Feasible Predictions of Thermoelecrical Properties including Anharmonic Effects ?

Christian Carbogno & Florian Fiebig

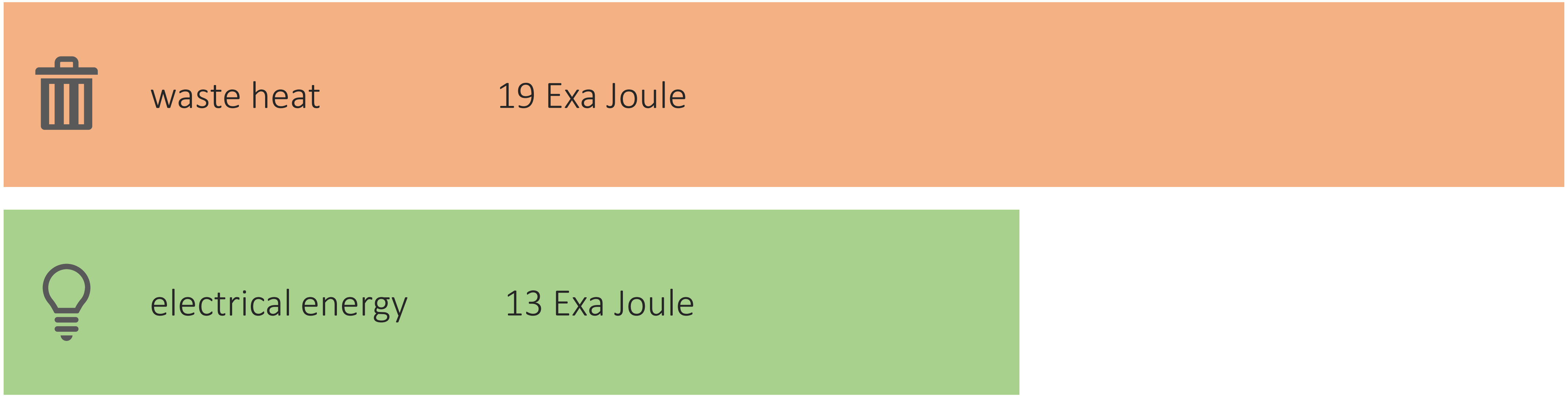
The NOMAD Laboratory at the FHI of the Max-Planck-Gesellschaft

and IRIS-Adlershof of the Humboldt-Universität zu Berlin

NOVEL MATERIALS DISCOVERY

MAX-PLANCK-GESELLSCHAFT

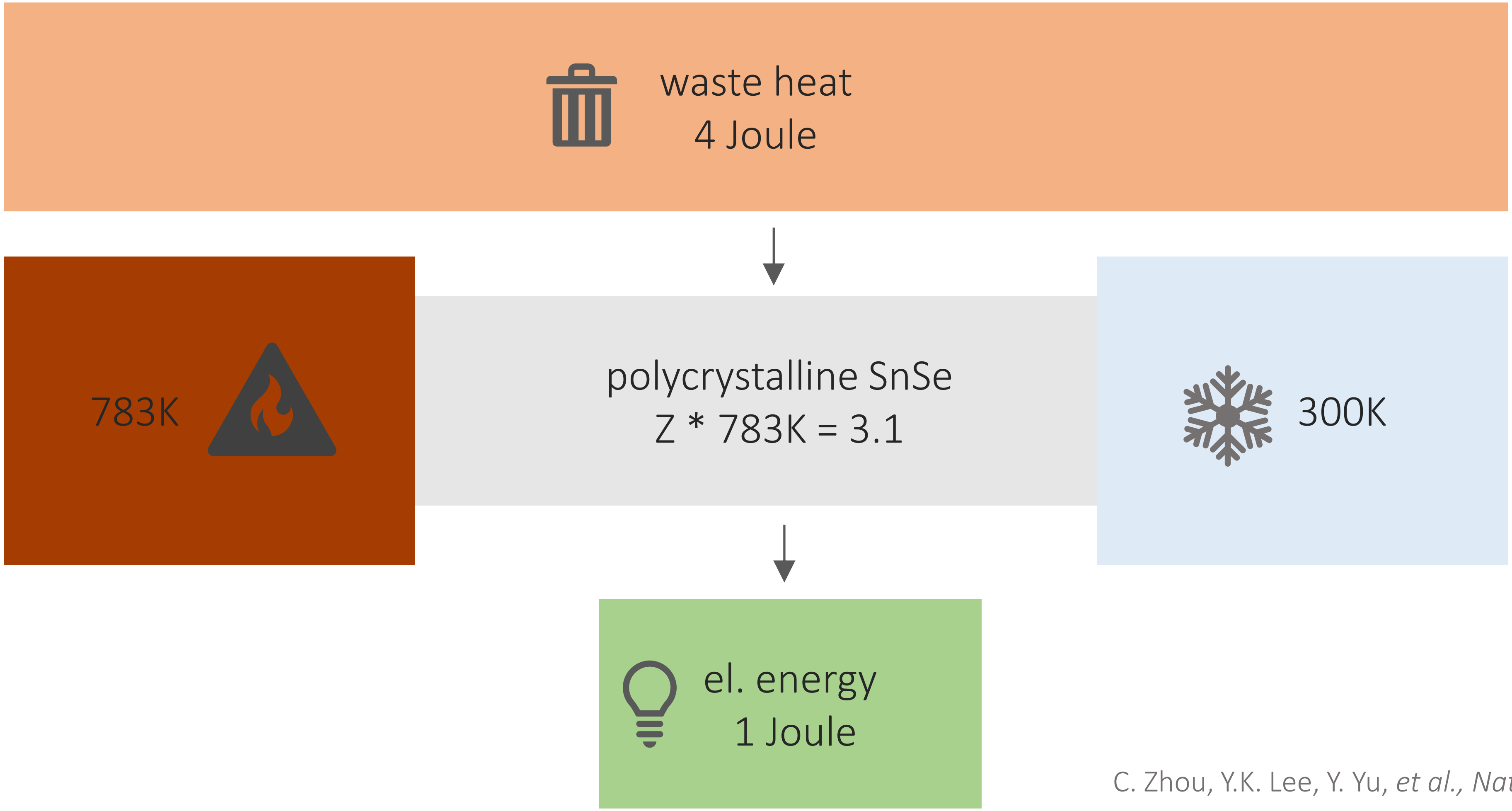
We are wasting energy as waste heat.



US power plants in 2012 fueled by coal, natural gas, and nuclear.

D. Gingerich, M. Mauter, *Environmental Science & Technology* **2015** *49* (14), 8297-8306.

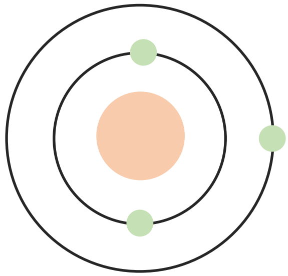
Recycling waste heat is possible with thermoelectrial materials.



