

# The Curl equations for an induced Renner-Teller type model

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**Abstract** : When a set of three states appears strongly coupled within the set but interacts very weakly with other states of the Hilbert space, these three states form a sub-Hilbert space and thereby, one can express the non-adiabatic coupling (NAC) elements in terms of adiabatic-diabatic transformation (ADT)/mixing angles obviously representing the same sub-space. It has been possible to demonstrate that those explicit forms of the NAC terms satisfy the Curl equations – the necessary conditions to ensure the adiabatic-diabatic transformation in order to remove the NAC terms (could be 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 elements among the electronic states. While formulating the extended Born-Oppenheimer (EBO) equations [*J Chem Phys* 124 074101 (2006)] for the ground adiabatic state, we demonstrate the necessity for the existence of zero Curls of the NAC terms and discuss briefly about their analytical validity at and around the conical intersection. Considering a three state diabatic Hamiltonian, namely, the so called induced Renner-Teller model, we calculate the NAC terms and their Curls analytically, and explore the nature of these quantities, when the three states are either degenerate at a point or approaching to form three states degeneracy at the same point.

**Keywords** : Curl equation, Non-adiabatic coupling, Renner-Teller, extended Born-Oppenheimer equation

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## 1. Introduction

Since the relevant Schrödinger equation (SE) of any molecular process – essentially governed by coulombic interactions, can provide enough accurate solutions, namely, the observables such as reactive/non-reactive cross sections or spectroscopic quantities, a major theoretical interest has been motivated toward the development of numerical algorithm to solve the SE, particularly, with the approximation arising from the Born-Oppenheimer [1] and Born-Huang [2] treatment. On the other hand, it is well

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established fact by now that even if a molecular process takes place on the ground state, the excited electronic states can affect the ground very strongly due to the presence of so called "non-adiabatic coupling" and therefore, the necessity of a rigorous theoretical treatment of any BO system has been well accepted. As soon as the electronic excitations are included in the molecular processes, the Hellmann-Feynman theorem [3] predicts the presence of NAC terms with singularity in the configuration space and these singularities arise due to the fact that electronic states are degenerate at certain points or along a line (seam) in the configuration space [4]

Though the existence of singularity in non-adiabatic coupling terms had been overlooked for a quite longer period of time, Longuet-Higgins demonstrated that such singularity destroys the single-valuedness of electronic wavefunction in many molecular systems and therefore, any dynamical calculations for the nuclei need to be performed with care. Herzberg and Longuet-Higgins' (HLH) [5] corrected the multi-valued electronic wavefunction by employing a complex phase factor, known as Longuet-Higgins' phase, in an *ad hoc* manner. In an alternative approach, Mead and Truhlar [6] incorporated a vector potential in the nuclear Hamiltonian to generalize the BO equation as a reminiscent of the complex phase factor treatment of Herzberg and Longuet-Higgins. Kuppermann *et al* [7] and many others [8] evaluated the integral and differential scattering cross sections of H<sub>3</sub> isotopic system, Adhikari *et al* [9] calculated the transition probabilities of a two arrangement channel pseudo Jahn-Teller model and clearly justify the effect of Longuet-Higgins' phase, also known as geometric phase (GP), on reactive/non-reactive transition probabilities leading to a demand to explore the origin of GP from first principles.

Any first principle based theory based on BO treatment starts with the fact that slow-moving nuclei is distinguishable from fast-moving electrons in molecular systems and intends to introduce the BO approximation by neglecting the non-adiabatic coupling (NAC) elements. Since such approximation has been considered as independent of the eigenspectrum of the system, the ordinary BO equations are being frequently used for calculations even for systems with large NAC terms. On the other hand, even if the projection of the total wavefunction on the upper electronic state(s) are negligibly small at sufficiently low energies, the coupling terms arising due to the products between the singularly large NAC terms and the amplitudes of the excited state(s) wavefunctions could be finite in magnitude leading to the breakdown of BO approximation. Therefore, it is a matter of contemporary research how elegantly one can incorporate the NAC terms in the SE and perform the numerical calculations. Since the NAC terms appear in the adiabatic representation of SE with singularity in the configuration space, it is convenient to perform an 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. Such

transformation for a given sub-Hilbert space is guaranteed only when the NAC terms satisfy the so called Curl conditions. Moreover, the formulation of extended BO equations is possible only when the relevant Curls of the NAC terms are zero at and around the conical intersection (CI). Therefore, the Curls of the NAC terms is an important aspect to explore in order to pursue the first principle based BO treatment.

Baer *et al* [10–13] made the first attempts to carry out the first principle based BO treatment of two coupled electronic states as sub-Hilbert space and formulated a new set of two coupled BO equations by grafting the effects of NAC terms into the diagonal to obtain the single surface Extended Born-Oppenheimer (EBO) equations. Varandas and Xu [14] demonstrated an alternative approach for the first principle based BO treatment of two state adiabatic nuclear SE by casting the NAC elements in terms of electronic basis functions angle (mixing angle), found the one-to-one correspondence among mixing [14], adiabatic-diabatic transformation (ADT) [15], and Longuet-Higgins' phase [5] angles and derived the single surface EBO equation in the vicinity of degeneracy. At the first time again, Baer *et al* [16] and Adhikari *et al* [17] had performed the BO treatment for any  $N (\geq 3)$  state coupled BO system in the adiabatic representation of nuclear SE, and formulated the EBO equations considering a model situation of the adiabatic Hamiltonian. This formulation does not have the scope to demonstrate (a) how the Curl conditions are being satisfied – a necessity to pursue adiabatic-diabatic transformation; (b) how the Curls could be, if at all, are zeros around CI(s) - a necessary condition to formulate EBO equation. Sarkar *et al* [18,19] has 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 [18,19] EBO equations in terms of electronic basis functions/ADT angles.

In this article, we briefly demonstrate the formulation of the explicit forms of the non-adiabatic coupling elements in terms of ADT angles by considering the validity of ADT condition for any three state sub-Hilbert space and how those explicit forms of the NAC terms satisfy Curl conditions, which ensures adiabatic-diabatic transformation. 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. On the other hand, 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 mention about the analytical proof for the validity of such relations. With these theoretical background, we consider a diabatic Hamiltonian known as induced Renner-Teller model, analytically calculate the electronic basis functions, non-adiabatic coupling elements, and their Curl and divergence equations. The nature of all these quantities are being explored at the situation of three state degeneracy or when those states are approaching to form three state degeneracy.

## 2. The theoretical background on the Born-Oppenheimer treatment of a three state sub-Hilbert space

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

$$\Psi(\mathbf{n}, \mathbf{e}) = \sum_{i=1}^3 \psi_i(\mathbf{n}) \xi_i(\mathbf{e}, \mathbf{n}), \quad (1)$$

where  $\xi_i(\mathbf{e}, \mathbf{n})$ s are the electronic eigenfunctions with nuclear coordinate dependent expansion coefficients,  $\psi_i(\mathbf{n})$ s subsequently termed as nuclear wavefunction and the sets of nuclear and electronic coordinates are defined as  $\mathbf{n}$  and  $\mathbf{e}$ , 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 :

$$\begin{aligned} \hat{H} &= \hat{T}_n + \hat{H}_e(\mathbf{e}, \mathbf{n}), \\ \hat{T}_n &= \frac{\hbar^2}{2m} \sum_n \nabla_n^2, \\ \hat{H}_e(\mathbf{e}, \mathbf{n}) \xi_i(\mathbf{e}, \mathbf{n}) &= u_i(\mathbf{n}) \xi_i(\mathbf{e}, \mathbf{n}) \end{aligned} \quad (2)$$

