woptic: Transport Properties with Wannier Functions and Adaptive k-Integration

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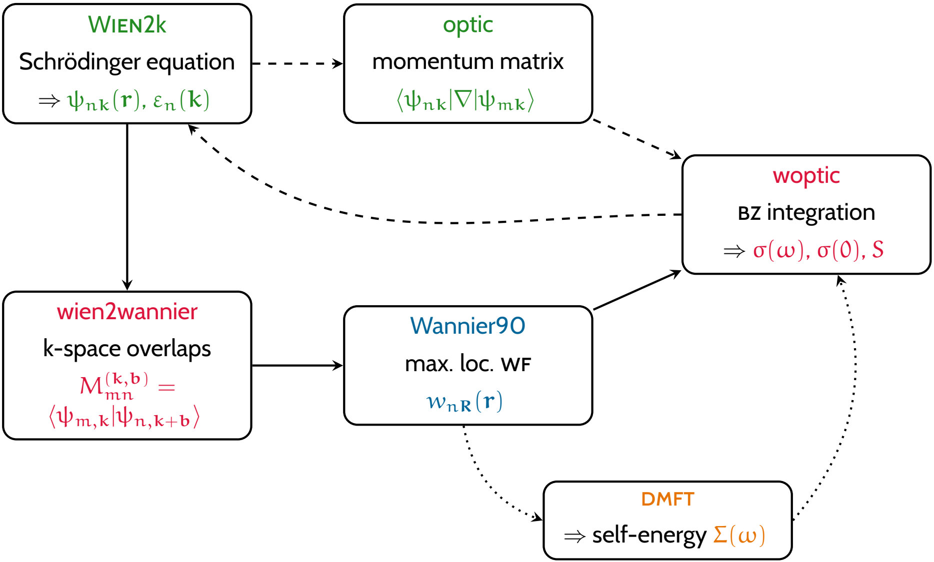
About this presentation

- On the menu:
  - band-structure calculation with WIEN2k (briefly)
  - maximally localized Wannier functions with wien2wannier and Wannier90
  - conductivity, thermopower with woptic
- explanations alternating with sample calculation
- ask **questions** – *It is better to uncover a little than to cover a lot*
- if you want to **try your own hand**, come to me

Anatomy of a calculation



Where to learn WIEN2k

PENNSTATE

WIEN2013: HANDS ON WORKSHOP ON THE WIEN2K PACKAGE

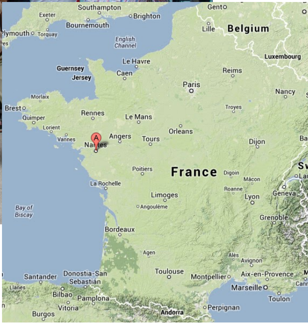
Materials Simulation Center

University Park, PA August 12-16, 2013

Where to learn WIEN2k

UNIVERSITÉ DE NANTES

Next year, in Nantes



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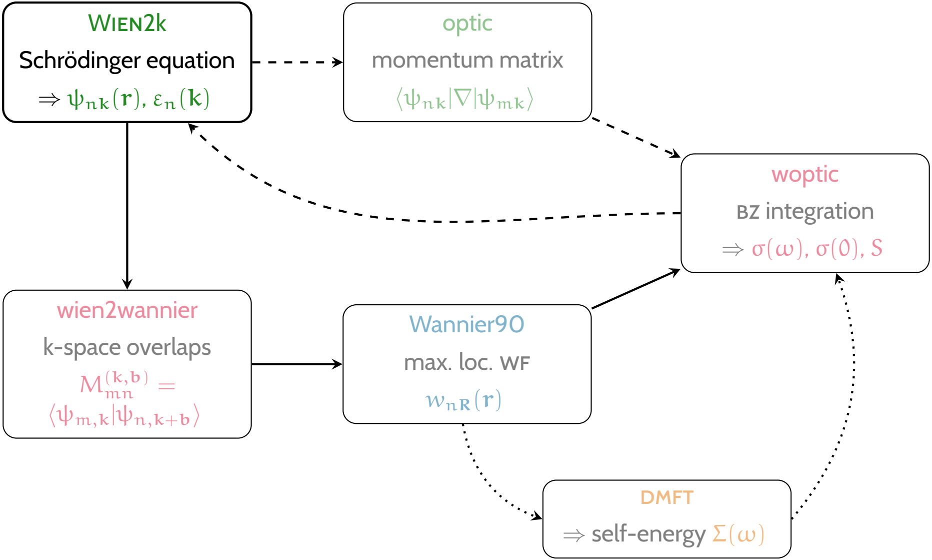


