Jahn-Teller effect among electronic resonant states of H_3

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Molecular Physics

Born-Oppenheimer approximation - electrons move fast, nuclei moves slow

Step 1. Solving for the electronic Hamiltonian

$V_i(Q) = \langle \phi_i \mid \mathcal{H}_{el} \mid \phi_i \rangle$ – adiabatic potential energy curves/surface

Step 2. Hamiltonian describing the nuclei

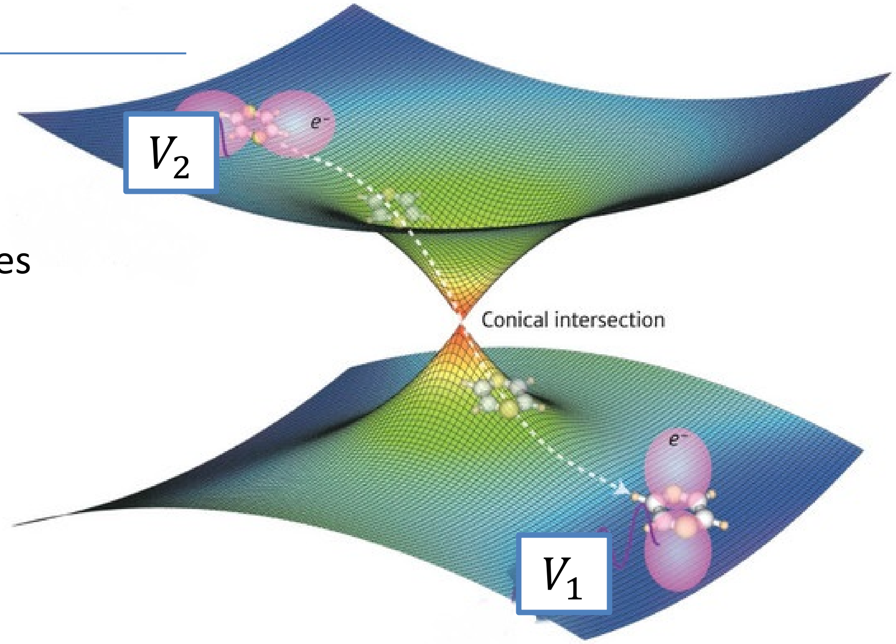
$\mathcal{H} = T_N + V_i + F(\tau)$

Non-adiabatic coupling: $\tau_{ij}(Q) = \langle \phi_i \vert \nabla \vert \phi_j \rangle$

Conical Intersection

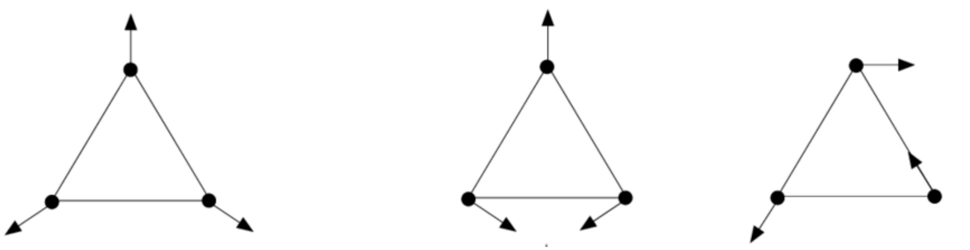
- Degeneracy in the potential energy surfaces
- Non-radiative transitions between electronic states
- The non-adiabatic coupling diverges
- Geometric phase (Berry phase)

$\oint \langle \phi_i \vert \nabla \vert \phi_i \rangle dQ = \pi \qquad \vert \phi_i \rangle \rightarrow - \vert \phi_i \rangle$



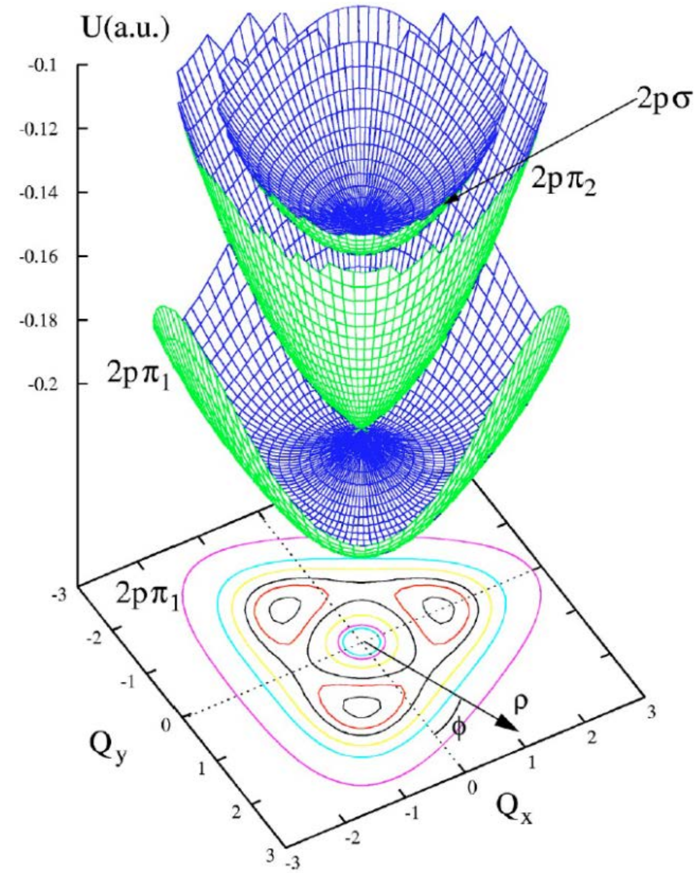
The Jahn-Teller effect (1937)

The symmetric configuration for degenerate electronic states are not stable



Q_s $\quad Q_x=\rho\cos\varphi, \quad Q_y=\rho\sin\varphi$

$$\hat{V} = \mathbf{1}\left(V_E + \delta_E\rho^2\right) + k\rho\begin{pmatrix}\cos\varphi & \sin\varphi \\ \sin\varphi & -\cos\varphi\end{pmatrix} + g\rho^2\begin{pmatrix}\cos 2\varphi & -\sin 2\varphi \\ -\sin 2\varphi & -\cos 2\varphi\end{pmatrix}$$

