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The Electronic Non-Adiabatic Coupling Matrix: A Numerical Study of the Curl Condition and the Quantization Condition Employing the Mathieu Equation†

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In this article, we discuss the electronic nonadiabatic coupling matrix, $\boldsymbol{\tau}$, which under certain conditions is characterized by two interesting features: (1) its components fulfill an extended Curl equation (*Chem. Phys. Lett.* 1975, *35,* 112, (see Appendix 1)) and (2) it is quantized in the sense that the topological **D** matrix, presented as an exponentiated line integral over the $\boldsymbol{\tau}$ matrix, is a unitary diagonal matrix (*Chem. Phys. Lett.* 2000, *319*, 489). These features can be shown to exist if the relevant group of states forms a Hilbert subspace, namely, a group of states that are strongly coupled with each other but are only weakly coupled with all other states. The numerical study is carried out applying the eigenfunctions of the Mathieu equation.

I. Introduction

It is well-known that molecular processes are governed by Coulombic interactions and therefore are accurately treated by applying the relevant Schrödinger equation (SE). The connection between the solutions of the SE and observables such as cross sections or spectroscopic measurements is well established from the early days of quantum theory so that the main theoretical interest is in developing numerical algorithms to solve the SE. The basic theory that enables the quantum mechanical treatment of realistic molecular systems was presented by Born and Oppenheimer (BO) and later completed by Born and Huang.[1,2] Any additional theoretical treatment is essentially considered as overdoing. Indeed, as long as the main attention is given to processes taking place on the ground electronic state, no rigorous additional theoretical input is needed.

The situation changes once electronic excited states have to be included to account for possible electronic transitions. Hints toward potential difficulties follow from the Hellmann−Feynman theorem[3] which points at the possibility that the BO approach may lead to magnitudes, the nonadiabatic coupling terms (NACT), which are singular. The singularities can be considered as mishaps caused by the fact that electronic states become degenerate at certain points in configuration space.[4] In numerous cases it was assumed that singular NACTs are rare and therefore can be ignored. The Hellmann−Feynman theorem was ignored for sometime until, two decades later, Longuet-Higgins and others revealed that singularities may affect the single-valuedness of some of the electronic eigenfunctions.[5−8] However, that these singularities may also affect the single-valuedness of the diabatic potential energy surfaces (PES), which are the ones to be applied in dynamical treatments, was revealed only a few years ago.[9−11]

An example where singularities play an important role is field theory,[12] namely, the theory of elementary particles, where the relevant (singular) vector potentials are connected with the creation and annihilation of elementary particles. We recently pointed out that the appropriate theoretical approach to handle the singularities in molecular physics is similar to approaches within field theory and elementary particles.[13−16]

Because the singular NACTs appear in the nuclear adiabatic BO−SEs, these equations cannot be solved unless the singularities are eliminated rigorously.[17−20] In ref 17, where this issue was discussed for the first time, it was revealed that a necessary condition for being able to eliminate the NACTs from the BO−SE is the fulfillment of a Curl condition (to be discussed in section **II**; see eq 4). In the process of eliminating the NACTs (a process also known as gauge transformation[13]), the adiabatic PESs (see next section) are transformed to become diabatic PESs. This transformation was termed the *adiabatic-to-diabatic transformation* (ADT).[17] It is obvious that the newly formed diabatic potentials, just like the original adiabatic ones, have to be single-valued in the region of interest. It was shown that for them to be single-valued, the matrix $\boldsymbol{\tau}$ that contains the NACTs (see next section) has to be quantized.[9−11] The quantization feature depends on the number of states that are included in the calculation and is probed via a matrix **D** to be introduced in the forthcoming section.

In section **II** brief discussion is given concerning the nonadiabatic matrix $\boldsymbol{\tau}$, the topological matrix **D**, and the extended (non-Aeblian) Curl matrix, **F** (related to the Curl condition). The Mathieu equation and its solutions are briefly discussed in the third section, numerical results for the elements of both the **D** matrix and the **F** matrix are presented in the fourth section, and Discussion and Conclusions are the fifth section.

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II. Theoretical Background

The nonadiabatic coupling matrix element, the NACT, $\boldsymbol{\tau}_{ji}$, is defined as

$$\boldsymbol{\tau}_{ji} = \langle \zeta_j | \nabla \zeta_i \rangle; \quad i > j = \{1,...\} \tag{1}$$

where the grad operator is expressed with respect to (mass-scaled) nuclear coordinates, ν, and the $\zeta_k(e|\nu)$ functions, $k = j,i$, are the eigenfunctions of the electronic Hamiltonian $\mathbf{H}_e(e|\nu)$:

$$(\mathbf{H}_e(e|\nu) - u_k(\nu))\zeta_k(e|\nu) = 0; \quad k = j,i \tag{2}$$

Here, $u_k(\nu)$ is the kth, adiabatic PES, and e stands for the electronic coordinates.

