CSBI calculator manual

2023.10.18 ver.1.0.0

Toru Sasaki (*Graduate School of Science, Tokyo Institute of Technology, Japan*)

Table of contents

1. What is this program?
2. Download and launch the program
3. Input data
4. Results data
5. Supplement
    i. Analytical function of potential surface

1. What is this program?

This is a program that calculates intermolecular vibrational eigen values and eigen vectors by solving time independent Schrödinger equation for small molecule-large oblate molecule system. Coupled-stretch-bend-internal-rotation (CSBI) model potential is used for analytical potential function. Following items are required for the calculation.

- A symmetry, mass and rotational constants of small molecule
- Mass and rotational constants of large molecules
- Equilibrium intermolecular distance
- Potential parameters of CSBI potential function (5. Supplement)

By using this information, this program calculates energy eigen values and eigen vectors.

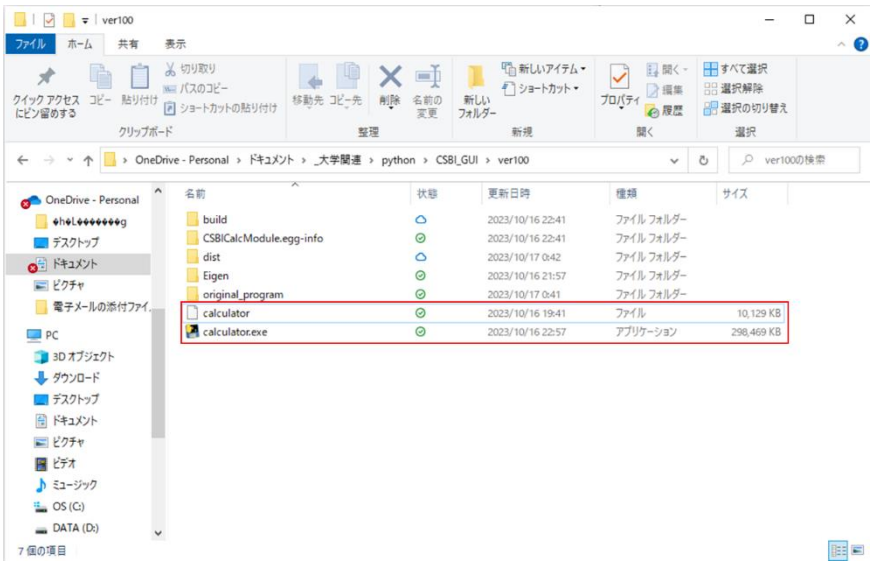
2. Download and launch the program

Windows

Double-click calculation.exe file in folder, then program will launch.

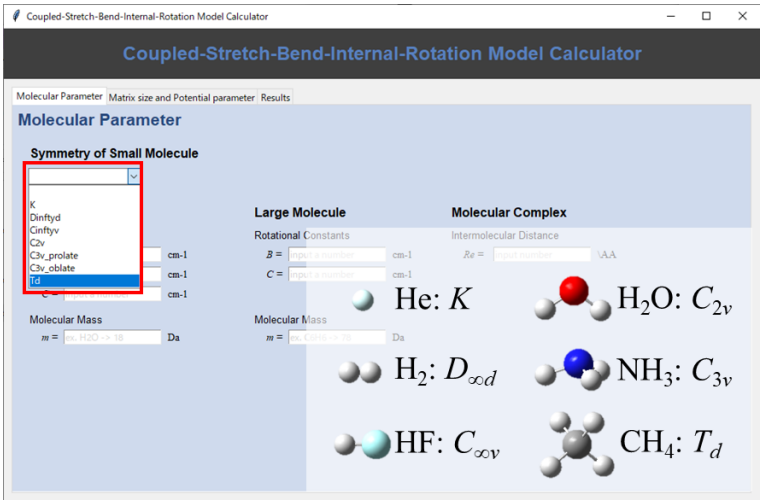
Linux

In the folder with the calculator file, running `. /calculator` command to launch the program.