$$Z = \frac{\sigma}{\kappa} S^2$$

C. Zhou, Y.K. Lee, Y. Yu, *et al.*, *Nature Materials*, **20**, 1378–1384 (2021).

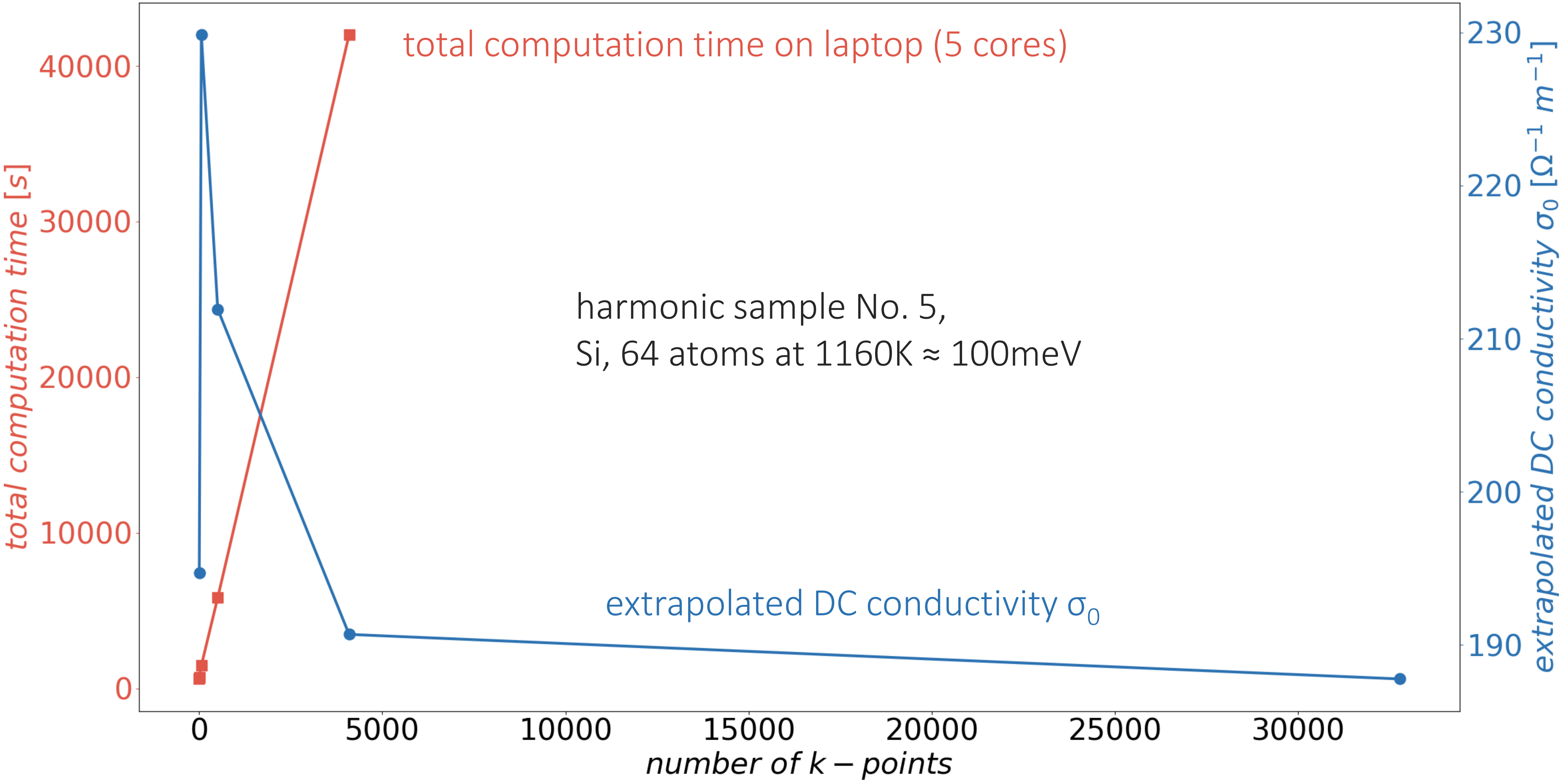
To include anharmonicities, use Kubo-Greenwood.



	Boltzmann transport	Kubo-Greenwood transport	Experiment
nuclear motion	harmonic	all orders	
electronic response	1st order	all orders	
nuclear thermal conductivity CuI at 300K [W/mK]	6.55 [1]	1.38 [2]	1.68 [3]
electronic mobility Si at 300K [cm²/Vs]	1366 [4]		1350 [5]

[1] A. Togo, L. Chaput, and I. Tanaka, Physical Review B **91**, 094306 (2015).
[2] F. Knoop, Dissertation, theoretische Physik, Humboldt-Universität zu Berlin, 2022.
[3] D. L. Perry, *Handbook of Inorganic Compounds*, Zeroth (CRC Press, Apr. 2016).
[4] S. Poncé, E. Margine, F. Giustino: Phys. Rev. B **97**, 121201(R), 2018.
[5] P. Norton, T. Braggins, and H. Levinstein, Phys. Rev. B **8**, 5632, 1956.

Kubo-Greenwood needs an expensive, dense **k**-grid.



We have the chance to converge Kubo-Greenwood with a cheaper **k**-grid.

We have the chance to converge Kubo-Greenwood with a cheaper **k**-grid.

Why are many **k**-points needed ?

How can we make **k**-points cheaper ?

→ DFT output -> conductivities

illustration in the band diagramm

more **k**-points -> higher conductivities ?

Fluxes can be computed from the Autocorrelation.

Fluxes ← Onsager-Coefficients ← Autocorrelation

$$\langle \mathbf{J}_e \rangle = \frac{1}{q}\left(q L_{11} \mathbf{E} + \frac{L_{12} \nabla T}{T} \right)$$

$$\langle \mathbf{J}_q \rangle = \frac{1}{q}\left(q L_{21} \mathbf{E} + \frac{L_{22} \nabla T}{T} \right)$$

$$L_{mn}(\omega) = \frac{1}{3V} \langle \hat{\mathbf{J}}_m(t - i\hbar\tau); \hat{\mathbf{J}}_n \rangle_{\omega + i\varepsilon}$$

B. Holst, M. French, R. Redmer, Phys. Rev. B **83**, 235120, 2011.

Autocorrelation can be computed from DFT results.

Autocorrelation

Total Flux Operator

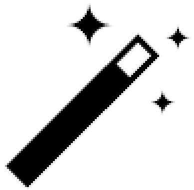
Wick‘s Theorem

Three Integrations

Kubo-Greenwood

$$\langle \hat{\mathbf{J}}_m(t - i\hbar\tau); \hat{\mathbf{J}}_n \rangle_{\omega+i\varepsilon} = \lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\; e^{i(\omega+i\varepsilon)t}\int_0^\beta \mathrm{d}\tau\; \mathrm{Tr}\{\hat{\varrho}_0 \hat{\mathbf{J}}_m\,(t - i\hbar\tau)\cdot \hat{\mathbf{J}}_n\}$$

$$\hat{\mathbf{J}}_m = \frac{q^{2-m}}{m_e}\sum_{\mathbf{k}\mathbf{k}'\nu\nu'}\langle \mathbf{k}\nu|\hat{\mathbf{p}}|\mathbf{k}'\nu'\rangle\,\epsilon^{m-1}_{\mathbf{k}\nu\mathbf{k}'\nu'}\,\hat{a}^\dagger_{\mathbf{k}\nu}\hat{a}_{\mathbf{k}'\nu'}$$



$$L_{mn}(\omega) = \frac{2\pi q^{4-m-n}}{3Vm_e^2\omega}\sum_{\mathbf{k}\nu\mu}\langle \mathbf{k}\nu|\hat{\mathbf{p}}|\mathbf{k}\mu\rangle\cdot\langle \mathbf{k}\mu|\hat{\mathbf{p}}|\mathbf{k}\nu\rangle\times\epsilon^{m+n-2}_{\mathbf{k}\nu\mathbf{k}\mu}(f_{\mathbf{k}\nu} - f_{\mathbf{k}\mu})\delta(E_{\mathbf{k}\mu} - E_{\mathbf{k}\nu} - \hbar\omega)$$

B. Holst, M. French, R. Redmer, Phys. Rev. B **83**, 235120, 2011.

We have the chance to converge Kubo-Greenwood with a cheaper **k**-grid.

