Extended Born - Oppenheimer equation for tri - state system

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December 31, 2021

ABSTRACT

We present explicit form of non - adiabatic coupling (NAC) elements of nuclear Schroedinger equation (SE) for a coupled tri - state electronic manifold in terms of mixing angles of real electronic basis functions. If the adiabatic - diabatic transformation (ADT) angles are the mixing angles of electronic basis, ADT matrix transforms NAC terms to exactly zeros and brings diabatic form of SE. ADT and NAC matrices satisfy a curl condition and find a novel relation among the mixing angles for irrotational case. We also find that extended Born - Oppenheimer (EBO) equations have meaningful solution and can reproduce numerically exact results only when the equations are gauge invariant.

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Herzberg and Longuet-Higgins (HLH) [1] made an interesting observation in molecular dynamics— a real valued electronic wavefunction changes sign when the nuclear coordinates encircles a closed path around a conical intersection. This is so-called geometric phase (GP) effect, where the total wavefunction is not well behaved and the Born-Oppenheimer (BO) treatment [2] breaks down. HLH corrected this problem in an *ad hoc* way by multiplying a complex phase factor with real double-valued electronic wavefunction such that the resulting complex electronic wavefunction is single valued. Mead and Truhlar [3] generalized the BO equation by introducing a vector potential into the nuclear Hamiltonian to account this effect and the approach is reminiscent of HLH complex phase factor treatment. The effect has been found to show up immense significance, particularly, in scattering processes[4].

The BO treatment is based on the fact that slow-moving nuclei can be distinguished from fast-moving electrons in molecular systems. This distinction leads to the BO approximation, which includes the assumption that NAC terms are negligibly small and the upper electronic states do not affect the wavefunction on the lower state. Though the implication of this assumption is considered to be independent on the energy of the system, the ordinary BO equation was also applied for cases with large NAC terms assuming that upper electronic states are classically closed at low energies. Even if the components of total wavefunction on the upper electronic state(s) are negligibly small at enough low energies, their product with large NAC terms are definite values and the BO approximation breaks down for those cases.

Since NAC terms appear as off-diagonal elements in the SE [5], formulations of EBO equation are the attempts [6-7] to include the effect of off-diagonal (non-adiabatic) elements on the single surface equation. Baer [7] derived a new set of potential energy coupled BO equations for two electronic states, where the effects of NAC terms are being translated on the diagonal. At enough low energy, Baer assumed that upper electronic state is classically closed and approximate EBO equations for both the surfaces were formed. This EBO equation was used to calculate transition probabilities in a two-arrangement-channel model [8-9] and reproduced the correct results obtained from rigorously derived diabatic SE. Varandas and Xu [10] expressed NAC elements of adiabatic nuclear SE in terms of nuclear coordinate dependent mixing angle of two real electronic wavefunctions, found that ADT angle [11] is identical (up to an additive constant) with the mixing
angle and indeed, formulated single surface EBO equations in the vicinity of degeneracy.

Baer et al. [12-13] considered coupled BO equations for N (≥ 2) adiabatic nuclear SE and derived single surface EBO equations for a model situation (not a general case). These EBO equations contain the effect of NAC terms where the ground adiabatic PES have a degeneracy with excited surfaces along a single line. Even though this derivation was not persuaded for a general situation, the formulation shows that such an extension is viable and those EBO equations will have meaningful solution only when they are gauge invariant.

In this article, we carry out the BO treatment of a coupled three state electronic manifold from first principles. The BO expansion of molecular wavefunction and the total electron - nuclei Hamiltonian in the adiabatic representation are given by:

