

Manual of Forcefit

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If Forcefit is utilized in your work, please cite as:

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1. Introduction

Forcefit is a python code to obtain internal force constants from Cartesian second derivatives (Hessians) calculated by frequency analysis task of Gaussian program. The algorithm employed in this code is totally from Seminario's work, see *Int. J. Quantum Chem.*, **30**, 1271 (1996). In the Seminario's study, eigenanalysis of particular pair interaction matrix is applied to deal with force constants for bonds or for any pair of atoms in general. Force constants for the angles are obtained from their corresponding two-pair interaction matrices of the two bonds or distances forming the angle, and the dihedral force constants are similarly obtained using their corresponding three-pair interaction matrices.

The potential energy function is shown below:

$$V = \sum_{\text{bonds}} k_b (b - b_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_\phi (\phi - \phi_0)^2 + \sum_{\text{impropers}} k_\omega (\omega - \omega_0)^2$$

in which b , θ , ϕ , and ω correspond to bond length, bond angle, dihedral angle, and improper dihedral (out-of-plane), respectively; b_0 , θ_0 , ϕ_0 , and ω_0 are their equilibrium values; k_b , k_θ , k_ϕ , and k_ω are the respective force constants (the indexes for bonds, angles, dihedrals, and impropers are not shown). How to obtain an invariant force constant corresponding to any internal coordinate will be described in the next section.

IMPORTANT NOTE: The force constants reported by Forcefit are the k_b , k_θ , k_ϕ and k_ω in above equation. In many literatures as well as GROMACS program, there is a 1/2 term in front of the force constant, therefore, if you want to comply with their convention, you must manually multiply the force constants reported by Forcefit by a factor of 2!

2. Methods

2.1 Bond force constants

The force $\delta F_A = (\delta F_{x_A}, \delta F_{y_A}, \delta F_{z_A})$ on atom A due to a displacement $\delta r_B = (\delta x_B, \delta y_B, \delta z_B)$ of atom B can be expressed as:

$$\begin{bmatrix} \delta F_{x_A} \\ \delta F_{y_A} \\ \delta F_{z_A} \end{bmatrix} = - \begin{bmatrix} \frac{\partial^2 E}{\partial x_A \partial x_B} & \frac{\partial^2 E}{\partial x_A \partial y_B} & \frac{\partial^2 E}{\partial x_A \partial z_B} \\ \frac{\partial^2 E}{\partial y_A \partial x_B} & \frac{\partial^2 E}{\partial y_A \partial y_B} & \frac{\partial^2 E}{\partial y_A \partial z_B} \\ \frac{\partial^2 E}{\partial z_A \partial x_B} & \frac{\partial^2 E}{\partial z_A \partial y_B} & \frac{\partial^2 E}{\partial z_A \partial z_B} \end{bmatrix} \begin{bmatrix} \delta x_B \\ \delta y_B \\ \delta z_B \end{bmatrix}$$

or in a compact notation:

$$\delta F_A = [k_{AB}] \delta r_B$$

The interatomic force constant matrix $[k_{AB}]$ defined including the minus sign allows an analytical study of the interaction between the two atoms, A and B . The matrix has three eigenvalues λ_i^{AB} and three eigenvectors \hat{v}_i^{AB} ($i = 1, 2, 3$) which we assume to have unit norm. $\hat{\mu}_{AB}$ represents the unit vector of displacement from atoms A to B , then the force constant k_{AB} is solved from the equation below

$$k_{AB} = \sum_{i=1}^3 \lambda_i^{AB} |\hat{\mu}_{AB} \cdot \hat{v}_i^{AB}|$$

The k_{AB} calculated from the above equation meets the invariance which is a fundamental requirement for any physical quantity.

2.2 Angle force constants

For bonds $A-B$ and $C-B$ which have unit vectors $\hat{\mu}_{AB}$ and $\hat{\mu}_{CB}$, the corresponding interatomic matrices $[k_{AB}]$ and $[k_{CB}]$ can be extracted from the Hessian obtained by frequency calculation of molecule. $[k_{AB}]$ and $[k_{CB}]$ have eigenvalues λ_i^{AB} and λ_i^{CB} , and eigenvectors \hat{v}_i^{AB} and \hat{v}_i^{CB} ($i = 1, 2, 3$). Define $\hat{\mu}_N$ as the unit vector perpendicular to the plane ABC

$$\hat{\mu}_N = \frac{\hat{\mu}_{CB} \times \hat{\mu}_{AB}}{|\hat{\mu}_{CB} \times \hat{\mu}_{AB}|}$$

then the unit vectors perpendicular to the bonds $A-B$ and $C-B$ on the plane ABC are

$$\hat{\mu}^{PA} = \hat{\mu}_N \times \hat{\mu}^{AB}$$

and

$$\hat{\mu}^{PC} = \hat{\mu}^{CB} \times \hat{\mu}_N$$

They denote the direction of small displacements of atoms A and C due to the opening or closing of the angle $A-B-C$. The bond angle force constant k_θ then can be solved via the following equation, where R_{AB} and R_{CB} are the length of the bonds.

