The decoupled anharmonic mode approximation (DAMA) Hands-on tutorial

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Overview

- Comparison DAMA to harmonic approximation
- State of implementation, future plans
- Getting started (download code)
  - File structure
- Hands on
  - Setup
  - Phonons P
  - PES sampling (Vibrational modes)
  - Calculation Eigenstates
  - Calculation properties Dama
- Useful routines

Method: The free energy contains the information about the thermal properties

- At *T>0* Free energy is relevant, which can be calculated from the partition function *Z(T)*

$$Z(T) = \Omega'_1 \cdots \Omega'_N$$

- The contributions to *Z* from each mode q_μ can be calculated from the eigenenergies of the modes E^j_μ

- The eigenenergies must be calculated for each decoupled mode

$$E^{j\prime}_\mu = E^0_\mu + E^j_\mu$$

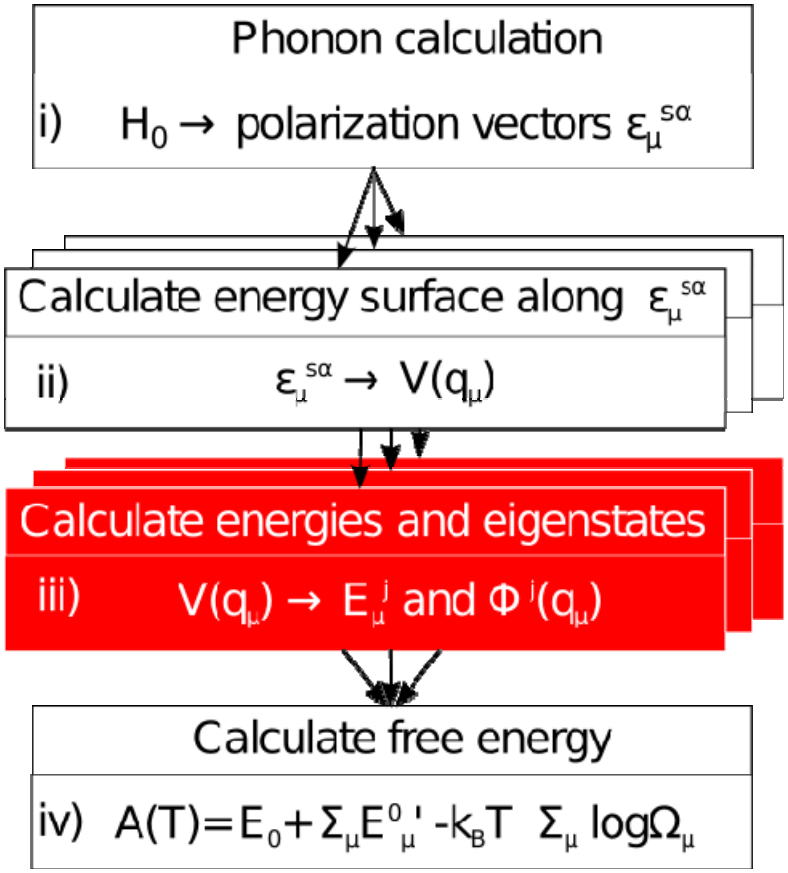
$$A(T) = E_0 - k_B T \log\left(\Omega'_1 \cdots \Omega'_N\right) = \underbrace{E_0}_{\text{ground state energy}} + \underbrace{\sum_\mu E^0_\mu}_{\text{zero point energy}} - T \cdot \underbrace{k_B \sum_\mu \log \Omega_\mu}_{\text{entropy}}$$

Mode decoupling and general procedure of DAMA

- Optimization of atomic positions
  - $V_1 = 0$
- Rotation of coordinates eliminate coupling between modes up to order 2 (Normal-Modes):

$$u^{s\alpha} = \sum_{\mu=1}^{3N} \frac{1}{\sqrt{M_s}} \epsilon_\mu^{s\alpha} q_\mu$$
$$P^{s\alpha} = \sum_{\mu=1}^{3N} \sqrt{M_s} \epsilon_\mu^{s\alpha} p_\mu$$

- DAMA rotates coordinates but keeps all diagonal terms of *V*
- Supercell: Brillouin zone sampled by Γ-point



Gorelli, Elatresh (2012) Lattice dynamics of dense lithium. Phys. Rev. Lett., **108**

