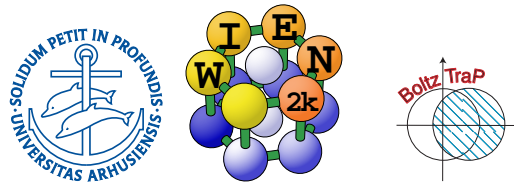


LDA+ U and Semiclassic transport



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LDA+U

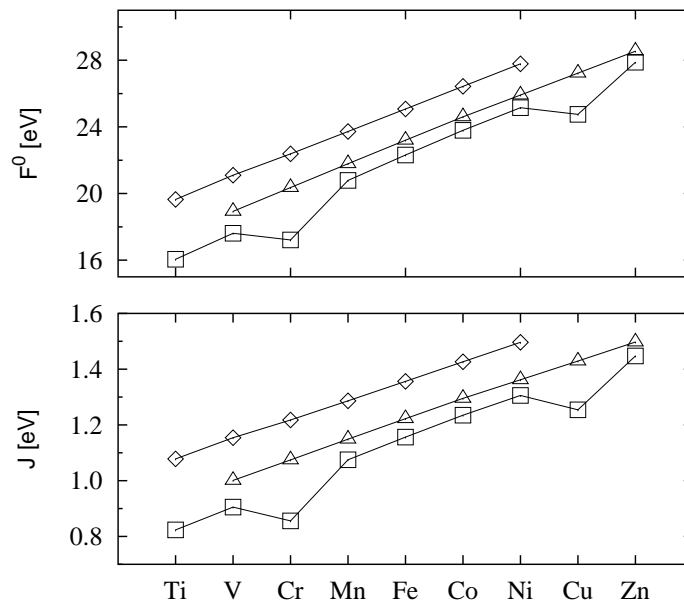
$$E^{LDA+U}(n, \hat{n}) = E^{LDA}(n) + E^{orb}(\hat{n}) - E^{DCC}(n)$$

- 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 already 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

$$F_{nl}^k = \int_0^\infty r^2 dr \int_0^\infty (r')^2 dr' \frac{r_{<}^k}{r_{>}^{k+1}} \phi_{nl}^2(r) \phi_{nl}^2(r') = U^{atomic/unscreened}$$



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

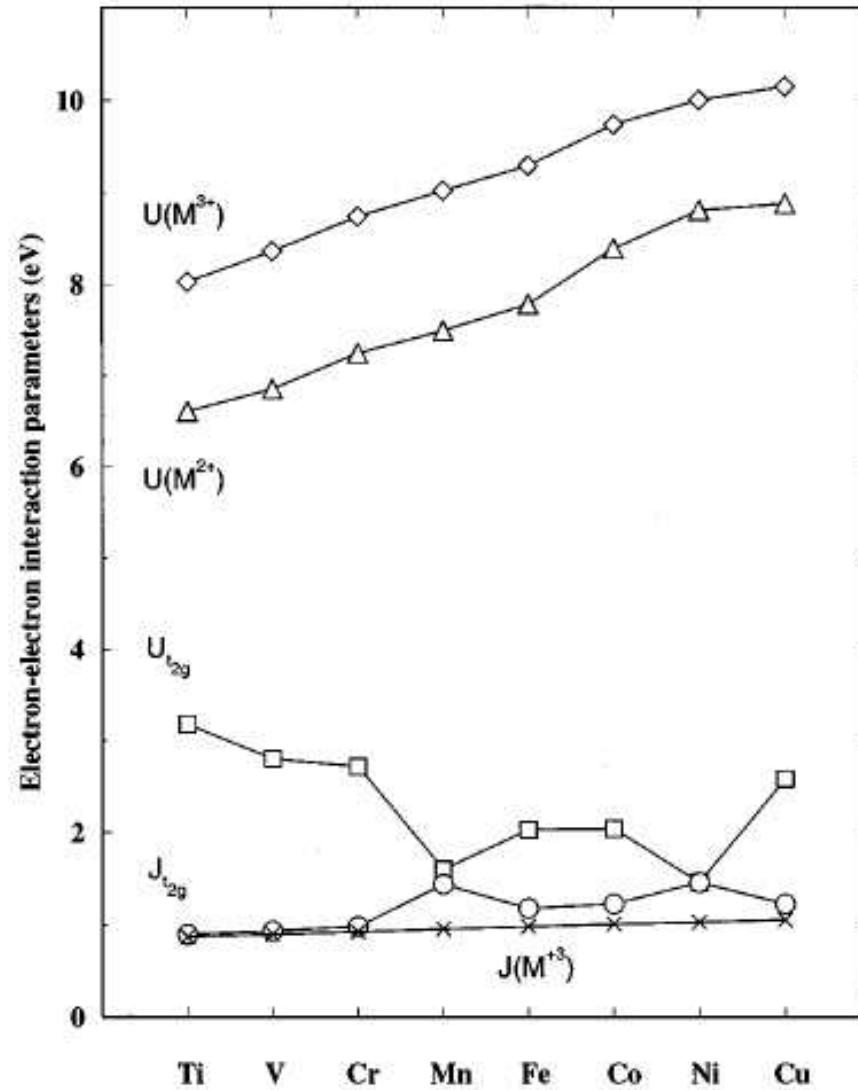
Due to screening the effective U in solids is much smaller than F^0 for atoms. To calculate the effective U Anisimov and Gunnarsson, constructed a supercell and set the hopping integrals connecting the $3d$ orbital of one atom with all other orbitals to zero. The number of electrons in this non-hybridizing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

