Dynamics of gas-phase elementary processes in the quantum regime

Sergio Rampino

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Perugia, 7 June 2017

I. Introduction

School on Open Science Cloud - Quantum Dynamics I

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1. A + BC reactions

$$A + BC \rightarrow AB + C$$

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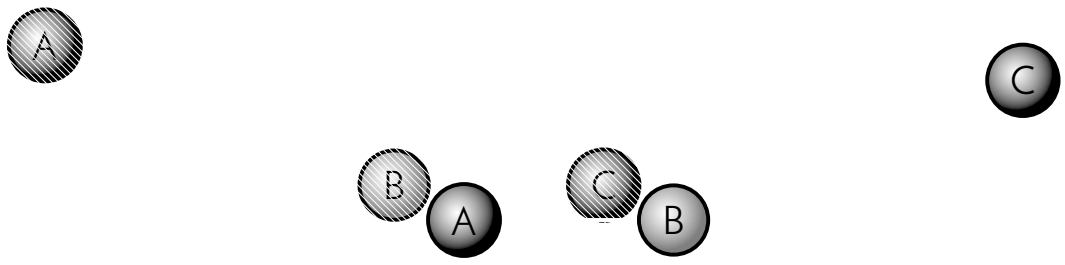

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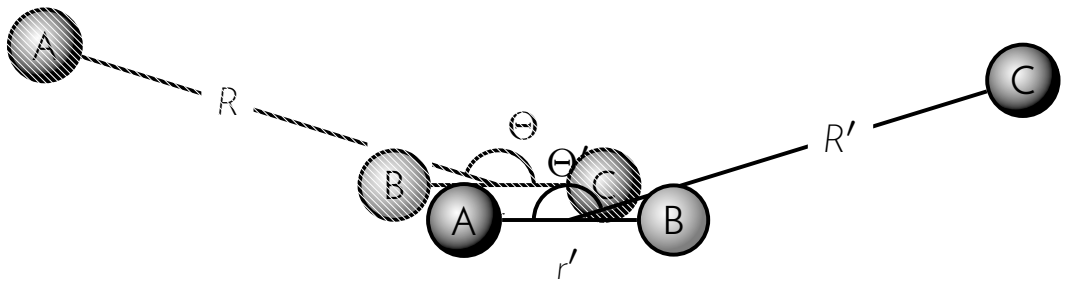

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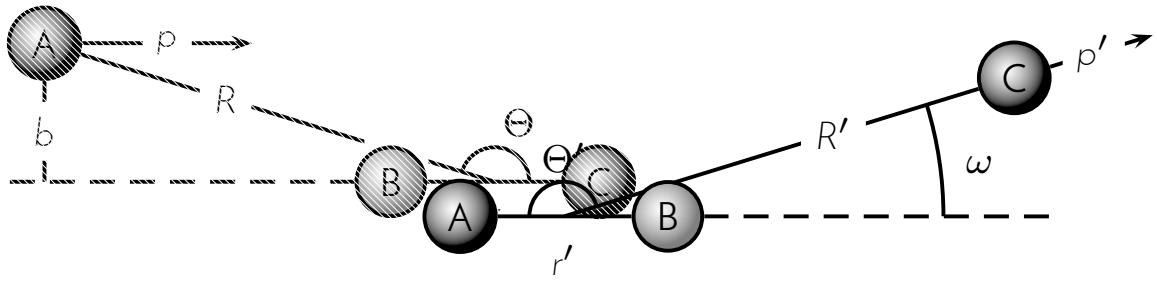

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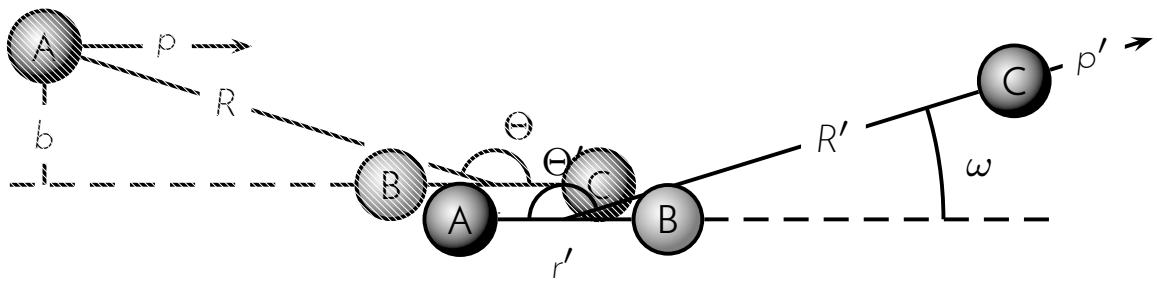

Atom-diatom collisions

Atom A colliding with molecule BC (in a given vibro-rotational state *v,j*) with a certain velocity and impact parameter *b*

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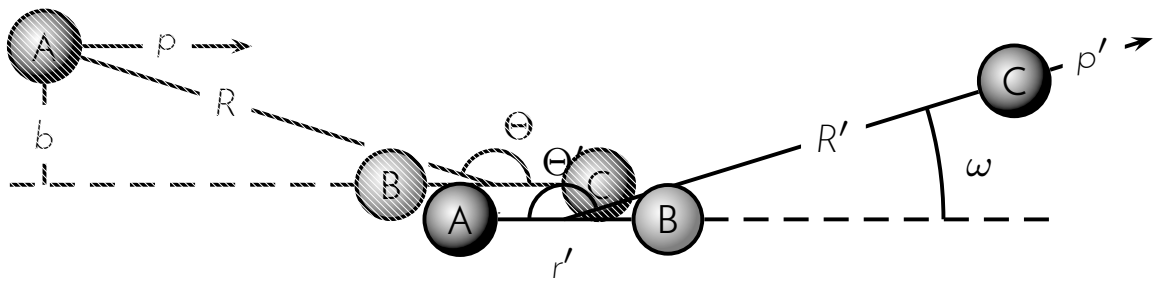


Atom-diatom collisions

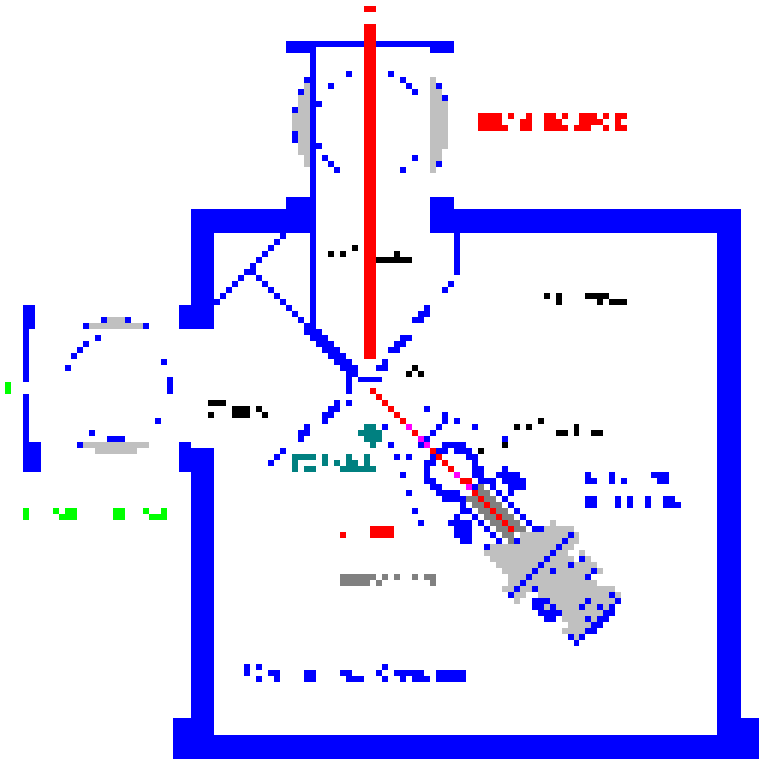
Atom A colliding with molecule BC (in a given vibro-rotational state v,j) with a certain velocity and impact parameter b

Reaction cross section

$$\sigma_{v,j} = \pi b_{max}^2 \frac{N_{v,j}^R}{N_{v,j}}$$

I. Introduction

2. Crossed molecular beams



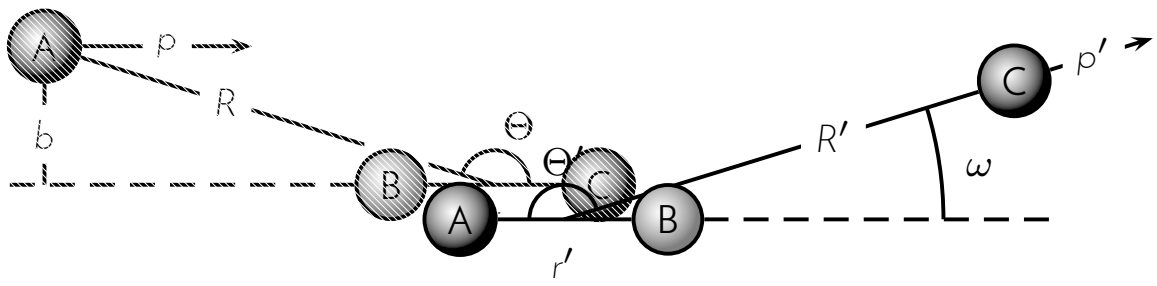
I. Introduction

2. Crossed molecular beams

Crossed-molecular-beam machine at Perugia (Prof. Casavecchia)

