energies
- Crystal structures
- Phonon Frequencies (restoring force=electron energy)
- Identification of relevant electronic orbital

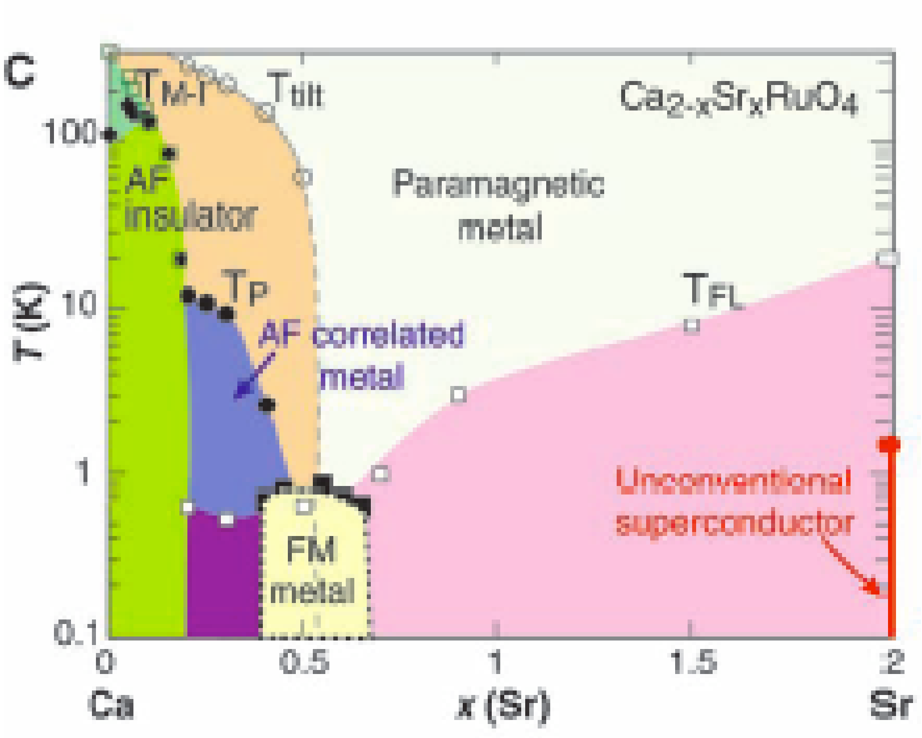
Not so good for:

- Dynamics
- Thermodynamics
- Phase transitions
- Local moment/Mott physics

Density Functional Theory: Issues

$$\Phi[\{n(r)\}] = \Phi_{univ}[\{n(r)\}] + \int (dr) V_{lattice}(r) n(r)$$

Density is not the optimal variable: phases with quite different physical properties have almost the same density



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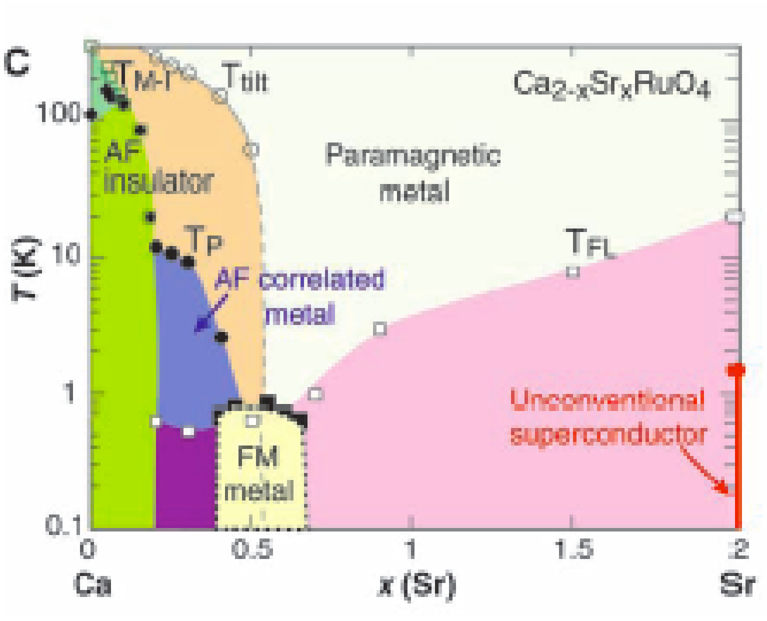
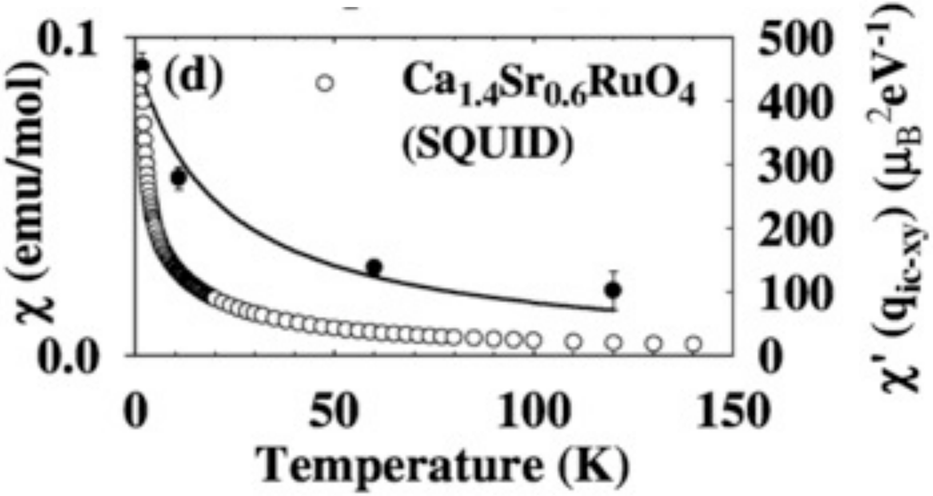
Density Functional Theory: Issues

