Localized Electrons with Wien2k

LDA+*U*, EECE, MLWF, DMFT

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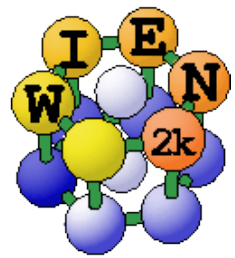
WIEN2013@PSU, Aug 14



LDA vs. Localized Electrons

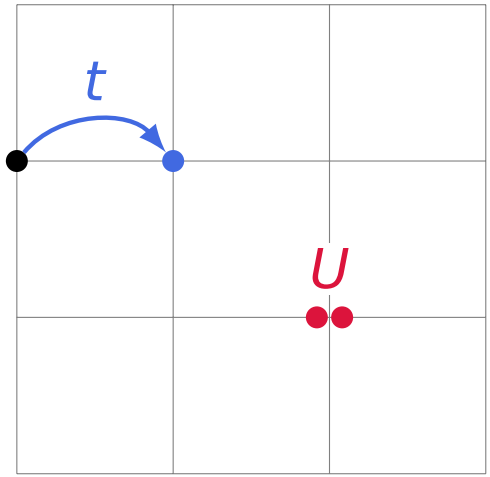
- LDA/GGA has problems with strongly correlated systems
  - localized orbitals ($3d, 4f$)

⇝ explicitly add "Coulomb interaction"

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

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

The Hubbard Model

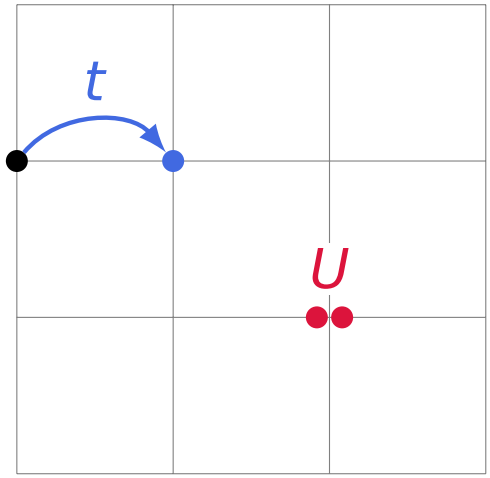


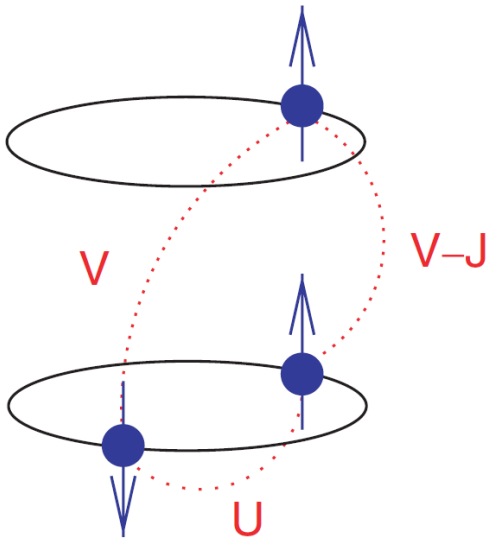
single-band Hubbard model:

$$H = -t \sum_{\langle i\,j\rangle\,\sigma} c^{+}_{i\sigma} c_{j\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

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

The Hubbard Model





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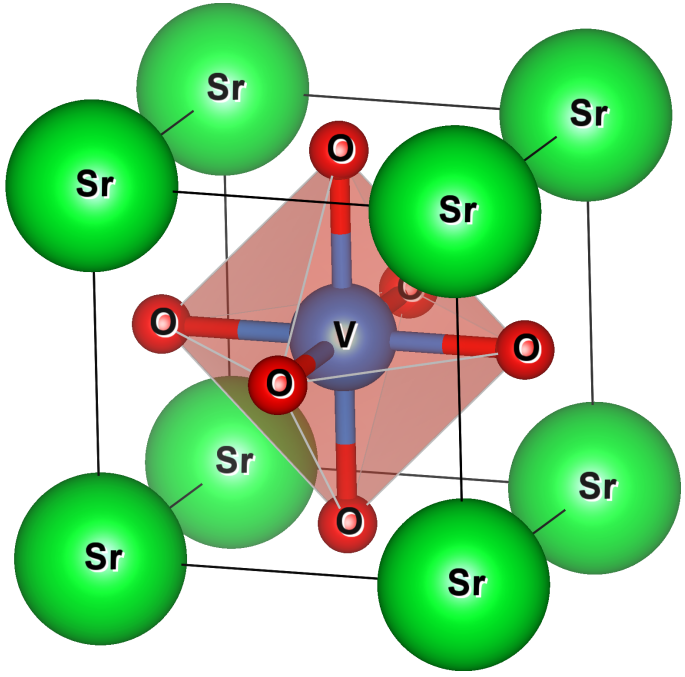
multi-band generalization:

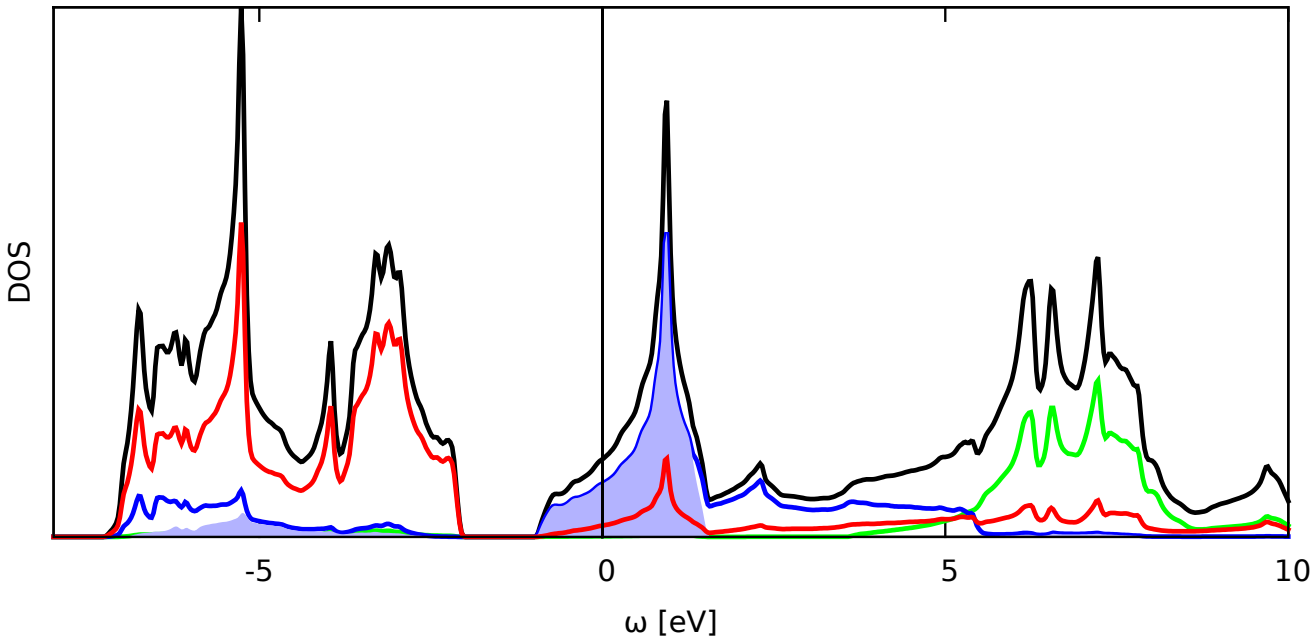
$$U \hat{n}_{\uparrow} \hat{n}_{\downarrow} \rightarrow \sum_{ijkl} U_{ijkl} c^{+}_{i} c^{+}_{j} c_{l} c_{k}$$

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

Strontium Vanadate $SrVO_3$

- correlated metal
- cubic perovskite
  - VO_6 octahedra
- isolated t_{2g}^1 manifold





Outline

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:

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

mean-field Hubbard term (multi-band)

$$\hat{n}_i \to n_i = \langle \hat{n}_i \rangle$$

double-counting correction (LDA contains part of U)

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

LDA+U: Effects

$$E = E^{\mathrm{LDA}} + \tfrac{1}{2} U \sum_{i \neq j} n_i n_j - \tfrac{1}{2} U N(N-1)$$

- orbital energies $\epsilon_i = \dfrac{\partial E}{\partial n_i} = \epsilon_i^{\mathrm{LDA}} + U\,(1/2 - n_i)$

$\Rightarrow$ unoccupied states $\uparrow$, occupied states $\downarrow$

- creates / enlarges gaps ($\rightsquigarrow$ Mott insulators)
- breaks symmetries ($\rightsquigarrow$ spin order, orbital order, . . .)

LDA+U: Practicalities

- conceptually simple, computationally cheap
- ambiguities in practice:
- U values?
  - ⇝ constrained LDA [Madsen and Novák, `wien2k.at`]
    - enforce occupation of target orbital
    - $U \sim \Delta E_{\text{tot}}$
- 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]

LDA+*U*: Program Flow

- must be spin-polarized

lapwdm density matrix $n_{ij} = \langle \hat{n}_i \hat{n}_j \rangle$ (*case*.dmat*up*,*dn*)

orb LDA+*U* potential (*case*.vorb*up*,*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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lapw2        -up,dn
lapwdm       -up,dn
lcore        -up,dn
mixer -orb
```

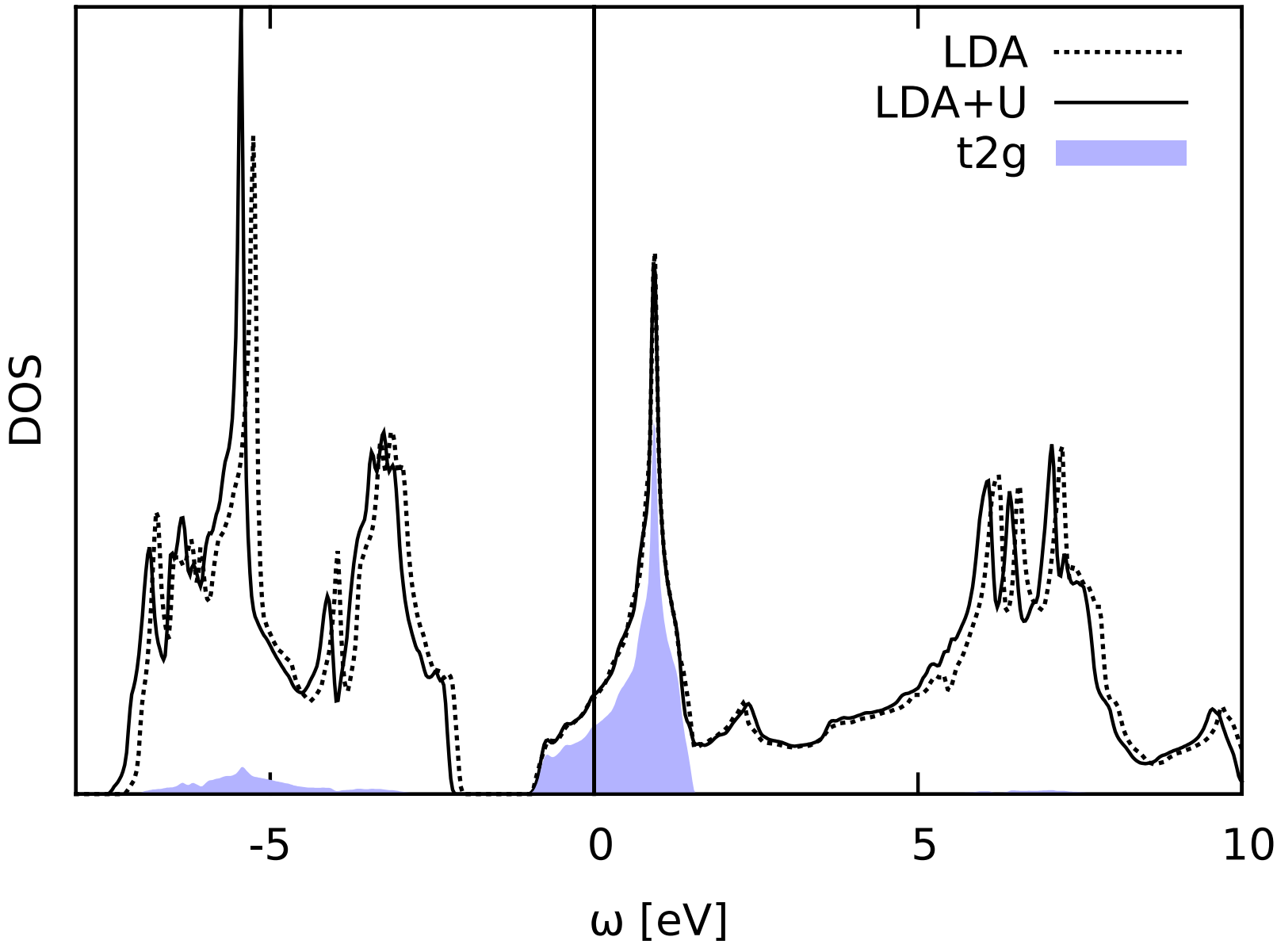
case.indm[c]

