Methods for understanding

the angular scattering of chemical reactions

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Antonio Laganà Celebration
“Virtual environments and detailed simulations of molecular processes”
Bettona, Italy

4th-5th November, 2015

Outline

- **The research of Antonio Laganà at the University of Manchester.**

- **Nearside-Farside (NF) theory of scattering.**
- **Local Angular Momentum (LAM) analysis.**
- ***Glories* in the angular scattering.**
- ***Hidden rainbows* in the angular scattering.**
- **Complex angular momentum theory, Regge poles.**

- ***No detailed discussion* of:**
  - **Resummation theory.**
  - **Uniform semiclassical theories.**
  - **Applications of Heisenberg's Scattering Matrix Programme.**
  - **Parameterized scattering matrix.**
  - **Reactions in the time domain.**

The Journal of Physical Chemistry, Vol. 83, No. 1, 1979

Comparison of Quasi-Classical, Transition State Theory, and Quantum Calculations of Rate Constants and Activation Energies for the Collinear Reaction $X + F_2 \rightarrow XF + F$ (X = Mu, H, D, T)

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Department of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom, and Institut für Theoretische Chemie und Strahlenchemie, Universität Wien, A-1090 Wien, Austria *(Received June 28, 1978)*

MOLECULAR PHYSICS, 1979, VOL. 38, NO. 2, 657–667

Quasiclassical dynamics of light+heavy–heavy atom reactions: the reaction $X+F_2 \rightarrow XF+F$ (X=Mu, H, D, T)

by J. N. L. CONNOR and A. LAGANÀ†

Department of Chemistry, University of Manchester,
Manchester M13 9PL, U.K.

CHEMICAL PHYSICS LETTERS 1979 Volume 62,

UNI- AND BIMODAL PRODUCT ENERGY DISTRIBUTIONS FOR THE REACTIONS H + Cl_2 ($v = 1$) AND D + Cl_2 ($v = 1$)

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Computer Physics Communications 17 (1979) 145–148

QUASICLASSICAL SMOOTH SAMPLING STUDY OF THRESHOLD BEHAVIOUR FOR THE COLLINEAR REACTION X + F_2 → XF + F (X = Mu, H, D, T)

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Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

J.N.L. CONNOR, A. LAGANÀ (Socio):

Studio teorico della reazione $H + Cl_2 \rightarrow HCl + Cl$.

Gli studi di dinamica molecolare trovano una esemplare applicazione nella trattazione teorica delle reazioni $X +$

IL NUOVO CIMENTO VOL. 63 B, N. 1 116 11 Maggio 1981

On Differences between Quasi-Classical and Quantum-Mechanical Vibrational Product Distributions in the Collinear $H + Cl_2$ $(v = 2)$ and $D + Cl_2$ $(v = 2)$ Reactions (*).

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J. Chem. Phys. 75(7), 1 Oct. 1981

Quasiclassical dynamics of light+heavy–heavy and heavy+heavy–light atom reactions: The reaction $X+F_2 \rightarrow XF+F(X=Mu, H)$

J. N. L. Connor, A. Laganà,[a] A. F. Turfa, and J. C. Whitehead

Department of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom

MOLECULAR PHYSICS, 1981, VOL. 44, No. 2, 403–410

On the evaluation of the classical phase for reactive molecular collisions in semiclassical collision theory

by J. N. L. CONNOR

Department of Chemistry, University of Manchester, Manchester M13 9PL, England

and ANTONIO LAGANÀ

Dipartimento di Chimica, Università degli Studi, I-06100 Perugia, Italy

MOLECULAR PHYSICS, 1982, VOL. 46, No. 6, 1231–1250

Semiclassical and quasiclassical calculation of reaction probabilities for collinear $X + F_2 \rightarrow XF + F$ (X = Mu, H, D, T)

by J. N. L. CONNOR, C. J. EDGE† and A. LAGANÀ‡
Department of Chemistry, University of Manchester,
Manchester M13 9PL, England

THE REACTION $X + Cl_2 \rightarrow XCl + Cl$ (X = Mu, H, D). II. COMPARISON OF EXPERIMENTAL DATA WITH THEORETICAL RESULTS DERIVED FROM A NEW POTENTIAL ENERGY SURFACE

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Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

Chemical Physics 65 (1982) 29–48

J. Chem. Phys. 80 (3), 1 February 1984

The uniform asymptotic swallowtail approximation: Application to the collinear H + F_2 chemical reaction

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(Received 5 October 1983; accepted 16 November 1983)

action

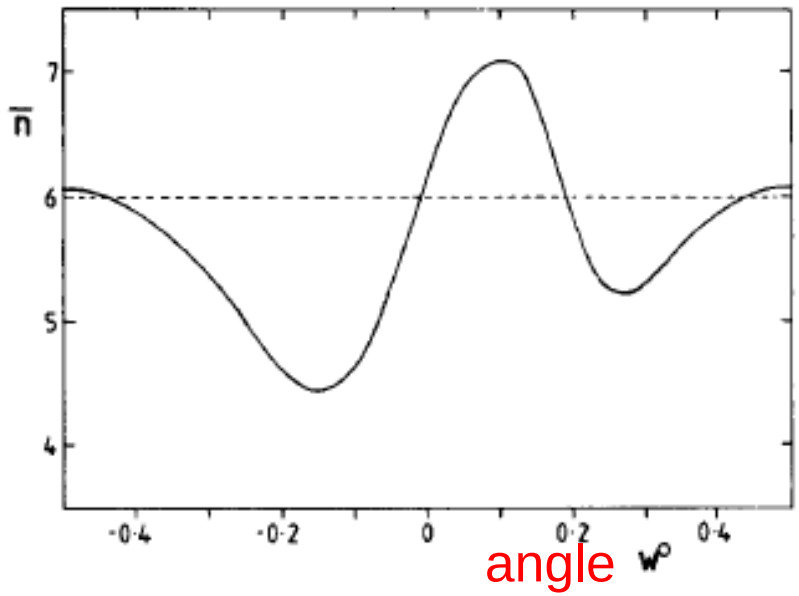
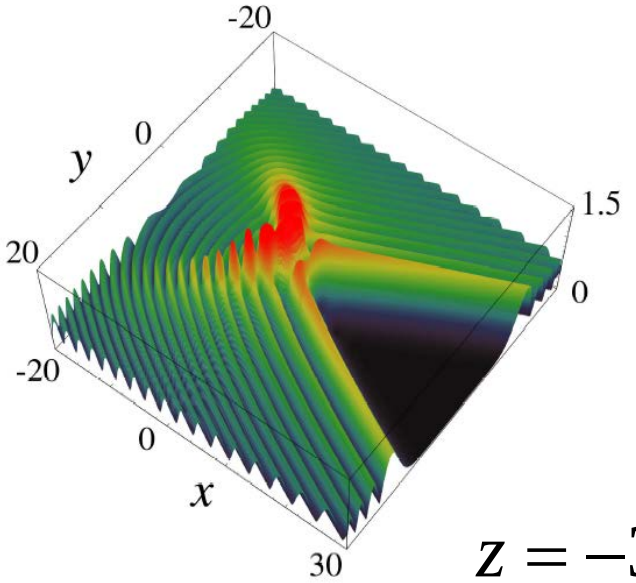


