

VCSRF: Representation of a Transformed VCHAM Potential on the Grid

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

$$\tilde{\mathbf{W}}(\mathbf{q}) = \mathbf{U}^\dagger(\mathbf{q})\mathbf{W}(\mathbf{q})\mathbf{U}(\mathbf{q}). \quad (1)$$

In general, the transformed potential $\tilde{\mathbf{W}}(\mathbf{q})$ 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

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

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

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

$$\tilde{W}_{ij,\alpha}^{(1)}(q_\alpha) = \tilde{W}_{ij}(q_\alpha; \mathbf{q}_0^\alpha) - \tilde{W}_{ij}^{(0)}, \quad (4)$$

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

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

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 $\gamma_{\alpha\beta}^{(i)}$ and $\mu_{\alpha\beta}^{(i,j)}$ 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 $\gamma_{\alpha\beta}^{(i)}$ and $\mu_{\alpha\beta}^{(i,j)}$ 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):

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

with

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

$$\tilde{W}_{ij,\kappa}^{(1)}(Q_\kappa) = \tilde{W}_{ij}(Q_\kappa; \mathbf{Q}_0^\kappa) - \tilde{W}_{ij}^{(0)}, \quad (8)$$

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

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 $\tilde{\mathbf{W}}$, 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 $Q_\kappa = \{q_{\kappa_1}, q_{\kappa_2}, \dots, q_{\kappa_{n_\kappa}}\}$ 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 $\sum_{a=1}^{n_\kappa} \binom{n_\kappa}{a}$ UCs are replaced by a single first-order CC.