```
-9.        Emin [Ry]
1          #atoms
2  1  2    atom, #l, l
0 0        mode
```

case.inorb

```
1 1 0     mode, #atoms, ipr
PRATT 1.0  mixing
  2 1 2    atom, #l, l
  1        double-counting
0.26 0.00  U,J [Ry] (Ueff=U-J)
```

LDA+U: $SrVO_3$



On-Site Hybrid Functionals (-eece)

- split states as in LDA+$U \rightarrow \rho_{\text{sel}}, \psi_{\text{sel}}$
- 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

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

  - on-site Hartree-Fock

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

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

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

[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
```

EECE: Program Flow

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

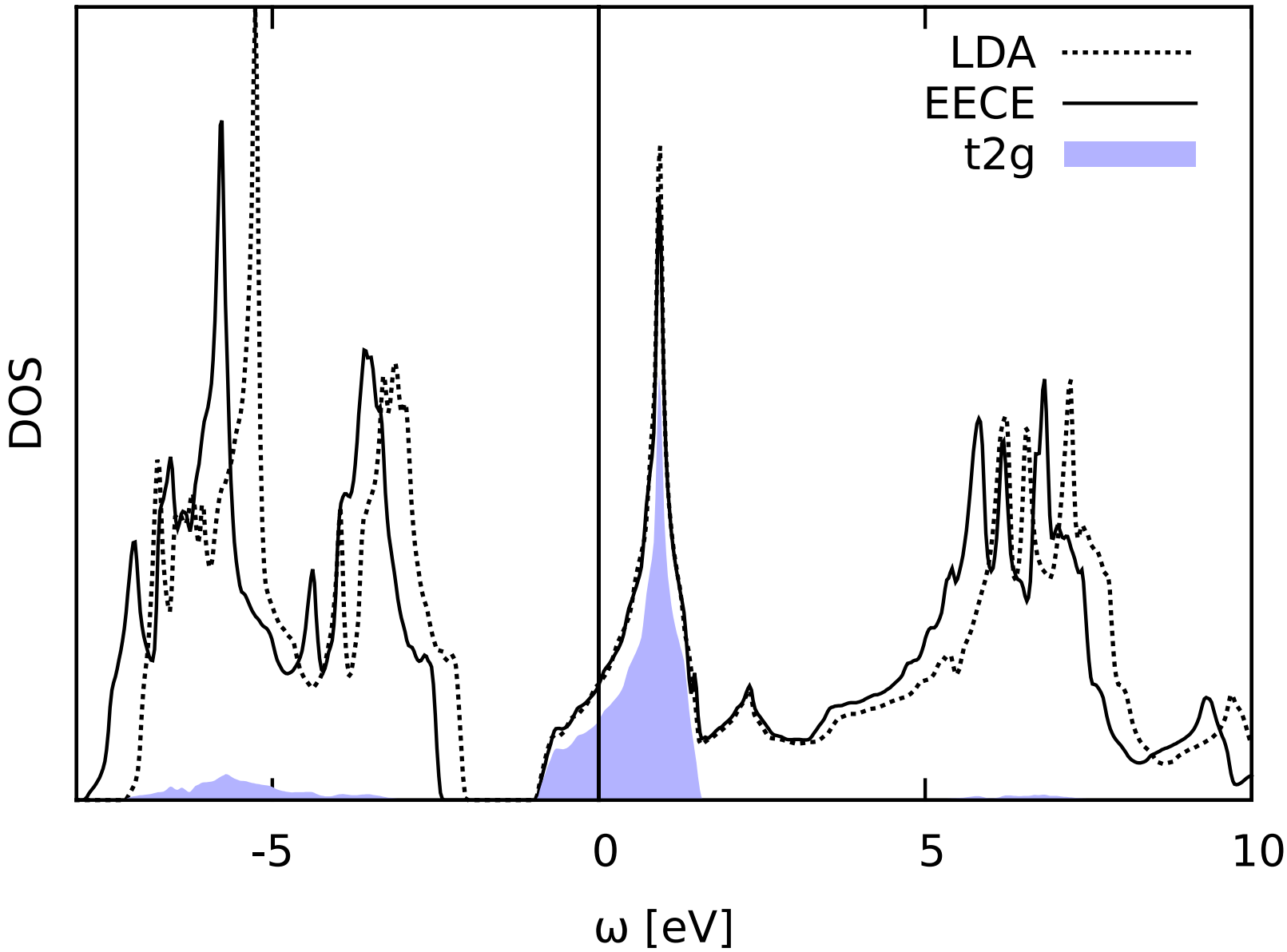
case.ineece

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

case.inorb, *case*.indm[c]