$$F_{eff}^0 = \varepsilon_{3d\uparrow}((n+1)/2, n/2) - \varepsilon_{3d\uparrow}((n+1)/2, n/2 - 1) \\ - \varepsilon_F((n+1)/2, n/2) + \varepsilon_F((n+1)/2, n/2 - 1)$$

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

Anisimov and Gunnarsson, PRB 43, 7570

U and J in a solid



E^{orb}

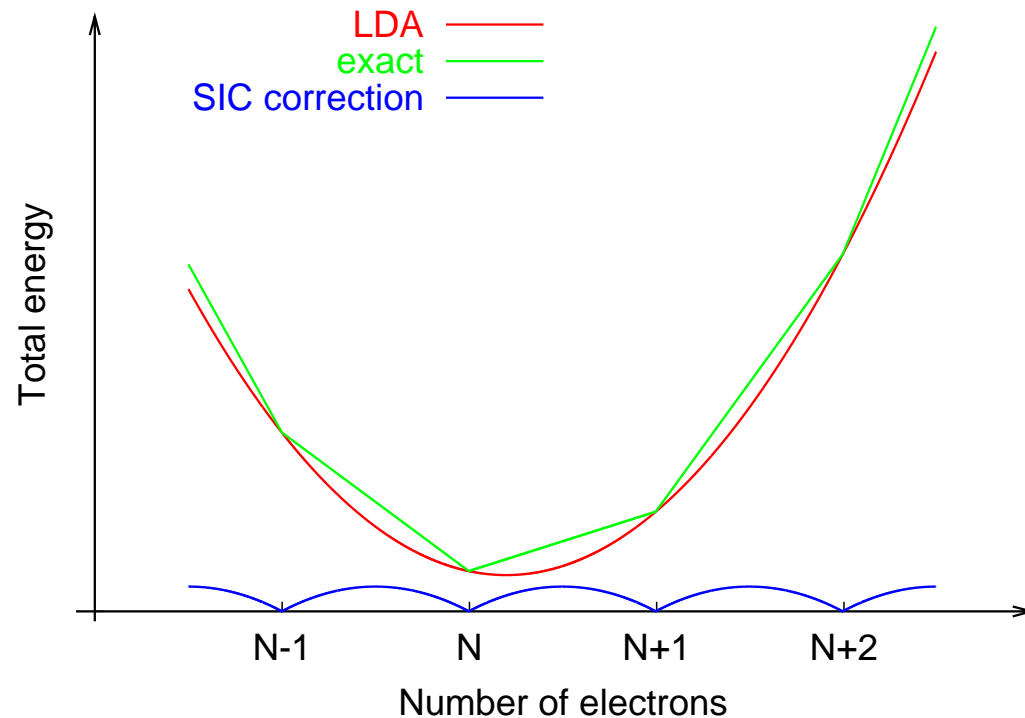
$$E^{orb}(\hat{n}) = -\frac{U - J}{2} \sum_{\sigma} Tr(\hat{n}^{\sigma} \cdot \hat{n}^{\sigma})$$

