Beyond Born–Oppenheimer Constructed Diabatic Potential Energy Surfaces for HeH_2^+

Koushik Naskar[1], Satyam Ravi[1,2], Satrajit Adhikari[1,*], Michael Baer[3], and Narayanasami Sathyamurthy[4]

[1]School of Chemical Sciences, Indian Association for the Cultivation of Science
2A & 2B Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, West Bengal, India

[2]School of Advanced Sciences and Languages VIT Bhopal University, Bhopal, 466114, India

[3]The Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

[4]Indian Institute of Science Education and Research Mohali, SAS Nagar, Manauli 140306, India

*E-mail: pcsa@iacs.res.in

Poster presenter's e-mail: pckn@iacs.res.in

Beyond Born-Oppenheimer (BBO) Theory

Molecular Schrodinger Equation:

$$\hat{H}(e,n)\left|\Psi(e,n)\right\rangle = E\left|\Psi(e,n)\right\rangle$$

Molecular Hamiltonian:

$$\hat{H}(e,n) = \hat{T}_n(n) + \hat{H}_e(e;n)$$

Total molecular wave function:

$$\Psi(e,n) = \sum_{i=1}^{N} \psi_i(n)\xi_i(e;n)$$

Electronic Schrodinger Equation:

$$\hat{H}_e(e;n)\xi_i(e;n) = u_i(n)\xi_i(e;n)$$

Schrodinger Equation in Adiabatic Representation:

$$\left[-\frac{1}{2}\left(\vec{\nabla}+\vec{\tau}\right)^2 + \left(\boldsymbol{u}-\boldsymbol{E}\right)\right]\boldsymbol{\psi} = 0$$

Non-Adiabatic Coupling Terms (NACTs)

$$\vec{\tau}_{ij} = \left\langle \xi_i \left| \vec{\nabla} \right| \xi_j \right\rangle$$

NACTs from Hellmann-Feynman Theorem:

$$\vec{\tau}_{ij} = \frac{\left\langle \xi_i \left| \vec{\nabla}_n \hat{H}_e \right| \xi_j \right\rangle}{\left(u_j - u_i\right)}$$

Cauchy's Residue Theorem

$$\int_0^{2\pi} \tau_{ij}^{\phi}(\phi)\, d\phi = n\pi$$

1. H. Hellmann, *Einfuhrang in die Quantenchemie* (Franz Duetiche, Leipzig, 1937)
2. R. Feynman, *Phys. Rev.* **56**, 340 (1939); S. T. Epstein, *Am. J. Phys.* **22**, 613 (1954)
3. A.L. Cauchy, "Oeuvres complètes, Ser. 1" , *Paris* **4** (1890)

Adiabatic to Diabatic Transformation (ADT):

Transforming the nuclear wave function $\psi(s_n) = A(s_n)\phi^d(s_n)$

The ADT matrix, ***A*** satisfies the **ADT condition** $\vec{\nabla}_n A + \vec{\tau} A = 0$

Schrodinger Equation in diabatic representation, $\left[-\frac{1}{2}\nabla^2 + (W - E)\right]\phi^d = 0$

Diabatic Potential Energy (PE) matrix, $W = A^{\dagger} u A$

- The adiabatic-to-diabatic transformation matrix, ***A*** is orthogonal

- ***A*** matrix for a 2 state problem $\begin{pmatrix} \cos\Theta_{12} & \sin\Theta_{12} \\ -\sin\Theta_{12} & \cos\Theta_{12} \end{pmatrix}$ Θ_{12} is the ADT angle

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

- For three state problem, three Euler like ADT angles are required to construct the ADT matrix:

$$A = \begin{pmatrix} \cos\Theta_{12} & \sin\Theta_{12} & 0 \\ -\sin\Theta_{12} & \cos\Theta_{12} & 0 \\ 0 & 0 & 1 \end{pmatrix}.\begin{pmatrix} \cos\Theta_{13} & 0 & \sin\Theta_{13} \\ 0 & 1 & 0 \\ -\sin\Theta_{13} & 0 & \cos\Theta_{13} \end{pmatrix}.\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\Theta_{23} & \sin\Theta_{23} \\ 0 & -\sin\Theta_{23} & \cos\Theta_{23} \end{pmatrix}$$

❑ Features of Adiabatic to Diabatic Transformation:

- For a *N* dimensional electronic manifold, the ADT matrix can be considered as a product of elementary rotation matrices constituted with mixing angles between any two electronic states for the N-state sub-Hilbert space (SHS).

$$\mathrm{A} = P_n\{\mathrm{A}^{12}(\Theta_{12}).\mathrm{A}^{13}(\Theta_{13}).\mathrm{A}^{23}(\Theta_{23}).....\mathrm{A}^{N-1,N}(\Theta_{N-1,N})\},\ n=1,...\Lambda!; \quad \Lambda = {}^{N}C_2 = \frac{N(N-1)}{2}$$