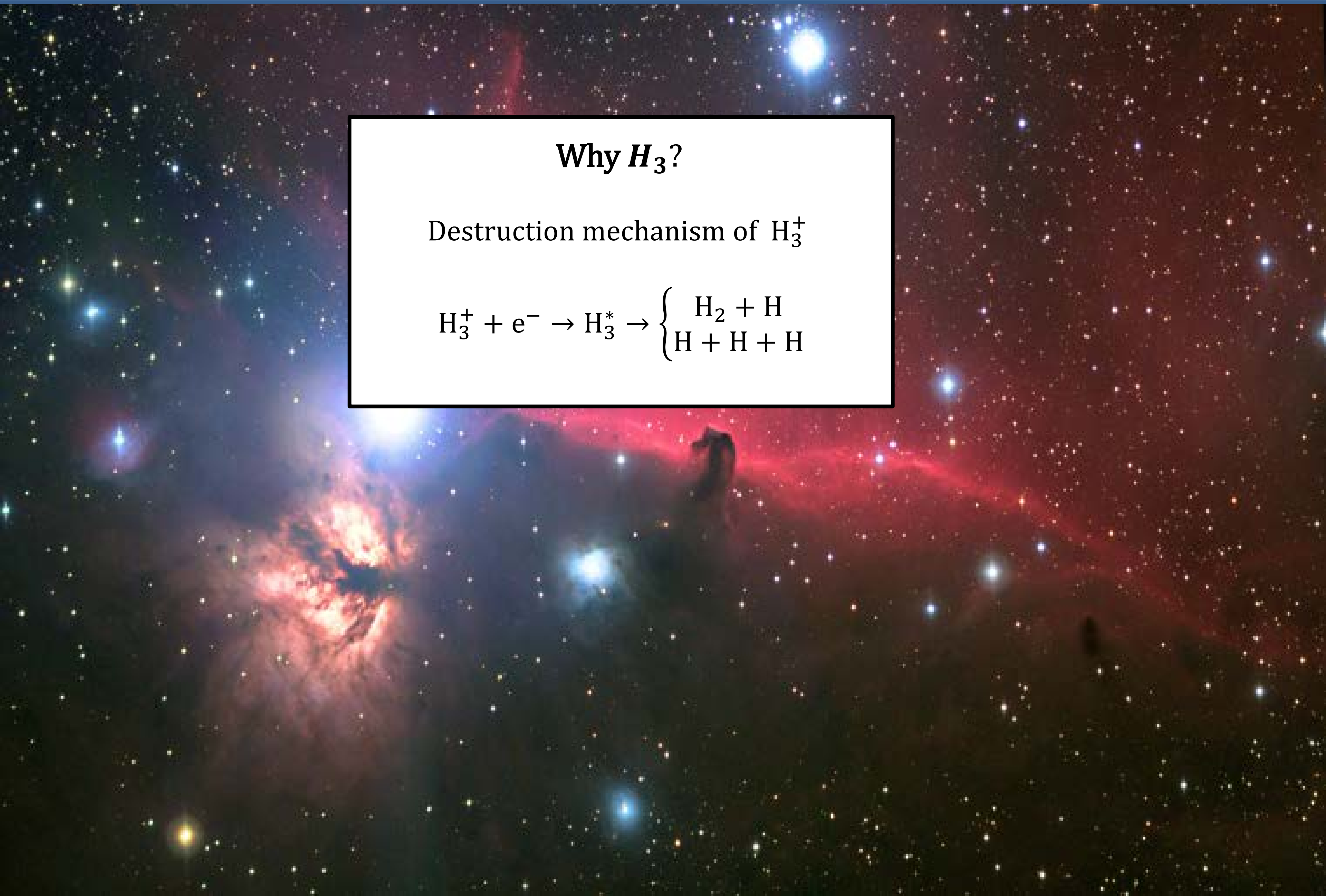


Adiabatic potential energy surfaces

Implications:

- Conical intersection at $\rho = 0$
- The non-adiabatic coupling diverges
- Non trivial geometric phase

Jahn-Teller effect among electronic resonant states of H_3



Why H_3?

Destruction mechanism of H_3^+

$$H_3^+ + e^- \rightarrow H_3^* \rightarrow \begin{cases} H_2 + H \\ H + H + H \end{cases}$$

Resonant electronic states of H_3

(~ Short lived states)

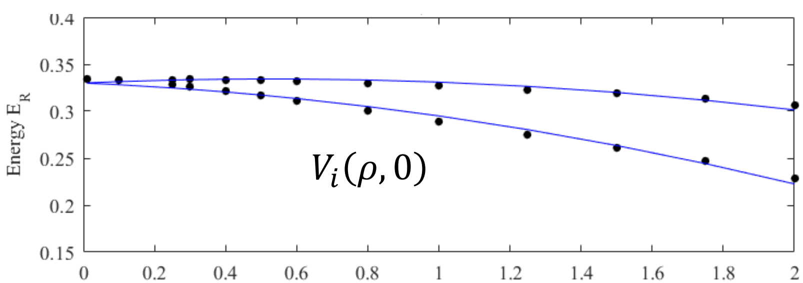
Complex potential: $\tilde{V}_i(\boldsymbol{Q}) = V_i(\boldsymbol{Q}) - i\frac{1}{2}\Gamma_i(\boldsymbol{Q})$

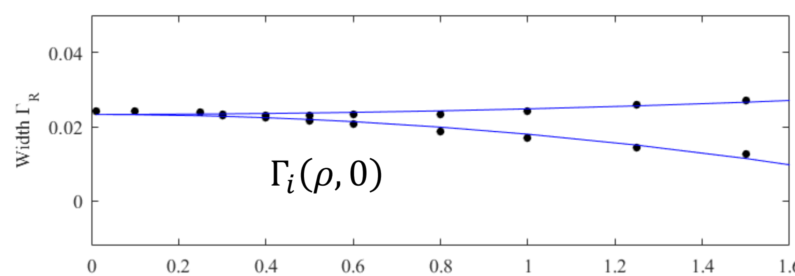
Fixed nuclei electron scattering calculations (Complex Kohn variational method)

A Jahn-Teller Hamiltonian for the resonant electronic states of H_3

Complex Jahn-Teller parameters

$$\hat{V}(\boldsymbol{Q} = \rho, \varphi) = \mathbf{1}\left((V_E + i\Gamma_E) + (\delta_E + i\gamma_E)\rho^2\right) + (\alpha + i\beta)\rho\begin{pmatrix}\cos\varphi & \sin\varphi \\ \sin\varphi & -\cos\varphi\end{pmatrix} + (\gamma + i\delta)\rho^2\begin{pmatrix}\cos 2\varphi & -\sin 2\varphi \\ -\sin 2\varphi & -\cos 2\varphi\end{pmatrix}$$





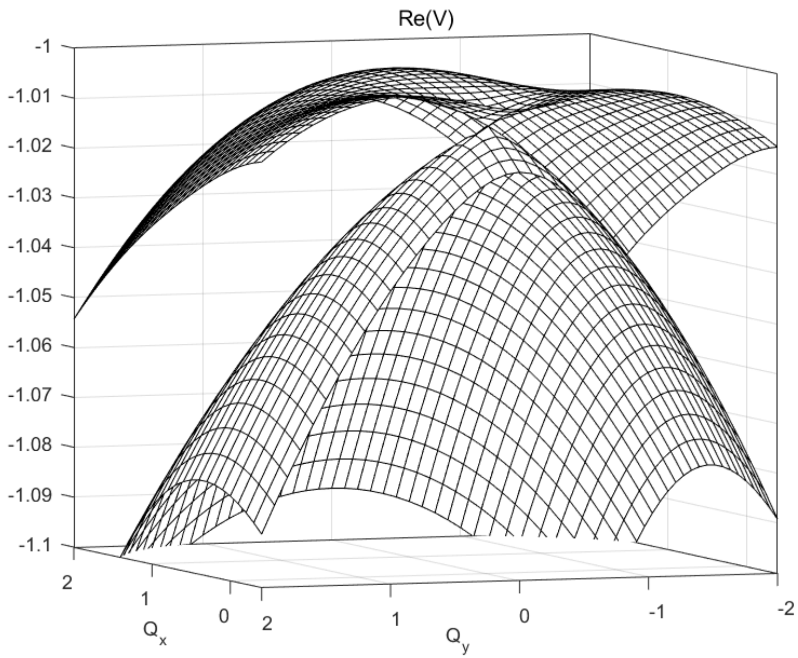
...	ϵ_E	δ_E	α	γ	Γ_E	γ_E	β	δ
$\phi = 89$	0.33	-0.017	0.0163	0.0017	-0.0117	0.0010	0.0001	0.0017

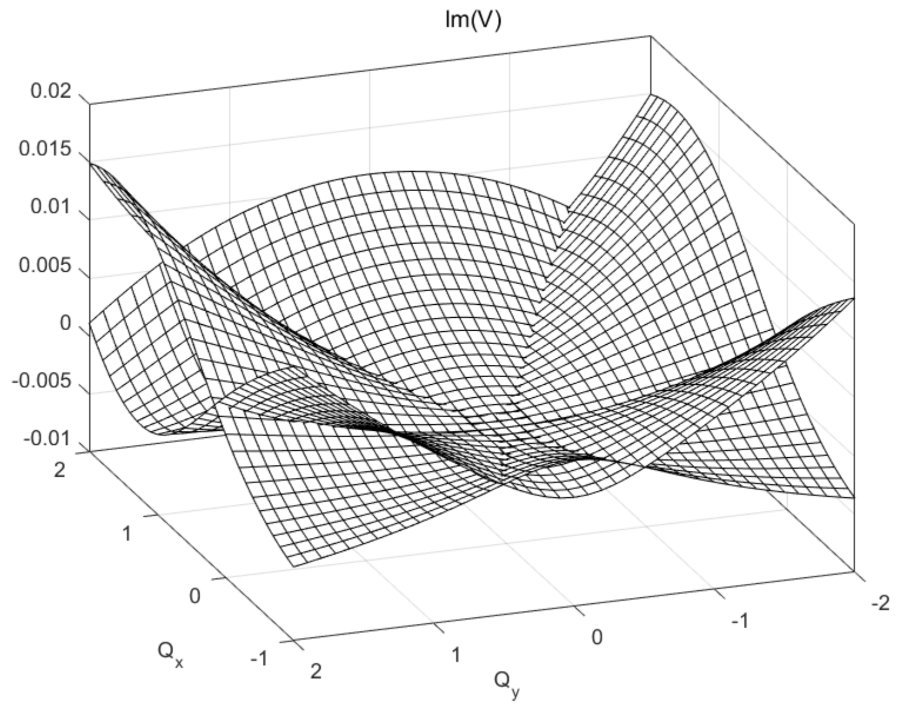
H. Estrada *et al*, JCP, 84, 152 (1986)
S. Feuerbacker *et al* JCP, 120, 3201 (2004)
S. Feuerbacker *et al* JCP, 121, 5 (2004)

