Chapter 1

Introduction

The Born-Oppenheimer (BO) treatment\textsuperscript{1,2} introduces the distinction between the fast and slow moving electrons and nuclei with two important outcomes \textit{viz.} the adiabatic Potential Energy Surfaces (PESs) and the Non-Adiabatic Coupling terms (NACTs). When a molecular process is assumed to occur “exclusively” on the ground adiabatic surface, the relevant Schrödinger equation (SE) is expected to provide enough accurate solutions for the observable – such as reactive/non-reactive cross-sections or spectroscopic quantities. On the contrary, the excited electronic states quite often affect the ground state dynamics very strongly due to the so called “non-adiabatic coupling” and the BO approximate equation fails to calculate correct transition probabilities. Calculations on charge transfer\textsuperscript{3–7} reactions and scattering cross sections\textsuperscript{8–13} on single-surface, two-surface and three-surface show serious discrepancies between single and multiple surface results. In this connection, it is important to note that it is more than 85 years since von Neumann and Wigner\textsuperscript{14} first discussed the existence of conical intersections (CIs) between PESs in polyatomic molecules. This was based upon a detailed analysis of the spectral representation of a symmetric (Hermitian) matrix and yielded the Neumann-Wigner theorem, which states
that in general two real parameters (three in the Hermitian case) need to be independently varied in order to achieve an eigenvalue degeneracy. Eight years later, Jahn and Teller proved in their seminal paper\textsuperscript{15} that a polyatomic molecule in an orbitally degenerate electronic state is unstable with respect to linear displacement along some non-totally symmetric coordinates. They proved, by exhaustively looking at all possible molecular point groups, that these non-totally symmetric vibrations always exist; therefore there will always be modes of vibration which lift the degeneracy and lower the symmetry.

The Jahn-Teller (JT) geometry is a CI between the two components of the degenerate electronic state. Any geometry of a molecule at which the electronic state is degenerate lies on a CI seam between the PESs of the components of the degenerate electronic state. CIs can also occur between electronic PESs in Abelian point groups and when there is no symmetry. These so-called accidental intersections are not required by symmetry, as in the JT case, but occur rather due to the nature of the two electronic states involved. On the other hand, in a Renner-Teller\textsuperscript{16} (RT) active molecule the degeneracy of electronic states is lifted to second order in nuclear displacements, where the two surfaces depict “glancing intersections” as suggested by Herzberg.\textsuperscript{17} The most important extension of the original JT theorem is the Psuedo Jahn-Teller effect (PJT), which includes excited states in the vibronic coupling interactions. The first suggestion\textsuperscript{18} of what has been called the PJT was given in 1957, showing that when two or more electronic states are not exactly degenerate but are very close in energy (pseudodegenerate), the JT effect is not removed but modified, producing structural distortions and further splitting of the term. In the presence of electronic degeneracy, the PJT effect is still very important as an additional (to the JT and RT) source of instability (for linear systems there is no RT instability without the PJT). Subsequently, Bersuker proposed a theorem\textsuperscript{19} of structural instability as: together,
the JT and PJT effects are the only source of structural instability of polyatomic systems in the high-symmetry configurations. Nevertheless, CIs have been shown to be of considerable importance in photochemical processes in recent years, where the points of intersection represent funnels for radiationless decay in polyatomic molecules. Since CIs are ubiquitous in polyatomic molecules, they become the crucial mechanistic elements of the rapidly growing area of non-adiabatic chemistry. Indeed, this effect of non-adiabaticity in various problems of chemical physics has been explored by employing different schemes. As for example, Tully et al. proposed a simplified approach to treat non-adiabatic transitions, in which a multidimensional classical trajectory is allowed to hop at an avoided crossing seam between adiabatic PESs with a transition probability. Martinez et al. developed ab initio multiple spawning (AIMS) method to solve the electronic and nuclear SE simultaneously. This approach allows multi-electronic state dynamics taking account of the inter-electronic state coupling so that non-adiabatic effects can be incorporated. A general treatment of CI was given by Yarkony with an extensive study on the diabatization procedure, namely, Coupled diabatic surface fitting (CDSF) method which simultaneously fits and diabatizes ab initio electronic structure data, producing a coupled quasi-diabatic state representation. Takatsuka et al. proposed phase space averaging and natural branching method to study non-adiabatic chemical dynamics under intense laser field.

