

Ab - initio non-adiabatic couplings among three lowest singlet states of H_3^+ : Construction of multisheeted diabatic potential energy surfaces

Bijit Mukherjee, Saikat Mukherjee and Satrajit Adhikari*

Department of Physical Chemistry
Indian Association for the Cultivation of Science
Jadavpur, Kolkata -700 032, INDIA

E-mail: pcsa@iacs.res.in

Abstract. We calculate the adiabatic potential energy surfaces and non-adiabatic interactions among the three lowest singlet states ($1^1A'$, $2^1A'$ and $3^1A'$) of H_3^+ in hyperspherical coordinates for a fixed hyperradius, $\rho = 9$ bohr as functions of hyperangles, θ ($0 \leq \theta \leq 90^\circ$) and ϕ ($0 \leq \phi \leq 360^\circ$). All *ab initio* calculations are performed using MRCI level of methodology implemented in quantum chemistry package, MOLPRO. The ground ($1^1A'$) and the first excited ($2^1A'$) states exhibit several conical intersections as functions of ϕ for $\theta \geq 70^\circ$. Subsequently, we carry out adiabatic to diabatic transformation (ADT) to obtain ADT angles for constructing single-valued, continuous, smooth and symmetric 3×3 diabatic potential energy matrix to perform accurate scattering calculations.

1. Introduction

The Born - Oppenheimer (BO) treatment, one of the most fundamental theories in quantum chemistry, separates the motions of fast moving electrons from the slow moving nuclei.^{1,2} This results into two important quantities, *viz.*, the adiabatic potential energy surfaces (PESs) and the non-adiabatic coupling terms (NACTs) among the electronic states. It is the NACTs, which dictate the contributions of the excited electronic states into a molecular process even if it is occurring on the ground electronic state. In order to calculate correct transition probabilities for various processes or study radiationless decay and scattering processes, one has to take into account the NACTs between the electronic states. These coupling terms become sharp functions of nuclear coordinates close to conical intersections (CIs) in the nuclear configuration space (CS), those which occur at the avoided crossings or degenerate points between the adiabatic PESs. Thus, in order to perform stable numerical calculations, one has to carry out a unitary transformation to obtain the so called diabatic representation, where the kinetic couplings among the electronic states become smooth functions of nuclear coordinates. The transformation from adiabatic to diabatic representation of Schrödinger Equation (SE) for a given sub-Hilbert space is guaranteed to produce “correct” and “accurate” diabatic PESs under the following conditions: (a) The non-removable components of NACTs are approximately zero³; (b) The vector fields created by the NACTs satisfy the so called Curl Conditions.^{4,5} Baer⁶ and his co-workers^{7,8} carried out the beyond BO treatment for two state sub-Hilbert space and formulated the diabatic Hamiltonian matrix in terms of adiabatic PESs and adiabatic to diabatic transformation (ADT)



angles.^{9–11} Sarkar *et al.* generalized^{12–15} the BO treatment for any three/four coupled electronic states, where the explicit form of NACTs, Curl - Divergence equation and diabatic Hamiltonian matrix are derived in terms of ADT angles. This approach paves^{16,17} a practical way to handle the NACTs with singularities at any point(s) or along a seam in the CS to construct continuous, single-valued, symmetric and smooth diabatic PESs to carry out scattering processes.

