Beyond Born-Oppenheimer treatment on spectroscopic and scattering processes

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Abstract. We review the formulation of beyond Born-Oppenheimer (BBO) theory based on first principle for the construction of diabatic potential energy surfaces (PESs) both for few important spectroscopic systems, viz., Na$_3$ cluster, NO$_2$ radical as well as scattering process like D$^+$ + H$_2$. The essential theoretical development leading to the BBO equations are thoroughly discussed. It has been found that the above molecular systems possess numerous nonadiabatic interactions that range from Jahn-Teller, Renner-Teller types of conical intersections along with strong pseudo Jahn-Teller couplings between various electronic states. We have calculated the adiabatic PESs and nonadiabatic coupling terms for those systems and subsequently performed adiabatic-to-diabatic transformation to construct smooth, symmetric and continuous diabatic potential energy matrix. Nuclear dynamics has been performed on the diabatic PESs of Na$_3$ and NO$_2$ to simulate the photoelectron spectra that match quite well with the experimentally measured ones. Moreover, we have carried out reactive scattering dynamics on the adiabatic and diabatic surfaces of H$_3^+$ system to reproduce experimental cross sections for reactive charge and non-charge transfer processes.

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1. Introduction

Electronic nonadiabatic phenomena are ubiquitous in nature. Chemical processes starting from natural phenomena like photosynthesis, vision, excited state chemical reactions, solar energy conversion, photochemistry, etc. all involve electronically excited states. As a result, a violation of Born-Oppenheimer (BO) approximation\textsuperscript{1,2} is common rather than a rarity. Adiabatic potential energy surfaces (PESs) and nondiabatic coupling terms (NACTs) are the two major outcomes of the BO treatment that form the driving force governing the motion of atoms in molecular systems. While the former ones (PESs) define physically realizable solutions of the Schrödinger equation (SE) under BO treatment on which nuclei move, the latter (NACTs) are responsible for excited state dynamics and electronic transitions from one surface to another. Even ground state dynamics leading to rovibrational transitions become inaccurate if NACTs are non-negligible and that is the reality in general. It has been observed that calculations on photoexcitation spectra, charge transfer reactions\textsuperscript{3–7} and scattering cross-sections\textsuperscript{8–18} on single-, two- and three-surfaces show significant anomalies between single and multiple surface results.

NACTs are usually sharp functions that encounter singularities\textsuperscript{19,20} in nuclear configuration space (CS) whenever electronic degenerate states occur. These degeneracies often forming conical intersections (CIs) are key mechanistic elements in understanding radiationless transitions in polyatomic molecules. On the other hand, in order to handle numerical inaccuracies due to singularities of NACTs in the SE at CIs, we adopt a different representation known as \textit{diabatic} representation of the corresponding SE. This is achieved by a unitary transformation of the adiabatic SE commonly known as \textit{adiabatic-to-diabatic transformation} (ADT). In the diabatic framework, the vibronic couplings appear in the potential energy matrix which use to be smooth functions of the nuclear coordinates.

CIs render extremely fast and efficient switching paths for a molecule between its excited and ground electronic states. As observed by Longuet-Higgins, BO adiabatic eigenfunctions acquire phases and flip their sign while moving in a closed contour in nuclear configuration space (CS) around a CI.\textsuperscript{21,22} Herzberg and Longuet-Higgins corrected the multi-valuedness of the wavefunctions for Jahn-Teller (JT) CI model in an \textit{ad hoc} manner by introducing a complex phase factor known as Longuet-Higgins phase.\textsuperscript{23} Varandas \textit{et al.} investigated the above phenomenon in a re-
alistic molecular system (LiNaK) where it was shown that the dominant coefficients of adiabatic electronic eigenfunctions undergo sign flip along a loop enclosing a JT-CI.\textsuperscript{24} To cope with the singular nature of the NACTs, Hobey and McLachlan first discussed the ADT method to eliminate the NACTs from the close-coupled BO equations for a single degree of freedom (DOF),\textsuperscript{25} followed by Smith who attempted ADT for diatomic molecules.\textsuperscript{26} M. Baer studied the atom-diatom collision problem in detail and derived a set of differential equations for ADT matrix elements satisfying the ADT condition,\textsuperscript{27} where he suggested a solution in integral form along a two dimensional contour in nuclear configuration space.\textsuperscript{28} On the other hand, Mead, Truhlar and Kendrick discussed the removable and non-removable components of NACTs, where it has been shown that the ADT can at best remove the longitudinal component of the NACTs.\textsuperscript{29,30} Also, it has been observed that at the close proximity of a degeneracy, the removable part of the coupling blows up, but the non-removable component remains insignificant.\textsuperscript{31} The ADT angle(s) can be computed by integrating the derivative coupling at and around the CI point(s) or seam(s), and the close line integrals of such couplings will result into $n\pi$, $n$ being any integer.\textsuperscript{28,32,33}

Baer’s approach involving line integral over the NACTs to transform the adiabatic SE to diabatic framework for two-electronic state sub-Hilbert space (SHS) has been successful.\textsuperscript{27} It has been shown that such transformation for a given SHS is guaranteed only when the NACT vector fields satisfy the so-called “Curl condition”.\textsuperscript{34} Adhikari and co-workers have generalized the beyond Born-Oppenheimer (BBO) treatment for any three or more coupled electronic states with detailed analysis of curl conditions in terms of ADT angles, where the explicit form of NACTs, the ADT equations, the curl-divergence equations and diabatic PESs in terms of those angles are formulated.\textsuperscript{16,35–44} The aforementioned approach is further theoretically developed and reformulated by Adhikari \textit{et al.}, which leads to a practical way to use the “Curl condition” for the formulation of approximated Extended Born-Oppenheimer (EBO) equation.\textsuperscript{14,18} In addition, molecular symmetry (MS) has been incorporated to assign the appropriate irreducible representation of the NACTs by correcting their signs\textsuperscript{37,38} at different points in the nuclear CS so that the calculated diabatic PES matrix is totally symmetric. Thus, the present theory \textit{per se} is complete and is expected to provide single-valued, continuous, smooth, and symmetric diabatic PESs to carry out nuclear dynamics. The BBO theory has been implemented to explore its workability while investigating Jahn-Teller (JT),\textsuperscript{45} Pseudo Jahn-Teller (PJT)\textsuperscript{46} as well as Renner-Teller (RT)\textsuperscript{47} effects on various floppy molecules of spectroscopic interest.\textsuperscript{37–41} Electronic structure-wise complicated molecular systems like NO\textsubscript{2}\textsuperscript{39,40} and NO\textsubscript{3}\textsuperscript{48–50} have been thoroughly studied and the corresponding experimental photoelectron spectra are reproduced. Also, the theory has been applied to multisurface scattering process D$^+$+H\textsubscript{2} to calculate charge transfer reactive cross sections and the results are in quite good agreement with experimentally measured quantities.\textsuperscript{51}

This review focuses on the development and application of BBO theory on few of the spectroscopically important molecules like Na\textsubscript{3} cluster and NO\textsubscript{2} radical as well as D$^+$+H\textsubscript{2} collision process. The basic theoretical concepts leading to the necessary equations of BBO theory are first presented, followed by descriptions of the current methodology in understanding various nonadiabatic interactions in the above realistic molecular systems. Finally, we summarize our findings and key observations on the nonadiabaticities within those systems in a concluding section.
2. Beyond Born-Oppenheimer theory

2.1. Two state electronic sub-Hilbert space

The properties of molecular system can be observed by solving the time independent molecular SE:

\[ H(\vec{r}, \vec{R}) \Psi(\vec{r}, \vec{R}) = E \Psi(\vec{r}, \vec{R}), \tag{1} \]

where \( H(\vec{r}, \vec{R}) \) is the total molecular Hamiltonian and \( \Psi(\vec{r}, \vec{R}) \) is the molecular wave function. The electronic and nuclear coordinates are collectively denoted as \( \vec{r} \) and \( \vec{R} \), respectively. The molecular Hamiltonian is expressed as the sum of nuclear kinetic energy \( (T(\vec{R})) \) and electronic non-relativistic Hamiltonian \( (H^e(\vec{r}|\vec{R})) \), which depends parametrically on the nuclear coordinates:

\[ H(\vec{r}, \vec{R}) = T(\vec{R}) + H^e(\vec{r}|\vec{R}). \tag{2} \]

On the other hand, the molecular wavefunction is expressed upon the BO expansion for two-state SHS as:

\[ \Psi(\vec{r}, \vec{R}) = \sum_{i=1}^{2} \psi^{ad}_i(\vec{R}) \xi_i(\vec{r}|\vec{R}), \tag{3} \]

where the expansion coefficients, \( \psi^{ad}_i(\vec{R}) \) appear as the nuclear wavefunctions and \( \xi_i(\vec{r}|\vec{R}) \) are the eigenfunctions of the electronic Hamiltonian with eigenvalues \( u_i(\vec{R}) \):

\[ H^e(\vec{r}|\vec{R}) \xi_i(\vec{r}|\vec{R}) = u_i(\vec{R}) \xi_i(\vec{r}|\vec{R}). \tag{4} \]

Here we briefly discuss the BBO treatment for two state sub-Hilbert space\(^{28,34}\) to transform the adiabatic SE to the diabatic one through a unitary transformation matrix. The time independent molecular SE and the BO expansion of the molecular wavefunction leads to adiabatic representation of the nuclear SE in mass-weighted coordinates as:

\[ \sum_{j=1}^{2} \left( H_{ij} + (u_j - E) \delta_{ij} \right) \psi^{ad}_j(\vec{R}) = 0, \quad i = 1, 2 \tag{5} \]

where

\[ H_{ii} = -\frac{\hbar^2}{2} (\nabla^2_n + \tau^{(2)}_{ii}), \]
\[ H_{ij} = -\frac{\hbar^2}{2} (2\tau^{(1)}_{ij} \nabla_n + \tau^{(2)}_{ij}) = H^\dagger_{ji}, \quad i \neq j. \]

\( \tau^{(1)}_{ij} \) and \( \tau^{(2)}_{ij} \) are the elements of nonadiabatic coupling matrices of the first and second kind, respectively, which are defined as:

\[ \tau^{(1)}_{ij} = \langle \xi_i(\vec{r}|\vec{R}) | \nabla_n \xi_j(\vec{r}|\vec{R}) \rangle, \quad \tau^{(2)}_{ij} = \langle \xi_i(\vec{r}|\vec{R}) | \nabla^2_n \xi_j(\vec{r}|\vec{R}) \rangle, \tag{6} \]

and are related by:

\[ \tau^{(2)} = \tau^{(1)} + \nabla_n \tau^{(1)}. \tag{7} \]

The adiabatic SE can be written in more compact form as:

\[-\frac{\hbar^2}{2} \left( \nabla_n + \tau \right)^2 \psi^{ad} + (U - E) \psi^{ad} = 0, \tag{8} \]
where the antisymmetric $\vec{\tau}$ matrix is given as:

$$\vec{\tau} = \begin{pmatrix} 0 & \tilde{\tau}_{12} \\ -\tilde{\tau}_{12} & 0 \end{pmatrix}. \quad \text{(9)}$$

When the two states in concern constitute a SHS, it is possible to transform ($\psi^{ad} = A\psi^{dia}$) the adiabatic nuclear SE (Eq. 8) to the diabatic one as below,

$$-\frac{\hbar^2}{2} \nabla_n^2 \psi^{dia} + (W - E)\psi^{dia} = 0; \quad W = A^\dagger UA, \quad \text{(10)}$$

with $U_{ij} = u_i \delta_{ij}$, under the condition:

$$\vec{\nabla}_n A + \vec{\tau} A = 0. \quad \text{(11)}$$

The above equation is known as Adiabatic-to-Diabatic Transformation (ADT) condition, where the ADT matrix $A(\theta_{12})$ is constructed by angle of rotation ($\theta_{12}(\vec{R})$), commonly called mixing angle or ADT angle as:

$$A(\theta_{12}) = \begin{pmatrix} \cos \theta_{12} & \sin \theta_{12} \\ -\sin \theta_{12} & \cos \theta_{12} \end{pmatrix}. \quad \text{(12)}$$

When the above model form of $A$ (Eq. 12) and the antisymmetric form of $\vec{\tau}$ (Eq. 9) matrices are substituted in the ADT equation (Eq. 11), a simple manipulation leads to the following differential equation for ADT angle:

$$\vec{\nabla}_n \theta_{12} = -\tilde{\tau}_{12}. \quad \text{(13)}$$

The elements of the diabatic Hamiltonian matrix can be written in terms of ADT angle after incorporating the ADT matrix in Eq. 10 as:

$$W_{11} = u_1 \cos^2 \theta_{12} + u_2 \sin^2 \theta_{12},$$
$$W_{22} = u_1 \sin^2 \theta_{12} + u_2 \cos^2 \theta_{12},$$
$$W_{12} = (u_1 - u_2) \sin \theta_{12} \cos \theta_{12}. \quad \text{(14)}$$

In summary, for a two-state SHS, ab initio calculations provide the adiabatic PESs, $u_1$ and $u_2$, and the NACT, $\tilde{\tau}_{12}$ for each nuclear configuration and thereby, the ADT angle is obtained by solving Eq. 13 for those nuclear configurations, which can be used to construct the ADT matrix (Eq. 12) and subsequently, diabatic potential energy matrix elements (Eq. 14).

### 2.2. Three state electronic sub-Hilbert space

For a three state system, the total molecular wave function is expressed as:

$$\Psi(\vec{r}, \vec{R}) = \sum_{i=1}^{3} \psi_i(\vec{R}) \xi_i(\vec{r} | \vec{R}).$$

The matrix form of the kinetically coupled SE in adiabatic representation is same as given in Eq. 8:

$$-\frac{\hbar^2}{2} \left( \vec{\nabla}_n + \vec{\tau} \right)^2 \psi^{ad} + (U - E) \psi^{ad} = 0,$$
where the nonadiabatic coupling (NAC) and the adiabatic PES matrices are defined as:

\[
\vec{\tau} = \begin{pmatrix}
0 & \tilde{\tau}_{12} & \tilde{\tau}_{13} \\
-\tilde{\tau}_{12} & 0 & \tilde{\tau}_{23} \\
-\tilde{\tau}_{13} & -\tilde{\tau}_{23} & 0
\end{pmatrix} \quad \text{and} \quad U = u_i \delta_{ij} I. \tag{15}
\]

Within this SHS, we can find the ADT matrix \( A \) which would transform \((\psi^{ad} = A\psi^{dia})\) the SE from the adiabatic representation into the diabatic representation as:

\[
\left(-\frac{1}{2} \nabla_n^2 + W - E\right) \psi^{dia} = 0, \quad W = A^\dagger U A,
\]

under the condition:

\[
\vec{\nabla}_n A + \vec{\tau} A = 0, \tag{17}
\]

which is the ADT equation.

The model form of \( A \) matrix for a three state SHS can be constructed by taking the product of three 3×3 rotation matrices, \( A_{12}(\theta_{12}), A_{23}(\theta_{23}) \) and \( A_{13}(\theta_{13}) \) in different order, where one of them is given by:

\[
A(\theta_{12}, \theta_{23}, \theta_{13}) = A_{12}(\theta_{12}) \cdot A_{23}(\theta_{23}) \cdot A_{13}(\theta_{13}),
\]

\[
= \begin{pmatrix}
\cos \theta_{12} & \sin \theta_{12} & 0 \\
-\sin \theta_{12} & \cos \theta_{12} & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \theta_{23} & \sin \theta_{23} \\
0 & -\sin \theta_{23} & \cos \theta_{23}
\end{pmatrix}
\begin{pmatrix}
\cos \theta_{13} & 0 & \sin \theta_{13} \\
0 & 1 & 0 \\
-\sin \theta_{13} & 0 & \cos \theta_{13}
\end{pmatrix}
\]

\[
= \begin{pmatrix}
\cos \theta_{12} \cos \theta_{13} & \sin \theta_{12}\cos \theta_{23} & \cos \theta_{12} \sin \theta_{13} \\
-\sin \theta_{12} \sin \theta_{13} \sin \theta_{23} & \sin \theta_{12} \cos \theta_{23} + \sin \theta_{12} \cos \theta_{13} \sin \theta_{23} & -\sin \theta_{12} \sin \theta_{13} \\
-\cos \theta_{12} \sin \theta_{13} \sin \theta_{23} & \cos \theta_{12} \cos \theta_{23} + \cos \theta_{12} \cos \theta_{13} \sin \theta_{23} & -\sin \theta_{12} \sin \theta_{13}
\end{pmatrix}. \tag{18}
\]

Upon solving the ADT equation, Eq. 17, using the form of \( A \) in Eq. 18, we will obtain the following set of differential equations for the ADT angles:

\[
\vec{\nabla}_n \theta_{12} = -\tilde{\tau}_{12} + \tan \theta_{23}(\tilde{\tau}_{13} \cos \theta_{12} - \tilde{\tau}_{23} \sin \theta_{12}) , \tag{19a}
\]

\[
\vec{\nabla}_n \theta_{23} = -(\tilde{\tau}_{13} \sin \theta_{12} + \tilde{\tau}_{23} \cos \theta_{12}) , \tag{19b}
\]

\[
\vec{\nabla}_n \theta_{13} = -\frac{1}{\cos \theta_{23}}(\tilde{\tau}_{13} \cos \theta_{12} - \tilde{\tau}_{23} \sin \theta_{12}) . \tag{19c}
\]

