Strongly correlated systems and the DFT+DMFT approach

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lecture notes

Autumn School on Correlated Electrons

http://www.cond-mat.de/events/correl.html

manuscripts/full books can be dowloaded
• what are correlations?
• the quantum-many problem and DFT
• from the many-body problem to simple models
• the metal insulator transition in DMFT and Hartree-Fock
• building material-specific many-body models from DFT
• the LDA+DMFT scheme and comparison with LDA+$U$
• conclusions
what are correlations?
all of solid state physics is about correlations
classical N-body problem

one body: no interactions

two-body: analytically solvable problem

three-body: chaotic behavior possible
solution very difficult
many objects with simple two-body interactions can give rise to a very complex system
correlations

many objects with simple two-body interactions can give rise to a very complex system
emergent behavior

(from NASA website)
Sundman’s method failed to apply to the $n$-body problem for $n > 3$. It took about 7 decades until the general case was solved. In 1991, a Chinese student, Quidong (Don) Wang, published a beautiful paper [Wal], [D1], in which he provided a convergent power series solution of the $n$-body problem. He omitted only the case of solutions leading to singularities—collisions in particular. (To understand the complications raised by solutions with singularities, see [D2].)

Did this mean the end of the $n$-body problem? Was this old question—unsuccessfully attacked by the greatest mathematicians of the last 3 centuries—merely solved by a student in a moment of rare inspiration? Though he provided a solution as defined in sophomore textbooks, does this imply that we know everything about gravitating bodies, about the motion of planets and stars? Paradoxically, we do not; in fact we know nothing more than before having this solution.

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*The Solution of the $n$-body Problem*

Florin Diacu

or papers or learned about at normal presentations. we
don’t know a reference, have no idea who proved
that result, how, and when. Usually a colleague men-
tioned it at some conference dinner, during a coffee-
break, or in a friendly discussion in our Department. It
is striking, it sticks to our mind, and after a while it is
part of our mathematical heritage—we just know it.
Then we tell it further under similar circumstances, and
so the wheel turns on. We will call this component of
our knowledge folk-mathematics.

Without denying the positive role folk-mathematics
plays in spreading information, we must admit that re-
sults gathered through it are sometimes misleading or
misunderstood. A typical example is the Cantor set.
Everybody knows that the middle-third Cantor set has
zero Lebesgue measure, and many believe that the mid-
dle-fifth analogue has positive measure. Intuitively this
sounds plausible: if we remove each time a smaller seg-
ment, the remaining quantity should be larger. Unfor-
tunately, the intuition leads us astray this time. For any

Dedicating to Philip Holmes, his deep mathematics, for his warm
and candid poetry, and for the immense intellectual joy he has in-
stilled in me during the time our book took shape.
exact solutions do not help

The following section deals with this apparent paradox.

**The Foundations of Mathematics**

What Sundman and Wang did is in accord with the way solutions of initial value problems are defined; everything is apparently all right; but there is a problem, a big one: these series solutions, though convergent on the whole real axis, have very slow convergence. One would have to sum up millions of terms to determine the motion of the particles for insignificantly short intervals of time. The round-off errors make these series unusable in numerical work. From the theoretical point of view, these solutions add nothing to what was previously known about the n-body problem.

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**References**


emergent behavior

(from NASA website)
emergence at work

sand dunes

(photo from wikipedia)

traffic jam

(photo from wikipedia)

flocking

(photo from wikipedia)
the theory of nearly everything

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \]

The underlying laws needed for the description of all chemistry as well as a large part of physics are now entirely known. The only problem that remains is that the exact equations of quantum mechanics are too difficult to be solved. It is therefore necessary to derive approximations that allow us to calculate the properties of complex molecular systems with an acceptable computational effort.

P.M.A. Dirac 1929

Paul Adrien Maurice Dirac
Nobel Prize in Physics 1933
emergent behavior

The effectiveness of this message may be indicated by the fact that I heard it quoted recently by a leader in the field of materials science, who urged the participants at a meeting dedicated to “fundamental problems in condensed matter physics” to accept that there were few or no such problems and that nothing was left but extensive science, which he seemed to equate with device engineering.

The main fallacy in this kind of thinking is that the reductionist hypothesis does not by any means imply a “constructionist” one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe. In fact, the more the ele-

4 August 1972, Volume 177, Number 4047

http://www.emergentuniverse.org
the dream machine

Z, M, e...
equations + your computer

all physics
what are correlations?

hallmarks are emergent cooperative phenomena

e.g. examples: phase transitions

prediction is very difficult

typically theory comes after experiments

.. and even many decades after (superconductivity)

after we understood the mechanism everything is simpler…
an example: anti-ferromagnetism

Heisenberg model: effective interaction

\[ H = \frac{1}{2} \Gamma \sum_{\langle ij \rangle} S_i \cdot S_j \]
a prediction: antiferromagnetism

prediction: Néel (1932)
from mean-field theory

experiment: Shull and Smart (1949)
but the theory was wrong…

Bethe: ground state of linear Heisenberg chain has $S=0$
static mean-field ground state is wrong

Anderson: broken symmetry & quantum fluctuations
after we understood the mechanism everything is simpler…

