User Guide for SC-QHA Code

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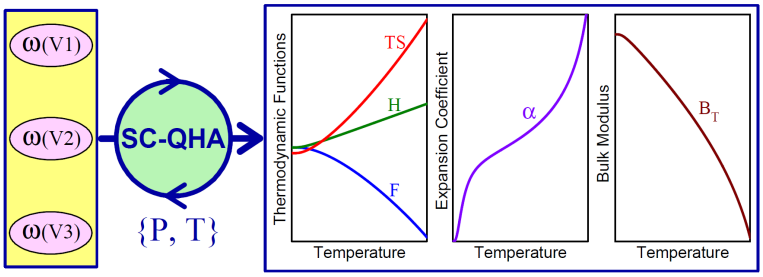
(A) Brief introduction of SC-QHA method and code:



The self-consistent quasiharmonic approximation (SC-QHA) method is an efficient and accurate first-principles method to calculate various thermodynamic properties of solids. The related physical formula, computational algorithm, and selected applications of SC-QHA can be found in **Reference [1]**, and the **online supplementary material** includes the formula derivation steps and detailed testing calculations.

The source code folder (SRC/) includes the 1st-order and 2nd-order SC-QHA methods (i.e., expansion_1st.x and expansion_2nd.x), and the example folder (Example/) includes the SC-QHA calculation results for diamond. The code can be readily compiled using the Makefile in the SRC/ folder:

(1) Specify the compiler in Makefile (default: gfortran), save and exit Makefile;
(2) Type Linux command "make"

(B) Calculation Steps:

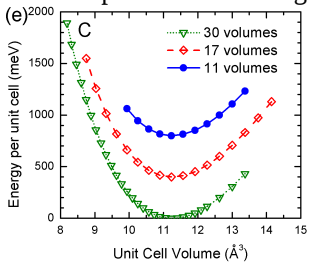
(1)Finely optimize the unit-cell shapes and relax the atomic positions for many volumes around the equilibrium volume.

(2)Fit the Energy-Volume relationship using an equation of state (EOS) using softwares like gnuplot, Origin, and xmgrace. Here, 4-parameter or 5-parameter Birch-Murnaghan (BM4 and BM5) EOS is allowed, due to their superior performance in nearly all of the cases we have considered.

Birch-Murnaghan EOS (**Reference [2]**):

$$E(V)=z_q(1)+z_q(2)*V^{-2/3}+z_q(3)*V^{-4/3}+z_q(4)*V^{-6/3}+z_q(5)*V^{-8/3}$$

where, the z_q's are the fitting coefficients. An example of diamond is given below:



It should be noted:
In the EOS fitting, the units for **Energy** and **Volume** must be **meV** and **Angstrom^3**.

(3)Use the **Phonopy code [3]** to calculate the phonon spectra for 2 or 3 volumes (equally spaced), which is used to calculate the Frequency-Volume and Grueneisen-Volume relationships.

(4)When the DFT calculations of the forces are finished, generate phonon frequencies and eigenvectors in the Brillouin zone using Phonopy, and the input file mesh.conf can be written like (e.g., for diamond):

```
ATOM_NAME = C
DIM = 2 2 2
MP = 20 20 20
EIGENVECTORS = .true.
FORCE_CONSTANTS = Write
```

(5)Use SC-QHA code to calculate various thermodynamic properties, e.g., thermodynamic functions, thermal expansion, and bulk modulus. The input parameters of SC-QHA code are written in a ***namelist*** (Fortran90 term) like:

```
&input
  ……
/
```