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

\[
\tilde{\tau}_{12} = -\vec{\nabla}_n \theta_{12} - \sin \theta_{23} \vec{\nabla}_n \theta_{13} , \tag{20a}
\]

\[
\tilde{\tau}_{23} = \sin \theta_{12} \cos \theta_{23} \vec{\nabla}_n \theta_{13} - \cos \theta_{12} \vec{\nabla}_n \theta_{23} , \tag{20b}
\]

\[
\tilde{\tau}_{13} = -\cos \theta_{12} \cos \theta_{23} \vec{\nabla}_n \theta_{13} - \sin \theta_{12} \vec{\nabla}_n \theta_{23} . \tag{20c}
\]
When the same model form of ADT matrix is substituted in Eq. 16, the elements of diabatic potential matrix can be expressed in terms of adiabatic PESs and ADT angles as the following:

\[
W_{11} = u_1(\cos \theta_{12} \cos \theta_{13} - \sin \theta_{12} \sin \theta_{13} \sin \theta_{23})^2 + u_2(\sin \theta_{12} \cos \theta_{13} + \cos \theta_{12} \sin \theta_{13} \sin \theta_{23})^2
\]
\[+ u_3 \sin^2 \theta_{13} \cos^2 \theta_{23}, \tag{21a}\]
\[
W_{22} = u_1 \sin^2 \theta_{12} \cos^2 \theta_{23} + u_2 \cos^2 \theta_{12} \cos^2 \theta_{23} + u_3 \sin^2 \theta_{23}, \tag{21b}\]
\[
W_{33} = u_1(\cos \theta_{12} \sin \theta_{13} + \cos \theta_{13} \sin \theta_{12} \sin \theta_{23})^2 + u_2(\sin \theta_{12} \sin \theta_{13} - \cos \theta_{12} \cos \theta_{13} \sin \theta_{23})^2
\]
\[+ u_3 \cos^2 \theta_{13} \cos^2 \theta_{23}, \tag{21c}\]
\[
W_{12} = u_1 \sin \theta_{12} \cos \theta_{23}(\cos \theta_{12} \sin \theta_{13} \sin \theta_{23}) - u_2 \cos \theta_{12} \cos \theta_{23}(\sin \theta_{12} \cos \theta_{13} + \cos \theta_{12} \sin \theta_{13} \sin \theta_{23})
\]
\[- u_3 \sin \theta_{13} \sin \theta_{23} \cos \theta_{23}, \tag{21d}\]
\[
W_{13} = u_1(\cos \theta_{12} \sin \theta_{13} - \sin \theta_{12} \sin \theta_{13} \sin \theta_{23})(\cos \theta_{12} \sin \theta_{13} + \cos \theta_{12} \sin \theta_{13} \sin \theta_{23})
\]
\[+ u_3 \sin \theta_{13} \cos \theta_{13} \sin^2 \theta_{23}, \tag{21e}\]
\[
W_{23} = u_1 \sin \theta_{12} \cos \theta_{23}(\sin \theta_{12} \cos \theta_{13} \sin \theta_{23}) + u_2 \cos \theta_{12} \cos \theta_{23}(-\sin \theta_{12} \sin \theta_{13} + \cos \theta_{12} \cos \theta_{13} \sin \theta_{23})
\]
\[- u_3 \cos \theta_{13} \sin \theta_{23} \cos \theta_{23}. \tag{21f}\]

While constructing the diabatic PESs for a three-state SHS, one needs to perform ab initio calculations for adiabatic PESs and NACTs over the interested range of nuclear CS, plugged in those NACTs to the ADT condition and calculate those angles as required in Eq. 21.

2.3. The extended Born-Oppenheimer equations for three-state SHS

We can use the analytic form of the NAC elements (Eqs. 20) to formulate the explicit form of Curl equation for each NAC element in terms of the ADT angles:

\[
(\nabla_n \times \tilde{\tau}_{12})_\perp = C_{12} = Z_{12} = -\cos \theta_{23}(\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13}), \tag{22a}\]
\[
(\nabla_n \times \tilde{\tau}_{23})_\perp = C_{23} = Z_{23} = \cos \theta_{12} \cos \theta_{23}(\nabla_q \theta_{12} \nabla_p \theta_{13} - \nabla_p \theta_{12} \nabla_q \theta_{13})
\]
\[+ \sin \theta_{12} \sin \theta_{23}(\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13})
\]
\[- \sin \theta_{12}(\nabla_q \theta_{12} \nabla_p \theta_{23} - \nabla_p \theta_{12} \nabla_q \theta_{23}), \tag{22b}\]
\[
(\nabla_n \times \tilde{\tau}_{13})_\perp = C_{13} = Z_{13} = \sin \theta_{12} \cos \theta_{23}(\nabla_q \theta_{12} \nabla_p \theta_{13} - \nabla_p \theta_{12} \nabla_q \theta_{13})
\]
\[+ \cos \theta_{12} \sin \theta_{23}(\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13})
\]
\[- \cos \theta_{12}(\nabla_q \theta_{12} \nabla_p \theta_{23} - \nabla_p \theta_{12} \nabla_q \theta_{23}), \tag{22c}\]

where \((\nabla_n \times \tilde{\tau}_{ij})_\perp\) represents the perpendicular component of the curl. The Curl due to vector product of NACTs and analyticity of ADT matrix are defined as: \(C_{ij} = (\tilde{\tau}_q \tau_p)_{ij} - (\tilde{\tau}_p \tau_q)_{ij}\) and \(Z_{ij} = \nabla_p \tau_q^{ij} - \nabla_q \tau_p^{ij}\), respectively. The Cartesian coordinates \(p\) and \(q\) denote nuclear DOFs. The set of Eqs. 22 provide us the functional form of Curl condition over the nuclear CS to validate the existence of three state SHS. It should be noted that the same curl conditions (Eqs. 22) are identically zero for a two-state SHS. Moreover, the divergence of each NAC element of three state SHS can also be deduced as shown below:

\[
\nabla_n \cdot \tilde{\tau}_{12} = 2 \sin \theta_{12} \cos \theta_{12} \cos^2 \theta_{23}(\nabla_n \theta_{13} \cdot \nabla_n \theta_{13})
\]
\[- 2 \sin \theta_{12} \cos \theta_{12}(\nabla_n \theta_{23} \cdot \nabla_n \theta_{23})
\]
\[ - 3 \cos^2 \theta_{12} \cos \theta_{23}(\nabla_n \theta_{13} \cdot \nabla_n \theta_{23})
\]
\[+ \sin^2 \theta_{12} \cos \theta_{23}(\nabla_n \theta_{13} \cdot \nabla_n \theta_{23}) - \sin \theta_{23} \nabla_n^2 \theta_{13} - \nabla_n^2 \theta_{12}. \tag{23a}\]
\[ \nabla_n \cdot \vec{r}_{23} = 2 \sin \theta_{12} \sin \theta_{23} \cos \theta_{23} (\nabla_n \theta_{13} \cdot \nabla_n \theta_{13}) + 3 \cos \theta_{12} \cos \theta_{23} (\nabla_n \theta_{12} \cdot \nabla_n \theta_{23}) + 3 \sin \theta_{12} (\nabla_n \theta_{12} - \nabla_n \theta_{23}) + \sin \theta_{12} \cos \theta_{23} \nabla_n^2 \theta_{12} - \cos \theta_{12} \nabla_n^2 \theta_{23}. \]  

(23b)

\[ \nabla_n \cdot \vec{r}_{13} = 2 \sin \theta_{12} \sin \theta_{23} \cos \theta_{23} (\nabla_n \theta_{12} \cdot \nabla_n \theta_{12}) + 3 \sin \theta_{12} \cos \theta_{23} (\nabla_n \theta_{12} \cdot \nabla_n \theta_{13}) - 3 \cos \theta_{12} (\nabla_n \theta_{12} - \nabla_n \theta_{23}) - \cos \theta_{12} \sin \theta_{23} (\nabla_n \theta_{13} \cdot \nabla_n \theta_{23}) - \cos \theta_{12} \cos \theta_{23} \nabla_n^2 \theta_{13} - \sin \theta_{12} \nabla_n^2 \theta_{23}. \]  

(23c)

In general, \( \nabla_n \theta_{ij} \)s and \( \nabla_n^2 \theta_{ij} \)s are non-zero at and around a CI in nuclear CS. From Eq. 23, it is evident that the divergence of the vector field \( \vec{r} \) is non-zero for any arbitrary value of \( \theta_{ij} \) and thus, the vector field should have a non-zero curl. When one or more CI(s) between two electronic states \( i \) and \( (i+1) \) exist(s), the NACT \( \vec{r}^{(i+1)} \) will become singular at the CI point and those functions will decay as \( 1/r \), where \( r \) is the distance from the CI.\(^{52}\) Such vector fields can be resolved into two components, viz. longitudinal and transverse,\(^{53,54}\) where the curl of the former is, by definition, zero but that of the latter may or may not. Though the Abelian (longitudinal) and non-Abelian (transverse) magnitude of the curl equations are the key issue for the formulation of extended Born-Oppenheimer (EBO) equation,\(^{14}\) we need to explore the validity of Curl Condition for a given sub-Hilbert space to construct the diabatic potential energy matrix. It may be noted that Curl Condition is independent of Abelian or non-Abelian nature of the curl of the NACTs. Moreover, the curl and Divergence equations of NACTs are the key elements to establish the existence of time independent (standing) Wave Equations.\(^{34,55,56}\)

We recall the matrix representation of a three-state adiabatic SE:

\[ -\frac{\hbar^2}{2} \left( \vec{\nabla}_n + \vec{r} \right)^2 \psi^{ad} + (U - E) \psi^{ad} = 0, \quad U_{ij} = u_i \delta_{ij}, \]

whereas the NAC matrix \( \vec{r} \) is defined in Eq. 15.

We can choose the model form of \( A \) matrix in the following way:

\[ A(\theta_{12}, \theta_{23}, \theta_{13}) = A_{23}(\theta_{23}) \cdot A_{13}(\theta_{13}) \cdot A_{12}(\theta_{12}), \]

\[ = \begin{pmatrix} \cos \theta_{12} \cos \theta_{13} & \sin \theta_{12} \cos \theta_{13} & \sin \theta_{13} \\ -\sin \theta_{12} \cos \theta_{23} - \cos \theta_{12} \sin \theta_{13} \sin \theta_{23} & \cos \theta_{12} \cos \theta_{23} - \sin \theta_{12} \sin \theta_{13} \sin \theta_{23} & \cos \theta_{12} \sin \theta_{23} \\ \sin \theta_{12} \sin \theta_{23} - \cos \theta_{12} \sin \theta_{13} \cos \theta_{23} & -\cos \theta_{12} \sin \theta_{23} - \sin \theta_{12} \sin \theta_{13} \sin \theta_{23} & \cos \theta_{13} \sin \theta_{23} \end{pmatrix}. \]  

(24)

Upon solving the ADT equation \( [\vec{\nabla}_n A + \vec{r} A = 0] \), using the above form of \( A \), we will obtain the following set of differential equations for the ADT angles:

\[ \vec{\nabla}_n \theta_{12} = - (\cos \theta_{13})^{-1} (\vec{r}_{12} \cos \theta_{23} - \vec{r}_{13} \sin \theta_{23}), \]

\[ \vec{\nabla}_n \theta_{13} = - (\vec{r}_{12} \sin \theta_{23} + \vec{r}_{13} \cos \theta_{23}), \]

\[ \vec{\nabla}_n \theta_{23} = - \vec{r}_{23} - \tan \theta_{13} (-\vec{r}_{12} \cos \theta_{23} + \vec{r}_{13} \sin \theta_{23}). \]
The electronic basis functions can be chosen as the columns of $A^\dagger$ matrix:

$$
\xi_1 = \begin{pmatrix} \cos \theta_{12} \cos \theta_{13} \\ \sin \theta_{12} \cos \theta_{13} \\ \sin \theta_{13} \end{pmatrix} ; \xi_2 = \begin{pmatrix} -\sin \theta_{12} \cos \theta_{23} - \cos \theta_{12} \sin \theta_{13} \sin \theta_{23} \\ \cos \theta_{12} \cos \theta_{23} - \sin \theta_{12} \sin \theta_{13} \sin \theta_{23} \\ \cos \theta_{13} \sin \theta_{23} \end{pmatrix} ; \xi_3 = \begin{pmatrix} \sin \theta_{12} \sin \theta_{23} - \cos \theta_{12} \sin \theta_{13} \cos \theta_{23} \\ -\cos \theta_{12} \cos \theta_{23} - \sin \theta_{12} \sin \theta_{13} \sin \theta_{23} \\ \cos \theta_{13} \sin \theta_{23} \end{pmatrix} .
$$

(25)

The explicit form of NAC matrix ($\tau$) in terms of ADT angles can be derived by incorporating the form of the electronic basis sets (Eq. 25) in $\tau_{ij} = \langle \xi_i | \nabla_n | \xi_j \rangle$ which gives:

$$
\tau = \begin{pmatrix}
0 & -\cos \theta_{13} \cos \theta_{23} \nabla_n \theta_{12} & \cos \theta_{13} \sin \theta_{23} \nabla_n \theta_{12} \\
\cos \theta_{13} \cos \theta_{23} \nabla_n \theta_{12} & 0 & -\sin \theta_{13} \nabla_n \theta_{12} \\
-\cos \theta_{13} \sin \theta_{23} \nabla_n \theta_{12} & \sin \theta_{13} \nabla_n \theta_{12} & 0 \\
\sin \theta_{23} \nabla_n \theta_{13} & \sin \theta_{13} \nabla_n \theta_{12} + \nabla_n \theta_{23} & 0
\end{pmatrix} .
$$

(26)

If we can rearrange the NAC matrix as the product of a vector function and a scalar matrix under certain conditions at and around the point of CI, it is possible to consider a unitary transformation matrix, $G (\psi^{ad} = G \phi)$ that diagonalizes the NAC matrix with eigenvalues $i\bar{\omega}$ and the adiabatic SE (Eq. 8) takes the following form:

$$
-\frac{\hbar^2}{2} \left( \nabla_n + i\bar{\omega} \right)^2 \phi + (V - E) \phi = 0,
$$

(27)

$$
V = G^\dagger U G, \quad i\bar{\omega} = G^\dagger \tau G,
$$

(28)

where $0$ and $\pm i\bar{\omega}$ are the eigenvalues of the NAC matrix ($\tau$) (Eq. 26).

In other words, since the eigenvalues of NACM are vectors, it has to be expressed as the product of a vector function, $\nabla_n \eta(\eta \equiv \theta_{12}$ or $\theta_{13}$ or $\theta_{23})$ and an ADT angle dependent antisymmetric scalar matrix, $g(\theta_{12}, \theta_{13}, \theta_{23})$:

$$
\tau = \nabla_n \eta \cdot g(\theta_{12}, \theta_{13}, \theta_{23}).
$$

(29)

The vectors $\nabla_n \theta_{13}$ and $\nabla_n \theta_{23}$ in terms of its Cartesian components can be expressed as:

$$
\nabla \theta_{13} = i\nabla p \theta_{13} + j\nabla q \theta_{13} + \ldots,
$$

(30a)

$$
\nabla \theta_{23} = i\nabla p \theta_{23} + j\nabla q \theta_{23} + \ldots,
$$

(30b)

and are rewritten as:

$$
\nabla_n \theta_{13} = \tau \frac{\nabla p \theta_{13}}{\nabla p \theta_{12}} \nabla p \theta_{12} + j \frac{\nabla q \theta_{13}}{\nabla q \theta_{12}} \nabla q \theta_{12} + \ldots,
$$

(31a)

$$
\nabla_n \theta_{23} = \tau \frac{\nabla p \theta_{23}}{\nabla p \theta_{12}} \nabla p \theta_{12} + j \frac{\nabla q \theta_{23}}{\nabla q \theta_{12}} \nabla q \theta_{12} + \ldots,
$$

(31b)

Assuming the following relations to be true:

$$
\left( \frac{\nabla p \theta_{13}}{\nabla p \theta_{12}} \right) = \left( \frac{\nabla q \theta_{13}}{\nabla q \theta_{12}} \right) \quad \text{and} \quad \left( \frac{\nabla p \theta_{23}}{\nabla p \theta_{12}} \right) = \left( \frac{\nabla q \theta_{23}}{\nabla q \theta_{12}} \right)
$$

(32)
we can write:

\[
\vec{\nabla}_n \theta_{13} = \bar{i} \left( \frac{\nabla_p \theta_{13}}{\nabla_p \theta_{12}} \right) \nabla_p \theta_{12} + \bar{j} \left( \frac{\nabla_p \theta_{13}}{\nabla_q \theta_{12}} \right) \nabla_q \theta_{12} + \ldots,
\]

\[
= \left( \frac{\nabla_p \theta_{13}}{\nabla_p \theta_{12}} \right) \vec{\nabla}_n \theta_{12} = \left( \frac{\nabla_q \theta_{13}}{\nabla_q \theta_{12}} \right) \vec{\nabla}_n \theta_{12} = \ldots,
\] (33a)

\[
\vec{\nabla}_n \theta_{23} = \bar{i} \left( \frac{\nabla_p \theta_{23}}{\nabla_p \theta_{12}} \right) \nabla_p \theta_{12} + \bar{j} \left( \frac{\nabla_p \theta_{23}}{\nabla_q \theta_{12}} \right) \nabla_q \theta_{12} + \ldots,
\]

\[
= \left( \frac{\nabla_p \theta_{23}}{\nabla_p \theta_{12}} \right) \vec{\nabla}_n \theta_{12} = \left( \frac{\nabla_q \theta_{23}}{\nabla_q \theta_{12}} \right) \vec{\nabla}_n \theta_{12} = \ldots,
\] (33b)

leading to the \( \vec{\tau} \) matrix:

\[
\vec{\tau} = \vec{\nabla}_n \theta_{12} \begin{bmatrix}
0 & -\sin \theta_{23} \left( \frac{\nabla_q \theta_{13}}{\nabla_q \theta_{12}} \right) & -\cos \theta_{23} \left( \frac{\nabla_q \theta_{13}}{\nabla_q \theta_{12}} \right) \\
\sin \theta_{23} \left( \frac{\nabla_q \theta_{13}}{\nabla_q \theta_{12}} \right) & 0 & -\sin \theta_{13} - \left( \frac{\nabla_p \theta_{23}}{\nabla_p \theta_{12}} \right) \\
\cos \theta_{23} \left( \frac{\nabla_q \theta_{13}}{\nabla_q \theta_{12}} \right) & \sin \theta_{13} + \left( \frac{\nabla_p \theta_{23}}{\nabla_p \theta_{12}} \right) & 0
\end{bmatrix}
\] (34)

with eigenvalues: 0, \( \pm i\bar{\omega} \), where

\[
\bar{\omega} = \vec{\nabla}_n \theta_{12} \left[ 1 + \left( \frac{\nabla_p \theta_{13}}{\nabla_p \theta_{12}} \right)^2 \frac{1}{2} + \left( \frac{\nabla_p \theta_{13}}{\nabla_p \theta_{12}} \right)^2 \frac{1}{2} + 2\sin \theta_{13} \left( \frac{\nabla_p \theta_{23}}{\nabla_p \theta_{12}} \right) \right]^{1/2}.
\] (35)

The assumptions in Eq. 32 to obtain the form of NACM in the above Eq. 34 implicate zero curl \( \tau^{pq}_{ij} \) around the CI point, which is demonstrated below. Indeed, the entire formulation of EBO equation for any three-state SHS depends whether at least approximately, curl \( \tau^{pq}_{ij} \)'s are zeros around CIs.