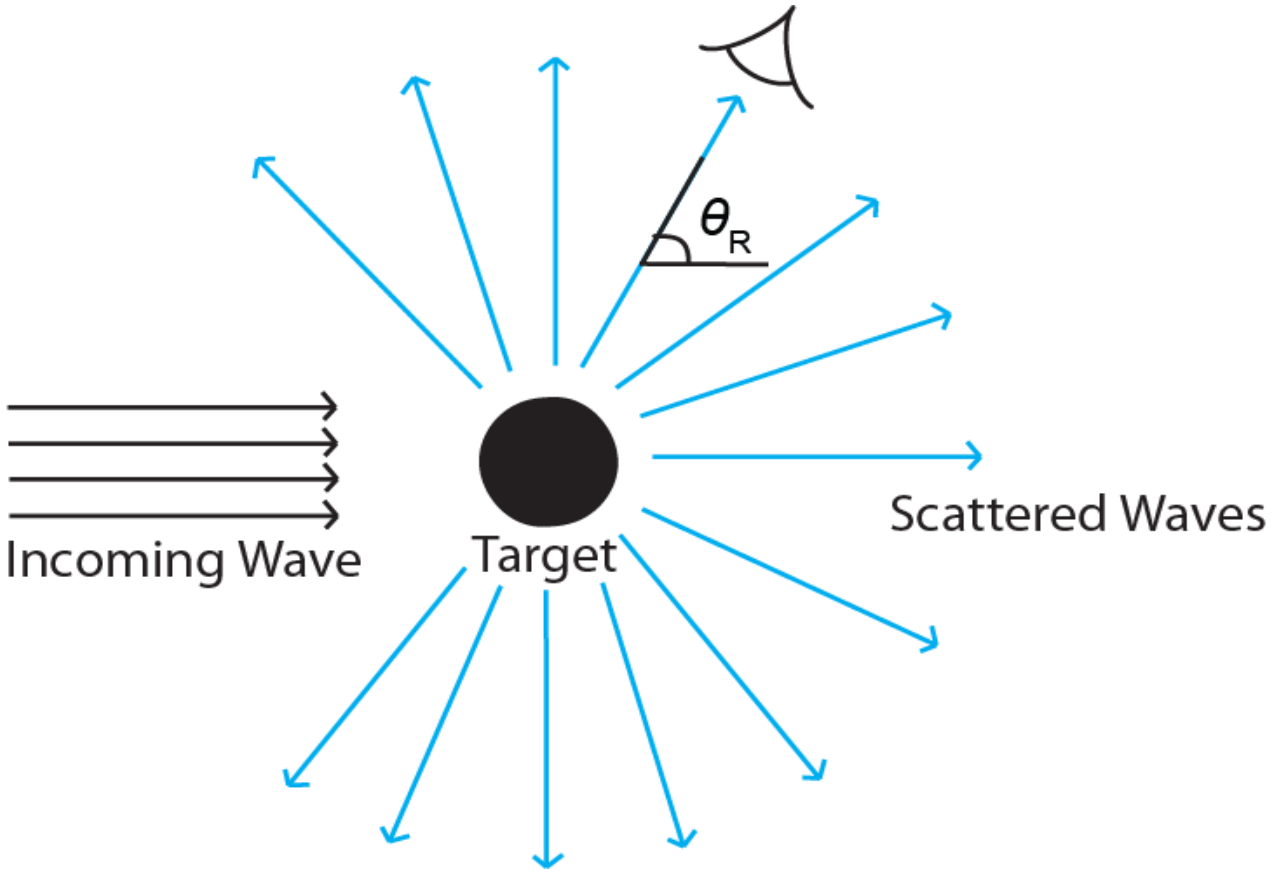
FIG. 1. Plot of the quantum number variable $\bar{n}$ against initial angle variable w^{0} for the collinear H + $F_2(n=0) \rightarrow HF(\bar{n})$ + F reaction at a translational energy $E_0^{\text{trans}} = 9.958$ kJ mol^{-1}.

$$\left| \int_{-\infty}^{\infty} \exp\left[\mathrm{i}\left(u^5 + z u^3 + y u^2 + x u \right) \right] \right|$$



$z = -3$

Differential Cross Section (DCS)
(or angular distribution)



Experimental information:

2008

PNAS | April 29, 2008 | vol. 105 | no. 17 | 6227–6231

HF($v' = 3$) forward scattering in the F + H_2 reaction: Shape resonance and slow-down mechanism

Xingan Wang*, Wenrui Dong*, Minghui Qiu†, Zefeng Ren*, Li Che*, Dongxu Dai*, Xiuyan Wang*, Xueming Yang*‡, Zhigang Sun*§, Bina Fu*, Soo-Y. Lee§, Xin Xu¶, and Dong H. Zhang*‡

*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China; †Department of Physics, Dalian Jiaotong University, Dalian 116028, Liaoning, China; §School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637616; and ¶Department of Chemistry, Xiamen University, Xiamen 361005, Fujian, China

Edited by Richard N. Zare, Stanford University, Stanford, CA, and approved February 8, 2008 (received for review November 15, 2007)

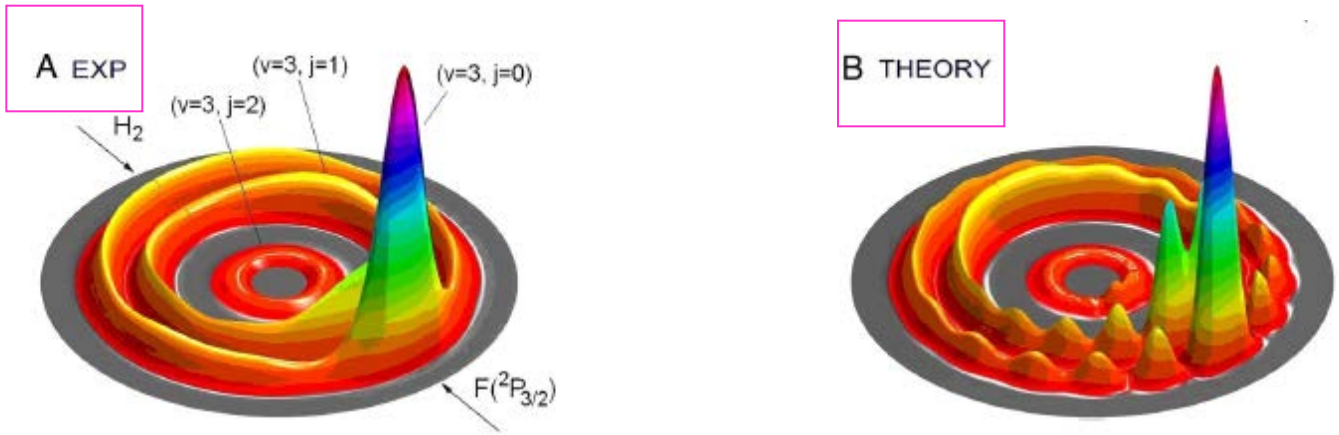


Fig. 2. Experimental (*A*) and theoretical (*B*) three-dimensional DCS contour plots for the $F(^2P_{3/2}) + H_2(j = 0) \rightarrow HF(v' = 3, j') + H$ reaction at the collision energy 0.94 kcal/mol.

differential cross section

$$\sigma_{i,f}(\theta) = \left| f_{i,f}(\theta) \right|^2$$

n.b., $\theta \equiv \theta_{\mathrm{R}}$

PWS scattering amplitude

$$f_{i,f}(\theta) = \frac{1}{2\,\mathrm{i}\,k_i} \sum_{J=0}^{\infty} (2J+1) S_{i,f}^{J} P_J(\cos\theta)$$

