Important Notes on Beyond Born-Oppenheimer Theory

Satrajit Adhikari

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The Time independent molecular Schrödinger Equation (SE) is:

$$\hat{\mathbf{H}}(s_e, s_n)|\Psi(s_e, s_n)\rangle = E|\Psi(s_e, s_n)\rangle, \tag{1}$$

where, $\hat{\mathbf{H}}(s_e, s_n)$ is the total molecular Hamiltonian and $|\Psi(s_e, s_n)\rangle$ is the molecular wave function. Now, the molecular Hamiltonian is sum of the nuclear kinetic energy and the electronic Hamiltonian:

$$\hat{\mathbf{H}}(s_e, s_n) = \hat{\mathbf{T}}_n(s_n) + \hat{\mathbf{H}}_e(s_e|s_n). \tag{2}$$

The nuclear kinetic energy in atomic units is given by:

$$\hat{\mathbf{T}}_n(s_n) = -\frac{1}{2}\sum_A \left(\frac{\nabla^2_{s_n,A}}{M_A}\right), \tag{3}$$

whereas, the electronic Hamiltonian is:

$$\hat{\mathbf{H}}_e(s_e|s_n) = -\frac{1}{2}\sum_i \nabla^2_{s_e,i} - \sum_i\sum_A \frac{Z_A}{r_{iA}} + \sum_i\sum_{j>i}\frac{1}{r_{ij}} + \sum_A\sum_{B>A}\frac{Z_A Z_B}{R_{AB}}. \tag{4}$$

The first term is the elctronic kinetic energy, the second term is the electron-nuclear Coulomb attraction, the third term is the electron-electron repulsion whereas the forth term is nuclear-nuclear Coulomb potential. The second and the fourth terms bring the parametric dependence on the nuclear coordinates within the electronic Hamiltonian. All the quantities are in atomic units. The electronic Hamiltonian satisfies the time-independent electronic SE:

$$\hat{\mathbf{H}}_e(s_e|s_n)|\xi_i(s_e|s_n)\rangle = u_i(s_n)|\xi_i(s_e|s_n)\rangle. \tag{5}$$

$|\xi_i(s_e|s_n)\rangle$s are electronic wave functions and $u_i(s_n)$ are the adiabatic potential energies both of which depend parametrically on the nuclear coordinates. Since, the electronic wave functions form complete set, i.e.

$$\langle\xi_i|\xi_j\rangle = \delta_{ij}; \quad \sum_i |\xi_i\rangle\langle\xi_i| = \mathbf{I}.$$

The total molecular wave function $|\Psi(s_e, s_n)\rangle$ can be expanded in terms of this basis set:

$$|\Psi(s_e, s_n)\rangle = \sum_i \psi_i(s_n)|\xi_i(s_e|s_n)\rangle, \tag{6}$$

what we know as the Born-Oppenheimer Expansion.

We use the above expansion of $|\Psi(s_e, s_n)\rangle$ and put it in Eq. (1):

$$(\hat{\mathbf{T}}_n + \hat{\mathbf{H}}_e) \sum_i \psi_i |\xi_i\rangle = E \sum_i \psi_i |\xi_i\rangle. \tag{7}$$

Applying a bra $\langle \xi_j|$ from the left on the above equation:

$$\sum_i \langle \xi_j | (\hat{\mathbf{T}}_n + \hat{\mathbf{H}}_e) \psi_i |\xi_i\rangle = E \sum_i \psi_i \langle \xi_j | \xi_i \rangle \tag{8}$$

$$\Rightarrow \sum_i \Big(\langle \xi_j | \hat{\mathbf{T}}_n \psi_i |\xi_i\rangle + \delta_{ji}(u_i - E)\psi_i \Big) = 0. \tag{9}$$

Now, $\hat{\mathbf{T}}_n$ in atomic units is:

$$\hat{\mathbf{T}}_n(s_n) = -\frac{1}{2} \sum_A \left(\frac{\nabla^2_{s_{n,A}}}{M_A} \right),$$

which can be converted in terms of mass-weighted coordinates by taking a transformation $s_{n,A} \rightarrow \sqrt{M_A} s_{n,A}$, i.e. $\tilde{s}_{n,A} = \sqrt{M_A} s_{n,A}$:

$$\hat{\mathbf{T}}_n(\tilde{s}_n) = -\frac{1}{2} \sum_A \nabla^2_{\tilde{s}_{n,A}} \equiv -\frac{1}{2} \nabla^2_n. \tag{10}$$

Now, taking Eq. (9) and using the above form of $\hat{\mathbf{T}}_n$, we have:

$$\sum_i \left\{ -\frac{1}{2} \langle \xi_j(s_e|s_n) | \nabla^2_n \psi_i(s_n) | \xi_i(s_e|s_n) \rangle + \delta_{ji}(u_i - E)\psi_i(s_n) \right\} = 0 \tag{11}$$

$$\Rightarrow \sum_i \left\{ -\frac{1}{2}\delta_{ji}\nabla^2_n - \langle \xi_j | \vec{\nabla}_n | \xi_i \rangle . \vec{\nabla}_n - \frac{1}{2} \langle \xi_j | \nabla^2_n | \xi_i \rangle + \delta_{ji}(u_i - E) \right\} \psi_i = 0$$

$$\Rightarrow \sum_i \left\{ -\frac{1}{2}\delta_{ji}\nabla^2_n - \vec{\tau}^{(1)}_{ji} . \vec{\nabla}_n - \frac{1}{2}\tau^{(2)}_{ji} + \delta_{ji}(u_i - E) \right\} \psi_i = 0, \tag{12}$$

where, $\langle \xi_j | \vec{\nabla}_n | \xi_i \rangle = \vec{\tau}^{(1)}_{ji}$ and $\langle \xi_j | \nabla^2_n | \xi_i \rangle = \tau^{(2)}_{ji}$ are the Non-Adiabatic Coupling Terms (NACTs) of first order and second order, respectively. We follow a little digression from the above equation and discuss some crucial properties of the NACTs.

Digression 1: Properties of the NACTs:

1) The elements $\vec{\tau}^{(1)}_{ij}$ constitute a skew-symmetric matrix:

$$\vec{\boldsymbol{\tau}}^{\dagger} = -\vec{\boldsymbol{\tau}} \tag{13}$$

Proof:

$$\because \langle \xi_i | \xi_j \rangle = \delta_{ij}$$

$$\Rightarrow \vec{\nabla}_n \langle \xi_i | \xi_j \rangle = 0$$

$$\Rightarrow \langle \vec{\nabla}_n \xi_i | \xi_j \rangle + \langle \xi_i | \vec{\nabla}_n \xi_j \rangle = 0.$$

If the electronic wave functions $|\xi_i\rangle$s are all real, then the above equation can be written as:

$$\langle \xi_j | \vec{\nabla}_n \xi_i \rangle + \langle \xi_i | \vec{\nabla}_n \xi_j \rangle = 0$$

$$\Rightarrow \vec{\tau}_{ji}^{(1)} + \vec{\tau}_{ij}^{(1)} = 0$$

$$\Rightarrow \vec{\tau}_{ji}^{(1)} = -\vec{\tau}_{ij}^{(1)}. \tag{14}$$

Hence,

$$\vec{\boldsymbol{\tau}}^{\dagger} = -\vec{\boldsymbol{\tau}}.$$

2) The second order NACT elements satisfy the following condition:

$$\boldsymbol{\tau}^{(2)} = \vec{\boldsymbol{\tau}}^{(1)}.\vec{\boldsymbol{\tau}}^{(1)} + \vec{\boldsymbol{\nabla}}_n.\vec{\boldsymbol{\tau}}^{(1)} \tag{15}$$

Proof:

$$\because \langle \xi_i | \vec{\nabla}_n | \xi_j \rangle = \vec{\tau}_{ij}^{(1)},$$

applying $\vec{\nabla}_n.$ on both sides of the above equation:

$$\begin{aligned}
\vec{\nabla}_n.\langle \xi_i | \vec{\nabla}_n | \xi_j \rangle &= \vec{\nabla}_n.\vec{\tau}_{ij}^{(1)} \\
\Rightarrow \langle \vec{\nabla}_n \xi_i | \vec{\nabla}_n \xi_j \rangle + \langle \xi_i | \nabla_n^2 | \xi_j \rangle &= \vec{\nabla}_n.\vec{\tau}_{ij}^{(1)} \\
\Rightarrow \tau_{ij}^{(2)} &= \vec{\nabla}_n.\vec{\tau}_{ij}^{(1)} - \langle \vec{\nabla}_n \xi_i | \vec{\nabla}_n \xi_j \rangle \\
\Rightarrow \tau_{ij}^{(2)} &= \vec{\nabla}_n.\vec{\tau}_{ij}^{(1)} - \sum_k \langle \vec{\nabla}_n \xi_i | \xi_k \rangle.\langle \xi_k | \vec{\nabla}_n \xi_j \rangle \\
\Rightarrow \tau_{ij}^{(2)} &= \vec{\nabla}_n.\vec{\tau}_{ij}^{(1)} - \sum_k \vec{\tau}_{ki}^{(1)}.\vec{\tau}_{kj}^{(1)}.
\end{aligned}$$

From Eq. (14), we have

$$\tau_{ij}^{(2)} = \sum_k \vec{\tau}_{ik}^{(1)}.\vec{\tau}_{kj}^{(1)} + \vec{\nabla}_n.\vec{\tau}_{ij}^{(1)}. \tag{16}$$

In matrix notation:

$$\boldsymbol{\tau}^{(2)} = \vec{\boldsymbol{\tau}}^{(1)}.\vec{\boldsymbol{\tau}}^{(1)} + \vec{\boldsymbol{\nabla}}_n.\vec{\boldsymbol{\tau}}^{(1)}.$$

The above equation written in the form:

$$\vec{\boldsymbol{\nabla}}_n.\vec{\boldsymbol{\tau}}^{(1)} = \boldsymbol{\tau}^{(2)} - |\vec{\boldsymbol{\tau}}^{(1)}|^2, \tag{17}$$

is called the **Divergence Equation**.

