wien2wannier and woptic: From Wannier Functions to Optical Conductivity

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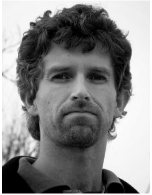
Outline

- brief introduction to maximally localized Wannier functions
- some applications of Wannier functions
- woptic: conductivity $\sigma(\omega)$, thermopower S from LDA+DMFT

Big Thanks to:

Original code authors

Philipp Wissgott
Waltzing Atoms



Jan Kuneš
Institute of Physics, Prague

As well as

Karsten Held

Peter Blaha

European Research Council
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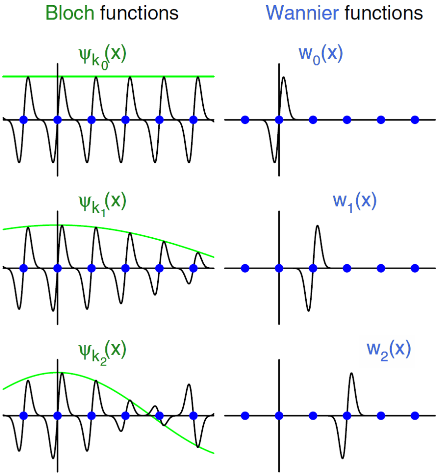
From Bloch to Wannier



from Marzari *et al.*

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

Transform $\mathbf{k} \leftrightarrow \mathbf{R}$;
$\mathbf{r}$ is spectator

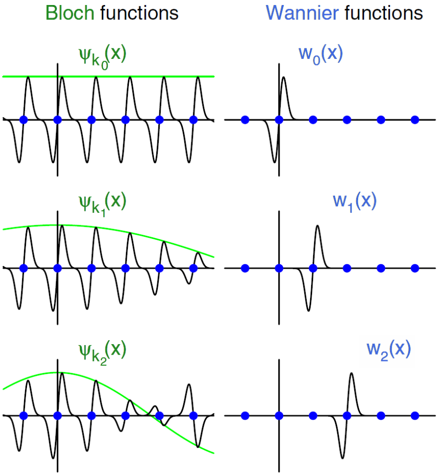
Properties:

"periodicity" $w_{\mathbf{R}}(\mathbf{r}) \equiv w_0(\mathbf{r}-\mathbf{R})$

orthonormality

$$\langle w\, n\mathbf{R} | w\, m\mathbf{R}'\rangle = \delta_{nm}\delta_{\mathbf{R}\mathbf{R}'}$$

Gauge freedom



from Marzari *et al.*

But $|\psi\,\mathbf{k}\rangle$ carries arbitrary phase $\phi(\mathbf{k})$

$$\Rightarrow |w\,\mathbf{R}\rangle = \frac{V}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k}\; e^{i(\phi(\mathbf{k})-\mathbf{k}\mathbf{R})}\, |\psi\,\mathbf{k}\rangle$$

strongly non-unique (shape, localization)

$\rightsquigarrow$ choose $\phi(\mathbf{k})$ for maximum localization of $|w\,\mathbf{R}\rangle$

Maximally localized WF (Marzari-Vanderbilt) [Marzari et al., RMP (2012)]

In the multiband case, $e^{i\phi(\mathbf{k})} \longrightarrow$ unitary matrix

$$|w\, n\mathbf{R}\rangle = \int_{\mathrm{BZ}} d\mathbf{k}\, e^{-i\mathbf{k}\mathbf{R}} \sum_m U^{(\mathbf{k})}_{mn} |\psi\, m\mathbf{k}\rangle$$

Total spread

$$\Omega := \sum_n \langle \Delta \mathbf{r}^2 \rangle_n = \widetilde{\Omega}[U] + \Omega_I$$

gauge dependent

gauge independent

$\rightsquigarrow$ MLWF procedure: minimize $\widetilde{\Omega}[U]$ (Wannier90)

