The molecular symmetry adapted non-adiabatic coupling terms and diabatic Hamiltonian matrix

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Abstract.
We calculate the adiabatic Potential Energy Surfaces (PESs) and the Non-Adiabatic Coupling Terms (NACTs) for the excited electronic states (2\textsuperscript{2}E\textsuperscript{′} and 1\textsuperscript{2}A\textsuperscript{′}\textsubscript{1}) of Na\textsubscript{3} cluster at the MRCI level by using \textit{ab initio} quantum chemistry package (MOLPRO), where the NACTs are adapted with Molecular Symmetry (MS) by employing appropriate Irreducible Representations (IREPs). Such terms are incorporated into the Adiabatic to Diabatic Transformation (ADT) equations to obtain the ADT angles to construct the continuous, single-valued, symmetric and smooth 3 x 3 diabatic Hamiltonian matrix.

1. Introduction
Since the non-adiabatic coupling terms (NACTs) have important roles\textsuperscript{1-12} in the description of scattering and radiation - less processes in molecular system, it is a matter of contemporary research how gracefully one can handle the NACTs instead of neglecting them forcibly\textsuperscript{13-20}. As the adiabatic potential energy surfaces (PESs) and the NACTs are physically indicative and the removable components of those NACTs are usually very sharp functions of nuclear coordinates with singularities\textsuperscript{21,22} in the configuration space (CS), one needs to perform a unitary transformation to obtain the diabatic representation, where couplings among the electronic states are smooth functions of nuclear coordinates and thereby, the dynamical calculations on the diabatic PESs would be numerically accurate and stable. Such a transformation from adiabatic to diabatic representation of SEs for a given sub - Hilbert space is guaranteed only when the vector fields created by the NACTs satisfy the so called Curl Conditions,\textsuperscript{17,23} \textit{i.e.} the non - removable components of NACTs are approximately zero.

Baer and Alijah\textsuperscript{24} predicted the existence of quantization of NACTs for a given sub - Hilbert space to construct continuous and single valued diabatic potential matrix. Such quantization was confirmed by Yarkony \textit{et al.}\textsuperscript{25} for removable component of NACTs with singularity in the CS. Sarkar \textit{et al.}\textsuperscript{7-12} has generalized the Born - Oppenheimer (BO) treatment of any three/four coupled electronic states with detailed analysis of Curl Conditions in terms of electronic basis functions/ADT angles, where the explicit form of NACTs, their Curl - Divergence equations,
Curl Condition and diabatic PESs in terms of Adiabatic to Diabatic Transformation (ADT) angles were formulated. This approach provides a practical way to handle the NACTs with singularity at certain point(s)/seam in the CS, and help to construct continuous, single valued, smooth and symmetric diabatic PESs. Finally, since molecular symmetry (MS) imposes certain constraints on the CIs and NACTs with respect to the symmetry adapted nuclear coordinates, it is necessary to incorporate MS in the \textit{ab initio} calculated NACTs to calculate ADT angles to construct diabatic PESs and thereby, one may expect to observe “correct” features of nuclear dynamics and spectral profiles.

The spectroscopy of alkali metal clusters is an intense area of research with convenient one-electron - valence configuration and few vibrational degrees of freedom (DOF) for easy analysis both by experimental measurements and theoretical calculations. L. Wöst et al.\textsuperscript{27–29} and W. E. Ernst et al.\textsuperscript{30–32} have done extensive work to generate the absorption spectra of Na\textsubscript{3}, where those trimers are also important for exhibiting JT interaction in D\textsubscript{3h} symmetry between the excited 2\textsuperscript{2}E\textsuperscript{′} states. In Li\textsubscript{3} system, R. G. Sadygov and D. R. Yarkony showed\textsuperscript{33} unusual CIs of C\textsubscript{2v} symmetry along with that of D\textsubscript{3h} symmetry. H. Koizumi and I. B. Bersuker modified\textsuperscript{34} the existing PJT model Hamiltonian\textsuperscript{35} for excited states (2\textsuperscript{2}E\textsuperscript{′} and 1\textsuperscript{2}A\textsubscript{i}'\textsuperscript{1}) of Na\textsubscript{3} cluster in such a way that the corresponding adiabatic PESs for 2\textsuperscript{2}E\textsuperscript{′} states show four CIs. We had also demonstrated the \textit{ab initio} calculated PESs and NACTs of 2\textsuperscript{2}E\textsuperscript{′} and 1\textsuperscript{2}A\textsubscript{i}'\textsuperscript{1} states of Na\textsubscript{3} cluster at the SA-CASSCF level, where four CIs were reported\textsuperscript{36–38} between the states of 2\textsuperscript{2}E\textsuperscript{′} symmetry.

