Dynamical adiabatic theory of atomic collisions

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Ratko Janev (1939-2019)

(1965 - 1972) Instutute of Nuclear Sciences , Vinca - Belgrade

(1972 - 1987) Institute of Physics, Belgrade

(1987-1999) International Atomic Energy Agency, Vienna

(1999 - 2019) Macedonian Academy of Sciences and Arts, Skopje

(1999 - 2000) National Institute of Fusion Science, Tokyo

(2000 - 2002) Juelich Reserch Center, Germany

(2005 -2019) Institute of Applied Physics and Computational Mathematics, Beijing

(1972 - 1987) Institute of Physics, Belgrade

Founder of the Group for Theory of Atomic Collisions:

High energy atomic collisions - Dževad Belkić (Karolinska Institute, Stockholm)

Ion - surface interactions - Nataša Nedeljković (Faculty of Physics, Belgrade)

Low energy atomic collisions - Tasko Grozdanov (Institute of Physics, Belgrade), Predrag Krstić (Institute for Advanced Computational Science , Stony Brook)

My first and the last paper with R. Janev:
Physical Review A 17 (1978), 880
Eur. Phys. J. D (2018) 72: 14

Dynamical adiabatic theory of atomic collisions

Overview

- Introduction
- Dynamical adiabatic representation
- Hidden crosings in HeH^{2+} system
- Application to electron capture process: $H^{+}+He(1s)^{+} \rightarrow H(1s)+He^{2+}$
- Concluding remarks

Introduction

Motivation

- Incompatibility of standard (i.e. Born-Oppenheimer) adiabatic basis with physical boundary conditions in slow atomic collisions

Solutions for impact-parameter formulation:

- "Electronic translational factors" attached to basis functions [D.R. Bates and R. McCarroll 1958]

- Non-stationary scaling of length - Dynamical adiabatic basis. [E.A. Solov'ev 1976, 1982]

  (1) Boundary conditions.
  -All non-adiabatic couplings $W_{ij}(R) = \langle i|\partial/\partial R|j\rangle \to 0$ as $R \to \infty$.
  (In the standard adiabatic basis some $W_{ij}(R) \to const$ as $R \to \infty$.)

  .

  (2) Rotational transitions.
  -Transformed into radial transitions in rotating frame.
  (In standard adiabatic - need numerical close-coupling calculations.)

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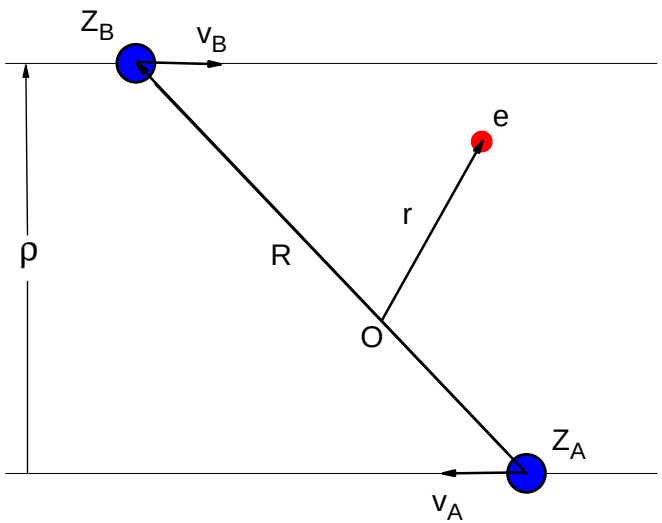
  (3) Ionization process.
  -Described using a basis of the complete discrete orthogonal wave-packets.

Solution for quantum formulation:

- Hyperspherical coordinates (E.A. Solov'ev and S.I. Vinitsky, 1985)

Dynamical adiabatic representation



(i) Non-stationary scaling of electronic coordinates:

$$\mathbf{q} = \hat{O}_z[\varphi(t)]\mathbf{r}/R(t),$$

$\hat{O}_z[\varphi(t)]$ - rotation matrix to molecular (rotating with internuclear axis) frame.

