Electronic Transport Properties in PAOFLOW 2.0

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Abstract

Regardless of its success, the constant relaxation time approximation has limited validity. Temperature and energy dependent effects are important to match experimental trends even in simple situations. We present the implementation of relaxation time approximation models in the calculation of Boltzmann transport in PAOFLOW 2.0 and apply those to model band-structures and thermoelectric materials. In addition, using a self-consistent fitting of the model parameters to experimental conductivity data, we provide a flexible tool to extract scattering rates with high accuracy. We also introduce a method to examine the importance of interband coherence on electronic conductivity and test the validity of the assumption that interband scattering can be ignored in transport..

Introduction

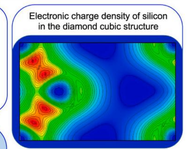
PAOFLOW

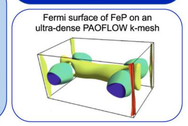
- Installable software package, written in Python 3.8
- Highly parallelized for manycore systems

Construct Hamiltonians from projections of DFT wavefunctions on an atomic orbital basis

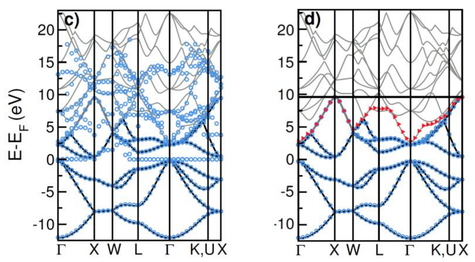
Construct analytical tight binding Hamiltonians

- Compute advanced materials properties:
  - Band structure
  - Ultra-dense k-mesh interpolation
  - Fermi surface
  - Spin texture
  - Weyl point search
  - Transport quantities
  - Scattering models for non-constant relaxation time
  - Spin Hall and anomalous Hall conductivities
  - Real space PAO wavefunctions for spatially resolved quantities





$$\bar{H} = AEA^{\dagger} \longrightarrow \bar{H}_{\kappa} = \bar{H} + \kappa Q_{\mathcal{N}}$$



Electronic Transport

$$\mathscr{L}_{\alpha} = \frac{\tau}{4\pi^3}\int \sum_n \mathbf{v}_n(\mathbf{k})\mathbf{v}_n(\mathbf{k})\left(-\frac{\partial f_0}{\partial E}\right)[\varepsilon_n(\mathbf{k})-\mu]^{\alpha}\, d\mathbf{k}, \quad \text{Constant Relaxation Time Approximation (CRTA)}$$

$$\mathscr{L}_{\alpha} = \frac{1}{4\pi^3}\int \sum_n \tau_n(\mathbf{k})\mathbf{v}_n(\mathbf{k})\mathbf{v}_n(\mathbf{k})\left(-\frac{\partial f_0}{\partial E}\right)[\varepsilon_n(\mathbf{k})-\mu]^{\alpha}\, d\mathbf{k}, \quad \text{Relaxation Time Approximation (RTA)}$$

$$\begin{aligned}\text{Electronic conductivity } \sigma &= e^2\mathscr{L}_0,\\ \text{Seebeck coefficient } S &= -\frac{1}{Te}[\mathscr{L}_0]^{-1}\cdot\mathscr{L}_1,\\ \text{Thermal conductivity } \kappa_{el} &= \frac{1}{T}\left(\mathscr{L}_2-\mathscr{L}_1\cdot[\mathscr{L}_0]^{-1}\cdot\mathscr{L}_1\right),\end{aligned}$$

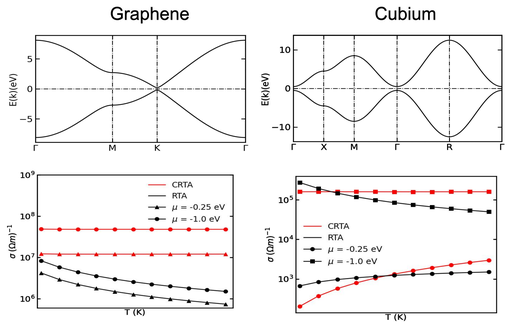
$$\tau_{ac}(E,T) = \frac{2\pi\hbar^4\rho v^2}{(2m^*)^{\frac{3}{2}}k_BTD_{ac}^2\sqrt{E}}, \qquad \tau_{imp}(E,T) = \frac{E^{\frac{3}{2}}\sqrt{2m^*}4\pi\varepsilon^2}{(log(1+\frac{1}{\chi})-\frac{1}{1+\chi})\pi n_I Z_i^2 e^4}$$