In the present article we concentrate on two subjects:

(a) Having the definition of the $\boldsymbol{\tau}$ matrix (which is a vector of matrixes), we introduce the matrix $\mathbf{F}$, defined as:

$$\mathbf{F}_{qp} = \frac{\partial}{\partial p}\boldsymbol{\tau}_q - \frac{\partial}{\partial q}\boldsymbol{\tau}_p - [\boldsymbol{\tau}_q,\boldsymbol{\tau}_p]; \quad \{p,q;n\} \tag{3}$$

where p and q are (Cartesian) internal coordinates (n stands for their number), $\boldsymbol{\tau}_q$ and $\boldsymbol{\tau}_p$ are, respectively, the q and the p components of $\boldsymbol{\tau}$, and $\mathbf{F}_{qp}$ is recognized as the (p,q) component of the tensorial Yang-Mills field.[21] The set of equations in eq 3 can be written also in a more compact way:

$$\mathbf{F} = Curl\boldsymbol{\tau} - [\boldsymbol{\tau} \times \boldsymbol{\tau}] \tag{3$'$}$$

It was shown that in case of a complete Hilbert space, the components of $\mathbf{F}$ are zero at every point in the configuration space (for details, see Appendix 1 in ref 17). Thus,

$$\boldsymbol{F} = \mathbf{0} \tag{4}$$

In other words, every set of states that forms a Hilbert space yields a zero YM field. As it turns out, eq 4 enables the elimination of the NACTs from the BO−SE or, in others words, guarantees the validity of the ADT. However, because eq 4 is fulfilled for a complete Hilbert space, it just guarantees the elimination of the NACTs for such a case. A few years ago, the validity of eq 4 was extended for groups of states which do not form a complete Hilbert space but are characterized by the feature that, in the region of interest, the states included in such a group are strongly coupled with each other but are only weakly coupled with all the states not included in the group (see Appendix in ref 22). In what follows, we define such a group of states as a Hilbert *subspace*.

Consequently, eq 4 can be used as a means to determine (for a given region) whether one is able to eliminate the NACTs from the BO−SE. This is a mathematical procedure known as *diabatization*.

However, eq 4 is a very inconvenient method to check whether indeed a group of states can be diabatized. It is a complicated expression (from a numerical point of view) because it has to be carried out at every point in the region of interest and it cannot be carried out at singular points, namely, at points where the $\boldsymbol{\tau}$ matrix elements are not analytical functions of the (nuclear) coordinates. Therefore, this condition is never considered in realistic cases.

In what follows, we briefly show how to modify eq 4 to include the singular points.[23] To simplify the presentation, we assume the existence of one singular point so that eq 4 can be "extended" in the following way:

$$\mathbf{F} = \mathbf{g}(q_1,q_2,...,q_n)\prod_{j=1}^{n'}\delta(q_j - q_{j0}) \tag{4$'$}$$

Here the matrix $\mathbf{g}$, like $\mathbf{F}$, is a tensorial matrix, the coordinates $(q_{10},q_{20},...,q_{n'0})$ are the position coordinates of the singularity (also known as the point of the conical intersection (CI)[24,25]), and $\delta(q_j - q_{j0})$ is the corresponding Dirac-δ function. It is important to emphasize that in case the coordinates q_j, $j = 1,..,n$ are not Cartesian coordinates, n' is not necessarily equal to n. In fact, in most cases $n' < n$. Equation 4$'$ takes an interesting form in the case of a two-state system defined in terms of two (polar) coordinates (q,ϕ), namely:

$$\mathbf{F} = \epsilon\frac{1}{q}\pi f(\phi)\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\delta(q) \tag{5}$$

where ϵ is the unit vector in the direction of $\mathbf{F}$ and $f(\phi)$ was found to be equal to the angular component of $\boldsymbol{\tau}_{\mathbf{12}}(q,\phi)$, namely, to $\boldsymbol{\tau}_{\phi\mathbf{12}}(q,\phi)$.[23a]

(b) The second subject is related to a feature of $\boldsymbol{\tau}$ that, under certain conditions, satisfies quantization conditions. We start by saying that it can be shown that for a group of states that spans a Hilbert space, the $\boldsymbol{\tau}$ matrix is quantized, and that the following matrix, $\mathbf{D}(\Gamma)$, defined as[9−11]

$$\mathbf{D}(\Gamma) = \wp \exp(-\oint_\Gamma \mathbf{ds}\cdot\boldsymbol{\tau}) \tag{6}$$

is a diagonal unitary matrix for any contour, Γ, defined in the multidimensional region of configuration space (because the integration is done along a contour, we frequently termed this integration as a *line integral*).[19−20] This implies that its numbers along the diagonal are of norm 1, which in the case of real eigenfunctions are ±1. Here, $\mathbf{ds}$ is a differential vector along Γ, the dot represents a scalar product, and the symbol $\wp$ is a path-ordering operator. Again, as in the previous case, it can be shown that a group of states which does not form a Hilbert space but is isolated from "the rest of the world" in a given region in configuration space will approximately fulfill the relevant quantization condition. Consequently, the extent to which the $\mathbf{D}$ matrix is diagonalized is another way of finding out to what extent this group of states forms a Hilbert subspace. As a final comment on this subject, we mention the fact that the number of −1s along the diagonal, designated as K and defined as the topological number, is contour dependent, i.e., $K = K(\Gamma)$, and yields information regarding the various CIs surrounded by Γ.[26] This number was shown to be always even, which implies that the $\mathbf{D}$ matrix is not only unitary but also that its determinant is equal to 1. In other words, $\mathbf{D}$ belongs to the SO(N) symmetry group (where N is the dimension of the Hilbert subspace).

