Master's Project,2024

Conical intersections and non-adiabatic coupling terms in pyridine radical cation ($\mathbf{C_5H_5}N^+$):Three state beyond Born-Oppenheimer treatment

Project Report
Under Supervision of

Professor Satrajit Adhikari

by
Aiyush Saha
Roll NO:2021UG006
Registration No:202101000202006
School of Chemical Sciences
Indian Association For The Cultivation Of Science(IACS)

CERTIFICATE

This is to certify that the work contained in this project report entitled "**Conical intersections and non-adiabatic coupling terms in pyridine radical cation ($C_5H_5N^+$):Three state beyond Born-Oppenheimer treatment** " submitted by **Aiyush Saha** to Indian Association for the Cultivation of Science towards partial requirement for his Master's project for 7th semester has been carried out by him under my supervision and that it has not been submitted elsewhere for the award of any degree.

<div align="right">

Dr.Satrajit Adhikari
Senior Professor
School of Chemical Sciences
IACS,KOLKATA

</div>

ACKNOWLEDGEMENT

Contents

Abstract

Explicit forms of Adiabatic to Diabatic Transformation (ADT) equations have been devised for coupled three-state electronic manifold in terms of ADT angles. The numerical instability originated from singularity of NACTs is removed by using ADT matrices, which transform the adiabatic Schrodinger equation (SE) to its diabatic form. In this project,Pyridine Radical Cation ($C_5H_5N^+$) is selectively choosen for demonstration of ADT equations for three coupled electronic mainfield.We examine the NACTs among the lowest three electronic states of ($C_5H_5N^+$) in which many types of non-adiabatic interactions i.e. Pseudo Jahn-Teller (PJT) interactions and accidental conical intersections (CIs) are prevailing. For C_5H_5N+ cation $Q_3 - Q_7$ and $Q_5 - Q_{16}$ normal mode pairs are taken as nuclear configuration spaces (CSs) to investigate the utility of Beyond BornOppenheimer (BBO) equations for three coupled electronic states.Intense vibronic coupling prevailing within the low-lying three electronic states of this cation, namely in the Franck-Condon region is the key mechanistic element for dictating the photoelectron spectrum. We have calculated ab initio adiabatic potential energy surfaces (PESs) and NACTs among the lowest three electronic states at the Complete Active Space Self-Consistent Field (CASSCF) level using MOLPRO quantum chemistry package. Subsequently, ADT is carried out using those newly developed equations to validate the positions of the CIs, evaluate the ADT angles and construct smooth, symmetric and continuous diabatic PESs for the molecular systems.

Introduction

The Born-Oppenheimer (BO) approximation[1, 2] appears to be an excellent starting point that decouples the mechanics of fast-moving electrons from the slow-moving nuclei on the basis of their mass difference (mass of nuclei » mass of electron).The treatment of this approximation helps to solve the molecular Schrodinger Equation (SE). There are many molecular process like charge transfer spectra likephotochemical reactions, measurements of scattering cross sections and charge transfer reactions; in these situations, the treatement of BO approximation actually fails. So, whenever the excited electronic structures are involved in a given molecular process, the failure of BO approximation comes out.[3, 4]In such cases, the non-adiabatic coupling terms (NACTs) appears as very important phenomenon. Actually, the non-adiabatic coupling terms (NACTs) are neglected from SE in case of BO approximation.

According to Longuet-Higgins (LH) treatment,[5] while travelling along a close path to encircle a point ofconical intersction, multivaluedness of the eigenfunctions come out. To get rid of this multi-valuedness, a phase factor is incorporated and subsequently, a vector potential is introduced into the nuclear Hamiltonian.[6]On the other hand, when the electronic states becomes degenerate or near degenerate, Hellman-Feynman[7] theorem predicts the possibility of singularities in NACTs. This singular characteristics can be eliminated by transforming adiabatic representation to a different representation or basis, known as the diabatic representation. As a result, the singular kinetic coupling terms are converted into the off-diagonal terms in the diabatic potential energy matrix, which are smoothly varying functions of nuclear coordinates.This kind of unitary transformation is known as the Adiabatic -to- Diabatic transformation (ADT). Vector field created by the NACTs can be resolved into longitudinal and transverse components, where the former is presented as the derivative of a scalar and the latter by the curl of a vector.By performing ADT, the longitudinal component (removable part), can be eliminated.[8, 9]but the transverse or the non-removable part may be neglected at the close proximity of a CI.