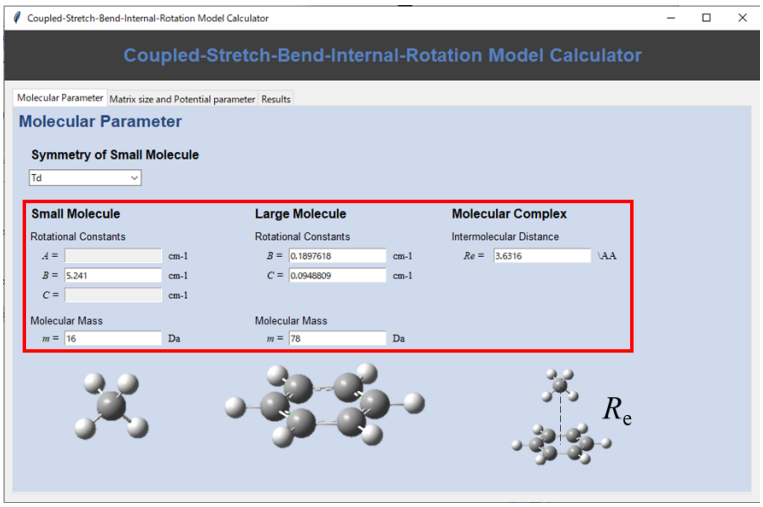


3. Input data

1. Choose a symmetry of small molecule. The input symmetry limits boxes of rotation constants A, B, and C that can be entered.



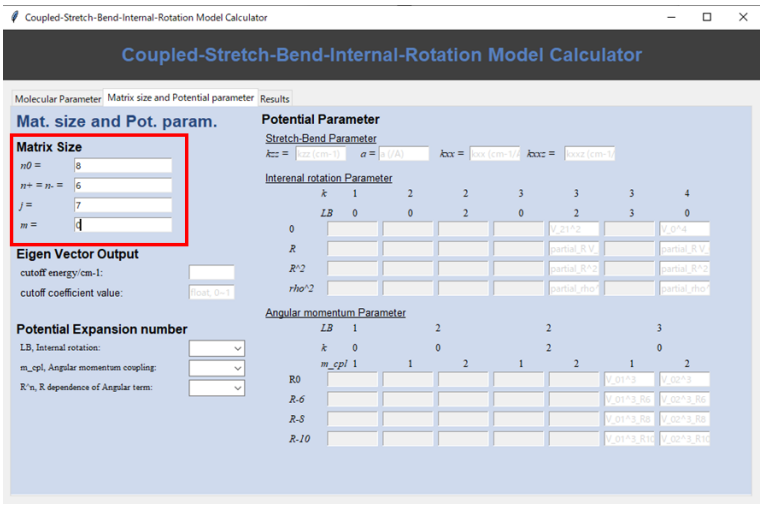
2. Enter the rotational constants, mass, equilibrium intermolecular distance. The unit of these number are cm^{-1} and Å.



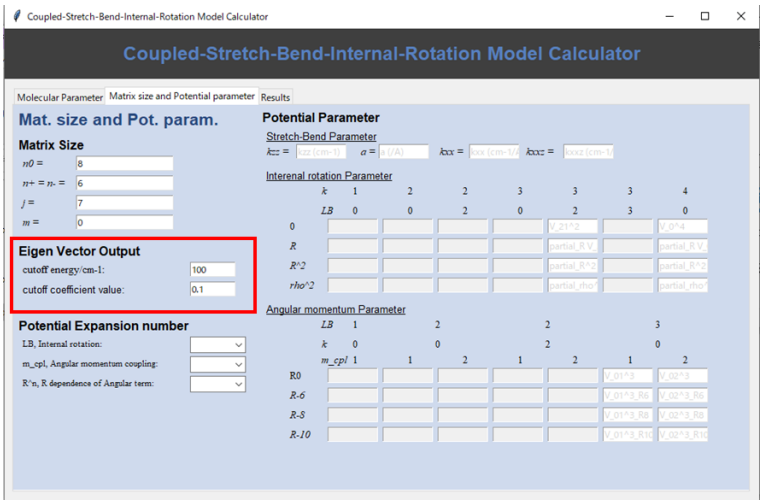
3. Determine the dimension of Hamiltonian matrix. The larger the dimension, the more exact the value, but the higher the computational cost. In benzene-methane system, we used following values.