Bloch waves

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

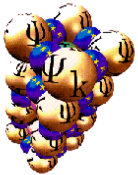
$$\text{with} \quad \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}\, u_{n\mathbf{k}}(\mathbf{r});$$

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

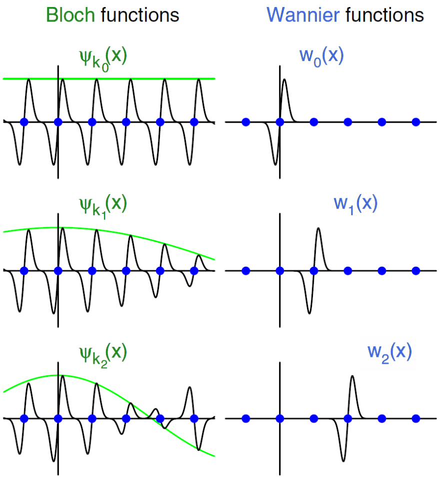
(Simultaneous eigenbasis of $\widehat{H}$ and translation operators $\widehat{T}_{\mathbf{R}}$)

"Usual" basis for solid-state calculations

But for many applications, a localized basis is preferable



Fourier transforms of the Bloch waves



from Marzari *et al.*

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

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

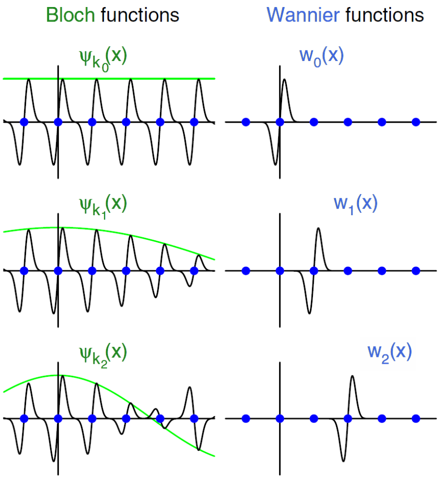
Properties:

"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.*

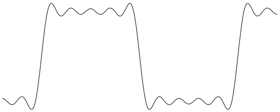
$|\psi\, n\mathbf{k}\rangle$ carries arbitrary phase $\phi(\mathbf{k})$

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

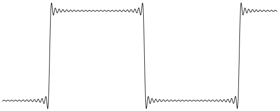
strongly non-unique (shape, spread)

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

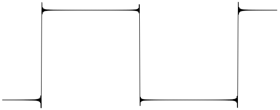
“Gauge” freedom



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



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



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

[Wikipedia, “Gibbs phenomenon”]

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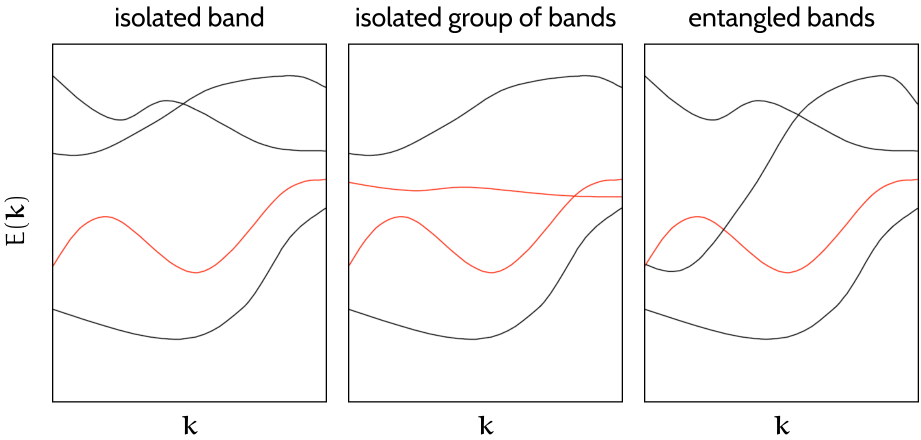
strongly non-unique (shape, spread)