To clarify the subject of quantization, we consider a case of a two-state system. Because the matrix $\mathbf{D}$ is a unitary matrix, it will be written as

$$\mathbf{D} = \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix} \tag{7}$$

where it can be shown that α is given by the following line integral:[17]

$$\alpha = \oint_\Gamma \boldsymbol{\tau}_{12}(s)\cdot\mathbf{ds} = k\pi \tag{8}$$

Here, $\boldsymbol{\tau}_{12}$ is the only nonzero term of the 2 × 2 $\boldsymbol{\tau}$ matrix and k

is some number. It was shown that the condition for the two states to form a Hilbert subspace is that k is an integer (or zero).[9−11] This requirement is reminiscent of the ordinary Bohr–Sommerfeld quantization law for the angular momentum[27] (which in this particular case is the matrix element, $\boldsymbol{\tau}_{12}$). Returning to the **D** matrix in eq 7, it is seen that for it to become the topological matrix as explained above, K is allowed to have two values, $K = 0$ or 2, but never $K = 1$.[26]

Thus far we discussed two mathematical items: the **F** matrix and the **D** matrix. Having an **F** matrix which is zero at every point (where it is not singular) in a given region guarantees the diabatization in that region, and having a diagonal **D** matrix for every contour in that region guarantees single-valued diabatization. This can be said in a more mathematical way: The fulfillment of the Curl condition (eq 4) is a necessary and sufficient condition for diabatization. The quantization is a necessary condition for single-valued diabatization. We already mentioned that because of numerical “inconveniences”, the Curl condition is not likely to be considered in realistic cases. However, probing the quantization condition is a much friendlier act and can be easily carried out in realistic molecular studies (as we and others frequently do).

The fulfillment of the Curl equation and the quantization condition are the subjects of the present article. In general, if one of the two conditions is satisfied, we expect the other to be satisfied as well. (This statement is not necessarily correct in case of singularities.) In the following study we consider a model based on the eigenfunctions of the Mathieu equation,[28−31] which not only yields details related to the meaning of the above two features of the $\boldsymbol{\tau}$ matrix but also explains the interrelation between the two. Recalling that N is (also) the dimension of the $\boldsymbol{\tau}$ matrix, we discuss two aspects: (1) how, for a given value of N, increasing the region Λ harms the fulfillment of both features and (2) to what extent increasing N for a given region Λ improves the fulfillment of both features.

III. The Mathieu Equation: A Summary of the Two-State System

The electronic SE to be considered is written for one electronic (circular) coordinate, θ, and is expressed in terms of two nuclear polar coordinates, ϕ and q:[28−31]

$$\left(-\frac{1}{2}E_{\mathrm{el}}\frac{\partial^2}{\partial\theta^2} - G(q,\phi)\cos(2\theta-\phi) - u_j(q,\phi)\right)\zeta_j(\theta|q,\phi) = 0 \tag{9}$$

Here E_{el} is a characteristic electronic quantity, $G(q,\phi)$ is the nuclear-electronic interaction coefficient, and $u_j(q,\phi)$ and $\zeta_j(\theta|q,\phi)$ are the jth eigenvalue and eigenfunction, respectively, which parametrically depend on the nuclear coordinates. Equation 9 is recognized as the well-known Mathieu equation. For the present study, we assumed $G(q,\phi)$ to be independent of ϕ and linearly dependent on q, namely, equal to kq (here, k is a given constant not related to k in eq 8). This choice of the interaction term has several numerical advantages: (1) It forms singular NACTs (or degenerate eigenvalues) at $q = 0$, only. Therefore, in what follows, the value of q yields the distance of a point in configuration space from the position of the singularity point. (2) The eigenvalues of eq 9 depend on q but are independent of ϕ, and the eigenfunctions of eq 9 are such that the resulting NACTs are also ϕ independent (but depend on q). This fact makes our whole study ϕ independent.

To simplify somewhat the forthcoming treatment, we introduce a new parameter, x, defined as:

$$x = q(k/E_{\mathrm{el}}) \tag{10}$$

Thus, the parameter x replaces q as the radial coordinate. As was mentioned earlier, the size of the Λ region (in configuration space) plays an important role in our study. The present notation q is the (nuclear) coordinate directly associated with the size of the Λ region. Thus, the larger the q, the larger the Λ region. The same applies now for x (which replaces q), so that the larger *the* x, the larger the Λ region. The numerical study concentrates on the dependence of various functions on x.

Equation 9 is based on two nuclear coordinates (q,ϕ), and therefore $\boldsymbol{\tau}$ has two components, $\boldsymbol{\tau}_q$ and $\boldsymbol{\tau}_\phi$ (even with the simplified G function). It was shown that in the case of $N = 2$ and small enough x values, the corresponding two matrix elements $\boldsymbol{\tau}_{q12}$ and $\boldsymbol{\tau}_{\phi 12}$ become:[29]

$$\boldsymbol{\tau}_{\phi 12}(x,\phi) = -\frac{1}{2q}\left(1 + \frac{x^2}{32}\right); \quad \boldsymbol{\tau}_{q12}(x,\phi) = 0 \tag{11}$$

(in fact, $\boldsymbol{\tau}_{q12}$ is zero for any x value). Next, by choosing the contour Γ to be a circle centered at $x = 0$, it was shown that the topological angle α (see eq 8) takes the form:

$$\alpha = q\int_0^{2\pi}\boldsymbol{\tau}_{\phi 12}\,\mathrm{d}\phi = -\pi\left(1 + \frac{x^2}{32}\right) \tag{12}$$

Similarly, it can be shown that the only nonzero element of the **F** tensor, i.e., $F_{q\phi 12}$, is:

$$F_{q\phi 12} = \pi\frac{1}{q}f(\phi)\delta(q) - \frac{x^2}{32q^2} \tag{13}$$

where the first term on the right-hand side is due to eq 5 and the second is the result of the relevant two-state (two-coordinate) Curl expression when applied to the two components of $\boldsymbol{\tau}$, as given in eq 11:

$$\frac{1}{q}\left(\frac{\partial(q\boldsymbol{\tau}_{\phi 12})}{\partial q} - \frac{\partial\boldsymbol{\tau}_{q12}}{\partial\phi}\right) = -\frac{x^2}{32q^2}$$

Recalling eq 10, the expression in eq 13 becomes:

$$F_{q\phi 12} = \pi\frac{1}{q}f(\phi)\delta(q) - \frac{k^2}{32{E_{\mathrm{el}}}^2} \tag{13$'$}$$

Thus, at every point that $q > 0$, the vector $F_{q\phi 12}$ is a constant and therefore is never equal to zero (unless $E_{\mathrm{el}} \rightarrow \infty$). This fact implies that the two lowest states of the Mathieu equation can never form a Hilbert subspace.

