調和近似

分子のハミルトニアン

$$\hat{H} = -\sum_{i=1}^{3N} \frac{1}{2m_i} \frac{\partial^2}{\partial x_i^2} + V(\mathbf{x}), \tag{1}$$

調和近似 : 平衡点aの周りで2次のテイラー展開

$$V(\mathbf{x}) \simeq V_0(\mathbf{a}) + \frac{1}{2} \sum_{i,j}^{3N} h_{ij}(x_i - a_i)(x_j - a_j), \tag{2}$$

$$h_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}\Big|_{\mathbf{x}=\mathbf{a}}. \tag{3}$$

$$\hat{H} = -\sum_{i=1}^{3N} \frac{1}{2m_i} \frac{\partial^2}{\partial x_i^2} + \frac{1}{2} \sum_{i,j}^{3N} h_{ij}(x_i - a_i)(x_j - a_j). \tag{4}$$

荷重変位座標

$$\xi_i = \sqrt{m_i}(x_i - a_i), \tag{5}$$

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{3N} \frac{\partial^2}{\partial \xi_i^2} + \frac{1}{2} \sum_{i,j}^{3N} h'_{ij} \xi_i \xi_j. \tag{6}$$

$$h'_{ij} = \frac{\partial^2 V}{\partial \xi_i \partial \xi_j}\Big|_{\xi=\mathbf{0}} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial x_i \partial x_j}\Big|_{\mathbf{x}=\mathbf{a}}. \tag{7}$$

基準座標

$$\mathbf{L}^\dagger \mathbf{h}' \mathbf{L} = \begin{bmatrix} 0 & & & & & & \\ & \ddots & & & \mathbf{0} & & \\ & & 0 & & & & \\ & & & \omega_1^2 & & & \\ & & & & \omega_2^2 & & \\ & \mathbf{0} & & & & \ddots & \\ & & & & & & \omega_{3N-6}^2 \end{bmatrix} \tag{8}$$

調和近似

$$Q_i = \sum_{j=1}^{3N} L_{ji}\xi_j = \sum_{j=1}^{3N} L_{ji}\sqrt{m_i}(x_i - a_i). \tag{9}$$

$$\hat{H} = \sum_{i=1}^{f}\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \frac{\omega_i^2 Q_i^2}{2}\right] + \sum_{i=f+1}^{3N} -\frac{1}{2}\frac{\partial^2}{\partial Q_i^2}, \tag{10}$$

振動ハミルトニアン

$$\hat{H}_v^{\mathrm{Harm}} = \sum_{i=1}^{f}\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \frac{\omega_i^2 Q_i^2}{2}\right]. \tag{11}$$

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \frac{\omega_i^2 Q_i^2}{2}\right]\zeta_{n_i}^{(i)}(Q_i) = \epsilon_{n_i}^{(i)}\zeta_{n_i}^{(i)}(Q_i), \tag{12}$$

$$\epsilon_{n_i}^{(i)} = \hbar\omega_i(n_i + \frac{1}{2}). \tag{13}$$

$$\hat{H}_v^{\mathrm{Harm}}\zeta_{\mathbf{n}} = E_{\mathbf{n}}\zeta_{\mathbf{n}}, \tag{14}$$

$$\zeta_{\mathbf{n}}(\mathbf{Q}) = \prod_{i=1}^{f}\zeta_{n_i}^{(i)}(Q_i), \tag{15}$$

$$E_{\mathbf{n}} = \sum_{i=1}^{f}\hbar\omega_i(n_i + \frac{1}{2}), \tag{16}$$

調和振動子波動関数の性質

関数形

$$\zeta_n(Q) = N_n H_n(q) e^{-q^2/2}, \tag{17}$$

$$N_n = \frac{1}{\sqrt{\pi^{1/2} 2^n n!}}, \tag{18}$$

$$q = \sqrt{\frac{\omega}{\hbar}} Q, \tag{19}$$

$$H_{n+1} = 2qH_n - 2nH_{n-1}, \tag{20}$$

$$H_0 = 1, \tag{21}$$

$$H_1 = 2q. \tag{22}$$

第2量子化

$$\hat{b} = \left(\frac{\omega}{2\hbar}\right)^{1/2} \left(\hat{Q} + \frac{i\hat{P}}{\omega}\right), \tag{23}$$