Idea: choose $|w\,\mathbf{k}\rangle := e^{i\phi(\mathbf{k})}|\psi\,\mathbf{k}\rangle$ 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



$$|w\,\mathbf{k}\rangle = e^{i\phi(\mathbf{k})}|\psi\,\mathbf{k}\rangle$$

[pictures by J. Kuneš]

Maximally localized WF

[Marzari et al., RMP (2012)]

In the multiband case, $e^{i\phi(k)} \longrightarrow$ unitary matrix $[U^{+}U = 1]$,

$$|w\, n\mathbf{R}\rangle = \int_{\mathrm{BZ}} \mathrm{d}k\, e^{-ik\mathbf{R}} \sum_{m} U_{mn}^{(k)} |\psi\, mk\rangle$$

Maximally localized WF

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Total spread $\Omega := \sum_{n} \left(\langle \mathbf{r}^2 \rangle_n - \langle \mathbf{r} \rangle_n^2 \right) = \widetilde{\Omega}[U] + \Omega_I$

gauge dependent

gauge independent

Maximally localized WF

[Marzari et al., RMP (2012)]

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Total spread $\Omega := \sum_n \left(\langle \mathbf{r}^2\rangle_n - \langle \mathbf{r}\rangle_n^2\right) = \widetilde{\Omega}[U] + \Omega_I$