Equation 13′ was derived with the assumptions that $\boldsymbol{\tau}_{12}$ does not have a z-component and that $\boldsymbol{\tau}_{\phi 12}$ is independent of z. As a result of that, $F_{q\phi 12}$ is a vector perpendicular to the (q,ϕ) plane.

As a final point in this subsection, we mention the fact that the two expressions, presented in eqs 11 and 13 (or eq 13′) have to fulfill Stokes’ theorem,[32a] which states:

$$\oint_\Gamma \boldsymbol{\tau}_{12}(s)\cdot\mathbf{ds} = \oint\!\!\oint \mathrm{d}\sigma\cdot Curl(\boldsymbol{\tau}_{12}(\mathrm{s})) \tag{14}$$

Assuming the surface, σ, to be a circular area of a given radius, q, surrounding the point $q = 0$ and employing eqs 11 and 13′, it is seen that eq 14 is fulfilled if and only if:

$$\int_0^{2\pi} d\phi f(\phi) = 1 \tag{15}$$

In a previous publication,[23a] this condition was termed as the *quantization of the pseudo-electromagnetic field* along the seam (reminiscent of Dirac's quantization of the magnetic monopole[32b]). It is interesting that the condition in eq 15 was derived in ref 23a assuming the two states form a Hilbert subspace. Here it is shown to be fulfilled even in that case where the two states do not form a Hilbert subspace.

IV. The Mathieu Equation: A Numerical Study of the Multistate System

The numerical study is divided into two parts. (a) In the first part, we study the interrelation between the size of configuration space expressed in terms of x and the size of the Hilbert subspace expressed in terms of N when applied to the topological matrix **D**. In other words, we intend to show that for a fixed value of x, increasing N causes the unitary **D** matrix to become more and more diagonal, which is an indication that the group of states converges toward becoming a Hilbert subspace. The opposite is expected when x is increased for a fixed N value. In such a case, the **D** matrix becomes less diagonal, implying that the relevant group of states distances itself from being a Hilbert subspace. (b) In the second part, we study the interrelation between the size of configuration space (expressed, as before, in terms of x) and the behavior of the Yang-Mills field **F**. We intend to show that for a fixed x value, increasing N causes more and more elements of the **F** matrix elements (in their absolute values) to decay to zero. In the previous section, we showed that in case of $N = 2$ the (1,2) element of the 2×2 **F** matrix is a constant and therefore never becomes zero. However, in a recent publication it was shown, analytically, that increasing N from 2 to 4 causes the (1,2) element of the 4×4 **F** matrix element to approach zero for small enough x values.[30] In fact, it was this observation which motivated us to extend our study to much larger groups of states.

To solve the Mathieu equation, we expand the $\zeta_j(\theta|q,\phi)$ eigenfunctions in the Fourier series. For our purposes and in the notation of ref 31a, we select the following two families of solutions:

$$\begin{aligned} ce_{2n+1}(z,-x) &= \sum_{m=0}^{\infty} A_{2m+1}^{2n+1}(-x)\cos(2m+1)z \\ se_{2n+1}(z,-x) &= \sum_{m=0}^{\infty} B_{2m+1}^{2n+1}(-x)\sin(2m+1)z \end{aligned} \tag{16}$$

where z is given as:

$$z = \theta - \frac{\phi}{2} \tag{17}$$

Here, the cosine series stands for the $\zeta_j(\theta|q,\phi)$ functions with odd j values and the sine function for those with the even j values.

It is well-known that the geometrical series, as presented in eqs 16 and 17, does not converge at points close to the real axis. This feature may affect the rate of convergence for points on the real axis. Because of that, the convergence in each case was treated with care. In this respect it is important to mention that we had to include 200 terms in each case to guarantee the required convergence. This slow convergence enforced numerically, rather than analytically, calculated coefficients to avoid inaccuracies.

IV.1. The Topological D Matrix and the Size of Configuration Space. The expression to calculate the **D** matrix is given in eq 6, but because in all our forthcoming numerical treatments we assume the contour Γ to be a circle centered at the point of the *CI*, eq 6 simplifies in the following way:

$$\mathbf{D}(q) = \wp \exp\left(-q\int_0^{2\pi} d\phi\, \boldsymbol{\tau}_\phi(q,\phi)\right) \tag{18}$$

where $\boldsymbol{\tau}_\phi(q,\phi)$ is the ϕ component of $\boldsymbol{\tau}$:

$$\boldsymbol{\tau}_{\phi jk} = \frac{1}{q}\left\langle \zeta_j \middle| \frac{\partial}{\partial\phi}\zeta_k \right\rangle \tag{19}$$

and we recall that in all our applications x replaces q. In fact, the calculation of the **D** matrix becomes even simpler for the present model because none of the $\boldsymbol{\tau}(q,\phi)$ matrix elements is ϕ dependent, and therefore the integration in eq 18 can be done immediately:

$$\mathbf{D}(x) = \exp(-2\pi q \boldsymbol{\tau}_\phi(q)) \tag{18′}$$

The study of the **D** dependence on x and N, i.e., $\mathbf{D}(N,x)$, is presented in terms of the diagonal elements of the **D** matrix, namely, $\mathbf{D}_{jj}$ $\{j = 1,N\}$. In the converged case (that is, the case for which the group of N states forms a Hilbert subspace in the circular region defined by x) we expect these diagonal elements to be ±1, and the rest (the off-diagonal ones) to become zero. For our particular model the diagonal elements are all expected to become -1 when N is an even number but for the case where N is an odd number, one of the diagonals is $+1$ and the rest are, as before, -1. In what follows, we consider the even case only. Therefore, for a given N and x, a significant deviation of a diagonal term from -1 implies that within the region defined by x the considered N states *do not* form a Hilbert subspace.

