

Input: system coordinates $\mathbf{X} \in \mathbb{R}^{3N}$, the function for computing a thermodynamic property f , Lanczos order m , number of samples n , finite displacement δ

Output: The approximate trace of $f(\mathbf{D}(\mathbf{X}))$ where \mathbf{D} is the mass-weighted Hessian matrix.

Algorithm:

$\Gamma \leftarrow 0$

for $l = 1$ to n **do**

1. Generate a Rademacher random vector \mathbf{v}_l with unit norm.

2. Apply $m + 1$ steps of Lanczos to the Hessian using \mathbf{v}_l as the starting vector: $\mathbf{T} = \text{Lanczos}(\mathbf{D}(\mathbf{X}), \mathbf{v}_l, m + 1)$, in which the matrix-vector multiplication involved is realized as

$\mathbf{D}\mathbf{x} = \mathbf{M}^{-\frac{1}{2}} \frac{\mathbf{g}(\mathbf{X} + \delta\mathbf{x}) - \mathbf{g}(\mathbf{X} - \delta\mathbf{x})}{2\delta}$ where \mathbf{g} is the nuclear gradient.

3. $\mathbf{Y}, \boldsymbol{\Theta} = \text{eig}(\mathbf{T})$ where \mathbf{y}_k and θ_k are the k -th eigenvector and eigenvalue of \mathbf{T}

4. $\tau_k \leftarrow$ the first entry of \mathbf{y}_k

5. $\Gamma \leftarrow \Gamma + \sum_{k=0}^m \tau_k^2 f(\theta_k)$

end for

Output $\Gamma = \frac{3N}{n} \Gamma$