The molecular ion H_3^+ being an important hydrogenic compound, exists in substantial amount in interstellar space. This species, first spectroscopically observed by Oka,¹⁸ soon gained much theoretical and experimental attention owing to its important role being played in astrophysics. This seemingly simple ion only with two electrons possesses a rich electronic structure making it a target for a large number of *ab initio* calculations. Until now many accurate PESs near the ground state equilibrium geometry have been reported.^{19,20} Meyer *et al.*¹⁹ carried out calculations using full configuration interaction and the obtained local PESs were fitted using 69 carefully selected points with energies up to 25000 cm^{-1} , and then, achieved near spectroscopic accuracy. Röhse *et al.*²⁰ applied CISD-R12 method to achieve higher accuracy and Cencek *et al.*²¹ included both adiabatic and relativistic corrections. In spite of the large amount of work on H_3^+ , very less attention has been paid on its excited states. Schaad and Hicks²² performed a systematic study of excited electronic states of H_3^+ which included the detailed study of the ground triplet state only. Later on, a complete PES has been reported,^{23–25} including vibrational^{24–27} and rovibrational^{23,28} calculations. Several diabatic PESs have been made using the singlet states of H_3^+ , few of which are: the Preston and Tully surface,²⁹ the Kamisaka-Bian-Nobusada-Nakamura³⁰ surface, the double many-body expansion potential surface constructed by Varandas *et al.*³¹ using dressed DIM method. Recently, *ab initio* calculated NACTs and adiabatic PESs are employed to construct “first principle based and accurate” diabatic PESs by Mukherjee *et al.*³² In this article, we explore the non-adiabaticities among the lowest three singlet states of H_3^+ by calculating the adiabatic PESs and NACTs for the states $1^1A'$, $2^1A'$, $3^1A'$ in the hyperspherical coordinates using the *ab initio* quantum chemistry package MOLPRO.³³ We employ beyond BO theory for three state sub-Hilbert space, calculate ADT angles by plugging NACTs in ADT equations, and construct diabatic Hamiltonian matrix for a fixed ρ as a function of θ and ϕ using adiabatic PESs and ADT angles.

2. Theory

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 CIs among the states anywhere in the nuclear CS. The BO expansion^{1,2} of the molecular wavefunction for this subspace of the Hilbert space and the total electron - nuclei Hamiltonian in the adiabatic representation are:

$$\begin{aligned}
 |\Psi(s_e, s_n)\rangle &= \sum_{i=1}^3 \psi_i(s_n) |\xi_i(s_e|s_n)\rangle, \\
 \hat{\mathbf{H}} &= \hat{\mathbf{T}}_{s_n} + \hat{\mathbf{H}}_e(s_e|s_n), \\
 \hat{\mathbf{T}}_{s_n} &= -\frac{\hbar^2}{2} \sum_i \left(\frac{\nabla_{s_n,i}^2}{m_i} \right), \\
 \hat{\mathbf{H}}_e(s_e|s_n) |\xi_i(s_e|s_n)\rangle &= u_i(s_n) |\xi_i(s_e|s_n)\rangle,
 \end{aligned} \tag{1}$$

where the eigenfunctions $[\xi_i(s_e|s_n)]$ of the electronic Hamiltonian, $\hat{\mathbf{H}}_e(s_e|s_n)$, are defined by the sets of nuclear (s_n) and electronic (s_e) coordinates with nuclear coordinate dependent eigenvalues, $u_i(s_n)$. $\hat{\mathbf{T}}_{s_n}$ 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 [$\hat{\mathbf{H}}\Psi(s_e, s_n) = E\Psi(s_e, s_n)$], we can arrive at the following compact form of kinetically coupled nuclear equation:

$$-\frac{\hbar^2}{2m} \left(\vec{\nabla} + \vec{\tau} \right)^2 \psi + (\mathbf{u} - E) \psi = 0, \quad (2)$$

where the non - adiabatic coupling and adiabatic PES matrices have the following form:

$$\vec{\tau} = \begin{pmatrix} 0 & \vec{\tau}_{12} & \vec{\tau}_{13} \\ -\vec{\tau}_{12} & 0 & \vec{\tau}_{23} \\ -\vec{\tau}_{13} & -\vec{\tau}_{23} & 0 \end{pmatrix} \quad \text{and} \quad \mathbf{u} = \begin{pmatrix} u_1 & 0 & 0 \\ 0 & u_2 & 0 \\ 0 & 0 & u_3 \end{pmatrix}, \quad (3)$$

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

$$\vec{\tau}_{ij} = \langle \xi_i(s_e|s_n) | \vec{\nabla} \xi_j(s_e|s_n) \rangle. \quad (4)$$

