Beyond Born-Oppenheimer treatment for the construction of triple-sheeted accurate diabatic Hamiltonian matrix of F+H₂ system

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Abstract. We intend to study the non-adiabatic interactions among the three lowest adiabatic states (1¹A’, 1²A”, and 2²A’) of F+H₂ triatomic reactive system in hyperspherical coordinates for a fixed hyperradius at ρ = 7.5 bohr as functions of hyperangles, θ (0° ≤ θ ≤ 90°) and φ (0° ≤ φ ≤ 360°). The adiabatic potential energy surfaces are calculated using MRCI level of methodology whereas the non-adiabatic coupling terms between those states are calculated from the analytic gradient methods implemented in MOLPRO quantum chemistry package. The ground (1¹A’) and the first excited (1²A”) states exhibit conical intersection (CI) and seam of CI along C₂v geometries, whereas the first (1²A”) and the second (2²A’) excited states undergo Renner-Teller coupling at linear geometries. We carry out adiabatic-to-diabatic transformation (ADT) by solving ADT equations to obtain ADT angles for constructing single-valued, continuous and symmetric 3 × 3 diabatic potential energy matrix so that subsequent accurate scattering calculations can be performed.

1. Introduction
The elementary chemical reaction F+H₂ has been for decades of outstanding interest both from experimental¹–¹³ and theoretical¹⁴–³⁵ aspects. Though the system is limited to three atoms, yet it presents great challenges in obtaining a full quantum description of the reaction, but equally attracts rich experimental probes since this reaction is highly exoergic (~32 kcal mol⁻¹), the energy source for powerful chemical lasers and exhibits interesting quantum mechanical resonances. Early experiments date back to the end of sixties in the last century mainly initiated by studies using chemical lasers¹–³ and chemiluminescence techniques⁴,⁵ followed by high resolution molecular beam experiments by Y. T. Lee and his group⁶,⁷ which provided the first vibrationally resolved differential cross sections for its various isotopic variants. Vib-rotational resolved differential cross section experiments⁸ and calculations⁹ by Toennies et al. also confirmed previous observations. With the advancement of experimental sophistication, higher resolution molecular cross beam studies were carried out during the last decade to investigate energy and angular
dependence of FH and FD products and reaction resonances of this benchmark system. From the theoretical point of view, F+H$_2$ traces a long history of \textit{ab initio} studies with attempts to develop accurate potential energy surfaces (PESs). For more than four decades until now, substantial number of PESs have appeared in the literature. H. F. Schaefer III group was one of the few who came up with the first \textit{ab initio} PESs in 1970s followed by empirical and semiempirical PESs of London-Eyring-Polanyi-Sato (LEPS) type given by Muckerman (M5) and Takayanagi and Sato (TS) and Truhlar group (T5, T5A). Subsequent renewed investigations by Truhlar and co-workers on the \textit{ab initio} treatments of transition state for the title reaction produced modified PESs called SEC5 and SEC6. The global \textit{ab initio} PES constructed by Stark and Werner (SW) could able to draw sophisticated theoretical analysis of the existing high resolution experimental works unlike the previous PESs that failed to account multiple experimental observations. In subsequent works, Werner \textit{et al.} constructed a series of PESs by taking successive corrections in terms of spin-orbit effect of the same system. On the basis of UCCSD(T) (spin unrestricted coupled cluster method with all single and double excitations and perturbative accounts of triple excitations) calculations, D. H. Zhang group gave another family of global PESs that provide good estimates of exothermicity ($\sim$32 kcal mol$^{-1}$), resonance states in reactant channels and reproduce experimental observations like reaction rate constant, branching ratios of the reaction F+HD/H$_2$, forward/backward scattering and peaks due to partial wave resonances of reaction F+HD. For a complete overview and more detailed history of PESs constructed for this system, the authors request the readers to go through the reference section and references therein.