gauge dependent

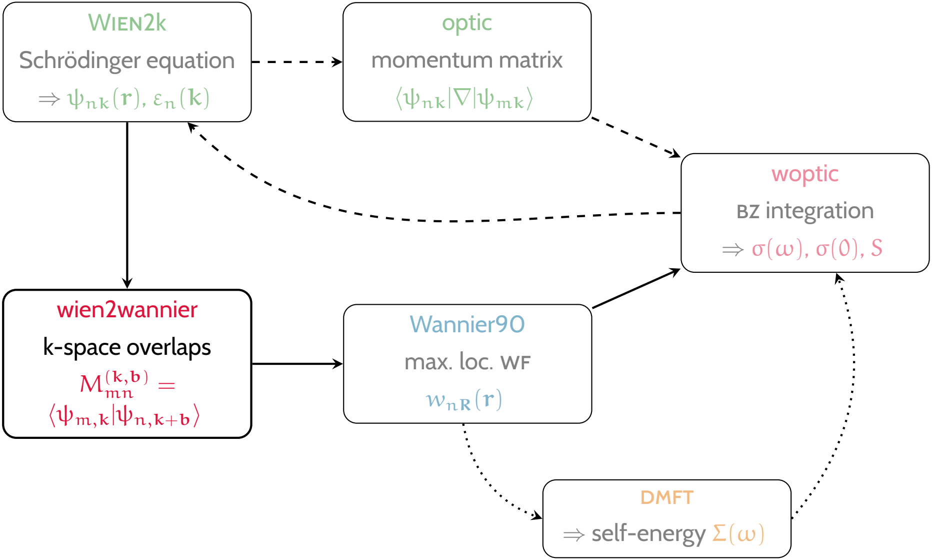
gauge independent

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

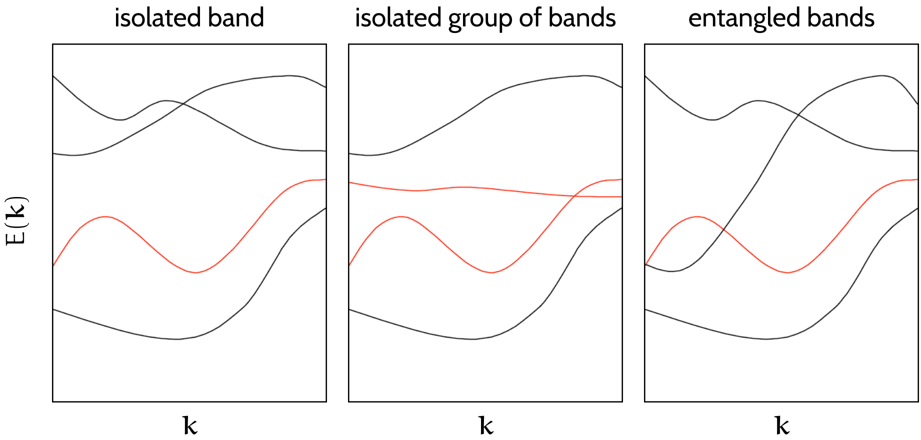
- input: $M^{(k,b)}_{mn} = \langle \psi\, mk | e^{-ib(k+b)} | \psi\, nk\rangle$
- optional input: $A^{(k)}_{mn} = \langle \psi\, mk |\, g\, nk\rangle$
- output: $U^{(k)}_{nm}$, $\left(H^{(\mathbf{R})}_{nm}\right)$

wien2wannier

Anatomy of a calculation



From bands to WF

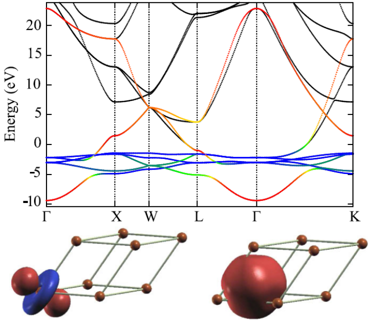


$$|w\,\mathbf{k}\rangle = e^{i\phi(\mathbf{k})}|\psi\,\mathbf{k}\rangle \qquad |w\,n\mathbf{k}\rangle = U_{mn}^{(\mathbf{k})}|\psi\,m\mathbf{k}\rangle$$

[pictures by J. Kuneš]

Disentanglement

Cu (fcc):



from Marzari *et al.*

5 d-like WF,

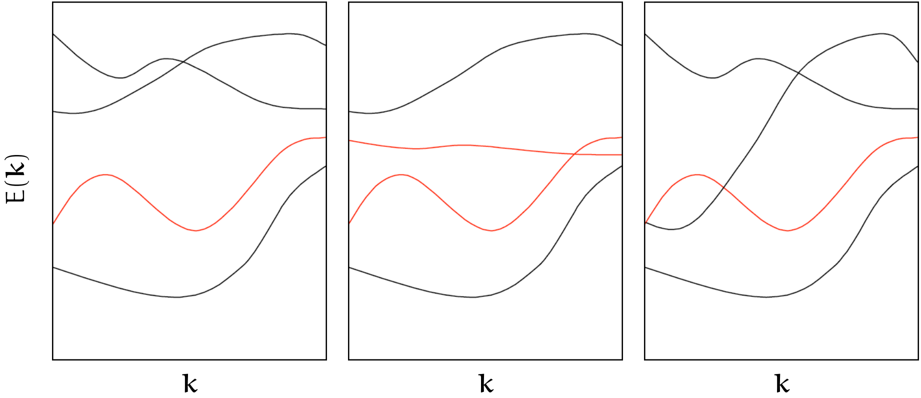
2 interstitial s-like WF

- 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 $\Omega_I[V]$

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

From bands to WF

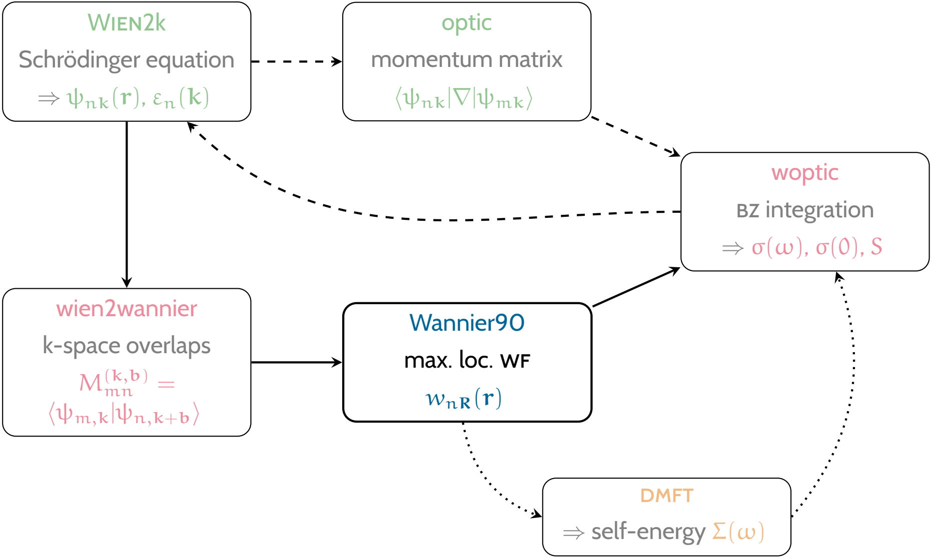
isolated band | isolated group of bands | entangled bands



