Constrained RPA method for calculating the Hubbard U from first principles.

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Collaborators

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Tutorials (Friday) given by
Rei Sakuma and Christoph Friedrich
The external perturbation is screened by the electrons.

Example:

\[
\delta \varphi(r, t) = -\frac{Z}{r}
\]

Screening charge
(neglect Friedel oscillations)
In semiconductors or insulators the screening, due to the band gap, is not complete.

\[-\frac{Z}{\varepsilon r}\]
SCREENING IN TERMS OF LINEAR RESPONSE FUNCTION

Linear response function

\[ \delta \rho(rt) = \int dr'dt' R(rt, r't') \delta \varphi(r't') \rightarrow R(rt, r't') = \frac{\delta \rho(rt)}{\delta \varphi(r't')} \]

\[ \delta V_{tot}(rt) = \delta \varphi(rt) + \delta V_H(rt) \]

\[ \delta V_{tot} = \delta \varphi + \nu \delta \rho = [1 + \nu R] \delta \varphi = \varepsilon^{-1} \delta \varphi \]

\[ \varepsilon^{-1} = \frac{\delta V_{tot}}{\delta \varphi} = [1 + \nu R] \]

Bare Coulomb interaction \[ \nu(1-2) = \frac{1}{|r_1 - r_2|} \] Coulomb potential at 2 from a point charge at 1

\[ W = \varepsilon^{-1} \nu = \nu + \nu R \nu \]

\[ W(1,2) \] is the screened Coulomb potential at 2 of a point charge located at 1
GREEN FUNCTION

\[ iG(1,2) = \frac{\langle \Psi_0 \mid T[\hat{S}\hat{\varphi}^+(1)\hat{\varphi}^+(2)] \mid \Psi_0 \rangle}{\langle \Psi_0 \mid \hat{S} \mid \Psi_0 \rangle} \]

\[ \hat{S} = T \exp \left[ -i \int d3 \varphi(3) \hat{\rho}(3) \right] \]

\[ \varphi \text{ is an external perturbation} \]

\[ \Psi_0 \text{ is the exact ground state without the perturbation: } \hat{H}\Psi_0 = E_0 \Psi_0 \]

The field operator in the interaction picture is independent of \( \varphi \)

\[ \hat{\varphi}(rt) = e^{i\hat{H}t} \hat{\varphi}(r)e^{-i\hat{H}t} \]

\[ R(1,2) = \frac{\delta \rho(1)}{\delta \varphi(2)} = -i \frac{\delta G(1,1^+)}{\delta \varphi(2)} \bigg|_{\varphi=0} = \frac{\delta}{\delta \varphi(2)} \frac{\langle \Psi_0 \mid T[\hat{S}\hat{\rho}(1)] \mid \Psi_0 \rangle}{\langle \Psi_0 \mid \hat{S} \mid \Psi_0 \rangle} \bigg|_{\varphi=0} \]

\[ \frac{\delta \hat{S}}{\delta \varphi(2)} \bigg|_{\varphi=0} = -i T \left[ \hat{S}\hat{\rho}(2) \right] = -i \hat{\rho}(2) \]

\[ \hat{S}(\varphi = 0) = 1 \]

\[ R(1,2) = -i \langle \Psi_0 \mid T[\hat{\rho}(1)\hat{\rho}(2)] \mid \Psi_0 \rangle - \rho(1)\rho(2) \]

The Kubo formula

\[ = -i \langle \Psi_0 \mid T[\Delta\hat{\rho}(1)\Delta\hat{\rho}(2)] \mid \Psi_0 \rangle \quad \Delta\hat{\rho} = \hat{\rho} - \rho \]
Using \[ \Delta \hat{\rho}(rt) = e^{i\hat{H}t} \Delta \hat{\rho}(r) e^{-i\hat{H}t} \]

and inserting a complete set of eigenstates of \( H \) in between the density fluctuation operators and Fourier transforming yields the Lehmann or spectral representation of the response function:

