EFFECTIVE ELECTRON-ELECTRON INTERACTION IN MANY-ELECTRON SYSTEMS

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OUTLINE

- Examples of correlated materials. Typical electronic structure.
- The Hubbard model and the role of *U*.
- Herring's definition of $U \rightarrow$ constrained LDA.
- Screening and linear response theory.
- Constrained RPA (cRPA) method.
- Examples.



EXAMPLES OF CORRELATED MATERIALS La2CuO4 LDA -0 Cu 2 La 0.8 Cu $\operatorname{Cu} d_{x^2 - y^2}$ 0 0 0.6 -2 0.4 -4 La2-SrxCuO4 300 $\mathbf{O} p_{x,y}$ Optimal doping level Overdoped Underdoped Temperature (K) regime regime 0.2 -6 Antiferromagnetic Superconductor insulator -8 0 0.0 0.3 0.1 0.2 Amount of Sr (x) = hole doping level Anti-ferromagnetic insulator but metallic in LDA



The $\alpha\text{--}\gamma$ Phase Transition in Cerium

(a) α -Ce fcc smaller volume



The α - γ transition in Ce is isostructural (fcc). γ phase has a larger volume than α phase.

Experimental spectra: drastic reduction in the QP weight in going from the α - to γ -phase.

LDA or GW spectra: little change.



Sakuma et al, PRB 86, 245126 (2012)

BEDT-TTF ORGANIC CONDUCTORS



BEDT-TTF=bis(ethylenedithio)tetrathiafulvaene



 $Cu_2(CN)_3$ insulator



Metallic in LDA!



CHARACTERISTICS OF CORRELATED MATERIALS

- Partially filled narrow band (3d or 4f) crossing the Fermi level
- Failure of LDA or mean-field theory
- Slight change of parameters can induce large change in materials properties,



THE HUBBARD MODEL



Kotliar and Vollhardt, Physics Today 2004

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

One-band Hubbard model:

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

(A similar Hamiltonian was also introduced independently around the same time by Gutzwiller, and Kanamori)

CORRELATED ELECTRONS: THE ROLE OF U



Strongly correlated (U/t >> 1): If one electron is found on one site then the other electron is to be found on the other site with high probability

 \rightarrow The two electrons *cannot* be treated as independent:

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left(\uparrow \downarrow \rangle - |\downarrow \uparrow \rangle \right)$$



Energetically unfavourable when U/t > 1



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



Model Approaches: Good for strongly correlated systems but need parameters



•Dynamical Mean-Field Theory (DMFT)



Electron correlations in narrow energy bands

By J. HUBBARD

Theoretical Physics Division, A.E.R.E., Harwell, Didcot, Berks

(Communicated by B. H. Flowers, F.R.S.—Received 23 April 1963)

$$H = \sum_{i,j} \sum_{\sigma} T_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{1}{2} I \sum_{i,\sigma} n_{i\sigma} n_{i,-\sigma}$$

The most obvious approximation has been the neglect of all the interaction terms in (6) other than the (ii|1/r|ii) term. For the sake of comparison one may note that *I* has the order of magnitude 20 eV for 3*d*-electrons in transition metals. The largest of the neglected terms are those of the type (ij|1/r|ij) where *i* and *j* are nearest neighbours. From (9) these integrals can be estimated to have the order of magnitude (2/R) Ry ~ 6 eV (R = interatomic spacing in Bohr units). Actually this figure should be reduced appreciably to allow for the screening of the interactions of electrons on different atoms by the conduction electron gas. This screening effect may be allowed for approximately by multiplying the above estimate by a factor $e^{-\kappa R}$ where κ is an appropriate screening constant. In the case of 3*d* transition metals $e^{-\kappa R} \sim \frac{1}{3} - \frac{1}{2}$, reducing the (ij|1/r|ij) term to the order of magnitude 2 to 3 eV. For the case in which *i* and *j* are now nearest neighbours

$$(ij|1/r|ij) \sim \frac{2\mathrm{e}^{-\kappa|\mathbf{R}_i-\mathbf{R}_j|}}{|\mathbf{R}_i-\mathbf{R}_j|} \operatorname{Ry}$$

HERRING'S DEFINITION OF U

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

U is the energy cost of moving an electron from one site to another.



