ME 697R: Computational Methods for Nanoscale Energy Transport

Chapter 5: First Principles Method
Section 5.5: Development of Empirical Interatomic Potentials using DFT

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Potential Energy Surface

Atomic configurations near equilibrium

Density Functional Theory (DFT)

Potential Energy

Classical potentials

\[ E = f(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \]

\[ F = -\frac{dE}{dr_{ij}} \]
Fitting to ab initio Calculations

Potential Energy

$E_i$ vs $r_{ij}$

DFT

ab-initio calculated energy surfaces

Varying the potential parameters

Calculate total energy

Be able to reproduce the energy surface?

Matches bulk properties?

Potential parameters obtained

Y

N

N

Y

Fitting to ab initio Calculations

Potential Energy

$E_i$ vs $r_{ij}$

DFT

ab-initio calculated energy surfaces

Varying the potential parameters

Calculate total energy

Be able to reproduce the energy surface?

Matches bulk properties?

Potential parameters obtained

Y

N

N

Y
Specifying a series of structures with their corresponding energies. Typically the structures would include the equilibrium configuration and as many distinct distortions about this point in order to probe as many different interatomic distances between atoms as possible.

Unless the fitted potentials are able to reproduce the ab initio data very accurately, it is usually desirable to weight the fit in favor of configurations nearer the equilibrium structure.

One approach that has been taken is to use a Boltzmann factor weighting based on the energy difference to the minimum energy configuration, with an appropriate choice of temperature to the task ultimately to be performed.
Benefits of Fitting to ab-initio Calculations

- By fitting the outcomes of a single Hamiltonian it is possible to guarantee that the training set is fully consistent (i.e. there are no differences in temperature, pressure, sample quality, or variable uncertainties in the observables).

- Data can be obtained for materials where no experimental information exists or at geometries that are significantly perturbed from the equilibrium one.

- The data from quantum mechanical methods is free of statistical mechanical effects, such as thermal vibrations and zero point motion.

- Can take into account anharmonic effects.
Having obtained an apparently successful fit, it is important to assess the quality of the results. There are plenty of pitfalls, and convergence should only be taken as a first step towards success.

Make sure the fitted potential can well reproduce the bulk properties, at least part of those properties which are directly related to your application.
Example: Silica

- Potential form:
  \[ U_{ij}(r) = U_{ij}^{\text{Coulomb}}(r) + f_0(b_i + b_j) \exp \left[ \frac{(a_i + a_j - r)}{(b_i + b_j)} \right] - c_i c_j / r^6 \]

- Fitted parameters
  
  Not fitted, determined from charge analysis

<table>
<thead>
<tr>
<th>Q/e</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (kcal^{1/2} Å^{-3} mol^{-1/2})</th>
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</thead>
<tbody>
<tr>
<td>O</td>
<td>-1.200</td>
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<td>0.175 66</td>
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<tr>
<td>Si</td>
<td>+2.400</td>
<td>0.8688</td>
<td>0.032 85 70.37</td>
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</table>