3) The NAC matrices satisfy the **Curl condition**:

$$\vec{\boldsymbol{\nabla}}_q.\vec{\boldsymbol{\tau}}_p - \vec{\boldsymbol{\nabla}}_p.\vec{\boldsymbol{\tau}}_q = [\vec{\boldsymbol{\tau}}_p, \vec{\boldsymbol{\tau}}_q] \tag{18}$$

where, p and q are the nuclear coordinates and the R.H.S is the commutator of the NACTs.

Proof:

Let us consider the $ij$the component of the L.H.S i.e.,

$$\begin{aligned}
(\vec{\boldsymbol{\nabla}}_q.\vec{\boldsymbol{\tau}}_p - \vec{\boldsymbol{\nabla}}_p.\vec{\boldsymbol{\tau}}_q)_{ij} &= \vec{\nabla}_q.\vec{\tau}_p^{ij} - \vec{\nabla}_p.\vec{\tau}_q^{ij} \\
&= \vec{\nabla}_q.\langle\xi_i|\vec{\nabla}_p|\xi_j\rangle - \vec{\nabla}_p.\langle\xi_i|\vec{\nabla}_q|\xi_j\rangle \\
&= \langle\vec{\nabla}_q\xi_i|\vec{\nabla}_p\xi_j\rangle + \langle\xi_i|\vec{\nabla}_q.\vec{\nabla}_p|\xi_j\rangle \\
&- \langle\vec{\nabla}_p\xi_i|\vec{\nabla}_q\xi_j\rangle - \langle\xi_i|\vec{\nabla}_p.\vec{\nabla}_q|\xi_j\rangle.
\end{aligned}$$

Since the $|\xi_k\rangle$s are analytical, $\left[\vec{\nabla}_p, \vec{\nabla}_q\right]|\xi_k\rangle = 0$, thus the above expression reduces to:

$$\begin{aligned}
(\vec{\boldsymbol{\nabla}}_q.\vec{\boldsymbol{\tau}}_p - \vec{\boldsymbol{\nabla}}_p.\vec{\boldsymbol{\tau}}_q)_{ij} &= \langle\vec{\nabla}_q\xi_i|\vec{\nabla}_p\xi_j\rangle - \langle\vec{\nabla}_p\xi_i|\vec{\nabla}_q\xi_j\rangle \\
&= \sum_k \left(\langle\vec{\nabla}_q\xi_i|\xi_k\rangle\langle\xi_k|\vec{\nabla}_p\xi_j\rangle - \langle\vec{\nabla}_p\xi_i|\xi_k\rangle\langle\xi_k|\vec{\nabla}_q\xi_j\rangle\right) \\
&= -\sum_k \left(\vec{\tau}_q^{(ik)}.\vec{\tau}_p^{(kj)} - \vec{\tau}_p^{(ik)}.\vec{\tau}_q^{(kj)}\right) \\
&= (\vec{\boldsymbol{\tau}}_p.\vec{\boldsymbol{\tau}}_q)^{ij} - (\vec{\boldsymbol{\tau}}_q.\vec{\boldsymbol{\tau}}_p)^{ij} \\
&= [\vec{\boldsymbol{\tau}}_p, \vec{\boldsymbol{\tau}}_q]_{ij}\,. \qquad \text{Verified}
\end{aligned}$$

Eq. (17) and (18) are collectively known as the **Curl-Div Equations** satisfaction of which establishes the validity of the Hilbert-Space.

4) The NACTs satisfy the following definition which is reminiscent of the Hellmann-Feynman Theorem:

$$\vec{\tau}_{ji} = \frac{\langle\xi_j|\vec{\nabla}_n\hat{\mathbf{H}}_e|\xi_i\rangle}{u_i - u_j} \tag{19}$$

Proof:

Consider the electronic SE in Eq. (5)

$$\hat{\mathbf{H}}_e(s_e|s_n)|\xi_i(s_e|s_n)\rangle = u_i(s_n)|\xi_i(s_e|s_n)\rangle.$$

Applying $\vec{\nabla}_n$ on both sides of the equation, we get:

$$\begin{aligned}
\vec{\nabla}_n\hat{\mathbf{H}}_e(s_e|s_n)|\xi_i(s_e|s_n)\rangle &= \vec{\nabla}_n u_i(s_n)|\xi_i(s_e|s_n)\rangle \\
\Rightarrow \left(\vec{\nabla}_n\hat{\mathbf{H}}_e\right)|\xi_i\rangle + \hat{\mathbf{H}}_e\left(\vec{\nabla}_n|\xi_i\rangle\right) &= \left(\vec{\nabla}_n u_i\right)|\xi_i\rangle + u_i\left(\vec{\nabla}_n|\xi_i\rangle\right).
\end{aligned}$$

Applying $\langle\xi_j|$ (where, $j \neq i$) on both sides, we will have then:

$$\begin{aligned}
\langle\xi_j|\vec{\nabla}_n\hat{\mathbf{H}}_e|\xi_i\rangle + \langle\xi_j|\hat{\mathbf{H}}_e\vec{\nabla}_n|\xi_i\rangle &= \left(\vec{\nabla}_n u_i\right)\langle\xi_j|\xi_i\rangle + u_i\langle\xi_j|\vec{\nabla}_n|\xi_i\rangle \\
\Rightarrow \langle\xi_j|\vec{\nabla}_n\hat{\mathbf{H}}_e|\xi_i\rangle + u_j\langle\xi_j|\vec{\nabla}_n|\xi_i\rangle &= 0 + u_i\langle\xi_j|\vec{\nabla}_n|\xi_i\rangle \\
\Rightarrow \vec{\tau}_{ji} &= \frac{\langle\xi_j|\vec{\nabla}_n\hat{\mathbf{H}}_e|\xi_i\rangle}{u_i - u_j}.
\end{aligned}$$

Now, we come back to Eq. (12) and use Eq. (16) to have:

$$\begin{aligned}
\sum_i \left\{-\frac{1}{2}\delta_{ji}\nabla_n^2 - \vec{\tau}_{ji}^{(1)}.\vec{\nabla}_n - \frac{1}{2}\sum_k \vec{\tau}_{jk}^{(1)}.\vec{\tau}_{ki}^{(1)} - \frac{1}{2}\vec{\nabla}_n.\vec{\tau}_{ji}^{(1)} + \delta_{ji}(u_i - E)\right\}\psi_i &= 0 \\
\Rightarrow -\frac{1}{2}\sum_i \left\{\delta_{ji}\nabla_n^2\psi_i + 2\vec{\tau}_{ji}^{(1)}.(\vec{\nabla}_n\psi_i) + \sum_k \vec{\tau}_{jk}^{(1)}.\vec{\tau}_{ki}^{(1)}\psi_i + (\vec{\nabla}_n.\vec{\tau}_{ji}^{(1)})\psi_i - 2\delta_{ji}(u_i - E)\psi_i\right\} &= 0.
\end{aligned}$$

The above expression can be simplified as:

$$\sum_i \left[-\frac{1}{2}\sum_k \left\{(\delta_{jk}\vec{\nabla}_n + \vec{\tau}_{jk}).(\delta_{ki}\vec{\nabla}_n + \vec{\tau}_{ki})\right\} + \delta_{ji}(u_i - E)\right]\psi_i = 0,$$

which in matrix notation becomes:

$$\left[-\frac{1}{2}(\vec{\boldsymbol{\nabla}}_n + \vec{\boldsymbol{\tau}})^2 + \mathbf{u} - E\right]\boldsymbol{\psi} = 0. \tag{20}$$

Here, $\vec{\boldsymbol{\tau}}$ is the Non-Adiabatic Coupling matrix (NACM) and $\mathbf{u}$ is the Adiabatic Potential Energy Matrix. This is the **adiabatic representation** of the molecular SE where it becomes kinetically coupled. Born - Oppenheimer approximation or the adiabatic approximation comes into play whenever the NACT matrix, $\vec{\boldsymbol{\tau}}$ is neglected in Eq. (20). Under this approximation, the nuclear SE becomes uncoupled.

$$\left(-\frac{1}{2}\boldsymbol{\nabla}_n^2 + \mathbf{u} - E\right)\boldsymbol{\psi} = 0.$$

It is evident from Eq. (19) that close to any degeneracy point in the nuclear configuration space, the NACTs take up substantial magnitudes, often tending to blow up. So, we can not just neglect them from the SE by applying the BO approximation. Yet within the adiabatic representation they are not numerically amenable. So the pursuit for a different representation begins where we could avoid such singularities and can have numerically tractable solutions of the electronic SE.