I. Introduction

3. Dynamics and kinetics



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Reaction cross section

$$\sigma_{v,j} = \pi b_{max}^2 \frac{N_{v,j}^R}{N_{v,j}}$$

Thermal rate coefficient

$$k_{v,j}(T) = \langle v \rangle \sigma_{v,j} = \sqrt{\frac{8 k_B T}{\pi \mu}} \pi b_{max}^2 \frac{N_{v,j}^R}{N_{v,j}}$$

II. Potential energy surface

II. Potential energy surface

4. Born-Oppenheimer approximation

Schrödinger equation for a molecular system

$$i\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{\xi},t)=\hat{H}\Psi(\boldsymbol{\xi},t)$$

where $\boldsymbol{\xi}$ is the set of nuclear ($\boldsymbol{q}$) and electronic ($\boldsymbol{Q}$) coordinates

Closed form solution for for very simple models only

II. Potential energy surface

4. Born-Oppenheimer approximation

Born-Oppenheimer approximations: the grounds

Electrons are 1822 times ligher than the protons and neutrons constituting the nuclei

Underlying assumption:

The electrons rearrange instantaneously around the moving nuclei (electronically adiabatic approximation)

II. Potential energy surface

4. Born-Oppenheimer approximation

Due to the Born-Oppenheimer approimation, expand Ψ

$$\Psi(\mathbf{q}, \mathbf{Q}, t) = \sum_{n}^{\infty} \psi_n(\mathbf{q}, t)\phi_n(\mathbf{Q}; \mathbf{q})$$

and rewrite the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \sum_n \psi_n(\mathbf{q}, t)\phi_n(\mathbf{Q}; \mathbf{q}) = \left[\hat{T}_{\mathbf{q}} + \hat{V}\right] \sum_n \psi_n(\mathbf{q}, t)\phi_n(\mathbf{Q}; \mathbf{q})$$

where $\hat{H} = \hat{T}_{\mathbf{q}} + \hat{V}$

II. Potential energy surface

4. Born-Oppenheimer approximation

Electronic structure: ϕ's eigensolution of

$$\hat{V}\phi_n(\mathbf{Q};\mathbf{q}) = V_n(\mathbf{q})\phi_n(\mathbf{Q};\mathbf{q})$$

Nuclear dynamics: B-O equation of motion

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{q},t) = \left[\hat{T}_{\mathbf{q}}(\mathbf{q}) + V(\mathbf{q})\right]\psi(\mathbf{q},t)$$

where $n = 0$ (dynamics on the electronic ground state) has been dropped

II. Potential energy surface

4. Born-Oppenheimer approximation

Nuclei move on the Potential Energy Surface $V(\boldsymbol{q})$

$$i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{q},t) = \left[\hat{T}_{\boldsymbol{q}}(\boldsymbol{q}) + V(\boldsymbol{q})\right]\psi(\boldsymbol{q},t)$$

the ensemble of the values $V_n(\boldsymbol{q})$ of the energy of the nth electronic state at all nuclear geometries

II. Potential energy surface

5. Analytic formulations

Aguado-Paniagua global fitting scheme

$$V(r_1, r_2, r_3) = V_1^{(2)}(r_1) + V_2^{(2)}(r_2) + V_3^{(2)}(r_3) + V^{(3)}(r_1, r_2, r_3)$$

$$V^{(2)}(r) = c_0 \frac{e^{-\alpha r}}{r} + \sum_{i=1}^{I} c_i (r e^{-\gamma^{(2)} r})^i$$

$$V^{(3)}(r_1, r_2, r_3) = \sum_{ijk}^{M} d_{ijk} (r_1 e^{-\gamma_1^{(3)} r_1})^i (r_2 e^{-\gamma_2^{(3)} r_2})^j (r_3 e^{-\gamma_3^{(3)} r_3})^k$$

$i + j + k \neq i \neq j \neq k$ $\qquad$ $i + j + k \leq M$

Many-body-expansion polynomial formulation

II. Potential energy surface

5. Analytic formulations

Shepard interpolation scheme

$$V(\boldsymbol{q}) = \sum_{i=1}^{N_{\mathrm{Sh}}} w_i(\boldsymbol{q}) T_i(\boldsymbol{q})$$

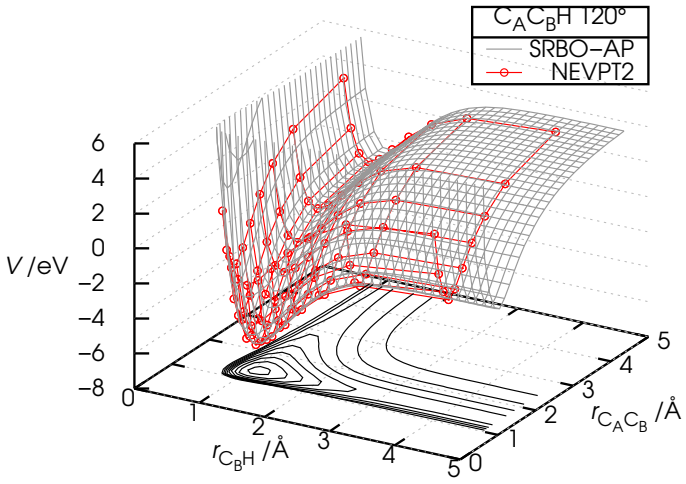
$$T_i(\boldsymbol{q}) = V_i + \sum_{\alpha=1}^{N_q} \Delta q_\alpha \left.\frac{\partial V}{\partial q_\alpha}\right|_i + \frac{1}{2!} \sum_{\alpha=1}^{N_q} \sum_{\beta=1}^{N_q} \Delta q_\alpha \Delta q_\beta \left.\frac{\partial^2 V}{\partial q_\alpha \partial q_\beta}\right|_i$$

$$w_i = \frac{1}{d_i} \Bigg/ \sum_{j=1}^{N_{\mathrm{Sh}}} w_j \qquad\qquad d_i = \sqrt{\sum_{\alpha=1}^{N_q} (\Delta q_\alpha)^2}$$

Weighed sum of second-order Taylor expansions around a set of N_{Sh} electronic energies

II. Potential energy surface

6. Representations



Many-body expansion

$$V(r_1, r_2, r_3) =$$

$$V_1^{(2)}(r_1) + V_2^{(2)}(r_2) + V_3^{(2)}(r_3) +$$

$$V^{(3)}(r_1, r_2, r_3)$$

Configuration-space sampling

$f = 2$
10-point SRBO grids
5-point angular grid

Ab initio

PC-NEVPT2/CASSCF
DKH Hamiltonian
ANO-RCC basis set

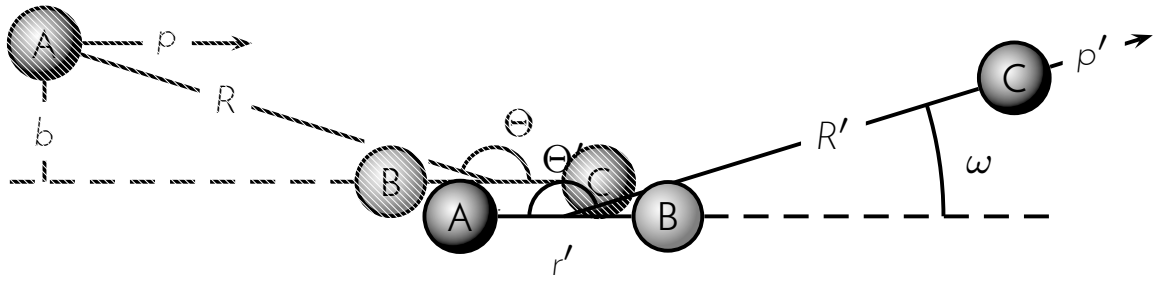
Fitting

775 *ab initio* energies
6th-degree polynomial fit for two-body terms
7th-degree polynomial fit for three-body term

III. Coordinates

III. Coordinates

7. Arrangement and process coordinates



Bond lengths (BL)

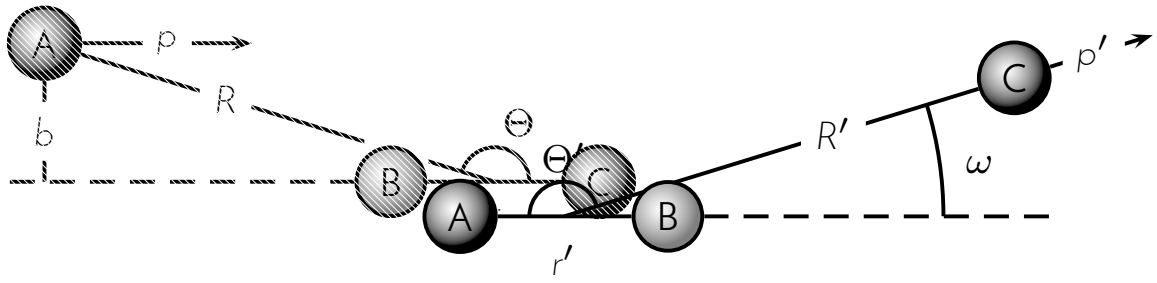
* the BC (reactant) internuclear distance r_{BC}
* the AB (product) internuclear distance r_{AB}
* the angle formed by r_{BC} and r_{AB}

Features

* ``process'' coordinates
* non orthogonal coordinates
* commonly employed in PES representations and inspection