We present the explicit form of Curl Condition of NACTs in terms of the ADT angles:

\[
curl \tau^{pq}_{12} = (\vec{\nabla}_n \times \vec{\tau}_{12}) \downarrow = \sin \theta_{13} \cos \theta_{23} (\nabla_p \theta_{12} \nabla_q \theta_{13} - \nabla_q \theta_{12} \nabla_p \theta_{13}) + \sin \theta_{23} \cos \theta_{13} (\nabla_p \theta_{12} \nabla_q \theta_{23} - \nabla_q \theta_{12} \nabla_p \theta_{23}) - \cos \theta_{23} (\nabla_p \theta_{13} \nabla_q \theta_{23} - \nabla_q \theta_{13} \nabla_p \theta_{23})
\] (36a)

\[
curl \tau^{pq}_{13} = (\vec{\nabla}_n \times \vec{\tau}_{13}) \downarrow = -\sin \theta_{13} \sin \theta_{23} (\nabla_p \theta_{12} \nabla_q \theta_{13} - \nabla_q \theta_{12} \nabla_p \theta_{13}) + \cos \theta_{23} \cos \theta_{13} (\nabla_p \theta_{12} \nabla_q \theta_{23} - \nabla_q \theta_{12} \nabla_p \theta_{23}) + \sin \theta_{23} (\nabla_p \theta_{13} \nabla_q \theta_{23} - \nabla_q \theta_{13} \nabla_p \theta_{23})
\] (36b)

\[
curl \tau^{pq}_{23} = (\vec{\nabla}_n \times \vec{\tau}_{23}) \downarrow = -\cos \theta_{13} (\nabla_p \theta_{12} \nabla_q \theta_{13} - \nabla_q \theta_{12} \nabla_p \theta_{13}).
\] (36c)

Consider curl of \( \vec{\tau}_{23} \) in Cartesian and in Polar coordinates:

\[
(\vec{\nabla}_n \times \vec{\tau}_{23}) \downarrow = \curl \tau^{pq}_{23} = -\cos \theta_{13} \left[ \frac{\partial \theta_{12}}{\partial x} \frac{\partial \theta_{13}}{\partial y} - \frac{\partial \theta_{12}}{\partial y} \frac{\partial \theta_{13}}{\partial x} \right],
\] (37)

\[
(\vec{\nabla}_n \times \vec{\tau}_{23}) \downarrow = \curl \tau^{pq}_{23} = -\cos \theta_{13} \left[ \frac{\partial \theta_{12}}{\partial r} \frac{\partial \theta_{13}}{\partial \theta} - \frac{\partial \theta_{12}}{\partial \theta} \frac{\partial \theta_{13}}{\partial r} \right].
\] (38)
If we set the origin of the coordinate system \([r = 0 \ (x = 0, y = 0)]\) at the CI point, the Jacobian for the transformation from Cartesian to polar given by:

\[
J(r, \theta) = \begin{vmatrix}
\frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} \\
\frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta}
\end{vmatrix} = r, \quad (39)
\]

vanishes at \(r = 0\). On the other hand, if the CI point is away from the origin of the coordinate system, the parametric representation for the vector equation of a conical surface predicts \(J(r, \theta) = 0\) at the singularity (see Figure 1).

Identifying the Jacobian determinant \(J(r, \theta) \approx 0\) around the CI point, we conclude \(\text{curl} \ \mathbf{\tau}_{23}^{xy}\) is either identically or approximately zero around the CI and similar prediction can be made for \(\text{curl} \ \mathbf{\tau}_{12}^{xy}\) and \(\text{curl} \ \mathbf{\tau}_{13}^{xy}\).

Coming back to the SE after unitary transformation (Eq. 27):

\[
-\frac{\hbar^2}{2} \left( \nabla_n + i\omega \right)^2 \phi + (V - E) \phi = 0, \\
V = G^\dagger U G, \quad i\omega = G^\dagger \mathbf{\tau} G,
\]

rewriting the product, \(V \phi\), for the \(i\)th equation as:

\[
(V \phi)_i = u_1 \phi_i + \sum_{j=2}^{3} G^*_{ij} (u_j - u_i) \psi_{ad}^i, \quad i = 1, 2, 3 \quad (40)
\]

and imposing BO approximation: \(|\psi_{ad}^1| \gg |\psi_{ad}^i|\), \(i = 2, 3\), i.e. at enough low energy, both the upper electronic states are classically closed, we arrive to the single surface adiabatic nuclear SE (i.e. EBO equation):

\[
-\frac{\hbar^2}{2} \left( \nabla_n + i\omega \right)^2 \phi_i + (u_i - E) \phi_i = 0, \quad i = 1, 2, 3. \quad (41)
\]

2.4. Molecular symmetry adaptation of the NACTs

Electronic structure theory methods give adiabatic PESs by considering the BO approximation, where the nuclear geometries are kept freezed and thus point group symmetry can define the irreducible representations (IREPs) of those surfaces. On the other hand, the true nature of NACTs essentially lies on the non-rigidity of a molecule and for their case, point groups become inappropriate for assigning the IREPs. As a result, standard electronic structure packages do not provide any symmetry information of NACTs. It is a necessity to consider higher symmetry operations that include feasible permutation - inversion of the nuclei and their rotation in the space to define nodal patterns of NACTs, which is called molecular symmetry (MS) group of a molecule. For a molecule having identical atoms, the permutation-inversion symmetry plays a key role in unraveling the complex spectra and dynamics of a molecule. In general, for any molecule which shows large amplitude motions, the notion of a point group is of limited applicability and one needs to invoke a larger set of symmetries to account the molecular processes.
Since the time scale of a given laboratory experiment is generally too short to allow certain nuclear permutations, it is indeed necessary to take into account all the elements of the complete group of a Hamiltonian. Therefore, one needs to consider only the feasible transformation, which can be attained without crossing an ‘insuperable’ energy barrier, to constitute the MS group.

In general a MS group contains $h$ symmetry operations, $\hat{O}_i$, $i = 1, 2, \ldots, h$, including the identity operation $E$, all feasible permutations $P$ of the spatial as well as spin coordinates of the equivalent nuclei, the inversion $E^*$ of all nuclear coordinates $\vec{R}$ and electronic coordinates $\vec{r}$, and the inversion-permutation $P \cdot E^*$. Each symmetry operation $\hat{O}$ of the MS group of a molecule transforms the vibronic modes, the three Euler angles to describe the orientations of a rigid body in a three dimensional Euclidean space and the nuclear spin. We can express $\hat{O}$ as a product of three different operations:\[^{59}\]

$$\hat{O} = \hat{O}_a \hat{O}_b \hat{O}_c$$  \hspace{1cm} (42)

where $\hat{O}_a$ changes vibronic DOFs, $\hat{O}_b$ rotates the Euler angles, $\hat{O}_c$ permutes the nuclear spin. On the contrary, the symmetry operations of the point group of a molecule transform only its vibronic DOFs.

**Figure 2** Schematic representation of Eq. 43b. The operation 123 denotes permutation of nuclear coordinates which is equivalent with the successive operation of $C^1_3$, $R^{2\pi}$ and $P_{123}$. $C^1_3$ acts on electronic and nuclear space coordinates rotating the vibrational displacements and electronic coordinates with a molecular fixed axes. $R^{2\pi}$ depicts bodily rotation of the molecule about the molecular fixed axis and $P_{123}$ permutes the spins of the nuclei. Figure redrawn from Ref. [37].

### 2.4.1. MS adaptation to NACTs for $D_{3h}$ (M) group

Let us take the example of sodium trimer (Na$_3$ cluster) that belongs to the point group $D_{3h}$.\[^{37}\] The system-fixed $x - y - z$ axes are located on the Na$_3$ cluster such that the $xy$ plane is the molecular plane (plane of symmetry, $\sigma_h$) and the $z$ axis is the threefold symmetry axis ($C_3$). Thus, the relations between the MS group $[D_{3h}(M)]$ and the corresponding point group $[D_{3h}]$ operations are as follows (one representative element...
from each class of the MS group is shown):  

\[ E = E \cdot R_{0}^{i} \cdot p_{0} \]  

(43a)  

\[ (123) = C_{1}^{1} \cdot R_{0}^{123} \]  

(43b)  

\[ (23) = C_{2x} \cdot R_{0}^{23} \cdot p_{23} \]  

(43c)  

\[ E^{*} = \sigma_{xy} \cdot R_{0}^{i} \cdot p_{0} \]  

(43d)  

\[ (132)^{*} = S_{3}^{-1} \cdot R_{x}^{132} \]  

(43e)  

\[ (23)^{*} = \sigma_{xz} \cdot R_{y} \cdot p_{23} \]  

(43f)  

where "\( R_{\phi}^{\pi} \)'s are the members of the corresponding molecular rotation group and "\( p \)'s denote nuclear permutation. Figure 2 illustrates Eq. 43b schematically. We represent the symmetry elements of the system in Figure 3(a), where the planar system is considered to be on the \( xy \) plane. Figure 3(b) depicts a modified version of the projection of the same point group, where the effects of the symmetry operations are indicated without showing the symmetry elements. If one considers a point \( E \) above the \( xy \) plane representing the identity operation, the different symmetry operations acted separately upon that point would displace the same to different positions. Figure 3(b) shows all such positions together indicating the appropriate symmetry operations in each case.

The following two important theorems on MS group can relate the IREPs of a NACT for different nuclear coordinates as well as different NACTs for the same nuclear mode:

**Theorem 1:** When the IREP of a particular NACT, say \( \tau^{ij}_{l} \), along a specific symmetry adapted nuclear coordinate \( R_{l} \) is known, the IREP of another one, \( \tau^{ij}_{k} \) between the same electronic states \( i, j \) for a different symmetry adapted nuclear coordinate, \( R_{k} \), can be determined by the following relation:

\[ \Gamma(\tau^{ij}_{k}) = \Gamma \left( \frac{\partial}{\partial R_{k}} \right) \times \Gamma \left( \frac{\partial}{\partial R_{l}} \right) \times \Gamma(\tau^{ij}_{l}) \]  

(44)

where

\[ \tau^{ij}_{k} = \langle \xi_{i}(\vec{r}) | \frac{\partial}{\partial R_{k}} \left( \xi_{j}(\vec{r}) \vec{R} \right) \rangle \]  

(45)

It should be noted that this is valid only for those symmetry adapted coordinates that belong to 1-d IREP. The possible combination of the IREPs of the NACTs can be determined by fixing each of the NACTs \( [\tau^{i}_{k}, (k = \rho, \phi, x and y)] \) in succession to the totally symmetric representation \( (A'_{1}) \). As \( D_{3h}(M) \) MS group is isomorphic with \( D_{3h}(M) \) MS group, we have extended the character table for MS group \( D_{3h}(M) \) by the following prescription.

If we choose \( \tau_{\rho} = A'_{1} \), we get the other three as \( \tau_{\phi} = A''_{1} \), \( \tau_{x} = \tau_{y} = E'' \) from Table 1 and Eq. 44. On the other hand, choosing \( \tau_{\phi} = A'_{1} \) will give \( \tau_{\phi} = A''_{1} \), \( \tau_{x} = \tau_{y} = E' \). Though it seems that we should find four such combination of the IREPs of the NACTs, only the above two possibilities survive (see the last two columns of Table 1). This is because when we try to
Table 1 Extended character table of molecular symmetry group $D_{3h}(M)$

| $D_{3h}(M)$ | $E$ | (123) | $E^*$ | (123)$^*$ | coord. | deriv. | 1st comb | 2nd comb |
|-------------|-----|-------|-------|-----------|--------|--------|----------|----------|
| $A_1^*$     | 1   | 1     | 1     | 1         | 1      |        | $\tau_\rho$ | $\tau_\phi$ |
| $A_2^*$     | 1   | -1    | 1     | 1         | -1     | $\phi$ | $\frac{i \pi}{3}$ | $\frac{i \pi}{3}$ |
| $E'$        | 2   | -1    | 0     | 2         | -1     | 0      | $x, y$   | $\frac{i \pi}{2}$ |
| $A_1''$     | 1   | 1     | -1    | -1        | 1      | $\rho$ | $\frac{i \pi}{3}$ | $\frac{i \pi}{3}$ |
| $A_2''$     | 1   | -1    | -1    | -1        | 1      | $\tau_x, \tau_y$ | $\tau_x, \tau_y$ |
| $E''$       | 2   | -1    | 0     | -2        | 1      | 0      | $\tau_x, \tau_y$ | $\tau_x, \tau_y$ |

find out the combination of the IREPs of the $\tau_k$s fixing $\tau_x$ or $\tau_y$ to $A_1^*$, the IREP for $\tau_y$ or $\tau_x$ turns into reducible representation contradicting the construction of Character Table as shown in Table 1.

Figure 4 Nodal patterns of IREPs of $D_{3h}$ point group. Figure redrawn from Ref. [37].

Figure 4 depicts the nodal patterns$^{59,60}$ of the NACTs belonging to all possible IREPs in which the profiles of the NACTs are presented as functions of normal mode coordinates $Q_x$ (bending) and $Q_y$ (asymmetric stretching). The outer and inner concentric circles depict the patterns for negative and positive values of $Q_s$ (symmetric stretching) or, in other words, the smaller and the larger concentric circles in Figures 3(b) and 4 represent points above and below the $xy$ plane, respectively. Considering only the smaller circles of Figure 4, we pursue the finding of the correct combination of IREPs from the two possible ones (see Table 1). For this purpose, we utilize the quantization rule$^{62}$ (Eq. 46) of the contour integrals over the NACTs evaluated along a closed loop $L_g$ of nuclear coordinate $\vec{R}$ around a single CI:

$$\oint d\vec{R} \cdot \tau(\vec{R} | L_g) = \pm \pi$$  \hspace{1cm} (46)$$

This is illustrated in Figure 5. The above contour integral can be divided into three components,$^{61}$ namely, one torsional (tor) and two radial (rad) lines that create the loop:

$$\oint d\vec{R} \cdot \tau(\vec{R} | L_g) = I_{\text{rad},1} + I_{\text{tor}} + I_{\text{rad},2} = \pm \pi,$$
where

\[ I_{\text{rad},1} = \int_0^{\rho_1} d\rho \tau_{\rho}(\rho, \phi_1|L_g), \quad I_{\text{tor}} = \int_{\phi_1}^{\phi_2} d\phi \tau_{\phi}(\rho_1, \phi|L_g) \]

and

\[ I_{\text{rad},2} = \int_0^{\rho_1} d\rho \tau_{\rho}(\rho, \phi_2|L_g) \]

Using the IREPs of the integrands \((\tau_{\rho}/\tau_{\phi})\) as defined in Table 1, we incorporate the sign of their magnitudes according to the inner circle of Figure 4 and then perform those integrations. It appears that: (i) for the first combination, \(I_{\text{rad},1} + I_{\text{rad},2} = 0\) (from Figure 5(a)) and \(I_{\text{tor}} = 0\) (from Figure 5(b)), making it incompatible with the quantization rule (Eq. 46); (ii) the second combination gives non-zero residue for the contour integral (see Figure 5(c and d)) and hence lefts out to be the only feasible one.

