Existence of Diabatic Potentials and the Quantization of the Nonadiabatic Matrix

Michael Baer†

Institute of Atomic and Molecular Science, Taipei, Taiwan, ROC 10764, and Department of Physics and Applied Mathematics, Soreq NRC, Yavne 81800, Israel

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In this work are considered nonadiabatic matrices which were *not* derived from first principles. For this type of nonadiabatic matrices we derived the conditions for such an $N \times N$ matrix to yield an $N \times N$ diabatic potential matrix which is continuous throughout configuration space. It is shown that these conditions are very close to being quantization type conditions which select from all possible matrices only a certain group. The final theoretical results are supported by examples (a) for the $N = 2$ case and (b) for the $N = 3$ case.

I. Introduction

In a recent publication we discussed difficulties related to the application of electronic nonadiabatic matrices, $\boldsymbol{\tau}$, which are not obtained from first principles and which are therefore incapable, in general, of producing physical diabatic potentials.[1] It was then found, for one class of nonadiabatic models, that, provided their parameters fulfill certain conditions, they will form physically meaningful diabatic potentials. In this article the discussion of this subject is extended to any type of nonadiabatic matrices. Moreover, it is shown that the condition to be satisfied by these matrices is reminiscent of the Bohr−Sommerfeld "quantization" law as is applied to angular momentum operators.[2]

In the next section is presented the theory that led to the "quantization" of the nonadiabatic coupling matrix, in the third section a few examples are discussed, and the conclusions are summarized in the fourth section.

II. "Quantization" of the Nonadiabatic Coupling Matrix along a Closed Path

II.1. Necessary Conditions for an Adiabatic-to-Diabatic Transformation Matrix To Produce Unique Diabatic Potentials. To study the necessary conditions for having a uniquely defined diabatic potential matrix, we assume the existence of an adiabatic−diabatic transformation (ADT) matrix $\mathbf{A}(s,s_0)$ which transforms a given adiabatic potential matrix $\mathbf{u}(s)$ to a diabatic potential matrix $\mathbf{W}(s,s_0)$:[3−6]

$$\mathbf{W}(s,s_0) = \mathbf{A}^{\dagger}(s,s_0)\,\mathbf{u}(s)\,\mathbf{A}(s,s_0) \tag{1}$$

Here $\mathbf{A}^{\dagger}(s,s_0)$ is the complex conjugate of $\mathbf{A}(s,s_0)$, s_0 is a given initial point in configuration space (CS), and s is some other point. Next, it is assumed that $\mathbf{W}(s,s_0)$ is uniquely defined throughout CS, and our aim is to derive the features to be fulfilled by $\mathbf{A}(s,s_0)$ in order to ensure the uniqueness of $\mathbf{W}(s,s_0)$. In this respect it is important to mention that $\mathbf{u}(s)$ is also assumed to be uniquely defined throughout CS.

To reveal the features of $\mathbf{A}(s,s_0)$, we introduce a closed path Γ defined in terms of a continuous parameter λ so that the starting point s_0 of the path is at $\lambda = 0$. Next we define β as the value attained by λ once the path completes a full cycle and returns to its starting point. Thus, for instance, in the case of a circle $\beta = 2\pi$.

Having introduced these definitions, we can now express our assumption regarding the uniqueness of $\mathbf{W}(s,s_0)$ in the following way: At *each point* s_0 in CS the diabatic potential matrix $\mathbf{W}(\lambda)$ $(\equiv \mathbf{W}(s,s_0))$ fulfills the relation

$$\mathbf{W}(\lambda{=}0) = \mathrm{W}(\lambda{=}\beta) \tag{2}$$

Following eq 1, this requirement implies that for every point s_0 we have

$$\mathbf{A}^{\dagger}(0)\,\mathbf{u}(0)\,\mathbf{A}(0) = \mathbf{A}^{\dagger}(\beta)\,\mathbf{u}(\beta)\,\mathbf{A}(\beta) \tag{3}$$