- Resulting physical properties compared to experiment

<table>
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<th>a-quartz</th>
<th>a-cristobalite</th>
<th>a-cristobalite</th>
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<th>Coesite</th>
<th>Stishovite</th>
<th>Stishovite</th>
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<tbody>
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<td></td>
<td>Obs. (^a)</td>
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<td>Obs. (^b)</td>
<td>This work</td>
<td>Obs. (^c)</td>
<td>This work</td>
<td>Obs. (^d)</td>
<td>This work</td>
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<td>a (Å)</td>
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<td>5.02</td>
<td>4.978</td>
<td>4.99</td>
<td>7.1356</td>
<td>7.23</td>
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<td>b (Å)</td>
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<td>5.02</td>
<td>4.978</td>
<td>4.99</td>
<td>12.3692</td>
<td>12.74</td>
<td>4.180</td>
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<td>c (Å)</td>
<td>5.405</td>
<td>5.54</td>
<td>6.948</td>
<td>6.66</td>
<td>7.1736</td>
<td>7.43</td>
<td>2.666</td>
<td>2.75</td>
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<tr>
<td>(\alpha, \beta, \gamma)</td>
<td>(\gamma = 120^\circ)</td>
<td>120°</td>
<td>(\beta = 120.34^\circ)</td>
<td>120.8°</td>
<td>(\gamma = 120^\circ)</td>
<td>120°</td>
<td>(\beta = 120.34^\circ)</td>
<td>120.8°</td>
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<td>Si-O(1) (Å)</td>
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<td>1.601</td>
<td>1.56</td>
<td>1.605</td>
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<td>1.63</td>
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<td>1.614</td>
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<td>1.64</td>
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<td>142°</td>
<td>143.7°</td>
<td>147°</td>
<td>146.8°</td>
<td>142°</td>
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<td>Density (g/cm(^3))</td>
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<td>2.318</td>
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<td>2.921</td>
<td>2.72</td>
<td>4.283</td>
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<td>Bulk modulus (Mbar)</td>
<td>0.38(3)</td>
<td>0.337</td>
<td>0.172</td>
<td>0.96(3)</td>
<td>1.08</td>
<td>3.35</td>
<td>3.11</td>
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<td>Energy (kcal/mol)</td>
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<td>-1236.9</td>
<td>-1234.1</td>
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</table>
Example: Potential Fitting on PbTe

- Crystal structure

Interpenetrating FCC structure

Blue: Pb atom  82
Green: Te atom  52

lattice parameters

NaCl structure (B1)

\[ a = 6.462 \text{ Å} \quad T = 300 \text{ K} \]

Space group : Fm3m
Select the Potential Form

- The potential form should be as simple as possible. Normally simple lattice structure indicates that simple potentials may be derived for this material.

- Consider two-body potential first. Assume all interaction between Pb-Pb, Pb-Te, Te-Te are of the Buckingham form:

  \[ \varphi(r_{ij}) = A_{ij} \exp\left(-r_{ij}/\rho_{ij}\right) - C_{ij}/r_{ij}^6, \]

- Nine parameters to be determined.
Energy Surface Calculations

- Code used for \textit{ab initio} calculations:
  - \textbf{Wien2k} (based on Full Potential Linearized Augmented Plane Wave method)
  - Also \textbf{ABINIT, VASP}... can be used, but appropriate pseudo-potentials should be chosen. Read literature!

- Scan the configurations:
  - The equilibrium crystal structure.
  - Increase and decrease the lattice constant, while the internal coordinates (symmetry) are unchanged.
  - Fix the lattice constant, while displace the internal coordinates (symmetry).
  - Vary both the lattice constant and internal coordinates
  - The number of configurations should be much larger than the number of unknown parameters. We used around 30 in our work.
GULP Input File

```
fit c6 relax

#small1001
cell
6.55157 6.55157 6.55157 90 90 90 0 0 0 0 0
fractional
Pb 0.00000 0.00000 0.00000 0.666000 0 0 0
Pb 0.50000 0.50000 0.50000 0.666000 0 0 0
Pb 0.50000 0.00000 0.50000 0.666000 0 0 0
Pb 0.00000 0.50000 0.50000 0.666000 0 0 0
Te 0.50000 0.50000 0.50000 -0.666000 0 0 0
Te 0.00000 0.50000 0.50000 -0.666000 0 0 0
Te 0.50000 0.00000 0.50000 -0.666000 0 0 0
observables
energy ev
-1.1178823 100.0
end
shift 1.0

#small1002

```

0 means fixed during fitting

• Calculated total energy (shifted)
• Weighting factor
• Effective charges
• Parameter: energy shift

Fit to experimental properties at the same time

• Initial guess parameters
• Cutoff range

 vary
 shift
 end

cell
6.55157 6.55157 6.55157 90 90 90 1 1 1 1 1 1
fractional
Pb 0.0 0.0 0.0 0.666 1 1 1
Te 0.5 0.5 0.5 -0.666 1 1 1
observables
gs
elastic
t 1.106 0.1
elastic
t 2 3.0 0.1
elastic
t 4 13.1 0.1
end