**Theorem 2:** Consider a loop-type sequence of \(N\) molecular states with same spin multiplicity, say \(N\) doublet states, \(D_a, D_b, D_c, \ldots, D_y, D_z = a\), of \(Ni_3\) cluster. The NACTs are: \(\tau_{a,b,c}, \ldots, \tau_{y,z} = a\), and their product is represented as:

\[ \tau_{k}^{a,b,c, \ldots, y,z = a} = \tau_{k}^{a,b,c, \ldots, y,z = a}. \tag{47} \]

In terms of the IREPs, one can have the following relation:

\[ \Gamma(\tau_{k}^{a,b,c, \ldots, y,z = a}) = \Gamma(\xi_a(\vec{r} | \vec{R}))^2 \times \Gamma(\xi_b(\vec{r} | \vec{R}))^2 \times \ldots \times \Gamma(\xi_y(\vec{r} | \vec{R}))^2 \times \Gamma \left( \frac{\partial}{\partial R_k} \right)^N \tag{48} \]

It is evident from the above relation that for 1-d IREPs, we will have:

\[ \Gamma(\tau_{k}^{a,b,c, \ldots, y,z = a}) = \begin{cases} \Gamma \left( \frac{\partial}{\partial R_k} \right) \quad & \text{when } N \text{ is odd} \\ \Lambda' \quad & \text{when } N \text{ is even} \end{cases} \tag{49} \]

The above equation (Eq. 49) states the second theorem. While we implement the second theorem on the NACTs, we also discuss the associated property of the wavefunctions of a system near a CI. Whenever there is a CI between two electronic states \(i\) and \((i+1)\), the corresponding electronic eigenfunctions \(\xi_i(\vec{r} | \vec{R})\) and \(\xi_{i+1}(\vec{r} | \vec{R})\) may change their signs along the nuclear coordinate \(\vec{R}\) at the time of crossing the CI. If all the CIs in CS are connected with symmetry related set of coordinates, and there is a flip of sign in the wavefunctions for one of...
the CIs, same switching will occur for all the other CIs too and hence, the wavefunctions \( \xi_i(\vec{r}|\vec{R}) \) and \( \xi_{i+1}(\vec{r}|\vec{R}) \) will have the same IREP. As a result, the NACTs \( \tau_k^{i,j} \) and \( \tau_k^{(i+1),j} \) \((i < j)\), also interchange their signs (see Eq. 45) with the same IREP, i.e.,

\[
\Gamma(\tau_k^{i,j}) = \Gamma(\tau_k^{(i+1),j}).
\] (50)

To understand the situation, we again consult the excited electronic states \( 2^2E' \) and \( 1^2A'_1 \) of Na\(_3\) system and designate them as 1, 2 and 3, respectively. Existence of multiple CIs between states 1 and 2 have been predicted.\(^\text{37}\) Thus, according to the crossing rule (Eq. 50) \( \tau_k^{13} \) and \( \tau_k^{23} \) should interchange their respective signs while crossing each CI and hence, should bear same IREP.

Implementing Eq. 48 on a three-state SHS created by the states \( 2^2E' \) and \( 1^2A'_1 \) in Na\(_3\) system, the second theorem gives the following relation:

\[
\Gamma(\tau_k^{1,2,3,1}) = \Gamma(\tau_k^{12}) \times \Gamma(\tau_k^{23}) \times \Gamma(\tau_k^{31}) = \Gamma(\tau_k^{12}) \times \Gamma(\tau_k^{23})^2
\] (51)

where \( \Gamma(\tau_k^{ij}) = \Gamma(\tau_k^{ji}) \) for any \( i, j \) and the crossing rule (Eq. 50) between states \( i \) and \((i + 1)\) has been incorporated. Considering \( \Gamma(\tau_p^{12}) = A''_1 \) and \( \Gamma(\tau_p^{23}) = A'_1 \) from the second combination of Table 1, we can obtain \( \Gamma(\tau_p^{12}) = A''_2 \) and \( \Gamma(\tau_p^{12}) = A'_2 \) from Eq. 51 and 49, where \( \Gamma(\tau_p^{1,2,3,1}) = \Gamma\left(\frac{\partial}{\partial \rho}\right) \) and \( \Gamma(\tau_p^{1,2,3,1}) = \Gamma\left(\frac{\partial}{\partial \phi}\right) \).

Still now we have dealt with 1-d IREPs where Eq. 49 has been successfully implemented. Similarly, the above treatment is extended to 2-d IREP cases where we have established the following working equations:\(^\text{37}\)

As we have, \( \Gamma(\tau_p^{23}) = \Gamma\left(\frac{\xi_2(\vec{r}|\vec{R})}{\xi_3(\vec{r}|\vec{R})}\right) \)

\[ \Rightarrow \Gamma(\tau_p^{23}) = \Gamma(\xi_2(\vec{r}|\vec{R})) \times \Gamma\left(\frac{\partial}{\partial \chi}\right) \times \Gamma(\xi_3(\vec{r}|\vec{R})) \]

\[ \Rightarrow \Gamma(\tau_p^{23}) = \Gamma(\xi_2(\vec{r}|\vec{R})) \times E' \times \Gamma(\xi_3(\vec{r}|\vec{R})). \] (52a)

Therefore, \( \Gamma(\tau_p(\vec{r}|\vec{R})) \times \Gamma(\xi_3(\vec{r}|\vec{R})) = A'_1 \) (52b)

Similarly, for \( \Gamma(\tau_p^{13}) = E' \), we have:

\[ \Gamma(\xi_1(\vec{r}|\vec{R})) \times \Gamma(\xi_3(\vec{r}|\vec{R})) = A'_1. \] (52c)

It is clear from Eqs. 52b and 52c that \( \xi_1(\vec{r}|\vec{R}) \), \( \xi_2(\vec{r}|\vec{R}) \) and \( \xi_3(\vec{r}|\vec{R}) \) must belong to 1d IREP, which means,

\[
\Gamma(\xi_1(\vec{r}|\vec{R})) \times \Gamma(\xi_2(\vec{r}|\vec{R})) \times \Gamma(\xi_3(\vec{r}|\vec{R})) = A'_1
\] (53)

When we use Eq. 48 for the Na\(_3\) case and substitute Eq. 53, we obtain:

\[
\Gamma(\tau_p^{1,2,3,1}) = \Gamma(\xi_1(\vec{r}|\vec{R}))^2 \times \Gamma(\xi_2(\vec{r}|\vec{R}))^2 \times \Gamma(\xi_3(\vec{r}|\vec{R}))^2 \times \Gamma\left(\frac{\partial}{\partial \chi}\right)^3 = A'_1 \times \Gamma\left(\frac{\partial}{\partial \chi}\right)^3 = (E')^3
\] (54)
Thus, from Table 1 and Eq. 51,
\[
\Gamma(\tau_1^{1,2,3,1}) = \Gamma(\tau_2^{12}) \times (\tau_3^{23})^2 = \Gamma(\tau_2^{12}) \times (E')^2
\]  
(55)
Equating Eqs. 54 and 55, one gets \(\Gamma(\tau_2^{12}) = E'\) and similarly, \(\Gamma(\tau_2^{12}) = E'\). In Table 2, we present the IREPs for all kind of NACTs in a compact manner.\(^{37,38}\)

### Table 2 Extended character table of molecular symmetry group \(D_{3h}(M)\) with different NAC elements

| \(D_{3h}(M)\) | \(E\) | \((123)\) | \((12)\) | \((23)\) | \(E'\) | \((123)*\) | \((12)*\) | \((23)*\) | coord. deriv. | \(\tau_2^{12}\) | \(\tau_1^{12}\) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| \(A_1'\) | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | \(\phi\) | \(\frac{\partial}{\partial \rho}\) | \(\frac{\partial}{\partial \rho}\) |
| \(A_2'\) | 1 | 1 | -1 | 1 | 1 | 1 | 1 | 1 | \(\phi\) | \(\frac{\partial}{\partial \rho}\) | \(\frac{\partial}{\partial \rho}\) |
| \(E'\) | 2 | -1 | 0 | 2 | -1 | 0 | 0 | 0 | \(x, y\) | \(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}\) | \(\tau_x, \tau_y\) | \(\tau_x, \tau_y\) |
| \(A_1''\) | 1 | 1 | -1 | 1 | -1 | -1 | 1 | 1 | \(\rho\) | \(\frac{\partial}{\partial \rho}\) | \(\frac{\partial}{\partial \rho}\) |
| \(A_2''\) | 1 | 1 | -1 | -1 | 1 | 1 | 1 | 1 | \(\rho\) | \(\frac{\partial}{\partial \rho}\) | \(\frac{\partial}{\partial \rho}\) |
| \(E''\) | 2 | -1 | 0 | -2 | 1 | 0 | 0 | 0 | \(\rho\) | \(\frac{\partial}{\partial \rho}\) | \(\frac{\partial}{\partial \rho}\) |

### 3. Implementation of BBO theory: The excited states of Na\(_3\) cluster

Alkali trimers are well known for exhibiting significant effects of JT and PJT interactions in their corresponding spectral features.\(^{46,63}\) Due to one-electron-valence configuration and only three vibrational DOFs, these clusters can be convenient for theoretical calculation\(^{64–68}\) and thereby, to interpret the experimentally measured data.\(^{69,70}\) Yarkony et al. confirmed the presence of \(D_{3h}\) CIs in Li\(_3\) cluster along with unusual CIs at \(C_{2v}\) geometries.\(^{64}\) de Vivie-Riedle et al. performed full configuration interaction calculation for ground and excited states of Na\(_3\) cluster to generate PESs and transition dipole moment, and carried out dynamics to reproduce experimental spectrum.\(^{65}\) In subsequent works, Köppel et al. simulated\(^{66}\) the experimental spectra by using model Hamiltonian both under JT and PJT conditions on the same system. Koizumi and Bersuker\(^{67}\) extended the PJT model Hamiltonian\(^{68}\) and predicted four CIs between the two sheets of the excited \(2^2E'\) state of Na\(_3\) cluster. We have performed \textit{ab initio} calculation for adiabatic PESs and NACTs of \(2^2E'\) and \(1^2A_1'\) states of the Na\(_3\) cluster with Multi Configuration Space Self Consistent Field (MCSCF) as well as Multi Reference Configuration Interaction (MRCI) methodology and confirmed six CIs between the two sheets of \(2^2E'\) state, where three CIs\(^{35,36}\) are at \(C_{2v}\) geometry and the other three CIs collapse\(^{37}\) at the point of \(D_{3h}\) symmetry.

#### 3.1. \textit{Ab initio} calculation for PESs and NACTs

Na\(_3\) cluster possesses three vibrational modes, namely the symmetric stretching \((Q_x)\), bending \((Q_z)\) and antisymmetric stretching mode \((Q_y)\). The “breathing mode” \(Q_\rho\) retains the \(D_{3h}\) symmetry, whereas \(Q_x\) and \(Q_y\) transform the \(D_{3h}\) equilateral triangle into a \(C_{2v}\) isosceles and a \(C_s\) scalene triangle, respectively. \textit{Ab initio} calculations for adiabatic PESs and NACTs are performed as a function of the polar coordinates: \(\rho = \sqrt{Q_x^2 + Q_y^2}\) and \(\phi = \tan^{-1} \frac{Q_y}{Q_x}\) to incorporate the inherent symmetry of the molecule.
We have employed Gaussian (3s,3p) triple zeta basis set in the \textit{ab initio} calculations, where such basis has been augmented with a single set of \textit{d} functions (\(\zeta_d = 0.1\)) to incorporate the electron correlation effects and two diffuse \textit{s} functions (\(\zeta_{4s} = 0.008736, \zeta_{5s} = 0.00345\))\(^{37}\) for more accurate excited state description. The excited state PESs (\(2^2E'\) and \(1^2A_1'\)) and NACTs are first calculated at MCSCF level\(^{35,36}\) and subsequently, MRCI methodology has been employed to calculate those quantities as functions of the normal modes \(Q_x\) and \(Q_y\) for fixed \(Q_z\).\(^{37}\) All the \textit{ab initio} calculations are done using MOLPRO quantum chemistry package.\(^{71}\) It can be shown that the 4th, 5th and 6th excited states of \(\text{Na}_3\) form a SHS within the range of configuration space taken up for the investigation. MRCI \textit{ab initio} calculations have been carried out with the first 6 states, where those reference states were calculated first by MCSFCF approach involving first 20 electronic states in order to reach the closest possible variational minimum with respect to exact energies. For the evaluation of the PESs of \(2^2E'\) and \(1^2A_1'\) excited states, an active space has been chosen with 15 orbitals as closed shell and 3 unpaired electrons distributed over 12 \textit{active} orbitals generating 572 configuration state functions (CSFs). The energy of the lowest \(2^2E'\) state calculated at MRCI level is found to be lower by \(\approx 1538.95\) cm\(^{-1}\) than the MCSCF energy. Figure 6 presents the contour plots of PESs for \(2^2E'\) and \(1^2A_1'\), where the embedded energies are the relative energy values given in Hartree unit.

The energies are represented in scaled units by subtracting the minimum energy (\(-482.5668\) Hartree) of the lower \(2^2E'\) state. The NACTs among \(2^2E'\) and \(1^2A_1'\) states are calculated by using DDR method implemented in MOLPRO. All the MRCI calculations for the adiabatic PESs and NACTs have been carried out over the range \(\rho = 0.0\) to 0.9 Å and \(\phi = 0\) to \(2\pi\). The functional forms of \(\rho\) and \(\phi\) components of NACTs are presented in terms of normal mode coordinates \(Q_x\) and \(Q_y\) as shown in Figure 7. Apparently, it has been observed that there are 4 CIs between the \(2^2E'\) states of \(\text{Na}_3\) system, one of them being at \((Q_x, Q_y) = (0, 0)\) \([\rho, \phi = (0, 0)]\) and the other three at \(\rho \approx 0.03\) Å, \(\phi = \pi/3, \pi\) and \(5\pi/3\). Yet, a deeper and careful investigation revealed that the CI at \(\rho = 0\) could be a consequence of the collapse of three CIs.\(^{37}\)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Adiabatic PESs of \(\text{Na}_3\) cluster, where the surfaces at each point are scaled with the minimum energy of the lower \(2^2E'\) state (\(-482.5668\) Hartree). Panels (a) and (b) display the lower and upper \(2^2E'\) state and panel (c) shows \(1^2A_1'\) state. Results are adapted from Ref. [37].}
\end{figure}
Figure 7 The Nonadiabatic Coupling Terms of Na$_3$ as functions of $Q_x$ and $Q_y$. In panels (a and d), the outer most contour line (dotted) starts with 0 and the inner ones (solid) rise up with an increment of 6 Å$^{-1}$, whereas for panels (b, c, e, and f) the outer most contour line (dotted) starts with 0 and the inner ones (solid) rise up with an increment of 0.2 Å$^{-1}$. Results are adapted from Ref. [37].

Figure 8 Panel (a): Circular contours encircling one or multiple conical intersections. Panel (b): $c_i$ is the coefficient of the dominant configuration in MRCI wavefunction of the ground state. Results are adapted from Ref. [37].

3.2. Longuet-Higgins’ sign change

We followed Longuet-Higgins$^{21,22}$ prescription to locate the CIs by noting down the numerical magnitude of the dominant coefficient of adiabatic electronic wavefunction around a close loop of one or multiple CI(s).$^{24}$ This has been well illustrated in Figure 8 which displays: (a) the four loops with successively encircle one or multiple CI(s) and (b) the corresponding sign changes.
of the dominant coefficients of the MRCI wavefunction. The figure shows that if adiabatically
transporting along a close path encircles an odd number of CI(s), the MRCI wavefunction will
change sign, whereas encircling even (or no) CI(s) does not flip the sign.

3.3. Molecular symmetry adapted NACTs

As it is known that existing quantum chemistry packages can not provide appropriate IREPs
of the NACTs, we have constructed MS adapted NACTs through the following two steps:37 (a)
An overall sign correction is performed for each of the NACTs according to the nodal patterns
of the respective IREPs to which they belong; (b) The signs of the NACTs \( \tau_{k}^{13} \) and \( \tau_{k}^{23} \) \([ k = \rho, \phi] \)
are interchanged at the point of CI to incorporate the crossing rule (Eq. 50). A comparison
between sign corrected and uncorrected NACTs is drawn in Figure 9. It presents \( \tau_{ij}^{\rho} \) \( k \)
and \( \tau_{ij}^{\phi} \) at the point of CI to incorporate the crossing rule (Eq. 50). A comparison
between sign corrected and uncorrected NACTs is drawn in Figure 9. It presents \( \tau_{ij}^{\rho} \) \( k \)
and \( \tau_{ij}^{\phi} \) as obtained from MOLPRO package and lower panels (c, d)
depict the IREP adapted (dotted line) ones with appropriate crossing due to CIs (solid line).

![Figure 9](image_url)

**Figure 9** Upper panels (a, b) show \( \tau_{ij}^{\rho} \) vs. \( \phi \) for a fixed \( \rho = 0.03 \) Å before MS adaptation and lower panels (c, d) represent
the same after MS adaptation. Results are adapted from Ref. [37].

The conclusion that can be drawn from the above discussion is that MS determines the proper
sign of NACTs, the magnitude of which are obtained from \textit{ab initio} calculation. Though the
NACTs strictly follow the inherent symmetry of the system even with large magnitude at and
around the CI point(s), in general, any \textit{ab initio} package can provide only approximate values
around those critical point(s). On the other hand, it is important to note that the singularity
of the NACTs along with their sign in the CS are much more important to describe the system
accurately through diabatic surfaces rather than their absolute magnitude wherever applicable.