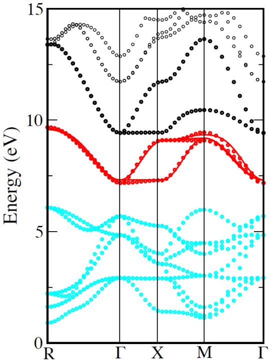
$|w\,\mathbf{k}\rangle = e^{i\phi(\mathbf{k})}|\psi\,\mathbf{k}\rangle$ $\qquad$ $|w\,n\mathbf{k}\rangle = U^{(\mathbf{k})}_{mn}|\psi\,m\mathbf{k}\rangle$ $\qquad$ $|w\,n\mathbf{k}\rangle = U^{(\mathbf{k})}_{in}V^{(\mathbf{k})}_{mi}\,|\psi\,m\mathbf{k}\rangle$

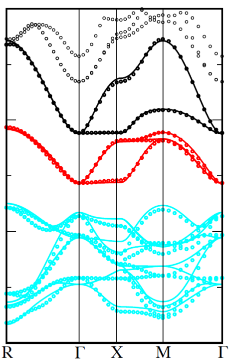
[pictures by J. Kuneš]

Anatomy of a calculation



Choice of Wannier subspace



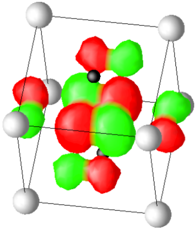


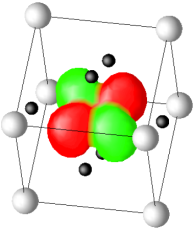
$SrVO_3$:

V-e_g

V-t_{2g}

O-p





V-centered xy orbital

Applications of MLWF

- analysis of chemical bonding
- electric polarization and orbital magnetization
  ⇝ BerryPI
- 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 $H(\mathbf{k}) = U^{+}(\mathbf{k})\, \varepsilon(\mathbf{k})\, U(\mathbf{k})$

  ⇝ realistic dynamical mean-field theory (DMFT)

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): $\widehat{H} = \widehat{H}_0 + \lambda(t)\widehat{B}$

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

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

$\rightsquigarrow$ momentum matrix elements $\langle\psi|\nabla|\psi\rangle$

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

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

el. current operator

heat-current operator

Calculating optical conductivity and thermopower

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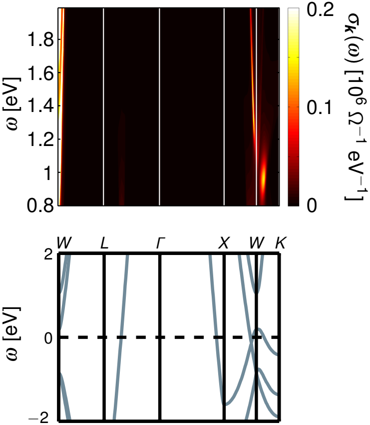
Adaptive k-integration