- input: $M^{(\mathbf{k},\mathbf{b})}_{mn} = \langle \psi\, m\mathbf{k} | e^{-i\mathbf{r}(\mathbf{k}+\mathbf{b})} | \psi\, n\mathbf{k} \rangle$
- optional input: $A^{(\mathbf{k})}_{mn} = \langle \psi\, m\mathbf{k} | g\, n\mathbf{k} \rangle$
- output: $U^{(\mathbf{k})}_{nm}$, $(H^{(\mathbf{R})}_{nm}, \dots)$

wien2wannier

Maximally localized WF (Marzari-Vanderbilt) [Marzari et al., RMP (2012)]

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wien2wannier

wien2wannier

- MLWF from full-potential LAPW code WIEN2k
- interface to Wannier90
  - $A_{mn}^{(\mathbf{k})}$, $M_{mn}^{(\mathbf{k},\mathbf{b})}$
  - initial projections: atom-centered basis functions, rotations
- real-space plots (`wplot`)

  $\rightsquigarrow$ XCrySDen, VESTA
- available from `wien2k.at → unsupported`

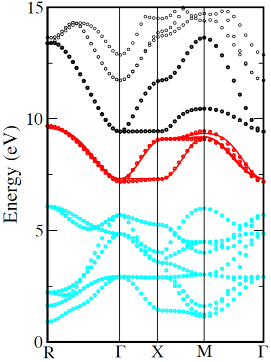
  to be included in WIEN2k 14.1 distribution

Applications of MLWF

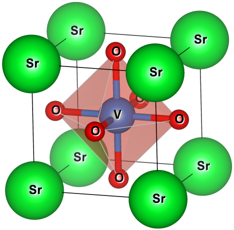
- analysis of chemical bonding
- electric polarization and orbital magnetization
  - ⤳ BerryPI [Ahmed et al., Comp. Phys. Commun. (2013)]
- Wannier interpolation $\mathcal{K} \to \widetilde{\mathcal{K}}$

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

- Wannier functions as basis functions
  - ▸ tight-binding model $H(\mathbf{k}) = U^{+}(\mathbf{k})\,\varepsilon(\mathbf{k})\,U(\mathbf{k})$
  - ⤳ realistic dynamical mean-field theory (DMFT)



$SrVO_3$:

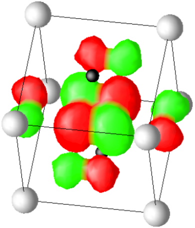


V-e_g

V-t_{2g}

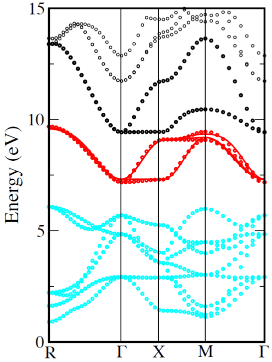
O-p

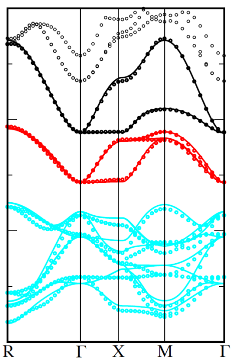
3-band projection



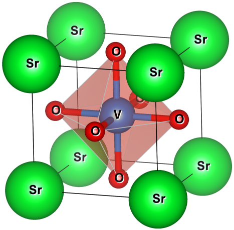
V-centered t_{2g} orbital

[Kuneš et al., Comp. Phys. Commun. (2010)]





$SrVO_3$:



V-e_g

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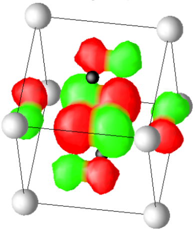
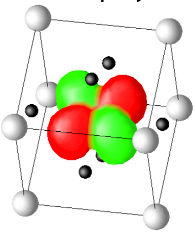
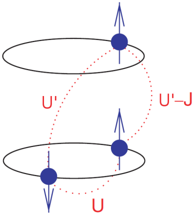


14-band projection



V-centered t_{2g} orbital



[Held, Adv. Phys (2007)]