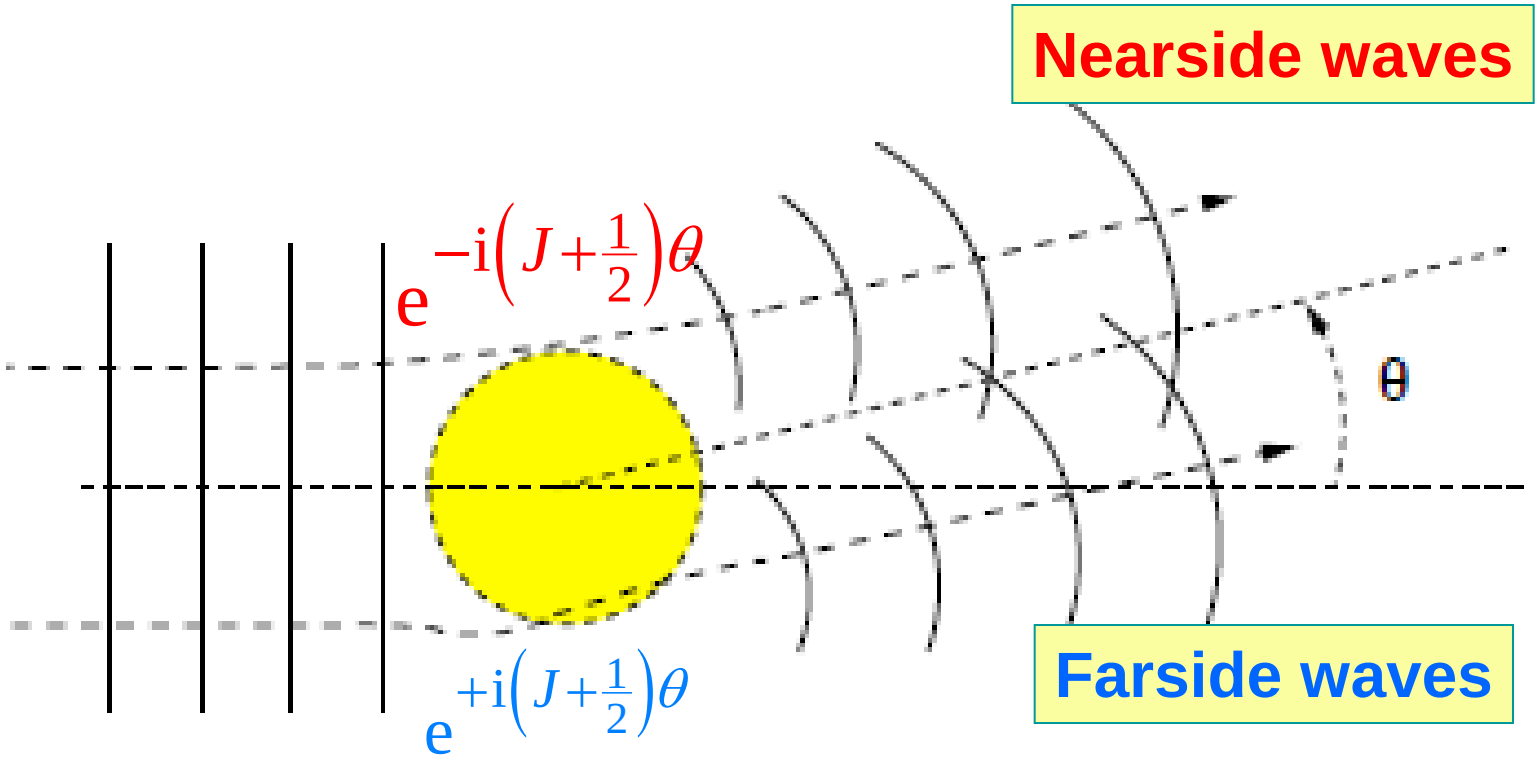
n.b., $S \equiv \tilde{S}$

$J_{\max} >> 1$ Localization Principle

S^J = Scattering matrix element.

$P_J(\bullet)$ = Legendre polynomial.

Nearside-Farside picture of scattering



Nearside-Farside theory has been applied to:

- Forward glory, sideward and backward scattering
- Rainbow and rotational rainbow scattering.
- Diffraction effects.
- Geometric phases.
- Contribution of angular momentum to angular scattering (NF-LAM theory).
- Direct and delayed mechanisms.
- QP decomposition.
- Semiclassical limit of NF theory (*a huge topic*).
- Used with time-dependent scattering theories.
- Used with complex angular momentum theories.
- Complex-mode reactions.
- etc.

FULLER Nearside-Farside Decomposition

$$f(\theta) = f_{\mathrm{N}}(\theta) + f_{\mathrm{F}}(\theta)$$

where

$$f_{\mathrm{N}}(\theta) = \frac{1}{2\mathrm{i}k} \sum_{J=0}^{\infty} (2J+1)\, \tilde{S}_J \, \frac{1}{2}\left[P_J(\cos\theta) + \frac{2\mathrm{i}}{\pi} Q_J(\cos\theta) \right]$$

$$f_{\mathrm{F}}(\theta) = \frac{1}{2\mathrm{i}k} \sum_{J=0}^{\infty} (2J+1)\, \tilde{S}_J \, \frac{1}{2}\left[P_J(\cos\theta) - \frac{2\mathrm{i}}{\pi} Q_J(\cos\theta) \right]$$

$P_J(\bullet)$ = Legendre polynomial. $Q_J(\bullet)$ = Legendre function of the 2nd kind.

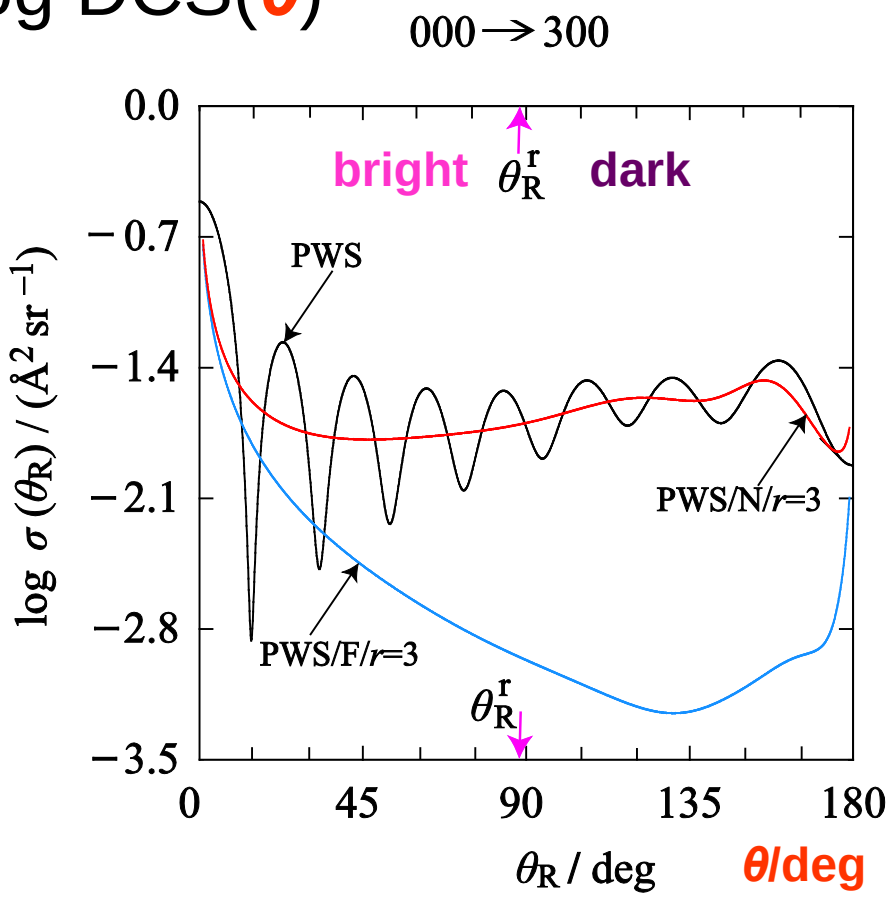
---

n.b., $P_J(\cos\theta) \pm \frac{2\mathrm{i}}{\pi} Q_J(\cos\theta) \underset{J>>1}{\propto} \exp\left\{ \mp \mathrm{i}\left[\left(J+\frac{1}{2}\right)\theta - \frac{1}{4}\pi \right] \right\}$ **Travelling angular waves**

Nearside-Farside analysis of the angular distribution for the F + H_2 reaction (2008 expt)

$$\sigma(\theta) = \left| f_N(\theta) + f_F(\theta) \right|^2, \quad \sigma_N(\theta) = \left| f_N(\theta) \right|^2, \quad \sigma_F(\theta) = \left| f_F(\theta) \right|^2$$

log DCS(***θ***)