- Elementary rotation matrices A^{mn} are given by :

$$\left[\mathrm{A}^{mn}(\Theta_{mn})\right]_{ij} = \delta_{ij}; \quad \{i,j\} \neq \{m,n\}.$$

$$\left[\mathrm{A}^{mn}(\Theta_{mn})\right]_{mm} = \cos\Theta_{mn} = \left[\mathrm{A}^{mn}(\Theta_{mn})\right]_{nn}; \quad m \neq n$$

$$\left[\mathrm{A}^{mn}(\Theta_{mn})\right]_{mn} = \sin\Theta_{mn} = -\left[\mathrm{A}^{mn}(\Theta_{mn})\right]_{nm}; \quad m \neq n$$

$$\mathrm{A}^{14}(\Theta_{14}) = \begin{pmatrix} \cos\Theta_{14} & 0 & 0 & \sin\Theta_{14} \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\sin\Theta_{14} & 0 & 0 & \cos\Theta_{14} \end{pmatrix}$$

- Using the ADT condition we get Λ unique coupled differential equation in the form:

$$\vec{\nabla}_n \boldsymbol{A} + \vec{\tau}\boldsymbol{A} = \boldsymbol{0} \quad \Rightarrow \quad \vec{\nabla}_n \Theta_{ij} = \sum_{m=1}^{\Lambda} c^{(m)} \vec{\tau}_{(m)}$$

1. M. Baer, *Chem. Phys. Letters*, **35,** 112 (1975)
2. M. Baer, *Chem. Phys. Letters*, **35,** 112 (1975).
3. Z. H. Top and M. Baer, *J. Chem. Phys.* **66**, 1363 (1977).
4. K. Naskar, S. Mukherjee, B. Mukherjee, S. Ravi, S. Mukherjee, S. Sardar and S. Adhikari, *J. Chem. Theory Comput.*, **16**, 1666−1680 (2020).

Application of BBO Theory for Scattering Processes: *Ab - initio* PESs, NACTs and Diabatic PESs of HeH_2^+ system

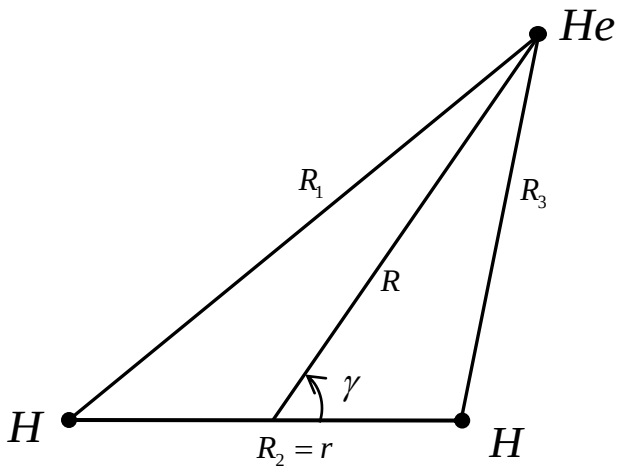
- The *ab–initio* calculations on the four lowest singlet states of HeH_2^+ ($1^1A'$, $2^1A'$, $3^1A'$ and $4^1A'$) are performed by **MOLPRO - 2018** quantum chemistry package in hyperspherical coordinate as a function hyperangles (θ, φ) for fixed values of hyperradius (ρ)

- MCSCF calculation is performed with three (3) electrons distributed over eight (8) orbitals followed by MRCI calculation using **cc- pVQZ** basis set.

$$R_1 = \frac{\rho}{\sqrt{2}} d_3 \left[1 + \sin\theta \cos(\varphi + \varepsilon_3)\right]^{1/2},$$

$$R_2 = \frac{\rho}{\sqrt{2}} d_1 \left[1 + \sin\theta \cos\varphi\right]^{1/2},$$

$$R_3 = \frac{\rho}{\sqrt{2}} d_2 \left[1 + \sin\theta \cos(\varphi - \varepsilon_2)\right]^{1/2}.$$