3.4. ADT angles and their residues

After substituting the MS adapted NACTs in Eqs. 19 and solving those stiff differential equations
over a 2d grid of geometries in polar coordinates \((\rho, \phi)\), we obtained the ADT angles.
It is noteworthy to mention that one can integrate two sets of coupled ($\rho$ and $\phi$) differential equations (Eqs. 19) with infinitely different paths, where each path will produce a set of $\rho$ - $\phi$ dependent ADT angles, but such angles obtained from any choice of path are expected to show gauge invariance.\cite{37}

Figure 10 The different 2d rectangular contour paths along which the ADT angles are solved. Figure redrawn from Ref. \cite{37}.

In our calculations we have considered two different 2d rectangular contour paths for solving the ADT equations. Figure 10 demonstrates such paths. **P.I:** The differential equations for the $\phi$ grid are integrated with positive increment from $\phi = 0$ to $2\pi$ for each positive step integration of the differential equations for the $\rho$ grid from 0 to $\rho_{max}$; **P.II:** The differential equations for the $\rho$ grid are integrated with positive increment from $\rho = 0$ to $\rho_{max}$ for each positive step integration of the differential equations for the $\phi$ grid from 0 to $2\pi$. The calculated ADT angles ($\theta_{ij}(\rho, \phi)$) using **P.I** are displayed as functions of $\rho$ and $\phi$ in panels (a - c) of Figure 11, whereas those obtained by **P.II** scheme are presented in the panels (d - f) of the same figure. The ADT matrices constructed from those path dependent ADT angles are related through an orthogonal transformation which would predict the same calculated observable for all cases.

Figure 11 The form of the ADT angles solved on a 2d contour integral by using **P.I** scheme (a-c) and by using **P.II** scheme (d-f). Results are adapted from Ref. \cite{37}. 

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3.5. The curl equations and diabatic potential matrix

In this molecular system, a Curl Condition\(^{28}\) for each NACT, \(\tau_{ij}\), has been derived and proved to exist by considering the analyticity of the ADT matrix \(A\) for a pair of nuclear degrees of freedom (DOF):

\[
\frac{\partial}{\partial p} \tau_{ij}^p - \frac{\partial}{\partial q} \tau_{ij}^q = (\tau_q \tau_p)_{ij} - (\tau_p \tau_q)_{ij},
\]

(56)

where the curl due to vector product of NACTs and analyticity of ADT matrix are given by

\[
C_{ij} = (\tau_q \tau_p)_{ij} - (\tau_p \tau_q)_{ij}
\]

and \(Z_{ij} = \frac{\partial}{\partial p} \tau_{ij}^p - \frac{\partial}{\partial q} \tau_{ij}^q\), respectively with \(\nabla_p = \frac{\partial}{\partial p}\) and \(\nabla_q = \frac{\partial}{\partial q}\). The Cartesian coordinates \(p\) and \(q\) are the nuclear DOFs.

We have calculated the root mean square deviation (RMSD) between the mathematical \(Z_{ij}\) and ADT \(C_{ij}\) curl employing the equation:

\[
\chi_{\text{Curl} \tau_{ij}}(\rho_k) = \frac{1}{N} \sqrt{\sum_{l}^N (C_{ij}(\rho_k, \phi_l) - Z_{ij}(\rho_k, \phi_l))^2}.
\]

This allowed us to explore the numerical validity of the Curl Condition (Eq. 57). Since it is hard to visualize the differences between the two types of curls as functions of \(\rho\) and \(\phi\), we have scaled both the quantities, i.e. the mathematical \(Z_{ij}\) and the ADT \(C_{ij}\) curls by the maximum magnitude of either one of them and depicted their RMSD values in Figure 12. The calculated RMSD values for curl \(\tau_{12}\) appeared as absolutely zero, hence, the other two RMSDs for curl \(\tau_{13}\) and \(\tau_{23}\) are presented in Figure 12 (a and b) for schemes, P.I and P.II, respectively, where their negligibly small magnitude describe the validity of the Curl Condition and thereby, show the existence of the three-state sub-Hilbert space consisting of \(^2E'\) and \(^1A'_1\) states of \(\text{Na}_3\) system.

Herzberg and Longuet-Higgins had observed the unique properties of the diagonal elements of the ADT matrix that undergo sign change along a closed contour enclosing a CI point while solving the JT CI model.\(^{23}\) Such scheme was later on implemented on multi-states model systems.\(^{12,13,62}\) This observation has been drawn for \(\text{Na}_3\) cluster also, where the calculated diagonal element(s) of the ADT matrix, \(A_{11}\) and \(A_{22}\) show six sign changes.\(^{37}\) Figure 13 depicts those diagonal elements in which panel (a) and (c) show \(A_{11}/A_{22}\) components, and panel (b) and (d) exhibit \(A_{33}\) components which do not change sign. These are presented as function of \(\phi\) at asymptotic \(\rho\). The six sign changes in \(A_{11}/A_{22}\) element indicate the presence of six CIs between the \(E'\) states, which allowed us to conclude that the three central CIs collapse at \(\rho = 0\) to result into one CI making the total count four.
Figure 13 The diagonal elements of Adiabatic to diabatic Transformation matrix are shown. The left panels (a, b) show the ADT matrix elements obtained from the ADT angles solved on a 2d contour integral by using P.I scheme and the right panels (c, d) display the same obtained by employing P.II scheme. Results are adapted from Ref. [37].

The functional nature of the diabatic matrix elements are shown in Figure 14, calculated from ADT angles obtained by Eqs. 19 by using one of the contour paths. It has been found that whatever be the path chosen for integration, the diabatic surfaces are calculated from the BBO theory are continuous, single valued, smooth and symmetric. [37]

Figure 14 The contour plots of diabatic PESs (eV) and the coupling elements (eV) calculated by incorporating ADT angles into Eqs. 21, where those angles are obtained by solving Eqs. 19 on a 2d contour integral by using P.I scheme. Results are adapted from Ref. [37].
3.6. Nuclear dynamics and absorption spectra

It is well known that the theoretically calculated spectrum \(^{65,66}\) for system \(B\) of Na\(_3\) cluster matches quite well with experimental one for \(Q_s = 3.7\) Å. The diabatic surfaces calculated from BBO theory enabled us to carry out dynamical calculations of this system to simulate its absorption spectra.\(^{37}\)

We have performed dynamics over a 2D grid with the normal mode coordinates, \(Q_x\) and \(Q_y\), employing FFT - Lanczos method to calculate the auto-correlation function \((C(t))\). Spectra can be obtained by Fourier transform of \(C(t)\) according to the relation:

\[
I(\omega) \propto \omega \int_{-\infty}^{\infty} C(t) \exp(i\omega t) dt, \quad (57)
\]

where

\[
C(t) = \langle \psi(t)|\psi(0) \rangle, \quad (58)
\]

\[
= \langle \psi^*(\frac{t}{2})|\psi(\frac{t}{2}) \rangle. \quad (59)
\]

It has to be noted that Eq. \(^{59}\) is more accurate, computationally faster and is more convenient to implement than Eq. \(^{58}\), but it is valid only if the initial wavefunction is real and the Hamiltonian is symmetric. We considered a Gaussian wavepacket (GWP) as the time-independent solution of the Hamiltonian \([H(Q_x, Q_y) = T_n + \frac{1}{2}(Q_x^2 + Q_y^2)]\) and performed the diabatization with the ADT matrix to obtain the diabatic wavefunctions with different initial positions of the GWP. The dynamics has been carried out thrice locating the initial wavefunction on each of the three states, \(2^2E'\) (state 1 and 2) and \(1^2A_1'\) (state 3), and then, convoluted those results to achieve the final spectrum. In each of the three cases, the wavefunctions are expanded along 128\(\times\)128 plane wave basis functions, the number of which are enough to reach the convergence. In Figure 15, the direct comparison of that calculated absorption spectrum with the experimental outcome obtained by W. E. Ernst and O. Golonzka\(^{70}\) are presented. The absorption spectra\(^{37}\) in Figure 15(b and c) are calculated by performing the dynamics on the diabatic surfaces constructed by the ADT angles obtained by integrating Eqs. 19 for two paths of integration, \(P.I\) and \(P.II\), respectively. The similarity of the obtained results in peak positions as well as in the intensity pattern establishes workability of the BBO theory on the excited state dynamics of Na\(_3\) cluster.

![Figure 15](image-url)
4. Construction of multistate multimode diabatic Hamiltonian of NO₂

Nitrogen dioxide (NO₂) radical has long been of chemical interest owing to the difficulty it presents for experimental measurement as well as theoretical calculations of its spectral properties. After exhaustive research, it is now well established that the complexity of the visible NO₂ spectrum, from near IR to near UV, is due to the CIs between the two lowest electronic states, namely, the $X^2A_1$ ground and $A^2B_2$ first excited state. The ground state of NO₂ ($^2A_1$) and the first excited state ($^2B_2$) undergoes strong JT type coupling via the asymmetric distortion. Moreover, the ground state is significantly affected by RT interactions with the upper excited electronic states in those regions of nuclear CS where the molecule attains linear geometry.

Three strongly coupled vibrational normal modes and the denser bound/quasi bound electronic states are the main causes of the difficulties to probe the molecule. This has led to enormous studies having both experimental and theoretical calculations. A model diabatic Hamiltonian was constructed with linear vibronic coupling between the two strongly coupled $X^2A_1$ and $A^2B_2$ states of NO₂ and dynamics has been carried out to obtain the photoelectron spectra. Global ab initio PESs for the ground and first excited electronic states of NO₂ were calculated by Schinke et al. at MRCI level followed by diabatization and quantum dynamics calculations. Other quantum dynamical calculations have also been carried out either by the MCTDH method or wavepacket dynamics taking into effect the $X^2A_1/A^2B_2$ CI to study the nonadiabaticity between those electronic states of NO₂. An effective Hamiltonian was used to investigate the nonadiabatic dynamics on the two lowest electronic states of this radical using both quantum mechanical and quasi classical techniques. Takatsuka et al. have carried out wavepacket dynamics involving the $X^2A_1/A^2B_2$ CI with a femtosecond pump pulse and subsequently, the time resolved photoelectron spectrum was theoretically investigated, in which the optical control of CIs was monitored in real time by full quantum mechanical calculations. Our group has performed a thorough investigation on the electronic structure, topological effect and nuclear dynamics of NO₂ molecule, where the adiabatic PESs, CIs between the ground ($X^2A_1$) and the first excited state ($A^2B_2$), and the corresponding NACTs between those states are calculated to achieve enough accuracy in dynamics. It has been shown that the coupling between the electronic states ($X^2A_1$ and $A^2B_2$) of NO₂ is essentially through the asymmetric stretching mode, where the functional form of such interaction is distinctly symmetric and non-linear. In summary, NO₂ poses great challenges while unraveling the signatures of nonadiabatic effect in its complex spectra and thus, becomes a non-trivial example requiring BBO treatment.

4.1. Ab initio calculations

We have calculated the adiabatic PESs and NACTs by employing MRCI approach for the ground ($X^2A_1$) and first excited ($A^2B_2$) electronic states of NO₂ with respect to the three modes, the bending ($Q_1$), the symmetric stretching ($Q_2$) and the asymmetric stretching ($Q_3$) as functions of each pair of normal modes fixing the other one at equilibrium. A CCSD(T)/cc-pVTZ geometry optimization calculation produced $C_{2v}$ symmetry with NO bond distance of 1.2126 Å and the
O-N-O bond angle of \( \approx 133.7^\circ \), which is in good agreement with experimental observation\(^{73}\) as well as theoretical calculations\(^{86}\). The equilibrium energy minima is found to be -204.7997 Hartree, whereas the frequencies for bending mode (\( \omega_1 \)), symmetric stretching (\( \omega_2 \)), and asymmetric stretching (\( \omega_3 \)) are calculated to be 0.094 eV, 0.167 eV and 0.209 eV, respectively, which are also in accordance with previous results\(^{76,84,86}\). All our calculations are based on MCSCF level of theory followed by MRCI calculation implemented in MOLPRO\(^{71}\) quantum chemistry package. Dunning’s Correlation Consistent Polarized Valence Triple Zeta (cc-pVTZ) Basis set\(^{98}\) has been employed with [10s,5p,2d,1f]/[4s,3p,2d,1f] contraction scheme for both kind of atoms, nitrogen and oxygen. The configuration active space consisted of 6 electrons in the core orbitals with 17 electrons in 10 active orbitals. The NACTs between the two states are obtained by numerical finite difference method, namely, the DDR procedure as implemented in MOLPRO.

Dimensionless coordinates have been employed throughout the study of this radical which are defined as:

\[
\xi_i = \sqrt{\frac{\omega}{\hbar}} Q_i, \quad \xi_j = \sqrt{\frac{\omega}{\hbar}} Q_j
\]

(60)

with \( \omega = \sqrt{\omega_i \omega_j} \) and \( \omega_i, \omega_j \) are the normal mode frequencies. To get the advantage of inherent symmetry of the system, we have used the polar coordinates \( (\rho(\xi_i, \xi_j) \) and \( \phi(\xi_i, \xi_j) \)) expressed in terms of those dimensionless coordinates, \( \xi_i \) and \( \xi_j \) as given below:

\[
\rho(\xi_i, \xi_j) = \sqrt{\xi_i^2 + \xi_j^2} \\
\phi(\xi_i, \xi_j) = \tan^{-1} \left( \frac{\xi_j}{\xi_i} \right) \quad i, j = 1, 2, 3 \quad \text{and} \quad i < j.
\]

(61)

The \textit{ab initio} results obtained are quite interesting with varied features. Figure 16 depicts the functional forms of NACTs for \( Q_1 - Q_2 \) mode showing singularities along a \( C_{2v} \) seam and a strong RT coupling when the molecule attains linear geometry with the bond lengths 0.882 Å. Figure 17 exhibits both \( \rho \) and \( \phi \) components of the other NAC elements for \( Q_1 - Q_3 \) and \( Q_2 - Q_3 \) pairs of normal mode coordinates. Three singularities from JT type symmetry allowed accidental CI\(^{39}\) (SAACI) arises at the \( Q_1 - Q_3 \) mode at \( \rho \approx 1.0 \) and two RT couplings exists at \( \rho \approx 1.0 \) (see panels a and b of Figure 17). On the other hand, a sharp SAACI for \( Q_2 - Q_3 \) mode is observed at \( \phi = \pi \), whereas RT regions are observed at \( \rho \approx 1.2 \) around \( \phi = \pi/3, 5\pi/3 \) (see panels c and d of Figure 17). One of the key observations is that the RT interaction which was previously predicted\(^{95}\) to exist only between \( X^2 A_1 \) and the higher lying \( ^2 B_1 \) electronic states,
could be now isolated between $X^2A_1$ and $A^2B_2$ states also at different regions of CS of normal coordinates whenever the molecule attains linear geometry.

![Figure 17](a) (b) (c) (d)

**Figure 17** Same as Figure 16. Panels (a) and (b) show the $\rho$ and $\phi$ components of NACT for $\xi_1 - \xi_3$ mode, whereas panels (c) and (d) exhibit $\tau_\rho$ and $\tau_\phi$ are displayed for $\xi_2 - \xi_3$ mode, respectively. Results are adapted from Ref. [40].

Our *ab initio* calculated adiabatic PESs at different geometries agreed quite well with other existing results and the NACTs are obtained at more level of calculations (MRCI/cc-pVTZ basis set) enabled us to calculate diabatic PESs that are expected to be accurate enough. It is noteworthy to mention that as the two electronic states change their sign along the nuclear coordinate at the point of CI, the NACTs remain unaffected and hence MS determined IREPs of the NACTs are not required in this case.

### 4.2. ADT angles and diabatic PESs

Using the *ab initio* calculated NACTs, we solved the ADT equation (Eq. 13) over a two dimensional contour as functions of each pair of normal modes:

$$\frac{\partial}{\partial Q_i} \theta(Q_i, Q_j) = -\tau_{Q_i}(Q_i, Q_j),$$  \hspace{1cm} (62a)

$$\frac{\partial}{\partial Q_j} \theta(Q_i, Q_j) = -\tau_{Q_j}(Q_i, Q_j).$$  \hspace{1cm} (62b)

The functional form of the calculated ADT angles for $Q_1 - Q_2$, $Q_1 - Q_3$ and $Q_2 - Q_3$ pairs of modes are shown in Figure 18(a-c), respectively. Our obtained results reveal that the ADT angle for $Q_1 - Q_2$ (a) attains the numerical value of $2\pi$ in the region of RT coupling and the magnitude $\pi$ for the JT type CIs along the $C_{2v}$ seam. Figure 18(b, c) displays the JT type
SAACIs\cite{100} where again it can be observed that the ADT angle reaches the value of $\pi$ validating the presence of those CIs, whereas a magnitude of $2\pi$ establishes the existence of RT coupling.

Within the chosen nuclear CS, the couplings of the $X^2A_1$ and $A^2B_2$ states with other low lying electronic states ($B^2B_1$, $C^2A_2$) are negligibly small, hence it would be a good approximation that they form a two-state SHS. The solution of the ADT equation provides continuous, single-valued and smooth diabatic PESs for different pairs of normal modes. The calculated ADT angles are plugged in Eq. 14 and subsequently the elements of the diabatic potential energy matrix are evaluated. The diagonal elements of diabatic PESs are depicted in Figure 19, whereas the coupling elements are presented in Figure 20.

