

Dynamics of gas-phase elementary processes in the quantum regime

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II. Potential
energy surface

III. Coordinates

IV. Reaction
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V. Applications

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1. A + BC reactions
2. Crossed molecular beams
3. Dynamics and kinetics

II. Potential energy surface

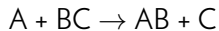
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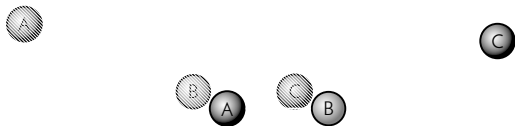
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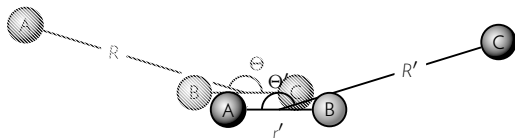
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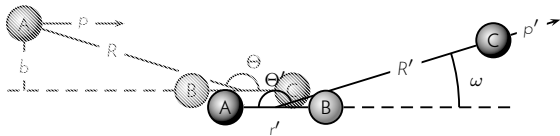
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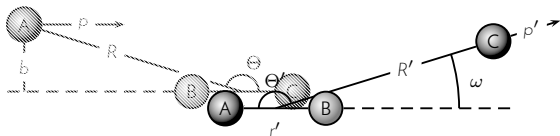
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1. A + BC reactions



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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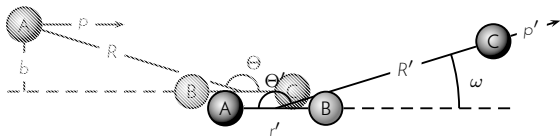
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1. A + BC reactions



Atom-diatom collisions

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

Reaction cross section

$$\sigma_{v_i} = \pi b_{\max}^2 \frac{N_{v_i}^R}{N_{v_i}}$$

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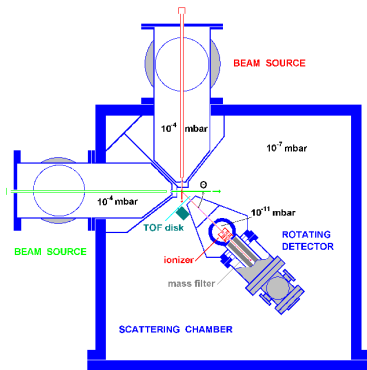
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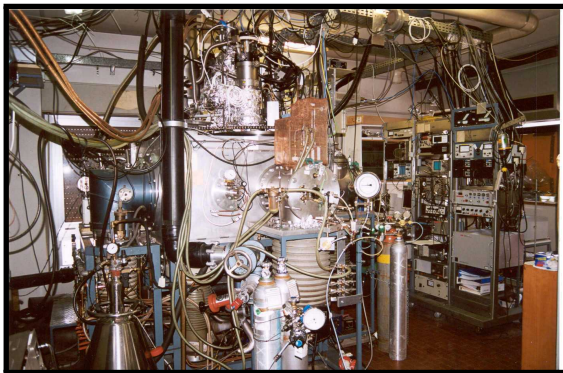
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Crossed-molecular-beam machine at Perugia (Prof. Casavecchia)

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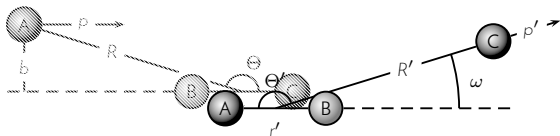
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Atom-diatom collisions

Atom A colliding with molecule BC (in a given vibro-rotational state $v_{i,j}$) with a certain velocity and impact parameter b

Reaction cross section

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

Thermal rate coefficient

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

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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 (\mathbf{q}) and electronic (\mathbf{Q}) coordinates

Closed form solution for for very simple models only

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4. Born-Oppenheimer approximation

Born-Oppenheimer approximations: the grounds

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

Underlying assumption:

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

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4. Born-Oppenheimer approximation

Due to the Born-Oppenheimer approximation, 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

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

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

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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

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4. Born-Oppenheimer approximation

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

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

the ensemble of the values $V_n(\mathbf{q})$ of the energy of the n th electronic state at all nuclear geometries

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5. Analytic formulations

Aguado-Paniagua global fitting scheme

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

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

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

$$i + j + k \neq i \neq j \neq k$$

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

Many-body-expansion polynomial formulation

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Shepard interpolation scheme