"buck"
core Pb core 500000 0.182239 200 0.00 16.00 1 1 1
"buck"
core Te core 500000 0.236482 649.786427 0.00 16.00 1 1 1
"buck"
core Te core 500000 0.222757 200 0.00 16.00 1 1 1

dump every 500000.res
```
### Parameter fitting

#### Initialization of parameters

<table>
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<tr>
<th>Atom Types</th>
<th>Potential</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Cutoffs(Ang)</th>
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<tbody>
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<td>Pb c Pb c</td>
<td>Buckingham</td>
<td>0.500E+06 0.162</td>
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<td>0.00</td>
<td>0.000</td>
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#### List of variables to be fitted

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<table>
<thead>
<tr>
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<th>Parameter Type</th>
<th>Species</th>
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<td>0.102259</td>
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<td>Buckingham C</td>
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#### Final values of parameters :

---

<table>
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<tr>
<th>Parameter No.</th>
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<th>Species</th>
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<tr>
<td>10</td>
<td>0.604815</td>
<td>Buckingham C</td>
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</tbody>
</table>

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Back Checking the Properties

- Confirm the correctness of fitted potential: using GULP

Input file

```
opti comp prop c6

cell
6.55157 6.55157 6.55157 90.0 90.0 90.0
fractional 8

Pb core 0.5 0.5 0.0 0.666 0 0 0
Pb core 0.01 0.02 0.02 0.666 1 1 1
Pb core 0.52 0.0 0.51 0.666 1 1 1
Pb core 0.03 0.48 0.52 0.666 1 1 1
Te core 0.51 0.01 0.02 -0.666 1 1 1
Te core 0.02 0.49 0.02 -0.666 1 1 1
Te core 0.02 0.03 0.07 -0.666 1 1 1
Te core 0.52 0.51 0.51 -0.666 1 1 1

buck
Pb   core  Pb   core  84203.209   0.075415   61.011668  0.00 16.00
buck
Te   core  Pb   core  92131.469   0.255164   585.69477  0.00 16.00
buck
Te   core  Te   core  1773611.7   0.256533   0.60491809  0.00 16.00
```

Arbitrary small deviations from equilibrium internal structure

Internal coordinates are allowed to change

These are the fitted parameters from previous step
Predicted Properties

- Confirm the correctness of fitted potential: Bulk properties

### Initial internal coordinates

<table>
<thead>
<tr>
<th>No.</th>
<th>Atomic Label</th>
<th>x (Frac)</th>
<th>y (Frac)</th>
<th>z (Frac)</th>
<th>Charge</th>
<th>Occupancy (Frac)</th>
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<td>0.510000</td>
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### Final fractional coordinates of atoms:

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<th>y (Frac)</th>
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<th>Radius (Angs)</th>
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<td>0.500000</td>
<td>0.500000</td>
<td>0.500000</td>
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</table>

### Final Cartesian lattice vectors (Angstroms):

- a: 6.518352, -0.000113, 0.000011
- b: 0.000113, 6.518659, -0.000140
- c: 0.000011, -0.000140, 6.518914

### Elastic Constant Matrix: (Units=GPa)

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<tr>
<th>Indices</th>
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<th>2</th>
<th>3</th>
<th>4</th>
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<th>6</th>
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<td>0.0001</td>
<td>-0.0013</td>
<td>11.0327</td>
</tr>
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</table>

### Final cell parameters and derivatives:

- a: 6.518352 Angstroms, dE/ds1(xx) = -0.002707 eV/strain
- b: 6.518659 Angstroms, dE/ds2(yy) = 0.004900 eV/strain
- c: 6.518914 Angstroms, dE/ds3(zz) = -0.003652 eV/strain
- alpha: 90.022455 Degrees, dE/ds4(ys) = -0.000817 eV/strain
- beta: 90.998511 Degrees, dE/ds5(xz) = 0.000669 eV/strain
- gamma: 90.001972 Degrees, dE/ds6(xy) = -0.000659 eV/strain
Lattice Thermal conductivity v.s. temperature has been calculated which agrees with experimental values reasonably well.