15th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

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Self-consistent ab-initio lattice dynamics (SCAILD): Theory and numerical examples

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Trieste
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Outline

• Standard methods for calculating phonons.
• The Self Consistent Ab Initio Lattice Dynamical (SCAILD) method
• Results
• Some Benchmarks
• The Future ?!
• Standard methods for calculating phonons.

Frozen phonon method

Direct method

Linear response

All quasi harmonic methods!

(quasi = only the effect of the thermal-expansion is taking into account when calculating the phonon frequencies $\omega_{qs}$)
\[ \begin{align*}
&\Gamma \quad H \quad R \quad \Gamma \quad N \\
\end{align*} \]

\[ E \quad bcc \quad hcp \]

\text{Ampitude}
The Self Consistent Ab Initio Lattice Dynamical (SCAILD) Method
\[ U_R = \frac{1}{\sqrt{N}} \sum_{k_s} \epsilon_{k_s} R_{k_s} \epsilon^{iR_k} \]
Alternative Perspective:
Dynamical Stabilization By Phonon-Phonon Interaction
1) Calculate starting guess
\[ \mathbf{R} = \mathbf{R}_0 + \mathbf{U} \Rightarrow \Phi(\mathbf{R}) \]
\[ \Rightarrow \tilde{D}(k) = \sum_{\mathbf{R}} \Phi(\mathbf{R}) e^{-i\mathbf{R}k} \Rightarrow \omega_{ks}^0 \]

2) Calculate atomic displacements
\[ U_R = \frac{1}{\sqrt{N}} \sum_{ks} \epsilon_{ks} \mathcal{R}_{ks} e^{i\mathbf{R}k} \]
\[ \mathcal{R}_{ks}^2 = \frac{\hbar}{M\omega_{ks}} \left[ \frac{1}{2} + \bar{n}\left(\frac{\hbar\omega_{ks}}{k_B T}\right) \right] \]

3) Calculate forces
\[ \mathbf{F}_R = -\langle \Psi \mid \frac{\partial \mathcal{H}}{\partial \mathbf{R}} \mid \Psi \rangle \]

4) Calculate new frequencies
\[ \bar{\omega}_{ks}^2 = -\frac{1}{M} \frac{\epsilon_{ks} \mathbf{F}_k}{\mathcal{R}_{ks}} \]
\[ \Omega_{ks}^2 = \frac{1}{m_k} \sum_{S \in S(k)} \bar{\omega}_{S-1ks}^2 \Rightarrow \omega_{ks}^2(N) = \frac{1}{N} \sum_{i=1}^{N} \Omega_{ks}^2(i) \]
The mean-field frequencies

\[ \bar{\omega}_{ks}^2 = -\frac{1}{M} \frac{\epsilon_{ks} F_k}{\mathcal{R}_{ks}} \]

\[ \bar{\omega}_{ks}^2 = \omega_{ks}^2 \left( 1 + \frac{1}{2} \sum_{k_1, k_2} \sum_{s_1, s_2} A(k, k_1, k_2, s, s_1, s_2) \frac{\mathcal{R}_{k_1 s_1} \mathcal{R}_{k_2 s_2}}{\mathcal{R}_{ks} \omega_{ks}^2} + \ldots \right) \]

\[ \mathcal{R}_{ks}^2 = \frac{\hbar}{M \omega_{ks}} \left[ \frac{1}{2} + \bar{n} \left( \frac{\hbar \omega_{ks}}{k_B T} \right) \right] \]

\[ A(k, k_1, k_2, s, s_1, s_2) = \]

\[ \frac{1}{(MN)^{3/2}} \sum_{R, R_1, R_2} \sum_{\alpha, \beta, \gamma} \Phi_{\alpha\beta\gamma}(R, R_1, R_2) \epsilon_{ks} \epsilon_{k_1 s_1} \epsilon_{k_2 s_2} e^{i(Rk + R_1 k_1 + R_2 k_2)} \]
Principal Results/Publications

(I) Entropy driven stabilization of energetically unstable crystal structures explained from first principles theory.


(II) Ab initio study of interacting lattice vibrations and stabilization of the $\beta$-phase in Ni-Ti shape-memory alloy


(III) Dynamical stability of body center cubic iron at the Earths core conditions


(IV) Entropically Stabilized Local Dipole Formation in Lead Chalcogenides

Results

\[ \omega \text{ [THz]} \]

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Zr</th>
<th>Hf</th>
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<tbody>
<tr>
<td></td>
<td>1293 K</td>
<td>1188 K</td>
<td>2073 K</td>
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</tbody>
</table>

\[ \omega \text{ [THz]} \]

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
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<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 K</td>
<td></td>
<td></td>
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<tr>
<td>0 K</td>
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Cubic Phase of $ZrO_2$


(a) quasiharmonic

(b) 2570 K
$\omega$ [THz]

$\beta$-NiTi Phonon dispersion calculated with SCAILD.

 Experiment

BCC Fe up to Earth Inner Core Conditions

![Graph showing temperature and pressure conditions for BCC Fe up to Earth's inner core conditions. The graph includes data points for bcc-Fe unstable, bcc-Fe stable, and bcc-Fe melting, with pressure and temperature axes ranging from 0 to 9000 K and 0 to 385 GPa, respectively.](image-url)
Some Benchmark Calculations
Phonons of $\text{Ni}_2\text{MnGa}$

$T = 0 \text{ K}$

Calc.
Ni$_2$MnGa

$T=300K$, SCAILD Calc.
Cubic

BaTiO$_3$

(a) 0 K

(b) T=421 K
Future developments:

- Free energies, Calc. Running!
- Phonon lifetimes, Calc. Running!
How do I get access to the scaild code?

Send me an email (petros.souvatzis@fysik.uu.se) requesting a password, then go to:

http://web.mac.com/petros.souvatzis/Webbplats_2/SCAILD.html

And download!
THANK YOU!

The Grandfather of Olivia Newton John (Max Born)

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