Curl Condition for a Four-State Born−Oppenheimer System Employing the Mathieu Equation

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Received: April 6, 2008; Revised Manuscript Received: July 14, 2008

When a group of four states forms a subspace of the Hilbert space, i.e., appears to be strongly coupled with each other but very weakly interacts with all other states of the entire space, it is possible to express the nonadiabatic coupling (NAC) elements either in terms of s or in terms of electronic basis function angles, namely, mixing angles presumably representing the same sub-Hilbert space. We demonstrate that those explicit forms of the NAC terms satisfy the curl conditions—the necessary requirements to ensure the adiabatic−diabatic transformation in order to remove the NAC terms (could be often singular also at specific point(s) or along a seam in the configuration space) in the adiabatic representation of nuclear SE and to obtain the diabatic one with smooth functional form of coupling terms among the electronic states. In order to formulate extended Born−Oppenheimer (EBO) equations [*J. Chem. Phys.* 2006, *124*, 074101] for a group of four states, we show that there should exist a coordinate independent ratio of the gradients for each pair of ADT/mixing angles leading to zero curls and, thereafter, provide a brief discussion on its analytical validity. As a numerical justification, we consider the first four eigenfunctions of the Mathieu equation to demonstrate the interesting features of nonadiabatic coupling (NAC) elements, namely, the validity of curl conditions and the nature of curl equations around CIs.

I. Introduction

Since the molecular processes are governed by Coulombic interactions, it is a well-established fact that the relevant Schroedinger equation (SE) can treat those processes accurately and provide the solutions as the observable such as reactive/nonreactive cross sections or spectroscopic quantities leading to the main theoretical interest in developing numerical algorithm to solve the SE. The fundamental theoretical development by Born−Oppenheimer[1] and thereafter Born−Huang[2] help us to pursue the quantum mechanical treatment of realistic molecular system as long as the process takes place exclusively on the ground electronic state. Indeed, the situation changes almost immediately when the excited electronic states affect the ground due the presence of so-called "nonadiabatic coupling", i.e., the coupling among the electronic states and, thereby, further rigorous theoretical treatment is required. When the electronic excitations are included in the molecular processes, the Hellmann−Feynman theorem[3] points out the existence of NAC terms with singularity any where in the configuration space. These singularities arise due to the fact that electronic states become degenerate at certain points or along a line (seam) in the configuration space.[4] At this junction, we may mention that singularities dictate a crucial role in the theory of elementary particles[5] leading to vector potentials connected with the creation and annihilation of elementary particles. It may be interesting to note that the required theoretical approach to handle the singularities of NAC terms in molecular physics[6,7] is similar to that of used in field theory and elementary particles.

For a quite longer period, the presence of singularity in nonadiabatic coupling terms[7] had been overlooked until Longuet-Higgins[8,9] and others[10,11] demonstrated that such singularity destroy the single-valuedness of electronic wave function in many molecular systems and therefore, it is not worth pursuing dynamical calculations for the nuclei on the multivalued diabatic potential energy surfaces (PES). Herzberg and Longuet-Higgins (HLH)[12] corrected this deficiency by multiplying a complex phase factor, known as Longuet-Higgins' phase, leading to a single-valued wave function. This "modification" of the electronic eigenfunctions is not an outcome of any first principles based theory but imposed in an ad hoc manner. In an alternative manner, Mead and Truhlar[13] introduced a vector potential in the nuclear Hamiltonian to generalize the Born−Oppenheimer (BO) equation, which is a reminiscent of the complex phase factor treatment of Herzberg and Longuet-Higgins. With these theoretical predictions, Kuppermann et al.[14] and many others[15] calculated integral and differential scattering cross sections of the H_3 isotopic system; Adhikari and Billing[16] evaluated the transition probabilities of a two -arrangement channel pseudo-Jahn−Teller model[17] and clearly demonstrate the effect of Longuet-Higgins' phase, also known as geometric phase (GP), on reactive/nonreactive transition probabilities with a demand to explore the origin of GP from first principles.

The development of any first principles based theory by including BO treatment considers the fact that slow-moving nuclei are distinguishable from fast-moving electrons in molecular systems and intends to impose the BO approximation by neglecting the effect of upper electronic state(s) on the lower with the implication that the nonadiabatic coupling (NAC) elements are negligibly small. Such approximation has been

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10.1021/jp8029709 CCC: $40.75
Published on Web 09/11/2008

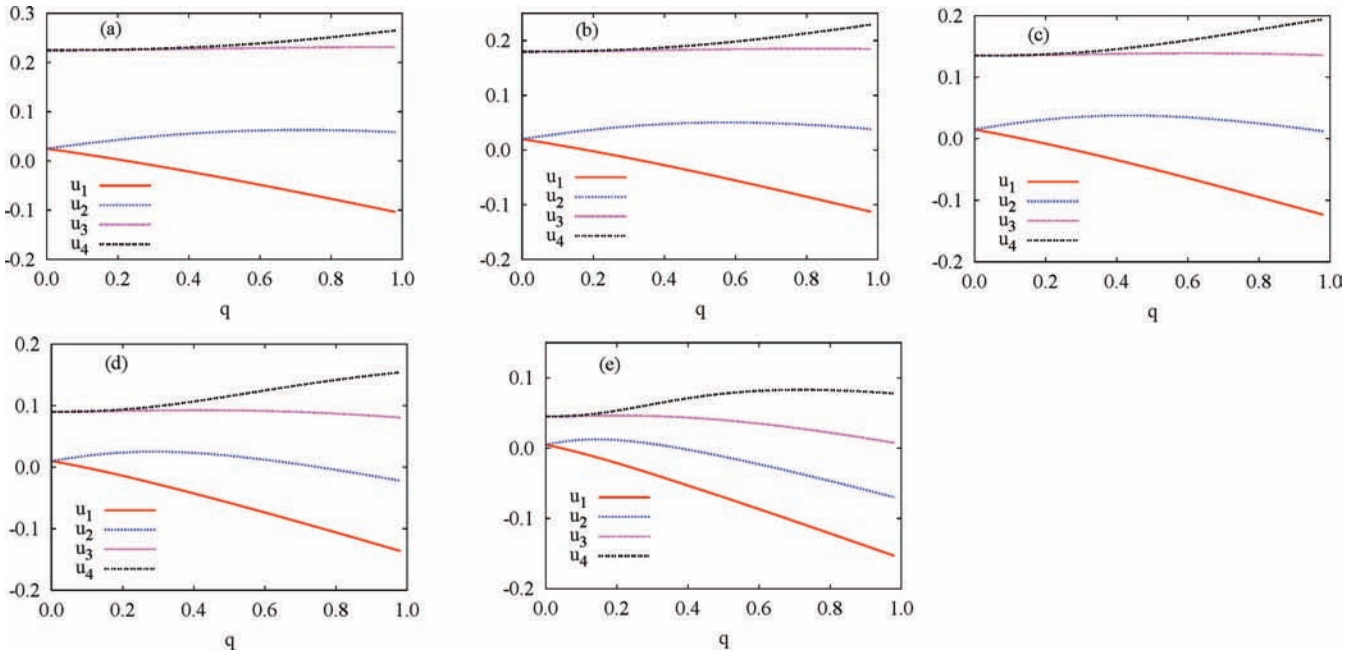

Figure 1. First four adiabatic potentials where $k = 0.2$ and (a) $E_{el} = 0.05$, (b) $E_{el} = 0.04$, (c) $E_{el} = 0.03$, (d) $E_{el} = 0.02$, and (e) $E_{el} = 0.01$.

assumed to be independent of the eigenspectrum of the system and, thereby, the ordinary BO equations are being frequently used for calculations even for systems with large NAC terms. Even if the components of the total wave function on the upper electronic state(s) are negligibly small at enough low energies, the products between the singularly large NAC terms and the amplitudes of the excited state(s) wave functions could be finite in magnitude leading to the breakdown of BO approximation. Therefore, one needs to pursue theoretical development in such a way that the beyond Born−Oppenheimer effects are included in the dynamical calculations. While developing such theories, Mead and Truhlar (MT)[18] mentioned that the consideration of the entire Hilbert space ($n = N$) to incorporate the couplings among the electronic states is indeed a trivial approach to demonstrate. In the same article,[18] they explore the curl of the nonadiabatic coupling for any realistic description of the electronic wave function. A general vector field can be decomposed into longitudinal and transverse components, where the longitudinal component can be expressed as a derivative of a scalar and the transverse component by the curl of a vector. The ADT can at best remove the longitudinal component of the derivative coupling. The longitudinal and transverse components are referred to as the removable and nonremovable couplings.

The general characteristics of the removable and nonremovable components have been discussed by Kendrick, Mead, and Truhlar.[19] When the energy eigenvalues are well separated, the removable and nonremovable couplings will be of the same order. At sufficiently low energies (well below the energy of the upper state), these coupling can be ignored in dynamics calculations due to the $1/M$ prefactor. At the close proximity of a degeneracy, only the removable coupling is singular and according to the degenerate perturbation theory, the nonremovable couplings are insignificant.[20] It means that the ADT angle can be obtained by integrating the derivative coupling at and around the same region. On the contrary, away from the conical intersection, the contribution from the nonremovable coupling appears in path-dependent integrals for the ADT angles and, therefore, closed line integrals of the derivative coupling[21] will not be multiples of π. The inclusion of more electronic states can reduce this problem;[22] however, this greatly increases the computational cost of ab initio quantum chemistry and dynamical calculations.

One can separate the removable and nonremovable couplings by solving Poisson's equation for the ADT angle λ.[23] As there are many possible definitions for the boundary conditions on λ,[24] there is no unique solution. Moreover, the solution of Poisson's equation is computationally too expensive to be carried out for molecules of more than three atoms. Since the Born−Oppenheimer approximation implies that it is not necessary to find the best diabatic basis, one can find a diabatic basis for which the residual couplings can be neglected and such a basis is referred to as quasidiabatic basis. The requirements for a quasidiabatic basis are easier to satisfy: (a) the singularity in the derivative coupling must be transformed away; (b) the residual couplings must be negligible. It is desirable for a diabatic basis to estimate the residual couplings to ensure that no spurious couplings have been incorporated. If it is necessary, the residual couplings could be perturbatively included in scattering calculations.

It is a matter of contemporary research how elegantly one can handle the NAC terms instead of neglecting them forcibly. Since the definition of NAC terms appears in the adiabatic representation of SE and those terms are usually very sharp functions of nuclear coordinates with singularity in the configuration space, one may wish to perform a unitary transformation to obtain the diabatic representation of those SEs, where couplings among the electronic states are slowly varying functions of nuclear coordinates and, therefore, the dynamical calculations on the diabatic PESs are numerically accurate and stable. On the other hand, the transformation from adiabatic to diabatic representation of SEs for a given sub-Hilbert space is guaranteed only when the NAC terms being vector fields satisfy the so-called curl conditions. Moreover, it has been shown analytically that the formulation of extended BO equations is possible only when there exists a coordinate-independent ratio of the gradients for each pair of ADT/mixing angles implying zero curls of the NAC terms. Therefore, the nature of the curls

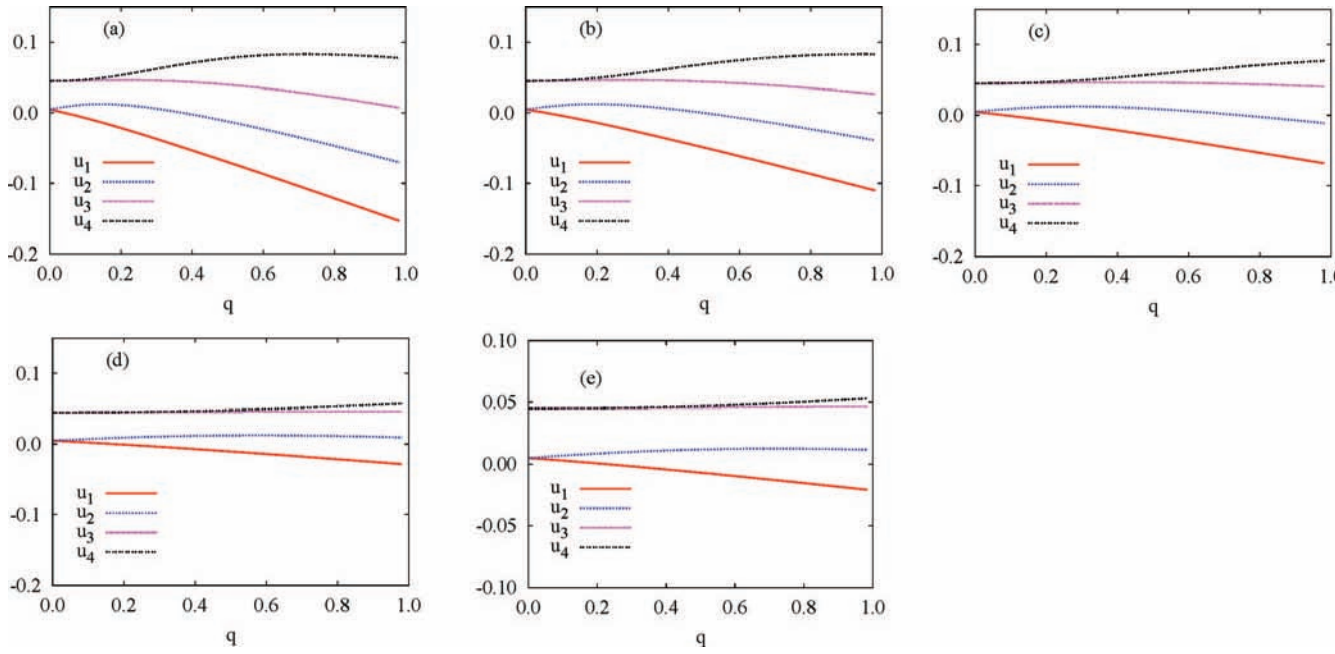

Figure 2. First four adiabatic potentials where $E_{el} = 0.01$ and (a) $k = 0.20$, (b) $k = 0.15$, (c) $k = 0.10$, (d) $k = 0.05$, and (e) $k = 0.04$.

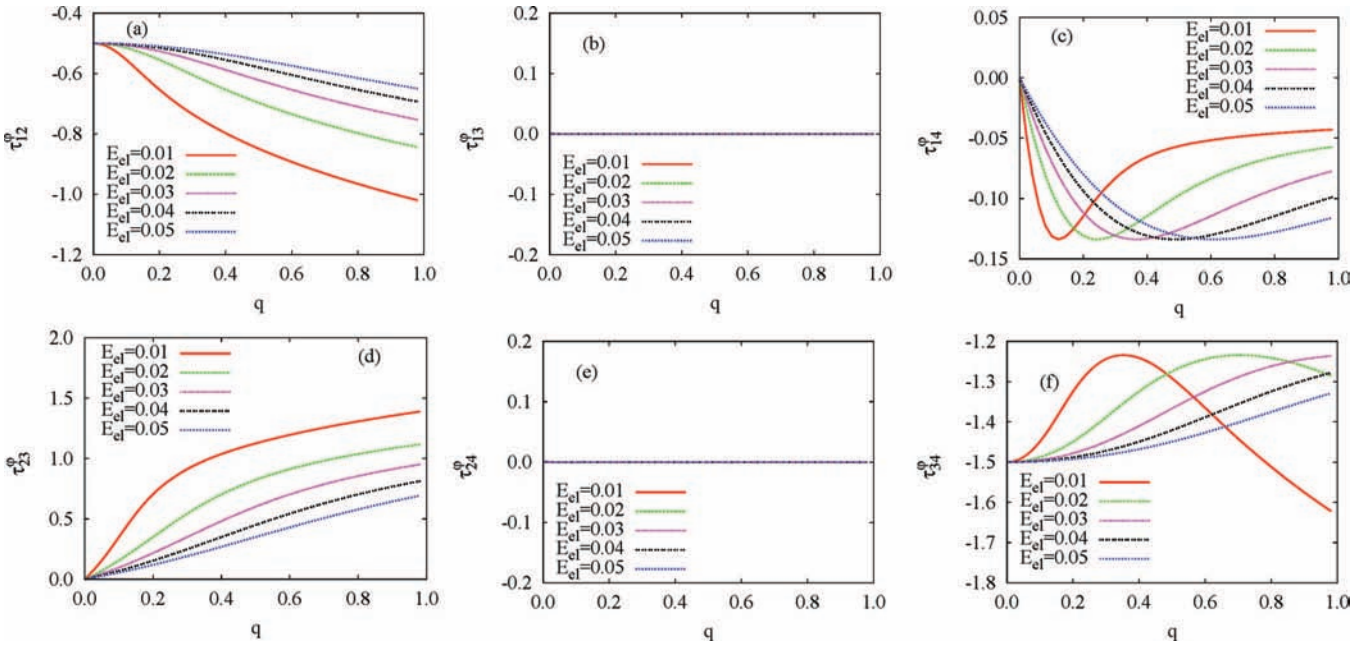

Figure 3. ϕ components of nonadiabatic coupling elements: (a) τ^{ϕ}_{12}, (b) τ^{ϕ}_{13}, (c) τ^{ϕ}_{14}, (d) τ^{ϕ}_{23}, (e) τ^{ϕ}_{24}, and (f) τ^{ϕ}_{34} as a function of q with different E_{el} where $k = 0.2$.

of the NAC terms is a crucial aspect to explore in order to carry out the first principles based theoretical development on BO treatment.

