Alexey V. Akimov, Initial version: 12/5/2015; latest revision: 06/12/2016

Let's start with a simple case:

$$HC = CE, \tag{1a}$$

or

$$C^T H = EC^T. \tag{1b}$$

with orthonormality condition:

$$C^T C = I. \tag{2}$$

We then get:

$$\frac{dH}{dR} C + H \frac{dC}{dR} = \frac{dC}{dR} E + C \frac{dE}{dR}, \tag{3}$$

and

$$\frac{dC^T}{dR} C + C^T \frac{dC}{dR} = 0. \tag{4}$$

The derivative coupling is

$$D = C^T \frac{dC}{dR}. \tag{5}$$

From Eq. 4 and 5 we can see that:

$$D^T + D = 0. \tag{6}$$

Multiplying Eq. 3 by C^T from the left, we obtain:

$$C^T \frac{dH}{dR} C + C^T H \frac{dC}{dR} = C^T \frac{dC}{dR} E + C^T C \frac{dE}{dR}. \tag{7}$$

Using Eq. 1b, we get:

$$C^T \frac{dH}{dR} C + EC^T \frac{dC}{dR} = C^T \frac{dC}{dR} E + C^T C \frac{dE}{dR}. \tag{8}$$

Using definition Eq. 5 and orthonormality condition Eq. 2, the Eq. 8 simplifies:

$$C^T \frac{dH}{dR} C = \frac{dE}{dR} + DE - ED. \tag{9}$$

The matrix $X = DE - ED$ is symmetric with zero diagonal elements. Moreover, it has the following structure:

$$X = \begin{pmatrix} 0 & (E_1 - E_0)D_{01} & (E_2 - E_0)D_{02} & \dots \\ (E_1 - E_0)D_{01} & 0 & (E_2 - E_1)D_{12} & \dots \\ (E_2 - E_0)D_{02} & (E_2 - E_1)D_{12} & 0 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}. \tag{10}$$

On the contrary, the matrix $\frac{dE}{dR}$ is diagonal.

Therefore, one can split the matrix $C^T \frac{dH}{dR} C$ into diagonal matrix and symmetric matrix with all diagonal elements zero. In this way we can compute gradients and NACs as:

$$\frac{dE_i}{dR} = \left(C^T \frac{dH}{dR} C \right)_{ii} = \sum_{a,b} \left(C^T \right)_{ia} \left(\frac{dH}{dR} \right)_{ab} C_{bi} = \sum_{a,b} \left(\frac{dH}{dR} \right)_{ab} C_{ai} C_{bi} , \tag{11}$$

$$X_{ij} = \left(E_j - E_i \right) D_{ij} = \left(C^T \frac{dH}{dR} C \right)_{ij} \Rightarrow D_{ij} = \frac{1}{\left(E_j - E_i \right)} \sum_{a,b} \left(\frac{dH}{dR} \right)_{ab} C_{ai} C_{bj} . \tag{12}$$

Now let us consider more general case – non-orthogonal basis:

$$HC = SCE , \tag{13a}$$

or

$$C^T H = EC^T S . \tag{13b}$$

with orthonormality condition:

$$C^T SC = I . \tag{14}$$

We then get:

$$\frac{dH}{dR} C + H \frac{dC}{dR} = \frac{dS}{dR} CE + S \frac{dC}{dR} E + SC \frac{dE}{dR} , \tag{15}$$

and

$$\frac{dC^T}{dR} SC + C^T \frac{dS}{dR} C + C^T S \frac{dC}{dR} = 0 . \tag{16}$$

The derivative coupling is

$$D = C^T \frac{d}{dR} \left(SC \right) . \tag{17}$$

From Eq. 16 and 17 we can see that:

$$\frac{dC^T}{dR} SC + D = 0 , \tag{18a}$$

$$C^T S \frac{dC}{dR} + D^T = 0 . \tag{18b}$$

Summing Eq. 18a and 18b and using Eq. 16, we get:

$$D + D^T = C^T \frac{dS}{dR} C . \tag{19}$$

Multiplying Eq. 15 by C^T from the left, we obtain:

$$C^T \frac{dH}{dR} C + C^T H \frac{dC}{dR} = C^T \frac{dS}{dR} CE + C^T S \frac{dC}{dR} E + C^T SC \frac{dE}{dR} . \tag{20}$$

Using 13b and 14

$$C^T \frac{dH}{dR} C + EC^T S \frac{dC}{dR} = C^T \frac{dS}{dR} CE + C^T S \frac{dC}{dR} E + \frac{dE}{dR} . \tag{21}$$

Using Eq. 17:

$$C^T \frac{dH}{dR} C + EC^T S \frac{dC}{dR} = DE + \frac{dE}{dR} . \tag{22}$$

Using Eq. 18b:

$$C^T \frac{dH}{dR} C - ED^T = DE + \frac{dE}{dR}. \tag{23a}$$

or

$$C^T \frac{dH}{dR} C = \frac{dE}{dR} + DE + ED^T. \tag{23b}$$

Using Eq. 19, we get:

$$C^T \frac{dH}{dR} C = \frac{dE}{dR} + DE + E\left(C^T \frac{dS}{dR} C - D \right), \tag{24a}$$

or

$$C^T \left(\frac{dH}{dR} - E \frac{dS}{dR} \right) C = \frac{dE}{dR} + DE - ED. \tag{25}$$

The structure of the matrixes on the right-hand side is the same as in the orthogonal case, Eq. 9. The only difference is that one now has additional term in effective Hamiltonian matrix, due to non-orthogonality of the basis functions. Apparently, the Eq. 9 is recovered as the special case of Eq. 25, when $S = I$.

Second order NAC and the derivatives of the first order NAC

Consider the case of orthogonal states first. Also, we are only interested in kinetic-energy-like terms, so we have only $\frac{d^2}{dR_\alpha^2}$ and no cross-terms like $\frac{d^2}{dR_\alpha dR_\beta}$. In the present case, we have generalized the theory to the complex-valued coefficients C.

From the definition, Eq. 5, we obtain:

$$T = C^+ \nabla^2 C = C^+ (\nabla^+ \nabla) C = (C^+ \nabla^+)(\nabla C) = (\nabla C)^+ (\nabla C) = D^+ C^+ C D = D^+ D, \tag{26}$$

The symmetry of T:

$$T^+ = (D^+ D)^+ = D^+ D = T, \tag{27}$$

as it should be