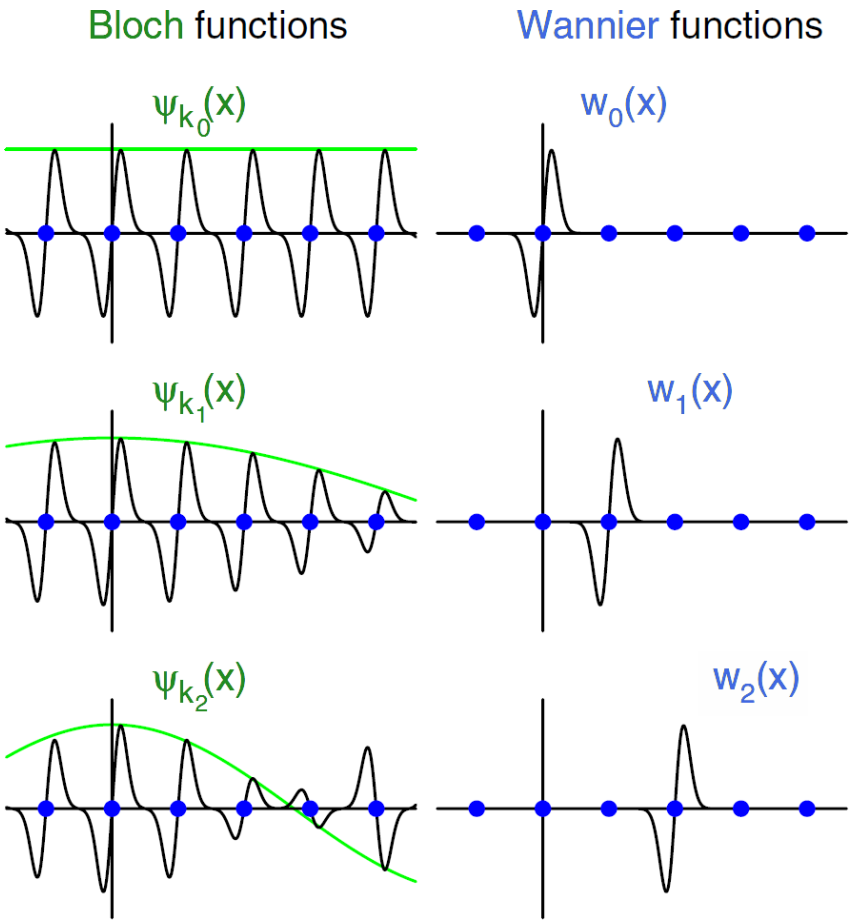
(generated automatically)

EECE: $SrVO_3$



Outline

Wannier Functions

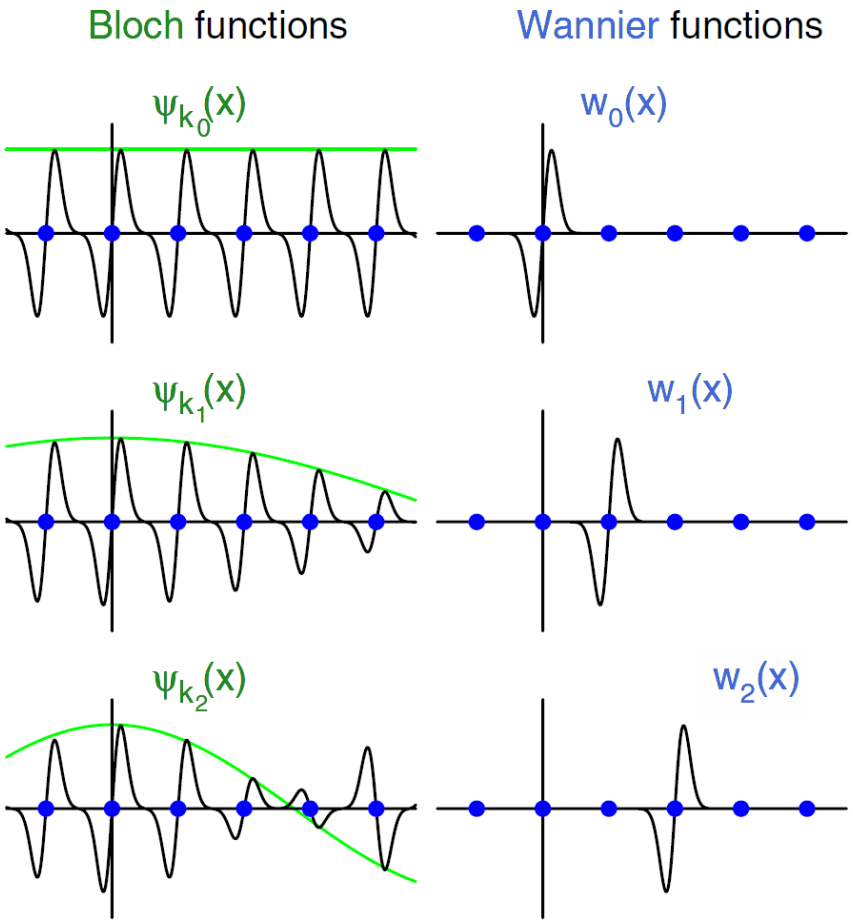


from Marzari *et al.*

- Fourier transforms of Bloch functions:

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

Wannier Functions



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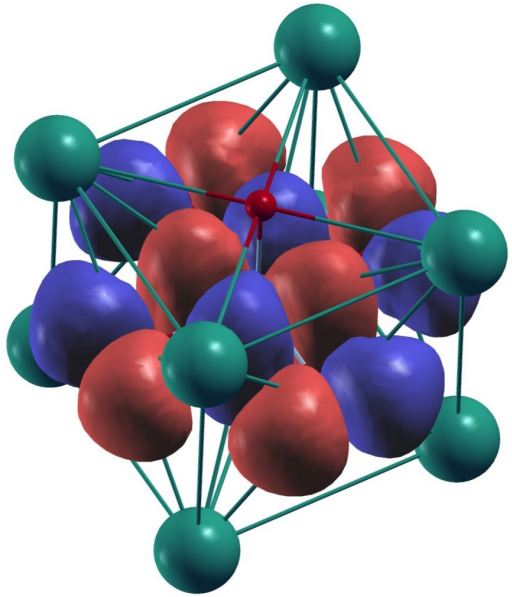
- "gauge" freedom:

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

⇝ choose $U(\boldsymbol{k})$ to minimize spread $\langle \Delta \boldsymbol{r}^2 \rangle$

Maximally Localized Wannier Functions



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

$\rightsquigarrow$ minimize $\tilde{\Omega}$

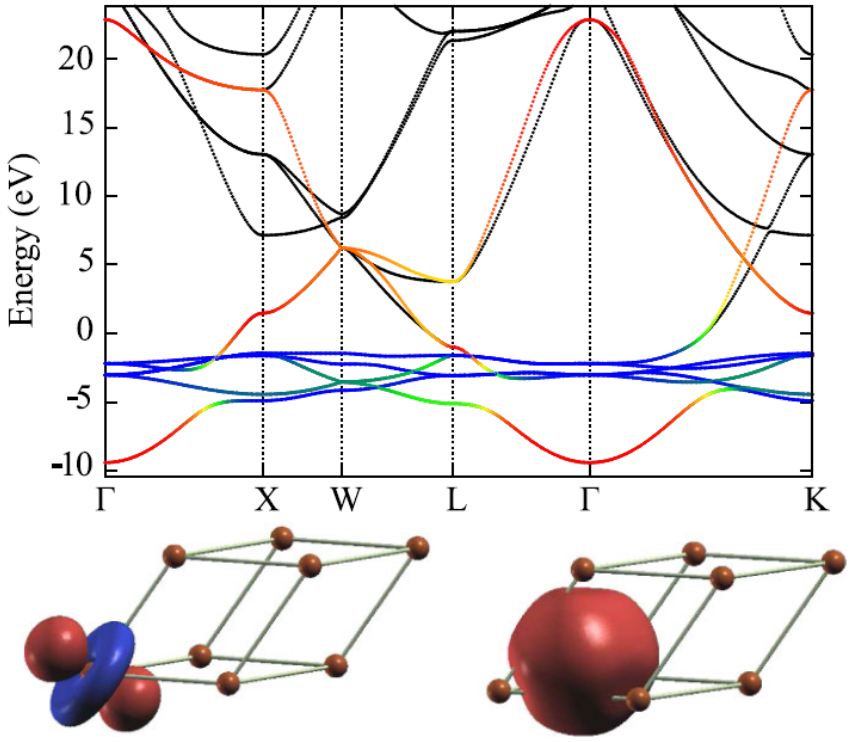
- `wannier90` computes $U(\boldsymbol{k})$ in this way

[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
  - $V(\boldsymbol{k})$ $\left(J(\boldsymbol{k}) \times N\right)$

- selection determines Ω_{I}

⇝ minimize also Ω_{I}

MLWF: Applications

- analysis of chemical bonding
- electric polarization and orbital magnetization
  - ⇝ Oleg Rubel's talk (tomorrow, 10:30)
- Wannier interpolation $\mathcal{K} \rightarrow \mathcal{G}$

$$H(\boldsymbol{k})|_{\mathcal{K}} \xrightarrow{\mathcal{F}} H(\boldsymbol{R})|_{\mathcal{K}^{-1}} \xrightarrow{\mathcal{F}^{-1}} H(\boldsymbol{k})|_{\mathcal{G}}$$

- Wannier functions as basis functions
  - tight-binding model $H(\boldsymbol{k}) = U^{+}(\boldsymbol{k})\,\epsilon(\boldsymbol{k})\,U(\boldsymbol{k})$
  - ⇝ realistic dynamical mean-field theory (DMFT)

wannier90

case.win

```
num_bands          = 3
num_wann           = 3
num_iter           = 1000
num_print_cycles =  100

dis_froz_min       = 7.
dis_froz_max       = 9.

bands_plot_project = 1
```

case.wout

```
Final 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

wien2wannier

case.w2win