\[
R(r,r';\omega) = \sum_n \left\{ \frac{\langle \Psi_0 | \Delta \hat{\rho}(r') | n \rangle \langle n | \Delta \hat{\rho}(r) | \Psi_0 \rangle}{\omega - E_n + E_0 + i\delta} - \frac{\langle \Psi_0 | \Delta \hat{\rho}(r) | n \rangle \langle n | \Delta \hat{\rho}(r') | \Psi_0 \rangle}{\omega + E_n - E_0 - i\delta} \right\}
\]
TIME-DEPENDENT HARTREE APPROXIMATION (RANDOM-PHASE APPROXIMATION)

\[ R(1,2) = \frac{\delta \rho(1)}{\delta \varphi(2)} = -i \frac{\delta G(1, 1^+)}{\delta \varphi(2)} \]

\[ GG^{-1} = 1 \rightarrow \frac{\delta G}{\delta \varphi} G^{-1} + G \frac{\delta G^{-1}}{\delta \varphi} = 0 \rightarrow \frac{\delta G}{\delta \varphi} = -G \frac{\delta G^{-1}}{\delta \varphi} G \]

From the equation of motion

\[
\left[ i \frac{\partial}{\partial t} - h_0 - \varphi - V_H - \Sigma \right] G = 1 \rightarrow G^{-1} = -\left[ h_0 + \varphi + V_H + \Sigma \right] \rightarrow \frac{\delta G^{-1}}{\delta \varphi} = -\left[ 1 + \frac{\delta V_H}{\delta \varphi} + \frac{\delta \Sigma}{\delta \varphi} \right]
\]

\[
R = iG \frac{\delta G^{-1}}{\delta \varphi} G = -iG \left[ 1 + \frac{\delta V_H}{\delta \varphi} + \frac{\delta \Sigma}{\delta \varphi} \right] G
\]

Time-dependent Hartree (Random-Phase Approximation) \[ \frac{\delta \Sigma}{\delta \varphi} = 0 \rightarrow R = -iG \left[ 1 + \frac{\delta V_H}{\delta \varphi} \right] G \]
\[ R(1,2) = -iG(1,2)G(2,1^+) - i \int d3G(1,3) \frac{\delta V_H(3)}{\delta \varphi(2)} G(3,1^+) \]

\[ \frac{\delta V_H(3)}{\delta \varphi(2)} = \int d4\nu(3 - 4) \frac{\delta \rho(4)}{\delta \varphi(2)} = \int d4\nu(3 - 4) R(4,2) \]

\[ P(1,2) = -iG(1,2)G(2,1^+) \quad \text{Polarisation function} \]

\[ R(1,2) = P(1,2) + \int d3d4P(1,3)\nu(3 - 4)R(4,2) \]
\[ P(r, r'; \omega) = -i \int d\omega \ G(r, r'; \omega + \omega')G(r', r; \omega') \]

\[ G^0 (r, r'; \omega) = \sum_n^{occ} \frac{\varphi_n (r) \varphi_n^* (r')}{\omega - \epsilon_n - i\delta} + \sum_m^{unocc} \frac{\varphi_n (r) \varphi_n^* (r')}{\omega - \epsilon_m + i\delta} \]

\[ P^0 (r, r'; \omega) = \sum_n^{occ} \sum_m^{unocc} \left\{ \frac{\varphi_n^* (r) \varphi_m (r) \varphi_n (r') \varphi_m^* (r')}{\omega - \epsilon_m + \epsilon_n + i\delta} - \frac{\varphi_n (r) \varphi_m^* (r) \varphi_n^* (r') \varphi_m (r')}{\omega + \epsilon_m - \epsilon_n - i\delta} \right\} \]

\[ P^0 (r, r'; \omega) = \sum_\alpha \left[ \frac{b^*_\alpha (r) b_\alpha (r')}{\omega - \Delta_\alpha} - \frac{b_\alpha^* (r) b_\alpha (r')}{\omega + \Delta_\alpha} \right] \]

\[ b_\alpha = \varphi_n^* \varphi_m, \quad \Delta_\alpha = \epsilon_m - \epsilon_n - i\eta, \quad \epsilon_m > \mu, \ \epsilon_n < \mu \]
First-Principles Methods:
Parameter-free but insufficient for strongly correlated systems