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

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

\[
\hat{T}_n = -\frac{\hbar^2}{2m} \sum_n \nabla_n^2 ,
\]

\[
\hat{H}_e(\mathbf{e}, \mathbf{n}) \xi_i(\mathbf{e}, \mathbf{n}) = u_i(\mathbf{n}) \xi_i(\mathbf{e}, \mathbf{n}) ,
\]

where \( \mathbf{n} \) and \( \mathbf{e} \) are the sets of nuclear and electronic coordinates, respectively, \( \xi_i(\mathbf{e}, \mathbf{n}) \) is the eigenfunction of the electronic Hamiltonian, \( \hat{H}_e(\mathbf{e}, \mathbf{n}) \) with eigenvalue, \( u_i(\mathbf{n}) \), also \( \psi_i(\mathbf{n}) \) is the nuclear coordinate dependent expansion coefficient and \( \hat{T}_n \) is the nuclear kinetic energy (KE) operator. When we substitute equation (1) in the time - independent SE and multiply by electronic basis, \( \xi_i(\mathbf{e}, \mathbf{n}) \), the matrix representation of adiabatic nuclear equation takes the following form after integrating over the electronic coordinates, \( \mathbf{e} \),

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

\[
H_{ii} = -\frac{\hbar^2}{2m} (\nabla_n^2 + 2 \tau_{1i} \cdot \vec{\nabla} + \tau_{2i}^2 ) + u_i(\mathbf{n}) ,
\]

\[
H_{ij} = -\frac{\hbar^2}{2m} (2 \tau_{1j} \cdot \vec{\nabla} + \tau_{2j}^2 ) = H_{ji}^\dagger ,
\]

\[
\tau_{1i} = \langle \xi_i(\mathbf{e}, \mathbf{n}) | \vec{\nabla} | \xi_j(\mathbf{e}, \mathbf{n}) \rangle , \quad \tau_{2i} = \langle \xi_i(\mathbf{e}, \mathbf{n}) | \nabla_n^2 | \xi_j(\mathbf{e}, \mathbf{n}) \rangle ,
\]

\[
\langle \xi_i(\mathbf{e}, \mathbf{n}) | \xi_j(\mathbf{e}, \mathbf{n}) \rangle = \delta_{ij} .
\]
We define the following three real orthonormal functions as the electronic basis set \((\xi_1, \xi_2 \text{ and } \xi_3)\) where \(\alpha(n), \beta(n) \text{ and } \gamma(n)\) are the nuclear coordinate dependent mixing angles (e.g. \(\alpha(n)\) is the mixing angle between electronic states 1 and 2),

\[
\begin{align*}
\xi_1 &= \begin{pmatrix} \cos \alpha \cos \beta \\ \sin \alpha \cos \beta \\ \sin \beta \end{pmatrix}, \\
\xi_2 &= \begin{pmatrix} -\cos \alpha \sin \beta \sin \gamma - \sin \alpha \cos \gamma \\ -\sin \alpha \sin \beta \sin \gamma + \cos \alpha \cos \gamma \\ \cos \beta \sin \gamma \end{pmatrix}, \\
\xi_3 &= \begin{pmatrix} -\cos \alpha \sin \beta \cos \gamma + \sin \alpha \sin \gamma \\ -\sin \alpha \sin \beta \cos \gamma - \cos \alpha \sin \gamma \\ \cos \beta \cos \gamma \end{pmatrix},
\end{align*}
\]

and rewrite the kinetically coupled nuclear SE (equation (2)) as below,

\[
-\frac{\hbar^2}{2m} \begin{pmatrix} \vec{\nabla} & \vec{t}_1 & \vec{t}_2 \\ -\vec{t}_1 & \vec{\nabla} & \vec{t}_3 \\ -\vec{t}_2 & -\vec{t}_3 & \vec{\nabla} \end{pmatrix}^2 \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} + \begin{pmatrix} u_1 - E & 0 & 0 \\ 0 & u_2 - E & 0 \\ 0 & 0 & u_3 - E \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = 0,
\]

(4)

where the NAC matrix \((\vec{\tau}(\equiv \vec{\tau}^{(1)})\)) is defined as,

\[
\vec{\tau} = \begin{pmatrix} 0 & \vec{t}_1 & \vec{t}_2 \\ -\vec{t}_1 & 0 & \vec{t}_3 \\ -\vec{t}_2 & -\vec{t}_3 & 0 \end{pmatrix},
\]

