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Beyond Born-Oppenheimer treatment in pyridine Radical cation ($C_5H_5N^+$)

Project Report
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CERTIFICATE

This is to certify that the work contained in this project report entitled "**Beyond Born-Oppenheimer treatment in pyridine Radical cation $(\mathbf{C_5H_5}N^+)$**" submitted by **Aiyush Saha** to Indian Association for the Cultivation of Science towards partial requirement for his Master's project for 8th semester has been carried out by him under my supervision and that it has not been submitted elsewhere for the award of any degree.

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Aiyush Saha
BS-MS 4th year

Contents

Abstract

Explicit forms of Adiabatic to Diabatic Transformation (ADT) equations have been devised for a coupled four-state electronic manifold in terms of ADT angles. The numerical instability originated from the singularity of Non-Adiabatic Coupling Terms (NACTs) is removed by using ADT matrices, which transform the adiabatic Schrödinger equation (SE) to its diabatic form. In this project, Pyridine Radical Cation $(C_5H_5N^+)$ is selectively chosen for demonstration of ADT equations for four coupled electronic states. We examine the NACTs among the lowest four 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 the $C_5H_5N^+$ cation, the Q_{11}–Q_{12},Q_5–Q_{16} and Q_3–Q_7 normal mode pairs is taken as the nuclear configuration space (CS) to investigate the utility of Beyond Born-Oppenheimer (BBO) equations for four coupled electronic states. Intense vibronic coupling prevailing within the low-lying four 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 four electronic states at the Complete Active Space Self-Consistent Field (CASSCF) level using the 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 system.

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 representa- tion 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 four electronic state.detailed study on their workability a realistic molecular system pyridine cation to generate the diabatic surfaces.

Beyond Born-Oppenheimer: Theory & 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:

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

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

$$\mathbf{A} = \mathbf{A}_{12}(\Theta_{12}) \cdot \mathbf{A}_{13}(\Theta_{13}) \cdot \mathbf{A}_{14}(\Theta_{14}) \cdot \mathbf{A}_{23}(\Theta_{23}) \cdot \mathbf{A}_{24}(\Theta_{24}) \cdot \mathbf{A}_{34}(\Theta_{34}) \quad (3.12)$$

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 four electronic state sub-Hilbert space.

ADT equation for the coupling of four-coupled electronic states are:

$$\begin{aligned}
\vec{\nabla}\Theta_{12} = &-\vec{\tau}_{12} - \sin\Theta_{12}\left(\vec{\tau}_{13}\tan\Theta_{13} + \vec{\tau}_{14}\sec\Theta_{13}\tan\Theta_{14}\right) \\
&- \cos\Theta_{12}\left(\vec{\tau}_{23}\tan\Theta_{13} + \sec\Theta_{13}\vec{\tau}_{24}\tan\Theta_{14}\right)
\end{aligned} \quad (3.13)$$

$$\begin{aligned}
\vec{\nabla}\Theta_{13} = &-\vec{\tau}_{13}\cos\Theta_{12} + \vec{\tau}_{23}\sin\Theta_{12} - \vec{\tau}_{14}\cos\Theta_{12}\sin\Theta_{13}\tan\Theta_{14} \\
&+ \vec{\tau}_{24}\sin\Theta_{12}\sin\Theta_{13}\tan\Theta_{14} - \vec{\tau}_{34}\cos\Theta_{13}\tan\Theta_{14}
\end{aligned} \quad (3.14)$$

$$\vec{\nabla}\Theta_{23} = -\cos\Theta_{13}\Big[\vec{\tau}_{13}\sin\Theta_{12}\sec\Theta_{13} + \cos\Theta_{23}\sec\Theta_{14}(\vec{\tau}_{34} - \vec{\tau}_{24}\sin\Theta_{12}\tan\Theta_{13})\tan\Theta_{24}$$
$$+ \sin\Theta_{12}\sec\Theta_{13}\tan\Theta_{13}\vec{\tau}_{14}\tan\Theta_{14} + \sin\Theta_{23}\vec{\tau}_{14}\sec\Theta_{14}\tan\Theta_{24}$$
$$+ \cos\Theta_{12}\,(\vec{\tau}_{23}\sec\Theta_{13} + \tan\Theta_{13}\cos\Theta_{23}\vec{\tau}_{14}\sec\Theta_{14}\tan\Theta_{24}$$
$$+ \sec\Theta_{13}\,(\tan\Theta_{13}\vec{\tau}_{24}\tan\Theta_{14} + \sin\Theta_{23}\vec{\tau}_{24}\sec\Theta_{14}\tan\Theta_{23}))\Big]$$