(ii) Introducing new wavefunction $f(\mathbf{q},\tau)$ (in a.u.):

$$\Psi(\mathbf{r},t) = R^{-3/2}\exp\left[i\frac{r^2}{2R}\frac{dR}{dt}\right]f(\mathbf{q},\tau),$$

$$\exp\left[i\frac{r^2}{2R}\frac{dR}{dt}\right]|_{Rr_j^{-1}\to\infty} = \exp[i(\mathbf{v}_j\cdot\mathbf{r}_j + \frac{1}{2}v_j^2 t)], j = A, B.$$

(iii) A new time-like variable: $d\tau = dt/R(t)^2$.

Modified time dependent Schrödinger equation

$$H(\tau)f(\mathbf{q},\tau) = i\frac{\partial f(\mathbf{q},\tau)}{\partial\tau},$$

$$H(\tau) = -\tfrac{1}{2}\Delta_q - R(\tau)\left(\frac{Z_A}{|\mathbf{q}+\alpha\hat{\mathbf{q}}_1|} + \frac{Z_B}{|\mathbf{q}-\beta\hat{\mathbf{q}}_1|}\right) + \omega L_3 + \tfrac{1}{2}\omega^2 q^2$$

$$\omega = \rho v, v = |\mathbf{v}_A - \mathbf{v}_B|,$$

$$R(\tau) = \rho/\cos\omega\tau, \quad L_3 = -i\left(q_1\frac{\partial}{\partial q_2} - q_2\frac{\partial}{\partial q_1}\right), \quad \Pi_3(q_3\to -q_3)$$

Adiabatic expansion

$$f(\mathbf{q},\tau) = \sum_j g_j(\tau)\Phi_j(\mathbf{q},R(\tau),\omega)\exp\left(-i\int_0^\tau E_j(R(\tau'),\omega)d\tau'\right)$$

Dynamical adiabatic basis depends on two parameters: $\omega = \rho v$ and real (*or complex*) values of R

$$H(R,\omega)\Phi_j(\mathbf{q},R,\omega) = E_j(R,\omega)\Phi_j(\mathbf{q},R,\omega)$$

Relation to standard adiabatic eigenvalues: $E_j(R,\omega=0) = \varepsilon_j(R)R^2$

Numerical method: Lagrange-mesh method [T.P. Grozdanov and E.A. Solov'ev, 2013,2014]

Prolate spheroidal coordinates $\{\xi,\eta,\phi\}$: $N_\xi \times N_\eta$ mash points $(\xi_i = hx_i, \eta_j)$ $(i = 1,...,N_\xi, j = 1,...,N_\eta)$, related to zeros of the Laguerre and Legendre polynomials: $L_{N_\xi}(x_i) = 0$ and $P_{N_\eta}(\eta_j) = 0$,

$$h_m^{\pi_3}(\phi) = \begin{cases} [(1+\delta_{m,0})\pi]^{-1/2}\cos m\phi & \text{for } \pi_3 = 1 \\ (\pi)^{-1/2}\sin m\phi & \text{for } \pi_3 = -1. \end{cases}$$

$m = |m_1| = 0,1,...,M$

Matrix elements by using Gaussian quadratures - all analytic.