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

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

$$w_i = \frac{1}{d_i} \left/ \sum_{j=1}^{N_{Sh}} w_j \right.$$

$$d_i = \sqrt{\sum_{\alpha=1}^{N_q} (\Delta q_{\alpha})^2}$$

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

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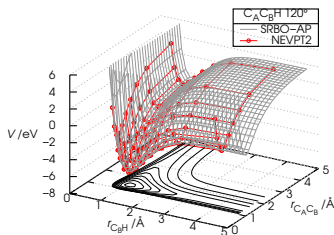
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Many-body expansion

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

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

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

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

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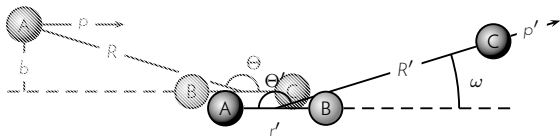
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Bond lengths (BL)

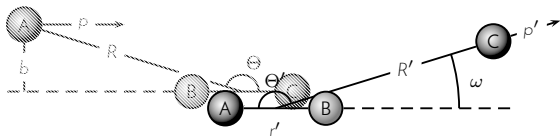
- * the BC (reactant) internuclear distance r_{BC}
- * the AB (product) internuclear distance r_{AB}
- * the angle formed by r_{BC} and r_{AB}

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

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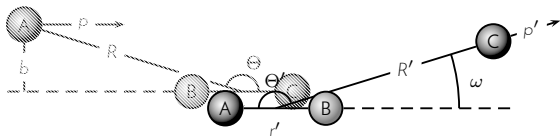
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Delves hyperspherical coordinates

$$* \rho = \sqrt{R^2 + r^2}$$

$$* \theta_a = \arctan \frac{r}{R}$$

$$* \Theta$$

Features

* "arrangement" coordinates

* orthogonal coordinates

* used in hyperspherical TI methods

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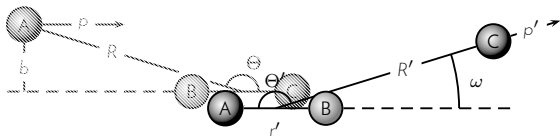
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Bond Order (BL) coordinates

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

Features

- * "process" coordinates
- * non orthogonal coordinates
- * physical space inverted and confined in a finite volume

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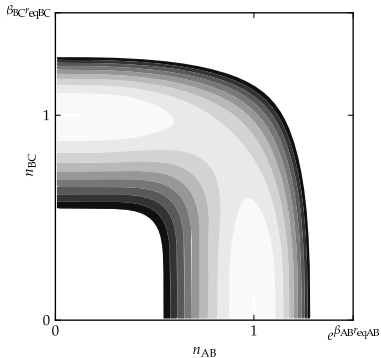
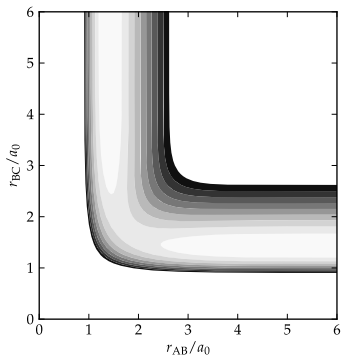
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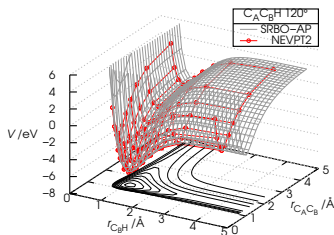
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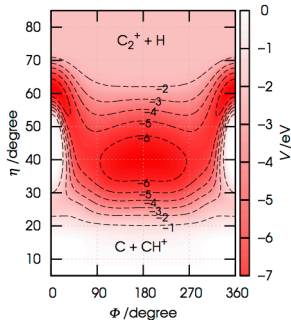
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Rectangular relaxed plot

reaction coordinate

$$\eta = \arctan(r_{\text{CH}}/r_{\text{CC}})$$

angular coordinate

$$\Phi = \widehat{\text{CCH}}$$

overall-size coordinate

$$\rho = (r_{\text{CH}}^2 + r_{\text{CC}}^2)^{1/2}$$

RRX plot

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

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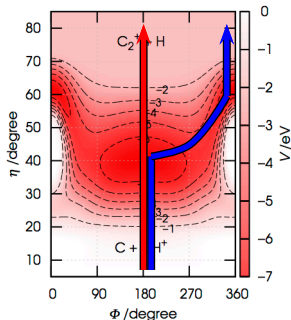
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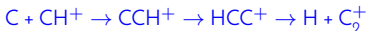


