Denote

- $E = \{E_1, E_2, \ldots, E_m\}$ be the sequence of energy profile generated by Quantum Mechanics method, where $|E|$ is the number of points sampled.
- C be the off-set constant.
- $(K_{i,j})$ be the sequence of force constants: in particular, $K_{i,j}$ denotes the force constant corresponding to j^{th} multiplicity of i^{th} angle. Also, by abuse of notation, denote K be the number of multiplicities used.
- M be the main multiplicity.
- $(\varphi_{i,j})$ be the sequence of angles: in particular, $\varphi_{i,j}$ denotes the j^{th} angle at i^{th} moment. Also, by abuse of notation, denote φ be the number of angles.
- $(\delta_{i,j})$ be the sequence of interactions: in particular, $\delta_{i,j}$ denotes interaction of the j^{th} angle at i^{th} moment.
- $RMSE((K_{i,j}), C) = \sqrt{\frac{1}{|E|}\sum_{m=1}^{|E|}\left[E_m - C - \sum_{i=1}^{\varphi}\sum_{j=1}^{K} K_{i,j}\cos(j \times \varphi_{m,i})\right]^2}$ denote the normalized root-mean-square-error corresponding to a choice of force constants.
- $Mag((K_{i,j})) = \sqrt{\frac{2}{K(K-1)}\sum_{i=1}^{K}\sum_{j=1}^{i}\left(K_{i,M} - K_{j,M}\right)^2}$ be a measure of differences between principal force constant of different angles.
- $SoftSgn(x) = \begin{cases} \frac{x}{|x|} = \begin{cases} 1 \; if \; x > 0 \\ -1 \; if \; x < 0 \end{cases} & if \; |x| \geq \varepsilon \\ \frac{x}{\varepsilon} \; otherwise \end{cases}$ be the soft sign function used. In the implementation, $\varepsilon = 10^{-4}$ was used.
- $Sgn((K_{i,j})) = \sqrt{\sum_{i=1}^{K}\sum_{j=1}^{i}\left[K_{i,M} \times SoftSgn(K_{i,M}) - K_{j,M} \times SoftSgn(K_{j,M})\right]^2}$.
- $Err((K_{i,j}), C) = RMSE((K_{i,j}), C) + 0.1 \times Mag((K_{i,j})) + 1000 \times e^{-RMSE((K_{i,j}),C)} \times Sgn((K_{i,j}))$ be the main target function.

The algorithm consists of 3 steps:

1. Pre-calculation

- Calculate $\rho_{i,j}$ to be the Pearson correlation coefficient between $(\delta_{i,k})_k$ and $\left(\cos(j \times \varphi_{i,k})\right)_k$: in particular

$$\rho_{i,j} = \frac{|E|\sum_{k=1}^{|E|}\delta_{i,k}\cos(j \times \varphi_{i,k}) - \left(\sum_{k=1}^{|E|}\delta_{i,k}\right)\left(\sum_{k=1}^{|E|}\cos(j \times \varphi_{i,k})\right)}{\sqrt{|E|\sum_{k=1}^{|E|}\delta_{i,k}^2 - \left(\sum_{k=1}^{|E|}\delta_{i,k}\right)^2}\sqrt{|E|\sum_{k=1}^{|E|}cos^2(j \times \varphi_{i,k}) - \left(\sum_{k=1}^{|E|}\cos(j \times \varphi_{i,k})\right)^2}}$$

2. Pre-optimization

   We find the optimal set of principle force constant, by minimizing $Err((K_{i,j}), C)$ with respect to the constraint

$$\forall j \neq M, K_{i,j} = 0$$

   Denote $r = RMSE((K'_{i,j}))$ where $((K'_{i,j}), C') = arg \min_{(K_{i,j}),C} Err((K_{i,j}), C)$.

3. Optimization

- Let $W = 0.01 \times \sqrt{\frac{1}{r}\left(\sum_m E_m^2\right)}$, $w = \sum_{i=1}^{\varphi}\sum_{j=1}^{K}\frac{1}{\rho_{i,j}\delta_i + \varepsilon_0}$, and $w_{i,j} = \frac{\frac{1}{\rho_{i,j}\delta_i + \varepsilon_0}}{w}$, where $\varepsilon_0 = 10^{-3}$.
- Minimize the following function

$$Err((K_{i,j}), C) + W \times \sqrt{\sum_{i=1}^{\varphi}\sum_{j=1, j\neq M}^{K} w_{i,j} \times K_{i,j}^2}$$