Ground state is not the only interest: different phases at different temperatures: need theory with local moments, entropic effects





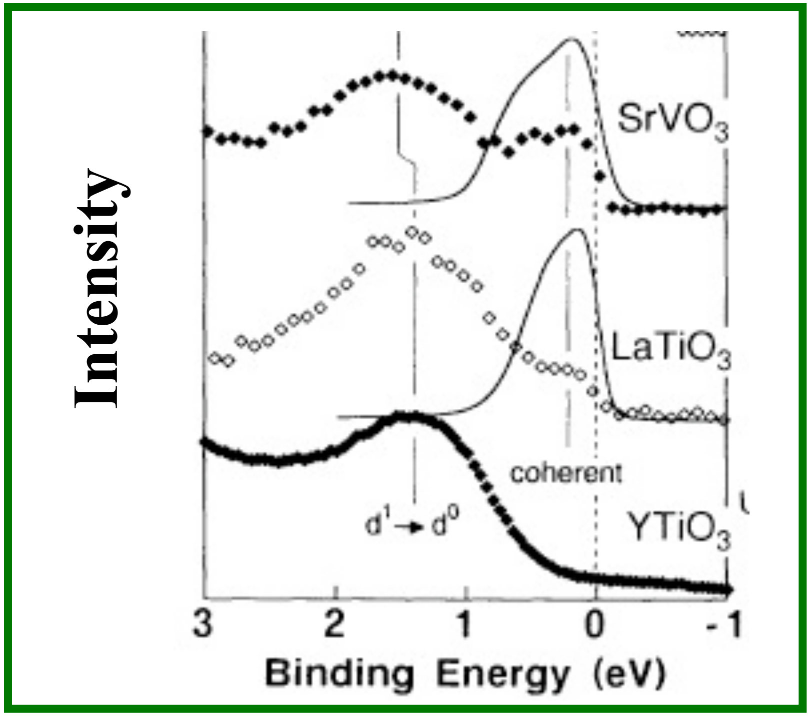
$$\chi \sim \frac{1}{T}$$

Local magnetic moment?

Density Functional Theory: Issues

Ground state is not the only interest: excitation spectrum also important

Photoemission (electron removal spectrum)



dots: data
lines: band theory

Shakeoff (side) band present in data, absent in band theory

A. Fujimori et al Phys. Rev. Lett. **69**, 1796 (1992

Summary: density functional theory

- Quantities of interest obtained from solution of auxiliary problem + self consistency condition
- Uncontrolled but in practice very useful approximation
- Built to get ground state density, energy=>difficulties with excitation spectrum, higher T behavior, phase transitions to other ground states

To deal with excitation spectrum: fermi liquid theory

landau100.itp.ac.ru

Qualitative Arguments I: Landau/Peierls

nndb.com

Consider `free' (no potential) fermions interacting via short ranged interaction (physical example: ^{3}He)

Neglect interactions:

$$\mathrm{H} = -\sum_i \frac{\nabla_i^2}{2m}$$

Solution: antisymmetrized product ('Slater Determinant') of plane waves

$$\mathrm{Det}\left[e^{i\vec{k}_j\cdot\vec{r}_i}\right]$$

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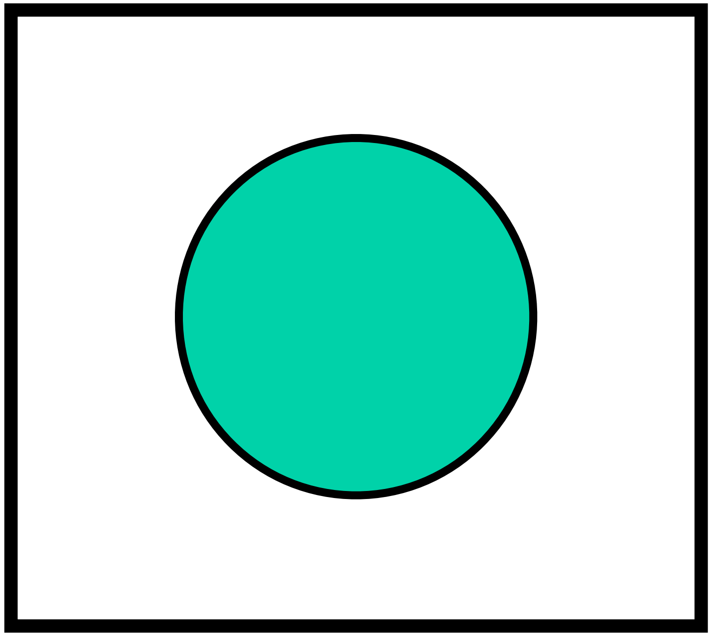
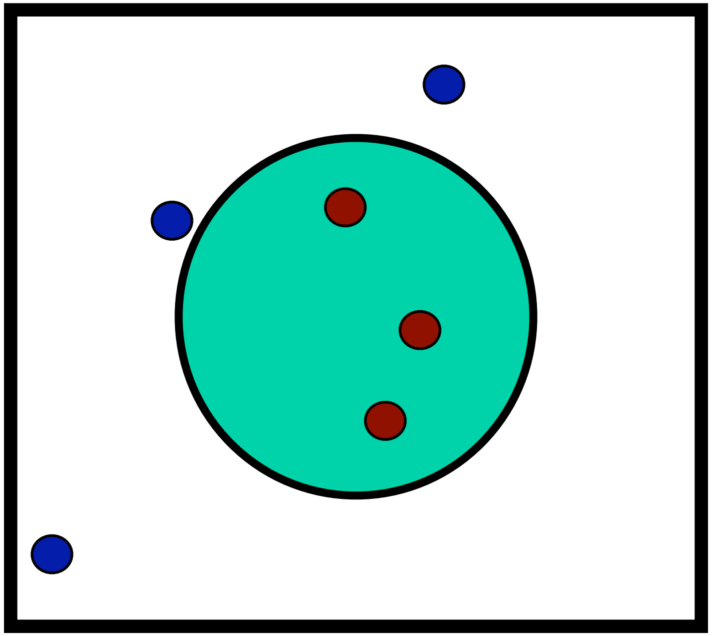
Physical Content