Why are many **k**-points needed ?

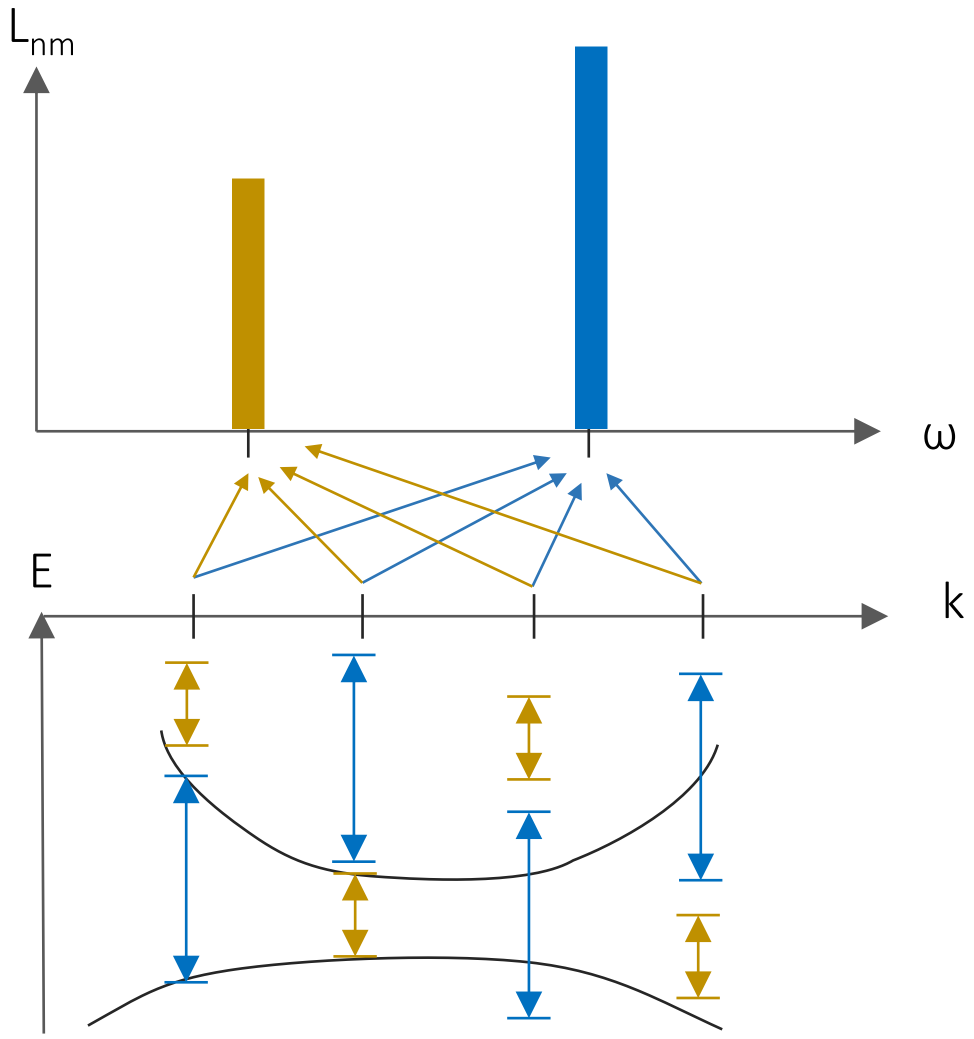
How can we make **k**-points cheaper ?

DFT output -> conductivities

→ illustration in the band diagramm

more **k**-points -> higher conductivities ?

Each k-point contributes to $L_{nm}(\omega)$ at all frequencies ω.



$$L_{mn}(\omega) = \frac{2\pi q^{4-m-n}}{3Vm_e^2\omega} \sum_{\mathbf{k}\nu\mu} \langle \mathbf{k}\nu|\hat{\mathbf{p}}|\mathbf{k}\mu\rangle \cdot \langle \mathbf{k}\mu|\hat{\mathbf{p}}|\mathbf{k}\nu\rangle$$
$$\times \epsilon_{\mathbf{k}\nu\mathbf{k}\mu}^{m+n-2}(f_{\mathbf{k}\nu} - f_{\mathbf{k}\mu})\delta(E_{\mathbf{k}\mu} - E_{\mathbf{k}\nu} - \hbar\omega)$$

We have the chance to converge Kubo-Greenwood with a cheaper **k**-grid.

Why are many **k**-points needed ?

DFT output -> conductivities

illustration in the band diagramm

→ more **k**-points -> higher conductivities ?

How can we make **k**-points cheaper ?

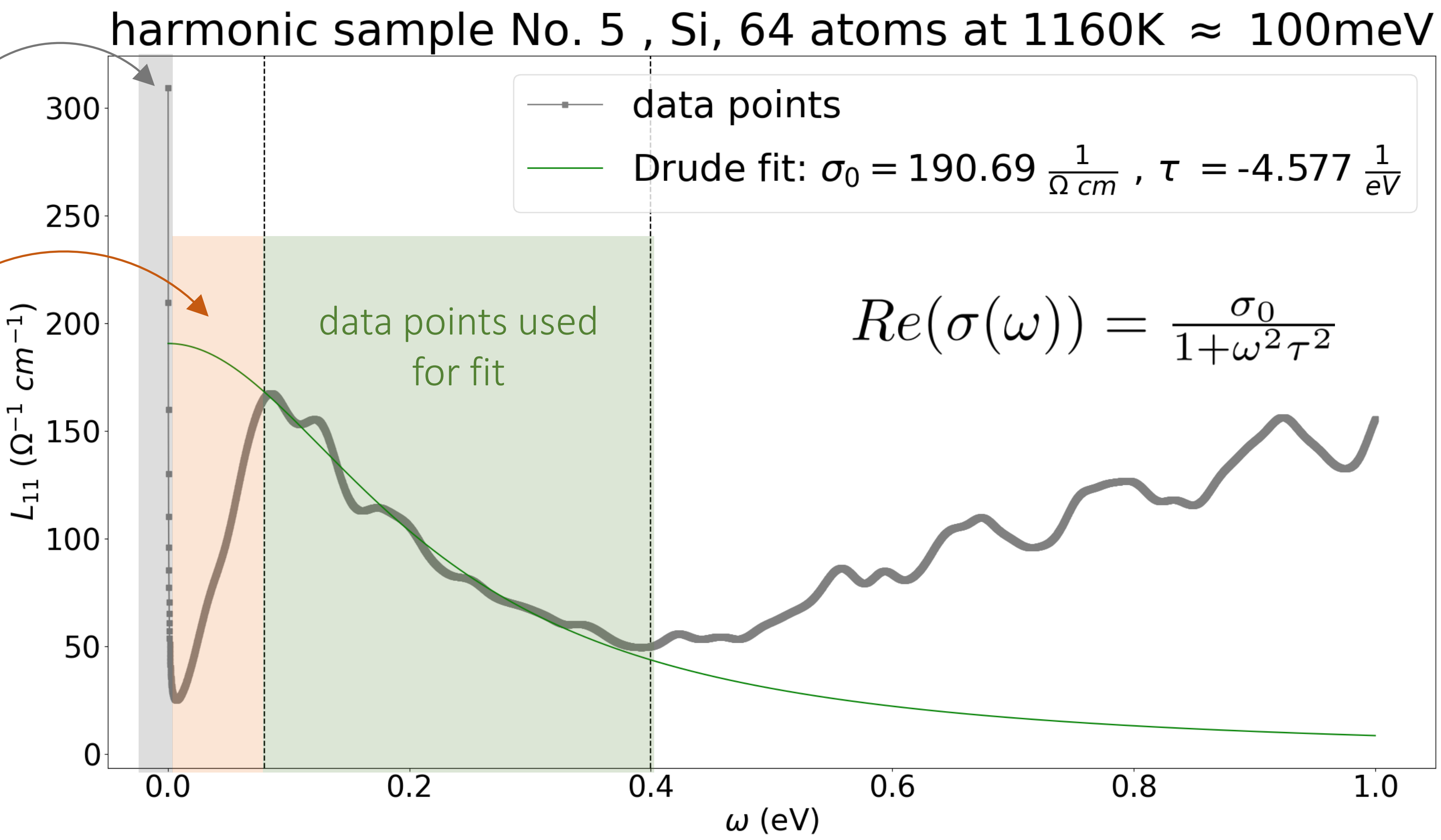
$L_{nm}(\omega)$ is an average.