To continue, we introduce another transformation matrix, $\mathbf{D}$, defined as

$$\mathbf{D} = \mathbf{A}(\beta)\mathbf{A}^{\dagger}(0) \tag{4}$$

which for every s_0 and a given path Γ connects between $\mathbf{u}(\beta)$ and $\mathbf{u}(0)$:

$$\mathbf{u}(\beta) = \mathbf{D}\,\mathbf{u}(0)\,\mathbf{D}^{\dagger} \tag{5}$$

The $\mathbf{D}$ matrix is by definition a unitary matrix (it is a product of two unitary matrices), and at this stage, except for being dependent on Γ and, eventually, on the initial point s_0, it is rather arbitrary. In what follows we shall derive some features of $\mathbf{D}$.

Since the adiabatic eigenvalues are uniquely defined at each point in CS, we have $\mathbf{u}(0) \equiv \mathbf{u}(\beta)$ and therefore eq 5 can also be written as

$$\mathbf{u}(0) = \mathbf{D}\,\mathbf{u}(0)\,\mathbf{D}^{\dagger} \tag{6}$$

Performing the multiplication, it can be shown that it yields the following system of relations between the adiabatic eigenvalues $u_j(0)$ and the $\mathbf{D}$-matrix elements:

$$\sum_{j=1}(D^{\dagger}_{kj}\,D_{kj} - \delta_{kj})u_j(0) = 0; \quad k = 1, ..., N \tag{7}$$

Equation 7 has to hold at every arbitrary point s_0 $(\equiv\lambda = 0)$ and for an essential, arbitrary set of nonzero adiabatic eigenvalues, $u_j(0)$, $j = 1, ..., N$. Due to the arbitrariness of the $u_j(0)$'s,

† Guest Professor at the Institute of Atomic and Molecular Science, Tapei, Taiwan.

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eqs 7 can be satisfied if and only if the **D**-matrix elements fulfill the relation[11]

$$(D_{jk})^{\dagger}D_{jk} = \delta_{jk}; \quad j, k = 1, ..., N \tag{8}$$

or

$$D_{jk} = \delta_{jk} \exp(i\chi_k) \tag{9}$$

Thus **D** is a diagonal matrix which contains in its diagonal complex numbers whose norm is 1.

Recalling eq 4, we obtain

$$\mathbf{A}(\beta) = \mathbf{D}\mathbf{A}(0) \tag{10}$$

It is noticed that $\mathbf{A}(\beta)$ does not have to be identical to $\mathbf{A}(0)$; namely, it does not have to be uniquely defined at every point in CS in order to be able to produce physically meaningful diabatic potentials, but then, upon following a closed path, it has to fulfill the conditions specified by eqs 9 and 10.

II.2. "Quantization" of the Nonadiabatic Coupling Matrix. Our next step is to derive $\mathbf{A}(\beta)$, and this we do by applying the first-order vector equation:[3]

$$\nabla\mathbf{A} + \boldsymbol{\tau}\mathbf{A} = 0 \tag{11}$$

where $\boldsymbol{\tau}$, as was mentioned earlier, is the nonadiabatic coupling matrix. This equation does not necessarily yield a uniquely defined **A** matrix. Uniquely defined **A** matrices are guaranteed if and only if all the $\boldsymbol{\tau}$-matrix elements are regular functions at *every* point in CS. Here, purposely, we consider cases where the $\boldsymbol{\tau}$-matrix elements are not regular throughout CS, and the question we intend to answer is: What kind of conditions have to be imposed on the $\boldsymbol{\tau}$-matrix elements in order for them to yield an **A** matrix that transforms (see eq 1) the adiabatic potential matrix to a *uniquely* defined diabatic potential matrix? Equation 11 can always be solved, by simply integrating it along a path (in case of a single variable, this path is a straight line). The only difficulty one may encounter in the multidimensional case is that the solution may not be uniquely defined. As we have seen in the previous paragraph, this deficiency does not necessarily rule out the possibility of forming uniquely defined diabatic potentials. Thus, what we intend to do is as follows: We shall integrate eq 11 along a line and look for conditions to be imposed on the $\boldsymbol{\tau}$-matrix elements so that the **A** matrix, even if not uniquely defined in CS, will yield a uniquely defined diabatic potential matrix. The formal solution of eq 11 can be written as an ordered integral[7,8]