In Figure 1, the diagonal matrix elements $\mathbf{D}_{jj}(N,x)$ are presented as a function of x for five different values of N: 2, 4, 6, 8, and 12. In Figure 1a, $\mathbf{D}_{22}$ is presented as a function of x calculated for $N = 2$; in Figure 1b, $\mathbf{D}_{22}$ and $\mathbf{D}_{44}$ are presented as calculated for $N = 4$; in Figure 1c, $\mathbf{D}_{22}$, $\mathbf{D}_{44}$, and $\mathbf{D}_{66}$ are presented as calculated for $N = 6$; in Figure 1d, $\mathbf{D}_{44}$, $\mathbf{D}_{66}$, and $\mathbf{D}_{88}$ are presented as calculated for $N = 8$; and in Figure 1e, $\mathbf{D}_{88}$ and $\mathbf{D}_{1212}$ are presented as calculated for $N = 12$. We noticed that all curves related to the various j and N values start with the value $\mathbf{D}_{jj}(N,x \approx 0) = -1.0$ and then increase (that is, approach zero or even $+1$) in different paces as x increases. However, the rate of increase becomes slower the larger is the N value. For instance, two states (i.e., $N = 2$) form a Hilbert subspace only as long as $x \le 1.0$ (see Figure 1a), but eight states (i.e., $N = 8$) form a Hilbert subspace, which holds as long as $x \le 6.0$ (see Figure 1d). Thus, for a given x, the larger the N the closer the set of states comes to being a Hilbert subspace. These results also imply that the larger the region in the configuration space, the larger the size of the set of states has to be to become a Hilbert subspace. In this respect, we mention that the relevant measure for a region in the configuration space is the area (and not the radius). Therefore, the previous eight lower states of the Mathieu equation are able to form a Hilbert subspace in a region which is about 40 times larger than a region in which two states can form a Hilbert subspace.

Another observation is related to the rate of increase of $\mathbf{D}_{jj}(N,x)$, for a fixed N value but for different j values. We noticed

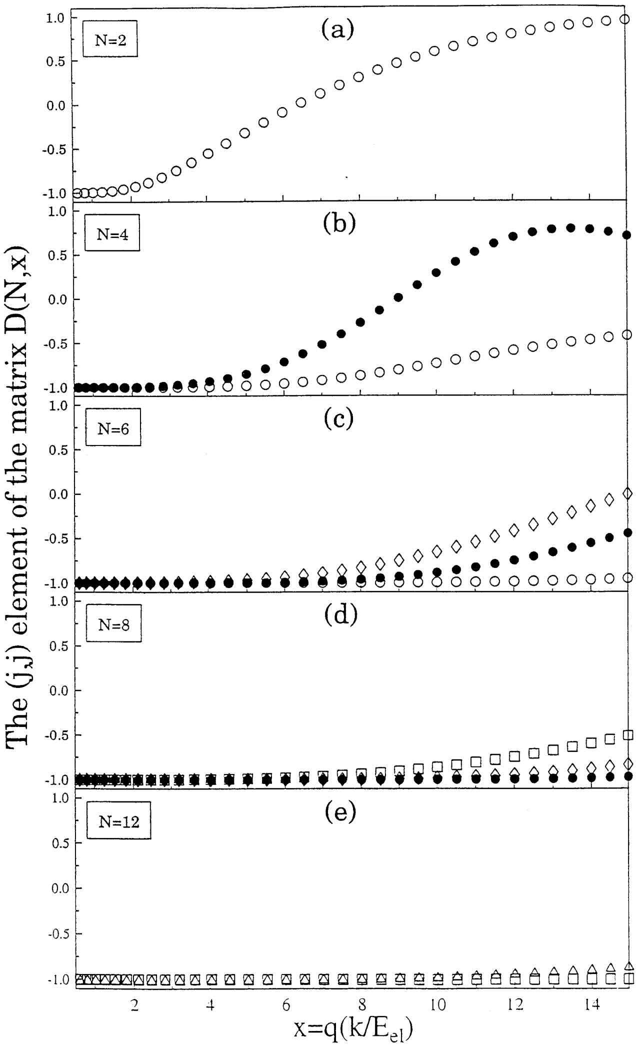

Figure 1. Diagonal matrix elements $\mathbf{D}_{jj}(N,x)$, calculated as a function of x for various N values. (a) Results for $\mathbf{D}_{22}(N = 2,x)$; (b) results for $\mathbf{D}_{jj}(N = 4,x)$, $j = 2,4$; (c) results for $\mathbf{D}_{jj}(N = 6,x)$, $j = 2,4,6$; (d) results for $\mathbf{D}_{jj}(N = 8,x)$, $j = 4,6,8$; (e) results for $\mathbf{D}_{jj}(N = 12,x)$, $j = 8,12$. Empty circles $j = 2$; full circles $j = 4$; diamonds $j = 6$; squares $j = 8$; triangles $j = 12$.

that the larger the j value, the larger the rate of increase. Thus, for instance, in Figure 1c the sixth diagonal element $\mathbf{D}_{66}(N = 6,x)$ increases faster as compared to the diagonal elements $\mathbf{D}_{22}(N = 6,x)$ and $\mathbf{D}_{44}(N = 6,x)$ calculated for the same N value (i.e., $N = 6$). In fact in all cases, the last diagonal element along the diagonal, namely $\mathbf{D}_{NN}(N,x)$, shows as x increases, the largest deviations from -1.0. It is important to mention that the $\mathbf{D}_{jj}(N,x)$ matrix element is related to the jth highest adiabatic state and that $\mathbf{D}_{NN}(N,x)$, therefore, is related to the *highest* adiabatic state of the considered set of states.