Method: Numerical solution to calculate eigenstates of *any potential shape*

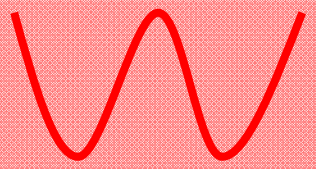
- In DAMA the eigenenergies are calculated solving numerically the full hamiltonian for each decoupled mode

$$H_\mu = \frac{p_\mu^2}{2} + V_\mu^{diag}(q_\mu)$$

$$V_\mu^{diag}(q_\mu) = \frac{c_p}{D\, q_\mu^2 - C} + \sum_j c_j \, \sin\left(j \cdot \kappa\,(q_\mu - a)\right)$$

- The potential is fitted to analytic functions (sampling the coulomb repulsion at large q_μ)
- As a basis we use plane waves

$$b_k = \sqrt{\frac{2}{b-a}} \cdot \sin\left(k\,\kappa(q_\mu - a)\right)$$

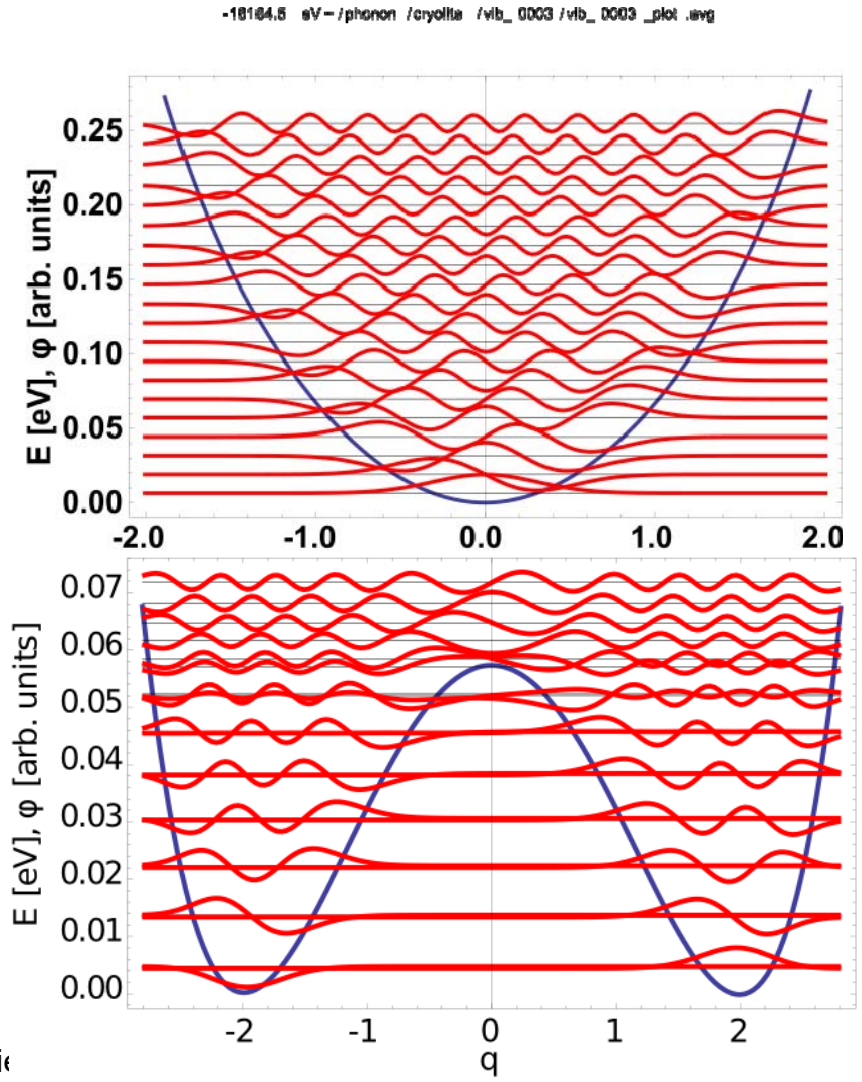


- The Hamiltonian then corresponds to a matrix, which can be numerically diagonalized
  - eigenvalues correspond to the vibrational energies
  - eigenvectors cprrespond to the coefficients of the basis functions

$$\langle b_j | H_\mu | b_k \rangle$$

Result: Vibrational modes

- Calculations suggest appearance of tunnelling states in the high temperature phase with a degenerate vibrational spectrum
- Double well states can explain large vibrational ellisoids



