ANTONIO LAGANA
CELEBRATION
NOVEMBER 2015

Wavepacket Approach to Quantum Reactive Scattering

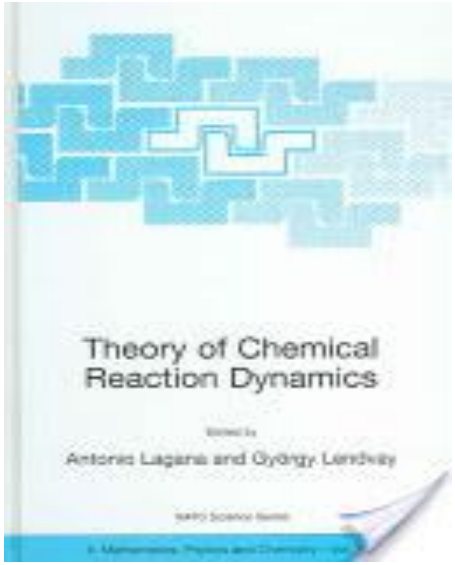
Gabriel Balint-Kurti

Telluride 1997

Antonio has been a great **initiator of collaborative projects** especially through the European COST project

Nature 2000:

For example, **Antonio Laganà**, a professor of computational chemistry at the University of Perugia in Italy, is trying to establish a research network in what he calls **meta-computing.**



Theory of Chemical Reaction Dynamics

Antonio Laganà, György Lendvay

Springer Science & Business Media, 1 Jul 2004

The theoretical treatment of chemical reaction dynamics has undergone spectacular development during the last few years, prompted by experimental progress.

A comparison of time-dependent and time-independent quantum reactive scattering—Li + HF → LiF + H model calculations

Gabriel G. Balint-Kurti, Fahrettin Gögtas, Steven P. Mort, and Alison R. Offer
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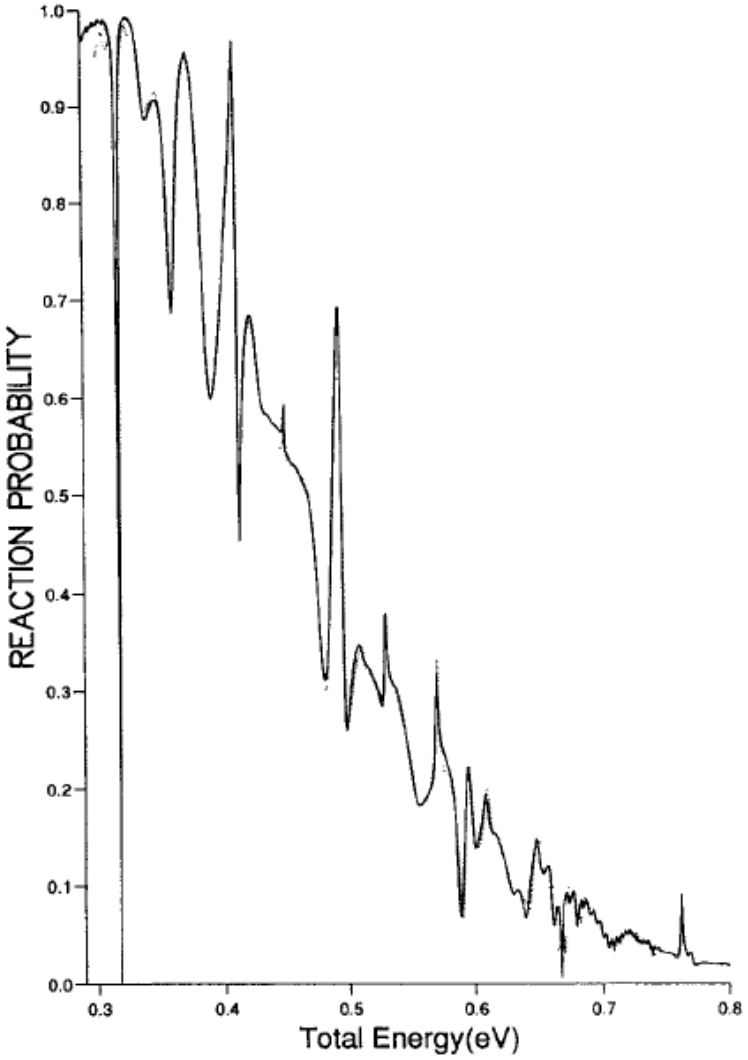
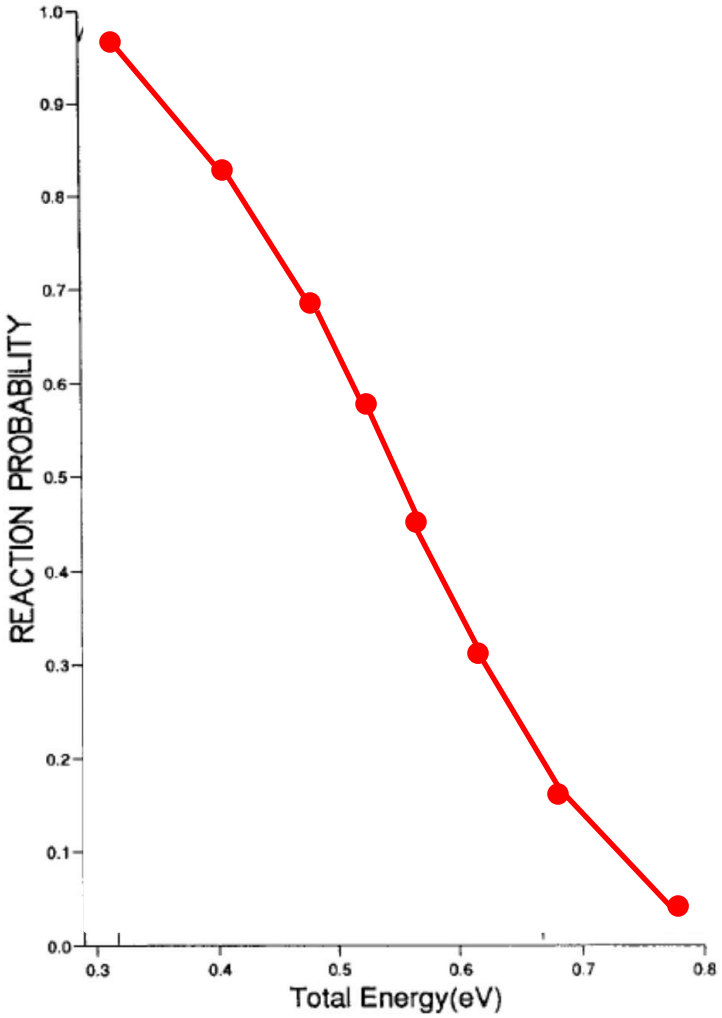
Antonio Laganà and Osvaldo Gervasi
Dipartimento di Chimica, Laboratorio di Chimica Generale, Università di Perugia, Via Elce di Sotto, 8-06100 Perugia, Italy

(Received 25 May 1993; accepted 17 August 1993)

Li + HF → LiF +H model
My initial Time-dependent wavepacket calculations

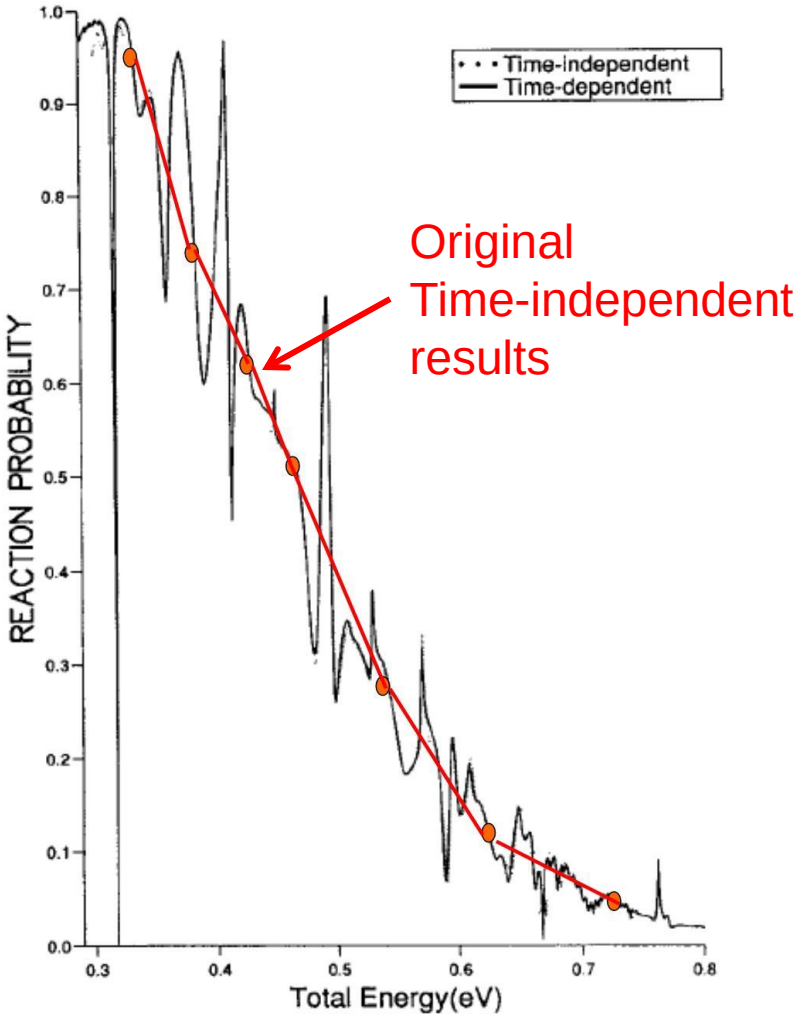


Antonio's time-independent quantum calculations for the same model

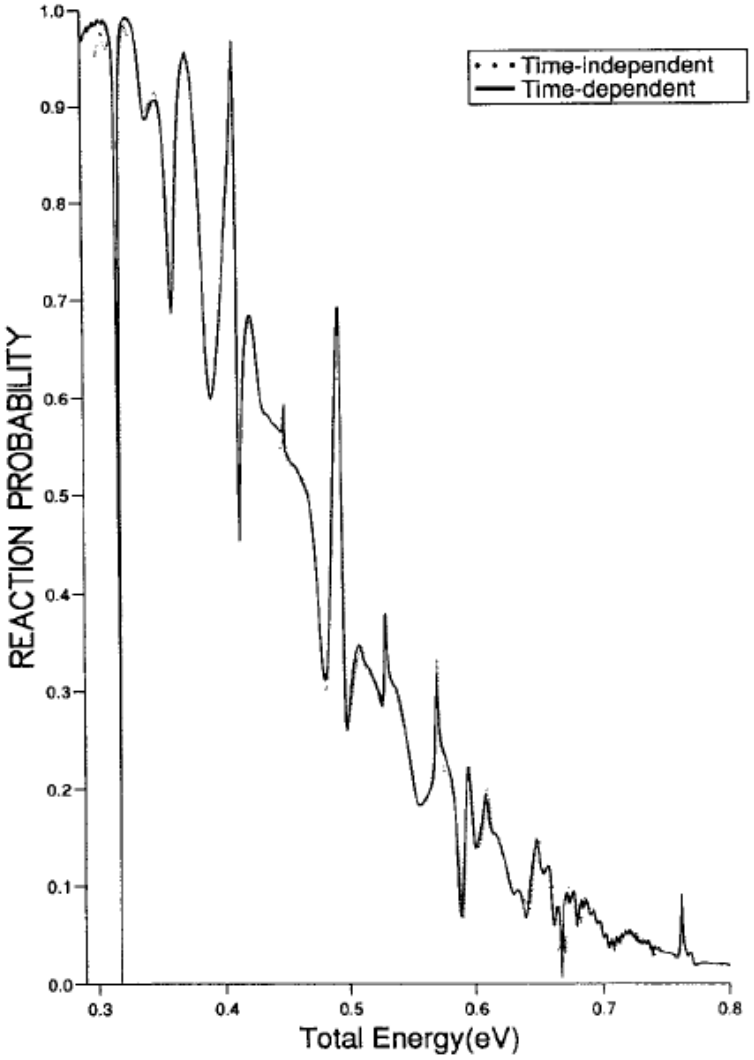


The red line illustrates the time-independent quantum results which Antonio first produced – smooth curve – no sharp resonant features.

It was only after Antonio repeated the calculations using a finer energy mesh that we obtained agreement!



Li + HF → LiF +H comparison of quantum time independent & time dependent calculations Fixed angle model calculations



Reactive Scattering

- Time-independent

  Rotational-Vibrational basis sets

  Solve large set of coupled second order differential Equations

  Obtain complete **S** matrix at one collision energy

  gives ALL cross sections including many of no interest.