Going to the Diabatic Representation:

Method 1: Choosing an electronic basis set, parameterized by a fixed nuclear coordinate, i.e. the

total molecular wave function is written as:

$$|\Psi(s_e, s_n)\rangle = \sum_i \tilde{\psi}_i(s_n)|\xi_i(s_e|s_0)\rangle, \tag{21}$$

where, $\tilde{\psi}_i(s_n) \equiv \tilde{\psi}_i(s_n|s_0)$, depends parametrically on s_0, and $|\xi_i(s_e|s_0)\rangle$'s satisfy the corresponding electronic SE:

$$\hat{\mathbf{H}}_e(s_e|s_0)|\xi_i(s_e|s_0)\rangle = u_i(s_0)|\xi_i(s_e|s_0)\rangle.$$

Using the above form of $|\Psi(s_e, s_n)\rangle$, Eq. (7) becomes:

$$(\hat{\mathbf{T}}_n(s_n) + \hat{\mathbf{H}}_e(s_e|s_n)) \sum_i \tilde{\psi}_i(s_n)|\xi_i(s_e|s_0)\rangle = E \sum_i \tilde{\psi}_i(s_n)|\xi_i(s_e|s_0)\rangle.$$

Applying bra $\langle\xi_j(s_e|s_0)|$ from the left on the above equation:

$$\sum_i \left[\delta_{ji}(\hat{\mathbf{T}}_n(s_n) - E) + \langle\xi_j(s_e|s_0)|\hat{\mathbf{H}}_e(s_e|s_n)|\xi_i(s_e|s_0)\rangle\right] \tilde{\psi}_i(s_n) = 0$$

$$\Rightarrow \sum_i \left[\delta_{ji}(-\frac{1}{2}\nabla_n^2 - E) + \mathbf{V}_{ji}(s_n|s_0)\right] \tilde{\psi}_i(s_n) = 0, \tag{22}$$

where,

$$\mathbf{V}_{ji}(s_n|s_0) = \langle\xi_j(s_e|s_0)|\hat{\mathbf{H}}_e(s_e|s_n)|\xi_i(s_e|s_0)\rangle.$$

$$\text{Now,} \qquad \hat{\mathbf{H}}_e(s_e|s_n) = \hat{\mathbf{T}}_n(s_n) + \hat{\mathbf{U}}(s_e|s_n),$$

$$\text{and,} \qquad \hat{\mathbf{H}}_e(s_e|s_0) = \hat{\mathbf{T}}_n(s_n) + \hat{\mathbf{U}}(s_e|s_0),$$

$$\therefore \qquad \hat{\mathbf{H}}_e(s_e|s_n) = \hat{\mathbf{H}}_e(s_e|s_0) + (\hat{\mathbf{U}}(s_e|s_n) - \hat{\mathbf{U}}(s_e|s_0)).$$

So, we can write

$$\mathbf{V}_{ji}(s_n|s_0) = u_i(s_0) + \langle\xi_j(s_e|s_0)|\hat{\mathbf{U}}(s_e|s_n) - \hat{\mathbf{U}}(s_e|s_0)|\xi_i(s_e|s_0)\rangle.$$

Thus, Eq. (22) becomes potentially coupled which in the matrix representation becomes:

$$\left(-\frac{1}{2}\nabla_n^2 + \mathbf{V} - E\right)\tilde{\boldsymbol{\psi}} = 0. \tag{23}$$

Thus we transform Eq. (20) into Eq. (23) where all the couplings are transferred from the kinetic energy part to the potential energy part. Eq. (23) is in the **Diabatic Representation** where the off-diagonal terms of the potential energy matrix assume non-zero values.

Digression 2: How are the electronic basis sets $|\xi_i(s_e|s_0)\rangle$ and $|\xi_i(s_e|s_n)\rangle$ related?

We can see that:

$$\begin{aligned}\vec{\nabla}_n|\xi_i(s_e|s_n)\rangle &= \sum_j |\xi_j(s_e|s_n)\rangle\langle\xi_j(s_e|s_n)|\vec{\nabla}_n|\xi_i(s_e|s_n)\rangle \\ &= \sum_j \vec{\tau}_{ji}|\xi_j(s_e|s_n)\rangle \\ &= -\sum_j \vec{\tau}_{ij}|\xi_j(s_e|s_n)\rangle.\end{aligned}$$

In matrix notation, $\vec{\boldsymbol{\nabla}}_n|\boldsymbol{\xi}(s_e|s_n)\rangle = -\vec{\boldsymbol{\tau}}|\boldsymbol{\xi}(s_e|s_n)\rangle$.

In other words, we have to solve the differential equation:

$$\vec{\boldsymbol{\nabla}}_n|\boldsymbol{\xi}(s_e|s_n)\rangle + \vec{\boldsymbol{\tau}}|\boldsymbol{\xi}(s_e|s_n)\rangle = 0, \tag{24}$$

to establish the relation between $|\xi_i(s_e|s_0)\rangle$ and $|\xi_i(s_e|s_n)\rangle$.
Now for a first order vectorial linear differential equation of type:

$$\vec{\boldsymbol{\nabla}}\boldsymbol{\Omega} + \vec{\boldsymbol{\tau}}\boldsymbol{\Omega} = 0,$$

where, $\boldsymbol{\Omega}$ is a scalar matrix, we can show that the approximated solution can be written in the form:

$$\boldsymbol{\Omega}(s) = \zeta \exp\left(-\int_{s_0}^{s} \vec{\boldsymbol{\tau}}(s').d\vec{s}'\right)\boldsymbol{\Omega}(s_0). \tag{25}$$

ζ is the ordering operator which defines the order of integration along the given contour ($s_0 \to s_1 \to s_2, ... \to s$).

Having knowledge of the above equation, we can write the solution of Eq. (24) as:

$$|\boldsymbol{\xi}(s_e|s_n)\rangle = \zeta \exp\left(-\int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n\right)|\boldsymbol{\xi}(s_e|s_0)\rangle,$$

or, we can write,

$$|\boldsymbol{\xi}(s_e|s_n)\rangle = \tilde{\mathbf{A}}(s_n|s_0)|\boldsymbol{\xi}(s_e|s_0)\rangle, \tag{26}$$

where,

$$\tilde{\mathbf{A}}(s_n|s_0) = \zeta \exp\left(-\int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n\right), \tag{27}$$

is the transformation matrix operating on the electronic basis set $|\boldsymbol{\xi}(s_e|s_0)\rangle$ to give $|\boldsymbol{\xi}(s_e|s_n)\rangle$. It can be shown that the matrix $\tilde{\mathbf{A}}(s_n|s_0)$ is orthogonal.

We see that:

$$\begin{aligned}
\tilde{\mathbf{A}}(s_n|s_0)^\dagger \tilde{\mathbf{A}}(s_n|s_0) &= \zeta \exp\left(-\int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n\right)^\dagger \zeta \exp\left(-\int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n\right) \\
&= \exp\left(-\zeta \int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}^\dagger(s'_n).d\vec{s}'_n\right) \exp\left(-\zeta \int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n\right) \\
&= \exp\left(\zeta \int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n\right) \exp\left(-\zeta \int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n\right) \\
&= \mathbf{I}
\end{aligned}$$

Thus, $\tilde{\mathbf{A}}(s_n|s_0)$ is orthogonal.