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

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



The orbital dependent potential

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

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

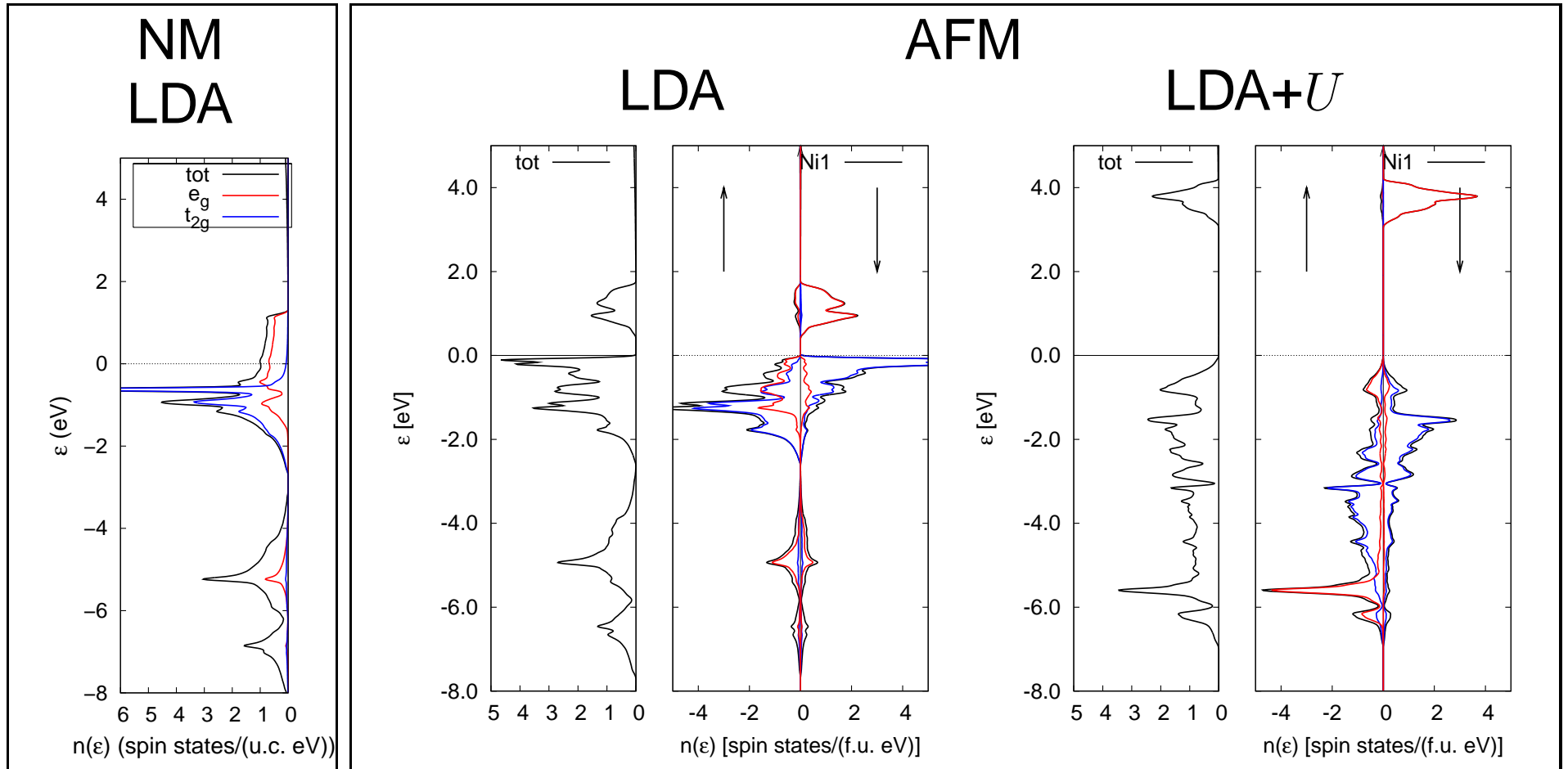
The orbital dependent potential

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

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

- 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 crystalline 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.
 - $F_{eff}^0 = 5.96$ eV.