- Wavepackets (Time-Dependent & Time-Independent)

  Wavepacket represented by its values at grid points

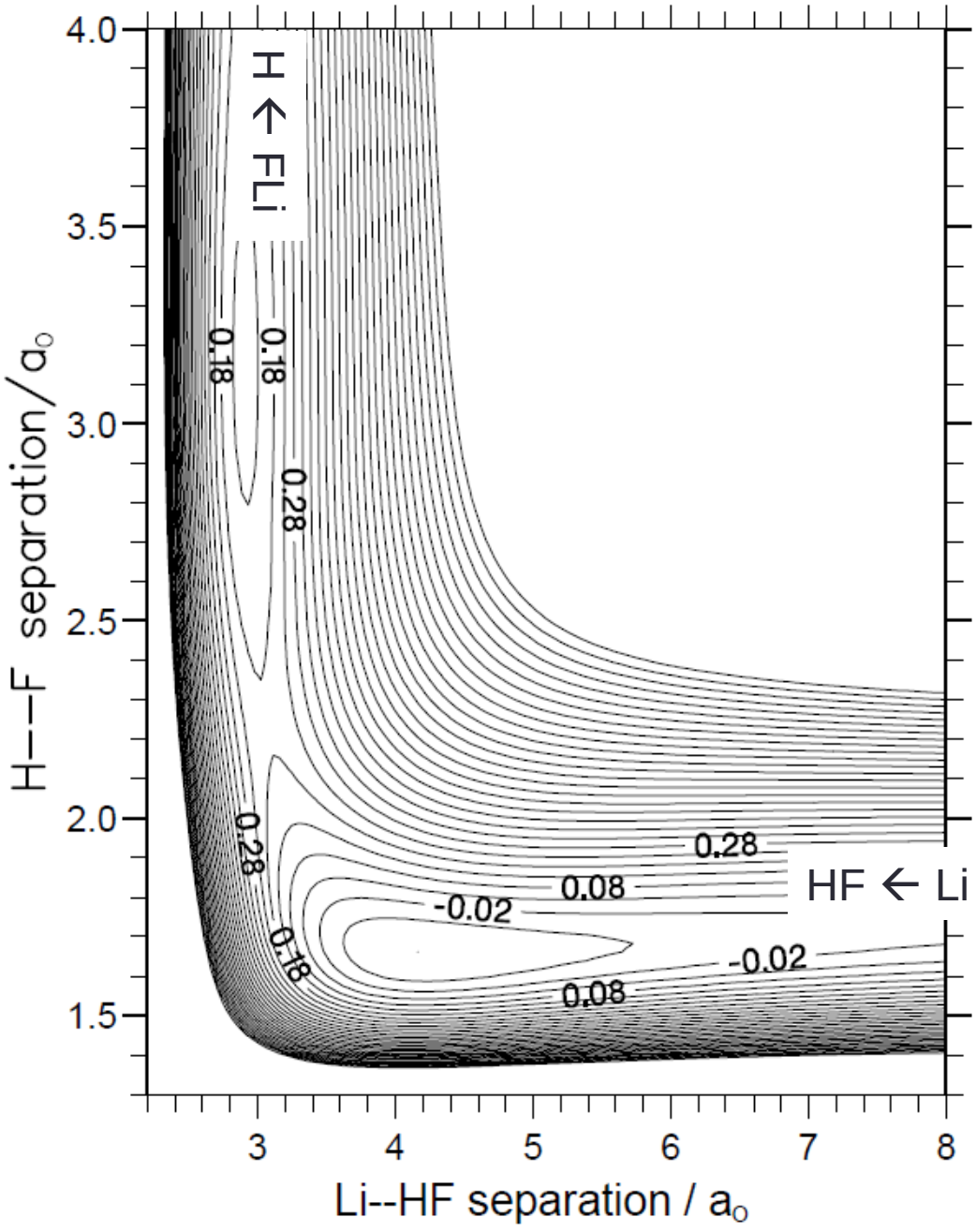
  – **no basis sets**

  Propagate wavepacket forward in time by applying time evolution operator to wavepacket

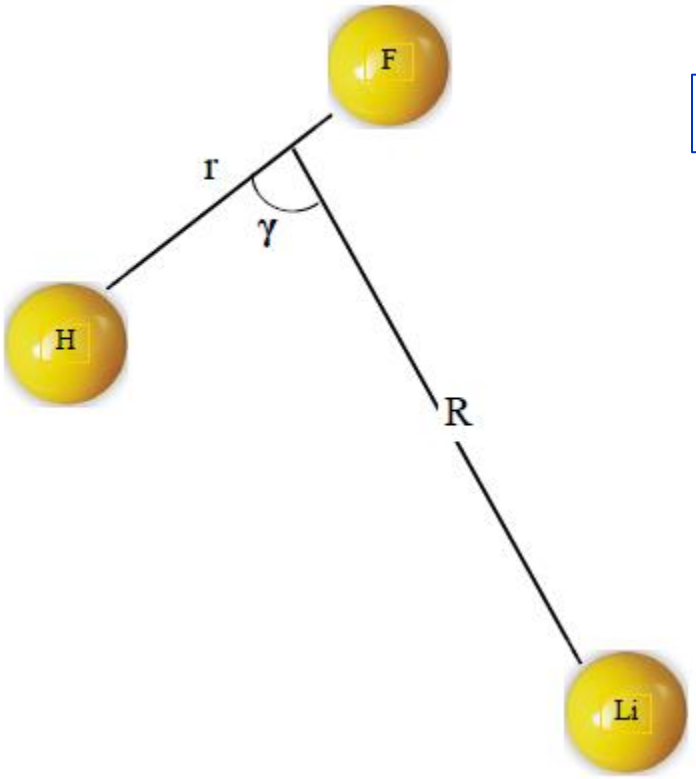
  Obtain cross sections at all energies, starting only from desired quantum state.

Li + FH ⟶ LiF + H

Fixed Li-F-H angle



Initial Wavepacket

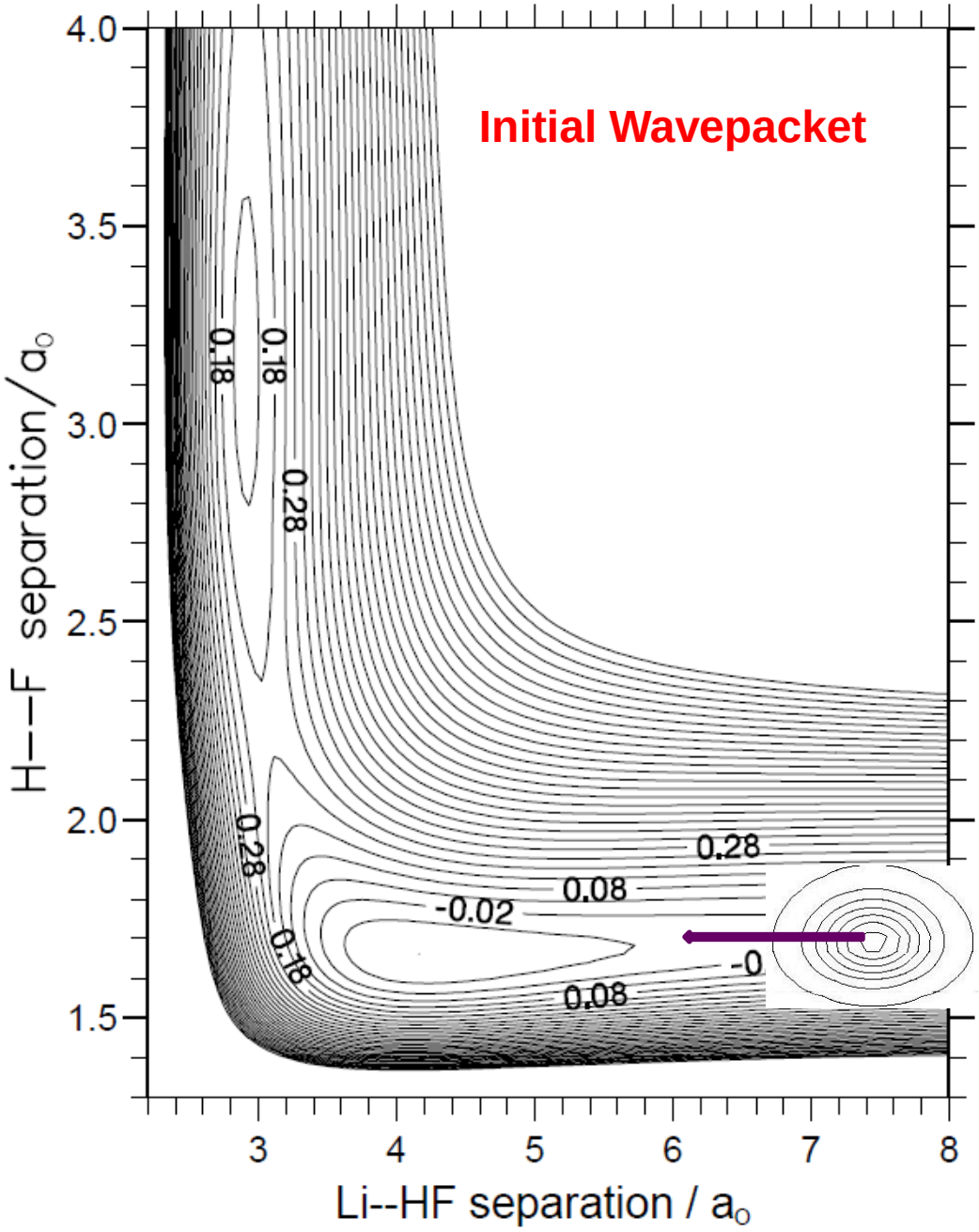


Rotational-vibrational wavefunction of HF

$$\Psi = e^{-ikR} e^{-\alpha(R-R_o)^2} \Phi_{v,j}(r,\gamma)$$

Gaussian wavepacket

Plane wave moving to smaller R


Initial Wavepacket
H--F separation / a_o
Li--HF separation / a_o
4.0
3.5
3.0
2.5
2.0
1.5
3
4
5
6
7
8
0.18
0.18
0.28
0.28
0.28
0.08
-0.02
0.18
-0
0.08

Find how much of the initial wavepacket corresponds to relative kinetic energy E.

The wavepacket is localised in space – contains a range of energies by Hiesenberg's theorem.

$$g(k') = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ik'R} e^{-ikR} e^{-\alpha(R-R_o)^2} dR$$

Amplitude of wavepacket at energy $E=k^2\hbar^2/2\mu$

R dependence of wavepacket

Wavepacket Propagation

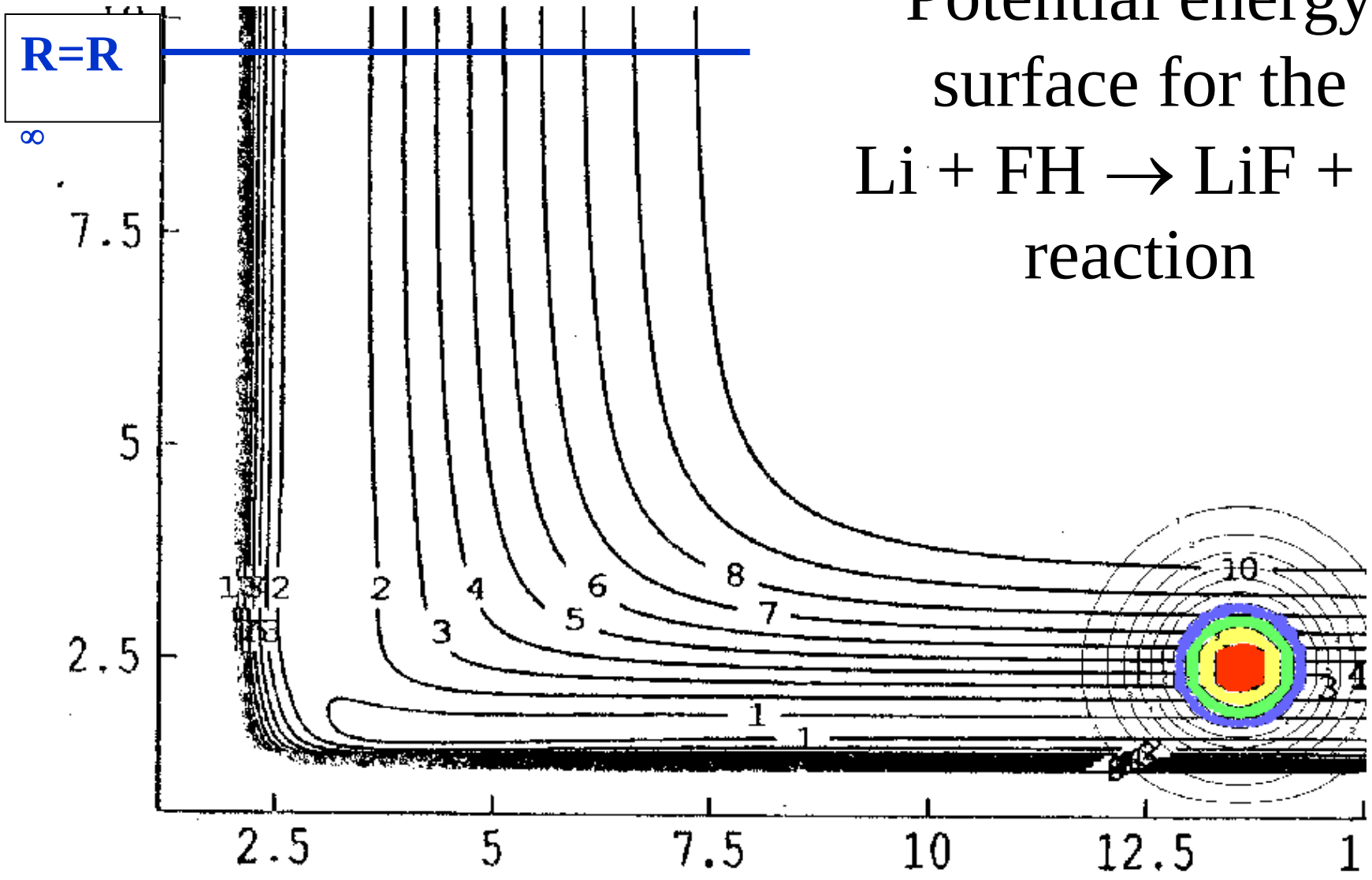
$$\Psi(t+\tau) = e^{-i\hat{H}\tau/\hbar}\,\Psi(t)$$