Owing to such wealth of theoretical investigation, it can be inferred that the reaction F+H$_2$ $\rightarrow$ HF+H possesses substantial difficulties for multiple reasons. Firstly, the strong correlation of the eleven electrons that makes the \textit{ab initio} results highly sensitive to the choice on the level of electronic structure calculations and basis sets. Secondly, the spin-orbit coupling effect due to the open-shell F atom, making this particular system one of the prototypes for its study. Lastly, rich non-adiabatic interactions that are present in the system, the investigation of which is going on at present with great interest. Werner \textit{et al.} calculated global PESs for the ground and excited states based on which multisurface scattering calculations were performed. In their work, they concluded about the necessity of including three PESs for a complete description of the reaction. More recently, Das \textit{et al.} have carried out thorough investigation in understanding the role of Jahn-Teller (JT) and Renner-Teller (RT) conical intersections (CIs) in this reaction. While doing so, they have calculated a set of two diabatic PESs based on \textit{ab initio} calculated non-adiabatic coupling terms (NACTs). It was shown that the JT CI is formed by a $\Sigma$-state, assigned as 1A’ and one of the two II-states (of the same symmetry) assigned as 2A’, whereas the RT CIs are formed by the corresponding two degenerate II-states, designated as 2A’ and 1A” along the collinear HHF axis. Thus, it is necessary to go beyond Born-Oppenheimer (BO) picture to encapsulate the non-adiabatic interactions among the various electronic states that are present within the three state sub-Hilbert Space.

One has to take into account the NACTs for performing accurate multi-surface scattering calculations. NACTs along with adiabatic PESs are the two most important outcomes of the BO treatment. NACTs dictate the contributions from the excited electronic states on a molecular process even if it is occurring on the ground state. Since these coupling terms are often blown up in the neighborhood of a CI in the nuclear configuration space (CS), it is convenient to transform the kinetically coupled adiabatic Schrödinger equation (SE) to the \textit{diabatic} representation where potential coupling elements appear as smooth functions of nuclear coordinates. This \textit{adiabatic-to-diabatic} transformation requires two necessary conditions to be fulfilled. Firstly,
the vector fields created by the NACTs have to satisfy the so called Curl Conditions.\textsuperscript{38,39} Secondly, the non-removable components of the NACTs are approximately zero.\textsuperscript{40} Baer\textsuperscript{41} and his co-workers\textsuperscript{42} have carried out detailed beyond BO treatment for two state sub-Hilbert space in which they have formulated diabatic potential energy matrix in terms of adiabatic PESs and adiabatic to diabatic transformation (ADT) angles.\textsuperscript{43-46} Adhikari et al. have generalized the BO treatment for any three/four coupled electronic states, where the explicit form of NACTs and Curl- Divergence equation are derived in order to formulate diabatic Hamiltonian matrix.\textsuperscript{47-53}

We carry out beyond BO treatment for the lowest three states ($1^2A'$, $1^2A''$, and $2^2A'$), which form a sub-Hilbert space, by calculating \textit{ab initio} adiabatic PESs and NACTs, discuss about the nature of JT CI and RT interaction, obtain ADT angles by plugging those NACTs in the ADT equations and thereby, construct smooth, continuous and symmetric diabatic PESs at a fixed $\rho$ as a function of $\theta$ and $\phi$ in hyperspherical coordinates.

2. Theory
A three-state electronic sub-Hilbert space has been considered ($1^2A'$, $1^2A''$, $2^2A'$), which forms a complete space for the present collision process, F+H\textsubscript{2}. The CIs are present among these three states in the nuclear CS. The BO expansion\textsuperscript{36,37} of the molecular wavefunction for this sub-Hilbert space and the total electron-nuclei Hamiltonian in the adiabatic representation are:

$$|\Psi(s_e, s_n)\rangle = \sum_{i=1}^{3} \psi_i(s_n)|\xi_i(s_e|s_n)\rangle,$$

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

$$\hat{T}_{s_n} = -\frac{\hbar^2}{2m} \sum_i \left( \frac{\nabla^2_{s_{n,i}}}{m_i} \right),$$