Method 2: By carrying out a transformation of the nuclear wave function $\boldsymbol{\psi}$ in the adiabatic representation to another wave function $\boldsymbol{\phi}^d$ for the Diabatic representation. They are related in the following way:

$$\boldsymbol{\psi}(s_n) = \mathbf{A}(s_n)\boldsymbol{\phi}^d(s_n) \tag{28}$$

Using, the above expression of $\boldsymbol{\psi}$, we work out the L.H.S of the SE in Eq. (20):

$$-\frac{1}{2}(\vec{\boldsymbol{\nabla}}_n + \vec{\boldsymbol{\tau}})^2 \mathbf{A}\boldsymbol{\phi}^d + (\mathbf{u} - E)\mathbf{A}\boldsymbol{\phi}^d = 0 \tag{29}$$

Now,

$$\begin{aligned}
(\vec{\boldsymbol{\nabla}}_n + \vec{\boldsymbol{\tau}})^2 \mathbf{A}\boldsymbol{\phi}^d &= (\vec{\boldsymbol{\nabla}}_n + \vec{\boldsymbol{\tau}}).(\vec{\boldsymbol{\nabla}}_n + \vec{\boldsymbol{\tau}})\mathbf{A}\boldsymbol{\phi}^d \\
&= (\vec{\boldsymbol{\nabla}}_n + \vec{\boldsymbol{\tau}}).\left\{\mathbf{A}\vec{\boldsymbol{\nabla}}_n\boldsymbol{\phi}^d + (\vec{\boldsymbol{\nabla}}_n\mathbf{A})\boldsymbol{\phi}^d + \vec{\boldsymbol{\tau}}\mathbf{A}\boldsymbol{\phi}^d\right\} \\
&= 2(\vec{\boldsymbol{\nabla}}_n\mathbf{A}).\vec{\boldsymbol{\nabla}}_n\boldsymbol{\phi}^d + \mathbf{A}\boldsymbol{\nabla}_n^2\boldsymbol{\phi}^d + (\boldsymbol{\nabla}_n^2\mathbf{A})\boldsymbol{\phi}^d \\
&+ (\vec{\boldsymbol{\nabla}}_n.\vec{\boldsymbol{\tau}})\mathbf{A}\boldsymbol{\phi}^d + 2\vec{\boldsymbol{\tau}}.(\vec{\boldsymbol{\nabla}}_n\mathbf{A})\boldsymbol{\phi}^d + 2\vec{\boldsymbol{\tau}}.\mathbf{A}(\vec{\boldsymbol{\nabla}}_n\boldsymbol{\phi}^d) + \boldsymbol{\tau}^2\mathbf{A}\boldsymbol{\phi}^d
\end{aligned}$$

which can be simplified to

$$(\vec{\boldsymbol{\nabla}}_n + \vec{\boldsymbol{\tau}})^2 \mathbf{A}\boldsymbol{\phi}^d = \mathbf{A}\boldsymbol{\nabla}_n^2\boldsymbol{\phi}^d + 2(\vec{\boldsymbol{\nabla}}_n\mathbf{A} + \vec{\boldsymbol{\tau}}\mathbf{A}).\vec{\boldsymbol{\nabla}}_n\boldsymbol{\phi}^d + \left\{(\vec{\boldsymbol{\tau}} + \vec{\boldsymbol{\nabla}}_n).(\vec{\boldsymbol{\nabla}}_n\mathbf{A} + \vec{\boldsymbol{\tau}}\mathbf{A})\right\}\boldsymbol{\phi}^d \tag{30}$$

If we choose the matrix $\mathbf{A}$ such that it satisfies the following equation,

$$\vec{\boldsymbol{\nabla}}_n\mathbf{A} + \vec{\boldsymbol{\tau}}\mathbf{A} = 0 \tag{31}$$

we could reduce Eq. (29) into

$$-\frac{1}{2}\mathbf{A}\boldsymbol{\nabla}_n^2\boldsymbol{\phi}^d + (\mathbf{u} - E)\mathbf{A}\boldsymbol{\phi}^d = 0 \tag{32}$$

Digression 3: Properties of A matrix:

We can show that $\mathbf{A}$ matrix is orthogonal:
Multiplying Eq. (31) by $\mathbf{A}^\dagger$ from the left, we get:

$$\mathbf{A}^\dagger \vec{\boldsymbol{\nabla}}_n \mathbf{A} + \mathbf{A}^\dagger \vec{\boldsymbol{\tau}} \mathbf{A} = 0 \tag{33}$$

Taking dagger of Eq. (31) and then multiplying $\mathbf{A}$ from right, we get:

$$(\vec{\boldsymbol{\nabla}}_n \mathbf{A}^\dagger)\mathbf{A} - \mathbf{A}^\dagger \vec{\boldsymbol{\tau}} \mathbf{A} = 0 \tag{34}$$

Adding Eq. (34) with (33) we obtain:

$$\begin{aligned} \mathbf{A}^\dagger \vec{\boldsymbol{\nabla}}_n \mathbf{A} + (\vec{\boldsymbol{\nabla}}_n \mathbf{A}^\dagger)\mathbf{A} &= 0 \\ \Rightarrow \vec{\boldsymbol{\nabla}}_n (\mathbf{A}^\dagger \mathbf{A}) &= 0 \\ \Rightarrow \mathbf{A}^\dagger \mathbf{A} &= \text{const.} \end{aligned}$$

By choosing appropriate boundary conditions, we can write:

$$\mathbf{A}^\dagger \mathbf{A} = \mathbf{A}\mathbf{A}^\dagger = \mathbf{I} \tag{35}$$

Having knowing the orthogonality property of $\mathbf{A}$ matrix, we left multiply Eq. (32) by $\mathbf{A}^\dagger$ and obtain the SE in **diabatic representation**:

$$-\frac{1}{2}\boldsymbol{\nabla}_n^2 \boldsymbol{\phi}^d + (\mathbf{W} - E)\boldsymbol{\phi}^d = 0 \tag{36}$$

where,

$$\mathbf{W} = \mathbf{A}^\dagger \mathbf{u} \mathbf{A} \tag{37}$$

The $\mathbf{W}$ matrix is the new potential energy matrix in the diabatic representation having non-zero off-diagonal terms. Thus Eq. (36) also represents the SE in the **diabatic representation** where we have couplings embedded in the potential energy matrix.

Both the methods (1) and (2) provide us the routes for adiabatic-to-diabatic (ADT) transformation. But we can show that the two methods are equivalent that results into the same diabatic representation.

Method (1) and (2) are equivalent:
The condition in Eq.(31) is an important relation in the adiabatic-to-diabatic (ADT) transformation procedure called as the **ADT equation**. We can write the solution of the ADT equation by exploiting the form of the solution given in Eq.(25), i.e.:

$$\mathbf{A}(s_n) = \zeta \exp\left(- \int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n \right) \mathbf{A}(s_0). \tag{38}$$

By choosing appropriate boundary conditions, we can have $\mathbf{A}(s_0) = \mathbf{I}$ which simplifies the above expression as:

$$\mathbf{A}(s_n) = \zeta \exp\left(- \int_{s_0}^{s_n} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n \right). \tag{39}$$

We see from Eq. (27) and (39), that:

$$\tilde{\mathbf{A}}(s_n|s_0) = \mathbf{A}(s_n). \tag{40}$$

Now, recalling the expression for the total molecular wave function, which we write in the matrix form as:

$$\Psi(s_e, s_n) = \boldsymbol{\xi}^T(s_e|s_n)\boldsymbol{\psi}(s_n).$$

Now, from Eq. (26) we can write:

$$\begin{aligned} \Psi(s_e, s_n) &= \boldsymbol{\xi}^T(s_e|s_0)\tilde{\mathbf{A}}^\dagger\boldsymbol{\psi}(s_n) \\ &= \boldsymbol{\xi}^T(s_e|s_0)\mathbf{A}^\dagger\boldsymbol{\psi}(s_n) \qquad \text{(from Eq. (40))} \\ &= \boldsymbol{\xi}^T(s_e|s_0)\boldsymbol{\phi}^d(s_n) \qquad \text{(from Eq. (28))} \end{aligned}$$

Comparing the above expression with the matrix form of Eq. (21), we affirm that:

$$\tilde{\boldsymbol{\psi}}(s_n) = \boldsymbol{\phi}^d(s_n).$$

Thus, the diabatic wave functions in the two different methods are actually same which would lead to the same diabatic representation of the SE. And, it is needless to mention that the potentials in this particular representation from the two methods are also same:

$$\mathbf{V} = \mathbf{W}.$$

Path Dependent ADT Matrices:

We consider the following ADT equations characterized by the nuclear coordinates p and q:

$$\frac{\partial}{\partial p}\mathbf{A}(p,q) + \boldsymbol{\tau}_p\mathbf{A}(p,q) = 0 \tag{41a}$$

$$\frac{\partial}{\partial q}\mathbf{A}(p,q) + \boldsymbol{\tau}_q\mathbf{A}(p,q) = 0 \tag{41b}$$

We know that the solution for any of these scalar equation is given by Eq. (38), i.e.

$$\mathbf{A}(s|\Gamma) = \zeta \exp\left(- \int_{s_0}^{s} \vec{\boldsymbol{\tau}}(s'_n).d\vec{s}'_n \right) \mathbf{A}(s_0), \tag{42}$$

where, Γ is the contour of integration from $(s_0 \to s)$.

