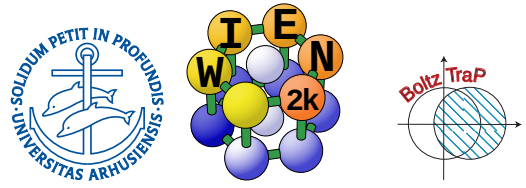
LDA+U and Semiclassic transport



Georg Madsen

georg@chem.au.dk

University of Aarhus

LDA+U

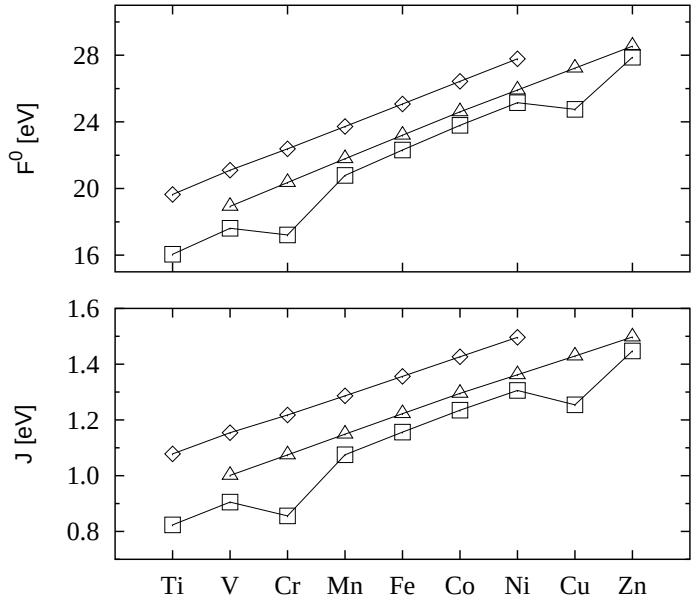
$$E^{LDA+U}(n,\hat{n}) = E^{LDA}(n) + E^{orb}(\hat{n}) - E^{DCC}(n)$$

- identify a set of atomic like orbitals which are treated in a non-LDA manner.
  - treated with an orbital dependent potential with an associated on-site Coulomb and exchange interactions, U and J.
  - identify the electron-electron interactions that are allready present in LDA and correct for the double counting

U and J in an atom

U: the cost in Coulomb energy by placing two electrons on the same site. F^0 of the unscreened Slater integrals in atom

$$F^k_{nl} = \int_0^\infty r^2 dr \int_0^\infty (r')^2 dr' \frac{r^k_<}{r^{k+1}_>} \phi^2_{nl}(r)\phi^2_{nl}(r') = U^{atomic/unscreened}$$



F^0 increases with increased ionicity and as the d-wave function is contracted across the 3d transition series.