In this article, we recalculate \textit{ab initio} PESs and NACTs of 2\textsuperscript{2}E\textsuperscript{′} and 1\textsuperscript{2}A\textsubscript{i}'\textsuperscript{1} states of Na\textsubscript{3} cluster at the MRCI level, incorporate sign correction of the NACTs according to the proper IREPs of MS group [D\textsubscript{3h}(M)], solve the ADT equations with those MS adapted NACTs to obtain the ADT angles and construct the diabatic PESs as functions of nuclear coordinates to demonstrate the workability of our beyond BO theory.

2. Theory
2.1. Beyond Born - Oppenheimer theory for three - state sub - Hilbert space
We assume a three - state electronic sub - Hilbert space (i.e., a complete space for the present case) with conical intersections (CIs) among the states anywhere in the nuclear configuration space (CS). The Born - Oppenheimer\textsuperscript{39,40} (BO) expansion of the molecular wavefunction for this subspace of the Hilbert space and the total electron - nuclei Hamiltonian in the adiabatic representation are:

\[
\Psi(s_e, s_n) = \sum_{i=1}^{3} \psi_i(s_n) \xi_i(s_e; s_n),
\]

\[
\hat{H} = \hat{T}_{sn} + \hat{H}_e(s_e, s_n),
\]

\[
\hat{T}_{sn} = -\frac{\hbar^2}{2} \sum_i \left( \frac{\nabla_{s_n,i}^2}{m_i} \right),
\]

\[
\hat{H}_e(s_e, s_n) \xi_i(s_e; s_n) = u_i(s_n) \xi_i(s_e; s_n)
\]  \hspace{1cm} (1)

where the eigenfunctions \([\xi_i(s_e; s_n)]\) of the electronic Hamiltonian, \(\hat{H}_e(s_e, s_n)\), are defined by the sets of nuclear \((s_n)\) and electronic \((s_e)\) coordinates with nuclear coordinate dependent eigenvalues, \(u_i(s_n)\). \(\hat{T}_{sn}\) is the nuclear kinetic energy (KE) operator and the expansion coefficient, \(\psi_i(s_n)\), are actually the nuclear wavefunctions.

When the total electron - nuclear Hamiltonian and the BO expansion of the molecular wavefunction [Eq. (1)] for a sub - Hilbert space are substituted in the time independent SE \([\hat{H}\Psi(s_e, s_n) = E\Psi(s_e, s_n)]\), we can arrive at the following compact form of kinetically coupled nuclear equation:
where the non-adiabatic coupling and adiabatic PES matrices have the following form:

\[
\mathbf{\tau} = \begin{pmatrix}
0 & \bar{\tau}_{12} & \bar{\tau}_{13} \\
-\bar{\tau}_{12} & 0 & \bar{\tau}_{23} \\
-\bar{\tau}_{13} & -\bar{\tau}_{23} & 0
\end{pmatrix}
\quad \text{and} \quad U_{ij} = u_i \delta_{ij},
\]

respectively. The non-adiabatic coupling matrix elements are defined as:

\[
\bar{\tau}_{ij} = \langle \xi_i(s_c; s_n) | \mathbf{\nabla} \xi_j(s_c; s_n) \rangle.
\]

If the three states constitute a sub-Hilbert space, it is possible to transform (\(\psi = \mathbf{A}\psi^d\)) the adiabatic nuclear SE [Eq. (2)] to the diabatic one:

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

under the condition:

\[
\mathbf{\nabla} \mathbf{A} + \mathbf{\tau} \mathbf{A} = 0.
\]

This equation is known as the Adiabatic - Diabatic Transformation (ADT) condition. In order to find a meaningful solution of Eq. (6), we have to ensure that the chosen form of \(\mathbf{A}\) matrix must (a) be orthogonal at any point in CS; (b) have elements that are cyclic functions with respect to a parameter.