$$n_{0,\max} = 8, \qquad n_{+,\max} = n_{-,\max} = 6, \quad j_{\max} = 7$$

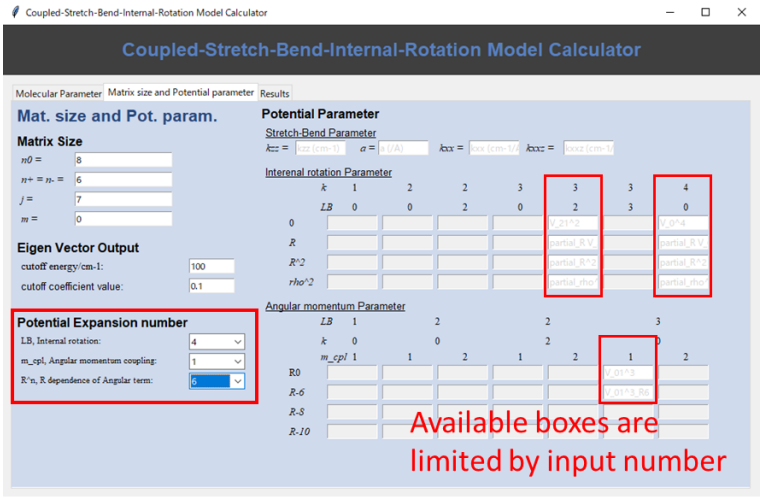
m is good quantum number of this model system and must be smaller than $j_{\max}$. The program computes only one m case. If you want data for more than one m, please run the program multiple times. In benzene methane system, we needed $m = 0, 1, 2$.



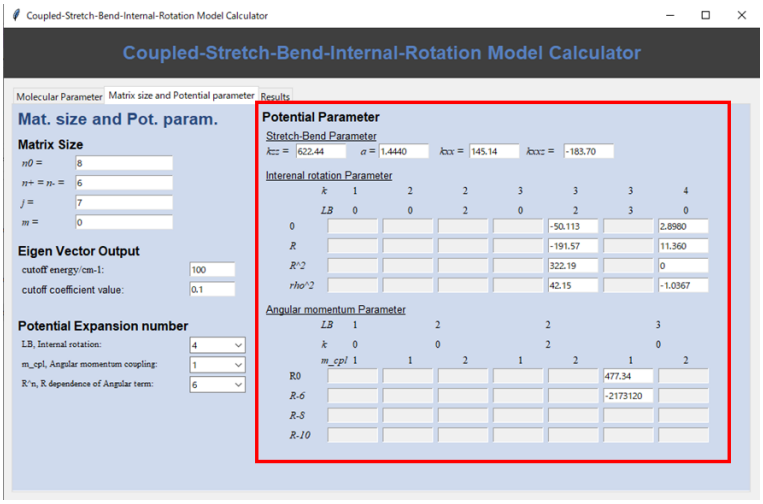
4. Enter some limitations for output of eigen vector.
   i. Cutoff energy is a parameter that determines how far up to the higher energy levels are output from the ground state.
   ii. Cutoff coefficient is a parameter that determines how small the eigenvector coefficients are output. If all eigenvectors are required (e.g., for spectral calculations), enter -1.



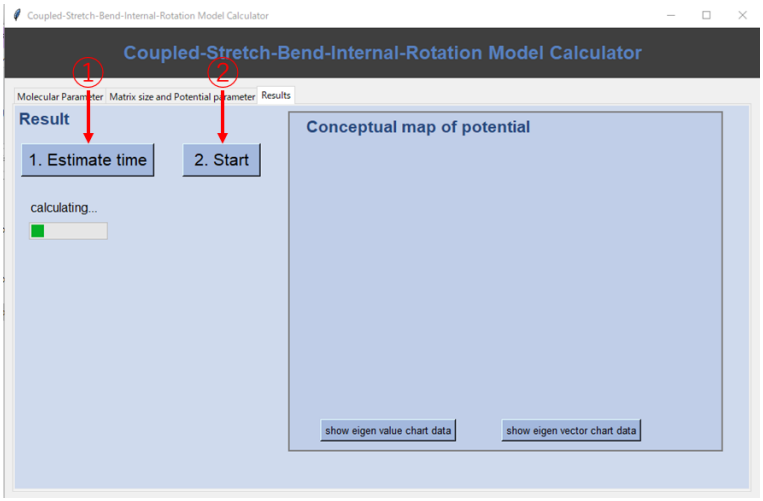
5. Choose the number of expansion terms. These inputs change the input boxes on the right side.