$$(3.15)$$

$$\vec{\nabla}\Theta_{14} = -\vec{\tau}_{14}\cos\Theta_{12}\cos\Theta_{13} + \vec{\tau}_{24}\sin\Theta_{12}\cos\Theta_{13} + \vec{\tau}_{34}\sin\Theta_{13} \qquad (3.16)$$

$$\vec{\nabla}\Theta_{24} = \sin\Theta_{23}\,(-\sin\Theta_{12}\sin\Theta_{13}\vec{\tau}_{24}\sec\Theta_{14} + \cos\Theta_{13}\vec{\tau}_{34}\sec\Theta_{14})$$
$$- \sin\Theta_{12}\cos\Theta_{23}\vec{\tau}_{14}\sec\Theta_{14}$$
$$+ \cos\Theta_{12}\,(\sin\Theta_{13}\sin\Theta_{23}\vec{\tau}_{14}\sec\Theta_{14} - \cos\Theta_{23}\vec{\tau}_{24}\sec\Theta_{14}) \qquad (3.17)$$

$$\vec{\nabla}\Theta_{34} = \sin\Theta_{12}\Big(-\sin\Theta_{23}\vec{\tau}_{14}\sec\Theta_{14}\sec\Theta_{24} + \sin\Theta_{13}\cos\Theta_{23}\vec{\tau}_{24}\sec\Theta_{14}\sec\Theta_{24}$$
$$+ \cos\Theta_{12}\,\{-\sec\Theta_{24}\,(\sin\Theta_{13}\cos\Theta_{23}\vec{\tau}_{14}\sec\Theta_{14} + \sin\Theta_{23}\vec{\tau}_{24}\sec\Theta_{14})\}\Big)$$
$$- \cos\Theta_{13}\cos\Theta_{23}\vec{\tau}_{34}\sec\Theta_{14}\sec\Theta_{24} \qquad (3.18)$$

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 performed *ab initio* calculations on the pyridine radical cation focusing on the lowest four coupled electronic states, namely $^2A_1$, $^2A_2$, $^2B_1$, and $^2B_2$. The Complete Active Space Self-Consistent Field (CASSCF) method was employed within the MOLPRO package using a (5 electrons, 6 orbitals) active space and Dunning's cc-pVTZ basis set under C_{2v} symmetry. One-dimensional potential energy surfaces (PESs) were generated for all vibrational modes, while detailed *ab initio* calculations focused on the Q_{11}–Q_{12},Q_5–Q_{16},Q_3–Q_7 normal mode pairs to investigate nonadiabatic interactions.

Optimized vibrational frequencies and ionization energies were compared with experimental data to validate our approach. Nonadiabatic coupling terms (NACTs) between the electronic states were calculated using the Coupled Perturbed Multi-Configuration Self-Consistent Field (CP-MCSCF) method. Important insights from these *ab initio* studies and the adiabatic-to-diabatic transformation on this system are discussed.

4.1 Results and Discussion:

Frequency data comparison table

a_1 and b_1 modes:

Vibrational Modes	MP2/cc-PVDZ (cm^{-1})	MP2/cc-PVTZ (cm^{-1})	CCSD/cc-PVTZ (cm^{-1})	Expt. (cm^{-1})
a_1 modes				
q1	598	601	607	603
q2	1006	1007	1005	991
q3	1044	1048	1052	1060
b_1 modes:				
q12	713	726	711	703
q13	740	759	752	747

b_1 and a_2 modes:

Vibrational Modes	MP2/cc-PVDZ (cm^{-1})	MP2/cc-PVTZ (cm^{-1})	CCSD/cc-PVTZ (cm^{-1})	Expt. (cm^{-1})
b_1 mode				
q16	655	651	654	654
a_2 modes				
q22	1628	1621	1656	1574
q25	880	895	880	850
q26	902	900	912	884

Table 4.1: For the pyridine radical cation, vibrational frequency calculations were carried out using various levels of *ab initio* theory, including MP2 and CCSD with different basis sets (cc-PVDZ and cc-PVTZ). These computations were performed for four electronic states of the radical cation. Among all tested methods, the best agreement with experimental vibrational frequencies was observed using the CCSD method with the cc-PVTZ basis set. This level of theory consistently produced values closest to the experimental data across various vibrational modes, demonstrating its superior accuracy for modeling the pyridine radical cation.