Baer et al.[7,17,25−27] made the first attempt to pursue the first principles based BO treatment on two coupled electronic states as sub-Hilbert space, performed the adiabatic−diabatic transformation of SE, and derived a new set of two coupled BO equations by grafting the effects of NAC terms into the diagonal to formulate the single surface extended Born−Oppenheimer (EBO) equations. In an alternative approach, Varandas and Xu[28] reformulated the two-state adiabatic nuclear SE by casting the NAC elements in terms of nuclear coordinate dependent electronic basis functions angle (mixing angle), found the one-to-one correspondence between mixing[28] and adiabatic−diabatic transformation (ADT)[29] angles and then derived the single-surface EBO equation in the vicinity of degeneracy. Both the formulations with two-dimensional sub-Hilbert space have the following inbuilt features: (a) the components of NAC term satisfy the curl condition; (b) the curl of the NAC term is zero. On the other hand, in the BO treatment for any N (≥ 3) state coupled BO system in the adiabatic representation of nuclear SE, the transformation from adiabatic to diabatic equations and the formulation of EBO equations have been carried out by Baer et al.[30] and Adhikari et al.[31] considering a model situation instead of including the general features of any BO system. Moreover, the formulation does not have the scope to demonstrate (a) how the curl conditions are being satisfied—a necessity to pursue adiabatic−diabatic transformation and (b) how the curls are

zeros around conical intersection(s) (CI(s))—a necessary condition to formulate approximate/rigorous EBO equation. Sarkar and Adhikari[32,33] performed a generalized BO treatment of any three coupled electronic states with a detailed analysis of curl conditions and thereby carried out adiabatic−diabatic transformation of nuclear SE, and finally formulated approximate[32] as well as rigorous[33] EBO equations in terms of electronic basis functions/ADT angles.

In this article, we present the explicit forms of the nonadiabatic coupling elements in terms of ADT angles by considering the validity of ADT condition for any four-state sub-Hilbert space. Since the NAC terms could be singular in the nuclear configuration space, it is a necessity to transform the adiabatic representation of SE to the diabatic in order to ensure accurate and stable numerical calculations but this transformation is possible only when each pair of components of the NAC terms satisfy the curl conditions. Considering the explicit forms of the NAC terms for any four-state sub-Hilbert space, we explore the validity of curl conditions. Since the necessary condition to derive the EBO equations is the existence of a relation among the ADT angles implicating zero curls at least around the CIs, we briefly demonstrate the analytical proof for the validity of such relations. The principal aim of this article is to perform numerical calculations by employing Mathieu equation[34−40] considering its first four adiabatic states to evaluate adiabatic potential energy surfaces, components of NAC terms, validity of curl conditions, and the nature of curl/divergence equations. Though similar calculations were being performed[41−43] on the same system to evaluate the NAC terms and their behavior at and around the seam, presently we are performing a much more detailed analysis.

II. Born−Oppenheimer Treatment of a Four-State Sub-Hilbert Space

The investigations performed so far on the validity/existence of sub-Hilbert space require a detailed discussion. When the derivative coupling is large, the nonremovable part is a relatively small component, whereas if the derivative coupling is small, the nonremovable term is a relatively significant component of the coupling vector. Kuppermann,[24,44] Baer,[45,46] and Yarkony[21,47] carried out investigations on this issue to demonstrate the possibility of the existence of sub-Hilbert space. The nonremovable couplings have been reported for the H_3 system.[24] It was observed that the nonremovable couplings are at least an order of magnitude lower than the derivative coupling when the energy difference is less than 180 mH and the nonremovable coupling is comparable to the derivative coupling when the energy difference is greater than 180 mH. Baer et al.[45,46] studied a tetra-atomic system, $C_2H_2^+$, to investigate the topological effect for both the two-state (Abelian) and multistate (non-Abelian) case. In case of a tetra-atomic systems, topological effects are revealed when one atom surrounds the triatom axis or when two atoms surround (at a time) the two atoms. In other words, it was shown that for a tetra-atomic system not only a triatom axis but even a two-atom axis forms a seam that contains degeneracy points. For the treatment of nonadiabatic coupling terms, they distinguish between the case where the NAC matrix is of 2×2 dimension and the case where it is of the 3×3 dimension. Thus, the first case applies to the two-state Hilbert subspace and the second to the three-state Hilbert subspace. On the other hand, Yarkony[21] investigated the nonremovable part of the derivative couplings by considering the integral of derivative coupling along closed loops in the vicinity of the $1^2A'-2^2A'$ seam of conical intersections in the H_3 system. It has been noticed that for radial coordinate $\rho \rightarrow 0$, the contribution of the nonremovable part decreases rapidly. For this case, as ρ increases the upper state approaches the energy of manifold of Rydberg states so that the contribution from derivative couplings to this states becomes significant.

We carry out the first principles based BO treatment for any four-state electronic sub-Hilbert space assuming the presence of conical intersection(s) anywhere in the nuclear configuration space. Since these four states are considered as either decoupled or approximately decoupled from rest of the states of a molecular system, the BO expansion of the wave function for this subspace of the Hilbert space is given by

$$\Psi(\mathbf{n},\mathbf{e}) = \sum_{i=1}^{4} \psi_i(\mathbf{n})\xi_i(\mathbf{e},\mathbf{n}) \tag{1}$$

where $\xi_i(\mathbf{e},\mathbf{n})$ are the electronic eigenfunctions with nuclear coordinate dependent expansion coefficients, $\psi_i(\mathbf{n})$ subsequently termed as nuclear wave function and the sets of nuclear and electronic coordinates are defined as **n** and **e**, respectively.

In the adiabatic representation of Schroedinger equation, the total electron−nuclei Hamiltonian ($\hat{H}$), the nuclear kinetic energy (KE) operator ($\hat{T}_n$) and the eigenvalue [$u_i(\mathbf{n})$]—eigenfunction [$\xi_i(\mathbf{e},\mathbf{n})$] equation for the electronic Hamiltonian [$\hat{H}_e(\mathbf{e},\mathbf{n})$] are presented as

$$\hat{H} = \hat{T}_n + \hat{H}_e(\mathbf{e},\mathbf{n})$$

$$\hat{T}_n = -\frac{\hbar^2}{2m}\sum_n \nabla_n^2$$

$$\hat{H}_e(\mathbf{e},\mathbf{n})\xi_i(\mathbf{e},\mathbf{n}) = u_i(\mathbf{n})\xi_i(\mathbf{e},\mathbf{n}) \tag{2}$$

The BO expansion for the sub-Hilbert space of molecular wave function, $\Psi(\mathbf{n},\mathbf{e})$ (eq 1) and the total electron−nuclear Hamiltonian, $\hat{H}$ (eq 2) are being substituted in the time-independent Schroedinger equation, $\hat{H}\Psi(\mathbf{n},\mathbf{e}) = E\Psi(\mathbf{n},\mathbf{e})$, to obtain the following matrix representation of adiabatic nuclear SE:

$$\sum_{j=1}^{4}(H_{ij} - E\delta_{ij})\psi_j(\mathbf{n}) = 0, \quad i = 1,2,3,4$$

$$H_{ii} = -\frac{\hbar^2}{2m}(\nabla^2 + 2\vec{\tau}_{ii}^{(1)}\cdot\vec{\nabla} + \tau_{ii}^{(2)}) + u_i(n)$$

$$H_{ij} = -\frac{\hbar^2}{2m}(2\vec{\tau}_{ij}^{(1)}\cdot\vec{\nabla} + \tau_{ij}^{(2)}) = H_{ji}^{\dagger}$$

$$\vec{\tau}_{ij}^{(1)} = \langle \xi_i(\mathbf{e},\mathbf{n})|\vec{\nabla}|\xi_j(\mathbf{e},\mathbf{n})\rangle, \quad \tau_{ij}^{(2)} =$$

$$\langle \xi_i(\mathbf{e},\mathbf{n})|\nabla^2|\xi_j(\mathbf{e},\mathbf{n})\rangle, \quad \langle \xi_i(e,n)|\xi_j(\mathbf{e},\mathbf{n})\rangle = \delta_{ij} \tag{3}$$

where $\vec{\tau}_{ij}^{(1)}$ and $\tau_{ij}^{(2)}$ are the elements of nonadiabatic coupling matrices of the first [$\tau^{(1)}$] and second [$\tau^{(2)}$] kind, respectively.

For a given Hilbert/sub-Hilbert space, the two kinds of NAC matrices are related as

$$\tau^{(2)} = \vec{\tau}^{(1)}\cdot\vec{\tau}^{(1)} + \vec{\nabla}\vec{\tau}^{(1)} \tag{4}$$

leading to the following compact form of kinetically coupled nuclear equations:

$$-\frac{\hbar^2}{2m}(\vec{\nabla} + \vec{\tau})^2\Psi + (U - E)\Psi = 0 \tag{5}$$

where the adiabatic PES matrix elements are defined as $U_{ij} = u_i\delta_{ij}$ with the NAC matrix [$\tau(\equiv\vec{\tau}^{(1)})$] elements as

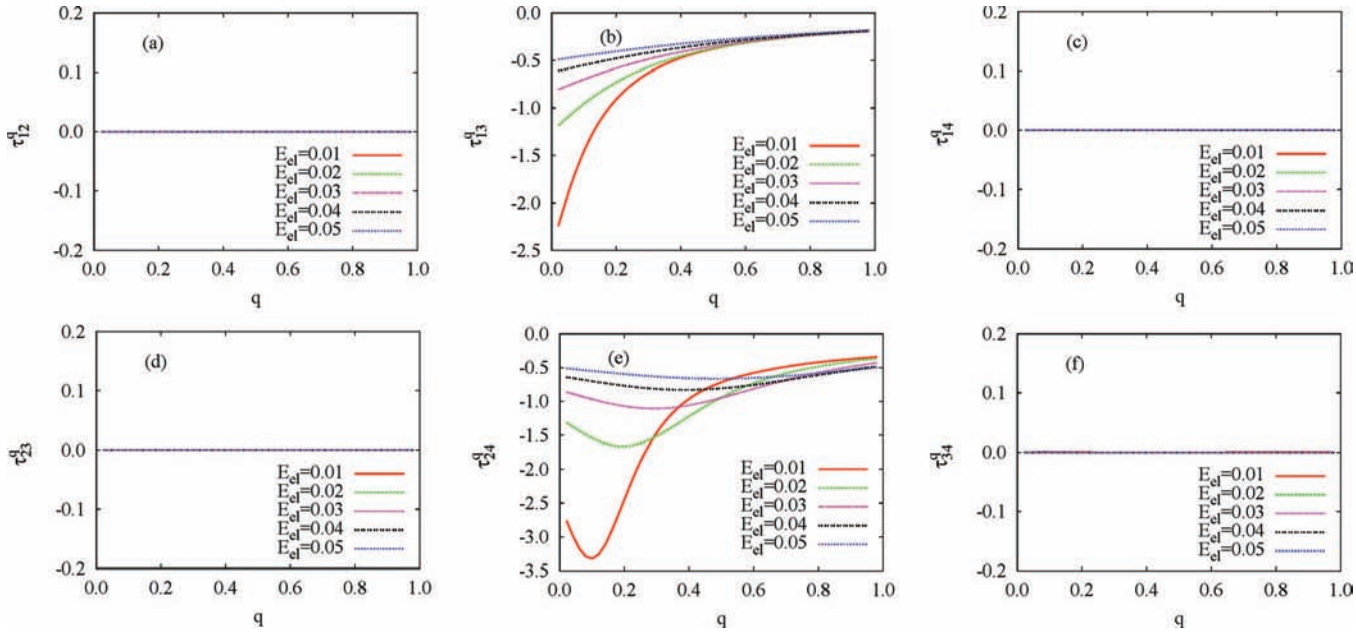

Figure 4. q components of nonadiabatic coupling elements: (a) τ^q_{12}, (b) τ^q_{13}, (c) τ^q_{14}, (d) τ^q_{23}, (e) τ^q_{24}, and (f) τ^q_{34} as a function of q with different E_{el} where $k = 0.2$.

$$\vec{\tau} = \begin{pmatrix} 0 & \vec{\tau}_{12} & \vec{\tau}_{13} & \vec{\tau}_{14} \\ -\vec{\tau}_{12} & 0 & \vec{\tau}_{23} & \vec{\tau}_{24} \\ -\vec{\tau}_{13} & -\vec{\tau}_{23} & 0 & \vec{\tau}_{34} \\ -\vec{\tau}_{14} & -\vec{\tau}_{24} & -\vec{\tau}_{34} & 0 \end{pmatrix} \tag{6}$$

Since the four states constitute the sub-Hilbert space, i.e., the complete space at present, it is possible to transform ($\Psi = \mathbf{A}\Psi^d$) the adiabatic nuclear SE (eq 5) to the diabatic one and the diabatic matrix equations are presented as below

$$-\frac{\hbar^2}{2m}\nabla^2\Psi^d + (W - E)\Psi^d = 0, \quad W = A^\dagger U A \tag{7}$$

under the condition

$$\vec{\nabla}\mathbf{A} + \tau\mathbf{A} = 0 \tag{8}$$

This equation is known as adiabatic−diabatic transformation (ADT) condition.[29] In order to obtain its meaningful solution, one need to ensure that the chosen form of **A** matrix is orthogonal at any point in configuration space and its elements are cyclic functions with respect to a parameter. At present, considering a four-dimensional Hilbert space, any chosen (model) form of the ADT matrix (**A**) consisting of 16 elements has to be an orthogonal matrix with the fulfillment of 10 relations. These orthonormality conditions demand six independent variables [$\theta_{12}(\mathbf{n})$, $\theta_{13}(\mathbf{n})$, $\theta_{14}(\mathbf{n})$, $\theta_{23}(\mathbf{n})$, $\theta_{24}(\mathbf{n})$, and $\theta_{34}(\mathbf{n})$], commonly called ADT/mixing angles, to construct the four-state **A** matrix by taking the product of six rotation matrices, $\mathbf{A}_{12}(\theta_{12})$, $\mathbf{A}_{13}(\theta_{13})$, $\mathbf{A}_{14}(\theta_{14})$, $\mathbf{A}_{23}(\theta_{23})$, $\mathbf{A}_{24}(\theta_{24})$, and $\mathbf{A}_{34}(\theta_{34})$ in various ways. We define these six rotation matrices and one of the ways of their product (**A**) can be taken as

$$\mathbf{A}(\theta_{34}, \theta_{24}, \theta_{14}, \theta_{23}, \theta_{13}, \theta_{12}) = \mathbf{A}_{34}(\theta_{34})\cdot\mathbf{A}_{24}(\theta_{24})\cdot\mathbf{A}_{14}(\theta_{14})\cdot\mathbf{A}_{23}(\theta_{23})\cdot\mathbf{A}_{13}(\theta_{13})\cdot\mathbf{A}_{12}(\theta_{12})$$

$$= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \cos\theta_{34} & \sin\theta_{34} \\ 0 & 0 & -\sin\theta_{34} & \cos\theta_{34} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\theta_{24} & 0 & \sin\theta_{24} \\ 0 & 0 & 1 & 0 \\ 0 & -\sin\theta_{24} & 0 & \cos\theta_{24} \end{pmatrix} \cdot \begin{pmatrix} \cos\theta_{14} & 0 & 0 & \sin\theta_{14} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\sin\theta_{14} & 0 & 0 & \cos\theta_{14} \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\theta_{23} & \sin\theta_{23} & 0 \\ 0 & -\sin\theta_{23} & \cos\theta_{23} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \cos\theta_{13} & 0 & \sin\theta_{13} & 0 \\ 0 & 1 & 0 & 0 \\ -\sin\theta_{13} & 0 & \cos\theta_{13} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \cos\theta_{12} & \sin\theta_{12} & 0 & 0 \\ -\sin\theta_{12} & \cos\theta_{12} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{9}$$

It may be noted that there can be as many as 6! different ways of taking the product of rotation matrices to construct the ADT matrix, **A**, but the explicit form of $\vec{\tau}$ matrix elements derived by considering those ADT matrices are essentially same except the interchange of their forms along with a multiplication by the factor ± 1.

