Details on the calculations

Viola Ferretti

1 Single-parabolic-band model

L_i is the transport integral, given by:

$$L_i = \int \mathcal{T}(E)(E-\mu)^i \left(-\frac{\partial f}{\partial E}\right) dE \tag{1}$$

μ is the chemical potential (in eV), or the Fermi energy E_F as long as the temperature is less than 10^2 K, which is the vast majority of the cases of interest. E is the energy of the charge carrier and $f_0 = \frac{1}{\exp\left(\frac{E-E_F}{k_B T}\right)+1}$ is the Fermi-Dirac distribution function. $\mathcal{T}(E)$ is defined as:

$$\mathcal{T}(E) = v^2(E)\tau(E)\mathcal{D}(E) \tag{2}$$

where v is the group velocity, τ is the relaxation time and $\mathcal{D}$ is the density of states of the carriers, defined in $J^{-1}m^{-3}$. Assuming that short-range impurity scattering dominates:

$$\tau(E) = C\left[D(E)\right]^{-1} \tag{3}$$

where C is the scattering coefficient (dimensions $W^{-1}m^{-3}$), that depends on the DOS through the material dimensions and the confinement length. This condition can be derived from Fermi's golden rule and is suitable for scattering mechanisms involving electron-phonon interactions (occurring at 300-700 K).
To work with dimensionless quantities, the reduced chemical potential $\eta = \mu/k_B T$ is introduced. The integrals L_i can be written in function of simpler integrals F_i, given by:

$$F_i(\eta) = \int \eta^i f_0 d\eta \tag{4}$$

Thus one has:

$$\begin{cases} L_0 = \frac{C}{m}\left(k_B T\right) F_0 \\ \\ L_1 = \frac{C}{m}\left(k_B T\right)^2 \left(2F_1 - \eta F_0\right) \\ \\ L_2 = \frac{C}{m}\left(k_B T\right)^3 \left(3F_2 - 4\eta F_1 + \eta^2 F_0\right) \end{cases} \quad \Longrightarrow \quad \begin{cases} \sigma = \frac{q^2 C}{m}\left(k_B T\right) F_0 \\ \\ S = \frac{k_B}{q}\frac{(2F_1 - \eta F_0)}{F_0} \\ \\ \kappa_e = \frac{k_B^3 T^2 C}{m}\left(3F_2 - 4\eta F_1 + \eta^2 F_0 - \frac{(2F_1 - \eta F_0)^2}{F_0}\right) \end{cases} \tag{5}$$

with m and q the effective mass and the charge of the carrier.
By defining the constants $S_0 = \frac{k_B}{q} \simeq 87 \mu V/K$, $\sigma_= \frac{q^2 C k_B T}{m}$ and $\kappa_0 = \frac{C k_B^3 T^2}{m}$ one gets:

$$\begin{cases} \sigma = \sigma_0 F_0 \\ \\ S = S_0 \frac{(2F_1 - \eta F_0)}{F_0} \\ \\ \kappa_e = \kappa_0 \left(3F_2 - 4\eta F_1 + \eta^2 F_0 - \frac{(2F_1 - \eta F_0)^2}{F_0}\right) \end{cases} \tag{6}$$

In the end one can compute the final figure of merit ZT via the following equation:

$$ZT = \frac{S^2 \sigma T}{\kappa} \tag{7}$$

The lattice thermal conductivity κ_L can be written in units of κ_0 as $\kappa_L = r_\kappa \kappa_0$, where r_κ is a parameter that can be changed by the user during the simulation, together with μ.

2 Double-parabolic-band model

The mathematical procedure is similar to the one applied for the single-band model. In fact, the thermoelectric quantities still depend on the transport integrals L_i, which take the form of eq.1. The difference is that now both a valence and a conduction band and the energy gap between the two are considered. In addition, bands are considered symmetric. This is useful to describe the bipolar effect due to the presence of both negative and positive charge carriers, i.e. electrons in the conduction band and holes in the valence band. Therefore, now the transport integrals are distinguished between the two bands:

$$\begin{cases} L_{i,c} = \int_0^\infty \mathcal{T}(E)(E-\mu)^i \left(-\frac{\partial f}{\partial E}\right) dE \\ \\ L_{i,v} = \int_{-\infty}^0 \mathcal{T}(E)(E-\mu)^i \left(-\frac{\partial f}{\partial E}\right) dE \end{cases} \tag{8}$$