$$\mathbf{A}(s) = \exp\left(-\int_{s_0}^{s} \mathrm{d}\mathbf{s}\cdot\boldsymbol{\tau}\right)\mathbf{A}(s_0) \tag{12}$$

where the integration is performed along a path Γ that combines s and s_0. For a closed path eq 12 becomes similar to eq 10 so that the **D** matrix can be derived from the expression

$$\mathbf{D} = \exp\left(\oint_{\Gamma} \mathrm{d}\mathbf{s}\cdot\boldsymbol{\tau}\right) \tag{13}$$

Equation 13 shows a very important feature of the **D** matrix, namely, that it depends solely on the path Γ while not depending on any particular point on the path. Next in order for this matrix to yield a physical diabatic potential matrix, it also has to fulfill the condition given in eq 9. These two conditions form the general "quantization" condition to be imposed on a $\boldsymbol{\tau}$ matrix.

It is important to mention that although $\boldsymbol{\tau}$ is a vector of matrices, the fact that we encounter in eq 13 the scalar product $\boldsymbol{\tau}\cdot\mathbf{ds}$ (which is equal to $\boldsymbol{\tau}_s\,\mathrm{ds}$, where $\boldsymbol{\tau}_s$ is a scalar matrix) permits continuing the derivation as though a scalar and not a vector matrix is involved. Next we rewrite eq 13 in a more "explicit" form as[7]

$$\mathbf{D} = \prod_{k=0}^{M} \mathbf{G}^{\dagger}(s_k)\,\mathbf{E}(s_k)\,\mathbf{G}(s_k) \tag{14}$$

where $\{s_k, k = 0, 1, ..., M\}$ is a series of points along Γ (the point s_M, the last point in this series, is identical to s_0), $\mathbf{G}(s_k)$ is a unitary matrix that diagonalizes $\boldsymbol{\tau}(s_k)$ at s_k ($\mathbf{G}^{\dagger}(s_k)$ is its complex conjugate) and $\mathbf{E}(s_k)$ is a diagonal matrix with elements

$$E_n(s_k) = \exp\left(-i\int_{s_{k-1}}^{s_k} \mathrm{d}s\cdot t_n(s)\right) \tag{15}$$

where it is assumed that s_k is close enough to s_{k-1} to allow the expansion in eq 14. The order in eq 14 is such that the $k = 0$ term is the most right-hand one in the product. The matrix $\mathbf{it}(s)$ is the diagonal matrix that contains the eigenvalues of $\boldsymbol{\tau}(s)$ as calculated at a point s on Γ (we recall that since all $\boldsymbol{\tau}(s)$ matrices are antisymmetric, they all have imaginary (or zero) eigenvalues $\mathrm{i}t_n(s)$).

To get some insight into what this relation implies for the **D** matrix we make a simplifying assumption, namely, that $\mathbf{G}(s)$ is a slowly varying (or nonvarying) function of the coordinates along a given path so that for each two adjacent points we may assume

$$\mathbf{G}(s_k)\,\mathbf{G}^{\dagger}(s_{k-1}) \sim \mathbf{I} \tag{16}$$

If this is the case, then eq 15 can be written as

$$\mathbf{D} = \mathbf{G}^{\dagger}(\lambda{=}\beta)\exp\left(-i\oint_{\Gamma}\mathrm{d}s\; t(s)\right)\mathbf{G}(\lambda{=}0) \tag{17}$$

