Vibrational Self-Consistent Field Method

Vibrational Schrödinger equation

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{f} \frac{\partial^2}{\partial Q_i^2} + V^{n\mathrm{MR}}(\mathbf{Q}), \tag{1}$$

$$V^{n\mathrm{MR}}(\mathbf{Q}) \;\; = \;\; \sum_{i=1}^{f} V_i + \sum_{i>j}^{f} V_{ij} + \cdots + \sum_{i_1>i_2>\cdots>i_n}^{f} V_{\mathbf{i}_n}, \tag{2}$$

$$\hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle, \tag{3}$$

VSCF wave function

$$\Phi_{\mathbf{r}}(\mathbf{Q}) = \prod_{i=1}^{f} \phi_{r_i}^{(i)}(Q_i), \tag{4}$$

$$E_{\mathbf{r}}^{\mathrm{VSCF}} = -\frac{1}{2}\sum_{i=1}^{f} \langle \phi_{r_i}^{(i)} | \frac{\partial^2}{\partial Q_i^2} | \phi_{r_i}^{(i)} \rangle + \langle \Phi_{\mathbf{r}} | V^{n\mathrm{MR}} | \Phi_{\mathbf{r}} \rangle, \tag{5}$$

Variational principles

$$L = E_{\mathbf{r}}^{\mathrm{VSCF}} - \sum_{i=1}^{f} \epsilon_{r_i}^{(i)} (\langle \phi_{r_i}^{(i)} | \phi_{r_i}^{(i)} \rangle - 1), \tag{6}$$

$$\delta L = \sum_{i=1}^{f} \langle \delta\phi_{r_i}^{(i)} | \left[-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \langle \prod_{j\neq i} \phi_{r_j}^{(j)} | V | \prod_{j\neq i} \phi_{r_j}^{(j)} \rangle - \epsilon_{r_i}^{(i)} \right] | \phi_{r_i}^{(i)} \rangle + c.c., \tag{7}$$

VSCF equation

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_i^2} + \bar{V}_i(Q_i)\right]|\phi_{r_i}^{(i)}\rangle = \epsilon_{r_i}^{(i)}\,|\phi_{r_i}^{(i)}\rangle\,, \tag{8}$$

$$\bar{V}_i(Q_i) \;=\; \langle\prod_{j\neq i}^{f}\phi_{r_j}^{(j)}|V^{n\mathrm{MR}}|\prod_{j\neq i}^{f}\phi_{r_j}^{(j)}\rangle \tag{9}$$

Integral over the potential using DVR method

$$\begin{aligned}\langle\Phi_{\mathbf{r}}|V^{n\mathrm{MR}}|\Phi_{\mathbf{r}}\rangle = \sum_{i=1}^{f}\langle\phi_{r_i}^{(i)}|V_i|\phi_{r_i}^{(i)}\rangle + \sum_{i>j}^{f}\langle\phi_{r_i}^{(i)}\phi_{r_j}^{(j)}|V_{ij}|\phi_{r_i}^{(i)}\phi_{r_j}^{(j)}\rangle + \dots\\ \dots + \sum_{i_1>\dots>i_n}^{f}\langle\phi_{r_{i_1}}^{(i_1)}\dots\phi_{r_{i_n}}^{(i_n)}|V_{i_1\dots i_n}|\phi_{r_{i_1}}^{(i_1)}\dots\phi_{r_{i_n}}^{(i_n)}\rangle\,,\end{aligned} \tag{10}$$

$$\begin{aligned}\bar{V}_i(Q_i) \;=\; & V_i(Q_i) + \sum_{j\neq i}^{f}\langle\phi_{r_j}^{(j)}|V_{ij}|\phi_{r_j}^{(j)}\rangle + \sum_{j_1>j_2\neq i}^{f}\langle\phi_{r_{j_1}}^{(j_1)}\phi_{r_{j_2}}^{(j_2)}|V_{ij_1j_2}|\phi_{r_{j_1}}^{(j_1)}\phi_{r_{j_2}}^{(j_2)}\rangle + \dots\\ & + \sum_{j_1>\dots>j_{n-1}\neq i}^{f}\langle\phi_{r_{j_1}}^{(j_1)}\dots\phi_{r_{j_{n-1}}}^{(j_{n-1})}|V_{ij_1\dots j_{n-1}}|\phi_{r_{j_1}}^{(j_1)}\dots\phi_{r_{j_{n-1}}}^{(j_{n-1})}\rangle + \mathrm{const.},\end{aligned} \tag{11}$$