```
BOTH
 21  23    min band, max band
  3   3    LJMAX, #Wannier functions
2             #terms
 2 2 -2     0.00000000    0.70710677 atom, L, M, 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    0.00000000
```

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

MLWF: Program FLow

0. normal SCF run $\longrightarrow$ converged density, band structure
1. `prepare_w2wdir.sh, init_w2w`: prepare input files
2. x `lapw1` *-options* $\longrightarrow$ eigenvectors on full k-mesh
3. `w2w` *case* $\longrightarrow$ overlap $\langle u_{m\boldsymbol{k}} | u_{n\boldsymbol{k}} \rangle$
4. `shift_energy` *case*
5. `wannier90.x` *case* $\longrightarrow$ $U(\boldsymbol{k})$

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

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

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

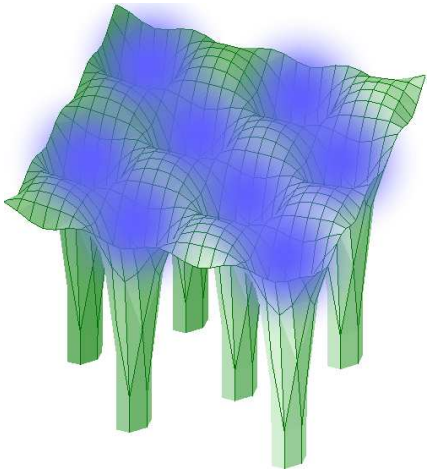
`http://www.wien2k.at/reg_user/unsupported/wien2wannier/`

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