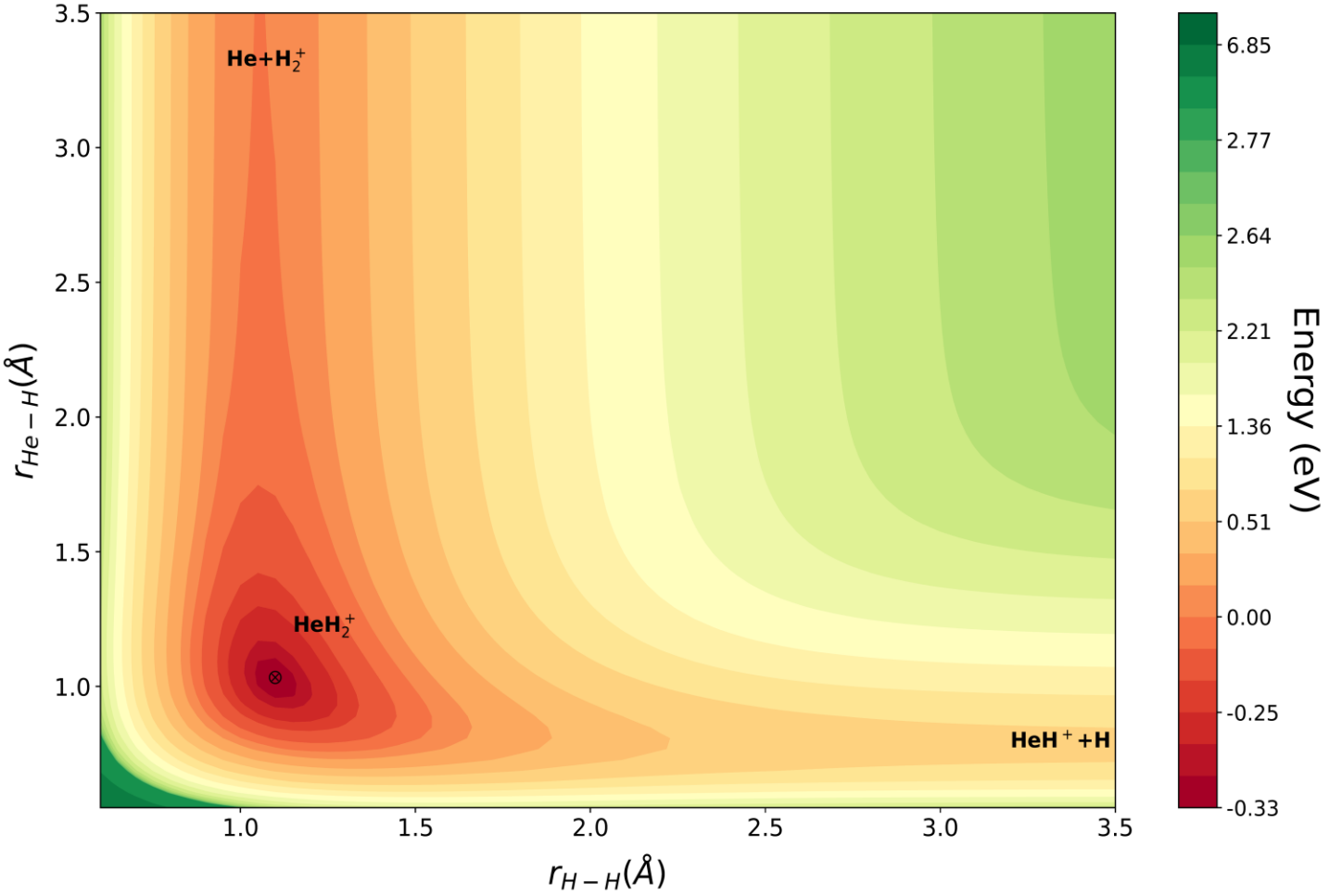


$$d_i = \sqrt{m_i(m_j + m_k)/\mu M} \qquad \mu = \sqrt{m_1 m_2 m_3 / M}$$

$$\varepsilon_3 = 2\tan^{-1}(m_2/\mu) \qquad \varepsilon_3 = 2\tan^{-1}(m_2/\mu)$$

1. B. R. Johnson, J. Chem. Phys **73**, 5051, 1980

Adiabatic PESs of HeH_2^+ system



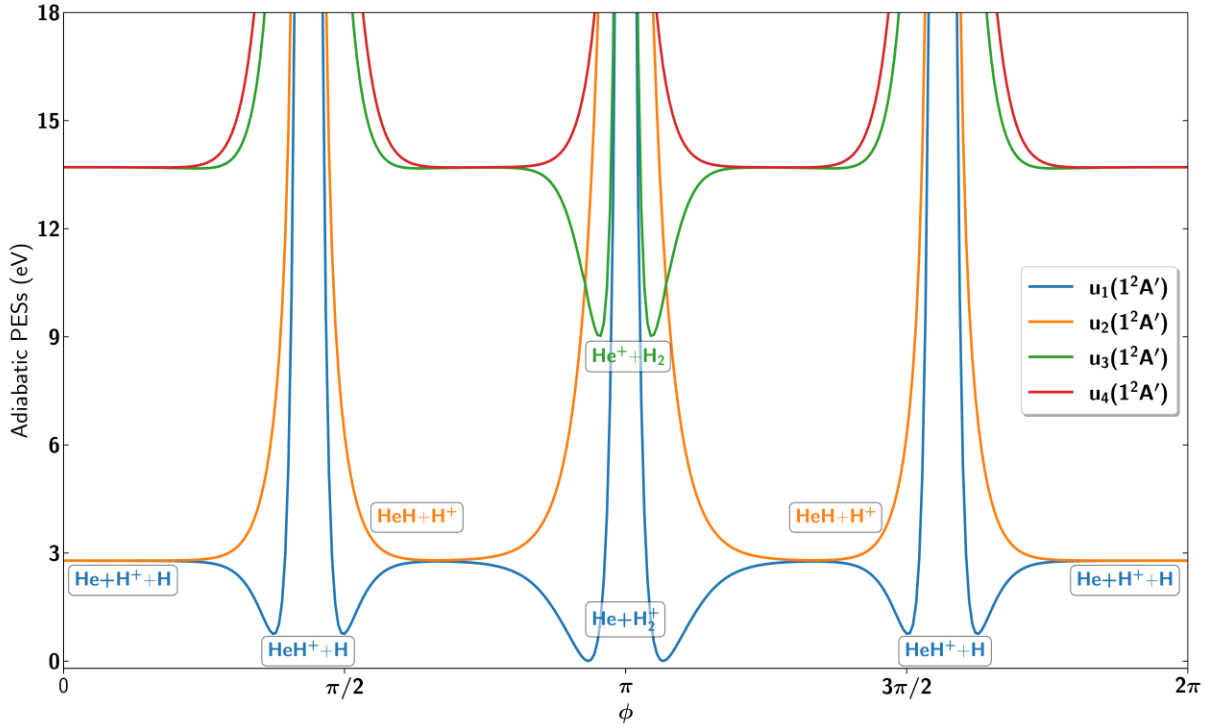
Global minima	
r_{HH}	1.09 Å
r_{HeH}	1.02 Å
V	-0.34 eV