Their relations with the functions F_i is the following:

$$\begin{cases} L_{i,c} = \frac{g\tau_0}{2\pi\hbar^2 L} (k_B T)^{i+1} \left[F_{i+1,c}(\eta-\delta) + (\eta-\delta) F_{i,c}(\eta-\delta)\right] \\ \\ L_{i,v} = L_{i,c} = -\frac{g\tau_0}{2\pi\hbar^2 L} (k_B T)^{i+1} \left[F_{i+1,v}(\eta+\delta) + (\eta+\delta) F_{i,v}(\eta-\delta)\right] \end{cases} \tag{9}$$

where L is the confinement length, g accounts for degeneracy, and $\delta = \Delta/k_B T$, Δ being such that $E_g = 2\Delta$. The F_i integrals are given by:

$$\mathcal{F}_{i,c(v)}(\eta) = \int_{-\eta\ (-\infty)}^{\infty\ (-\eta)} \frac{x^i e^x}{(e^x+1)^2} dx \tag{10}$$

Assuming electron-hole symmetry, i.e.:

$$\begin{cases} \mathcal{F}_{0,c}(\eta) = \mathcal{F}_{0,v}(-\eta) \\ \mathcal{F}_{1,c}(\eta) = -\mathcal{F}_{1,v}(\eta) \\ \mathcal{F}_{2,c}(\eta) = \mathcal{F}_{2,v}(-\eta) \end{cases} \tag{11}$$

and defining $S_0 = \frac{k_B}{q} \simeq 87\mu V/K$, $\sigma_= \frac{q^2 C k_B T}{m}$ and $\kappa_0 = \frac{C k_B^3 T^2}{m}$, one gets:

$$\begin{cases} \sigma_{c(v)} = \sigma_0 \mathcal{F}_{0,c(v)} \\ \\ S_{c(v)} = -S_0 \frac{\mathcal{F}_{1,c(v)}}{\mathcal{F}_{0,c(v)}} \\ \\ \kappa_{e,c(v)} = \kappa_0 \left(\mathcal{F}_{2,c(v)} - \frac{\mathcal{F}_{1,c(v)}^2}{\mathcal{F}_{0,c(v)}}\right) \end{cases} \tag{12}$$

The physical quantities to compute are now:

$$\begin{cases} \sigma = \sigma_c + \sigma_v \\ \\ S = \frac{\sigma_c S_c + \sigma_v S_v}{\sigma_c + \sigma_v} \\ \\ \kappa_e = \frac{\sigma_c \sigma_v}{\sigma_c + \sigma_v} (S_c - S_v)^2 + (\kappa_{e,c} + \kappa_{e,v}) \end{cases} \tag{13}$$

and eventually ZT is calculated through eq.7.
The parameters that the user can set in this simulation are r_k (which is introduced to account for the lattice thermal conductivity, as previously explained), μ and δ.

3 Double-Dirac-band model

Because this is a double-band model, the procedure follows the steps of the simulation for parabolic bands. However, now the transport integrals L_i are dependent on both the integrals of type F_i and on new functions G_i:

$$L_{i,c(v)} = \frac{C v_F^2 (K_B T)^i}{2} \left(\mathcal{F}_{i,c(v)}(\eta - \delta) - \mathcal{G}_{i,c(v)}(\delta, \eta) \right) \tag{14}$$

with:

$$\begin{cases} \mathcal{F}_{i,c(v)}(\eta) = \int_{-\eta\ (-\infty)}^{\infty\ (-\eta)} \frac{x^i e^x}{(e^x+1)^2} dx \\ \\ \mathcal{G}_{i,c(v)}(\delta, \eta) = \int_{\delta-\eta\ (-\infty)}^{\infty\ (-\delta-\eta)} \frac{\delta^2}{(x+\eta)^2} \frac{x^i e^x}{(e^x+1)^2} dx \end{cases} \tag{15}$$

In the end, substituting these functions in the set of equations 12 and then applying equations 13, one finds σ, S, κ_e in units of $\sigma_0 = e^2 v_F^2 C/2$, $S_0 = k_B/e$ and $\kappa_0 = v_F^2 C k_B^2 T/2$, respectively; eventually ZT through equation 7.
The parameters to be set by the user are r_k, μ and δ.

References

[1] Hung, Nguyen T., Ahmad RT Nugraha, and Riichiro Saito. "Universal curve of optimum thermoelectric figures of merit for bulk and low-dimensional semiconductors." Physical Review Applied 9.2 (2018): 024019.

[2] Naithani, Harshita, Eckhard Müller, and Johannes de Boor. "Developing a two-parabolic band model for thermoelectric transport modelling using Mg2Sn as an example." Journal of Physics: Energy 4.4 (2022): 045002.

[3] Hasdeo, Eddwi H., et al. "Optimal band gap for improved thermoelectric performance of two-dimensional Dirac materials." Journal of Applied Physics 126.3 (2019).