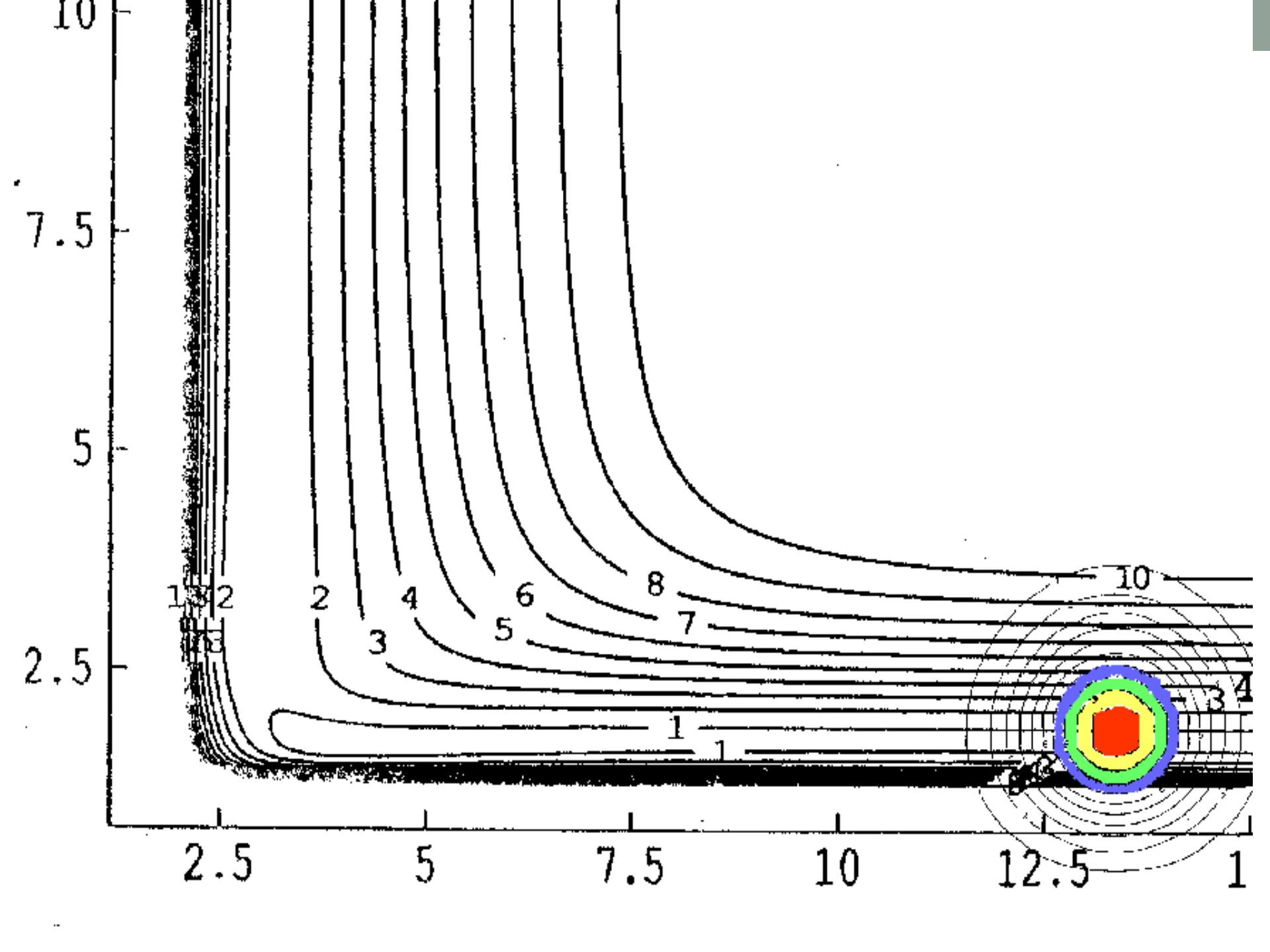
Time Evolution Operator

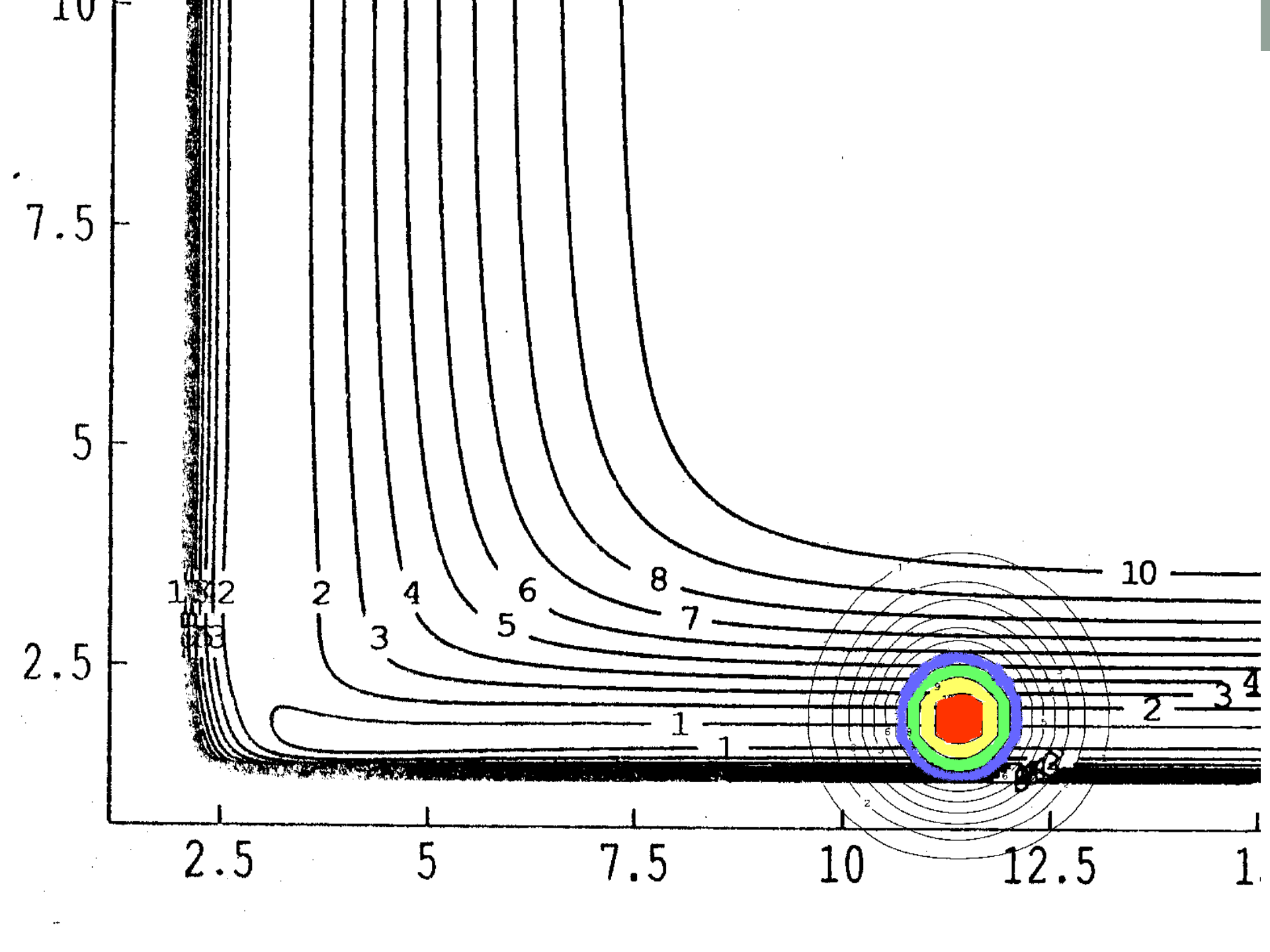
Kosloff introduced the expansion of the Time Evolution operator as an expansion in Chebyshev Polynomials (T_n).

$$e^{-i\hat{H}t/\hbar} = \sum_n A_n(t) T_n\left(-\hat{H}\right)$$

Potential energy surface for the $Li + FH \rightarrow LiF + H$ reaction




10
7.5
5
2.5
2.5
5
7.5
10
12.5
1
1
2
3
4
5
6
7
8
10


10
7.5
5
2.5
10
8
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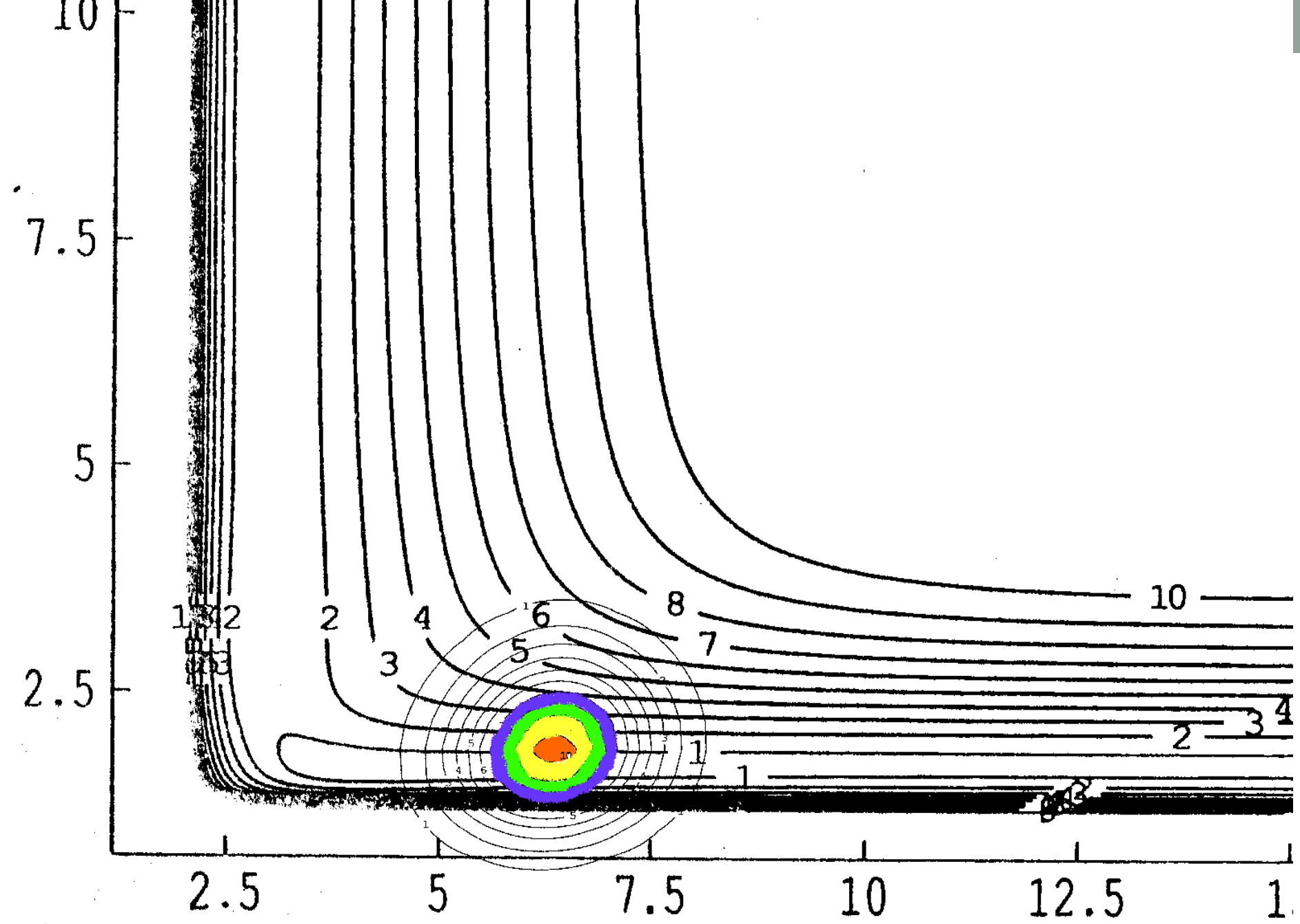
2
1
1
2
3
4
2.5
5
7.5
10
12.5