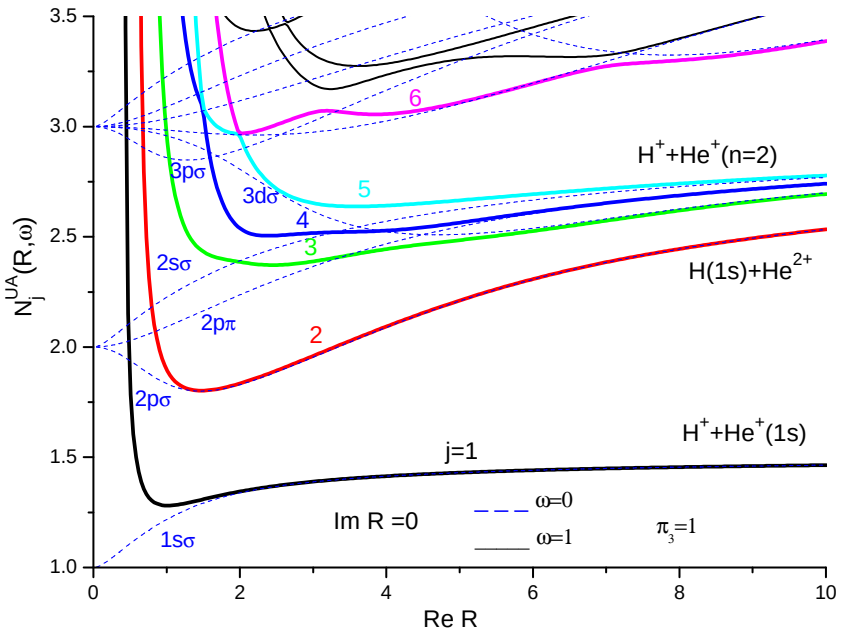
HeH^{2+} SYSTEM ($Z_A = 1, Z_B = 2$). ELECTRON CAPTURE PROCESSES

$$He^{2+} + H(1s) \rightarrow He^{+}(n = 2) + H^{+}$$ [T.P. Grozdanov and E.A. Solov'ev, 2015]

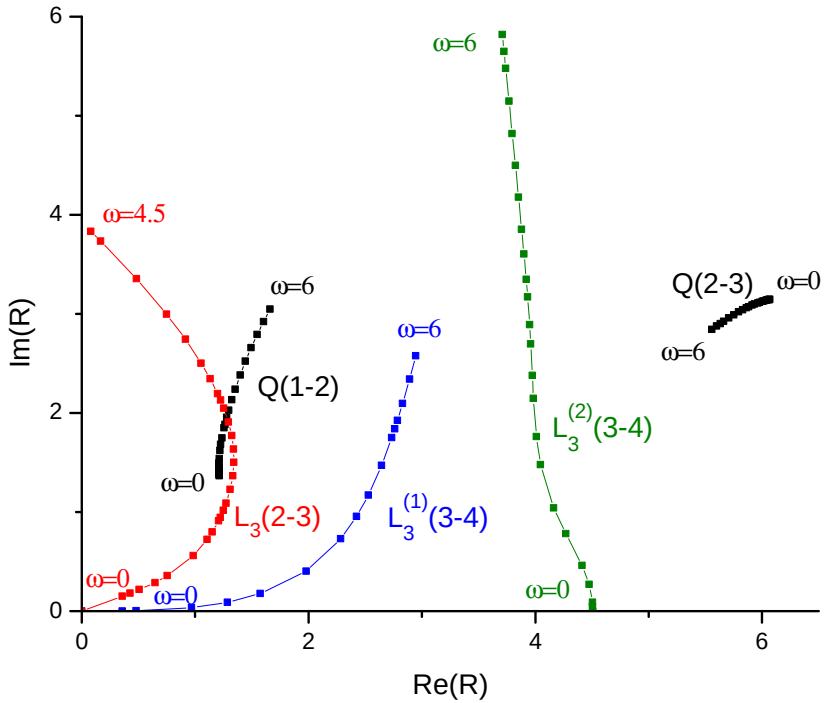
$$H^{+} + He^{+}(1s) \rightarrow H(1s) + He^{2+}$$ [T.P. Grozdanov and E.A. Solov'ev, 2018]

Effective united-atom principal quantum number:

$$N_{UA}(R, \omega) = (Z_A + Z_B)R[-2E(R, \omega)]^{-1/2}$$



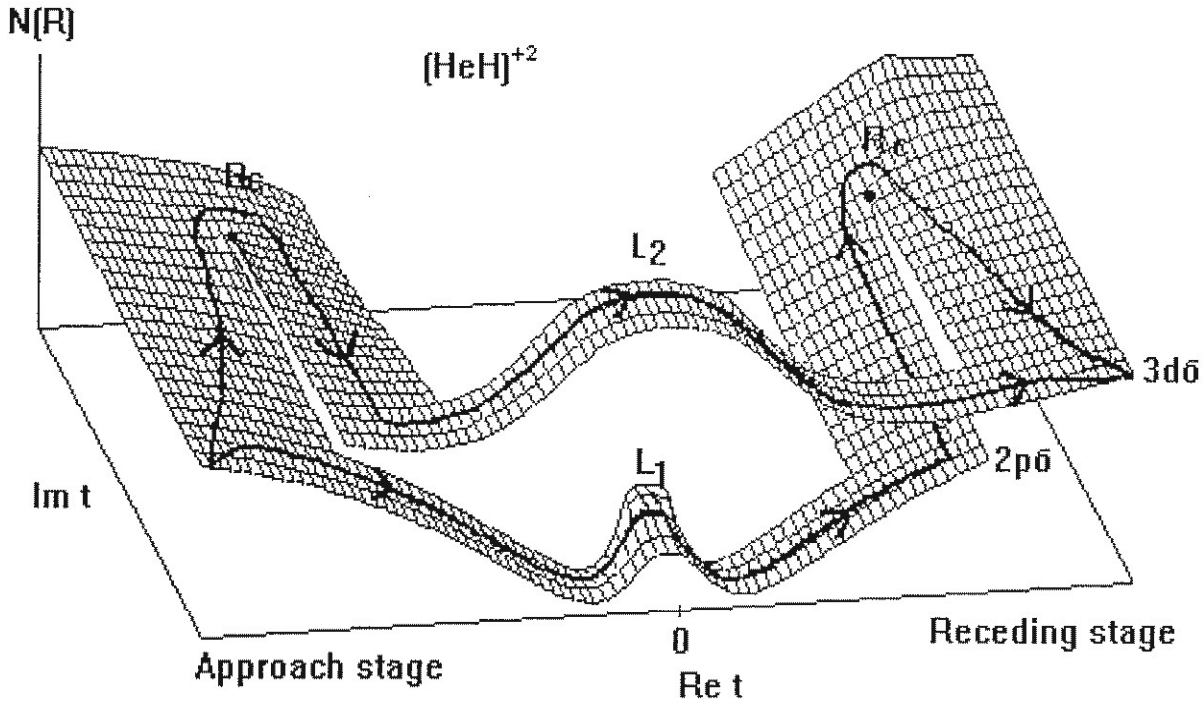
Hidden crosssings: Q- and L_3- series of branch points



TRANSITION PROBABILITIES

Example: one branch point, two paths

[R.K. Janev, J. Pop-Jordanov, E.A. Solov'ev, 1997]



$$P = \left| \sum_{k=1,2} A^{(k)} \exp\{-i\phi^{(k)} - in^{(k)}\pi/2\} \right|^2,$$

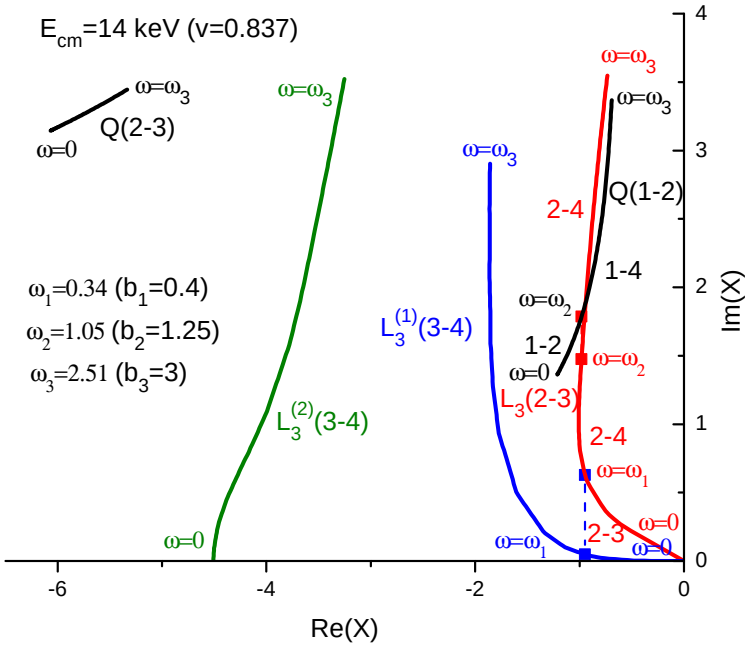
$A^{(k)} = \sqrt{1-p}\sqrt{p}, \quad \phi^{(k)} = \mathrm{Re} \int_{L_k} E(R(t))dt, \quad n^{(k)} = \pm 1$