As the model form of (3×3) \(\mathbf{A}\) has to be an orthogonal matrix and the ortho-normality conditions demand the fulfillment of six relations, three independent variables, viz., Euler like angles of rotation \([\theta_{12}(s_n), \theta_{23}(s_n) \text{ and } \theta_{13}(s_n)]\), commonly called ADT angles, are the natural requirement to construct the three-state \(\mathbf{A}\) matrix by taking the product of three (3×3) rotation matrices, \(\mathbf{A}_{12}(\theta_{12}), \mathbf{A}_{23}(\theta_{23}), \text{ and } \mathbf{A}_{13}(\theta_{13})\) as shown below:

\[
\mathbf{A}(\theta_{12}, \theta_{23}, \theta_{13}) = \mathbf{A}_{12}(\theta_{12}) \cdot \mathbf{A}_{23}(\theta_{23}) \cdot \mathbf{A}_{13}(\theta_{13}).
\]

The above model form of \(\mathbf{A}\) matrix [Eq. (7)] and the anti-symmetric form of \(\mathbf{\tau}\) matrix [Eq. (3)] are substituted in Eq. (6), where the simple manipulation as performed by Top and Baer and Alijah and Baer leads to the following equations for ADT angles:

\[
\begin{align*}
\mathbf{\nabla} \theta_{12} &= -\bar{\tau}_{12} + \tan \theta_{23}(\bar{\tau}_{13} \cos \theta_{12} - \bar{\tau}_{23} \sin \theta_{12}), \\
\mathbf{\nabla} \theta_{23} &= -\bar{\tau}_{23} \sin \theta_{12} + \bar{\tau}_{23} \cos \theta_{12}, \\
\mathbf{\nabla} \theta_{13} &= -\frac{1}{\cos \theta_{23}}(\bar{\tau}_{13} \cos \theta_{12} - \bar{\tau}_{23} \sin \theta_{12}),
\end{align*}
\]

which in turn brings the explicit form of \(\tau\) matrix elements in terms of ADT angles:

\[
\begin{align*}
\bar{\tau}_{12} &= -\mathbf{\nabla} \theta_{12} - \sin \theta_{23} \mathbf{\nabla} \theta_{13}, \\
\bar{\tau}_{23} &= \sin \theta_{12} \cos \theta_{23} \mathbf{\nabla} \theta_{13} - \cos \theta_{12} \mathbf{\nabla} \theta_{23}, \\
\bar{\tau}_{13} &= -\cos \theta_{12} \cos \theta_{23} \mathbf{\nabla} \theta_{13} - \sin \theta_{12} \mathbf{\nabla} \theta_{23}.
\end{align*}
\]

The components of \textit{ab initio} calculated NACTs are substituted in Eq. (8) and those coupled stiff differential equations are solved by using “Backward Differentiation Formula (BDF)” to
calculate the ADT angles. When we substitute those ADT angles in Eq. (10), the diabatic potential matrix elements are obtained as given below:

\[
W_{11} = u_2 \cos^2 \theta_{23} \sin^2 \theta_{12} + u_3 (\cos \theta_{12} \sin \theta_{13} + \cos \theta_{13} \sin \theta_{12} \sin \theta_{23})^2 + u_1 (\cos \theta_{12} \cos \theta_{13} - \sin \theta_{12} \sin \theta_{13} \sin \theta_{23})^2, \tag{10a}
\]

\[
W_{22} = u_2 \cos^2 \theta_{12} \cos^2 \theta_{23} + u_3 (-\sin \theta_{12} \sin \theta_{13} + \cos \theta_{12} \cos \theta_{13} \sin \theta_{23})^2 + u_1 (-\cos \theta_{13} \sin \theta_{12} - \cos \theta_{12} \sin \theta_{13} \sin \theta_{23})^2, \tag{10b}
\]

\[
W_{33} = u_3 \cos^2 \theta_{13} \cos^2 \theta_{23} + u_1 \cos^2 \theta_{23} \sin^2 \theta_{13} + u_2 \sin^2 \theta_{23}, \tag{10c}
\]