U and J in a solid

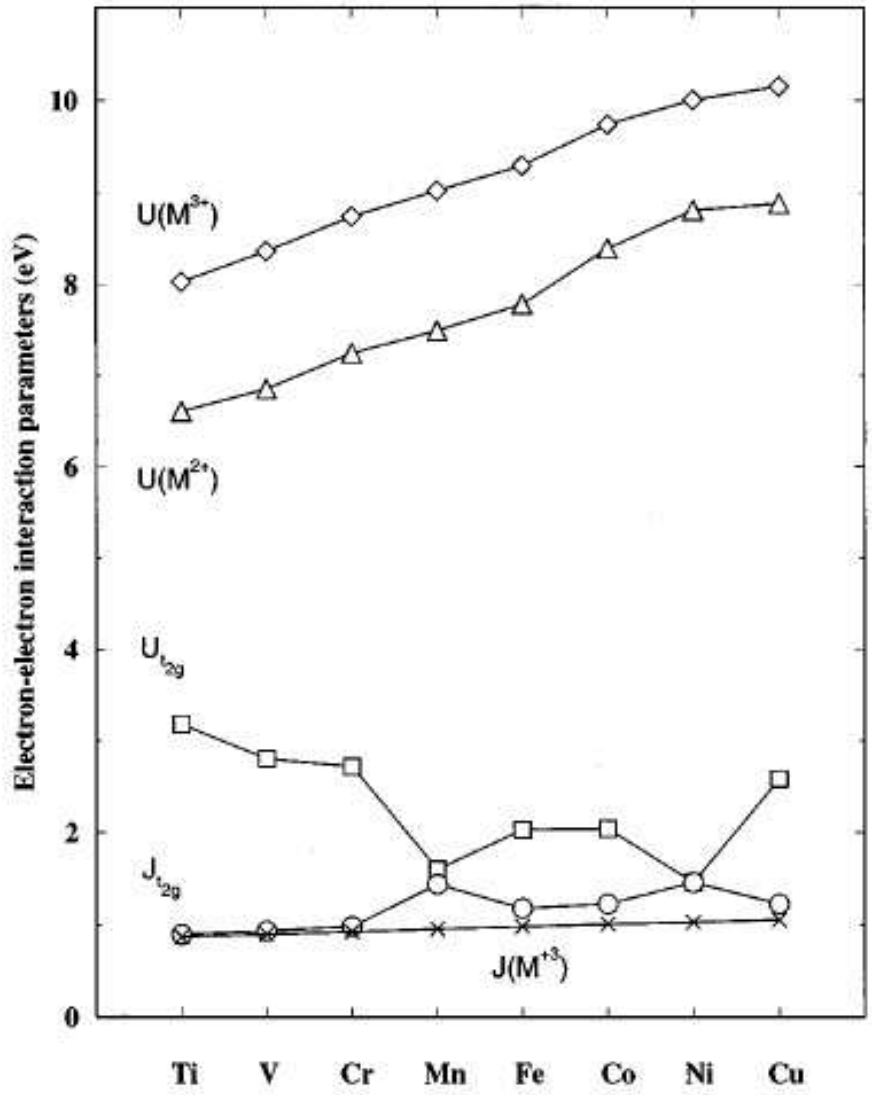
Due to screening the effective U in solids is much smaller than F^0 for atoms. To calculate the effective U Anisimov and Gunnarsson, constructed a supercell and set the hopping integrals connecting the $3d$ orbital of one atom with all other orbitals to zero. The number of electrons in this non-hybridizing d-shell was varied and F^0_{eff} was then calculated from

$$\begin{aligned} F^0_{eff} =& \varepsilon_{3d\uparrow}((n+1)/2, n/2) - \varepsilon_{3d\uparrow}((n+1)/2, n/2-1) \\ & - \varepsilon_F((n+1)/2, n/2) + \varepsilon_F((n+1)/2, n/2-1) \end{aligned}$$

where $\varepsilon_{3d\uparrow}$ is the spin-up $3d$ eigenvalue.

Anisimov and Gunnarsson, PRB **43**, 7570

U and J in a solid



I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).

E^{orb}

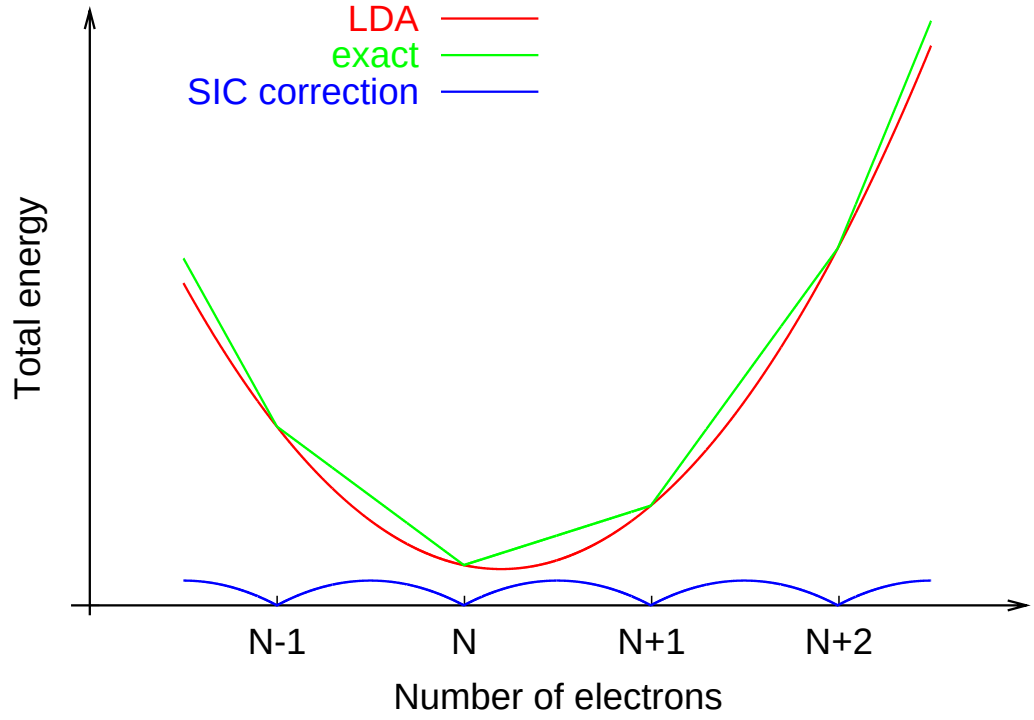
$$E^{orb}(\hat{n}) = -\frac{U-J}{2}\sum_{\sigma} Tr(\hat{n}^{\sigma}\cdot\hat{n}^{\sigma})$$