10
7.5
5
2.5
2.5
5
7.5
10
12.5
1
10
8
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4
3
2
1
1
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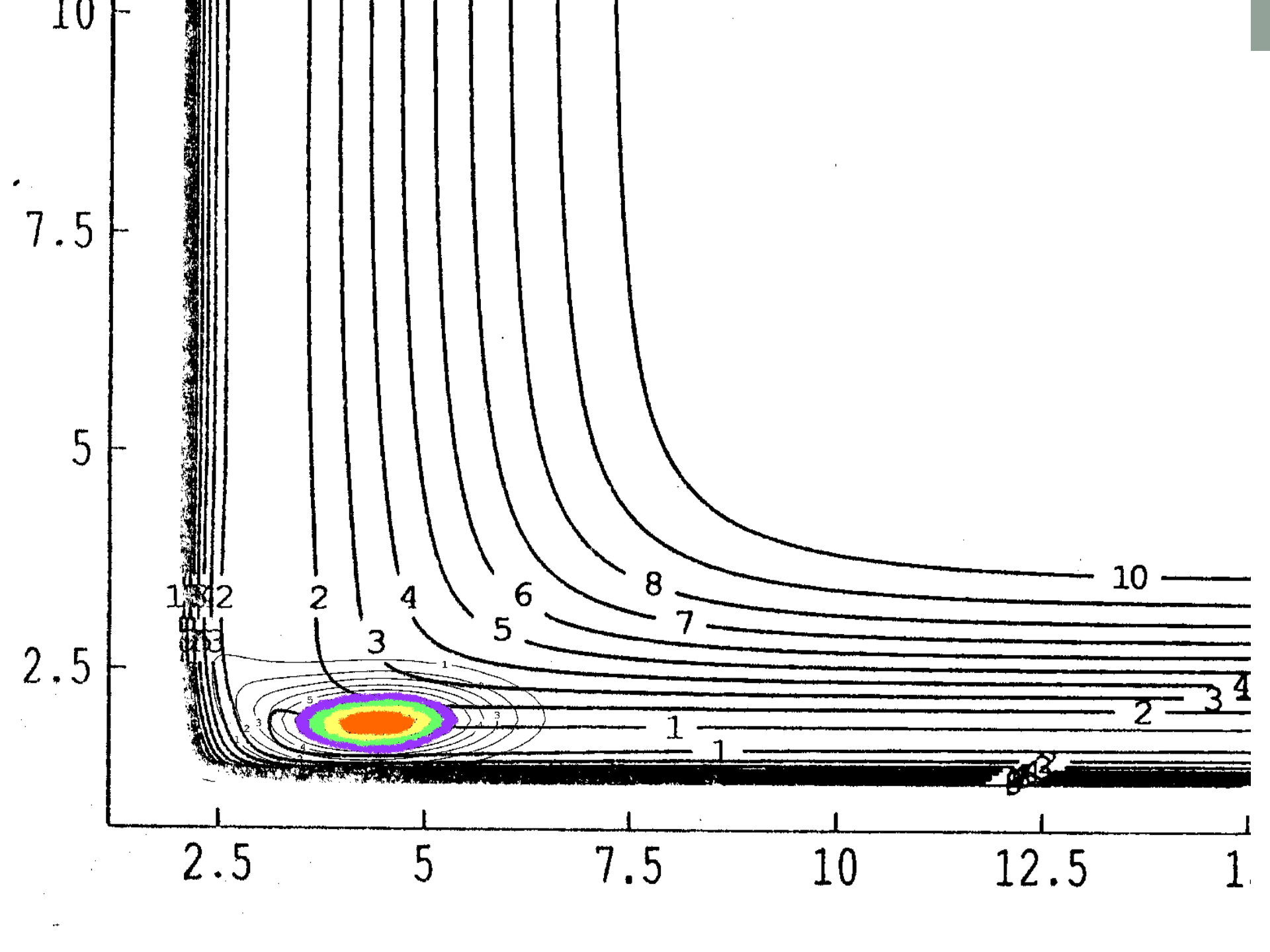
3
4
2
3
4


10
7.5
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2.5
2
4
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7
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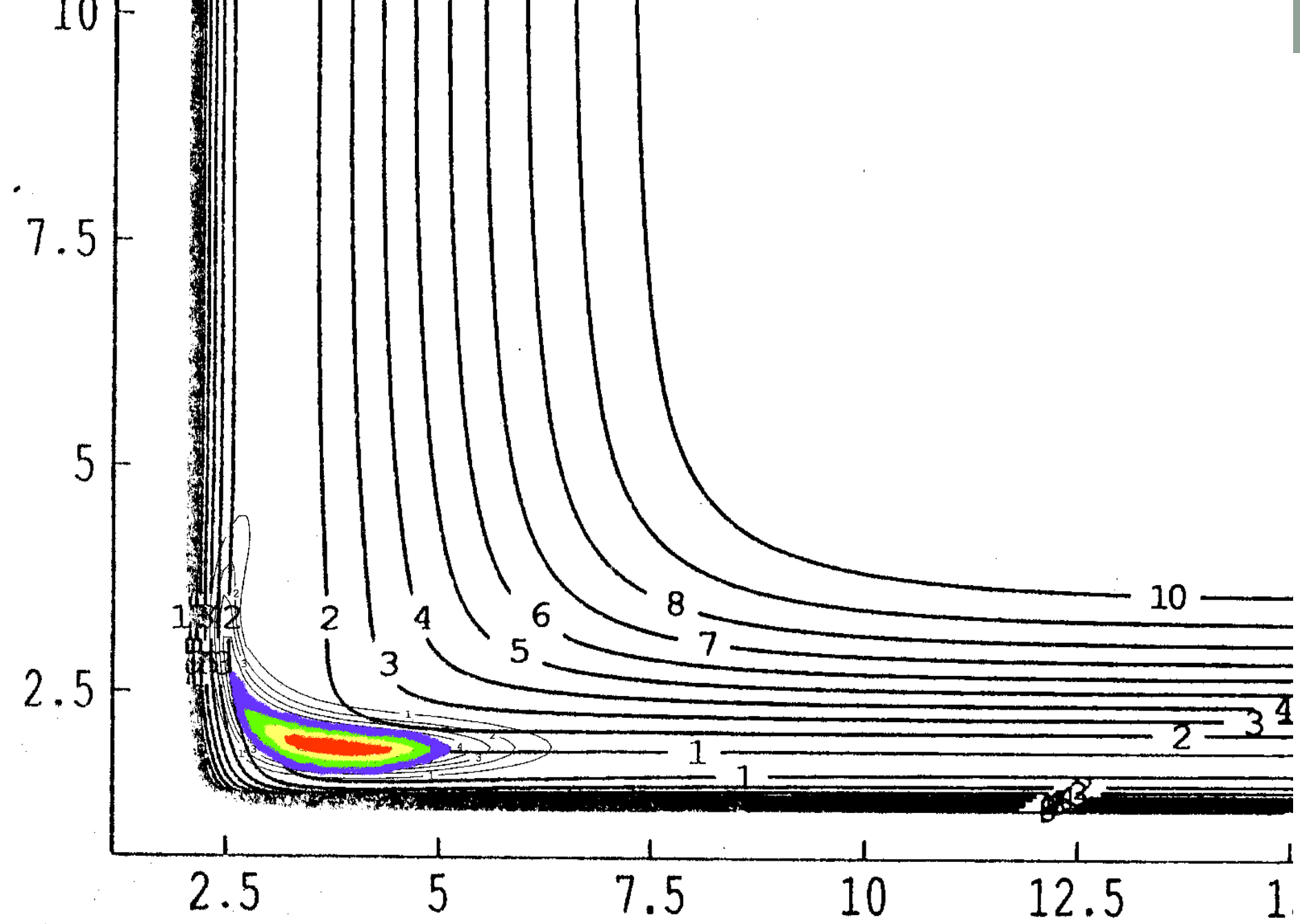
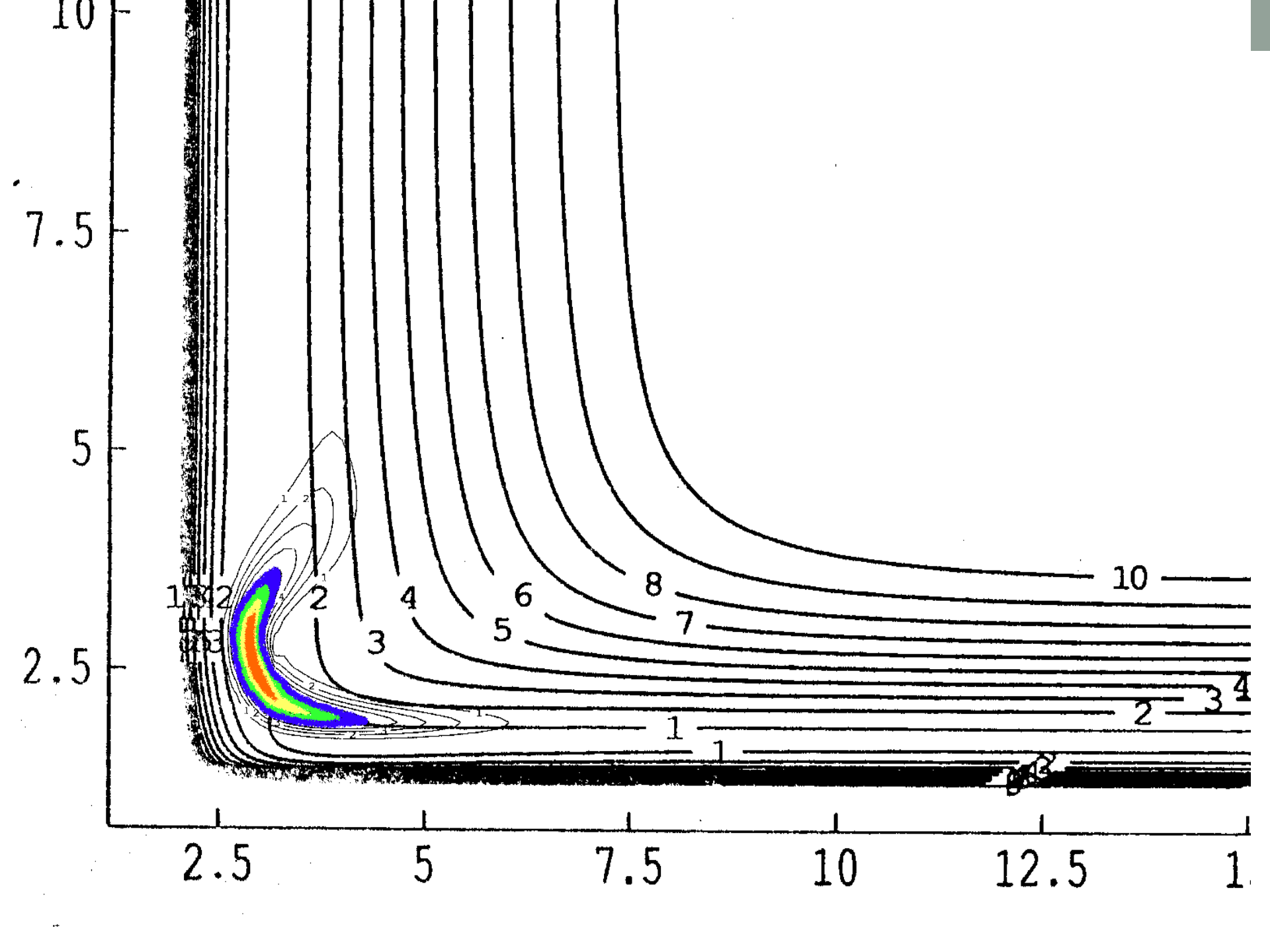
3
2
1
2.5
5
7.5
10
12.5