$$\hat{H}_e(s_e|s_n)|\xi_i(s_e|s_n)\rangle = u_i(s_n)|\xi_i(s_e|s_n)\rangle,$$ (1)

where the eigenfunctions $||\xi_i(s_e|s_n)\rangle|$ of the electronic Hamiltonian, $\hat{H}_e(s_e|s_n)$, are defined by the sets of nuclear ($s_n$) and electronic ($s_e$) coordinates while the eigenvalues, $u_i(s_n)$ depend on nuclear coordinates. $\hat{T}_{s_n}$ is the nuclear kinetic energy (KE) operator and the expansion coefficient, $\psi_i(s_n)$, are the nuclear wavefunctions. Using the BO expanded molecular wavefunction [Eq. (1)] for the given sub-Hilbert space, we can reduce the total molecular time independent SE into the following compact form of kinetically coupled nuclear equation:

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

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

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

respectively. The non-adiabatic coupling matrix elements have the following definition:

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

The validity of the three state sub-Hilbert space make it possible to transform the adiabatic nuclear SE [Eq. (2)] to the diabatic one through an orthogonal transformation, $\psi = A\psi^d$. The required SE in diabatic representation becomes:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi^d + (W - E) \psi^d = 0, \quad W = A^\dagger uA$$ (5)
under the condition:

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

This equation is known as the ADT condition. The model form of \((3\times3)\) \(A\) has to be an orthogonal matrix and the orthonormality conditions demand the fulfillment of six relations involving three independent variables, which are Euler like angles of rotation \([\Theta_{12}(s_n), \Theta_{23}(s_n)\) and \(\Theta_{13}(s_n)]\), commonly called ADT angles. These are the natural requirement to construct the three-state \(A\) matrix for which product of three \((3\times3)\) rotation matrices \(A_{12}(\Theta_{12}), A_{23}(\Theta_{23}),\) and \(A_{13}(\Theta_{13})\) are taken as shown below:

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

The above model form of \(A\) matrix [Eq. (7)] and the anti-symmetric form of \(\vec{\tau}\) matrix [Eq. (3)] are substituted in Eq. (6), where simple manipulations as performed by Baer et al. lead to the following differential 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 form of \(\vec{\tau}\) matrix elements in terms of the 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 \textit{ab initio} calculated NACTs are substituted in Eq. (8) to obtain the ADT angles which along with the adiabatic PESs, are used to calculate the diabatic potential matrix elements as given in Eq. (5). The explicit expressions of \(W\) matrix elements are:

\[
W_{11} = u_1(\cos \Theta_{12} \cos \Theta_{13} - \sin \Theta_{12} \sin \Theta_{13} \sin \Theta_{23})^2 \\
+ u_2(\sin \Theta_{12} \cos \Theta_{13} + \cos \Theta_{12} \sin \Theta_{13} \sin \Theta_{23})^2 + u_3 \sin^2 \Theta_{13} \cos^2 \Theta_{23}, \quad (10a)
\]
\[
W_{22} = u_1 \sin^2 \Theta_{12} \cos^2 \Theta_{23} + u_2 \cos^2 \Theta_{12} \cos^2 \Theta_{23} + u_3 \sin^2 \Theta_{23}, \quad (10b)
\]
\[
W_{33} = u_1 \sin \Theta_{12} \sin \Theta_{13} + \cos \Theta_{12} \sin \Theta_{13} \sin \Theta_{23})^2 \\
+ u_2(\sin \Theta_{12} \sin \Theta_{13} - \cos \Theta_{12} \cos \Theta_{13} \sin \Theta_{23})^2 + u_3 \cos^2 \Theta_{13} \cos^2 \Theta_{23}, \quad (10c)
\]
\[
W_{12} = u_1 \sin \Theta_{12} \cos \Theta_{23}(\cos \Theta_{12} \cos \Theta_{13} - \sin \Theta_{12} \sin \Theta_{13} \sin \Theta_{23}) \\
- u_2 \cos \Theta_{12} \cos \Theta_{23}(\sin \Theta_{12} \cos \Theta_{13} + \cos \Theta_{12} \sin \Theta_{13} \sin \Theta_{23}) \\
+ u_3 \sin \Theta_{13} \sin \Theta_{23} \cos \Theta_{23}, \quad (10d)
\]
\[
W_{13} = u_1 \cos \Theta_{12} \cos \Theta_{13} - \sin \Theta_{12} \sin \Theta_{13} \sin \Theta_{23}) (\cos \Theta_{12} \sin \Theta_{13} + \sin \Theta_{12} \cos \Theta_{13} \sin \Theta_{23}) \\
+ u_2(\sin \Theta_{12} \cos \Theta_{13} + \cos \Theta_{12} \sin \Theta_{13} \sin \Theta_{23})(\sin \Theta_{12} \sin \Theta_{13} - \cos \Theta_{12} \cos \Theta_{13} \sin \Theta_{23}) \\
- u_3 \sin \Theta_{13} \cos \Theta_{13} \cos^2 \Theta_{23}, \quad (10e)
\]
\[
W_{23} = u_1 \sin \Theta_{12} \cos \Theta_{23}(\cos \Theta_{12} \sin \Theta_{13} \sin \Theta_{23}) \\
+ u_2 \cos \Theta_{12} \cos \Theta_{23}(\sin \Theta_{12} \sin \Theta_{13} + \cos \Theta_{12} \cos \Theta_{13} \sin \Theta_{23}) \\
- u_3 \cos \Theta_{13} \sin \Theta_{23} \cos \Theta_{23}. \quad (10f)
\]
3. Ab initio calculation for PESs and NACTs

We have employed hyperspherical coordinates to map the triatomic potential energy surface of FH$_2$ in order to represent all the reaction arrangement channels evenhandedly. The hyperradius $\rho$ solely determines the overall size of the triangle, whereas the two hyperangles $\theta$ ($0 \leq \theta \leq 90^\circ$) and $\phi$ ($0 \leq \phi \leq 360^\circ$) corresponding to spherical latitude and longitude, respectively, describe the shape of the triangle. All the ab initio calculations are carried out in terms of the interparticle distances of the three nuclei that are related to the hyperspherical coordinates $^{54}$ as:

\[
R_1 = \frac{\rho}{\sqrt{2}} d_3 [1 + \sin \theta \cos (\phi + \epsilon_3)]^{1/2}, \quad (11a)
\]
\[
R_2 = \frac{\rho}{\sqrt{2}} d_1 (1 + \sin \theta \cos \phi)^{1/2}, \quad (11b)
\]
\[
R_3 = \frac{\rho}{\sqrt{2}} d_2 [1 + \sin \theta \cos (\phi - \epsilon_2)]^{1/2}, \quad (11c)
\]

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 F+H$_2$, $m_1 = m_F = 19$ amu, $m_2 = m_3 = m_H = 1.008$ amu, $M = 21.016$ amu, $\mu = 0.958$ amu, $d_1 = 1.379$, $d_2 = d_3 = 1$ and $\epsilon_2 = \epsilon_3 = 92.91^\circ$. $R_1$ and $R_3$ are the bond distances between the F atom and the two H atoms whereas $R_2$ is between the two H atoms. At $\phi = 0^\circ$ and $180^\circ$, the two F-H bonds are equivalent and the geometries attain C$_2v$ symmetry for all $\theta's$. For, $\theta = 0^\circ$, the triangle remains isosceles since it again goes to C$_2v$ symmetry and the shape is constant for all $\phi's$, whereas $\theta = 90^\circ$ corresponds to the collinear arrangement of the triatom. At the collinear geometries, the arrangement is HHF for $87.1^\circ < \phi < 272.9^\circ$, while for other values of $\phi$, the arrangement is HFH.