In the realm of nonadiabatic chemistry, a wide variety of diabatization methods has been proposed by several theoreticians, namely vibronic coupling model (VCM) [10–14]exact factorisation (EF) scheme,[15–17]direct dynamical approaches[18–22] and many others,[23–28]but the first principle based formalism developed by M.

Baer.[8, 9, 29–34]may be considered as one of the accurate ones. While investigating atom-diatom collision reactions, M. Baer formulated a set of coupled differential equations to transform adiabatic PESs and NACTs for a given sub-Hilbert space (SHS) to diabatic Hamiltonian.[8, 9, 29]The accuracy of such Adiabatic to-Diabatic Transformation (ADT) is assured if NACT vector field satisfies the so-called "curl condition" over the interested domain of nuclear CS for a given SHS.[9, 30]If all the electronic states constituting thesub-space are involved in the ADT calculation, the mixing (ADT) angles along a closed contour encircling JT or Renner-Teller (RT) type CI(s)/seam(s) acquire the magnitude of integer (n) multiple of π or 2π[9, 32, 33] respectively.

Adhikari et *al.*[35–42]uccessfully generalized the BBO treatment for any three or more coupled electronic states formulating explicit expressions of NACTs, ADT equations, curl-divergence equations and diabatic potential energy matrix elements. Recently, an efficient generalized algorithm and program, 'ADT'[43]hasbeen developed in order to formulate the analytic expressions of several ADT quantities (ADT equations,dia- batic potential energy matrix, etc.) as well as to obtain numerical solutions of those quantities for Nnumber of coupled electronic states with M nuclear degrees of freedom (DOFs). It is important to mention that the workability of such a complete theory on BBO approach has been already verified for realistic prototypical systems of spectroscopic interest[38–42] to calculate their photoelectron spectra as well as triatomic scattering systems to compute their reactive cross sections.

This research work is mainly based on formulation of BBO equations for three electronic state.detailed study on their workability a realistic molecular system pyridine cation to generate the diabatic surfaces.

Beyond Born-Oppenheimer: Theory and Methodology

According to the Born-Oppenheimer treatment, total molecular wavefunction can be written as a linear combination of the electronic wavefunctions where the nuclear counterpart is represented by the combiningcoefficients as written in the following equation. While considering a sub-Hilbert space of finite dimension, total electron-nuclei wavefunction takes the following form:

$$|\psi(s_e, s_n)\rangle = \sum_{i=1}^{n} \psi_i(s_n)|\xi_i(s_e|s_n)\rangle. \tag{3.1}$$

The following time-independent Schrodinger equation consists of this wavefunction which is the eigenfunction of the Hamiltonian operator and the corresponding eigenvalue represents the total energy of the molecular system:

$$\hat{H}(s_e, s_n)|\psi(s_e, s_n)\rangle = E|\psi(s_e, s_n)\rangle \tag{3.2}$$

The molecular Hamiltonian can be divided into two parts, i.e., (i) nuclear kinetic energy operator ($\hat{T}_n$) and (ii) electronic Hamiltonian ($\hat{H}_e(s_e|s_n)$).

$$\hat{H}(s_e, s_n) = \hat{T}_n(s_n) + \hat{H}_e(s_e|s_n) \tag{3.3}$$

where the nuclear kinetic energy operator is defined as:

$$\hat{T}_n = -\frac{1}{2}\sum_i \frac{\nabla^2_{s_{n,i}}}{m_i} \tag{3.4}$$

On the other hand, The Born-Oppenheimer expansion i.e. electronic wavefunctions ($\xi_i(s_e|s_n)\rangle$ are eigenfunctions of electronic Hamiltonian $\hat{H}_e(s_e|s_n)$ The operator with eigenvalue $u_i(s_n)$, which is nuclear coordinate dependent. The adiabatic potential energy surface is represented by this $u_i(s_n)$. Therefore, the electronic eigenvalue equation is presented as follows:

$$\hat{H}_e(s_e|s_n)|\xi_i(s_e|s_n)\rangle = u_i(s_n)|\xi_i(s_e|s_n)\rangle \tag{3.5}$$