Reaction paths

path 1: collinear MEP



path 2: absolute MEP



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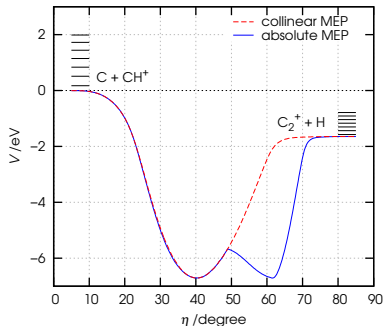
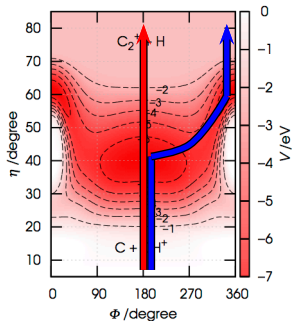
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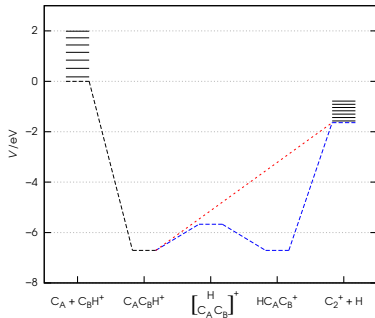
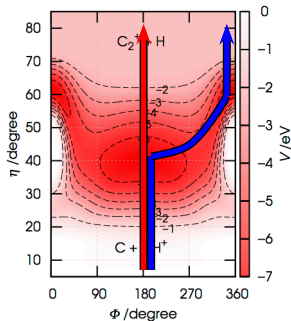
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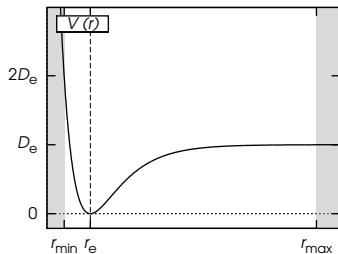
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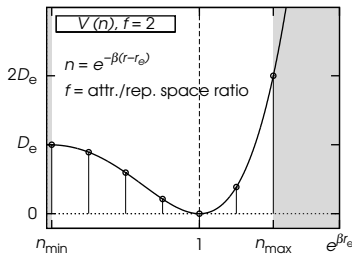
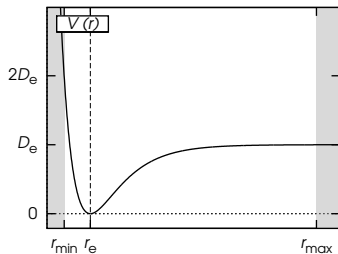
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9. Configuration-space sampling



SRBO approach

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

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

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

S Rampino, **Configuration-space sampling in potential energy surface fitting: a space-reduced bond-order grid approach**, *The Journal of Physical Chemistry A* 120, 4683-4692 (2016)

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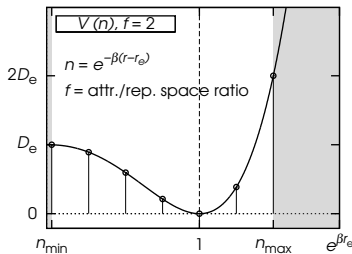
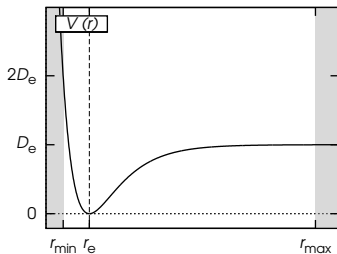
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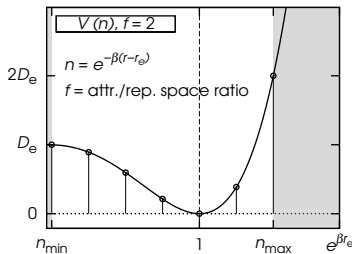
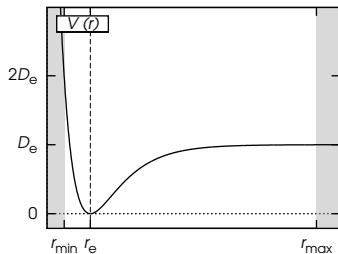
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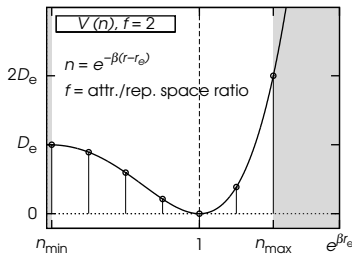
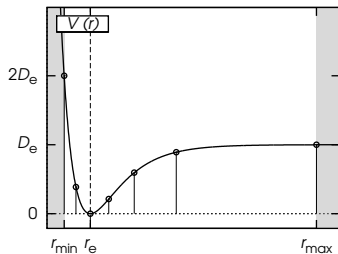
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QCT calculations