1. replaced by
   charge degrees of freedom irrelevant

2. instead of electronic Hamiltonian
   spin-only Hamiltonian

3. simple (wrong) method sufficient
   static mean-field solution
the quantum many-body problem and DFT
the theory of nearly everything

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|r_i - r_i'|} - \sum_{i, \alpha} \frac{Z_{\alpha}}{|r_i - R_{\alpha}|} - \sum_{\alpha} \frac{1}{2M_{\alpha}} \nabla_{\alpha}^2 + \frac{1}{2} \sum_{\alpha \neq \alpha'} Z_{\alpha} Z_{\alpha'} |R_{\alpha} - R_{\alpha'}| \]

The underlying laws needed for the description of all chemistry as well as a large part of physics are now entirely known. The only problem that remains is that the exact equations of quantum mechanics are too difficult to be solved. It is therefore necessary to derive approximations that allow us to calculate the properties of complex molecular systems with an acceptable computational effort.

P.M.A. Dirac 1929
the many-body problem

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i, \alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_{\alpha} \frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \]

Born-Oppenheimer Ansatz

\[ \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_\alpha\}) = \psi(\{\mathbf{r}_i\}; \{\mathbf{R}_\alpha\}) \Phi(\{\mathbf{R}_\alpha\}) \]

electronic Hamiltonian

\[ \hat{H}_e = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \]

\[ = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \]
a single iron atom

26 electrons, 78 arguments, $10^{78}$ values
10 X 10 X 10 grid

$$\psi_0(r_1, r_1, \ldots, r_{26})$$
independent electrons

exact solution for $V_{ee}=0$

$$\hat{h}_e^0(r) = -\frac{1}{2} \nabla^2 - \sum_{\alpha} \frac{Z_\alpha}{|r - R_\alpha|} = -\frac{1}{2} \nabla^2 + \nu_{\text{ext}}(r)$$

e.g. Bloch states, bands

many-body states

$$\psi(\{r_i\}; \{R_\alpha\}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix}
\psi_{k_1 \uparrow}(r_1) & \psi_{k_1 \uparrow}(r_2) & \cdots & \psi_{k_1 \uparrow}(r_{N_e}) \\
\psi_{k_1 \downarrow}(r_1) & \psi_{k_1 \downarrow}(r_2) & \cdots & \psi_{k_1 \downarrow}(r_{N_e}) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_{k_{N_e/2} \uparrow}(r_1) & \psi_{k_{N_e/2} \uparrow}(r_2) & \cdots & \psi_{k_{N_e/2} \uparrow}(r_{N_e}) \\
\psi_{k_{N_e/2} \downarrow}(r_1) & \psi_{k_{N_e/2} \downarrow}(r_2) & \cdots & \psi_{k_{N_e/2} \downarrow}(r_{N_e})
\end{vmatrix}$$

unfortunately Coulomb repulsion is large
a way out: density-functional theory

\[ E[n] = F[n] + \int dr \, v_{\text{ext}}(r)n(r) + E_{nn} = F[n] + V[n] + E_{nn} \]

universal

\[ n(r) = n_0(r) = \sum_{n}^{occ} |\psi_n(r)|^2 \]

auxiliary independent electrons model

\[ F[n] = T_0[n] + E_H[n] + E_{xc}[n] = T_0[n] + \frac{1}{2} \int dr \int dr' \, \frac{n(r)n(r')}{|r - r'|} + E_{xc}[n] \]

Hartree Coulomb energy
long range and large

\[ \hat{h}_e^0(r) \, \psi_n(r) = \left[ -\frac{1}{2} \nabla^2 + v_R(r) \right] \psi_n(r) = \varepsilon_n \psi_n(r) \]

Kohn-Sham equations

\[ v_R(r) = -\sum_{\alpha} \frac{Z_\alpha}{|r - R_{\alpha}|} + \int dr' \, \frac{n(r')}{|r - r'|} + \frac{\delta E_{xc}[n]}{\delta n} \]
from DFT to LDA, GGA,…

\[ E_{xc}[n] = \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}') (g(\mathbf{r}, \mathbf{r}') - 1)}{|\mathbf{r} - \mathbf{r}'|} \]

\[ E_{xc}[n] = \int d\mathbf{r} \epsilon_{xc}^{\text{LDA}}(n(\mathbf{r})) n(\mathbf{r}) \]

homogeneous electron gas

Walter Kohn

Nobel Prize in Chemistry (1998)

Kohn-Sham equations

understand and predict properties of solids, molecules, biological systems, geological systems…
when LDA, GGA, … fails

*anomalous phenomena*

Mott insulators
heavy-Fermions
unconventional superconductivity
spin-charge separation

………

*strongly correlated systems*
localized electrons

\[ \psi_{nlm}(\rho, \theta, \phi) = R_{nl}(\rho)Y_l^m(\theta, \phi) \]

\[ R_{nl}(\rho) = \sqrt{\frac{2Z}{n}}^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} e^{-\rho/n} \left( \frac{2\rho}{n} \right)^l L_{n-l-1}^{2l+1} \left( \frac{2\rho}{n} \right) \]