CI offers more subtle and important impact on single and multi-surface dynamics through the geometric phase effect, first discovered by Longuet-Higgins (LH). The geometric phase effect is known to be broadly applicable as a result of Berry’s highly influential work in 1984. This signature property of a CI requires that the BO adiabatic electronic
wavefunction acquires a phase and changes sign when transported along a closed loop in the configuration space (CS) - a pseudo-rotation path surrounding (only) that point of degeneracy.\textsuperscript{38-41} Varandas, Tennyson and Murrel applied this LH theorem on a realistic system \textit{LiNaK} to demonstrate\textsuperscript{42} that the dominant coefficient, $c_i$, of the electronic eigenfunction actually undergoes a sign-change along a close loop encircling a CI. Though Herzberg and Longuet-Higgins (HLH)\textsuperscript{43} predicted the multi-valuedness of the electronic eigenfunction for the JT CI model and corrected it in an \textit{ad hoc} manner, it had an important consequence, namely, such a model Hamiltonian under transformation produces NACTs between the two adiabatic PESs. On the contrary, the Adiabatic to Diabatic Transformation (ADT) technique to eliminate the NAC terms from BO close-coupling equations was first discussed by Hobey and McLachlan\textsuperscript{44} for a single degree of freedom only and attempted by Smith for a diatomic molecule.\textsuperscript{45} M. Baer derived a general formulation\textsuperscript{46} on the diabatization of two adiabatic PESs for atom-molecule collisions along with ADT condition, where the ADT matrix elements were shown to be obtained by solving the differential equations for ADT angles along a two-dimensional contour, and the existence and uniqueness of the solution of those equations was predicted to be guaranteed by the validity of “Curl Condition”.\textsuperscript{47,48} Mead and Truhlar introduced a vector potential\textsuperscript{49} in the nuclear SE to treat CI between two adiabatic PESs. Moreover, an elaborate discussion\textsuperscript{50,51} was made about the characteristics of the removable and non-removable components of the NACTs, where the ADT can at best remove the longitudinal component of the derivative coupling.\textsuperscript{46,47} At the close proximity of a degeneracy, only the removable coupling is singular and the non-removable coupling is insignificant.\textsuperscript{52} The ADT angle(s) can be calculated by integrating the derivative coupling at and around the CI point(s),\textsuperscript{47} where the closed line integrals of the derivative coupling will be multiples
On the other hand, when the non-removable couplings are not negligible, the residue of such closed line integrals does not appear as multiples of $\pi$. Though the removable and non-removable couplings can be separated by solving Poisson’s equation for the ADT angle, the solution of Poisson’s equation is computationally expensive due to many possible definitions for the boundary conditions on such angles. Indeed, one can reduce the magnitude of non removable coupling by including more number of electronic states, which again increases the computational cost enormously. In any case, the requirements for diabatization through ADT around CI point(s) are the following: (a) The singularity in the derivative coupling must be transformed away; (b) The residual couplings must be negligible.