Nuclei move classically on the PES
Quantization introduced 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

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

Outcomes

opacity function

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

reactive probability

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

cross section

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

thermal rate coefficient

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

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The nuclei Schrödinger equation

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

must have solution

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

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Time evolution operator

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

Ground equation for TD methods

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

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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

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Wavepacket method

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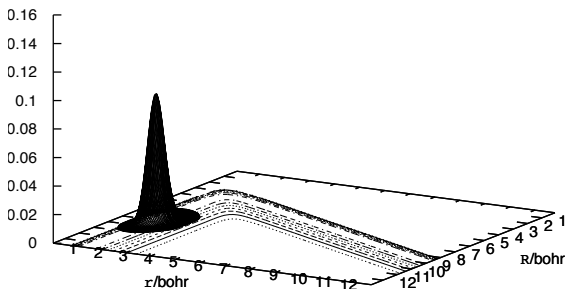
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Wavepacket method

1. set up a (v, j) wavepacket

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



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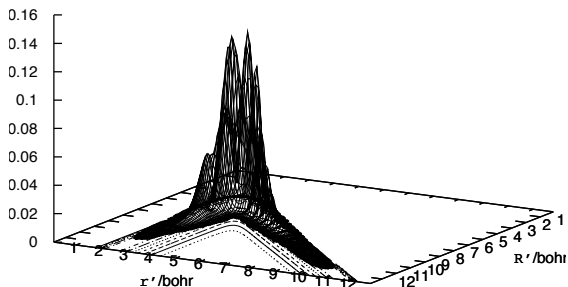
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Wavepacket method

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

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



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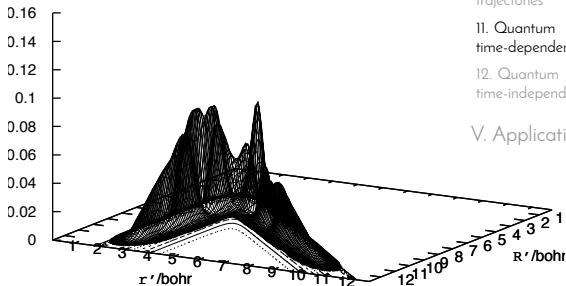
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Wavepacket method

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

$$S_{cv',av}(E) = -\frac{1}{\langle \psi_{cv'} | \Phi_{E_{cv'}}^+ \rangle \langle \Phi_{E_{av}}^- | \psi_{av} \rangle} \int_0^\infty e^{\frac{iEt}{\hbar}} \langle \psi_{cv'} | e^{-\frac{i\hat{H}t}{\hbar}} | \psi_{av} \rangle dt$$



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

in

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

and get the ground equation for TI methods

$$\hat{H}\psi(\mathbf{q}, t_0) = E\psi(\mathbf{q}, t_0) \quad (3)$$

time factored out

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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

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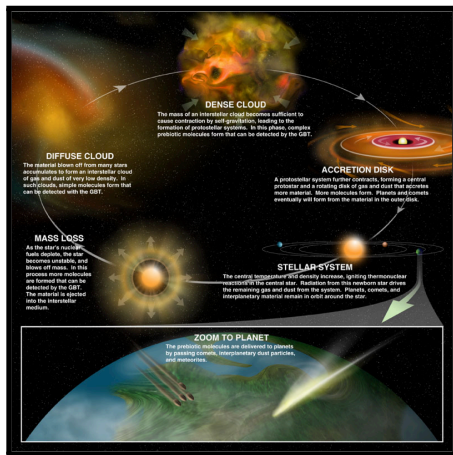
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 $C_2^+ + H$: dynamics