\[
W_{12} = W_{21} = u_2 \cos \theta_{12} \cos^2 \theta_{23} \sin \theta_{12} + u_3 \left((-\sin \theta_{12} \sin \theta_{13} + \cos \theta_{12} \cos \theta_{13} \sin \theta_{23}) \times \left(\cos \theta_{12} \sin \theta_{13} + \cos \theta_{13} \sin \theta_{12} \sin \theta_{23}\right) - u_1 \left(\cos \theta_{13} \sin \theta_{12} + \cos \theta_{12} \sin \theta_{13} \sin \theta_{23}\right) \times \left(\cos \theta_{12} \cos \theta_{13} - \sin \theta_{12} \sin \theta_{13} \sin \theta_{23}\right)\right), \tag{10d}
\]

\[
W_{13} = W_{31} = \cos \theta_{23} \left((-u_1 - u_3) \cos \theta_{12} \cos \theta_{13} \sin \theta_{13} + \sin \theta_{12} (-u_2 + u_3 \cos^2 \theta_{13} + u_1 \sin^2 \theta_{13}) \sin \theta_{23}\right), \tag{10e}
\]

\[
W_{23} = W_{32} = -\cos \theta_{23} \left((-u_1 - u_3) \cos \theta_{13} \sin \theta_{12} \sin \theta_{13} - \cos \theta_{12} (u_2 - u_1 \sin^2 \theta_{13} - u_3 \cos^2 \theta_{13}) \sin \theta_{23}\right). \tag{10f}
\]

One can use Eqs. (9) to formulate the explicit form of Curl equation\(^7\) for each NACT in terms of ADT angles:

\[
\text{Curl } \tau_{12}^{pq} = C_{12} = Z_{12} = -\cos \theta_{23} (\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13}), \tag{11a}
\]

\[
\text{Curl } \tau_{23}^{pq} = C_{23} = Z_{23} = \cos \theta_{12} \cos \theta_{23} (\nabla_q \theta_{12} \nabla_p \theta_{13} - \nabla_p \theta_{12} \nabla_q \theta_{13}) - \sin \theta_{12} \sin \theta_{23} (\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13}) + \sin \theta_{12} (\nabla_q \theta_{12} \nabla_p \theta_{23} - \nabla_p \theta_{12} \nabla_q \theta_{23}), \tag{11b}
\]

\[
\text{Curl } \tau_{13}^{pq} = C_{13} = Z_{13} = \sin \theta_{12} \cos \theta_{23} (\nabla_q \theta_{12} \nabla_p \theta_{13} - \nabla_p \theta_{12} \nabla_q \theta_{13}) + \cos \theta_{12} \sin \theta_{23} (\nabla_q \theta_{23} \nabla_p \theta_{13} - \nabla_p \theta_{23} \nabla_q \theta_{13}) - \cos \theta_{12} (\nabla_q \theta_{12} \nabla_p \theta_{23} - \nabla_p \theta_{12} \nabla_q \theta_{23}), \tag{11c}
\]

where the Curl due to vector product of NACTs and analyticity of ADT matrix are defined as: \(C_{ij} = (\tau_q \tau_p)_{ij} - (\tau_p \tau_q)_{ij}\) and \(Z_{ij} = \frac{\partial}{\partial p} \tau_{ij} - \frac{\partial}{\partial q} \tau_{ij}\), respectively with \(\nabla_p = \frac{\partial}{\partial p}\) and \(\nabla_q = \frac{\partial}{\partial q}\).

The Cartesian coordinates \(p\) and \(q\) denote nuclear DOFs.

### 2.2. Molecular symmetry adaptation to NACTs for \(D_{3h}(M)\) group

The “true” symmetry group for the electron - nuclei Hamiltonian of molecules is called molecular symmetry (MS) group which, in general, contains \(R\) symmetry operations, \(\hat{O}_i\), \(i=1,2,...,R\), 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 \(s_k\) and electronic coordinates \(s_e\), 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 angles (Euler) to describe the orientations of a rigid body in a three dimensional Euclidean space and the nuclear spin, which enables us to express \(\hat{O}\) as a product of three different operations, \(^{42}\) i.e., \(\hat{O} = \hat{O}_a \cdot \hat{O}_b \cdot \hat{O}_c\); where
\( \hat{O}_a \) produces change in vibronic degrees of freedom (DOF), \( \hat{O}_b \) changes the Euler angles and \( \hat{O}_c \) permutes the nuclear spin. At this point, we take the example of sodium trimer that belongs to the point group \( D_{3h} \). If one locates the system-fixed \((x,y,z)\) axes on a \( \text{Na}_3 \) cluster such that the xy plane be the molecular plane (plane of symmetry, \( \sigma_h \)) and the z axis be the threefold symmetry axis \((C_3)\), 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):