$$L_{mn}(\omega) = \frac{\frac{2\pi q^{4-m-n}}{3Vm_e^2\omega}\sum_{\mathbf{k}\nu\mu}\langle\mathbf{k}\nu|\hat{\mathbf{p}}|\mathbf{k}\mu\rangle\cdot\langle\mathbf{k}\mu|\hat{\mathbf{p}}|\mathbf{k}\nu\rangle\times\epsilon_{\mathbf{k}\nu\mathbf{k}\mu}^{m+n-2}(f_{\mathbf{k}\nu}-f_{\mathbf{k}\mu})\delta(E_{\mathbf{k}\mu}-E_{\mathbf{k}\nu}-\hbar\omega)}{\text{number of }\mathbf{k}-points}$$

DC conductivity can be extrapolated from the Drude peak in $L_{11}(\omega)$.

divergence due to $\frac{1}{\omega}$

Vanishing energy differences live in lower dimensions. They are hard to hit with a k-point.



We have the chance to converge Kubo-Greenwood with a cheaper **k**-grid.

Why are many **k**-points needed ?

→

How can we make **k**-points cheaper ?

DFT output -> conductivities

illustration in the band diagramm

more **k**-points -> higher conductivities ?

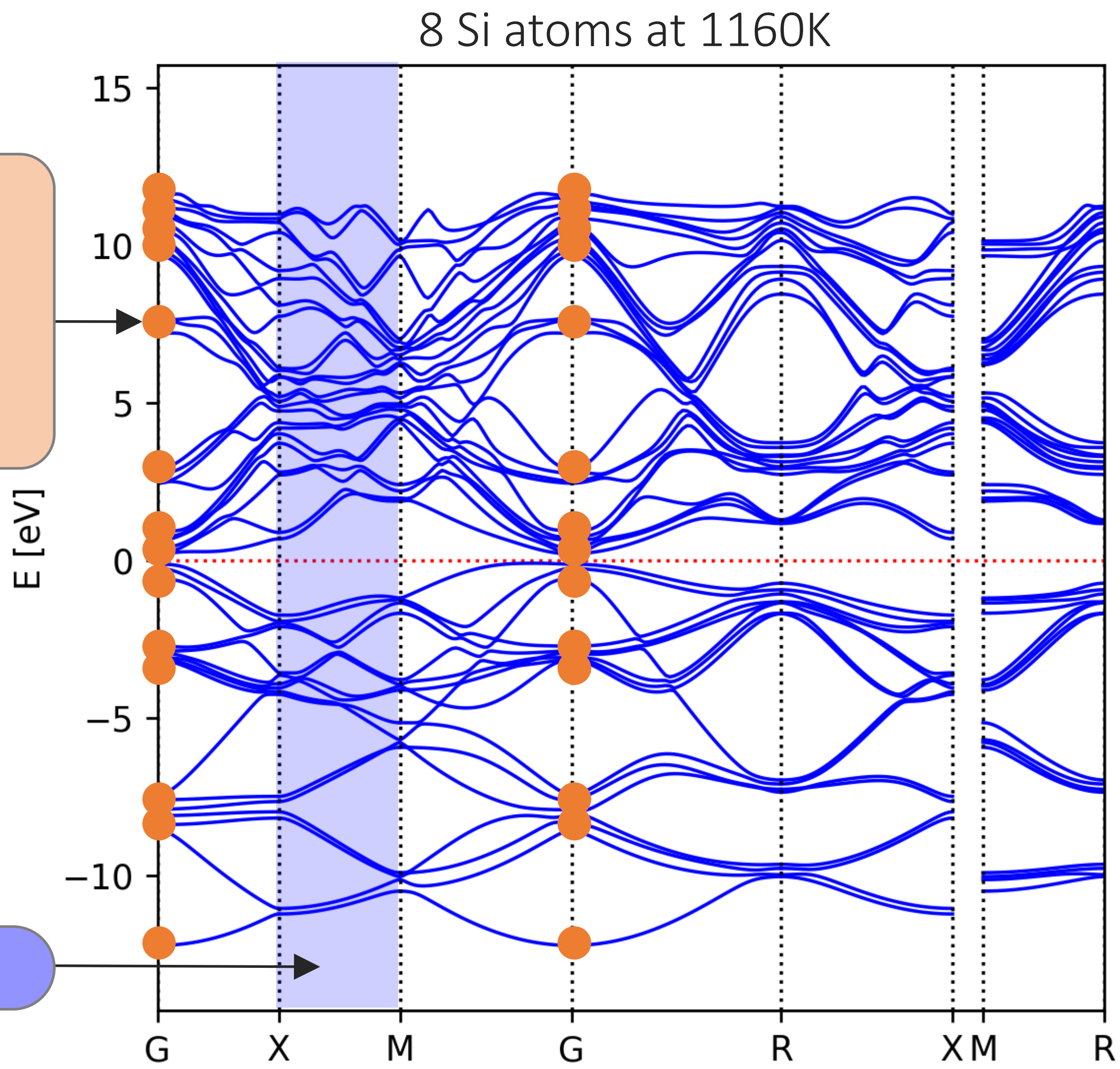
There are expensive **k**-points and cheap ones.

k_grid 1 1 1 → 1 **k**-point (SCF) → 29s time

Self-Consistent Field iterations = expensive

Fourier-Interpolation = cheap

output band ...50... → 50 **k**-points (FI) → 0.7s time



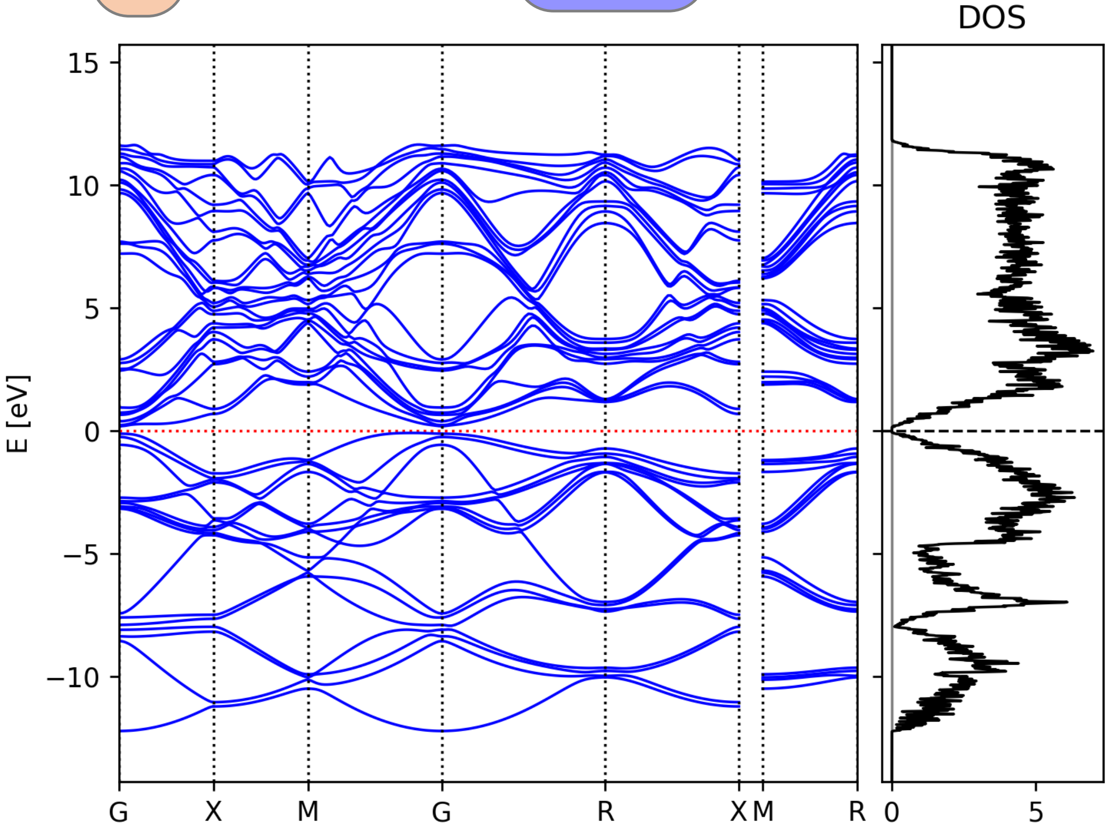
We can get similar results with the cheap and the expensive **k**-points.