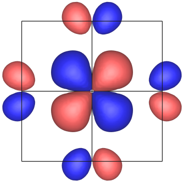
Local Coulomb interaction in cubic symmetry:

- U intra-orbital repulsion
- U' inter-orbital repulsion
- J Hund's exchange

$U = U' + 2J$

U, U', J for t_{2g} Wannier orbitals

[Ribic, EA, et al., arXiv:1405.7232]



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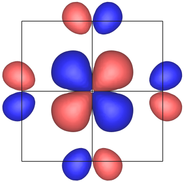
$U = U' + 2J$ for atomic orbitals

ϟ in crystal: hybridization $\Rightarrow$ 3 independent parameters

	$SrVO_3$ (3d)	$BaOsO_3$ (5d)
$\frac{U-U'}{2J}$	1.06	1.32

U, U', J for t_{2g} Wannier orbitals

[Ribic, EA, et al., arXiv:1405.7232]



Local Coulomb interaction in cubic symmetry:

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- U' inter-orbital repulsion
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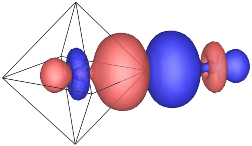
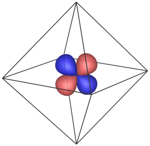
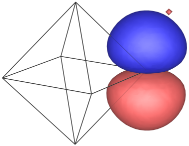


$U = U' + 2J$ for atomic orbitals

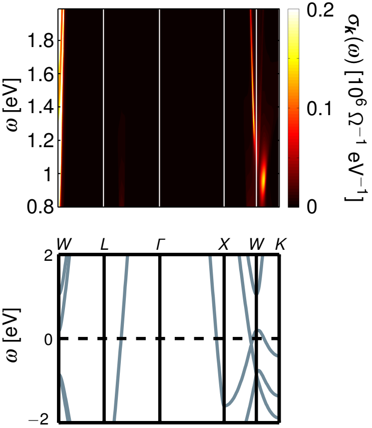
↯ in crystal: hybridization $\Rightarrow$ 3 independent parameters

	$SrVO_3$ $(3d)$	$BaOsO_3$ $(5d)$	$BaOsO_3$ $t_{2g} + p$
$\frac{U - U'}{2J}$	1.06	1.32	0.98



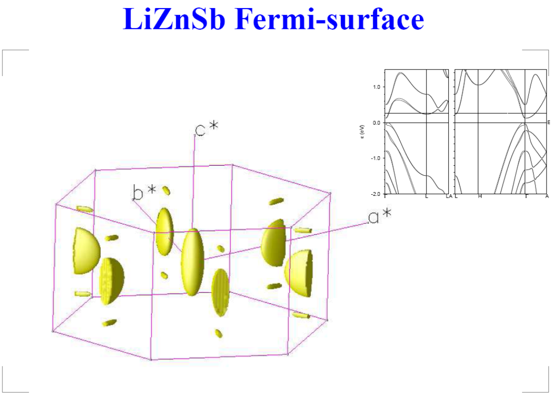


- adaptive k-integration
- optical conductivity $\sigma(\mathbf{k}, \omega)$



(Aluminum)

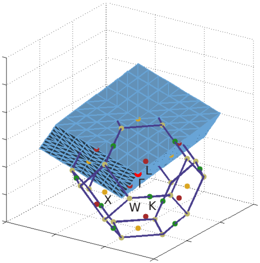
- including local self-energy $\Sigma(\omega)$ (DMFT)
- thermopower
- full matrix elements $\langle\psi|\nabla|\psi\rangle$ from WIEN2k



[J. Sofo]

Tetrahedral mesh management

- tetrahedron T has integration error estimate ϵ_T
- refine T if $\epsilon_T \geqslant \Theta \max_{T'} \epsilon_{T'}$
  - "harshness" $\Theta \in [0, 1]$
- enforce "regularity"
  - at most one "hanging node"
  - for stable convergence
- enforce "shape stability"
  - no heavily-distorted octahedra
  - avoid large integration errors