(5)

with matrix elements,

\[
\begin{align*}
\vec{t}_1 &= -\cos \beta \cos \gamma \vec{\nabla} \alpha - \sin \gamma \vec{\nabla} \beta, \\
\vec{t}_2 &= \cos \beta \sin \gamma \vec{\nabla} \alpha - \cos \gamma \vec{\nabla} \beta, \\
\vec{t}_3 &= -\sin \beta \vec{\nabla} \alpha - \vec{\nabla} \gamma.
\end{align*}
\]

(6)
When we substitute \( \Psi = A \Psi^d \) in equation (4) with the following choice of ADT matrix,

\[
A = \begin{pmatrix}
\cos \alpha \cos \beta & \sin \alpha \cos \beta & \sin \beta \\
-\sin \alpha \cos \gamma & \cos \alpha \cos \gamma & \cos \beta \sin \gamma \\
-\cos \sin \beta \sin \gamma & -\sin \alpha \sin \beta \sin \gamma & \\
\sin \alpha \sin \gamma & -\cos \alpha \sin \gamma & \cos \beta \cos \gamma \\
-\cos \alpha \sin \gamma & -\sin \alpha \sin \beta \cos \gamma & \sin \alpha \sin \beta \cos \gamma \\
\end{pmatrix},
\]

(7)

adiabatic nuclear SE is being transformed to the potentially coupled diabatic nuclear SE,

\[
\sum_{j=1}^{3} \{ (-\frac{\hbar^2}{2m} \nabla^2 - E) \delta_{ij} + W_{ij} \} \psi^d_j = 0, \quad i = 1, 2, 3,
\]

\[
W = A^\dagger UA, \quad U_{ij} = u_i \delta_{ij}.
\]

(8)

Since we find that the above form of \( \bar{\tau} \) (equation (5) and (6)) and \( A \) (equation (7)) matrices satisfy the ADT condition [11],

\[
\bar{\nabla} A + \bar{\tau} A = 0,
\]

(9)

we arrive an equation (known as curl condition) for each NAC element, \( \bar{\tau}_{ij} \), considering the analyticity of the transformation matrix \( A \) for any two nuclear coordinates, \( p \) and \( q \),

\[
\frac{\partial}{\partial p} \bar{\tau}_{ij}^q - \frac{\partial}{\partial q} \bar{\tau}_{ij}^p = (\bar{\tau}^q \bar{\tau}^p)_{ij} - (\bar{\tau}^p \bar{\tau}^q)_{ij},
\]

\[
\bar{\tau}_{ij}^p = < \xi_i | \nabla_p | \xi_j >, \quad \bar{\tau}_{ij}^q = < \xi_i | \nabla_q | \xi_j >.
\]

(10)

The curl condition for each pair of electronic basis, \( \{ | \xi_1 >, | \xi_2 > \} \), \( \{ | \xi_1 >, | \xi_3 > \} \) and \( \{ | \xi_2 >, | \xi_3 > \} \) is satisfied and the explicit forms of curl equations are the following,

\[
Curl \bar{\tau}_{12} = [\bar{\tau} \times \bar{\tau}]_{12} = \sin \beta \cos \gamma [\nabla_p \alpha \nabla_q \beta - \nabla_q \alpha \nabla_p \beta] + \sin \gamma \cos \beta [\nabla_p \alpha \nabla_q \gamma - \nabla_q \alpha \nabla_p \gamma]
\]

\[
- \cos \gamma [\nabla_p \beta \nabla_q \gamma - \nabla_q \beta \nabla_p \gamma],
\]

\[
Curl \bar{\tau}_{13} = [\bar{\tau} \times \bar{\tau}]_{13} = -\sin \beta \sin \gamma [\nabla_p \alpha \nabla_q \beta - \nabla_q \alpha \nabla_p \beta] + \cos \gamma \cos \beta [\nabla_p \alpha \nabla_q \gamma - \nabla_q \alpha \nabla_p \gamma]
\]

\[
+ \sin \gamma [\nabla_p \beta \nabla_q \gamma - \nabla_q \beta \nabla_p \gamma],
\]

\[
Curl \bar{\tau}_{23} = [\bar{\tau} \times \bar{\tau}]_{23} = \cos \beta [\nabla_p \alpha \nabla_q \gamma - \nabla_q \alpha \nabla_p \gamma].
\]