When we substitute the above model form of **A** matrix (eq 9) and the antisymmetric form of $\vec{\tau}$ matrix (eq 6) in eq 8, simple manipulation leads to the differential equations[48,49] for ADT angles, which in turn provide the explicit form of $\vec{\tau}$ matrix elements in terms of ADT angles:

$$\vec{\tau}_{12} = -\cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{12} - \sin\theta_{23}\cos\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{13} - \sin\theta_{24}\vec{\nabla}\theta_{14} \quad (10a)$$

$$\vec{\tau}_{13} = \cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\cos\theta_{34}\vec{\nabla}\theta_{12} - \cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\sin\theta_{24}\sin\theta_{34}\vec{\nabla}\theta 12 - \cos\theta_{23}\cos\theta_{14}\cos\theta_{34}\vec{\nabla}\theta_{13} + \sin\theta_{23}\cos\theta_{14}\sin\theta_{24}\sin\theta_{34}\vec{\nabla}\theta_{13}\cos\theta_{24}\sin\theta_{34}\vec{\nabla}\theta_{14} \quad (10b)$$

$$\vec{\tau}_{14} = -\cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\sin\theta_{34}\vec{\nabla}\theta_{12} + \cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\sin\theta_{24}\cos\theta_{34}\vec{\nabla}\theta 12 + \cos\theta_{23}\cos\theta_{14}\sin\theta_{34}\vec{\nabla}\theta_{13} + \sin\theta_{23}\cos\theta_{14}\sin\theta_{24}\cos\theta_{34}\vec{\nabla}\theta_{13}\cos\theta_{24}\sin\theta_{34}\vec{\nabla}\theta_{14} \quad (10c)$$

$$\vec{\tau}_{23} = -\sin\theta_{13}\cos\theta_{24}\cos\theta_{34}\vec{\nabla}\theta_{12} - \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\sin\theta_{24}\cos\theta_{34}\vec{\nabla}\theta_{12} - \cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\sin\theta_{34}\vec{\nabla}\theta_{12} + \cos\theta_{23}\sin\theta_{14}\sin\theta_{24}\cos\theta_{34}\vec{\nabla}\theta_{13} - \sin\theta_{23}\sin\theta_{14}\sin\theta_{34}\vec{\nabla}\theta_{13} - \cos\theta_{24}\cos\theta_{34}\vec{\nabla}\theta_{23} - \sin\theta_{34}\vec{\nabla}\theta_{24} \quad (10d)$$

$$\vec{\tau}_{24} = -\sin\theta_{13}\cos\theta_{24}\sin\theta_{34}\vec{\nabla}\theta_{12} - \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\sin\theta_{24}\sin\theta_{34}\vec{\nabla}\theta_{12} - \cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\cos\theta_{34}\vec{\nabla}\theta_{12} - \cos\theta_{23}\sin\theta_{14}\sin\theta_{24}\sin\theta_{34}\vec{\nabla}\theta_{13} - \sin\theta_{23}\sin\theta_{14}\cos\theta_{34}\vec{\nabla}\theta_{13} + \cos\theta_{24}\sin\theta_{34}\vec{\nabla}\theta_{23} - \cos\theta_{34}\vec{\nabla}\theta_{24} \quad (10e)$$

$$\vec{\tau}_{34} = -\sin\theta_{13}\sin\theta_{24}\vec{\nabla}\theta_{12} + \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{12} - \cos\theta_{23}\sin\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{13} - \sin\theta_{24}\vec{\nabla}\theta_{23} - \vec{\nabla}\theta_{34} \quad (10f)$$

In an alternative manner, if we replace the so-called ADT angles [$\theta_{12}(\mathbf{n})$, $\theta_{13}(\mathbf{n})$, $\theta_{14}(\mathbf{n})$, $\theta_{23}(\mathbf{n})$, $\theta_{24}(\mathbf{n})$, and $\theta_{34}(\mathbf{n})$] by electronic basis function angles, namely, mixing angles [$\alpha(\mathbf{n})$, $\beta(\mathbf{n})$, $\gamma(\mathbf{n})$, $\lambda(\mathbf{n})$, $\delta(\mathbf{n})$, and $\eta(\mathbf{n})$] in the ADT matrix, **A** (eq 9) and the columns of the $\mathbf{A}^{\dagger}$ matrix are substituted in eq 3 as electronic basis functions, we obtain the same set of equations for NAC elements (eqs 10a−f) as functions of mixing angles and, thereby, show the one-to-one correspondence among ADT and mixing angles.

Once the nonadiabatic coupling elements $\vec{\tau}_{12}$, $\vec{\tau}_{13}$, $\vec{\tau}_{14}$, $\vec{\tau}_{23}$, $\vec{\tau}_{24}$ and $\vec{\tau}_{34}$ are evaluated by using ab initio calculation for a particular nuclear configuration, the solutions of eqs 10a−f provide the ADT angles for the same nuclear configuration and then one can transform the adiabatic representation of Schroedinger equation with the kinetic coupling $\vec{\boldsymbol{\tau}}$ matrix among the electronic states (eq 5) to the diabatic representation with potential coupling, namely, the **W** matrix (eq 7) among the same states. This transformation guarantees the uniquely defined diabatic potential energy matrix in the configuration space only when the following curl conditions of the NAC elements are valid. At this junction, we must note that the derivative coupling matrix, $\vec{\tau}$, evaluated from ab initio calculations will satisfy the curl condition as well as provide zero curls if the sub-Hilbert space (namely four states in this case) partitioning is rigorous, but otherwise not. In our present numerical study by employing the Mathieu equation, it appears that as long as the four states form a sub-Hilbert space for a set or various sets of parametric values, the calculated NAC terms have zero curl and satisfy curl condition.

A curl condition for each NAC element, $\vec{\tau}_{ij}$, has been derived[29] and proved to exist for an isolated group of states (sub-Hilbert space) by considering the analyticity of the ADT matrix **A** for a pair of nuclear degrees of freedom

$$\text{curl}\ \tau_{ij}^{pq} = \frac{\partial}{\partial p}\tau_{ij}^{q} - \frac{\partial}{\partial q}\tau_{ij}^{q} = (\boldsymbol{\tau}^{q}\boldsymbol{\tau}^{p})_{ij} - (\boldsymbol{\tau}^{q}\boldsymbol{\tau}^{q})_{ij}$$

$$\tau_{ij}^{p} = \langle\xi_i|\nabla_p\xi_i\rangle, \quad \tau_{ij}^{q} = \langle\xi_i|\nabla_q\xi_j\rangle \quad (11)$$

where p and q are in Cartesian coordinates with $\nabla_p = \partial/\partial p$ and $\nabla_q = \partial/\partial q$. While defining the conditions for a strictly diabatic electronic basis of molecular system, Mead and Truhlar[18] reformulated the curl equation and explored its consequences.

At present, for a given four-dimensional sub-Hilbert space, we demonstrate that the explicit forms of the NAC elements in terms of ADT/mixing angles satisfy the curl conditions, i.e., the difference between the cross derivatives of any two components of a NAC element with respect to a pair of nuclear coordinates ($Z_{ij} = (\partial/\partial p\tau_{ij}^{q}) - (\partial/\partial q\tau_{ij}^{p})$) appears to be analytically equal to the corresponding element arising from the difference of the products taken at different order between the component NAC matrices [$C_{ij} = (\boldsymbol{\tau}^{q}\boldsymbol{\tau}^{p})_{ij} - (\boldsymbol{\tau}^{p}\boldsymbol{\tau}^{q})_{ij}$]. Since the compact expressions of the curl and divergence equations for the explicit forms of NAC elements (eqs 10a−f] are as such lengthy, we present only two of them:

$$\begin{aligned}\text{curl}\ \tau_{12}^{pq} = Z_{12} = C_{12} = {} & \sin\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24}(\nabla_p\theta_{12}\nabla_q\theta_{13} - \nabla_q\theta_{12}\nabla_p\theta_{13}) + \\ & \cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\cos\theta_{24}(\nabla p\theta_{12}\nabla_q\theta_{23} - \nabla_q\theta_{12}\nabla_p\theta_{23}) + \cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\cos\theta_{24}(\nabla_p\theta 12\nabla_q\theta_{14} - \nabla_q\theta_{12}\nabla_p\theta_{14}) + \\ & \cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\sin\theta_{24}(\nabla_p\theta_{12}\nabla_q\theta_{24} - \nabla_q\theta_{12}\nabla_p\theta_{24}) - \cos\theta_{23}\cos\theta_{14}\cos\theta_{24}(\nabla_p\theta_{13}\nabla_q\theta_{23} - \nabla_q\theta_{13}\nabla_p\theta_{23}) + \\ & \sin\theta_{23}\sin\theta_{14}\cos\theta_{24}(\nabla_p\theta_{13}\nabla_q\theta 14 - \nabla_q\theta_{13}\nabla_p\theta_{14}) + \sin\theta_{23}\cos\theta_{14}\sin\theta_{24}(\nabla_p\theta_{13}\nabla_q\theta_{24} - \nabla_q\theta_{13}\nabla_p\theta_{24}) - \\ & \cos\theta_{24}(\nabla_p\theta_{14}\nabla_q\theta_{24} - \nabla_q\theta_{14}\nabla_p\theta_{24}) \quad (12a)\end{aligned}$$

$$\begin{aligned}\text{div}\ \vec{\tau}_{12} = {} & -\cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24}\nabla^2\theta_{12} - \sin\theta_{23}\cos\theta_{14}\cos\theta_{24}\nabla^2\theta_{13} - \sin\theta_{24}\nabla^2\theta_{14} + \\ & \sin\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{13} + \cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{23} + \\ & \cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{14} + \cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\sin\theta_{24}\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{24} - \cos\theta_{23}\cos\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{23} + \\ & \sin\theta_{13}\sin\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{24} + \sin\theta_{13}\cos\theta_{14}\sin\theta_{24}\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{24} - \cos\theta_{24}\vec{\nabla}\theta_{14}\cdot\vec{\nabla}\theta_{24} \quad (12b)\end{aligned}$$

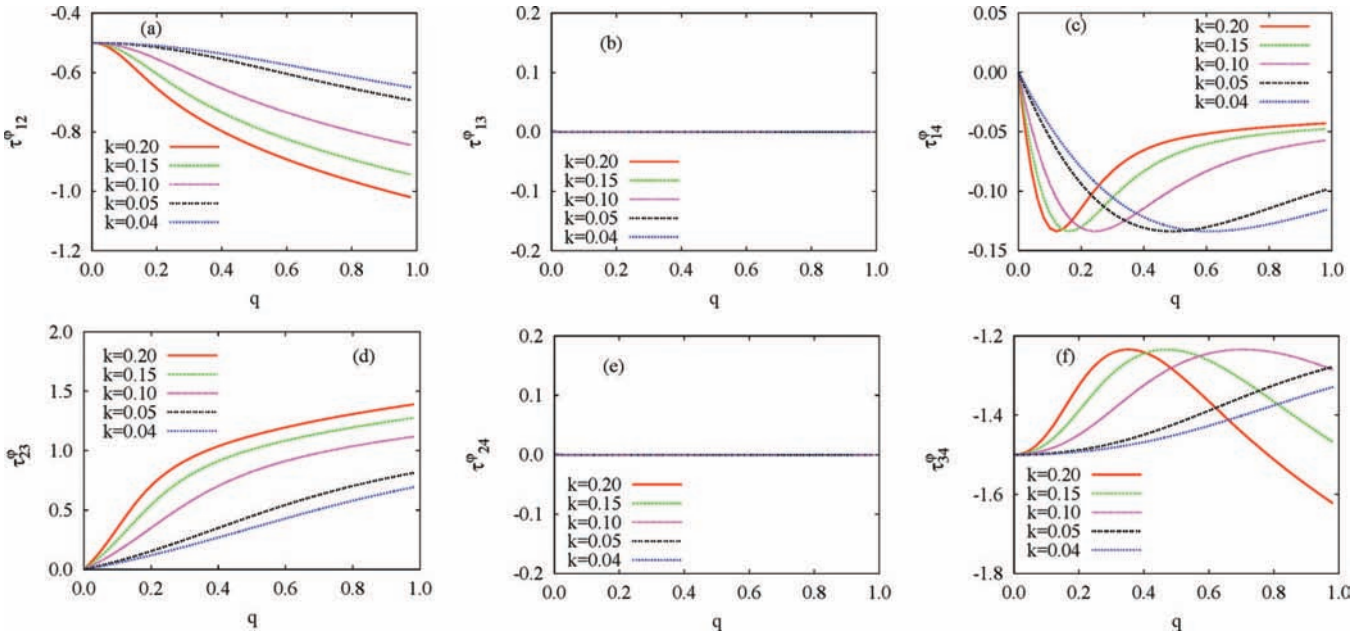

Figure 5. ϕ components of nonadiabatic coupling elements: (a) τ^{ϕ}_{12}, (b) τ^{ϕ}_{13}, (c) τ^{ϕ}_{14}, (d) τ^{ϕ}_{23}, (e) τ^{ϕ}_{24}, and (f) τ^{ϕ}_{34} as a function of q with different k where $E_{el} = 0.01$.

$$\begin{aligned}\text{curl}\ \tau^{pq}_{34} &= Z_{34}\\ &= C34\\ &= (-\cos\theta_{13}\sin\theta_{24} - \sin\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24})(\nabla_p\theta_{12}\nabla_q\theta_{13} - \nabla_q\theta_{12}\nabla_p\theta_{13}) - (\sin\theta_{13}\cos\theta_{24} +\\ &\quad \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\sin\theta_{24})(\nabla_p\theta_{12}\nabla_q\theta_{24} - \nabla_q\theta_{12}\nabla_p\theta_{24}) + \cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\cos\theta_{24}(\nabla_p\theta 12\nabla_q\theta 23 -\\ &\quad \nabla_q\theta_{12}\nabla_p\theta_{23}) + \cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\cos\theta_{24}(\nabla_p\theta_{12}\nabla_q\theta_{14} - \nabla_q\theta_{12}\nabla_p\theta_{14}) + \sin\theta_{23}\sin\theta_{14}\cos\theta_{24}(\nabla_p\theta_{13}\nabla_q\theta_{23} -\\ &\quad \nabla_q\theta_{13}\nabla_p\theta_{23}) - \cos\theta_{23}\cos\theta_{14}\cos\theta_{24}(\nabla_p\theta_{13}\nabla_q\theta 14 - \nabla_q\theta_{13}\nabla_p\theta_{14}) + \cos\theta_{23}\sin\theta_{14}\sin\theta_{24}(\nabla_p\theta_{13}\nabla_q\theta_{24} -\\ &\quad \nabla_q\theta_{13}\nabla_p\theta_{24}) - \cos\theta_{24}(\nabla_p\theta_{23}\nabla_q\theta 24 - \nabla_q\theta_{23}\nabla_p\theta_{24}) \qquad (13a)\end{aligned}$$

$$\begin{aligned}\text{div}\ \vec{\tau}_{34} &= \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24}\nabla^2\theta_{12} - \sin\theta_{13}\sin\theta_{24}\nabla^2\theta_{12} - \cos\theta_{23}\sin\theta_{14}\cos\theta_{24}\nabla^2\theta_{13} - \sin\theta_{24}\nabla^2\theta_{23} - \nabla^2\theta_{34} -\\ &\quad (\sin\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24} + \cos\theta_{13}\sin\theta_{24})\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{13} + \cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{23} +\\ &\quad \cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{14} + \sin\theta_{23}\sin\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{23} + \cos\theta_{13}\cos\theta_{14}\cos\theta_{24}\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{14} -\\ &\quad (\sin\theta_{13}\cos\theta_{24} + \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\sin\theta_{24})\vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{23} + \cos\theta_{23}\sin\theta_{14}\sin\theta_{24}\vec{\nabla}\theta_{13}\cdot\vec{\nabla}\theta_{24} - \cos\theta_{24}\vec{\nabla}\theta_{23}\cdot\vec{\nabla}\theta_{24} \qquad (13b)\end{aligned}$$

and similar expressions can be evaluated for the other NAC elements.