Since for each N the last element (related to the highest state) shows the largest deviation from -1.0, we present in Figure 2 the $\mathbf{D}_{NN}(N,x)$ matrix elements as a *function* of N for different x values. We noticed that the various $\mathbf{D}_{NN}(N,x)$ curves decay asymptotically toward the value -1 as N increases, but the rate of decay becomes slower as x becomes larger (i.e., the larger is the region in configuration space). Thus, it is noticed that at $x = 4$, for example, the rate of decay is very fast (all diagonal elements for $N \geq 4$ are already -1.0), but for $x = 16$ the rate of decay is so slow that we reach the value of -1.0 only when $N \geq 16$.

In summary, we show here that the more the region in the configuration space is extended, the larger the size of a set of states is required to be to be able to become a Hilbert subspace. We already had hints for this tendency in our studies related to real molecular systems, namely, the C_2H molecule[33] and the H + H_2 system.[34] However, the important message of this study is that the convergence to the required size of the function space is relatively fast. This is the case because the region increases as x^2 and not as x. Indeed, assuming that for a given region the required size of a Hilbert subspace is $N = 2$, then the required size for a region almost 2 orders of magnitude larger is obtained for $\sim N = 10$.

IV.2. The Yang-Mills F Matrix and the Size of Configuration Space. The Yang-Mills field, described in terms of the **F** matrix and presented in eqs 3 and 3′, is made up of two expressions:

$$\mathbf{F} = \mathbf{H} - \mathbf{T} \tag{20}$$

where

$$\mathbf{H} = curl\boldsymbol{\tau} \quad \text{and} \quad \mathbf{T} = \boldsymbol{\tau} \times \boldsymbol{\tau} \tag{21}$$

The **H** matrix elements, expressed in terms of polar coordinates, are given in the form:

$$\mathbf{H}_{jk} = \frac{1}{q}\left\{\frac{\partial}{\partial q}\left\langle \zeta_j \middle| \frac{\partial}{\partial \phi}\zeta_k \right\rangle - \frac{\partial}{\partial \phi}\left\langle \zeta_j \middle| \frac{\partial}{\partial q}\zeta_k \right\rangle\right\}$$

or:

$$\mathbf{H} = \frac{1}{q}\left(\frac{\partial \tilde{\boldsymbol{\tau}}_\phi}{\partial q} - \frac{\partial \boldsymbol{\tau}_q}{\partial \phi}\right) \tag{22}$$

where $\tilde{\tau}_\phi$ is defined as:

$$\tilde{\boldsymbol{\tau}}_{\phi jk} = \left\langle \zeta_j \middle| \frac{\partial \zeta_k}{\partial \phi} \right\rangle \Rightarrow \tilde{\boldsymbol{\tau}}_\phi = q\boldsymbol{\tau}_\phi \tag{23}$$

and the **T** matrix follows from the expression:

$$\mathbf{T} = \frac{1}{q}(\tilde{\boldsymbol{\tau}}_\phi \boldsymbol{\tau}_q - \boldsymbol{\tau}_q \tilde{\boldsymbol{\tau}}_\phi) \tag{24}$$

Here $\boldsymbol{\tau}_q(q,\phi)$ is defined in a similar way as $\tilde{\boldsymbol{\tau}}_\phi$ but with respect to q. Because all the expressions in eqs 22 and 24 are multiplied by $(1/q)$, the numerical study will be performed for the same expressions but ignoring $(1/q)$.

The dependence of the various matrixes, $\mathbf{Z} = \mathbf{H}, \mathbf{T}, \mathbf{F}$, on x and N is presented in Figures 3−5 in terms of several off-diagonal elements of the kind $\mathbf{Z}_{jk}(N,q)$ where $j \neq k$.

To grasp the importance of the two matrixes **H** and **T** that make up for **F**, we show in Figure 3, a and b, several off-diagonal elements of these matrixes as a function of N calculated at $x = 10$. It is well noticed that most of these elements are relatively large (>0.1) and therefore differ from zero for all practical purposes.

The situation changes when considering the **F** matrix elements. In Figure 4, the off-diagonal elements of the **F** matrix are presented (note the logarithmic scales along both axes): in Figure 4a, results are shown for $x = 1$ and in Figure 4b, for $x = 10$ (the same x value as applied in Figure 3). It is well noticed that the various numerical values of this matrix are by far much smaller than those of the corresponding elements of the **H** and the **T** matrixes, and they become smaller and smaller as N increases. The interesting aspect of this study is the very fast decrease of most of these matrix elements with N and the