$$|\phi_r^{(i)}\rangle \;=\; \sum_{s=0}^{M-1} c_{sr}^{(i)}\,|\zeta_s^{(i)}\rangle\,, \tag{12}$$

$$\;=\; \sum_{s=0}^{M-1} d_{sr}^{(i)}\,|\chi_s^{(i)}\rangle\,. \tag{13}$$

$$\bar{V}_i(Q_i^{[k]}) \;=\; V_i(Q_i^{[k]}) + \sum_{j\neq i}^{f}\sum_{k_j=0}^{M-1} d_{k_jr_j}^{(j)*}d_{k_jr_j}^{(j)}V_{ij}(Q_i^{[k]},Q_j^{[k_j]}) + \dots\,, \tag{14}$$

VSCF equation in matrix form

$$\mathbf{c}^{(i)\dagger}\mathbf{h}^{(i)}\mathbf{c}^{(i)} = \epsilon^{(i)} \tag{15}$$

$$h^{(i)}_{s's} = -\frac{1}{2}\langle\zeta^{(i)}_{s'}|\frac{\partial^2}{\partial Q_i^2}|\zeta^{(i)}_s\rangle + \sum_{k=0}^{M-1} x^{(i)*}_{ks'} x^{(i)}_{ks} \bar{V}_i(Q_i^{[k]}), \tag{16}$$

Iterative algorithm

set up kinetic energy matrix
loop until convergence
    calculate total energy / mean field matrix
    check convergence
        - exit if converged
    loop over mode i
        - get kinetic and mean field matrix for i
        - diagonalize / store eigenvectors
    end of loop
    update coefficients
end of loop

VSCF Configuration Functions

VSCF configuration functions

$$|\Phi_{\mathbf{p}}\rangle = \prod_{i=1}^{f} |\phi_{p_i}^{(i)}\rangle \,, \tag{17}$$

$$\langle \Phi_{\mathbf{q}} | \Phi_{\mathbf{p}} \rangle = \delta_{\mathbf{qp}} = \prod_{i=1}^{f} \delta_{q_i p_i} \,, \tag{18}$$

- the number of configurations:

$$N_{\mathrm{conf}} = M^f \,, \tag{19}$$

(M is the number of basis sets for each mode)

Excited configurations

- one-mode excitation:

$$|\Phi_{p_i}^{q_i}\rangle \equiv |\phi_{p_1}^{(1)} \ldots \phi_{p_{i-1}}^{(i-1)} \phi_{q_i}^{(i)} \phi_{p_{i+1}}^{(i+1)} \ldots \phi_{p_f}^{(f)}\rangle \,, \tag{20}$$

- many-mode excitation:

$$|\Phi_{\mathbf{p}}\rangle \,, \left\{ |\Phi_{p_i}^{q_i}\rangle \right\} , \left\{ |\Phi_{p_{i_1} p_{i_2}}^{q_{i_1} q_{i_2}}\rangle \right\} , \ldots , \left\{ |\Phi_{\mathbf{p}_{i_f}}^{\mathbf{q}_{i_f}}\rangle \right\} , \tag{21}$$

- the number of *m*-mode excitation:

$$N_{\mathrm{conf}}^{(m)} = \begin{pmatrix} f \\ m \end{pmatrix} (M-1)^m \,, \tag{22}$$

$$N_{\mathrm{conf}} = \sum_{m=0}^{f} N_{\mathrm{conf}}^{(m)} = \sum_{m=0}^{f} \begin{pmatrix} f \\ m \end{pmatrix} (M-1)^m \,, \tag{23}$$