Since $\vec{\nabla}\ \theta_{ij}$s and, in general, $\nabla^2\theta_{ij}$s are nonzero around the conical intersection, the divergences of the vector field ($\vec{\tau}_{ij}$) are nonvanishing for any arbitrary values of ADT/mixing angles and therefore the vector field may show up nonzero curl[50,51] also. On the other hand, if a nonadiabatic coupling term of the kind $\vec{\tau}_{ii+1}(\mathbf{n})$, exhibits a ($i$, $i+1$) CI associated with a singularity (pole) at the same point, it decays like $1/r$ where r is the distance from the CI. The theory of electrodynamics predicts that such vector field could be resolved into irrotational (longitudinal) and solenoidal (transverse) components,[50,51] where the curl of longitudinal part is zero but curl of transverse part may or may not. At the same time, experimental observations on so-called solenoids tend to argue that if an infinitely long contour line (seam) due to conical intersection is considered as infinitesimally narrow "solenoid", the seam should produce zero field outside of the line but ab initio calculations[52,53] show the presence of nonzero $\vec{\tau}$ in the space surrounding the seam. In a similar context, Mead and Truhlar predicted[18] that for a molecular system with three or more nuclei, it is possible to obtain approximate but useful diabatic basis set only if the transverse (solenoidal) part of the nonadiabatic coupling is negligible, i.e., if the component of the coupling terms due to the internuclear distance dependence of the configurational wave function is enough small with respect to the internuclear distance dependence of the configurational coefficients. Thus, the existing knowledge of the vector field ($\vec{\tau}_{ij}$) cannot say quantitatively about the nature of their curls and therefore, the following section demonstrates that in order to perform further theoretical development like the formulation of single surface EBO equation, it is necessary to find out the nature of curl τ^{pq}_{ij}s quantitatively, at least around the point/seam of CI, for a given sub-Hilbert space.

Since, in the adiabatic representation of SE (eq 5), the electronic states interact through kinetic coupling terms

$$-\frac{\hbar^2}{2m}(\vec{\nabla} + \vec{\boldsymbol{\tau}})^2\Psi + (\mathbf{U} - E)\Psi = 0, \quad U_{ij} = u_i\delta_{ij} \qquad (14)$$

in order to formulate the EBO equation, one needs to bring the effect of the off-diagonal NAC terms to the diagonal. The

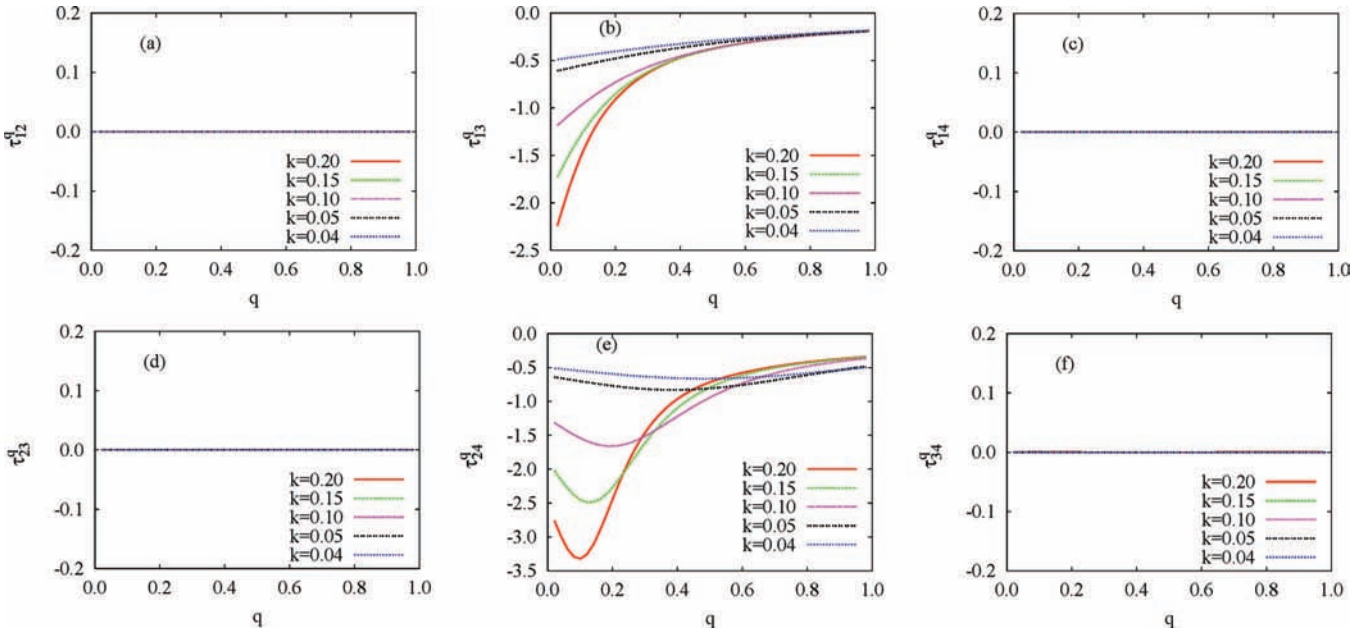

Figure 6. q components of nonadiabatic coupling elements: (a) τ^q_{12}, (b) τ^q_{13}, (c) τ^q_{14}, (d) τ^q_{23}, (e) τ^q_{24}, and (f) τ^q_{34} as a function of q with different k where $E_{el} = 0.01$.

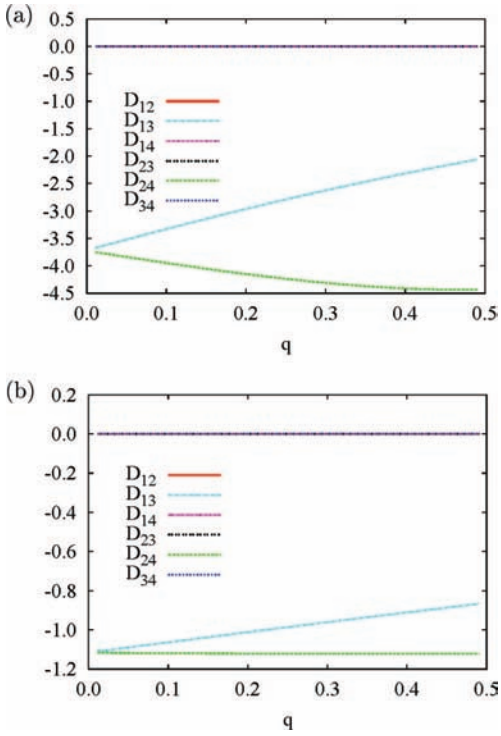

Figure 7. Divergence of the nonadiabatic coupling elements as a function of q where (a) $E_{el} = 0.05$, $k = 0.20$, and (b) $E_{el} = 0.01$, $k = 0.04$.

convenient way of pursuing such operation is to carry out a unitary transformation on eq 14 by a matrix, **G** ($\Psi = \mathbf{G}\Phi$), i.e., the **G** matrix diagonalizes all the components of $\boldsymbol{\tau}$ under the condition, namely, components of the $\boldsymbol{\tau}$ matrix commute with each other [curl $\tau^{\phi q}_{ij} = [\boldsymbol{\tau}^{\phi}, \boldsymbol{\tau}^{q}] = 0$] leading to the following form:

$$-\frac{\hbar^2}{2m}(\mathbf{G}^{\dagger}\vec{\nabla}\mathbf{G} + i\vec{\omega})^2\Phi + (\mathbf{V} - E)\mathbf{\Phi} = 0, \quad \mathbf{V} = \mathbf{G}^{\dagger}\mathbf{U}\mathbf{G}, \quad i\vec{\omega} = \mathbf{G}^{\dagger}\vec{\boldsymbol{\tau}}\mathbf{G} \quad (15)$$

The eigenvalues ($\pm i\vec{\omega}$) of the NAC matrix, $\vec{\boldsymbol{\tau}}$, should be vectors in order to obtain physically meaningful (a scalar) Hamiltonian (eq 15) and thereby one can impose the BO approximation, $|\psi_1| \gg |\psi_i|$, $i = 2, 3, 4$, by considering the upper electronic states as classically closed at low enough energy, to formulate the single surface adiabatic nuclear SE (EBO): [30−33]

$$-\frac{\hbar^2}{2m}(\vec{\nabla} + i\vec{\omega}_1)^2\phi_1 - \frac{\hbar^2}{2m}\left[-2\left(\frac{\vec{\nabla}G^d_{11}}{G^d_{11}}\right)\vec{\nabla}\phi_1 + 2\left(\frac{\vec{\nabla}G^d_{11}}{G^d_{11}}\right)^2\phi_1 - \left(\frac{\nabla^2 G^d_{11}}{G^d_{11}}\right)\phi_1 - i\vec{\omega}_1\left(\frac{\vec{\nabla}G^d_{11}}{G^d_{11}}\right)\phi_1 - \left(\frac{\vec{\nabla}G^d_{12}}{G^d_{11}}\right)\vec{\tau}_{21}\phi_1 - \left(\frac{\vec{\nabla}G^d_{13}}{G^d_{11}}\right)\vec{\tau}_{31}\phi_1 - \left(\frac{\vec{\nabla}G^d_{14}}{G^d_{11}}\right)\vec{\tau}_{41}\phi_1\right] + (u_1 - E)\phi_1 = 0 \quad (16)$$

On the other hand, since the straightforward diagonalization of $\boldsymbol{\tau}$ matrix (eq 6) gives scalar eigenvalues

$$i\omega = \pm i\sqrt{\frac{A}{2} \pm \frac{1}{2}\sqrt{A^2 - 4B^2}}$$
$$A = \vec{\tau}_{12}\cdot\vec{\tau}_{12} + \vec{\tau}_{13}\cdot\vec{\tau}_{13} + \vec{\tau}_{23}\cdot\vec{\tau}_{23} + \vec{\tau}_{14}\cdot\vec{\tau}_{14} + \vec{\tau}_{24}\cdot\vec{\tau}_{24} + \vec{\tau}_{34}\cdot\vec{\tau}_{34}$$
$$B = \vec{\tau}_{14}\cdot\vec{\tau}_{23} - \vec{\tau}_{13}\cdot\vec{\tau}_{24} + \vec{\tau}_{12}\cdot\vec{\tau}_{34} \quad (17)$$

but the requirement of eq 15 dictates that the eigenvalues ($\pm i\vec{\omega}$) of $\vec{\boldsymbol{\tau}}$ matrix must be vectors, the only possibility remains that the $\vec{\boldsymbol{\tau}}$ matrix could be written as the product of a vector function, $\vec{\nabla}\,\eta$ ($\eta \equiv \theta_{12}$ or θ_{13} or θ_{14} or θ_{23} or θ_{24} or θ_{34}) and a ADT/mixing angle dependent antisymmetric scalar matrix, $\mathbf{g}(\theta_{12}, \theta_{13}, \theta_{23}, \theta_{14}, \theta_{24}, \theta_{34})$. It is quite straightforward to find from the elements of the $\vec{\boldsymbol{\tau}}$ matrix (eq 10a) that if the following identities, $(\nabla_p\theta_{13}/\nabla_p\theta_{12}) = (\nabla_q\theta_{13}/\nabla_q\theta_{12})$, $(\nabla_p\theta_{14}/\nabla_p\theta_{12}) = (\nabla_q\theta_{14}/\nabla_q\theta_{12})$, $(\nabla_p\theta_{23}/\nabla_p\theta_{12}) = (\nabla_q\theta_{23}/\nabla_q\theta_{12})$, $(\nabla_p\theta_{24}/\nabla_p\theta_{12}) = (\nabla_q\theta_{24}/\nabla_q\theta_{12})$, and $(\nabla_p\theta_{34}/\nabla_p\theta_{12}) = (\nabla_q\theta_{34}/\nabla_q\theta_{12})$ for any pair of nuclear coordinates, namely, p and q are assumed to be true, one can write, $\vec{\boldsymbol{\tau}} = \vec{\nabla}\,\eta\cdot\mathbf{g}(\theta_{12}, \theta_{13}, \theta_{14}, \theta_{23}, \theta_{24}, \theta_{34})$, with the eigenvalues ($\pm\vec{\imath}\,\omega$) as presented in Appendix A. Therefore, we need to explore the validity of these identities (see eqs 12a and

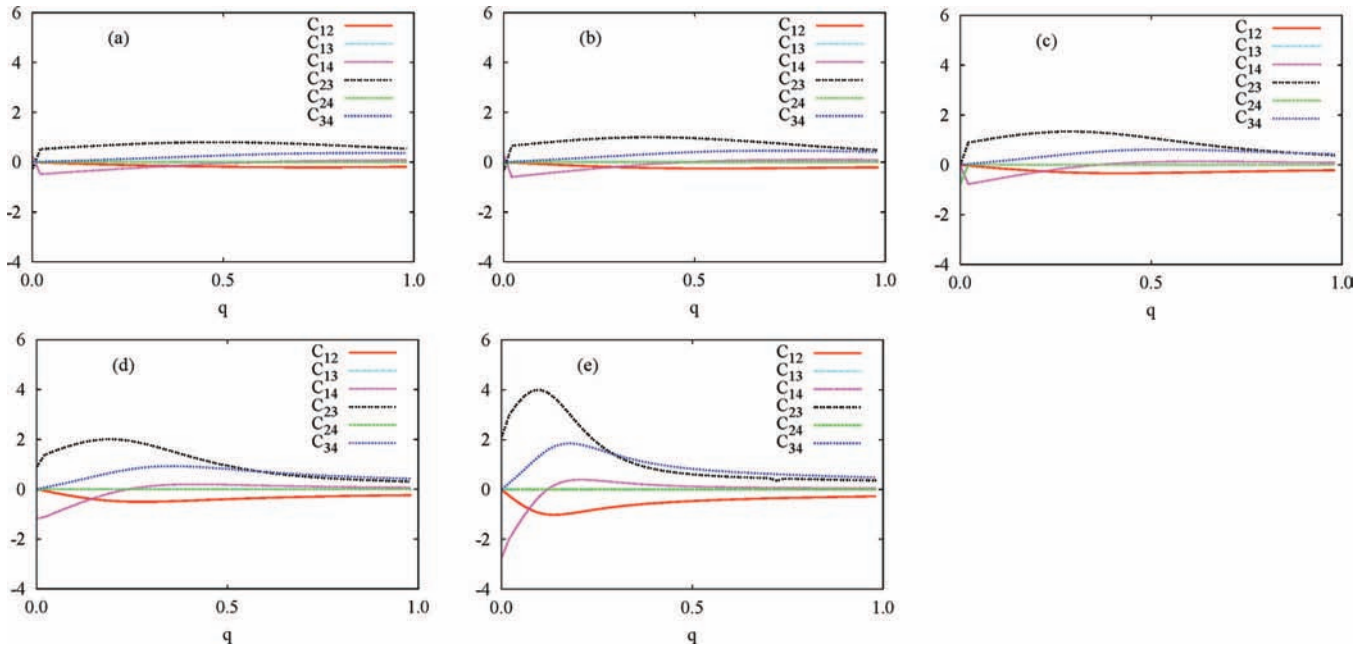

Figure 8. Curls of the nonadiabatic coupling elements calculated by using the equation $C_{ij} = (\boldsymbol{\tau}^{\phi}\boldsymbol{\tau}^{q})_{ij} - (\boldsymbol{\tau}^{q}\boldsymbol{\tau}^{\phi})_{ij}$ as a function of q where $k = 0.2$ and (a) $E_{el} = 0.05$, (b) $E_{el} = 0.04$, (c) $E_{el} = 0.03$, (d) $E_{el} = 0.02$, and (e) $E_{el} = 0.01$.