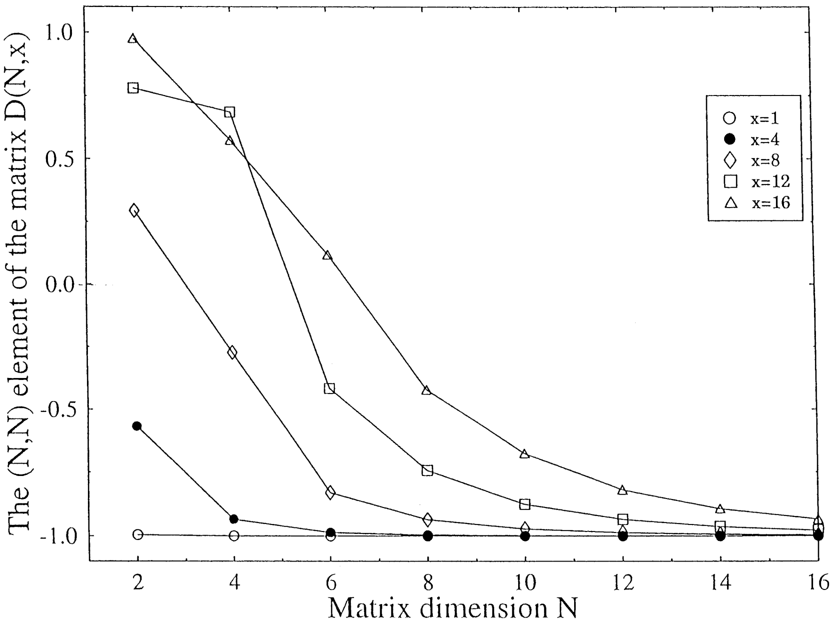

Figure 2. Highest diagonal matrix elements $\mathbf{D}_{NN}(N,x)$, calculated as a function of N for various x values. Empty circles $x = 1.0$; full circles $x = 4.0$; diamonds $x = 8.0$; squares $x = 12.0$; triangles $x = 16.0$.

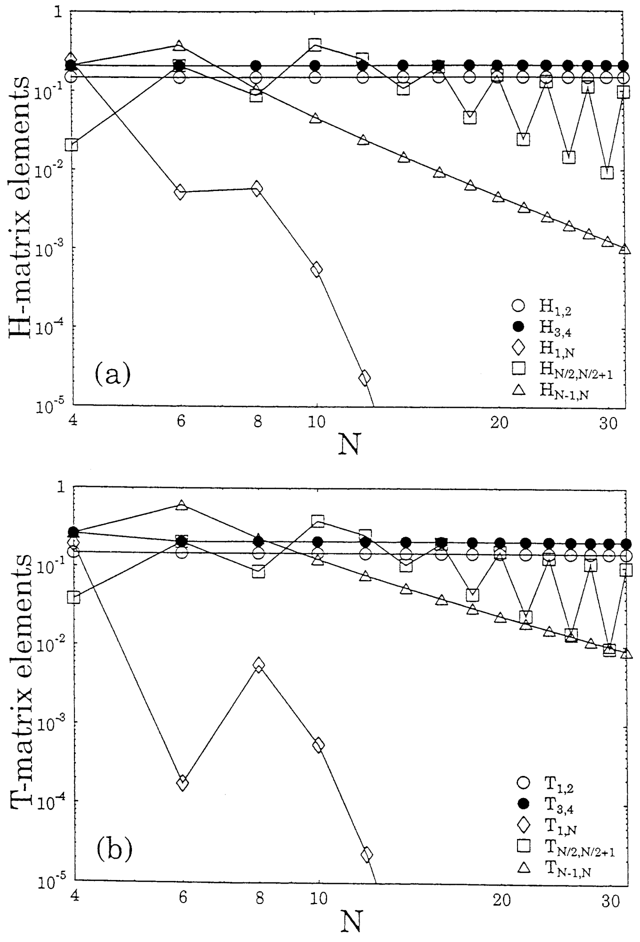

Figure 3. Off-diagonal matrix elements $\mathbf{Z}_{jk}(N,x)$; $\mathbf{Z} = \mathbf{H},\mathbf{T}$, calculated as a function of N (note the logarithmic scale) for $x = 8.0$. (a) $\mathbf{Z} = \mathbf{H}$; (b) $\mathbf{Z} = \mathbf{T}$. Empty circles (1,2) off-diagonal matrix element; full circles (3,4) off-diagonal matrix element; diamonds (1,N) off-diagonal matrix element; squares (N/2,N/2 + 1) off-diagonal matrix element; triangles ($N-1$,N) off-diagonal matrix element.

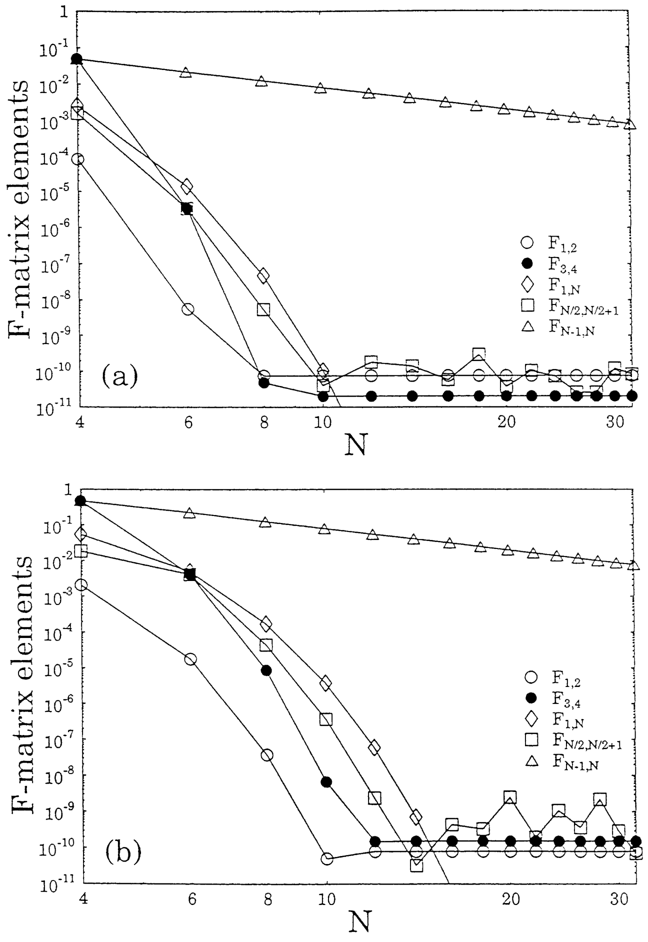

Figure 4. Off-diagonal matrix elements $\mathbf{F}_{jk}(N,x)$ calculated as a function of N for two x values. (a) $x = 1.0$; (b) $x = 10.0$. Note the logarithmic scales along both the abscissa and the ordinate.