$$\tau_{pop}(E,T) = \sum_i \frac{Z(E,T,\omega_i^l)E^{\frac{1}{2}}}{C(E,T,\omega_i^l)-A(E,T,\omega_i^l)-B(E,T,\omega_i^l)} \qquad \tau_{op}(E,T) = \frac{\sqrt{2k_BT}\,\pi x_o\hbar^2\rho}{m^{*\frac{3}{2}}D_{op}^2[\,N_{op}\sqrt{x+x_o}+(N_{op}+1)\Theta(x-x_o)\sqrt{x-x_o}\,]},$$

$$\tau_{pac}(E,T) = \frac{\sqrt{2E}2\pi\epsilon^2\hbar^2\rho v^2}{p^2e^2\sqrt{m^*}k_BT}\times\left[1-\frac{\varepsilon_o}{2E}\log(1+4\frac{E}{\varepsilon_o})+\frac{1}{1+4\frac{E}{\varepsilon_o}}\right]$$

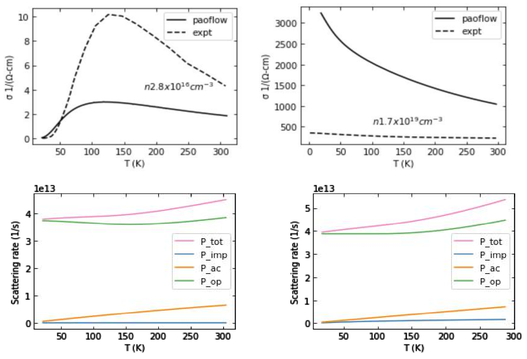
$$\frac{1}{\tau_{total}(E,T)} = \frac{1}{\tau_{imp}(E,T)}+\frac{1}{\tau_{ac}(E,T)}+\frac{1}{\tau_{op}(E,T)}+\frac{1}{\tau_{pop}(E,T)}+\frac{1}{\tau_{pac}(E,T)}.$$

CRTA vs RTA

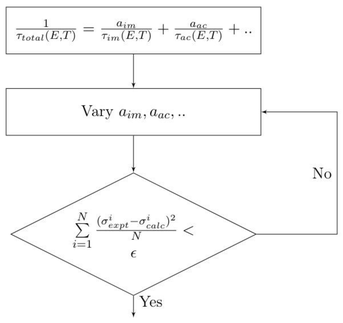


- Metals - Conductivity decreases as temperature increases.
- Semiconductors - Conductivity increases as temperature increases.
- This behavior is not captured by the CRTA.
- RTA models are able to capture the experimental behaviour by introducing relevant dissipation phenomena.

RTA in Semiconductors



- Quantifies scattering mechanisms and scattering trends in the system.
- Identify contribution of different scattering mechanisms - scattering due to optical phonons is the most dominant in this system, followed by acoustic phonons and then impurity scattering.
- Room for improvement -
  - Temperature dependence of dominant prefactors in the scattering model not considered.
  - Models do not include interband scattering.
  - Scattering has strong dependence to extrinsic factors like size of dopant, disorder, etc

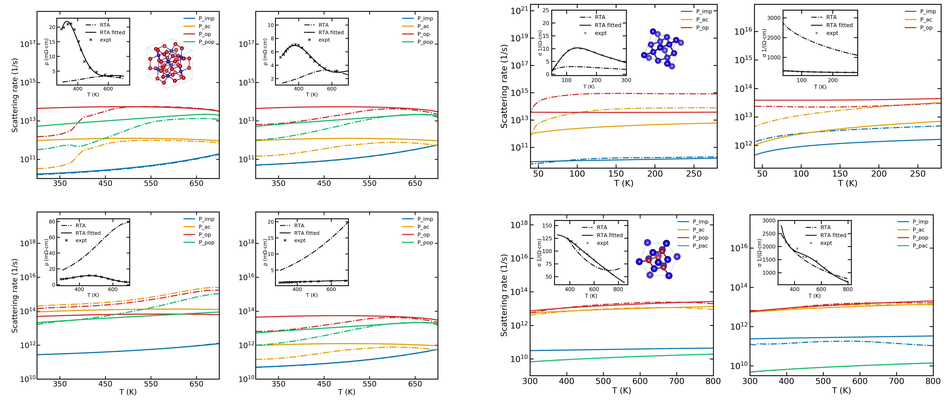


- Introduced a self consistent automated relaxation time calculation method.
- Allows description of scattering mechanisms in specific experimental samples.
- Captures variations in scattering mechanism due to variation in experimental conditions - useful for scattering engineering.