1 **k**-point (SCF)

4396 **k**-points (FI)

29s time

59s time

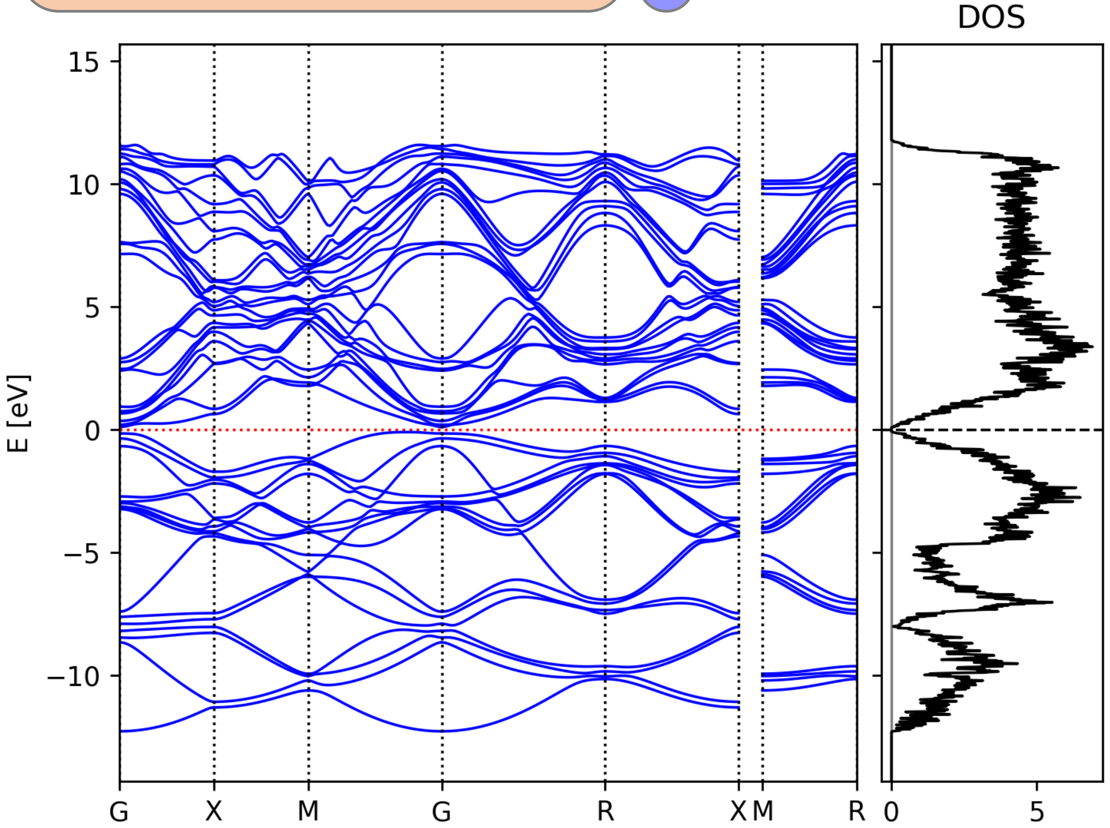


16 x 16 x 16 =
4096 **k**-points (SCF)

4396 **k**-points (FI)

