Predicting Thermoelectric Properties From First Principles

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State-of-the-Art Thermoelectric Materials

Strategy for improving ZT

Alloy

Quantum Confinement

Phonon-blocking/ Electron-transmitting Interface

Computing Thermoelectric Properties

First principles electronic structure

Parameter fitting (Genetic Algorithm)

Tight binding calculation

Boltzmann Transport Equation
Green Kubo formalism

Figure of Merit

\[ ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_{ph}} \]

Electronic contribution:
- Seebeck coefficient
- Electrical conductivity
- Thermal conductivity

Lattice contribution:
- Thermal conductivity

First principles Force Fields

Boltzmann Transport Equation
Green Kubo formalism
Materials Design Software - EZTB

Atoms
- StructureBuilder
- ForceFieldKeating
- ForceFieldReaxFF
- ElasticMinimization
- Atomic Positions

Electrons
- CrystalStructure
- TightBinding
- EigenSolver
- BandStructure
- LanczosSolver
- Minimization
- GeneticAlgorithm
- PoissonSolver

Optics
- Absorption
  - Chi2
  - Chi3
- Band Structure
  - Density of States
- Transport
  - RelaxationTime
  - Boltzmann
  - GreenKubo
  - NonEquilGreenFct
- ZT

ab initio data
Experimental data

Completed
Initiated
Caltech
New

CMDF2005 - Aug 23-24, 2005

Applied Cluster Computing Technologies group
http://hpc.jpl.nasa.gov
EZTB - Software Technology

1. **C++**
   Object Oriented eases development and maintenance

2. **Python and SWIG wrapping**
   Improves portability
   Facilitates development of new process flows
   Integration into CMDF

3. **XML data representation**
   Improves portability
   Enables scripting instructions

4. **Web Portal Middleware (JPL-WIGLAF)**
   Simple remote browser access
   Job monitoring on cluster computers
Web Enabling Materials Design Software

Example python script

- Read crystal
- Set up crystal
- Set up H
- Diagonalize H
Tight Binding Model

Tight Binding Hamiltonian

\[ H = \sum_{i \nu} \varepsilon_{i}^{(\nu)} + \sum_{ij \mu \nu} t_{ij}^{(\mu \nu)} \]

- \( i \): neighbors (1st, 2nd, …)
- \( \nu \): \( \text{sp}^3\text{d}^5\text{s}^* \), 20 orbitals
- Spin-orbit term: on-site

Structure Definition

- Uniform Bulk: primitive vectors, atom basis
- Nanostructures: atomic positions
- Material: tight binding parameters fitted to \textit{ab initio} and experimental data

\( \sigma \) anti-bonding

\( \sigma \) bonding

\( \pi \) anti-bonding

\( \pi \) bonding

\( \text{sp} \ \sigma \) bond
Empirical Relaxation Time Approximation

Linear response expressions for the charge and heat currents:

\[ j^e = L^{11} E + L^{12} (-\nabla T) \]
\[ j^q = L^{21} E + L^{22} (-\nabla T) \]

Electrical conductivity:
\[ \sigma = L^{11} \]

Thermal conductivity \((j^e=0)\):
\[ \kappa_e = L^{22} - L^{21} (L^{11})^{-1} L^{12} \]

Seebeck coefficient \((j^e=0)\):
\[ S = (L^{11})^{-1} L^{12} \]

Linearized Boltzmann Transport Equation yields the linear coefficients:

\[ L^{11} = \Lambda^{(0)} \]
\[ L^{21} = T L^{12} = -\frac{1}{e} \Lambda^{(1)} \]
\[ L^{22} = \frac{1}{e^2 T} \Lambda^{(2)} \]

\[ \Lambda_{mn}^{(\alpha)} = e^2 \tau \int \frac{d^3 k}{4 \pi^3} \left( -\frac{\partial f}{\partial \varepsilon} \right) v_m(k) v_n(k) (\varepsilon(k) - \mu)^\alpha \]

\[ v_n(k) = \frac{1}{\hbar} \frac{\partial \varepsilon(k)}{\partial k_n} \]

