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# Electronic non-adiabatic transitions
# Derivation of the general adiabatic–diabatic transformation matrix

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In 1969 Smith [1] presented a transformation which enables one to go from the adiabatic to the diabatic framework. We extended this method, which was originally devised for the atom–atom case, to the atom–diatom case [2–4] and also applied it successfully for the few cases we studied [5]. According to the extended version of Smith's method the transformation matrix is derived as a solution of a first-order vector differential equation

$$\nabla \,.\, \mathbf{A} + \mathbf{t}\mathbf{A} = 0, \tag{1}$$

where $\nabla$ is a vectorial operator

$$\nabla = \left(\frac{\partial}{\partial x_1};\ \dots;\ \frac{\partial}{\partial x_N}\right) \tag{2}$$

and $\mathbf{t}$ is a vector matrix

$$\mathbf{t} = (\mathbf{t}_{x_1};\ \dots;\ \mathbf{t}_{x_N}). \tag{3}$$

Here, the order of $\mathbf{A}$ and $\mathbf{t}$ is $n$ where $n$ is the number of states included in the treatment and the $x_i$, $i=1, \dots, N$, are a set of $N$ independent nuclear coordinates. For instance in the case of three atoms $N=3$ and $x_i = R, r, \gamma$ (the translational, vibrational and angular coordinates respectively) so that $\nabla$ becomes

$$\nabla = \left(\frac{\partial}{\partial R}, \frac{\partial}{\partial r}, \frac{\partial}{\partial \gamma}\right) \tag{4}$$

and the corresponding $\mathbf{t}$ matrix is

$$\mathbf{t} = (\mathbf{t}_R, \mathbf{t}_r, \mathbf{t}_\gamma). \tag{5}$$

The matrices $\mathbf{t}_{x_i}$, $i=1, \dots, N$, are antisymmetric with elements

$$t_{x_i kl} = -\langle \zeta_k | \frac{\partial}{\partial x_i} | \zeta_l \rangle, \quad i=1, \dots, N; \quad k, l = 1, \dots, n, \tag{6}$$

where $\zeta_k$ and $\zeta_l$ are the electronic adiabatic basis functions. Equation (1) has a unique solution when and only when each pair of the component matrices $\mathbf{t}_x$ and $\mathbf{t}_y$ fulfil the condition [2]

$$\frac{\partial}{\partial x}\mathbf{t}_y - \frac{\partial}{\partial y}\mathbf{t}_x = [\mathbf{t}_y, \mathbf{t}_x]. \tag{7}$$

The solution was discussed in detail for the two state case ($n=2$) where the number of variables were $N=1$ [1–6] and $N=2, 3$ [2–4]. Some attempts to solve this equation were also made for the three state case ($n=3$) [4]. In this Note we present a general method which yields a solution for any value of $n$ and $N$. In order to solve equation (1), that is in order to derive $\mathbf{A}$ at a point $(x_1^1, \ldots, x_N^1)$ once its value is known at $(x_1^0, \ldots, x_N^0)$, we suggest obtaining the solution in a propagative way. What is meant by that is starting at the point $(x_1^0, \ldots, x_N^0)$ we propagate to the first intermediate point $(x_1^1, x_2^0, x_3^0, \ldots, x_N^0)$ and then to the second point $(x_1^1, x_2^1, x_3^0, \ldots, x_N^0)$ and so on until we reach the final point $(x_1^1, \ldots, x_N^1)$. While in the $i$th step we consider the $i$th component of equation (1), that is

$$\frac{\partial}{\partial x_i}\mathbf{A}+\mathbf{t}_{x_i}\mathbf{A}=0 \tag{8}$$

and assume that $\mathbf{A}$ is already known at the point $(x_1^1, \ldots, x_{i-1}^1, x_i^0, x_{i+1}^0, \ldots, x_N^0)$. To do that we define a matrix $\mathbf{A}_i$ as

$$\mathbf{A}_i=\mathbf{A}(x_1^1, \ldots, x_{i-1}^1, x_i^1, x_{i+1}^0, \ldots, x_N^0). \tag{9}$$

Then the final solution of equation (8) can be written as

$$\mathbf{A}_i=\mathbf{B}_i\mathbf{A}_{i-1}, \tag{10}$$

where

$$\mathbf{B}_i=\exp\left[-\mathbf{T}_i\right] \tag{11}$$

and

$$\mathbf{T}_i=\int_{x_i^0}^{x_i^1} dx_i\, \mathbf{t}_{x_i}(x_1^1, \ldots, x_{i-1}^1, x_i, x_{i+1}^0, \ldots, x_N^0). \tag{12}$$

Repeating the process $N$ times we get

$$\mathbf{A}(x_1^1, \ldots, x_N^1)=\left(\prod_{i=0}^{N-1}\mathbf{B}_{N-i}\right)\mathbf{A}(x_1^0, \ldots, x_N^0). \tag{13}$$

To find $\mathbf{B}_i$ we have to find the eigenvalues of $\mathbf{T}_i$ and the matrix $\mathbf{S}_i$ that diagonalizes $\mathbf{T}_i$. Since $\mathbf{T}_i$ is antisymmetric it has only imaginary (or zero) eigenvalues and $\mathbf{S}_i$ is unitary

$$\mathbf{T}_i\mathbf{S}_i=\mathbf{S}_i\boldsymbol{\lambda}_i, \tag{14}$$

where $\boldsymbol{\lambda}_i$ is a diagonal matrix. If we now define $\mathbf{E}^{(i)}$ as a (diagonal) matrix with the following matrix elements

$$\mathbf{E}_{kl}^{(i)}=\exp\left(\lambda_k^{(i)}\right)\delta_{kl} \tag{15}$$

where $\lambda_k^{(i)}$ is the $k$th eigenvalue of $\mathbf{T}_i$, then the $\mathbf{B}_i$ matrix can be written as

$$\mathbf{B}_i=\mathbf{S}_i\mathbf{E}^{(i)}\mathbf{S}_i^{\dagger}. \tag{16}$$

Substituting equation (16) in equation (13) leads to

$$\mathbf{A}(x_1^1, \ldots, x_N^1)=\left(\prod_{i=0}^{N-1}\mathbf{S}_{N-i}\mathbf{E}^{(N-i)}\mathbf{S}_{N-i}^{\dagger}\right)\mathbf{A}(x_1^0, \ldots, x_N^0) \tag{17}$$

which is the desired solution.

## References

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