III. Coordinates

7. Arrangement and process coordinates



Reactant (and product) Jacobi coordinates

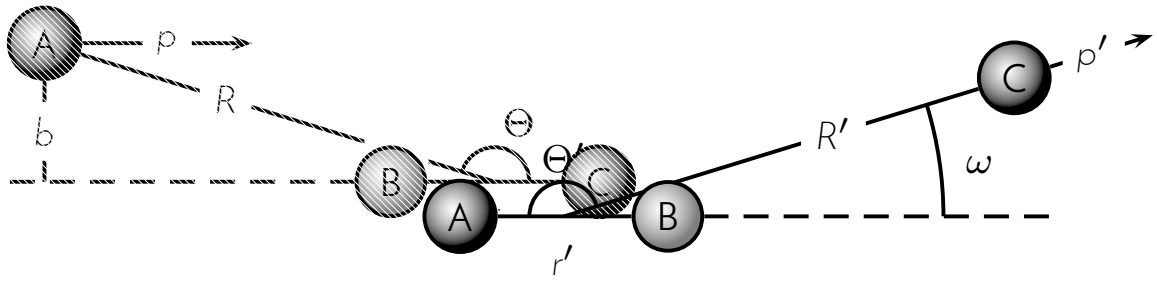
* the BC (reactant) internuclear distance r
* the A-BC distance R
* the angle Θ formed by R and r

Features

* "arrangement" coordinates
* orthogonal coordinates
* used in wavepacket TD methods

III. Coordinates

7. Arrangement and process coordinates



Delves hyperspherical coordinates

* $\rho = \sqrt{R^2 + r^2}$
* $\theta_a = \arctan \frac{r}{R}$
* Θ

Features

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* orthogonal coordinates
* used in hyperspherical TI methods

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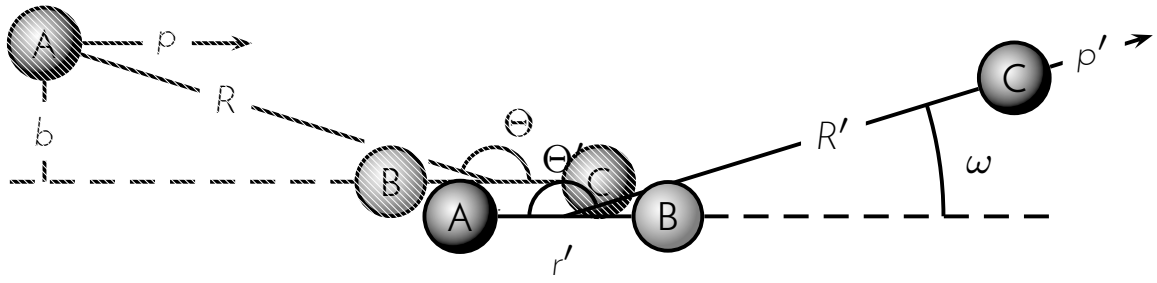

Bond Order (BL) coordinates

* $n_{BC} = e^{-\beta_{BC}(r_{BC} - r_{eqBC})}$
* $n_{AB} = e^{-\beta_{AB}(r_{AB} - r_{eqAB})}$
* the angle formed by r_{AB} and r_{BC}

Features

* ``process'' coordinates
* non orthogonal coordinates
* physical space inverted and confined in a finite volume

III. Coordinates

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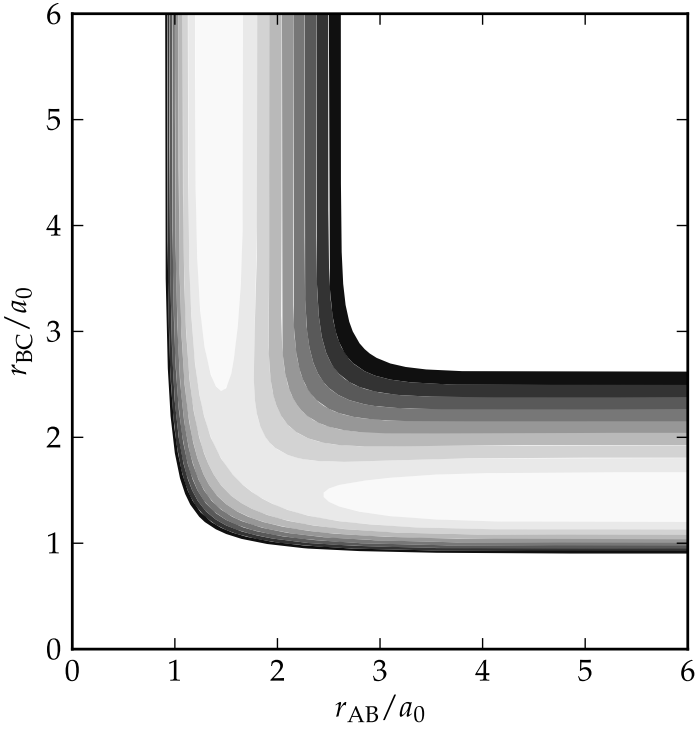
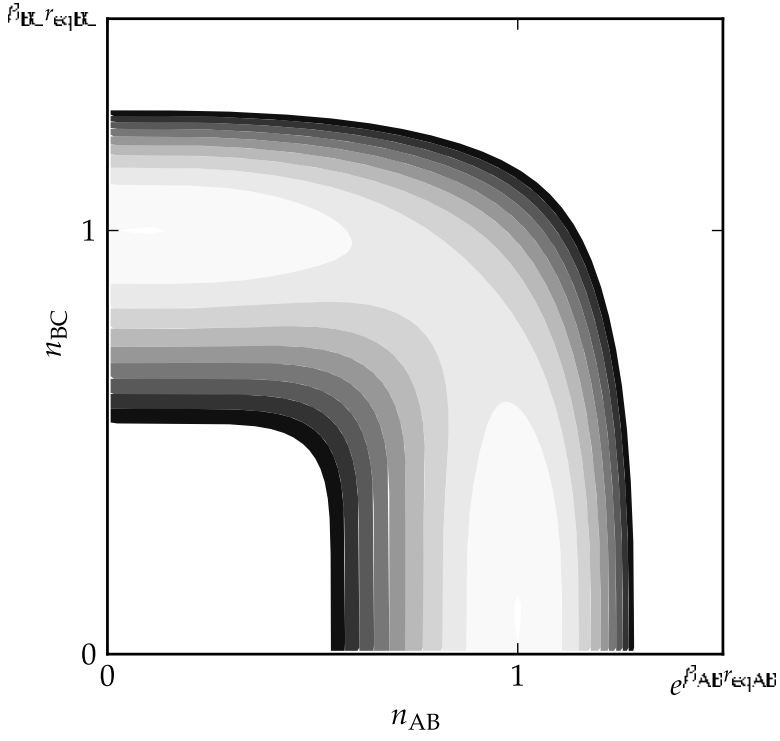
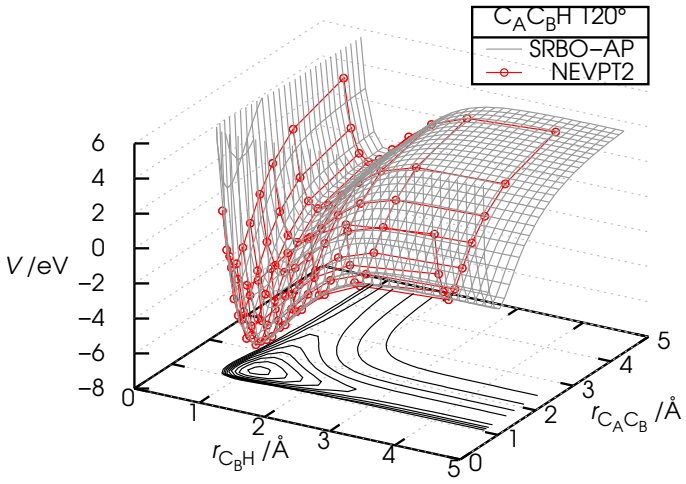




III. Coordinates

8. PES representations



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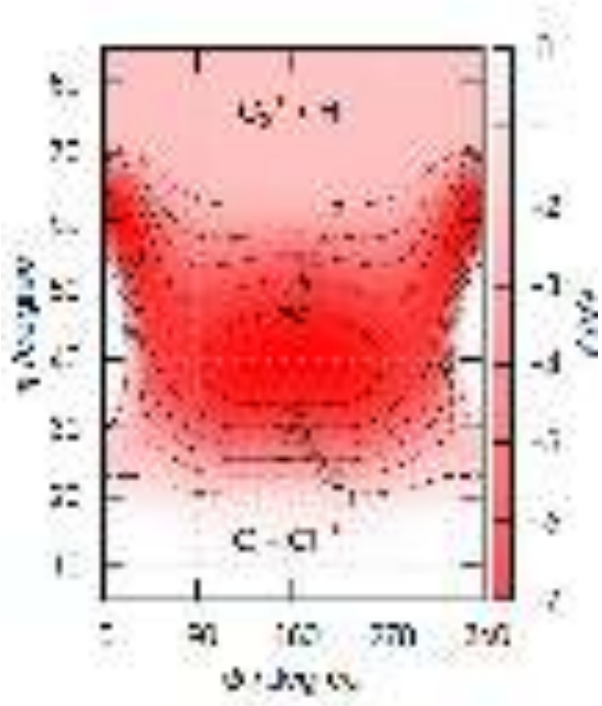