Ionization Energy Calculations:

Method	1st (eV)	2nd (eV)	3rd (eV)
MP2/cc-PVTZ geometry followed by HF/Koopmans[1]	9.44	10.42	11.37
MP2/cc-PVTZ geometry followed by EOM-IP-CCSDT[1]	9.69	9.72	10.43
MP2/cc-PVDZ geometry followed by MCSCF	8.98	9.00	10.28
MP2/cc-PVDZ geometry followed by MRCI	9.37	9.39	10.69
MP2/cc-PVTZ geometry followed by MCSCF	8.96	9.02	10.31
MP2/cc-PVTZ geometry followed by MRCI	9.50	9.53	10.85
Expt.[2]	**9.66**	**9.85**	**10.51**

Table 4.2: Here are the calculated ionization energies (in eV) for the pyridine radical cation using various computational methods, considering only 4-state results. Among all, the MP2/cc-PVTZ geometry followed by MRCI method provides the best agreement with the experimental values and can be considered the most reliable approach in this study.

4.1.1 1-D Potential Energy Surfaces

Here, we present one-dimensional potential energy surfaces (PESs) of the pyridine radical cation for four coupled electronic states. These surfaces are computed along selected vibrational modes and provide insight into the state-specific nuclear motion and potential energy variation relevant to the molecule's spectroscopic and reactive behavior.
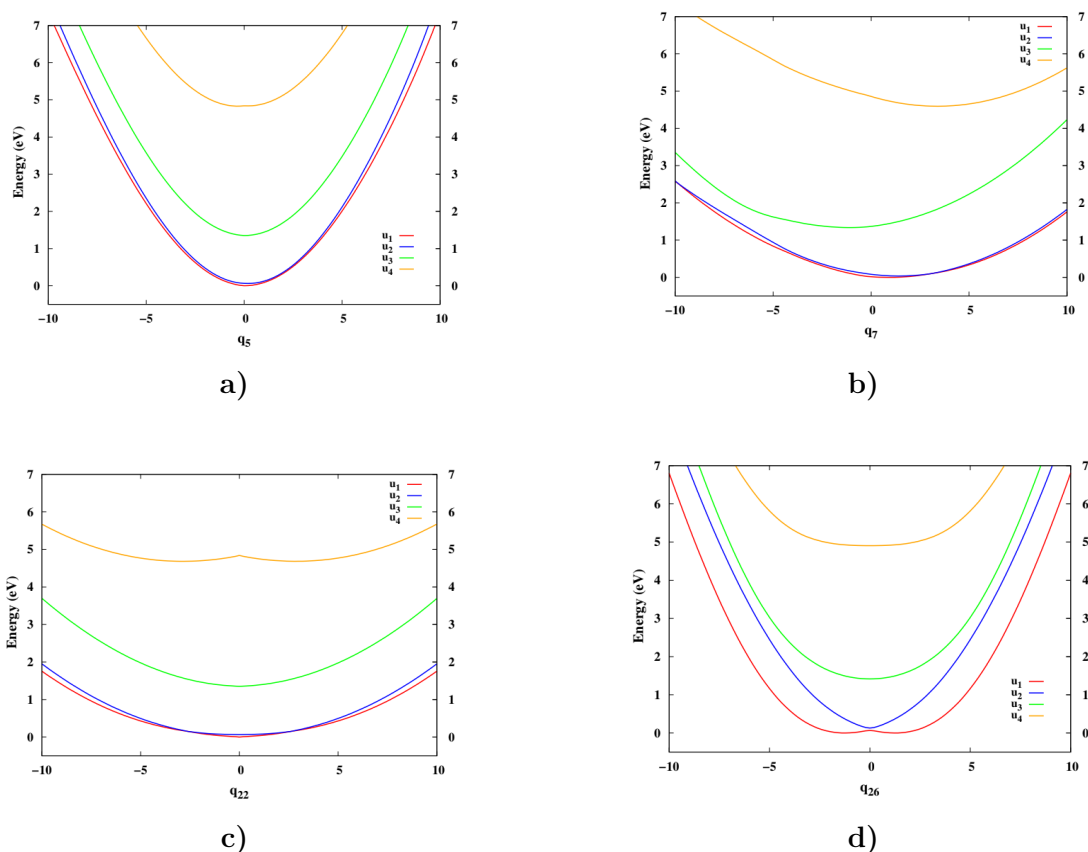

