

qha: A Python package for quasi-harmonic free energy calculation for multi-configuration systems [1]

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[1] Qin, T. *et al. Computer Physics Communications*. 2018.

Quasi-harmonic approximation (QHA)

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- a useful tool to compute materials thermodynamic properties at high T , P
- a good approximation when T is not too close to T_M
- Born–Oppenheimer approximation: static contribution + vibrational contribution (QHA on phonon spectra)
- deal with multiple configuration systems

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- the order-disorder phase boundary between ice-VIII and ice-VII [2]
- the relative stability of hydrous defects in Mg_2SiO_4 -forsterite at high P and T [3]
- the effect of disorder and iron concentration on the spin crossover diagram of Fe^{3+} -bearing MgSiO_3 -bridgmanite [4]

[2] Umemoto, K. *et al. Chemical Physics Letters*. 2010.

[3] Qin, T. *et al. American Mineralogist*. 2018.

[4] Shukla, G. & Wentzcovitch, R. M. *Physics of the Earth and Planetary Interiors*. 2016.

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- single configuration system:

$$Z(T, \nu) = \exp(-E(\nu)/k_B T) \prod_{\mathbf{q}, s} \frac{\exp(-\hbar\omega_{\mathbf{q}s}(\nu)/2k_B T)}{1 - \exp(-\hbar\omega_{\mathbf{q}s}(\nu)/k_B T)}, \quad (1)$$

$$F(T, \nu) = -k_B T \ln Z(T, \nu). \quad (2)$$

- multi-configuration systems:

$$Z(T, \nu) = \sum_{n=1}^{N_c} g_n Z_n(T, \nu), \quad (3)$$

$$F(T, \nu) = -k_B T \ln Z(T, \nu). \quad (4)$$

- finite strain equation of state fitting to string $\{F(T, \nu)\}$'s to a continuous function $F(T, V)$

Flow chart

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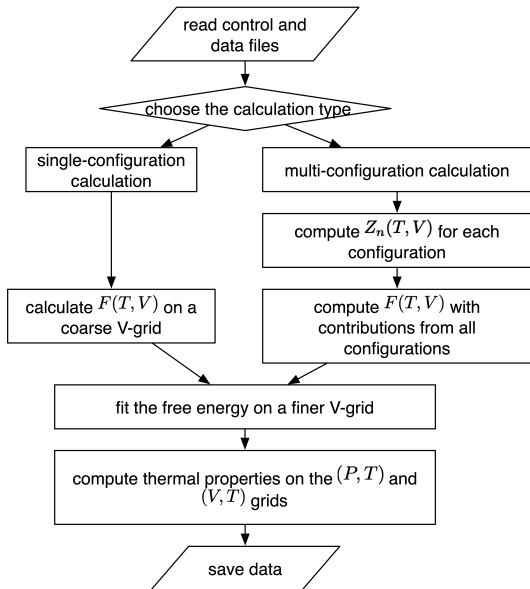
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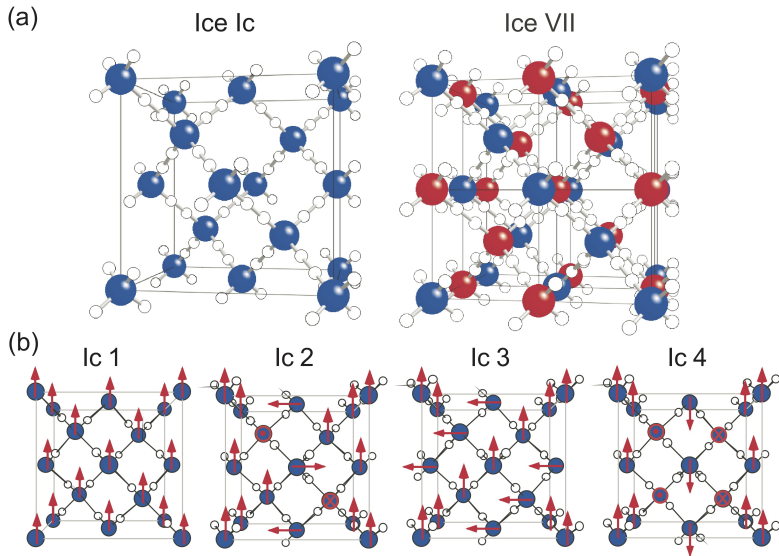
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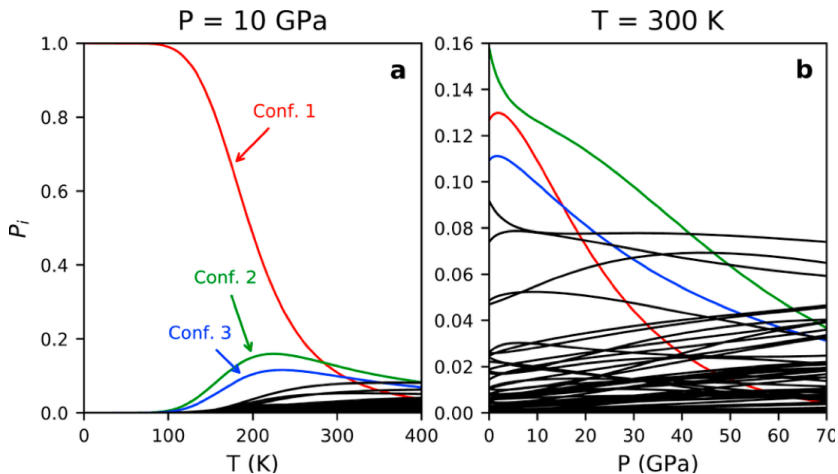
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$$\text{Possibilities } P_i(V, T) = \frac{g_i \exp\left(\frac{-E_i(V)}{k_B T}\right)}{Z(V, T)} \text{ of the 52 configurations}$$