We carry out two consecutive steps of integration in two different paths Γ_1 and Γ_2 to reach a specific point and find the corresponding ADT matrices, $\mathbf{A}_1(p,q)$ and $\mathbf{A}_2(p,q)$ by employing Eq. (42). The two diff paths on the pq plane are chosen as follows:

$$\textbf{S.I:} \qquad (p_0, q_0) \to (p_0 + \Delta p, q_0) \to (p_0 + \Delta p, q_0 + \Delta q)$$
$$\textbf{S.II:} \qquad (p_0, q_0) \to (p_0, q_0 + \Delta q) \to (p_0 + \Delta p, q_0 + \Delta q)$$

The corresponding ADT matrices for both the paths and steps are given by:

$$\textbf{S.I:} \qquad \mathbf{A}(p_0 + \Delta p, q_0) = \exp\left(-\int_{p_0}^{p_0+\Delta p} \boldsymbol{\tau}_p(p, q_0)dp\right)\mathbf{A}(p_0, q_0) \tag{43a}$$

$$\mathbf{A}(p_0 + \Delta p, q_0 + \Delta q) = \exp\left(-\int_{q_0}^{q_0+\Delta q} \boldsymbol{\tau}_q(p_0 + \Delta p, q)dq\right)\mathbf{A}(p_0 + \Delta p, q_0) \tag{43b}$$

$$\textbf{S.II:} \qquad \mathbf{A}(p_0, q_0 + \Delta q) = \exp\left(-\int_{q_0}^{q_0+\Delta q} \boldsymbol{\tau}_q(p_0, q)dq\right)\mathbf{A}(p_0, q_0) \tag{44a}$$

$$\mathbf{A}(p_0 + \Delta p, q_0 + \Delta q) = \exp\left(-\int_{p_0}^{p_0+\Delta p} \boldsymbol{\tau}_p(p, q_0 + \Delta q)dp\right)\mathbf{A}(p_0, q_0 + \Delta q) \tag{44b}$$

When Eqs. (43a) and (44a) are substituted in Eqs. (43b) and (44b), respectively, the corresponding ADT matrices for two different chosen paths will be:

$$\begin{aligned}\textbf{S.I:} \qquad \mathbf{A}_1 &\equiv \mathbf{A}(p_0 + \Delta p, q_0 + \Delta q) \\ &= \exp\left(-\int_{q_0}^{q_0+\Delta q} \boldsymbol{\tau}_q(p_0 + \Delta p, q)dq - \int_{p_0}^{p_0+\Delta p} \boldsymbol{\tau}_p(p, q_0)dp\right)\mathbf{A}(p_0, q_0)\end{aligned} \tag{45a}$$

$$\begin{aligned}\textbf{S.II:} \qquad \mathbf{A}_2 &\equiv \mathbf{A}(p_0 + \Delta p, q_0 + \Delta q) \\ &= \exp\left(-\int_{p_0}^{p_0+\Delta p} \boldsymbol{\tau}_p(p, q_0 + \Delta q)dp - \int_{q_0}^{q_0+\Delta q} \boldsymbol{\tau}_q(p_0, q)dq\right)\mathbf{A}(p_0, q_0)\end{aligned} \tag{45b}$$

Next we take dagger on Eq. (45a):

$$\mathbf{A}_1^\dagger = \mathbf{A}^\dagger(p_0, q_0)\exp\left(\int_{q_0}^{q_0+\Delta q} \boldsymbol{\tau}_q(p_0 + \Delta p, q)dq + \int_{p_0}^{p_0+\Delta p} \boldsymbol{\tau}_p(p, q_0)dp\right) \tag{46}$$

and then multiply it with Eq. (45b) to get:

$$\begin{aligned}\mathbf{A}_1^\dagger\mathbf{A}_2 &= \mathbf{A}^\dagger(p_0, q_0)\exp\Big[\int_{p_0}^{p_0+\Delta p}\Big(\boldsymbol{\tau}_p(p, q_0 + \Delta q) - \boldsymbol{\tau}_p(p, q_0)\Big)dp \\ &+ \int_{q_0}^{q_0+\Delta q}\Big(\boldsymbol{\tau}_q(p_0 + \Delta p, q) - \boldsymbol{\tau}_q(p_0, q)\Big)dq\Big]\mathbf{A}(p_0, q_0)\end{aligned} \tag{47a}$$

Considering a midpoint $(\bar{p},\bar{q})$ in the planer interval as $p_0 \leq \bar{p} \leq p_0+\Delta p$ and $q_0 \leq \bar{q} \leq q_0+\Delta q$ and assuming $\Delta p, \Delta q$ are small enough, we use the definition of numerical differentiation as well as integration around the midpoint $(\bar{p},\bar{q})$ and safely write Eq. (47a) as:

$$\begin{aligned}\mathbf{A}_1^\dagger \mathbf{A}_2 &= \mathbf{A}^\dagger(p_0,q_0)\exp\left(-\Delta q\int_{p_0}^{p_0+\Delta p}\frac{\partial \boldsymbol{\tau}_p(p,\bar{q})}{\partial q}dp+\Delta p\int_{q_0}^{q_0+\Delta q}\frac{\partial \boldsymbol{\tau}_q(\bar{p},q)}{\partial p}dq\right)\mathbf{A}(p_0,q_0)\\ &= \mathbf{A}^\dagger(p_0,q_0)\exp\left[-\Delta q\Delta q\left(\frac{\partial \boldsymbol{\tau}_p(\bar{p},\bar{q})}{\partial q}-\frac{\partial \boldsymbol{\tau}_q(\bar{p},\bar{q})}{\partial p}\right)\right]\mathbf{A}(p_0,q_0) \qquad (47b)\end{aligned}$$

which in turn takes the following form:

$$\mathbf{A}_1^\dagger \mathbf{A}_2 = \mathbf{A}^\dagger(p_0,q_0)\exp\left(-\Delta q\Delta q(\mathrm{curl}\boldsymbol{\tau})_{pq}\right)\mathbf{A}(p_0,q_0) \qquad (47c)$$

Since the argument of the exponential in Eq. (47c) is not a null matrix, the product matrix ($\mathbf{B}=\mathbf{A}_1^\dagger\mathbf{A}_2$) does not appear as unit matrix, and thereby, the ADT matrices, $\mathbf{A}_1(p,q)$ and $\mathbf{A}_2(p,q)$, are not the same at the point $(p_0+\Delta p, q_0+\Delta q)$ for two different chosen paths of integration, **S.I** and **S.II**. If the curl of the NAC matrix is zero (i.e. curl$\boldsymbol{\tau}$), both the chosen path (even any path) will produce the same ADT matrices. On the contrary, the product matrix ($\mathbf{B}=\mathbf{A}_1^\dagger\mathbf{A}_2$) is an orthogonal one as shown below:

$$\begin{aligned}\mathbf{B}^\dagger\mathbf{B} &= \mathbf{A}^\dagger(p_0,q_0)\exp\left(\Delta q\Delta q(\mathrm{curl}\boldsymbol{\tau})_{pq}\right)\mathbf{A}(p_0,q_0)\mathbf{A}^\dagger(p_0,q_0)\exp\left(-\Delta q\Delta q(\mathrm{curl}\boldsymbol{\tau})_{pq}\right)\mathbf{A}(p_0,q_0)\\ &= \mathbf{I} \qquad (48)\end{aligned}$$

where, curl$\vec{\boldsymbol{\tau}}$ is a skew - symmetric matrix, i.e. $(\mathrm{curl}\vec{\boldsymbol{\tau}})^\dagger = -\mathrm{curl}\vec{\boldsymbol{\tau}}$. Therefore, the ADT matrices, $\mathbf{A}_1(p,q)$ and $\mathbf{A}_2(p,q)$, are related through an orthogonal transformation matrix, $\mathbf{B}$.

Two state systems: The Jahn-Teller Model and the Longuet-Higgins phase:

At the point of degeneracy between the electronic states the diabatic potentials behave linearly as a function of nuclear coordinates:

$$\mathbf{W} = k\begin{pmatrix} y & x \\ x & -y \end{pmatrix}, \qquad (49)$$

where, (x,y) are some generalized nuclear coordinates and k is force constant. The eigenvalues of $\mathbf{W}$ are the adiabatic potential energies and the eigen vectors form the columns of the ADT matrix. So, we diagonalize $\mathbf{W}$ choosing the polar coordinates:

$$y=\rho\cos\phi \quad \text{and} \quad x=\rho\sin\phi$$

On solving we obtain the eigenvalues as:

$$u_1 = k\rho \quad \text{and} \quad u_2 = -k\rho,$$

where, $\rho = \{0, \infty\}$ and $\phi = \{0, 2\pi\}$. As given in the below figure, the two surfaces u_1 and u_2 form cone-like PESs with a common apex. At $\rho = 0$, they become degenerate.

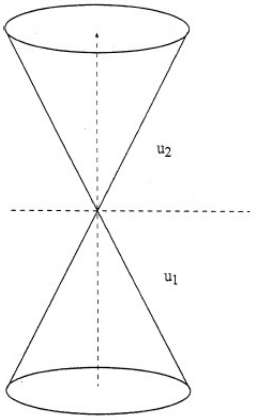

Figure 1: The two interacting cones within the Jahn-Teller Model.