We have calculated the three lowest adiabatic PESs (1$^2A'$, 1$^2A''$, 2$^2A'$) of the system and the NACTs between those states by MOLPRO quantum chemistry package $^{55}$ as functions of hyperangles, $\theta$ ($0 \leq \theta \leq 90^\circ$) and $\phi$ ($0 \leq \phi \leq 360^\circ$) for a fixed value of hyperradius $\rho$ = 7.5 bohr. The ab initio data points for those three PESs are calculated in C$_1$ symmetry using Dunning’s correlation consistent quintuple zeta (cc-pV5Z) basis set. The MCSCF calculations are performed involving the first three (3) electronic states firstly with nine (9) electrons being distributed over ten (10) active orbitals followed by same level of calculations using those orbitals with an active space of seven (7) electrons distributed over eight (8) active orbitals. Then, these orbitals are used as reference for internally contracted MRCl calculations with the same active space (7 electrons in 8 active orbitals) for the three (3) electronic states. The three adiabatic states correlate to 2$^2\Sigma^+$ and 2$^2\Pi$ states in the collinear arrangements. The 2$^2\Sigma^+$ and one of the 2$^2\Pi$ states at collinear geometry form a symmetry allowed accidental CI at jacobi coordinates $R = 5.45$ bohr and $r = 1.4$ bohr, where $r$ is the distance between the two H atoms and $R$ being the distance between the center of mass of H$_2$ molecule and F atom. This is in agreement

![Figure 1](image-url)
Figure 2. 1D cuts of three adiabatic singlet states as function of $\phi$ for different $\theta$s: (a) $10^\circ$, (b) $24^\circ$, (c) $40^\circ$, (d) $50^\circ$, (e) $70^\circ$ and (f) $90^\circ$. The dashed red line represents the ground state ($1^2A'$), the blue solid line depicts the first excited state ($1^2A''$) and the meagenda circles represent the second excited state ($2^2A'$). All the energies are in hartree scaled with respect to the asymptote. At around $\theta = 24^\circ$ and $\phi = 180^\circ$, the lowest two states interact strongly while at $\theta = 90^\circ$, the upper two states exhibit RT interactions.
with the findings of Stark and Werner in their article on SW PES. To map the result into the hyperspherical coordinates, we varied $\rho$ and $\phi$ keeping $\theta$ at 90° such that the particles remain at collinear configurations. Figure 1 depicts collinear arrangements along the hyperradius $\rho$, where the location of CI is at $\rho = 7.5$ bohr, $\phi = 164.4^\circ$ and $\theta = 90^\circ$ (corresponding to $R = 5.45$ bohr and $r = 1.4$ bohr). At $\rho > 7.5$ bohr, the $^2\Pi$ state is lower than that of $^2\Sigma$ state, where $\rho < 7.5$ bohr, the two states cross each other. This is the main reason we perform calculations at $\rho = 7.5$ bohr in order to scan the nature of CIs in $\theta - \phi$ space at non-linear geometries through our study of NACTs. Calculations in $\theta - \phi$ space at other values of $\rho$ are going on so that a set of global multisheeted diabatic PESs can be constructed.

### Table 1. Comparison of the ground state energies of F+H$_2$ system in different geometries at $\rho = 7.5$. All the energies are in hartree units, scaled with respect to the asymptote.

| $\theta$ | $\phi$ | Present work | SW |
|---------|-------|-------------|----|
| 0°      | 0°    | 0.1723      | 0.1723 |
| 45°     | 60°   | 0.1064      | 0.1073 |
| 45°     | 120°  | 0.1182      | 0.1178 |
| 60°     | 60°   | 0.0320      | 0.0333 |
| 60°     | 120°  | 0.0599      | 0.0612 |
| 75°     | 60°   | -0.0362     | -0.0361 |
| 75°     | 120°  | 0.0014      | 0.0018 |
| 89°     | 60°   | -0.0505     | -0.0495 |
| 89°     | 120°  | -0.0214     | -0.0210 |