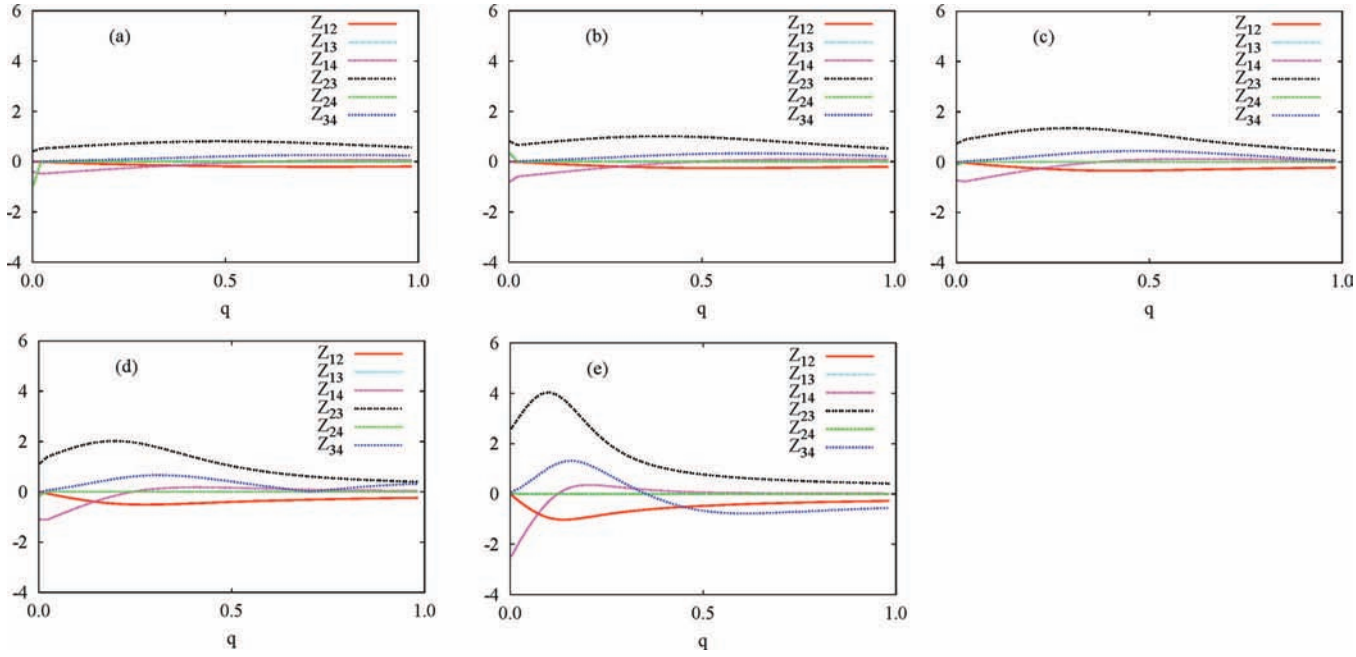

Figure 9. Curls of the nonadiabatic coupling elements calculated by using the equation $Z_{ij} = (\partial/\partial q)\tau_{ij}^{\phi} - (\partial/\partial \phi)\tau_{ij}^{q}$ as a function of q where $k = 0.2$ and (a) $E_{el} = 0.05$, (b) $E_{el} = 0.04$, (c) $E_{el} = 0.03$, (d) $E_{el} = 0.02$, and (e) $E_{el} = 0.01$.

13a) or whether the components of NAC terms commutes (eq 11) with each other at and around CI(s), i.e.

$$\text{curl } \tau_{ij}^{\phi q} = [\boldsymbol{\tau}^{\phi}, \boldsymbol{\tau}^{q}] = 0 \tag{18}$$

In the following sections, we explore the validity of the curl condition as well as the identities leading to zero curl along the seam of the CI using the Mathieu equation as the model system. At this juncture, we remind that (a) the validity of the curl condition (eqs 12a and 13a) implies that the adiabatic−diabatic transformation can provide uniquely defined diabatic PESs, on which stable and accurate numerical calculations can be performed; and (b) the zero curls bring the extended Born−Oppenheimer (EBO) equation; i.e, the transformation of eq 14 to eq 15 and then approximation to eq 16 are justified. Therefore, one can carry out accurate ground-state calculations with an expection that eq 16 takes into account the effect of upper electronic states.

III. Mathieu Equation as the Model System

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

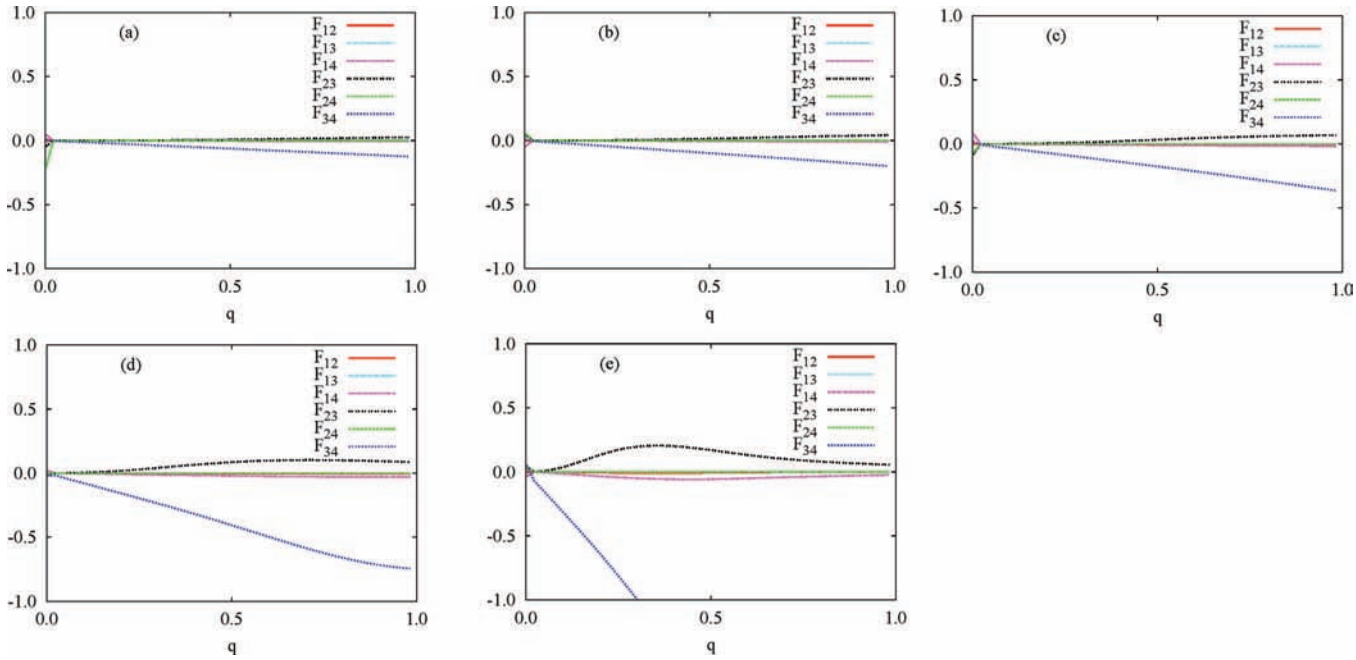

Figure 10. Off-diagonal elements of the matrix **F** (**F** = $C - Z$) as a function of q where $k = 0.2$ and (a) $E_{el} = 0.05$, (b) $E_{el} = 0.04$, (c) $E_{el} = 0.03$, (d) $E_{el} = 0.02$, and (e) $E_{el} = 0.01$.

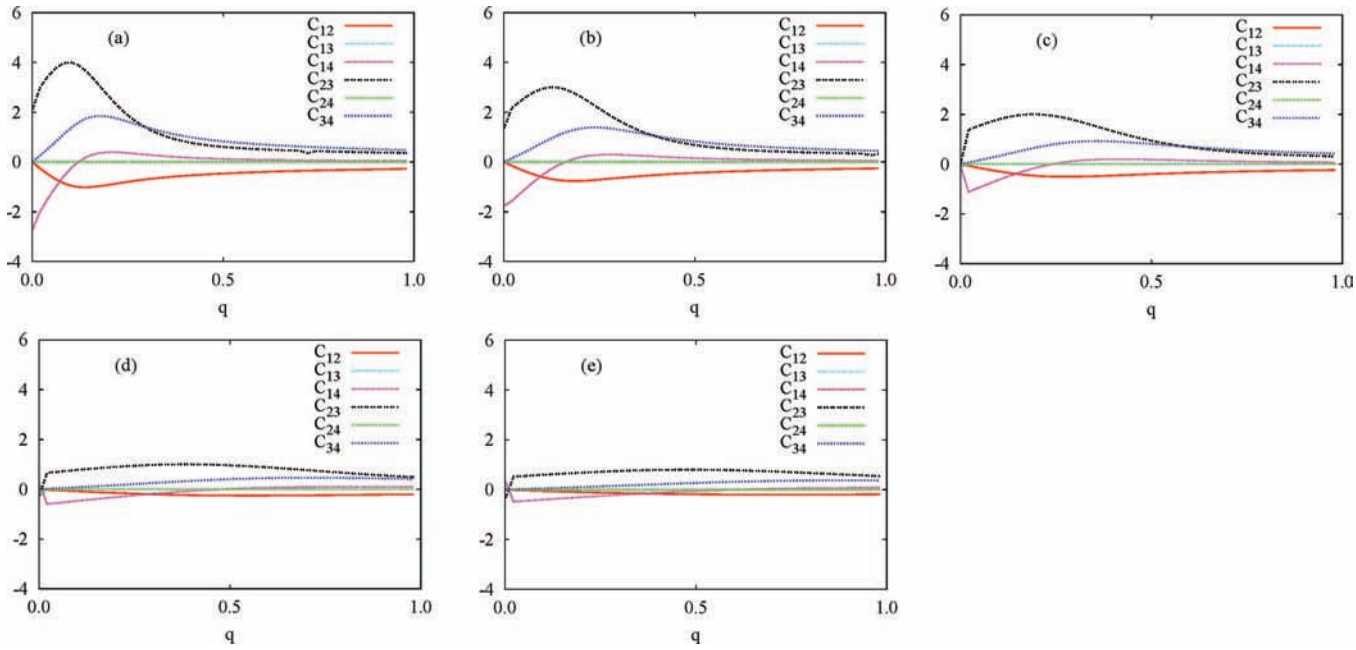

Figure 11. Curls of the nonadiabatic coupling elements calculated by using the equation $C_{ij} = (\boldsymbol{\tau}^{\phi}\boldsymbol{\tau}^{q})_{ij} - (\boldsymbol{\tau}^{q}\boldsymbol{\tau}^{\phi})_{ij}$ as a function of q where $E_{el} = 0.01$ and (a) $k = 0.20$, (b) $k = 0.15$, (c) $k = 0.10$, (d) $k = 0.05$, and (e) $k = 0.04$.

$$\left(-\frac{1}{2}E_{el}\frac{\partial^2}{\partial\theta^2} - G(q,\phi)\cos(2\theta-\phi) - u_j(q,\phi)\right)\xi_j(\theta|q,\varphi) = 0 \tag{19}$$

where E_{el} is a characteristic electronic quantity, $G(q,\phi)$ is the nuclear−electronic interaction coefficient, and $u_j(q,\phi)$ and $\xi_j(\theta|q,\phi)$ are the jth eigenvalue and eigenfunction, respectively, which parametrically depend on the nuclear coordinates. Equation 19 is recognized as the well-known Mathieu equation.[34−40] For the degenerate systems, we consider the above symmetrical system where the degeneracy is at the origin, but for a nonsymmetrical system where the degeneracy is shifted to some point in configuration space, one have to consider the following extended Mathieu equation.

$$\left\{-E_{el}\frac{\partial^2}{\partial\theta^2} - k[(q\cos\phi - a)\cos 2\theta + (q\sin\phi - b)\sin 2\theta] - u_j(q,\phi)\right\}\xi_j(\theta|q,\phi) = 0 \tag{20}$$

As can be seen, the interaction due to the nuclear motion at the point (a, b) is zero, which means that the degeneracy of the electronic states is left at this point. The difference between the two is with respect to the location of CI. In the first model the CI is located at the origin and in the latter, it is located at

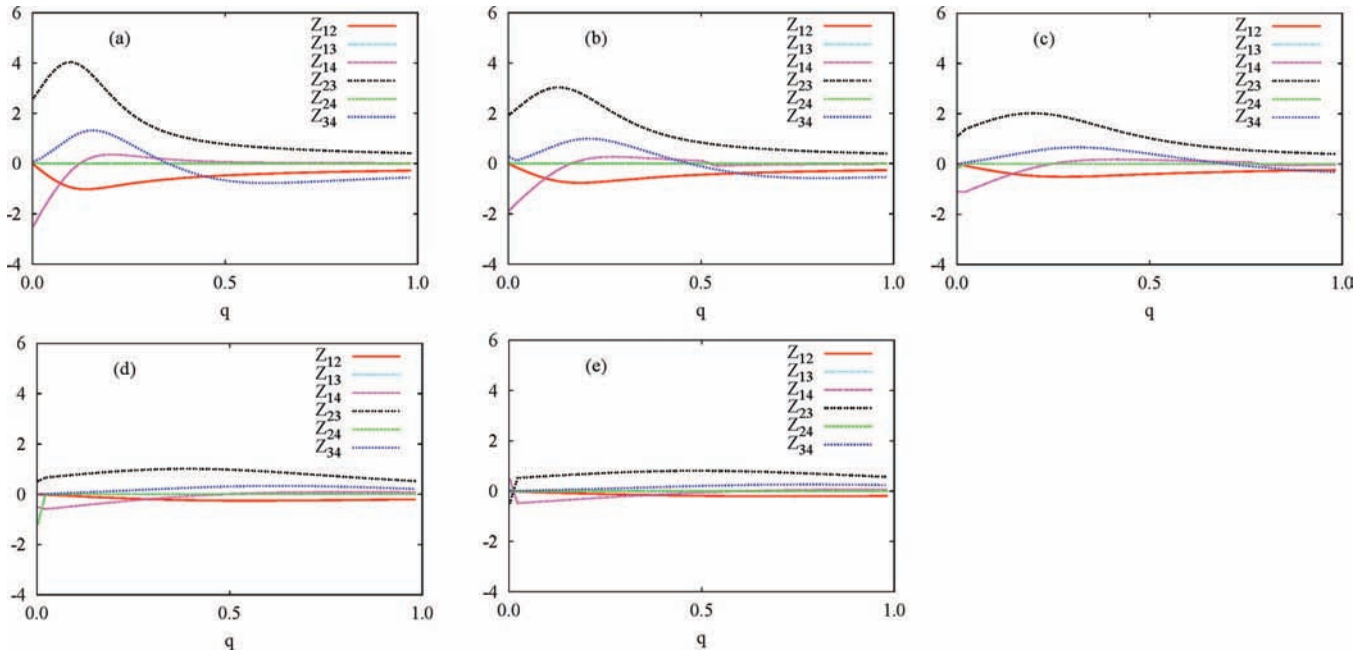

Figure 12. Curls of the nonadiabatic coupling elements calculated by using the equation $Z_{ij} = (\partial/\partial q)\tau_{ij}^{\phi} - (\partial/\partial\phi)\tau_{ij}^{q}$ as a function of q where $E_{el} = 0.01$ and (a) $k = 0.20$, (b) $k = 0.15$, (c) $k = 0.10$, (d) $k = 0.05$, and (e) $k = 0.04$.