\[
\begin{align*}
E &= \ E \cdot R^0 \cdot p_0 \\
(123) &= C_1^1 \cdot R^{\frac{2\pi}{3}} \cdot p_{123} \\
(23) &= C_2 \cdot R^{\pi} \cdot p_{23} \\
E^* &= \sigma_{xy} \cdot R^\pi \cdot p_0 \\
(132)^* &= S_{3}^{-1} \cdot R^{\frac{2\pi}{3}} \cdot p_{132} \\
(23)^* &= \sigma_{xz} \cdot R^\pi \cdot p_{23}
\end{align*}
\]

where \( "R^\phi\)’s are members of the corresponding molecular rotation group and \( "p\)’s denote nuclear permutation. There are two important theorems on MS, which relate the IREPs with different NACTs.

(i) Theorem 1:
The first theorem states that when the IREP of a particular NACT, say \( \tau_{ij}^k \), is known for a specific symmetry adapted nuclear coordinate \( s_l \), the IREP of another one, \( \tau_{ij}^k \) between the same electronic states \( i,j \) for a different symmetry adapted nuclear coordinate, \( s_k \), can be found out by the following relation:

\[
\Gamma(\tau_{ij}^k) = \Gamma \left( \frac{\partial}{\partial s_k} \right) \times \Gamma \left( \frac{\partial}{\partial s_l} \right) \times \Gamma (\tau_{ij}^l),
\]

(13)

where

\[
\tau_{ij}^k = \langle \xi_i(s_e; s_n) | \frac{\partial}{\partial s_k} (\xi_j(s_e; s_n)) \rangle.
\]

(14)

The possible combination of the IREPs of the NACTs can be determined by fixing each of them \( \{\tau_k, (k=\rho, \phi, x \text{ and } y)\} \) in succession to the totally symmetric representation \( (A'_1) \). If we choose \( \tau_{\rho} = A'_1 \), the IREPs of other three NACTs appear as \( \tau_{\phi} = A''_1, \tau_x = \tau_y = E'' \) from Eq. (13). Though there would be four such combination of the IREPs of the NACTs, only two possibilities survive as theorem 1 is valid only for those \( \Gamma \left( \frac{\partial}{\partial s_l} \right) \) that belong to 1-d IREP (i.e., for \( l=\rho, \phi \)).

In other words, when we try to 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).

Since we need to select the correct combination from the above two possible ones, we utilize the following quantization rule\(^\text{17} \) [Eq. (15)] of the contour integrals over the NACTs evaluated along a closed loop \( L_g \) of nuclear coordinate \( s_n \) around a single conical intersection (CI):

\[
\oint ds_n \cdot \tau(s_n|L_g) = \pm \pi.
\]

(15)

It appears that the second combination is compatible with the quantization rule producing non-zero residue.
Table 1 Extended character table of molecular symmetry group $D_{3h}(M)$ with different NAC elements

| $D_{3h}(M)$   | $E$ (123) | (12) (13) (23) | $E^*$ (123)$^*$ | (12)$^*$ (13)$^*$ (23)$^*$ | coord. deriv. | $\tau_k^{23}$ $\tau_k^1$ $\tau_k^2$ |
|---------------|-----------|----------------|-----------------|-----------------|----------------|-----------------|
| $A_1'$        | 1         | 1              | 1              | 1              | 1              | $\tau_\phi$    |
| $A_2'$        | 1         | 1              | -1             | 1              | -1             | $\phi$         |
| $E'$          | 2         | -1             | 0              | 2              | -1             | $x,y$          |
| $A_1''$       | 1         | 1              | 1              | -1             | -1             | $\tau_\rho$    |
| $A_2''$       | 1         | 1              | -1             | -1             | 1              | $\rho$         |
| $E''$         | 2         | -1             | 0              | -2             | 1              | 0              |