When the Born-Oppenheimer expansion of the molecular wavefunction is substituted in the total Hamiltonian (Eq. 3.2) and it is projected with various electronic wavefunctions, the adiabatic Schrödinger equation, which is kinetically coupled, takes the following matrix form:

$$\left(-\frac{1}{2}(\nabla_n + \boldsymbol{\tau})^2 + U - E\right)\psi = 0 \tag{3.6}$$

where $U_{ij} = u_i \delta_{ij}$ and $\boldsymbol{\tau}$ is the non-adiabatic coupling matrix (NACM) defined as:

$$\boldsymbol{\tau}_{ij} = \langle \xi_i(s_e|s_n)|\nabla \xi_j(s_e|s_n)\rangle \tag{3.7}$$

The adiabatic representation of the Schrödinger equation is impossible to solve as the Non-Adiabatic Coupling Terms (NACTs) reach infinity at the degenerate points. This can be proved with the help of the Hellmann-Feynman theorem. Therefore, we realize the drawback of adiabatic representations, which indicates the fundamental necessity of a different representation where the non-adiabatic interactions appear as continuous, smooth, and single-valued diabatic coupling terms. This transformation can be done by using an orthogonal rotation matrix, which can be represented as A. Therefore, the nuclear wavefunctions look like the following form:

$$\psi = A\varphi_d \tag{3.8}$$

In this orthogonal transformation, ψ and φ_d symbolize the adiabatic and diabatic nuclear wavefunctions, respectively.

While incorporating the above-mentioned form of wavefunction, the diabatic representation of the nuclear Schrödinger equation takes the following form:

$$-\frac{1}{2}\nabla_n^2 \varphi_d + (W - E)\varphi_d = 0 \tag{3.9}$$

where

$$W = A^\dagger U A \tag{3.10}$$

under the condition:

$$\nabla_n A + \boldsymbol{\tau} A = 0 \tag{3.11}$$

which is known as the adiabatic-to-diabatic transformation (ADT) condition.

The ADT condition in Eq.3.11 can be used as the precursor for devising the ADT equations. For an N-electronic states sub-Hilbert space, the model ADT matrix can be constructed by multiplying $\binom{N}{2}$ rotation matrices in a particular way. These matrices can be arranged in $\binom{N}{2}!$ different ways, but we carry out the formulation for a particular order of multiplication. However, any one of the possible arrangements produces the same numerical value of the diabatic potential energy matrices, as they are related by orthogonal transformation.

For any one of the rotation matrices $A_{ij}(\theta_{ij})$, where the ii and jj elements become $\cos\theta_{ij}$ and the ij and ji elements take the form of $\sin\theta_{ij}$ and $-\sin\theta_{ij}$,

respectively. Among the remaining elements, diagonal terms are 1, while the off-diagonal terms acquire the magnitude of 0.

For three state sub-Hilbert space the order of multiplication is taken as

$$\mathbf{A} = \mathbf{A}_{12}(\Theta_{12}) \cdot \mathbf{A}_{13}(\Theta_{13}) \cdot \mathbf{A}_{23}(\Theta_{23}) \tag{3.12}$$

When this model rotation matrix and NACM are incorporated in the Eq.3.11, a set of differential equations (ADT equations) can be derived by solving the matrix form of ADT condition. But due to absence of any analytic solution of these differential equations, they are integrated numerically to obtain the ADT angles which are used to construct the ADT matrix at each and every grid points in the interested domain of the nuclear configuration space. During transformation of the adiabatic potential energy surfaces (PESs) to the diabatic one, a similarity transformation [Eq. (3.10)] is mandatory such that the NACTs take the form of diabatic coupling terms which appear as the off-diagonal elements of the diabatic potential energy matrix. We have extensively derived the ADT equations for three electronic state sub-Hilbert space.

ADT equation for '1-2' coupling of three coupled electronic state is:

$$\nabla_{\vec{\theta}_{12}} = -\vec{\tau}_{13} - \tan\theta_{13}\left(\vec{\tau}_{23}\cos\theta_{12} + \vec{\tau}_{13}\sin\theta_{12}\right) \tag{3.13}$$

Diabatization removes the singularity of the NACTs, and therefore, those surfaces and couplings can be used for carrying out nuclear dynamics to reproduce the photodetachment spectra.