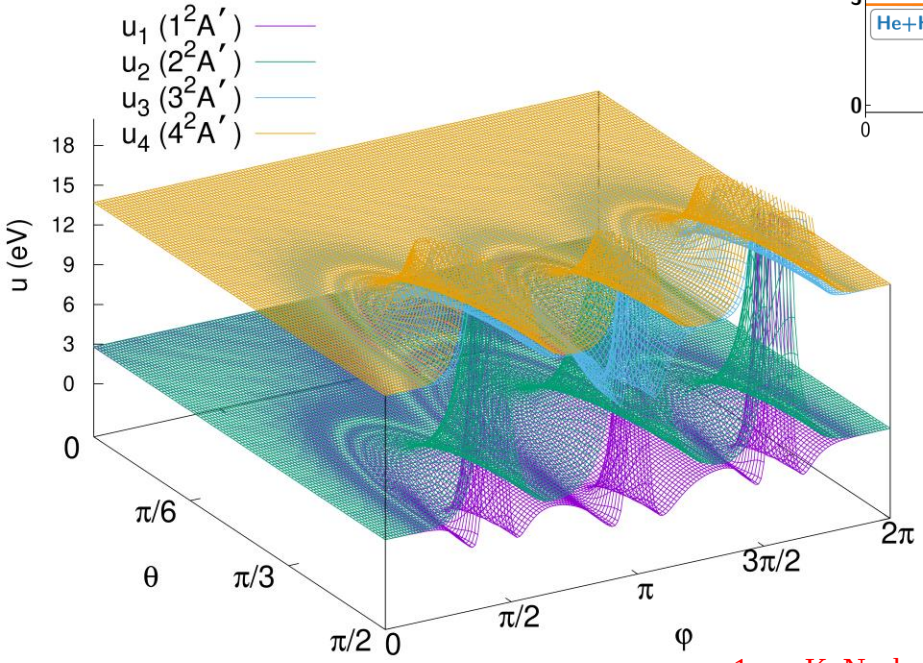
➢ Adiabatic ground electronic state of the HeH_2^+ system in collinear geometry