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

$$\begin{aligned} \sum_{j=1}^3 (H_{ij} - E\delta_{ij}) \psi_j(\mathbf{n}) &= 0, \quad i = 1, 2, 3 \\ H_{ii} &= -\frac{\hbar^2}{2m} (\nabla^2 + 2\tau_{ii}^{(1)} \cdot \nabla + \tau_{ii}^{(2)}) + u_i(\mathbf{n}), \\ H_{ij} &= -\frac{\hbar^2}{2m} (2\tau_{ij}^{(1)} \cdot \nabla + \tau_{ij}^{(2)}) = H_{ji}^\dagger, \\ \tau_{ij}^{(1)} &= \langle \xi_i(\mathbf{e}, \mathbf{n}) | \nabla | \xi_j(\mathbf{e}, \mathbf{n}) \rangle, \quad \tau_{ij}^{(2)} = \langle \xi_i(\mathbf{e}, \mathbf{n}) | \nabla^2 | \xi_j(\mathbf{e}, \mathbf{n}) \rangle, \\ \langle \xi_i(\mathbf{e}, \mathbf{n}) | \xi_j(\mathbf{e}, \mathbf{n}) \rangle &= \delta_{ij}, \end{aligned} \quad (3)$$

where  $\tau_{ij}^{(1)}$  and  $\tau_{ij}^{(2)}$  are the elements of non-adiabatic coupling matrices of the first

$[\tau^{(1)}]$  and second  $[\tau^{(2)}]$  kind, respectively and for a given sub-Hilbert space, the two kinds of NAC matrices are related as :

$$\tau^{(2)} = \tau^{(1)} \cdot \tau^{(1)} + \nabla \tau^{(1)}, \quad (4)$$

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

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

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

$$\tau = \begin{pmatrix} 0 & \tau_{12} & \tau_{13} \\ -\tau_{12} & 0 & \tau_{23} \\ -\tau_{13} & -\tau_{23} & 0 \end{pmatrix}. \quad (6)$$

Since the three states constitute the sub-Hilbert space, *i.e.*, the complete space, 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,

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

under the condition:

$$\nabla \mathbf{A} + \tau \mathbf{A} = 0. \quad (8)$$

This equation is known as Adiabatic-Diabatic Transformation (ADT) condition [15]. The eq. (8) can ensure meaningful solution only when the chosen form of  $\mathbf{A}$  matrix has the following features : (a) It is orthogonal at any point in configuration space; (b) Its' elements are cyclic functions with respect to a parameter, *i.e.*, starting with an unit diagonal matrix, the chosen form of  $\mathbf{A}$  matrix has to generate a diagonal matrix with even number ( $-1$ )s after completing the cycle. Since the model form of  $\mathbf{A}$  has to be an orthogonal matrix and the ortho-normality conditions demand the fulfillment of six relations for a three-dimensional Hilbert space with nine elements, three independent variables namely Euler like angles of rotation  $[\theta_{12}(n), \theta_{23}(n)$  and  $\theta_{13}(n)]$ , commonly called ADT angles, are the natural requirement to construct the three state  $\mathbf{A}$  matrix by taking the product of three rotation matrices,  $\mathbf{A}_{12}(\theta_{12})$ ,  $\mathbf{A}_{23}(\theta_{23})$ , and  $\mathbf{A}_{13}(\theta_{13})$  and one of the ways of their product yields :

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

$$= \begin{pmatrix} \cos \theta_{12} \cos \theta_{13} & \sin \theta_{12} \cos \theta_{23} & \cos \theta_{12} \sin \theta_{13} \\ -\sin \theta_{12} \sin \theta_{13} \sin \theta_{23} & & + \sin \theta_{12} \cos \theta_{13} \sin \theta_{23} \\ -\sin \theta_{12} \cos \theta_{13} & \cos \theta_{12} \cos \theta_{23} & -\sin \theta_{12} \sin \theta_{13} \\ -\cos \theta_{12} \sin \theta_{13} \sin \theta_{23} & & + \sin \theta_{12} \cos \theta_{13} \sin \theta_{23} \\ -\sin \theta_{13} \cos \theta_{23} & -\sin \theta_{23} & \cos \theta_{13} \cos \theta_{23} \end{pmatrix}. \quad (9)$$

When we substitute the above model form of  $\mathbf{A}$  matrix [eq. (9)] and the anti-symmetric form of  $\tau$  matrix [Eq. (6)] in eq. (8), a simple manipulation brings the explicit expression of  $\tau$  matrix elements in terms of ADT angles :

$$\tau_{12} = -\nabla\theta_{12} - \sin\theta_{23}\nabla\theta_{13} , \quad (10a)$$

$$\tau_{23} = \sin\theta_{12} \cos\theta_{23}\nabla\theta_{13} - \cos\theta_{12}\nabla\theta_{23} , \quad (10b)$$

$$\tau_{13} = -\cos\theta_{12} \cos\theta_{23}\nabla\theta_{13} - \sin\theta_{12}\nabla\theta_{23} . \quad (10c)$$

In a similar manner, if we replace the so called ADT angles [ $\theta_{12}(\mathbf{n})$ ,  $\theta_{13}(\mathbf{n})$ , and  $\theta_{23}(\mathbf{n})$ ] by electronic basis functions angles, namely, mixing angles [ $\alpha(\mathbf{n})$ ,  $\beta(\mathbf{n})$ , and  $\gamma(\mathbf{n})$ ] in the ADT matrix,  $\mathbf{A}$  [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. (10)] as functions of mixing angles and thereby, show the one-to-one correspondence among ADT and mixing angles. Since the *ab initio* calculation can provide the non-adiabatic coupling elements  $\tau_{12}$ ,  $\tau_{23}$  and  $\tau_{13}$  for a particular nuclear configuration and the solution of eqs. (10) are the ADT angles for the same nuclear configuration, one can construct the ADT matrix  $\mathbf{A}$  and transform the adiabatic SE [eq. (5)] to the diabatic equations [eq. (7)]. On the other hand, if we have the total electron-nuclear Hamiltonian of a molecular system in the diabatic representation, one can calculate the ADT matrix by diagonalizing the  $\mathbf{W}$  matrix [eq. (7)] and thereby, obtain the NAC elements through eq. (8).

At this junction, we may mention that the adiabatic-diabatic 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. A Curl condition for each NAC element,  $\tau_{ij}$ , has been derived [15] and proved to exist for an isolated group of states (sub-Hilbert space) by considering the analyticity of the ADT matrix  $\mathbf{A}$  for a pair of nuclear degrees of freedom,

$$\text{Curl } \tau_{ij}^{pq} = \frac{\partial}{\partial p} \tau_{ij}^q - \frac{\partial}{\partial q} \tau_{ij}^p = (\tau^q \tau^p)_j - (\tau^p \tau^q)_j ,$$

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

where  $p$  and  $q$  are in *Cartesian coordinates* with  $\nabla_p = \frac{\partial}{\partial p}$  and  $\nabla_q = \frac{\partial}{\partial q}$  .

At present, for a given three dimensional sub-Hilbert space, we present that the explicit forms of the NAC elements in terms of ADT angles satisfy [eq. (10)] 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  $\left[ \frac{\partial}{\partial p} \tau_{ij}^q - \frac{\partial}{\partial q} \tau_{ij}^p \right]$  appears to be analytically equal with the corresponding element arising from the

difference of the products taken at different order between the component NAC matrices  $[(\tau^q \tau^p)_{ij} - (\tau^p \tau^q)_{ij}]$  as below :

$$\text{Curl } \tau_{12}^{pq} = [\tau \times \tau]_{12}^{pq} = -\cos \theta_{23} (\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13}) \quad (12a)$$

$$\begin{aligned} \text{Curl } \tau_{23}^{pq} = [\tau \times \tau]_{23}^{pq} = & \cos \theta_{12} \cos \theta_{23} (\nabla_q \theta_{12} \nabla_p \theta_{13} - \nabla_p \theta_{12} \nabla_q \theta_{13}) \\ & - \sin \theta_{12} \sin \theta_{23} (\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13}) \\ & + \sin \theta_{12} (\nabla_q \theta_{12} \nabla_p \theta_{23} - \nabla_p \theta_{12} \nabla_q \theta_{23}) \end{aligned} \quad (12b)$$