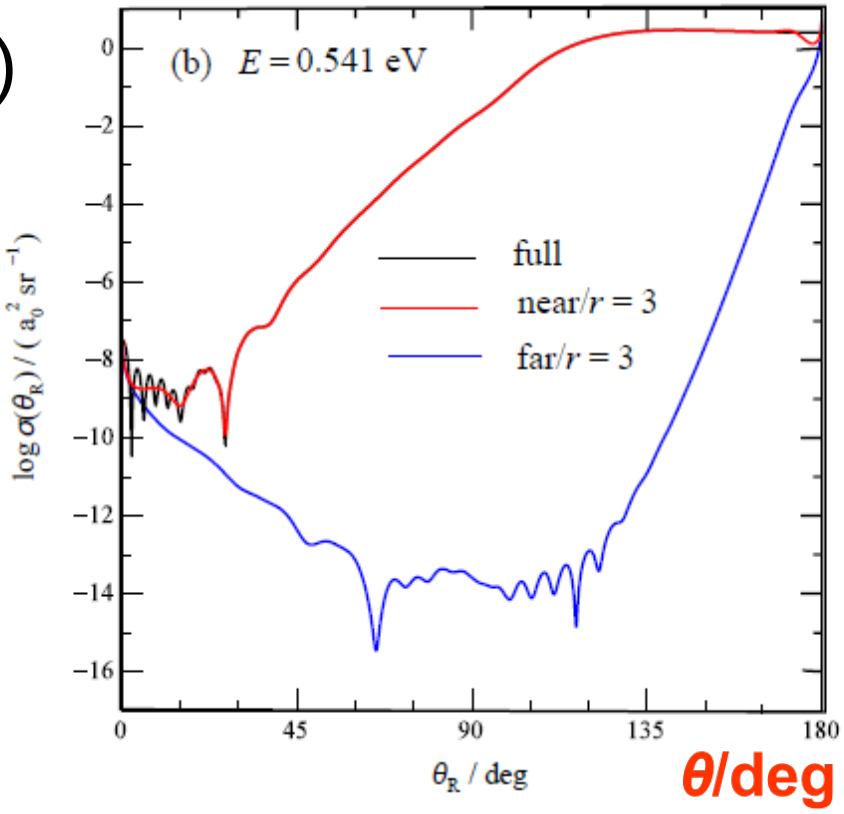


(0,0,0) → (3,0,0)
***E* = 0.3112 eV**
FXZ pes

Phys. Chem. Chem. Phys., 2011

$CH_4 + Cl \rightarrow CH_3 + HCl$

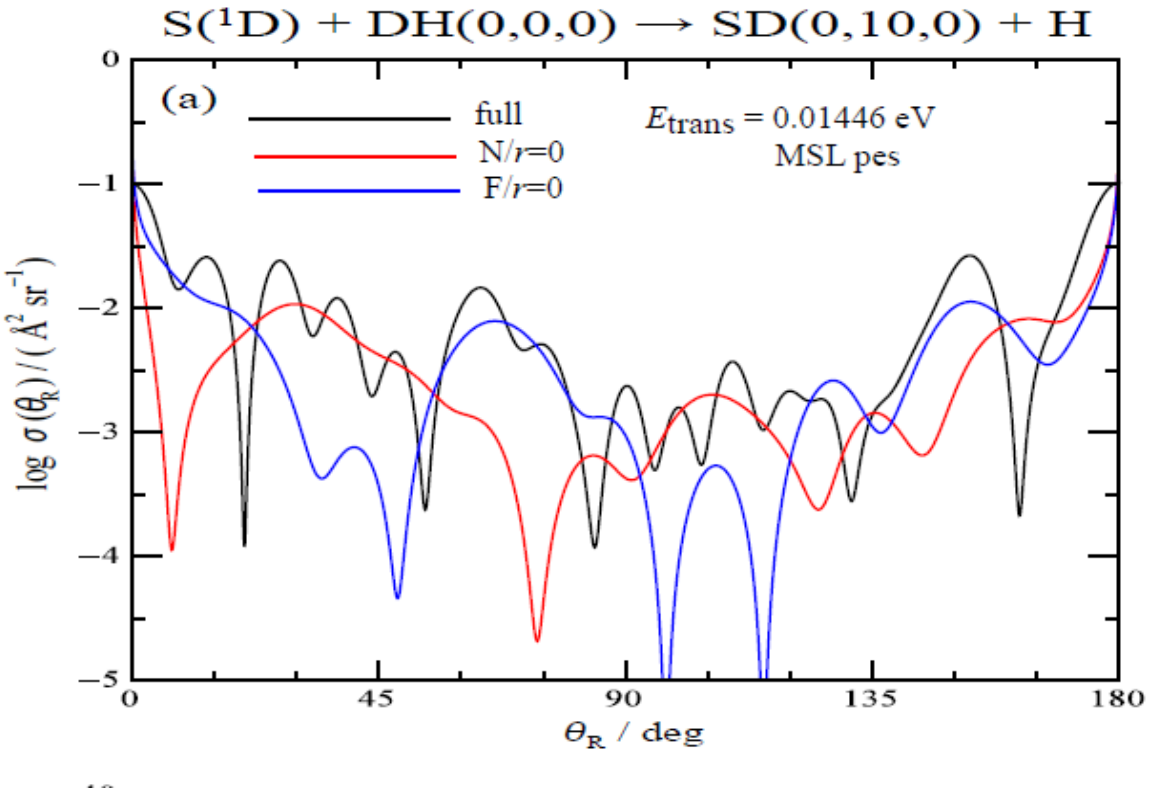
log DCS(***θ***)



A. J. Totenhofer, J. N. L. Connor and G. Nyman (*accepted*)

$S(^1D) + DH(0,0,0) \rightarrow SD(0,10,0) + H$

log DCS(***θ***)



***θ*/deg**

Marlies Hankel

AIP Advances 2015, vol. **5**

MSL = Maiti-Schatz-Lendvay 4.2 eV

Nearside-Farside theory for Local Angular Momentum (LAM)

Full LAM:

$$\mathrm{LAM}(\theta) = \frac{\mathrm{d}\arg f(\theta)}{\mathrm{d}\theta}$$

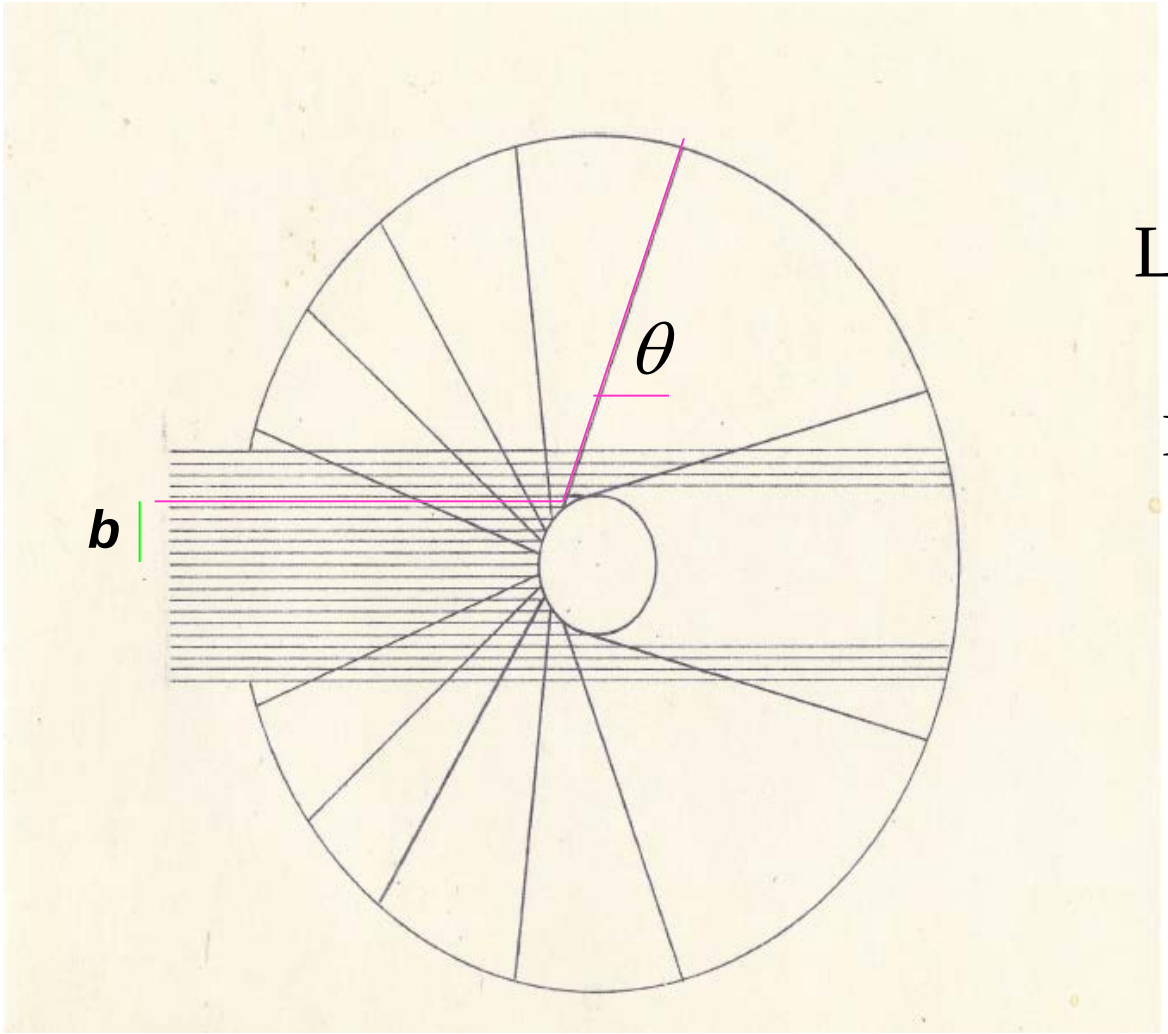
Nearside and Farside LAMs:

$$\mathrm{LAM}_{\mathrm{N}}(\theta) = \frac{\mathrm{d}\arg f_{\mathrm{N}}(\theta)}{\mathrm{d}\theta}$$

$$\mathrm{LAM}_{\mathrm{F}}(\theta) = \frac{\mathrm{d}\arg f_{\mathrm{F}}(\theta)}{\mathrm{d}\theta}$$

Also $\mathrm{LIP}(\theta) = \mathrm{LAM}(\theta)/k,$ $\mathrm{LIP}_{\mathrm{N}}(\theta),$ $\mathrm{LIP}_{\mathrm{F}}(\theta)$