fact that they decrease to values as small as 10^{-10} (recalling the large values of the **H** and **T** matrix elements). The only exception is the *last* off-diagonal element $\mathbf{F}_{N-1N}(x)$, which decreases with N but at a very slow rate.

Comparing the results for $x = 1$ and $x = 10$, we noticed that in both cases the various values decrease to $\sim 10^{-10}$, but in the

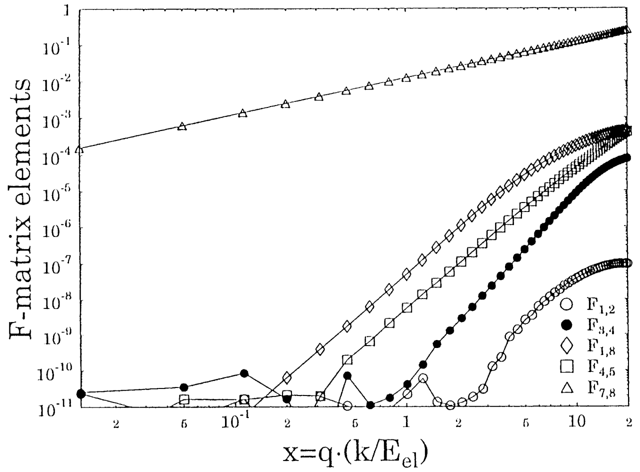

Figure 5. Off-diagonal matrix elements $\mathbf{F}_{jk}(N,x)$ calculated as a function of x for $N = 8$. Note the logarithmic scales along both the abscissa and the ordinate.

case of $x = 1$, the rate of decrease is faster. The reason is that it is easier for a given group of states to become a Hilbert subspace the smaller is the x value, namely, the smaller is the region surrounding the CIs.

This feature is even better seen in Figure 5 where the same **F** matrix elements are presented but as a function of x calculated for a fixed value of N (=8). The results in this figure support what is claimed in the previous paragraph, that is, that these matrix elements tend to increase as a function of x (when calculated for a fixed N value).

V. Conclusions

In this article, we considered the nonadiabatic coupling matrix $\boldsymbol{\tau}$ which, under certain conditions, is characterized by two interesting features: (1) its components fulfill the Curl condition (see eqs 2−4), and (2) it is quantized in the sense that the **D** matrix presented in eq 6 is a unitary diagonal matrix. These features can be shown to exist if the relevant group of states forms a Hilbert space. In case this group does not form a Hilbert space, the fulfillment of these relations depends on the various CIs in the configuration space (namely, on the positions and the spatial distribution of their NACTs) and the size of the region in the configuration space that surrounds them.

It has been known for quite some time that a region surrounding a CI can always be made small enough so that the 2 × 2 **D** matrix becomes a unitary diagonal matrix, which implies that the two relevant states form a Hilbert subspace in this (reduced) region.[33−38] (In fact, we recently revealed[34] that even this statement is not always true.) From studies that were extended to three states,[33,34] we learned that in a given region where two states are not enough for forming a Hilbert subspace of two states we can form a Hilbert subspace of three states. In other words, there are regions where the 2 × 2 **D** matrix may not be a unitary diagonal matrix, but the corresponding 3 × 3 is such a matrix. Thus, it seems that the larger the region, the more states are required to make the relevant **D** matrix diagonal (and the **F** matrix a zero matrix). This article is devoted to this subject.

The idea was to consider for this purpose a simple model for which the "electronic" eigenstates can be easily produced; thus, the above-mentioned relations can be studied quantitatively. On the basis of our previous experience, we chose for this task the Mathieu equation. This equation is characterized by one electronic coordinate, θ, and two nuclear coordinates (q,ϕ). The term that couples the electronic and the nuclear motions and depends on all three of them is written in the present application as a product $[G(q)\cos(2\theta-\phi)]$, which yields NACTs that are independent of the polar coordinate ϕ, a fact which simplifies significantly the numerical treatment.

The numerical results support the basic theoretical expectations: for a given, arbitrary size of a region in configuration space, we can always find (usually) a final set of states that forms a Hilbert subspace. In addition, we also revealed two practical findings: (1) It is true that the larger the region, the more states are required for the group to become a Hilbert subspace, but we found that the convergence toward a Hilbert subspace is relatively fast (this fact, however, depends on the distribution of the various CIs). (2) We found that for both matrices, i.e., the **D** matrix and the **F** matrix, the elements that relate to the higher states converge more slowly than those related to the lower states. In other words, it is always the Nth diagonal term of the **D** matrix that is the last one to reach ±1, and it is always the $(N,N-1)$ off-diagonal term of the **F** matrix that is last to become close to zero.

In this article we analyzed the matrices **F** and **D** by considering a model. As a final statement, we reiterate the importance of these two matrices: The diabatization is guaranteed by the Curl condition (eq 4), which implies that **F** has to be zero at every point in the region of interest but single-valued diabatization is guaranteed only by the quantization of the $\boldsymbol{\tau}$ matrix as expressed in terms of the **D** matrix in that same region.

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