$$\begin{aligned} \text{Curl } \tau_{13}^{pq} = [\tau \times \tau]_{13}^{pq} = & \sin \theta_{12} \cos \theta_{23} (\nabla_q \theta_{12} \nabla_p \theta_{13} - \nabla_p \theta_{12} \nabla_q \theta_{13}) \\ & + \cos \theta_{12} \sin \theta_{23} (\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13}) \\ & - \cos \theta_{12} (\nabla_q \theta_{12} \nabla_p \theta_{23} - \nabla_p \theta_{12} \nabla_q \theta_{23}) \end{aligned} \quad (12c)$$

where the Divergence of  $\tau_{ij}$ s [eq. (10)] are given by :

$$\begin{aligned} \text{div } \tau_{12} = & 2 \sin \theta_{12} \cos \theta_{12} \cos^2 \theta_{23} (\nabla \theta_{13} \cdot \nabla \theta_{13}) \\ & - 2 \sin \theta_{12} \cos \theta_{12} (\nabla \theta_{23} \cdot \nabla \theta_{23}) - 3 \cos^2 \theta_{12} \cos \theta_{23} (\nabla \theta_{13} \cdot \nabla \theta_{23}) \\ & + \sin^2 \theta_{12} \cos \theta_{23} (\nabla \theta_{13} \cdot \nabla \theta_{23}) - \sin \theta_{23} \nabla^2 \theta_{13} - \nabla^2 \theta_{12} \end{aligned} \quad (13a)$$

$$\begin{aligned} \text{div } \tau_{23} = & 2 \sin \theta_{12} \sin \theta_{23} \cos \theta_{23} (\nabla \theta_{13} \cdot \nabla \theta_{13}) \\ & + 3 \cos \theta_{12} \cos \theta_{23} (\nabla \theta_{12} \cdot \nabla \theta_{23}) + 3 \sin \theta_{12} (\nabla \theta_{12} \cdot \nabla \theta_{23}) \\ & + \sin \theta_{12} \sin \theta_{23} (\nabla \theta_{13} \cdot \nabla \theta_{23}) - \sin \theta_{12} \cos \theta_{23} \nabla^2 \theta_{12} - \cos \theta_{12} \nabla^2 \theta_{23} \end{aligned} \quad (13b)$$

$$\begin{aligned} \text{div } \tau_{13} = & 2 \sin \theta_{12} \sin \theta_{23} \cos \theta_{23} (\nabla \theta_{12} \cdot \nabla \theta_{12}) \\ & + 3 \sin \theta_{12} \cos \theta_{23} (\nabla \theta_{12} \cdot \nabla \theta_{13}) - 3 \cos \theta_{12} (\nabla \theta_{12} \cdot \nabla \theta_{23}) \\ & - \cos \theta_{12} \sin \theta_{23} (\nabla \theta_{13} \cdot \nabla \theta_{23}) - \cos \theta_{12} \cos \theta_{23} \nabla^2 \theta_{13} - \sin \theta_{12} \nabla^2 \theta_{23} \end{aligned} \quad (13c)$$

Since  $\nabla \theta_{ij}$ s and in general,  $\nabla^2 \theta_{ij}$ s are non-zero around the conical intersection, the Divergence of the vector field  $(\tau_{ij})$  are non-vanishing for any arbitrary values of ADT angles and therefore, the vector field may show up non-zero Curl [20,21]. On the other hand, as the non-adiabatic coupling terms may show up singularity (pole) in the configuration space, such vector fields could be resolved into irrotational (longitudinal) and solenoidal (transverse) components [20,21]. The theory of electrodynamics reminds that the Curl of longitudinal part (of vector field) is zero but Curl of transverse part may or may not. The experimental observations on so-called solenoids may bring the argument that if the seams due to conical intersection are considered as infinitesimal narrow "solenoids", seams should produce zero field outside of them. On the contrary, the *ab initio* calculations [22,23] show the presence of non-zero  $\tau$  in the space around

the seams. Thus, it is an important issue to explore the nature of the Curls of the vector fields ( $\tau_{ij}$ s) since the following section demonstrates-in order to carry out further theoretical development like the formulation of single surface EBO equation, it is necessary to know the nature of Curl  $\tau_{ij}^{\rho q}$  quantitatively, at least around the point/seam of CI, for a given sub-Hilbert space.

While formulating EBO equation, we start from the adiabatic representation of SE [eq. (5)] with kinetic coupling terms,

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

and carry out an unitary transformation on eq. (14) by a matrix,  $G(\Psi = G\Phi)$ , such that it leads to the following form :

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

where the eigenvalues ( $\pm i\omega$ ) of the NAC matrix,  $\tau$  should be vectors in order to obtain physically meaningful (a scalar) Hamiltonian [eq. (15)] before one can impose the BO approximation,  $|\psi_1\rangle \gg |\psi_i\rangle$ ,  $i = 2, 3$ , by considering the upper electronic states as classically closed at low enough energy, to formulate the single surface adiabatic nuclear SE (EBO) [16–19]. Since the straight forward diagonalization of  $\tau$  matrix [eq. (10)] gives scalar eigenvalues,

$$\begin{aligned} & \sqrt{\tau_{12} \cdot \tau_{12} + \tau_{23} \cdot \tau_{23} + \tau_{13} \cdot \tau_{13}} \\ & = \pm \left\{ \sum_i \left[ \left( \frac{\partial \theta_{12}}{\partial p_i} \right)^2 + \left( \frac{\partial \theta_{23}}{\partial p_i} \right)^2 + \left( \frac{\partial \theta_{13}}{\partial p_i} \right)^2 + 2 \sin \theta_{23} \left( \frac{\partial \theta_{13}}{\partial p_i} \right) \left( \frac{\partial \theta_{12}}{\partial p_i} \right) \right] \right\}^{1/2} \\ & p_i \equiv x, y, z, \dots \end{aligned} \quad (16)$$

but the requirement of eq. (15) dictates that the eigenvalues ( $\pm i\omega$ ) of  $\tau$  matrix must be vectors, the only possibility remains that the  $\tau$  matrix could be written as the product of a vector function,  $\nabla\eta$  ( $\eta \equiv \theta_{12}$  or  $\theta_{23}$  or  $\theta_{13}$ ) and a ADT/mixing angle dependent anti-symmetric scalar matrix,  $\mathcal{G}(\theta_{12}, \theta_{23}, \theta_{13})$ . It is quite easy to find from

the elements of  $\tau$  matrix [eq. (10)] that if the following identities,  $\left( \frac{\nabla_p \theta_{13}}{\nabla_p \theta_{12}} \right) = \left( \frac{\nabla_q \theta_{13}}{\nabla_q \theta_{12}} \right)$ ,

$$\left( \frac{\nabla_p \theta_{23}}{\nabla_p \theta_{12}} \right) = \left( \frac{\nabla_q \theta_{23}}{\nabla_q \theta_{12}} \right) \quad \text{for any pair of nuclear coordinates, namely, } p \text{ and } p \text{ are valid}$$



at and around the degeneracy point, one can write,

$$\tau = \nabla\theta_{12} \begin{pmatrix} 0 & -1 - \sin\theta_{23} \left( \frac{\nabla_{\rho}\theta_{13}}{\nabla_{\rho}\theta_{12}} \right) & -\sin\theta_{23} \left( \frac{\nabla_{\rho}\theta_{13}}{\nabla_{\rho}\theta_{12}} \right) & \\ & & -\cos\theta_{12} \cos\theta_{23} \left( \frac{\nabla_{\rho}\theta_{13}}{\nabla_{\rho}\theta_{12}} \right) & \\ 1 + \sin\theta_{23} \left( \frac{\nabla_{\rho}\theta_{13}}{\nabla_{\rho}\theta_{12}} \right) & 0 & -\cos\theta_{12} \left( \frac{\nabla_{\rho}\theta_{23}}{\nabla_{\rho}\theta_{12}} \right) & \\ \sin\theta_{12} \left( \frac{\nabla_{\rho}\theta_{23}}{\nabla_{\rho}\theta_{12}} \right) & \cos\theta_{12} \left( \frac{\nabla_{\rho}\theta_{23}}{\nabla_{\rho}\theta_{12}} \right) & 0 & \\ + \cos\theta_{12} \cos\theta_{23} \left( \frac{\nabla_{\rho}\theta_{13}}{\nabla_{\rho}\theta_{12}} \right) & -\sin\theta_{12} \cos\theta_{23} \left( \frac{\nabla_{\rho}\theta_{13}}{\nabla_{\rho}\theta_{12}} \right) & & \end{pmatrix}$$

