VCSRF: Block Diagonalisation

We consider a unitary transformation of the diabatic basis $\{\Phi_i\}$ to yield a new basis $\{\Phi_i^{BD}\}$,

$$\Phi_i^{BD} = \sum_{j=1}^{N} S_{ji}\Phi_j, \tag{1}$$

such that the matrix representation of the potential in the new basis $\{\Phi_i^{BD}\}$, $\boldsymbol{W}_{BD}$, has a given block diagonal form:

$$\boldsymbol{W}_{BD} = \begin{pmatrix} \boldsymbol{W}_{BD,1} & & & \\ & \boldsymbol{W}_{BD,2} & & 0 \\ 0 & & \ddots & \\ & & & \boldsymbol{W}_{BD,n} \end{pmatrix}, \tag{2}$$

where the sub-matrices $\boldsymbol{W}_{BD,i}$ are $N_i \times N_i$ square matrices. In order to calculate the transformation matrix $\boldsymbol{S}$, we make use of the method developed by Cederbaum *et al.*[1] Within this scheme, the transformation matrix $\boldsymbol{S}$ is constructed such that

$$||\boldsymbol{S} - \boldsymbol{1}|| = minimum, \tag{3}$$

where $||\boldsymbol{A}||$ denotes the Euclidean norm of the matrix $\boldsymbol{A}$. That is, the transformation matrix $\boldsymbol{S}$ will bring the potential matrix $\boldsymbol{W}$ into block diagonal form, but beyond this will do nothing else. This constraint is found to be necessary as there exists an infinite number of unitary transformations that will bring the potential matrix into a given block diagonal form. Through the enforcement of this requirement, it can be shown that

$$\boldsymbol{S} = \boldsymbol{U}\boldsymbol{U}_{BD}^{\dagger}\left(\boldsymbol{U}_{BD}\boldsymbol{U}_{BD}^{\dagger}\right)^{-\frac{1}{2}}. \tag{4}$$

Here, $\boldsymbol{U}$ denotes the matrix of eigenvectors of the diabatic potential $\boldsymbol{W}$, and $\boldsymbol{U}_{BD}$ the block-diagonal part of $\boldsymbol{U}$. By way of example, for the transformation

$$
\boldsymbol{W} = \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix} \rightarrow \boldsymbol{W}_{BD} = \begin{pmatrix} W_{BD,11} & W_{BD,12} & 0 \\ W_{BD,21} & W_{BD,22} & 0 \\ 0 & 0 & W_{BD,33} \end{pmatrix},
$$
$$(5)$$

the corresponding block-diagonal part of $\boldsymbol{U}$ would be

$$
\boldsymbol{U}_{BD} = \begin{pmatrix} U_{11} & U_{12} & 0 \\ U_{21} & U_{22} & 0 \\ 0 & 0 & U_{33} \end{pmatrix}. \tag{6}
$$

References

[1] L. S. Cederbaum and J. Schirmer and H. -D. Meyer, J. Phys. A, **22**, 2427 (1989)