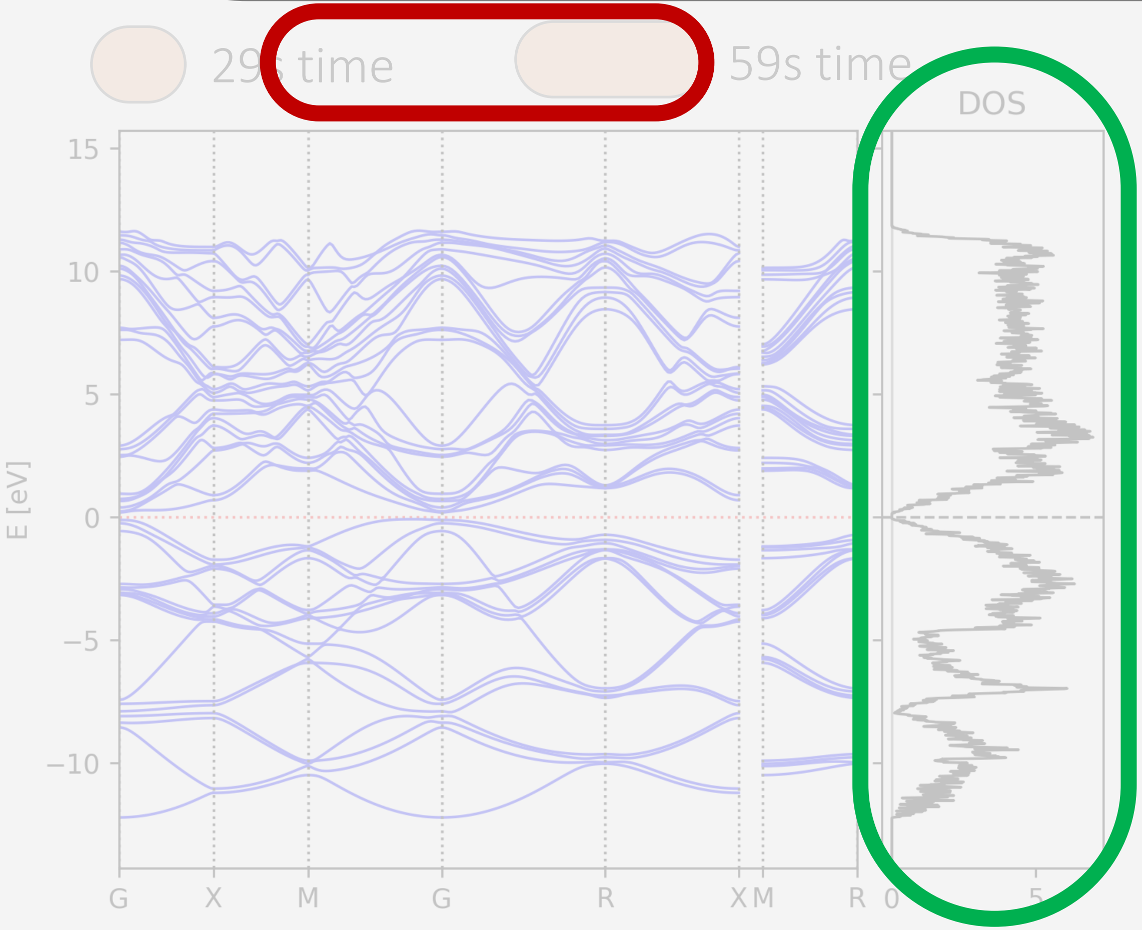
187s time

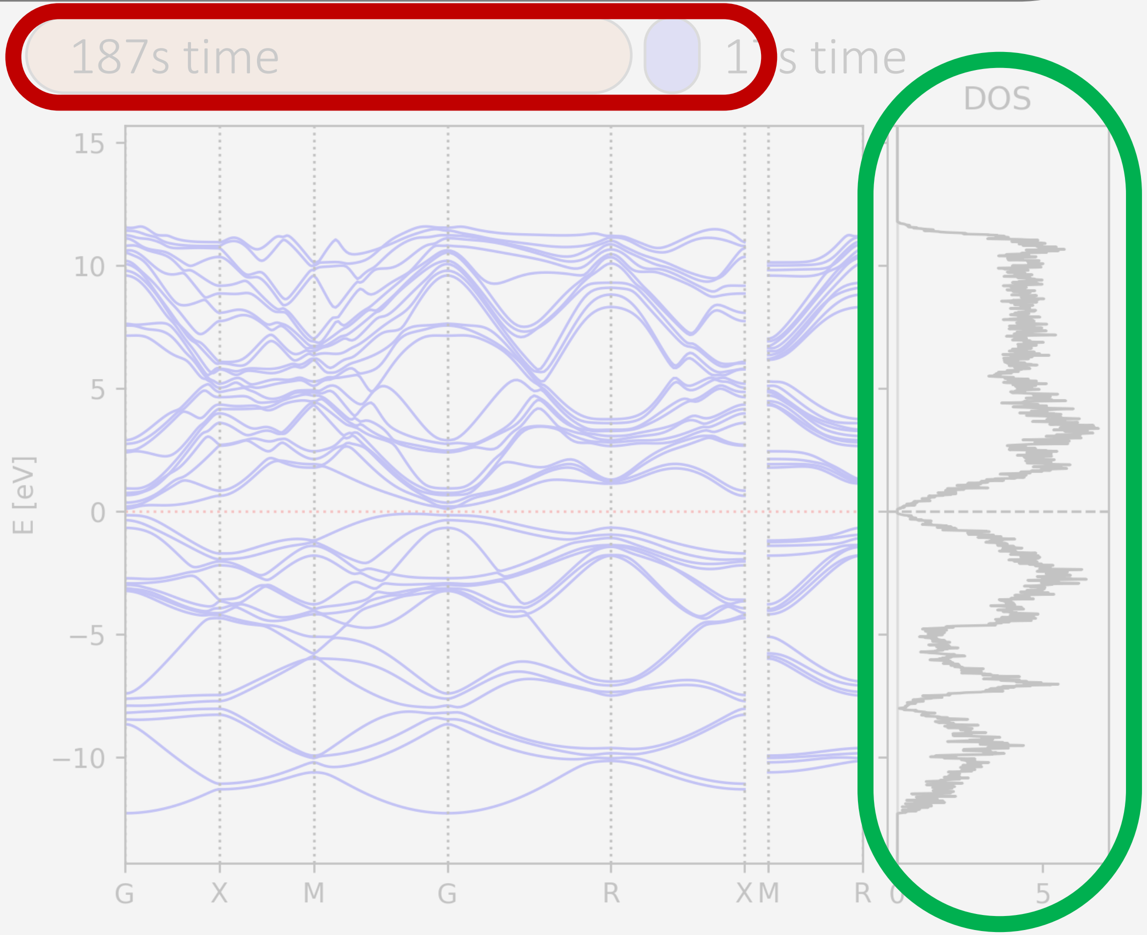
17s time



We can get similar results with the cheap and the expensive **k**-points.

Is the difference in results worth the extra cost ?

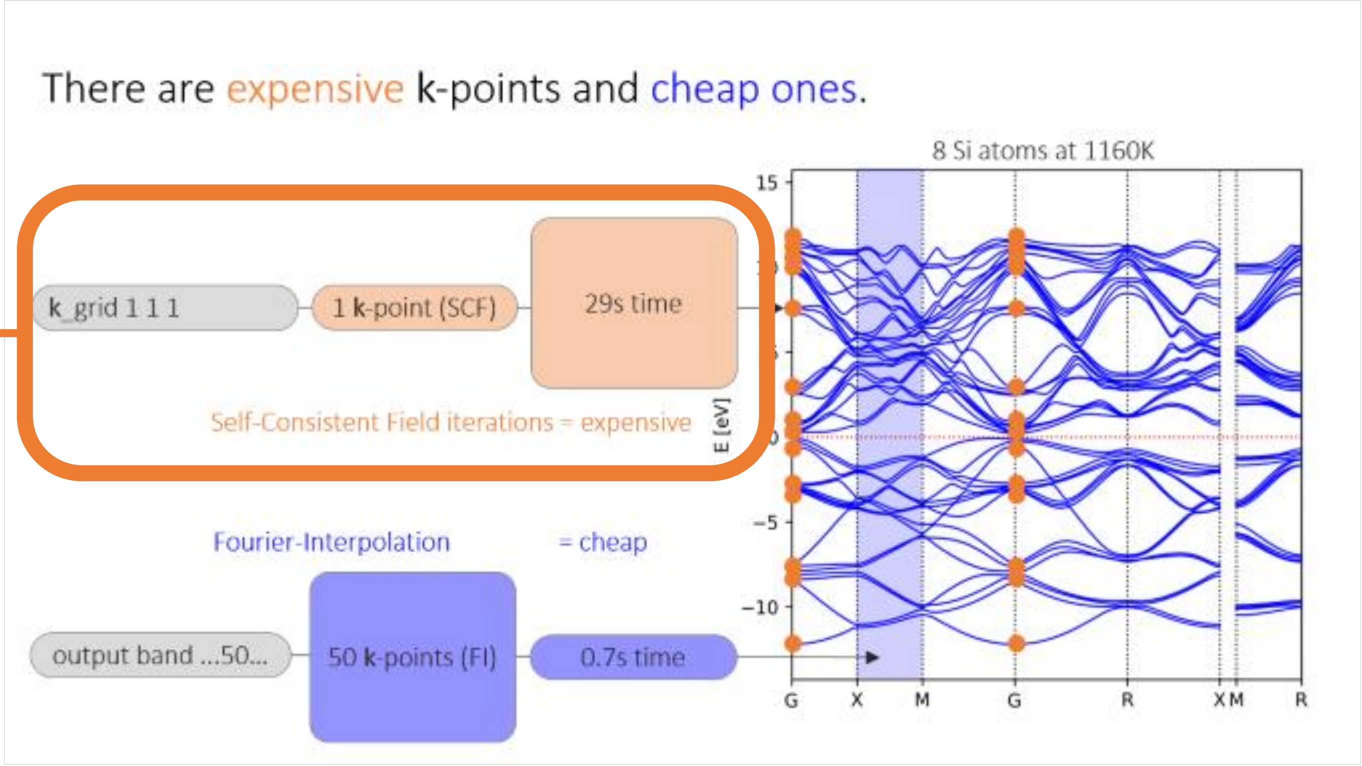




Currently we are only using the expensive **k**-points for Kubo-Greenwood.

$L_{nm}(\omega)$ is an average.