HERRING'S DEFINITION OF U

Example: 3d transition metal with configuration $3d^n 4s^1$

$$U = [E(3d^{n-1}4s^2) - E(3d^n4s^1)] + [E(3d^{n+1}4s^0) - E(3d^n4s^1)]$$

Ionisation energy Electron affinity

$$= E(3d^{n-1}4s^2) - 2E(3d^n4s^1) + E(3d^{n+1}4s^0)$$

$$U = \frac{\partial^2 E}{\partial n_d^2}$$



CONSTRAINED LDA (CLDA)

Dederichs, Blugel, Zeller, and Akai, PRL 53, 2512 (1984)



$$E[q] = \min \left\{ E_{LDA}[\rho(r)] + v_d(n_d - q) \right\} \qquad v_d = \text{Lagrange multiplier}$$

$$U = \frac{\partial^2 E[q]}{\partial q^2}$$

Cococcioni and de Gironcolo, PRB 71, 035105 (2005) Hybertsen, Schluter, and Christensen, PRB 39, 9028 (1989)



KOHN-SHAM EQUATION IN CONSTRAINED LDA

$$E[q] = \min\left\{E_{LDA}[\rho(r)] + v_d(n_d - q)\right\}$$

$$\left(-\frac{1}{2}\nabla^2 + V_{ext} + V_H + V_{xc} + v_d P_d\right)\psi_{kn} = \varepsilon_{kn}\psi_{kn}$$

Additional non-local potential acting on the impurity site

$$P_d = |\varphi_d\rangle \langle \varphi_d|,$$

$$n_d = \sum_{kn}^{occ} |\langle \varphi_d | \psi_{kn} \rangle|^2$$





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 $\Rightarrow U = \frac{\partial^2 E}{\partial n_d^2} = \frac{\partial \varepsilon_d}{\partial n_d}$

Janak's theorem



External perturbation

$$V_{ext}(r,t) \rightarrow \rho_{ind}(r,t) \qquad \rightarrow V_{ind}(r,t) = \int dr' v(r - r') \rho_{ind}(r',t)$$

$$V_{scr}(r,t) = V_{ext}(r,t) + V_{ind}(r,t)$$
Coulomb potential 1/lr-r'l

The external perturbation is *screened* by the electrons.

Example: Proton in an electron gas



SCREENED POTENTIAL



In semiconductors or insulators the screening is not complete, due to the band gap.

$$-\frac{Z}{\varepsilon r}$$



SCREENING WITHIN LINEAR RESPONSE THEORY

response function perturbing $\rho_{ind}(rt) = \int dr' dt' \frac{R(r, r'; t - t')}{R(r, r'; t - t')} V_{ext}(r't')$

Screened field

$$V_{scr}(rt) = V_{ext}(rt) + V_{ind}(rt), \qquad V_{ind}(rt) = \int dr' v(r-r') \rho_{ind}(r't)$$

= $V_{ext}(rt) + \int dr' v(r-r') \rho_{ind}(r't)$
= $V_{ext}(rt) + \int dr' v(r-r') \int dr'' dt' R(r',r'';t-t') V_{ext}(r''t')$
 $V_{scr}(r,\omega) = V_{ext}(r,\omega) + \int dr' dr'' v(r-r') R(r',r'';\omega) V_{ext}(r'',\omega)$

$$V_{ext}(r,\omega) = V_{ext}(r,\omega) + \int dr' dr'' V(r-r'') R(r'',r''';\omega) V_{ext}(r''',$$

$$V_{scr}(\omega) = [1 + vR(\omega)] V_{ext}(\omega)$$

$$\varepsilon^{-1}(\omega)$$



SCREENED COULOMB INTERACTION

$$V_{ext}(rt;r't') = v(r-r')\delta(t-t')$$

$$V_{ext}(r,r';\omega) = v(r-r')$$

Instantaneous Coulomb potential at point *r* arising from a point charge (electron) at *r*'. (r't') =parameters

$$V_{scr}(r,\omega) = V_{ext}(r,\omega) + \int dr_1 dr_2 v(r-r_1) R(r_1, r_2; \omega) V_{ext}(r_2, \omega)$$
General formula

