4th-order Taylor Expansion PES

Quartic Force Field (QFF)

$$
\begin{aligned}
V^{\mathrm{QFF}}(\mathbf{Q}) &= \sum_{i=1}^{f} c_i Q_i + \sum_{i,j=1}^{f} c_{ij} Q_i Q_j + \sum_{i,j,k=1}^{f} c_{ijk} Q_i Q_j Q_k \\
&\quad + \sum_{i,j,k,l=1}^{f} c_{ijkl} Q_i Q_j Q_k Q_l,
\end{aligned} \tag{1}
$$

$$
c_i = \frac{\partial V}{\partial Q_i}, \tag{2}
$$

$$
c_{ij} \equiv \frac{h_{ij}}{2} = \frac{1}{2}\frac{\partial^2 V}{\partial Q_i \partial Q_j}, \tag{3}
$$

$$
c_{ijk} \equiv \frac{t_{ijk}}{3!} = \frac{1}{3!}\frac{\partial^3 V}{\partial Q_i \partial Q_j \partial Q_k}, \tag{4}
$$

$$
c_{ijkl} \equiv \frac{u_{ijkl}}{4!} = \frac{1}{4!}\frac{\partial^4 V}{\partial Q_i \partial Q_j \partial Q_k \partial Q_l}. \tag{5}
$$

3rd and 4th-order terms by numerical differentiations

$$
\frac{\partial^2 V}{\partial Q_i \partial Q_j} = \sum_{k,l=1}^{3N} L_{ki}^{*} \left[\frac{1}{\sqrt{m_k m_l}} \frac{\partial^2 V}{\partial x_k \partial x_l} \right] L_{lj}, \tag{6}
$$

$$
t_{ijk} \simeq \frac{h_{jk}(+\delta_i) - h_{jk}(-\delta_i)}{2\delta_i}, \tag{7}
$$

$$
h_{jk}(+\delta_i) \equiv \frac{\partial^2 V}{\partial Q_j \partial Q_k}|_{Q_i=\delta_i}, \tag{8}
$$

$$
\delta_i = const \times \sqrt{\frac{\hbar}{\omega_i}}, \tag{9}
$$

$$u_{ijkl} \simeq \frac{h_{ij}(+\delta_k+\delta_l) - h_{ij}(+\delta_k-\delta_l) - h_{ij}(-\delta_k+\delta_l) + h_{ij}(-\delta_k-\delta_l)}{4\delta_k\delta_l}, \tag{10}$$

$$h_{ij}(\pm\delta_k \pm \delta_l) \equiv \frac{\partial^2 V}{\partial Q_i \partial Q_j}|_{Q_k=\pm\delta_k, Q_l=\pm\delta_l}, \tag{11}$$

$$u_{ijkk} \simeq \frac{h_{ij}(+\delta_k) + h_{ij}(-\delta_k) - 2h_{ij}}{\delta_k^2}, \tag{12}$$

n-mode represenation (nMR) QFF

$$V^{\mathrm{QFF}}(\mathbf{Q}) = \sum_{i=1}^{f} V_i^{\mathrm{QFF}} + \sum_{i>j}^{f} V_{ij}^{\mathrm{QFF}} + \sum_{i>j>k}^{f} V_{ijk}^{\mathrm{QFF}} + \sum_{i>j>k>l}^{f} V_{ijkl}^{\mathrm{QFF}}, \tag{13}$$

$$V_i^{\mathrm{QFF}} = g_i Q_i + \frac{h_{ii}}{2} Q_i^2 + \frac{t_{iii}}{3!} Q_i^3 + \frac{u_{iiii}}{4!} Q_i^4, \tag{14}$$

$$\begin{aligned} V_{ij}^{\mathrm{QFF}} &= h_{ij} Q_i Q_j + \frac{t_{iij}}{2} Q_i^2 Q_j + \frac{t_{ijj}}{2} Q_i Q_j^2 \\ &+ \frac{u_{iiij}}{3!} Q_i^3 Q_j + \frac{u_{iijj}}{4} Q_i^2 Q_j^2 + \frac{u_{ijjj}}{3!} Q_i Q_j^3, \end{aligned} \tag{15}$$

$$\begin{aligned} V_{ijk}^{\mathrm{QFF}} &= t_{ijk} Q_i Q_j Q_k \\ &+ \frac{u_{iijk}}{2} Q_i^2 Q_j Q_k + \frac{u_{ijjk}}{2} Q_i Q_j^2 Q_k + \frac{u_{ijkk}}{2} Q_i Q_j Q_k^2, \end{aligned} \tag{16}$$

$$V_{ijkl}^{\mathrm{QFF}} = u_{ijkl} Q_i Q_j Q_k Q_l, \tag{17}$$

Grid PES

Lagrange interpolation of ab initio energy based on DVR grid points, $Q_i^{[k]}$.