- $\hat{n}$ is the orbital occupation matrix (OOM).
  - Rotationally invariant
  - Depends on “atomic orbitals” (projection of wave-function onto basis functions corresponding to certain atomic l-values)

Double counting correction.

Fully localized limit, $n_\sigma = Tr(\hat{n}^\sigma)/(2l+1)$.

$$E_{FLL}^{DCC} = -\left(\frac{U}{2}n(n-1) - \frac{J}{2}\sum_\sigma n^\sigma(n^\sigma - 1)\right) = -\frac{U-J}{2}\sum_\sigma (2l+1)n^\sigma$$



Anisimov et al., PRB **48**, 16929

The orbital dependent potential

The orbital dependent potentials entering the Kohn-Sham equation that arise from the $E^{orb} - E^{DCC}_{FLL}$ correction to the total energy

$$\Delta V^{U\sigma}_{FLL} = \frac{\partial(E^{orb} - E^{DCC}_{FLL})}{\partial n^{\sigma}} = -(U - J)(\hat{n}^{\sigma} - \frac{1}{2}I)$$

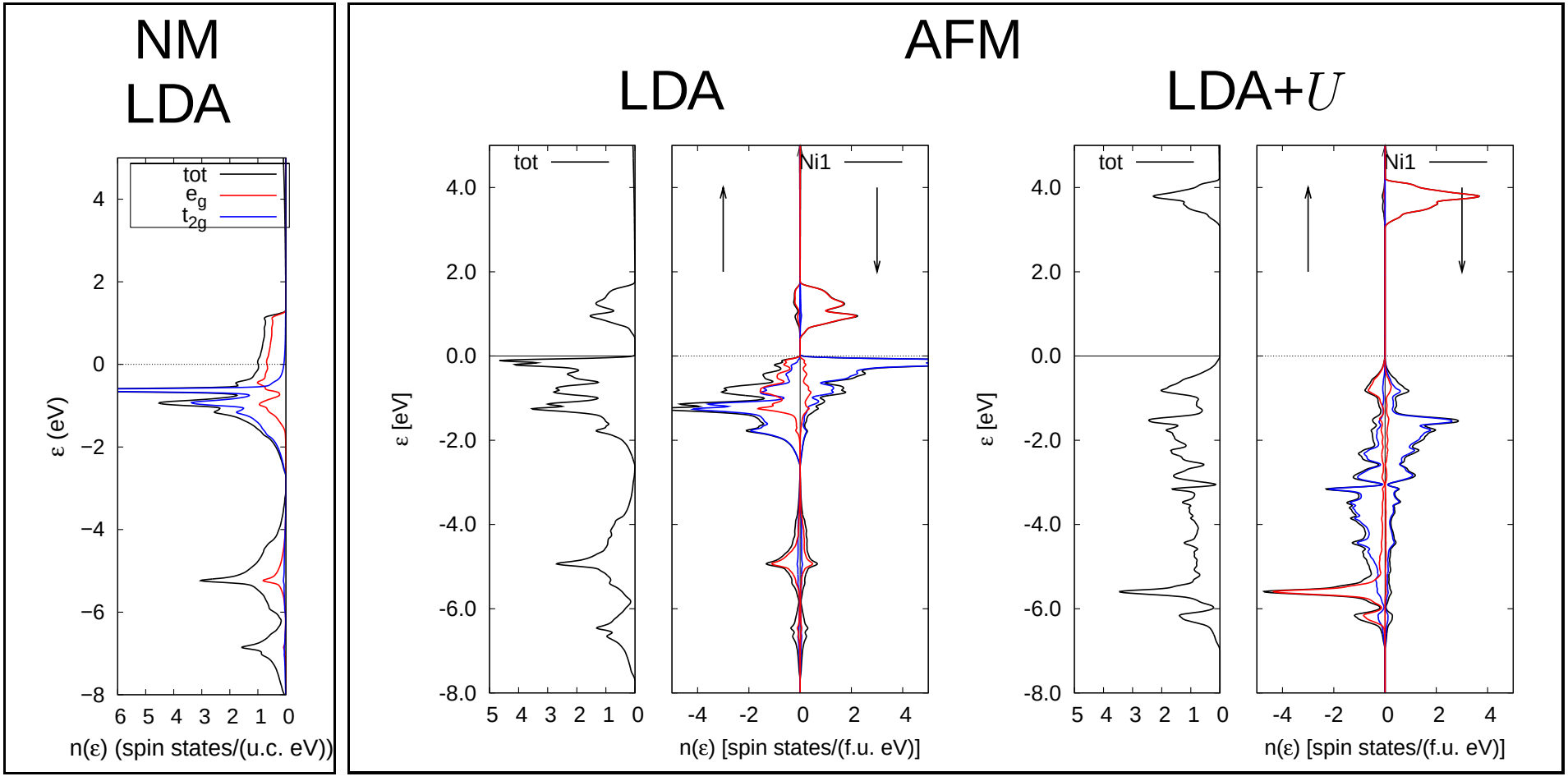
The orbital dependent potential

The orbital dependent potentials entering the Kohn-Sham equation that arise from the $E^{orb} - E^{DCC}_{FLL}$ correction to the total energy