Complex adiabatic potential energy surfaces

$$\hat{V}(\rho,\varphi) = \mathbf{1}\left((V_E+i\Gamma_E) + (\delta_E+i\gamma_E)\rho^2\right) + (\alpha+i\beta)\rho\begin{pmatrix}\cos\varphi & \sin\varphi \\ \sin\varphi & -\cos\varphi\end{pmatrix} + (\gamma+i\delta)\rho^2\begin{pmatrix}\cos 2\varphi & -\sin 2\varphi \\ -\sin 2\varphi & -\cos 2\varphi\end{pmatrix}$$

- Non-hermitian Hamiltonian
- Complex adiabatic potential energy surfaces

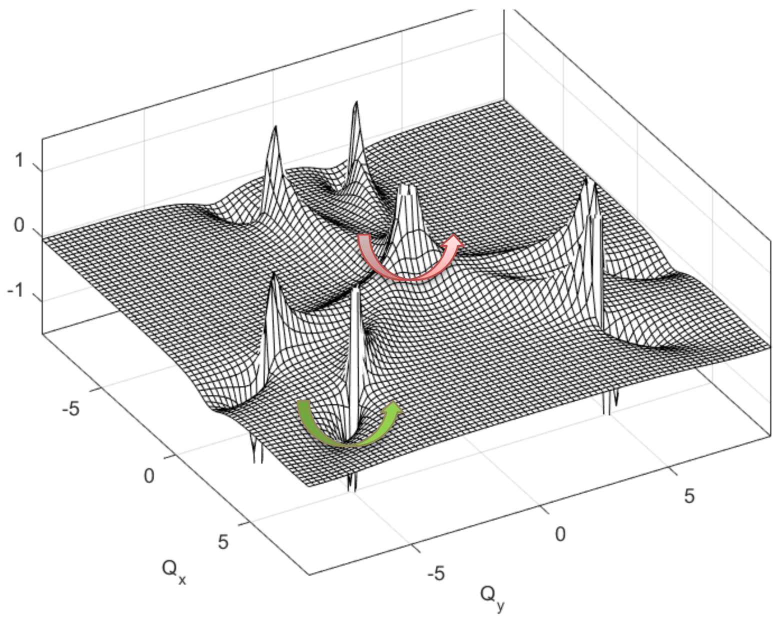




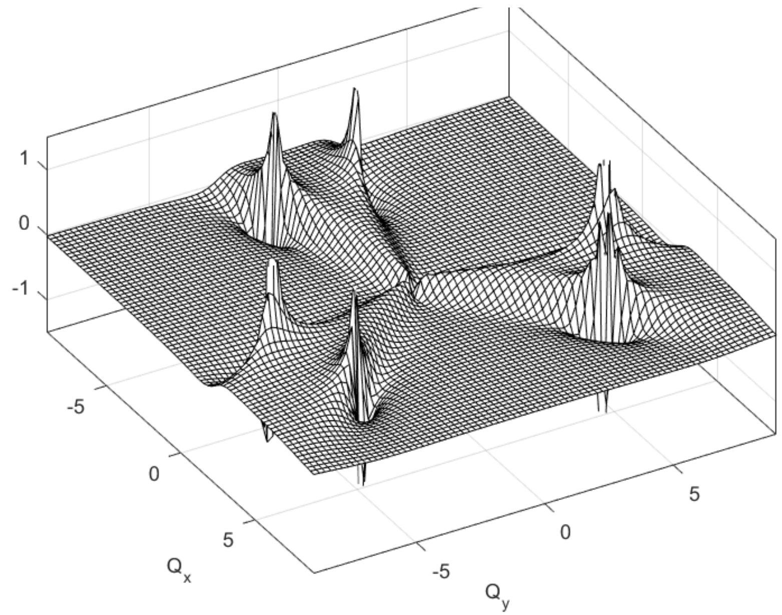
Complex non-adiabatic coupling and the Geometric phase

$$\tau_{ij}(Q) = \langle \phi_i | \nabla | \phi_j \rangle$$

Re(τ)



Im(τ)

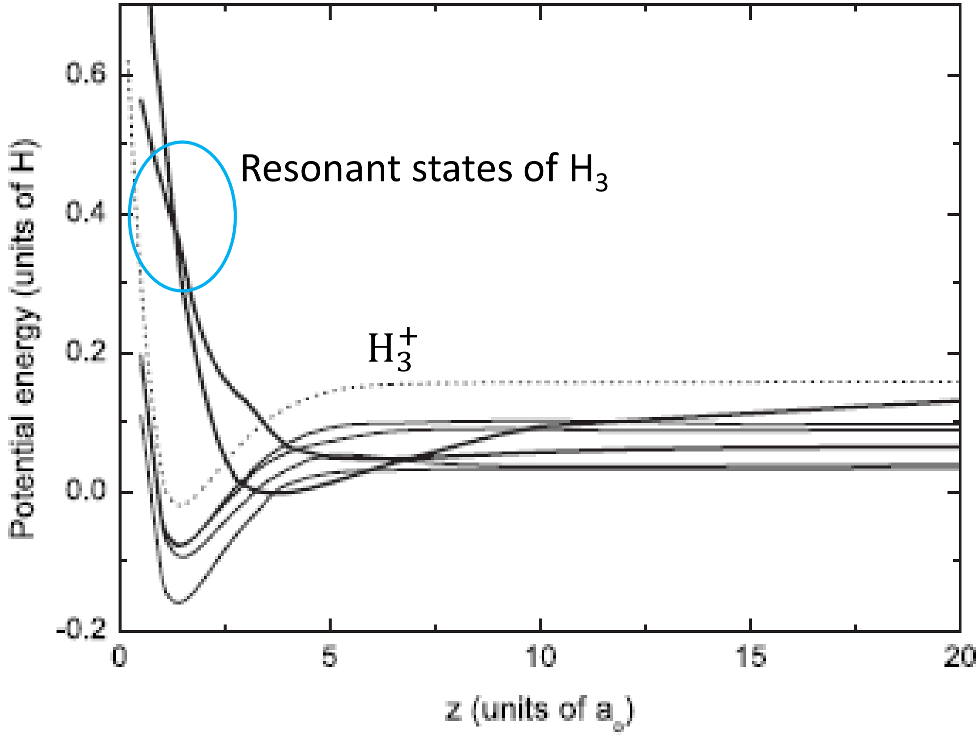


1 central complex intersection
Conical intersection
Geometric phase: π

6 outer intersections
Exceptional points (non-hermitian degeneracies)
Geometric phase: $\pi/2$

Continuation

Stationary topological properties → Dynamics of the nuclei



Dissociative recombination

$$H_3^+ + e^- \rightarrow H_3^* \rightarrow \begin{cases} H_2 + H \\ H + H + H \end{cases}$$

Ion-pair formation

$$H_3^+ + e^- \rightarrow H_3^* \rightarrow H_2^+ + H^-$$

Autoionization

$$H_3^+ + e^- \rightarrow H_3^* \rightarrow H_3^+ + e^-$$

Associative ionization

$$H_2^+ + H^- \rightarrow H_3^* \rightarrow H_3^+ + e^-$$

J. B. Roos et al, PRA, 76, 042703 (2007).

Thank you!