Hamiltonian matrix element

$$H_{\mathbf{qp}} = \langle \Phi_{\mathbf{q}} | \hat{H} | \Phi_{\mathbf{p}} \rangle \,, \tag{24}$$

$$\hat{H} = \sum_{m=1}^{n} \hat{H}_m, \tag{25}$$

$$\hat{H}_1 = \sum_{i=1}^{f} \left[-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + V_i \right], \tag{26}$$

$$\hat{H}_2 = \sum_{i>j}^{f} V_{ij}, \tag{27}$$

$$\vdots$$

$$\hat{H}_n = \sum_{i_1 > i_2 > \ldots > i_n}^{f} V_{\mathbf{i}_n}, \tag{28}$$

- one-mode operator:

$$\langle \Phi_{\mathbf{p}} | \hat{H}_1 | \Phi_{\mathbf{p}} \rangle = \sum_{i=1}^{f} \langle \phi_{p_i}^{(i)} | -\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + V_i | \phi_{p_i}^{(i)} \rangle \,, \tag{29}$$

$$\langle \Phi_{p_i}^{q_i} | \hat{H}_1 | \Phi_{\mathbf{p}} \rangle = \langle \phi_{p_i}^{(i)} | -\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + V_i | \phi_{p_i}^{(i)} \rangle \,, \tag{30}$$

$$\langle \Phi_{\mathbf{p}_{\mathbf{i}_m}}^{\mathbf{q}_{\mathbf{i}_m}} | \hat{H}_1 | \Phi_{\mathbf{p}} \rangle = 0, \;\; (m > 1) \tag{31}$$

- two-mode operator:

$$\langle \Phi_{\mathbf{p}} | \hat{H}_2 | \Phi_{\mathbf{p}} \rangle = \sum_{i>j}^{f} \langle \phi_{p_i}^{(i)} \phi_{p_j}^{(j)} | V_{ij} | \phi_{p_i}^{(i)} \phi_{p_j}^{(j)} \rangle \,, \tag{32}$$

$$\langle \Phi_{p_i}^{q_i} | \hat{H}_2 | \Phi_{\mathbf{p}} \rangle = \sum_{j \neq i}^{f} \langle \phi_{p_i}^{(i)} \phi_{p_j}^{(j)} | V_{ij} | \phi_{p_i}^{(i)} \phi_{p_j}^{(j)} \rangle \,, \tag{33}$$

$$\langle \Phi_{p_i p_j}^{q_i q_j} | \hat{H}_2 | \Phi_{\mathbf{p}} \rangle = \langle \phi_{p_i}^{(i)} \phi_{p_j}^{(j)} | V_{ij} | \phi_{p_i}^{(i)} \phi_{p_j}^{(j)} \rangle \,, \tag{34}$$

$$\langle \Phi_{\mathbf{p}_{\mathbf{i}_m}}^{\mathbf{q}_{\mathbf{i}_m}} | \hat{H}_2 | \Phi_{\mathbf{p}} \rangle = 0, \;\; (m > 2) \tag{35}$$

- general rule:

$$\langle \Phi^{\mathbf{q}_{\mathbf{i}_m}}_{\mathbf{p}_{\mathbf{i}_m}} | \hat{H}_{m'} | \Phi_{\mathbf{p}} \rangle = 0, \ (m > m') \tag{36}$$

$$\langle \Phi^{\mathbf{q}_{\mathbf{i}_m}}_{\mathbf{p}_{\mathbf{i}_m}} | \hat{H} | \Phi_{\mathbf{p}} \rangle = 0, \ (m > n) \tag{37}$$

- Brillouin's theorem:

$$\langle \Phi^{q_i}_{r_i} | \hat{H} | \Phi_{\mathbf{r}} \rangle = 0, \tag{38}$$

(r is a reference VSCF state)