Since the NACTs are usually very sharp functions of nuclear coordinates with singularities, one needs to perform an unitary transformation to obtain the diabatic representation of SE, where potential couplings among the electronic states are slowly varying functions of nuclear coordinates and thereby, the dynamical calculations could be numerically accurate and stable. Such a transformation for a given sub- Hilbert space (i. e. an isolated group of states form a complete space) is guaranteed only when the vector fields created by the NACTs satisfy the so called Curl Conditions at every point in the region of interest in order to eliminate the NACTs. It may be noted that this condition is not fulfilled at degenerate points (or CI points) and nevertheless, the NACTs can be eliminated if the line integrals are quantized forming a sub space. Sarkar et al. generalized the BO treatment for any three/four coupled electronic states 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 ADT angles were formulated.
This approach provides a practical way to handle the NACTs with singularity at certain point(s)/seam in CS, and help to construct continuous, single-valued diabatic PESs.\textsuperscript{68–71} Moreover, it has been proved\textsuperscript{72} that there is no unique diabatic representation of the PES matrix due to the path dependent solution of the ADT condition, where all such diabatic matrices will be related through orthogonal transformation and provide same observable, namely, cross-sections/rate constants on dynamical calculations and help to construct continuous and single-valued diabatic PESs. Finally, since molecular symmetry (MS) imposes certain constrains 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 obtain ADT angles to construct\textsuperscript{72–74} smooth and symmetric diabatic PESs and thereby, one may expect to observe “correct” features of nuclear dynamics and spectral profiles.

1.1 Adiabatic representation

In the adiabatic representation, time independent molecular SE describing the motion of nuclei and electrons is usually written as:

\[
\hat{H}(s_e, s_n)|\Psi(s_e, s_n)\rangle = E|\Psi(s_e, s_n)\rangle, \tag{1.1}
\]

where \(\hat{H}(s_e, s_n)\) and \(|\Psi(s_e, s_n)\rangle\) are the total molecular Hamiltonian and wavefunction, respectively. Such Hamiltonian can be expressed as a sum of the nuclear kinetic energy (\(\hat{T}_n(s_n)\)), depends on the nuclear coordinate \((s_n)\) and the electronic Hamiltonian \((\hat{H}_e(s_e|s_n))\), which contains the nuclear Coulomb interactions and depends parametrically
1.1 Adiabatic representation

on the nuclei coordinates.

\[ \hat{H}(s_e, s_n) = \hat{T}_n(s_n) + \hat{H}_e(s_e|s_n). \quad (1.2) \]

The nuclear kinetic energy is given by:

\[ \hat{T}_n(s_n) = -\frac{\hbar^2}{2m} \sum_n \nabla^2_{s_n,n}. \quad (1.3) \]

The electronic Hamiltonian satisfies the time-independent electronic SE:

\[ \hat{H}_e(s_e|s_n)\xi_i(s_e|s_n) = u_i(s_n)\xi_i(s_e|s_n), \quad (1.4) \]

where \( \xi_i(s_e|s_n) \)'s are electronic wavefunctions and \( u_i(s_n) \) are the adiabatic potential energies both of which depend parametrically on the nuclear coordinates. Since the electronic eigenfunctions form complete set, the total molecular wave function \(|\Psi(s_e, s_n)\rangle\) can be expanded in terms of this basis set \(|\xi_i(s_e|s_n)\rangle\)'s, which is known as the Born-Oppenheimer Expansion:

\[ |\Psi(s_e, s_n)\rangle = \sum_i \psi_i(s_n)\xi_i(s_e|s_n), \quad (1.5) \]

where the nuclear coordinate dependent expansion coefficients, \( \psi_i(s_n) \)'s subsequently termed as nuclear wavefunction, and the sets of nuclear and electronic coordinates are defined as \( s_n \) and \( s_e \), respectively. Substituting Eq.(1.5) and Eq.(1.2) in the time-independent SE as:

\[ (\hat{T}_n + \hat{H}_e) \sum_i \psi_i|\xi_i\rangle = E \sum_i \psi_i|\xi_i\rangle. \quad (1.6) \]
Performing the corresponding differentiation with respect to the nuclear coordinates and integrating with respect to the electronic coordinates, the explicit form of the BO system of coupled equations are:

\[-\frac{\hbar^2}{2m} \nabla^2 \psi_k + (u_k - E) \psi_k - \frac{\hbar^2}{2m} \sum_{j=1}^{N} (2\tilde{\tau}^{(1)}_{kj} \cdot \nabla + \tau^{(2)}_{kj}) \psi_k = 0. \quad k = 1, \ldots, N \tag{1.7}\]