Overview implementation

- Present
  - Calculation of eigenstates
  - Free energy (Phase transitions, thermal expansion)
  - Atomic mean square deviation
  - Vibrational DOS
- Planned (2018)
  - Calculation of elastic constants and bulk modulus at T>0
  - Reciprocal space sampling
- Further ideas
  - Plotting of cube files (probability density)
  - Structure optimization at T>0

Get started

- Download from adams-science.com/dama
  - Dama routines (gzip)
  - Dama source (gzip)
  - Dama exerices (gzip)
- Transfer to supercomputer, uncompress
- Compile source (adjust Makefile)
- Add bin_dama to you path
  - export PATH=~/bin_dama:$PATH

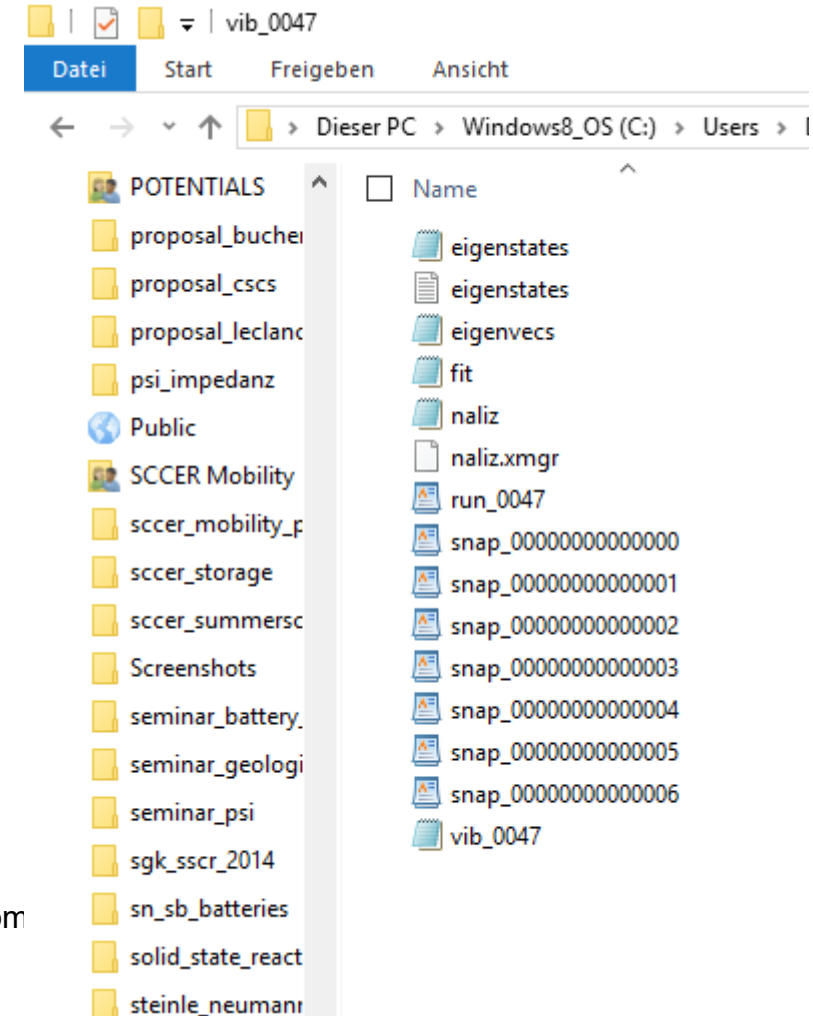
Workflow overview

- S: Set up unicell & optimize
- P: Calculate phonon modes (decoupling; use ph.x or by hand)
- V: Sample potential energy surface
  - Setup vib_0000 to vib_xxxx
  - Run SCF calculations
- E: Calculate eigenstates for each mode (vib_0000 to vib_xxxx) using eigenstates.x (DAMA kernel)
- D: Calculate properties of solid using eigenanalysis.x (DAMA evaluation and synthesis)