(ii) Theorem 2:
To state the second theorem [see Eq. (18)], we need to consider a loop-type sequence of $N$ molecular states with same spin multiplicity, say $N$ doublet states, $D_a, D_b, D_c, \ldots, D_y, D_z = a$, for the $Na_3$ cluster. The corresponding NACTs are $\tau_{k,a,b}^k, \tau_{k,b,c}^k, \ldots, \tau_{k,y,z}^k = a^k$, and their product is:

$$\tau_{k,a,b,c,\ldots,y,z}^k = \tau_{k,a}^k \tau_{k,b}^k \tau_{k,c}^k \ldots \tau_{k,y}^k \tau_{k,z}^k.$$  

(16)

In terms of the IREPs, one can write:

$$\Gamma(\tau_{k,a,b,c,\ldots,y,z}^k) = \Gamma(\tau_{k,a}^k) \times \Gamma(\tau_{k,b}^k) \times \ldots \times \Gamma(\tau_{k,y}^k).$$

(17)

(a) For 1-d IREPs:

$$\Gamma(\tau_{k,a,b,c,\ldots,y,z}^k) = \begin{cases} 
\Gamma \left( \frac{\partial}{\partial s_k} \right) A_1' \quad \text{when } N \text{ is odd} \\
\Gamma \left( \frac{\partial}{\partial s_k} \right) A_2' \quad \text{when } N \text{ is even} 
\end{cases}$$

(18)

If there is a CI between two electronic states $i$ and $(i + 1)$, the corresponding electronic eigenfunctions $\xi_i(s_e; s_n)$ and $\xi_{i+1}(s_e; s_n)$ will change their signs along the nuclear coordinate $s_n$ at the time of crossing the CI. Therefore, while implementing the second theorem [Eq. (18)] on the NACTs, we need to interchange the signs of the NACTs $\tau_{k,i,j}^k$ and $\tau_{k,i+1,j}^k$, $i < j$, at the point of CI with the same IREP i.e.

$$\Gamma(\tau_{k,i,j}^k) = \Gamma(\tau_{k,i+1,j}^k).$$

(19)

(b) For 2-d IREPs:

Since Eq. (18) is only valid to find out the 1-d IREPs, we need to establish similar working equations for 2-d IREP cases as given below:

$$\Gamma(\tau_{x,y}^{23}) = \Gamma(\xi_2(s_e; s_n)) \frac{\partial}{\partial x} (\xi_3(s_e; s_n)))$$

$$= \Gamma(\xi_2(s_e; s_n)) \times \Gamma \left( \frac{\partial}{\partial x} \right) \times \Gamma(\xi_3(s_e; s_n))$$

(20)
As \( \Gamma \left( \frac{\partial}{\partial x} \right) = E' \) and \( \Gamma(\tau_{23}^{23}) = E' \) [see Table (1)], it appears from Eq. (20):
\[
\Gamma(\xi_2(s_c; s_n)) \times \Gamma(\xi_1(s_c; s_n)) = A_1',
\]
(21a)

Similarly, for \( \Gamma(\tau_{13}^{13}) = E' \), we have:
\[
\Gamma(\xi_1(s_c; s_n)) \times \Gamma(\xi_3(s_c; s_n)) = A_1'.
\]
(21b)

Thus,
\[
\Gamma(\xi_1(s_c; s_n))^2 \times \Gamma(\xi_2(s_c; s_n))^2 \times \Gamma(\xi_3(s_c; s_n))^2 = A_1'.
\]
(21c)

When we use Eq. (16) for the present case and substitute Eq. (21c), we obtain:
\[
\Gamma(\tau_{12}^{12,3,1}) = \Gamma(\xi_1(s_c; s_n))^2 \times \Gamma(\xi_2(s_c; s_n))^2 \times \Gamma(\xi_3(s_c; s_n))^2 \times \Gamma \left( \frac{\partial}{\partial x} \right)^3 = (E')^3
\]
\[
= \Gamma(\tau_{12}^{12}) \times \Gamma(\tau_{23}^{23})^2
\]
\[
= \Gamma(\tau_{12}^{12}) \times (E')^2
\]
(22)

Therefore, one gets \( \Gamma(\tau_{12}^{12}) = E' \) and similarly, \( \Gamma(\tau_{12}^{12}) = E' \).