Ground state: 'filled fermi sea'



2 dimensional picture of region of k space with occupied states in green

Excited states: particle-hole pairs



Label wave function by excitations above ground state

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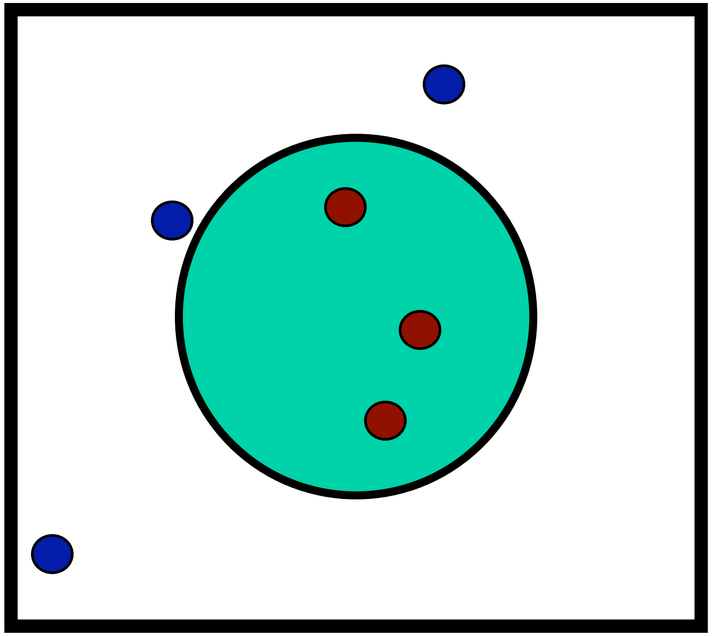
Physical content II

Noninteracting fermions

Excited states:

particle-hole pairs

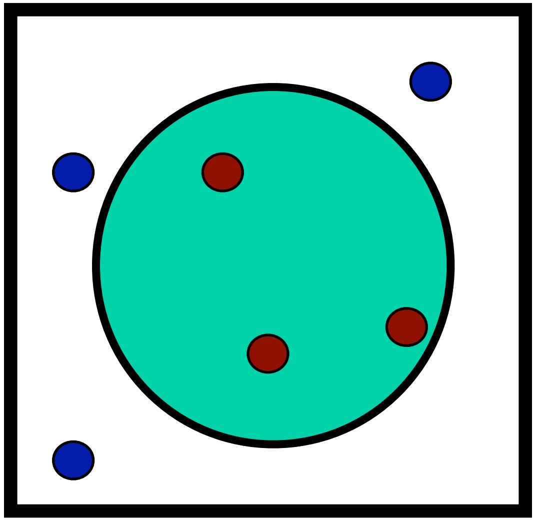


- **Particle (or hole) energy ~ distance from fermi surface:**

$$E = v_F \left||k| - k_F\right|$$

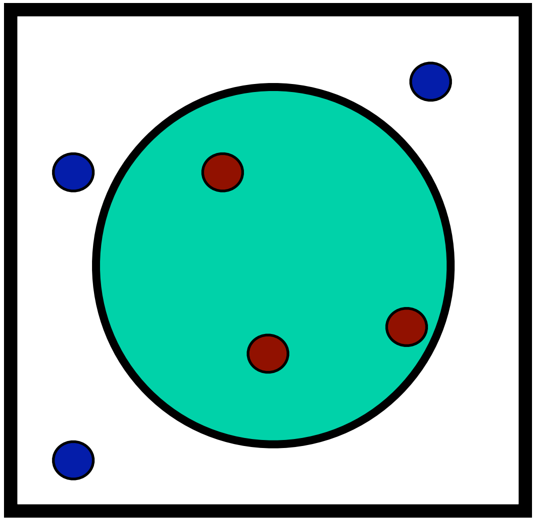
- **Susceptibilities, specific heat coefficient constant (at low T) and proportional to particle mass m**

Physical content: III



Noninteracting case: each particle and hole propagates freely.

Physical content: III



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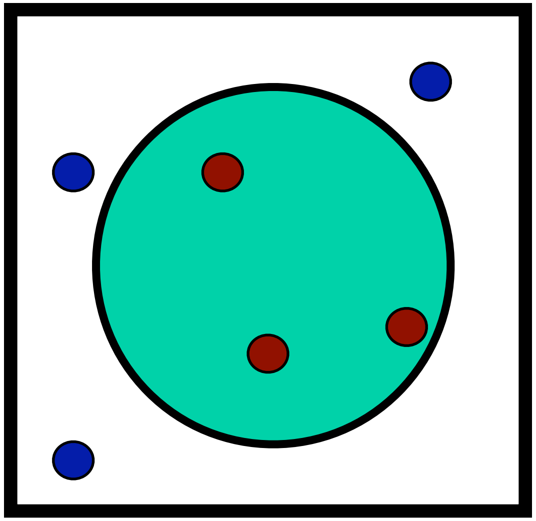