(hydrogen-like atom: Appendix B)
Fermi liquid

in some limit an interacting electron system can be described via independent quasi-electrons

one-to-one correspondence between electrons & quasiparticles

\[
\frac{m^*}{m} = 1 + \frac{1}{3} F_1^s > 1, \quad F_1^s > 0
\]

enhanced masses

\[
\frac{\chi}{\chi_P} = \frac{1}{1 + F_0^a} > 1, \quad F_0^a < 0
\]

enhanced Pauli susceptibility

\(F_0^a\) and \(F_1^s\): Landau parameters

E. Pavarini, Electronic structure calculations with DMFT, Springer (2014)
weak correlations

if Fermi-liquid theory works we can deal with correlations in a relatively simple way

- static mean-field
- simple xc functionals: LDA, GGA,…
- many-body perturbation theory

and we can talk about weak correlations
a qualitative failure: Mott insulators
an example: KCuF$_3$

$\text{K}^+ \ Cu^{2+} \ F^-$

$\text{K} \ 4s^0 \ Cu \ 3d^9 \ F \ 2p^6$

odd number of electrons
LDA band structure

Partially filled d-like bands, metallic

In reality: insulator, paramagnetic for $T > 40$ K

Energy (eV)

K 4s  Cu 4s

Cu 3d

F 2p

LDA, GGA, ...
what about real materials?

\[
H_{e}^{NR} = - \sum_{i'\sigma} \sum_{m'm'} t_{m,m'}^{i,i'} c_{i'm'\sigma}^{\dagger} c_{i'\sigma} \\
+ \frac{1}{2} \sum_{i'i'j'j} \sum_{\sigma\sigma'} \sum_{mm'} \sum_{\tilde{m}\tilde{m}'} U_{mm'\tilde{m}\tilde{m}'}^{i'j'i'j'} c_{i'm'\sigma}^{\dagger} c_{j'm'\sigma'}^{\dagger} c_{j'\sigma'} c_{i'\tilde{m}\sigma} 
\]

back to the many-body problem
from the many-body problem to simple models
from ab-initio to simple models

energy scales

- $10^9$ eV: quarks
- $10^7$ eV: proton
- $10^5$ eV: nucleus
- $10^3$ eV: atom, molecule, crystal

simple low-energy models
let us simplify ( a lot :) 

real Hamiltonian 

\[ H_{e}^{\text{NR}} = - \sum_{i i' \sigma} \sum_{m m'} t_{m, m'}^{i, i'} c_{i m}^{\dagger} c_{i' m'}^\sigma + \frac{1}{2} \sum_{ii' jj'} \sum_{\sigma \sigma'} \sum_{mm'} \sum_{\tilde{m} \tilde{m}'} U_{mm' \tilde{m} \tilde{m}'}^{ii' jj'} c_{i m}^{\dagger} c_{i m}^{\dagger} c_{j \tilde{m}'}^{\dagger} c_{j \tilde{m}'}^{\dagger} c_{i' \tilde{m}} c_{i' \tilde{m}} \]

hoppings + crystal field

Coulomb

one band Hubbard model

\[ H = \varepsilon_d \sum_i \sum_\sigma c_{i \sigma}^{\dagger} c_{i \sigma} - t \sum_{\langle ii' \rangle} \sum_\sigma c_{i \sigma}^{\dagger} c_{i' \sigma} + U \sum_i n_{i \uparrow} n_{i \downarrow} = H_d + H_T + H_U \]
LDA band structure

-8
-6
-4
-2
0
2
4
6
8

Z
X
P

energy (eV)

K 4s  Cu 4s

Cu 3d

F 2p

LDA, GGA, ...

partially filled d-like bands, metallic

in reality: insulator, paramagnetic for T>40 K
high-$T_c$ superconducting cuprates

$\text{HgBa}_2\text{Cu}_2\text{O}_4$

$\text{CuO}_2$ planes
Band-Structure Trend in Hole-Doped Cuprates and Correlation with $T_{\text{c max}}$

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(Received 4 December 2000; published 10 July 2001)

By calculation and analysis of the bare conduction bands in a large number of hole-doped high-temperature superconductors, we have identified the range of the intralayer hopping as the essential, material-dependent parameter. It is controlled by the energy of the axial orbital, a hybrid between Cu 4s, apical-oxygen 2p_z, and farther orbitals. Materials with higher $T_{\text{c max}}$ have larger hopping ranges and axial orbitals more localized in the CuO_2 layers.
The model describes the Mott metal-insulator transition.

\[ H = \varepsilon_d \sum_i \sum_{\sigma} c_{i\sigma}^\dagger c_{i\sigma} - t \sum_{\langle ii' \rangle} \sum_{\sigma} c_{i\sigma}^\dagger c_{i'\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} = H_d + H_T + H_U \]

\[
\begin{align*}
\varepsilon_d &= -t_{1,1}^{i,i} \\
t &= t_{1,1}^{i,i'} \\
U &= U_{1111}
\end{align*}
\]

\( U = 0 \): half-filled band, **metal**

\( t = 0 \): \( N_s \) atoms, **insulator**

half filling

= 1 electron per site
the $U=0$ limit

$$H_d + H_T = \sum_k \sum_{\sigma} [\varepsilon_d + \varepsilon_k] c_{k\sigma}^\dagger c_{k\sigma}$$

hypercubic lattice

$$\varepsilon_k = -2t \sum_{\nu=1}^{d} \cos(k_{r\nu} a)$$
## Atomic Limit ($t=0$) & Half Filling