Figure 4.1: One-dimensional potential energy surfaces (PESs) for the pyridine radical cation along vibrational modes q_5, q_7, q_{22}, and q_{26}. Each panel (a–d) corresponds to a different mode, showing how four coupled electronic states vary with nuclear displacement.

4.1.2 1D Cuts and Topological Features of Adiabatic PESs for the $Q_3 - Q_7$ Pair in Pyridine Radical Cation:
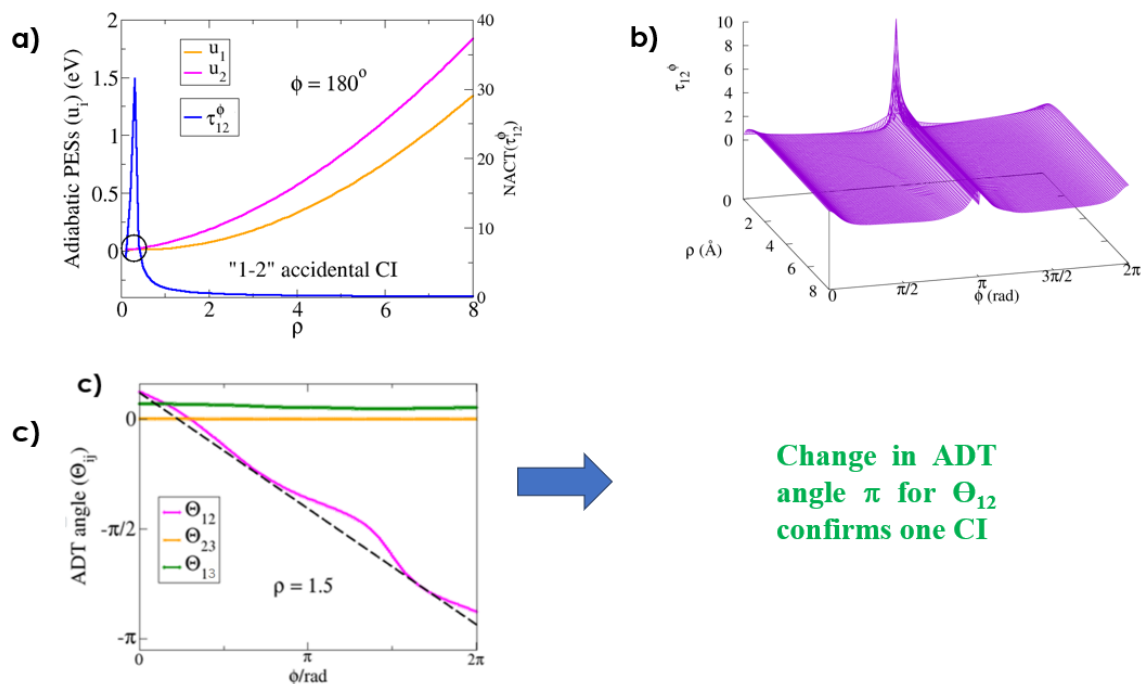

Figure 4.2: 1D cuts of adiabatic PESs of pyridine cation for $Q_3 - Q_7$ pairwise modes along ϕ at (a) $\phi = 180$ where ρ and ϕ are the polar coordinates. ρ is in dimensionless units. In diagram (b), the location of the "1-2" NACT is depicted over the 2D functional form of τ_{12}^ϕ. The first diagram (c) shows 1D functional forms of ADT angles, Θ_{12}, Θ_{23}, and Θ_{13} for the $Q_3 - Q_7$ pair.