Rectangular relaxed plot

reaction coordinate
$\eta = \arctan\left(r_{CH}/r_{CC}\right)$

angular coordinate
$\Phi = \widehat{CCH}$

overall-size coordinate
$\rho = \left(r_{CH}^2 + r_{CC}^2\right)^{1/2}$

RRX plot
$\min_{\rho} V(\eta, \Phi)$

L Pacifici, M Pastore, E Garcia, A Laganà, S Rampino, **A dynamics investigation of the C + CH^+ → C_2^+ + H reaction on an ab initio bond-order like potential**, *The Journal of Physical Chemistry A* 120, 5125-5135 (2016)

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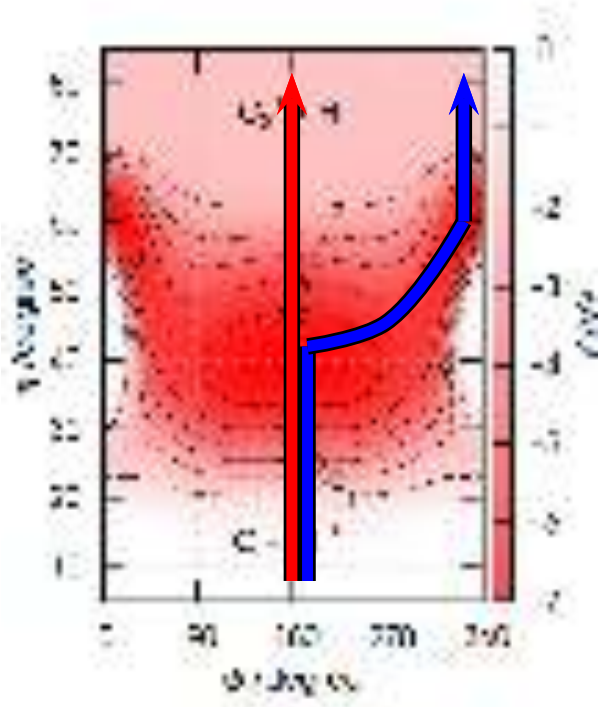

Reaction paths

path 1: collinear MEP

$C + CH^+ \rightarrow CCH^+ \rightarrow C_2^+ + H$

path 2: absolute MEP

$C + CH^+ \rightarrow CCH^+ \rightarrow HCC^+ \rightarrow H + C_2^+$

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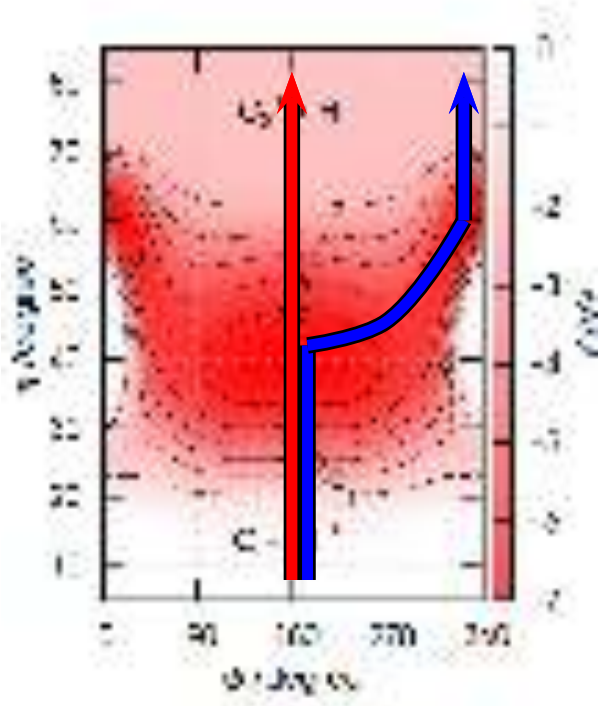

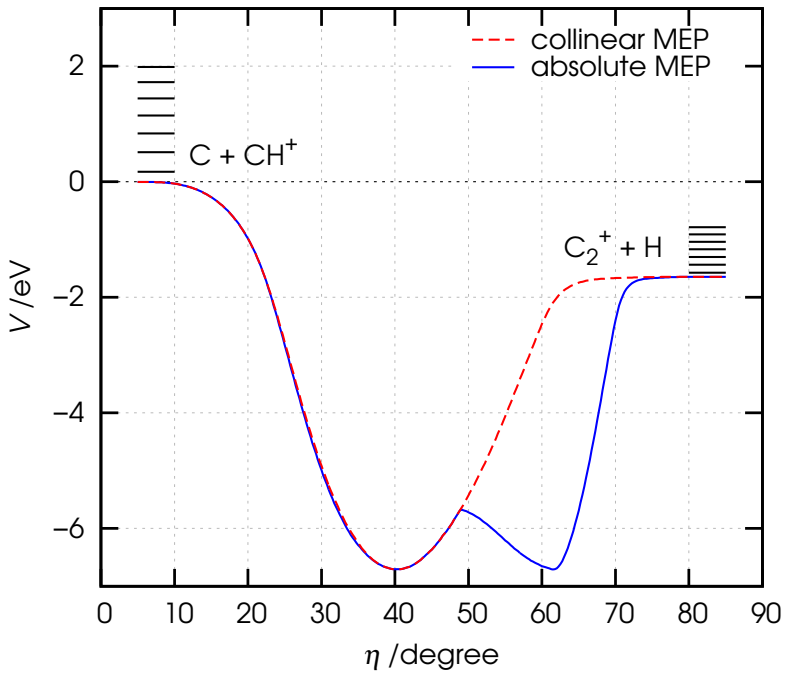

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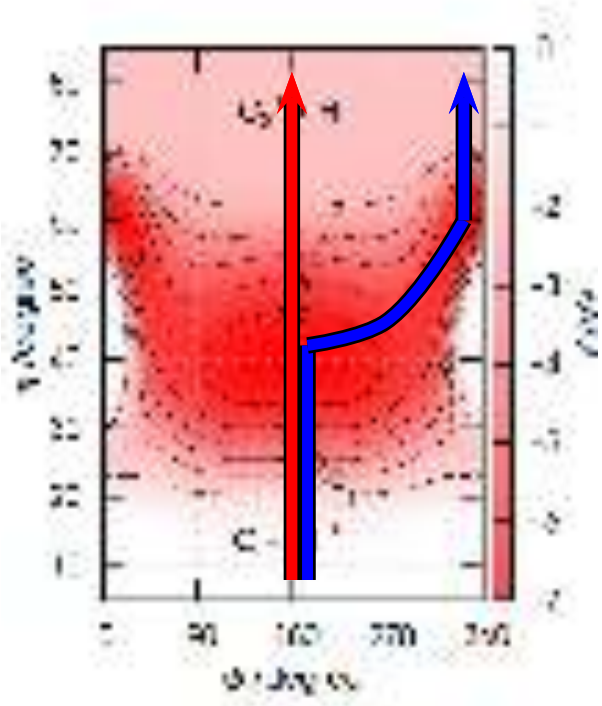

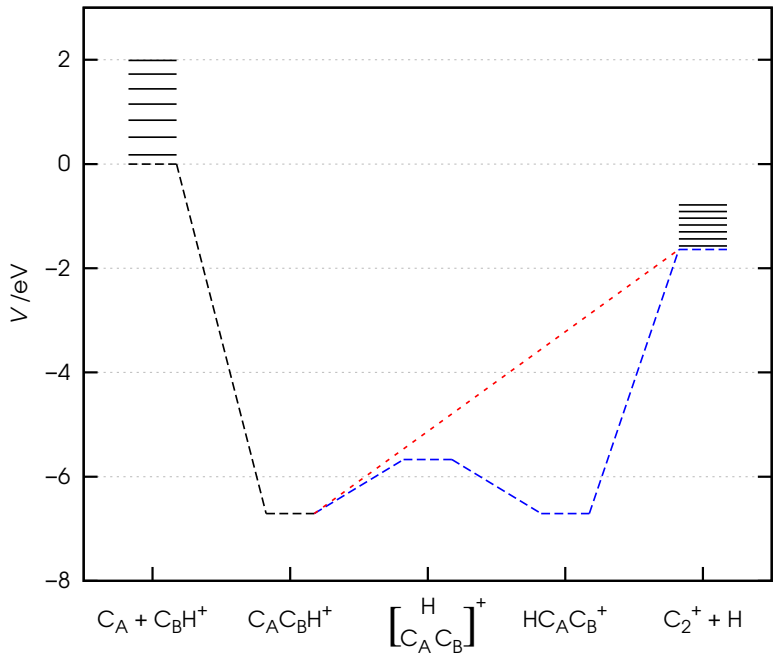

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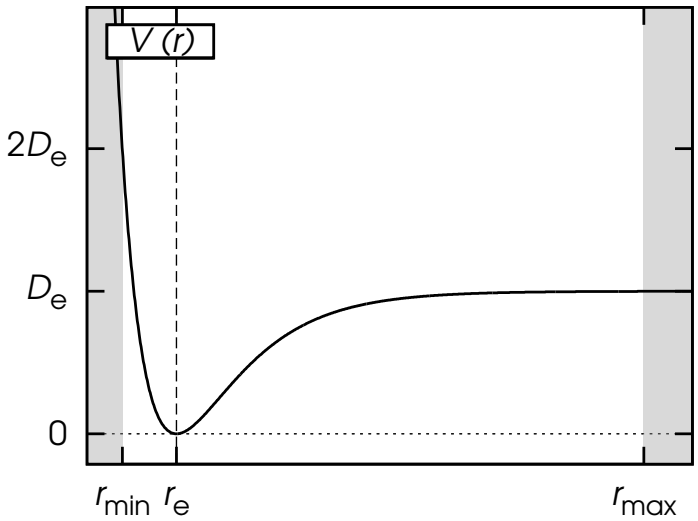
9. Configuration-space sampling