LDA+DMFT

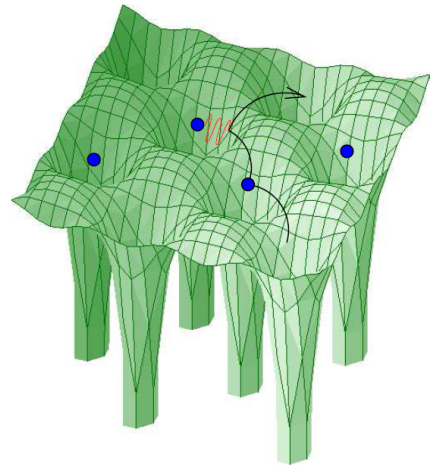
LDA

- realistic calculations
- fails for strong correlations



model Hamiltonians

- simplified, abstract model
- full correlations



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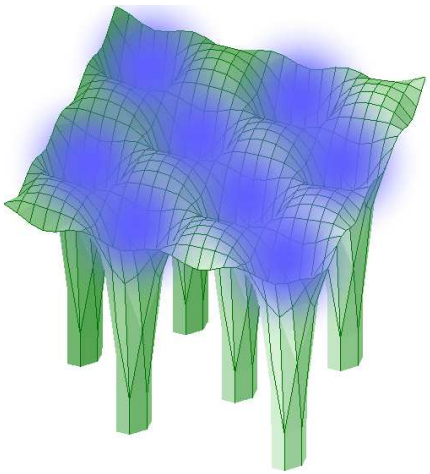
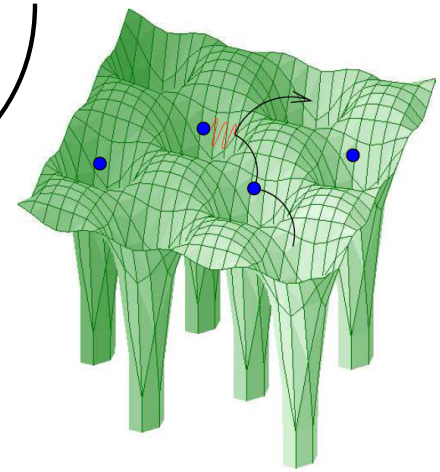


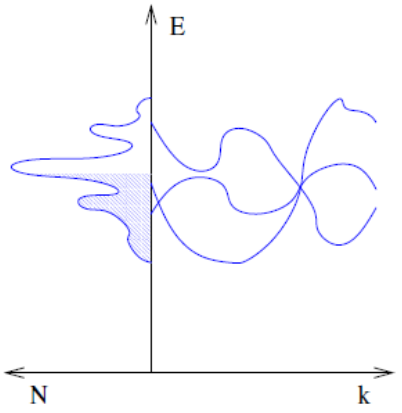


LDA+DMFT

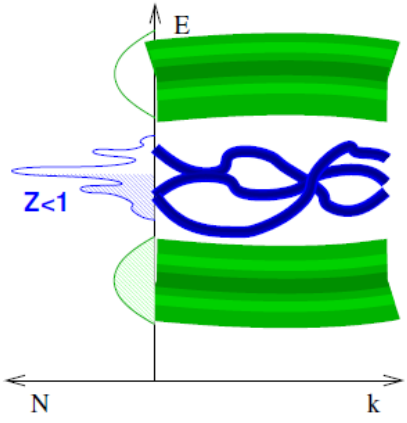
⇒ realistic calculation including
most important correlation effects

Held, Adv. Phys. 56, 829 (2007)
Kotliar et al., Rev. Mod. Phys. 78, 865 (2006)

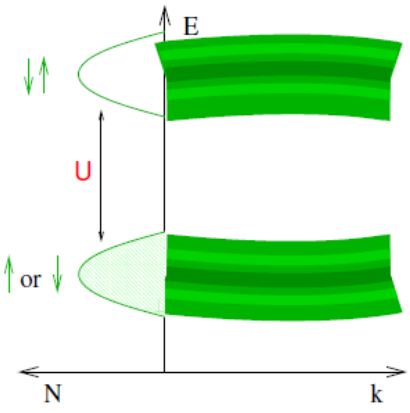
Correlation Regimes



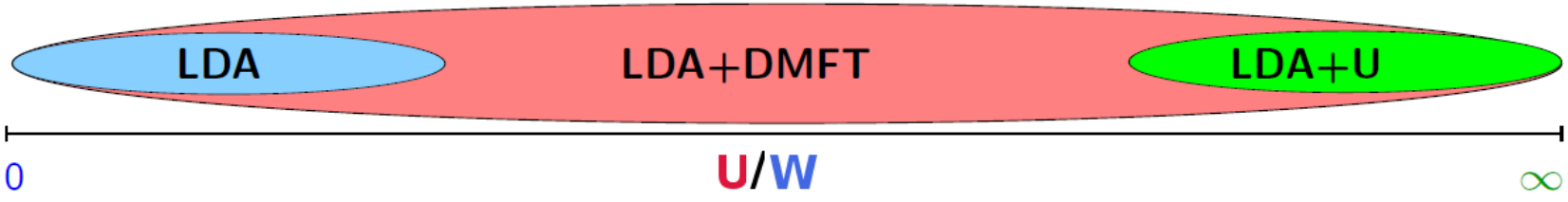
weakly correlated metal



strongly correlated metal

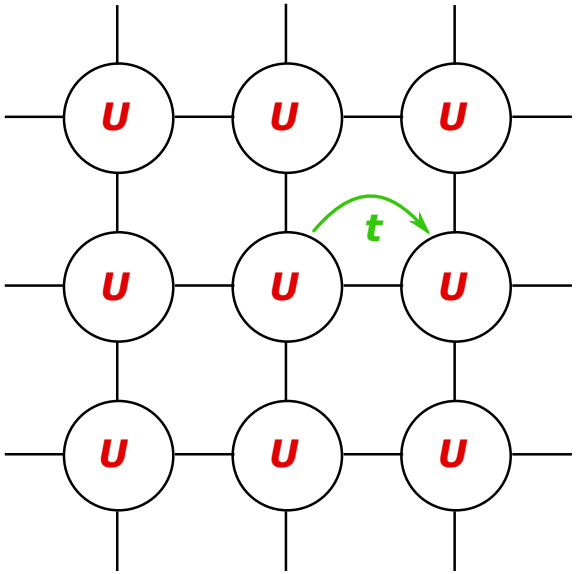


Mott insulator



U: screened local interaction W: bandwidth, $\sim t$

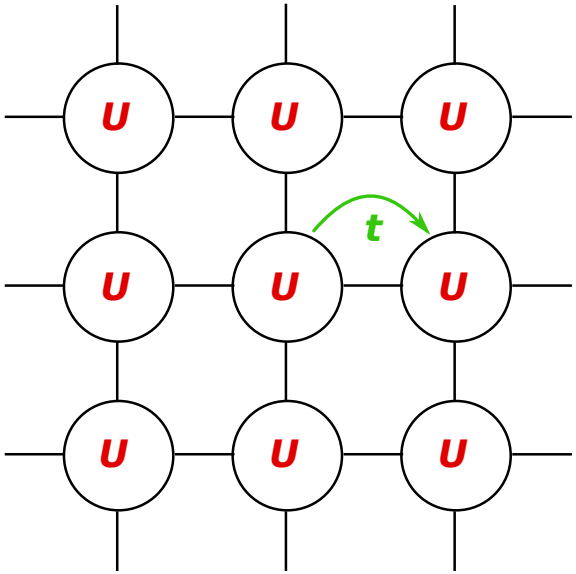
From lattice models to DMFT

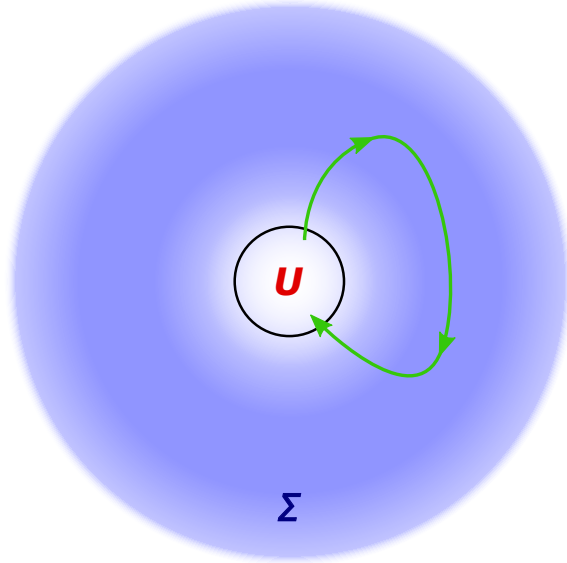