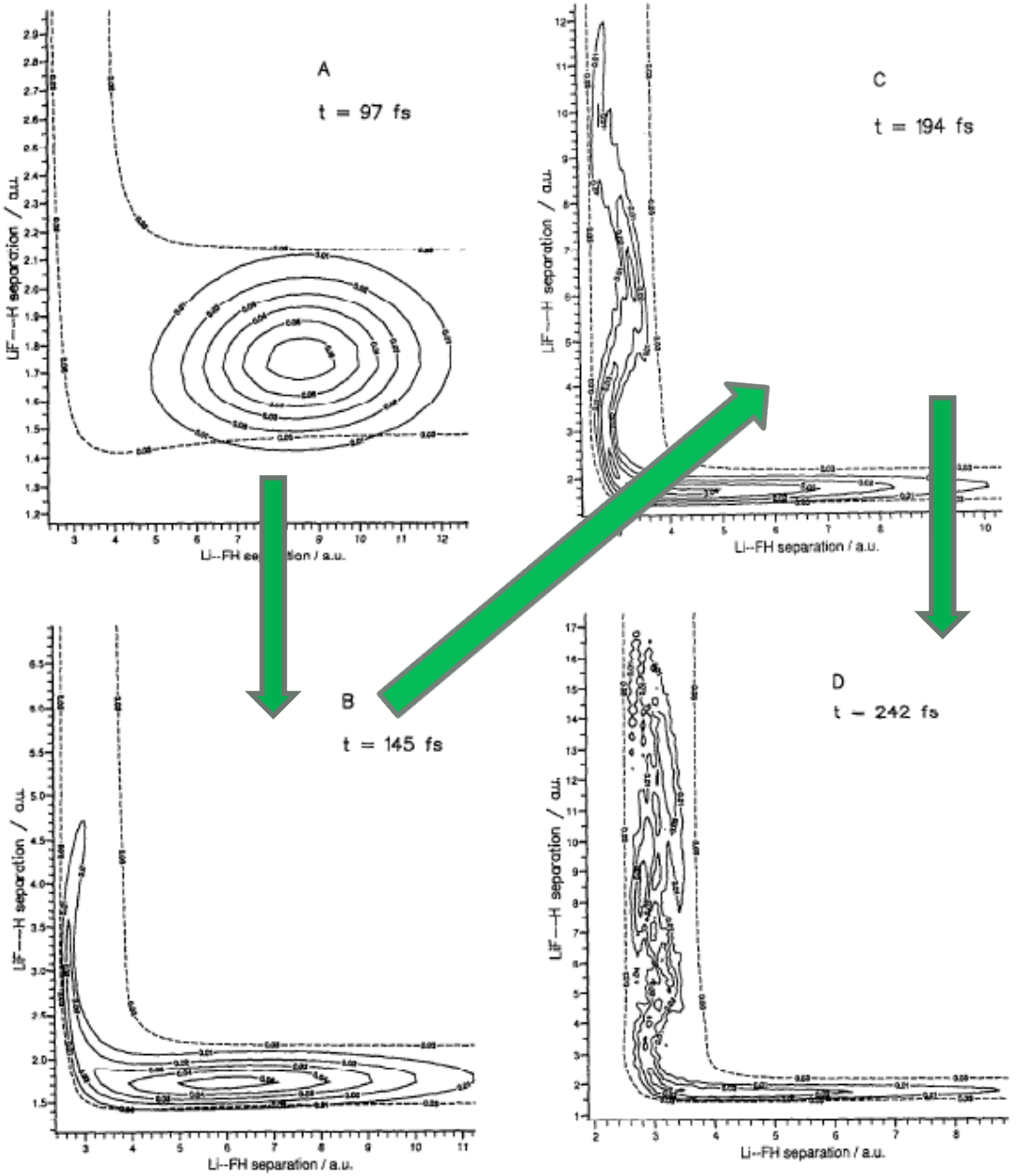

10
7.5
5
2.5
2.5
5
7.5
10
12.5
1
10
8
7
6
5
4
3
2
1
1


10
7.5
5
2.5
2
3
4
5
6
7
8
10
1
2.5
5
7.5
10
12.5

$$Li + FH \longrightarrow LiF + H$$

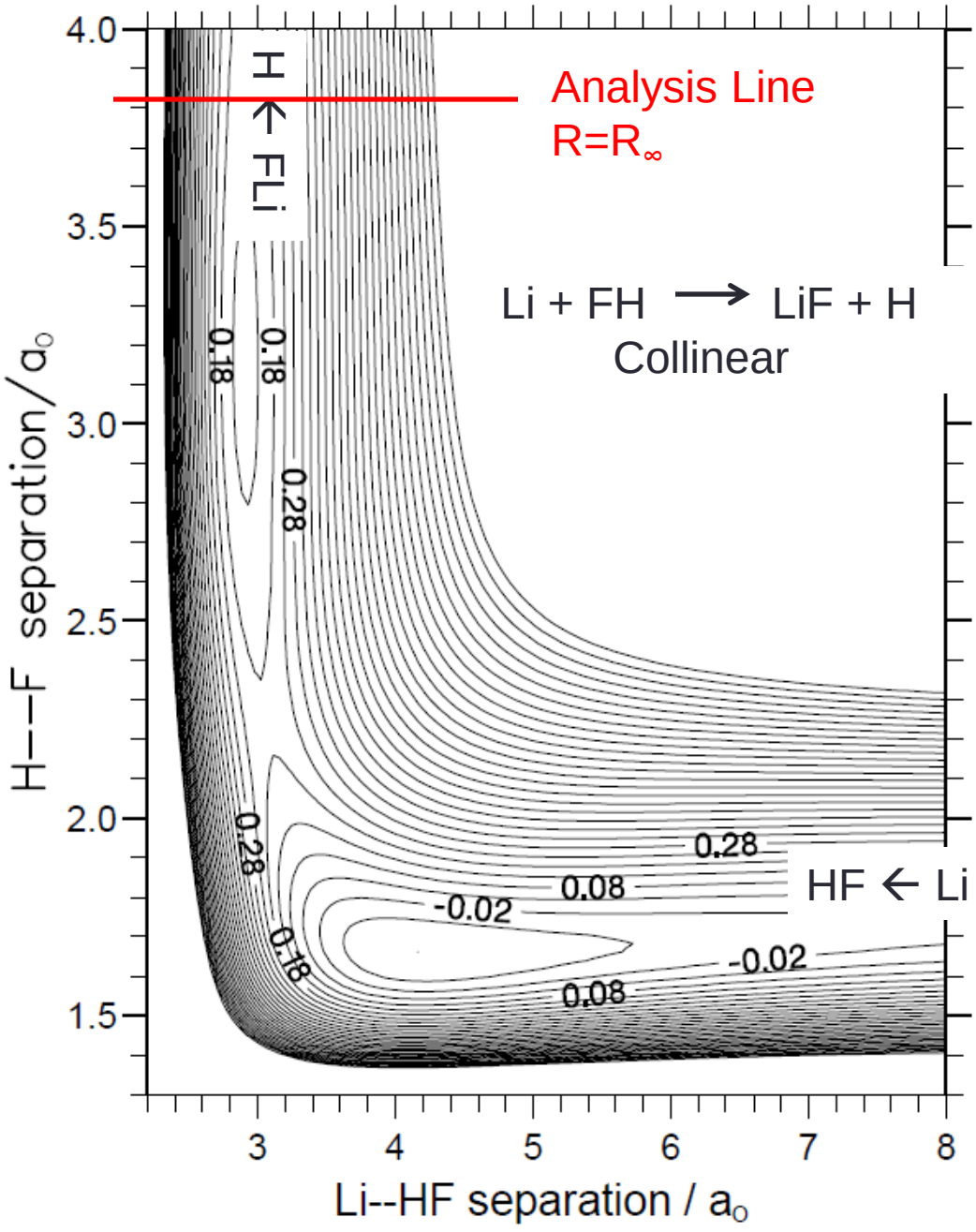
Collinear

Snapshots during propagation



S matrix & Cross Sections

Take cut through wavepacket at each time step as it passes through the analysis line $\Psi(r,R=R_\infty;t)$



S matrix & Cross Sections

$$C_{v' \leftarrow v}(t) = \int \phi_{v'}(r)\, \Psi(r, R=R_\infty; t) r^2 dr$$

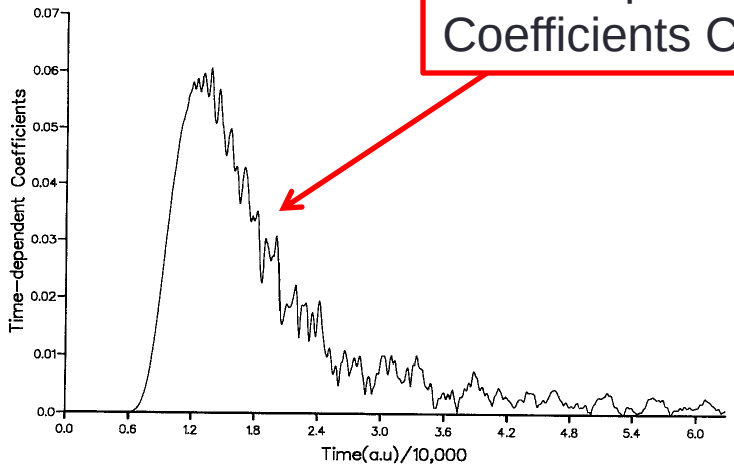
Use Fourier Transform to convert Time → Energy

$$A_{v' \leftarrow v}(E) = \frac{1}{2\pi} \int e^{iEt/\hbar}\, C_{v' \leftarrow v}(t) dt$$

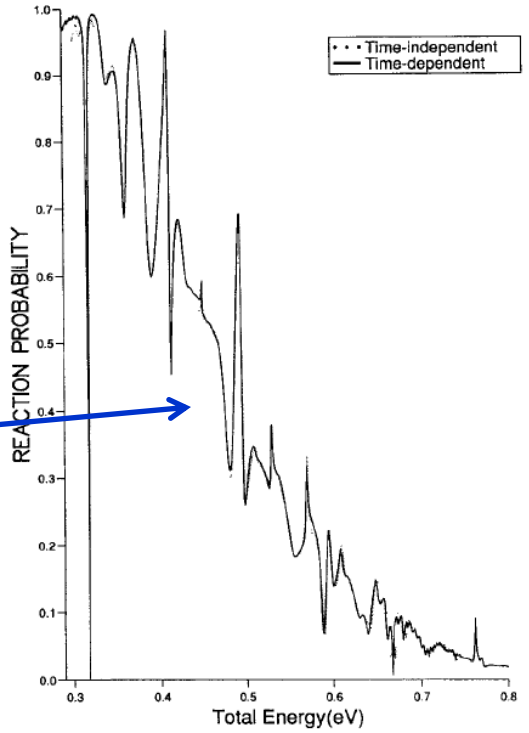
$$S_{v' \leftarrow v} = \hbar \left(\frac{k_v k_{v'}}{\mu \mu'} \right)^{1/2} \frac{A_{v' \leftarrow v}(E)}{g(-k_v)}$$

Li + HF → LiF +H collinear

Time-Dependent Coefficients C(t)



Reaction Probability



$O + H_2$ Electronically non-adiabatic Reactive Scattering

S. K. Gray, G. G. Balint-Kurti,
G. C. Schatz, J. J. Lin, X. Liu,
S. Harich & X. Yang,
JCP, 113, 7330 (2000).

$$O(^1D) + H_2 \rightarrow OH(^2\Pi) + H$$

The reactants give rise to 5 potential energy surfaces.