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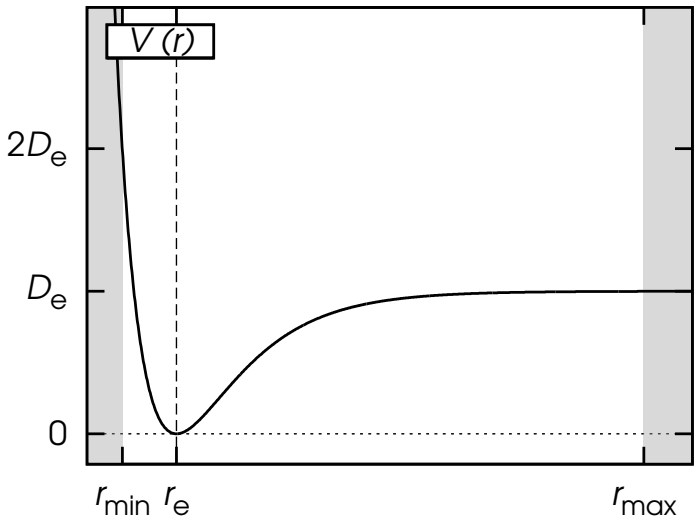

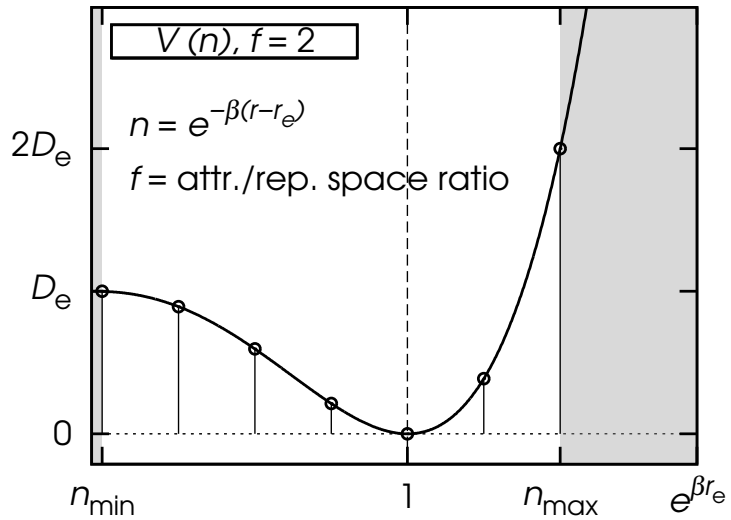

SRBO approach

switch from BL to BO space
introduce space-reduction param *f*

$$n = e^{-\beta(r-r_e)}$$

$$f = \frac{1-n_{min}}{n_{max}-1} = \frac{1-e^{-\beta(r_{max}-r_e)}}{e^{-\beta(r_{min}-r_e)}-1}$$

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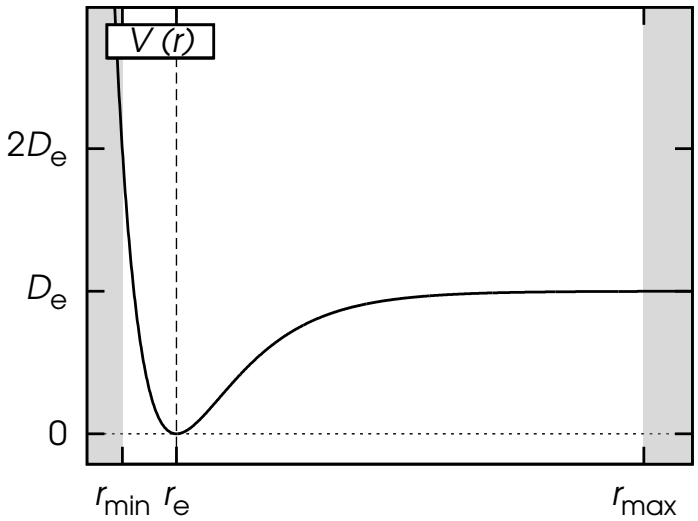

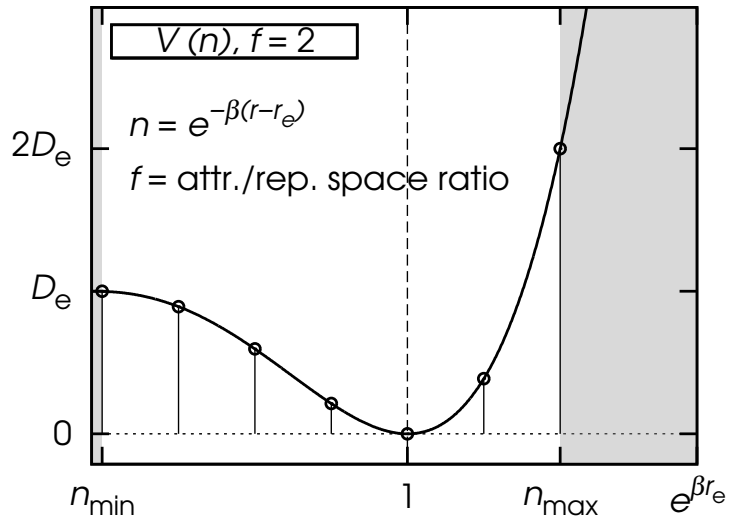

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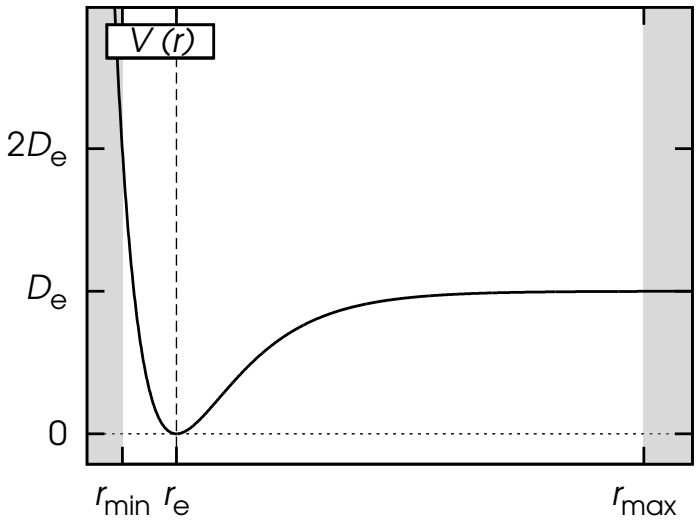

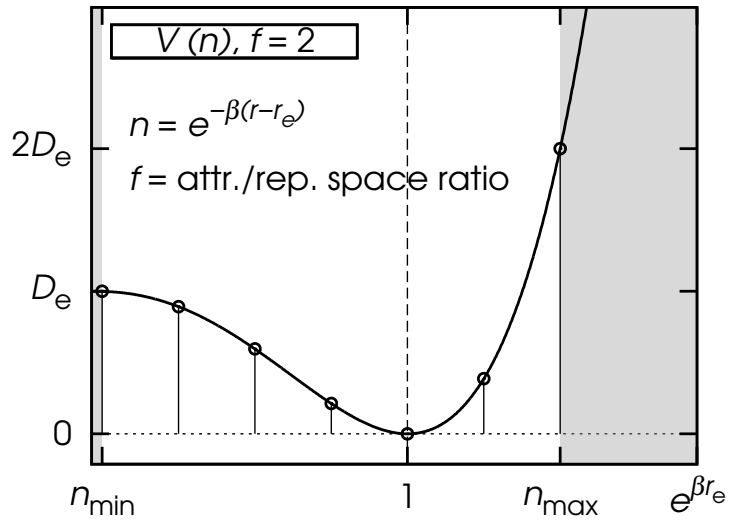

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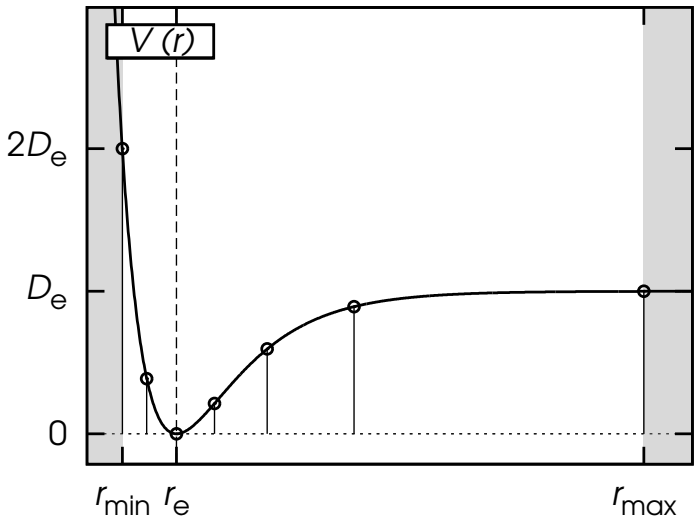