4. Ab initio calculations for PESs and NACTs

We have chosen Q_3-Q_7 and Q_5-Q_{16} normal mode pairs of Pyridine Radical Cation (C_5H_5N+)to perform the ab initio calculations of the lowest three electronic states, namely: $^2A_1$, $^2A_2$, and $^2B_1$We have adopted Complete Active Space Self-Consistent Field (CASSCF) level of calculations provided in the MOLPRO quantum chemistry package to calculate the adiabatic PESs.The ab initio energy values are obtained in C_{2v} symmetry employing Dunning's correlation consistent cc-pVDZ basis set.The state-averaged CASSCF calculations have been done employing a a 5-electrons in 6-orbitals (5e, 6o) configuration active space (CAS).The NACT components along Cartesian coordinates between the five electronic states in the given nuclear configuration space are evaluated by implementing the Coupled-Perturbed Multi-Configuration Space Self-Consistent Field (CP-MCSCF) method. We will discuss the important results that have been obtained from the *ab initio* investigations and the subsequent outcome from the adiabatic-to-diabatic transformation on this particular system.
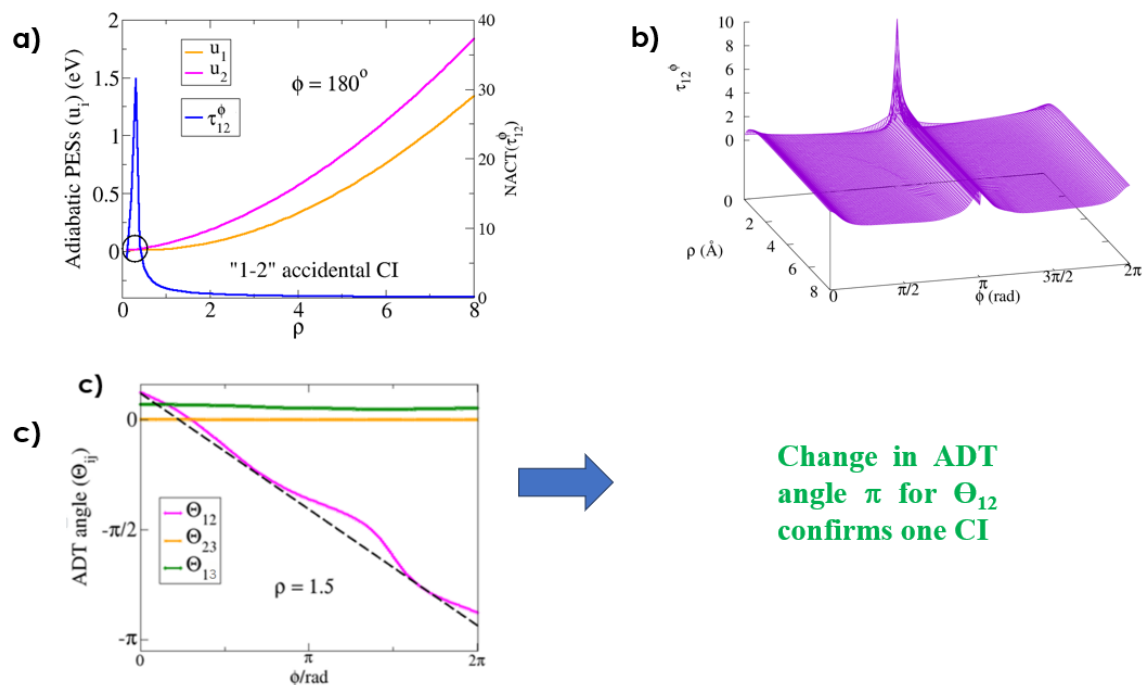
4.1 Results and Discussion:

Figure 4.1: 1D cuts of adiabatic PESs of pyridine cation for $Q_3 - Q_7$ pairwise modes along ϕ at (a) $\phi = 180$ where ρ and ϕ are the polar coordinates. ρ is in dimensionless units. In diagram (b), the location of the "1-2" NACT is depicted over the 2D functional form of τ_{12}^{ϕ}. The first diagram (c) shows 1D functional forms of ADT angles, Θ_{12}, Θ_{23}, and Θ_{13} for the $Q_3 - Q_7$ pair.
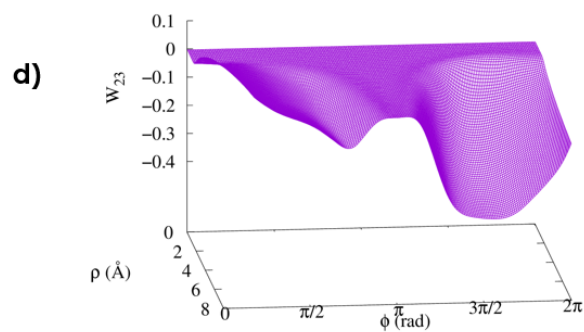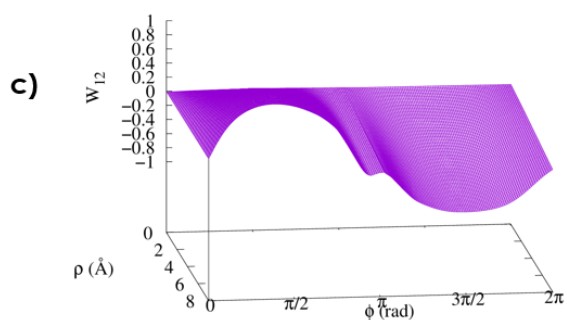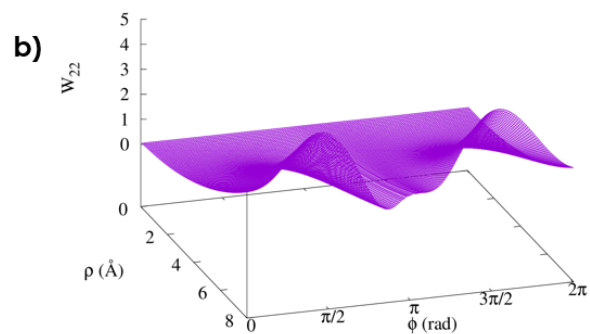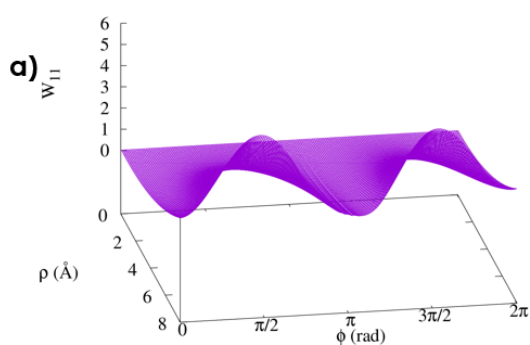
Figure 4.2: The left panel (a-d) represents some representative diabatic PESs and couplings, namely, W_{11}, W_{22}, W_{12} and W_{23} for the Q_3-Q_7 pair.It is important to note that all the diabatic PESs as well as couplings are smooth, continuous and single-valued functions of nuclear coordinates.
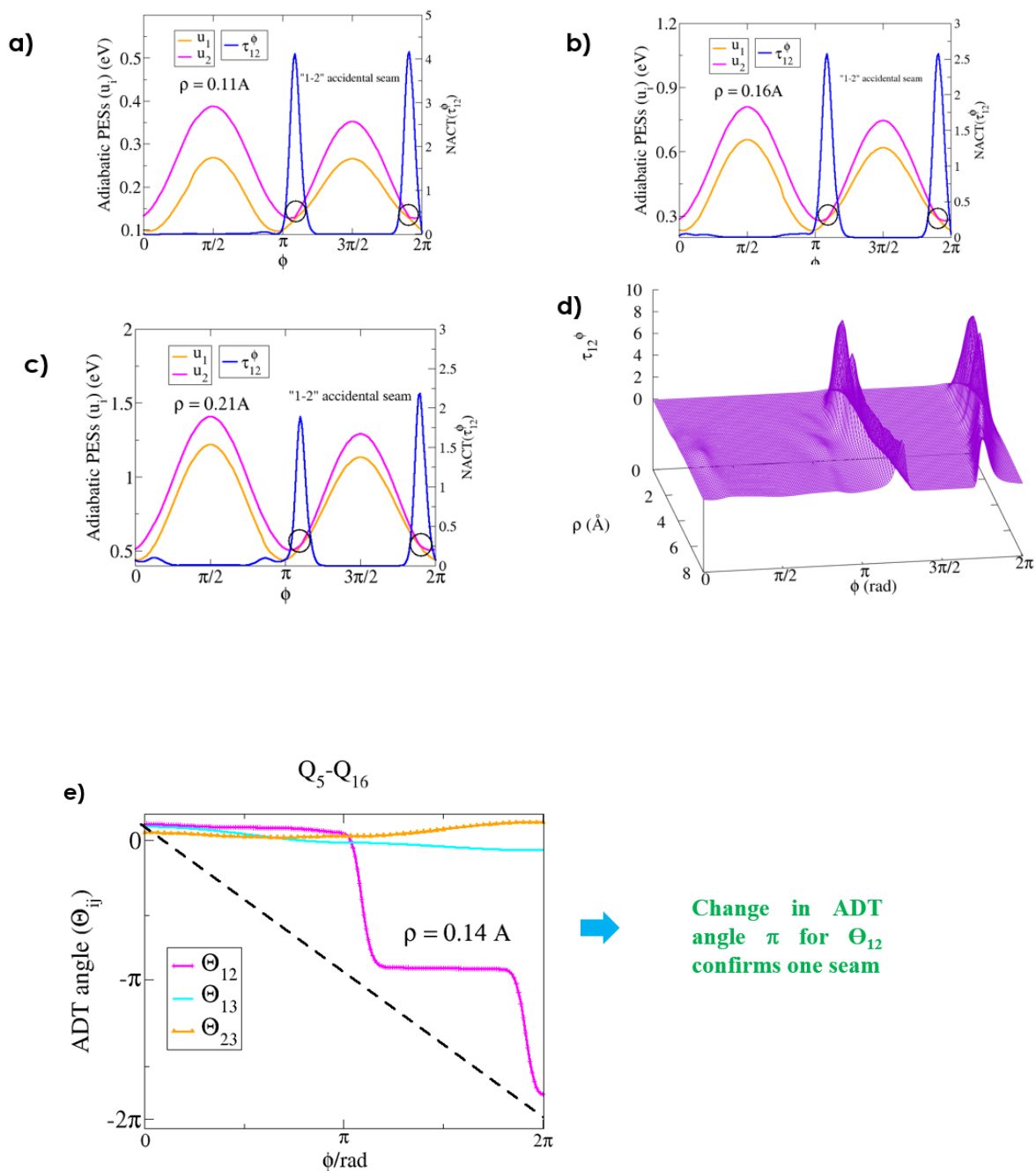
Figure 4.3: The 1D cuts of adiabatic potential energy surfaces (PESs) of the pyridine cation are plotted for the Q_5 and Q_{16} pairwise vibrational modes along the polar coordinate (in dimensionless units) for ρ values = 0.11, 0.16 and 0.21 A (d) 2 D Surface of NACT (e)functional forms of ADT angles, 12, 13, and 23 for the Q5 Q16 pair.