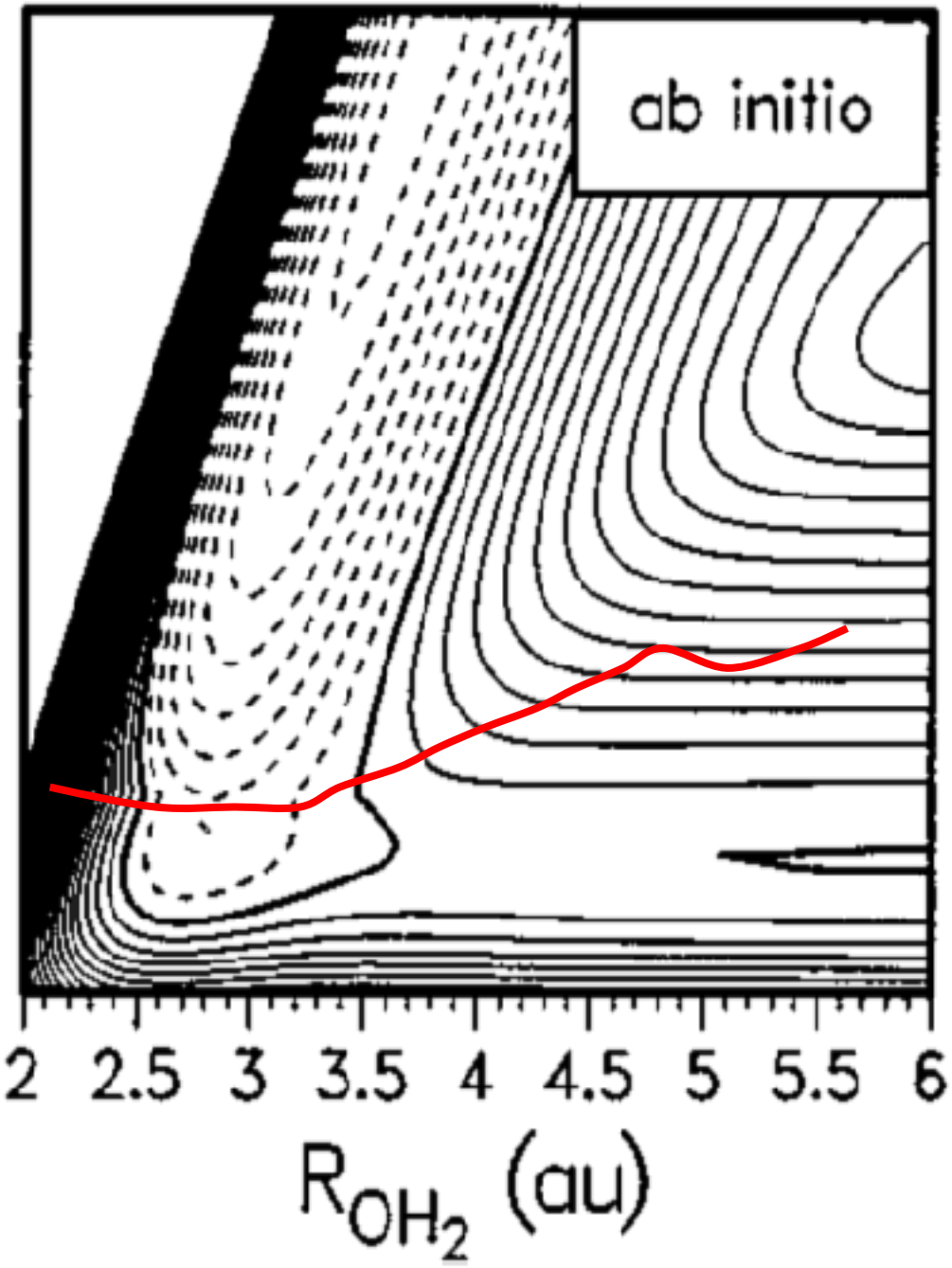
Only 3 of them participate in the reaction.

3 potential energy surfaces

X^1A'

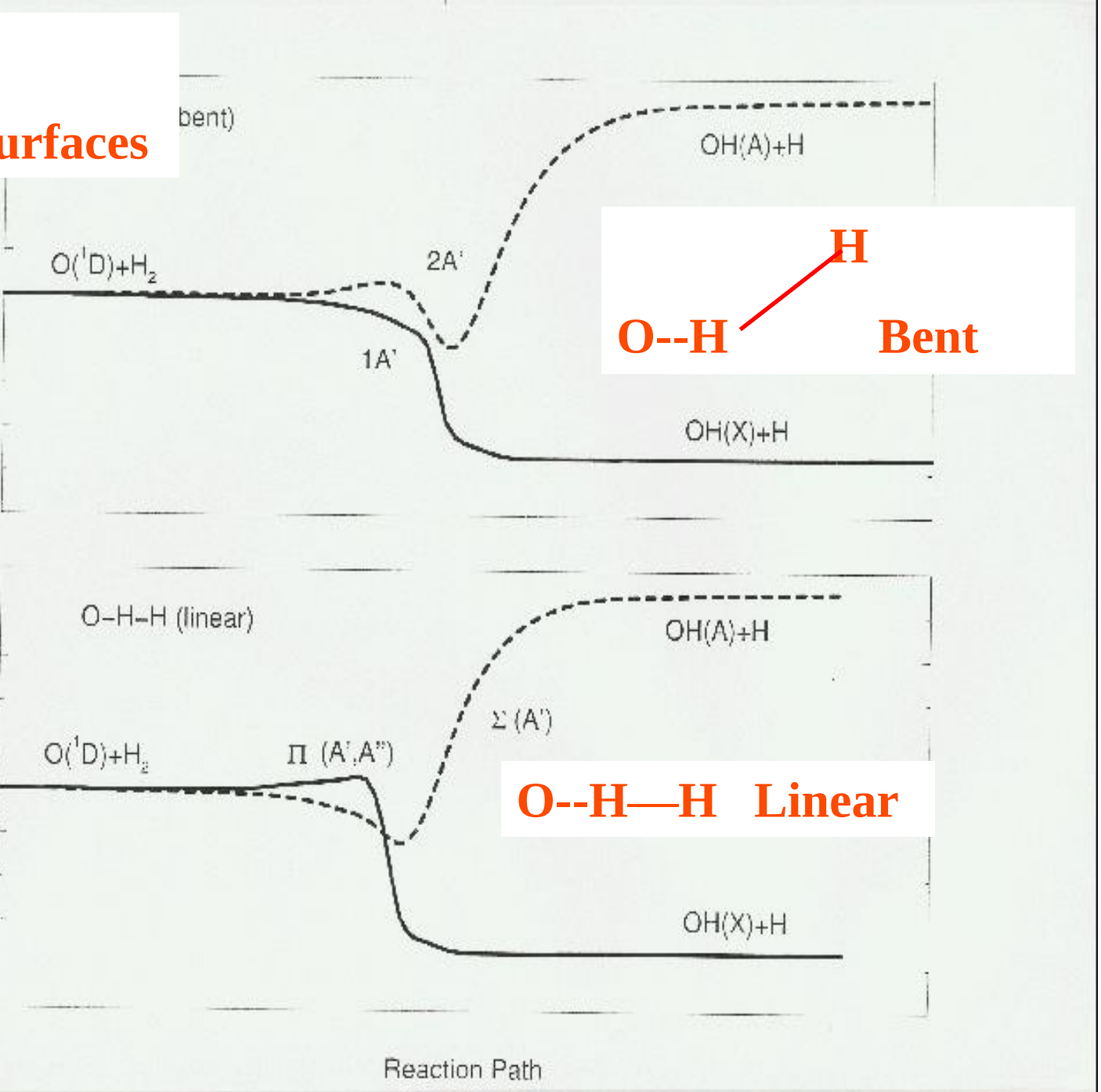
$2^1A'$

$1^1A''$



O-H-H collinear surface from Schatz, Papaioannou, Pederson, Harding, Hollebeek, Ho & Rabitz
JCP 107, 2340 (1997)

urfaces



H

O--H Bent

O--H—H Linear

OBJECTIVE:

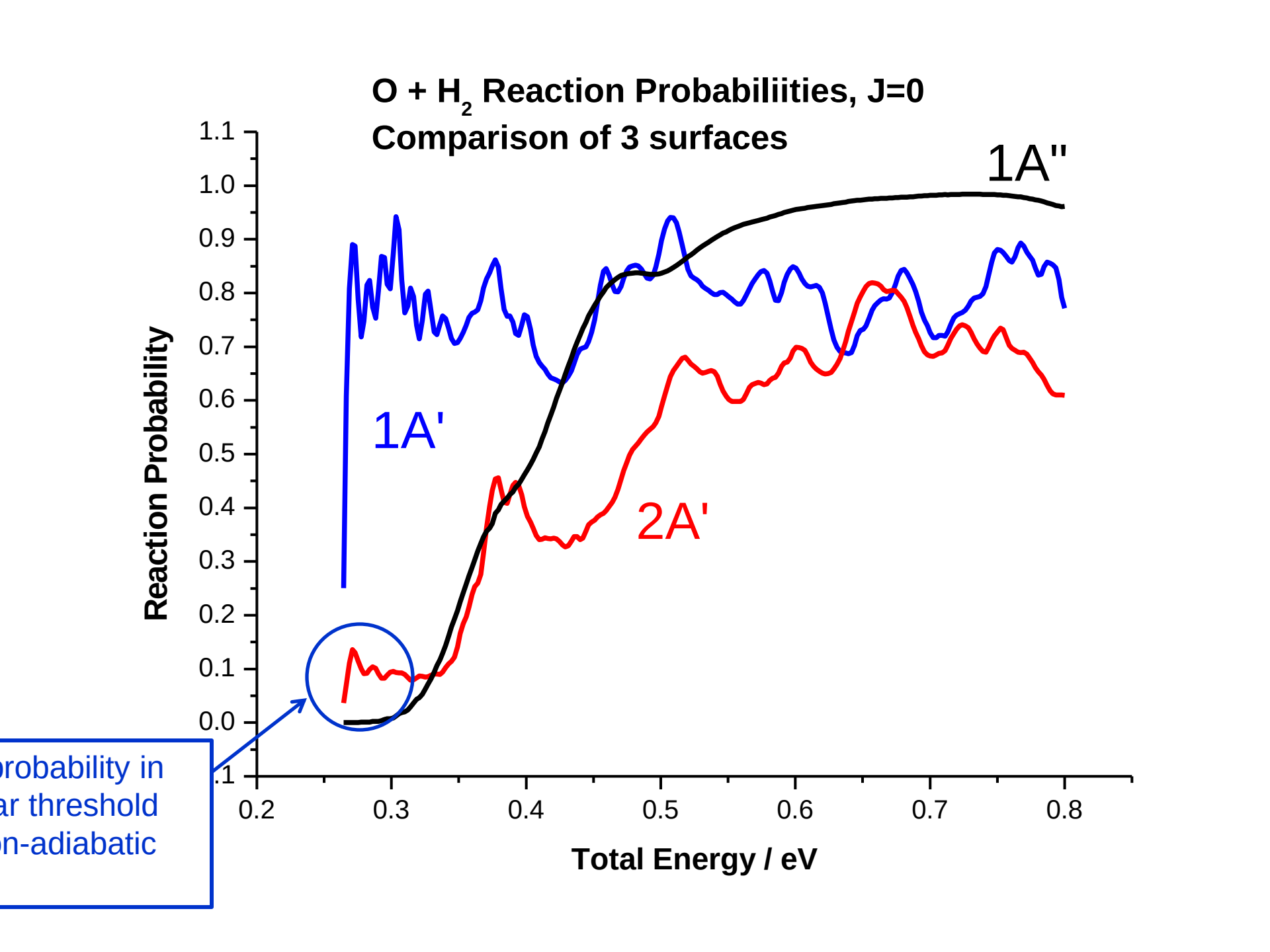
To compute ratio σ(j=1)/σ(j=0)

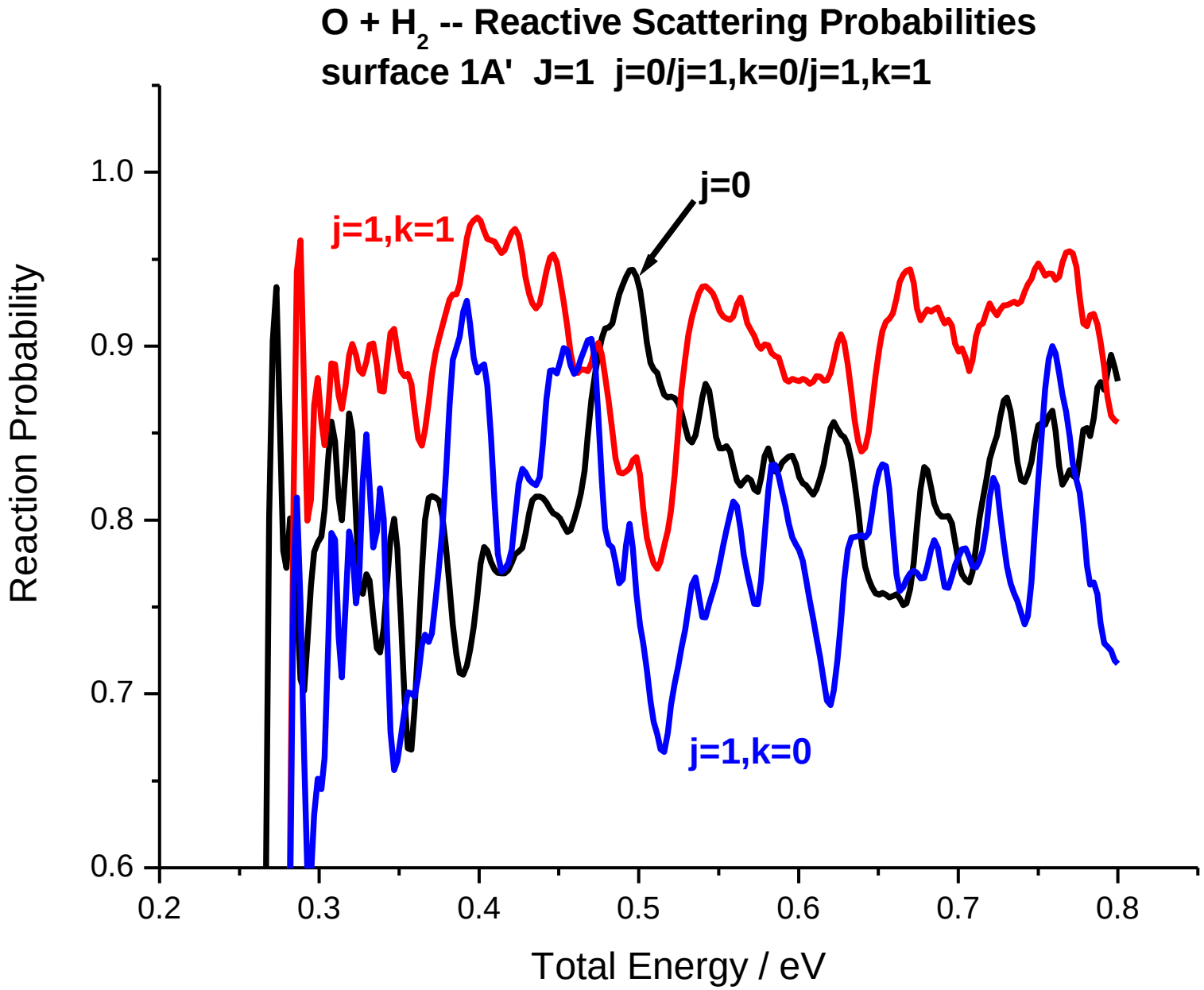
σ(j=1) --- Total reactive cross section starting from H_2(j=1)