The ground state ($^12A'$) energy of F+H$_2$ appears as 0.1722978 hartree at $\theta = 0^\circ$ in which the two F-H bonds are equivalent having values 5.31 bohr and the H-H bond is 7.31 bohr leading to $C_{2v}$ geometries for all values of $\phi$. At the same geometries, the first and the second excited states have energies 0.1722928 and 0.1751432 hartree, respectively. The 1D potential energy curves of the three adiabatic states as function of $\phi$ for various $\theta$s are presented in Figure 2. We compare our ground state ($^12A'$) PES of F+H$_2$ at $\rho = 7.5$ bohr, which has been calculated without the inclusion of spin-orbit coupling, with that of the SW PES for few geometries in Table 1. In Table 2 we compare the obtained collinear barrier with earlier calculations.

### Table 2. Comparison of the calculated collinear barriers (in KCal mol$^{-1}$) with earlier calculations.

| Collinear barrier |
|-------------------|
| This work         | 1.824 |
| SW$^{22}$         | 1.921 |
| ASW$^{24}$        | 1.971 |
| FXZ$^{26}$        | 2.222 |
| SEC5$^{20}$       | 1.570 |

We have employed State-Averaged MCSCF (SA-MCSCF) analytic gradient method implemented in MOLPRO to calculate the NACTs ($\tau_k^{ij}[k = \theta, \phi], i = j = 1, 2, 3, i < j, i \neq j$)
among the three states. The strong non-adiabatic interactions between the ground \((1^2A')\) and the first excited \((1^2A'')\) states lead to one CI seam at \(\phi = 0^\circ\) for \(\theta\) starting from close to \(10^\circ\) to all along \(90^\circ\), and one CI at region \(\phi = 180^\circ\) and \(\theta \approx 25^\circ\). The former one at \(C_{2v}\) geometries is termed as \(C_{2v}\) seam. In this case, with increasing values of \(\theta\) from \(10^\circ\) to \(90^\circ\), the F-H\(_2\) perpendicular distance shortens and finally reduces to zero at \(\theta = 90^\circ\), which is a collinear arrangement. The latter CI also arises at \(C_{2v}\) geometry but located around a specific point \((\phi = 180^\circ\) and \(\theta \approx 25^\circ\)), where the F-H distances become \(\approx 2.8\) bohr and H-H distance is \(\approx 3.1\) bohr.

![Figure 3](image-url)

**Figure 3.** Functional forms of the \(\tau_{ij}^{\theta\phi}\) as plotted in terms of \(\theta\) and \(\phi\) for \(\rho = 7.5\) bohr. (a) \(\tau_{12}^{\theta\phi}\), representing the singularities at \(C_{2v}\) seams. (b) and (c) are \(\tau_{13}^{\theta\phi}\) and \(\tau_{23}^{\theta\phi}\), depicting the PJT and RT interactions, respectively.

In addition, the first \((1^2A'')\) and the second excited state \((2^2A')\) exhibit RT interactions which are evident at linear geometries for \(\theta = 90^\circ\) and \(\phi\) close to \(180^\circ\). Moreover, the ground state and the second excited state undergo pseudo Jahn-Teller (PJT) interaction at the same geometries \((\theta = 90^\circ\) and \(\phi\) close to \(180^\circ\)). Figures 3 and 4 display the \(\theta\) and \(\phi\) components of the NACTs, respectively, for each pair of states that enable us to figure out the JT-type and RT CIs as well as PJT interactions.
4. ADT and diabatic potential matrix