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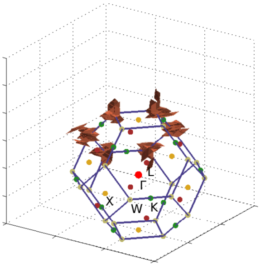

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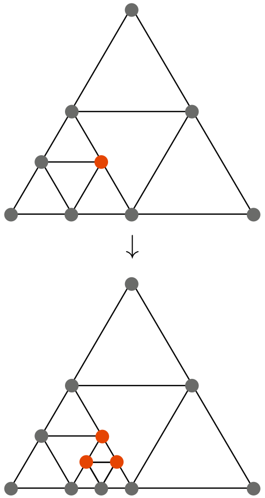

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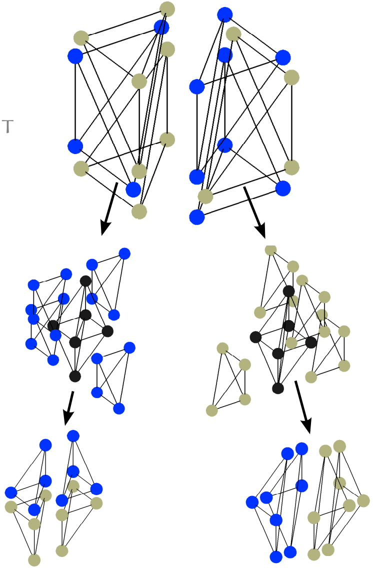
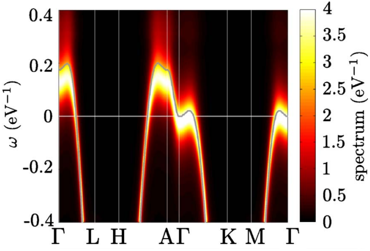


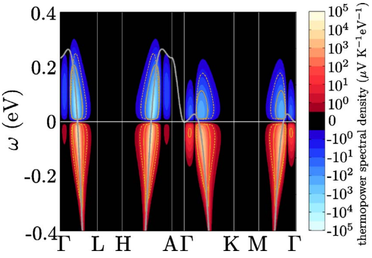
"Kuhn triangulation"

[Ong, SIAM J. Sci. Comput. (1994);

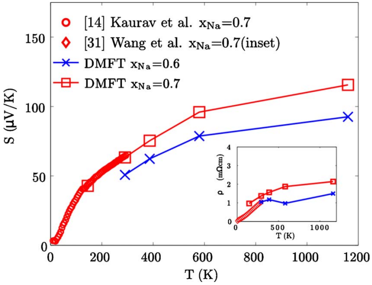
Endres & Krysl, Int. J. Numer. Meth. Engng. (2004)]



0.4
0.2
0
-0.2
-0.4
ω (eV^{-1})
Γ L H AΓ K M Γ
4
3.5
3
2.5
2
1.5
1
0.5
0
spectrum (eV^{-1})

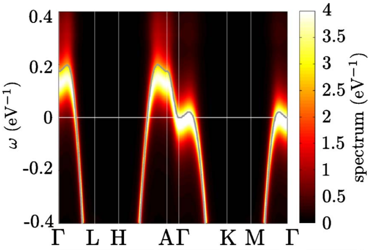


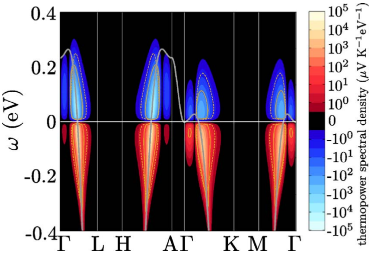
0.4
0.2
0
-0.2
-0.4
ω (eV)
Γ L H AΓ K M Γ
10^5
10^4
10^3
10^2
10^1
10^0
0
-10^0
-10^1
-10^2
-10^3
-10^4
-10^5
thermopower spectral density (μV K^{-1}eV^{-1})