Handout from Prof. Michael Polanyi's 1st year physical chemistry lectures at the University of Manchester. About 1946.



$$b = R\cos(\theta/2)$$

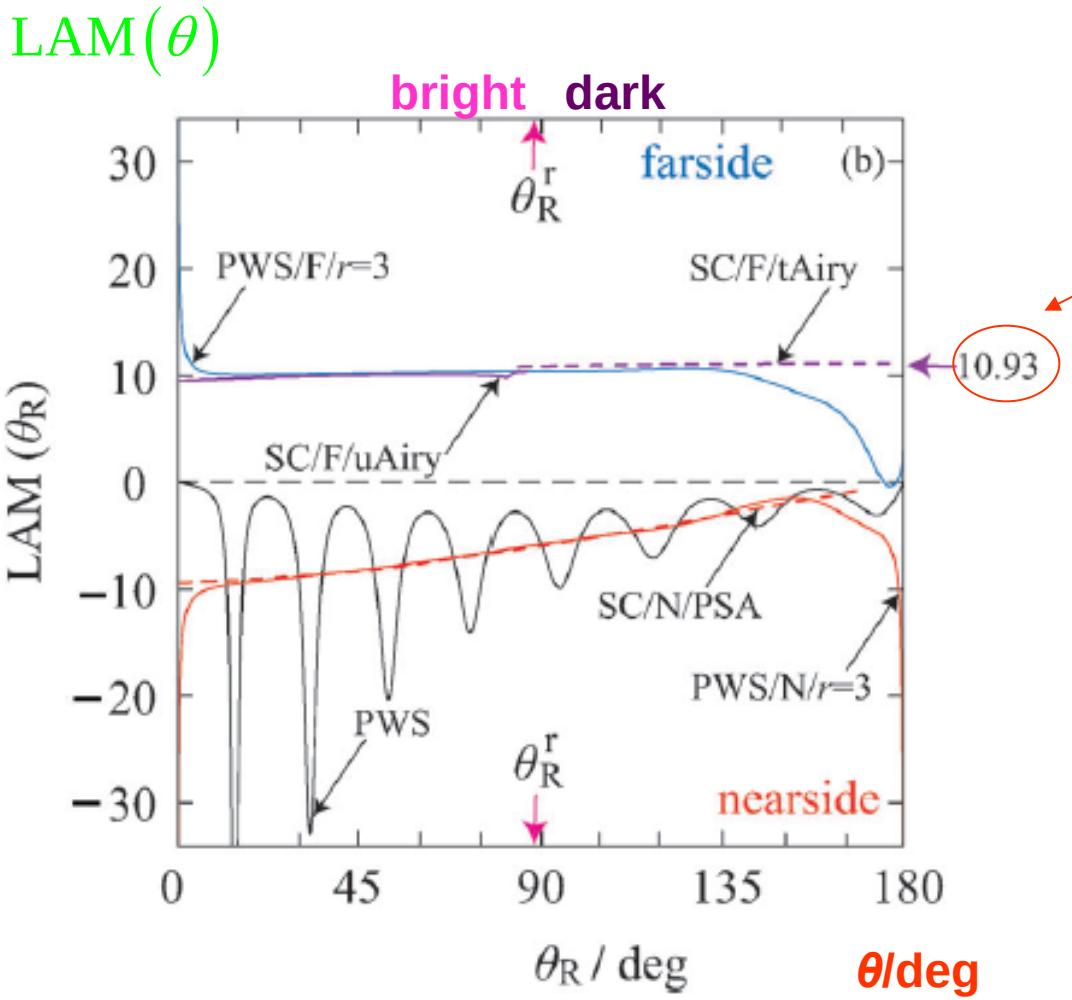
$$\mathrm{LIP_N}(\theta) = b(\theta)$$

$$\mathrm{LAM_N}(\theta) = -kR\cos(\theta/2)$$

R = radius of the sphere

Nearside-Farside LAM analysis of the angular distribution

for the F + H_2 reaction (2008 expt)



Thiele rational interpolation
*(J_0 = 10.4 + 0.5*i*)*

(0,0,0) → (3,0,0)
***E* = 0.3112 eV**
FXZ pes

Phys. Chem. Chem. Phys., 2011

Advantages of Nearside-Farside (NF) Theory

- It is exact (although approximate NF decompositions can be used when convenient).
- The input is exact (or approximate) S matrix elements as calculated by standard (or non-standard) computer programs.
- It is easily incorporated into existing computer programs.
- Semiclassical techniques such as stationary phase or saddle point Integration are not invoked, although the semiclassical picture is still evident.
- Resummation can be applied to the partial series, followed by a NF decomposition. This can improve the physical usefulness of the NF decomposition.
- NF and resummation can be incorporated into LAM-LIP analysis

Recent comments by Nobel Laureates

First, Marcus in his Spiers Memorial Lecture on the *Interplay of Theory and Computation in Chemistry* writes:[12] **(2010)**

> *"There are also major advantages of analytical theories that may capture in a single equation an entire field and relate experiments of one type to those of another. Such a theory has a generic quality."*

Second, Zewail in a personal perspective on *The Future of Chemical Physics* writes:[17] **(2010)**

> *"... large-scale computations without a 'final' theoretical condensate (or better yet, a 'simple equation') are like large-scale experiments which produce numerous results that do not boil down to a meaningful finding."*

Glory seen from an airplane

Phys. Chem. Chem. Phys., 2004, 6, 377–390

RESEARCH PAPER

PCCP
www.rsc.org/pccp

Theory of forward glory scattering for chemical reactions

J. N. L. Connor

Department of Chemistry, University of Manchester, Manchester, UK M13 9PL

Molecular Physics, Vol. 103, No. 13, 10 July 2005, 1715–1725

Taylor & Francis
Taylor & Francis Group

Theory of forward glory scattering for chemical reactions: new derivation of a uniform semiclassical formula for the scattering amplitude

J. N. L. CONNOR*

School of Chemistry, The University of Manchester, Manchester M13 9PL, UK

Molecular Physics, Vol. 104, No. 1, 10 January 2006, 159–175

Taylor & Francis
Taylor & Francis Group

Theory of forward glory scattering for chemical reactions: accuracy of semiclassical approximations using a *J*-shifted Eckart parameterization for the scattering matrix element

CHENGKUI XIAHOU† and J. N. L. CONNOR*

School of Chemistry, The University of Manchester, Manchester M13 9PL, UK

Phys. Chem. Chem. Phys., 2011, **13**, 12981–12997 **2011**

Rainbows and glories in the angular scattering of the state-to-state F + H_2 reaction at E_{trans} = 0.04088 eV

Chengkui Xiahou,[a] J. N. L. Connor*[a] and Dong H. Zhang[b]