$$E(Q_i) = \sum_{k=0}^{M-1} E_k L_k(Q_i), \tag{18}$$

$$L_k(Q_i^{[k']}) = \delta_{kk'}, \tag{19}$$

$$\pi(Q_i) = \prod_{k=0}^{M-1} (Q_i - Q_i^{[k]}), \tag{20}$$

$$\pi_k(Q_i) = \frac{\pi(Q_i)}{Q_i - Q_i^{[k]}} = \prod_{k' \neq k}^{M-1} (Q_i - Q_i^{[k']}), \tag{21}$$

$$L_k(Q_i) = \frac{\pi(Q_i)}{\pi_k(Q_i^{[k]})} = \prod_{k' \neq k}^{M-1} \frac{(Q_i - Q_i^{[k']})}{(Q_i^{[k]} - Q_i^{[k']})}, \tag{22}$$

(ex.) when M = 1:

$$\begin{aligned} E(Q_i) &= E_0 \frac{Q_i - Q_i^{[1]}}{Q_i^{[0]} - Q_i^{[1]}} + E_1 \frac{Q_i - Q_i^{[0]}}{Q_i^{[1]} - Q_i^{[0]}}, \\ &= \frac{E_1 - E_0}{Q_i^{[1]} - Q_i^{[0]}} (Q_i - Q_i^{[0]}) + E_0, \end{aligned} \tag{23}$$

nMR Grid PES

$$V^{grid}(\mathbf{Q}) = \sum_{i=1}^{f} V_i^{grid} + \sum_{i>j}^{f} V_{ij}^{grid} + \cdots + \sum_{i_1>i_2>\cdots>i_n}^{f} V_{\mathbf{i}_n}^{grid} \tag{24}$$

$$V_i^{grid}(Q_i) = E(Q_i), \tag{25}$$

$$V_{ij}^{grid}(Q_i, Q_j) = E(Q_i, Q_j) - V_i^{grid}(Q_i) - V_j^{grid}(Q_j), \tag{26}$$

$$V_{\boldsymbol{i}_m}^{grid}(Q_{i_1}, \ldots, Q_{i_m}) = E(Q_{i_1}, \ldots, Q_{i_m}) - \sum_{l=1}^{m-1} \sum_{\boldsymbol{i}_l \in \boldsymbol{i}_m} V_{\boldsymbol{i}_l}^{grid}(Q_{i_1}, \ldots, Q_{i_l}), \tag{27}$$

$$V_{\boldsymbol{i}_m}^{grid}(Q_{i_1}, \ldots, Q_{i_m}) = 0, if\ any\ Q_i = 0. \tag{28}$$

$$V^{grid}\left(Q_1^{[k_1]}, \ldots, Q_f^{[k_f]}\right) = E\left(Q_1^{[k_1]}, \ldots, Q_f^{[k_f]}\right) = V^{ab\ initio}. \tag{29}$$

Multiresolution method

[r] : Resolution (QFF/Grid, level of ab initio)

$$V^{[r]} = \sum_{i \in r} V_i^{[r]} + \sum_{\mathbf{i}_2 \in r} V_{ij}^{[r]} + \cdots + \sum_{\mathbf{i}_n \in r} V_{\mathbf{i}_n}^{[r]}, \tag{30}$$

Multiresolution PES

$$V(\mathbf{Q}) = \sum_r V^{[r]}, \tag{31}$$

(ex.) Divide the resolution by coupling order:

$$V^{[high]} = \sum_{i=1}^{f} V_i^{[high]}, \tag{32}$$

$$V^{[mid]} = \sum_{i>j}^{f} V_{ij}^{[mid]} + \sum_{i>j>k}^{f} V_{ijk}^{[mid]}, \tag{33}$$

$$V^{[low]} = \sum_{i>j>k>l}^{f} V_{ijkl}^{[low]}, \tag{34}$$

$$\begin{aligned} V &= V^{[high]} + V^{[mid]} + V^{[low]} \\ &= \sum_{i=1}^{f} V_i^{[high]} + \sum_{i>j}^{f} V_{ij}^{[mid]} + \sum_{i>j>k}^{f} V_{ijk}^{[mid]} \sum_{i>j>k>l}^{f} V_{ijkl}^{[low]}, \end{aligned} \tag{35}$$