We substitute the \textit{ab initio} calculated NACTs in Eq. (8) and integrate those differential equations by Backward Differentiation Formula over a 2D grid of geometries represented by $46 \times 180$ grid points in hyperspherical coordinates $\theta$ and $\phi$. It is established that the solutions for the two sets of coupled differential equations (for $\theta$ and $\phi$) are not unique and depend on the contour of integration. Each contour will generate different sets of $\theta - \phi$ dependent ADT angles ($\Theta_{12}, \Theta_{13}, \Theta_{23}$). The various sets of ADT angles thus obtained due to different choices of paths show gauge invariance and the different ADT matrices appear related through orthogonal transformation. In the present study, we consider a rectangular path, where the differential equations for the $\theta$ grid are integrated with positive increment from $\theta = 0^\circ$ to $90^\circ$ for each positive step integration of the differential equations for the $\phi$ grid from $0^\circ$ to $360^\circ$. Figure 5 displays the functional form of the calculated ADT angles for the ground-first excited state ($\Theta_{12}$), ground-second excited states ($\Theta_{13}$) and the first-second excited states($\Theta_{23}$). The ADT angle, $\Theta_{12}$ attains the numerical value of $\pi$ at $\phi = 0^\circ/360^\circ$ establishing the JT-type CI seam at
Figure 5. The functional forms of the ADT angles solved on a 2D contour integral as functions of $\theta$ and $\phi$ for $\rho = 7.5$ bohr. (a) $\Theta_{12}$ attains $\pi$ in magnitude and in change in magnitude at the corresponding $C_{2v}$ seams. (b) and (c) $\Theta_{13}$ and $\Theta_{23}$ attain $\pi$ and $2\pi$ corresponding to the PJT and RT interaction respectively.
those geometries.\textsuperscript{44,45} Moreover, at $\phi = 180^\circ$, the overall change in numerical value of $\Theta_{12}$ is $\pi$ at the asymptotic $\theta (= 90^\circ)$ depicting the other $C_{2v}$ CI. On the other hand, $\Theta_{23}$ attains $2\pi$ in the region of RT coupling at $\theta = 90^\circ$ and $\phi$ close to $180^\circ$.\textsuperscript{46}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{diabatic_coupling_elements}
\caption{The diabatic coupling elements among the three states as functions of $\theta$ and $\phi$.}
\end{figure}

Finally, in Figure 6, the elements of the diabatic potential matrix are displayed which appear as single-valued, continuous, smooth and symmetric. In the diabatic representation, the crossing of the lowest two PESs is evident from Figure 7 along the $C_{2v}$ seams, while the coupling elements are now analytic functions of nuclear coordinates representing the inter-state mixing in the diabatic representation.
Figure 7. The crossing of diabatic PESs of ground and the first excited states as functions of $\theta$ and $\phi$.

5. Summary
We have calculated the lowest three adiabatic states of F+H$_2$ namely, the $1^2A'$, $1^2A''$ and $2^2A'$ states without including the spin-orbit coupling and the NACTs between those states using MOLPRO quantum chemistry package in hyperspherical coordinates for a fixed hyperradius at $\rho = 7.5$ bohr. It has been found that the states interact at various regions of the nuclear CS resulting into CI seams, PJT interactions and RT couplings. The ground and the first excited states undergo JT-type interaction to form CI seam at $\phi$ close to 0° and 360° while $\theta$ from 10° all along to 90° and CI at the region $\{\phi = 180^\circ, \theta \approx 25^\circ\}$. The first and the second excited states show RT couplings at $\theta = 90^\circ$ and $\phi$ around 180°, whereas the ground and the second excited states have PJT interactions found at regions close to $\{\theta = 90^\circ, \phi = 180^\circ\}$. These interactions are validated by the calculations of ADT angles which gave the theoretically predicted numerical value, i.e. $\pi$ for JT-type CI$^{44,45}$ and $2\pi$ for RT coupling.$^{46}$ Since these three states constitute a sub-Hilbert space over the range of selected CS, the curl conditions are obeyed and the diabatic potential matrix elements are constructed using the obtained ADT angles. It turned out that the elements of the diabatic PES matrix are single-valued, smooth and symmetric and can be represented by analytic functions of the hyperangles $\theta$ and $\phi$ unlike the NACTs in adiabatic representation.

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