Jahn-Teller effect among electronic resonant states of H_3

Extracting complex Jahn-Teller parameters

1) Jahn-Teller potential: $\hat{V}(\rho,\varphi) = \mathbf{1}\left(V_E + \delta_E\rho^2\right) + k\rho\begin{pmatrix}\cos\varphi & \sin\varphi \\ \sin\varphi & -\cos\varphi\end{pmatrix} + g\rho^2\begin{pmatrix}\cos 2\varphi & -\sin 2\varphi \\ -\sin 2\varphi & -\cos 2\varphi\end{pmatrix}$

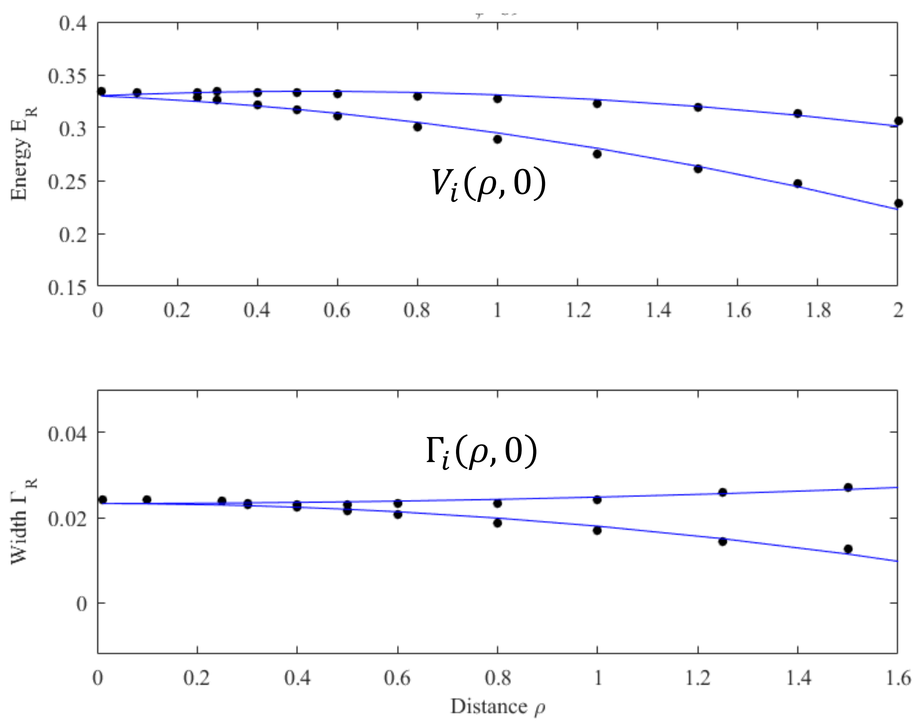
2) Resonant states : $\tilde{V}_i(\rho,\varphi) = V_i(\rho,\varphi) - i\frac{1}{2}\Gamma_i(\rho,\varphi)$

Complex Jahn-Teller parameters

$(V_E + \delta_E\rho^2) \quad \rightarrow \quad (V_E + i\Gamma_E + (\delta_E + i\gamma_E)\rho^2)$

$k \quad \rightarrow \quad \alpha + i\beta$

$g \quad \rightarrow \quad \gamma + i\delta$



ϵ_E	δ_E	α	γ	Γ_E	γ_E	β	δ
0.33	-0.017	0.0163	0.0017	-0.0117	0.0010	0.0001	0.0017

H. Estrada *et al*, JCP, 84, 152 (1986)
S. Feuerbacker *et al* JCP, 120, 3201 (2004)
S. Feuerbacker *et al* JCP, 121, 5 (2004)

Electronic resonant states of H_3

Local complex potential $\tilde{V}_i(\boldsymbol{R}) = V_i(\boldsymbol{R}) - i\frac{1}{2}\Gamma_i(\boldsymbol{R})$

Computed using electron scattering calculations.

$$|\Psi(x,t)|^2 = |\psi(x)e^{-iEt}|^2 = |\psi(x)e^{-i(E_R - \frac{i\Gamma}{2})t}|^2 = |\psi(x)|^2 e^{-\Gamma t}$$

A Jahn-Teller Hamiltonian that describes the resonant states of H_3?

Influence the non-adiabatic couplings and the Berry phase?

T.F. O'Malley, Phys Rev, 150 (1966).

Dissociative recombination of H_3^+

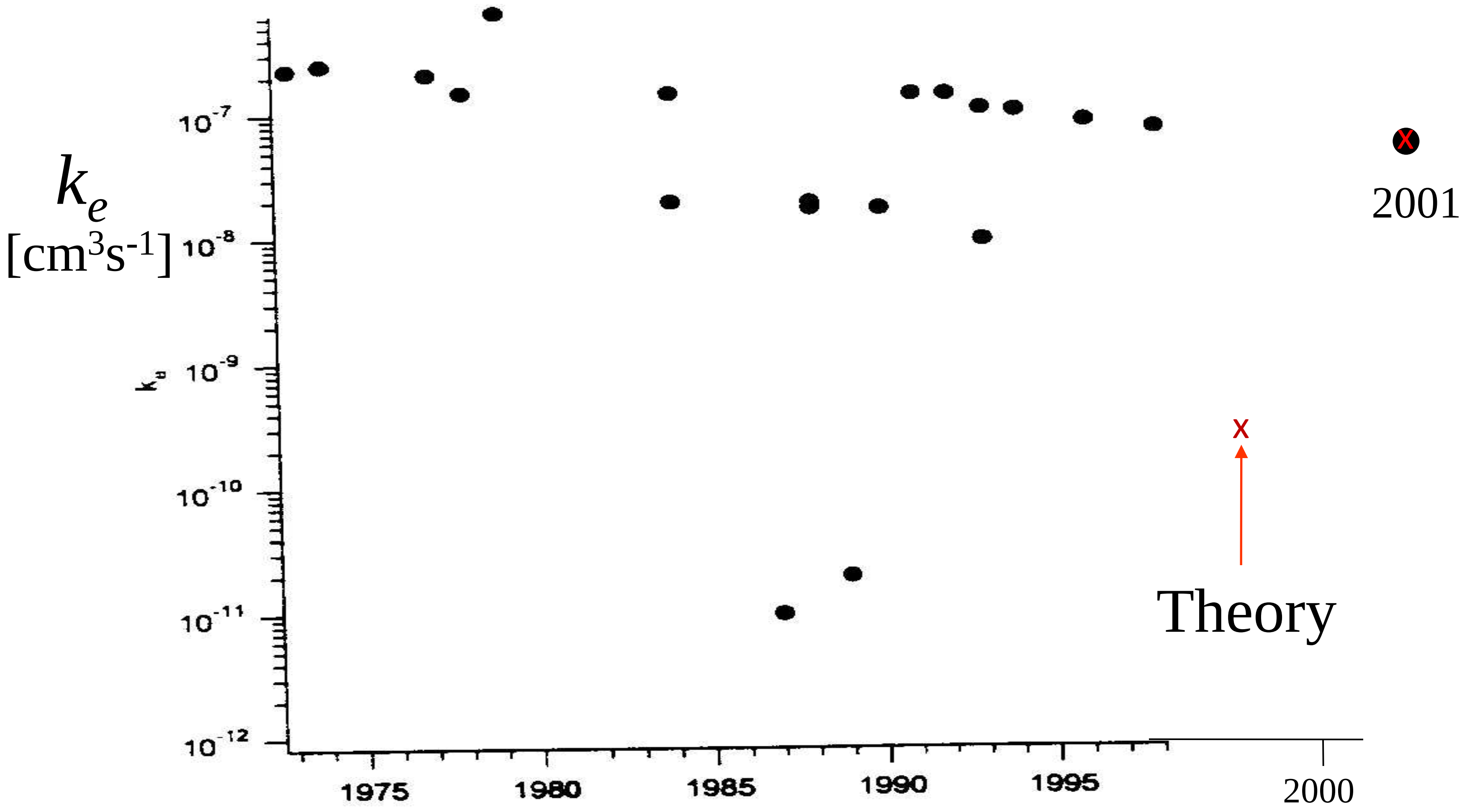
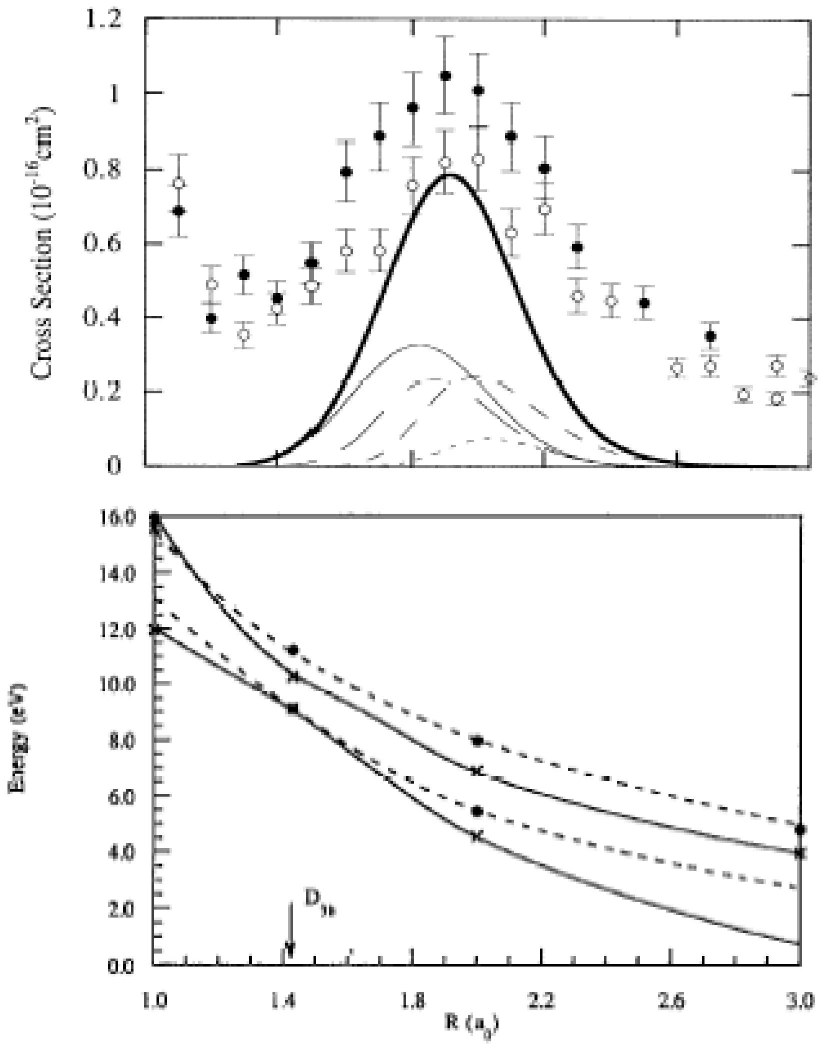


