VCSRF: Representation of a Transformed VCHAM Potential on the Grid

We condider a given potential $\boldsymbol{W}(\boldsymbol{q})$ furnished by the VCHFIT program, and a transformed potential $\tilde{\boldsymbol{W}}(\boldsymbol{q})$ yielded by a unitary transformation $\boldsymbol{U}(\boldsymbol{q})$:

$$\tilde{\boldsymbol{W}}(\boldsymbol{q}) = \boldsymbol{U}^{\dagger}(\boldsymbol{q})\boldsymbol{W}(\boldsymbol{q})\boldsymbol{U}(\boldsymbol{q}). \tag{1}$$

In general, the transformed potential $\tilde{\boldsymbol{W}}(\boldsymbol{q})$ will not be in the product form required for use with MCTDH. In order to proceed, the VCSRF program can be used to represent the transformed potential as a cut-HDMR expansion, which for f degrees of freedom q_α reads

$$\tilde{W}_{ij}(\boldsymbol{q}) = \tilde{W}^{(0)}_{ij} + \sum_{\alpha=1}^{f} \tilde{W}^{(1)}_{ij,\alpha}(q_\alpha) + \sum_{\alpha<\beta=1}^{f} \tilde{W}^{(2)}_{ij,\alpha\beta}(q_\alpha, q_\beta) + \cdots \tag{2}$$

To second-order, the component functions, also known as uncombined clusters (UCs), are given by

$$\tilde{W}^{(0)}_{ij} = \tilde{W}_{ij}(\boldsymbol{q}_0), \tag{3}$$

$$\tilde{W}^{(1)}_{ij,\alpha}(q_\alpha) = \tilde{W}_{ij}\left(q_\alpha; \boldsymbol{q}^{\alpha}_0\right) - \tilde{W}^{(0)}_{ij}, \tag{4}$$

$$\tilde{W}^{(2)}_{ij,\alpha\beta}(q_\alpha, q_\beta) = \tilde{W}_{ij}\left(q_\alpha, q_\beta; \boldsymbol{q}^{\alpha\beta}_0\right) - \tilde{W}^{(1)}_{ij,\alpha}(q_\alpha) - \tilde{W}^{(1)}_{ij,\beta}(q_\beta) - \tilde{W}^{(0)}_{ij}, \tag{5}$$

With higher-order terms being defined analogously. Here, $\boldsymbol{q}_0$ denotes the coordinates of the reference point, and, for example, $\boldsymbol{q}^{\alpha}_0$ denotes the (f-1)-dimensional coordinate vector $(q_{0,1}, \ldots, q_{0,\alpha-1}, q_{0,\alpha+1}, \ldots, q_{0,f})$.

It is evident that a vibronic coupling Hamiltonian of order N will be reproduced *exactly* by a cut-HDMR expansion of order $n \leq N$. For example, a second-order model containing bi-linear $\gamma^{(i)}_{\alpha\beta}$ and $\mu^{(i,j)}_{\alpha\beta}$ terms would be represented exactly by a second-order cut-HDMR expansion in terms of the UCs, whilst a second-order model containing only quadratic $\gamma^{(i)}_{\alpha\beta}$ and $\mu^{(i,j)}_{\alpha\beta}$ terms

would be reproduced exactly with only a first-order cut-HDMR expansion in terms of the UCs.

In order to reduce the combinatorial scaling of the number of UCs entering into the cut-HDMR expansion, we note that the transformed potential may equivalently be written in terms of the p combined modes Q_κ of the MCTDH calculation to be made. Subsequently, the cut-HMDR expansion of the transformed potential may be re-written also in terms of component functions of the combined modes, termed combined clusters (CCs):

$$\tilde{W}_{ij}(\boldsymbol{Q}) = \tilde{W}_{ij}^{(0)} + \sum_{\kappa=1}^{p} \tilde{W}_{ij,\kappa}^{(1)}(Q_\kappa) + \sum_{\kappa<\nu=1}^{p} \tilde{W}_{ij,\kappa\nu}^{(2)}(Q_\kappa, Q_\nu) + \cdots \tag{6}$$

with

$$\tilde{W}_{ij}^{(0)} = \tilde{W}_{ij}(\boldsymbol{Q}_0), \tag{7}$$

$$\tilde{W}_{ij,\kappa}^{(1)}(Q_\kappa) = \tilde{W}_{ij}\left(Q_\kappa; \boldsymbol{Q}_0^\kappa\right) - \tilde{W}_{ij}^{(0)}, \tag{8}$$

$$\tilde{W}_{ij,\kappa\nu}^{(2)}(Q_\kappa, Q_\nu) = \tilde{W}_{ij}\left(Q_\kappa, Q_\nu; \boldsymbol{Q}_0^{\kappa\nu}\right) - \tilde{W}_{ij,\kappa}^{(1)}(Q_\kappa) - \tilde{W}_{ij,\nu}^{(1)}(Q_\nu) - \tilde{W}_{ij}^{(0)}. \tag{9}$$

The first-order CCs, $\tilde{W}_{ij,\kappa}^{(1)}(Q_\kappa)$, can be used directly on the multi-dimensional product grids defined by the DVRs of the corresponding physical coordinates q_α that the combined modes Q_κ are comprised of. The second- and higher-order CCs, $\tilde{W}_{ij,\kappa\nu}^{(2)}(Q_\kappa, Q_\nu)$, etc., may be put into product form using the potfit algorithm.

To understand the savings made from the use of CCs in the cut-HDMR expansion of $\tilde{\boldsymbol{W}}$, we note that each CC can be written as a sum of UCs. By way of example, the first-order CC defined with respect to the combined mode $Q_\kappa = \left\{q_{\kappa_1}, q_{\kappa_2}, \ldots, q_{\kappa_{n_\kappa}}\right\}$ can be written as the sum of all UCs up to order n_κ defined in terms of the corresponding physical coordinates. Thus, a total of $\sum_{a=1}^{n_\kappa} \begin{pmatrix} n_\kappa \\ a \end{pmatrix}$ UCs are replaced by a single first-order CC.