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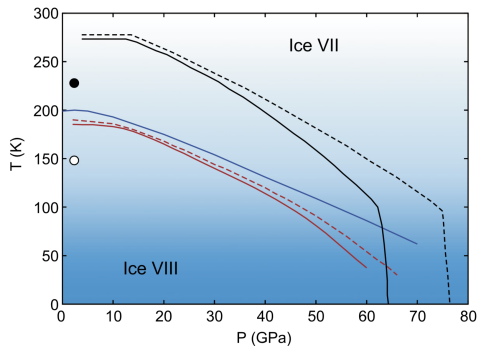
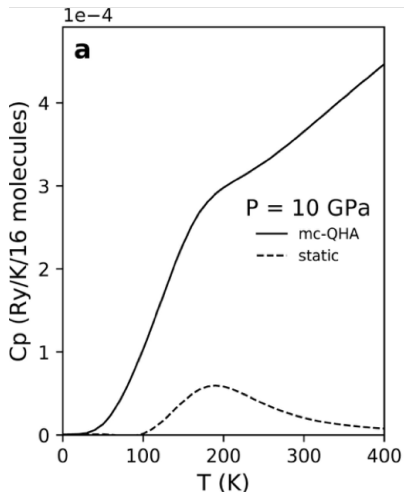
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[2] Blue line: static, red lines: QHA results, black lines: experimental results, solid lines: H₂O, dashed lines: D₂O

[2] Umemoto, K. et al. *Chemical Physics Letters*. 2010

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- addresses the thermodynamic properties of multi-configuration systems
- directly samples the free energy in Brillouin zone
- balances the speed and flexibility

other codes

- address single configuration systems
- integrate the vibrational density of states $g(\omega)$ to get F [5]
- less flexible and extensible [6]

[5] Petretto, G. *et al. Scientific Data*. 2018

[6] https://github.com/dalcorso/thermo_pw

Applications or extensibilities

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MineralsCloud / qha

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A pure Python package for calculating thermodynamic properties under quasi-harmonic approximation, using data from ab-initio calculations

thermodynamic-properties quasi-harmonic-approximation python3 scientific-computing ab-initio phonon Manage train

384 commits 8 branches 16 releases 1 environment 4 contributors GPL-3.0

branch: master New pull request Create new file Upload files Find file Clone or download

Author	Commit Message	Time
shigeki99	Deprecate the use of TeXify app	Latest commit: ed23d57 on Jan 9
github	Update issue & pull-request templates	8 months ago
ebcs	Merge branch 'master' into develop	a month ago
examples	fix: Remove deprecated 'plot_results' keyword	2 months ago
qha	Update version number	a month ago
gfigione	Update gfigione	7 months ago
travis.yml	fix: Update 'travis.yml' 'local-dir'	a month ago
LICENSE.txt	fix: Change 'setup.py' for Windows users	10 months ago
README.md	Deprecate the use of TeXify app	a month ago
setup.py	Create 'basic_io' subpackage	5 months ago

qha: A Powerful Python toolkit for quasi-harmonic approximation

(TOC)

[docs](#) [status](#)

Contributors

This repository is now maintained by [Tian Qin](#) and [Qi Zhang](#). Thanks to the contribution from [Chenming Luo](#).

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<https://github.com/MineralsCloud/qha>

■ Extensibilities to materials research

- thermoelastic properties of materials [7]
- metals with phonon frequencies varying at different electronic temperatures (introduced in seission H17.00005, Tuesday)
- calculate the geotherm and isentrope [8]

[7] Wu, Z. & Wentzcovitch, R. M. *Physical Review B*. 2011

[8] Cardona, J. J. V. et al. *Geophysical Research Letters*. 2017

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- qha is a fast, user-friendly Python package for traditional QHA calculations
- qha can calculate multi-configuration system's equation of state and other thermodynamic properties
- qha is extensible and will form a more complete toolchain in the near future

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4. Qin, T., Zhang, Q., Wentzcovitch, R. M. & Umemoto, K. qha: A Python package for quasiharmonic free energy calculation for multi-configuration systems. *Computer Physics Communications* (2018).
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6. Umemoto, K., Wentzcovitch, R. M., de Gironcoli, S. & Baroni, S. Order–disorder phase boundary between ice VII and VIII obtained by first principles. *Chemical Physics Letters* **499**, 236–240 (2010).
7. Wu, Z. & Wentzcovitch, R. M. Quasiharmonic thermal elasticity of crystals: An analytical approach. *Physical Review B* **83**, 184115 (May 2011).