Model Approaches:
Good for strongly correlated systems but need parameters

- Local Density Approximation (LDA)
- GW method

- Dynamical Mean-Field Theory (DMFT)

\[ \Sigma = \Sigma_{\text{DMFT}} + \Sigma_{r} + \Sigma_{rd} \]

e.g., GW approximation

GW+DMFT: PRL 90, 86402 (2003), PRL 102, 176402 (2009)

We insist that the parameters are determined from first-principles
Typical electronic structure of correlated materials:
Partially filled narrow band (3d or 4f) crossing the Fermi level

Slight change of parameters can induce large change in materials properties.
E.g., by slight distortion or pressure the ratio of the effective Coulomb interaction $U$/bandwidth changes and the materials can undergo phase transitions (metal-insulator).

→ competition between kinetic energy and $U$. 

SrVO$_3$ perovskite

La/YTiO$_3$

→ many configurations close in energy
→ strong correlations
→ one-particle description can be problematic

The main action takes place here
The usual approach is to model the narrow band by a Hubbard model.

One-band Hubbard model:

\[
H = \frac{W}{4} \sum_{<ij>} c_j^+ c_i + U \sum_i n_{i\uparrow} n_{i\downarrow}
\]

Kotliar and Vollhardt, Physics Today 2004
Iron-based high-temperature superconductors

2D square lattice of Fe  
Fe - magnetic moment

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tc (K)</th>
<th>Reference</th>
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</table>

- a) Y. Kamihara et al., Tokyo, JACS
- b) X.H. Chen, et al., Beijing, cm/0803.3790
- c) G.F. Chen et al., Beijing, cm/0803.3603
- d) Z.A. Ren et al., Beijing, unpublished
Fe 3d
(As 4p)
(Fe 3d)
As 4p
O 2p

Fe 3d
(Se 4p)
(Fe 3d)
Se 4p
BEDT-TTF organic conductors

BEDT-TTF = bis(ethylenedithio)tetrathiafulvaene

\[ \kappa - (BEDTTF)_2 \quad Cu(NCS)_2 \]

Exp: metal

\[ \kappa - (BEDTTF)_2 \quad Cu_2(CN)_3 \]

Exp: insulator

LDA band structures

\[ \kappa-(\text{BEDT-TTF})_2\text{Cu[N(CN)_2]}\text{Cl} \]

P. Limelette et al., PRL 91 (2003) 016401
See also:
Kagawa et al. cond-mat/0307304

**FIG. 6:** Temperature-dependence of the resistivity at different pressures. The data (circles) are compared to a DMFT-NRG calculation (diamonds), with a pressure dependence of the bandwidth as indicated. The measured residual resistivity \( \rho_0 \) has been added to the theoretical curves.
Zeolites constitute a huge family of nonporous crystalline aluminosilicates which have a wide variety of intriguing properties.\(^1\) Because of their capability of hosting various ions, atoms, molecules, and clusters in their subnanometric pores with rich possibilities of crystal structure, they have versatile functionalities such as high catalytic activities, sorption characteristics, and ion-exchange abilities.

Nakamura, Koretsune, and Arita, PRB80, 174420 (2009)
Alkali-cluster-loaded sodalites

Na-sodalite

K-sodalite

FIG. 3. (Color online) Calculated \textit{ab initio} band structures (red solid lines) of (a) sodium electro-sodalite and (b) potassium electro-sodalite. The blue dotted dispersions are obtained by the $t_1$-$t_2$ model, where $t_1$ and $t_2$ are nearest and next-nearest transfers, respectively. For the values, see the text. The zero of energy is the Fermi level.