Figure 4.4: The left panel (a-d) represents some representative diabatic PESs and couplings, namely, W_{11}, W_{22}, W_{12} and W_{23} for the Q_5-Q_{16} pair.It is important to note that all the diabatic PESs as well as couplings are smooth, continuous and single-valued functions of nuclear coordinates.
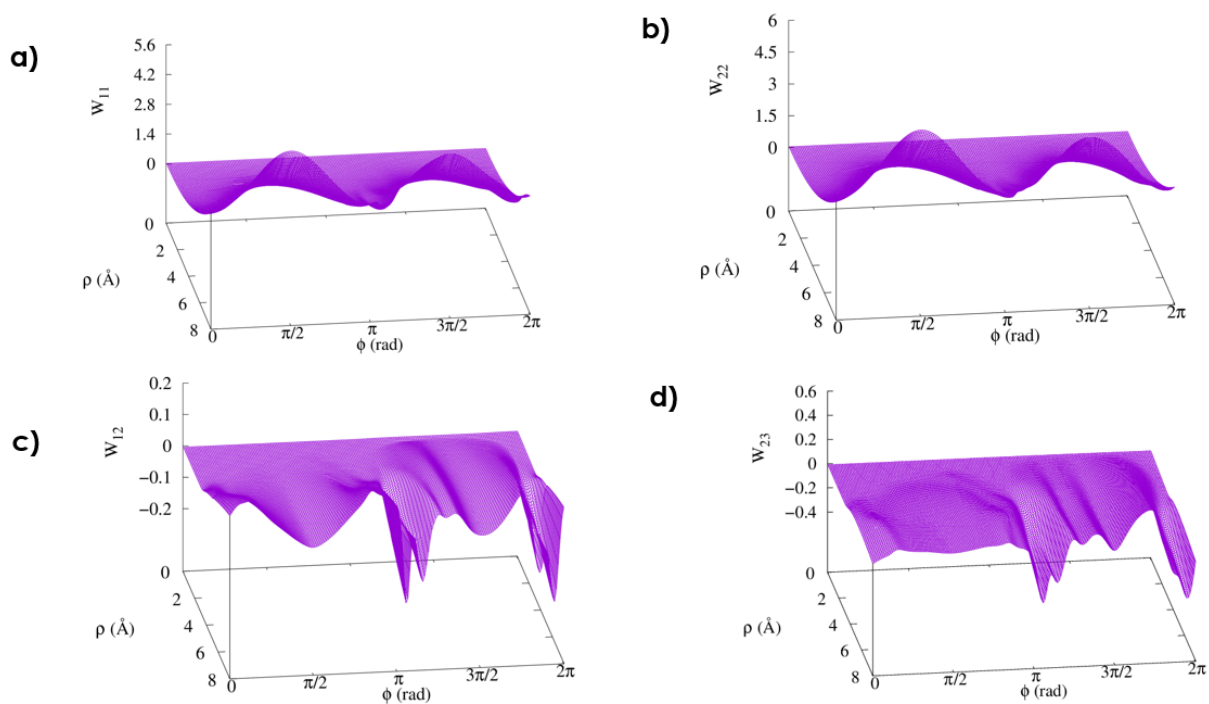
Conclusion:

Till now several theoretical developments were carried out on BBO theories and many investigations are pursued on quantum dynamics, where the appropriate number of coupled electronic states for the construction of a sub-Hilbert space is highly relevant to devise the ADT equations and expressions of NACTs. In the context of non-adiabatic chemistry, ADT equations upto four electronic states have already been deduced to generate the diabatic PESs for several realistic systems on which dynamics has been performed thoroughly with utmost care.In this research work, explicit expressions of ADT angles as well as NACTs for three-state sub-Hilbert space are derived, which are able to construct the diabatic surfaces for the calculation of the experimental observables. ADT condition is assumed to be valid for the given sub-Hilbert space but the applicability of those equations in realistic ground needs to be properly justified. For this reason, the molecular species, pyridine is taken into account, where the non-adiabatic interactions between the first three electronic states are notably strong.

In this context, we need to stress upon the fact that this study shows the workability of the developed ADT equations for three coupled electronic states, where the adiabatic PESs and NACTs are computed at CASSCF level of theory. In near future, with the help of the present theory, we intend to construct diabatic surfaces using more accurate adiabatic PESs and NACTs (at the MRCI level) in order to carry out dynamics and demonstrate experimentally observed photoelectron spectra available for this system.

References

[1] M. Born and K. Huang. *Dynamical Theory of Crystal Lattices.* Oxford University Press, Oxford, 1954.

[2] M. Born and R. Oppenheimer. "Zur Quantentheorie der Molekeln". In: *Ann. Phys.* 389.20 (Jan. 1927), pp. 457–484. ISSN: 0003-3804. DOI: 10.1002/andp.19273892002.

[3] M. Baer, G. Niedner-Schatteburg, and J.P. Toennies. In: *J. Chem. Phys.* 91 (1989), p. 4169.

[4] M. Baer et al. In: *J. Chem. Phys.* 93 (1990), p. 4845.

[5] F. Aguilon et al. In: *J. Chem. Phys.* 104 (1996), p. 4530.

[6] M. Sizun et al. In: *Chem. Phys.* 209 (1996), pp. 327–353.

[7] I. Last, M. Gilibert, and M. Baer. In: *J. Chem. Phys.* 107 (1997), p. 1451.

[8] D. Grimbert, V. Sidis, and V. Cobut. In: *J. Chem. Phys.* 108 (1998), p. 6331.

[9] R. Baer et al. In: *J. Chem. Phys.* 105 (1996), p. 9141.

[10] D. M. Charutz, R. Baer, and M. Baer. In: *Chem. Phys. Letts.* 265 (1997), p. 629.