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

Screened Coulomb interaction

$$W = v + vRv$$

Kubo's formula for retarded response function:

$$R(rt,r't') = -i\langle \Psi | [\hat{\rho}(rt),\hat{\rho}(r't')] | \Psi \rangle \theta(t-t')$$

Need a good approximation for *R*



POLARISATION FUNCTION

Definition of polarisation function *P*: Response function with respect to the screened field





$$\rho_{ind} = RV_{ext} = P(V_{ext} + V_{ind})$$

$$V_{ind} = V \rho_{ind} = V R V_{ext}$$

$$RV_{ext} = P(V_{ext} + vR\rho_{ind}) = P(1+vR)V_{ext}$$

Since V_{ext} is arbitrary:
$$R = P + PvR$$
$$W = v + vRv = v + vPv + vPvPv + ...$$
$$W = v + vPw$$
$$ext{ c.f. } W = v + vRv$$

TIME-DEPENDENT HARTREE APPROXIMATION or RANDOM-PHASE APPROXIMATION (RPA)

In RPA, approximate *P* by the non-interacting response function: $P(1,2) = -iG(1,2)G(2,1^{+}) \quad 1 \stackrel{\bullet}{\longrightarrow} 2 \quad \text{Plain bubble}$

The response of an interacting system to an external perturbation is assumed to be given by the response to the total (screened) field as if the system were non-interacting.





THE NON-INTERACTING LINEAR RESPONSE FUNCTION

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

SCREENING PROCESS





To reduce the Coulomb interaction the spin-up electron jumps to the excited state \rightarrow polarisation.

Screening or correlation amounts to lowering interaction energy



CONSTRAINED RPA (CRPA): A METHOD FOR CALCULATING U

Key physical idea:

U should be obtained as a screened Coulomb interaction **without screening** from the electrons residing in the subspace that defines the Hubbard model.



PRB 70, 195104 (2004)

CRPA FORMULA FOR $\,U\,$

Fully screened interaction

$$W = v + vPW \rightarrow W = (1 - vP)^{-1}v$$

$$W = [1 - vP_r - vP_d]^{-1}v$$

= $[(1 - vP_r)\{1 - (1 - vP_r)^{-1}vP_d\}]^{-1}v$ (AB)^{-1} = B^{-1}A^{-1}
= $(1 - W_rP_d)^{-1}((1 - vP_r)^{-1}v)$
 W_r

 $W = (1 - W_r P_d)^{-1} W_r$

 $U = W_r = (1 - vP_r)^{-1}v$

the effective interaction in the *d*-subspace (the Hubbard *U*)

 $U = v + vP_rU$



POLARISATION FUNCTION IN RPA

Full system

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

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

$$P_r = P - P_d$$

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

Independent of band-structure 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 Hubbard U is determined by two main factors:

- Screening, *i.e.*, the polarisation *P*
- The choice of orbitals when computing the matrix elements $U_{ii,kl}(\omega)$



CONNECTION BETWEEN cRPA AND cLDA

$$\frac{\partial^2 E}{\partial n_i \partial n_j} = \frac{\partial \varepsilon_i}{\partial n_j} = \left\langle \varphi_i \varphi_i \, | \, \varepsilon^{-1} (v + f_{xc}) \, | \, \varphi_j \varphi_j \right\rangle \qquad \qquad f_{xc} = \frac{\delta^2 E_{xc}}{\delta \rho^2}$$

In cLDA, calculate
$$U = \frac{\partial \varepsilon_i}{\partial n_i}$$
 with constrained hopping

In cRPA, calculate \mathcal{E}^{-1} with constrained screening, i.e., removing screening channels already included in the model.