3. Ab initio calculation for NACTs and its MS Adaptation

![Fig. 1](image-url) The functional forms of the components of Non-Adiabatic Coupling (NAC) matrix elements as functions of \( Q_x \) and \( Q_y \).
The vibrational modes involved in this calculation are: Symmetric stretching (Q₁), bending (Q₂) and antisymmetric stretching (Q₃). The "breathing mode" Q₄ preserves the D₃h symmetry, whereas Q₅ and Q₆ distort the D₃h equilateral triangle. We have calculated the excited state PESs (2²E' and 1²A₁') and NACTs by the MRCI level of theory with MOLPRO ab initio program. The triple zeta or TZV basis functions augmented with a single set of d functions (ζ₄ = 0.1) are used to describe the electron correlation effects in a better way and two diffuse s functions (ζ₅₈ = 0.008736, ζ₅₈ = 0.00345) are employed to improve the excited state description. Calculations at SA-CASSCF level were already presented as functions of the normal modes Qₖ and Qₙ for three fixed Qₖ, namely 3.4, 3.7 and 4.0 Å, respectively. Since the 4th, 5th (2²E') and 6th (1²A₁') excited states of Na₂₃ cluster are the ones to be explored, the first 20 electronic states (generating 572 CSFs) are being involved at CASSCF reference to attain the closest possible variational minimum with respect to the exact energies and to ensure the formation of three state sub-Hilbert space within the range of CS of our investigation. Then, more accurate MRCI calculations are performed by incorporating the first six (6) states of the system obtained from the SA-CASSCF calculation and the finite numerical difference method (DDR) is applied to calculate NACTs among 2²E' and 1²A₁' states. The functional forms of the component of NACTs in normal mode coordinates (Qₖ) and (Qₙ) are shown in Fig. 1. All these calculations are carried out over the range ρ = 0.0 to 0.9 Å and φ = 0 to 2π for a fixed Qₖ = 3.7 Å. Fig. 1 displays there are four (4) CIs between the 2²E' states of Na₂₃ cluster as reported earlier, where one of them is located at (Q₂, Q₅) = (0, 0) [ρ, φ] = (0.0)] and the other three at ρ ≈ 0.03 Å, φ = π/3, π and 5π/3 with ρ = (Q₂² + Q₅²)½ and φ = tan⁻¹(Q₅/Q₂).

The ab initio calculation can only provide the magnitudes of the NACTs, but their correct sign (“+” or “−”) at each point of the CS are determined by employing molecular symmetry. We have incorporated MS adaptation scheme to NACTs through the following two steps: (i) The sign of each of the NACTs are fixed according to the nodal pattern of the corresponding IREP's as shown in panels (b, c) of Fig. 2, whereas the panels (a, d) depict the numerical magnitude of τᵢⱼ and τᵢₖ as obtained from MOLPRO package; (ii) The signs of τ₁₃ and τ₁₃ [k=ρ,φ] are interchanged at the point of CI to include crossing which is presented in panels (c, f) of Fig. 2.

Fig. 2 Panels (a, d) show τᵢⱼ vs. φ for a fixed ρ=0.03Å before MS adaptation. The IREP adapted τᵢⱼ is displayed in panels (b, e), whereas panels (c, f) represent the same with appropriate crossing due to CIs.
4. ADT angles ($\theta_{ij}$) and their residues ($\bar{\theta}^k_{ij}$)

The MS adapted NACTs are plugged into Eqs. (8) on a 2D grid of geometries in polar coordinates ($\rho, \phi$) ranging from $\rho = 0$ to 0.9 Å and $\phi = 0$ to $2\pi$ to obtain the ADT angles. The Backward Differentiation Formula is used to solve such stiff differential equations with appropriate relative and absolute error tolerances to attain the required level of convergence. Fig. 3 describes the rectangular contour path - the differential equations for the $\rho$ grid are integrated with positive increment from $\rho = 0$ to $\rho_{\text{max}}$ for each positive step integration of the differential equations for the $\phi$ grid from 0 to $2\pi$. It may be noted one can integrate two sets of coupled ($\rho$ and $\phi$) differential equations [Eqs. (8)] with different chosen paths, where each path will produce a set of ADT angles and such angles obtained from any choice of path are expected to show gauge invariance.