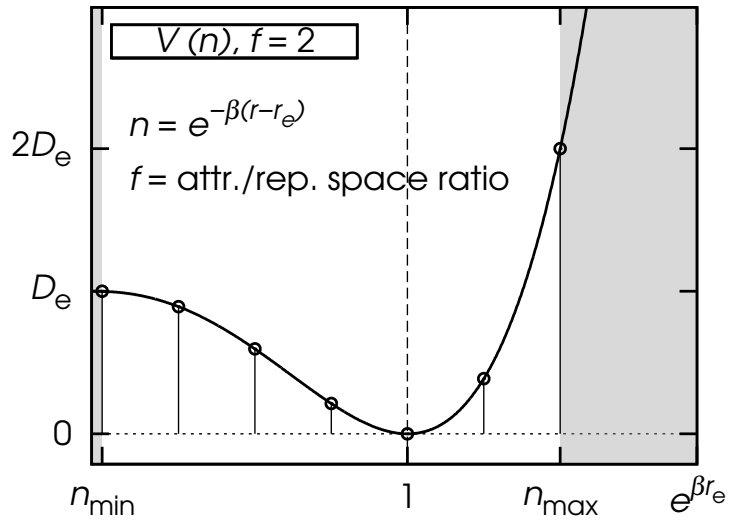

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IV. Reaction dynamics

IV. Reaction dynamics

10. Quasi-classical trajectories

QCT calculations

Nuclei move classically on the PES
Quantization introcued at some degree

Trajectory

impact parameter b
collision energy E_{tr}
atom-diatom orientation angles
diatom's quantum-like internal states (v, j)

$N_{v,j}(E_{tr}, b)$: total trajectories
$N^{R}_{v,j}(E_{tr}, b)$: reactive trajectories

Outcomes

opacity function

$$P_{v,j}(E_{tr}, b) = \frac{N^{R}_{v,j}(E_{tr},b)}{N_{v,j}(E_{tr},b)}$$

reactive probability

$$P_{v,j}(E_{tr}) = \frac{N^{R}_{v,j}(E_{tr})}{N_{v,j}(E_{tr})}$$

cross section

$$\sigma_{v,j} = \pi b^{2}_{max} \frac{N^{R}_{v,j}}{N_{v,j}}$$

thermal rate coefficient

$$k_{v,j}(T) = \langle v \rangle \sigma_{v,j} = \sqrt{\frac{8 k_B T}{\pi \mu}} \pi b^{2}_{max} \frac{N^{R}_{v,j}}{N_{v,j}}$$

IV. Reaction dynamics

11. Quantum time-dependent

The nuclei Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{q},t) = \left[\hat{T}_{\boldsymbol{q}}(\boldsymbol{q}) + V(\boldsymbol{q})\right]\psi(\boldsymbol{q},t)$$

must have solution

$$\psi(\boldsymbol{q},t) = \hat{U}(t,t_0)\psi(\boldsymbol{q},t_0)$$

IV. Reaction dynamics

11. Quantum time-dependent

Time evolution operator

$$\hat{U}(t, t_0) = e^{\frac{-i\hat{H}\Delta t}{\hbar}}$$

Ground equation for TD methods

$$\psi(\boldsymbol{q}, t) = e^{\frac{-i\hat{H}\Delta t}{\hbar}} \psi(\boldsymbol{q}, t_0)$$

IV. Reaction dynamics

11. Quantum time-dependent

Typical TD technique: the wavepacket method

- set up a state selected reactant wp on a discrete grid
- evolve in time
- analyze

Features

- initial value method
- makes use of discrete grids
- 1 reactant state and a wide range of scattering energies per run