The corresponding eigenvectors are:

$$\begin{aligned} \eta_1 &= \left(\frac{1}{\sqrt{\pi}}\cos\frac{\phi}{2}, \frac{1}{\sqrt{\pi}}\sin\frac{\phi}{2}\right), \\ \eta_2 &= \left(\frac{1}{\sqrt{\pi}}\sin\frac{\phi}{2}, -\frac{1}{\sqrt{\pi}}\cos\frac{\phi}{2}\right). \end{aligned}$$

The components of the two eigenvectors (η_1, η_2) when multiplied with the diabatic electronic basis set, $(|\xi_1^d\rangle, |\xi_2^d\rangle)$, we obtain the corresponding adiabatic electronic basis set, $(|\xi_1^a\rangle, |\xi_2^a\rangle)$, which is as follows:

$$\begin{aligned} |\xi_1^a\rangle &= \frac{1}{\sqrt{\pi}}\cos\frac{\phi}{2}|\xi_1^d\rangle + \frac{1}{\sqrt{\pi}}\sin\frac{\phi}{2}|\xi_2^d\rangle, \\ |\xi_2^a\rangle &= \frac{1}{\sqrt{\pi}}\sin\frac{\phi}{2}|\xi_1^d\rangle - \frac{1}{\sqrt{\pi}}\cos\frac{\phi}{2}|\xi_2^d\rangle. \end{aligned} \tag{50}$$

The adiabatic functions show an interesting characteristic: they change sign whenever they are brought upon the same point by a rotation from ϕ to $\phi + 2\pi$. This implies that the electronic adiabatic functions are not single-valued while surrounding a point of degeneracy.

In order to get rid of the multi-valuedness of the electronic eigenfunctions, Longuet-Higgins introduced a complex phase factor (in quite some *ad-hoc* manner) which takes care of the sign of the wave functions, i.e.:

$$|\zeta_j\rangle = \exp(i\phi/2)|\xi_j^a\rangle; \quad j = 1, 2. \tag{51}$$

The $|\zeta_j\rangle$s become single-valued, however instead of being real, they become complex. This has a direct influence in the expression of NACTs, which will be now be modified as:

$$\begin{aligned}
\vec{\tau}'_{ij} &= \langle\zeta_i|\vec{\nabla}|\zeta_j\rangle \\
&= \langle\xi_i^a|e^{(-i\phi/2)}\vec{\nabla}|e^{(i\phi/2)}\xi_j^a\rangle \\
&= \frac{i\vec{\nabla}\phi}{2}\langle\xi_i^a|e^{(-i\phi/2)}e^{(i\phi/2)}|\xi_j^a\rangle + \langle\xi_i^a|e^{(-i\phi/2)}e^{(i\phi/2)}|\vec{\nabla}\xi_j^a\rangle \\
&= \frac{i\vec{\nabla}\phi}{2}\delta_{ij} + \vec{\tau}_{ij} \qquad (52)
\end{aligned}$$

Hence,

$$\begin{aligned}
\text{for, } i = j \quad \vec{\tau}'_{jj} &= \frac{i\vec{\nabla}\phi}{2} \\
\text{for, } i \neq j \quad \vec{\tau}'_{ij} &= \vec{\tau}_{ij}
\end{aligned}$$

This change in definition of the NACTs will also affect the BO equation. Consider for an isolated single state expressed in terms of the newly defined complex electronic eigen function, the BO equation will be modified as:

$$\left[-\frac{1}{2}\left(\vec{\nabla} + i\vec{\alpha}\right)^2 + u - E\right]\psi = 0, \qquad (53)$$

where,

$$\vec{\alpha} = \frac{\vec{\nabla}\phi}{2}, \qquad (54)$$

whereas, for the ordinary case where the electronic eigen function is real, the BO equation for a single state will be:

$$\left(-\frac{1}{2}\nabla^2 + u - E\right)\psi = 0,$$

It is because $\vec{\tau}'_{11} \neq 0, \vec{\tau}'_{11} = i\alpha$ for the former case whereas for the latter case $\vec{\tau}_{11} = 0$ by virtue.
The Eq. (53) is called as the **Extended Born - Oppenheimer Equation** (given for a single state) which describes the effect of Jahn-Teller CI originating from two interacting states.

The quasi-Jahn-Teller Model: Mathieu Equation:

We define a model Hamiltonian that describes the atomic system within a degenerate manifold of electronic states $|\zeta_i\rangle$, $i = 1, ..., N$ coupled to a nuclear system in the following way:

$$\hat{\mathbf{H}} = -\frac{1}{2}E_{el}\frac{\partial^2}{\partial\theta^2} + \hat{\mathbf{T}}_n + F(q,\phi) - G(q,\phi)\cos(2\theta - \phi), \qquad (55)$$

where, E_{el} is a characteristic electronic energy value, θ is an electronic phase angle, q and ϕ are nuclear coordinates, $\hat{\mathbf{T}}_n$ is the nuclear kinetic energy operator described in terms of the polar

coordinates:

$$\hat{\mathbf{T}}_n = -\frac{1}{2}\left(\frac{\partial^2}{\partial q^2} + \frac{1}{q}\frac{\partial}{\partial q} + \frac{1}{q^2}\frac{\partial^2}{\partial \phi^2}\right), \tag{56}$$

and, $F(q,\phi)$ and $G(q,\phi)$ are two general nuclear potentials which for the present purpose, we can regard as the harmonic oscillator potential $\frac{1}{2}q^2$ and a linear coupling term q, respectively. Thus, the Hamiltonian becomes:

$$\hat{\mathbf{H}} = -\frac{1}{2}E_{el}\frac{\partial^2}{\partial \theta^2} + \hat{\mathbf{T}}_n + \frac{1}{2}q^2 - q\cos(2\theta - \phi). \tag{57}$$

The last term couples the nuclear motion with the electronic motion.

The electronic eigenfunctions are solutions of the following electronic SE:

$$\left(-\frac{1}{2}E_{el}\frac{\partial^2}{\partial \theta^2} - q\cos(2\theta - \phi) - \tilde{u}_i(q,\phi)\right)\xi_i(\theta, q, \phi) = 0, \tag{58}$$

where, $\tilde{u}_i(q,\phi)$ are the electronic eigenvalues.

It can be shown that the approximate solutions of Eq. (58), related to the two lowest eigenvalues, are:

$$\xi_1 = \frac{1}{\sqrt{\pi}}\cos\left(\theta - \frac{\phi}{2}\right) \quad \text{and} \quad \xi_2 = \frac{1}{\sqrt{\pi}}\sin\left(\theta - \frac{\phi}{2}\right),$$

corresponding to the eigenvalues:

$$\tilde{u}_i = \frac{1}{2}E_{el} \mp q; \quad i = 1, 2.$$

The two lowest adiabatic PESs are then:

$$\begin{aligned} u_i(q,\phi) &= \tilde{u}_i(q,\phi) + \frac{1}{2}q^2; \quad i = 1, 2 \\ \Rightarrow u_i(q,\phi) &= \frac{1}{2}E_{el} \mp q + \frac{1}{2}q^2; \quad i = 1, 2. \end{aligned} \tag{59}$$

Next, we find the magnitude of the NACT, τ_{12}; as the electronic wave functions does not depend upon q, the radial component of the NACT does not exist. The angular component τ_{12}^{ϕ} is given by:

$$\begin{aligned} \tau_{12}^{\phi} &= \langle \xi_1 | \frac{1}{q}\frac{\partial}{\partial \phi} | \xi_2 \rangle \\ &= \frac{1}{q\pi}\int_0^{2\pi} \cos\left(\theta - \frac{\phi}{2}\right)\frac{\partial}{\partial \phi}\sin\left(\theta - \frac{\phi}{2}\right) d\theta \\ &= -\frac{1}{2q\pi}\int_0^{2\pi} \cos^2\left(\theta - \frac{\phi}{2}\right) d\theta = -\frac{1}{2q\pi}.\pi \\ &= -\frac{1}{2q}. \end{aligned}$$