Approximation based on $\lambda_{\mathbf{pq}}$

$$\lambda_{\mathbf{pq}} = \sum_{i=1}^{f} |p_i - q_i|, \tag{39}$$

$$\hat{H}^k = \sum_{i=1}^{f} \frac{P_i^2}{2} + \sum_{i=1}^{f} c_i Q_i + \sum_{i,j=1}^{f} c_{ij} Q_i Q_j + \ldots + \sum_{i_1, i_2, \ldots, i_k}^{f} c_{\mathbf{i}_k} Q_{i_1} Q_{i_2} \ldots Q_{i_k}, \tag{40}$$

We assume the following equations, which are exact for HO, hold also for VSCF:

$$Q_i \,|\phi^{(i)}_{p_i}\rangle \simeq a\,|\phi^{(i)}_{p_i-1}\rangle + a'\,|\phi^{(i)}_{p_i+1}\rangle\,, \tag{41}$$

$$P_i \,|\phi^{(i)}_{p_i}\rangle \simeq b\,|\phi^{(i)}_{p_i-1}\rangle - b'\,|\phi^{(i)}_{p_i+1}\rangle\,, \tag{42}$$

Then, we obtain,

$$\langle \Phi_{\mathbf{q}} | \hat{H}^k | \Phi_{\mathbf{p}} \rangle \simeq 0, \ (\lambda_{\mathbf{pq}} > k) \tag{43}$$

$$\langle \Phi_{\mathbf{q}} | \hat{H} | \Phi_{\mathbf{p}} \rangle \simeq \langle \Phi_{\mathbf{q}} | \hat{H} - \hat{H}^{\lambda_{\mathbf{pq}}} | \Phi_{\mathbf{p}} \rangle\,, \tag{44}$$

Vibrational Configuration Interaction

VCI wavefunction

$$|\Psi_{\mathbf{p}}\rangle = \sum_{\mathbf{q}} C_{\mathbf{qp}} |\Phi_{\mathbf{q}}\rangle \,, \tag{1}$$

VCI equation

$$H_{\mathbf{q'q}} = \langle \Phi_{\mathbf{q'}} | \hat{H} | \Phi_{\mathbf{p}} \rangle \,, \tag{2}$$

$$\mathbf{C}^{\dagger}\mathbf{HC} = E, \tag{3}$$

Truncated VCI

VCI[m] : m-mode excitation

$$\begin{aligned} |\Psi_{\mathbf{r}}^{\mathrm{VCI}[m]}\rangle \;&=\; C_{\mathbf{qr}}\Phi_{\mathbf{r}} + \sum_{i=1}^{f} \sum_{q_i \neq r_i}^{q_{max}} C_{r_i}^{q_i} |\Phi_{r_i}^{q_i}\rangle + \sum_{i_1 > i_2}^{f} \sum_{q_{i_1} \neq r_{i_1}}^{q_{max}} \sum_{q_{i_2} \neq r_{i_2}}^{q_{max}} C_{r_{i_1} r_{i_2}}^{q_{i_1} q_{i_2}} |\Phi_{r_{i_1} r_{i_2}}^{q_{i_1} q_{i_2}}\rangle + \ldots \\ &+ \sum_{i_1 > i_2 > \ldots > i_m}^{f} \sum_{\mathbf{q_{i_m}} \neq \mathbf{r_{i_m}}}^{q_{max}} C_{\mathbf{r_{i_m}}}^{\mathbf{q_{i_m}}} |\Phi_{\mathbf{r_{i_m}}}^{\mathbf{q_{i_m}}}\rangle \end{aligned} \tag{4}$$

$$N_{\mathrm{conf}}^{\mathrm{VCI}[m]} = \sum_{m'=0}^{m} \begin{pmatrix} f \\ m' \end{pmatrix} q_{max}^{m'}, \tag{5}$$

(qmax is max quanta of excitation)