$$\Delta V^{U\sigma}_{FLL} = \frac{\partial(E^{orb} - E^{DCC}_{FLL})}{\partial n^{\sigma}} = -(U - J)(\hat{n}^{\sigma} - \frac{1}{2}I)$$

- stabilizes an orbital that is more than half occupied
- destabilize an orbital that is less than half occupied.

NiO. Electronic structure.



TbN properties

LDA

B_{xc}	$\#g$	s_z	l_z	E
[001]	16	5.827	1.470	-23531.760614
[011]	8	5.836	1.353	-23531.760272
[111]	12	5.836	1.347	-23531.760239

Magneto crystallline anisotropy energy

LDA+U

B_{xc}	s_z	l_z	E
[001]	5.870	1.854	-23531.693142
[011]	5.870	1.580	-23531.691680
[111]	5.870	1.515	-23531.691371

- Obey Hund's 2nd rule
- Enhanced MCAE

Calculating U within APW

- Within the LAPW method one cannot identify individual hopping terms
- Remove hybridization by:
  - putting the d-states into the core
  - performing a two-window calculation.
- NiO with the impurity sites on the FCC sites in a $2 \times 2 \times 2$ supercell.
  - F^0_{eff}=5.96 eV.

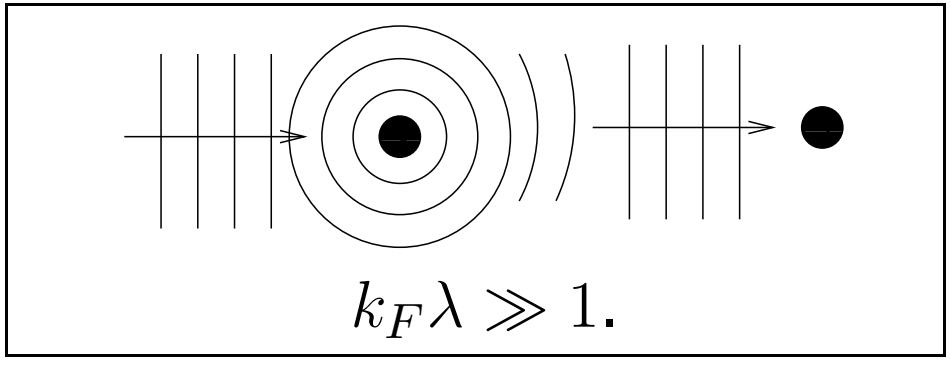
Madsen and Novak, Europhys. Lett., 69, p777