Fig. 5 Laboratory measurement of k_e over the years.

T. Oka, 1999

Dissociative recombination of H_3^+

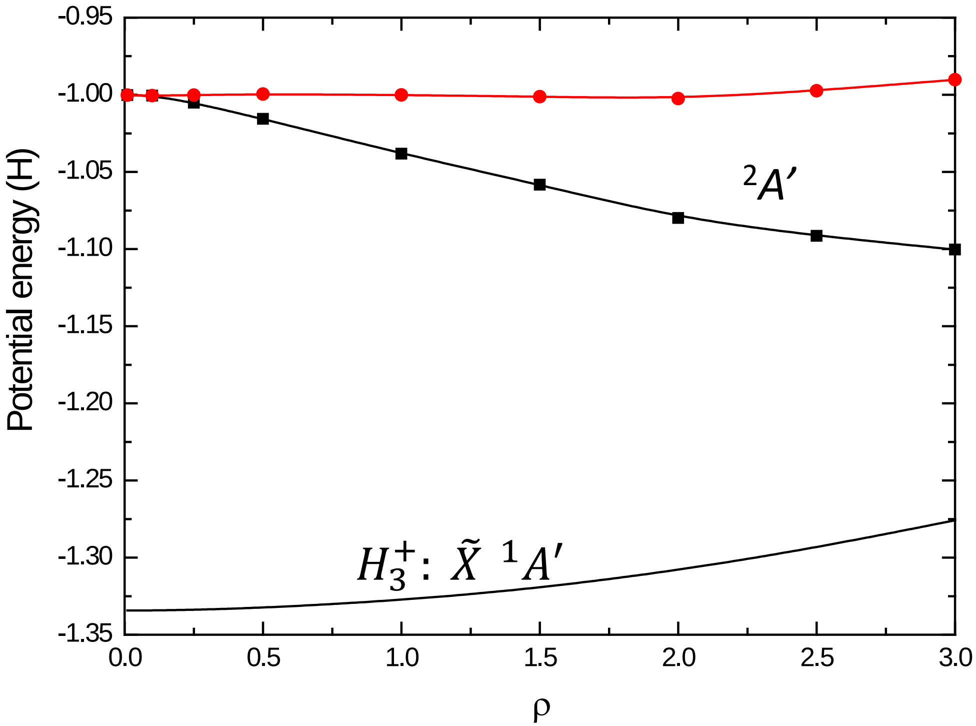


Electron scattering calculations at higher energies revealed electronic resonant states of H_3

Jahn-Teller conical intersection among the resonant states

M. Larsson *et al*, PRL, 70, 430 (1993)
A. E. Orel & K. C. Kulander, PRL, 71, 4315 (1993)
A. E. Orel *et al*. J. Chem. Phys. 100, 1756 (1994)

Electron scattering calculations



Fixed nuclei electron scattering calculations

Complex Kohn variational method

→ Fixed nuclei T- or S-matrix

Trial wavefunction:

$$\Psi = \sum_{\Gamma} \hat{A}\left[\Phi(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N) F_{\Gamma\Gamma_0}(\boldsymbol{r}_{N+1})\right] + \sum_{\mu} d_{\mu} \Theta(\boldsymbol{r}_1, \dots, \boldsymbol{r}_{N+1})$$

Target MRCI wave function

Correlation and polarization

$$F_{\Gamma\Gamma_0}(\boldsymbol{r}) = \sum_i c_i \phi_i(\boldsymbol{r}) + \sum_{lm} \left[f_l(k_l r)\delta_{ll_0}\delta_{mm_0} + T_{ll_0mm_0} g_l^+(k_l r)\right] \frac{Y_{lm}}{r}$$

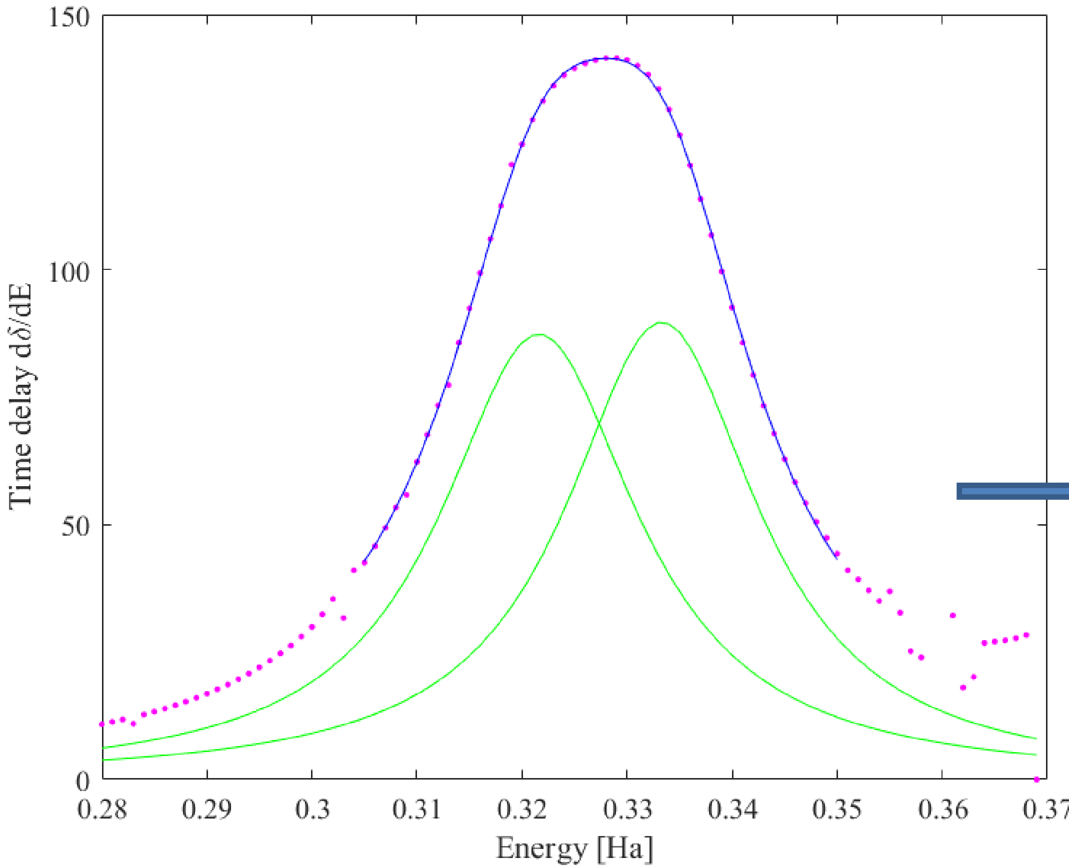
T. N. Rescigno *et al.*, in *Modern Electronic Structure Theory* vol 1, ed D. R. Yarkony (Singapore: World Scientific, 1995), p. 501.