[11] S. Adhikari and G. D. Billing. In: *J. Chem. Phys.* 111 (1999), p. 40.

[12] A. J. C. Varandas and Z. R. Xu. In: *J. Chem. Phys.* 112 (2000), p. 2121.

[13] M. Baer et al. In: *Phys. Rev. A* 62 (2000), p. 32506.

[14] S. Adhikari et al. In: *Phys. Rev. A* 62 (2000), p. 32507.

[15] B. Sarkar and S. Adhikari. In: *J. Chem. Phys.* 124 (2006), p. 074101.

[16] B. Sarkar and S. Adhikari. In: *Indian J. Phys.* 81 (9) (2007), p. 925.

[17] B. Sarkar and S. Adhikari. In: *Int. J. Quan. Chem.* 109 (2009), p. 650.

[18] B. Sarkar and S. Adhikari. In: *J. Phys. Chem. A* 112 (2008), p. 9868.

[19] A. K. Paul et al. In: *J. Chem. Phys.* 131 (2009), p. 124312.

[20] A. K. Paul, B. Sarkar, and S. Adhikari. *Recent Advances in Spectroscopy.* Ed. by R. K. Chaudhuri et al. Astrophysics and Space Science Proceedings, Springer - Verlag, Berlin, Heidelberg, 2010. Chap. 7, p. 63.

[21] A. K. Paul, S. Ray, and S. Adhikari. *Vibronic Interactions and the Jahn - Teller Effect: Theory and Applications.* Ed. by M. Atanasov, C. Daul, and P. L. W. Tregenna-Piggott. Progress in Theoretical Chemistry and Physics 23, Springer, 2012. Chap. 15, p. 281.

[22] A. K. Paul et al. In: *Chem. Phys. Letts.* 508 (2011), p. 300.

[23] A. K. Paul et al. In: *J. Chem. Phys.* 135 (2011), p. 034107.

[24] S. Mukherjee et al. In: *J. Phys. Chem. A* 117 (2013), p. 3475.

[25] S. Mukherjee et al. In: *J. Phys.: Conf. Ser.* 428 (2013), p. 012008.

[26] S. Mukherjee and S. Adhikari. In: *Chem. Phys.* 440 (2014), p. 116.

[27] S. Mukherjee, D. Mukhopadhyay, and S. Adhikari. In: *J. Chem. Phys.* 141 (2014), p. 204306.

[28] S. Mukherjee et al. In: *J. Chem. Phys.* 143 (2015), p. 244307.

[29] H. C. Longuet-Higgins et al. In: *Proc. R. Soc. London, Ser. A* 244 (1958), p. 1.

[30] H. C. Longuet - Higgins. In: *Adv. Spectrosc. (NY)* 2 (1961), p. 429.

[31] H. C. Longuet - Higgins. In: *Proc. R. Soc. London, Ser. A* 344 (1975), p. 147.

[32] H. C. Longuet - Higgins. In: *Mol. Phys.* 6 (1963), p. 445.

[33] M. V. Berry. In: *Proc. R. Soc. London, Ser. A* 392 (1984), p. 45.

[34] M. S. Child. In: *Adv. Chem. Phys.* 124 (2002), p. 1.

[35] D. E. Manolopoulos and M. S. Child. In: *Phys. Rev. Lett.* 82 (1999), p. 2223.

[36] A. J. C. Varandas, J. Tennyson, and J. N. Murrel. In: *Chem. Phys. Lett.* 61 (1979), p. 431.

[37] G. Herzberg and H. C. Longuet - Higgins. In: *Discuss. Faraday Soc.* 35 (1963), p. 77.

[38] W. D. Hobey and A. D. Mclachlan. In: *J. Chem. Phys.* 33 (1960), p. 1695.

[39] F. T. Smith. In: *Phys. Rev.* 179 (1969), p. 111.

[40] M. Baer. In: *Chem. Phys. Lett.* 35 (1975), p. 112.

[41] C. A. Mead and D. G. Truhlar. In: *J. Chem. Phys.* 70 (1979), p. 2284.

[42] C. A. Mead and D. G. Truhlar. In: *J. Chem. Phys.* 77 (1982), p. 6090.

[43] C. A. Mead. In: *J. Chem. Phys.* 78 (1983), p. 807.