Boltzmann Equation

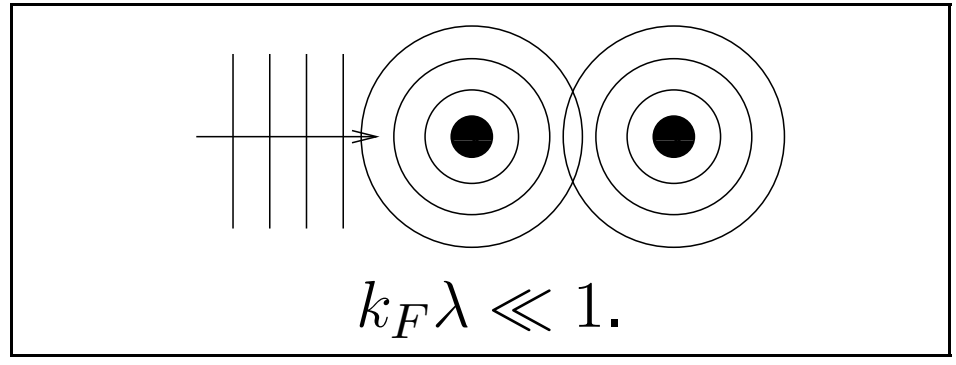
The *steady state* distribution $f_{\mathbf{k}}$ is constant in time

$$\left.\frac{\partial f_{\mathbf{k}}}{\partial t}\right|_{\text{diff}} + \left.\frac{\partial f_{\mathbf{k}}}{\partial t}\right|_{\text{field}} + \left.\frac{\partial f_{\mathbf{k}}}{\partial t}\right|_{\text{scatt}} = 0$$

Assumption:
$\mathbf{k}$ should be a good quantum number. i.e. wavelength of electron small compared to mean free path. $k_F\lambda >> 1$.