$$\hat{b}^\dagger = \left(\frac{\omega}{2\hbar}\right)^{1/2} \left(\hat{Q} - \frac{i\hat{P}}{\omega}\right). \tag{24}$$

$$\hat{b} \left|\zeta_n\right\rangle = \sqrt{n} \left|\zeta_{n-1}\right\rangle, \tag{25}$$

$$\hat{b}^\dagger \left|\zeta_n\right\rangle = \sqrt{n+1} \left|\zeta_{n+1}\right\rangle. \tag{26}$$

$$\hat{b} \left|\zeta_0\right\rangle = 0. \tag{27}$$

$$\hat{Q} = \left(\frac{\hbar}{2\omega}\right)^{1/2} (\hat{b} + \hat{b}^\dagger), \tag{28}$$

$$\hat{P} = -i \left(\frac{\hbar\omega}{2}\right)^{1/2} (\hat{b} - \hat{b}^\dagger). \tag{29}$$

調和振動子波動関数の性質

重要な関係式

$$\langle\zeta_{n+1}|\hat{Q}|\zeta_n\rangle = \left(\frac{\hbar}{2\omega}\right)^{1/2}\sqrt{n+1}, \tag{30}$$

$$\langle\zeta_{n-1}|\hat{Q}|\zeta_n\rangle = \left(\frac{\hbar}{2\omega}\right)^{1/2}\sqrt{n}, \tag{31}$$

$$\langle\zeta_{n'}|\hat{Q}|\zeta_n\rangle = 0 \quad \text{(otherwise)}. \tag{32}$$

$$\langle\zeta_{n+2}|\hat{P}^2|\zeta_n\rangle = -\left(\frac{\hbar\omega}{2}\right)\sqrt{(n+1)(n+2)}, \tag{33}$$

$$\langle\zeta_{n-2}|\hat{P}^2|\zeta_n\rangle = -\left(\frac{\hbar\omega}{2}\right)\sqrt{n(n-1)}, \tag{34}$$

$$\langle\zeta_n|\hat{P}^2|\zeta_n\rangle = \hbar\omega(n+\frac{1}{2}), \tag{35}$$

$$\langle\zeta_{n'}|\hat{P}^2|\zeta_n\rangle = 0 \quad \text{(otherwise)}, \tag{36}$$

$$\hat{H} = \hbar\omega(\hat{b}^\dagger\hat{b} + \frac{1}{2}) \tag{37}$$

$$\hat{b}^\dagger\hat{b}\,|\zeta_n\rangle = n\,|\zeta_n\rangle\,, \tag{38}$$

$$E_n = \hbar\omega(n+\frac{1}{2}) \tag{39}$$

1次元振動Schrödinger方程式を解く

1次元振動Schrödinger方程式

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_1^2} + V_1(Q_1)\right]|\phi_n\rangle = \epsilon_n |\phi_n\rangle \,. \tag{40}$$

$$x_i = a_i + \frac{L_{i1}}{\sqrt{m_i}} Q_1. \tag{41}$$

変分法

$$|\phi_n\rangle = \sum_{m=0}^{M-1} c_{mn} |\zeta_m\rangle \,, \tag{42}$$

$$\sum_{m=0}^{M-1} h_{m'm} c_{mn} = c_{m'n}\epsilon_n, \tag{43}$$

$$h_{m'm} \equiv \langle\zeta_{m'}| - \frac{1}{2}\frac{\partial^2}{\partial Q_1^2} + V_1(Q_1)|\zeta_m\rangle \,. \tag{44}$$

$$\mathbf{c}^\dagger\mathbf{h}\mathbf{c} = \begin{bmatrix} \epsilon_0 & & & \mathbf{0} \\ & \epsilon_1 & & \\ & & \ddots & \\ \mathbf{0} & & & \epsilon_M \end{bmatrix}, \tag{45}$$