Relaxation time fitted to experiment
Silicon Band Structure

Empirical tight-binding method with spds* orbitals

\[ E_{\text{gap}} = 1.12 \text{ eV} \]
Computed ZT for Bulk

Relaxation time (n-Si)
(from fitting to experimental mobility)

Electron Density (1/cm^3)

0.0E+00
5.0E-14
1.0E-13
1.5E-13
2.0E-13
2.5E-13
1.E+14
1.E+15
1.E+16
1.E+17
1.E+18
1.E+19
1.E+20

Relaxation Time (s)

n-Si

Electron Density (1/cm^3)

T=300K

n-Ge

Electron Density (1/cm^3)

n-Bi₂Te₃

Electron Density (1/cm^3)

Electrical Conductivity (Ω⁻¹cm⁻¹)

0.000
0.002
0.004
0.006
0.008
1.E+13
1.E+15
1.E+17
1.E+19
1.E+21

0.7
0.6
0.5
0.4
0.3
0.2
0.1

0
1000
2000
3000
4000
5000

0.0E+00
0.000
0.004
0.008
0.012
0.016
0.020
0.024
0.028
0.032
0.036
0.040
0.044
0.048
0.052
0.056
0.060
0.064
0.068
0.072
0.076
0.080
0.084
0.088
0.092
0.096
0.100
1.E+13
1.E+15
1.E+17
1.E+19
1.E+21

ZT

Experiment
Theory
Experiment
Theory
Experiment
Theory
Experiment
Theory
n-Doped Silicon Nanowires

Si-NW 2x2

ZT figure of merit

- Semi-classical model for the electronic contribution to transport
- Lattice contribution to the thermal conductivity adjusted for finite-size effects
Beyond Relaxation Time Approximation

Boltzmann Transport Equation (BTE)

\[-\frac{\partial f_n(k)}{\partial \varepsilon_n} e F \cdot v_n(k) + \frac{\partial f_n(k)}{\partial T} \nabla T \cdot v_n(k) = C_n(k)\]

\[v_n(k) = \frac{1}{\hbar} \frac{\partial \varepsilon(k)}{\partial k_n}\]

\[C_n(k) = \frac{V}{8\pi^3} \sum_{n'} \int dk' \left\{ -S_{nn'}(k,k') f_n(k)(1 - f_n'(k')) + S_{n'n}(k',k) f_n'(k')(1 - f_n(k)) \right\}\]

Electrical conductivity:

\[\sigma_{\alpha\beta} = \frac{e^2}{F_\beta} \sum_n \int \frac{d^3k}{4\pi^3} f_n(k) v_\alpha(k)\]

Thermal conductivity:

\[\kappa_{\alpha\beta}^{el} = \frac{e^2}{\nabla_\beta T} \sum_n \int \frac{d^3k}{4\pi^3} f_n(k) v_\alpha(k)(\varepsilon(k) - \mu)\]

Seebeck coefficient:

\[S = \frac{F}{\nabla T}\]

\(f\) is obtained from BTE with \(F\) along \(e_\beta\) and with \(\nabla T = 0\)

\(f\) is obtained from BTE with \(\nabla T\) along \(e_\beta\) and \(F\) such that \(J_{el} = 0\)

For a given \(\nabla T\), \(F\) is such that \(J_{el} = 0\)
Sensitivity Studies

Inverse Problem optimization

$$\delta p = C_{pt} \delta t$$

Direct Model Eigenvalue problem

$$\delta t = C_{tp} \delta p$$

Variation of transport coefficients

$$\sigma_i(t + \delta t) = \sigma_i(t) + \frac{\partial \sigma_i}{\partial t_\alpha} \delta t_\alpha$$

Correlation matrices

$$\frac{\partial \sigma_i}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} \frac{\partial p_\beta}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} \left( C_{pt} \right)_{\beta\alpha}$$
## Silicon Band Structure