$k_F\lambda \gg 1.$



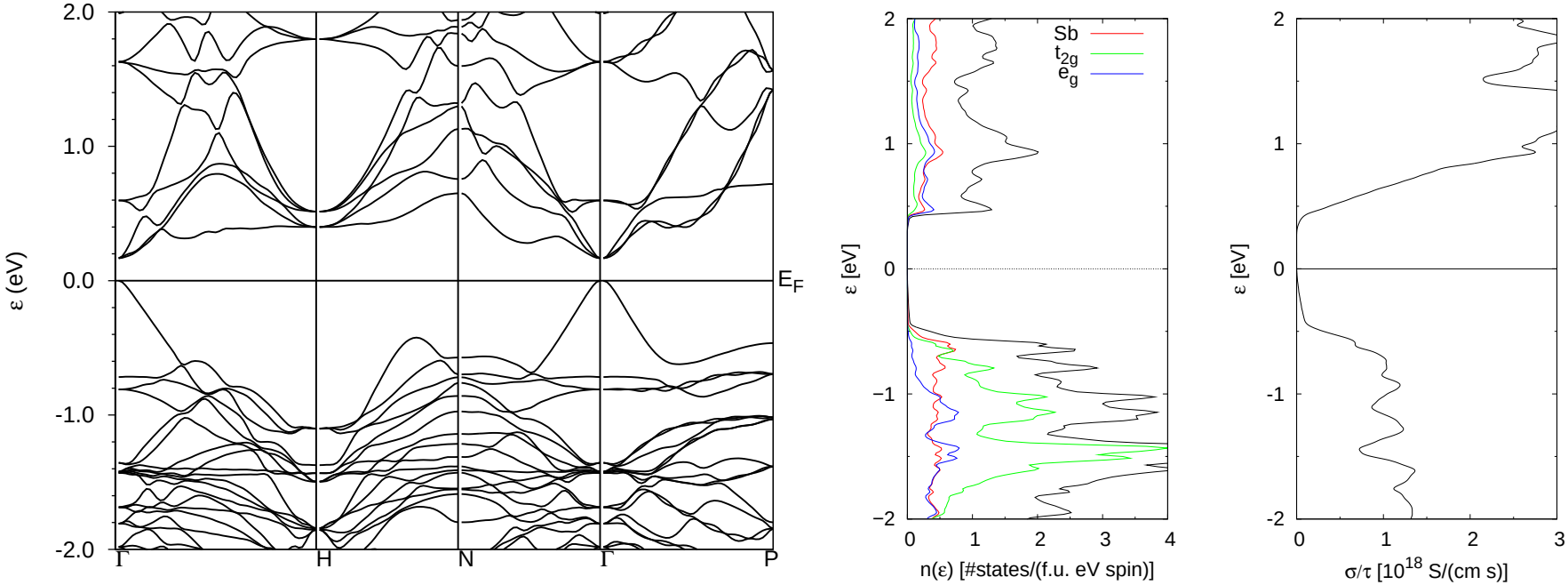
$k_F\lambda \ll 1.$

Transport distribution

$$\sigma_{\alpha\beta}(i,\mathbf{k}) = e^2 \tau_{i,\mathbf{k}} v_\alpha(i,\mathbf{k}) v_\beta(i,\mathbf{k})$$

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{1}{N} \sum_{i,\mathbf{k}} \sigma_{\alpha\beta}(i,\mathbf{k}) \frac{\delta(\varepsilon - \varepsilon_{i,\mathbf{k}})}{d\varepsilon}$$

$CoSb_3$



Rigid band approximation

$$\sigma_{\alpha\beta}(T;\mu) = \int \sigma_{\alpha\beta}(\varepsilon)\Big[-\frac{\partial f_\mu(T;\varepsilon)}{\partial\varepsilon}\Big]d\varepsilon$$

$$\nu_{\alpha\beta}(T;\mu) = \frac{1}{eT}\int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)\Big[-\frac{\partial f_\mu(T;\varepsilon)}{\partial\varepsilon}\Big]d\varepsilon$$

- $S = \nu/\sigma$, constant relaxationion time => S independent of τ.
- S and the effective mass, σ/τ, can be calculated as a function of temperature and chemical potential/doping

Program: BoltzTraP

Smoothed Fourier expansion of band energies

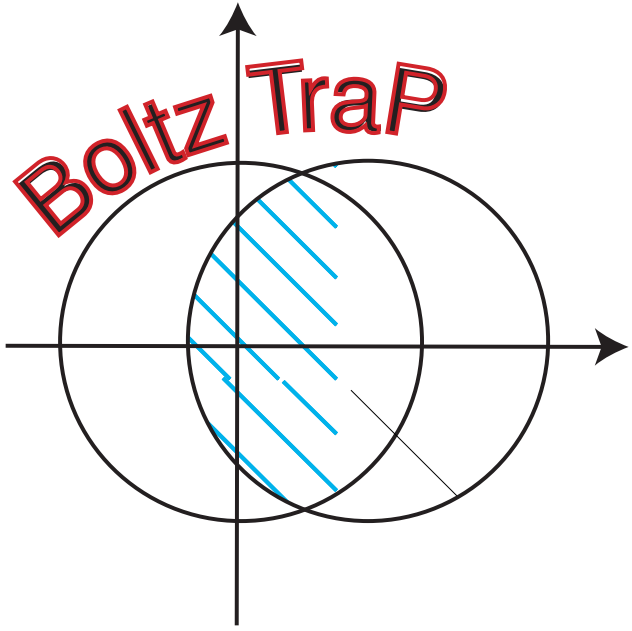
$$\varepsilon_i(\mathbf{k}) = \sum_{\mathbf{R}} \frac{1}{n_{\mathbf{R}}} c_{\mathbf{R},i} e^{i\mathbf{k}\cdot\mathbf{R}}$$

Pickett, Krakauer, Allen, PRB **38**, 2721

$$\frac{\partial \varepsilon_{i,\mathbf{k}}}{\partial k_\alpha} = \sum_{\mathbf{R}} \frac{i\mathbf{R}_\alpha}{n_{\mathbf{R}}} c_{\mathbf{R},i} e^{i\mathbf{k}\cdot\mathbf{R}}$$

Transport distribution

$$\sigma(\varepsilon) = \frac{1}{N} \sum \sigma_{i,\mathbf{k}} \frac{\delta(\varepsilon - \varepsilon_{i,\mathbf{k}})}{d\varepsilon}$$