6. Enter the potential parameters. In this example, we entered the value obtained from a fit to quantum chemical calculation data, but you can enter any float value. If not entered, it will be read as zero. The unit of these numbers are combinations of cm^{-1} and Å.

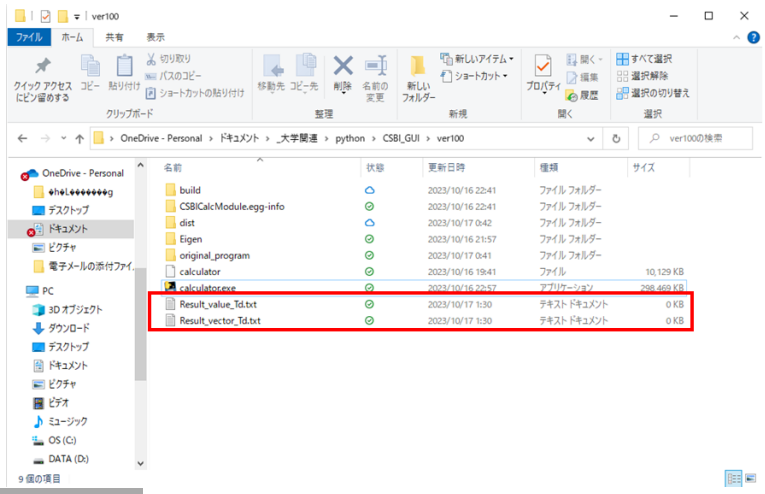


7. First, press 1. Estimate time, then press2. Start. When Estimate time is pressed, some information of potential and estimated calculation time calculated by using input data will be show. Press Start to start the diagonalization calculation.
   It is not a “bug” that the timer starts even though the calculation does not start when Estimate time is pressed. It is not a “bug” that the timer stops during the diagonalization calculation.



3. Result data

The eigen values and the eigen vectors will be saved as txt file in the same folder as the exe file.

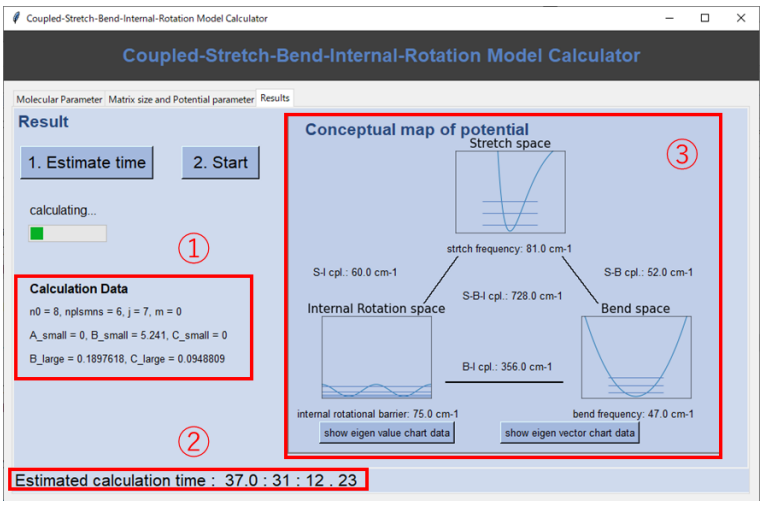


Pressing Estimate time, the data ①～③ based on the entered parameters are shown.

① It is the parameters used in calculation.