4.1.3 Representative Diabatic PESs and Couplings for the $Q_3 - Q_7$ Pair:
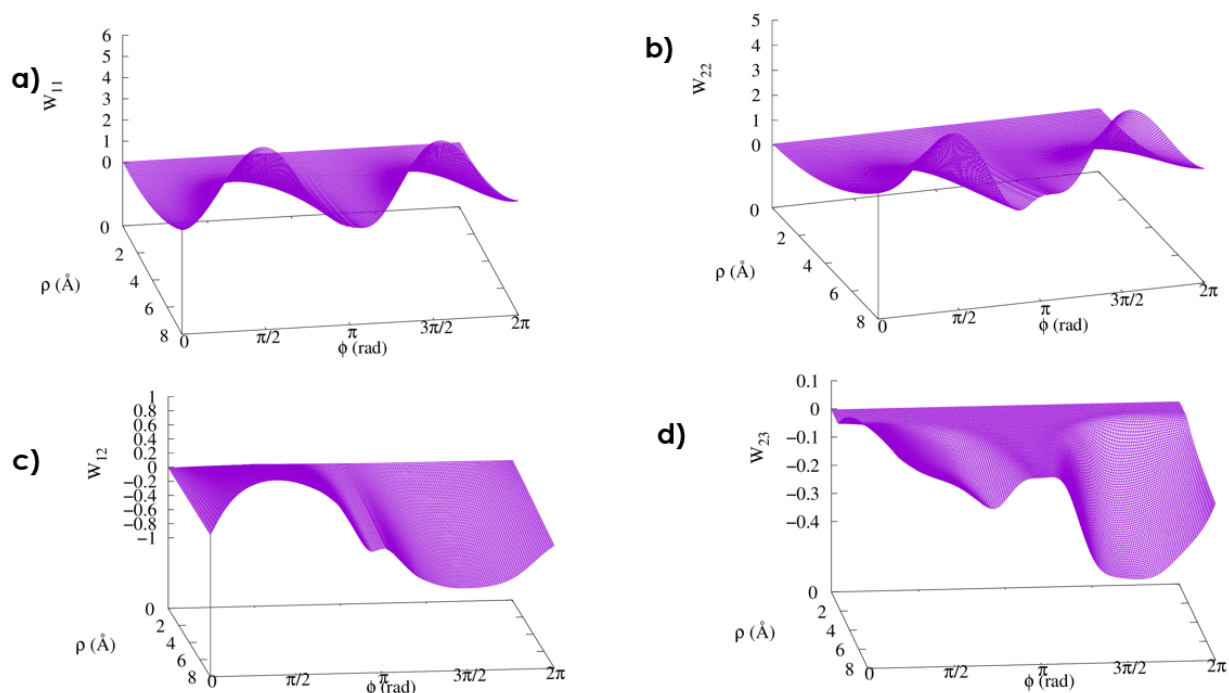
Figure 4.3: The left panel (a-d) represents some representative diabatic PESs and couplings, namely, W_{11}, W_{22}, W_{12} and W_{23} for the $Q_3 - Q_7$ pair.It is important to note that all the diabatic PESs as well as couplings are smooth, continuous and single-valued functions of nuclear coordinates.