Now, recalling the coupled adiabatic equations, we have:

$$\sum_i \left\{ -\frac{1}{2}\delta_{ji}\nabla_n^2 - \vec{\tau}_{ji}^{(1)}.\vec{\nabla}_n - \frac{1}{2}\sum_k \vec{\tau}_{jk}^{(1)}.\vec{\tau}_{ki}^{(1)} - \frac{1}{2}\vec{\nabla}_n.\vec{\tau}_{ji}^{(1)} + \delta_{ji}(u_i - E) \right\} \psi_i = 0,$$

where, ψ_is are the adiabatic nuclear wave functions. These equations can be written as:

$$\left(-\frac{1}{2}\nabla_n^2+\frac{1}{2}(\tau_{12}^2)_{11}+u_1-E\right)\psi_1+\left(-\vec{\tau}_{12}.\vec{\nabla}_n-\frac{1}{2}\vec{\nabla}_n.\vec{\tau}_{12}\right)\psi_2=0,$$
$$\left(\vec{\tau}_{12}.\vec{\nabla}_n+\frac{1}{2}\vec{\nabla}_n.\vec{\tau}_{12}\right)\psi_1+\left(-\frac{1}{2}\nabla_n^2+\frac{1}{2}(\tau_{12}^2)_{22}+u_2-E\right)\psi_2=0,$$

which upon simplification becomes:

$$\left(-\frac{1}{2q^2}\frac{\partial^2}{\partial\phi^2}+\frac{1}{8q^2}+u_1-E\right)\psi_1+\frac{1}{2q^2}\frac{\partial}{\partial\phi}\psi_2=0,$$
$$-\frac{1}{2q^2}\frac{\partial}{\partial\phi}\psi_1+\left(-\frac{1}{2q^2}\frac{\partial^2}{\partial\phi^2}+\frac{1}{8q^2}+u_2-E\right)\psi_2=0. \tag{60}$$

Though the above system of equations are solvable but we prefer to do it by transforming them into the diabatic representation. We employ the ADT matrix which transforms the nuclear wave functions as:

$$\boldsymbol{\psi}=\mathbf{A}\boldsymbol{\eta}$$

where, we choose $\mathbf{A}$ to be an orthogonal matrix as:

$$\mathbf{A}=\begin{pmatrix}\cos\alpha & \sin\alpha\\ -\sin\alpha & \cos\alpha\end{pmatrix}.$$

Thus, we have:

$$\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=\begin{pmatrix}\cos\alpha & \sin\alpha\\ -\sin\alpha & \cos\alpha\end{pmatrix}\begin{pmatrix}\eta_1\\ \eta_2\end{pmatrix}$$

α is called the ADT angle which constitutes the ADT matrix.

We can now solve the ADT equation [Eq. (31)] to obtain the explicit value of the ADT angle, α. Thus ADT equation will give us:

$$\begin{pmatrix}-\sin\alpha & \cos\alpha\\ -\cos\alpha & -\sin\alpha\end{pmatrix}\vec{\nabla}\alpha+\begin{pmatrix}0 & \vec{\tau}_{12}\\ -\vec{\tau}_{12} & 0\end{pmatrix}\begin{pmatrix}\cos\alpha & \sin\alpha\\ -\sin\alpha & \cos\alpha\end{pmatrix} = 0$$
$$\Rightarrow\begin{pmatrix}-\sin\alpha & \cos\alpha\\ -\cos\alpha & -\sin\alpha\end{pmatrix}\vec{\nabla}\alpha+\begin{pmatrix}-\vec{\tau}_{12}\sin\alpha & \vec{\tau}_{12}\cos\alpha\\ -\vec{\tau}_{12}\cos\alpha & -\vec{\tau}_{12}\sin\alpha\end{pmatrix} = 0$$

This gives:

$$-\sin\alpha\vec{\nabla}\alpha-\sin\alpha\vec{\tau}_{12}=0 \quad \text{or} \quad \cos\alpha\vec{\nabla}\alpha+\cos\alpha\vec{\tau}_{12}=0,$$

which gives:

$$\begin{aligned} \vec{\nabla}\alpha &= -\vec{\tau}_{12} \\ \Rightarrow \frac{1}{q}\frac{\partial\alpha}{\partial\phi} &= -\tau_{\phi}^{12} \\ \Rightarrow \frac{1}{q}\frac{\partial\alpha}{\partial\phi} &= \frac{1}{2q} \\ \Rightarrow \alpha &= \frac{\phi}{2}. \end{aligned}$$

So, we have:

$$\begin{aligned} \psi_1 = \eta_1\cos\alpha + \eta_2\sin\alpha \quad \text{and} \quad \psi_2 = -\eta_1\sin\alpha + \eta_2\cos\alpha \\ \text{or,} \quad \psi_1 = \eta_1\cos\frac{\phi}{2} + \eta_2\sin\frac{\phi}{2} \quad \text{and} \quad \psi_2 = -\eta_1\sin\frac{\phi}{2} + \eta_2\cos\frac{\phi}{2} \end{aligned}$$

Putting the above form of ψ_is in Eq. (60), we obtain the coupled diabatic SE:

$$\begin{aligned} \left(-\frac{1}{2q^2}\frac{\partial^2}{\partial\phi^2} + u_1\cos^2\frac{\phi}{2} + u_2\sin^2\frac{\phi}{2}\right)\eta_1 + \left((u_1-u_2)\sin\frac{\phi}{2}\cos\frac{\phi}{2}\right)\eta_2 &= E\eta_1 \\ \left((u_1-u_2)\sin\frac{\phi}{2}\cos\frac{\phi}{2}\right)\eta_1 + \left(-\frac{1}{2q^2}\frac{\partial^2}{\partial\phi^2} + u_1\sin^2\frac{\phi}{2} + u_2\cos^2\frac{\phi}{2}\right)\eta_2 &= E\eta_2 \end{aligned}$$

Thus, the coupling between the two states are through the potential energies (diabatic) which in the matrix form can be written as:

$$\mathbf{W} = \begin{pmatrix} u_1\cos^2\frac{\phi}{2} + u_2\sin^2\frac{\phi}{2} & (u_1-u_2)\sin\frac{\phi}{2}\cos\frac{\phi}{2} \\ (u_1-u_2)\sin\frac{\phi}{2}\cos\frac{\phi}{2} & u_1\sin^2\frac{\phi}{2} + u_2\cos^2\frac{\phi}{2} \end{pmatrix}$$

Using the values of the adiabatic energies given in Eq. (59), we have the diabatic SE as:

$$\begin{aligned} \left(T_n + \frac{1}{2}E_{el} + \frac{q^2}{2} - q\cos\phi\right)\eta_1 - q\sin\phi\eta_2 = E\eta_1 \\ -q\sin\phi\eta_1 + \left(T_n + \frac{1}{2}E_{el} + \frac{q^2}{2} + q\cos\phi\right)\eta_2 = E\eta_2 \end{aligned} \tag{61}$$

Eq. (61) is a set of equations which does not contain the first derivative terms and free of any terms responsible for singularity at the degeneracy point.

Formulation of the Beyond Born-Oppenheimer theory in three state electronic sub-Hilbert space:

For a three state system, the total molecular wave function can be written as:

$$|\Psi(s_e, s_n)\rangle = \sum_{i=1}^{3} \psi_i(s_n)|\xi_i(s_e|s_n)\rangle.$$

The SE in the adiabatic representation is as:

$$\left[-\frac{1}{2}(\vec{\boldsymbol{\nabla}}_n + \vec{\boldsymbol{\tau}})^2 + \mathbf{u} - E\right]\boldsymbol{\psi}^{ad} = 0,$$

where, the NAC and the adiabatic PES matrix are defined as:

$$\vec{\boldsymbol{\tau}} = \begin{pmatrix} 0 & \vec{\tau}_{12} & \vec{\tau}_{13} \\ -\vec{\tau}_{12} & 0 & \vec{\tau}_{23} \\ -\vec{\tau}_{13} & -\vec{\tau}_{23} & 0 \end{pmatrix} \quad \text{and} \qquad \mathbf{u} = u_i\delta_{ij}\mathbf{I},$$

respectively. Within the same sub-Hilbert space, we can find the ADT matrix $\mathbf{A}$ which would transform ($\boldsymbol{\psi}^{ad} = \mathbf{A}\boldsymbol{\psi}^{d}$) the SE from the adiabatic representation into the diabatic representation as:

$$\left(-\frac{1}{2}\boldsymbol{\nabla}_n^2 + \mathbf{W} - E\right)\boldsymbol{\psi}^{d} = 0, \quad \mathbf{W} = \mathbf{A}^{\dagger}\mathbf{u}\mathbf{A}, \tag{62}$$

under the condition:

$$\vec{\boldsymbol{\nabla}}_n\mathbf{A} + \vec{\boldsymbol{\tau}}\mathbf{A} = 0, \tag{63}$$

which is the ADT equation.