The two-state three-mode diabatic Hamiltonian is expressed as:

$$
H^{dia} = T_n + \begin{pmatrix} V_{11}(Q_1, Q_2, Q_3) & V_{12}(Q_1, Q_2, Q_3) \\ V_{12}(Q_1, Q_2, Q_3) & V_{22}(Q_1, Q_2, Q_3) \end{pmatrix},
$$

$$
T_n = -\frac{\hbar^2}{2} \sum_{i=1}^{3} \left( \frac{\partial^2}{\partial Q_i^2} \right).
$$

As we have considered only the coupling between two normal modes at a time and the adiabatic PESs and ADT angles are calculated as functions of pairwise normal modes, $(Q_i, Q_j)$ for $i, j = 1, 2, 3$; $i < j$, this leads us to write the following form of the elements of diabatic PESs matrix as:

$$
V_{11}(Q_1, Q_2, Q_3) \approx \sum_{i=1}^{3} \sum_{j=1}^{3} u_1(Q_i, Q_j) \cos^2 \theta(Q_i, Q_j) + \sum_{i=1}^{3} \sum_{j=1}^{3} u_2(Q_i, Q_j) \sin^2 \theta(Q_i, Q_j), \quad (64a)
$$

$$
V_{22}(Q_1, Q_2, Q_3) \approx \sum_{i=1}^{3} \sum_{j=1}^{3} u_1(Q_i, Q_j) \sin^2 \theta(Q_i, Q_j) + \sum_{i=1}^{3} \sum_{j=1}^{3} u_2(Q_i, Q_j) \cos^2 \theta(Q_i, Q_j), \quad (64b)
$$

$$
V_{12}(Q_1, Q_2, Q_3) \approx \sum_{i=1}^{3} \sum_{j=1}^{3} [u_1(Q_i, Q_j) - u_2(Q_i, Q_j)] \sin \theta(Q_i, Q_j) \cos \theta(Q_i, Q_j). \quad (64c)
$$

4.3. Dressed potential: Topological effect

In order to gain more insight into the vibronic structure of the molecule, we have calculated the dressed potentials by averaging over one of the normal coordinates, employing the vibrational manifold obtained from each of the adiabatic and diabatic PESs.\cite{100-102}
Figure 19 The diagonal elements of diabatic potential energy matrix of NO$_2$ are shown as functions of pairwise normal modes. Results are adapted from Ref. [40].
The prescription is as follows. Firstly, the dressed adiabatic potentials are obtained for the $i$th mode, $u_p^{d,Q_i}(Q_i)$, $p = 1, 2$ using the following expression:

$$u_p^{d,Q_i}(Q_i) = \langle \zeta_p^a(Q_j|Q_i)|u_p(Q_j|Q_i)|\zeta_p^a(Q_j|Q_i) \rangle,$$  \hspace{1cm} (65)

where $u_p(Q_j|Q_i)$s are the two adiabatic PESs, $\zeta_p^a(Q_j|Q_i)$s are the adiabatic vibrational ground eigenfunctions calculated on those surfaces and $u_p^{d,Q_i}(Q_i)$s are the dressed adiabatic potentials as functions of $Q_i$ averaged over $Q_j$. In a similar way, we have calculated the dressed diabatic potentials, $\bar{W}_{mn}^{Q_j}(Q_i)$, $m, n = 1, 2$, as functions of $Q_i$ averaged on $Q_j$, using the diabatic PESs, $W_{mn}(Q_j|Q_i)$, and the corresponding vibrational ground eigenfunctions, $\zeta_{mn}^d(Q_j|Q_i)$ as:

$$\bar{W}_{mn}^{Q_j}(Q_i) = \langle \zeta_{mn}^d(Q_j|Q_i)|W_{mn}(Q_j|Q_i)|\zeta_{mn}^d(Q_j|Q_i) \rangle.$$  \hspace{1cm} (66)

Finally, the dressed diabatic matrix, $\bar{W}^{Q_j}(Q_i)$, can be diagonalized to calculate the two adiabatic-via-dressed diabatic potential energy curves (PECs), $u_p^{d,Q_i}(Q_i)$, $p = 1, 2$ for each $i$th mode.

The calculated dressed adiabatic, diabatic and adiabatic-via-dressed diabatic curves as function of $Q_2$, taking average over $Q_3$, show substantial deviations from each other along $Q_2 < -0.05$ Å. On the other hand, while performing average over $Q_2$, those curves are distinctly different but symmetric as function of $Q_3$. A key finding in the present study of topological effects is summarized in Figure 21. We have plotted the dressed diabatic coupling elements along one coordinate $Q_i$, and averaged over the other coordinate $Q_j$ to investigate the effects of (i) only RT interaction along $Q_1 - Q_2$ mode; (ii) only JT type couplings by switching off the RT interactions for $Q_1 - Q_3$ and $Q_2 - Q_3$ modes; and (iii) both the JT type and RT couplings also for $Q_1 - Q_3$ and $Q_2 - Q_3$ modes. It was found that the dressed diabatic coupling curves as function of $Q_2$ averaged over $Q_3$ and vice versa show strong RT effect. Similar curves as function of $Q_1$ averaged over $Q_3$ and vice-versa show less prominent effects due to RT couplings.

The dressed diabatic couplings are non-linear as a function of each normal mode, whereas for the asymmetric stretching coordinate ($Q_3$), such couplings (see panel (c) of Figure 21) are non-linear as well as symmetric. In summary, when the ground and the excited states are coupled through asymmetric stretching coordinate ($Q_3$), the functional form of the coupling is constituted only with even power terms of a polynomial in $Q_3$.

4.4. Nuclear dynamics and photodetachment spectra of NO$_2^-$

As we know that photoelectron spectrum reveals the structural insights of a species, NO$_2^-$ can be a very good example for this owing to its complex spectra. The photoelectron spectra of this
The dressed diabatic coupling elements \([W_{ij}^{Qj}(Q_i)]\) are shown considering “RT effect”, “only JT coupling” and “JT + RT coupling” along each normal mode coordinate. In panel (a), \(\bar{W}^{Q1}_{ij}(Q_1)\) depicts only RT coupling whereas similar features between the “JT + RT coupling” and “only JT coupling” curves for \(\bar{W}^{Q2}_{ij}(Q_1)\) show less prominent RT effect. In panel (b), \(\bar{W}^{Q1}_{ij}(Q_2)\) shows again only RT coupling whereas the significantly different nature of the “JT + RT coupling” and “only JT coupling” curves of \(\bar{W}^{Q2}_{ij}(Q_2)\) confirms the presence of both JT and RT effects. In panel (c), pair of \(W_{ij}^{Q2}(Q_1)\) curves exhibit less prominent RT effect whereas pair of \(W_{ij}^{Q2}(Q_3)\) curves affirms the influence of RT effect along with the JT effect. It is noteworthy, that the coupling elements as function of asymmetric stretching coordinate \((Q_1)\) are symmetric and non-linear. Results are adapted from Ref. [40].

Figure 21

The dressed diabatic coupling elements \([W_{ij}^{Qj}(Q_i)]\) are shown considering “RT effect”, “only JT coupling” and “JT + RT coupling” along each normal mode coordinate. In panel (a), \(\bar{W}^{Q1}_{ij}(Q_1)\) depicts only RT coupling whereas similar features between the “JT + RT coupling” and “only JT coupling” curves for \(\bar{W}^{Q2}_{ij}(Q_1)\) show less prominent RT effect. In panel (b), \(\bar{W}^{Q1}_{ij}(Q_2)\) shows again only RT coupling whereas the significantly different nature of the “JT + RT coupling” and “only JT coupling” curves of \(\bar{W}^{Q2}_{ij}(Q_2)\) confirms the presence of both JT and RT effects. In panel (c), pair of \(W_{ij}^{Q2}(Q_1)\) curves exhibit less prominent RT effect whereas pair of \(W_{ij}^{Q2}(Q_3)\) curves affirms the influence of RT effect along with the JT effect. It is noteworthy, that the coupling elements as function of asymmetric stretching coordinate \((Q_1)\) are symmetric and non-linear. Results are adapted from Ref. [40].

Figure 22

The dressed diabatic coupling elements \([W_{ij}^{Qj}(Q_i)]\) are shown considering “RT effect”, “only JT coupling” and “JT + RT coupling” along each normal mode coordinate. In panel (a), \(\bar{W}^{Q1}_{ij}(Q_1)\) depicts only RT coupling whereas similar features between the “JT + RT coupling” and “only JT coupling” curves for \(\bar{W}^{Q2}_{ij}(Q_1)\) show less prominent RT effect. In panel (b), \(\bar{W}^{Q1}_{ij}(Q_2)\) shows again only RT coupling whereas the significantly different nature of the “JT + RT coupling” and “only JT coupling” curves of \(\bar{W}^{Q2}_{ij}(Q_2)\) confirms the presence of both JT and RT effects. In panel (c), pair of \(W_{ij}^{Q2}(Q_1)\) curves exhibit less prominent RT effect whereas pair of \(W_{ij}^{Q2}(Q_3)\) curves affirms the influence of RT effect along with the JT effect. It is noteworthy, that the coupling elements as function of asymmetric stretching coordinate \((Q_1)\) are symmetric and non-linear. Results are adapted from Ref. [40].

species was first observed\(^{74}\) in 1988 by Ervin et al., followed by the modified spectra obtained using 266 nm pulsed Nd:YAG laser by Weaver et al. The latter one showed the full bands of \(X^2A_1\) and \(A^2B_2\) state and the beginning of a third, \(C^2A_2\) state of NO\(_2\) in the spectral envelop. Vibronic levels of NO\(_2\) was studied by Delon et al. using laser induced dispersed fluorescence to characterize\(^{76,77}\) the effect of CI between the two lowest electronic states. Indeed, our aim has been to calculate the photoelectron spectra of NO\(_2^-\) that accounts \(X^2A_1\rightarrow A^2B_2\) transitions of NO\(_2\) molecule. For this purpose, we have employed our BBO constructed diabatic surfaces on which nuclear dynamics has been performed. The diabatic Hamiltonian in Eq. 64 has been used to solve the time dependent SE considering GWP for each mode. It should be noted that the nuclear dynamics has been carried out twice locating the initial wave function either on the state, \(X^2A_1\) or \(A^2B_2\), and finally convoluted the results to obtain the final spectra. What we show in Figure 22 is the direct comparison of our calculated spectra including both the JT and RT coupling (see panel (b)) and the “only JT coupling” case (see panel (c)) with the experimentally obtained results\(^{75}\) (see panel (a)). The close resemblance of the peak positions as well as in the intensity patterns of the calculated spectra considering both JT and RT couplings (panel (b)) depicts a reasonably fair agreement with the experimental one. On the other hand, in the absence of the RT interaction, the peak positions of the spectra mainly remain unchanged but an overall broadening can be observed (panel (c)).
Figure 23 Spectral profiles are shown after switching off different modes in the diabatic Hamiltonian. In panel (a), turning off $Q_1$ mode has destroyed the spectral progressions for both the envelops. In panel (b), absence of $Q_2$ mode makes the $\tilde{X}^2A_1$ peaks broadened and the also the progressions in $\tilde{A}^2B_2$ envelop are partially lost. In panel (c), absence of $Q_3$ mode affects the overall spectrum. Results are adapted from Ref. [40].

For better understanding the contribution from each normal mode towards the shaping of the spectral profile, we have carried out the dynamical calculations keeping one normal mode “switched off” at a time. This has led to three different spectral envelops due to turning off three different modes, illustrated in Figure 23. Cutting off the bending mode ($Q_1$) gives away the progressions in the bands of $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ states (see panel (a)). On dropping $Q_2$, we observed broadening of spectral profiles and partial loss of the progression of the peaks in the envelops of $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$, respectively (see panel (b), whereas switching off $Q_3$ does not affect significantly to the overall features of the spectral bands. Hence, from this study it can be concluded that the symmetric ($Q_1$) and the bending ($Q_2$) modes have the major contributions in the dominant progressions of the spectral peaks.

5. BBO approach for the construction of diabatic PESs and the reactive scattering calculation of $D^+ + H_2$ reaction

$H_3^+$ acts as a major source of proton donor\textsuperscript{103,104} in hydrogen plasmas for chemical reactions in the interstellar medium. Its dissociative recombination (DR) rate determines the densities of many astronomical species.\textsuperscript{105} Originally detected by Oka in 1980s,\textsuperscript{106} $H_3^+$ still remains a subject of numerous studies both theoretically and experimentally with extensive reviews.\textsuperscript{107,108} It serves as a prototype for the study of ion-molecule collision process on coupled electronic PESs. It is known that the charge transfer process $H^+ + H_2(v,j) \Leftrightarrow H + H_3^+(v',j')$ involve ground and first excited singlet electronic states.\textsuperscript{6} Moreover, depending upon the collision energy, the second excited singlet state also affects this reaction, thus, becoming a classic example of nonadiabatic event.

Only having two electrons, $H_3^+$ makes a natural target for \textit{ab initio} calculations due to its electronic simplicity. Very accurate local ground adiabatic PESs\textsuperscript{109–111} with relativistic corrections\textsuperscript{112} have been reported where all those surfaces have achieved spectroscopic accuracy.\textsuperscript{113,114} Fitted ground PES for $H^+ + H_2$ system\textsuperscript{115} using available \textit{ab initio} data points\textsuperscript{116,117} were used to study inelastic vibrational excitation using the classical trajectory method.\textsuperscript{118} Many groups have performed \textit{ab initio} calculations of ground electronic state for $H^+ + H_2$ system to obtain correct global behavior.\textsuperscript{119,120} Although ground state of $H_3^+$ has been extensively studied, only few have led thorough investigations on its higher excited electronic states.\textsuperscript{117,121,122} Varandas \textit{et al.} have computed adiabatic PESs for the excited states\textsuperscript{123–125} along with vibrational and rovibrational calculations.\textsuperscript{126,127} Nevertheless, it can be safely stated that there are surfaces\textsuperscript{119,128} available in the literature with major disadvantage of describing only the ground state accu.
rately and the study of electronically nonadiabatic chemical processes on those surfaces are
discarded. A few global PESs, namely, PESs by Preston-Tully,\textsuperscript{129} Kamisaka-Bian-Nobusada-
Nakamura (KBNN)\textsuperscript{130} surface, Aguado et al. PESs,\textsuperscript{131} and the double many-body
expansion (DMBE) potential surface constructed by Varandas et al.,\textsuperscript{132} are available which are all based
on diatomics-in-molecule (DIM) method. These surfaces have been used to study nonadiabatic
processes of H\textsubscript{3}\textsuperscript{+} considering the singlet states. Using the \textit{ab initio} data points calculated by
Ichihara and Yokoyama,\textsuperscript{122} Ushakov et al. have probed the collinear arrangement of H\textsuperscript{+} + H\textsubscript{2}
system using quantum mechanical and trajectory surface hopping methods to account nonadi-
abatic transitions involving the ground and first two excited singlet states.\textsuperscript{133} In another work,
quantum dynamical calculations within the vibrational close-coupling infinite-order-sudden ap-
proximation approach using two quasiadiabatic PESs have been done to obtain state-to-state
differential cross sections (DCS), total DCS and integral cross sections.\textsuperscript{134} Our group has led
a thorough investigation on the \textit{ab initio} calculated adiabatic PESs of the three lowest singlet
states of H\textsubscript{3}\textsuperscript{+} and the NACTs between those states in hyperspherical coordinates and depicted
the diabatic PESs.\textsuperscript{42} In a following work, Alijah et al. \textit{have also presented} \textit{ab initio} calculated
NACTs between the four lowest singlet states of H\textsubscript{3}\textsuperscript{+}.\textsuperscript{135}

Charge transfer processes occurring on multiple PESs have been the center of attention in the
nonadiabatic dynamics.\textsuperscript{130,132,136} Guided beam experimental technique is used to scan integral
cross-sections for the reaction H\textsuperscript{+} + D\textsubscript{2},\textsuperscript{137} in which rate constants\textsuperscript{138} at various collision energies
are acquired for the ion-atom exchange reactions H\textsuperscript{+} + D\textsubscript{2} and D\textsuperscript{+} + H\textsubscript{2}. On the other hand, a
temperature-variable selected ion flow-tube technique\textsuperscript{139} has been used to measure the forward
and reverse rate constants at 205 and 295 K. Gerlich have employed the merged beams technique to
estimate rate coefficients for D\textsuperscript{+} + (normal) H\textsubscript{2} from 180-350 K, collisional energies down to
the 1 meV magnitude are used to measure the reaction cross-sections.\textsuperscript{140} At high-energy regimes,
3D quantum scattering involving both time-dependent and time-independent calculations had
been carried out employing hyperspherical coordinates on three diabatic surfaces constructed by
the DIM approach.\textsuperscript{130,141–143} Further, those surfaces had been fitted to \textit{ab initio} data to explore the
multi-surface processes in D\textsuperscript{+} + H\textsubscript{2} reaction at J = 0. Moreover, time-independent scatter-
ing\textsuperscript{6,130,142,144} and time-dependent wave packet\textsuperscript{145–148} calculations had been performed for the
same energy range using DIM fitted diabatic PESs considering both centrifugal sudden and close
coupled methodologies with non-zero total angular momenta. Other essential works on the H\textsubscript{3}\textsuperscript{+}
charge transfer and non charge transfer processes are highlighted in recent review articles.\textsuperscript{149–151}

We have employed BBO theory to construct multi-sheeted diabatic PESs\textsuperscript{42} of H\textsubscript{3}\textsuperscript{+} system and
performed quantum dynamics\textsuperscript{156,152–154} using hyperspherical coordinates.\textsuperscript{54} In this reaction, the
following channels, namely, reactive non-charge transfer (RNCT), non-reactive charge transfer
(NRCT) and reactive charge transfer (RCT):
\begin{align*}
D^+ + H_2 &\rightarrow DH + H^+ \quad \text{RNCT} \\
D^+ + H_2 &\rightarrow D + H_2^+ \quad \text{NRCT} \\
D^+ + H_2 &\rightarrow DH^+ + H \quad \text{RCT}
\end{align*}
are investigated.