### Energy Levels

| State \( |N, S, S_z\rangle \) | \( N \) | \( S \) | \( E(N) \) |
|-----------------|-----|-----|-----|
| \( 0, 0, 0 \) | 0   | 0   | 0   |
| \( 1, \frac{1}{2}, \uparrow \) | 1   | 1/2 | \( \varepsilon_d \) |
| \( 1, \frac{1}{2}, \downarrow \) | 1   | 1/2 | \( \varepsilon_d \) |
| \( 2, 0, 0 \) | 2   | 0   | \( 2\varepsilon_d + U \) |

### Hamiltonian

\[
H_d + H_U = \varepsilon_d \sum_i n_i + U \sum_i \left[ -\left(S^i_z\right)^2 + \frac{n^2_i}{4} \right]
\]

**Emergence of the Spin!**

**Half Filling:** Highly degenerate states, \( 2^{N_S} \) degrees of freedom

**Insulating Behavior**
metal insulator transition

paramagnetic Mott insulator

\[ H = \varepsilon_d \sum_i \sum_\sigma c_{i\sigma}^\dagger c_{i\sigma} - t \sum_{<ii'>} \sum_\sigma c_{i\sigma}^\dagger c_{i'\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} = H_d + H_T + H_U \]

half filling

= 1 electron per site

\[
\begin{aligned}
\varepsilon_d &= -t_{1,1}^{i,i} \\
t &= t_{1,1}^{i,i'} \\
U &= U_{1111}^{iii} 
\end{aligned}
\]

\(U=0\): half-filled band, **metal**

\(t=0\): \(N_s\) atoms, **insulator**

*the model describes the Mott metal-insulator transition*
metal-insulator transition

DMFT: Metzner and Vollhardt, PRL 62, 324 (1989); Georges and Kotliar, PRB 45, 6479 (1992)


not explained by mean-field, Hartree-Fock, perturbation theory, Fermi-liquid etc....
the metal-insulator transition in DMFT and Hartree-Fock

these are toy version of LDA+DMFT and LDA+U
dynamical mean-field theory

\[ \hat{H} = -t \sum_{\sigma \langle ii' \rangle} c_{i \sigma}^\dagger c_{i' \sigma} + U \sum_i \hat{n}_{i \uparrow} \hat{n}_{i \downarrow} = \hat{H}_0 + \hat{U} \]

Hubbard model replaced by a self-consistent one-impurity Anderson model

Anderson model

\[ \hat{H}_{\text{eff}} = \sum_{\mathbf{k} \sigma} \varepsilon_{\mathbf{k}} \hat{n}_{\mathbf{k} \sigma} + \varepsilon_d \sum_{\sigma} \hat{n}_{d \sigma} + U \hat{n}_{d \uparrow} \hat{n}_{d \downarrow} + \sum_{\mathbf{k} \sigma} \sum_{\sigma} (V_{\mathbf{k} d} c_{\mathbf{k} \sigma}^\dagger d_{\sigma} + \overline{V}_{\mathbf{k} d} d_{\sigma}^\dagger c_{\mathbf{k} \sigma}) \]

self-consistent parameters
dynamical mean-field theory

Metzner and Vollhardt, PRL 62, 324 (1989); Georges and Kotliar, PRB 45, 6479 (1992)

\[ G^{i,j} \]

\[ H^{LDA} \]

\[ U^{i,i} \]

\[ G^{-1} = G^{-1} + \Sigma \]

\[ G = G^{i,i} \]
Anderson model

magnetic impurities in a bath

\[ \hat{H}_{\text{eff}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \hat{n}_{\mathbf{k}\sigma} + \varepsilon_d \sum_{\sigma} \hat{n}_{d\sigma} + U \hat{n}_{d\uparrow} \hat{n}_{d\downarrow} + \sum_{\mathbf{k}\sigma} \left( V_{kd} c_{\mathbf{k}\sigma}^\dagger d_{\sigma} + \overline{V}_{kd} d_{\sigma}^\dagger c_{\mathbf{k}\sigma} \right) \]

Kondo effect

Bethe Ansatz

NRG

ED/Lanczos

QMC
connections

\[ H = \varepsilon_d \sum_i \sum_{\sigma} c_i^\dagger c_{i\sigma} - t \sum_{\langle ii' \rangle} \sum_{\sigma} c_{i\sigma}^\dagger c_{i'\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} = H_d + H_T + H_U \]

impurity model (Anderson model)

\[ H_A = \sum_{\sigma} \sum_k \varepsilon_k n_{k\sigma} + \sum_{\sigma} \varepsilon_f n_{f\sigma} + U n_{f\uparrow} n_{f\downarrow} + \sum_{\sigma} \sum_k \left[ V_k c_k^\dagger c_{f\sigma} + h.c. \right] \]

self-consistency loop

solver: QMC
self-energy

\[ \varepsilon_k \to \varepsilon_k + \Sigma(\omega) \]

describes how energies are modified by correlations

depends on energy!

real part: shifts the energy

imaginary part: inverse lifetime of quasiparticles

\[ \varepsilon_k + \Sigma(\omega) - \omega = 0 \]

real solutions=poles of Green function=quasiparticle energies
Fermi-liquid

metallic phase

\[
\text{Re} \Sigma(\omega + i0^+) = U/2 + (1 - 1/Z) \omega + O(\omega^3), \quad (226)
\]
\[
\text{Im} \Sigma(\omega + i0^+) = -B \omega^2 + O(\omega^4). \quad (227)
\]