(11)
Since \( \vec{\tau}(\mathbf{n}) \) goes to zero rapidly enough as the radial coordinate tends to infinity \([14]\), \( \vec{\tau} \) may be resolved into an irrotational and a solenoidal part \([15-16]\). On the other hand, the explicit form of \( \text{div} \tau_{ij} \)s are given by:

\[
\begin{align*}
\text{div} \tau_{12} & = 2 \sin \beta \cos \beta \sin \gamma (\nabla \alpha)^2 + 3 \cos \beta \sin \gamma \nabla \alpha \nabla \gamma - 3 \cos \gamma \nabla \beta \nabla \gamma - \cos \beta \cos \gamma \nabla^2 \alpha \\
& - \sin \gamma \nabla^2 \beta - \sin \beta \cos \gamma \nabla \alpha \nabla \beta \\
\text{div} \tau_{13} & = 2 \sin \beta \cos \beta \cos \gamma (\nabla \alpha)^2 + 3 \cos \beta \cos \gamma \nabla \alpha \nabla \gamma + 3 \sin \gamma \nabla \beta \nabla \gamma + \cos \beta \sin \gamma \nabla^2 \alpha \\
& - \cos \gamma \nabla^2 \beta + \sin \beta \sin \gamma \nabla \alpha \nabla \beta \\
\text{div} \tau_{23} & = 2 \cos^2 \beta \sin \gamma \cos \gamma (\nabla \alpha)^2 - 2 \sin \gamma \cos \gamma (\nabla \beta)^2 - 3 \cos \beta \cos^2 \gamma \nabla \alpha \nabla \beta \\
& + \cos \beta \sin^2 \gamma \nabla \alpha \nabla \beta - \sin \beta \nabla^2 \alpha - \nabla^2 \gamma
\end{align*}
\]

(12)

Since \( \nabla \alpha \), \( \nabla \beta \) and \( \nabla \gamma \) (generally \( \nabla^2 \alpha \), \( \nabla^2 \beta \) and \( \nabla^2 \gamma \) also) are not zero in the vicinity of the conical intersection, \( \text{div} \tau_{ij} \neq 0 \) for any value of mixing angles, i.e., vector field \( \vec{\tau} \) corresponds to non-solenoidal case \([16-17]\). In the vicinity of the conical intersection, we presently handle only the irrotational part, i.e., \( \text{curl} \) equations are Abelian, \( \text{Curl} \tau_{ij} = 0 \). Thus, equations (11) have unique solution as below (if \( \beta \neq \frac{\pi}{2} \) or \( \neq \frac{3\pi}{2} \)),

\[
\begin{align*}
\nabla p \alpha \nabla q \beta & = \nabla q \alpha \nabla p \beta, \\
\nabla p \beta \nabla q \gamma & = \nabla q \beta \nabla p \gamma, \\
\nabla p \alpha \nabla q \gamma & = \nabla q \alpha \nabla p \gamma,
\end{align*}
\]

(13)

with the implication that nuclear coordinate dependent mixing angles are related by integer ratios,

\[
\alpha(\mathbf{n}) : \beta(\mathbf{n}) : \gamma(\mathbf{n}) = k : l : m.
\]

(14)

If an unitary transformation matrix, \( \mathbf{G} (\Psi = \mathbf{G}\Phi) \), diagonalizes NAC matrix, \( \vec{\tau} \), with eigenvalues, 0 and \( \pm i\vec{\omega} \), the adiabatic SE (equation (4)) transforms as,

\[
-\frac{\hbar^2}{2m} (\vec{\nabla}^2 + i\vec{\omega})^2 \Phi + (\mathbf{V} - E) \Phi = 0, \quad \mathbf{V} = \mathbf{G}^* \mathbf{U} \mathbf{G}, \\
\vec{\omega} = \pm \sqrt{\ell_1^2 + \ell_2^2 + \ell_3^2} \\
= \pm \{(\vec{\nabla} \alpha)^2 + (\vec{\nabla} \beta)^2 + (\vec{\nabla} \gamma)^2 + 2 \sin \beta \vec{\nabla} \alpha \vec{\nabla} \gamma\}^{\frac{1}{2}}.
\]