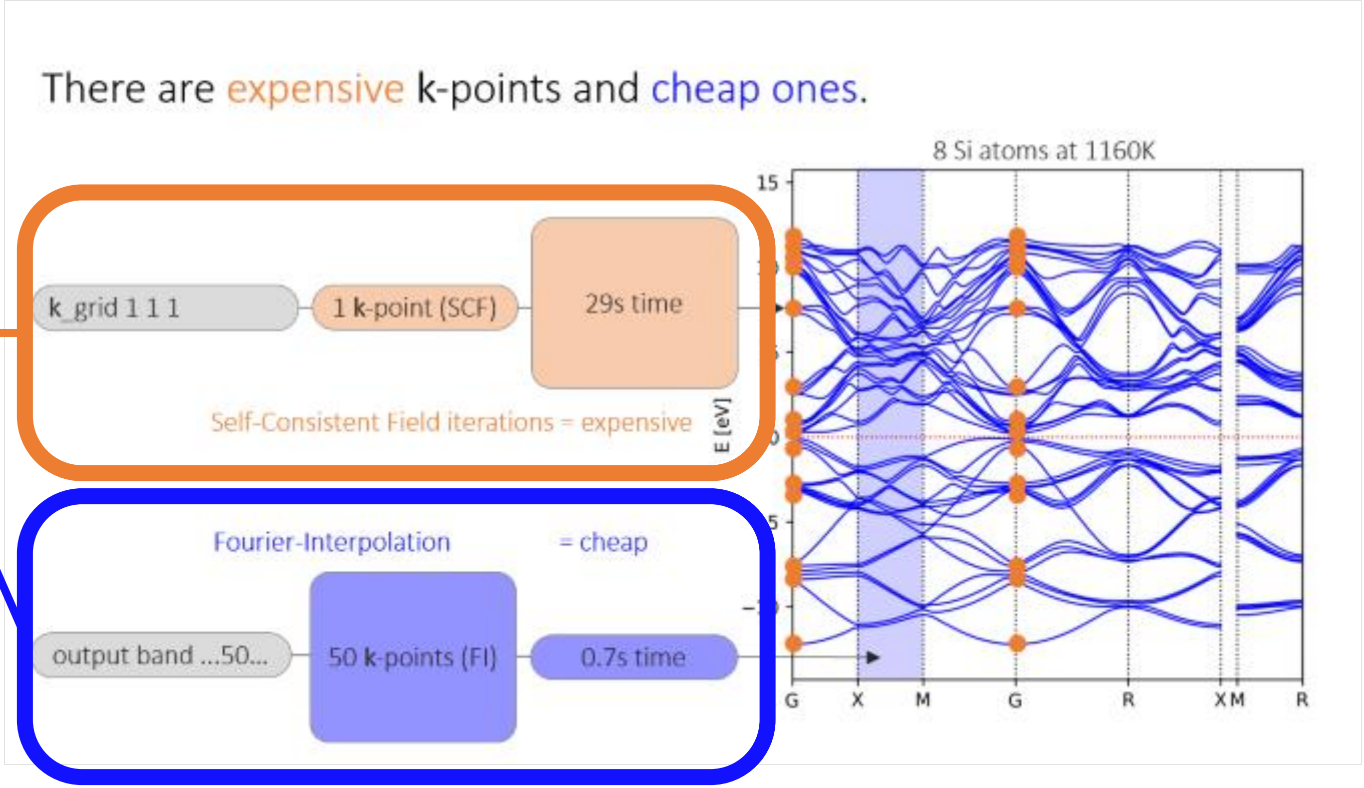
$$L_{mn}(\omega) = \frac{\frac{2\pi q^{4-m-n}}{3Vm_e^2\omega}\sum_{\mathbf{k}\nu\mu}\langle\mathbf{k}\nu|\hat{\mathbf{p}}|\mathbf{k}\mu\rangle\cdot\langle\mathbf{k}\mu|\hat{\mathbf{p}}|\mathbf{k}\nu\rangle\times\epsilon_{\mathbf{k}\nu\mathbf{k}\mu}^{m+n-2}(f_{\mathbf{k}\nu}-f_{\mathbf{k}\mu})\delta(E_{\mathbf{k}\mu}-E_{\mathbf{k}\nu}-\hbar\omega)}{\text{number of }\mathbf{k}\text{−}points}$$



We have the chance to converge Kubo-Greenwood with a cheaper **k**-grid.

$L_{nm}(\omega)$ is an average.

$$L_{mn}(\omega) = \frac{\frac{2\pi q^{4-m-n}}{3Vm_e^2\omega}\sum_{\mathbf{k}\nu\mu}\langle\mathbf{k}\nu|\hat{\mathbf{p}}|\mathbf{k}\mu\rangle\cdot\langle\mathbf{k}\mu|\hat{\mathbf{p}}|\mathbf{k}\nu\rangle\times\epsilon_{\mathbf{k}\nu\mathbf{k}\mu}^{m+n-2}(f_{\mathbf{k}\nu}-f_{\mathbf{k}\mu})\delta(E_{\mathbf{k}\mu}-E_{\mathbf{k}\nu}-\hbar\omega)}{\text{number of }\mathbf{k}-points}$$



We have the chance to converge Kubo-Greenwood with a cheaper **k**-grid.

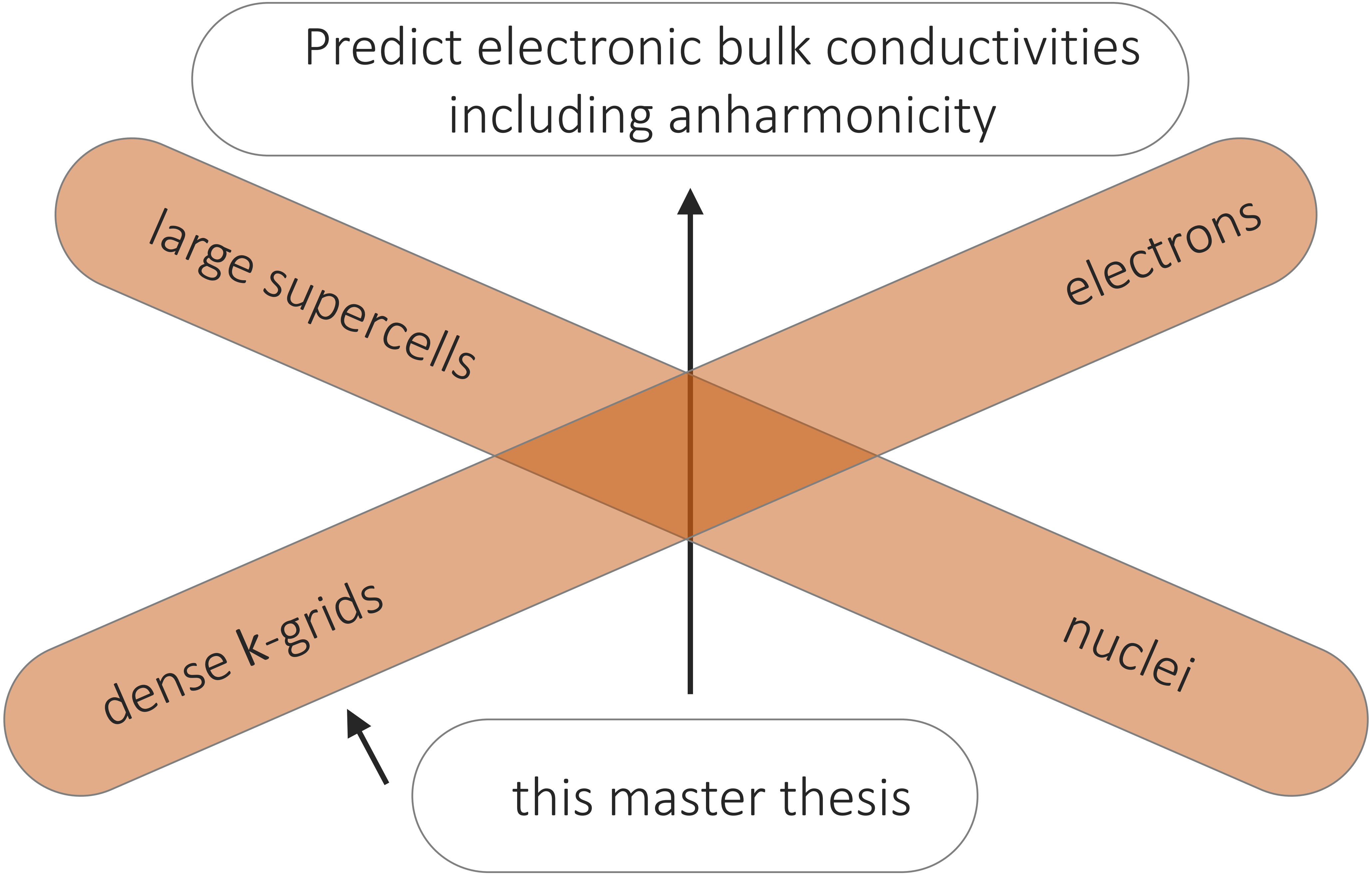
Why are many **k**-points needed ?