Parametrized Tight-Binding method with spds* orbitals

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Si</th>
<th>Si target</th>
<th>% deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c^\Gamma$</td>
<td>3.399</td>
<td>3.368</td>
<td>0.9</td>
</tr>
<tr>
<td>$E_v^\Gamma$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\Delta_0$</td>
<td>0.0472</td>
<td>0.045</td>
<td>4.9</td>
</tr>
<tr>
<td>$E_{c,min}^L$</td>
<td>2.383</td>
<td>2.400</td>
<td>0.7</td>
</tr>
<tr>
<td>$E_{X,min}^c$</td>
<td>1.131</td>
<td>1.118</td>
<td>1.2</td>
</tr>
<tr>
<td>$k_{min}^{[001]}$</td>
<td>81.3%</td>
<td>85.0%</td>
<td>4.4</td>
</tr>
<tr>
<td>$m_X^{(e)}$</td>
<td>0.891</td>
<td>0.916</td>
<td>2.7</td>
</tr>
<tr>
<td>$m_X^{(e)}$</td>
<td>0.201</td>
<td>0.190</td>
<td>5.8</td>
</tr>
<tr>
<td>$m_{L,1}^{(e)}$</td>
<td>3.433</td>
<td>2.000</td>
<td>71.7*</td>
</tr>
<tr>
<td>$m_{L,t}^{(e)}$</td>
<td>0.174</td>
<td>0.100</td>
<td>74.0*</td>
</tr>
<tr>
<td>$m_{[001]}^{1h}$</td>
<td>-0.214</td>
<td>-0.204</td>
<td>4.9</td>
</tr>
<tr>
<td>$m_{[110]}^{1h}$</td>
<td>-0.152</td>
<td>-0.147</td>
<td>3.4</td>
</tr>
<tr>
<td>$m_{[111]}^{1h}$</td>
<td>-0.144</td>
<td>-0.139</td>
<td>3.6</td>
</tr>
<tr>
<td>$m_{[001]}^{1h}$</td>
<td>-0.276</td>
<td>-0.275</td>
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</tr>
<tr>
<td>$m_{[110]}^{1h}$</td>
<td>-0.581</td>
<td>-0.579</td>
<td>0.3</td>
</tr>
<tr>
<td>$m_{[111]}^{1h}$</td>
<td>-0.734</td>
<td>-0.738</td>
<td>0.5</td>
</tr>
<tr>
<td>$m_{so}$</td>
<td>-0.246</td>
<td>-0.234</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Silicon Band Structure

Parametrized Tight-Binding method with spds* orbitals

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_s$</td>
<td>-2.15168</td>
</tr>
<tr>
<td>$E_p$</td>
<td>4.22925</td>
</tr>
<tr>
<td>$E_x^*$</td>
<td>19.11650</td>
</tr>
<tr>
<td>$E_d$</td>
<td>13.78950</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.01989</td>
</tr>
<tr>
<td>$ss\sigma$</td>
<td>-1.95933</td>
</tr>
<tr>
<td>$s^<em>s^</em>\sigma$</td>
<td>-4.24135</td>
</tr>
<tr>
<td>$ss^*\sigma$</td>
<td>-1.52230</td>
</tr>
<tr>
<td>$sp\sigma$</td>
<td>3.02562</td>
</tr>
<tr>
<td>$s^*p\sigma$</td>
<td>3.15565</td>
</tr>
<tr>
<td>$sd\sigma$</td>
<td>-2.28485</td>
</tr>
<tr>
<td>$s^*d\sigma$</td>
<td>-0.80993</td>
</tr>
<tr>
<td>$pp\sigma$</td>
<td>4.10364</td>
</tr>
<tr>
<td>$pp\pi$</td>
<td>-1.51801</td>
</tr>
<tr>
<td>$pd\sigma$</td>
<td>-1.35554</td>
</tr>
<tr>
<td>$pd\pi$</td>
<td>2.38479</td>
</tr>
<tr>
<td>$dd\sigma$</td>
<td>-1.68136</td>
</tr>
<tr>
<td>$dd\pi$</td>
<td>2.58880</td>
</tr>
<tr>
<td>$dd\delta$</td>
<td>-1.81400</td>
</tr>
</tbody>
</table>

Sensitivity Studies

N - Targets
1st principles experiments

M - Physical Quantities
Conductivity
Optical properties

Inverse Problem optimization

\[ \delta p = C_{pt} \delta t \]