where β (and λ) were defined in the previous paragraph. It is important to emphasize that although both **G** matrices are defined at the *same* point in CS, they are not necessarily identical, because it is not obvious that the $\boldsymbol{\tau}$ matrices are the same. In the case in which the $\boldsymbol{\tau}$ matrix is uniquely defined at each point in CS, eq 17 becomes

$$\mathbf{D} = \mathbf{G}^{\dagger}(s_0)\exp\left(-i\oint_{\Gamma}\mathrm{d}\mathbf{s}\cdot t(s)\right)\mathbf{G}(s_0) \tag{18}$$

It can be seen that the explicit representation of the **D** matrix in eq 17 is consistent with the requirement imposed on **D** as expressed in eq 5. Matrix **D** transforms $\mathbf{u}(0)$ to $\mathbf{u}(\beta)$ while moving along a closed path Γ in a certain direction. From eq 5 we also obtain that $\mathbf{D}^{\dagger}$ transforms $\mathbf{u}(\beta)$ to $\mathbf{u}(0)$ while moving along Γ but in the opposite direction. **D** matrix in eq 17 indeed possesses this feature. From eq 17 matrix $\mathbf{D}^{\dagger}$ is given in the form

$$\mathbf{D}^{\dagger} = \mathbf{G}^{\dagger}(\lambda{=}0)\exp\left(i\oint_{\Gamma}\mathrm{d}s\cdot t(s)\right)\mathbf{G}(\lambda{=}\beta) \tag{18'}$$

It is seen that it produces the backward transformation where we start with $\mathbf{G}(\beta)$, move with directional step sizes $(-\mathrm{d}s)$ (namely, backward), and end up with $\mathbf{G}(0)$.

In the previous section we showed that **D** has to be a diagonal matrix with numbers of norm 1 in its diagonal (but not necessarily a unit matrix). The **D** matrix is explicitly presented in eq 17 in terms of the eigenvalues of the $\boldsymbol{\tau}$ matrix. It is obvious that no arbitrary set of functions $t(s)$ would yield a **D** matrix with the features just mentioned. In other words the functions $t(s)$ (or the $\boldsymbol{\tau}$ matrix) have to have certain qualifications in order to form such diagonal **D** matrices. The conditions to be fulfilled by the $\boldsymbol{\tau}$ matrix (or better, its eigenvalues) are reminiscent of

the quantization of the component of the angular momentum operator along a closed path, as was assumed (by Bohr and Sommerfeld[2]) in the early days of quantum mechanics.

III. Quantization of Simplified Systems

In this section we discuss two simple examples to show that eq 18 indeed implies quantization.

III.1. Two-State System. The $\boldsymbol{\tau}$ matrix in this case is given as

$$\boldsymbol{\tau} = \begin{pmatrix} 0 & t \\ -t & 0 \end{pmatrix} \tag{19}$$

where t, at this stage, is an arbitrary function of the nuclear coordinates. The matrix **G** that diagonalizes $\boldsymbol{\tau}$ is of the form

$$\mathbf{G} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix} \tag{20}$$

and the corresponding eigenvalues are $\pm$it. Since **G** is a constant matrix, the matrix **D** can be derived explicitly (see eq 18):

$$\mathbf{D} = \begin{pmatrix} \cos(\oint t \cdot \mathrm{d}s) & -\sin(\oint t \cdot \mathrm{d}s) \\ \sin(\oint t \cdot \mathrm{d}s) & \cos(\oint t \cdot \mathrm{d}s) \end{pmatrix} \tag{21}$$

It is noticed that in order for **D** to be diagonal (and to have either (+1)'s or (−1)'s in the diagonal) the t matrix element along a given path Γ has to fulfill the condition

$$\frac{1}{2\pi} \oint_\Gamma t \cdot \mathrm{d}s = \frac{n}{2} \tag{22}$$

where n is an *integer*. These conditions are very close to being the Bohr−Sommerfeld quantization conditions (as applied to the eigenvalue of the $\boldsymbol{\tau}$ matrix).