$$= \nabla\theta_{12} \cdot \mathbf{g}(\theta_{12}, \theta_{23}, \theta_{13}), \tag{17}$$

with eigenvalues,

$$0, \pm i\omega \text{ and } \omega = \nabla\theta_{12} \left[ 1 + \left( \frac{\nabla_{\rho}\theta_{13}}{\nabla_{\rho}\theta_{12}} \right)^2 + \left( \frac{\nabla_{\rho}\theta_{23}}{\nabla_{\rho}\theta_{12}} \right)^2 + 2 \sin\theta_{23} \left( \frac{\nabla_{\rho}\theta_{13}}{\nabla_{\rho}\theta_{12}} \right) \right]^{1/2}.$$

Therefore, we need to explore the validity of these identities, i.e.,  $\text{Curl } \tau_j^{pq} = 0s$  [see eq. (12)] at and around Cl(s). Since the details of the proof to explore the validity of these identities are demonstrated in our previous articles [18,19], a brief discussion only is being presented here. We consider one of the above such identities either in polar or in Cartesian coordinates, where the ADT angles are assumed to be dependent, let say, on three nuclear coordinates and find its' nature by using the Jacobian determinant for the transformation from Cartesian to polar,

$$J(r, \theta, \phi) = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial y}{\partial r} & \frac{\partial z}{\partial r} \\ \frac{\partial x}{\partial \theta} & \frac{\partial y}{\partial \theta} & \frac{\partial z}{\partial \theta} \\ \frac{\partial x}{\partial \phi} & \frac{\partial y}{\partial \phi} & \frac{\partial z}{\partial \phi} \end{vmatrix} = \begin{vmatrix} \sin\theta \cos\phi & \sin\theta \sin\phi & \cos\phi \\ r \cos\theta \cos\phi & r \cos\theta \sin\phi & -r \sin\theta \\ -r \sin\theta \sin\phi & r \sin\theta \cos\phi & 0 \end{vmatrix} \tag{18}$$

or *vice versa*. If the origin of the coordinate system [ $r = 0$  ( $x = 0, y = 0, z = 0$ )] coincides with the point of conical intersection, various components of the Jacobian determinant vanishes at that point (CI) but the transformation remain valid with zero content at  $r = 0$ , along with  $\partial z/\partial\phi = 0$  (also at  $r \neq 0$ ),  $\partial y/\partial\phi = r\sin\theta\cos\phi = 0$ ,  $\partial z/\partial\theta = -r\sin\theta = 0$ ,  $\partial y/\partial\theta = r\cos\theta\sin\phi = 0$ . Even if the point of conical intersection(s) is away from the origin of the coordinate system, parametric representation for the vector equation of a conical surface predicts  $J(r,\theta) = 0$ ,  $J(r,\phi) = 0$  and  $J(\theta,\phi) = 0$  at the

singularity (CI) (see Appendix B of Ref. [18]). Thus, the quantities  $\left(\frac{\nabla_\rho\theta_{13}}{\nabla_\rho\theta_{12}}\right) = \left(\frac{\nabla_q\theta_{13}}{\nabla_q\theta_{12}}\right)$ ,

$\left(\frac{\nabla_\rho\theta_{23}}{\nabla_\rho\theta_{12}}\right) = \left(\frac{\nabla_q\theta_{23}}{\nabla_q\theta_{12}}\right)$  appear either identically or approximately zero around the conical intersection, and we intend to rewrite eq. (15) as,

$$-\frac{\hbar^2}{2m} [(\nabla + i\omega)^2\Phi] - \frac{\hbar^2}{2m} [(G^\dagger\nabla^2G\Phi - \nabla^2\Phi) + (i\omega G^\dagger\nabla G\Phi - i\omega\nabla\Phi) + (G^\dagger\nabla Gi\omega\Phi - \nabla i\omega\Phi)] + [(V - E)\Phi] = 0, \tag{19}$$

where  $G$  is the transformation matrix that diagonalizes the anti-symmetric scalar matrix,  $g(\theta_{12}, \theta_{13}, \theta_{23})$ . For symbolic convenience, now onwards we shall replace  $G^\dagger$  as  $G^d$  and its' element  $(G^\dagger)_{ij}$  as  $(G^d)_{ij}$  ( $\equiv G^d_{ij}$ ).

The  $i$ -th BO equation can be written from the matrix equation [eq. (19)] as below,

$$-\frac{\hbar^2}{2m} [(\nabla + i\omega)^2\Phi]_i - \frac{\hbar^2}{2m} \left[ \sum_k G^d_{ik}\nabla^2\psi_k - \sum_k \nabla^2(G^d_{ik}\psi_k) + \sum_k i\omega_i G^d_{ik}\nabla\psi_k - \sum_k i\omega_l (G^d_{ik}\psi_k) + \sum_{km} G^d_{ik}\nabla(\tau_{km}\psi_k) - \sum_{km} \nabla(G^d_{ik}\tau_{km}\psi_m) \right] + [(V - E)\Phi]_i = 0. \tag{20}$$

We manipulate the eq. (20) by considering the following aspects :

(a) Since the matrix representation of the ADT is given by,  $\Phi = G^d\psi$ , one can have the general identity

$$\psi_k = \frac{1}{G^d_{kk}} \phi_k - \sum_{l \neq k} \frac{G^d_{kl}}{G^d_{kk}} \psi_l \quad k, l = 1, 2, 3. \tag{21}$$

(b) The product,  $V\Phi$ , for the  $i$ -th equation can be rearranged as below,

$$(V\Phi)_i = u_i\phi_i + \sum_{j=2}^4 G^d_{ij}(u_j - u_i)\psi_j, \quad i = 1, 2, 3. \tag{22}$$

(c) We impose the BO approximation,  $|\psi_1\rangle \gg |\psi_i\rangle$ ,  $i = 2, 3$  (considering that at low enough energy, both the upper electronic states are classically closed) in the eq. (20) to write the ground state EBO equation as,

$$\frac{\hbar^2}{2m} (\nabla + i\omega_1)^2 \phi_1 - \frac{\hbar^2}{2m} \left[ -2 \left( \frac{\nabla G_{11}^d}{G_{11}^d} \right) \nabla \phi_1 + 2 \left( \frac{\nabla G_{11}^d}{G_{11}^d} \right)^2 \phi_1 - \left( \frac{\nabla^2 G_{11}^d}{G_{11}^d} \right) \phi_1 \right. \\ \left. + \left( \frac{\nabla G_{11}^d}{G_{11}^d} \right) \phi_1 - \left( \frac{\nabla G_{12}^d}{G_{11}^d} \right) \tau_{21} \phi_1 - \left( \frac{\nabla G_{13}^d}{G_{11}^d} \right) \tau_{31} \phi_1 \right] + (u_1 - E) \phi_1 = 0. \quad (23)$$

If we now introduce the approximation namely the transformation matrix ( $\mathbf{G}$ ) elements are slowly varying functions of nuclear coordinates and then, the matrix ( $\mathbf{G}$ ) commutes with the gradient operator  $\nabla$ , both eqs. (19) and (23) lead to the following approximate EBO equation [18] for the ground electronic state :

$$\frac{\hbar^2}{2m} (\nabla + i\omega)^2 \phi_1 + (u_1 - E) \phi_1 = 0, \quad (24)$$

where this equation [eq. (24)] with simple BO approximation becomes :

$$\frac{\hbar^2}{2m} \nabla^2 \phi_1 + (u_1 - E) \phi_1 = 0. \quad (25)$$

In the following sections, we explore the validity of the identities leading to zero Curl using an induced Renner-Teller type model, when the three states are either degenerate at a point or approaching to form three states degeneracy at the same point. At this junction, we remind that (a) since we start with a diabatic model Hamiltonian, the validity of Curl conditions are inbuilt but (b) the validity of zero Curls bring the Extended Born-Oppenheimer (EBO) equation, on which one can carry out accurate calculation on the ground state EBO equation by taking into account the effect of upper PESSs.