The quasiparticle residue \(Z\) defines the renormalized Fermi energy of the problem:

\[
\epsilon_F^* \equiv Z D \quad (228)
\]

This is also the Kondo temperature of the impurity model. Since the self-energy is momentum independent, \(Z\) directly yields the effective mass of quasiparticles (Müller-Hartmann, 1989c):

\[
\frac{m^*}{m} = \frac{1}{Z} = 1 - \frac{\partial}{\partial \omega} \text{Re} \Sigma(\omega + i0^+) \big|_{\omega=0}. \quad (229)
\]
Mott insulator

\[ \varepsilon_k + \Sigma(\omega) - \omega = 0 \]

\[ \Sigma(\omega) = C \frac{1}{\omega} - iD\delta(\omega) + \ldots \]
metal-insulator transition

Bethe lattice

G. Koltiar and D. Vollhardt

metallic phase

\[
\text{Re}\Sigma(\omega+i0^+) = \frac{U}{2} + (1 - 1/Z)\omega + O(\omega^3),
\]

\[
\text{Im}\Sigma(\omega+i0^+) = -B\omega^2 + O(\omega^4).
\]

The quasiparticle residue \( Z \) defines the renormalized Fermi energy of the problem:

\[
e_F^* = ZD
\]

This is also the Kondo temperature of the impurity model. Since the self-energy is momentum independent, \( Z \) directly yields the effective mass of quasiparticles (Müller-Hartmann, 1989c):

\[
\frac{m^*}{m} = \frac{1}{Z} = 1 - \frac{\partial}{\partial \omega} \text{Re}\Sigma(\omega+i0^+)\big|_{\omega=0}.
\]

insulating phase

\[
\text{Im}\Sigma(\omega+i0^+) = -\pi\rho_2 \delta(\omega) \quad \text{for} \quad \omega \in [-\Delta_g/2, \Delta_g/2]
\]

and that \( \text{Re}\Sigma \) has the following low-frequency behavior:

\[
\text{Re}\Sigma(\omega+i0^+) \approx \frac{\rho_2}{\omega} + O(\omega).
\]

A. Georges et al. RMP 63, 13 (1996)
compare with static mean-field

\[ H_U = U \sum_i n_{i \uparrow}n_{i \downarrow} \rightarrow H_U^{HF} \]

\[ H_U^{HF} = U \sum_i [n_{i \uparrow}\langle n_{i \downarrow} \rangle + \langle n_{i \uparrow} \rangle n_{i \downarrow} - \langle n_{i \uparrow} \rangle \langle n_{i \downarrow} \rangle] . \]

HF bands

\[ \varepsilon_{k \pm} - \mu = \frac{1}{2} (\varepsilon_{k} + \varepsilon_{k+Q_2}) \pm \frac{1}{2} \sqrt{(\varepsilon_{k} - \varepsilon_{k+Q_2})^2 + 4(mU)^2} \]

this is the simplest version of LDA+U
Mott transition: Hartree-Fock vs DMFT

Slater insulator

Hartree-Fock

\[ \Sigma_{i\uparrow}' \]

\[ T_{i-1} \quad T_i \quad T_{i+1} \]

LDA+U

Mott insulator

DMFT

\[ \Sigma_{\uparrow}'(\omega) \]

\[ \Sigma_{\downarrow}'(\omega) \]

LDA+DMFT
Hartree-Fock vs DMFT

(assuming the same supercell)

$$\sum_{i\sigma}^{\text{DMFT}}(\omega \to \infty) = \sum_{i\sigma}^{\text{HF}}$$

single cell HF

\[ \text{energy (eV)} \]

\[ \text{mU=0} \]

\[ \text{mU=2t} \]

\[ \text{Γ X M Γ} \]

\[ \text{Γ Γ X M Γ} \]
and real materials?

\[
\begin{align*}
\hat{H} &= -t \sum_{\sigma \langle ii' \rangle} c_{i\sigma}^\dagger c_{i'\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} = \hat{H}_0 + \hat{U}
\end{align*}
\]

many bands
U tensor
crystal-field
non-local U
......

\[
\begin{align*}
\hat{H}_e &= -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \\
&= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}
\end{align*}
\]

increasing number of free parameters, difficult to test theory
building material-specific many-body models from DFT
realistic models

basis functions

\[ \psi_{in\sigma}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{R}_i \cdot \mathbf{k}} \psi_{n\mathbf{k}\sigma}(\mathbf{r}) \]

localized Wannier functions from LDA (GGA,...)