IV. Reaction dynamics

11. Quantum time-dependent

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Wavepacket method

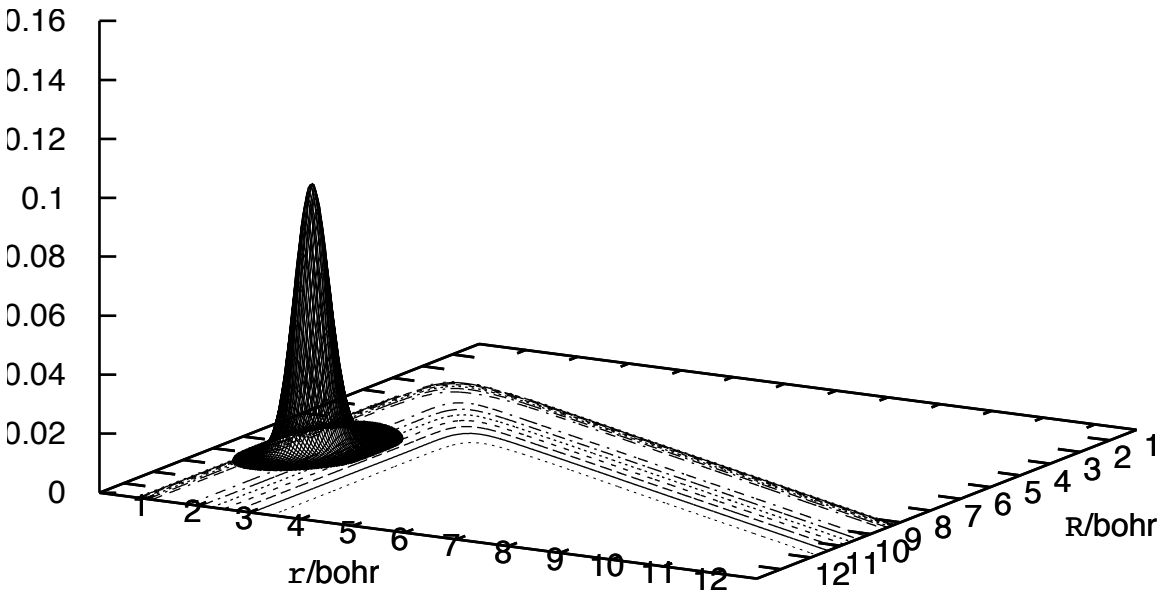
IV. Reaction dynamics

11. Quantum time-dependent

Wavepacket method

1. set up a (v, j) wavepacket

$$\psi(R, r, t_0) = e^{-ik(R-R_0)} e^{-\alpha(R-R_0)^2} \phi_0(r)$$



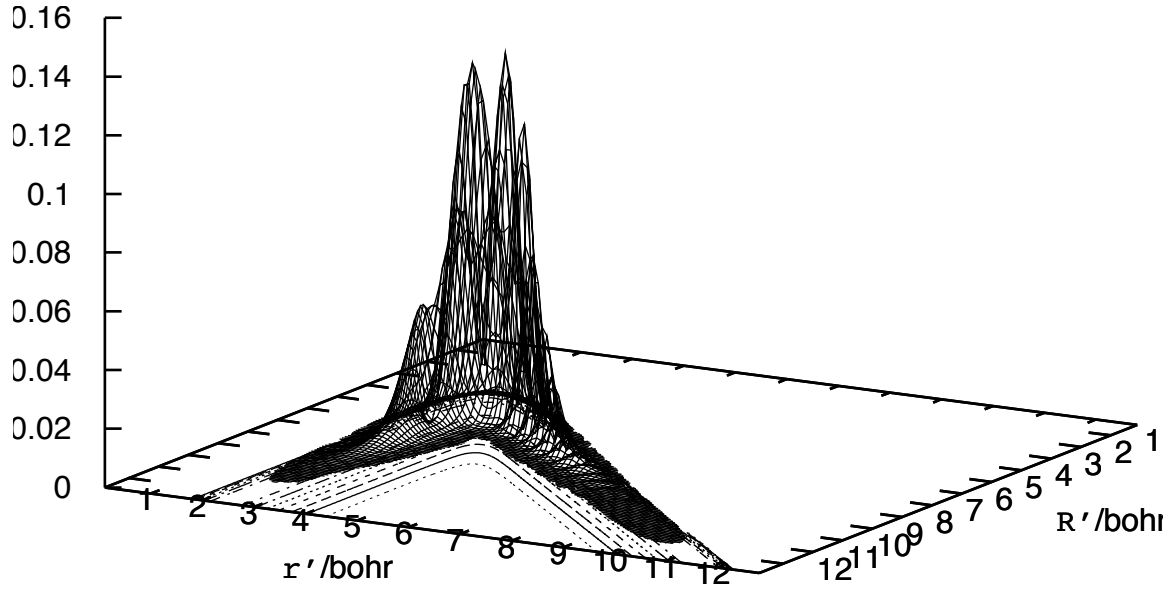
IV. Reaction dynamics

11. Quantum time-dependent

Wavepacket method

1. set up a (v, j) wavepacket
2. evolve in time

$$\psi(R, r, t) = e^{\frac{i\hat{H}(t-t_0)}{\hbar}} \psi(R, r, t_0)$$



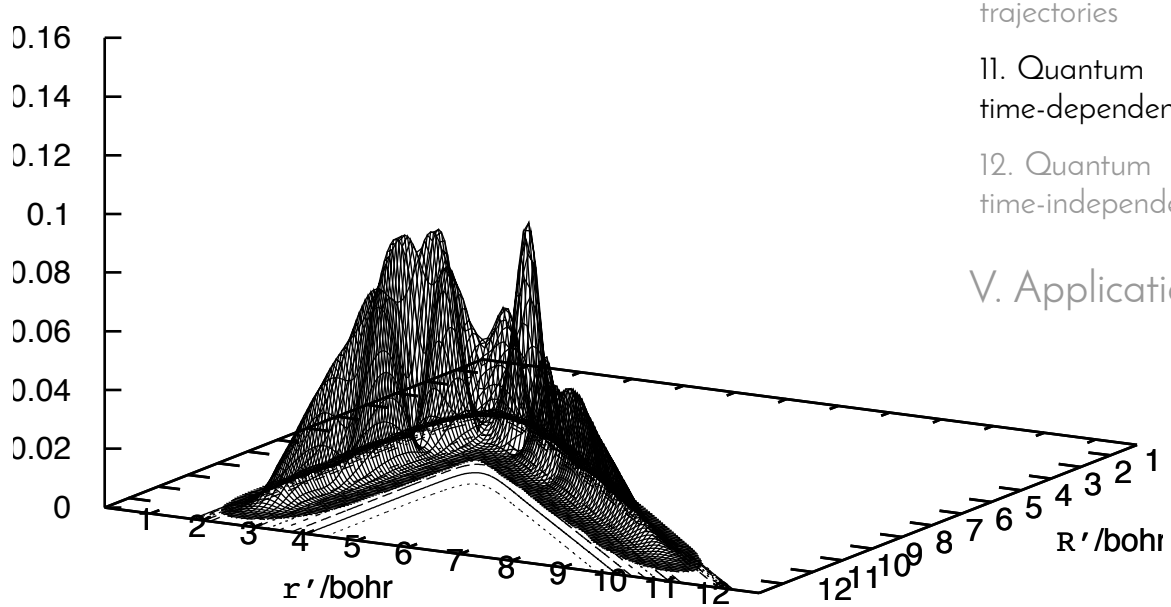
IV. Reaction dynamics

11. Quantum time-dependent

Wavepacket method

1. set up a (v, j) wavepacket
2. evolve in time
3. analyse far into the product region

$$S_{cv',av}(E) = -\frac{1}{\langle\psi_{cv'}|\Phi^{+}_{Ecv'}\rangle\langle\Phi^{-}_{Eav}|\psi_{av}\rangle}\int_0^\infty e^{\frac{iEt}{\hbar}}\langle\psi_{cv'}|e^{\frac{-i\hat{H}t}{\hbar}}|\psi_{av}\rangle\,\mathrm{d}t$$



IV. Reaction dynamics

12. Quantum time-independent

Insert

$$\psi(\boldsymbol{q}, t) = e^{\frac{-i\hat{H}\Delta t}{\hbar}} \psi(\boldsymbol{q}, t_0) \tag{1}$$

in

$$i\hbar \frac{\partial}{\partial t} \psi(\boldsymbol{q}, t) = \left[\hat{T}_{\boldsymbol{q}}(\boldsymbol{q}) + V(\boldsymbol{q}) \right] \psi(\boldsymbol{q}, t) \tag{2}$$

and get the ground equation for TI methods

$$\hat{H}\psi(\boldsymbol{q}, t_0) = E\psi(\boldsymbol{q}, t_0) \tag{3}$$

time factored out

IV. Reaction dynamics

12. Quantum time-independent

A typical TI approach: the hyperspherical method

- adopt ρ as a continuity variable
- divide ρ into sectors and expand ψ locally
- analyze ψ

Features

- not an initial value method
- expands in analytical basis functions
- all reactant states and 1 scattering energy per run

V. Applications

V. Applications

13. Astrochemistry

Grand-challenge

Develop a complete model for an interstellar cloud

Interstellar chemistry

low T (5-300 K)
low density (10^3-10^{14} cm^{-3})

· Gas-phase barrierless reactions involving ions or radicals

· Heterogeneous or multiphase processes involving dust grains and icy mantles

V. Applications

13. Astrochemistry

Processes

radiative association
associative detachment
dust-grain-catalysed reactions
photodissociation
colliaional dissociation
dissociative recombination
ion-neutral reactions
neutral-neutral reactions
charge-transfer reactions

Model setup

number densities of all species (hundreds)
physical conditions within the cloud
set of reactions (thousands)
reactions rates for all chemical processes

V. Applications

13. Astrochemistry

Processes

radiative association
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Processes

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Model setup

number densities of all species (hundreds)
physical conditions within the cloud
set of reactions (thousands)
reactions rates for all chemical processes

Kinetic databases

KIDA
http://kida.obs.u-bordeaux1.fr/
UDfA
http://udfa.ajmarkwick.net/

V. Applications

13. Astrochemistry

Processes

radiative association
associative detachment
dust-grain-catalysed reactions
photodissociation
colliaional dissociation
dissociative recombination
ion-neutral reactions
neutral-neutral reactions
charge-transfer reactions

Many of the reactions in these databases need to be studied/revised

Model setup

number densities of all species (hundreds)
physical conditions within the cloud
set of reactions (thousands)
reactions rates for all chemical processes

Kinetic databases

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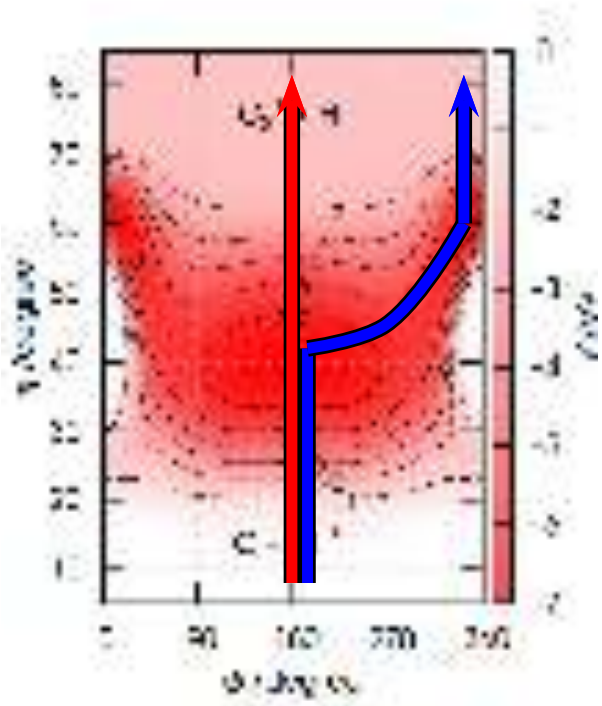
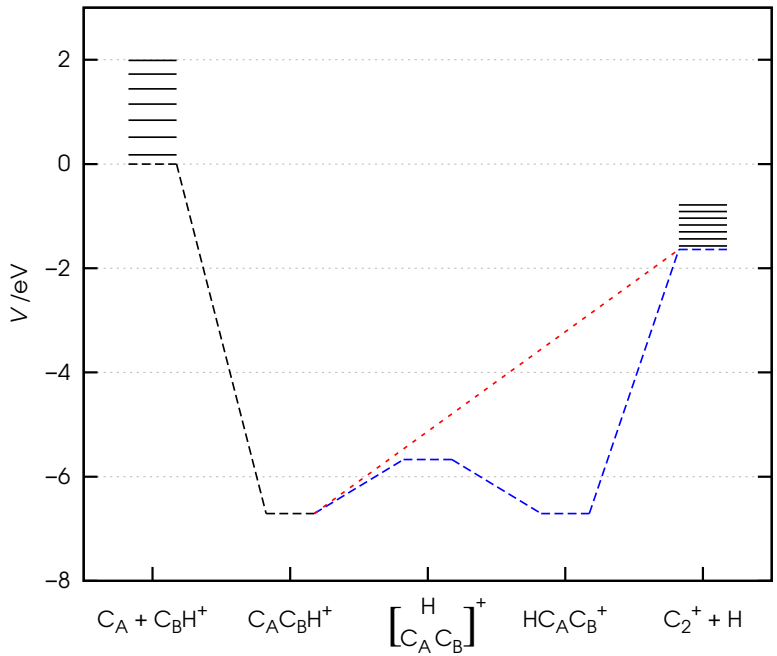
V. Applications

14. $C + CH^+ \rightarrow C_2^+ + H$: dynamics





L Pacifici, M Pastore, E Garcia, A Laganà, S Rampino, **A dynamics investigation of the $C + CH^+ \rightarrow C_2^+ + H$ reaction on an ab initio bond-order like potential**, *The Journal of Physical Chemistry A* 120, 5125-5135 (2016)