Received 4th April 2011, Accepted 25th May 2011

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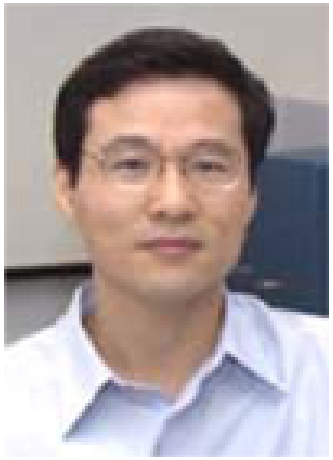
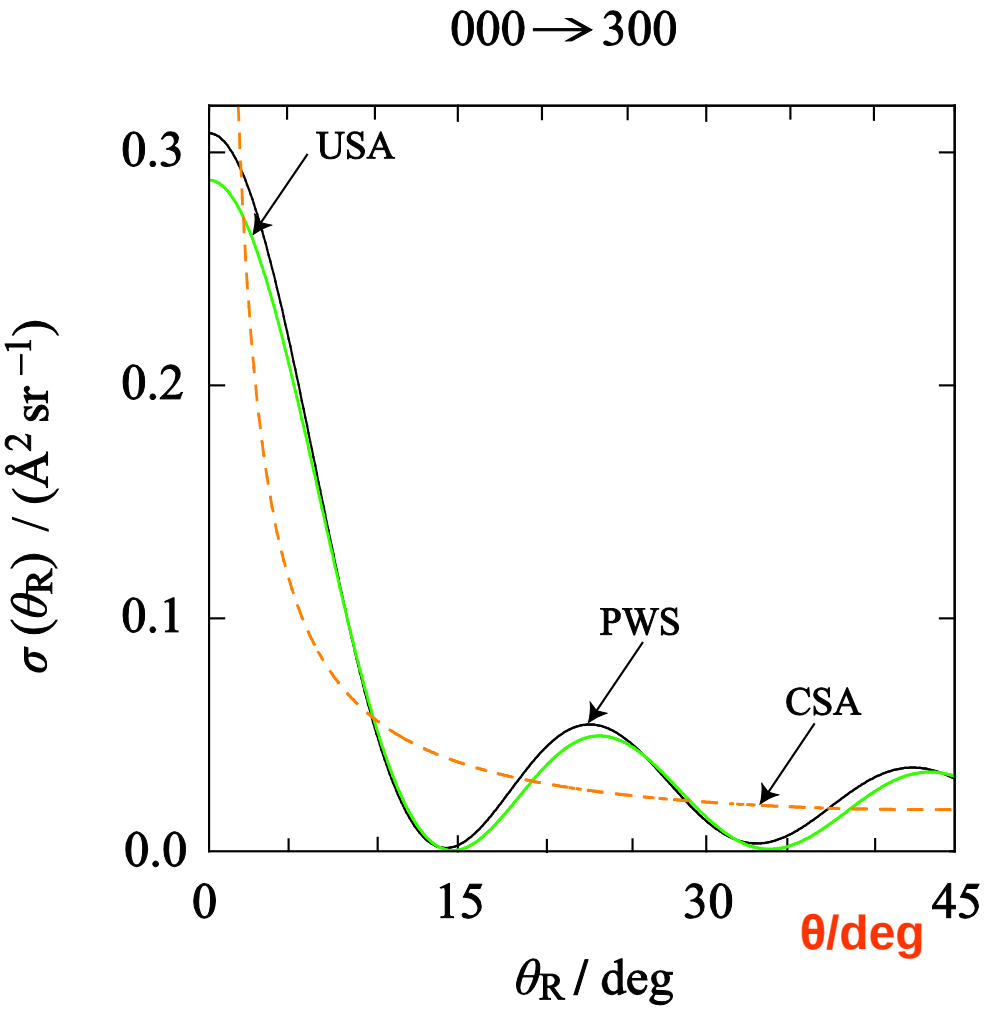
[b] *State Key Laboratory of Molecular Reaction Dynamics and Center for Theoretical and Computational Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, People's Republic of China*



Chengkui Xiahou

Dong Hui Zhang

Glory analysis for the F + H_2 reaction (2008 expt)



(0,0,0) → (3,0,0)
***E* = 0.3112 eV**
FXZ pes

Phys. Chem. Chem. Phys., 2011

Uniform Semiclassical Approximation (USA):

now called: **Uniform Bessel Approximation (UBA)**

$$I(\theta) = \frac{\pi}{2}\zeta(\theta)\left\{ \left[\sigma_-(\theta)^{1/2} + \sigma_+(\theta)^{1/2}\right]^2 J_0(\zeta(\theta))^2 + \left[\sigma_-(\theta)^{1/2} - \sigma_+(\theta)^{1/2}\right]^2 J_1(\zeta(\theta))^2 \right\}$$

where

(generic formula)

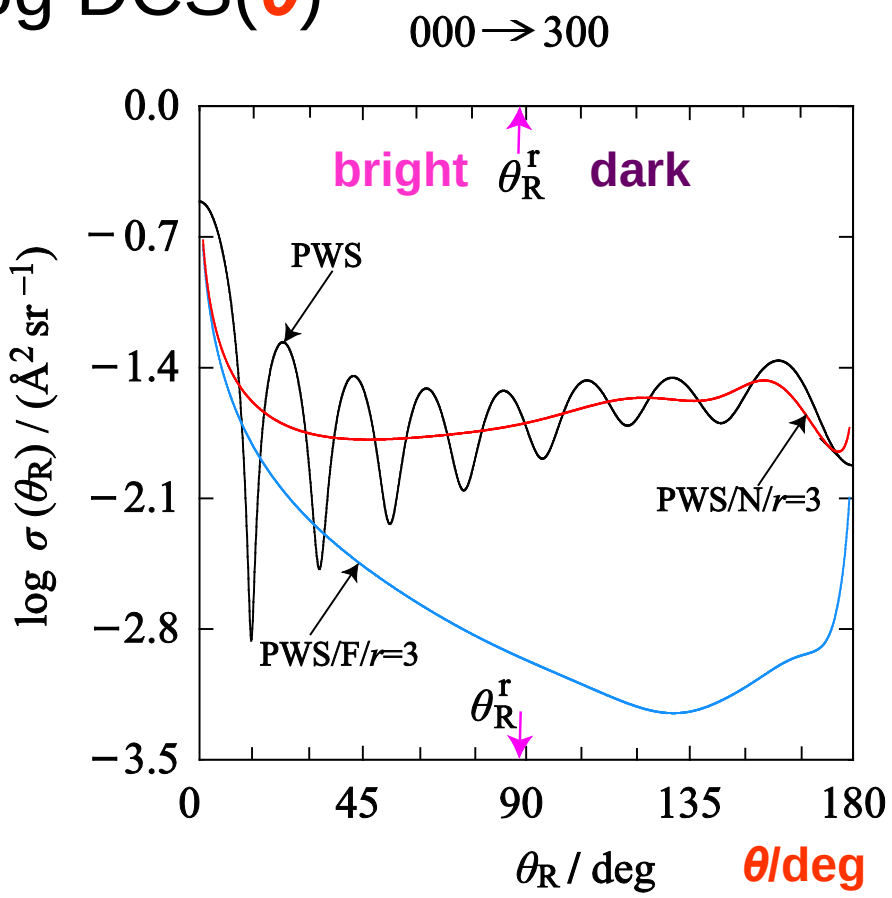
$$\zeta(\theta) = \tfrac{1}{2}\left[\beta_+(\theta) - \beta_-(\theta)\right]$$

Phys. Chem. Chem. Phys., 2004

Nearside-Farside analysis of the angular distribution for the F + H_2 reaction (2008 expt)

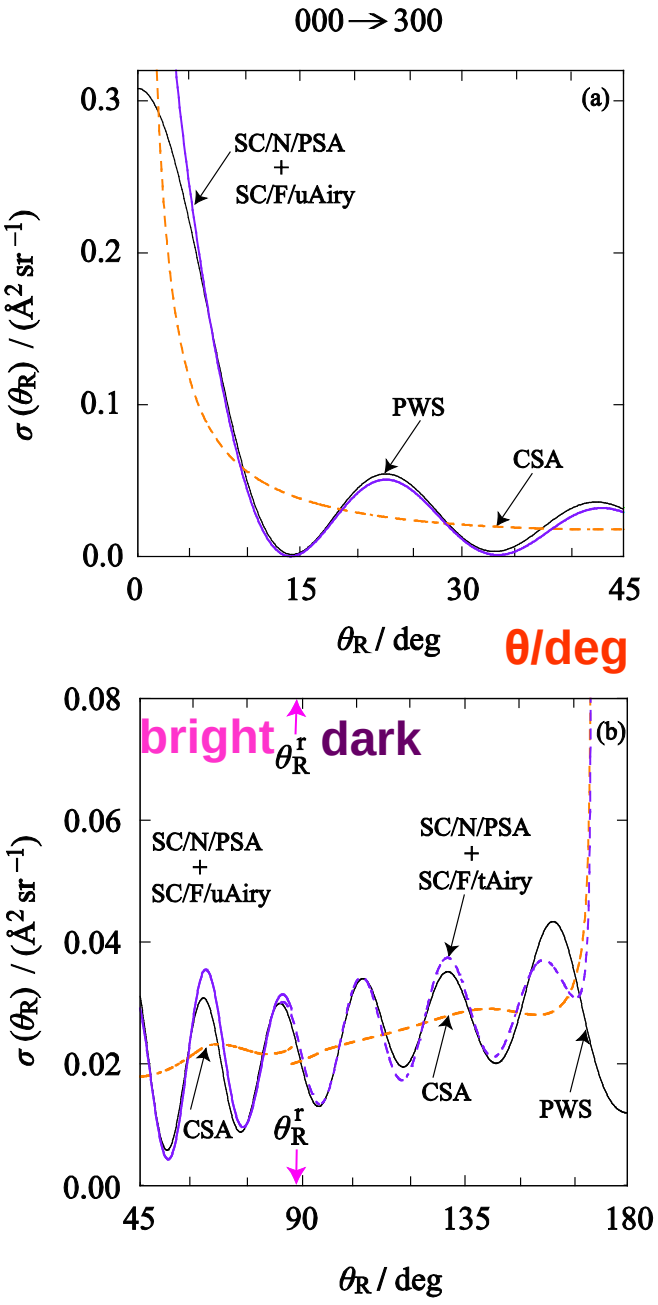
$$\sigma(\theta) = \left| f_N(\theta) + f_F(\theta) \right|^2, \quad \sigma_N(\theta) = \left| f_N(\theta) \right|^2, \quad \sigma_F(\theta) = \left| f_F(\theta) \right|^2$$

log DCS(***θ***)