Hamiltonian

\[ \hat{H}_e = \hat{H}^{\text{LDA}} + \hat{U} - \hat{H}_\text{DC} \]

\[ \hat{H}^{\text{LDA}} = -\sum_{\sigma} \sum_{in,i'n'} t^{i,i'}_{n,n'} c_{in\sigma}^\dagger c_{i'n'\sigma} \]

LDA Hamiltonian

\[ t^{i,i'}_{n,n'} = -\int d\mathbf{r} \bar{\psi}_{in\sigma}(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + v_R(\mathbf{r}) \right] \psi_{i'n'\sigma}(\mathbf{r}) \]
Coulomb and double counting

\[ \hat{U} = \frac{1}{2} \sum_{ii'jj'} \sum_{\sigma\sigma'} \sum_{nn'pp'} U_{npn'p'}^{ijij'} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{j'\sigma'} c_{i'\sigma'} \]

\[ \hat{U} = \frac{1}{2} U_{npn'p'}^{ijij'} = \langle i\sigma j\sigma' | \hat{U} | i'\sigma j'\sigma' \rangle \]

\[ = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \overline{\psi}_{i\sigma}(\mathbf{r}_1) \overline{\psi}_{j\sigma'}(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{j'\sigma'}(\mathbf{r}_2) \psi_{i'\sigma'}(\mathbf{r}_1) \]

**\[ \hat{H}_{DC} \]** long range Hartree and mean-field exchange-correlation already are well described by LDA (GGA,..)

up to here all electrons are the same....
light and heavy electrons

electrons

light (weakly correlated): LDA (GGA,..)

heavy (strongly correlated): U

\[ \hat{H}_e = \hat{H}^{\text{LDA}} + \hat{U}^l - \hat{H}^l_{\text{DC}} \]

eg. $l$ shell

short-range correction to LDA

local or almost local

for a $l$ shell, the local Coulomb interaction is

\[ \hat{U}^l = \frac{1}{2} \sum_i \sum_{\sigma \sigma'} \sum_{m_\alpha m'_\alpha} \sum_{m_\beta m'_\beta} U_{m_\alpha m_\beta m'_\alpha m'_\beta} c^\dagger_{im_\alpha \sigma} c^\dagger_{im_\beta \sigma'} c_{im'_\beta \sigma'} c_{im'_\alpha \sigma} \]

screening? cRPA, cLDA
Coulomb interaction tensor

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{k=0}^{\infty} \frac{r_k^k}{r_{k+1}^{k+1}} \frac{4\pi}{2k+1} \sum_{q=-k}^{k} Y_q^k(\theta_2, \phi_2) \overline{Y}_q^k(\theta_1, \phi_1)$$

$$U_{m_\alpha m_\beta m'_\alpha m'_\beta} = \sum_{k=0}^{2l} a_k(m_\alpha m'_\alpha, m_\beta m'_\beta) F_k$$

$$a_k(m_\alpha m'_\alpha, m_\beta m'_\beta) = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} \langle lm_\alpha | Y_q^k | lm'_\alpha \rangle \langle lm_\beta | \overline{Y}_q^k | lm'_\beta \rangle$$

$$F_k = \int dr_1 \ r_1^2 \int dr_2 \ r_2^2 \ R_{nl}(r_1) \frac{r_k^k}{r_{k+1}^{k+1}} R_{nl}(r_2).$$

O(3) symmetry

d electrons: F_0, F_2, F_4

radial integral

Slater integral
Coulomb interaction tensor

two-index terms

\[ \hat{U}^l \sim \frac{1}{2} \sum_{i\sigma} \sum_{mm'} U_{m,m'} \hat{n}_{i\sigma} \hat{n}_{i\sigma'} - \frac{1}{2} \sum_{i\sigma} \sum_{m \neq m'} (U_{m,m'} - J_{m,m'}) \hat{n}_{i\sigma} \hat{n}_{i\sigma'} \]

direct and exchange integrals

\[ U_{mm'mm'} = U_{m,m'} = \sum_{k=0}^{2l} a_k(\rho \rho') F_k, \]
\[ U_{mm'mm} = J_{m,m'} = \sum_{k=0}^{2l} a_k(\rho \rho') F_k \]
Coulomb tensor $d$ shell

| $U_{m,m'}^l$ | $|xy\rangle$ | $|yz\rangle$ | $|3z^2-r^2\rangle$ | $|xz\rangle$ | $|x^2-y^2\rangle$ |
|---|---|---|---|---|---|
| $|xy\rangle$ | $U_0$ | $U_0 - 2J_1$ | $U_0 - 2J_2$ | $U_0 - 2J_1$ | $U_0 - 2J_3$ |
| $|yz\rangle$ | $U_0 - 2J_1$ | $U_0$ | $U_0 - 2J_4$ | $U_0 - 2J_1$ | $U_0 - 2J_2$ |
| $|3z^2-r^2\rangle$ | $U_0 - 2J_2$ | $U_0 - 2J_4$ | $U_0$ | $U_0 - 2J_4$ | $U_0 - 2J_2$ |
| $|xz\rangle$ | $U_0 - 2J_1$ | $U_0 - 2J_1$ | $U_0 - 2J_4$ | $U_0$ | $U_0 - 2J_1$ |
| $|x^2-y^2\rangle$ | $U_0 - 2J_3$ | $U_0 - 2J_1$ | $U_0 - 2J_2$ | $U_0 - 2J_1$ | $U_0$ |

\[ U_{avg} = \frac{1}{(2l+1)^2} \sum_{m,m'} U_{m,m'} = F_0 \]

\[ U_{avg} - J_{avg} = \frac{1}{2l(2l+1)} \sum_{m,m'} (U_{m,m'} - J_{m,m'}) \]

\[ J_{avg} = (F_2 + F_4)/14 \]

**atomic 3d** \[ F_4/F_2 = 15/23 \]
do I need the full Coulomb tensor?

YES!