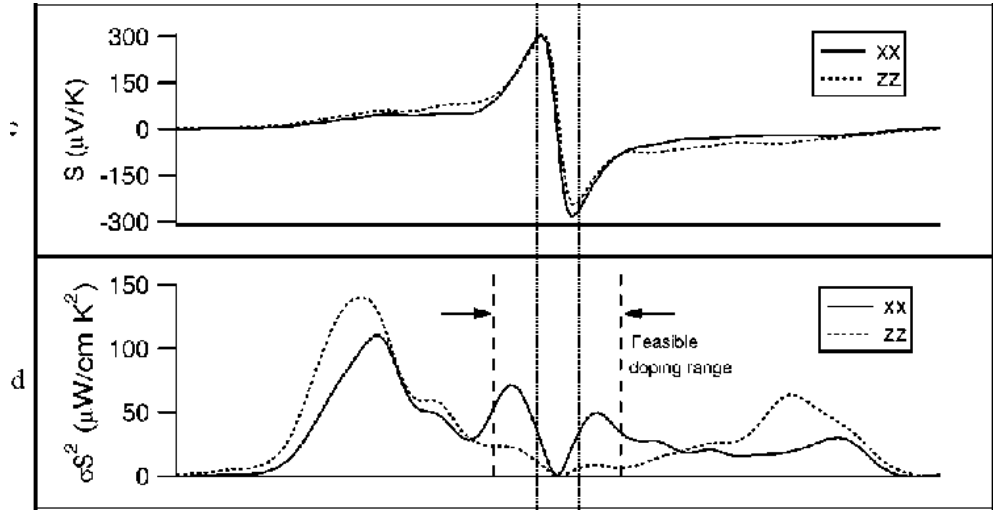


Rigid band approach

$$\sigma(\mu, T) = \int \sigma(\varepsilon) \left[-\frac{\partial f_\mu(T;\varepsilon)}{\partial \varepsilon} \right] \mathrm{d}\varepsilon$$

www.chem.au.dk/∼webuorg/gm/BoltzTraP.html

Testing BoltzTraP. Bi_2Te_3

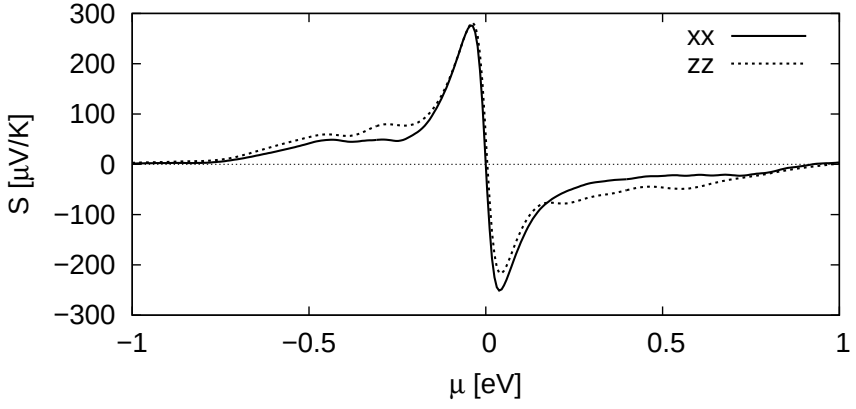


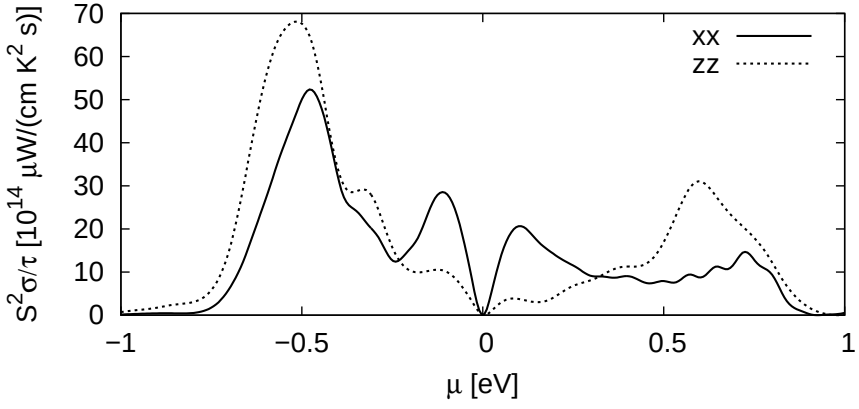
Calculate group velocities from momentum matrix elements.