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:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi^d + (\mathbf{W} - E) \psi^d = 0, \quad \mathbf{W} = \mathbf{A}^\dagger \mathbf{u} \mathbf{A} \quad (5)$$

under the condition:

$$\vec{\nabla} \mathbf{A} + \vec{\tau} \mathbf{A} = 0. \quad (6)$$

This equation is known as the ADT condition.⁶ 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 [$\Theta_{12}(s_n)$, $\Theta_{23}(s_n)$ 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 matrices⁹, $\mathbf{A}_{12}(\Theta_{12})$, $\mathbf{A}_{23}(\Theta_{23})$, and $\mathbf{A}_{13}(\Theta_{13})$ as shown below:

$$\mathbf{A}(\Theta_{12}, \Theta_{23}, \Theta_{13}) = \mathbf{A}_{12}(\Theta_{12}) \cdot \mathbf{A}_{23}(\Theta_{23}) \cdot \mathbf{A}_{13}(\Theta_{13}). \quad (7)$$

The above model form of \mathbf{A} matrix [Eq. (7)] and the anti - symmetric form of $\vec{\tau}$ matrix [Eq. (3)] are substituted in Eq. (6), where the simple manipulation as performed by Baer *et al.*^{9,10} leads to the following equations for ADT angles:

$$\vec{\nabla} \Theta_{12} = -\vec{\tau}^{12} + \tan \Theta_{23} (\vec{\tau}^{13} \cos \Theta_{12} - \vec{\tau}^{23} \sin \Theta_{12}), \quad (8a)$$

$$\vec{\nabla} \Theta_{23} = -(\vec{\tau}^{13} \sin \Theta_{12} + \vec{\tau}^{23} \cos \Theta_{12}), \quad (8b)$$

$$\vec{\nabla} \Theta_{13} = -\frac{1}{\cos \Theta_{23}} (\vec{\tau}^{13} \cos \Theta_{12} - \vec{\tau}^{23} \sin \Theta_{12}), \quad (8c)$$

which in turn brings the explicit form¹² of $\vec{\tau}$ matrix elements in terms of ADT angles:

$$\vec{\tau}_{12} = -\vec{\nabla} \Theta_{12} - \sin \Theta_{23} \vec{\nabla} \Theta_{13}, \quad (9a)$$

$$\vec{\tau}_{23} = \sin \Theta_{12} \cos \Theta_{23} \vec{\nabla} \Theta_{13} - \cos \Theta_{12} \vec{\nabla} \Theta_{23}, \quad (9b)$$

$$\vec{\tau}_{13} = -\cos \Theta_{12} \cos \Theta_{23} \vec{\nabla} \Theta_{13} - \sin \Theta_{12} \vec{\nabla} \Theta_{23}. \quad (9c)$$

The components of *ab initio* calculated NACTs are substituted in Eq. (8) to obtain the ADT angles. The diabatic potential matrix elements can be calculated by using those ADT angles and adiabatic PESs given in Eq. (5).

3. *Ab initio* calculation for PESs and NACTs:

The calculations of the PESs and NACTs for the H_3^+ system are carried out using the hyperspherical coordinates, namely, the hyperradius, ρ and the two hyperangles, θ and ϕ . The domains for these hyperangles are $0 \leq \theta \leq \pi/2$ and $0 \leq \phi \leq 2\pi$. The hyperradius ρ solely determines the size of the triangle formed by the three particles, whereas the two hyperangles describe the shape of the triangle. The *ab initio* calculations are performed in terms of the inter-particle distances of the three nuclei, which are related to the hyperspherical coordinates³⁴ as given below:

$$R_1 = \frac{\rho}{\sqrt{2}} d_3 [1 + \sin \theta \cos(\phi + \epsilon_3)]^{1/2}, \quad (10a)$$

$$R_2 = \frac{\rho}{\sqrt{2}} d_1 (1 + \sin \theta \cos \phi)^{1/2}, \quad (10b)$$

$$R_3 = \frac{\rho}{\sqrt{2}} d_2 [1 + \sin \theta \cos(\phi - \epsilon_2)]^{1/2}, \quad (10c)$$

where $d_i = \sqrt{m_i(m_j + m_k)/\mu M}$, $M = \sum_i m_i$, $\mu = \sqrt{(m_1 m_2 m_3/M)}$, $\epsilon_2 = 2 \tan^{-1}(m_3/\mu)$ and $\epsilon_3 = 2 \tan^{-1}(m_2/\mu)$. For H_3^+ , $m_1 = m_2 = m_3 = 1.008$ amu, $M = 3.024$ amu, $\mu = 0.582$ amu, $d_1 = d_2 = d_3 = 1.075$ and $\epsilon_2 = \epsilon_3 = 120.0$.