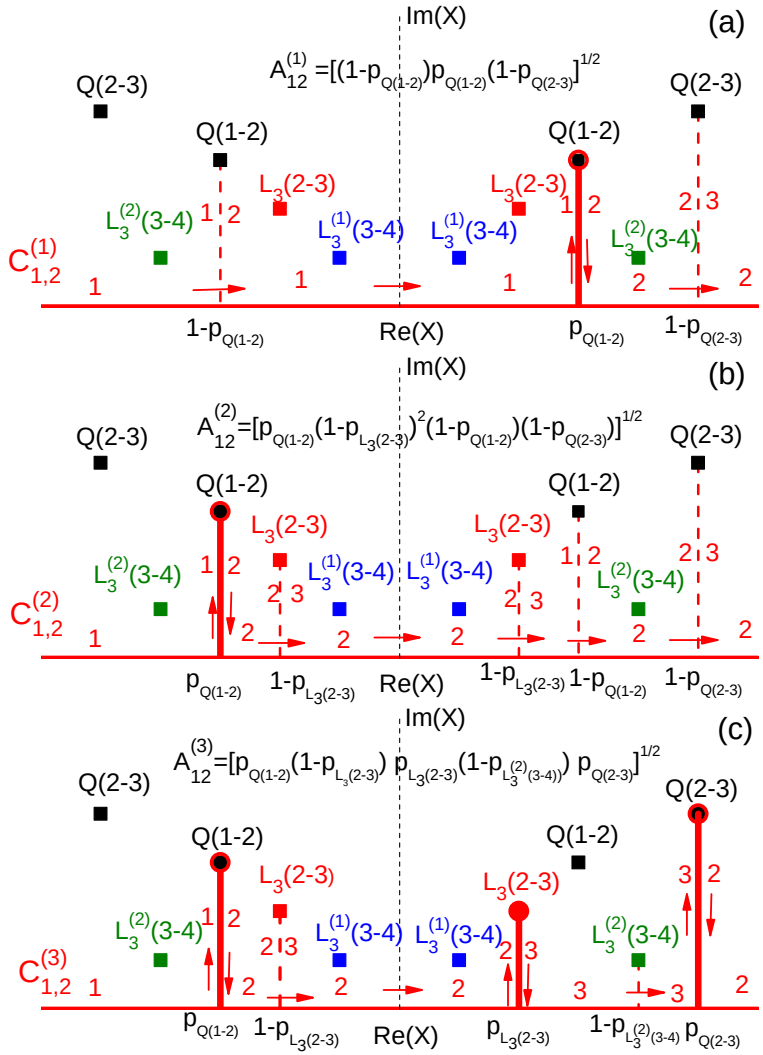
$p = e^{-2s}, \quad s = \left| \mathrm{Im} \int_{L_k} E(R(t))dt \right|$ – Stueckelberg parameter

$$P = 4e^{-2s}(1-e^{-2s})sin^2(\phi^{(1)}/2 - \phi^{(2)}/2)$$

TRANSITION PROBABILITIES: $H^+ + He^+(1s) \rightarrow H(1s) + He^{2+}$

"$X = vt$ - complex plane", $R^2 = X^2 + \rho^2$





$j_i = 1 \rightarrow j_f = 2$

$$P_{1,2} = \left| \sum_{k=1}^{9} A_{1,2}^{(k)} \exp\{-i\phi_{1,2}^{(k)} - in_{1,2}^{(k)}\pi/2\} \right|^2,$$

$$\phi_{1,2}^{(k)} = \mathrm{Re} \int_{C_{1,2}^{(k)}} \frac{E(R,\omega)}{R^2} dt,$$