(0,0,0) → (3,0,0)
***E* = 0.3112 eV**
FXZ pes

Phys. Chem. Chem. Phys., 2011



F + H_2 (2008 expt)

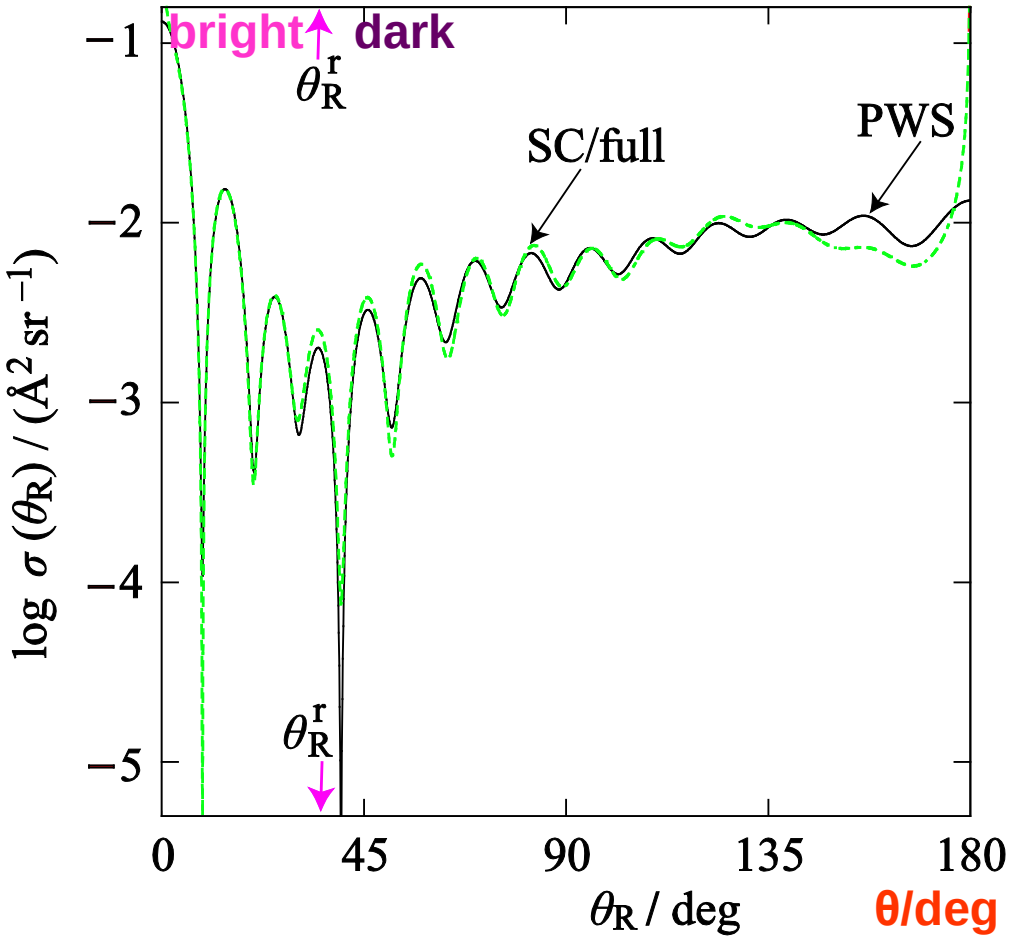
$$f_F(\theta_R) = (\bullet\bullet)\,\mathrm{Ai}(\bullet) + (\bullet\bullet\bullet)\,\mathrm{Ai}'(\bullet)$$

(generic formula)

(0,0,0) → (3,0,0)
***E* = 0.3112 eV**
FXZ pes

Phys. Chem. Chem. Phys., 2011

F + H_2 (1985 expt)



Black: PWS
Green: Semiclassical rainbow theory

(0,0,0) → (3,3,0)
***E*$_{trans}$ = 0.119 eV**
***E* = 0.3872 eV**
SW pes

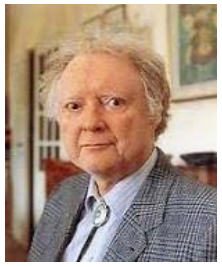
J. Phys. Chem., A, 2009

PCCP

The 6Hankel asymptotic approximation for the uniform description of rainbows and glories in the angular scattering of state-to-state chemical reactions: derivation, properties and applications

Chengkui Xiahou and J. N. L. Connor*

Phys. Chem. Chem. Phys., *2014*



THE JOURNAL OF CHEMICAL PHYSICS 138, 124310 (2013)

(*Poli di Regge*)

Resonance Regge poles and the state-to-state F + H_2 reaction: QP decomposition, parametrized S matrix, and semiclassical complex angular momentum analysis of the angular scattering

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(Received 31 December 2012; accepted 25 February 2013; published online 28 March 2013)

Complex angular momentum analysis of resonance scattering in the Cl+HCl→ClH+Cl reaction

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George C. Schatz
Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

(Received 29 March 1995; accepted 27 June 1995)

Journal of Chemical Physics, **volume 103, pages 5979-5998 (1995)**

Complex Angular Momentum Theory of Scattering

- CAM theory is completely general.
- CAM theory describes both resonance and non-resonance scattering.
- CAM theory correctly describes scattering into angular regions that are *classically allowed* or *classically forbidden*.

  "*Is a Regge rainbow all shadow? Answer: No!*"
- The standard definition of a resonance in CAM theory is a pole in the first quadrant of the CAM plane as characterized by its *position* and *residue* at a fixed value of the total energy, *E*.

Physical meaning of Regge poles

$$\frac{r_n}{J - J_n}, \qquad n = 0, 1, 2, \ldots$$

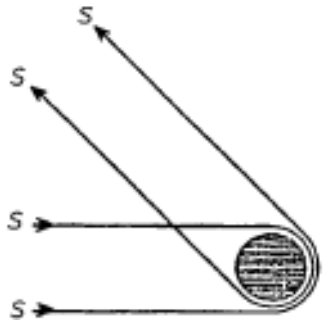
- **A Regge state is a short- or long lived "quasi-molecule" formed from the colliding partners. It corresponds to a pair of decaying surface waves that propagate around the interaction region.**

- **The surface waves decay like exp(- ImJ_n θ).**

- **1/(2 ImJ_n) determines the *life-angle* of the system.**

- **ReJ_n is related to the radius, *R*, of the interaction zone by Re$J_n \approx k\,R$.**

- **r_n is a measure of the probability of exciting the *n*th Regge state.**



S matrix = Q + P parameterization

$$\tilde{Q}_J^{\text{param}} = \left[A_0 + A_1 \exp\left(-\alpha J^2\right) \right] \exp\left[i \left(\text{polynomial up to } J^4 \right) \right]$$

Then

$$\tilde{S}_J^{\text{param}} = \left(\tilde{Q}_J^{\text{param}} + \sum_{n=0}^{n=3} \frac{\tilde{a}_n}{J - J_n} \right) \exp\left(i \tilde{\phi}_J \right)$$

$\tilde{\phi}_J$ = quadratic phase in J

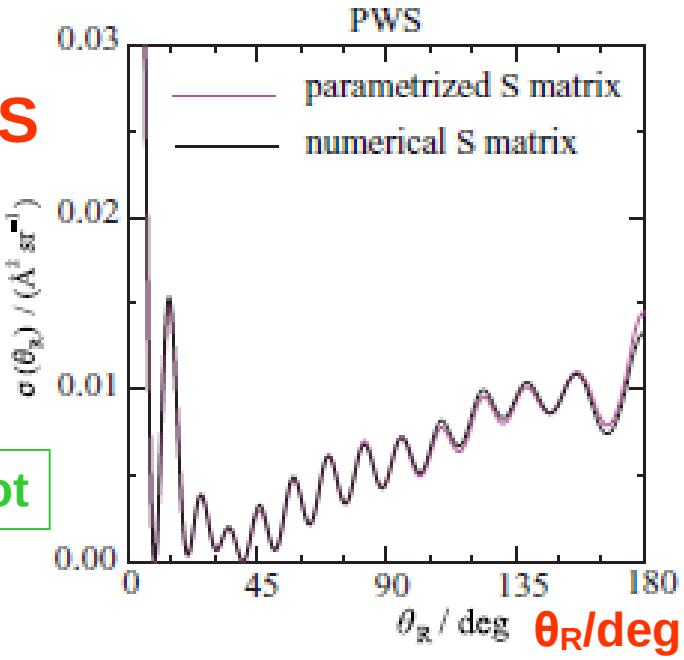
J_n = position of nth Regge pole, e.g., $J_0 = 16.4 + 0.9i$

Used to test the uniform CAM theory, etc

PWS DCSs

F + H_2 (1985 expt)

DCS



Linear plot

QP parameterized PWS

Numerical PWS

FIG. 2. Linear plot of PWS $\sigma(\theta_R)$ versus θ_R. Black curve: Numerical S matrix. Pink curve: Parametrized S matrix as given by Eq. (43).