In our present work, we have calculated the three lower adiabatic PESs ($1^1A'$, $2^1A'$ and $3^1A'$) and the NACTs, $\tau_k^{12}, \tau_k^{13}, \tau_k^{23}[k = \theta, \phi]$ for a fixed value of ρ ($= 9.0$ bohr) by varying θ and ϕ in increments of $\Delta\theta = 1^\circ$ and $\Delta\phi = 2^\circ$ within the aforesaid ranges. As the location of CIs is close to $\rho = 9.0$ bohr, the amplitudes of the NACTs are quite prominent in its corresponding θ - ϕ CS. The *ab initio* data points for the three PESs are obtained in C_s symmetry with the MOLPRO package³³ using Dunning's³⁵ correlation consistent *cc-pV5Z* basis set. We performed MCSCF calculations involving the first six (6) electronic states with an active space comprising two (2) electrons in ten (10) active orbitals generating fifty six (56) configuration state functions (CSFs). Taking the reference for the first three (3) singlet states, we subsequently carried out the internally contracted MRCI calculations. The calculated minimum energy of the ground singlet state ($1^1A'$) of H_3^+ at $\rho = 9$ bohrs is -1.175 hartree, appears at $\theta = 74^\circ$ and $\phi = \{55^\circ, 65^\circ, 145^\circ, 155^\circ, 295^\circ, 305^\circ\}$.

These configurations correspond to the inter-particle distances as: $R_1, R_2, R_3 = \{1.41, 8.52, 8.11\}$ bohrs. The ground state ($1^1A'$) energy of singlet H_3^+ appears as -1.0120 hartree at $\theta = 0^\circ$ in the equilateral arrangement with side lengths 6.84 bohrs. At the same geometry the first and second excited states remain degenerate ($1^1E'$) with energy -0.9968 hartree.

The ground ($1^1A'$) and the first excited ($2^1A'$) states exhibit three CIs at $\theta = 70^\circ$ with $\phi = \{60^\circ, 180^\circ, 300^\circ\}$ corresponding to isosceles geometries, whereas for $\theta \geq 70^\circ$, three semi-circular CI seams along $\phi = (30^\circ - 90^\circ), (150^\circ - 210^\circ)$ and $(270^\circ - 330^\circ)$ come into exist. The three CIs formed at $\theta = 70^\circ$ are due to the accidental degeneracy occurring at the three equivalent C_{2v} geometries while the six CI seams start at close to $\theta = 90^\circ$ corresponding to a particular scalene triangular geometry and end again at close to $\theta = 90^\circ$ corresponding to the equivalent scalene geometry traversing through the C_{2v} isosceles geometries. In addition to that,

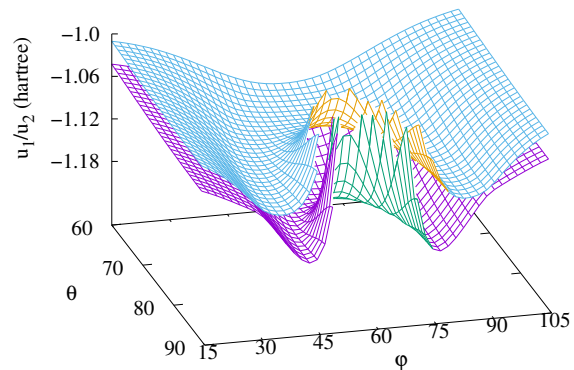


Figure 1 The CI seam between the ground ($1^1A'$) and first excited ($2^1A'$) states.

the pseudo Jahn-Teller (PJT) interaction comes into play between the upper two states ($2^1A'$ and $3^1A'$) at $\phi = \{0^\circ, 120^\circ, 240^\circ\}$. We depict one of the three CI seams between the two lowest singlet adiabatic PESs of H_3^+ system along $\phi = 15^\circ - 105^\circ$ in Figure 1. Since there is three-fold symmetry in the PESs, all the three CI seams are equivalent. On the other hand, the three lowest singlet adiabatic PESs of H_3^+ are depicted in Figure 2 for the fixed value of $\rho = 9$ bohrs over the entire range of θ and ϕ .