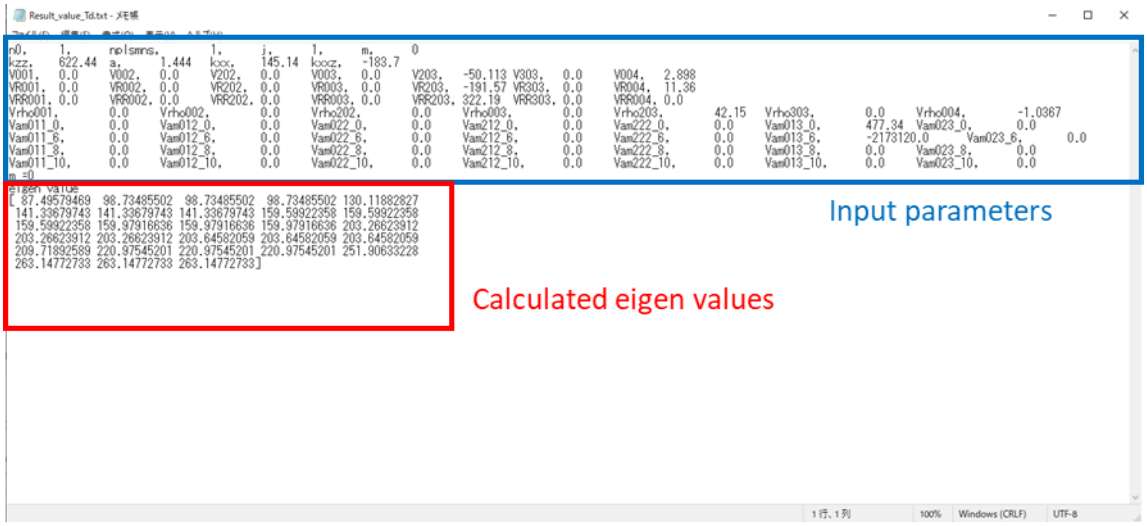
② It is an estimated calculation time based on $n_{0,\max}$, $n_{+,\max}$, $n_{-,\max}$, $j_{\max}$. Please use it only as a reference, because it is highly dependent on the parameter values and PC environment.

③ It is a relationship between molecular motions obtained from potential parameters. The vibration frequencies and barriers that characterize stretch, bend, and internal rotation are shown. In addition, the coupling among these motions are also shown. The displayed stretch Morse potential and bend harmonic potential are calculated functional forms. The internal rotation space shows the free rotation energy level calculated from the rotation constants and the cosine function representing the barrier.



Result_value.txt

A list of input parameter and calculated eigen values is output.



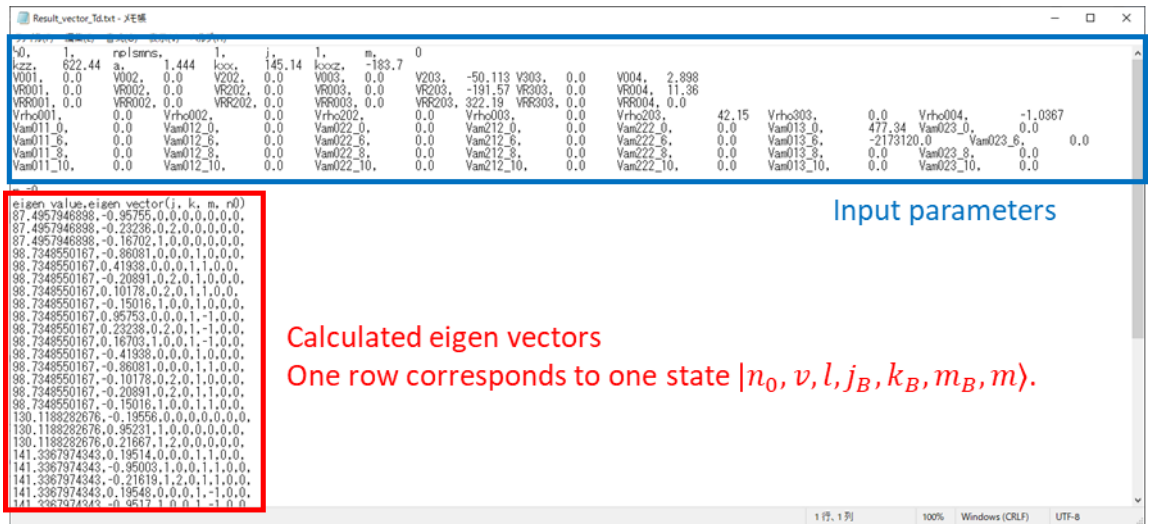
Result_vector.txt

A list of input parameters and calculated eigenvectors is output.