(15)
One can rewrite the product, $V \Phi$, for the $i$th equation as, $(V \Phi)_i = u_1 \Phi_i + \sum_{j=2}^{3} G_{ij}^* (u_i - u_l) \psi_j$, $i = 1, 2, 3$ and impose the BO approximation, $|\psi_1| \gg |\psi_i|$, $i = 2, 3$ (considering that at enough low energy, both the upper electronic states are assumed to be classically closed) to form the single surface adiabatic nuclear SE [12],

$$-rac{\hbar^2}{2m} (\nabla + i \omega_i)^2 \Phi_i + (u_1 - E) \Phi_i = 0, \quad i = 1, 2, 3.$$  

 Equation (14) simplifies both the adiabatic and diabatic equations (4) and (8), respectively for any arbitrary ratios of mixing angles, i.e., the NAC matrix takes the form, $\vec{t} = \vec{\nabla} \alpha \cdot g(\alpha)$, where $g(\alpha)$ is mixing angle dependent $3 \times 3$ matrix. At the same time, we know that EBO equations (16) have meaningful solution only when they satisfy the following gauge invariance condition [12] for systems of three electronic states,

$$\frac{1}{2\pi} \int_{0}^{2\pi} \omega(\vec{n}) \cdot d\vec{n} = m, \quad m = 1, 2, 3, ....$$

We choose different ratios of $\alpha(n)$, $\beta(n)$ and $\gamma(n)$ and calculate corresponding $\omega$ s as: (a) $\alpha = \beta = \gamma$, $\vec{\omega} = \pm \vec{\nabla} \alpha \{3 + 2 \sin \alpha\}^{\frac{1}{2}}$; (b) $\alpha = 2\beta = \gamma$, $\vec{\omega} = \pm \frac{\vec{\nabla} \alpha}{2} \{9 + 8 \sin \frac{\alpha}{2}\}^{\frac{1}{2}}$; (c) $2\alpha = \beta = 2\gamma$, $\vec{\omega} = \pm \vec{\nabla} \alpha \{6 + 2 \sin 2\alpha\}^{\frac{1}{2}}$ where $\alpha(n)$ is mixing as well as ADT angle (upto an additive constant) among the electronic states. It is important to note that in all such situations, divergence equations (12) have non-zero contributions. When $\alpha(n)$ is the function of two nuclear coordinates, $x(= q \cos \theta)$ and $y(= q \sin \theta)$ and is being equated as $\alpha(n) = \frac{\theta}{2}$, the product, $\vec{\nabla} \alpha(n) \cdot d\vec{n} = \frac{1}{2} d\theta$. For realistic systems, $\alpha(\theta)$ can be calculated as function of $\theta$ from the electronic eigenfunctions of the equation, $\tilde{H}_e(e, n) \xi_i(e, n) = u_i(n) \xi_i(e, n)$. Thus, the gauge invariant integrals for the above three cases are,

$$\Gamma_1 = \frac{1}{2\pi} \int_{0}^{2\pi} \frac{1}{2} \left\{3 + 2 \sin \frac{\theta}{2}\right\}^{\frac{1}{2}} d\theta = 4\sqrt{3} \int_{0}^{\frac{\pi}{2}} \left(1 - \frac{4}{5} \sin^2 \phi\right)^{\frac{1}{2}} d\phi = 1.03$$

$$\Gamma_2 = \frac{1}{2\pi} \int_{0}^{2\pi} \frac{1}{4} \left\{9 + 8 \sin \frac{\theta}{4}\right\}^{\frac{1}{2}} d\theta = 2\sqrt{17} \int_{0}^{\frac{\pi}{2}} \left(1 - \frac{16}{17} \sin^2 \phi\right)^{\frac{1}{2}} d\phi = 0.934$$