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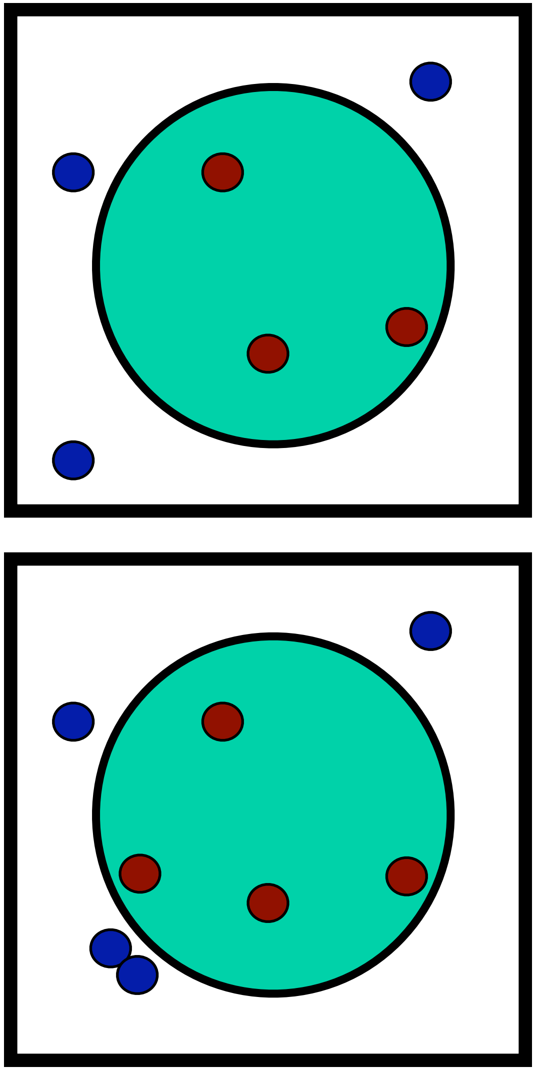

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As particle approaches fermi surface, phase space for decay decreases

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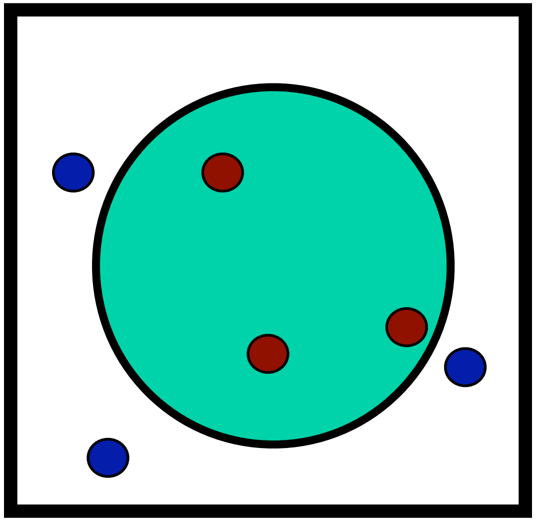

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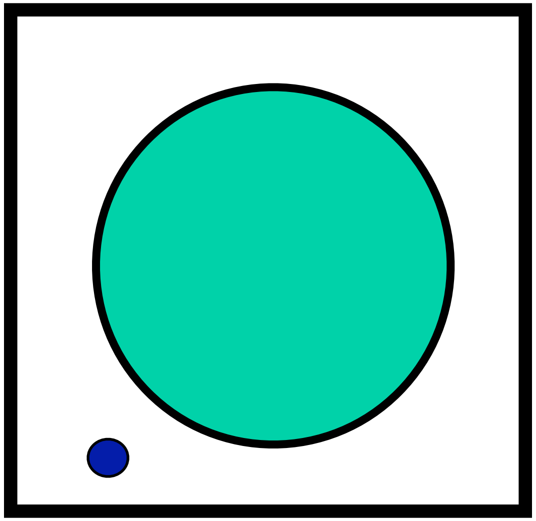
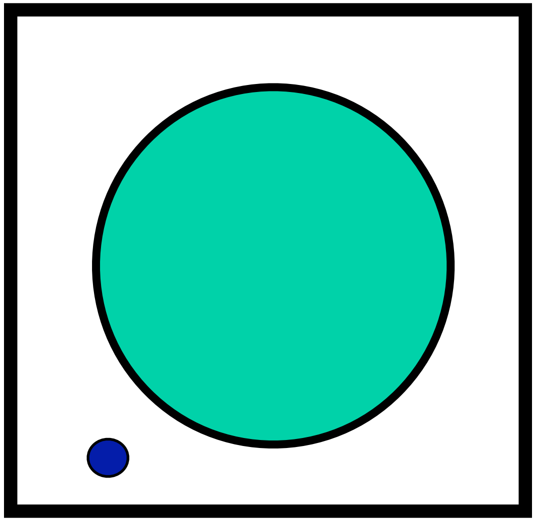


Hide other particles, so can
focus on decay of 1 particle

As particle approaches fermi surface, phase space for decay decreases



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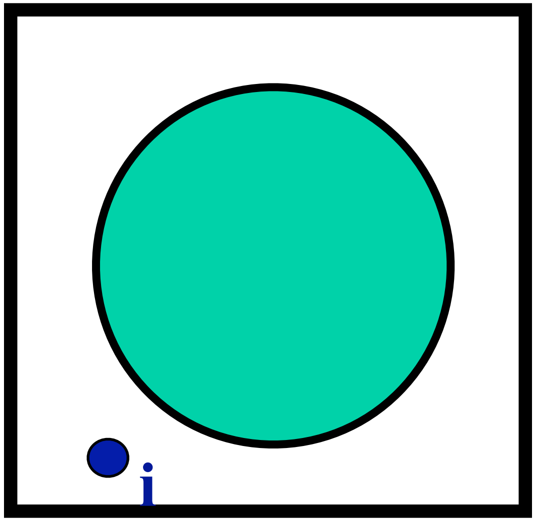
Energetics of decay:

As particle approaches fermi surface, phase space for decay decreases



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Energetics of decay:

Initial state: energy $E_{initial}$

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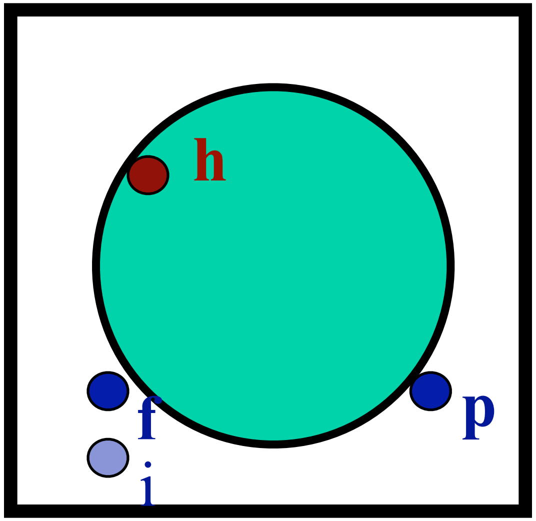

Energetics of decay:

Initial state: energy $E_{initial}$

Final state: energy $E_f + E_p + E_H$

Hide other particles, so can focus on decay of 1 particle

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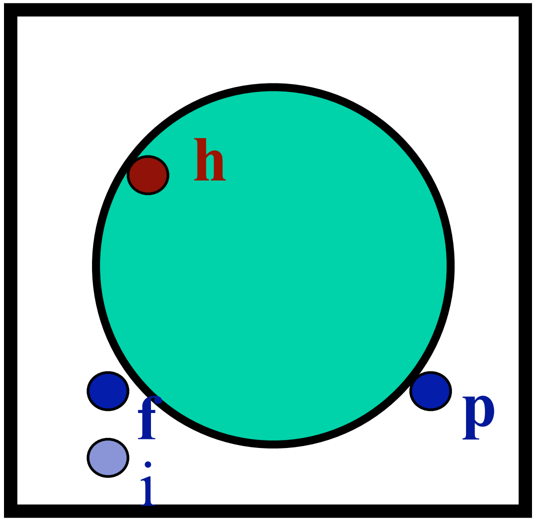
As particle approaches fermi surface, phase space for decay decreases



Hide other particles, so can focus on decay of 1 particle

Energetics of decay:

Initial state: energy $E_{initial}$

Final state: energy $E_f + E_p + E_H$

$= E_{initial}$

=>all 3 final states must be closer to fermi surface than initial state=>decay prob ~E^2

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Low energy excitations:

1. Decay process p->p + (p,h) is negligible
2. Modification of energetics due to other excitations not negligible

I gave a pictorial sketch of a perturbative argument for (1) and I ask you to believe (2).

Landau, then Luttinger, Ward, Nozieres, and others provided an increasingly sophisticated set of formal arguments justifying these statements and exploring their consequences.
Result: ‘Fermi Liquid Theory’

Fermi Liquid Theory References

Books

Abrikosov, Gorkov and Dzyaloshinksi, *Methods of Quantum Field Theory in Statistical Physics*
Pines and Nozieres: *Theory of Quantum Liquids*
Nozieres: *Interacting Fermi Systems*

Renormalization Group Point of View

R. Shankar, Rev. Mod. Phys. **66**, 129–192 (1994)

Result:

In many circumstances, low energy properties of interacting fermi systems are those of noninteracting systems, but with renormalized parameters.

Formalism: electron Green function

Define: Exact eigenstates $|\Psi^m_{N+1}(k)>$
of N+1 particle system
momentum k, energy E^m_k
relative to N-particle ground state $|GS>$

Define: electron Green function $G(k,\omega)$

$$= \int dt e^{-i\omega t} \mathcal{T} \left\langle GS \middle| \left\{ \psi_k(t), \psi^\dagger_k(0) \right\} \middle| GS \right\rangle$$

$\psi^\dagger_k$ creates electron in state
with wave function $\sim e^{i\vec{k}\cdot\vec{r}}$

$\mathcal{T}$ is time ordering symbol

Spectral representation

$$\mathbf{G}^R(k,\omega) = \int \frac{dx}{\pi} \frac{A(k,x)}{\omega - x - i\delta}$$

Spectral function $\mathbf{A}(k,\omega) = Im\left[G^R(k,\omega)\right]$

$$= \sum_m < GS|\psi_k|\Psi^m_{N+1} >< \Psi^m_{N+1}|\psi^\dagger_k|GS > \delta(\omega - E^m_{N+1})$$
$$+ \sum_m < GS|\psi^\dagger_k|\Psi^m_{N-1} >< \Psi^m_{N-1}|\psi_k|GS > \delta(\omega - E^m_{N-1})$$

Measures overlap of exact eigenstates with ‘single-particle state created by $\psi_k^\dagger$

Spectral representation II

Noninteracting system: $\psi_k^\dagger$ creates an exact eigenstate, say m=m$_1$

$$\psi_k^\dagger|GS>=|\Psi^m_{N+1}(k)>\delta_{m,m_1}$$

Spectral function is a delta function

$$\mathbf{A}(k,\omega)=\delta(\omega-E_k)$$

Spectral representation III

General interacting system: state created by $\psi_k^\dagger$ does not closely resemble any eigenstate; has overlap with all

$$<\Psi^m_{N+1}(k)|\psi_k^\dagger|GS>= f(m)$$

Spectral function is a smooth function

Spectral representation IV

Fermi liquid: as k-> k_F, the state created by $\psi_k^\dagger$ tends to have some overlap with one unique state, as well as with a continuum of others

$$<\Psi_{N+1}^m(k)|\psi_k^\dagger|GS>= Z_k\delta_{m,m_1} + f(m)$$

Spectral function tends to a delta function (quasiparticle peak) plus smooth ('incoherent part') background