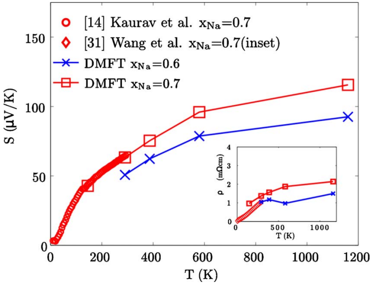


[14] Kaurav et al. x_{Na}=0.7
[31] Wang et al. x_{Na}=0.7(inset)
DMFT x_{Na}=0.6
DMFT x_{Na}=0.7
S (μV/K)
0
50
100
150
0
200
400
600
800
1000
1200
T (K)
ρ (mΩcm)
4
3
2
1
0
0
500
1000
T (K)

Some results for Na_xCoO_2







Thank you for your attention

Bloch waves

Bloch's theorem

$$\widehat{H} = -\nabla^2 + V(\mathbf{r}) \quad \text{with} \quad V(\mathbf{r}+\mathbf{R}) \equiv V(\mathbf{r})$$

has solutions $$\widehat{H}\,|\psi\, n\mathbf{k}\rangle = \varepsilon_n(\mathbf{k})\;|\psi\, n\mathbf{k}\rangle$$

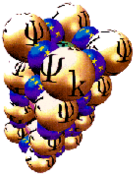
$$\text{with} \quad \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}\, u_{n\mathbf{k}}(\mathbf{r});$$

$$u_{n,\mathbf{k}}(\mathbf{r}+\mathbf{R}) \equiv u_{n,\mathbf{k}}(\mathbf{r}) \quad \text{and} \quad \varepsilon_n(\mathbf{k}+\mathbf{K}) \equiv \varepsilon_n(\mathbf{k})$$

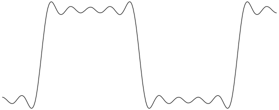
(Simultaneous eigenbasis of $\widehat{H}$ and translation operators $\widehat{T}_{\mathbf{R}}$)

"Usual" basis for solid-state calculations

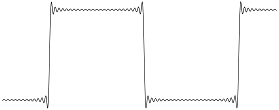
But for many applications, a localized basis is preferable



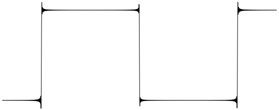
$\mathbf{r}$-localization and $\mathbf{k}$-smoothness



$\sin x + \frac{1}{3}\sin 3x + \cdots + \frac{1}{9}\sin 9x$



$\sin x + \frac{1}{3}\sin 3x + \cdots + \frac{1}{49}\sin 49x$



$\sin x + \frac{1}{3}\sin 3x + \cdots + \frac{1}{249}\sin 249x$

[Wikipedia, "Gibbs phenomenon"]

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

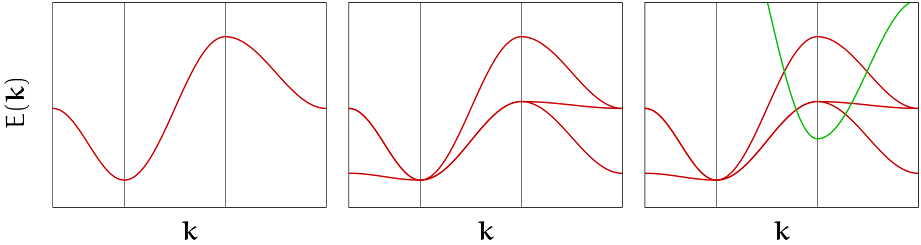
Idea: choose $\phi(\mathbf{k})$ for maximum localization of $|w\,\mathbf{R}\rangle$

Fourier series converges faster for smoother functions:

$$f \in C^p \Rightarrow |\widetilde{f}_n| \leqslant \frac{\text{const}}{|n|^p}$$

From bands to WF

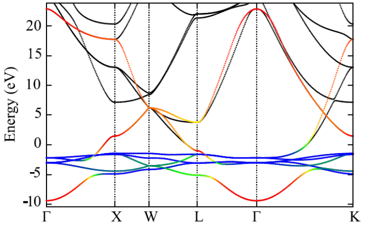
isolated band | isolated group of bands | entangled bands

