Localized Electrons with Wien2k LDA+U, EECE, MLWF, DMFT

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WIEN2013@PSU, Aug 14





LDA vs. Localized Electrons

LDA/GGA has problems with strongly correlated systems

- localized orbitals (3d, 4f)

1 LDA+U, EECE: add orbital-dependent potentials to LDA

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- insulators
- 2 DMFT: build many-body theory on top of LDA
 - correlated metals
 - partially-filled bands
 - Wannier functions as basis

The Hubbard Model



single-band Hubbard model:

$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^+ c_{j\sigma} + U \sum_i \widehat{n}_{i\uparrow} \widehat{n}_{i\downarrow}$$

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- "hopping" t (kinetic energy)
- interaction U

The Hubbard Model



single-band Hubbard model:

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- "hopping" t (kinetic energy)
- interaction U

multi-band generalization:

$$U \widehat{n}_{\uparrow} \widehat{n}_{\downarrow} \rightarrow \sum_{ijkl} U_{ijkl} c_i^+ c_j^+ c_l c_k$$

often parametrized with: intra-orbital *U*, inter-orbital *V*, Hund exchange *J*



Strontium Vanadate SrVO₃

- correlated metal
- cubic perovskite
 - VO₆ octahedra
- isolated t_{2g}^1 manifold





Outline

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Preliminaries

LDA+U, EECE — Orbital-Dependent Potentials LDA + Coulomb Repulsion U On-Site Hybrid/Hartree-Fock

B Wannier Functions and DMFT

LDA + Coulomb Repulsion U (-orb)

- split states into
 - "delocalized" → LDA
 - "localized" ->> LDA+U (usually, d or f states)
- augment LDA with local orbital-dependent energy:

$$E = E^{\text{LDA}} + \underbrace{\frac{1}{2}U\sum_{i \neq j}n_in_j}_{i \neq j} - \underbrace{\frac{1}{2}UN(N-1)}_{\text{double-counting correction}}$$

(multi-band)
(nulti-band)
(LDA contains part of U)
(n_i \rightarrow n_i = \langle \hat{n}_i \rangle

[Anisimov et al., Phys. Rev. B 48, 16929 (1993)]

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LDA+U: Effects

$$E = E^{\text{LDA}} + \frac{1}{2}U\sum_{i\neq j}n_in_j - \frac{1}{2}UN(N-1)$$

• orbital energies
$$\epsilon_i^{\sigma} = \frac{\partial E}{\partial n_i} = \epsilon_i^{\text{LDA}} + U(\frac{1/2 - n_i^{-\sigma}}{n_i})$$

- ⇒ unoccupied states ↑, occupied states ↓
 - creates / enlarges gaps (→ Mott insulators)

LDA+U: Practicalities

- conceptually simple, computationally cheap
- ambiguities in practice:
- U values?
 - - enforce occupation of target orbital
 - *U* ~ Δ*E*tot
- double-counting correction
 - 0 "around mean-field", $\frac{1}{2}UN(N \bar{n})$ [Czyżyk and Sawatzky, PRB 1994] metallic or less strongly correlated
 - 1 "self-interaction correction", $\frac{1}{2}UN(N-1)$ [Anisimov *et al.*, PRB 1993] strongly correlated systems

2 "HMF"

[Anisimov et al., PRB 1991]

[Madsen and Novák, wien2k.at]

LDA+U: Program Flow

must be spin-polarized

lapwdm density matrix $n_{ij} = \langle \hat{n}_i \hat{n}_j \rangle$ (case.dmatup,dn) orb LDA+U potential (case.vorbup,dn) lapw1 -orb includes LDA+U potential runsp -orb lapw0 orb -up,dn lapw1 -orb -up,dn lapw2 -up,dn lapwdm -up,dn lcore -up,dn mixer -orb

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LDA+U: Program Flow

 must be spin-polarized 				
lapwdm	density matrix $n_{ij} = \langle \hat{n}_i \hat{n}_j \rangle$ (<i>case</i> .dmat <i>up</i> , <i>dn</i>)			
orb	LDA+U potential (case.vorbup,dn)			
lapw1 -orb	includes LDA+U potential			

runsp -orblapw0orb-up, dnlapw1 -orb-up, dnlapw2-up, dnlcore-up, dnmixer -orb

<pre>case.indm[c]</pre>					
-9. 1 2 1 0 0	2	Emin #aton atom, mode	[Ry] ns #l,	ι	

case.inorb

1 1 0 m	ode, #atoms, ipr
PRATT 1.0	mixing
212	atom, #l, l
1	double-counting
0.26 0.00	U,J [Ry] (Ueff=U-J)

LDA+U: SrVO₃



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On-Site Hybrid Functionals (-eece)