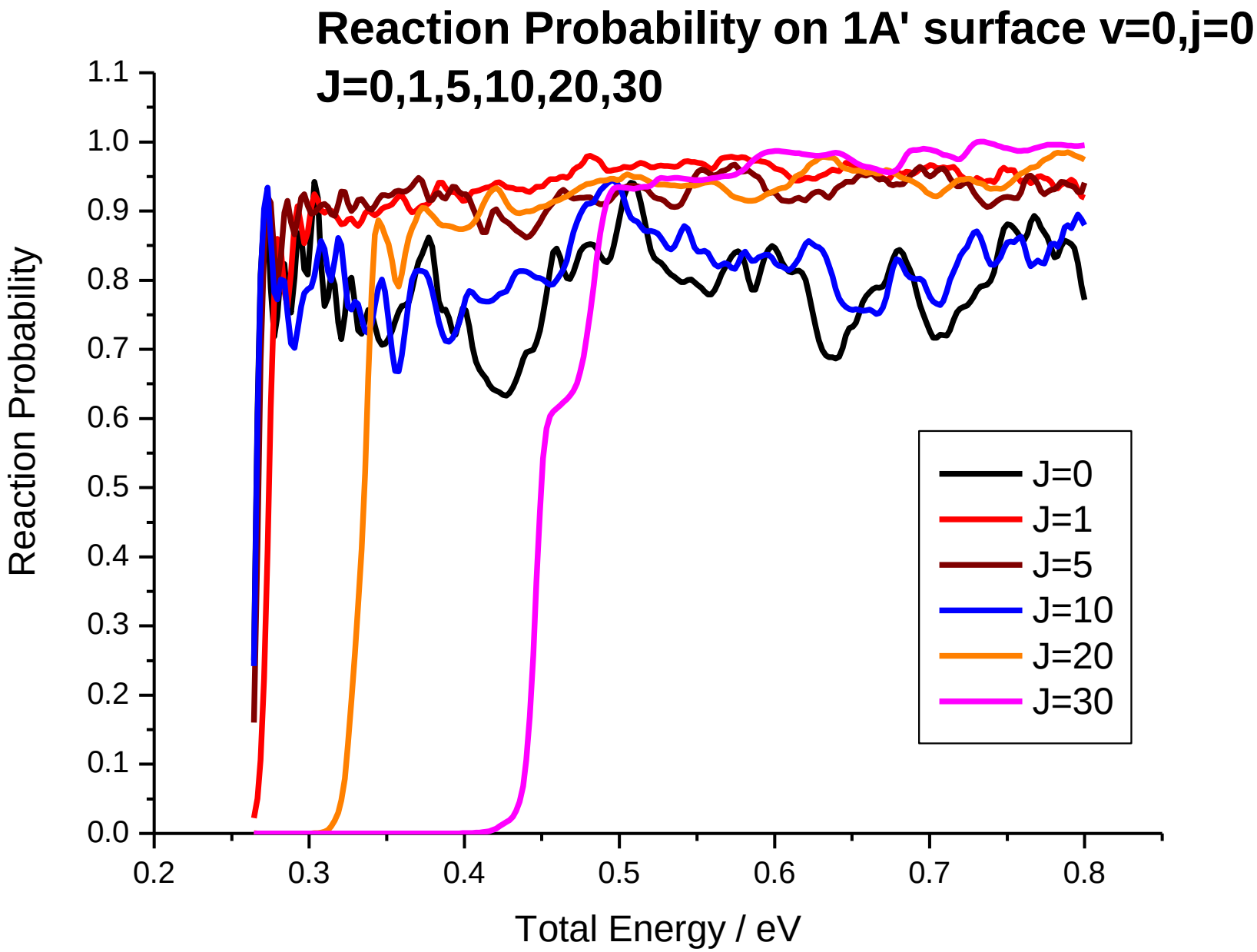
We use the helicity decoupling approximation.
Helicity (k)

k=0 for j=0

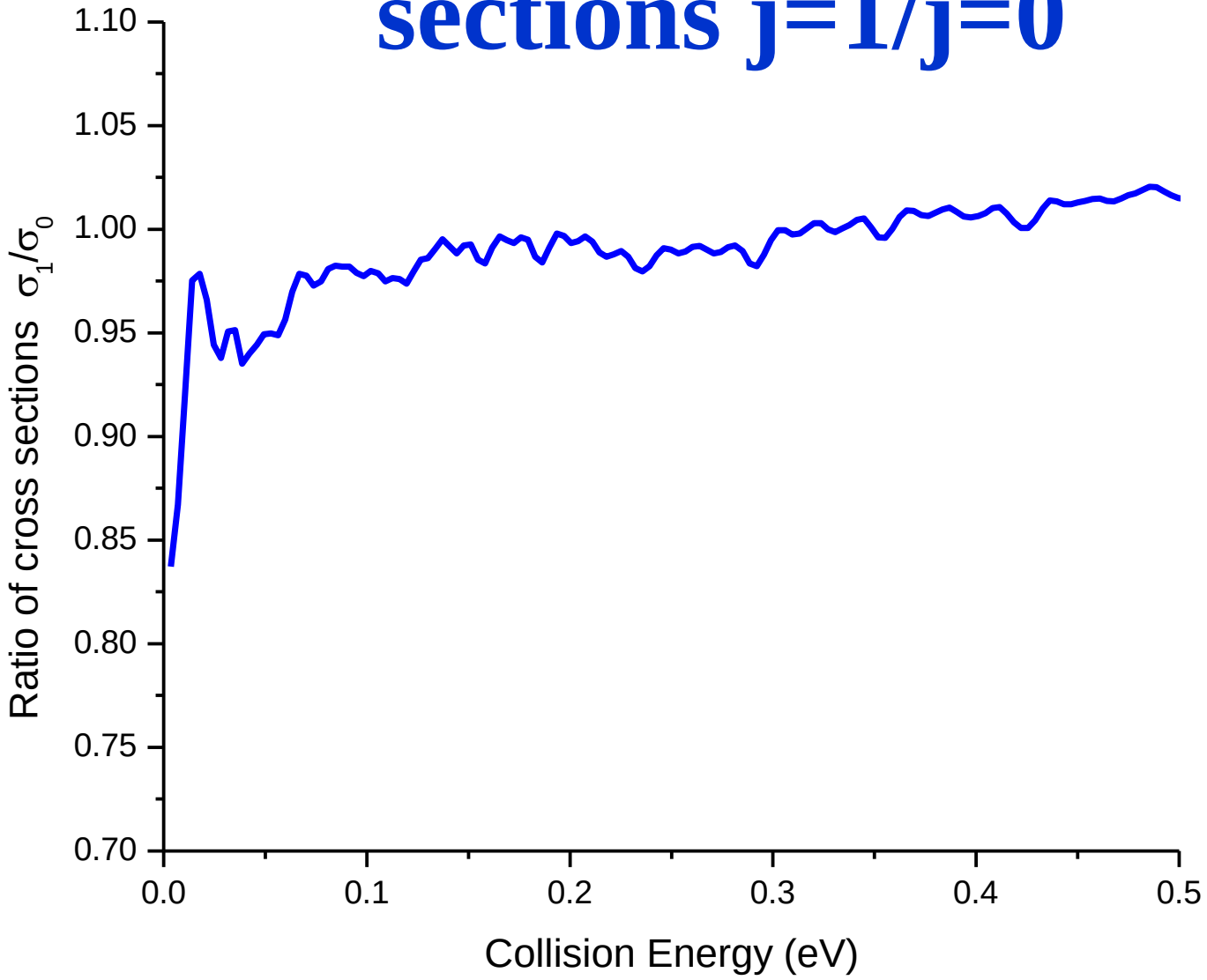
k=0 or 1 for j=1


O + H2 Reaction Probabiliities, J=0
Comparison of 3 surfaces
1A"
1A'
2A'
Reaction Probability
Total Energy / eV
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
robability in
ar threshold
n-adiabatic

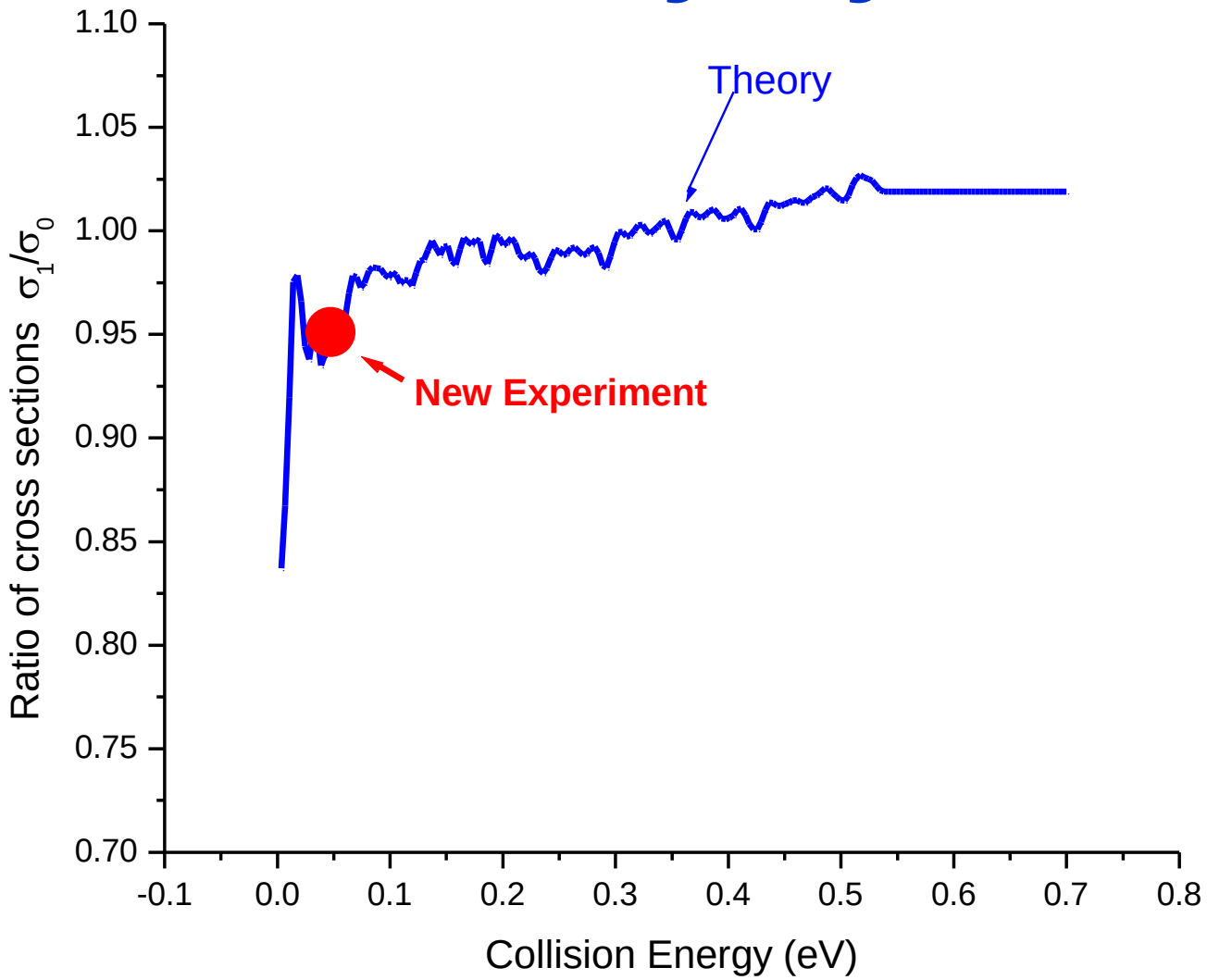

O + H2 -- Reactive Scattering Probabilities
surface 1A' J=1 j=0/j=1,k=0/j=1,k=1
Reaction Probability
1.0
0.9
0.8
0.7
0.6
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Total Energy / eV
j=0
j=1,k=1
j=1,k=0