\subsection*{5.1. \textit{Ab initio} calculation for PESs and NACTs}

Hyperspherical coordinates have been used to map the triatomic PESs\textsuperscript{155,156} so that all the
arrangement channels are represented evenhandedly. This involves a hyperradius \( \rho \), which solely
dictates the overall size of the triangle formed by the three particles and two hyperangles \( \theta \)
\((0 \leq \theta \leq 90^\circ)\) and \( \phi \) \((0 \leq \phi \leq 360^\circ)\) corresponding to the spherical latitudes and longitudes,
respectively. The latter two are responsible for the shape of the triangle. For three identical
particles, $\theta = 0^\circ$ represent equilateral triangle whereas $\theta = 90^\circ$ makes the arrangement collinear. The shape of the triangle will be acute isosceles for $\phi = 30^\circ$, $150^\circ$ and $270^\circ$, whereas obtuse isosceles triangle for $\phi = 90^\circ$, $210^\circ$ and $330^\circ$. All the \textit{ab initio} calculations for PESs and NACTs of H$_3^+$ system are carried out in terms of interparticle distances of the three H atoms, which are related to the hyperspherical coordinates as:

\begin{align}
R_1^2 &= \frac{\rho^2}{\sqrt{3}} [1 + \sin \theta \sin (\phi + 4\pi/3)], \\
R_2^2 &= \frac{\rho^2}{\sqrt{3}} [1 + \sin \theta \sin (\phi - 4\pi/3)], \\
R_3^2 &= \frac{\rho^2}{\sqrt{3}} [1 + \sin \theta \sin \phi].
\end{align}

In our work\cite{42} we have calculated the three lowest singlet adiabatic PESs ($1^1A'$, $2^1A'$, $3^1A'$) of H$_3^+$ and the NACTs between those states by MOLPRO quantum chemistry package\cite{71} as functions of hyperangles, $\theta$ ($0 \leq \theta \leq 90^\circ$) and $\phi$ ($0 \leq \phi \leq 360^\circ$) for a grid of hyperradius ranging from 1.5 to 20 Bohr. Dunning’s\cite{98} correlation consistent quintuple zeta (cc-pV5Z) basis set with (8s4p3d2f1g)/(5s4p3d2f1g) contraction scheme has been used in the \textit{ab initio} calculations. We have performed MCSCF calculations involving the first six electronic states with an active space chosen of 2 electrons distributed over 10 active orbitals. MRCI calculations are then carried out with the above reference orbitals for the first three singlet states.

Figure 24 1d cuts of lowest three adiabatic singlet PESs as a function of $\phi$ for different $\theta$s with a fixed $\rho = 10$ Bohr. The red solid line represents the ground ($1^1A'$) state, green dashed line and blue dot-dashed line depicts the first ($2^1A'$) and second ($3^1A'$) excited states, respectively. Results are adapted from Ref.\cite{42}.

![Figure 24](image-url)
The ground singlet state \( (1^1A') \) of \( H_4^+ \) provides an energy minima at -1.3437 Hartree with equilibrium \( D_{3h} \) structure. The energy minima for the first excited state happens to be at -1.1030 Hartree, whereas for the second excited state, it is -1.0001 Hartree. All these calculations are consistent with previously available results.\(^{192} \) Figure 24 represents 1d PECs of the three adiabatic singlet states as a function of \( \phi \) for various \( \theta \)s with a fixed \( \rho = 10 \) Bohr. It has been observed that there exist three CIs at \( \theta = 60^\circ \) with \( \phi = 30^\circ, 150^\circ, 270^\circ \) and six CIs for \( \theta \geq 60^\circ \) at different \( \phi \)s between the ground \( (1^1A') \) and first excited \( (2^1A') \) singlet states. Moreover, PJT interaction prevails between the first two excited states at \( \theta = 90^\circ, 210^\circ, 330^\circ \). Due to accidental degeneracy, the three CIs at \( \theta = 60^\circ \) with \( \phi = 30^\circ, 150^\circ, 270^\circ \) exist at \( C_{2v} \) geometry, whereas the six CIs for \( \theta \geq 60^\circ \) at different \( \phi \)s are originated for equivalent scalene triangle geometry formed by the triatom. The CI seams are formed along a semi-circular path while changing the scalene geometry of the triatom to an equivalent scalene triangle through an isosceles triangle. The contour plots of the two lowest singlet adiabatic PESs of \( H_4^+ \) system are displayed in Figure 25 using the stereographic projection defined as: \( \beta = \sin(\theta) \cos(\phi) \) and \( \gamma = \sin(\theta) \sin(\phi) \) for a fixed \( \rho = 10 \) Bohr. Those two PESs are projected on a same plane in Figure 25 displaying the CI seams in the CS, where the dot (*) represents the saddle point of the ground singlet state. The energies are shifted by -1.2 Hartree and presented in eV unit.

The numerical finite difference method (DDR) has been used to calculate the NACTs \( \tau_{kj}^{ij} \) \( (k = \theta, \phi, i = j = 1, 2, 3, i < j) \) among the states. As the two lowest surfaces form a semi-circular CI seam in the nuclear CS, it is reflected in the Figure 26 and 27 by the high amplitudes in the profiles of NACTs on the same seam. The CI seams between the ground and the first excited state exist within the range, \( 60^\circ \leq \theta \leq 90^\circ \) with \( \phi \approx (0^\circ - 60^\circ), (120^\circ - 180^\circ), (240^\circ - 300^\circ) \). As the profiles for PESs and NACTs show perfect repetition on \( 120^\circ \) interval due to inherent symmetry of the system \( (D_{3h}) \), we have depicted the range of \( \phi \) only between 0 to \( 120^\circ \) both in Figure 26 and 27. The \( \phi \) component of the NACT between the first two states \( (\tau_{12}^{12}) \) in Figure 27 exhibits maximum magnitude at \( \phi \approx 0^\circ \) and \( 60^\circ \) with \( \theta \approx 90^\circ \), whereas \( \tau_{12}^{12} \) shows a semi-circular CI seam in the CS, but unlike \( \tau_{12}^{12} \), it reaches a maximum at \( \theta \approx 60^\circ \) with \( \phi \approx 30^\circ \) (see Figure 26).

5.2. Adiabatic to diabatic transformation

After plugging-in the \( ab \) initio calculated NACTs in Eqs. 19, we solved those stiff differential equations over 2d grid of geometries as functions of \( \theta \) and \( \phi \) ranging from \( \theta = 0 \) to \( 90^\circ \) and \( \phi = 0 \) to \( 360^\circ \) to obtain the ADT angles. We have displayed the ADT angles \( [\theta_{ij}(\theta, \phi)] \) as functions of hyperangles for a fixed \( \rho = 10 \) Bohr in panels \( a - c \) of Figures 28 and the residues of the ADT angles \( \left[ \theta_{ij} = \int_0^{2\pi} \theta_{ij}(\theta_k, \phi) \cdot d\phi \right] \) are presented as function of \( \theta \) in Figures 29. Figure 29 reveals that the residue \( (\hat{\theta}_{ij}) \) for the ADT angle \( \theta_{12} \) becomes close to \( 4\pi \) at asymptotic \( \theta \). The diagonal element(s) of the ADT matrix, \( A_{11}/A_{22} \) for different \( \theta \)s clearly shows six sign changes as function of \( \phi \) in Figure 30 describing the presence of six CIs.

We have shown the elements of the diabatic potential energy matrix (see Eq. 21) in Figure 31.
using the stereographic projection as contour plots. The calculated functions are found out to be single-valued, continuous, smooth and symmetric. It is evident that the six crossing seams between the first two diabatic states have close relationship with the six avoided crossings between the corresponding adiabatic PESs. Our calculated diabatic PES matrix shows the correct symmetry of $\mathrm{H}_3^+$ system and is expected to provide very accurate observable on dynamical calculations.
Figure 29 The residues of the ADT angles as a function of $\theta$ for a fixed $\rho = 10$ Bohr. Results are adapted from Ref. [42].

Figure 30 1d cuts of the $(1,1)/(2,2)$ elements of ADT matrix at $\rho = 10$ Bohr as function of $\phi$ for different $\theta$s. Results are adapted from Ref. [42].

Figure 31 Contour plots of the diabatic potential energy matrix elements (in eV) in stereographic projection for a fixed $\rho = 10$ Bohr. Results are adapted from Ref. [42].
5.3. Time-Dependent 3D wave-packet methodology in hyperspherical coordinates for the $D^+ + H_2$ reaction

The initial wave packet can be represented in terms of $3-j$ symbols and modified spherical harmonics ($C_{j\mu}$):

$$\Phi_{a,K} = \sqrt{2\pi \sin \eta J(Rr_\eta|\rho\theta\phi)(2l+1)}\phi_{v\ell}(r) \chi(R)(-1)^j$$

$$\times \sum_{\mu} \left( \begin{array}{ccc} j & l & J \\ \mu & 0 & -\mu \end{array} \right) C_{j\mu}(\eta)A_{K\mu},$$

(68)

where symbols carry their usual meanings as defined elsewhere.\[136\]

According to Johnson’s hyperspherical coordinates,\[156\] the diabatic Hamiltonian operator related with the three-particle system is expressed as:

$$\hat{H} = \left\{ -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial \rho^2} + \frac{2}{\mu_R \rho^2} \hat{L}^2(\theta, \phi) + \frac{j_z^2 - \hat{j}_z^2}{\mu_R \rho^2 \cos^2 \theta} + \frac{j_z^2 - 4 \cos \theta \hat{j}_z \hat{P}_\phi}{2\mu_R \rho^2 \sin^2 \theta} \right\} + \hat{I} + \hat{V}_0(\rho, \theta, \phi),$$

(69)

where

$$\hat{j}_z = -i\hbar \left( \frac{\partial}{\partial \theta} \right),$$

(70)

$$\hat{P}_\phi = -i\hbar \left( \frac{\partial}{\partial \phi} \right),$$

(71)

$$\hat{L}^2(\theta, \phi) = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right],$$

(72)

$$\hat{V}_0(\rho, \theta, \phi) = \begin{bmatrix} V_{11} + \Delta V & V_{12} & V_{13} \\ V_{21} & V_{22} + \Delta V & V_{23} \\ V_{31} & V_{32} & V_{33} + \Delta V \end{bmatrix},$$

(73)

$$\Delta V(\rho, \theta) = -\frac{\hbar^2}{2\mu_R \rho^2} \left[ \frac{1}{4} + \frac{4}{\sin^2 2\theta} \right],$$

(74)

$$\mu_R = \sqrt{\frac{m_A m_B m_C}{m_A + m_B + m_C}},$$

(75)

and $\hat{I}$ is a unit matrix, $\hat{V}_0$ represents the ($3\times3$) interaction potential matrix for the triatomic system, and $\hat{j}_+, \hat{j}_-$ are the raising and lowering operators, respectively. The adiabatic $K$-component wavefunctions ($\Phi_{K,I}^a$) for different surfaces ($I = 1, 2, 3$) are transformed to the diabatic ones ($\Phi_{K,I}^d$) by using the matrix that diagonalizes $\hat{V}_0(\rho, \theta, \phi)$. The wavefunctions $\Phi_{K,I}^d$ in hyperspherical coordinates and the Hamiltonian (Eq. 69) are substituted into the time-dependent Schrödinger equation (TDSE) to obtain the following set of coupled equations in
orbital quantum numbers

The scattering amplitude corresponding to the channel specified by vibrational, rotational and
terms of \( K \)-component waves \( \Phi_{K,I}^d \) for each surface: \(^{136}\)

\[
\begin{align*}
  i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \Phi_{K,1}^d \\ \Phi_{K,2}^d \\ \Phi_{K,3}^d \end{bmatrix} &= \left\{ -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial \rho^2} + \frac{2}{\mu_R \rho^2} J^2(\theta, \phi) + \frac{\hbar K (hK - 4 \cos \theta \hat{P}_\theta)}{2\mu_R \rho^2 \sin^2 \theta} \right. \\
  &+ \frac{\hbar^2 [J(J + 1) - K^2]}{\mu_R \rho^2 \cos^2 \theta} + \Delta V(\rho, \theta) \left\} \begin{bmatrix} \Phi_{K,1}^d \\ \Phi_{K,2}^d \\ \Phi_{K,3}^d \end{bmatrix} \\
  &+ \begin{bmatrix} V_{11} + \Delta V & V_{12} & V_{13} \\
  V_{21} & V_{22} + \Delta V & V_{23} \\
  V_{31} & V_{32} & V_{33} + \Delta V \end{bmatrix} \begin{bmatrix} \Phi_{K,1}^d \\ \Phi_{K,2}^d \\ \Phi_{K,3}^d \end{bmatrix} \\
  &+ \frac{\sin \theta}{\mu_R \rho^2 \cos^2 \theta} \begin{bmatrix} \Phi_{K+2,1}^{d+} \\ \Phi_{K+2,2}^{d+} \\ \Phi_{K+2,3}^{d+} \end{bmatrix} + M_{K,K+2}^{d+} \begin{bmatrix} \Phi_{K-2,1}^{d-} \\ \Phi_{K-2,2}^{d-} \\ \Phi_{K-2,3}^{d-} \end{bmatrix},
\end{align*}
\]

(76)

where the diabatic wavefunctions \( \Phi_{K,I}^d \) and \( \Phi_{K\pm 2,I}^d \) are coupled via the coupling element:

\[
M_{K,K\pm 2} = \frac{\hbar^2}{2} \sqrt{(J \mp K)(J \pm K + 1)(J \mp K - 1)(J \pm K + 2)}. \quad (77)
\]

We represent the \( K \)-component waves \( \Phi_{K,I}^d(\rho, \theta, \phi) \) in a discrete way on three-dimensional grids in order to propagate the coupled wave packets in time.

The time-dependent wave packet is projected onto asymptotic eigenstates at a fixed value of \( R \) which makes the asymptotic propagation part of the problem even simpler to handle. \(^{157,158}\)
The scattering amplitude corresponding to the channel specified by vibrational, rotational and orbital quantum numbers \( \nu', j', l' \) for different surfaces \( (I = 1, 2, 3) \) can be evaluated as follows:

\[
u_{\nu'j'l'}^{\nu j l}(R; t) = 4R \int d \eta \int d \rho \rho \sin \eta \rho^{-5/2} (\sin 2 \theta)^{-1/2} \phi_{\nu'j'l'}^\nu(\rho, \theta) \times \sum_{K\mu' l' \nu'} g_{j'il'} A_{K\mu' l' \nu'} C_{j' l' \nu'}(\eta) \Phi_{K,I}^d(\rho, \theta, \phi),
\]

(78)

where the diabatic \( K \)-component wavefunctions \( \Phi_{K,I}^d \) are again transformed to the adiabatic ones \( \Phi_{K,I}^a \) at each time step of propagation and \( \phi_{\nu'j'l'}^\nu \) is a vibrational eigenfunction corresponding to the adiabatic state. The modified constant for \( 3 - j \) symbol is represented as:

\[
g_{j'il'} = \sqrt{2\pi(2l + 1)(-1)^{j-l}} \binom{j}{l} l \mu (J \mu) .
\]

(79)

The scattering amplitudes are Fourier transformed from time to energy space after the wave packet passes through the projection region and gets absorbed at the boundary:

\[
b_{\nu'j'l'}^{\nu j l}(E; R) = \frac{1}{\sqrt{2\pi}} \int dt \, u_{\nu'j'l'}^{\nu j l}(R; t) \exp(iEt/\hbar),
\]

(80)
and such amplitudes corresponding to the diabatic representation is then evaluated as:

\[
d_{1, v', j', l'} = \sum_v \{ b_{v, j, l} O_{v, v', j'}^{11} + b_{v, j, l} O_{v, v', j'}^{21} \},
\]

\[
d_{2, v', j', l'} = \sum_v \{ b_{v, j, l} O_{v, v', j'}^{22} + b_{v, j, l} O_{v, v', j'}^{12} \},
\]

(81)

where \( O_l \) and \( O_r \) are vibrational matrix elements:

\[
O_{v, v', j'}^\text{I} = \int_{r_c}^\infty \phi_{v}^{I} \phi_{v'}^{I'},
\]

\[
O_{v, v', j'}^\text{II} = \int_{r_c}^\infty \phi_{v}^{II} \phi_{v'}^{II'}.
\]

(82)

The state resolved reaction probability from the initial state \((v j l)\) to the product state \((v' j' l')\) on \( I^{th} \) surface could be calculated by taking the ratio of the outgoing and incoming fluxes,

\[
P_{v' j' l' \leftarrow v j l} = \frac{F_{v' j' l'}}{F_{v j l}},
\]

(83)

where

\[
F_{v' j' l'} = \frac{1}{\mu_{\text{out}}} k_{v' j'} |c_{v' j'}^l|^2,
\]

\[
F_{v j l} = \frac{1}{\mu_{\text{in}}} k_{v j} |c_{v j}^l|^2,
\]

(84)

(85)

where the scattering amplitude of the initial wave packet at energy \( E \) is denoted by \( c_{v j}^l \) and the wave vectors of the initial \((v j)\) and final \((v' j')\) channels are represented by \( k_{v j} \) and \( k_{v' j'} \), respectively, and \( \mu_{\text{in}} \) and \( \mu_{\text{out}} \) are the appropriate triatomic center of masses for the reactants and products, respectively. The weight of the scattering amplitudes in energy \( E \) and wave vector \( (k) \) space are related as:

\[
|c_{v j}^l|^2 = \left( \frac{\mu_{\text{in}}}{\hbar k} \right)^2 |c_{v j}^l|^2,
\]

(86)

where \( |c_{v j}^l|^2 \) has the analytic expression of a Gaussian wave packet as:

\[
|c_{v j}^l|^2 = \sqrt{2/\pi} \sigma \exp[-2\sigma^2(k - k_0)^2]
\]

(87)

with \( \sigma \) being the width of the Gaussian wavepacket.