Mode Coupling Strength

$$V_c = \sum_{i>j}^{f} V_{ij}^{\mathrm{QFF}} + \sum_{i>j>k}^{f} V_{ijk}^{\mathrm{QFF}} + \sum_{i>j>k>l}^{f} V_{ijkl}^{\mathrm{QFF}}, \tag{33}$$

Perturbation theory based on HO

$$E_{\mathbf{n}}^{(0)} = \sum_{i=1}^{f} \hbar\omega_i (n_i + \frac{1}{2}) \tag{34}$$

$$E_{\mathbf{n}}^{(1)} = \langle \zeta_{\mathbf{n}} | V_c | \zeta_{\mathbf{n}} \rangle \tag{35}$$

$$E_{\mathbf{n}}^{(2)} = \sum_{\mathbf{k} \neq \mathbf{n}} \frac{|\langle \zeta_{\mathbf{k}} | V_c | \zeta_{\mathbf{n}} \rangle|^2}{E_{\mathbf{n}}^{(0)} - E_{\mathbf{k}}^{(0)}} \tag{36}$$

MCS2

$$\eta_{ij} = \eta_{iijj}^{(1)} + \eta_{ij}^{(2)} + P_{ij}(\eta_{ijj}^{(2)} + \eta_{ijjj}^{(2)}), \tag{37}$$

- 2-mode, 1st order:

$$\eta_{iijj}^{(1)} \equiv \frac{u_{iijj}}{4} \langle 00 | Q_i^2 Q_j^2 | 00 \rangle , \tag{38}$$

- 2-mode, 2nd order:

$$\eta_{ij}^{(2)} \equiv \frac{|h_{ij} \langle 01 | Q_i Q_j | 10 \rangle|^2}{\hbar |\omega_i - \omega_j|}, \tag{39}$$

$$\eta_{ijj}^{(2)} \equiv \frac{|t_{ijj} \langle 02 | Q_i Q_j^2 | 10 \rangle|^2}{4\hbar |\omega_i - 2\omega_j|}, \tag{40}$$

$$\eta_{ijjj}^{(2)} \equiv \frac{|u_{ijjj} \langle 01 | Q_i Q_j^3 | 10 \rangle|^2}{36\hbar |\omega_i - \omega_j|} + \frac{|u_{ijjj} \langle 03 | Q_i Q_j^3 | 10 \rangle|^2}{36\hbar |\omega_i - 3\omega_j|}, \tag{41}$$

MCS3

$$\eta_{ijk} = \eta^{(2)}_{ijk} + \eta^{(2)}_{jki} + \eta^{(2)}_{kij} + P_{ijk}\eta^{(2)}_{ijjk}, \tag{42}$$

- 3-mode, 2nd order:

$$\eta^{(2)}_{ijk} \equiv \frac{|t_{ijk}\,\langle 011|Q_iQ_jQ_k|100\rangle\,|^2}{\hbar|\omega_i - \omega_j - \omega_k|}, \tag{43}$$

$$\eta^{(2)}_{ijjk} \equiv \frac{|u_{ijjk}\,\langle 021|Q_iQ_j^2Q_k|100\rangle\,|^2}{4\hbar|\omega_i - 2\omega_j - \omega_k|}, \tag{44}$$

MCS4

$$\eta_{ijkl} = \eta^{(2)}_{ijkl} + \eta^{(2)}_{jkli} + \eta^{(2)}_{klij} + \eta^{(2)}_{lijk}, \tag{45}$$

- 4-mode, 2nd order:

$$\eta^{(2)}_{ijkl} \equiv \frac{|u_{ijkl}\,\langle 0111|Q_iQ_jQ_kQ_l|1000\rangle\,|^2}{\hbar|\omega_i - \omega_j - \omega_k - \omega_l|}, \tag{46}$$

H_2CO

		2MCS	3MCS	4MCS
MCS > 1	direct	13	3	2
1e-4 < MCS < 1	QFF	2	10	1
MCS < 1e-5	neglect	0	7	12

C_2H_4

		2MCS	3MCS	4MCS
MCS > 1	direct	58	17	28
1e-4 < MCS < 1	QFF	8	54	36
MCS < 1e-5	neglect	0	149	431

Guanine ($C_5N_5OH_5$)

		2MCS	3MCS	4MCS
MCS > 1	direct	202	260	124
1e-4 < MCS < 1	QFF	658	9684	34185
MCS < 1e-4	neglect	1	1536	77621

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