Hund’s rules
multiplet structures
super-exchange
spin-state transitions
many-body states degeneracy
mass enhancements
Fermi surface

warning: some LDA+U implementations overlook this
screening

main effect of restricting Hilbert space is that parameters are renormalized!

Coulomb repulsion reduced…

atom  crystal

U ~ 25 eV  U ~ 5-6 eV
Screening effects

Can we calculate screened Coulomb integrals?

It is as difficult as the many-body problem.

Current approximations: cLDA and cRPA

\( c = \text{constrained} \)

States in the model (typically at the Fermi level) should **NOT** be included.

If you do it, you will count the screening twice.

Furthermore, the screening will be unrealistically large.
the LDA+DMFT approach
$H_{k}^{LDA} = \begin{pmatrix} H_{k}^{i, i' c} & H_{k}^{i, i' c} & \cdots \\ H_{k}^{i, i' c} & H_{k}^{i, i' c} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$

$G_{i c m_{\alpha}, i' c m'_{\alpha}}(i\nu_{n}) = \frac{1}{N_{k}} \sum_{k} \left[ \frac{1}{i\nu_{n}I - H_{k}^{LDA} - \Sigma(i\nu_{n}) + H_{DC}} \right]_{i c m_{\alpha}, i' c m'_{\alpha}}$

$G_{m_{\alpha}, m'_{\alpha}}(i\nu_{n}) = G_{i c m_{\alpha}, i' c m'_{\alpha}}(i\nu_{n})$

$G^{-1}(i\nu_{n}) = G^{-1}(i\nu_{n}) + \Sigma^{i c}(i\nu_{n})$

$\nu_{n} \rightarrow \tau \quad G(\tau)$

QMC

$G(\tau) \quad \tau \rightarrow \nu_{n}$

$\Sigma^{i c}(i\nu_{n}) = G^{-1}(i\nu_{n}) - G^{-1}(i\nu_{n})$

$\Sigma = \begin{pmatrix} \Sigma^{i c} & 0 & \cdots \\ 0 & \Sigma^{i c} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$

converged?

YES

DONE!

$\Sigma(i\nu_{n})$

$G(i\nu_{n})$
LDA+DMFT with Wannier functions

multiband Hubbard model

\[
H = H^{LDA} + \frac{1}{2} \sum_{imm'\sigma} U_{mm'} n_{im\sigma} n_{im'\sigma} \\
+ \frac{1}{2} \sum_{im(\neq m')\sigma} (U_{mm'} - J_{mm'}) n_{im\sigma} n_{im'\sigma},
\]

\[
U_{mm'} = U - 2J \delta_{m,m'} \quad J_{mm'} = J \delta_{m,m'}
\]

QMC solver

\[
G_{m,m'} = \sum_{k,n} \left[ \frac{1}{i\omega_n + \mu - H_{0k} - \Sigma(i\omega_n)} \right]_{m,m'}
\]

E. Pavarini, S. Biermann, A. Poteryaev, A.I. Lichtenstein, A.Georges, O.K. Andersen, PRL 2004
Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini,¹ S. Biermann,² A. Poteryaev,³ A. I. Lichtenstein,³ A. Georges,² and O. K. Andersen⁴

a small crystal field plays a key role
what impurity solver?

approximated numerically exact

iterative perturbation theory
Hubbard I
Gutzwiller approximation
Hartree-Fock
.....

ED or Lanczos
numerical Renormalization Group
quantum Monte Carlo
.....

among QMC:
Hirsch-Fye
continuous-time Hybridization Expansion
continuous-time Interaction Expansion
...

it depends on the problem
LDA+DMFT with Wannier functions

\[ H = - \sum_{ii'} \sum_{mm'} \sum_{\sigma} t_{im\sigma}^{ii'} c_{i'm\sigma}^\dagger c_{i'm\sigma} + U \sum_{im} n_{im\uparrow} n_{im\downarrow} + \frac{1}{2} \sum_{im \neq m', \sigma \sigma'} (U - 2J - J \delta_{\sigma \sigma'}) n_{im\sigma} n_{im'\sigma'} - J \sum_{m \neq m'} (c_{m\uparrow}^\dagger c_{m'\downarrow}^\dagger c_{m'\uparrow} c_{m\downarrow} + c_{m\downarrow}^\dagger c_{m'\uparrow}^\dagger c_{m'\downarrow} c_{m\uparrow}) \]

DMFT and cDMFT

quantum impurity solvers:
- general HF QMC
- general CT-INT QMC
- general CT-HYB QMC

- A. Flesch, E. Gorelov, E. Koch and E. Pavarini
  *Multiplet effects in orbital and spin ordering phenomena: A hybridization-expansion quantum impurity solver study*
CT-QMC solver

(performance of our general code on BlueGene)

FIG. 4. Convergence of the Krylov approximation

FIG. 3. Ferromagnetic spin polarization as a function of temperature in YTiO$_3$. The plot shows a transition at the critical temperature $T_c \sim 50$ K, slightly overestimating the experimental value $T_c \sim 30$ K, as one might expect from a mean-field calculations.