and a full explanation for the namelist file (e.g., “input_parameters”) is given below:

```
&input
 atom_No        = {Integer}     ! atom number
 q_No           = {Integer}     ! q-point number
 EOS            = {Character}   ! EOS type: 'BM4' or 'BM5'
 z_q(1)         = {Real}        ! 1st EOS coefficient
 z_q(2)         = {Real}        ! 2nd EOS coefficient
 z_q(3)         = {Real}        ! 3rd EOS coefficient
 z_q(4)         = {Real}        ! 4th EOS coefficient
 z_q(5)         = {Real}        ! 5th EOS coefficient, only applied for “BM5” EOS
 V_min          = {Real}        ! minimum volume from EOS fitting (in A^3)
 P_ext          = {Real}        ! external pressure (GPa), default: 0 GPa
 thermal        = {Logical}     ! .true./.false., default: .false., if .true., thermal expansion will be calculated.
 modes_file(1)  = {Character}   ! name of the 1st modes file with eigenvectors, e.g., 'modes_1.dat'
 modes_file(2)  = {Character}   ! name of the 2nd modes file
 modes_file(3)  = {Character}   ! name of the 3rd modes file, only applied for 2nd-order SC-QHA
 V_GC(1)        =  {Real}       ! the volumes corresponding to the modes files above
 V_GC(2)        =  {Real}
 V_GC(3)        =  {Real}       ! only applied for 2nd-order SC-QHA
 T_min          =  {Real}       ! minimum temperature, default: 1.0 K
 T_max          =  {Real}       ! maximum temperature, default: 3000.0 K
 delta_T        =  {Real}       ! temperature increment, default: 1.0 K
/
```

The SC-QHA code (e.g., 2nd-order SC-QHA) can be executed using command:

```
expand_2nd.x < input_parameters > output
```

More example results can found in the Example folder and **Reference [1]**.

(C) Special Application to Two-Dimensional (2D) Materials:

2D materials are intensively studied in recent years, and thermodynamic properties should be very important for their applications. For example, the thermal expansion of MoS_2 may cause the component spalling to its transistors **[4]**. The thermal expansion of both substrate and 2D materials may cause interfacial stress/strain, which can influence the device stability and optical properties **[5]**.

To apply SC-QHA code for 2D materials, there are two points may need to mention:

(1) The volume needs to be calculated using an arbitrary lattice constant *c* (e.g., *c*=1.0 Angstrom). Then, the 2D properties can be readily derived from the calculated "3D properties" using SC-QHA code, e.g.,

(i) 2D area (A) vs. 3D volume:

$$A_{2D} = V_{3D}/c$$

(ii) 2D vs. 3D thermal-expansion coefficient:

$$\alpha_{2D} = \frac{1}{A}\frac{dA}{dT} = \frac{1}{V}\frac{dV}{dT} = \alpha_{3D}$$

(iii) 2D vs. 3D bulk modulus:

$$B_{2D} = A\frac{d^2E}{dA^2} = cV\frac{d^2E}{dV^2} = cB_{3D}$$

(2) The working temperatures for 2D materials are always relatively low (e.g., < 800 K), and we have shown in **Reference [1]** that the 1st-order SC-QHA method is sufficient for such kind of low temperatures. Thus, we may only need to calculate the phonon spectra of **2 areas** (e.g., 0.2% and 2% expanded areas) for the thermal expansion of 2D materials.

References:

[1] L.F. Huang, X.Z. Lu, E. Tennessen, and J.M. Rondinelli, "*An efficient ab-initio quasiharmonic approach for the thermodynamics of solids*", Computational Materials Science **120**, 84-93 (2016).
[2] S.L. Shang, Y. Wang, D.E. Kim, and Z.K. Liu, "*First-principles thermodynamics from phonon and Debye model: Application to Ni and Ni_3Al*", Computational Materials Science **47**, 1040-1048 (2010).
[3] Atsushi Togo, http://atztogo.github.io/phonopy, Note: Version 1.9.3 will be fully compatible with our SC-QHA code.
[4] K. Sano et al., "*Large variability of contact resistance in Au/Cr/MoS_2 system and its suppression by Cr thinning*", Japanese Journal of Applied Physics **55**, 036501 (2016).
[5] L.F. Huang and Z. Zeng, "*Roles of mass, structure, and bond strength in the phonon properties and lattice anharmonicity of single-layer Mo and W dichalcogenides*", Journal of Physical Chemistry C **119**, 18779-18789 (2015).