### 3. The induced Renner-Teller type model

Degenerate electronic states are the typical examples for the cause of failure of adiabatic (BO) approximation. In the case of linear molecules, the coupling among the vibrational modes of degenerate electronic states is known as Renner-Teller (RT) effect [24]. Such effect commonly arises due to an isolated  $\Pi$  states of a molecule, namely, those  $\Pi$  states show negligible interaction with other electronic states. This situation corresponds the well-known RT case of two interacting ( $\Pi$ ) states through vibronic coupling with quadratic terms. On the other hand, the interaction between the  $\Pi$  states can be induced by a  $\Sigma$  state through a bending mode with linear coupling terms and thereby, demonstrate induced RT effect [25,26].

We consider two nuclear coordinates : the bending amplitude is denoted by a dimensionless normal coordinate,  $\rho$  and  $\phi$  is the vibrational azimuthal angle with respect to an arbitrary reference plane. These two coordinates can be termed as polar coordinates and related with Cartesian :  $x = \rho \cos\phi$  and  $y = \rho \sin\phi$ . In the diabatic representation (more precisely, crude adiabatic basis), we locate the system at the reference geometry given by  $\rho = 0$  and  $\phi = 0$  (i.e.,  $x = 0$  and  $y = 0$ ). When the nuclear vibration is assumed harmonic, the electronic Hamiltonian takes the following form after considering symmetry of the problem (RT system) within the first order expansion in  $\rho$  :

$$H_{\epsilon}^E = \begin{pmatrix} E_{\Pi} + \frac{1}{2}\omega\rho^2 & 0 & \lambda\rho \exp(i\phi) \\ 0 & E_{\Pi} + \frac{1}{2}\omega\rho^2 & \lambda\rho \exp(-i\phi) \\ \lambda\rho \exp(-i\phi) & \lambda\rho \exp(i\phi) & E_{\Sigma} + \frac{1}{2}\omega\rho^2 \end{pmatrix} \quad (26)$$

where the frequency of the harmonic potential is  $\omega$ ,  $E_{\Pi}$  and  $E_{\Sigma}$  are the energies of the  $\Pi$  and  $\Sigma$  states at the equilibrium geometry and  $\lambda$  is a coupling constant.

The electronic Hamiltonian [eq. (26)] under the following unitary transformation,

$$U_{\epsilon} = \frac{1}{\sqrt{2}} \begin{pmatrix} -i & 0 \\ i & 0 \\ 0 & \sqrt{2} \end{pmatrix} \quad (27)$$

takes the following form in polar coordinates  $\rho$  and  $\phi$  :

$$H_{\theta} = U_{\epsilon}^{\dagger} H_{\epsilon}^E U_{\epsilon} = \begin{pmatrix} E_{\Pi} + \frac{1}{2}\omega\rho^2 & 0 & \sqrt{2}\lambda\rho \cos\phi \\ 0 & E_{\Pi} + \frac{1}{2}\omega\rho^2 & -\sqrt{2}\lambda\rho \sin\phi \\ \sqrt{2}\lambda\rho \cos\phi & -\sqrt{2}\lambda\rho \sin\phi & E_{\Sigma} + \frac{1}{2}\omega\rho^2 \end{pmatrix} \quad (28)$$

where the kinetic energy operator of the nuclear motion is :

$$\hat{T}_N = -\frac{\omega}{2} \left( \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right). \quad (29)$$

#### 4. The non adiabatic coupling (NAC) elements and their Curl-divergence equations

We obtain the analytic form of the NAC terms by analyzing the eigenvectors of the

potentially coupled diabatic Hamiltonian ( $H_0$ ) [eq. (28)] matrix :

$$\mathbf{S} = \begin{pmatrix} \sin \phi & w_+ \cos \phi & w_- \cos \phi \\ \cos \phi & -w_+ \sin \phi & -w_- \sin \phi \\ 0 & -w_- & w_+ \end{pmatrix}, \tag{30}$$

with  $w_{\pm} = \frac{1}{\sqrt{2}} \left\{ \frac{[(E_{\Sigma} - E_{\Pi})^2 + 8\lambda^2 \rho^2]^{1/2} \pm (E_{\Sigma} - E_{\Pi})}{[(E_{\Sigma} - E_{\Pi})^2 + 8\lambda^2 \rho^2]^{1/2}} \right\}^{1/2}$ ,  $\rho^2 = x^2 + y^2$  and  $\Delta = \frac{1}{2}(E_{\Sigma} - E_{\Pi})$ ,

ie, the energy gap parameter between the  $\Pi$  and  $\Sigma$  states.

The matrix  $\mathbf{S}$  diagonalize the matrix  $H_0$  as

$$\mathbf{S}^\dagger H_0 \mathbf{S} = \mathbf{V} = \begin{pmatrix} V_{\Pi} & 0 & 0 \\ 0 & V_- & 0 \\ 0 & 0 & V_+ \end{pmatrix} \tag{31}$$

where the adiabatic potential energy surfaces are given by .

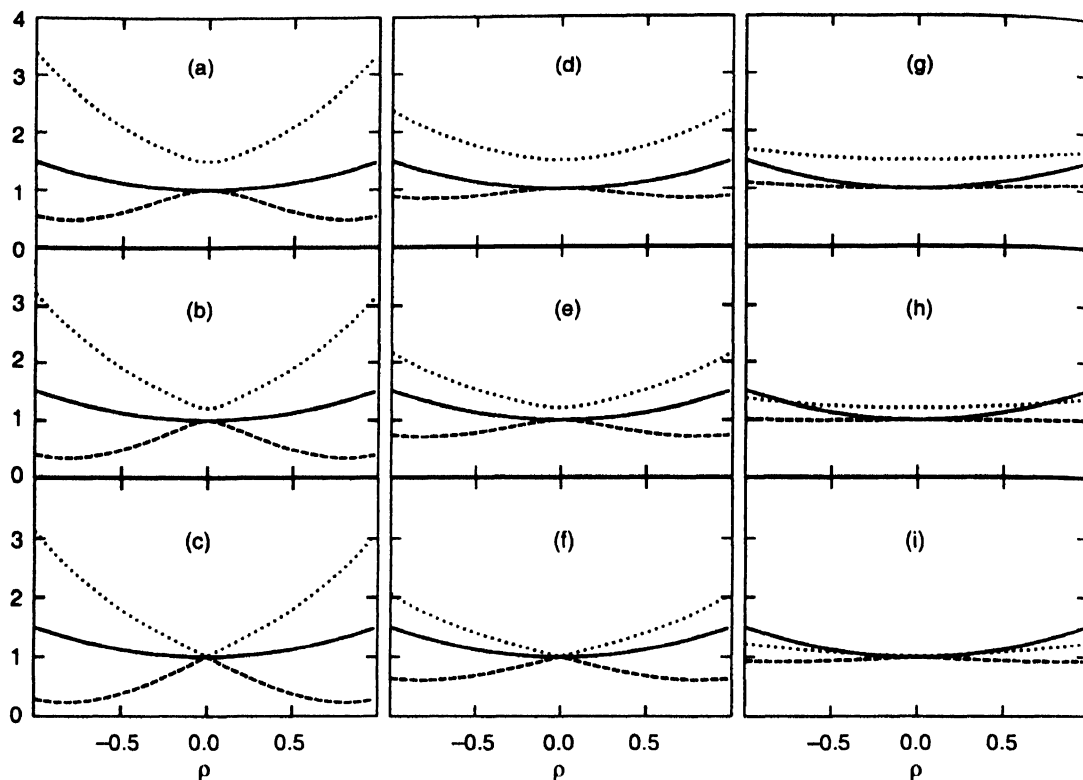
$$V_{\Pi} = E_{\Pi} + \frac{1}{2} \omega \rho^2 \tag{32}$$

$$V_{\pm} = \frac{1}{2}(E_{\Sigma} + E_{\Pi}) + \frac{1}{2} \omega \rho^2 \pm \sqrt{\left[ \frac{1}{2}(E_{\Sigma} + E_{\Pi}) \right]^2 + 2\lambda^2 \rho^2}. \tag{33}$$