lattice model

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

From lattice models to DMFT





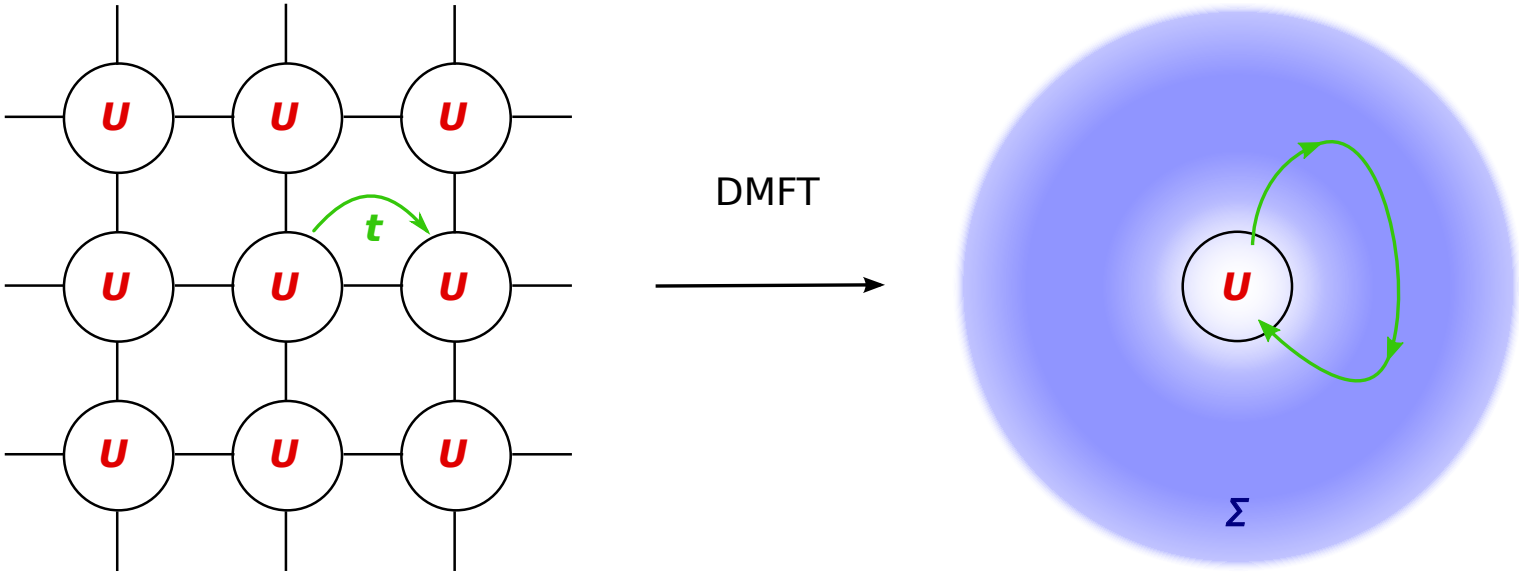
lattice model

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

impurity model

- one interacting site
- non-interacting “bath”

From lattice models to DMFT



lattice model

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

impurity model

- one interacting site
- non-interacting "bath"

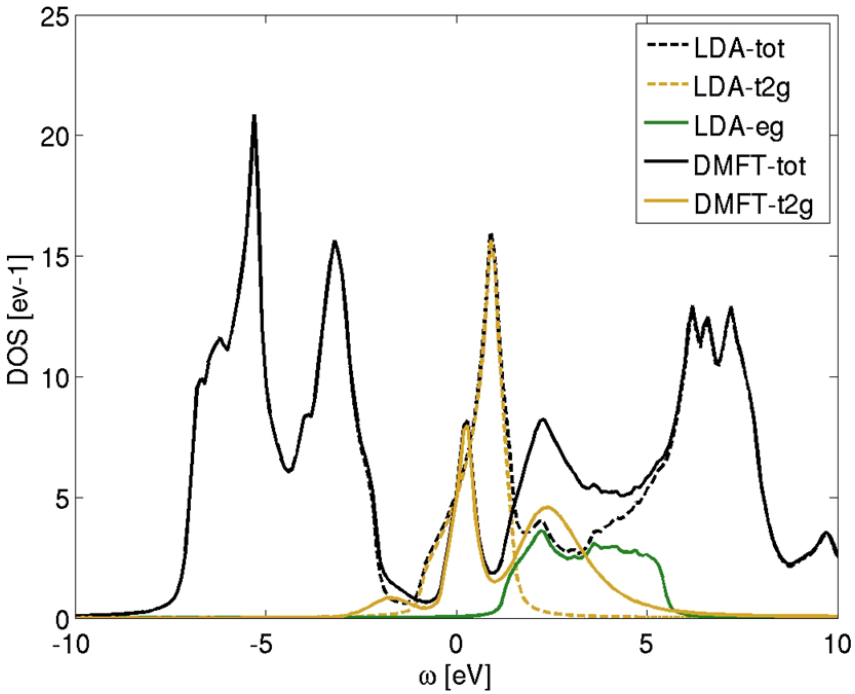
dynamical mean-field theory

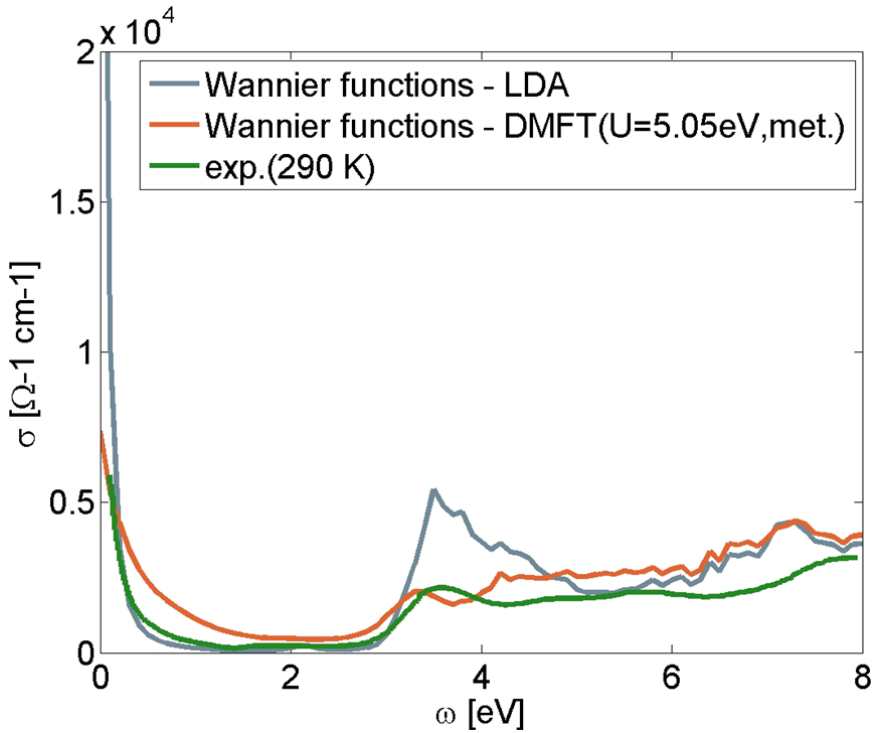
- lattice model $\mapsto$ impurity model
- self-energy $\Sigma(\omega)$

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

LDA+DMFT for $SrVO_3$

- DMFT basis: 3 degenerate t_{2g} Wannier functions
- $U = 5.05\,\text{eV}$, $T = 1160\,\text{K}$
  - 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_l^m
- computationally cheap
- double counting
- semi-empirical U, α

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