4.1.4 1D Cuts and Topological Features of Adiabatic PESs for the $Q_5 - Q_{16}$ Pair in Pyridine Radical Cation:
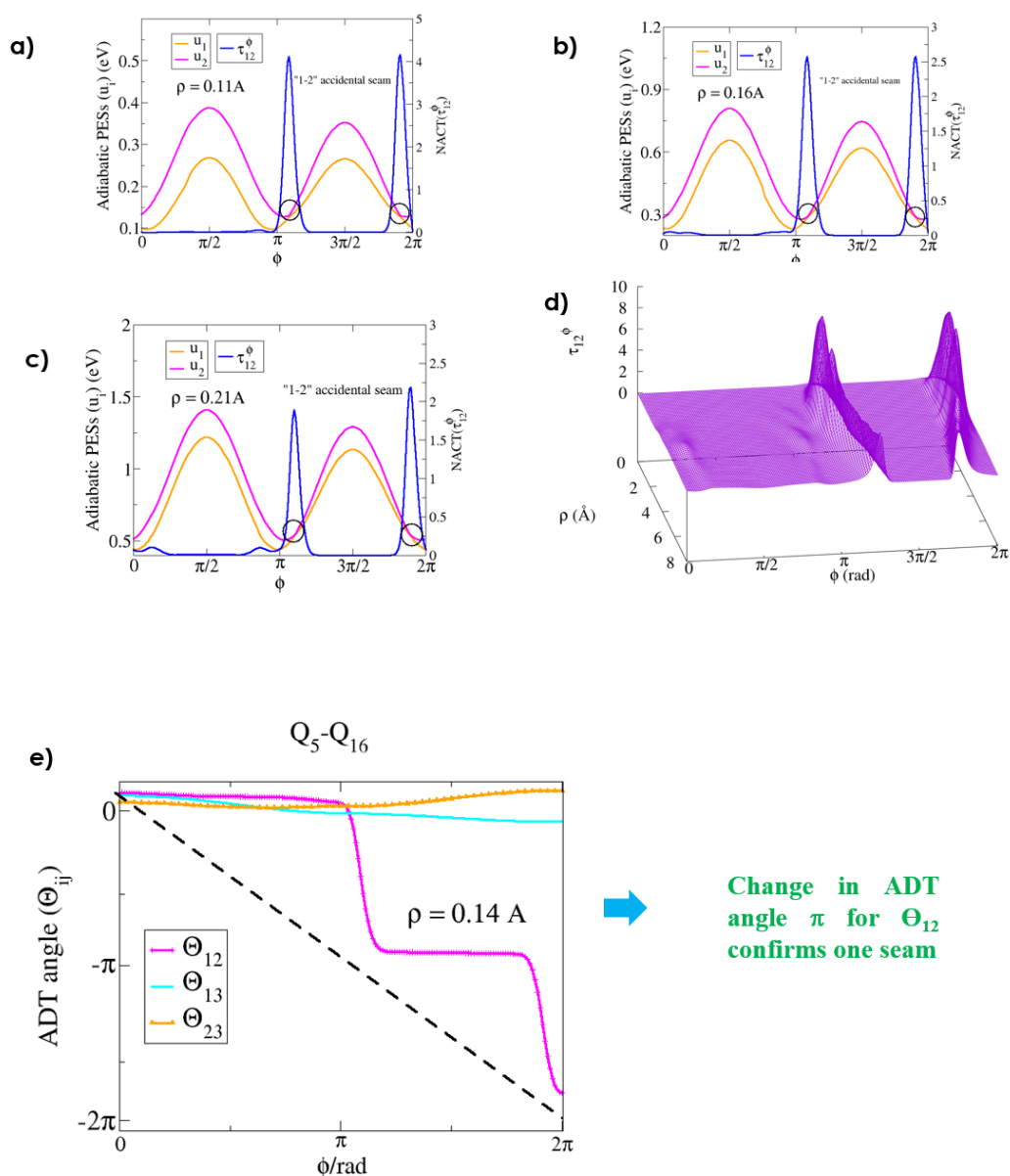

Figure 4.4: The 1D cuts of adiabatic potential energy surfaces (PESs) of the pyridine cation are plotted for the Q_5 and Q_{16} pairwise vibrational modes along the polar coordinate (in dimensionless units) for ρ values = 0.11, 0.16 and 0.21 A (d) 2 D Surface of NACT (e)functional forms of ADT angles $\Theta_{12}, \Theta_{13},$ and Θ_{23} for the $Q_5 - Q_{16}$ pair.