Figures 1(a)-(i) present adiabatic PESs as functions of the nuclear coordinate,  $\rho$  only (because surfaces are independent of  $\phi$ ) for various parametric values of the energy gap,  $2\Delta$  and coupling parameter,  $\lambda$ . Though the polar radius,  $\rho$ , is defined either for positive or with negative values, figures are plotted for both values just in order to keep better views. For any non-zero values of the gap,  $2\Delta$ , both the  $\Pi$  states show degeneracy at  $\rho = 0$  but split at  $\rho \neq 0$  gradually with increasing values of  $\lambda$ . On the other hand, as the gap decreases, the adiabatic surfaces tend to form degeneracy at a point.

Considering the definition of non-adiabatic coupling elements of the first kind [eq (3)], the derivative couplings among the electronic states can be calculated as

$$\mathbf{S}^\dagger \nabla \mathbf{S} = \begin{pmatrix} 0 & -w_+ \nabla \phi & -w_- \nabla \phi \\ w_+ \nabla \phi & 0 & w_+ \nabla w_- - w_- \nabla w_+ \\ w_- \nabla \phi & -w_+ \nabla w_- + w_- \nabla w_+ & 0 \end{pmatrix} \tag{34}$$



**Figure 1.** The three adiabatic potential energy curves as a function of  $\rho$  where (a), (b) and (c) are for  $\lambda = 1.0$ ,  $\omega = 1.0$  with  $\Delta$  values 0.5, 0.2 and 0.01, respectively. Figures 1(d), (e) and (f) are for  $\lambda = 0.5$ ,  $\omega = 1.0$  with values 0.5, 0.2 and 0.01, respectively. Figures 1(g), (h) and (i) are for  $\lambda = 0.1$ ,  $\omega = 1.0$  with  $\Delta$  values 0.5, 0.2 and 0.01, respectively.

where analytical forms of the  $\rho$  and 0 components ( $\tau^\rho$  and  $\tau^0$ ) of the NAC elements are :

$$\tau^\rho = \begin{pmatrix} 0 & -w_+ \nabla_\rho \phi & -w_- \nabla_\rho \phi \\ w_+ \nabla_\rho \phi & 0 & w_+ \nabla_\rho w_- - w_- \nabla_\rho w_+ \\ w_- \nabla_\rho \phi & -w_+ \nabla_\rho w_- + w_- \nabla_\rho w_+ & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & w_+ \nabla_\rho w_- - w_- \nabla_\rho w_+ \\ 0 & -w_+ \nabla_\rho w_- + w_- \nabla_\rho w_+ & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} \frac{\Delta\lambda}{(\Delta^2 + 2\lambda^2\rho^2)} \\ 0 & -\frac{1}{\sqrt{2}} \frac{\Delta\lambda}{(\Delta^2 + 2\lambda^2\rho^2)} & 0 \end{pmatrix} \quad (35)$$

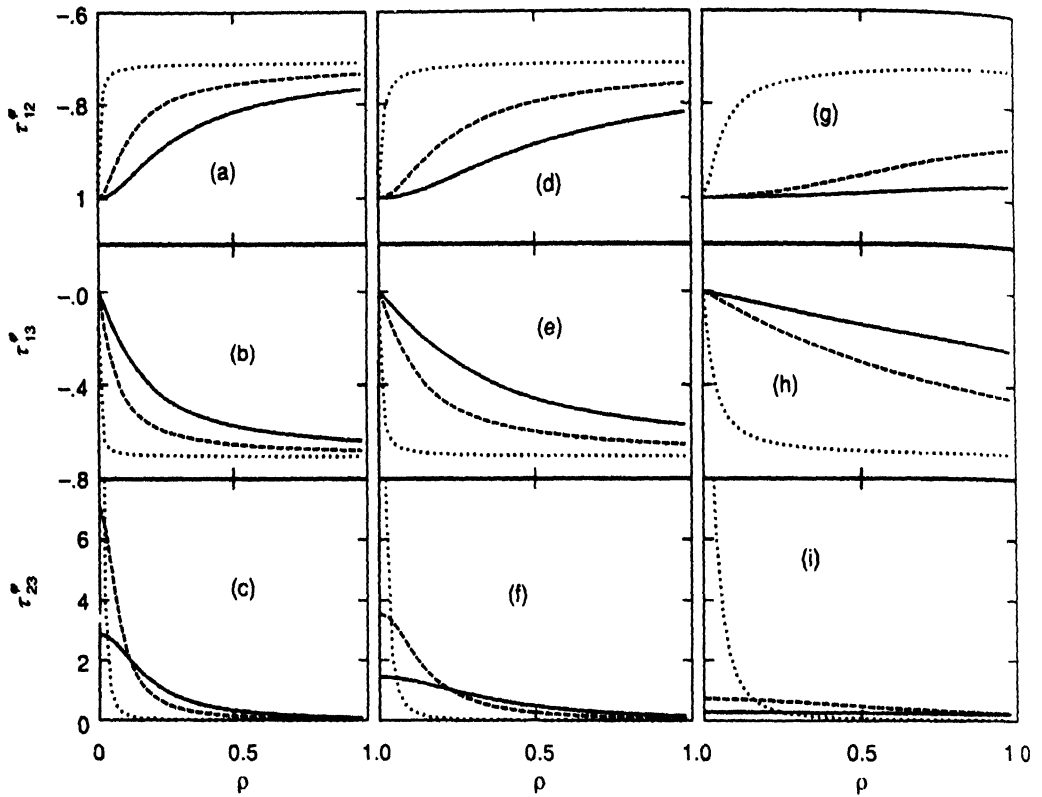
and

$$\begin{aligned} \tau^\phi &= \frac{1}{\rho} \begin{pmatrix} 0 & -w_+\nabla_\phi\phi & -w_-\nabla_\phi\phi \\ w_+\nabla_\phi\phi & 0 & w_+\nabla_\phi w_- - w_-\nabla_\phi w_+ \\ w_-\nabla_\phi\phi & -w_+\nabla_\phi w_- + w_-\nabla_\phi w_+ & 0 \end{pmatrix} \\ &= \frac{1}{\rho} \begin{pmatrix} 0 & -w_+ & -w_- \\ w_+ & 0 & 0 \\ w_- & 0 & 0 \end{pmatrix} \end{aligned}$$

$$= \frac{1}{\rho} \begin{pmatrix} 0 & -\frac{1}{\sqrt{2}} \left[ 1 + \frac{\Delta}{(\Delta^2 + 2\lambda^2\rho^2)} \right]^{1/2} & -\frac{1}{\sqrt{2}} \left[ 1 - \frac{\Delta}{(\Delta^2 + 2\lambda^2\rho^2)} \right]^{1/2} \\ \frac{1}{\sqrt{2}} \left[ 1 + \frac{\Delta}{(\Delta^2 + 2\lambda^2\rho^2)} \right]^{1/2} & 0 & 0 \\ \frac{1}{\sqrt{2}} \left[ 1 - \frac{\Delta}{(\Delta^2 + 2\lambda^2\rho^2)} \right]^{1/2} & 0 & 0 \end{pmatrix} \quad (36)$$

respectively.