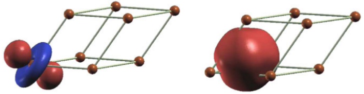


$|w\,\mathbf{k}\rangle = e^{i\phi(\mathbf{k})}|\psi\,\mathbf{k}\rangle$ $\qquad$ $|w\,n\mathbf{k}\rangle = U^{(\mathbf{k})}_{mn}|\psi\,m\mathbf{k}\rangle$ $\qquad$ $|w\,n\mathbf{k}\rangle = U^{(\mathbf{k})}_{in}V^{(\mathbf{k})}_{mi}\,|\psi\,m\mathbf{k}\rangle$

Disentanglement

Cu (fcc):





from Marzari *et al.*

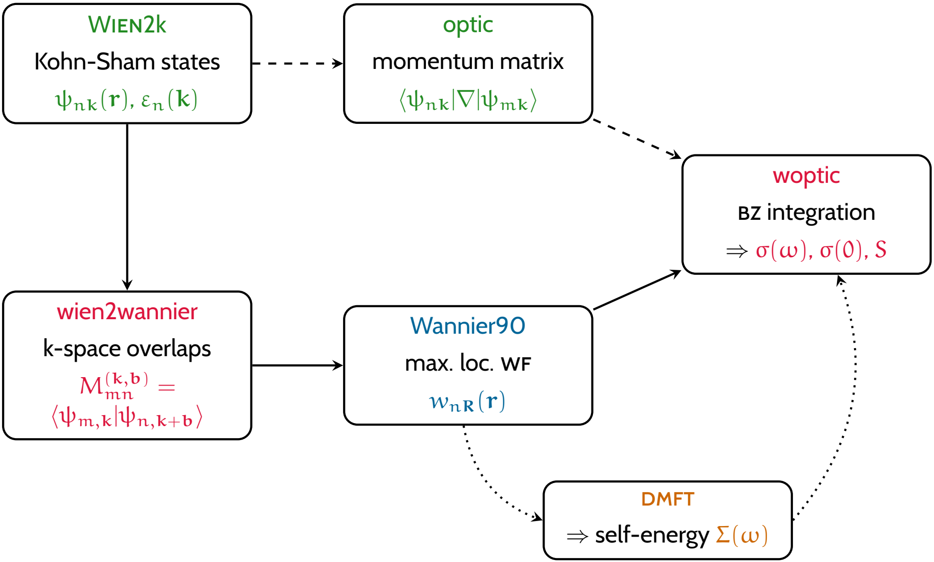
5 d-like WF,
2 interstitial s-like WF

- What to do when #bands $>$ #WF?
- Ansatz: Select "optimally smooth" subspace
  - $\rightsquigarrow$ rectangular matrix V_k (#bands(k) $\times$ #WF)
  - ! $\Omega_I = \Omega_I[V]$
  - ▸ minimize $\Omega_I[V]$

$$\Omega = \widetilde{\Omega}[U] + \Omega_I[V]$$

ϟ woptic not implemented with disentanglement

Anatomy of a calculation



Transport properties with WIEN2k

- BoltzTrap
  - semi-classical (Boltzmann)
  - band velocities $\partial\varepsilon(\mathbf{k})/\partial\mathbf{k}$ instead of momentum matrix elements $\langle\psi\,|\nabla|\,\psi\rangle$
- BoltzWann
  - similar, with Wannier functions
- **woptic**
  - quantum-mechanical linear response (Kubo)
  - adaptive BZ integration
  - inclusion of local self-energy $\Sigma(\omega)$
  - more information:
    - WIEN2k.at $\rightarrow$ reg. users $\rightarrow$ unsupported $\rightarrow$ wien2wannier
    - woptic preprint
    - Wissgott *et al.*, PRB (2012)