1次元振動Schrödinger方程式を解く

Discrete Variable Represenation 法

$$\hat{Q}_1 \left|\chi_m\right\rangle = Q_1^{[m]} \left|\chi_m\right\rangle \tag{46}$$

$$(\mathbf{Q}_1)_{mn} = \langle \zeta_m | \hat{Q}_1 | \zeta_n \rangle \,, \tag{47}$$

$$\mathbf{x}^\dagger \mathbf{Q_1} \mathbf{x} = \begin{bmatrix} Q_1^{[0]} & & & \mathbf{0} \\ & Q_1^{[1]} & & \\ & & \ddots & \\ \mathbf{0} & & & Q_1^{[M-1]} \end{bmatrix} . \tag{48}$$

$$\left|\chi_m\right\rangle = \sum_{m=0}^{M-1} x_{mn} \left|\zeta_m\right\rangle \tag{49}$$

$$V_1(Q_1) \left|\chi_m\right\rangle \simeq V_1(Q_1^{[m]}) \left|\chi_m\right\rangle \tag{50}$$

$$\mathbf{V}_1 = \mathbf{x} \begin{bmatrix} V_1(Q_1^{[0]}) & & & \mathbf{0} \\ & V_1(Q_1^{[1]}) & & \\ & & \ddots & \\ \mathbf{0} & & & V_1(Q_1^{[M-1]}) \end{bmatrix} \mathbf{x}^\dagger . \tag{51}$$

$$\langle \zeta_m | V_1(Q) | \zeta_n \rangle = \sum_{k=0}^{M-1} x_{mk}^* x_{nk} V_1(Q_1^{[k]}) \tag{52}$$

2次元振動Schrödinger方程式を解く

$$\begin{aligned}\hat{H}^{2\mathrm{D}} &= -\frac{1}{2}\frac{\partial^2}{\partial Q_1^2} - \frac{1}{2}\frac{\partial^2}{\partial Q_2^2} + V_1(Q_1) + V_2(Q_2) + V_{12}(Q_1, Q_2) \\ &= \hat{h}_1 + \hat{h}_2 + V_{12}(Q_1, Q_2) \end{aligned} \tag{53}$$

$$\hat{H}^{2\mathrm{D}} \left| \Phi_{n_1 n_2} \right\rangle = \epsilon_{n_1 n_2} \left| \Phi_{n_1 n_2} \right\rangle . \tag{54}$$

変分法

$$\left| \Psi_{n_1 n_2} \right\rangle = \sum_{m_1, m_2 = 0}^{M-1} C_{m_1 m_2, n_1 n_2} \left| \zeta_{m_1}^{(1)} \zeta_{m_2}^{(2)} \right\rangle , \tag{55}$$

$$\begin{aligned} H_{m_1' m_2', m_1 m_2} &= \langle \zeta_{m_1'}^{(1)} \zeta_{m_2'}^{(2)} | \hat{H}^{2\mathrm{D}} | \zeta_{m_1}^{(1)} \zeta_{m_2}^{(2)} \rangle , \\ &= (h_1)_{m_1' m_1} \delta_{m_2' m_2} + (h_2)_{m_2' m_2} \delta_{m_1' m_1} + (V_{12})_{m_1' m_2', m_1 m_2} \end{aligned} \tag{56}$$

$$\begin{aligned} (V_{12})_{m_1' m_2', m_1 m_2} &\equiv \langle \zeta_{m_1'}^{(1)} \zeta_{m_2'}^{(2)} | V_{12} | \zeta_{m_1}^{(1)} \zeta_{m_2}^{(2)} \rangle , \\ &= \sum_{k_1, k_2 = 0}^{M-1} x_{m_1' k_1}^{(1)*} x_{m_1 k_1}^{(1)} x_{m_2' k_2}^{(2)*} x_{m_2 k_2}^{(2)} V_{12}(Q_1^{[k_1]}, Q_2^{[k_2]}) \end{aligned} \tag{57}$$

$$\mathbf{C}^\dagger \mathbf{H} \mathbf{C} = \begin{bmatrix} E_{00} & & & & & \\ & E_{10} & & & \mathbf{0} & \\ & & \ddots & & & \\ & & & E_{01} & & \\ & \mathbf{0} & & & \ddots & \\ & & & & & E_{M-1 M-1} \end{bmatrix} . \tag{58}$$

