Chapter 6

Summary

The adiabatic potential energy surfaces (PESs) and non-adiabatic coupling terms (NACTs) are physically meaningful and uniquely defined in the configuration space (CS) and it is important to work in the adiabatic representation for any theoretical development on beyond Born-Oppenheimer (BO) treatment and its application on molecular system. As the NACTs could be singular at certain points in the CS, it is necessary to transform the kinetically coupled adiabatic Schrödinger equation (SE) to the potentially coupled diabatic one, where the PESs would be continuous and smooth enough to perform accurate and stable quantum dynamics. Since we start 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 in order to construct symmetric, single-valued, continuous and smooth diabatic PESs. The adiabatic PESs are calculated within BO approximation, where any quantum chemistry package can assign their irreducible representations (IREPs). 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 appro-
appropriate IREPs for NACTs. Thereby, it is theoretically and technically necessary to ensure that both the quantities, adiabatic PESs and NACTs belong to appropriate IREPs in order to obtain continuous, single-valued, smooth and symmetric diabatic PESs. In a series of work, we have developed our beyond BO 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 Chapter 3, we have carried out \textit{ab initio} calculation for adiabatic PESs and NACTs for the excited states of Na$_3$ and K$_3$ cluster at MRCI level using quantum chemistry package MOLPRO, adapted MS on those NACTs. The IREP adapted NACTs are substituted in Adiabatic to diabatic transformation (ADT) equation, the differential equations for the ADT angles ($\theta_{ij}$s) are solved by invoking stiff equation solver technique by Backward Differentiation Formula (BDF) over a 2D grid on normal modes, $Q_x$ and $Q_y$ ($\equiv \rho, \phi$) for a fixed $Q_s$, the validity of curl condition for the existence of three state sub-Hilbert space has been confirmed. The ADT angles and adiabatic PESs are used to construct the diabatic potential energy matrix by employing the analytic expressions of its elements in terms of ADT angles. We numerically demonstrate the collapse of three conical intersections (CIs) at the central point of those normal modes ($Q_x = 0, Q_y = 0$), where the diagonal elements of ADT matrix ($A_{11}/A_{22}$) show the expected number of sign change due to the CI points. The first two diagonal elements of the ADT matrix show six times sign changes within the domain of pseudo rotation (0 to $2\pi$) and confirm the existence of six CIs between the two $2^2E'$ states, where the three CIs collapse at the D$_{3h}$ symmetry point. Interestingly, the number of crossings along the seams between the diagonal elements of the diabatic PESs
also confirm the number of CIs. We have also shown numerically the gauge invariance for the various path dependent solution (ADT angles), which leads to different ADT matrices and those matrices are related with each other through orthogonal transformations. This became possible due to the incorporation of appropriate MS to the \textit{ab initio} calculated NACTs (known as sign correction). Nuclear dynamics has been carried out on the full diabatic Hamiltonian of Na$_3$ system with an aim to reproduce the experimentally measured photoelectron spectrum of system B of Na$_3$ cluster. The present work reproduces the pattern of latest experimental TPI spectrum by W. E. Ernst et al. reasonably well. In case of Potassium trimer, while exploring the topological effect due to the NACTs, we have calculated the \textit{dressed adiabatic}, \textit{dressed diabatic} and \textit{adiabatic-via-dressed diabatic} potential energy curves, and found a prominent role of non-adiabaticity in the system. Though there are multiple theoretical calculations including the present case on the low lying states of the K$_3$ cluster, the experimental measurement is yet to confirm those predictions.