$$\tau_{calc}^{original} = \left(\frac{1}{\tau_{imp}}+\frac{1}{\tau_{ac}}+\frac{1}{\tau_{pop}}\right)^{-1}$$

$$\tau_{calc}^{fitted} = \left(\frac{a_{imp}}{\tau_{imp}}+\frac{a_{ac}}{\tau_{ac}}+\frac{a_{pop}}{\tau_{pop}}\right)^{-1}$$

Extraction of Relaxation times – Examples



- Tested on $CoSb_3$, Si and Mg_3Sb_2. Models need to be modified depending on experimental sample.
- The extracted relaxation times were able to successfully corroborate experimental observations.

Interband Transitions and Boltzmann Transport

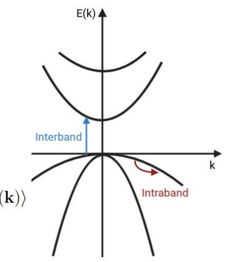
$$\sigma_{intra} = \frac{e^2}{4\pi^3}\int \sum_n \tau_n(\mathbf{k})\mathbf{v}_n(\mathbf{k})\mathbf{v}_n(\mathbf{k})\left(-\frac{\partial f}{\partial E}\right)_{E_n(\mathbf{k})} d\mathbf{k}$$

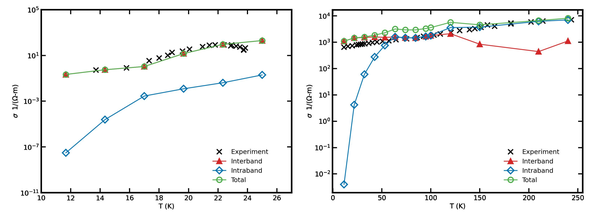
$$\sigma_{inter} = \frac{e^2}{4\pi^3}\int \sum_{n\neq n'} -\frac{1}{\tau_n(\mathbf{k})}\mathbf{X}_{n,n'}(\mathbf{k})\mathbf{X}_{n',n}(\mathbf{k})\frac{[f(E_n(\mathbf{k}))-f(E_{n'}(\mathbf{k}))](E_n(\mathbf{k})-E_{n'}(\mathbf{k}))}{\tau_n^{-2}(\mathbf{k})+(E_n(\mathbf{k})-E_{n'}(\mathbf{k}))^2} d\mathbf{k}$$

$$\sigma_{total} = \sigma_{intra} + \sigma_{inter}$$

Usually ignored

$$\mathbf{X}_{n,n'}(\mathbf{k}) = \frac{1}{i}\frac{\hbar}{m}\frac{\mathbf{P}_{n,n'}(\mathbf{k})}{(E_n(\mathbf{k})-E_{n'}(\mathbf{k}))} \qquad \mathbf{P}_{n,n'}(\mathbf{k}) = \langle\psi_n(\mathbf{k})|\,\hat{p}\,|\psi_m(\mathbf{k})\rangle = \langle u_n(\mathbf{k})|\,\frac{m_0}{\hbar}\nabla_{\mathbf{k}}\hat{H}(\mathbf{k})\,|u_m(\mathbf{k})\rangle$$





Studies on Phosphorus and $CoSb_3$ show that Interband effect on conductivity dominate at low temperatures while intraband effects are important at higher temperatures.

Conclusion

- User friendly post-processing tool for materials modelling - https://github.com/marcobn/PAOFLOW
- Easily calculate relaxation time of electrons due to scattering off phonons and impurities.
- Add your own relaxation time models easily.
- Automated calculation of relaxation time for sample specific studies.
- Description of interband contributions have been introduced.
- Effect of interband transitions are important at low temperatures and cannot be ignored.

References

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