U. von Barth,*The electronic structure of complex systems*, *Advanced Study Institute (1982)*M. Springer and FA, PRB 57, 4364 (1998).



ADVANTAGES OF CRPA

- Full matrix U
- Energy-dependent U
- Onsite and offsite U
- $U(r,r';\omega)$ is basis-independent:

Can use any band-structure method

• The concept of cRPA is general, can go beyond RPA .

JUSTIFICATION OF RPA:

Vertex corrections beyond RPA are expected to be large within the correlated subspace, These vertex corrections are taken care of by the Hubbard model.

For isolated *d*-subspace

 $U \sim \frac{1}{\alpha r} \quad \begin{array}{l} long \ range \\ (metallic \ screening \ is \ absent \\ \alpha > 1 \qquad \text{when calculating } U \end{array}$



MAXIMALLY LOCALISED WANNIER ORBITALS

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

$$\left|\psi_{kn}^{(w)}\right\rangle = \sum_{m} \left|\psi_{km}\right\rangle S_{mn}(k)$$

LDA wave functions

By varying *S*, minimise the extent of the orbitals

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

Marzari and Vanderbilt, PRB 56, 12847 (1997)



WANNIER ORBITALS OF SrVO3



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.



BEDT-TTF ORGANIC CONDUCTORS





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



CRPA FOR ENTANGLED BANDS

We first choose an energy window covering the 3d band and construct maximally localised Wannier orbitals



Marzari and Vanderbilt, PRB 56, 12847 (1997)



CRPA FOR ENTANGLED BANDS

Construct projection operator for the *d* subspace:

$$P = \sum_{m \in d} \left| \varphi_{mR} \right\rangle \left\langle \varphi_{mR} \right|$$

Define the *r* subspace:

$$\psi_{kn}^{r}\rangle = (1-P)|\psi_{kn}\rangle$$

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

Approximation: The off-diagonal elements are set to zero

_ Disentangled 3d band structure from maximally localised Wannier orbitals

Miyake et al PRB 80, 155134 (2009), also Sasioglu, Friedrich, and Bluegel PRB 2011



Fully screened interaction *W* of the 3d series

Hubbard U for the 3d series



NEAREST-NEIGHBOUR U and J





U and J for the Early Lanthanides



Nilsson et al PRB 88, 125123 (2013)



DYNAMIC (FREQUENCY-DEPENDENT) U



Miyake et al, unpublished





Strength of Effective Coulomb Interactions in Graphene and Graphite

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FIG. 3 (color online). Frequency dependence of the on-site and nearest-neighbor interaction obtained from cRPA for graphene (h = 21.2 Å) and graphite. For graphite $U_{00}(\omega) = U_{00}^A(\omega)$ is shown, which is virtually the same as $U_{00}^B(\omega)$. $|U_{00}^A(\omega) - U_{00}^B(\omega)| < 0.15 \text{ eV}$ for $\omega < 20 \text{ eV}$.





Werner et al, PHYSICAL REVIEW B 91, 125142 (2015)



FIG. 1. (Color online) LDA band structure (solid lines). In addition, the left panel shows the Wannier interpolated (disentangled) band structure for the one-band model and the right panel the corresponding band structure for the three-band model (thick dashed lines). The color coding in the right panel indicates the *d* character of the bands. The symmetry points are defined as $\Gamma = (0,0)$, $K = (\pi,\pi)$ and $X = (\pi,0)$ and the vertical axis is in eV.



EXCHANGE J AS A FUNCTION OF FREQUENCY







SUMMARY

cRPA provides a systematic and general scheme for determining U from realistic band structures
→bridging first-principles and model calculations of correlated materials.

Open problems:

- Entangled bands: not clear how to define the model.
- What is the best way of downfolding the energy-dependence of *U*? (How to construct a model with a static *U*)
- How to go beyond RPA: e.g., include ladder diagrams in P