It is important to note that all the NAC elements, both their  $\rho$  or  $\phi$  components, are independent of the nuclear coordinate,  $\phi$  but depends on  $\rho$  along with the parameters,  $\Delta$  and  $\rho$ . It appears that if the  $\phi$  components of the NAC terms are non-zero, invariably its'  $\rho$  components are zeros and *vice versa*, i.e.,  $\tau_{12}^\phi \neq 0$ ,  $\tau_{12}^\rho = 0$ ,  $\tau_{13}^\phi \neq 0$ ,  $\tau_{13}^\rho = 0$ ,  $\tau_{23}^\phi = 0$ , and  $\tau_{23}^\rho \neq 0$ . Moreover, each NAC element shows singularity, namely, the denominator approaches to zero in a faster manner than the numerator, at  $\rho \rightarrow 0$  under the condition  $\Delta = \alpha + \rho^n$  with  $\alpha = 0$  and  $n = 1$ . Figures 2(a)-(i) display the non-zero components of the NAC elements as functions of  $\rho$  for various values of  $\Delta$  and  $\lambda$ .



**Figure 2.** The components of the non adiabatic coupling elements as a function of  $\rho$  where (a), (b) and (c) are the three NAC terms ( $\tau_{12}^\rho$ ,  $\tau_{13}^\rho$ , and  $\tau_{23}^\rho$ ) for  $\omega = 1.0$ ,  $\lambda = 1.0$  with  $\Delta = 0.5$  (blue line),  $\Delta = 0.2$  (green line) and  $\Delta = 0.01$  (red line). Figures (d), (e) and (f) are for  $\lambda = 0.5$ , Figures (g), (h) and (i) are for  $\lambda = 0.1$ , respectively.

The Curl-Divergence equations for NAC elements are given by :

$$\text{Curl } \tau = \frac{1}{\rho} \left( \frac{\partial}{\partial \rho} \tau'_\phi - \frac{\partial}{\partial \phi} \tau'_\rho \right) = \frac{1}{\rho} (\tau_\rho \tau'_\phi - \tau_\phi \tau'_\rho) \quad \tau'_\phi = \rho \tau'_\phi$$

$$= \frac{1}{\rho} \begin{pmatrix} 0 & -\nabla_\rho w_+ & -\nabla_\rho w_- \\ \nabla_\rho w_+ & 0 & 0 \\ \nabla_\rho w_- & 0 & 0 \end{pmatrix} \tag{37}$$



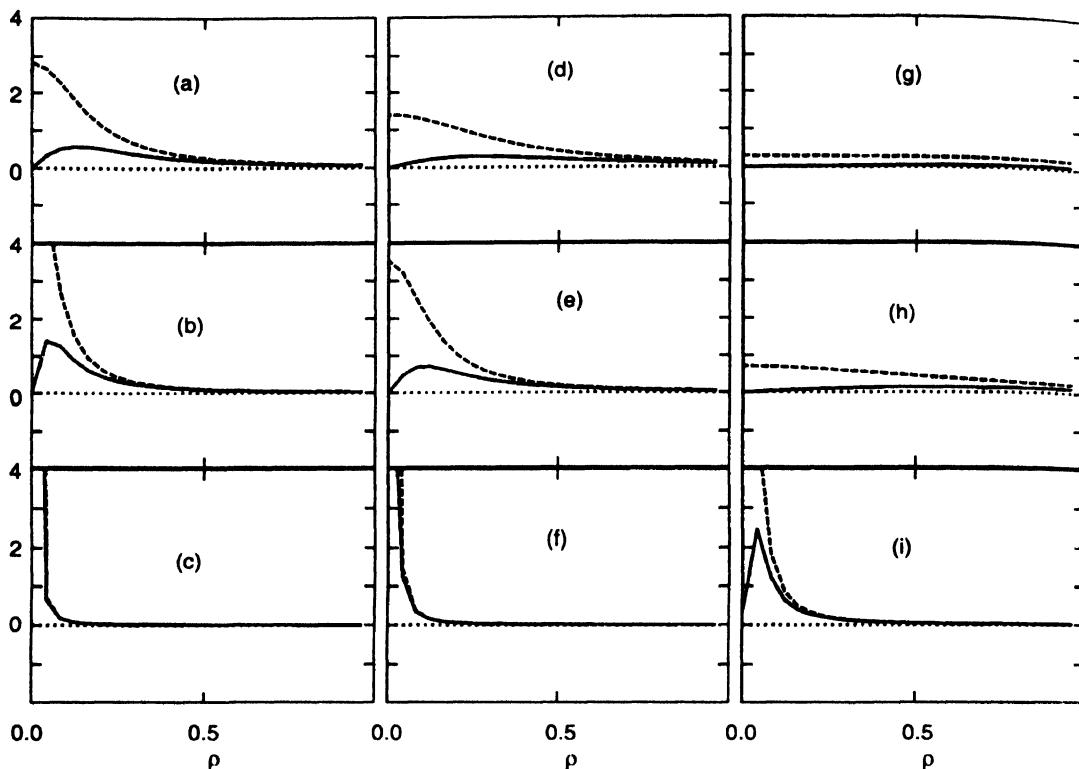
$$= \begin{pmatrix} 0 & \frac{\Delta\lambda^2}{\sqrt{2}(\Delta^2 + 2\lambda^2\rho^2)^{3/2}} \times & -\frac{\Delta\lambda^2}{\sqrt{2}(\Delta^2 + 2\lambda^2\rho^2)^{3/2}} \times \\ & \left[1 + \frac{\Delta}{\sqrt{\Delta^2 + 2\lambda^2\rho^2}}\right]^{-1/2} & \left[1 - \frac{\Delta}{\sqrt{\Delta^2 + 2\lambda^2\rho^2}}\right]^{-1/2} \\ -\frac{\Delta\lambda^2}{\sqrt{2}(\Delta^2 + 2\lambda^2\rho^2)^{3/2}} \times & 0 & 0 \\ \left[1 + \frac{\Delta}{\sqrt{\Delta^2 + 2\lambda^2\rho^2}}\right]^{-1/2} & & \\ \frac{\Delta\lambda^2}{\sqrt{2}(\Delta^2 + 2\lambda^2\rho^2)^{3/2}} \times & 0 & 0 \\ \left[1 - \frac{\Delta}{\sqrt{\Delta^2 + 2\lambda^2\rho^2}}\right]^{-1/2} & & \end{pmatrix} \quad (38)$$

and

$$\text{Div } \tau = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & w_+ \nabla_\rho^2 w_- - w_- \nabla_\rho^2 w_+ \\ 0 & -(w_+ \nabla_\rho^2 w_- - w_- \nabla_\rho^2 w_+) & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\frac{2\sqrt{2}\Delta\lambda^3\rho}{(\Delta^2 + 2\lambda^2\rho^2)^2} \\ 0 & \frac{2\sqrt{2}\Delta\lambda^3\rho}{(\Delta^2 + 2\lambda^2\rho^2)^2} & 0 \end{pmatrix} \quad (39)$$

Figures 3(a)-(i) present the Curl of NAC terms as functions of  $\rho$  for three different values of the parameters,  $\Delta$  and  $\lambda$ . It is quite clear that as the gap between the  $\Pi$  and  $\Sigma$  state,  $\Delta$ , and the force constant,  $\lambda$ , decreases, Curls of all the NAC elements approach to zero as functions of  $\rho$ . The analytical expressions of Curls of the NAC elements demonstrate that the Curls are zeros, namely, the numerator of the Curls approaches to zero in a faster manner than the denominator at  $\rho \rightarrow 0$  under the condition  $\Delta = \alpha + \rho^n$  with  $\alpha = 0$  and  $n = 4$ . Since  $\tau_{12}^\phi$  and  $\tau_{13}^\phi$  are independent of



**Figure 3.** The three Curl components of the NAC terms ( $\text{Curl}\tau_{12}$  (red),  $\text{Curl}\tau_{13}$  (green), and  $\text{Curl}\tau_{23}$  (blue)) as a function of  $\rho$  where (a), (b) and (c) are for  $\lambda = 1.0$ ,  $\omega = 1.0$  with  $\Delta$  values 0.5, 0.2 and 0.01, respectively. Figures (d), (e) and (f) are for  $\lambda = 0.5$ ,  $\omega = 1.0$  with  $\Delta$  values 0.5, 0.2 and 0.01, respectively. Figures (g), (h) and (i) are for  $\lambda = 0.1$ ,  $\omega = 1.0$  with  $\Delta$  values 0.5, 0.2 and 0.01, respectively.

