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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

SCREENING

External perturbation

$$\stackrel{\psi}{\delta \varphi(r,t)} \rightarrow \delta \rho(r,t) \rightarrow \delta V_H(r,t) = \int dr' v(r-r') \delta \rho(r',t)$$

$$\delta V_{tot}(r,t) = \delta \varphi(r,t) + \delta V_H(r,t)$$

The external perturbation is *screened* by the electrons.







r

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

$$W = \varepsilon^{-1}v = v + vRv$$

W(1,2) is the screened Coulomb potential at 2 of a point charge located at 1

GREEN FUNCTION

$$iG(1,2) = \frac{\left\langle \Psi_0 \mid T[\hat{S}\hat{\psi}(1)\hat{\psi}^+(2)] \mid \Psi_0 \right\rangle}{\left\langle \Psi_0 \mid \hat{S} \mid \Psi_0 \right\rangle} \quad \hat{S} = T \exp\left[-i\int d3 \,\varphi(3)\hat{\rho}(3)\right] \qquad 1 = r_1 t_1$$

\varphi is an external perturbation

 Ψ_0 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 φ $\hat{\psi}(rt) = e^{i\hat{H}t}\hat{\psi}(r)e^{-i\hat{H}t}$

$$R(1,2) = \frac{\delta\rho(1)}{\delta\varphi(2)} = -i\frac{\delta G(1,1^{+})}{\delta\varphi(2)}\Big|_{\varphi=0} = \frac{\delta}{\delta\varphi(2)} \frac{\left\langle \Psi_{0} \mid T[\hat{S}\hat{\rho}(1)] \mid \Psi_{0} \right\rangle}{\left\langle \Psi_{0} \mid \hat{S} \mid \Psi_{0} \right\rangle}\Big|_{\varphi=0}$$
$$\frac{\delta\hat{S}}{\delta\varphi(2)}\Big|_{\varphi=0} = -iT\left[\hat{S}\hat{\rho}(2)\right]\Big|_{\varphi=0} = -i\hat{\rho}(2) \qquad \hat{S}(\varphi=0) = 1$$
$$R(1,2) = -i\left[\left\langle \Psi_{0} \mid T[\hat{\rho}(1)\hat{\rho}(2)] \mid \Psi_{0} \right\rangle - \rho(1)\rho(2)\right] \qquad \text{The Kubo formula}$$

$$= -i \left\langle \Psi_0 \mid T[\Delta \hat{\rho}(1) \Delta \hat{\rho}(2)] \mid \Psi_0 \right\rangle \qquad \Delta \hat{\rho} = \hat{\rho} - \rho$$

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:

$$R(r,r';\omega) = \sum_{n} \left\{ \frac{\left\langle \Psi_{0} \mid \Delta \hat{\rho}(r') \mid n \right\rangle \left\langle n \mid \Delta \hat{\rho}(r) \mid \Psi_{0} \right\rangle}{\omega - E_{n} + E_{0} + i\delta} - \frac{\left\langle \Psi_{0} \mid \Delta \hat{\rho}(r) \mid n \right\rangle \left\langle n \mid \Delta \hat{\rho}(r') \mid \Psi_{0} \right\rangle}{\omega + E_{n} - E_{0} - i\delta} \right\}$$

TIME-DEPENDENT HARTREE APPROXIMATION (RANDOM-PHASE APPROXIMATION)

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

$$GG^{-1} = 1 \longrightarrow \frac{\delta G}{\delta \varphi} G^{-1} + G \frac{\delta G^{-1}}{\delta \varphi} = 0 \longrightarrow \frac{\delta G}{\delta \varphi} = -G \frac{\delta G^{-1}}{\delta \varphi} G$$