Nakamura, Koretsune, and Arita, PRB80, 174420 (2009)
The Hubbard model


Many-electron Hamiltonian is too complicated to be solved directly.

\[ H = \sum_{Rn, R'n'} \text{all} c_{Rn}^+ h_{Rn, R'n'} c_{R'n'} + \frac{1}{2} \sum_{R, nn', mm} \text{all} c_{Rn}^+ c_{Rn}^\prime \nu_{nn', mm'} c_{Rm}^+ c_{Rm}^\prime \]

→ Focus on the correlated subspace

\[ H_{\text{Hubbard}} = \sum_{Rn, R'n'} \text{correl.} c_{Rn}^+ h_{Rn, R'n'} c_{R'n'} + \frac{1}{2} \sum_{R, nn', mm} \text{correl.} c_{Rn}^+ c_{Rn}^\prime U_{nn', mm'} c_{Rm}^+ c_{Rm}^\prime \]

What is \( U \) and how do we calculate it?

Basic physical idea:
The Hubbard \( U \) should be obtained without the screening from the electrons residing in the subspace that defines the Hubbard model.
Related works on the Hubbard $U$

**Seminal work on $U$ (constrained LDA):**
VI Anisimov and O Gunnarsson, PRB 43, 7570 (1991)

**Improvement on constrained LDA**
M Cococcioni and S de Gironcoli, PRB 71, 035105 (2005)
Nakamura et al (PRB 2005)

**Random-Phase Approximation (RPA):**

**Constrained RPA (cRPA)**
→ PRB 70, 195104 (2004)
→ PRB 80, 155134 (2009) for entangled bands
Constrained RPA (cRPA): A method for calculating the Hubbard U

Polarisation:
\[ P = P_d + P_r \]

Fully screened interaction
\[
W = \frac{\nu}{1 - \nu P} = \frac{\nu}{1 - \nu P_r - \nu P_d} = \frac{\nu / (1 - \nu P_r)}{1 - \left[ \frac{\nu}{1 - \nu P_r} \right] P_d} = \frac{U}{1 - U P_d},
\]

Interpret \( U = \frac{\nu}{1 - \nu P_r} \)
as the Hubbard U.

\( P_r \) includes transitions between the \( d \)- and \( r \)-subspaces (self-screening)
Polarisation function in RPA: vertex $\Gamma = 1 \rightarrow P = -iGG$

\[
P(r, r'; \omega) = \sum_{i}^{\text{occ}} \sum_{j}^{\text{unocc}} \frac{\psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r')}{\omega - \varepsilon_j + \varepsilon_i \pm i\delta}
\]

Full system

\[
P_d(r, r'; \omega) = \sum_{i \in d}^{\text{occ}} \sum_{j \in d}^{\text{unocc}} \frac{\psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r')}{\omega - \varepsilon_j + \varepsilon_i \pm i\delta}
\]

Correlated bands

\[
P_r = P - P_d
\]

\[
U(r, r'; \omega) = \nu(r - r') + \int dr_1 dr_2 \nu(r - r_1) P_r(r_1, r_2; \omega)U(r_2, r'; \omega)
\]

Basis independent, can use any bandstructure method.

\[
U_{ij,kl}(\omega) = \int dr dr' \varphi_i(r)\varphi_j^*(r)U(r, r'; \omega)\varphi_k(r')\varphi_l(r')
\]

The matrix elements of $U$ evidently depend on the choice of the orbitals.
Maximally localised Wannier orbitals

\[ |\varphi_{nR}\rangle = \frac{V}{(2\pi)^3} \int d^3k \ e^{-ik \cdot R} |\psi^{(w)}_{kn}\rangle, \]

\[ |\psi^{(w)}_{kn}\rangle = \sum_m |\psi_{km}\rangle U_{mn}(k) \]

Minimise the extent of the orbitals

\[ \Omega = \sum_n \left( \langle \varphi_{n0}|r^2|\varphi_{n0}\rangle - |\langle \varphi_{n0}|r|\varphi_{n0}\rangle|^2 \right) \]
Fig. 4: Contour plot of the maximally localized Wannier function (MLWF) of SrVO$_3$. If we take the $x$ axis to be the horizontal direction and the $z$ axis to be the vertical direction, the Wannier function corresponds to $xz$. The red (blue) represents the positive (negative) contour. The Wannier function is centered at the vanadium site, which is located at the center of the cube. The green spheres at the corners are strontium atoms, and white spheres at the centers of the faces are oxygen atoms. The MLWF is optimized in the $t_{2g}$ model which consists of three $t_{2g}$-like states. We note that the Wannier function has tails on the oxygen sites.
Advantages of cRPA:

- Full matrix $U$
- Energy-dependent $U$
- Onsite and offsite $U$
- $U(r,r';\omega)$ is basis-independent for a given subspace:
  Can use any band-structure method

Justification of RPA:

$U$ is determined mainly by long-range screening. Short-range screening is taken care of by the Hubbard model. cRPA is general, can go beyond RPA.

$$U \sim \frac{1}{\alpha r}$$  

$\alpha > 1$  
is long range, because metallic screening is absent when calculating $U$. 

Constrained LDA

Super Cell

Transition metal or rare earth atom

“impurity”

Hopping from and to the 3d orbitals is cut off

Change the 3d charge on the impurity, keeping the system neutral, do a self-consistent calculation and calculate the change in the 3d energy level \( \rightarrow U(3d) \).
Controlling the screening channels: $U$ as a function of $P_d$ (eliminated transitions)

The O 2p plays a crucial role in determining $U$

$t_{2g} \rightarrow \text{all}$

$O_{2p} \rightarrow \text{all}$

$t_{2g} \rightarrow t_{2g}, e_g$

$bare interaction$

$U=3.5$ eV

\[ \text{Re} U(\omega) = v - \frac{2}{\pi} \int_0^\infty d\omega' \frac{\omega' \text{Im} U(\omega')}{\omega^2 - \omega'^2} \]

Miyake et al, unpublished
The dielectric constant is anisotropic. $U$ is almost isotropic and long ranged. Nearest-neighbour $U$/onsite $U \sim 0.45$

In many materials the correlated bands of interest are entangled with other more extended bands.

\[ H = \begin{pmatrix} d \text{ space} & 0 \\ 0 & r \text{ space} \end{pmatrix} \]

Approximation: The off-diagonal elements are set to zero.

Disentangled 3d band structure from maximally localised Wannier orbitals (using the procedure of Souza, Marzari and Vanderbilt)

PRB 80, 155134 (2009), also Sasioglu, Friedrich, and Bluegel PRB 2011
$U$ and $J$ of Ni as a function of frequency

Static $W$ for the 3d series

Difficult to screen a charge distribution without $l=0$ component
Application to LaFeAsO and FeSe

1111: LaFePO, LaFeAsO, ...
122: BaFe$_2$As$_2$, ...
111: LiFeAs, ...
11: FeSe, FeTe
...
...
LaFeAsO

Fe 3d
(As 4p)
(Fe 3d)
As 4p
O 2p

FeSe

Fe 3d
(Se 4p)
(Fe 3d)
Se 4p
Effective interaction in the cRPA


- strong family dependence in $U$
  (the 11 family is substantially more correlated)
- $t = 0.3\text{-}0.4$ eV in the $d$ model
- strongly orbital dependent in the $d$ model,
  due to the different extents of the Wannier orbitals

FeSe is probably
the most correlated
$U$ matrix in the $d$ model (in eV)


<table>
<thead>
<tr>
<th>LaFeAsO</th>
<th>$U$</th>
</tr>
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<tbody>
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<td>$xy$</td>
<td>$yz$</td>
</tr>
<tr>
<td>3.03</td>
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<td>1.80</td>
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<tr>
<td>1.80</td>
<td>1.62</td>
</tr>
<tr>
<td>1.91</td>
<td>1.52</td>
</tr>
</tbody>
</table>

$xy$  $yz$  $3z^2 - r^2$  $xz$  $x^2 - y^2$
Re and Im $U$ of BaFe$_2$As$_2$

Spectral functions of BaFe$_2$As$_2$


Talk by Philipp Werner on Thursday
Summary:
We do have a reliable scheme to calculate $U$ from first principles

Tutorials (Friday) given by Rei Sakuma and Christoph Friedrich