The terms, \(\tilde{\tau}^{(1)}_{ij}\) and \(\tau^{(2)}_{ij}\), are the elements of NACTs of the first \([\tilde{\tau}^{(1)}]\) and second \([\tau^{(2)}]\) kind, respectively and can be expressed as:

\[
\tilde{\tau}^{(1)}_{ij} = \langle \xi_i | (s_e | s_n) \nabla \xi_j (s_e | s_n) \rangle, \tag{1.8a}
\]
\[
\tau^{(2)}_{ij} = \langle \xi_i (s_e | s_n) | \nabla^2 \xi_j (s_e | s_n) \rangle. \tag{1.8b}
\]

For a given Hilbert/sub-Hilbert space, the two kinds of NAC matrices are related as:

\[
\tau^{(2)} = \tilde{\tau}^{(1)} \cdot \nabla \tilde{\tau}^{(1)} + \nabla \tau^{(1)} \tag{1.9}
\]

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

\[-\frac{\hbar^2}{2m} \left( \nabla + \tilde{\tau} \right)^2 \Psi + (U - E) \Psi = 0, \tag{1.10}\]

where \(\Psi(s_n)\) is a column vector that contains the nuclear functions \(\{\psi_k(s_n), k = 1, \ldots, N\}\) for \(N\) electronic state sub-Hilbert space, \(U\) is a diagonal matrix that contains the adiabatic potentials and \(\tau\) is the non-adiabatic coupling matrix. This equation is known as the kinetically coupled nuclear SE in the adiabatic framework for a given Hilbert/sub-Hilbert space. Since the adiabatic PESs and NACTs are physically meaningful and uniquely de-
fined in the CS, it is important to work in the adiabatic representation for any theoretical development in beyond BO treatment. On the contrary, the NACT blows up in magnitude with singularity at the point(s) of degeneracy in the CS. Therefore, the pursuit for a transformation from adiabatic representation to a different one begins, where we could avoid such singularities and will have numerically tractable solutions of the nuclear SE.

### 1.2 The Hellmann-Feynman Theorem and NACTs

Hellmann\(^5^9\) and Feynman\(^6^0\) independently derived a relation, which enables the calculation of forces that directly act on molecules. This theorem can be extended\(^6^1\) to a situation that yields a formula for the NACT.

We consider the electronic SE in Eq. 1.4:

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

Applying \(\vec{\nabla}_n\) on both sides of the equation results:

\[
\vec{\nabla}_n \hat{H}_e (s_e | s_n) |\xi_i (s_e | s_n)\rangle = \vec{\nabla}_n u_i (s_n) |\xi_i (s_e | s_n)\rangle
\]

\[
\Rightarrow \left( \vec{\nabla}_n \hat{H}_e \right) |\xi_i \rangle + \hat{H}_e \left( \vec{\nabla}_n |\xi_i \rangle \right) = \left( \vec{\nabla}_n u_i \right) |\xi_i \rangle + u_i \left( \vec{\nabla}_n |\xi_i \rangle \right).
\]

Next multiplying by \(|\xi_j (s_e | s_n)\rangle\) for \(j \neq i\) on both sides and recalling the definition of \(\tau_{ji}^n\),
1.3 The Curl Condition

We define the following tensorial vector $F_{pq}$ also known as Yang-Mills field:\(^{75}\)

$$F_{pq} = \vec{\nabla}_p \tilde{\tau}_q - \vec{\nabla}_q \tilde{\tau}_p - [\tilde{\tau}_p, \tilde{\tau}_q], \quad (1.12)$$

where, $p$ and $q$ are the two (nuclear) Cartesian coordinates and the third term of the R.H.S is the commutator of the NACTs.