Equation 22 presents the condition for the extended conical intersection case. It is important to indicate that if case n is an even integer, the diagonal of the **D** matrix contains (+1)'s (thus the **D** matrix becomes a unit matrix) and in this case the $\boldsymbol{\tau}$ matrix will not produce any topological (or symmetry) effects. However, if n is an odd integer, the diagonal of the **D** matrix contains (−1)'s and in this case the $\boldsymbol{\tau}$ matrix will produce topological (or symmetry) effects, as is well-known from the study of Herzberg and Longuet-Higgins[9] for the case in which $t\ \mathrm{d}s = (1/2)\mathrm{d}\varphi$, where φ is an angular *polar* coordinate.

III.2. The Three-State System. The second example is the following general three-state $\boldsymbol{\tau}$ matrix

$$\boldsymbol{\tau} = \begin{pmatrix} 0 & t_1 & t_2 \\ -t_1 & 0 & t_3 \\ -t_2 & -t_3 & 0 \end{pmatrix} \tag{23}$$

where t_j, $j = 1, 2, 3$ are, at this stage, arbitrary functions of the nuclear coordinates. The **G** matrix that diagonalizes $\boldsymbol{\tau}$ is of the form

$$\mathbf{G} = \frac{1}{\varpi\lambda\sqrt{2}} \begin{pmatrix} it_2\varpi - t_3t_1 & -it_2\varpi - t_3t_1 & t_3\lambda\sqrt{2} \\ it_3\varpi + t_2t_1 & -it_3\varpi + t_2t_1 & -t_2\lambda\sqrt{2} \\ \lambda^2 & \lambda^2 & t_1\lambda\sqrt{2} \end{pmatrix} \tag{24}$$

where λ and ϖ are defined as

$$\lambda = [t_2^{\,2} + t_3^{\,2}]^{1/2}; \quad \varpi = [t_1^{\,2} + t_2^{\,2} + t_3^{\,2}]^{1/2} \tag{25}$$

The three eigenvalues of the **G** matrix are $(0, \pm i\varpi)$. Next we derive the **D** matrix (see eq 18), where it is assumed that the s dependence of $\boldsymbol{\tau}(s)$ is such that the approximation expressed in eq 16 is fulfilled:

$$\mathbf{D} = \varpi^{-2} \begin{pmatrix} t_3^{\,2} + (t_1^{\,2} + t_2^{\,2})C_1 & t_1S_1\varpi - 2t_2t_3S_2 & -t_2S_1\varpi + 2t_1t_3S_2 \\ t_1S_1\varpi - 2t_2t_3S_2 & t_2^{\,2} + (t_1^{\,2} + t_3^{\,2})C_1 & -t_3S_1\varpi + 2t_1t_2S_2 \\ t_2S_1\varpi + 2t_1t_3S_2 & t_3S_1\varpi + 2t_1t_2S_2 & t_1^{\,2} + (t_2^{\,2} + t_3^{\,2})C_1 \end{pmatrix} \tag{26}$$

Here all t_j's are calculated at the end point and S_1, C_1, and S_2 are defined as follows:

$$S_1 = \sin(\oint_\Gamma \varpi\ \mathrm{d}s); \quad C_1 \cos(\oint_\Gamma \varpi\ \mathrm{d}s); \quad S_2 \sin^2\left(\frac{1}{2} \oint_\Gamma \varpi\ \mathrm{d}s\right) \tag{27}$$