1. K. Naskar, S. Ravi, S. Adhikari, M. Baer and N. Sathyamurthy; *J. Phys. Chem. A*, **127,** 3832 (2023)

Adiabatic PESs of HeH_2^+ system

Different channels for the HeH_2^+ system at asymptotic ρ

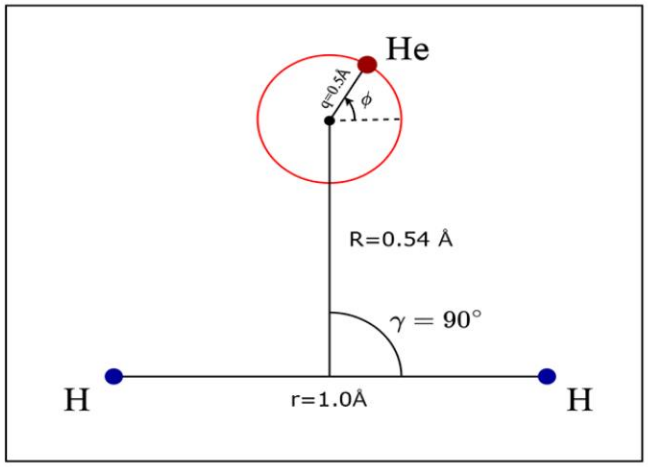




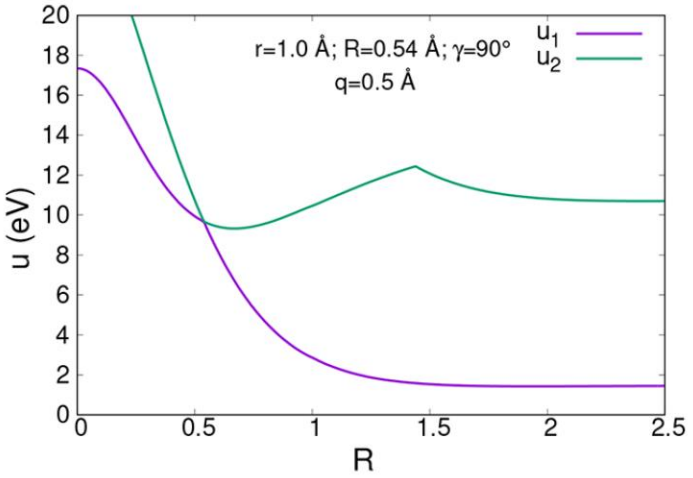
Adiabatic PESs for the HeH_2^+ system in hyperspherical coordinate

1. K. Naskar, S. Ravi, S. Adhikari, M. Baer and N. Sathyamurthy; *J. Phys. Chem. A*, **127,** 3832 (2023)

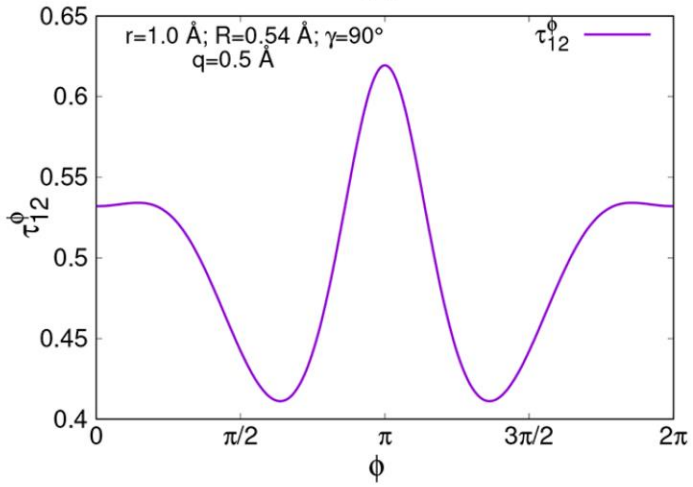
BBO Theory: Locating the conical intersections



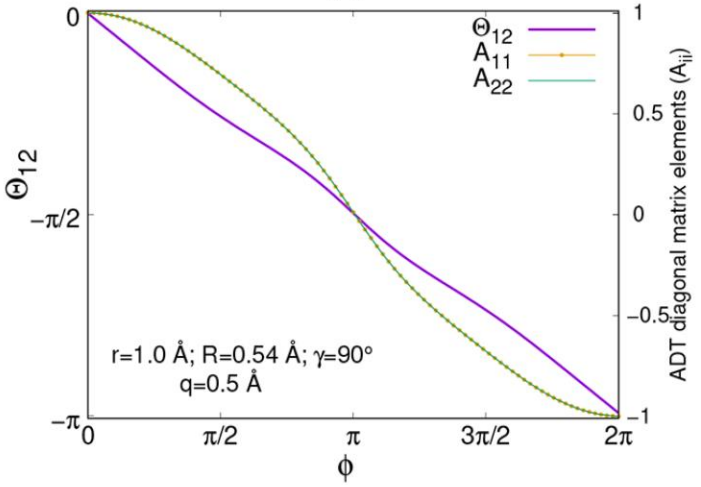
(a)



(b)



(c)