$$v_\alpha(i,\mathbf{k}) = \frac{1}{m_e}\langle\psi(i,\mathbf{k})|\hat{p}_\alpha|\psi(i,\mathbf{k})\rangle$$

Scheidemantel, Ambrosch-Draxl, Thonhauser, Badding, Sofo *Phys. Rev. B* **68**, p125210

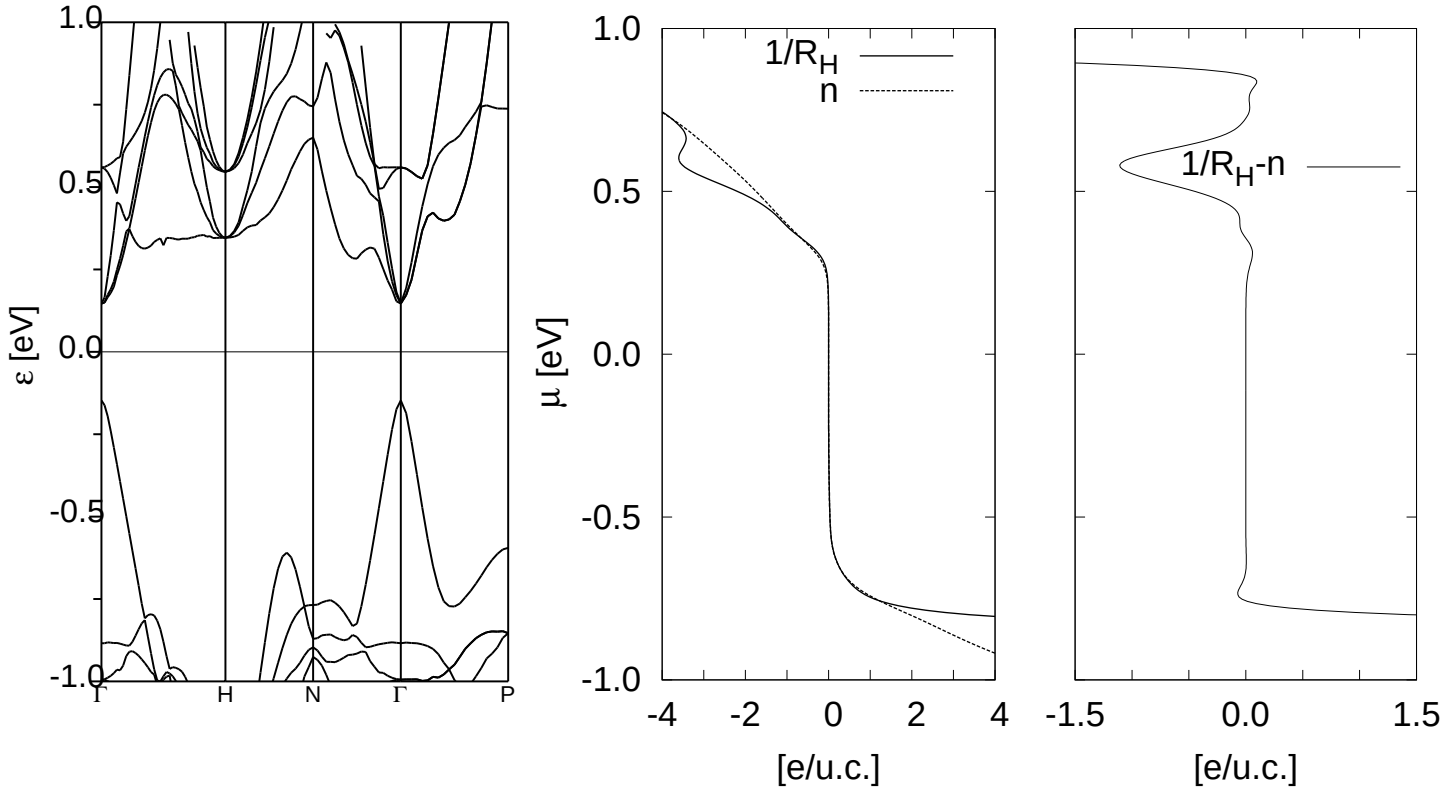
BoltzTraP:





Madsen, Singh, Comp. Phys. Comm. in press.

Hall coefficient. $CoSb_3$



- parabolic band makes Hall coefficient inversely proportional to the doping

Madsen, Singh, Comp. Phys. Comm. in press.