Electron scattering calculations

Eigenphase sum of the S-matrix: $\delta(\boldsymbol{R}, E) = \sum_i \delta_i \approx \delta_{bg}(E) + \sum_k \tan^{-1}\frac{\Gamma_k/2}{E-E_k}$

Time-delay matrix: $Tr\ Q = 2\frac{d\delta}{dE} = 2\frac{d\delta_{bg}}{dE} + \sum_k \frac{\Gamma_k}{(E-E_k)^2 + (\Gamma_k/2)^2}$

Breit-Wigner



ρ=0.4, φ=0

$E_1 = 0.322$
$\Gamma_1 = 0.023$

$E_2 = 0.333$
$\Gamma_2 = 0.023$

K. Aiba, et al, J. Phys. B. 40, F9 (2007).

Non-adiabatic interactions and Geometric phase

Non-adiabatic coupling: $F_{ij} = \langle v_i | \nabla v_j \rangle$

Single-valued eigenvectors: $|v_1\rangle = e^{i\theta/2}\begin{pmatrix} \sin\theta/2 \\ -\cos\theta/2 \end{pmatrix}, \quad |v_2\rangle = e^{i\theta/2}\begin{pmatrix} \cos\theta/2 \\ \sin\theta/2 \end{pmatrix}$

ADT angle: $\tan\theta = \frac{k\sin\varphi - g\rho\sin 2\varphi}{k\cos\varphi + g\rho\cos 2\varphi}$ $\Longrightarrow$ $\boldsymbol{F}^{\varphi} = \frac{1}{\rho}\begin{pmatrix} \frac{i}{2}\frac{d\theta}{d\varphi} & -\frac{1}{2}\frac{d\theta}{d\varphi} \\ \frac{1}{2}\frac{d\theta}{d\varphi} & \frac{i}{2}\frac{d\theta}{d\varphi} \end{pmatrix}$

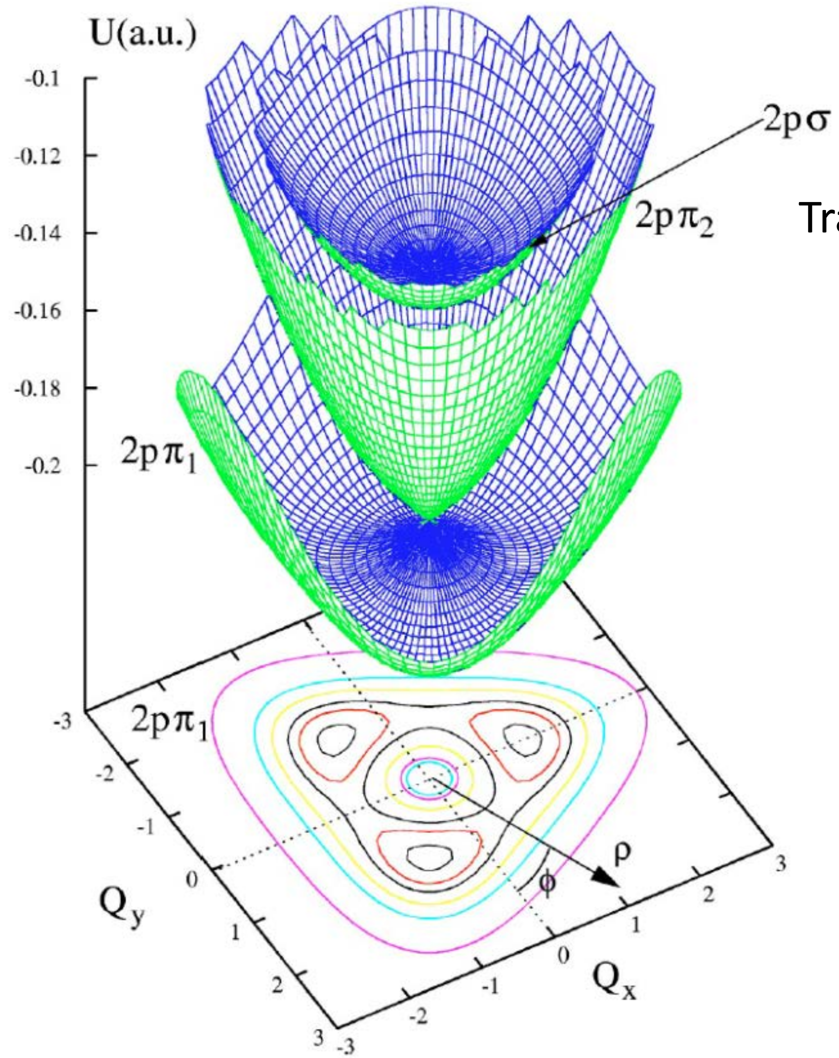
Non-adiabatic coupling for complex JT:

Complex ADT angle θ

Single-valued eigenvectors: $|v_1\rangle = e^{iRe\theta/2}\begin{pmatrix} \sin\theta/2 \\ -\cos\theta/2 \end{pmatrix}, \quad |v_2\rangle = e^{iRe\theta/2}\begin{pmatrix} \cos\theta/2 \\ \sin\theta/2 \end{pmatrix}$

M. Baer, *Beyond Born-Oppenheimer*, 2006

Non-adiabatic interactions and Geometric phase



Transporting a state around the conical intersection

$$|v_1(0)\rangle = -|v_1(2\pi)\rangle$$

Topological matrix

$$\boldsymbol{D} = \wp exp\left(-\oint d\boldsymbol{s}\cdot\boldsymbol{F}\right)$$

$$\boldsymbol{D} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$ ⟹ Geometric phase = π

M. Baer, *Beyond Born-Oppenheimer*, 2006

A theoretical curiosity

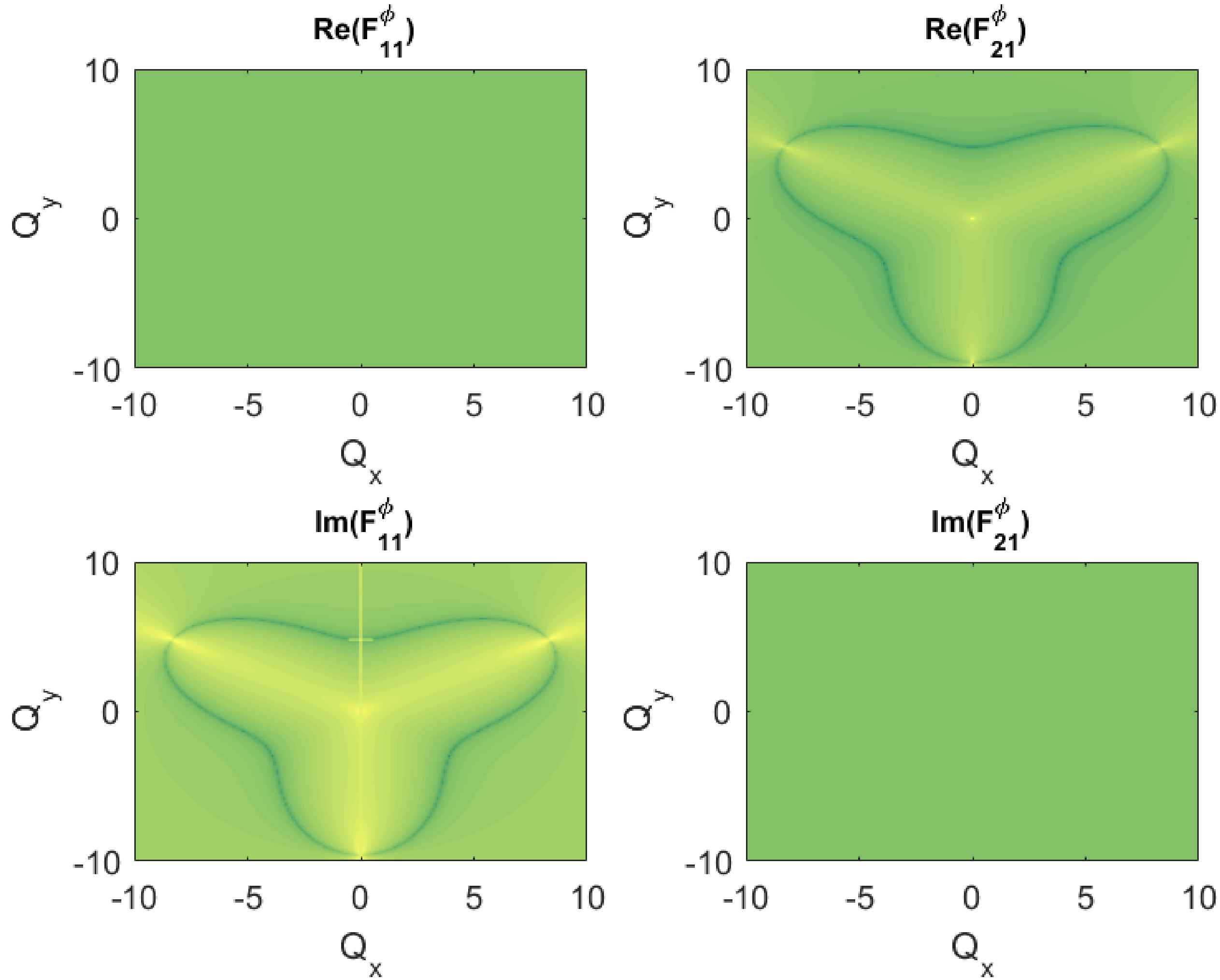
$$\hat{V} = \rho(k\cos(\varphi) + g\,\rho\cos(2\varphi))\begin{pmatrix}1 & \lambda \\ \lambda & -1\end{pmatrix} \qquad \lambda = \frac{k\sin\varphi - g\rho\sin 2\varphi}{k\cos\varphi + g\rho\cos 2\varphi}$$