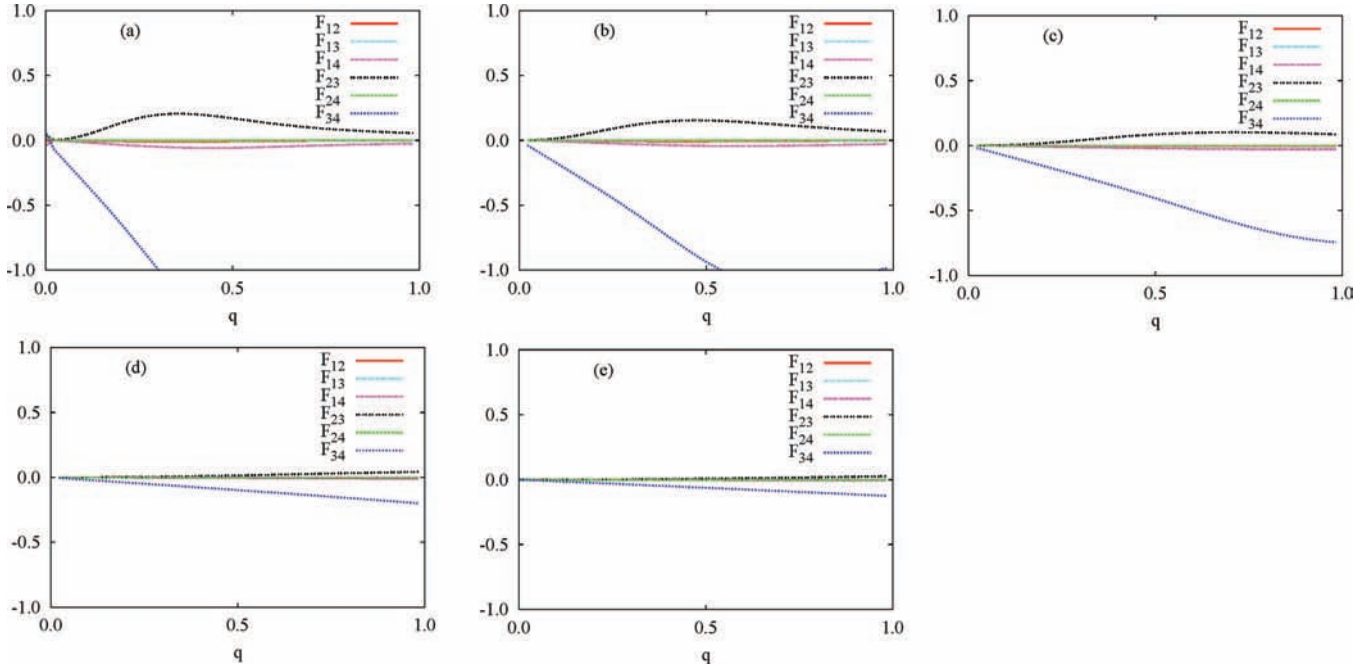

Figure 13. Off-diagonal elements of the matrix **F** (**F** = $C - Z$) as a function of q where $E_{el} = 0.01$ and (a) $k = 0.20$, (b) $k = 0.15$, (c) $k = 0.10$, (d) $k = 0.05$, and (e) $k = 0.04$.

some point (a, b) in the nuclear configuration space.

For the present study, we solve the symmetric case (eq 19) and assume $G(q,\phi)$ to be independent of ϕ and linearly dependent on q, namely, equal to kq with k as a given constant. This choice of the interaction term has several advantages: (1) it forms singular NAC elements (or degenerate eigenvalues) along the coordinate q only; (2) the eigenvalues of eq 19 depend on q but are independent of ϕ; (3) the eigenvectors are functions of ϕ and q, and their nature is such that the resulting NAC elements are ϕ independent but vary with q only.

To solve the Mathieu equation, we expand the $\xi_j(\theta|q,\phi)$ eigenfunctions in the Fourier series. We select the following two families of solutions:[34]

$$ce_{2n+1}(z,-x) = \sum_{m=0}^{\infty} A_{2m+1}^{2n+1}(-x)\cos(2m+1)z$$

$$se_{2n+1}(z,-x) = \sum_{m=0}^{\infty} B_{2m+1}^{2n+1}(-x)\sin(2m+1)z \qquad (21)$$

where x and z are given by

$$x = \frac{kq}{E_{el}}, \quad z = \theta - \frac{\phi}{2} \qquad (22)$$

Here, the cosine series stands for the $\xi_j(\theta|q,\phi)$ 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 21 and 22, do not converge at a point close to the real axis. This feature may affect the rate of convergence for points on the real axis and therefore the convergence in each case was treated with care. In this respect, it is important to mention that we have included 200 bases in each case to guarantee that the convergence though the required convergence arrives within 50 bases.

We need to perform a separate calculation using this nonsymmetrical Mathieu equation (eq 20) to investigate the nature of curls when the conical intersection is not at the origin.

IV. Numerical Calculations: Results and Discussion

IVa. Nonadiabatic Coupling Elements. Since we choose the nuclear−electronic interaction coefficient, $G(q,\phi)$ $(=kq)$, as independent of the nuclear coordinate ϕ, the adiabatic potential energies being the solutions of Mathieu equation are dependent only on the coordinate q. We present the first four adiabatic PESs (u_1, u_2, u_3, and u_4) as functions of q in Figure 1 for a fixed $k = 0.2$ with various E_{el} = (a) 0.05, (b) 0.04, (c) 0.03,(d) 0.02, and (e) 0.01, whereas in Figure 2 for a particular E_{el} = 0.01 with different k = (a) 0.20, (b) 0.15, (c) 0.10, (d) 0.05, and (e) 0.04. The solutions of Mathieu equation are such that adiabatic PESs show pairwise degeneracy, namely, between u_1 and u_2 and then, between u_3 and u_4 up to different values of q depending on the constants, E_{el} and k. In Figure 1a−e, for a fixed value of k (=0.2) and gradually decreasing values of E_{el}, both u_1 and u_2 come closer and closer to the set u_3 and u_4 but each individual set (set I, u_1 and u_2; and set II, u_3 and u_4) loses its degeneracy at different but smaller values of q. On the other hand, Figure 2a−e displays that for a fixed value of E_{el} with higher to lower values of k, the degeneracy within the individual set sustains more as functions of q. In summary, as the value of E_{el} decreases, each set of adiabatic states loses its degeneracy (Figure 1, a−e), but as the value k decreases, the same degeneracy increases (Figure 2, a−e).

Figure 3 presents the ϕ component of the nonadiabatic coupling terms, (a) τ^{ϕ}_{12}, (b) τ^{ϕ}_{13}, (c) τ^{ϕ}_{14}, (d) τ^{ϕ}_{23}, (e) τ^{ϕ}_{24}, and (f) τ^{ϕ}_{34}, and Figure 4 displays the q components, (a) τ^{q}_{12}, (b) τ^{q}_{13}, (c) τ^{q}_{14}, (d) τ^{q}_{23}, (e) τ^{q}_{24}, and (f) τ^{q}_{34}, as functions of q for various values of E_{el} (=0.05, 0.04, 0.03, 0.02, and 0.01) and a fixed k (=0.2). It is clear from the figures that as the E_{el} value decreases, both the ϕ as well as q components of the NAC terms undergo more and more changes as the functions of q, indicating increasingly stronger interaction among the adiabatic states. On the contrary, Figure 5 presents the ϕ component of the NAC terms, (a) τ^{ϕ}_{12}, (b) τ^{ϕ}_{13}, (c) τ^{ϕ}_{14}, (d) τ^{ϕ}_{23}, (e) τ^{ϕ}_{24}, and (f) τ^{ϕ}_{34}, and Figure 6 displays the q components, (a) τ^{q}_{12}, (b) τ^{q}_{13}, (c) τ^{q}_{14}, (d) τ^{q}_{23}, (e) τ^{q}_{24}, and (f) τ^{q}_{34} as functions of q with different values of k (=0.20, 0.15, 0.10, 0.05, 0.04) and a fixed E_{el} (= 0.01). It is again quite evident from the figures that as the k value decreases with a fixed E_{el}, both the ϕ and the q components of the nonadiabatic coupling terms show less and less changes as the functions of q leading to gradually lower interaction among the adiabatic states. Thus, as the value of E_{el} increases, the interaction among the adiabatic states through NAC terms decreases, but as the value k increases, the interaction elements among the same states increase.

Figures 3−6 demonstrate two interesting features. (a) If the ϕ component of a NAC element shows nonzero magnitude, invariably its q component appears zero or the vice versa as functions of the nuclear coordinate, q. This feature of the NAC terms obtained as the solution of Mathieu equation is being supported by the calculated divergence of the same NAC terms. Figure 7a,b displays the divergence of the NAC elements as functions of q for two different set of parametric values of E_{el} and k, where the NAC elements with nonzero ϕ component shows zero divergence but with nonzero q component presents nonzero divergence as expected from electrodynamics. (b) The choices of the parameters E_{el} and k are such that the four adiabatic states are interacting with each other, where all the NAC elements show nonzero values except $\bar{\tau}_{14}$ and $\bar{\tau}_{23}$ only at $q = 0$. More precisely, since either q or ϕ component of NAC elements is nonzero, it will be interesting to see how the curls of the NAC elements behave as functions of q for various chosen values of the parameters, E_{el} and k.

Figure 8 presents the curls of the NAC elements calculated by using the equation $C_{ij} = (\boldsymbol{\tau}^{\phi}\boldsymbol{\tau}^{q})_{ij} - (\boldsymbol{\tau}^{q}\boldsymbol{\tau}^{\phi})_{ij}$, Figure 9 displays the same quantities evaluated by using the equation, $Z_{ij} = (\partial/\partial q)\tau^{\phi}_{ij} - (\partial/\partial\phi)\tau^{q}_{ij}$, and Figure 10 demonstrates their difference, $F_{ij} = C_{ij} - Z_{ij}$, known as Yang−Mills field (curl condition) elements, as functions of q for various values of the parameter E_{el} (=0.05, 0.04, 0.03, 0.02, and 0.01) with a fixed k (=0.2). In a similar manner, Figures 11, 12 and 13 demonstrate the elements of the matrices, C_{ij}, Z_{ij}, and F_{ij}, respectively, as functions of q for various values of the parameter k (=0.20, 0.15, 0.10, 0.05, and 0.04) with a fixed E_{el} (=0.01). Figures 8 and 9 clearly indicate that as the E_{el} values decrease for a fixed k, the curls of the nonadiabatic coupling elements deviate more from zeros since the individual sets of states lose degeneracy due to the increasingly stronger interaction among themselves. Figures 11 and 12 demonstrate the same feature but in the other way; i.e., for a fixed E_{el} with decreasing values of k, the curls of the nonadiabatic coupling terms approach zero due to the lower interaction among the sets. On the other hand, Figures 10 and 13 present the validity of curl conditions, namely, as these four adiabatic states form a subspace, the curl conditions remain satisfied leading to zero Yang−Mills field; otherwise, such conditions are also deviating. In other words, we find when curls of the NAC terms are approaching zero for a set of parametric values, Yang−Mills field elements are also showing the same trend. On the contrary, when the NAC elements among the first four states tend to show zero curls and zero curl conditions (Yang−Mills fields) for a set of parametric values (e.g., $k = 0.04$ and $E_{el} = 0.01$), the nearest-neighbor NAC elements of the complementary space appear to vanish for the same set of parameters leading to the four state sub-Hilbert space. Figure 14 presents the nearest-neighbor nonzero NAC elements (τ^{ϕ}_{16}, τ^{ϕ}_{25}, τ^{q}_{15}, and τ^{q}_{26}) as functions of q for a fixed E_{el} = 0.01 with different values of $k = 0.20$, 0.15, 0.10, 0.05, and 0.04. The figure indicates that all the NAC elements in the complementary space gradually vanish as the k value decreases. Figure 15 demonstrates the relative magnitude of the subspace and the complementary space NAC elements when the first four states is about to decouple from the rest at $k = 0.04$ and E_{el} = 0.01.

Since the solution of the Mathieu equation shows conical intersections due to degeneracies at $q = 0$, the nature of the nonadiabatic coupling terms close to $q \rightarrow 0$ is important to investigate. Figures 8 and 9 as well as Figures 11 and 12 clearly indicate that if curls deviate from zero for various chosen values of k and E_{el}, it happens prominently well within $q < 0.25$. At $k = 0.2$, $E_{el} = 0.04$ and $k = 0.04$, $E_{el} = 0.01$, Figures 8−13 demonstrate that the curls and curl conditions are around zero for those values of q with the ratio x $(=kq/E_{el}) < 1$, leading to form a four-state sub-Hilbert space. In more specific terms, since the validity of curl condition ($F = C - Z = 0$) ensures the existence of sub-Hilbert space, we have calculated the

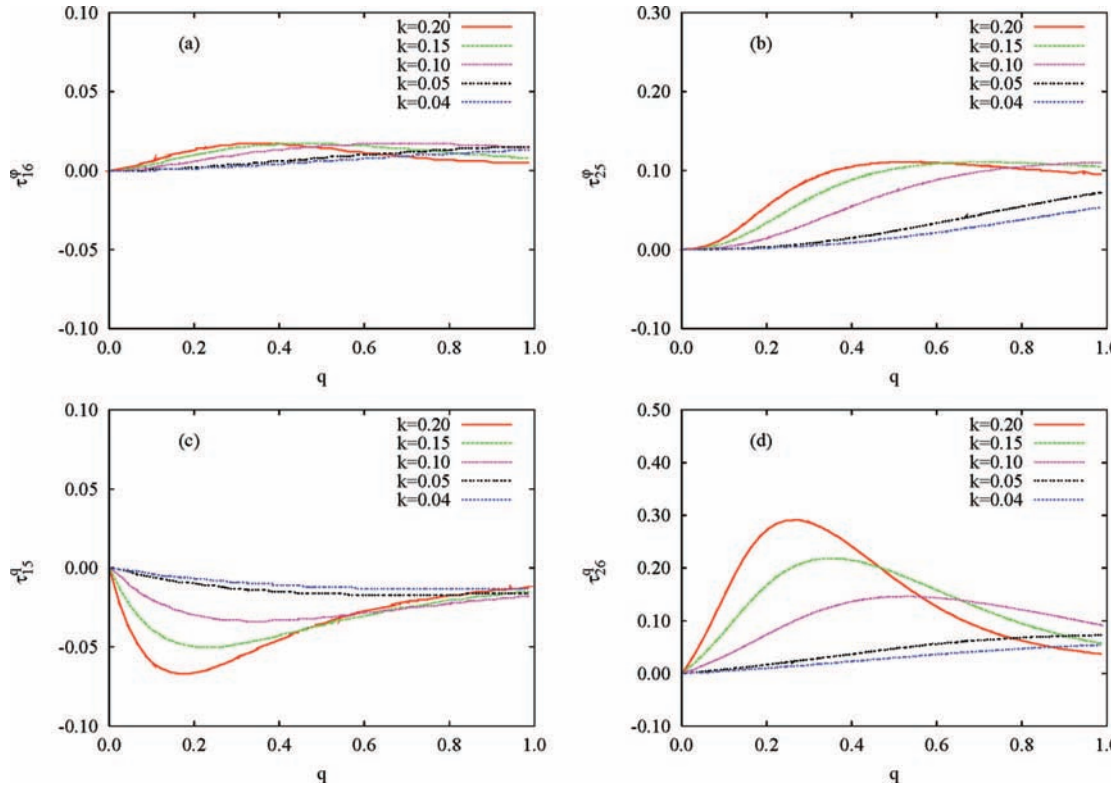

Figure 14. ϕ and q components of nonadiabatic coupling elements in the complementary space: (a) τ^{ϕ}_{16}, (b) τ^{ϕ}_{25}, (c) τ^{q}_{15}, and (d) τ^{q}_{26} as a function of q with different k where $E_{el} = 0.01$.