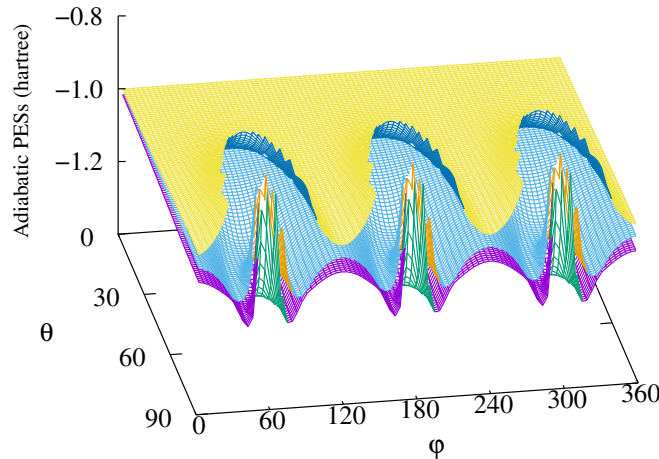


Figure 2 Adiabatic PESs of the lowest three singlet A' states of H_3^+ cluster.

We have employed the so called numerical finite difference method DDR in MOLPRO to calculate the NACTs ($\tau_k^{ij} [k = \theta, \phi], i = j = 1, 2, 3, i < j, i \neq j$) among the states. The ϕ component of the NACT, τ_ϕ^{12} takes up maximum magnitude along the three semi-circular CI seams for $\theta = 70^\circ$ to 90° and at ϕ s having values at $\{30^\circ, 90^\circ, 150^\circ, 210^\circ, 270^\circ, 330^\circ\}$. The corresponding NACT for the θ component (τ_θ^{12}) also blows up along the three CI seams in the same ranges of θ and ϕ as that of τ_ϕ^{12} , touching θ at $\theta \approx 70^\circ$ but unlike τ_ϕ^{12} , it reaches maximum at $\phi = \{60^\circ, 180^\circ, 300^\circ\}$ for $\theta \approx 70^\circ$. The maximum magnitudes of τ_k^{13} and $\tau_k^{23} [k = \theta, \phi]$ are quite smaller in comparison to $\tau_k^{12} [k = \theta, \phi]$. In case of $\tau_k^{23} [k = \theta, \phi]$, they exhibit pseudo-Jahn Teller (PJT) effect around $\theta = 90^\circ$. In Figure 3, the elements of the NACTs between the ground and the first excited state for (a) ϕ and (b) θ components are displayed as functions of the stereographic projections β and γ , which are defined as: $\beta = \sin \theta \cos \phi$ and $\gamma = \sin \theta \sin \phi$.

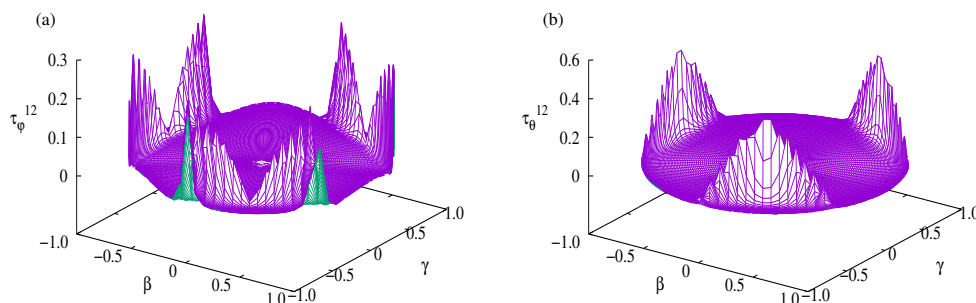


Figure 3 Functional forms of the non-adiabatic coupling (NAC) matrix elements (a) τ_ϕ^{12} and (b) τ_θ^{12} , between the ground and the first excited states as functions of β and γ . The NACTs blow up along the three CI seams.