Direct Model
Eigenvalue problem

\[ \delta t = C_{tp} \delta p \]

Variation of transport coefficients

\[ \sigma_i(t + \delta t) = \sigma_i(t) + \frac{\partial \sigma_i}{\partial t_\alpha} \delta t_\alpha \]

Correlation matrices

\[ \frac{\partial \sigma_i}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} \frac{\partial p_\beta}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} \left( C_{pt} \right)_{\beta\alpha} \]

Computational process I

1. Compute

\[ \left( C_{tp} \right)_{\alpha\beta} = \frac{\partial t_\alpha}{\partial p_\beta} \]

2. \[ C_{pt} = C_{tp}^{-1} \]

3. Compute

\[ \frac{\partial \sigma_i}{\partial p_\beta} \]

4. \[ \frac{\partial \sigma_i}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} \left( C_{pt} \right)_{\beta\alpha} \]
Sensitivity Studies

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Tight-Binding Parameters

Variation of transport coefficients

\[ \sigma_i(t + \delta t) = \sigma_i(t) + \frac{\partial \sigma_i}{\partial t_\alpha} \delta t_\alpha \]

Correlation matrices

\[ \frac{\partial \sigma_i}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} \frac{\partial p_\beta}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} (C_{pt})_{\beta \alpha} \]

Target evaluation inaccurate

Computational process I

1. Compute \((C_{tp})_{\alpha \beta} = \frac{\partial t_\alpha}{\partial p_\beta}\)

2. \(C_{pt} = C_{tp}^{-1}\)

3. Compute \( \frac{\partial \sigma_i}{\partial p_\beta} \)

4. \( \frac{\partial \sigma_i}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} (C_{pt})_{\beta \alpha} \)
**Sensitivity Studies**

- **Inverse Problem optimization**
  \[ \delta p = C_{pt} \delta t \]

- **Direct Model Eigenvalue problem**
  \[ \delta t = C_{tp} \delta p \]

**Targets**
- 1st principles experiments

**Tight-Binding Parameters**

**Physical Quantities**
- Conductivity
- Optical properties

**Variation of transport coefficients**
\[ \sigma_i(t + \delta t) = \sigma_i(t) + \frac{\partial \sigma_i}{\partial t_{\alpha}} \delta t_{\alpha} \]

**Correlation matrices (optimization)**
\[ \frac{\partial p_\alpha}{\partial t_\beta} \approx \frac{p_\alpha(t_1, \ldots, t_\beta + \delta t_\beta, \ldots, t_N) - p_\alpha(t)}{\delta t_\beta} \]

**Computational process II**
1. Compute
\[ (C_{pt})_{\alpha\beta} = \frac{\partial p_\alpha}{\partial t_\beta} \]
2. Compute
\[ \frac{\partial \sigma_i}{\partial p_\beta} \]
3. Compute
\[ \frac{\partial \sigma_i}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} (C_{pt})_{\beta\alpha} \]
Sensitivity Studies

Inverse Problem optimization

\[ \delta p = C_{pt} \delta t \]

Tight-Binding Parameters

Physical Quantities
Conductivity
Optical properties

N 

Targets
1st principles experiments

Direct Model
Eigenvalue problem

\[ \delta t = C_{tp} \delta p \]

M

Variation of transport coefficients

\[ \sigma_i(t + \delta t) = \sigma_i(t) + \frac{\partial \sigma_i}{\partial t_\alpha} \delta t_\alpha \]

Optimization inaccurate

Correlation matrices (optimization)

\[ \frac{\partial p_\alpha}{\partial t_\beta} \approx p_\alpha(t_1, \ldots, t_\beta + \delta t_\beta, \ldots, t_N) - p_\alpha(t) \]

\[ \frac{\partial \sigma_i}{\partial p_\beta} \]

Optimization in accurate

Optimization in accurate

N ≠ M

Computational process II

1. Compute

\[ \left( C_{pt} \right)_{\alpha\beta} = \frac{\partial p_\alpha}{\partial t_\beta} \]

