

Birch – Murnaghan Fits

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(If you are not interested in the procedure and only want a quick result, jump to the last section.)

Theoretical background

The dependence of the energy of a system on the lattice constant a can be described by the Birch–Murnaghan (BM) equation.:

$$E(a) = E_0 + \frac{9V_0 B_0}{16} \left\{ \left[\left(\frac{a_0}{a} \right)^2 - 1 \right]^3 B_0' + \left[\left(\frac{a_0}{a} \right)^2 - 1 \right]^2 \left[6 - 4 \left(\frac{a_0}{a} \right)^2 \right] \right\}$$

Where $E(a)$ is the total energy of the system, a_0 is the equilibrium lattice constant, $V_0 (= a_0^3)$ is the equilibrium volume, B_0 is the bulk modulus at zero pressure, B_0' is the derivative of the bulk modulus with respect to pressure:

$$B_0 = -V \left(\frac{\partial P}{\partial V} \right)_{P=0} ; \quad B_0' = \left(\frac{\partial B}{\partial P} \right)_{P=0}$$

Remarks:

The third-order isothermal BM-equation of state is based on the pressure expansion of the bulk modulus and consequently is valid only at moderate compression.

Assumptions: - Isotropic, cubic solid

- Constant temperature (isothermal)

- Moderate pressure

Fitting procedure

In order to apply a least square fitting to the BM-equation, the formula is expressed as linear regression. (More information about linear regression can be found on Wikipedia, where it is well explained: https://en.wikipedia.org/wiki/Linear_regression)

For this, $\left(\frac{1}{a} \right)^2$ will be substituted by b : $b = \frac{1}{a^2}$

Transforming the BM-equation gives

$$y(b) = c_0 + c_1 b + c_2 b^2 + c_3 b^3$$

Where $y(b) \equiv E(a)$ and $c_{0,1,2,3}$ are constants that can be expressed as functions of bulk modulus and volume. The physical meaning of $c_{0,1,2,3}$ is not important in the context of finding the equilibrium lattice constant a . Hence, they should be treated only as fitting parameters.

The LINEST function (linear least square curve fitting) can be applied to this formula, while using Libreoffice (or another software). But: Be careful, when using EXCEL! The fits slightly vary. (Rodrigo has found that Libreoffice gives more accurate results.)

Applying the LINEST matrix function:

Mark a 4x5 cell matrix and enter =LINEST("column of y-values"; "matrix of x-values"; 1; 1).

The y-values are in this case the energies $E(a)$; the x-values are b, b^2, b^3 (in a 3 x (number of values) matrix); 1 means that an intercept of the function (in this case c_0) is taken into account; 1 means that the statistics of the fit will be displayed.

The fitting procedure yields values for the constants $c_{0,1,2,3}$. In Libreoffice they will be displayed in reverse order: $c_{3,2,1,0}$

The results will be displayed as a 4 x 5 matrix:

The 1st row shows the results for $c_{3,2,1,0}$, the 2nd – 5th rows show the statistics.

Important: The 2nd row shows standard deviations of the results, which serve as fitting criterion. The 1st number in the 3rd row is the R^2 -value. The 2nd number in the 4th row are the degrees of freedom in this calculation, which should be > 2 .

Since the correct lattice constant a_0 corresponds to the minimum of the function $E(a)$, it can be found by setting $\frac{dE(a)}{da}$ to zero.

This is equal to setting $\frac{dy(b)}{db} = 0$:

$$0 = c_1 + 2c_2b + 3c_3b^2$$

$$b_{1,2} = \frac{-2c_2 \pm \sqrt{4c_2^2 - 12c_1c_3}}{6c_3}$$

There will be 2 values for b , but from the result for $a = \frac{1}{\sqrt{b}}$, it can be clearly distinguished, which is the reasonable result for the equilibrium lattice parameter a_0 .

Finding a_0 .

- 1.) Carry out at least 5 calculations for different initial lattice parameters a , better up to 10 calculations. (As more values you have, as better the fit.) In these calculations keep box size fix, but allow ions to relax (ISIF = 2 in INCAR, which is the default anyway, and IBRION = 1 (or 2, if you are far from equilibrium). If you know the approximate equilibrium lattice constant a_0 , take 2-4 a values on each side of the minimum, being spaced at equal distances of about 1% a_0 . (This may depend on the system). If you don't know a_0 , you might like to do a full geometry optimization (ISIF = 3) first and then do the BM-fitting.
- 2.) Check, if all calculations have converged to the desired electronic state. If yes, note the energies (energy(sigma->0)) for each initial lattice constant a .
- 3.) Download the Libreoffice file from Wiki. Enter the energies with the corresponding lattice constants in the 2 left columns. The resulting equilibrium lattice parameter will be displayed in the orange box in the right bottom corner. (It will be all calculated automatically. However, I cannot guarantee for any mistakes, while preparing the Libreoffice file. If you find any mistake in the file, let me know)