The model form of $\mathbf{A}$ matrix for a three state sub-Hilbert space can be constructed by taking the product of three (3×3) rotation matrices, $\mathbf{A}_{12}(\Theta_{12})$, $\mathbf{A}_{23}(\Theta_{23})$ and $\mathbf{A}_{13}(\Theta_{13})$ in different order, where one of them is given by:

$$\mathbf{A}(\boldsymbol{\Theta_{12}}, \boldsymbol{\Theta_{23}}, \boldsymbol{\Theta_{13}}) = \mathbf{A_{12}}(\boldsymbol{\Theta_{12}}) \cdot \mathbf{A_{23}}(\boldsymbol{\Theta_{23}}) \cdot \mathbf{A_{13}}(\boldsymbol{\Theta_{13}}),$$

$$
\begin{aligned}
&= \begin{pmatrix} \cos\Theta_{12} & \sin\Theta_{12} & 0 \\ -\sin\Theta_{12} & \cos\Theta_{12} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\Theta_{23} & \sin\Theta_{23} \\ 0 & -\sin\Theta_{23} & \cos\Theta_{23} \end{pmatrix} \begin{pmatrix} \cos\Theta_{13} & 0 & \sin\Theta_{13} \\ 0 & 1 & 0 \\ -\sin\Theta_{13} & 0 & \cos\Theta_{13} \end{pmatrix} \\
&= \begin{pmatrix} \cos\Theta_{12}\cos\Theta_{13} & \sin\Theta_{12}\cos\Theta_{23} & \cos\Theta_{12}\sin\Theta_{13} \\ -\sin\Theta_{12}\sin\Theta_{13}\sin\Theta_{23} & & +\sin\Theta_{12}\cos\Theta_{13}\sin\Theta_{23} \\ -\sin\Theta_{12}\cos\Theta_{13} & \cos\Theta_{12}\cos\Theta_{23} & -\sin\Theta_{12}\sin\Theta_{13} \\ -\cos\Theta_{12}\sin\Theta_{13}\sin\Theta_{23} & & +\cos\Theta_{12}\cos\Theta_{13}\sin\Theta_{23} \\ -\sin\Theta_{13}\cos\Theta_{23} & -\sin\Theta_{23} & \cos\Theta_{13}\cos\Theta_{23} \end{pmatrix}. \qquad (64)
\end{aligned}
$$

Upon solving the ADT equation, Eq. (63), using the form of $\mathbf{A}$ in Eq. (64), we will obtain the following set of differential equations for the ADT angles:

$$
\begin{aligned}
\vec{\nabla}_n\Theta_{12} &= -\vec{\tau}_{12} + \tan\Theta_{23}(\vec{\tau}_{13}\cos\Theta_{12} - \vec{\tau}_{23}\sin\Theta_{12}), && (65a)\\
\vec{\nabla}_n\Theta_{23} &= -(\vec{\tau}_{13}\sin\Theta_{12} + \vec{\tau}_{23}\cos\Theta_{12}), && (65b)\\
\vec{\nabla}_n\Theta_{13} &= -\frac{1}{\cos\Theta_{23}}(\vec{\tau}_{13}\cos\Theta_{12} - \vec{\tau}_{23}\sin\Theta_{12}). && (65c)
\end{aligned}
$$

On the other hand, the explicit form of $\vec{\boldsymbol{\tau}}$ matrix elements in terms of ADT angles can be obtained as:

$$
\begin{aligned}
\vec{\tau}_{12} &= -\vec{\nabla}_n\Theta_{12} - \sin\Theta_{23}\vec{\nabla}_n\Theta_{13}, && (66a)\\
\vec{\tau}_{23} &= \sin\Theta_{12}\cos\Theta_{23}\vec{\nabla}_n\Theta_{13} - \cos\Theta_{12}\vec{\nabla}_n\Theta_{23}, && (66b)\\
\vec{\tau}_{13} &= -\cos\Theta_{12}\cos\Theta_{23}\vec{\nabla}_n\Theta_{13} - \sin\Theta_{12}\vec{\nabla}_n\Theta_{23}. && (66c)
\end{aligned}
$$

When the same model form of ADT matrix is substituted in Eq. (62), the elements of diabatic

potential matrix can be expressed in terms of adiabatic PESs and ADT angles as the following:

$$
\begin{aligned}
W_{11} &= u_1(\cos\Theta_{12}\cos\Theta_{13} - \sin\Theta_{12}\sin\Theta_{13}\sin\Theta_{23})^2 + u_2(\sin\Theta_{12}\cos\Theta_{13} + \cos\Theta_{12}\sin\Theta_{13}\sin\Theta_{23})^2 \\
&+ u_3\sin^2\Theta_{13}\cos^2\Theta_{23}, \qquad (67a)\\
W_{22} &= u_1\sin^2\Theta_{12}\cos^2\Theta_{23} + u_2\cos^2\Theta_{12}\cos^2\Theta_{23} + u_3\sin^2\Theta_{23}, \qquad (67b)\\
W_{33} &= u_1(\cos\Theta_{12}\sin\Theta_{13} + \cos\Theta_{13}\sin\Theta_{12}\sin\Theta_{23})^2 + u_2(\sin\Theta_{12}\sin\Theta_{13} - \cos\Theta_{12}\cos\Theta_{13}\sin\Theta_{23})^2 \\
&+ u_3\cos^2\Theta_{13}\cos^2\Theta_{23}, \qquad (67c)\\
W_{12} &= u_1\sin\Theta_{12}\cos\Theta_{23}(\cos\Theta_{12}\cos\Theta_{13} - \sin\Theta_{12}\sin\Theta_{13}\sin\Theta_{23}) \\
&- u_2\cos\Theta_{12}\cos\Theta_{23}(\sin\Theta_{12}\cos\Theta_{13} + \cos\Theta_{12}\sin\Theta_{13}\sin\Theta_{23}) \\
&+ u_3\sin\Theta_{13}\sin\Theta_{23}\cos\Theta_{23}, \qquad (67d)\\
W_{13} &= u_1(\cos\Theta_{12}\cos\Theta_{13} - \sin\Theta_{12}\sin\Theta_{13}\sin\Theta_{23})(\cos\Theta_{12}\sin\Theta_{13} + \sin\Theta_{12}\cos\Theta_{13}\sin\Theta_{23}) \\
&+ u_2(\sin\Theta_{12}\cos\Theta_{13} + \cos\Theta_{12}\sin\Theta_{13}\sin\Theta_{23})(\sin\Theta_{12}\sin\Theta_{13} - \cos\Theta_{12}\cos\Theta_{13}\sin\Theta_{23}) \\
&- u_3\sin\Theta_{13}\cos\Theta_{13}\cos^2\Theta_{23}, \qquad (67e)\\
W_{23} &= u_1\sin\Theta_{12}\cos\Theta_{23}(\cos\Theta_{12}\sin\Theta_{13} + \sin\Theta_{12}\cos\Theta_{13}\sin\Theta_{23}) \\
&+ u_2\cos\Theta_{12}\cos\Theta_{23}(-\sin\Theta_{12}\sin\Theta_{13} + \cos\Theta_{12}\cos\Theta_{13}\sin\Theta_{23}) \\
&- u_3\cos\Theta_{13}\sin\Theta_{23}\cos\Theta_{23}. \qquad (67f)
\end{aligned}
$$

We can use the analytic form of the NAC elements [Eqs. (66)] to formulate the explicit form of Curl equation for each NAC element in terms of the ADT angles:

$$
\begin{aligned}
\text{Curl}\ \tau_{pq}^{12} = C_{12} = Z_{12} &= -\cos\Theta_{23}(\nabla_q\Theta_{23}\nabla_p\Theta_{13} - \nabla_p\Theta_{23}\nabla_q\Theta_{13}), \qquad (68a)\\
\text{Curl}\ \tau_{pq}^{23} = C_{23} = Z_{23} &= \cos\Theta_{12}\cos\Theta_{23}(\nabla_q\Theta_{12}\nabla_p\Theta_{13} - \nabla_p\Theta_{12}\nabla_q\Theta_{13}) \\
&- \sin\Theta_{12}\sin\Theta_{23}(\nabla_q\Theta_{23}\nabla_p\Theta_{13} - \nabla_p\Theta_{23}\nabla_q\Theta_{13}) \\
&+ \sin\Theta_{12}(\nabla_q\Theta_{12}\nabla_p\Theta_{23} - \nabla_p\Theta_{12}\nabla_q\Theta_{23}), \qquad (68b)\\
\text{Curl}\ \tau_{pq}^{13} = C_{13} = Z_{13} &= \sin\Theta_{12}\cos\Theta_{23}(\nabla_q\Theta_{12}\nabla_p\Theta_{13} - \nabla_p\Theta_{12}\nabla_q\Theta_{13}) \\
&+ \cos\Theta_{12}\sin\Theta_{23}(\nabla_q\Theta_{23}\nabla_p\Theta_{13} - \nabla_p\Theta_{23}\nabla_q\Theta_{13}) \\
&- \cos\Theta_{12}(\nabla_q\Theta_{12}\nabla_p\Theta_{23} - \nabla_p\Theta_{12}\nabla_q\Theta_{23}), \qquad (68c)
\end{aligned}
$$

where the Curl due to vector product of NACTs and analyticity of ADT matrix are defined as: $C_{ij} = (\boldsymbol{\tau}_q\boldsymbol{\tau}_p)_{ij} - (\boldsymbol{\tau}_p\boldsymbol{\tau}_q)_{ij}$ and $Z_{ij} = \frac{\partial}{\partial p}\tau_q^{ij} - \frac{\partial}{\partial q}\tau_p^{ij}$, respectively. The Cartesian coordinates p and q denote nuclear DOFs. The cross derivatives of those angles [Eqs. (68)] provide us the functional form of Curl condition over the configuration space to explore the existence of three state sub-Hilbert space.