$$V_{\pm} = \pm\rho\,(k\cos(\varphi) + g\,\rho\cos(2\varphi))\sqrt{1+\lambda^2}$$

Intersections where $V_{\pm} = 0$

A theoretical curiosity

$$V_{\pm} = \pm\rho\ \underline{(k\cos(\varphi) + g\ \rho\cos(2\varphi))}\ \sqrt{1+\lambda^2}$$



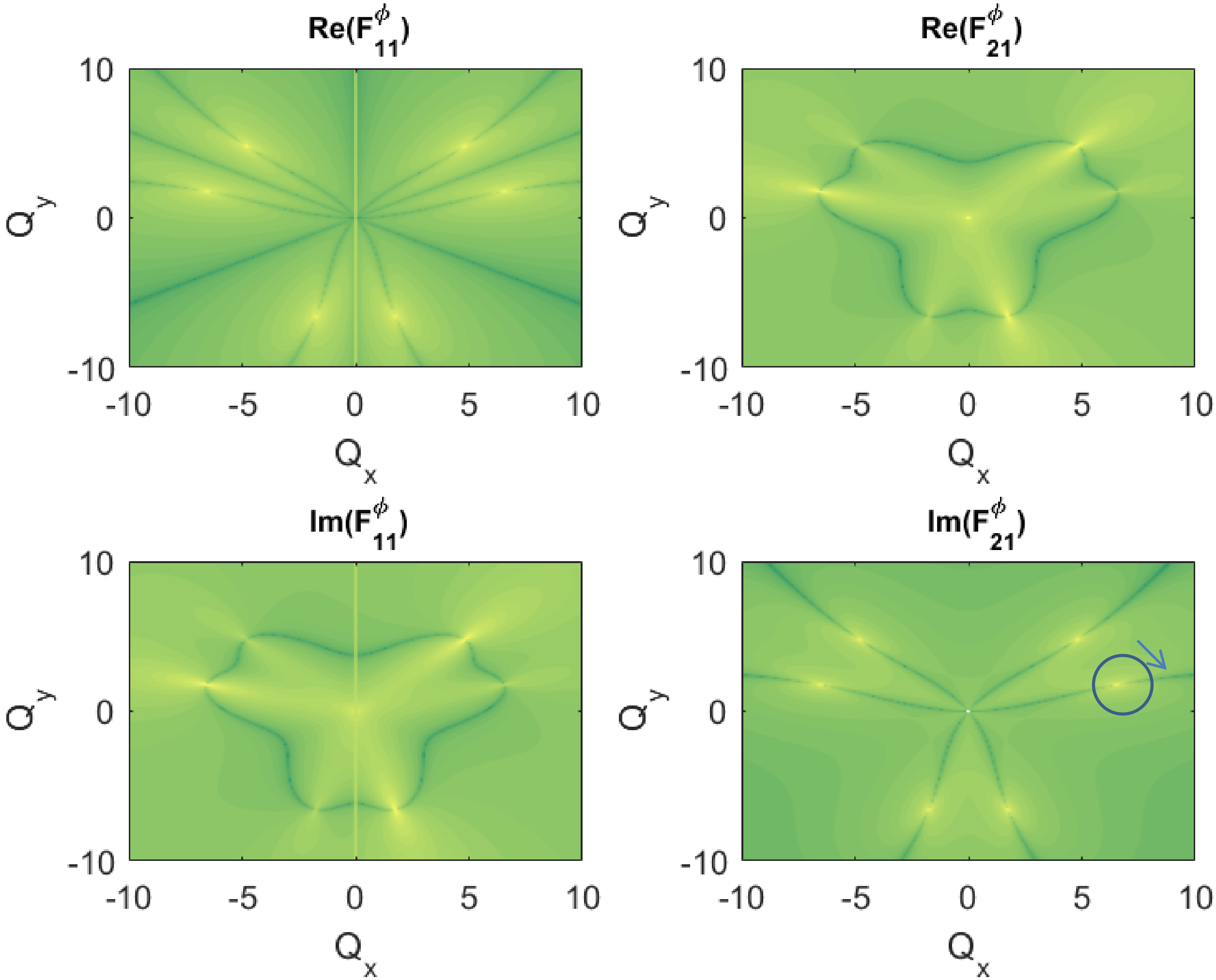
If k, g are real

Re(F_{11})=Im(F_{21})=0

1 inner conical intersection
+ 3 outer intersections

A theoretical curiosity

$$V_{\pm} = \pm\rho\,(k\cos(\varphi) + g\,\rho\cos(2\varphi))\,\sqrt{1+\lambda^2}$$



Complex JT

1 central conical intersection

+ 6 outer intersections

at $\lambda = \pm i$

Exceptional points

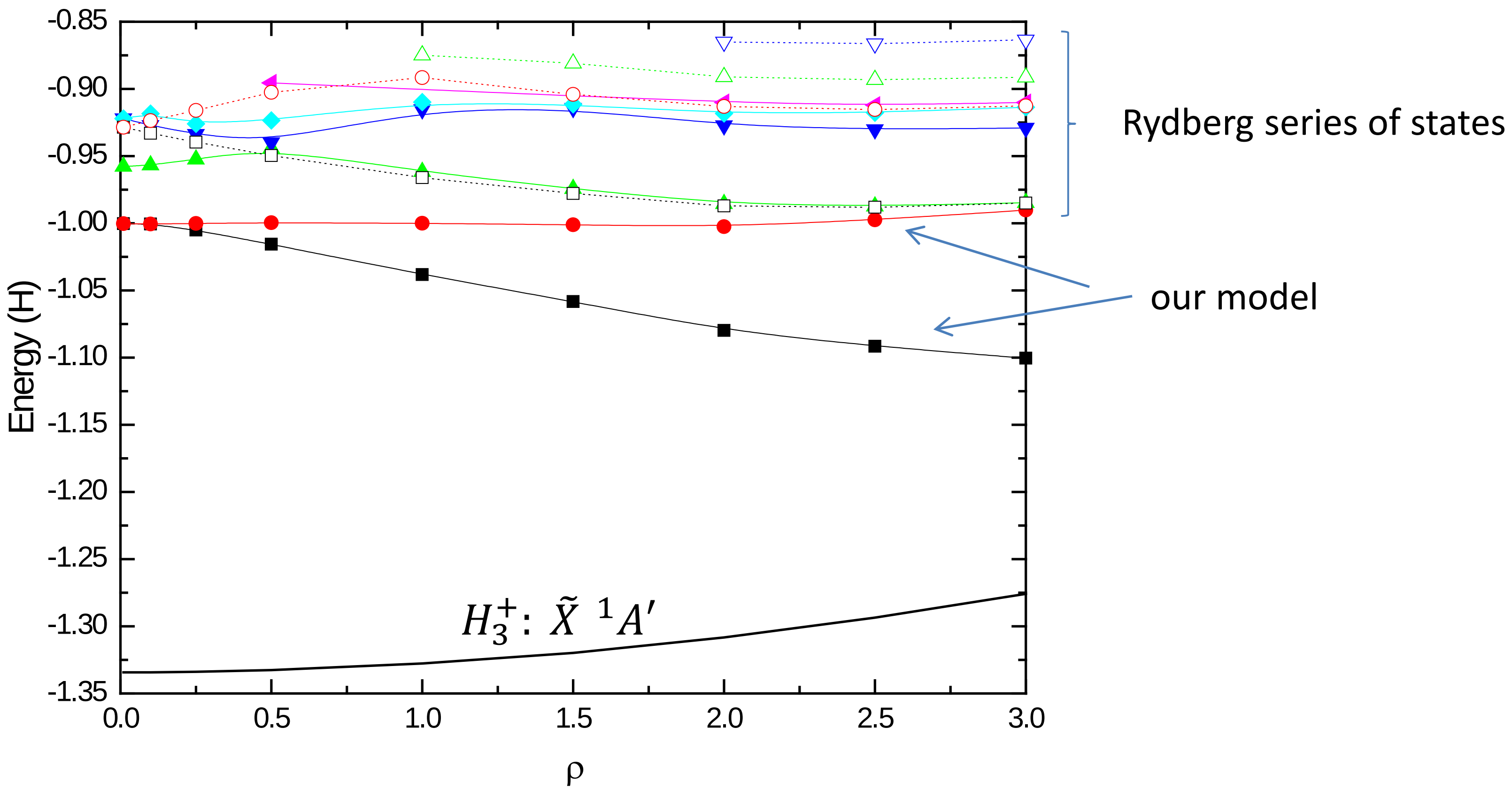
(non-hermitian degeneracies)