2次元振動Schrödinger方程式を解く

平均場近似（VSCF法）

$$|\Phi^{\rm VSCF}_{n_1n_2}\rangle = |\phi^{(1)}_{n_1}\phi^{(2)}_{n_2}\rangle\,, \tag{59}$$

$$\begin{aligned}
|\phi^{(i)}_n\rangle &= \sum_{m=0}^{M-1} c^{(i)}_{mn}\,|\zeta^{(i)}_m\rangle\,, & (60)\\
&= \sum_{m=0}^{M-1} d^{(i)}_{mn}\,|\chi^{(i)}_m\rangle\,. & (61)
\end{aligned}$$

$$\mathbf{d}^{(i)} = \mathbf{x}^{(i)\dagger}\mathbf{c}^{(i)} \tag{62}$$

$$\left[\hat{h}_1 + \langle\phi^{(2)}_{n_2}|V_{12}|\phi^{(2)}_{n_2}\rangle\right]|\phi^{(1)}_{n_1}\rangle = \epsilon^{(1)}_{n_1}\,|\phi^{(1)}_{n_1}\rangle\,, \tag{63}$$

$$\left[\hat{h}_2 + \langle\phi^{(1)}_{n_1}|V_{12}|\phi^{(1)}_{n_1}\rangle\right]|\phi^{(2)}_{n_2}\rangle = \epsilon^{(2)}_{n_2}\,|\phi^{(2)}_{n_2}\rangle\,, \tag{64}$$

$$\begin{aligned}
E^{\rm VSCF}_{n_1n_2} &= \langle\Phi^{\rm VSCF}_{n_1n_2}|\hat{H}^{\rm 2D}|\Phi^{\rm VSCF}_{n_1n_2}\rangle\,,\\
&= (h_1)_{n_1n_1} + (h_2)_{n_2n_2} + (V_{12})_{n_1n_2,n_1n_2} & (65)
\end{aligned}$$

$$\begin{aligned}
(h_i)_{n_in_i} &\equiv \langle\phi^{(i)}_{n_i}|\hat{h}_i|\phi^{(i)}_{n_i}\rangle\\
&= \sum_{m'_i,m_i=0}^{M-1} c^{(i)*}_{m'_in_i}c^{(i)}_{m_in_i}\,\langle\zeta^{(i)}_{m'_i}|\hat{T}_i|\zeta^{(i)}_{m_i}\rangle + \sum_{k=0}^{M-1} d^{(i)*}_{kn_i}d^{(i)}_{kn_i}V_i(Q^{[k]}_i), & (66)
\end{aligned}$$

$$\begin{aligned}
(V_{12})_{n_1n_2,n_1n_2} &\equiv \langle\phi^{(1)}_{n_1}\phi^{(2)}_{n_2}|V_{12}|\phi^{(1)}_{n_1}\phi^{(2)}_{n_2}\rangle\,,\\
&= \sum_{k_1,k_2=0}^{M-1} d^{(1)*}_{k_1n_1}d^{(1)}_{k_1n_1}d^{(2)*}_{k_2n_2}d^{(2)}_{k_2n_2}V_{12}(Q^{[k_1]}_1, Q^{[k_2]}_2) & (67)
\end{aligned}$$

$$\langle\phi^{(2)}_{n_2}|V_{12}|\phi^{(2)}_{n_2}\rangle = \sum_{k_2=0}^{M-1} d^{(2)*}_{k_2n_2}d^{(2)}_{k_2n_2}V_{12}(Q_1, Q^{[k_2]}_2), \tag{68}$$

問題

1. 式(23) – (29)を利用し、式(30) – (39)を導出せよ

2. 2次元の振動Schrödinger方程式を解くプログラムを作成し、ホルムアルデヒドのCH対称、逆対称伸縮の振動数を、変分法と平均場近似で求めよ。

ただし、ポテンシャルには以下の力の定数を用いよ

type	value / au
c_{55}	9.178689E-05
c_{555}	1.609595E-06
c_{5555}	1.830021E-08
c_{66}	9.641006E-05
c_{6666}	2.220306E-08
c_{665}	5.214792E-06
c_{5566}	1.232924E-07