Al optical conductivity $\sigma(\mathbf{k}, \omega)$



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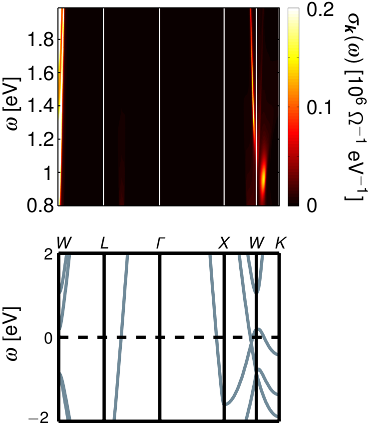
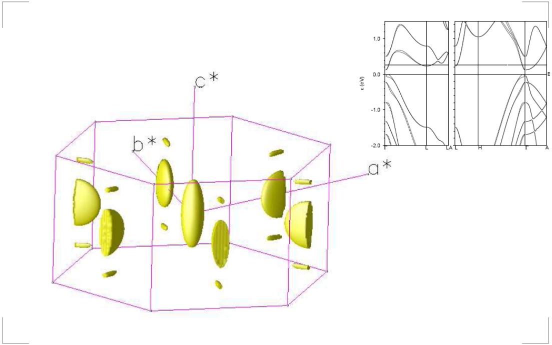
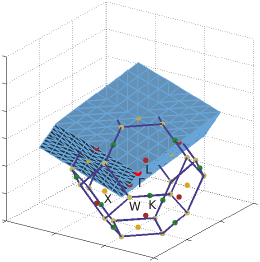


LiZnSb Fermi-surface



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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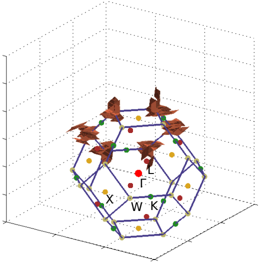

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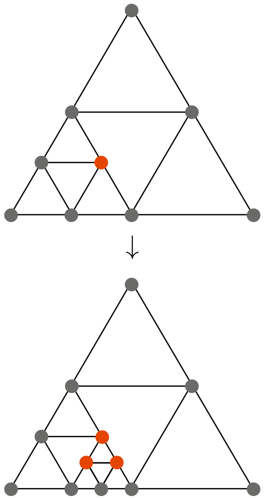

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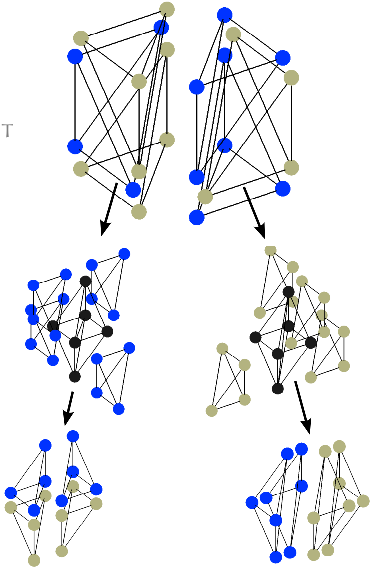
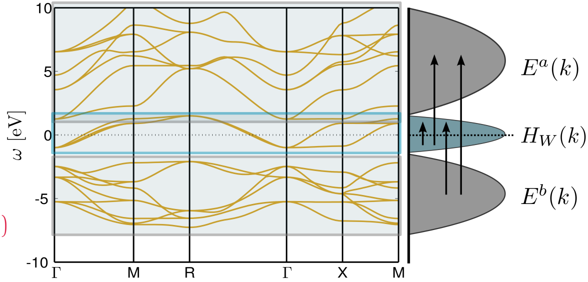


"Kuhn triangulation"

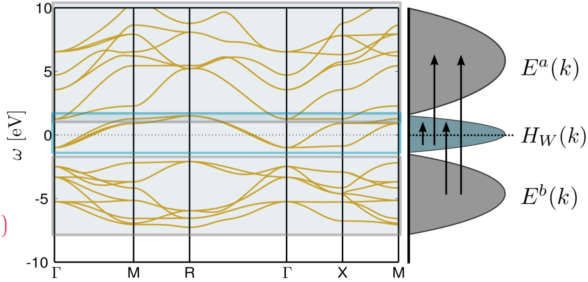
Interpolation and random-phase problem



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

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

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:

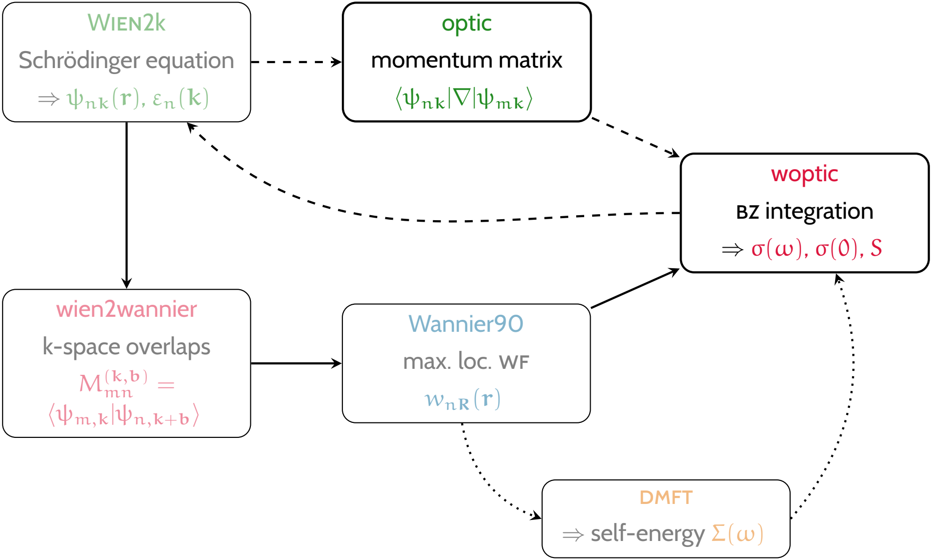
$\rightsquigarrow$ tr $\{ v(\mathbf{k}) \; A(\mathbf{k}) \; v(\mathbf{k}) \; A(\mathbf{k}) \}$ from DMFT

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

ϟ $|\psi\, n\mathbf{k}\rangle$ 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
- (planned) solution: interpolate $v(\mathbf{k})$

Anatomy of a calculation

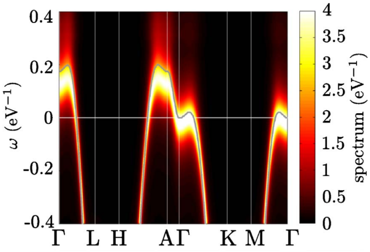


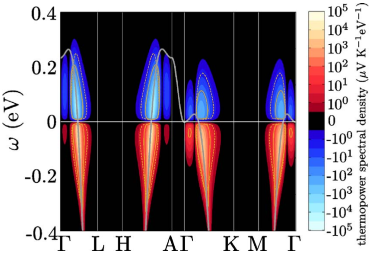
Limitations

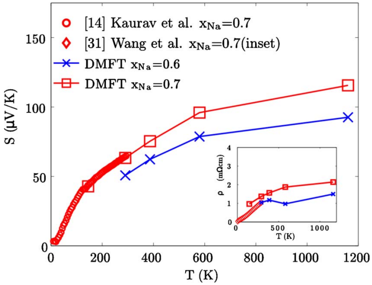
- Kohn-Sham eigenstates interpreted as excited states
  - ⇝ "scissors" operator: $\varepsilon_{\text{cond}}(\mathbf{k}) \leftarrow \varepsilon^{\text{LDA}}_{\text{cond}}(\mathbf{k}) + \Delta$
- careful with doping
  - rigid-band treatment
- disentanglement not implemented
- random-phase problem
  - for optical conductivity
  - when using self-energy
- not-so-mature code

Some results for Na_xCoO_2

[Wissgott *et al.*, PRB (2010)]



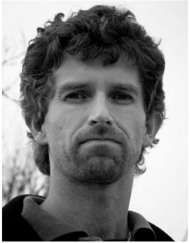




Big Thanks to ...

The code authors

Philipp Wissgott
TU Vienna



Jan Kuneš
Institute of Physics, Prague

As well as

Karsten Held

Peter Blaha

Alessandro Toschi

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The code authors

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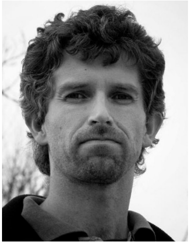

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Karsten Held

Peter Blaha

Alessandro Toschi

And to my audience for your patience!