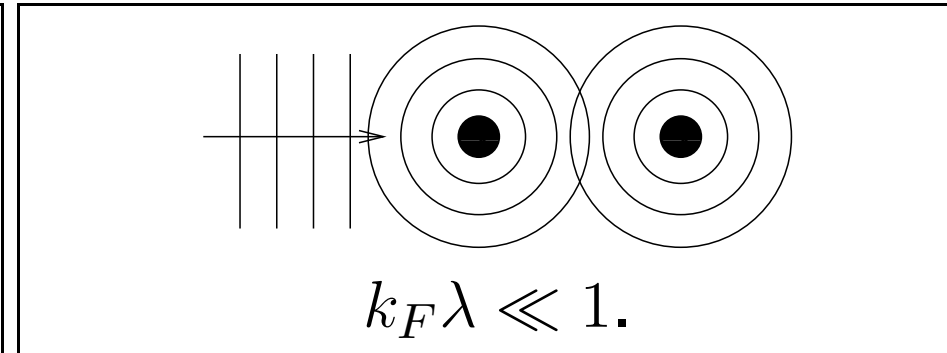
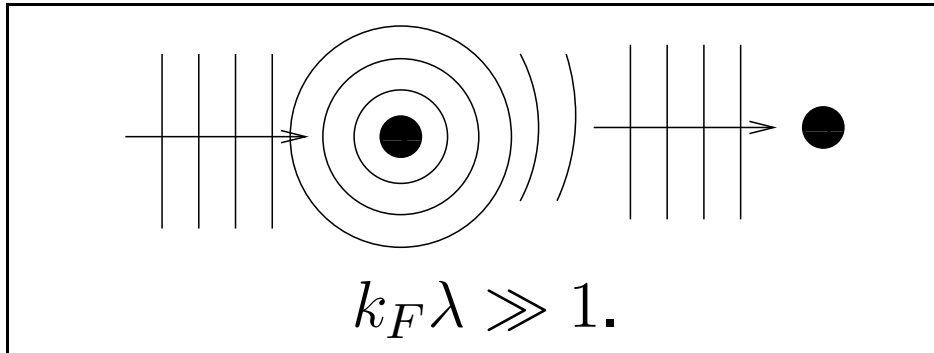
Boltzmann Equation

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. $k_F \lambda \gg 1$.