From the equation of motion

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

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

Time-dependent Hartree (Random-Phase Approximation) $\frac{\delta \Sigma}{\delta \varphi} = 0 \implies R = -iG \left[1 + \frac{\delta V_H}{\delta \varphi} \right] G$

$$R(1,2) = -iG(1,2)G(2,1^{+}) - i\int d3G(1,3)\frac{\delta V_{H}(3)}{\delta \varphi(2)}G(3,1^{+})$$

$$\frac{\delta V_H(3)}{\delta \varphi(2)} = \int d4v(3-4)\frac{\delta \rho(4)}{\delta \varphi(2)} = \int d4v(3-4)R(4,2)$$

$$P(1,2) = -iG(1,2)G(2,1^+)$$
 Polarisation function

$$R(1,2) = P(1,2) + \int d3d4P(1,3)v(3-4)R(4,2)$$

$$R = P + P - - R$$

$$P(r,r';\omega) = -i \int d\omega \ G(r,r';\omega+\omega')G(r',r;\omega')$$

$$G^{0}(r,r';\omega) = \sum_{n}^{occ} \frac{\varphi_{n}(r)\varphi_{n}^{*}(r')}{\omega - \varepsilon_{n} - i\delta} + \sum_{m}^{unocc} \frac{\varphi_{n}(r)\varphi_{n}^{*}(r')}{\omega - \varepsilon_{m} + i\delta}$$

$$P^{0}(r,r';\omega) = \sum_{n}^{occ} \sum_{m}^{unocc} \left\{ \frac{\varphi_{n}^{*}(r)\varphi_{m}(r)\varphi_{n}(r')\varphi_{m}^{*}(r')}{\omega - \varepsilon_{m} + \varepsilon_{n} + i\delta} - \frac{\varphi_{n}(r)\varphi_{m}^{*}(r)\varphi_{n}^{*}(r')\varphi_{m}(r')}{\omega + \varepsilon_{m} - \varepsilon_{n} - i\delta} \right\}$$

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

$$b_{\alpha} = \varphi_n^* \varphi_m, \quad \Delta_{\alpha} = \varepsilon_m - \varepsilon_n - i\eta, \quad \varepsilon_m > \mu, \ \varepsilon_n < \mu$$

First-Principles Methods: Parameter-free but insufficient for strongly correlated systems

Local Density Approximation (LDA)GW method

Model Approaches: Good for strongly correlated systems but need parameters

Dynamical Mean-Field Theory(DMFT)



Typical electronic structure of correlated materials: Partially filled narrow band (3d or 4f) crossing the Fermi level



La/YTiO3

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.

Evolution of the DOS.



The usual approach is to model the narrow band by a Hubbard model.

One-band Hubbard model:

$$H = \frac{W}{4} \sum_{\langle ij \rangle} c_j^+ c_i + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Iron-based high-temperature superconductors







κ -(BEDT-TTF)₂Cu[N(CN)₂]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 ρ_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



FIG. 3. (Color online) Calculated *ab initio* band structures (red solid lines) of (a) sodium electrosodalite and (b) potassium electrosodalite. 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

J. Hubbard, Proc. Roy. Soc. A276, 238 (1963)

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

$$H = \sum_{Rn,R'n'}^{all} c_{Rn}^{+} h_{Rn,R'n'} c_{R'n'} + \frac{1}{2} \sum_{R,nn',mm}^{all} c_{Rn'}^{+} c_{Rn'} v_{nn',mm'} c_{Rm'}^{+} c_{Rm'}$$

 \rightarrow Focus on the correlated subspace

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

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 ${\cal U}$

Seminal work on U (constrained LDA): O Gunnarsson, OK Andersen, O Jepsen, J Zaanen, PRB 39, 1708 (1989) 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): M Springer and FA, PRB 57, 4364 (1998) T Kotani, J. Phys.: Condens. Matter 12, 2413 (2000)

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:



Fully screened interaction

$$W = \frac{v}{1 - vP} = \frac{v}{1 - vP_r - vP_d}$$
$$= \frac{v/(1 - vP_r)}{1 - [v/(1 - vP_r)]P_d} = \frac{U}{1 - UP_d},$$

Interpret
$$U = \frac{v}{1 - vP_r}$$

as the Hubbard U.