Let us consider the $ij$th component of the first two terms in the R.H.S. of the above equation as:
1.3 The Curl Condition

\begin{align*}
\left( \vec{\nabla}_q \cdot \vec{\tau}_p - \vec{\nabla}_p \cdot \vec{\tau}_q \right)_{ij} &= \vec{\nabla}_q \cdot \tau^{ij}_p - \vec{\nabla}_p \cdot \tau^{ij}_q \\
&= \vec{\nabla}_q \cdot \langle \xi_i | \vec{\nabla}_p | \xi_j \rangle - \vec{\nabla}_p \cdot \langle \xi_i | \vec{\nabla}_q | \xi_j \rangle \\
&= \langle \vec{\nabla}_q \xi_i | \vec{\nabla}_p \xi_j \rangle + \langle \xi_i | \vec{\nabla}_q \cdot \vec{\nabla}_p | \xi_j \rangle \\
&\quad - \langle \vec{\nabla}_p \xi_i | \vec{\nabla}_q \xi_j \rangle - \langle \xi_i | \vec{\nabla}_p \cdot \vec{\nabla}_q | \xi_j \rangle.
\end{align*}

Assuming the eigenfunctions, $|\xi_k\rangle$s are analytic with respect to the nuclear coordinates, i.e. $[\vec{\nabla}_p, \vec{\nabla}_q] |\xi_k\rangle = 0$, the above expression reduces to:

\begin{align*}
\left( \vec{\nabla}_q \cdot \vec{\tau}_p - \vec{\nabla}_p \cdot \vec{\tau}_q \right)_{ij} &= \langle \vec{\nabla}_q \xi_i | \vec{\nabla}_p \xi_j \rangle - \langle \vec{\nabla}_p \xi_i | \vec{\nabla}_q \xi_j \rangle \\
&= \sum_k \left( \langle \vec{\nabla}_q \xi_i | \xi_k \rangle \langle \xi_k | \vec{\nabla}_p \xi_j \rangle - \langle \vec{\nabla}_p \xi_i | \xi_k \rangle \langle \xi_k | \vec{\nabla}_q \xi_j \rangle \right) \\
&= - \sum_k \left( \tau^{(ik)}_q \cdot \tau^{(kj)}_p - \tau^{(ik)}_p \cdot \tau^{(kj)}_q \right) \\
&= (\vec{\tau}_p \cdot \vec{\tau}_q)^{ij} - (\vec{\tau}_q \cdot \vec{\tau}_p)^{ij} \\
&= [\vec{\tau}_p, \vec{\tau}_q]_{ij}.
\end{align*}

Hence, it can be readily noted that for any arbitrary components $p$ and $q$ we have,

$$F_{pq} = \vec{\nabla}_q \cdot \vec{\tau}_p - \vec{\nabla}_p \cdot \vec{\tau}_q - [\vec{\tau}_p, \vec{\tau}_q] = 0.$$  \hfill (1.13)

This equation is known as *Curl equation*\textsuperscript{48}, which establishes the validity of the Hilbert-Space.
The BO expansion in diabatic representation for the molecular wavefunction, $\Psi(s_n, s_e)$ is given by:

$$|\Psi(s_e, s_n)\rangle = \sum_i \tilde{\psi}_i(s_n)|\xi_i(s_e|s_0)\rangle,$$  \hspace{1cm} (1.14)

where $s_0$ is a set of nuclear coordinates for a fixed point in CS. $\tilde{\psi}_i(s_n) \equiv \tilde{\psi}_i(s_n|s_0)$, depends parametrically on $s_0$ and $|\xi_i(s_e|s_0)\rangle$s are the electronic eigenfunctions satisfy the corresponding electronic SE:

$$\hat{H}_e(s_e|s_0)|\xi_i(s_e|s_0)\rangle = u_i(s_0)|\xi_i(s_e|s_0)\rangle,$$  \hspace{1cm} (1.15)

where $U_i(s_0)$ are the corresponding electronic eigenvalues as calculated for this fixed set of nuclear coordinates. Substituting Eqs. 1.14 and 1.15 in the time independent SE $[\hat{H}\Psi(s_e, s_n) = E\Psi(s_e, s_n)]$ and recalling that the coordinates $s_0$ are not variables, yields the following expression:

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

Next, multiplying the above equation by $\langle \xi_j(s_e|s_0)|$ and integrating over the electronic coordinates, we obtain:

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

$$\Rightarrow \sum_i \left[ \delta_{ji}(-\frac{1}{2}\nabla^2_n - E) + V_{ji}(s_n|s_0) \right] \tilde{\psi}_i(s_n) = 0,$$  \hspace{1cm} (1.16)
where $V_{ji}(s|s_0)$ is the $(j, i)$ diabatic matrix element given in the following form:

$$V_{ji}(s_n|s_0) = \langle \xi_j(s_e|s_0)|\hat{H}_e(s_e|s_n)|\xi_i(s_e|s_0)\rangle. \quad (1.17)$$

Again, $\hat{H}_e(s_e|s_n)$ operator is given as the sum of the electronic kinetic energy operator, $T_e(s_n)$ and the potential energy operator, $U_e(s_n)$:

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

where $U_e(s_n)$ is the Coulomb field, which governs the motion of the electrons. We also include Coulomb interactions due to the fixed nuclei and a similar expression holds for $\hat{H}_e(s_e|s_0)$ as:

$$\hat{H}_e(s_e|s_0) = \hat{T}_n(s_n) + \hat{U}(s_e|s_0).$$

Since the kinetic energy operator of the electrons does not depend on the nuclear coordinates, $\hat{H}_e(s_e|s_0)$ can be written as:

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

Having this relation, the expression of diabatic matrix element in Eq. 1.17 can be presented more elaborately as:

$$V_{ji}(s_n|s_0) = u_i(s_0) + \langle \xi_j(s_e|s_0)|\hat{U}(s_e|s_n)|\xi_i(s_e|s_0)\rangle.$$
Thus, Eq. 1.16 becomes potentially coupled and can be presented in the matrix representation as:

\[
\left( -\frac{\hbar^2}{2m} \nabla_n^2 + V - E \right) \tilde{\psi} = 0.
\] (1.18)

In other words, we transform Eq. 1.10 into Eq. 1.18, where all the couplings are transferred from the kinetic energy part to the potential one. The later one is the SE within the diabatic representation, where the diabatic potential matrix is a full one.

### 1.5 Adiabatic to Diabatic Transformation

The adiabatic representation of SE [Eq. 1.10] and the diabatic representation [Eq. 1.18] are expected to yield the same solution implies that they are related through an orthogonal transformation matrix. In order to derive this transformation matrix, we start with the adiabatic SE, eliminate the NACTs and form the relevant diabatic SE.

We start by replacing the nuclear wave function \( \psi \) in the adiabatic representation to another wave function \( \phi^d \) for the Diabatic representation. They are related in the following way:

\[
\psi(s_n) = A(s_n)\phi^d(s_n)
\] (1.19)

Here \( A \) is a matrix of the coordinates to be determined by the requirement that the \( \tau \) matrix in Eq. 1.10 will not appear in the SE for \( \Phi \). Using the above expression of \( \psi \) in Eq.
1.5 Adiabatic to Diabatic Transformation

1.10 yields:

$$\frac{-\hbar^2}{2m} (\vec{\nabla}_n + \vec{\tau})^2 A \phi^d + (u - E)A \phi^d = 0$$  \hspace{1cm} (1.20)

Next, we evaluate the following expression:

$$\begin{align*}
(\vec{\nabla}_n + \vec{\tau})^2 A \phi^d &= (\vec{\nabla}_n + \vec{\tau}).(\vec{\nabla}_n + \vec{\tau})A \phi^d \\
&= (\vec{\nabla}_n + \vec{\tau}). \left\{ A \vec{\nabla}_n \phi^d + (\vec{\nabla}_n A)\phi^d + \vec{\tau}A \phi^d \right\} \\
&= 2(\vec{\nabla}_n A).\vec{\nabla}_n \phi^d + A \nabla_n^2 \phi^d + (\nabla_n^2 A)\phi^d \\
&+ (\vec{\nabla}_n \cdot \vec{\tau})A \phi^d + 2 \vec{\tau}.(\vec{\nabla}_n A)\phi^d + 2 \vec{\tau} \cdot A \\
&= A \nabla_n^2 \phi^d + 2(\vec{\nabla}_n A + \vec{\tau}A).\vec{\nabla}_n \phi^d \\
&+ \left\{ (\vec{\tau} + \vec{\nabla}_n).(\vec{\nabla}_n A + \vec{\tau}A) \right\} \phi^d.  \hspace{1cm} (1.21)
\end{align*}$$