=> S P V E D

Files
S P V E D

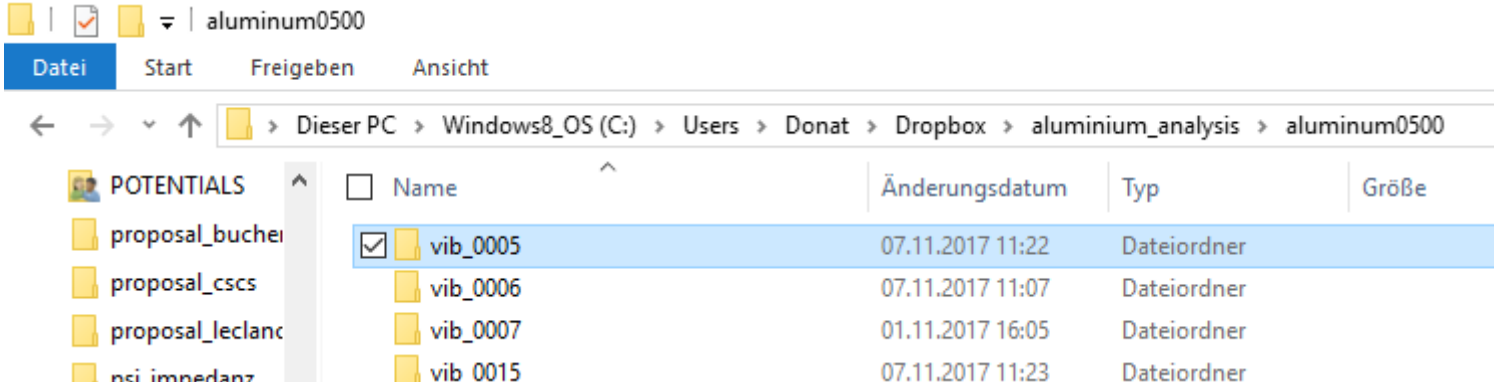
- aluminum0500/vib0047
- input PES: snap_00000000.xyz to snap_00000006.xyz and corresponding input alu0500_000001.inp, etc
  - Typically 7 positions for stable modes, and 21 for unstable ones
- vib_0047.xyz contains all positions (like movie)
- Input and output of eigenstates.x:
  - naliz.dat: input
  - eigenstates.dat: energies
  - eigenvecs.dat: wave functions
  - fit.dat: comparision of fit of Energy data to discrete sampling



Files

S P V E D

- Aluminum0500
- S: cryo.scf.inp pw.scf input, further pwscf input is generated by job.p
- P-V: movie: folder containing the original polarization vectors vib_0000.dat, vib_0001.dat etc.
- E-D: quality_2017_11_27.dat: comparison of vibrational frequency DAMA vs. Harmonic approximation
- D: Enaliz.dat input for eigenanalysis.x



Set up cell: job.p
S P V E D

- Perform Self-consistent calculation
  - Determine unit cell
  - Determine atomic positions (optimization)

Calculation of phonon modes (step_001)

S P V E D

- P: Calculate phonon modes (decoupling; use ph.x or by hand)
- Either run ph.x to generate matdyn.modes (containing polarizaiton vectors):
- Decompose cryo.scf.out (when optimization was performed):
  - `viz_pwscf_run.bash -i cryo.scf.out`
  - `getlast_xyz.bash -i run.xyz -b`
  - `cp snap_118.56.xyz snap.xyz`
- mkdir movie
  - `cd movie`
  - `ln -s ../matdyn.modes`
  - `ln -s ../snap.xyz`
  - `decompose_vib.bash`
  - `cd ..`
- Exercise: Determine polarization vector with lowest frequency ($\omega > 0$)

Calculation of phonon modes
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- Alternative to ph.x: by hand
- Advantage: large supercells can be handled (in ph.x supercells are difficult to handle)
- Write polarization vectors of unit cell containing displacement in x,y and z-direction
  - 3 vectors per non euqivalent atom in unit cell
  - copy vecotors to movie/vib_0000.dat, movie/vib_0001.dat, movie/vib_0002.dat, ..
- Generate displacements using cre_vib –l „0000 0001 0002“ –a 0.1 –n 2
  - Small smplitude of displacement, only one displacement +/-
- run resulting calculations in vib_0000, vib_0001, vib_0002, vib_0003, etc.
- Extract forces + coupling constants using get_coupling.bash
- Transfer coupling.dat to local computer to reconstruct forces in supercell and generate polarization vectors vib_0000.dat, vib_0001.dat etc. (eg. Using mgsio3_eigenmodes.nb)
- Move polarization vectors and vib_0000, etc to subdirectory coupling
- Transfer new polarization vectors back to original folder move/vib_0000.dat, movie/vib_0001.dat etc.