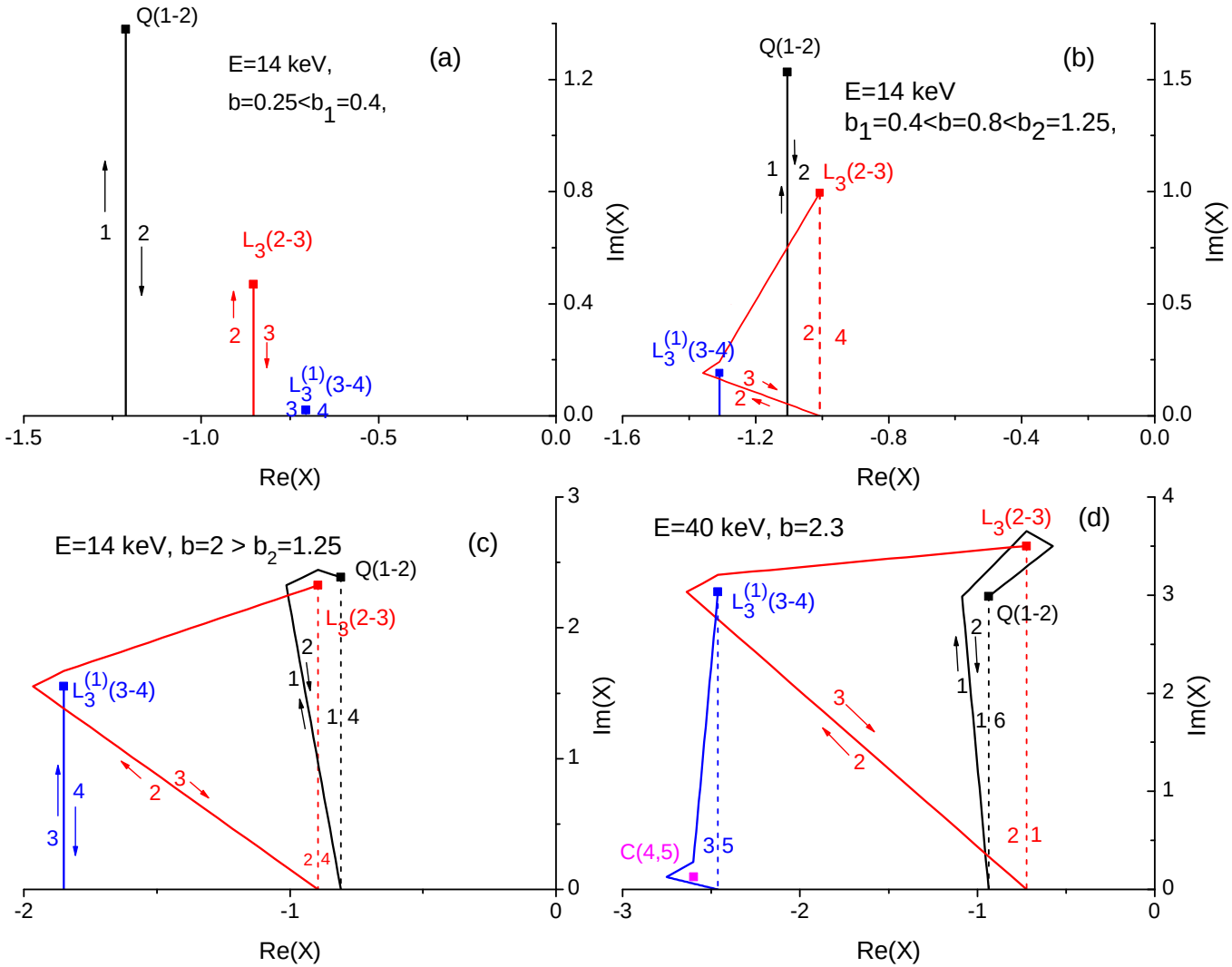
$$A_{1,2}^{(k)} = \prod_{A,B} \sqrt{p_A}\sqrt{1-p_B}$$

$$p_A = e^{-2s_A}, \quad s_A = \left| \mathrm{Im} \int_{C_A} \frac{E(R,\omega)}{R^2} dt \right|,$$