Now, choosing the matrix $A$ such that it satisfies the following equation,

$$\vec{\nabla}_n A + \vec{\tau}A = 0, \hspace{1cm} (1.22)$$

the kinetic contribution to the Hamiltonian becomes:

$$\begin{align*}
(\vec{\nabla}_n + \vec{\tau})^2 A \phi^d &= A \nabla_n^2 \phi^d \
&= A \nabla_n^2 \phi^d
\end{align*}$$  \hspace{1cm} (1.23)

and we could reduce Eq. 1.20 into

$$\begin{align*}
-\frac{\hbar^2}{2m} A \nabla_n^2 \phi^d + (u - E)A \phi^d &= 0. \hspace{1cm} (1.24)
\end{align*}$$
Multiplying by $A^\dagger$ – the complex conjugate matrix of $A$, we get

$$
-\frac{\hbar^2}{2m} \nabla_n^2 \phi^d + (W - E) \Phi = 0,
$$

(1.25)

where $W$ is given by

$$
W = A^\dagger u A
$$

(1.26)

This equation [Eq. 1.25] is the nuclear diabatic SE and $W$ is the corresponding diabatic potential. Since $A$ is the (orthogonal) transformation matrix that connects the two frameworks, it is termed as the *Adiabatic to Diabatic Transformation matrix* or ADT matrix. To conclude that derivation, we state that treatment of the SE, whether it is done in the adiabatic or the diabatic representation, yields the same solution. In other words, the transformation from the adiabatic framework to the diabatic one (or vice versa) does not affect the solution of SE, but the diabatic Hamiltonian could avoid the singularity due to the NACTs in the adiabatic representation.

## 1.6 Overview of Thesis

The thesis entitled, “Beyond Born-Oppenheimer Theory: Spectroscopic and Scattering Processes” presents a detailed theoretical development of beyond Born-Oppenheimer (BO) treatment for three-state sub-Hilbert space with the inclusion of molecular symmetry (MS) group adaptation to the *ab initio* calculated non-adiabatic coupling terms (NACTs). The theoretical background of the three-state beyond BO formalism by the adiabatic to diabatic transformation (ADT) to obtain diabatic PESs is provided in Chap-
1.6 Overview of Thesis

ter 2. The matrix equation for ADT involves with skew-symmetric matrix, NAC matrix, will generate path dependent solution (ADT angles) due to the choice of contour over the space coordinates. In this chapter, we have also proved that the gauge invariance for various ADT angles leads to different ADT matrices and those matrices are related with each other through orthogonal transformations. Calculations of adiabatic potential energy surfaces (PESs) by using electronic structure theory consider BO approximation, where the nuclear geometries are freezed and thereby, point group symmetry can define the Irreducible Representations (IREPs) of those surfaces. On the contrary, while calculating the NACTs to construct diabatic PESs, one need to consider the non rigidity of the molecule. Since the point group can not assign the IREPs of those NACTs, standard packages do not provide any information on their symmetry except the magnitude. Thus, 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 the nodal patterns (IREPs) of NACTs, which is called MS group of a molecule. In other words, when we transform the kinetically coupled adiabatic Schrödinger Equation (SE) to the diabatic one, it is important to make sure both the kinetic and potential energy terms in the adiabatic representation are consistent with appropriate symmetry, i.e. totally symmetric under the operation of each symmetry element of MS group, otherwise, the diabatic SE will lead to erroneous solution. Thereby, a detail formalism to assign IREPs to the NACTs by adapting the MS group is developed in Chapter 2. In the following chapters, we have applied our beyond BO theory on two types of systems: (a) Spectroscopic system, where the configuration space (CS) is confined around the equilibrium region to generate the photo-electron spectra; (b) Scattering process deals with an entire region of collision of a particle with a diatom to obtain the reaction cross-sections.
1.6 Overview of Thesis