4.1.5 Representative Diabatic PESs and Couplings for the $Q_5 - Q_{16}$ Pair:
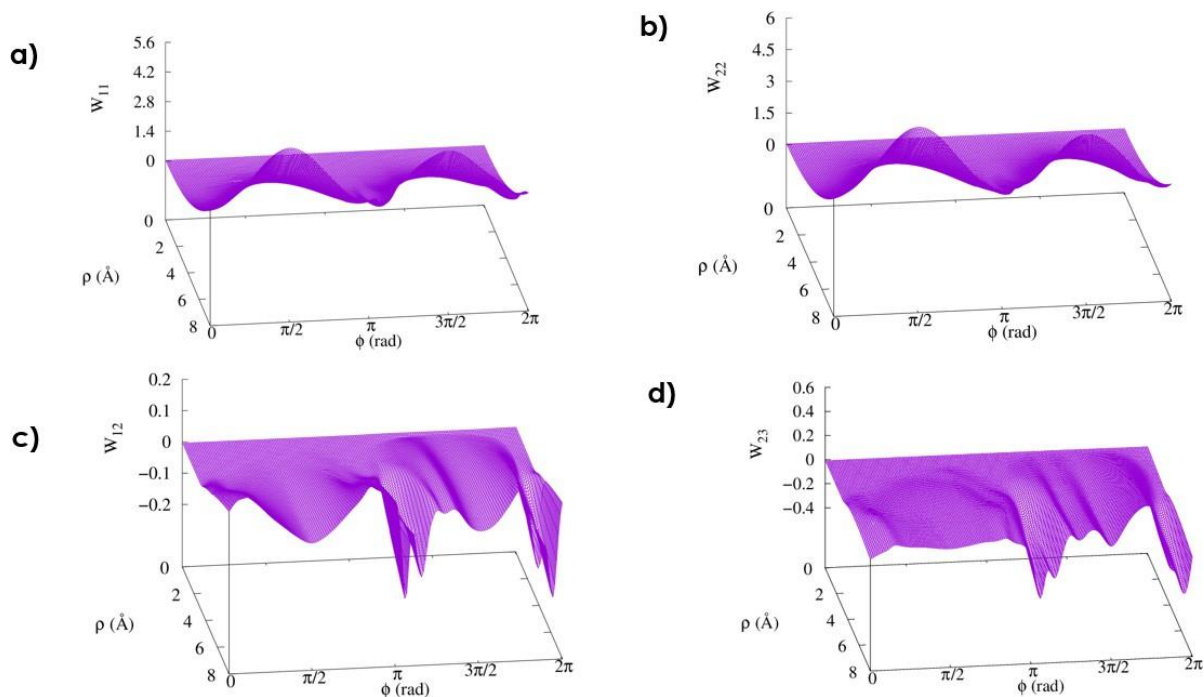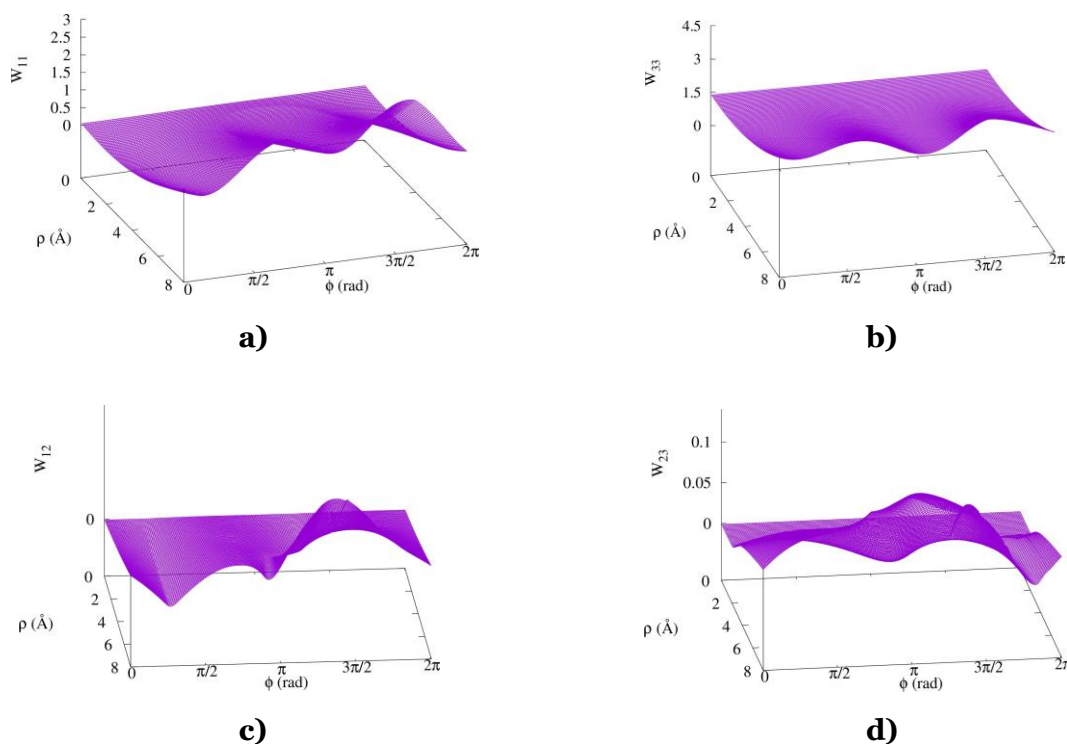