Yang−Mills field (F) elements for various chosen values of k and q with fixed E_{el} and presented those elements in Table 1. It is clear from the table that as the value of x becomes lower and lower ($\ll 1$), the magnitude of the F elements tends to virtually zero, forming a four-state sub-Hilbert space, but for all practical purposes of numerical calculation, even $x < 1$ situation may be considered (see Table 1) as sub-Hilbert space. Therefore, the solution of the Mathieu equation for the parametric space with $x \ll 1$ not only mimics a realistic molecular system but also shows the existence or presence of a four-state sub-Hilbert space.

IVb. Adiabatic−Diabatic Transformation (ADT) Angle. When we substitute the model form of **A** matrix (eq 9) and the antisymmetric form of the $\vec{\boldsymbol{\tau}}$ matrix (eq 6) in the ADT equation ($\nabla\mathbf{A} + \boldsymbol{\tau}\mathbf{A} = 0$), simple manipulation leads to the following differential equations for the ADT angles

$$\vec{\nabla}\theta_{12} = -\frac{1}{\cos\theta_{13}\cos\theta_{14}}[\cos\theta_{23}\{\vec{\tau}_{12}\cos\theta_{24} - \sin\theta_{24}(\vec{\tau}_{13}\sin\theta_{34} + \vec{\tau}_{14}\cos\theta_{34})\} - \sin\theta_{23}(\vec{\tau}_{13}\cos\theta_{34} - \vec{\tau}_{14}\sin\theta_{34})] \tag{23a}$$

$$\vec{\nabla}\theta_{13} = -\frac{1}{\cos\theta_{14}}[\sin\theta_{23}\{\vec{\tau}_{12}\cos\theta_{24} - \sin\theta_{24}(\vec{\tau}_{13}\sin\theta_{34} + \vec{\tau}_{14}\cos\theta_{34})\} + \cos\theta_{23}(\vec{\tau}_{13}\cos\theta_{34} - \vec{\tau}_{14}\sin\theta_{34})] \tag{23b}$$

$$\vec{\nabla}\theta_{23} = \frac{1}{\cos\theta_{14}}(\tan\theta_{13}[\cos\theta_{23}\{\vec{\tau}_{12}\cos\theta_{24} - \sin\theta_{24}(\vec{\tau}_{13}\sin\theta_{34} + \vec{\tau}_{14}\cos\theta_{34})\} - \sin\theta_{23}(\vec{\tau}_{13}\cos\theta_{34} - \vec{\tau}_{14}\sin\theta_{34})]) + \frac{1}{\cos\theta_{24}}\{\tan\theta_{14}\sin\theta_{24}(\vec{\tau}_{13}\cos\theta_{34} - \vec{\tau}_{14}\sin\theta_{34}) - (\vec{\tau}_{23}\cos\theta_{34} - \vec{\tau}_{24}\sin\theta_{34})\} \tag{23c}$$

$$\vec{\nabla}\theta_{14} = -\vec{\tau}_{12}\sin\theta_{24} - \cos\theta_{24}(\vec{\tau}_{13}\sin\theta_{34} + \vec{\tau}_{14}\cos\theta_{34}) \tag{23d}$$

$$\vec{\nabla}\theta_{24} = \tan\theta_{14}\{\vec{\tau}_{12}\cos\theta_{24} - \sin\theta_{24}(\vec{\tau}_{13}\sin\theta_{34} + \vec{\tau}_{14}\cos\theta_{34})\} - (\vec{\tau}_{23}\sin\theta_{34} - \vec{\tau}_{24}\cos\theta_{34}) \tag{23e}$$

$$\vec{\nabla}\theta_{34} = \frac{1}{\cos\theta_{24}}\{\tan\theta_{14}(\vec{\tau}_{13}\cos\theta_{34} - \vec{\tau}_{14}\sin\theta_{34}) + \sin\theta_{24}(\vec{\tau}_{23}\cos\theta_{34} - \vec{\tau}_{24}\sin\theta_{34}) - \vec{\tau}_{34}\cos\theta_{24}\} \tag{23f}$$

Numerically calculated τ^{q} and τ^{ϕ} matrix elements as presented in a previous section (IVa) are substituted in the q and ϕ components of the above differential equations and those coupled differential equations are solved to obtain six ADT angles as functions of q and ϕ. While solving those differential equations, we initialize all the ADT angles to zeros at $q = 0$ and $\phi = 0$. Figure 16 demonstrates that at $q \to 0$, the ADT angles start with zeros at $\phi = 0$ and end up with integral multiples of π at $\phi = 2\pi$, whereas at $q \neq 0$, the ADT angles often move away from zero to a particular value even at $\phi = 0$ and take the same magnitude (either with plus or minus sign) at $\phi = 2\pi$ such that the ADT angles at $\phi = 0$ and $\phi = 2\pi$ satisfy the single-valuedness of the ADT matrix. The same figure

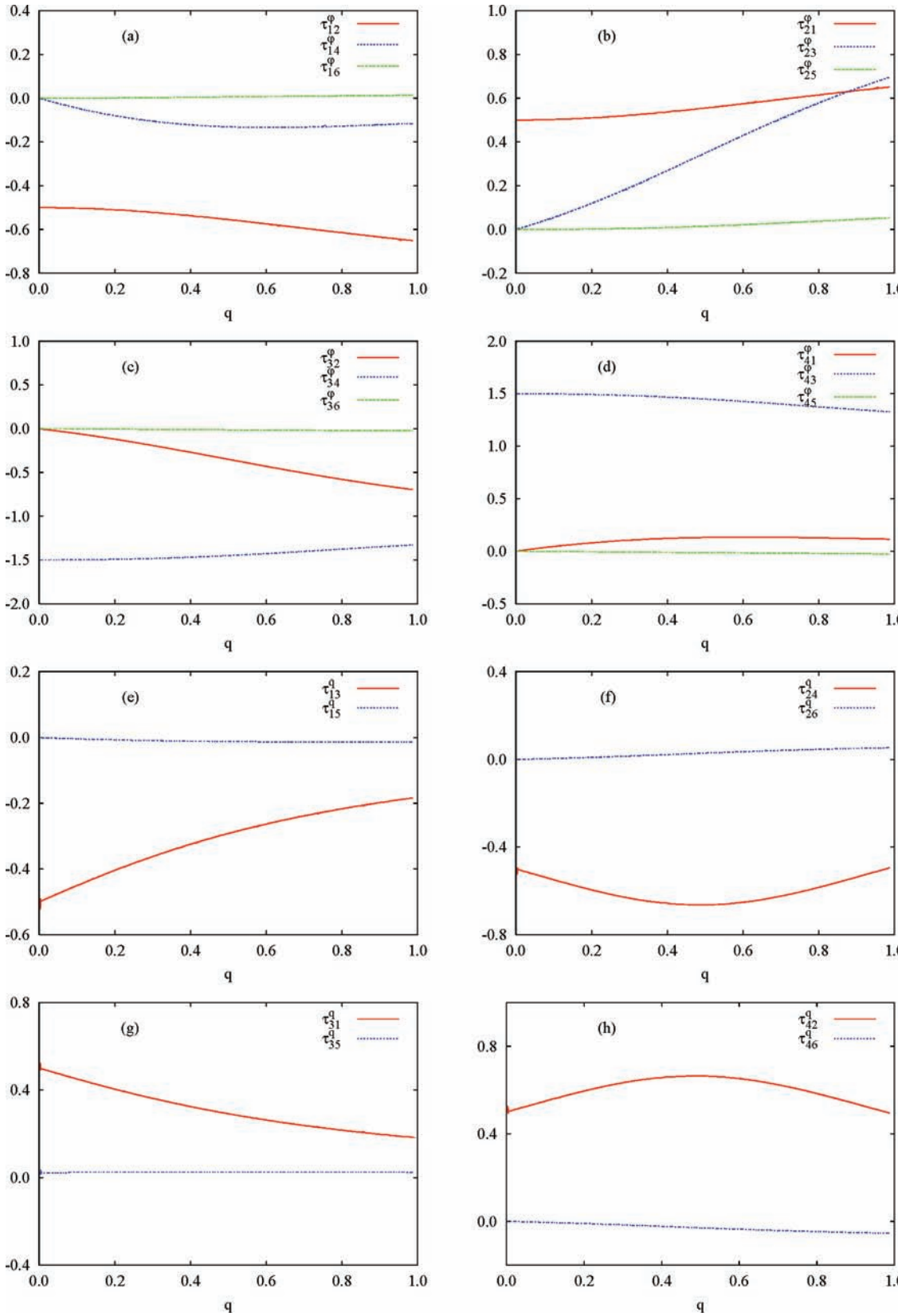

Figure 15. ϕ and q components of nonadiabatic coupling elements of the four-state subspace compared with the corresponding components of the complementary space elements: (a) τ^{ϕ}_{12}, τ^{ϕ}_{14}, and τ^{ϕ}_{16}; (b) τ^{ϕ}_{21}, τ^{ϕ}_{23}, and τ^{ϕ}_{25}; (c) τ^{ϕ}_{32}, τ^{ϕ}_{34}, and τ^{ϕ}_{36}; (d) τ^{ϕ}_{41}, τ^{ϕ}_{43}, and τ^{ϕ}_{45}; (e) τ^{q}_{13}, τ^{q}_{15}; (f) τ^{q}_{24}, τ^{q}_{26}; (g) τ^{q}_{31}, τ^{q}_{35}; (h) τ^{q}_{42}, τ^{q}_{46}, as a function of q where $k = 0.04$ and $E_{el} = 0.01$.

shows the ADT angles both for $E = 0.01$ and $k = 0.2$ as well as $E = 0.01$ and $k = 0.04$ cases. At this juncture, we are in a position to calculate the identities (the differences of the product of the cross derivatives) as defined in the curl equation (eq 12a) and later used while formulating the EBO equation (see the discussion following eq 17). Figure 17 presents a few such identities as functions of q and ϕ for the above two cases, namely, $E = 0.01$ and $k = 0.2$, and $E = 0.01$ and $k = 0.04$. It

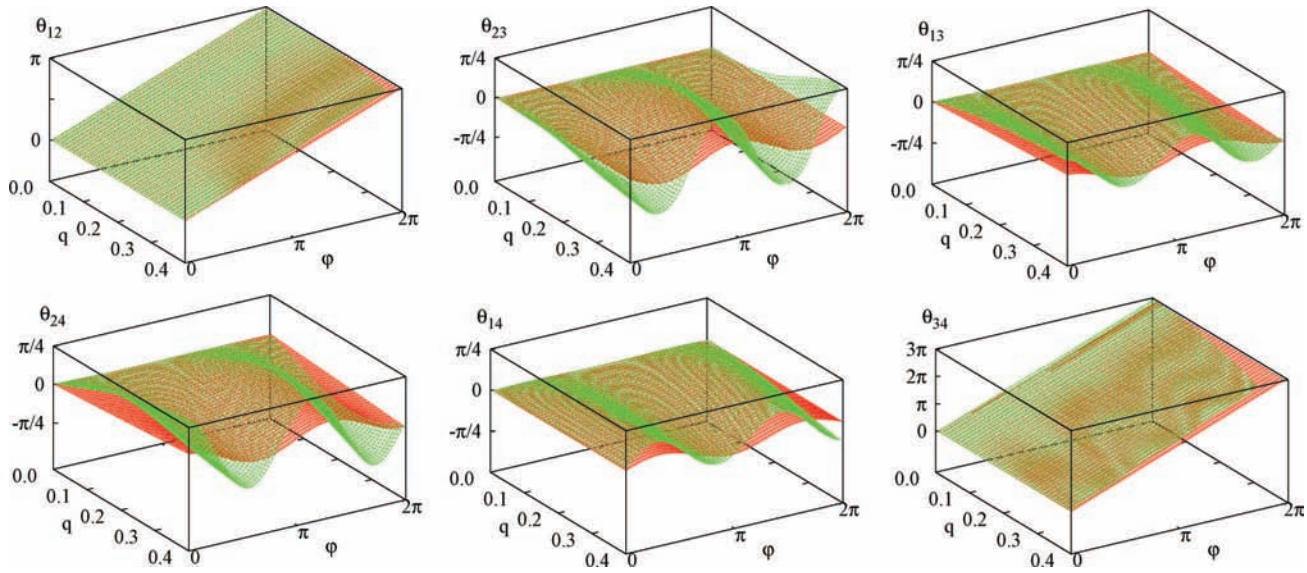

Figure 16. Adiabatic-to-diabatic transformation angles as a function of q and ϕ where $E_{el} = 0.01$, $k = 0.2$ (green) and $E_{el} = 0.01$, $k = 0.04$ (red), respectively.