V. Applications

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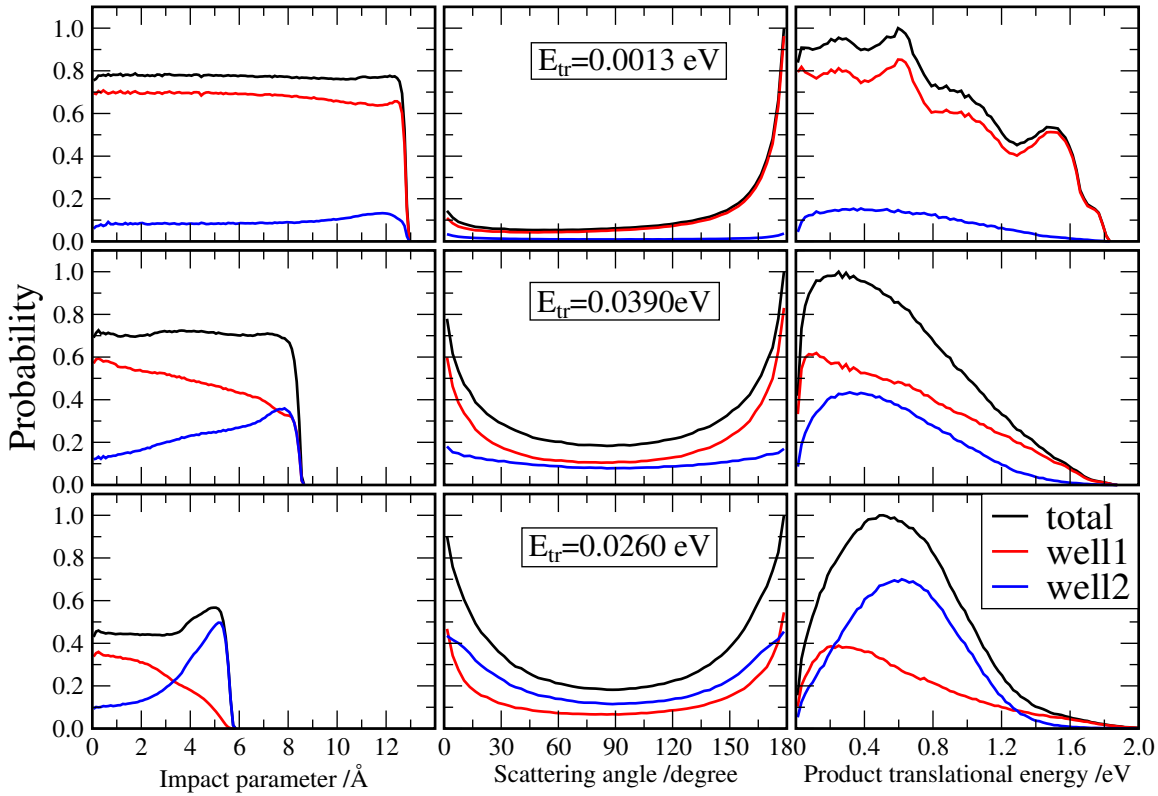


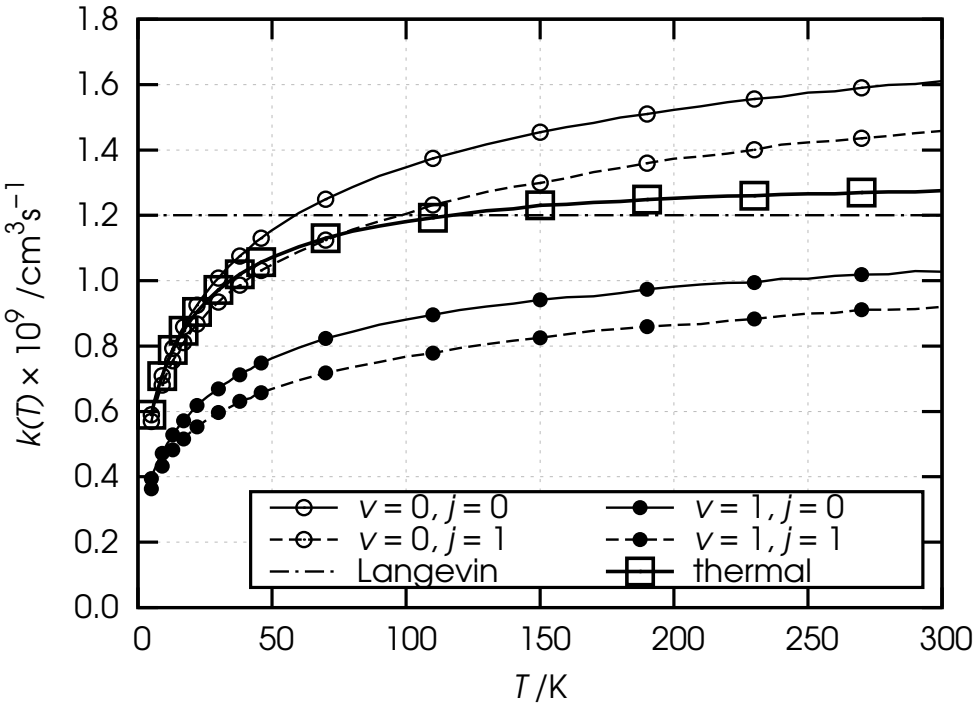
Opacity functions (10, 300, 2000 K)

capture-type mechanism at low collision energies
footprints of other mechanism showing up at higher collision energies

L Pacifici, M Pastore, E Garcia, A Laganà, S Rampino, **A dynamics investigation of the C + $CH^+ \rightarrow C_2^+$ + H reaction on an ab initio bond-order like potential**, *The Journal of Physical Chemistry A* 120, 5125-5135 (2016)

V. Applications

15. $C + CH^+ \rightarrow C_2^+ + H$: kinetics



Model vs dynamics

S Rampino, M Pastore, E Garcia, L Pacifici, A Laganà, **On the temperature dependence of the rate coefficient of formation of C_2^+ from $C + CH^+$**, *Monthly Notices of the Royal Astronomical Society* 460, 2368-2375 (2016)

V. Applications

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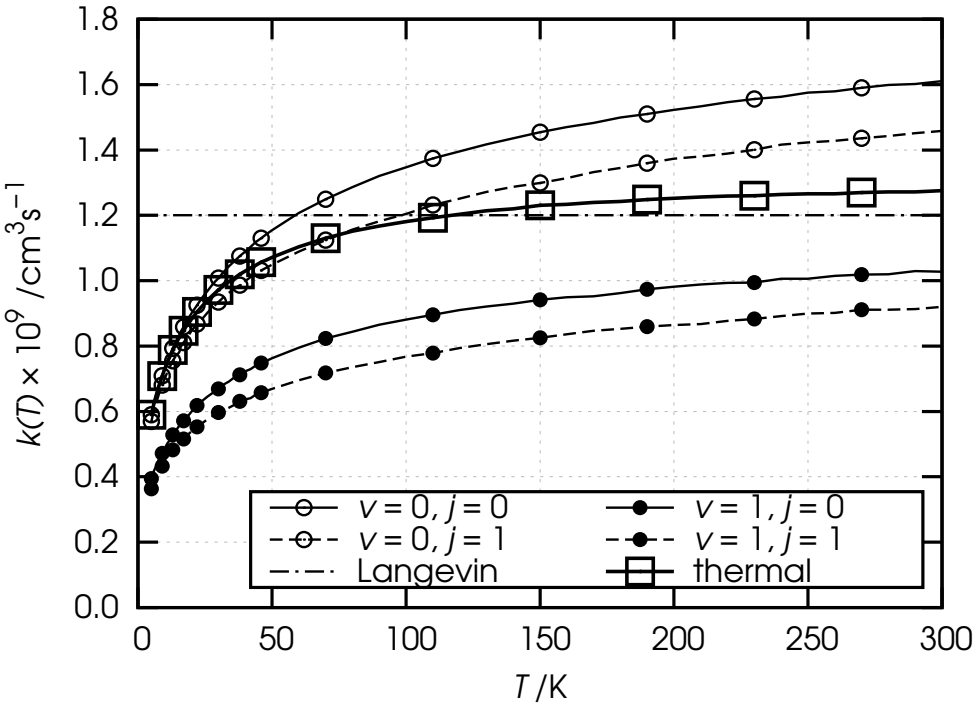

Model vs dynamics

factor two at low T

$k(T)$ doubles in 5-300 K

sharp increase in 5-50 K

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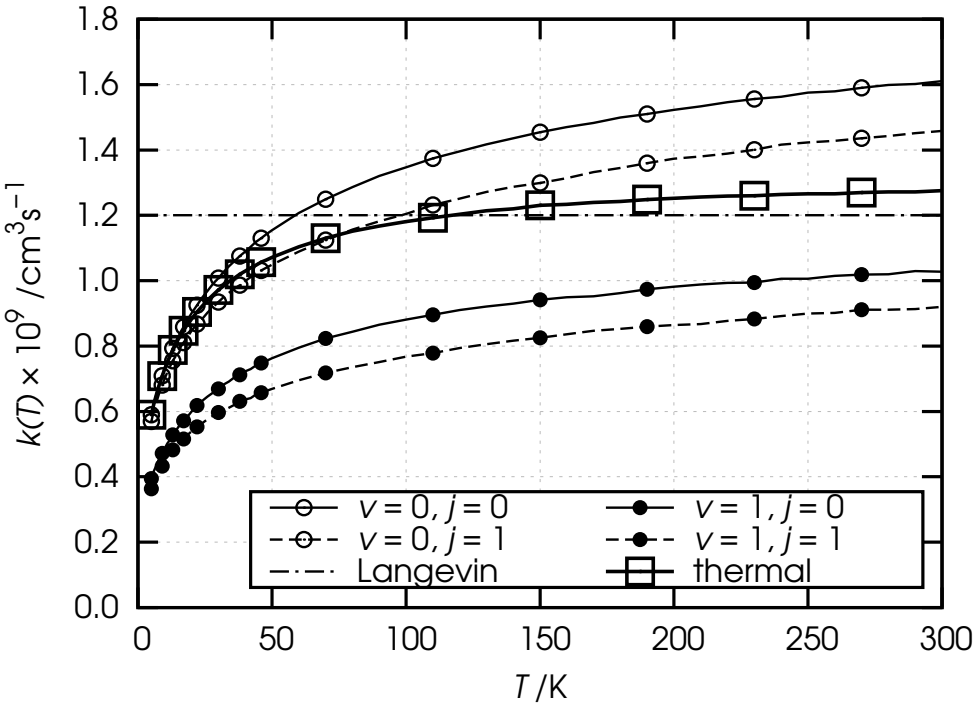

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Model calculations improperly enhance CH^+ consumption in kinetic models

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End