$\phi$  and the corresponding  $\rho$  components,  $\tau_{12}^\rho$  and  $\tau_{13}^\rho$  are zeros, the calculated divergence of these two elements are expected to be zeros. On the other hand, we find that the  $\phi$  component of the NAC element,  $\tau_{23}^\phi$  is zero but its'  $\rho$  component,  $\tau_{23}^\rho$  is non-zero and therefore, the element shows non-zero divergence as shown in Figure 4.

**5. The NAC elements at three state degeneracy and formulation of extended Born-Oppenheimer equation**

When the gap,  $\Delta$ , between the  $\Pi$  and  $\Sigma$  states is negligibly small or even at zero, the NAC matrices become :

$$\tau^\rho = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}; \quad \tau^\phi = \frac{1}{\rho} \begin{pmatrix} 0 & -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 0 & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 \end{pmatrix}, \quad (40)$$

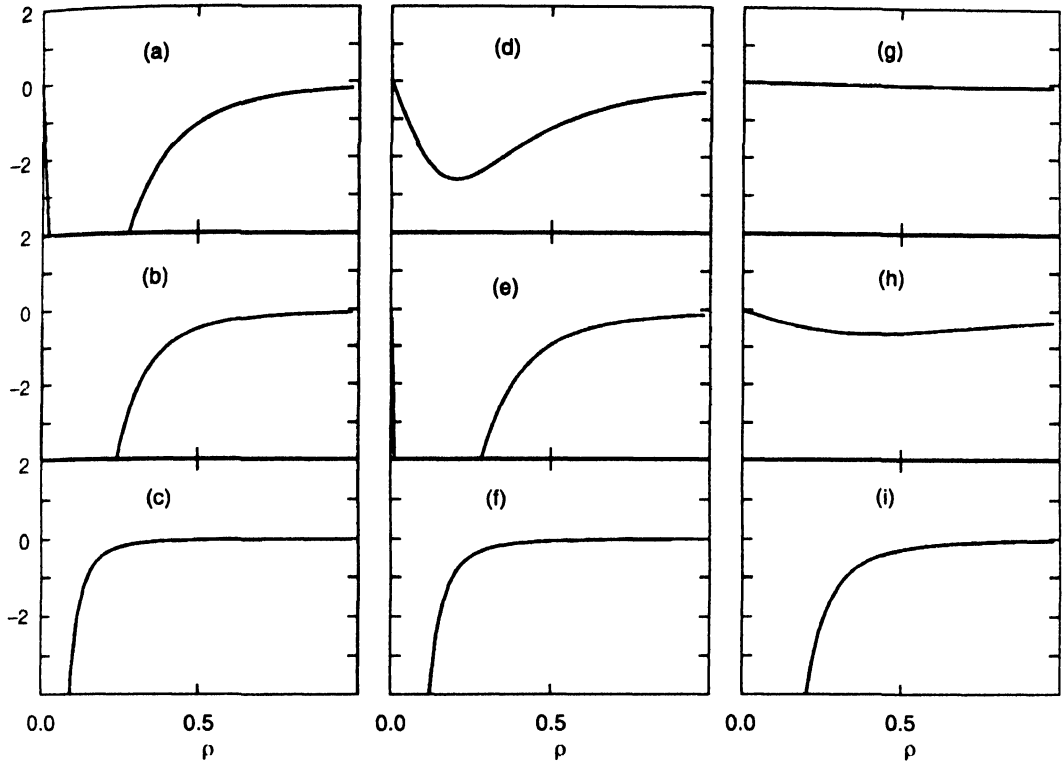


Figure 4. The divergence of the NAC terms ( $\text{div} \tau_{23}$ ) as a function of  $\rho$  where (a), (b) and (c) are for  $\lambda = 1.0$ ,  $\omega = 1.0$  with  $\Delta$  values 0.5, 0.2 and 0.01, respectively. Figures (d), (e) and (f) are for  $\lambda = 0.5$ ,  $\omega = 1.0$  with  $\Delta$  values 0.5, 0.2 and 0.01, respectively. Figures (g), (h) and (i) are for  $\lambda = 0.1$ ,  $\omega = 1.0$  with  $\Delta$  values 0.5, 0.2 and 0.01, respectively.

or in Cartesian coordinates :

$$\tau^x = \nabla_x \phi \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & 0 & 0 \\ -\frac{1}{\sqrt{2}} & 0 & 0 \end{pmatrix}; \quad \tau^y = \nabla_y \phi \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & 0 & 0 \\ -\frac{1}{\sqrt{2}} & 0 & 0 \end{pmatrix}. \quad (41)$$

Since the components of the NAC matrices commute with each other at the three state degenerate point, the total NAC matrix can be written as the product of a vector function and a scalar matrix, a condition to formulate EBO equation. The eigenvalues of the scalar matrix are 0 and  $\pm i$  with eigenvector matrix (G) :

$$G = \begin{pmatrix} \sqrt{2} & -\frac{1}{2}i & -\frac{1}{2}i \\ -\sqrt{2} & \frac{1}{2}i & \frac{1}{2}i \\ 0 & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \quad (42)$$

Since the matrix  $G$  is constant at the point of degeneracy, it obviously commutes with the operator  $\nabla$  in eq. (23) and therefore, the EBO equation [eq. (24)] takes the following form in Cartesian coordinates :

$$-\frac{\hbar^2}{2m} \{(\nabla_x + \nabla_x \phi)^2 + (\nabla_y + \nabla_y \phi)^2\} \Phi_1 + \left( E_{\Pi} + \frac{1}{2} \omega(x^2 + y^2) - E \right) \Phi_1 = 0. \quad (43)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \left( \nabla_x - i \frac{y}{x^2 + y^2} \right)^2 + \left( \nabla_y + i \frac{x}{x^2 + y^2} \right)^2 \Phi_1 + \left( E_{\Pi} + \frac{1}{2} \omega(x^2 + y^2) - E \right) \Phi_1 = 0. \quad (44)$$

## 6. Summary

Considering any three-state sub-Hilbert space as the complete one, we briefly present the generalized BO treatment assuming the validity of adiabatic-diabatic transformation condition,  $\nabla \mathbf{A} + \tau \mathbf{A} = 0$ , where the chosen form of the transformation matrix ( $\mathbf{A}$ ) has to be orthogonal at any point in the configuration space and its' elements should be cyclic functions with respect to a parameter. We demonstrate how (a) the  $\mathbf{A}$  matrix can be constructed by taking the product of six rotation matrices, (b) the same transformation matrix  $\mathbf{A}$  under the ADT condition can provide the explicit expressions of the NAC terms, and (c) the explicit form of Curl-Divergence equations for those NAC terms can be derived. The validity of Curl equation to ensure the ADT transformation leading to uniquely defined diabatic PESs and the proof of zero Curl at and around CI(s), a necessary condition to formulate EBO equation, are being presented. In order to justify these theoretical advancements, we start with a diabatic Hamiltonian known as induced Renner-Teller type model, analytically calculate the electronic basis functions, non-adiabatic coupling elements, and their Curl and divergence equations. The nature of all these quantities are investigated at the situation of three state degeneracy or when those states are approaching to form three state degeneracy. Finally, we present the analytical form of EBO equation for a three state degeneracy at a point.

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