Total integral cross sections (ICSs) at various collision energies can be calculated by summing over the state-to-state reaction probabilities for all those \( J \) values:

\[
\sigma_{v' j' \leftarrow v j}(E) = \frac{\pi}{\hbar^2} \sum_{J=0}^{J_{\text{max}}} \sum_{v'=0}^{v'_{\text{max}}} \sum_{j'=0}^{j'_{\text{max}}} (2J + 1) P_{v' j' \leftarrow v j}^J\left(E\right)
\]

(88)
Table 3  Data for initialization, projection and absorbing potential discussed in the text:

| Grid size:          |    |
|---------------------|----|
| $N_\rho$            | 256|
| $N_\theta$          | 64 |
| $N_\phi$            | 128|
| $(\rho_{\text{min}}, \rho_{\text{max}})/\text{Å}$ | (1.0, 10.0) |

| Translational wave packet: |    |
|-----------------------------|----|
| $R_0/\text{Å}$              | 5.50 ($\sim 6.56)^a$ |
| $R_f/\text{Å}$              | 1.70 ($\sim 2.75)^a$ |
| $\sigma/\text{Å}$           | 0.20 |
| $k_0$ ($\text{Å}^{-1}$)     | 36.3523 |

| Rovibrational energy:       |    |
|-----------------------------|----|
| $E_{vij}$ (eV)              | 0.269763 |

| Propagation:                |    |
|-----------------------------|----|
| $\Delta t$ (fs)             | 0.050 |
| Total time of propagation (fs) | $\sim 250$ |
| Average of the last five normalized Lanczos vectors | $10^{-8} - 10^{-7}$ |

| Absorbing potential:        |    |
|-----------------------------|----|
| $V_{\text{max}}$/eV         | 0.163 |
| $\rho I$ (Å)                | 8.0 |
| Active range of the absorbing potential (Å) | 8.0 - 10.0 |

| Projection:                 |    |
|-----------------------------|----|
| $R^*$ (Å)                   | 5.25 ($\sim 6.45)^a$ |
| vib. states                 | $v' = 0, \cdots, 10$ |
| rot. states                 | $j' = 0, \cdots, 12$ |

$^a$ The transformed values in $\rho$ - space are given in the parenthesis.

5.4. $D^+ + H_2$: reactive scattering dynamics

The BBO constructed diabatic surfaces\textsuperscript{42} allowed us to perform time-dependent coupled 3D wave packet $[\Phi_{K,I}^d(\rho, \theta, \phi)]$ dynamics in hyperspherical coordinates for the $D^+ + H_2$ ($v = 0; j = 0$) reaction on the lowest three singlet states ($1^1A', 2^1A'$ and $3^1A'$) of $H_3^+$. We have calculated state-to-state as well as total reaction probabilities for all three competitive processes, namely, RNCT, RCT and NRCT for $J = 0$ and $J \neq 0$ situations. Fully closed coupled (FCC) approach has been employed by inclusion of all helicity quantum numbers ($K$), as it had been illustrated elsewhere\textsuperscript{153} that all those $K$-component waves contribute significantly to the reaction probabilities for various total angular momenta, $J$. The Open Multi-Processing (OpenMP) parallelization is implemented for calculation of a set of $K$-component waves for a particular $J$ on a specific PES. On the other hand, the calculation on different PESs has been carried out by employing Message Passing Interface (MPI) parallelization, which can take care of the fact that dynamics on all the three states can be computed simultaneously at different computer nodes. We have used a large grid basis ($N_\rho = 256, N_\theta = 64, N_\phi = 128$) in all of our dynamical calculations since the interpolation of the wave packet on the $\rho$ coordinate at a particular $R$ ($=R^*$) during the projection demands higher number of grid points. We have used a linear absorbing potential and its explicit form is presented elsewhere.\textsuperscript{51,159} Table 3 presents the various dynamical parameters utilized in our calculations and their definitions are given in our previous publication.\textsuperscript{152}
5.4.1. Reaction probability: We have depicted our calculated total reaction probabilities as function of collision energy \(E_{\text{col}}=1.7 - 2.5 \text{ eV}\) for reactive non-charge transfer (RNCT) process for \(J=0\) case in panel (a) of Figure 32. The comparison of our results are shown with other theoretical calculations performed by Adhikari, Varandas and coworkers\(^{136}\) on DMBE PES\(^{132}\) and by Chu and Han\(^{146}\) on KBNN PES.\(^{130}\) It is evident that these are generally in good agreement with the previous calculations. As the fluctuations of the magnitude of reaction probability occur around \(\sim 0.7\) in the lower energy regime (1.7 - 2.0 eV) and \(\sim 0.6\) in the higher energy regime (2.0 - 2.5 eV), we concluded that RNCT reaction probability gradually decreased with the increase of collision energy. In addition, we have observed similar resonances over the entire energy regime as in the case of Chu and Han profile calculated on KBNN PES. The richer resonance structures in the reaction probability profile are due to the employment of enough accurate diabatic PES\(^{42}\) constructed by using the BBO theory. Although all other theoretical calculations show the average of total reaction probability is varying around similar values, our calculations exhibit higher average at lower energy and lower average at higher energy. The reaction probability as a function of collision energy for reactive charge transfer (RCT) process at zero total angular momentum case is displayed in panel (b) of Figure 32, where the results for other theoretical calculations are also presented. It is observed that all the profiles have similar threshold around \(\sim 1.8 \text{ eV}\). As the collision energy increases, the RCT reaction probability gradually increases. Finally, the reaction probabilities for the non-reactive charge transfer (NRCT) process for \(J = 0\) are demonstrated in panel (c) of Figure 32. Our calculations show a higher value of the reaction probability at the higher collision energy regime unlike other theoretical calculations. The obtained low value of reaction probability profile for NRCT process at low collision energy is an indication of the threshold for opening the charge transfer processes. The richer resonance structures in the reaction probability profiles are attributed to the effect of nonadiabatic interaction terms via the significant diabatic coupling elements of the potential energy matrix. Since the first two sheets of the diabatic PESs\(^{42}\) have six crossings along seams in certain configuration of \(\theta - \phi\) space over a wide range of hyperradius, \(\rho\) both in the reactant and product channels along with strong PJT coupling with the third state, we conclude
that these lead to the distinct behavior of our obtained reaction probability profiles compared to the previously calculated ones.

5.4.2. Total integral cross section: Panel (a) of Figure 33 displays the total integral cross section (ICS) for the RNCT process as a function of collision energy over the range 1.7 - 2.5 eV. Our calculations, carried out on the most recent as well as accurate diabatic PESs, are compared with the previous theoretical results obtained by Adhikari, Varandas and coworkers \cite{136} as well as by Chu, Varandas and Han \cite{148} on DMBE PES \cite{132} and by Chu and Han \cite{146} on the KBNN PES, \cite{130} and also with the available experimental measurements by Schlier et al. \cite{160}. It is clearly noticeable that the ICS profile for RNCT process decreases almost linearly with the increase of collision energy. Moreover, an appreciable agreement is found while comparing our obtained profile with the experimental results of Schlier et al. \cite{160} since it falls over the experimental error bars within the entire energy range of consideration. The ICS profile for RCT process presented in panel (b) of Figure 33, starts with very small value in the lower energy regime (\(~1.7\) eV) and thereafter, gradually increases as the collision energy increases. Our profile not only is in good agreement with the previous calculations by Adhikari, Varandas and coworkers, but also matches extremely well with the experimental measurements by Schlier et al. \cite{160} since it falls over the experimental error bars within the entire energy range of consideration. The ICS profile for NRCT process presented in panel (c) of Figure 33, starts with very small value in the lower energy regime (\(~1.7\) eV) and thereafter, gradually increases as the collision energy increases. Our profile not only is in good agreement with the previous calculations by Adhikari, Varandas and coworkers, but also matches extremely well with the experimental measurements by Schlier et al. \cite{160} since it falls over the experimental error bars within the entire energy range of consideration. It is noteworthy that the threshold energy for the RCT as well as NRCT process is manifested by small value of ICS at lower collision energy (\(~1.7\) eV). Indeed, the effect of nonadiabatic interaction terms via diabatic coupling on the scattering process as well as the use of FCC formalism \cite{153} over the previously employed approximate close coupled (ACC) one \cite{146,148} lead to the deviation of presently calculated cross sections from the previous theoretical calculations. All of our calculations clearly show that in the lower energy regime RNCT process is the prevailing one, whereas due to the enhanced competition between non-charge transfer and charge transfer processes with the increase of collision energy, the contributions from the RCT and NRCT processes also increase substantially.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure33.png}
\caption{Comparison of total integral cross section as function of collision energy for: (a) RNCT; (b) RCT and (c) NRCT processes with previous theoretical calculations performed by Adhikari, Varandas and coworkers \cite{136} on DMBE PES, Chu, Varandas and Han \cite{148} on DMBE PES and Chu and Han \cite{146} on KBNN PES. Also shown is the comparison with the experimental measurements of Schlier et al. \cite{160}. Results are adapted from Ref. \cite{51}.}
\end{figure}
6. Summary and future outlook

In the current perspective of beyond Born-Oppenheimer (BBO) theory, we observe that both adiabatic potential energy surfaces (PESs) and nonadiabatic coupling terms (NACTs) are important ingredients for constructing accurate diabatic PESs. The adiabatic PESs are physically meaningful quantities, experimentally realizable and uniquely defined in the nuclear configuration space (CS). Thus, it is important to work in the adiabatic representation for any theoretical development on BBO treatment and its application on molecular system. Nevertheless, the NACTs could be singular at certain points in the CS making it necessary to transform the kinetically coupled adiabatic SE to the potentially coupled diabatic one, where the PESs would be continuous and smooth enough to perform accurate and stable quantum dynamics. Since our methodology starts with the adiabatic Hamiltonian for a molecular system/process, it is necessary to ensure that all its terms are totally symmetric with respect to the elements of the molecular symmetry (MS) group designated for that system/process. Any quantum chemistry package can only assign the irreducible representations (IREPs) of the adiabatic PESs. On the contrary, as NACTs are calculated by using beyond BO treatment and the determination of the IREPs of electronic wavefunctions is difficult, such packages can not assign appropriate IREPs for NACTs. Hence, it is theoretically and technically necessary to ensure that both the quantities, adiabatic PESs and NACTs belong to appropriate IREPs in order to construct totally symmetric nuclear Hamiltonian. In a series of work, we have developed the BBO theory incorporating MS adaptation to the \textit{ab initio} calculated NACTs that provides a practical way to handle the NACTs with singularity at certain point(s)/seam and construct smooth and symmetric diabatic PESs to observe “correct” features of nuclear dynamics and spectral profiles.

In Section 3, we have reviewed our work on the excited states of Na$_3$ cluster, in which \textit{ab initio} calculation for adiabatic PESs and NACTs, have been performed at the MRCI level. The MS adapted NACTs were substituted in the Adiabatic to diabatic transformation (ADT) equation and those stiff differential equations were solved to calculate the ADT angles. We have shown the validity of curl condition for the chosen three-state sub-Hilbert space (SHS). The obtained ADT angles and adiabatic PESs were used to construct the diabatic potential energy matrix. We have demonstrated the collapse of three conical intersections (CIs) at the central point of the normal modes, where it was found that the diagonal elements of ADT matrix ($A_{11}/A_{22}$) show the expected number of sign change due to the CI points. Those two elements of the ADT matrix show six sign changes within the domain of pseudo rotation (0 to $2\pi$) and confirm the existence of six CIs between the two 2$^2$E$^\prime$ states, where the three CIs collapse at the D$_{3h}$ symmetry point. It was also established that the various path dependent solution (ADT angles) are gauge invariant. Thus, those may lead to different ADT matrices but those matrices are related with each other through orthogonal transformations. Subsequently, we have performed nuclear dynamics on the full diabatic Hamiltonian of Na$_3$ system with an aim to generate the photoelectron spectrum of system \textbf{B} of Na$_3$ cluster. Our calculated spectra reproduced the pattern of latest experimental spectrum obtained by W. E. Ernst \textit{et al.} in a fairly good agreement.

Section 4 presents a comprehensive study of NO$_2$ radical known for its complicated vibronic structure and photoelectron spectra. It provides a great opportunity to explore nonadiabatic effects through Jahn-Teller type and Renner-Teller type intersections between the PESs of the ground ($X^2A_1$) and first excited states ($A^2B_2$). Employing the BBO theory, we have calculated two state three-mode diabatic Hamiltonian of NO$_2$ with the intention to decipher the $X^2A_1 \rightarrow A^2B_2$ transitions and reproduce the experimental photoelectron spectrum. Firstly, \textit{ab initio} calculations for the adiabatic PESs of $X^2A_1$ and $A^2B_2$ and the NACTs between them are carried out as functions of pairwise normal mode coordinates. The NACTs depict several singularities of symmetry allowed accidental CIs, RT couplings and $C_{2v}$ seams in the CS, and
are used for solving the ADT equations. The calculated ADT angles with correct features of JT and RT type of CI, are used to construct the diabatic Hamiltonian. Those functions not only appear to be smooth and symmetric but also continuous and single-valued. Our study on the topological effect of this system revealed that both the JT-type coupling and the RT interaction contribute significantly on the nonadiabaticity through $Q_2 - Q_3$ mode. Moreover, the coupling between the electronic states through $Q_3$ mode is stronger, symmetric and non-linear which can be represented by a polynomial in $Q_3$ containing only the even power terms. Previous studies on the model Hamiltonian of NO$_2$ based on normal modes considered linear coupling between the electronic states, whereas our findings revealed that only the even power polynomial of $Q_3$ appears to be the contributing one. Thus, the selection rule for the transition of nuclear wave function from one electronic state to another arises due to the symmetric functional form of the coupling elements for the asymmetric stretching mode. Nuclear dynamics has been performed on the full diabatic Hamiltonian and subsequently, the photoelectron spectra was reproduced. A reduced dimensional study showed that $Q_1$ and $Q_2$ modes are responsible for generating the progression of the $A^2B_2$ band, while $Q_3$ mode has significant effect on the overall spectrum.

The BBO theory is employed for constructing global PESs for studying the scattering process D$^+$ + H$_2$ reaction. In Section 5, we have presented the ab initio calculated first three singlet adiabatic PESs of H$_3^+$ and the NACTs between those states employing hyperspherical coordinates. A semi-circular CI seam between the ground ($1^1A'$) and first excited ($2^1A'$) singlet states are our new observations which are represented as functions of hyperangles for each fixed hyperradius. For a fixed hyperradius, there are six CIs as a function of $\phi$ at each $\theta \geq 60^\circ$ due to the equivalent scalene geometry formed by the triatoms. We obtained the ADT angles by solving the three-state SHS ADT equations and thereby, constructed the diabatic potential energy matrix. The elements of the diabatic PES matrix are obtained to be single valued, continuous, symmetric and smooth functions of nuclear coordinates. A key feature of those diabatic PESs is the presence of six crossing seams exactly corroborating the number of avoided crossings in the adiabatic PESs. We have investigated the D$^+$ + H$_2$ reactive scattering dynamics using our newly constructed global multi-sheeted diabatic PESs for the lowest three singlet states ($1^1A'$, $2^1A'$ and $3^1A'$) of H$_3^+$ with zero as well as non-zero total angular momentum cases. Use of hyperspherical coordinates allows us to treat all the three competing processes, namely, reactive non-charge transfer (RNCT), non-reactive charge transfer (NRCT) and reactive charge transfer (RCT) process, evenhandedly. Our major focus has been on investigating the nonadiabatic effects which are known to contribute at higher energies beyond $\sim$ 1.8 eV. We have found that the total reaction probabilities are in good agreement with previous theoretical calculations, whereas for non-zero total angular momentum cases, the convergence profiles for the total reaction probabilities at various collision energies are in proper trend. Moreover, the total integral cross section profiles for RNCT, RCT and NRCT are in reasonably good agreement with the available experimental results thus validating the BBO treatment for the D$^+$ + H$_2$ scattering process.

Our studies on the above systems reveal that the first principle based formulation of BBO theory is complete by itself and provide realistic diabatic potential energy matrix paving the way for accurate quantum dynamical calculations. Our current research is focused on applying the theory in molecular systems known for their complex photoelectron spectra and found to possess rich Jahn-Teller and pseudo Jahn-Teller vibronic couplings, namely, benzene and trifluorobenzene radical cations (C$_6$H$_7^+$ and C$_6$F$_3$H$_7^+$). In addition, we look forward to employ the BBO formalism in order to construct global PESs for scattering systems like H + H$_2$ and F + H$_2$ reactions, of which the latter is known to exhibit strong Renner-Teller effect. Those highly coupled surfaces will be used for carrying out multisurface quantum dynamics to reproduce the reaction probabilities and integral cross sections.
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