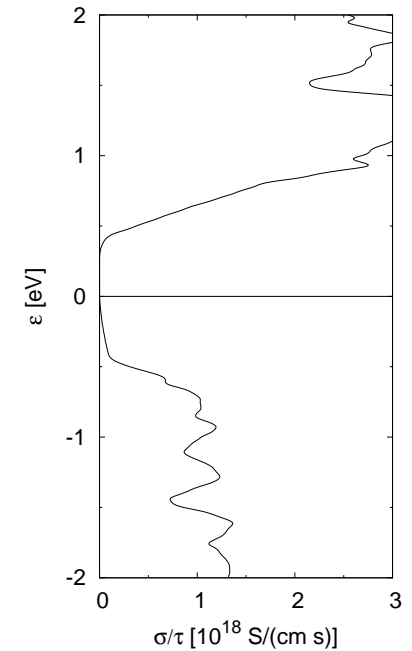
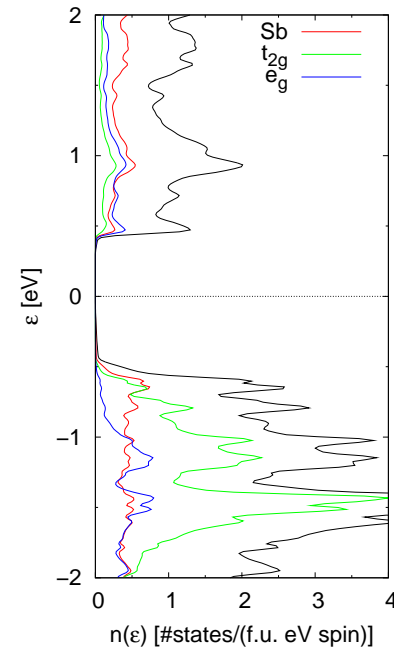
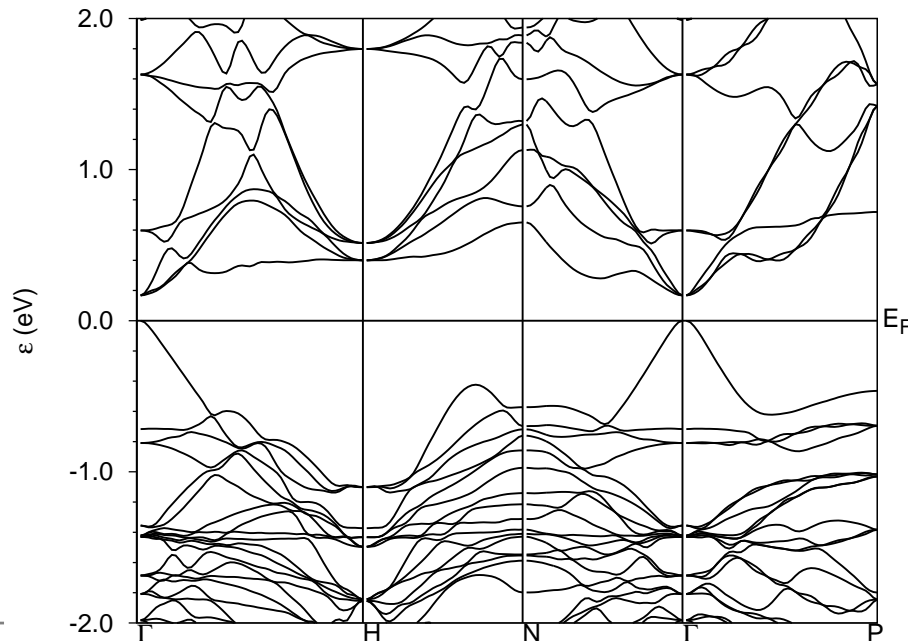


Transport distribution

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

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

CoSb₃



Rigid band approximation

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

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

- $S = \nu/\sigma$, constant relaxation time $\Rightarrow S$ 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

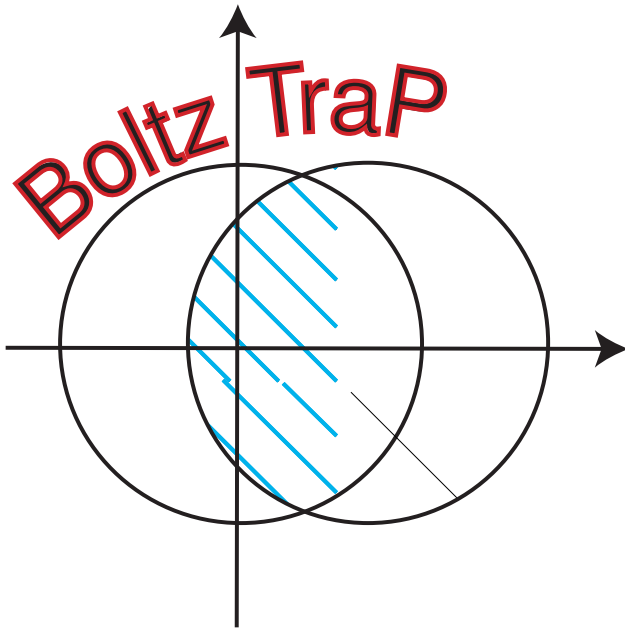
$$\varepsilon_i(\mathbf{k}) = \sum_{\mathbf{R}} \frac{1}{n_{\mathbf{R}}} c_{\mathbf{R},i} e^{i\mathbf{k}\cdot\mathbf{R}}$$