→ How can we make **k**-points cheaper ?

→ DFT output -> conductivities

→ illustration in the band diagramm

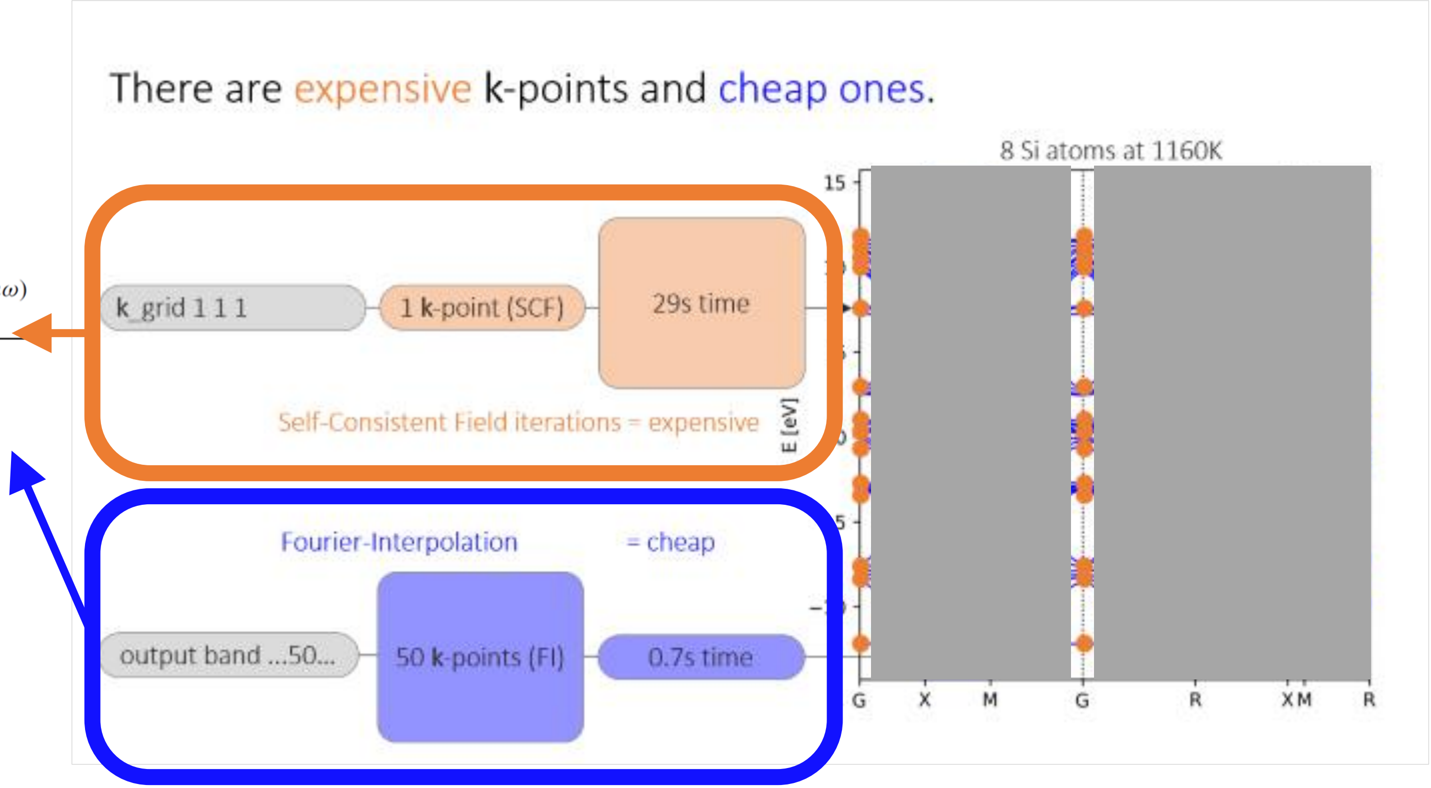
→ more **k**-points -> higher conductivities ?


Predict electronic bulk conductivities
including anharmonicity
large supercells
electrons
dense k-grids
nuclei
this master thesis

Resolve contributions to conducitivity, which we could not resolve before.

$L_{nm}(\omega)$ is an average.

$$L_{mn}(\omega) = \frac{\frac{2\pi q^{4-m-n}}{3Vm_e^2\omega}\sum_{\mathbf{k}\nu\mu}\langle\mathbf{k}\nu|\hat{\mathbf{p}}|\mathbf{k}\mu\rangle\cdot\langle\mathbf{k}\mu|\hat{\mathbf{p}}|\mathbf{k}\nu\rangle\times\epsilon_{\mathbf{k}\nu\mathbf{k}\mu}^{m+n-2}(f_{\mathbf{k}\nu}-f_{\mathbf{k}\mu})\delta(E_{\mathbf{k}\mu}-E_{\mathbf{k}\nu}-\hbar\omega)}{\text{number of }\mathbf{k}-points}$$



Thanks, Chris !

Ideas, feedback, questions ?

Literature

D. Gingerich, M. Mauter, *Environmental Science & Technology* **2015** *49* (14), 8297-8306.

C. Zhou, Y.K. Lee, Y. Yu, *et al.,* Polycrystalline SnSe with a thermoelectric figure of merit greater than the single crystal. *Nat. Mater.* **20**, 1378–1384 (2021).

A. Togo, L. Chaput, and I. Tanaka, “Distributions of phonon lifetimes in brillouin zones”, Physical Review B **91**, 094306 (2015).

D. L. Perry, *Handbook of Inorganic Compounds*, Zeroth (CRC Press, Apr. 2016).

F. Knoop, Heat transport in strongly anharmonic solids from first principles (Dissertation, theoretische Physik), Humboldt-Universität zu Berlin, 2022.

S. Poncé, E. Margine, F. Giustino: Towards predictive many-body calculations of phonon-limited carrier mobilities in semiconductors, Phys. Rev. B **97**, 121201(R), 2018

P. Norton, T. Braggins, and H. Levinstein: Drift and Conductivity Mobility in Silicon, Phys. Rev. B **8**, 5632, 1956

B. Holst, M. French, R. Redmer, Electronic transport coefficients from *ab initio* simulations and application to dense liquid hydrogen, Phys. Rev. B **83**, 235120, 2011.