In the two-dimensional table shown below, one horizontal row represents one component of an eigenvector. Each column corresponds to the following elements.

eigen value, coefficient, component of vector $(n_0, v, l, j_B, k_B, m_B, m)$

n_0 is a quantum number of 1-dimensional stretch vibration, v, l are quantum numbers of 2-dimensional bend vibration j_B, k_B, m_B は are quantum numbers of symmetric top internal rotation, m is good quantum number $l + m_B$.



5. Supplement

i.Analytical function of potential surface

As a practical problem, determination of the potential parameters requires fitting an analytic function to the energy grids calculated from quantum chemical calculations. For that case, here are the potentials defined in the program. $C_{l,m}(\theta,\phi)$ is renormalized spherical harmonics.

$$
\begin{aligned}
V(R,\rho,\omega_B) = {} & k_{zz}\left(1-e^{-a(R-R_e)}\right)^2 + k_{xx}\rho^2 + k_{xxz}\rho^2\left(1-e^{-a(R-R_e)}\right) \\
& + \sum_{L_B=1}\sum_{0<K_B<L_B} V_{K_B}^{L_B} T_{0,K_B}^{L_B} \\
& + \sum_{L_B=1}\sum_{0<K_B<L_B} \partial_R V_{K_B}^{L_B} T_{0,K_B}^{L_B}(\omega_B)(R-R_e) \\
& + \sum_{L_B=1}\sum_{0<K_B<L_B} \partial_R^2 V_{K_B}^{L_B} T_{0,K_B}^{L_B}(\omega_B)(R-R_e)^2 \\
& + \sum_{L_B=1}\sum_{0<K_B<L_B} \partial_\rho^2 V_{K_B}^{L_B} T_{0,K_B}^{L_B}(\omega_B)\rho^2 \\
& + \sum_{n=0,6,8,10}\sum_{L_B=1}\sum_{0<K_B<L_B} {V_{1,K_B}^{L_B}}^{(n)} \left[T_{1,K_B}^{L_B}(\omega_B) C_{1,-1}\left(\arcsin\frac{\rho}{R},0\right) - T_{-1,K_B}^{L_B}(\omega_B) C_{1,1}\left(\arcsin\frac{\rho}{R},0\right)\right] R^{-n}
\end{aligned}
$$

where $T_{m,k}^{j}(\omega_B)$ is defined as a symmetrized linear combination of rotational matrices.

$$
\begin{aligned}
T_{m,k}^{j}(\omega_B) &\coloneqq D_{m,k}^{j}(\omega_B) && \text{only even } k, \text{ for } D_{\infty d} \\
T_{m,k}^{j}(\omega_B) &\coloneqq D_{m,k}^{j}(\omega_B) && \text{for } C_{\infty v} \\
T_{m,k}^{j}(\omega_B) &\coloneqq D_{m,k}^{j}(\omega_B) - (-1)^k D_{m,-k}^{j}(\omega_B) && \text{only even } k, \text{ for } C_{2v} \\
T_{m,k}^{j}(\omega_B) &\coloneqq \left[1+2\cos\left(\frac{2\pi k}{3}\right)\right]\left\{D_{m,k}^{j}(\omega_B) - (-1)^k D_{m,-k}^{j}(\omega_B)\right\} && \text{only } k=0,3,6,\ldots, \text{ for } C_{3v} \\
T_{m,2}^{3}(\omega_B) &\coloneqq D_{m,2}^{3}(\omega_B) - D_{m,-2}^{3}(\omega_B) && \text{for } T_d \\
T_{m,0}^{4}(\omega_B) &\coloneqq \sqrt{14} D_{m,0}^{4}(\omega_B) - \sqrt{5}\left\{D_{m,4}^{4}(\omega_B) + D_{m,-4}^{4}(\omega_B)\right\}
\end{aligned}
$$