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

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



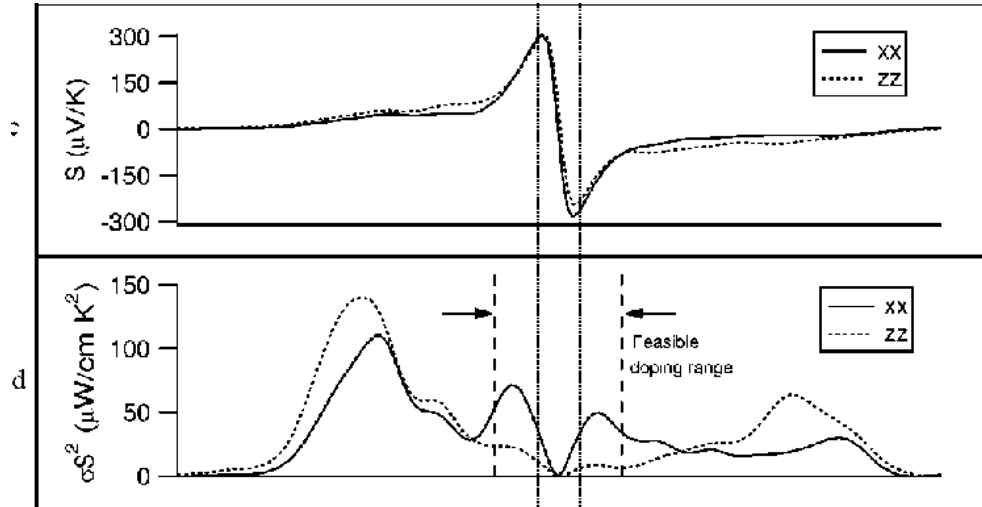
Rigid band approach

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

Testing BoltzTraP. Bi_2Te_3

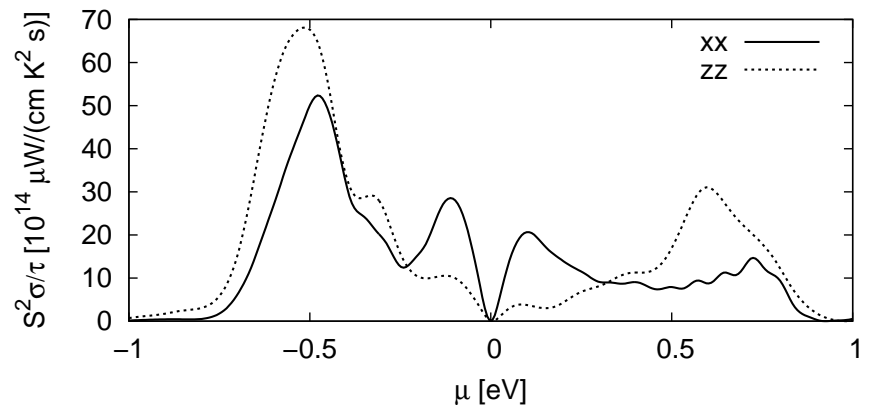
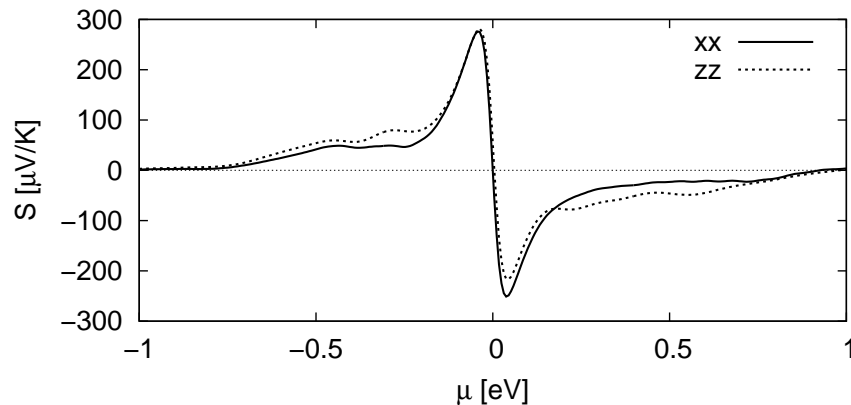
Calculate group velocities from momentum matrix elements.