VCI[m]-(k) : m-mode excitation, maximum sum of quanta k

$$\begin{aligned} |\Psi_{\mathbf{r}}^{\mathrm{VCI}[m]-(k)}\rangle \;&=\; C_{\mathbf{qr}}\Phi_{\mathbf{r}} + \sum_{i=1}^{f} {\sum_{q_i < k}}' C_{r_i}^{q_i} |\Phi_{r_i}^{q_i}\rangle + \sum_{i_1 > i_2}^{f} \sum_{q_{i_1} + q_{i_2} < k} C_{r_{i_1} r_{i_2}}^{q_{i_1} q_{i_2}} |\Phi_{r_{i_1} r_{i_2}}^{q_{i_1} q_{i_2}}\rangle + \ldots \\ &+ \sum_{i_1 > i_2 > \ldots > i_m}^{f} \sum_{q_{i_1} + q_{i_2} + \ldots + q_{i_m} < k} C_{\mathbf{r_{i_m}}}^{\mathbf{q_{i_m}}} |\Phi_{\mathbf{r_{i_m}}}^{\mathbf{q_{i_m}}}\rangle \end{aligned} \tag{6}$$

$$N_{\mathrm{conf}}^{\mathrm{VCI}[m]-(k)} = \sum_{m'=0}^{m} \begin{pmatrix} f \\ m' \end{pmatrix} \begin{pmatrix} k \\ m' \end{pmatrix}, \tag{7}$$

VCI matrix for a 2MR system

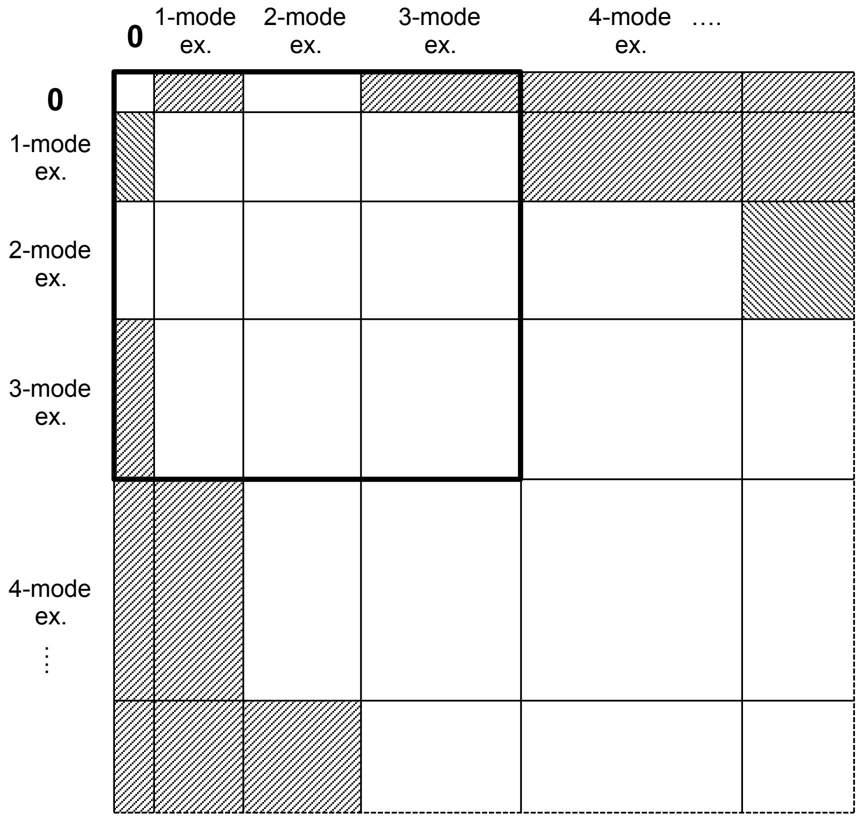

Table 1. The number of VSCF configuration functions in VCI[4] and VCI[4]-(6) with respect to the size of the molecule.

N [a]	f [b]	VCI[4] [c]	VCI[4]-(6)
4	6	24,337	887
6	12	691,489	12,888
9	21	8,051,527	119,652
12	30	36,409,681	498,981
15	39	108,598,231	1,427,895

[a] The number of atoms.
[b] The number of vibrational degrees of freedom ($3N$ - 6).
[c] $q_{\max}$ is taken to be 6.

問題

1. 振動版Brillouin’s定理である式(38)を証明せよ。

2. Table 1と同様にVCI[6], VCI[6]-(6)の配置数を自由度の数で表を作れ