$A = Q(1-2), Q(2-3), L_3(2-3), L_3^{(1)}(3-4), L_3^{(2)}(3-4)$

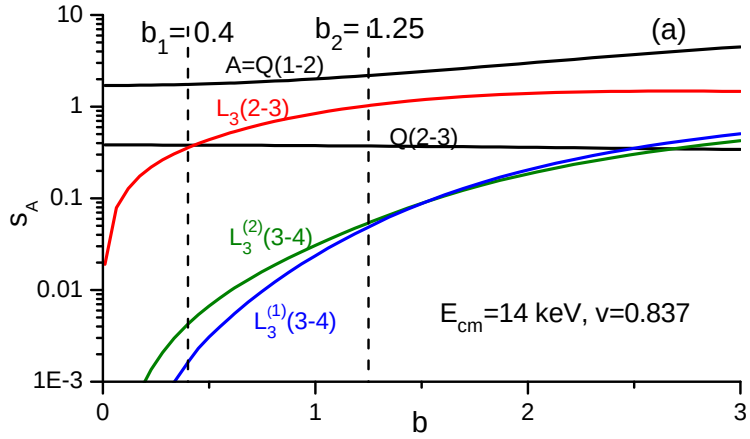
TRANSITION PROBABILITIES: $H^+ + He^+(1s) \rightarrow H(1s) + He^{2+}$