$$\Gamma_3 = \frac{1}{2\pi} \int_{0}^{2\pi} \frac{1}{2} \left\{6 + 2 \sin \theta\right\}^{\frac{1}{2}} d\theta = 2\sqrt{2} \int_{0}^{\frac{\pi}{2}} \left(1 - \frac{1}{2} \sin^2 \phi\right)^{\frac{1}{2}} d\phi$$

$$+ \quad 2\sqrt{2} \int_{0}^{\frac{\pi}{2}} \left(1 - \frac{1}{2} \sin^2 \phi\right)^{\frac{1}{2}} d\phi = 1.216$$

with the general form of incomplete elliptic integral of the second kind. It is quite obvious that since $\alpha(n)$ ($A$ is analytic) is analytic, the nature of these integrals will be generic for any functional form
of $\alpha(n)$. When three electronic states are coupled, the non-adiabatic effect of the upper states on the ground is equivalent to a potential developed due to elliptic motion of the nuclei around the point of conical intersection. Moreover, single surface EBO can be derived only for specific ratios of mixing/ADT angles, e.g., gauge invariance condition is approximately obeyed in case (a), whereas in the cases (b) and (c), integrals are either away or far away from the gauge condition.

Since the general form of $\vec{\tau}$ and $A$ (equations (5) - (7)) with any arbitrary ratios of mixing angles satisfies the equation, $\vec{\nabla}A + \vec{\tau}A = 0$, and ensures the ADT, uniquely defined diabatic potential matrix in configuration space is guaranteed by the unit matrix, $D = \exp\left(\int_0^{2\pi} \vec{\tau} \cdot d\vec{n}\right)$. The explicit expression of $D$ [13] is derived for the case (a) by using the corresponding $G$ matrix (equation (15)) as,

$$D = G \exp\left(-i \int_0^{2\pi} \vec{\omega}(n) \cdot d\vec{n}\right) G^* = \frac{1}{3 + 2si} \begin{pmatrix}
(si + 1)^2 & -(cs^2 + si) & (cs.si - cs) \\
+(1 + cs^2)C_1 & \times(3 + 2.si)^\frac{3}{2}S_1 & \times(3 + 2.si)^\frac{3}{2}S_1 \\
(3 + 2si)^\frac{3}{2}S_1 & (1 + 2si + 2si^2) & +2.cs(si^3 + cs^2 - si^2)S_2 \\
+2cs^3S_2 & +2.si.cs^2 + cs^4)C_1 \\
\end{pmatrix}$$

$$\times$$

$$\begin{pmatrix}
-(cs^2 + si) & (cs.si - cs)^2 & -(si + 1)(3 + 2.si)^\frac{3}{2}S_1 \\
+2.cs(si^3 + cs^2 - si^2)S_2 & (cs.si - cs) & --(si + 1)(3 + 2.si)^\frac{3}{2}S_1 \\
(3 + 2.si)^\frac{3}{2}S_1 & (si + 1)(3 + 2.si)^\frac{3}{2}S_1 & (cs^2 + si)^2 \\
+2(1 + si + si.cs^2)S_2 & +2.cs(si^3 + cs^2 - si^2)S_2 & +2.cs^4S_2 \\
\end{pmatrix}$$

$$\simeq \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{pmatrix}$$

(21)

where $si = \sin \alpha$, $cs = \cos \alpha$, $C_1 = \cos(2\pi\Gamma_1) \simeq 1$, $S_1 = \sin(2\pi\Gamma_1) \simeq 0$ and $S_2 = \sin^2(\pi\Gamma_1) \simeq 0$ and for the other two cases (b) and (c), $C_1 \neq 1$ and $S_1, S_2 \neq 0$.