Sample potential energy surface, step_002

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- Verify that cryo.scf.inp contains `calculation= ‘scf‘` and `restart_mode=‘from_scratch‘`
- For stables vibrational modes run
  - `cre_vib.bash –l „0000“ –a 0.5 –n 6`
- For unstables vibrational modes run
  - `cre_vib.bash –l „0056“ –a 3 –n 20`
- Indices can be provided as a list –l „0001 0002 0003“
  - List of *all indices* can be generated copying line `jl=`ls movie/vib_*dat ....`` from `cre_vib.bash`
- For all vib_0000, vib_0001, etc directories
  - Submit generated jobs
  - `nbearb` is a routine, that reads list_jobs.txt, and at each execution executes a n of lines (used to chain jobs, avoiding never ending loops)
  - `for fon in vib_3 ; do cd $fon ; ./nbearb –n -1 ; cd .. ; done`
- Exericse: write directory vib_0005, and pwscf calculations therein (modify vib_0005/job*vib*.p

Calculate eigenstates, step_003
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- Calculate eigenstates for each mode (vib_0000 to vib_xxxx) using eigenstates.x (DAMA kernel)
- Extraction of energy surface from pwscf.out and wring of DAMA input (naliz.dat) is implemented in resubmit.bash
  - resubmit.bash writes xmgrace input.
  - Generate visualization of PES and check quality fitting to discrete data from sampling:
  - `xmgrace -hardcopy -noask -noprint -nosafe -batch naliz.xmgr`
  - This is in contained in first line of naliz.xmgr
- adjust ymax (eventually ymin) in order to increase quality of fitting
  - Drop points in naliz.dat, that evidently did not converge
- Expercise: in vib_0010 extract all energies to naliz.dat and calculate eigenstates

Calculate free enegy and properties at T>0, step_004
S P V E D

- Calculate properties of solid using eigenanalysis.x (DAMA evaluation and synthesis)

- Expercise: Calculate free energy and MSD at 500 K (modify enaliz.dat)

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S P V E D

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Useful routines

S P V E D

- cre_fe_supercell.bash, cre_mg_supercell.bash: From calculation of unit cell create input for supercel calculations S and P_manual
- gen_all_phonvib.bash: Generates all possible polarization vectors (for manual determination of dynamical matrix and polarization vectors) P_manual
- get_coupling.bash: Extract elements of dynamical matrix for manual phonon calculations P_manual
- coupling_to_dama.bash: run before transfering true polarization files to mgo/movie (relevant when doing phonon calculation by hand) P_manual-V
- decomp_vib.bash: decomposes matdyn.modes into individual polarization vectors P-V
- cre_vib.bash: using movie/vib_0001.dat etc. Setup input for sampling of PES P-V

Useful routines
S P V E D

- V:
- cre_ela.bash: sample PES along further degrees of freedom (change of volume and volume conserving deformations of unit cel) V
- genjob.bash: Based on snap_00001.xyz, etc. generate all input files for pw.x V
- genjobpim.bash: snap_00001.xyz, etc. generate all input files for cp2k (PIM calculations) V
- vibjob.bash: in vib_0000 generate job_vib.p, containing all pw.x calculations V

- E:
- harmapp.bash: From lage vibrational in one vib_0001 interpolate PES for small amplitudes harmonically E

Useful routines
S P V E D

- recalcvib.bash: for vib_0000.dat file determine moment of inertia (i.e. equivalent mass) E
- resubmit.bash: extract PES from pw.x output, run eigenstates.x E
- filesresubmitpim.bash : extract PES from cp2k output E
- test_quality.bash: compare vibrational frequencies from E-D DAMA with those of ph.x (limited to small amplitudes)
- pim_test_quality.bash: adaptation of test_quality.bash for PIM
- calculations E-D
- mkdosgraph.bash: generate input for visualization of vibrational DOS (uses my_convolute.x) D
- phonon_dos.bash: generate phonon dos using output of ph.x
- getdosdata.bash: Extract QH vibrational frquencies from all vib_0000, vib_0001 directories D