Important concept: quasiparticle weight Z_k

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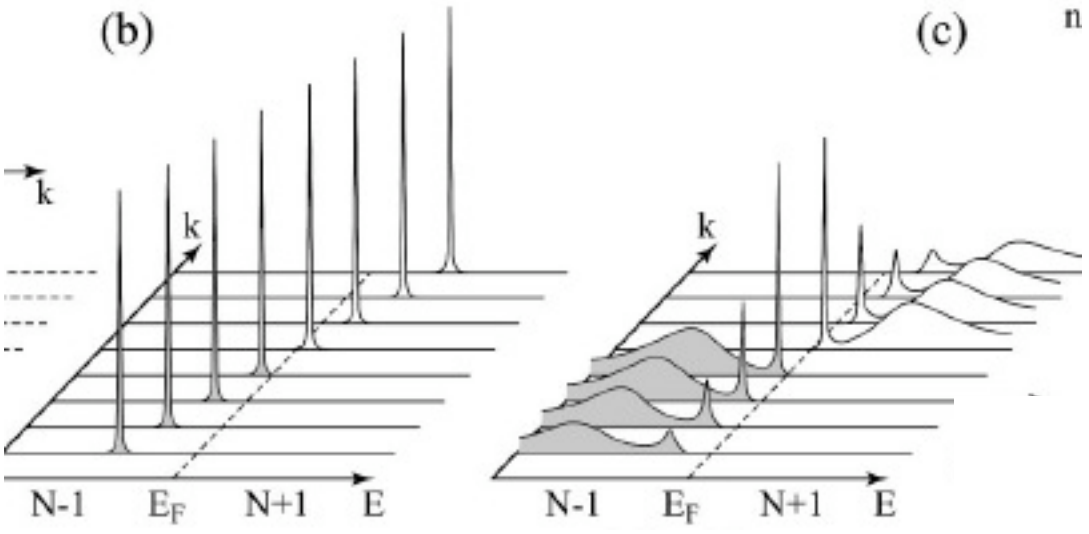
Angle-Resolved Photoemission (ARPES) measures (occupied state part of)

A (up to matrix element)

Noninteracting Fermi liquid



Z: relative weight of near fermi surface peak

v*: peak dispersion

Im Sigma: peak width

Fig. 3, Damascelli, Hussain and Shen RMP 75 473 (2003)

Spectral representation V

Alternative mathematical formulation: self energy

$$\mathbf{G}(k,\omega) = \frac{1}{\omega - \varepsilon_k - \Sigma(k,\omega)}$$

Self energy $\Sigma(k,\omega)$ expresses difference between actual electron propagation and electron propagation in reference noninteracting system with dispersion ε_k

Spectral representation V

Self energy has real and imaginary parts.

$$\mathbf{A}(k,\omega) = \frac{Im\Sigma(k,\omega)}{(\omega - \varepsilon_k - Re\Sigma(k,\omega))^2 + Im\Sigma(k,\omega)^2}$$

Real part expresses renormalization of dispersion, overlap with exact eigenstate.

Imaginary part expresses quasiparticle lifetime

Fermi liquid: $Im\Sigma(k,\omega\rightarrow 0)\rightarrow 0$

$$v_F^* = Z\left(\partial_k\varepsilon_k + \partial_k Re\Sigma(k,\omega)\right)_{k=k_F}$$

$$\mathbf{Z} = \left(1 - \frac{\partial Re\Sigma(k_F,\omega)}{\partial\omega}|_{\omega\rightarrow 0}\right)^{-1}$$

Fermi liquid theory

Arrangement of many-body physics formalism to focus on coherent part of G, with effect of incoherent parts being subsumed in renormalizations, interaction vertices etc.

Different perspective on spectral function, fermi liquid theory

Anderson impurity model

$$\begin{aligned} H_{AIM} &= \sum_{\sigma} \varepsilon_0 d^{\dagger}_{\sigma} d_{\sigma} + U n_{\uparrow} n_{\downarrow} \\ &+ \sum_{k\sigma} \left(V_k c^{\dagger}_{k\sigma} d_{\sigma} + H.c. \right) + \sum_{k\sigma} \varepsilon_k c^{\dagger}_{k\sigma} c_{k\sigma}. \end{aligned}$$

1 orbital (d), subject to interaction (U) and coupled to non-interacting continuum (c)

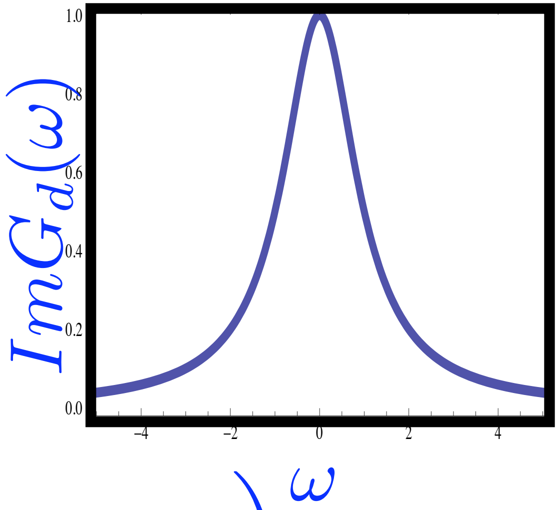
Not trivial because V-term does not commute with U term

0-dim model. Perturbation in U converges at all U

U=0: solvable hybridization problem:

Physics: scattering resonance in continuum.
Describe by Green function for d-electrons

$$\mathbf{G}_d(\omega) = \frac{1}{\omega - \varepsilon_d - \Delta(\omega)}$$



key parameter: hybridization function

$$\boldsymbol{\Delta}(\omega) = \sum_k V_k^2 \left(\mathcal{P}\frac{1}{\omega - \varepsilon_k} + i\pi\delta(\omega - \varepsilon_k) \right)$$

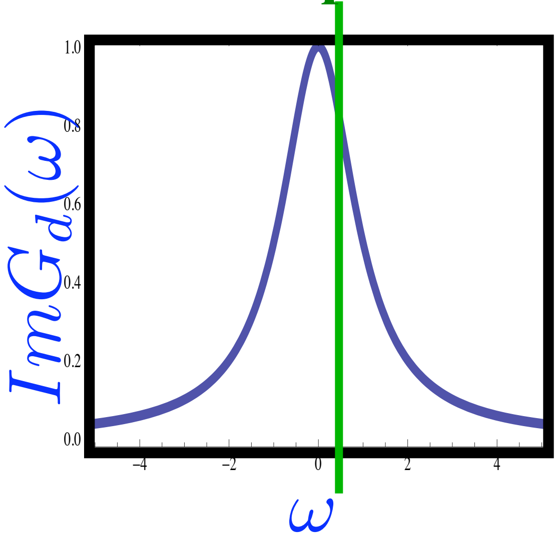
real part: level shift due to coupling to continuum
imaginary part: decay of electron from localized orbital to continuum

U=0: solvable hybridization problem:

Physics: scattering resonance in continuum. Describe by Green function for d-electrons

$$\mathbf{G}_d(\omega) = \frac{1}{\omega - \varepsilon_d - \Delta(\omega)}$$

key parameter: hybridization function



Chemical potential

Fill resonance up to chemical potential

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‘Friedel sum rule’

$$\mathbf{n_d = ArcTan\left[\frac{Im\ G_d^{-1}(\omega=\mu)}{Re\ G_d^{-1}(\omega=\mu)}\right]}$$

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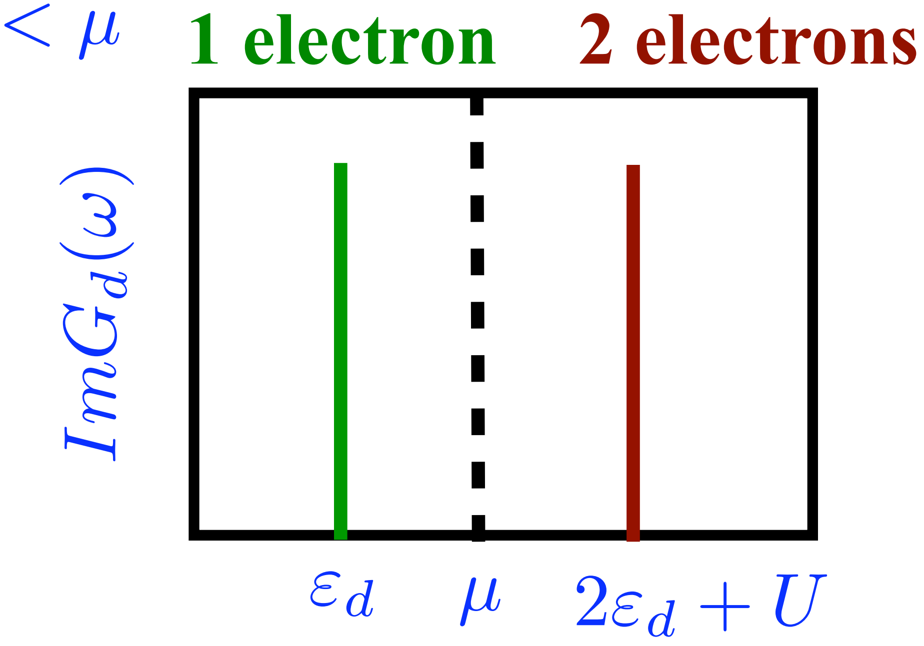
V=0: isolated ‘atom’

impurity occupation number n$_d$: conserved

If $\varepsilon_d < \mu$



Note: 2 1-electron states: up, down

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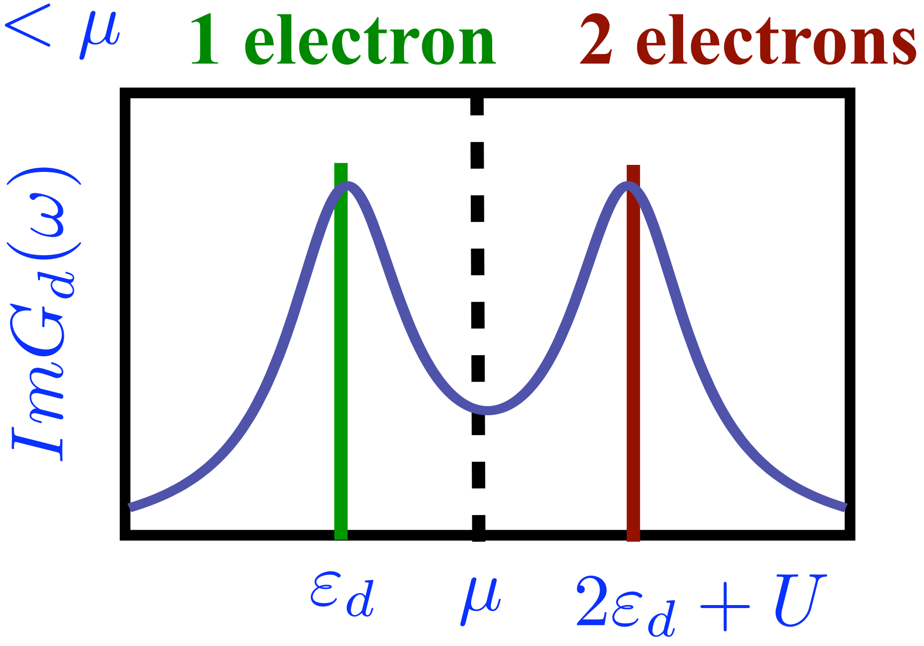
turn on V