- split states as in LDA+ $U \rightarrow \rho_{sel}, \Psi_{sel}$
- What's in a name?
 - "exact exchange for correlated electrons"
 - on-site hybrid/Hartree-Fock vs. full hybrid
- augment LDA with local orbital-dependent energy:
 - on-site hybrid

$$E = E^{\text{LDA}}[\rho] + \alpha \left(E_{\text{x}}^{\text{HF}}[\Psi_{\text{sel}}] - E_{\text{x}}^{\text{LDA}}[\rho_{\text{sel}}] \right)$$

• on-site Hartree-Fock

$$E = E^{\text{LDA}}[\rho] + \alpha(E_{\text{x}}^{\text{HF}}[\Psi_{\text{sel}}] - E_{\text{xc}}^{\text{LDA}}[\rho_{\text{sel}}])$$

• must choose α ; $E_{xc}[\rho]$ is not linear

[Novák et al. Phys. Stat. Sol. B 243, 563 (2006)]

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[Tran, Blaha, Schwarz, and Novák, Phys. Rev. B 74, 155108 (2006)]

EECE: Program Flow

must be spin-polarized

lapwdm density matrix $n_{ij} = \langle \hat{n}_i \hat{n}_j \rangle$ (*case*.dmat*up*,*dn*) lapw2, lapw0, orb EECE potential (*case*.vorb*up*,*dn*) lapw1 -orb includes EECE potential

runsp -eece

lapw0	
lapw1 -orb	-up,dn
lapw2	-up,dn
lcore	-up,dn
lapwdm	-up,dn
lapw2 -eece	-up,dn
lapw0 -eece	
orb	-up,dn
mixer -eece	

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EECE: Program Flow

runsp -eece

lapw0	
lapw1 -orb	-up,dn
lapw2	-up,dn
lcore	-up,dn
lapwdm	-up,dn
lapw2 -eece	-up,dn
lapw0 -eece	
orb	-up,dn
mixer -eece	

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must be spin-polarized

lapwdm density matrix $n_{ij} = \langle \hat{n}_i \hat{n}_j \rangle$ (*case*.dmat*up*,*dn*) lapw2, lapw0, orb EECE potential (*case*.vorb*up*,*dn*) lapw1 -orb includes EECE potential

case.ineece

- -9.0 1 Emin [Ry], #atoms
- 2 1 2 iatom nlorb lorb
- HYBR HYBR/EECE mode

0.25 α

case.inorb, case.indm[c]

(generated automatically)

EECE: SrVO₃



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Preliminaries

2 LDA+U, EECE — Orbital-Dependent Potentials

 Wannier Functions and DMFT Maximally Localized Wannier Functions Wannier90 Wien2Wannier Dynamical Mean-Field Theory at a Glance

Wannier Functions



from Marzari et al.

• Fourier transforms of Bloch functions:

$$|\mathbf{w} n\mathbf{R}\rangle = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{i\mathbf{k}\mathbf{R}} |\psi n\mathbf{k}\rangle$$

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Wannier Functions



from Marzari et al.

• Fourier transforms of Bloch functions:

$$|w n\mathbf{R}\rangle = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{i\mathbf{k}\mathbf{R}} |\psi n\mathbf{k}\rangle$$

• "gauge" freedom:

|w n**R** > =

$$\frac{V}{(2\pi)} \int_{\mathsf{BZ}} \mathrm{d}\boldsymbol{k} \sum_{m} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{R}} U_{mn}(\boldsymbol{k}) | \psi \, m \boldsymbol{k} \rangle$$

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→ choose $U(\mathbf{k})$ to minimize spread ($\Delta \mathbf{r}^2$)

Maximally Localized Wannier Functions

- choose U(k) to minimize spread → MLWF
- total spread $\Omega = \Omega_1 + \tilde{\Omega}$ can be split into gauge-invariant part and rest



- 🛶 minimize <u>Ω</u>
 - wannier90 computes U(k) in this way

[Marzari et al., Rev. Mod. Phys. 84, 1419 (2012)] http://wannier.org

wien2wannier provides interface to Wien2k

[Kuneš, Wissgott *et al.*, Comp. Phys. Commun. 181, 1888] http://www.wien2k.at/reg_user/unsupported/wien2wannier/

Disentanglement



from Marzari et al.

fcc-Cu, 5 *d*-like WF, 2 interstitial *s*-like WF

num_bands = 12
num_wann = 7

- other bands may cross target manifold
- must select bands to Wannierize
 - $V(\mathbf{k}) (J(\mathbf{k}) \times N)$
 - selection determines $\Omega_{\rm I}$