15. $C + CH^+ \rightarrow$
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Grand-challenge

Develop a complete model for an interstellar cloud

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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

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14. $\text{C} + \text{CH}^+ \rightarrow \text{C}_2^+ + \text{H}$: dynamics

15. $\text{C} + \text{CH}^+ \rightarrow \text{C}_2^+ + \text{H}$: kinetics

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Processes

radiative association
associative detachment
dust-grain-catalysed reactions
photodissociation
collisional 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

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associative detachment
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Processes

radiative association
associative detachment
dust-grain-catalysed reactions
photodissociation
collisional 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

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

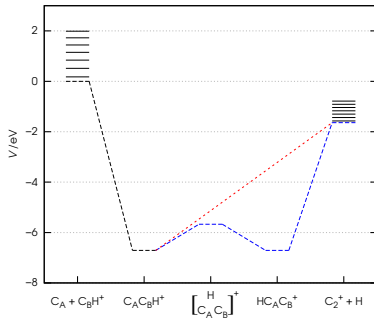
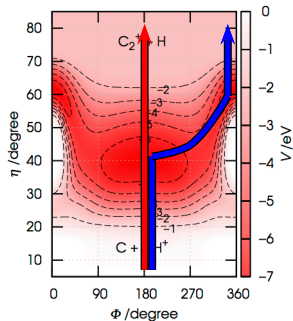
Kinetic databases

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

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



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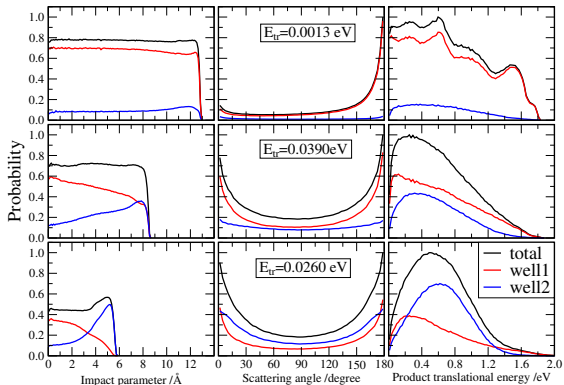
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Opacity functions (10, 300, 2000 K)

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)

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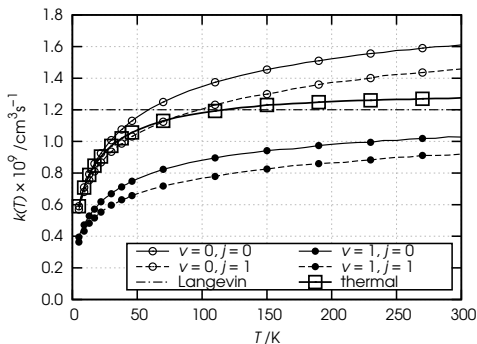
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Model vs dynamics

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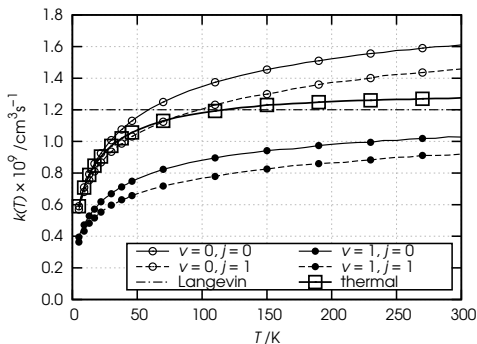
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Model vs dynamics

factor two at low T

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

sharp increase in 5-50 K

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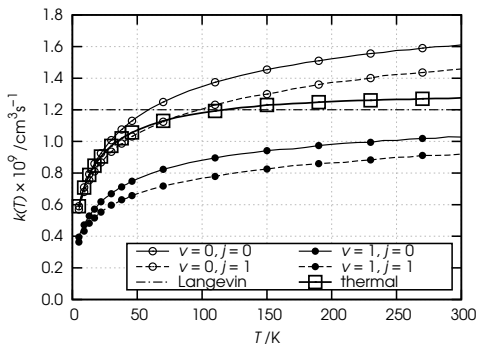
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Model vs dynamics

factor two at low T

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

sharp increase in 5-50 K

Model calculations improperly enhance
 CH^+ consumption in kinetic models

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End

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