(0,0,0) → (3,3,0)
E_{trans} = 0.119 eV
E = 0.3872 eV
SW pes

Semiclassical DCSs

124310-17 J. N. L. Connor

F + H_2 (1985 expt)

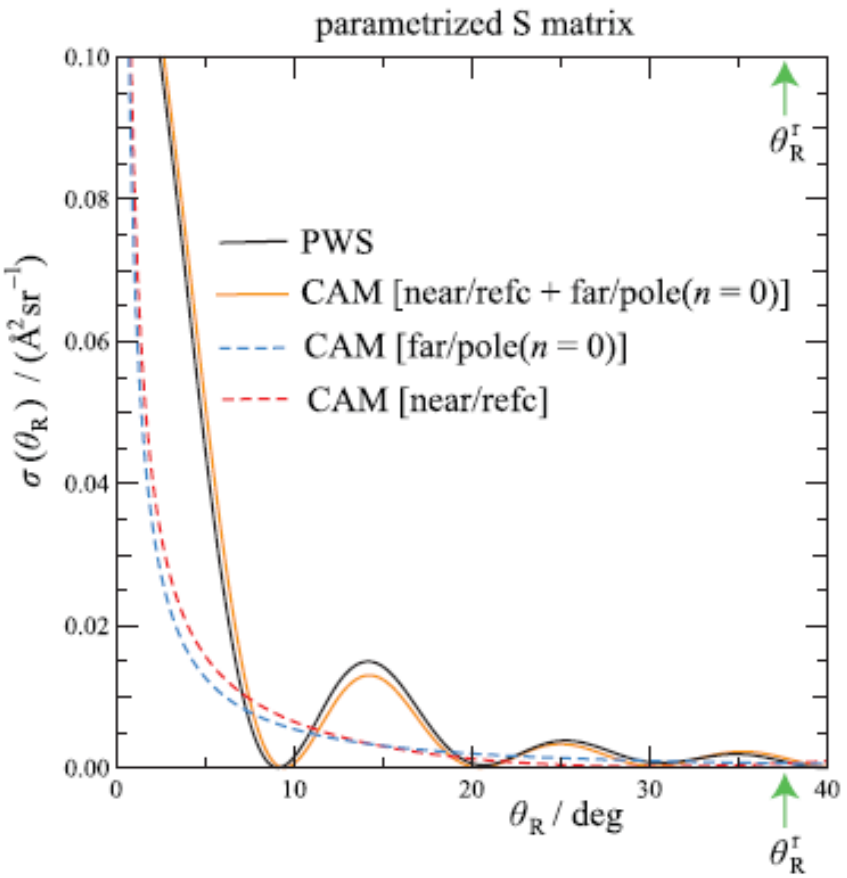


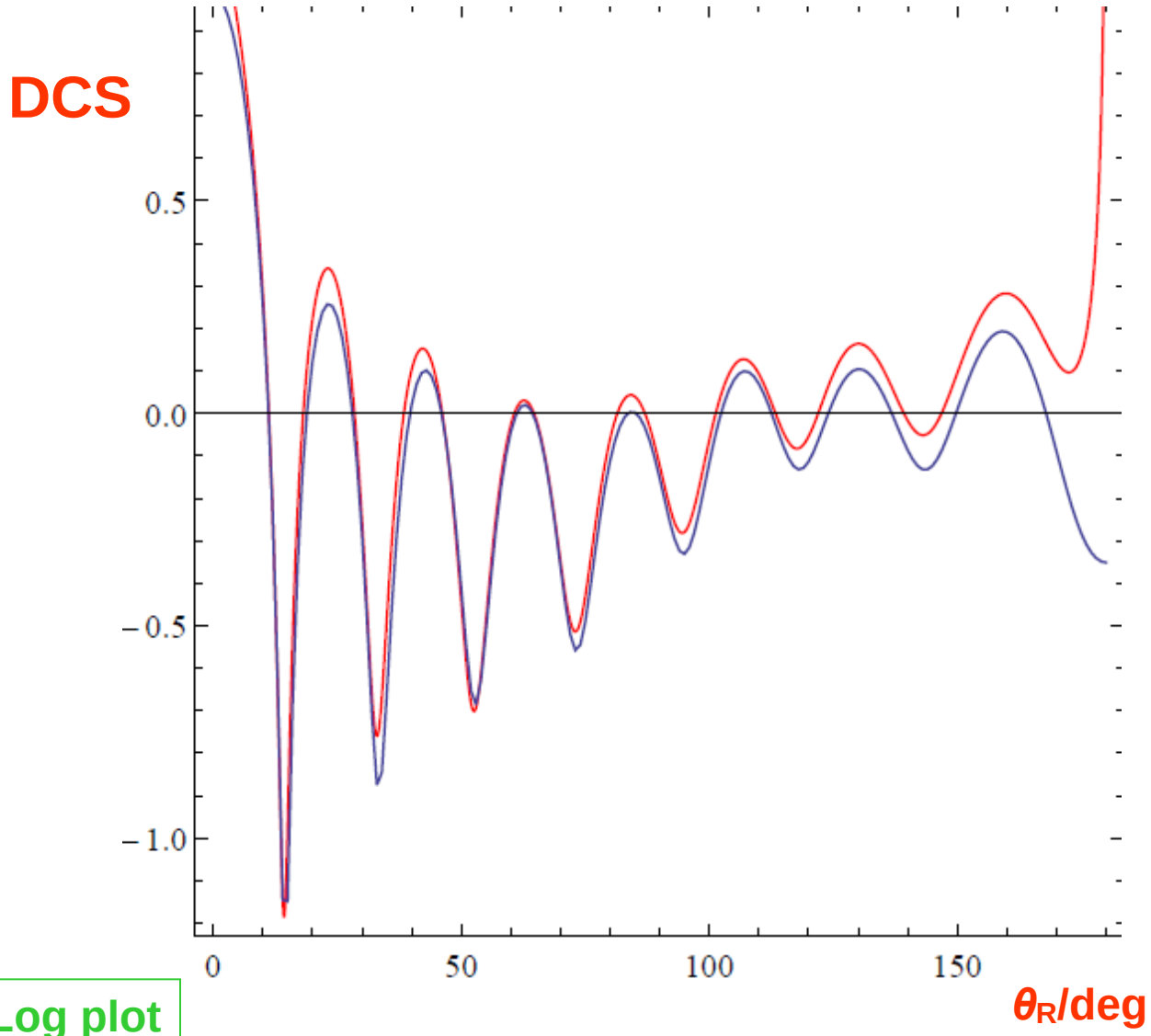
FIG. 14. Linear plot of $\sigma(\theta_R)$ versus θ_R for the parametrized S matrix with $0° \leq \theta_R \leq 40°$. Black curve: PWS. Orange curve: Uniform semiclassical CAM theory using the nearside refc subamplitude plus the farside $n = 0$ pole sub-subamplitude. Blue dashed curve: Uniform semiclassical CAM theory using the farside $n = 0$ pole sub-subamplitude. Red dashed curve: Uniform semiclassical CAM theory using the nearside refc subamplitude. The green arrows denote the position of the rainbow angle, $\theta_R^r = 37.6°$.

(0,0,0) → (3,3,0)
E_{trans} = 0.119 eV
E = 0.3872 eV
SW pes

(unpublished results)

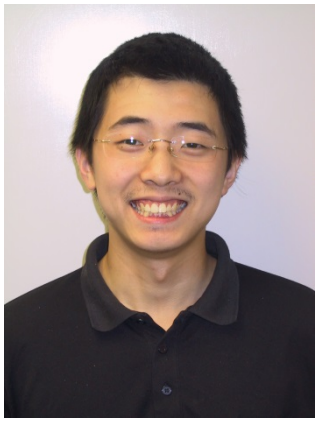
Uniform CAM and PWS DCSs

F + H_2 (2008 expt)



Uniform CAM

PWS



Xiao Shan

(0,0,0) → (3,0,0)
***E* = 0.3112 eV**
FXZ pes

Log plot

Thank you for listening!

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