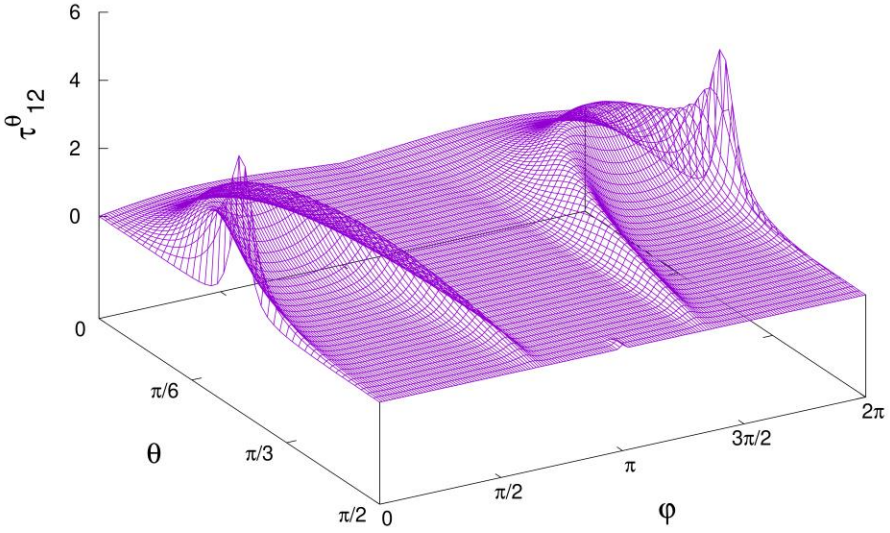


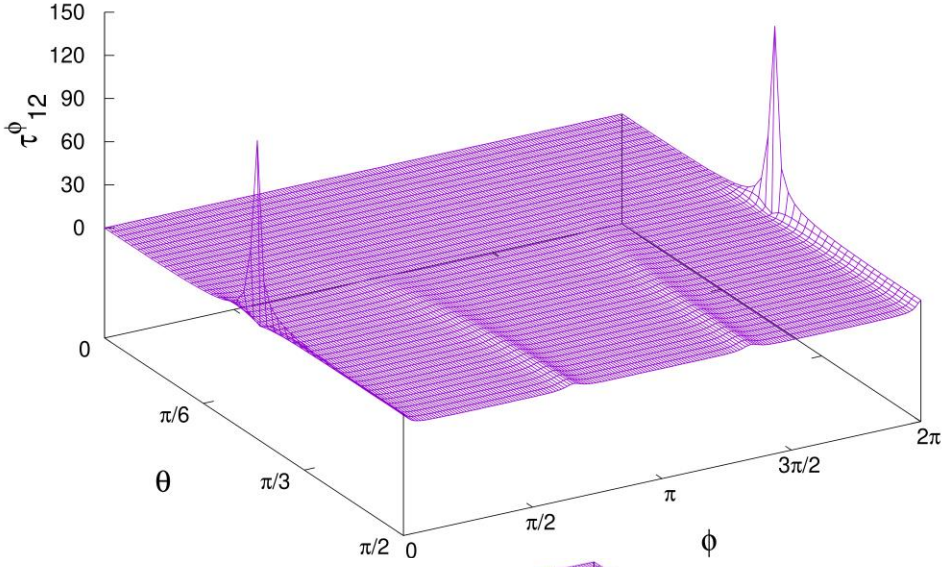
(d)

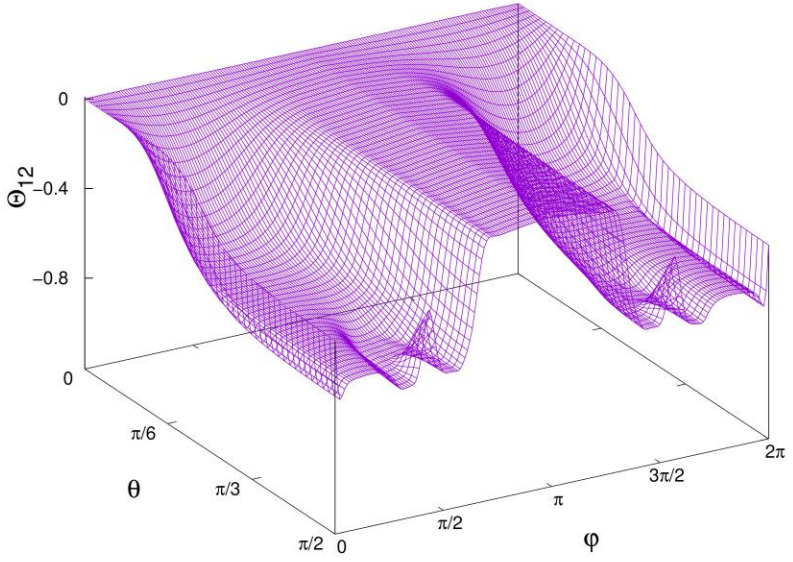
CI between ground and first excited state in C_{2v} configuration

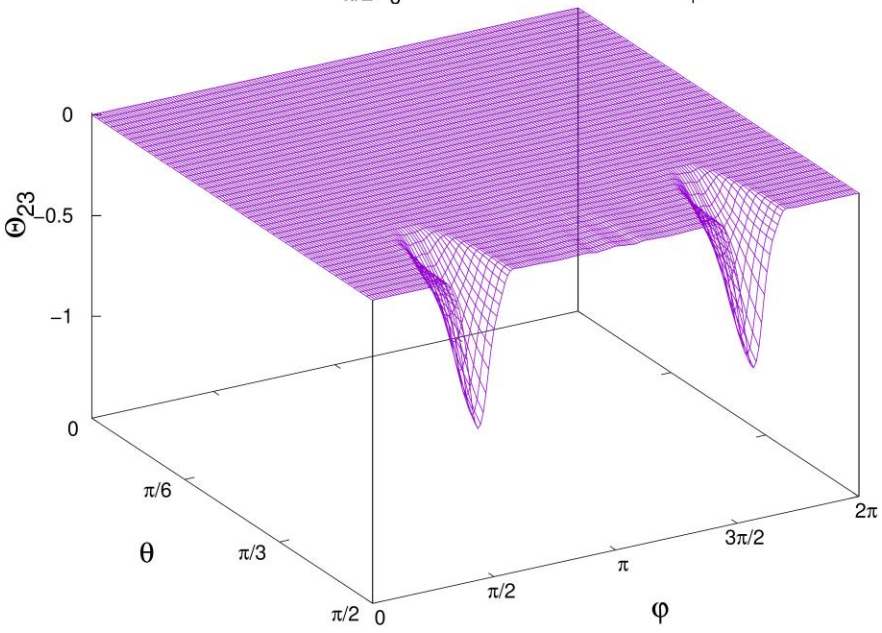
1. K. Naskar, S. Ravi, S. Adhikari, M. Baer and N. Sathyamurthy; *J. Phys. Chem. A*, **127,** 3832 (2023)