impurity occupation number n_d: not conserved

Guess: states broaden

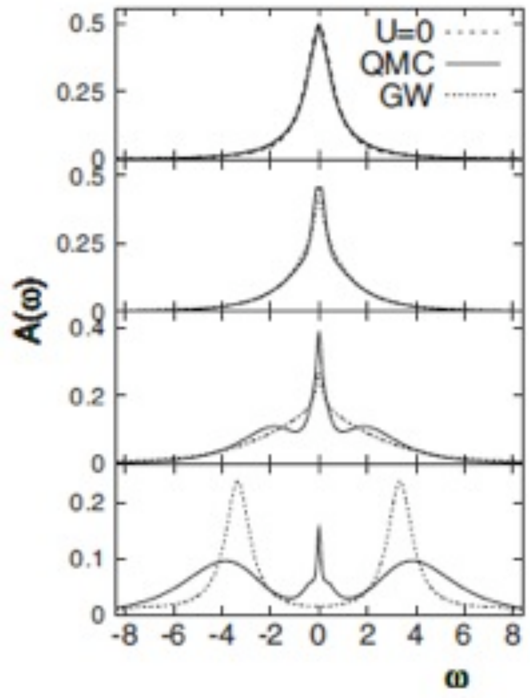
If $\varepsilon_d < \mu$



But recall Friedel sum rule

0-d system, no phase transition as function of U, so ratio of Im to Re G at chemical potential has to be consistent with density.

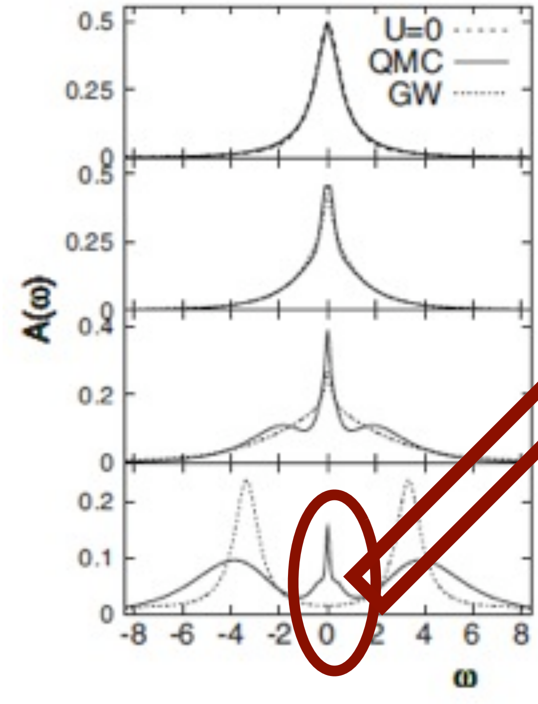
Result: 3 peak structure with ‘Kondo resonance’ in center



U increases ->

Wang, Spataru, Hybertsen, AJM PRB77 04511
(at largest U, T in calculation not low enough)

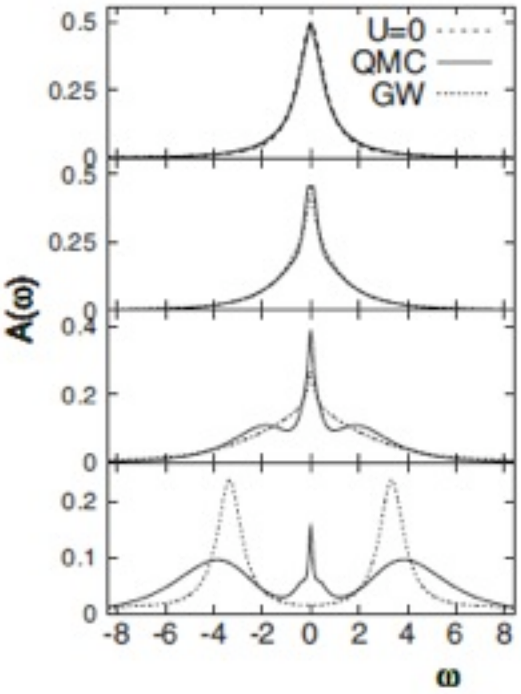
Low energy physics

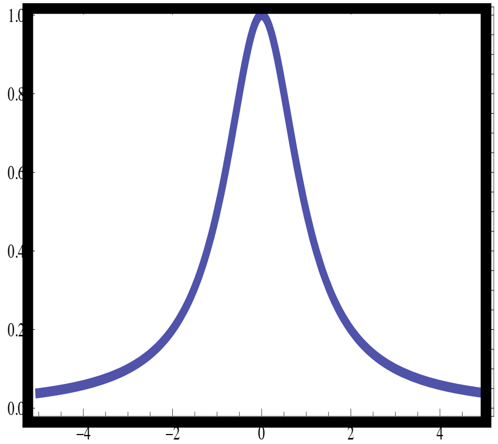


Renormalized scattering resonance

'Local fermi liquid theory'.
Weight of central peak <=>Z

How would density functional theory represent this solution





Only choice: one single scattering resonance, with properties tuned to reproduce energy

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We will see:

Anderson impurity model is an auxiliary problem whose solution gives insight into many-body electronic structure.