Phys. Rev. B 87, 195141

can include:

- full self-energy matrix in spin-orbital space
- full Coulomb matrix
- spin-orbit
an example: KCuF₃

insulator, paramagnetic for $T > 40$ K

AF-magnetic
LDA+U

non-magnetic
LDA

paramagnetic
LDA+DMFT

K 4s
Cu 4s
Cu 3d
F 2p


what can be done nowadays?
(some examples from my own work)
Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, and O. K. Andersen

A small crystal field plays a key role
early successes: details matter

mechanism of Mott transition in the series explained

Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic $3d^1$ Perovskites

E. Pavarini,$^1$ S. Biermann,$^2$ A. Poteryaev,$^3$ A. I. Lichtenstein,$^3$ A. Georges,$^2$ and O. K. Andersen$^4$

$t_{2g}^1$

$\Delta=200-300$ meV

LDA+DMFT 770 K

a small crystal field plays a key role
Orbital Fluctuations in the Different Phases of LaVO₃ and YVO₃

M. De Raychaudhury,¹,² E. Pavarini,³,⁴ and O. K. Andersen¹

Δ=100-200 meV
Nature of the Mott Transition in Ca$_2$RuO$_4$

E. Gorelov,$^1$ M. Karolak,$^2$ T. O. Wehling,$^2$ F. Lechermann,$^2$ A. I. Lichtenstein,$^2$ and E. Pavarini$^1$

layered ruthenates

CT-QMC INT

$\Delta=100$ meV
L-Pbca
no OO

$\Delta=300$ meV
S-Pbca
xy-OO

$\Sigma/eV$

$\omega/eV$

full U
origin of orbital order

KCuF₃ and LaMnO₃

what is the mechanism of orbital-order?

KK superexchange?

T_{KK} remarkably large

but el-ph coupling essential

spin-state transitions and multiplets

attention: approximated Coulomb=wrong spin states!

Importance of exchange anisotropy and superexchange for the spin-state transitions in $RCoO_3$ ($R =$ rare earth) cobaltates

Guoren Zhang,¹ Evgeny Gorelov,¹ Erik Koch,²,³ and Eva Pavarini¹,³
low-symmetry U and spin-orbit

Sr$_2$RuO$_4$

O(3) Coulomb

D$_{4h}$ Coulomb


Guoren Zhang, Evgeny Gorelov, Esmaeel Sarvestani, and Eva Pavarini
response functions

Green Function

\( k \)-dependent **Dyson** equation matrix

\[
G(k; i\nu_n) = G_0(k; i\nu_n) + G_0(k; i\nu_n) \Sigma(k; i\nu_n) G(k; i\nu_n)
\]

local **self-energy** approximation

\[
\Sigma(k; i\nu_n) \to \Sigma(i\nu_n)
\]

local **Dyson** equation

\[
G(i\nu_n) = G_0(i\nu_n) + G_0(i\nu_n) \Sigma(i\nu_n) G(i\nu_n)
\]

Susceptibility

\( q \)-dependent **Bethe-Salpeter** equation matrix

\[
\chi(q; i\omega_m) = \chi_0(q; i\omega_m) + \chi_0(q; i\omega_m) \Gamma(q; i\omega_m) \chi(q; i\omega_m)
\]

local **vertex** approximation

\[
\Gamma(q; i\omega_m) \to \Gamma(i\omega_m)
\]

local **Bethe-Salpeter** equation

\[
\chi(i\omega_m) = \chi_0(i\omega_m) + \chi_0(i\omega_m) \Gamma(i\omega_m) \chi(i\omega_m)
\]
Bethe-Salpeter equation
outlook

many-body problem

standard model

DFT(LDA)
excellent in many cases

qualitative failures of LDA
cannot be fixed in simple way

from LDA to many-body models

DMFT
what can we do with LDA+DMFT?

- Mott physics
- phase transitions
- from low to high temperature
- frequency dependence
- high pressure
- response functions
- non-local extensions
- total energy
- phonons
- forces (in progress)

- up to 5 correlated orbitals
- or 7 in some cases
- or few sites (depending on problem)
- approximated: interfaces
- approximated: disorder
- spin-orbit (but attention sign problem)
- to some extent non-equilibrium

- codes are NOT black boxes
- open problem: double counting, screening, non-local effects
keep in mind that

DMFT is designed for Hubbard-like physics

if the physics is different you might need something else….

emergence is the essence of the many-body problem
the right approach depends on the type of physics

it is not a good idea to expect that a single method solves all problems
... and perhaps some times simple methods are good enough

... but you have to know when...
The effectiveness of this message may be indicated by the fact that I heard it quoted recently by a leader in the field of materials science, who urged the participants at a meeting dedicated to “fundamental problems in condensed matter physics” to accept that there were few or no such problems and that nothing was left but extensive science, which he seemed to equate with device engineering.

The main fallacy in this kind of thinking is that the reductionist hypothesis does not by any means imply a “constructionist” one: the ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe. In fact, the more the ele-

http://www.emergentuniverse.org/
we have a good approximation of the dream machine

but only for some CLASSES of systems
these are the systems for which we DO understand the physics

to which today we can add strongly correlated transition-metal oxides
the dream machine

Z, M, e…

equations + your computer

+ you

some of physics
the dream machine

Z, M, e…

equations+
your computer

????????
lecture notes

Autumn School on Correlated Electrons

http://www.cond-mat.de/events/correl.html

manuscripts/full books can be downloaded
Thank you!