In panels (a - c) of Fig. 4, we display the three ADT angles [$\theta_{ij}(\rho, \phi)$] as functions of $\rho$ and $\phi$, where in panels (d - f), the residues of the ADT angles [$\bar{\theta}^k_{ij} = \int_{\phi}^{2\pi} \theta_{ij}(\rho_k, \phi) \cdot d\phi$] and their cumulative residues [$\bar{\theta}_{ij,l} = \sum_{k=1}^{l} |\theta_{ij}^{k+1} - \theta_{ij}^{k}|$] are shown as function of $\rho$.

The numerical magnitude of $\bar{\theta}^k_{ij}$ essentially determines the number of CIs between a pair of states and depicts the gauge invariance for the chosen path of integration. When a system has multiple CIs, the contribution for each CI on residue ($\bar{\theta}^k_{ij}$) could be positive or negative and thereby, the cumulative residue ($\bar{\theta}_{ij,l}$) could be a better way of showing the total change of residue. The panel (d) of Fig. 4 reveals that the cumulative residue ($\bar{\theta}_{ij,l}$) for the ADT angle $\theta_{12}$ become close to $4\pi$ at asymptotic $\rho$ showing four CIs between the $2^2E'$ states. On the other hand, the residue in the panel (e or f) of the Fig. 4 approaches to $\pi/2$ implying the gauge invariance of the path of contour integral.
We use the functional form of ADT angles (Fig. 4) to calculate the Curl condition by involving Eq. (11) to demonstrate the existence of sub - Hilbert space constituted by $2^2E'$ and $1^2A'_1$ states of Na$_3$ cluster. Fig. 5 displays the root mean square deviation (RMSD) between the mathematical ($Z_{ij}$) and ADT ($C_{ij}$) Curls for $\tau_{13}$, $\tau_{23}$ elements. Since the calculated RMSD values for Curl $\tau_{12}$ appears as absolutely zero, the other two RMSDs for Curl $\tau_{13}$ and Curl $\tau_{23}$ are presented (Fig. 5), where their negligibly small magnitude endorses the validity of three-state sub - Hilbert space.

5. ADT and diabatic potential matrix
When we incorporate those ADT angles in Eq. (7), diagonal element(s) of the ADT matrix, $A_{11}/A_{22}$ shows six sign changes in Fig. 6(a) and $A_{33}$ displays no sign change in Fig. 6(b) as function of $\phi$ at asymptotic $\rho$.

Though six sign changes in $A_{11}/A_{22}$ elements of A matrix could be due to six CIs between the $E'$ states, the residue / cumulative residue of the ADT angle $\theta_{12}$ indicates four CIs in the CS [see Fig. 4(d)]. One possibility could be due to the collapse of three central CIs on a single point at $\rho = 0$, but Longuet - Higgins’ sign change technique can not be implemented here to locate the number of CIs at the central point ($\rho = 0, \phi = 0$).

Fig. 7 depicts the functional form of the diabatic matrix elements calculated by substituting the $\theta_{ij}$s in Eqs. (10), where those ADT angles are obtained by integrating Eqs. (8) for the rectangular contour path of integration. The diabatic surfaces appear continuous, single valued, smooth and symmetric.

6. Summary
If few electronic states of a molecular system constitute a sub - Hilbert space over a range of CS, one can construct the diabatic Hamiltonian within the same range. We have calculated adiabatic PESs and NACTs for the states $2^2E'$ and $1^2A'_1$ of Na$_3$ system at MRCI level using quantum chemistry package MOLPRO, adapted MS on those NACTs, and solved the differential equations for the ADT angles ($\theta_{ij}$s) by invoking stiff equation solver technique [Backward Differentiation Formula (BDF)] over a 2D grid on normal modes, $Q_x$ and $Q_y$ ($\equiv \rho, \phi$) for a fixed $Q_z$. With
Fig. 7 The diabatic PES matrix elements (eV) as functions of the normal modes.

those ADT angles and the adiabatic PESs, we have constructed the diabatic potential energy matrix by employing the analytic expressions of its elements in terms of ADT angles [see Eq. (10)]. Calculated diabatic surfaces are not only symmetric and smooth functions but also show required number of crossings between its first two diagonal elements.

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