Geometric phase: $\pi/2$

N. Moiseyev, *Non-Hermitian Quantum Mechanics, 2011*

Continuation

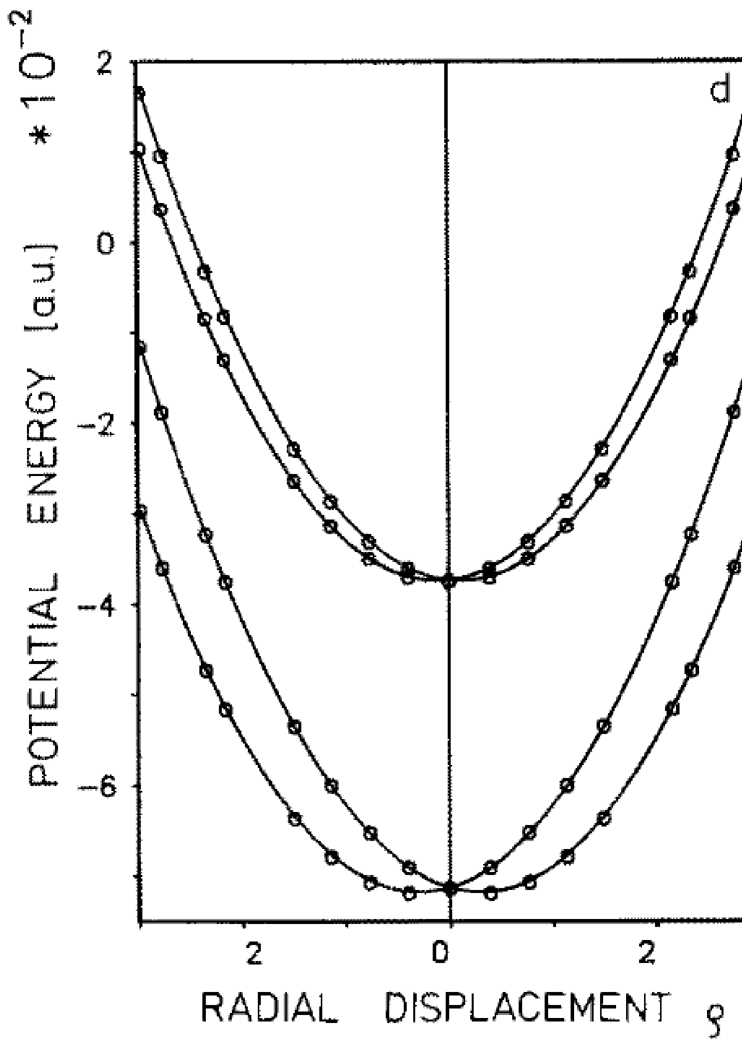
Not only one pair of coupled resonant states, but Rydberg series of states



Can the complex JT parameters be determined for the whole Rydberg series using a multi-channel quantum defect theory?

A. Staib, W. Domcke, Z. Phys. D. 16, 275 (1990)

Dissociative recombination of H_3^+



A Jahn-Teller Hamiltonian is fitted to describe the bound Rydberg states of H_3

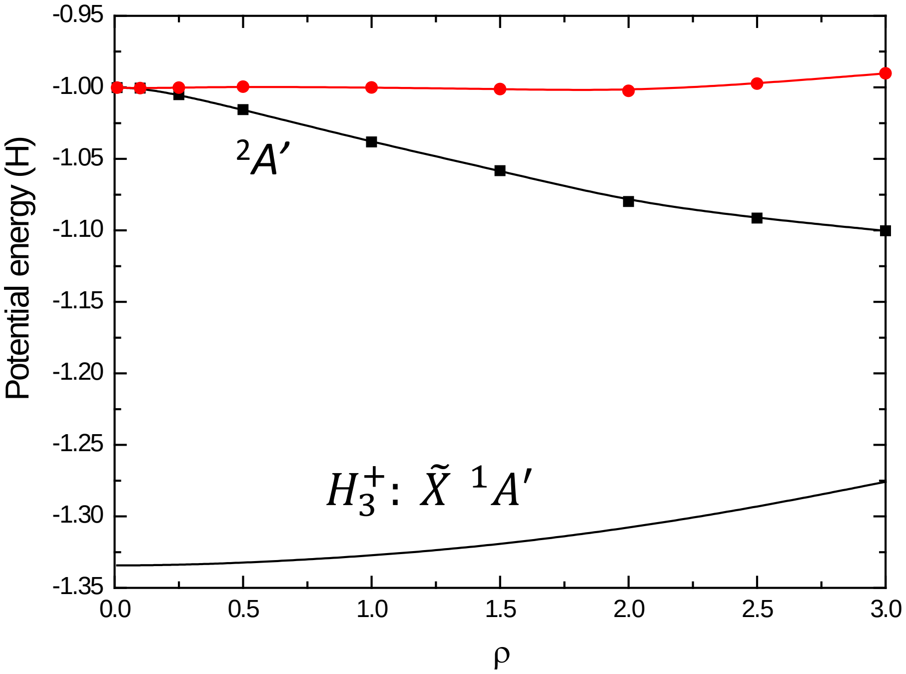
Important for spectroscopy of H_3

Important also for low energy e-H_3^+ collisions

$$Q_x = \rho \cos\varphi\ ,\ \ Q_y = \rho \sin\varphi$$

A. Staib, W. Domcke, Z. Phys. D. 16, 275 (1990)

Conical intersection among electronic resonant states



Electronic resonant states of H_3

Computed using electron scattering calculations.

Local Boomerang model

$$\tilde{V}_i(\boldsymbol{R}) = V_i(\boldsymbol{R}) - i\frac{1}{2}\Gamma_i(\boldsymbol{R})$$

What is the form of the Jahn-Teller Hamiltonian that describes the resonant states of H_3?

How will the fact that these state are resonant states influence the non-adiabatic couplings and the Berry phase?

C. W. McCurdy & J. Turner, JCP, 78, 6773 (1983).

Electron scattering calculations

Fixed nuclei electron scattering calculations are carried out with the ***Complex-Kohn variational method***

Trial wave function:

$$\Psi = \sum_{\Gamma} \hat{A}\left[\Phi(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N) F_{\Gamma\Gamma_0}(\boldsymbol{r}_{N+1})\right] + \sum_{\mu} d_{\mu} \Theta(\boldsymbol{r}_1, \dots, \boldsymbol{r}_{N+1})$$

Target MRCI wave function

Correlation and polarization

$$F_{\Gamma\Gamma_0}(\boldsymbol{r}) = \sum_i c_i \phi_i(\boldsymbol{r}) + \sum_{lm} \left[f_l(k_l r)\delta_{ll_0}\delta_{mm_0} + T_{ll_0 mm_0} g_l^{+}(k_l r)\right] \frac{Y_{lm}}{r}$$

Insert into a variational functional for the T-matrix

⟹ Fixed nuclei T- or S-matrix

T. N. Rescigno *et al.*, in *Modern Electronic Structure Theory* vol 1, ed D. R. Yarkony (Singapore: World Scientific, 1995), p. 501.