 P_r includes transitions between the *d*- and *r*-subspaces (self-screening)

PRB 70, 195104 (2004)

Polarisation function in RPA: vertex $\Gamma = 1 \rightarrow P = -iGG$

Full system
$$P(r, r'; \omega) = \sum_{i}^{occ} \sum_{j=d}^{unocc} \psi_{i}(r) \psi_{j}^{*}(r) \psi_{i}^{*}(r') \psi_{j}(r')$$
$$\omega - \varepsilon_{j} + \varepsilon_{i} \pm i\delta$$
Correlated bands
$$P_{d}(r, r'; \omega) = \sum_{i \in d}^{occ} \sum_{j \in d}^{unocc} \psi_{i}(r) \psi_{j}^{*}(r) \psi_{i}^{*}(r') \psi_{j}(r')$$
$$\omega - \varepsilon_{j} + \varepsilon_{i} \pm i\delta$$

$$P_r = P - P_d$$

$$= P - P_d$$

$$\omega - \varepsilon_j + \varepsilon_j$$

 $U(r,r';\omega) = v(r-r') + \int dr_1 dr_2 v(r-r_1) P_r(r_1,r_2;\omega) U(r_2,r';\omega)$

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

$$|\varphi_{n\mathbf{R}}\rangle = \frac{V}{(2\pi)^3} \int d^3k \; e^{-i\mathbf{k}\cdot\mathbf{R}} |\psi_{\mathbf{k}n}^{(\mathbf{w})}\rangle,$$

$$|\psi_{\mathbf{k}n}^{(\mathbf{w})}\rangle = \sum_{m} |\psi_{\mathbf{k}m}\rangle \mathcal{U}_{mn}(\mathbf{k}).$$

Minimise the extent of the orbitals

$$\Omega = \sum_{n} (\langle \varphi_{n0} | r^2 | \varphi_{n0} \rangle - |\langle \varphi_{n0} | \mathbf{r} | \varphi_{n0} \rangle|^2)$$

Wannier orbitals of SrVO3



Fig. 4: Contour plot of the maximally localized Wannier function (MLWF) of SrVO₃. 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';ω) 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 .

$$U \sim \frac{1}{\alpha r}$$
 is long range,
because metallic screening is absent when
 $\alpha > 1$ calculating U.



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). LDA Density of States of SrVO3







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

Miyake et al, unpublished

BEDT-TTF organic conductors



The dielectric constant is anisotropic. U is almost isotropic and long ranged. Nearest-neighbour U/onsite U ~0.45

Maximally localised Wannier orbitals of $\kappa - (BEDTTF)_2 Cu(NCS)_2$

Nakamura et al, J. Phys. Soc. Jpn. 78, 083710 (2009)



cRPA for entangled bands

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

 $H = \begin{pmatrix} d \text{ space } 0 \\ 0 & r \text{ space} \end{pmatrix}$ \bigwedge 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





Application to LaFeAsO and FeSe

1111: LaFePO, LaFeAsO, ...
122: BaFe₂As₂, ...
111: LiFeAs, ...
11: FeSe, FeTe

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Effective interaction in the cRPA

T.Miyake, K.Nakamura, R.Arita and M.Imada, JPSJ (2010)

- strong family dependence in U (the 11 family is substantially more correlated)
- t = 0.3-0.4 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)

c.f. K.Nakamura, R.Arita and M.Imada, J.Pys.Soc.Jpn.77, 093711(2008). T.Miyake et al., J.Phys.Soc.Jpn.77 Suppl.C99(2008).

		U					
	LaFeAsO	xy	yz	$3z^2 - r^2$	zx	$x^2 - y^2$	
	xy	3.03	1.80	1.78	1.80	1.91	
	yz	1.80	2.43	1.97	1.62	1.52	
	$3z^2 - r^2$	1.78	1.97	2.84	1.97	1.51	
	zx	1.80	1.62	1.97	2.43	1.52	
	$x^2 - y^2$	1.91	1.52	1.51	1.52	1.91	
xy	уz		$3z^2 - r^2$		XZ		x^2 - y^2

Werner et al, arXiv:1107.3128 (2011)

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