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



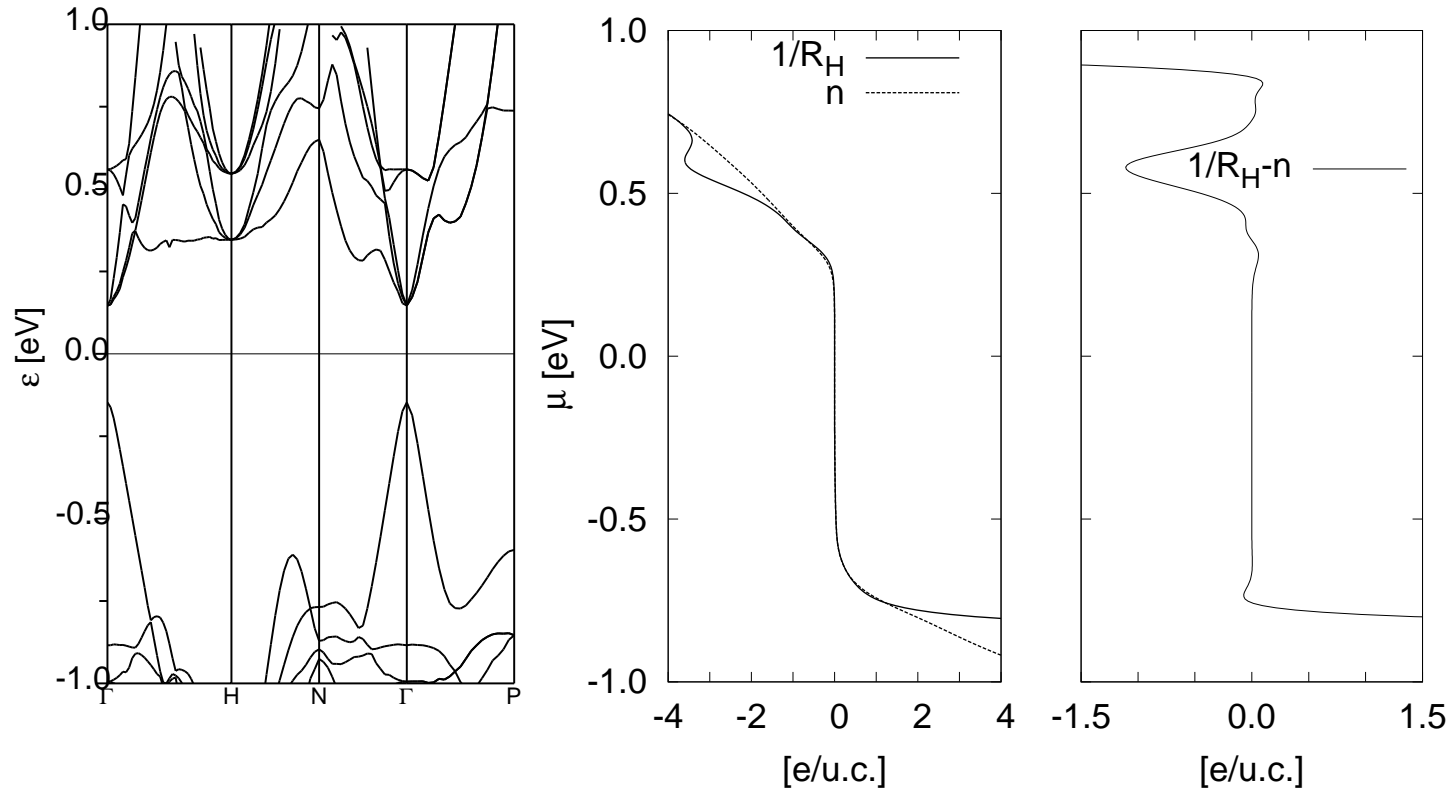
Scheidemantel, Ambrosch-Draxl, Thonhauser, Badding, Sofo *Phys. Rev. B* **68**, p125210

BoltzTraP:



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

Hall coefficient. CoSb_3



- parabolic band makes Hall coefficient inversely proportional to the doping