2. Compute

\[ \frac{\partial \sigma_i}{\partial p_\beta} \]

3. Compute

\[ \frac{\partial \sigma_i}{\partial t_\alpha} = \frac{\partial \sigma_i}{\partial p_\beta} \left( C_{pt} \right)_{\beta\alpha} \]
Sensitivity Studies

In inverse problem optimization, the variation of transport coefficients is given by:

\[ \delta \sigma_i = \partial \sigma_i / \partial t_\alpha \delta t_\alpha \]

Variation of transport coefficients

Correlation matrices (optimization)

\[ \partial \sigma_i \equiv \sigma_i(t_1, \ldots, t_\beta + \delta t_\beta, \ldots, t_N) - \sigma_i(t) \]

N ≠ M

1. Compute \[ \partial \sigma_i / \partial t_\alpha \]

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Sensitivity Studies

**Direct Model**

1. Compute \( \frac{\partial \sigma_i}{\partial t_\alpha} \)

**Inverse Problem optimization**

\[ \delta p = C_{p\ell} \delta t \]

\[ \delta t = C_{tp} \delta p \]

**Targets 1st principles experiments**

**Tight-Binding Parameters**

**Physical Quantities Conductivity Optical properties**

N ≠ M

1. **Variation of transport coefficients**

\[ \sigma_i(t + \delta t) = \sigma_i(t) + \frac{\partial \sigma_i}{\partial t_\alpha} \delta t_\alpha \]

2. **Correlation matrices (optimization)**

\[ \frac{\partial \sigma_i}{\partial t_\alpha} \equiv \frac{\sigma_i(t_1, \ldots, t_\beta + \delta t_\beta, \ldots, t_N) - \sigma_i(t)}{\delta t_\alpha} \]
Lattice Contribution to the Thermal Conductivity

1. Monte Carlo solution of the Boltzmann Transport Equation for phonons

Monte Carlo solution: Drift in real space

\[ \mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \mathbf{v}.\Delta t \]

Scattering (Normal, Umklapp)

Anharmonicity in Force Field \[ P_{NU} = 1 - \exp(\Delta t/\tau_{NU}) \]

\[ \tau_{NU}^{-1} = \tau_U^{-1} + \tau_N^{-1} \]

If random number < \( P_{NU} \) phonon scattered

Status

• Developed Monte Carlo Code
• Validating Code by comparing with
• Literature calculation for Si film
• Using empirical scattering rates

Plans

• Compute thermal conductivity for bulk Si, Ge, Bi₂Te₃ and Sb₂Te₃
• Substitute empirical scattering rates with first principal ones
• Thermal conductivity for nanostructures
Lattice Contribution to the Thermal Conductivity

2. Green-Kubo formula

Fluctuation Dissipation theorem

\[ \lambda_{\alpha\beta}(\omega) = \frac{1}{V k_B T^2} \int_0^\infty dt < j_\alpha(0) j_\beta(t) > e^{i\omega t} \]

\[ < j_\alpha(0) j_\beta(t) > = \sum_{i=0}^{N} j_\alpha(t_i) j_\beta(t_i + t) \]

Heat current

\[ j = \frac{d}{dt} \sum_i E_i r_i \]

Heat current auto-correlation function

Status

- First attempt for C, Tersoff potential
- Slow convergence of auto correlation function (1ns time-series for convergence)

Plans

- Validate code for thermal conductivity of C, Si, Ge
- Compute \( \lambda \) for \( Bi_2Te_3 \) (develop appropriate FF).
- Explore various nanostructure designs
Conclusion

Status
1. Electronic contribution to ZT
   • Computed within the empirical relaxation time approximation
   • Good agreement with experiment
   • Initiated BTE solution for acoustic phonon and ionized impurity scattering (deformation potentials fitted, experimental phonon energies)

2. Lattice contribution
   • Initiated code for BTE and Green-Kubo approach

Future plans
• Complete outlined computational framework
• Reduce the number of fitting parameters by using first principles results for the scattering processes
• Apply to other material classes such as skutterudites
• Compute $ZT$ for nano-patterned materials
• Propose materials with large $ZT$