In equation (15), the contribution of non-adiabatic effects appear as $\pm i\omega$ in the KE operator
(diagonal) as well as in the potential energy matrix (through $G$ matrix). Since single surface EBO equation is derived by neglecting the effect of $G$ matrix ($\sum_{j=2}^{3} G_{ij}^*(u_i - u_1)\psi_j$), diabatic and single surface EBO equations will not be equivalent irrespective of any arbitrary ratios of mixing angles. Alternatively, we can say that for any arbitrary ratios of mixing angles, the term, $\sum_{j=2}^{3} G_{ij}^*(u_i - u_1)\psi_j$, is not negligible and single surface EBO equations cannot be derived. The condition of gauge invariance and the existence of uniquely define diabatic potential from non-adiabatic terms clearly tell that only for specific ratios of mixing angles, single surface EBO equations is acceptable.

We justify our theory by performing numerical calculations on a two coordinate quasi-"JT scattering" model [13] in which the harmonic oscillator potential and linear coupling term are replaced by more general potentials. The adiabatic PESs $u_l$, $l = 1,2,3$ are given below:

\[
\begin{align*}
  u_1(x, y) &= \frac{1}{2} \mu (\omega_0 - \tilde{\omega}_1(x))^2 y^2 + A_1 \times f(x, y) \\
  u_2(x, y) &= \frac{1}{2} \mu \omega_0^2 y^2 - (D_1 - A_1) \times f(x, y) + D_1 \\
  u_3(x, y) &= \frac{1}{2} \mu \omega_0^2 y^2 - (D_2 - A_1) \times f(x, y) + D_2 \\
  \tilde{\omega}_1(x) &= \omega_1 \exp\left(-\frac{x}{\sigma_1}\right) \\
  f(x, y) &= \exp\left(-\frac{x^2 + y^2}{\sigma^2}\right)
\end{align*}
\] (22)

where $\mu = 0.58\; amu$, $A_1 = 3.0\; eV$, $D_1 = 5.0\; eV$, $D_2 = 10.0\; eV$, $\omega_0 = 39.14 \times 10^{13}\; s^{-1}$, $\omega_1 = 7.83 \times 10^{13}\; s^{-1}$, $\sigma = 0.3\; \AA$ and $\sigma_1 = 0.75\; \AA$, also Cartesian coordinates $x$ and $y$ are defined in the intervals $-\infty \leq x \leq \infty$ and $-\infty \leq y \leq \infty$ and related with polar coordinates as, $x = q \cos \theta$ and $y = q \sin \theta$. These adiabatic potentials describe a two arrangement channel system where $x \to \infty$ and $x \to -\infty$ are the reagents and products asymptote, respectively.

Introducing $\alpha(n) = \frac{\theta}{\pi} = \frac{1}{2} \tan^{-1}(\frac{y}{x})$, we construct diabatic potential matrices ($W$), vis-à-vis, diabatic and single surface EBO equations for all the three cases and then, initialize the wavefunction on the ground vibrational state with different initial KE at the asymptote of reagents, propagate the time dependent wavefunction using DVR [18] and project the final wavefunction with the asymptotic eigenfunctions of the Hamiltonian to calculate state-to-state vibrational transition probabilities. Dynamical calculations are carried out at total energy 1.20 and 1.80 eV. Since the point of conical intersection is at 3.0 eV, upper electronic states are expected to be classically closed at those energies. We demonstrate all the results in Table (I) - (III) for the cases (a) -
(c), respectively. Table(I) exhibits that reactive transition probabilities calculated by single surface EBO equations not only follow the correct symmetry but also achieve quantitative agreement with diabatic results whereas in Table (II) and (III), single surface EBO results are symmetry broken as well as inaccurate. Thus, these numerical results predict that only for the case (a), single surface EBO equation can be constructed.