NACTs and ADT Angles of HeH_2^+ system



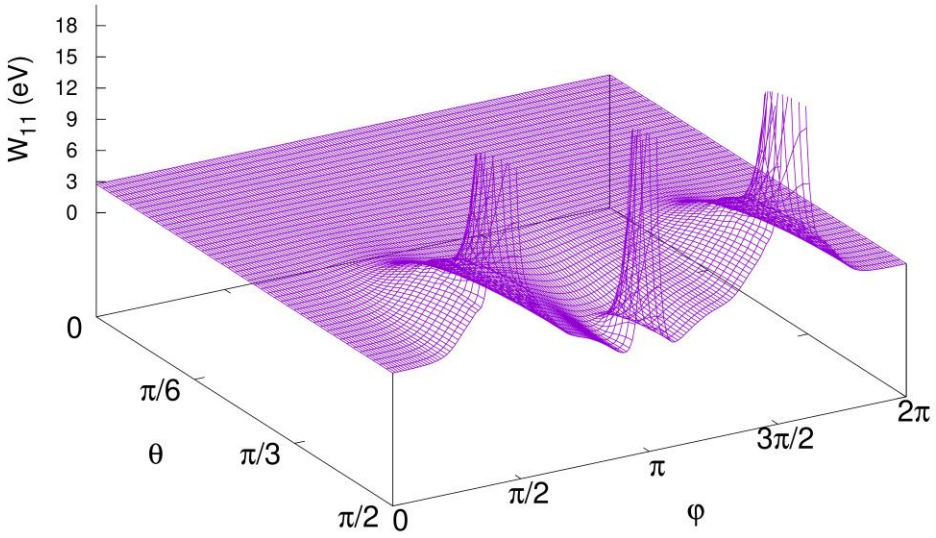


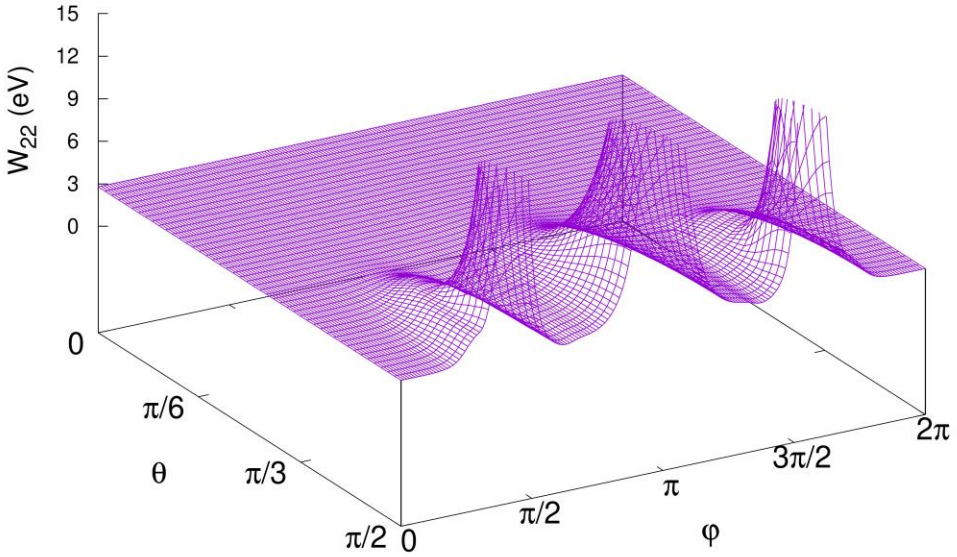


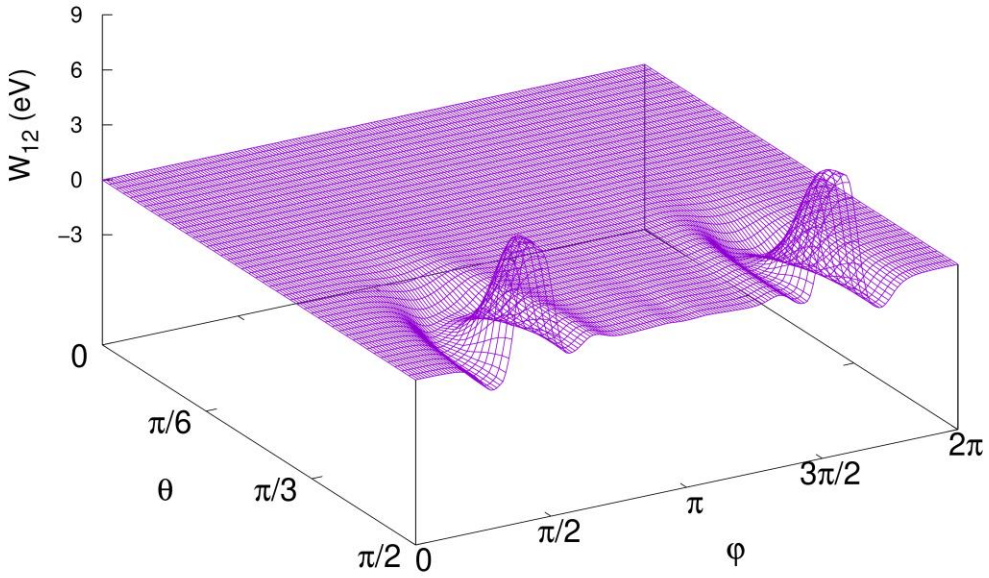


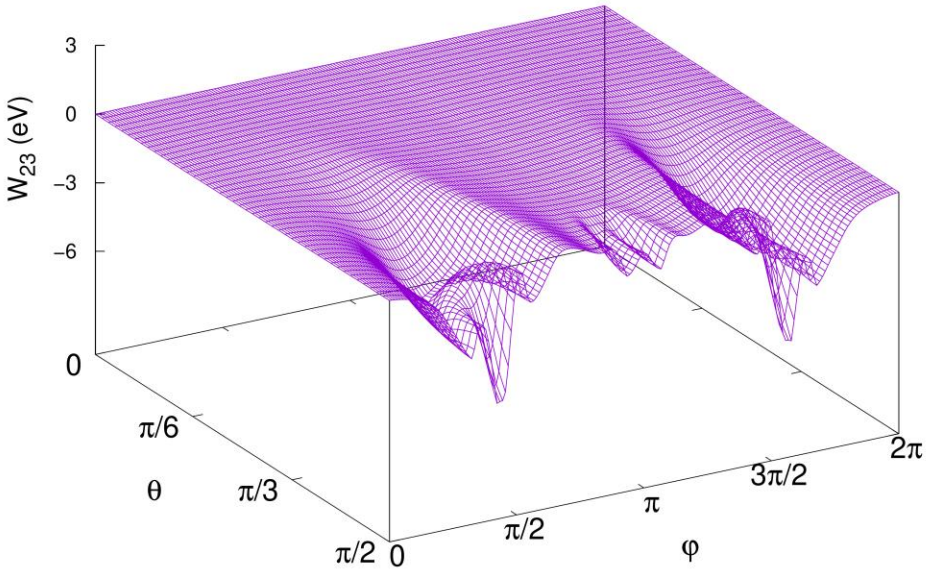
1. K. Naskar, S. Ravi, S. Adhikari, M. Baer and N. Sathyamurthy; *J. Phys. Chem. A*, **127,** 3832 (2023)

Diabatic PESs and couplings of HeH_2^+ system









1. K. Naskar, S. Ravi, S. Adhikari, M. Baer and N. Sathyamurthy; *J. Phys. Chem. A*, **127,** 3832 (2023)

Summary & Future Plans

- Ab-initio based adiabatic PESs and NACTs are calculated for lowest four states of HeH_2^+ system.
- Conical intersection (CI) is located between the states in collinear as well as C_{2v} configurations is located and validated by integrating the NACTs along appropriately chosen contours where the resulting ADT angle reaches multiple integers of π.
- ADT angles are determined by solving the ADT equations to construct the diabatic potential matrix for the HeH_2^+ system which are smooth, single-valued, continuous, and symmetric.

Future Plans

- Utilize the four state diabatic potential matrix to study the ground state proton transfer reaction $He+H_2^+ \rightarrow HeH^+ + H$ as well as the excited state hydrogen transfer reaction $He^+ + H_2 \rightarrow HeH^+ + H$

Acknowledgment

K.N. thanks CSIR, India [Grant No. 09/080(1068)/2018-EMR-I] for funding. SR thanks VIT Bhopal for the seed grant, Support for Excellence in Academic Research (SPEAR), (File No: VITB/SEEDGRANT/2022/08). S.A. acknowledges the SERB (Project No. CRG/2019/000793) for the research funding. S.A. also acknowledges IACS for the CRAY super-computing facility.