Reaction Probability on 1A' surface v=0,j=0
J=0,1,5,10,20,30
Reaction Probability
Total Energy / eV
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
J=0
J=1
J=5
J=10
J=20
J=30

$O+H_2$ ratio of reactive cross sections j=1/j=0



$O+H_2$ ratio of reactive cross sections j=1/j=0



Stephen Gray

An alternative method for propagating the wavepacket forward in time

$$i\hbar\frac{\partial\Psi}{\partial t}=\hat{H}\Psi$$

$$\Psi(t+\tau)=e^{-i\hat{H}\tau/\hbar}\Psi(t)$$

$$\Psi(t-\tau)=e^{+i\hat{H}\tau/\hbar}\Psi(t)$$

$$\Psi(t+\tau)=-\Psi(t-\tau)+2\,cos\left(\frac{\hat{H}\tau}{\hbar}\right)\Psi(t)$$

$$\Psi(t+\tau) = -\Psi(t-\tau) + 2\hat{H}\Psi(t)$$

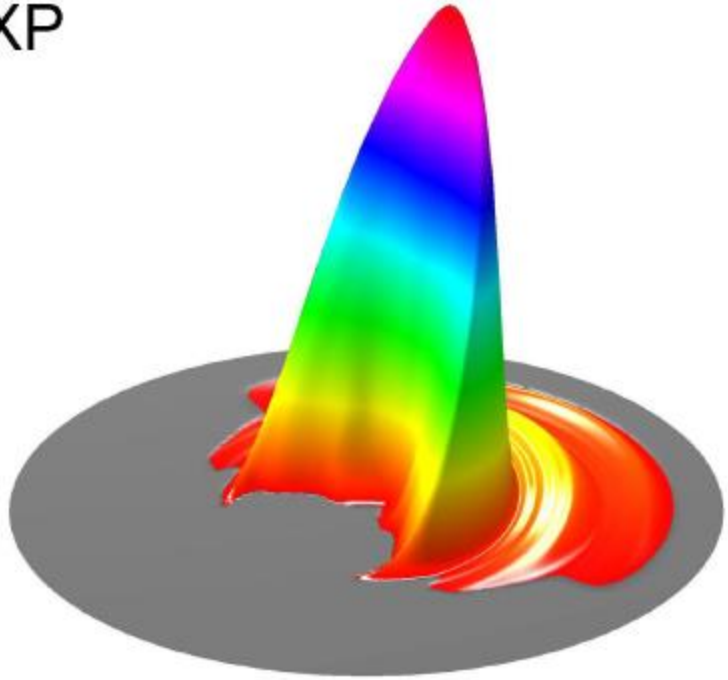
Using the alternative time propagation together with the functional mapping we can

1) **Use Real Wavepackets as no "i" appears in the propagation.**

2) **The propagation becomes much more efficient.**

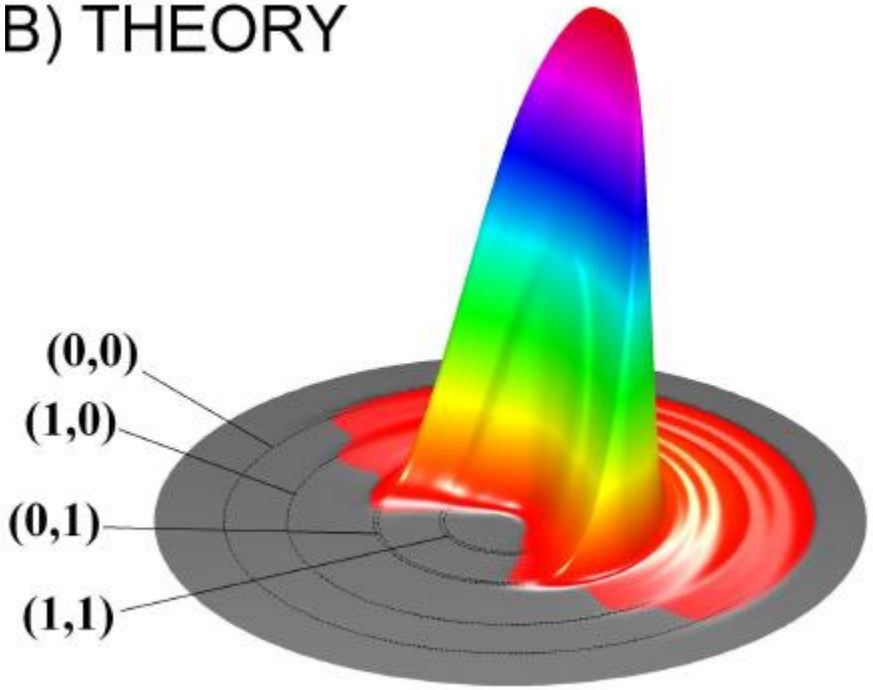
Some Examples of recent Wavepacket Calculations by other people

(A) EXP



HD + OH → H_2O + D reactive differential cross section

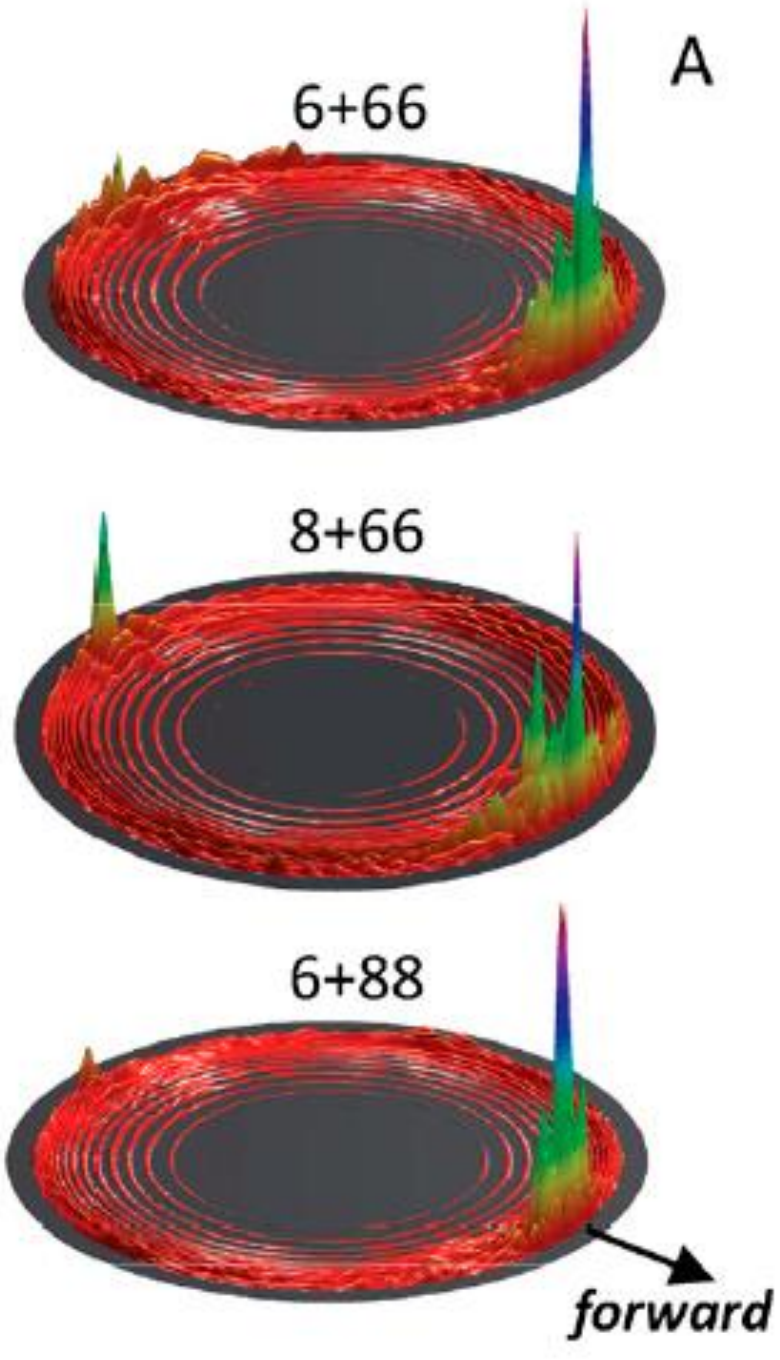
B) THEORY



C. Xiao, X. Xu, S. Liu, T. Wang, W. Dong, T. Yang, Z. Sun, D. Dai, X. Xu, **D. H. Zhang**, and X. Yang, Science 333, 440 (2011).

State-to-state quantum dynamics of
$O + O_2$ isotope exchange
Zhigang Sun,
Lan Liu,
Shi Ying Lin,
Reinhard Schinke,
Hua Guo,
and **Dong H. Zhang**
PNAS 107, 555 (2010)

Differential Reactive Cross Sections



Photodissociation Dynamics, Bristol 1994

Reviews

"Wavepacket Theory of Photodissociation and Reactive Scattering",

Adv. Chem. Phys. 128, 249 (2003).

"Time-dependent and time-independent wavepacket approaches to reactive scattering and photodissociation dynamics",

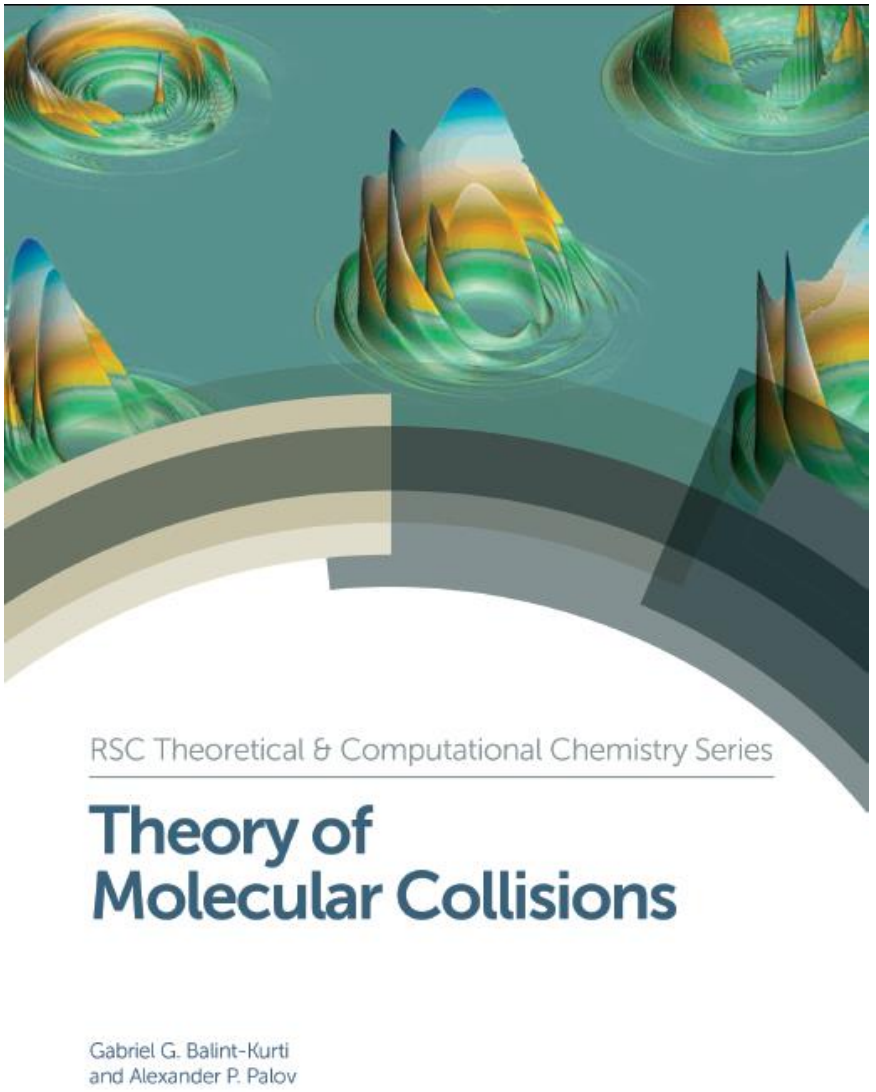
Internat. Rev. Phys. Chem., 27, 507 (2008).

"Wavepacket quantum dynamics",

Theoretical Chemistry Accounts, 127, 1 (2010).

Gabriel Balint-Kurti
and
Alexander Palov

Royal Society of Chemistry
2015



Cover: J. Aldegunde, P. G. Jambrina, M. P. de Miranda, V. S. Rábanos and F. J. Aoiz
Phys. Chem. Chem. Phys., 2011, **13**, 8345–8358