We have extensively studied two alkali trimers, viz., Na$_3$ and K$_3$ clusters and diabatic Hamiltonians are constructed using our MS based beyond BO theory in Chapter 3. We have calculated the adiabatic PESs for the excited electronic states of the two trimers and the NACTs between those states by MRCI level of theory. The NACTs are adapted with molecular symmetry to assign appropriate IREPs so that the elements of the Hamiltonian matrix are totally symmetric. The signs of the NACTs at each point of the CS are determined by employing appropriate IREPs arising due to MS group and such terms are incorporated into the ADT equations to obtain the ADT angles. Since those sign corrected NACTs and the corresponding ADT angles demonstrate the validity of Curl Condition for the existence of three-state ($2^2E'$ and $1^2A'_1$) sub-Hilbert space, it becomes possible to construct the continuous, single-valued, symmetric and smooth $3 \times 3$ diabatic Hamiltonian matrix. Finally, nuclear dynamics has been carried out on such diabatic surfaces to reproduce the pattern of experimental spectrum for system B of Na$_3$ cluster. We have also demonstrated that the dressed diabatic and adiabatic-via-dressed diabatic potential curves of K$_3$ cluster revealed prominent topological effect of non-adiabaticity of the system.

A thorough investigation has been performed for electronic structure, topological effect and nuclear dynamics of NO$_2$ molecule in Chapter 4. The adiabatic PESs of the ground ($X^2A_1$) and the first excited state ($A^2B_2$) are calculated by MRCI methodology and the corresponding NACTs are obtained to confirm the location of the conical intersections (CIs) between those states. We employ beyond Born-Oppenheimer theory for these two state sub-Hilbert space to carry out adiabatic to diabatic transformation (ADT) to obtain the ADT angles and thereby, to construct single-valued, smooth and continuous diabatic PESs. The analytic expressions for the adiabatic PESs and ADT angles are provided to
represent a two-state three-mode diabatic Hamiltonian of NO$_2$ for performing nuclear
dynamics to calculate the photo-electron spectra of its anion. It appears that not only
Jahn-Teller type coupling but also Renner-Teller interaction contribute significantly on
the overall spectrum. The coupling between the electronic states ($X^2A_1$ and $A^2B_2$) of
NO$_2$ is essentially through the asymmetric stretching mode, where the functional form of
such interaction is distinctly symmetric and non-linear.

Chapter 5 deals with the reactive scattering problem of D$^+$ + H$_2$ system in hyperspherical
coordinates. In order to construct an “accurate” diabatic PESs, we have calculated the adi-
abatic PESs and NACTs for the three lowest singlet states of H$_3^+$ using MRCI theory. The
NACTs between the ground and the first excited state translates along the seams on the $\theta$
- $\phi$ space, i.e. there are six CIs at each $\theta$ (60° $\leq$ $\theta$ $\leq$ 90°) within the domain, 0 $\leq$ $\phi$ $\leq$ 2$\pi$.

While transforming the adiabatic PESs to the diabatic ones, such surfaces have shown up
six crossings along those seams. Our beyond Born-Oppenheimer approach could incor-
porate the effect of NACTs accurately and construct single-valued, continuous, smooth
and symmetric diabatic PESs. The adiabatic PESs and ADT angles are fitted and ana-
lytic expression are provided to obtain the (3 $\times$ 3) diabatic Hamiltonian. We have carried
out time-dependent 3D wavepacket dynamics in hyperspherical coordinates for the D$^+$
+ H$_2$ ($v = 0; j = 0$) reaction employing our multi-sheeted diabatic PESs and total reaction
probabilities for the RNCT, RCT and NRCT processes are calculated for zero total angular
momentum, $J = 0$. 
References