Calculating optical conductivity and thermopower

Very schematically:

- linear response (Kubo formula): $\widehat{H} = \widehat{H}_0 + \lambda(t)\widehat{B}$

$$\rightsquigarrow \langle \widehat{A} \rangle (t) = \langle \widehat{A} \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' \lambda(t') \Big\langle \big[A(t), B(t') \big] \Big\rangle_0 + \cdots$$

- σ, S: current operators $\sim \widehat{\Psi}^{+} \nabla \widehat{\Psi} - \big(\nabla \widehat{\Psi}^{+}\big) \widehat{\Psi}$

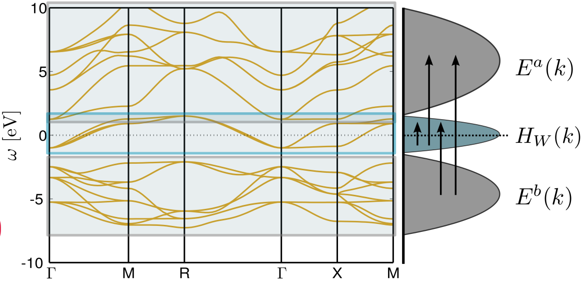
$$\chi^{\text{ret}}_{\text{el-el}}(\mathbf{r}-\mathbf{r}', t-t') \sim \theta(t-t') \Big\langle \big[\hat{j}(\mathbf{r}, t), \hat{j}(\mathbf{r}', t') \big] \Big\rangle_0$$

$$\chi^{\text{ret}}_{\text{el-heat}}(\mathbf{r}-\mathbf{r}', t-t') \sim \theta(t-t') \Big\langle \big[\hat{j}(\mathbf{r}, t), \widehat{Q}(\mathbf{r}', t') \big] \Big\rangle_0$$

el. current operator

heat-current operator

Interpolation and random-phase problem

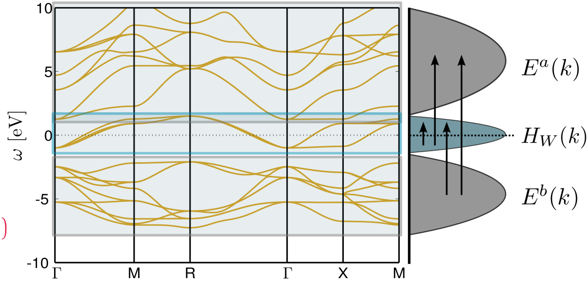


- DMFT in Wannier basis
  - $\rightarrow$ self-energy $\Sigma_i(\omega)$
  - $\rightarrow$ spectral function $A(\mathbf{k}, \omega)$

- in evaluation of χs:

$\rightsquigarrow$ tr $\left\{ v(\mathbf{k}) \; A(\mathbf{k}) \; v(\mathbf{k}) \; A(\mathbf{k}) \right\}$

Interpolation and random-phase problem



- DMFT in Wannier basis
  - $\rightarrow$ self-energy $\Sigma_i(\omega)$
  - $\rightarrow$ spectral function $A(\mathbf{k}, \omega)$
- in evaluation of χs:

$\rightsquigarrow$ tr $\{ v(\mathbf{k})\, A(\mathbf{k})\, v(\mathbf{k})\, A(\mathbf{k}) \}$ → from DMFT

→ momentum matrix $\langle w\, n\mathbf{k} | \nabla | w\, m\mathbf{k} \rangle$; from WIEN2k

↯ $|\psi\, n\mathbf{k}\rangle$ carries random phase $\phi_n(\mathbf{k})$, which propagates to v but not A

- problem with w–w ($v_{wx} A_{xy} v_{yz} A_{zw}$) and w–ψ ($v_{wi} A_{ii} v_{ix} A_{xw}$) terms

$\rightsquigarrow$ interpolate $v(\mathbf{k}) \rightarrow v(\tilde{\mathbf{k}})$