$$\frac{1}{k_\theta} = \frac{1}{R_{AB}^2 \sum_{i=1}^3 \lambda_i^{AB} |\hat{\mu}^{PA} \cdot \hat{v}_i^{AB}|} + \frac{1}{R_{CB}^2 \sum_{i=1}^3 \lambda_i^{AB} |\hat{\mu}^{PC} \cdot \hat{v}_i^{CB}|}$$

2.3 Dihedral force constants

Four atoms A , B , C , and D define a dihedral which is linked by bonds A - B , B - C , and C - D . The way of deriving dihedral force constant k_ϕ is similar to that used for bond angles. Unit vectors perpendicular to the planes ABC and BCD are given by

$$\hat{\mu}_{N_{ABC}} = \frac{\hat{\mu}^{CB} \times \hat{\mu}^{AB}}{|\hat{\mu}^{CB} \times \hat{\mu}^{AB}|}$$

$$\hat{\mu}_{N_{BCD}} = \frac{\hat{\mu}^{DC} \times \hat{\mu}^{BC}}{|\hat{\mu}^{DC} \times \hat{\mu}^{BC}|}$$

The dihedral angle force constant k_ϕ can be obtained via the following equation

$$\frac{1}{k_\phi} = \frac{1}{R_{AB}^2 |\hat{\mu}_{AB} \times \hat{\mu}_{BC}|^2 \sum_{i=1}^3 \lambda_i^{AB} |\hat{\mu}_{N_{ABC}} \cdot \hat{v}_i^{AB}|} + \frac{1}{R_{CD}^2 |\hat{\mu}_{BC} \times \hat{\mu}_{CD}|^2 \sum_{i=1}^3 \lambda_i^{DC} |\hat{\mu}_{N_{BCD}} \cdot \hat{v}_i^{DC}|}$$

2.4 Improper dihedral (out-of-plane) force constants

Let atoms B , C , and D be connected to the central atom A . Then the out-of-plane angle ω_{ABCD} is defined as the angle between planes ABC and BCD . The movement of atom A perpendicular to the plane BCD feels a restoring force from the bonds A - B , A - C , and A - D . The effective force constant for the movement of atom A perpendicular to BCD is given by the sum of the three bond contributions:

$$k_{AN} = \sum_{i=1}^3 \lambda_i^{AB} |\hat{\mu}^N \cdot \hat{v}_i^{AB}| + \sum_{i=1}^3 \lambda_i^{AC} |\hat{\mu}^N \cdot \hat{v}_i^{AC}| + \sum_{i=1}^3 \lambda_i^{AD} |\hat{\mu}^N \cdot \hat{v}_i^{AD}|$$

where $\hat{\mu}^N$ is the unit vector perpendicular to the plane BCD . Then the out-of-plane force constant for the angle ω_{ABCD} is

$$k_{\omega_{ABCD}} = h_{ABCD}^2 k_{AN}$$

where h_{ABCD} is the length of projection into the plane BCD of the altitude of triangle ABC (with base BC)

3. Usage of Forcefit

After finishing optimization and frequency calculation by Gaussian, move the obtained .fch file which contains the Hessian matrix to the same directory as forcefit.py. Make sure that only one .fch file is in the current directory, otherwise the code cannot recognize which .fch file should be used.

Open the *input.txt* file under the same directory as forcefit.py. First line is related to the calculation type, user can choose bond, angle, dihedral or improper. Second line tells the code which bond, angle, dihedral or improper term the user wants to calculate.

For example, if *input.txt* is prepared as follow:

```
bond  
1-2
```

Then the force constant of the bond between atoms 1 and 2 will be calculated.

If *input.txt* is prepared as

```
angle  
1-2-3
```

Then the force constant of the angle consisting of three atoms in the order of atoms 1, 2 and 3 will be calculated

If *input.txt* is prepared as

```
dihedral  
1-2-3-4
```

Then the force constant of the dihedral consisting of four atoms in the order of atoms 1, 2, 3 and 4 will be calculated.

If *input.txt* is prepared as

```
improper  
1-2-3-4
```

Then the out-of-plane force constant, which is caused by the movement of atom 1 perpendicular to the plane defined by atoms 2, 3, and 4, will be calculated.

After preparing the *input.txt* and run the code simply via the command *python ./forcefit.py*, then the desired result will be immediately obtained. Bond force constants are given in kcal/(mol·Å²). Angular, dihedral and improper force constants are given in kcal/(mol·rad²).