Figure 4.5: The left panel (a-d) represents some representative diabatic PESs and couplings, namely, W_{11}, W_{22}, W_{12} and W_{23} for the $Q_5 - Q_{16}$ pair. It is important to note that all the diabatic PESs as well as couplings are smooth, continuous functions of nuclear coordinates.

4.1.6 Two-Dimensional NACT Surfaces Showing Pseudo Jahn–Teller Interaction for the $Q_{11}-Q_{12}$ Pair:
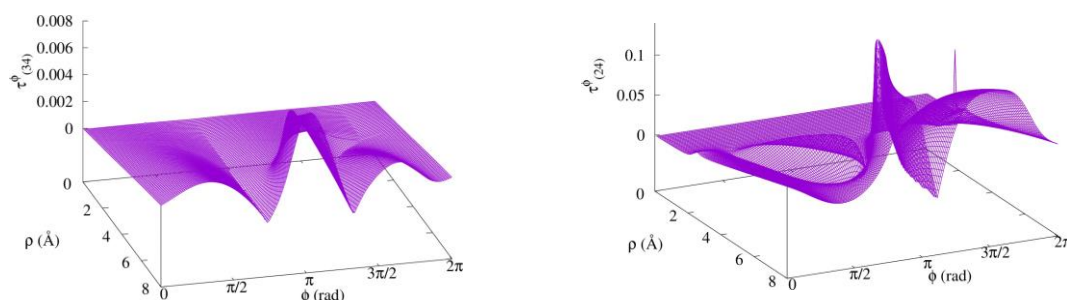
4.1.7 Representative Diabatic PESs and Couplings for the $Q_{11} - Q_{12}$ Pair:

Figure 4.7: The left panel (a-d) represents some diabatic PESs and couplings, namely, W_{11}, W_{33}, W_{12} and W_{23} for the $Q_{11} - Q_{12}$ pair. It is important to note that all the diabatic PESs as well as couplings are smooth, continuous functions of nuclear coordinates.

Conclusion:

Till now, several theoretical developments have been carried out on Beyond Born-Oppenheimer (BBO) theories, and many investigations have been pursued on quantum dynamics. In these studies, the appropriate number of coupled electronic states for constructing a sub-Hilbert space is highly relevant to devising the adiabatic-to-diabatic transformation (ADT) equations and expressions of nonadiabatic coupling terms (NACTs).

In the context of nonadiabatic chemistry, ADT equations for up to four coupled electronic states have already been deduced to generate diabatic potential energy surfaces (PESs) for several realistic systems, on which dynamics has been thoroughly performed. In this research, explicit expressions of ADT angles and NACTs for a four-state sub-Hilbert space are derived, enabling the construction of diabatic surfaces for calculating experimental observables. Although the ADT condition is assumed valid within the chosen sub-Hilbert space, its applicability to realistic systems requires careful justification.

For this reason, the molecular species pyridine is taken into account, where nonadiabatic interactions between the first four electronic states are notably strong. This study highlights the workability of the developed ADT equations for four coupled electronic states, with adiabatic PESs and NACTs computed at the CASSCF level of theory. In the near future, with the present theoretical framework, we intend to construct diabatic surfaces using more accurate adiabatic PESs and NACTs computed at the MRCI level to perform dynamics simulations and interpret experimentally observed photoelectron spectra for this system.

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