4. ADT and diabatic potential matrix

The *ab initio* calculated NACTs are substituted in ADT equations (Eqs. 8) and those stiff differential equations are solved by using Backward Differentiation Formula over a 2D grid of geometries represented by 89×180 grid points in hyperspherical coordinates (θ, ϕ) ranging from $\theta = 1^\circ$ to 89° and $\phi = 1^\circ$ to 359° . It is possible to integrate the two sets of coupled $(\theta$ and $\phi)$ differential equations (Eqs. 8) by choosing infinitely different paths and each path will generate different sets of θ - ϕ dependent ADT angles $(\Theta_{12}, \Theta_{23}, \Theta_{13})$.

Though the various sets of ADT angles obtained due to different choice of paths are expected to show gauge invariance, each set of such angles produces different ADT matrix and such matrices will be related through orthogonal transformation.¹⁴ At present case, we consider a rectangular path, where the differential equations for the θ grid are integrated with positive increment from $\theta = 1^\circ$ to 89° for each positive step integration of the differential equations for the ϕ grid from 1° to 359° . The obtained ADT angles are then used to calculate the elements of the ADT matrix. Figure 4 (a) and (b) represent 1D cuts of ADT angles (Θ_{12}) between the ground and the first excited state and ADT matrix elements (A_{11}/A_{22}) along the ϕ coordinate at various θ s $\{= 50^\circ, 70^\circ, 89^\circ\}$, respectively. Figure 4(a) shows that the ADT angle Θ_{12} approaches a magnitude of π for $\theta \geq 70^\circ$ whereas for the same values of θ , the A_{11}/A_{22} elements show six sign flips within the full ϕ range (see Figure 4(b)) which asserts the presence of six CIs. Finally, the elements of the diabatic potential matrix are displayed in Figure 5 which appeared as single-valued, continuous, smooth and symmetric. Only ϕ range $(0^\circ - 120^\circ)$ is used in the Figure 5 due to the overall three-fold symmetry in the CS. In Figure 6 we have depicted the two diagonal elements of the diabatic PESs crossing each other properly along the CI seam at $\phi = 30^\circ - 90^\circ$ and $\theta \geq 70^\circ$.

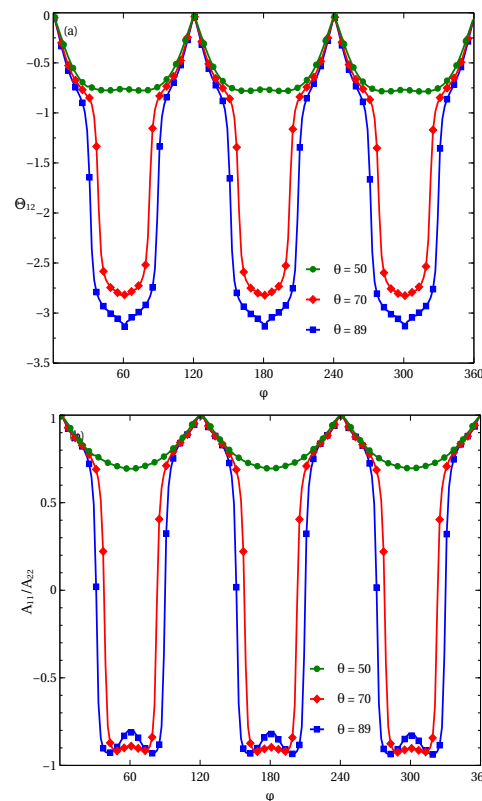


Figure 4 1D cuts of (a) Θ_{12} , (b) A_{11}/A_{22} elements of the ADT matrix as function of ϕ at various θ values.

5. Summary

We have calculated the first three singlet adiabatic PESs of H_3^+ and the NACTs between those states by MOLPRO quantum chemistry package in hyperspherical coordinates for a fixed hyperradius ($\rho = 9$ bohr). The ground ($1^1A'$) and the first excited ($2^1A'$) states exhibit three CIs as function of ϕ at $\theta = 70^\circ$ and six CIs for $\theta \geq 70^\circ$. Moreover, at $\phi = \{0^\circ, 120^\circ, 240^\circ\}$, the states $2^1A'$ and $3^1A'$ exhibit strong PJT interactions, which also contributes to the overall non-adiabaticity of the system. Since the three singlet states ($1^1A'$, $2^1A'$ and $3^1A'$) constitute a sub-Hilbert space over the range of the selected CS, we guarantee the validity of the curl conditions, and thus, construct the diabatic Hamiltonian. The elements of the diabatic PES matrix are found to be single-valued, continuous, symmetric and smooth functions of the hyperangles.