It is noticed that **D** becomes diagonal if and only if

$$\frac{1}{2\pi} \oint_\Gamma \varpi\ \mathrm{d}s = \frac{1}{2\pi} \oint_\Gamma [t_1^{\,2} + t_2^{\,2} + t_3^{\,2}]^{1/2}\ \mathrm{d}s = n \tag{28}$$

where n is an integer. Similar quantization laws exist if one of the t_j's becomes zero (if two out of the three t_j's become zero, then we are back to the two-state case and n is allowed to be half an integer). Returning now to eq 23, it is noticed that the elements of the $\boldsymbol{\tau}$ matrix cannot be arbitrary functions but have to be chosen in such a way that they fulfill the quantization law given in eq 28. This condition, as in the two-state case, limits significantly the number of 3×3 $\boldsymbol{\tau}$ matrices that can be employed to form physical diabatic potentials.

IV. Conclusions

In this work are considered arbitrary nonadiabatic matrices which were *not* derived from first principles. For this type of nonadiabatic matrices we derived the conditions to be fulfilled for such an $N \times N$ matrix to yield an $N \times N$ diabatic potential matrix which is continuous throughout CS. It is shown that these conditions are reminiscent of quantization type conditions which select, from all possible $\boldsymbol{\tau}$ matrices, only a certain group. To clarify the meaning of the theoretical outcome, we analyzed two simplified cases: the well-known two-state (e.g. conical intersection) model and a similar three-state model.

As for the two-state model our analysis shows that the only physically possible situation is that the average of the function $t(s)$ as calculated along a closed path Γ (see eq 22), i.e., t_Γ, either attains the value $^1/_2$ or is 1 (a case that does not lead to any topological effects). In other words our derivation shows that t_Γ cannot attain, for instance, the value $t_\Gamma = {}^1/_3$, because the diabatic potential that will be formed in that case will be multivalued in configuration space and therefore unsuitable for any further applications. Thus, Herzberg−Longuet-Higgins conical intersection model[9] (or its extended version) is the *only* possible physical model that can produce topological effects for a two-state system. All other two-state models either do not produce topological effects or are not physically acceptable.

To study the three-state model, the treatment was restricted to the case in which the $\boldsymbol{\tau}$ matrix eigenvectors form a smoothly behaving **G** matrix (see eq 16). The conditions that such a $\boldsymbol{\tau}$ matrix has to fulfill in order to yield a physical diabatic potential matrix are given in eq 28 and are very similar to the two-state model conditions for the case in which n is an *even* integer. In such a case the **D** matrix is the *unit* matrix, and just like in the two-state model with an even integer n, it will *never* produce topological effects. This does not necessarily imply that three-state systems cannot produce topological effects. Recently we

studied a three-state model with more than one point of degeneracy and found that the corresponding adiabatic-to-diabatic transformation matrix **A** will yield a diagonal **D** matrix (see eq 4) that has in its diagonal one (+1) and two (−1)'s.[10] It is not clear to us whether such a model system is capable of producing topological effects.

Finally we would like to make the following comment. It is well-known that the nonadiabatic coupling terms are momentum type operators. Since we referred here to motions along nonlinear paths, these operators present *angular* momentum type operators and these, according to the basic requirements of quantum mechanics, have to be quantized. If one applies nonadiabatic terms obtained from first principles, they are guaranteed to be properly quantized and therefore need not and should not be modified. However, if one intends to use model type coupling terms, they have to be quantized before they are applied. To do that we imposed, in a certain way, what is known as the Bohr−Sommerfeld quantization rule. We are, of course, aware that the Bohr−Sommerfeld quantization is done with respect to a single action variable without applying any diagonalization of a momentum matrix as we were forced to do here but the similarity is too striking not to name it, simply, the "generalized Bohr−Sommerfeld quantization rule". The next question to be asked is if this new type of quantization carries with it any physical significance. This aspect is not clear to us at this stage. There is some similarity between the quantized nonadiabatic coupling matrix eigenvalues and the electronic *spin*, but it is hard to believe that we encounter here a new measurable quantized observable.

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(11) One (less important) exceptional case will be discussed elsewhere.