MLWF: Applications

- analysis of chemical bonding
- electric polarization and orbital magnetization
 Oleg Rubel's talk (tomorrow, 10:30)
- Wannier interpolation $\mathcal{K} \to \mathcal{G}$ $H(\mathbf{k})|_{\mathcal{K}} \xrightarrow{\mathcal{F}} H(\mathbf{R})|_{\mathcal{K}^{-1}} \xrightarrow{\mathcal{F}^{-1}} H(\mathbf{k})|_{\mathcal{G}}$
- Wannier functions as basis functions
 - tight-binding model $H(\mathbf{k}) = U^+(\mathbf{k}) \epsilon(\mathbf{k}) U(\mathbf{k})$

wannier90

case.win

num_bands	=	3
num_wann	=	3
num_iter	=	1000
<pre>num_print_cycles</pre>	=	100

bands_plot_project = 1

case.wout	
-inal State	
WF centre and spread 1	
WF centre and spread 2	
WF centre and spread 3	
Sum of centres and spread	

[Marzari et al., Rev. Mod. Phys. 84, 1419 (2012)] http://wannier.org

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wien2wannier

ca	se	.W2	2win					
B01	ГΗ							
21	L	23	min band, ma	min band, max band				
3	3	3	LJMAX, #Wanı	LJMAX, #Wannier functions				
2			#terms					
2	2	-2	0.00000000	0.70710677	atom,	L,	Μ,	coeff
2	2	2	0.00000000	-0.70710677				
2								
2	2	- 1	0.00000000	0.70710677				
2	2	1	0.00000000	0.70710677				
2								
2	2	-1	0.70710677	0.00000000				
2	2	1	-0.70710677	0.0000000				

[Kuneš, Wissgott *et al.*, Comp. Phys. Commun. 181, 1888] http://www.wien2k.at/reg_user/unsupported/wien2wannier/

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MLWF: Program FLow

() normal SCF run \rightarrow converged density, band structure

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- prepare_w2wdir.sh, init_w2w: prepare input files
- $2 \times lapw1$ -options \rightarrow eigenvectors on full k-mesh
- **3** w2w case \rightarrow overlap $\langle u_{m\mathbf{k}} | u_{n\mathbf{k}} \rangle$
- 4 shift_energy case
- **5** wannier90.x case $\rightarrow U(\mathbf{k})$

wien2wannier Features

- spin-polarized cases, spin-orbit coupling
- any functional, LAPW, APW+LO basis
- disentanglement
- plotting: interface to XCrysDen / VESTA
- woptic: optical conductivity with Wannier functions

$$\sigma(\Omega) \sim \sum_{\boldsymbol{k},\omega} \frac{f(\omega) - f(\omega + \Omega)}{\Omega} \operatorname{tr} \left\{ VA(\boldsymbol{k}, \omega + \Omega) VA(\boldsymbol{k}, \omega) \right\}$$

[Wissgott, Kuneš et al. Phys. Rev. B 85, 205133]

- adaptive k-integration
- includes self-energy $\Sigma(\omega)$ (DMFT)

http://www.wien2k.at/reg_user/unsupported/wien2wannier/

LDA+DMFT

LDA

- realistic calculations
- fails for strong correlations

model Hamiltonians

- simplified, abstract model
- full correlations





LDA+DMFT



Correlation Regimes



U: screened local interaction

W: bandwidth, $\sim t$

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From lattice models to DMFT

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lattice model

- e⁻ hop between sites
- local repulsion (screened)

From lattice models to DMFT



Σ

lattice model

- e⁻ hop between sites
- local repulsion (screened)

impurity model

- one interacting site
- non-interacting "bath"

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From lattice models to DMFT



Σ

lattice model

- e⁻ hop between sites
- local repulsion (screened)

impurity model

- one interacting site
- non-interacting "bath"

dynamical mean-field theory

- lattice model → impurity model
- self-energy $\Sigma(\omega)$

Georges et al., RMP 1996, Kotliar & Vollhardt, Phys. Today 2004

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LDA+DMFT for SrVO₃

- DMFT basis: 3 degenerate t_{2g} Wannier functions
- *U* = 5.05 eV, *T* = 1160 K
 - DMFT(QMC) has finite T
 - low T is hard ("sign problem")



experiment: Makino et al., PRB 58, 4348 (1997) DMFT: Philipp Wissgott

LDA+U, EECE, DMFT compared

LDA+U, EECE

- density functionals
 - single-particle model
- good for insulators $(U \gg W)$
- work inside MT sphere basis: Y^m_l
- computationally cheap

LDA+DMFT

- "spectral density functional theory"
 - many-body physics
- basis: Wannier functions (or similar)
- whole U/W range
- sophisticated, expensive

- double counting
- semi-empirical U, α

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- semi-empirical U