In summary, we have used the generalized form of real orthogonal electronic basis functions in terms of mixing angles ($\alpha(n)$, $\beta(n)$ and $\gamma(n)$) among the three electronic states and expressed the NAC terms of adiabatic nuclear SEs with these angles. When ADT angles are chosen as mixing angles, adiabatic nuclear SEs transform to diabatic SEs, i.e, ADT and mixing angles are equal up to an additive constant. Since the NAC ($\vec{\tau}$), ADT ($A$) matrices satisfy the ADT condition and mixing angles are analytic, we find a curl condition is also satisfied with non-zero divergence for each element of $\vec{\tau}$ matrix. In irrotational case, solution of these curl equations imply that mixing/ADT angles are related with integer ratios. Consequently, both the adiabatic and diabatic nuclear SEs are being simplified extensively. Single surface EBO equations derived from adiabatic nuclear SEs have meaningful solution and quantitative agreement with corresponding diabatic case only for specific ratios of mixing angles where EBO equation is gauge invariant and provide uniquely defined diabatic potential energy matrix. We also find that the non-adiabatic effect associated with single surface EBO equation derived from three coupled electronic state is a potential that arises due to the elliptic motion of nuclei around the conical intersection.

We acknowledge Department of Science and Technology (DST, Government of India) for financial support through the project no. SP/S1/H-53/01. S.A. would like to thank Professor S. P. Bhattacharyya and Professor J. K. Bhattacharjee, I.A.C.S., Kolkata for their comments on curl and divergence equations.
TABLE I
Reactive state - to - state transition probabilities. Three diabatic surfaces are constructed considering the relation, $\alpha(n) = \beta(n) = \gamma(n)$ where the EBO is derived under the same situation.

| E (eV) | 0 $\rightarrow$ 0 | 0 $\rightarrow$ 1 | 0 $\rightarrow$ 2 | 0 $\rightarrow$ 3 | 0 $\rightarrow$ 4 | 0 $\rightarrow$ 5 | 0 $\rightarrow$ 6 |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1.20   | 0.0229$^a$      | 0.0000          | 0.0616          | 0.0000          | 0.0006          |                  |                  |
| 1.20   | 0.0279$^b$      | 0.0032          | 0.0656          | 0.0049          | 0.0010          |                  |                  |
| 1.80   | 0.1002          | 0.0000          | 0.0401          | 0.0000          | 0.0912          | 0.0000          | 0.0238          |
| 1.80   | 0.1194          | 0.0069          | 0.0524          | 0.0016          | 0.1196          | 0.0093          | 0.0139          |

$^a$ Diabatic

$^b$ EBO
TABLE II
Reactive state - to - state transition probabilities. Three diabatic surfaces are constructed considering the relation, $\alpha(n) = 2\beta(n) = \gamma(n)$ where the EBO is derived under the same situation.

| E (eV) | 0 → 0 | 0 → 1 | 0 → 2 | 0 → 3 | 0 → 4 | 0 → 5 | 0 → 6 |
|--------|-------|-------|-------|-------|-------|-------|-------|
| 1.20   | 0.0225 | 0.0000 | 0.0491 | 0.0000 | 0.0124 |
| 1.20   | 0.0114 | 0.0321 | 0.0298 | 0.0230 | 0.0002 |
| 1.80   | 0.1389 | 0.0001 | 0.0246 | 0.0000 | 0.0876 | 0.0000 | 0.0103 |
| 1.80   | 0.0732 | 0.0684 | 0.0389 | 0.0036 | 0.0835 | 0.0190 | 0.0129 |

*a* Diabatic  
*b* EBO
TABLE III
Reactive state - to - state transition probabilities. Three diabatic surfaces are constructed considering the relation, $2\alpha(n) = \beta(n) = 2\gamma(n)$ where the EBO is derived under the same situation.

| E (eV) | 0 → 0 | 0 → 1 | 0 → 2 | 0 → 3 | 0 → 4 | 0 → 5 | 0 → 6 |
|--------|-------|-------|-------|-------|-------|-------|-------|
| 1.20   | 0.0665$^a$ | 0.0000 | 0.0115 | 0.0000 | 0.0008 |
| 1.20   | 0.0315$^b$ | 0.0102 | 0.0629 | 0.0002 | 0.001  |
| 1.80   | 0.1220  | 0.0000 | 0.0390 | 0.0000 | 0.0697 | 0.0000 | 0.0027 |
| 1.80   | 0.1318  | 0.0309 | 0.0363 | 0.0064 | 0.0586 | 0.0573 | 0.0061 |

$^a$ Diabatic

$^b$ EBO
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