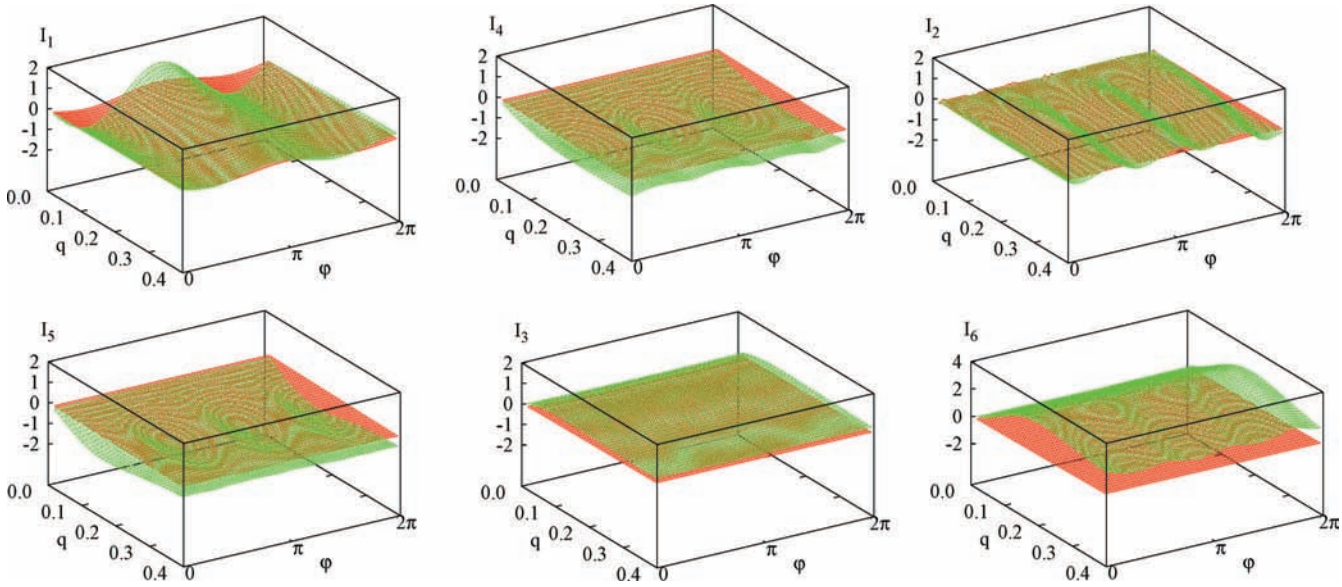

Figure 17. Identities (the differences of the product of the cross derivatives with respect to q and ϕ) for each pair of ADT angles as a function of q and ϕ where $E_{el} = 0.01$, $k = 0.2$ (green) and $E_{el} = 0.01$, $k = 0.04$ (red), respectively. Here $I_1 = (\nabla_q\theta_{12}\nabla_\phi\theta_{14} - \nabla_\phi\theta_{12}\nabla_q\theta_{14})$, $I_2 = (\nabla_q\theta_{12}\nabla_\phi\theta_{34} - \nabla_\phi\theta_{12}\nabla_q\theta_{34})$, $I_3 = (\nabla_q\theta_{13}\nabla_\phi\theta_{14} - \nabla_\phi\theta_{13}\nabla_q\theta_{14})$, $I_4 = (\nabla_q\theta_{13}\nabla_\phi\theta_{23} - \nabla_\phi\theta_{13}\nabla_q\theta_{23})$, $I_5 = (\nabla_q\theta_{14}\nabla_\phi\theta_{24} - \nabla_\phi\theta_{14}\nabla_q\theta_{24})$, $I_6 = (\nabla_q\theta_{23}\nabla_\phi\theta_{24} - \nabla_\phi\theta_{23}\nabla_q\theta_{24})$.

is quite clear that at $E = 0.01$ and $k = 0.04$, the identities are either zeros or varying very little around zeros as functions of q and ϕ leading to zero curls, whereas at $E = 0.01$ and $k = 0.2$, the same identities are showing substantially larger values essentially indicating nonzero curls.

TABLE 1: Elements of the Matrix F (F = $C - Z$) for Diferrent Values of k and q at $E_{el} = 0.01$

k	x ($q = 0.1$)	F_{12}	F_{14}	F_{23}	F_{34}
0.08	0.8	−0.000054	−0.001348	0.001996	−0.050028
0.04	0.4	−0.000003	−0.000188	0.000229	−0.012502
0.02	0.2	0.000000	−0.000025	0.000027	−0.003125
0.01	0.1	0.000000	−0.000003	0.000003	−0.000781
0.005	0.05	0.000000	0.000000	0.000000	−0.000195
k	x ($q = 0.3$)	F_{12}	F_{14}	F_{23}	F_{34}
0.08	2.4	−0.001097	−0.007698	0.021465	−0.150657
0.04	1.2	−0.000087	−0.001355	0.002412	−0.037544
0.02	0.6	−0.000006	−0.000200	0.000269	−0.009378
0.01	0.3	0.000000	−0.000027	0.000032	−0.002344
0.005	0.15	0.000000	−0.000004	0.000004	−0.000586

Finally, as the representative four states tend to form a sub-Hilbert space for a set or sets of parametric values, curls and Yang−Mills fields of the NAC terms tend to zeros leading to the validity of the adiabatic equation (eq 15) and the extended BO equations (eq 16). In other words, the formulation of eq 16 from eq 14 is only possible if the subspace is complete vis a vis NAC terms are curl free. At this juncture, we remind that curl-free NAC terms imply the commutation among the components of the NAC terms (i.e., the rhs of eq 11):

$$[\boldsymbol{\tau}^{\varphi}, \boldsymbol{\tau}^{q}] = 0 \tag{24}$$

as well as the validity of the following identities (eqs 12a and 13a]:

$$\nabla_p\theta_{ij}\nabla_q\theta_{jk} - \nabla_q\theta_{ij}\nabla_q\theta_{jk} = 0, \quad \{i \neq j \neq k\} = 1, 2, 3 \quad (25)$$

Since we know that when two operators commute with each other, they will have a common eigenfunction (**G**) (eq 15), i.e., **G** diagonalizes both the components of the $\vec{\boldsymbol{\tau}}$ matrix with eigenvalues $\pm i\vec{\omega}$. In this article, we just explore the condition to find out such sub-Hilbert space, where beyond BO equation (eqs 15 and 16) could be valid and the required calculations on the ground-state can be carried out.

V. Summary

The analytical derivations in the first part of this article (section II) were carried out by considering a four-state sub-Hilbert space. Since the ADT condition, $\vec{\nabla}\mathbf{A} + \vec{\tau}\mathbf{A} = 0$, is assumed to be valid for the same sub-Hilbert space, the explicit form of $\vec{\boldsymbol{\tau}}$ (eq 10), curl τ (eqs 12a and 13a), div τ (eqs 12b and 13b), EBO equation (eq 16), and differential equations for ADT angles (eq 23a) represent the nonadiabatic coupling terms and their nature for the space as defined by eq 1.

On the contrary, the solution of the Mathieu equation (eq 19) as defined by eq 21 are the so-called electronic eigenfunctions (ξ_is) in terms of Fourier series [where expansion coefficients depend on nuclear coordinates (q and ϕ) and Fourier functions are taken as functions of electronic (θ) and nuclear (ϕ) coordinates] and nuclear coordinate dependent adiabatic potential energy surfaces with conical intersections at $q = 0$. Therefore, it is worth mentioning that the present investigation is important and the results are crucial at smaller q values (let say ≤ 0.25). We have taken 200 bases (Fourier functions) to reach the convergence of the solution, i.e., the numerically "exact" electronic eigenfunctions and adiabatic PESs for any chosen values of the parameters, q, k, and E_{el}. In other words, when we solve the Mathieu equation with 200 bases for a specific parametric values of q, k, and E_{el}, automatically we have 200 electronic eigenfunctions also but we consider only the first four electronic eigenfunctions to calculate 4×4 $\boldsymbol{\tau}^q$ and $\boldsymbol{\tau}^\phi$ matrices and thereby, monitor their curls [$(\boldsymbol{\tau}^\phi\boldsymbol{\tau}^q)_{ij} - (\boldsymbol{\tau}^q\boldsymbol{\tau}^\phi)_{ij}$ and $(\partial/\partial q)\boldsymbol{\tau}^\phi_{ij} - (\partial/\partial\phi)\boldsymbol{\tau}^q_{ij}$] and curl condition [$(\boldsymbol{\tau}^\phi\boldsymbol{\tau}^q)_{ij} - (\boldsymbol{\tau}^q\boldsymbol{\tau}^\phi)_{ij} = (\partial/\partial q)\boldsymbol{\tau}^\phi_{ij} - (\partial/\partial\phi)\boldsymbol{\tau}^q_{ij}$] numerically, where the same $\boldsymbol{\tau}^q$ and $\boldsymbol{\tau}^\phi$ matrices are being used to evaluate ADT angles (eq 23a) and explore the explicit form of curls (eqs 12a and 13a) in terms of cross derivatives of ADT angles (derived by considering a four state sub-Hilbert space). At this juncture, it has to be categorically mentioned that our aim was to find out those specific values of k and E_{el}, where the first four electronic eigenfunctions (the numerically "exact" solution of Mathieu equation) will form a four-state subspace of the Hilbert space. In this regard, we wish to refer to Figures 14 and 15, where the nonadiabatic coupling elements in the complementary space (the fifth and sixth row−column elements) are approaching zero (Figure 14) as k decreases from 0.2 to 0.04 with a fixed $E_{el} = 0.01$ though the first 4×4 NAC matrix elements (Figure 15) are clearly nonzero at $k = 0.04$ and $E_{el} = 0.01$ leading a four state sub-Hilbert space. Figures 10 and 13 echo the same findings in a different manner.

On the other hand, since we know that the explicit form of the differential equation for the ADT angle (eq. 23a) are valid only with the consideration of four state sub-Hilbert space, the numerically calculated τ^q and τ^ϕ matrix elements could be the correct input to solve those differential equations of ADT angles and to obtain the identities of cross derivatives only when the values of the parameters, k and E_{el}, tend to form a four state sub-Hilbert space (see Figures 10, 13, and 15). The identities of cross derivatives (see Figure 17) are approaching zero as functions of q and ϕ at $k = 0.04$ and $E_{el} = 0.01$.

As the curls (numerically calculated by considering 4×4 component NAC matrices) tend to zero for specific parametric values of k and E_{el}, the components of NAC matrices, $\boldsymbol{\tau}^q$ and $\boldsymbol{\tau}^\phi$ commutes and a common **G** matrix (that can diagonalize $\boldsymbol{\tau}^q$ and $\boldsymbol{\tau}^\phi$ matrices simultaneously) is guaranteed to formulate EBO equation.

Acknowledgment. We acknowledge financial support from the Department of Science and Technology (DST, Government of India) through project no. SP/S1/H-53/01. B.S. acknowledges support from UGC, Government of India, through the DSA-SAP-III program.

Appendix A: Eigenvalues of NAC Matrix for a Four-Dimensional Hilbert Space

If the origin of the coordinate system coincides with the point of conical intersection or even if the point of conical intersection(s) is away from the origin of the coordinate system, the parametric representation for the vector equation of a conical surface predicts (see Appendix B of ref 32) the validity of the following identities: $(\nabla_p\theta_{13}/\nabla_p\theta_{12}) = (\nabla_q\theta_{13}/\nabla_q\theta_{12})$, $(\nabla_p\theta_{14}/\nabla_p\theta_{12}) = (\nabla_q\theta_{14}/\nabla_q\theta_{12})$, $(\nabla_p\theta_{23}/\nabla_p\theta_{12}) = (\nabla_q\theta_{23}/\nabla_q\theta_{12})$, $(\nabla_p\theta_{24}/\nabla_p\theta_{12}) = (\nabla_q\theta_{24}/\nabla_q\theta_{12})$, and $(\nabla_p\theta_{34}/\nabla_p\theta_{12}) = (\nabla_q\theta_{34}/\nabla_q\theta_{12})$ for any pair of nuclear coordinates, namely, p and q, at and around the point of conical intersection (CI). Moreover, in this article, the "exact" numerical solutions of the Mathieu equation for specific values of k and E_{el} show the existence of zero curls, i.e., $[\boldsymbol{\tau}^\phi, \boldsymbol{\tau}^q] = 0$. Such components of NAC matrices $\boldsymbol{\tau}^q$ and $\boldsymbol{\tau}^\phi$ lead to the validity of the above identities (see eqs 12a and 13a and Figure 17). When we substitute these identities in eq 10, the nonadiabatic coupling (NAC) terms takes the following form:

$$\vec{\tau}_{12} = -\vec{\nabla}\theta_{12}\Bigg[\cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24} + \sin\theta_{23}\cos\theta_{14}\cos\theta_{24}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right) + \sin\theta_{24}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)\Bigg] \quad (A1a)$$

$$\vec{\tau}_{13} = \vec{\nabla}\theta_{12}\Bigg[\cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\cos\theta_{34} + \cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\sin\theta_{24}\sin\theta_{34} - \cos\theta_{23}\cos\theta_{14}\cos\theta_{34}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right) + \sin\theta_{23}\cos\theta_{14}\sin\theta_{24}\sin\theta_{34}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right) - \cos\theta_{24}\sin\theta_{34}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)\Bigg] \quad (A1b)$$

and similarly other NAC terms. At this junction, we can recall eq 16 to find out the following quantities (A and B) considering the NAC elements as presented in eqs A1:

$$A = \vec{\tau}_{12}\cdot\vec{\tau}_{12} + \vec{\tau}_{13}\cdot\vec{\tau}_{13} + \vec{\tau}_{23}\cdot\vec{\tau}_{23} + \vec{\tau}_{14}\cdot\vec{\tau}_{14} + \vec{\tau}_{24}\cdot\vec{\tau}_{24} + \vec{\tau}_{34}\cdot\vec{\tau}_{34}$$

$$= \vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{12}\left\{1 + \left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)^2 + 2\cos\theta_{23}\sin\theta_{14}\cos\theta_{24}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\times \left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{23}\sin\theta_{14}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{24}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right) + 2\cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) + 2(\sin\theta_{13}\sin\theta_{23} - \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24})\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)\right\} \quad \text{(A2)}$$

$$B = \vec{\tau}_{14}\cdot\vec{\tau}_{23} - \vec{\tau}_{13}\cdot\vec{\tau}_{24} + \vec{\tau}_{12}\cdot\vec{\tau}_{34}$$

$$= \vec{\nabla}\theta_{12}\cdot\vec{\nabla}\theta_{12}\left\{\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + \sin\theta_{13}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + \cos\theta_{13}\sin\theta_{23}\cos\theta_{14}\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) - \cos\theta_{23}\cos\theta_{14}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\times \left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) + \cos\theta_{14}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24}\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + \sin\theta_{23}\cos\theta_{14}\cos\theta_{24}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + \sin\theta_{24}\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)\right\} \quad \text{(A3)}$$

and thereby

$$\bar{\omega}_i = \sqrt{\frac{A}{2} \pm \frac{1}{2}\sqrt{A^2 - 4B^2}}$$

$$= \pm\vec{\nabla}\theta_{12}\left[-\frac{1}{2}\left\{1 + \left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)^2\right] + 2\cos\theta_{23}\sin\theta_{14}\cos\theta_{24}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right) + \left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{23}\sin\theta_{14}\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{24}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right) + 2\cos\theta_{13}\cos\theta_{23}\sin\theta_{14}\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) + 2(\sin\theta_{13}\sin\theta_{23} - \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24})\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)\right\} \quad \text{(A4)}$$

$$\pm\frac{1}{2}\left\{[1 + \left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)^2 + 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right) + 2(\cos\theta_{13}\cos\theta_{23}\sin\theta_{14} + \cos\theta_{13}\sin\theta_{23}\cos\theta_{14})\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + 2(\sin\theta_{13}\sin\theta_{23} - \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24} + \cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24})\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + 2(\cos\theta_{23}\sin\theta_{14}\cos\theta_{24} + \sin\theta_{23}\cos\theta_{14}\cos\theta_{24})\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2(\sin\theta_{23}\sin\theta_{14} - \cos\theta_{23}\cos\theta_{14})\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{14}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{24}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)]\times \left[1 + \left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right)^2 + \left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)^2 + 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right) + 2(\cos\theta_{13}\cos\theta_{23}\sin\theta_{14} - \cos\theta_{13}\sin\theta_{23}\cos\theta_{14})\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + 2(\sin\theta_{13}\sin\theta_{23} - \cos\theta_{13}\sin\theta_{23}\sin\theta_{14}\cos\theta_{24} - \cos\theta_{13}\cos\theta_{23}\cos\theta_{14}\cos\theta_{24})\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) - 2\sin\theta_{13}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) + 2(\cos\theta_{23}\sin\theta_{14}\cos\theta_{24} - \sin\theta_{23}\cos\theta_{14}\cos\theta_{24})\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) + 2(\sin\theta_{23}\sin\theta_{14} + \cos\theta_{23}\cos\theta_{14})\left(\frac{\nabla_p\theta_{13}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{24}}{\nabla_p\theta_{12}}\right) + 2\sin\theta_{14}\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right) - 2\left(\frac{\nabla_p\theta_{23}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right) - 2\sin\theta_{24}\left(\frac{\nabla_p\theta_{14}}{\nabla_p\theta_{12}}\right)\left(\frac{\nabla_p\theta_{34}}{\nabla_p\theta_{12}}\right)\right]^{1/2}1/2}$$

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JP8029709