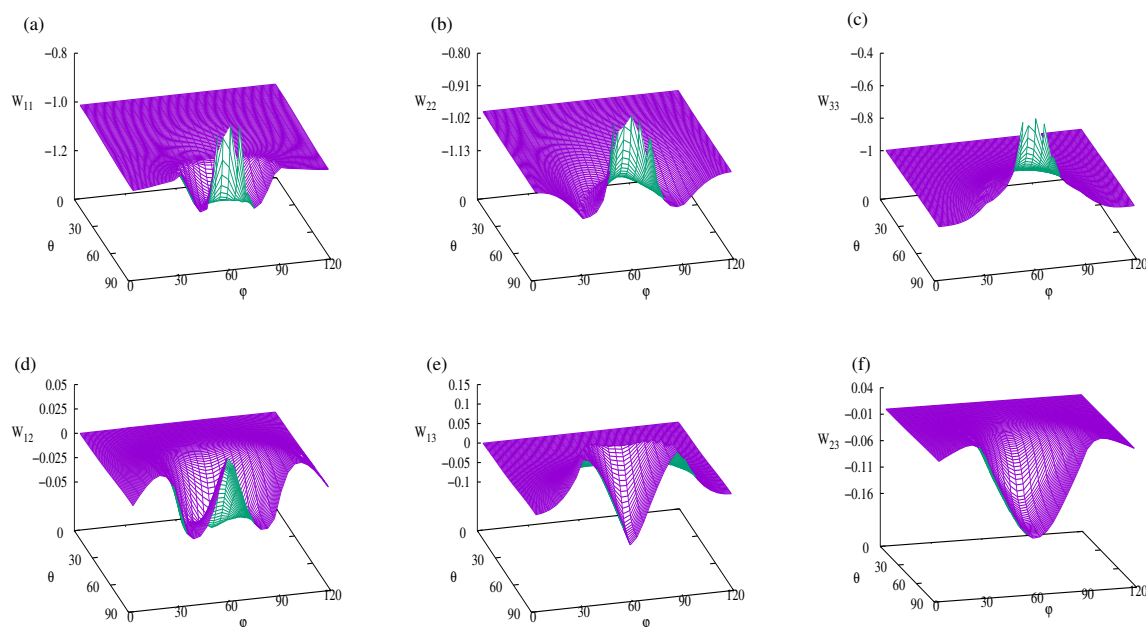


Figure 5 The diabatic PESs (panel (a)-(c)) and the coupling elements (panel (d)-(f)) as functions of θ and ϕ .

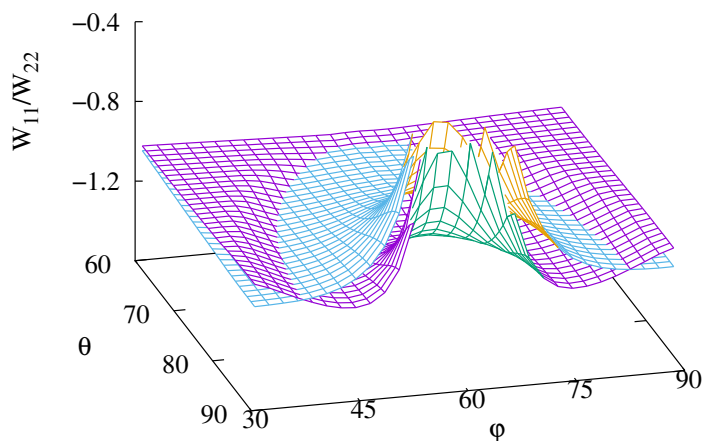


Figure 6 The crossing between the two diagonal elements of diabatic potential energy matrix as functions of θ and ϕ .

6. Acknowledgments

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