The optical spectrum of NO$_2$ molecule presents a very complex scenario and a thorough understanding of its spectral properties is a challenging problem that requires beyond BO treatment. This molecule is probably one of the best known examples that provides a great opportunity to explore non-adiabatic effects through the conical (Jahn-Teller type) and parabolic (Renner-Teller) intersections between the PESs of the ground and first excited states. In Chapter 4, a two state three-mode Hamiltonian of NO$_2$ is constructed with the intention to decipher the $X^2A_1 \rightarrow A^2B_2$ transitions and reproduce the experimental spectrum. We have carried out \textit{ab initio} calculations for the adiabatic PESs of the ground ($X^2A_1$) and the first excited states ($A^2B_2$) of NO$_2$, and the NACTs between them as functions of pairwise normal mode coordinates using MOLPRO package. The NACTs show
up several singularities of symmetry allowed accidental CI, RT coupling and $C_{2v}$ seam in the CS that depict the complex nature of strongly coupled states. The beyond BO theory for two-state sub-Hilbert space is employed to obtain ADT angles with correct features of JT and RT type of CI. We have used the ADT angles to calculate the diabatic PESs as functions of pairwise normal modes. The diagonal and off-diagonal coupling elements of diabatic PESs appear to be smooth and continuous along all the three modes and symmetric along the $Q_3$ mode. The fitting of adiabatic PESs and ADT angles are carried out to obtain analytic expressions for diabatic PESs considering the coupling only between each pairwise normal modes and finally, an accurate two-state three-mode diabatic Hamiltonian is provided. A detailed study of topological effect for the pairwise normal mode coordinates shows: (a) The RT interactions not only prevail in the $Q_1 - Q_2$ mode but also exhibit a dominant role in the $Q_2 - Q_3$ mode. The different functional forms of the *dressed coupling elements* corresponding to “only JT coupling” and “JT + RT coupling” depict the presence of RT effect in $Q_2 - Q_3$ mode. In other words, this investigation suggests that both the JT-type coupling and the RT interaction contribute significantly on the non-adiabaticity through $Q_2 - Q_3$ mode, whereas the RT interaction is less effective for $Q_1 - Q_3$ mode; (b) The $Q_1 - Q_3$ and $Q_2 - Q_3$ modes couple the two electronic states quite significantly compared to $Q_1 - Q_2$. It appears that the coupling between the electronic states through $Q_3$ mode is stronger, symmetric and non-linear, i.e. a polynomial in $Q_3$ containing only the even power terms. In summary, our calculated curves [*dressed adiabatic, dressed diabatic and adiabatic-via-dressed diabatic*] depict not only the significant contribution of the $Q_3$ mode on the inter-state coupling as predicted in the literature but also shows non-adiabatic effects arising only through the even power terms of the $Q_3$ mode. It is important to note that the model Hamiltonian based on normal modes constructed
so far only considered linear coupling (odd power polynomial of $Q_3$) between the electronic states, whereas in the present case, only the even power polynomial of $Q_3$ appears to be the contributing one. In other words, the selection rule for the transition of nuclear wave function from one electronic state to another arises essentially due to the symmetric functional form of the coupling elements for the asymmetric stretching mode. We have performed the nuclear dynamics on the full diabatic Hamiltonian and reproduced the experimental photo-detachment spectrum. The close resemblance in the peak positions and the intensity patterns of the calculated spectra depicts a reasonably good agreement with the experimental one. When the reduced dimensional nuclear dynamics is carried out, we find that the $Q_1$ 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. Since the calculated spectra obtained from our diabatic Hamiltonian matches quite well with the experimentally measured one, the present work endorses the formulation of beyond BO theory based on adiabatic to diabatic transformation and the construction of sufficiently “accurate” diabatic PESs.

We present *ab initio* calculated first three singlet adiabatic PESs of $H_3^+$ and the NACTs between those states by MOLPRO quantum chemistry package in hyperspherical coordinates. The interesting observation is a semi-circular CI seam between the ground ($1^1A'$) and first excited ($2^1A'$) singlet states as functions of hyperangles for each fixed hyperradius. In other words, 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, which may be the first observation within our understanding. Since, within a good approximation, the three singlet states constitute a sub-Hilbert space over the entire range of CS validating ADT
by the curl conditions, we construct the diabatic Hamiltonian employing our beyond BO theory. The elements of the diabatic PES matrix are appeared to be single valued, continuous, symmetric and smooth functions of nuclear coordinates. The striking feature of those diabatic PESs is the six crossing seams, which exactly corroborates with the number of avoided crossing in the adiabatic PESs. It is found that the non-adiabaticity has a profound effect on this system by calculating the dressed potential energy curves. The analytic expressions for the three adiabatic PESs and the ADT angles are evaluated by fitting procedure to construct the model three-state diabatic Hamiltonian. In Chapter 5, We have investigated \( \text{D}^+ + \text{H}_2 \) reactive scattering dynamics in hyperspherical coordinates for treating evenhandedly all the three competing processes, namely, reactive non-charge transfer (RNCT), non-reactive charge transfer (NRCT) and reactive charge transfer (RCT) processes involved in the reaction using our newly constructed global multi-sheeted diabatic PESs for the lowest three singlet states \((1^1A', 2^1A'\text{ and } 3^1A')\) of \( \text{H}_2^+ \) with zero total angular momentum. Our major focus has been on investigating the non-adiabatic effects which are known to contribute at higher energies beyond \( \sim 1.8 \text{ eV} \). The calculated probabilities for zero total angular momentum are compared with the previous results of Chu and Han’s using the KBNN PES as well as the calculation of Ghosh et al. using DMBE PESs. For \( J = 0 \), the present profile is found to be in good agreement with the Chu and Han’s result, which validates our beyond BO theory for scattering processes.