Deformation of paths

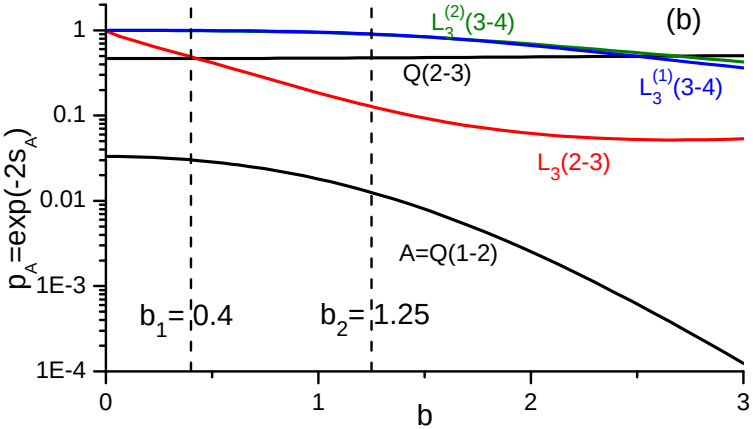


TRANSITION PROBABILITIES: $H^+ + He^+(1s) \rightarrow H(1s) + He^{2+}$

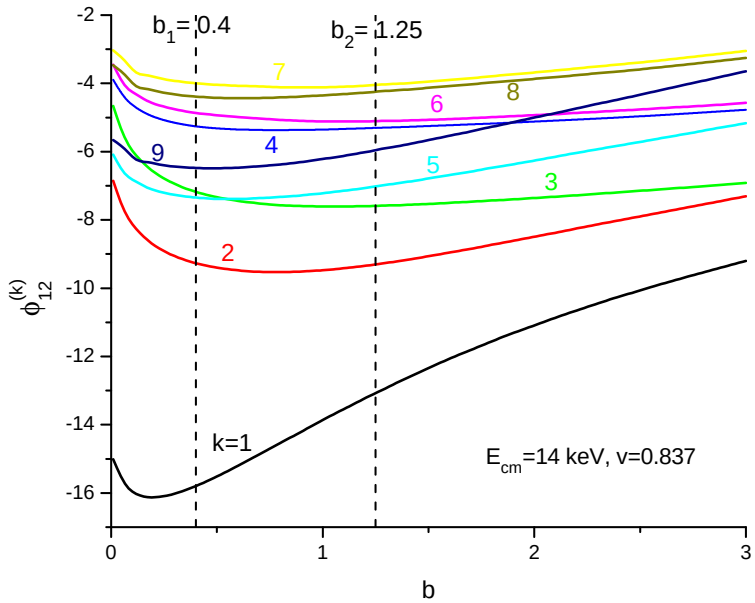
Stueckelberg parameters



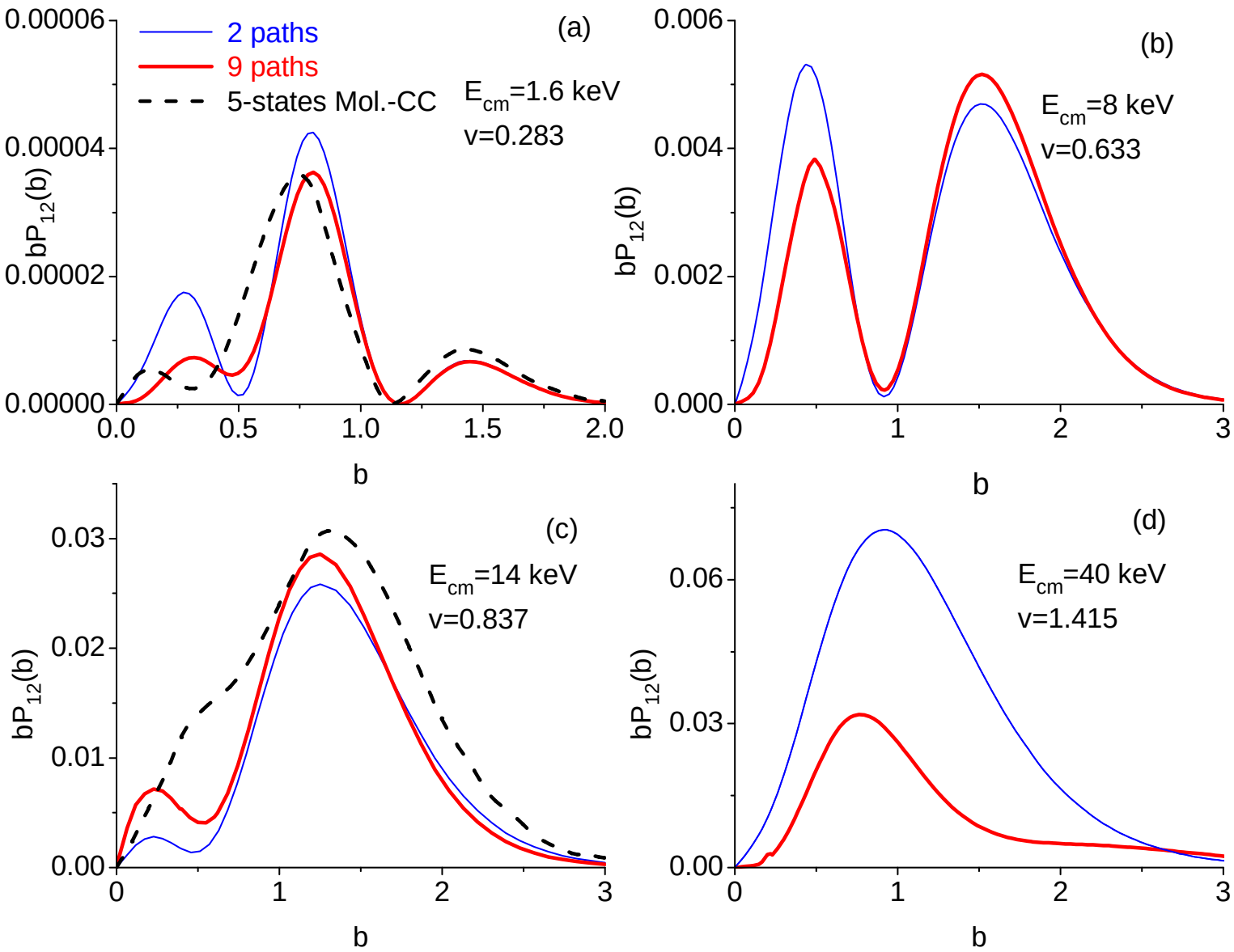
Single-pass probabilities



Phases $\phi_{1,2}^{(k)}$

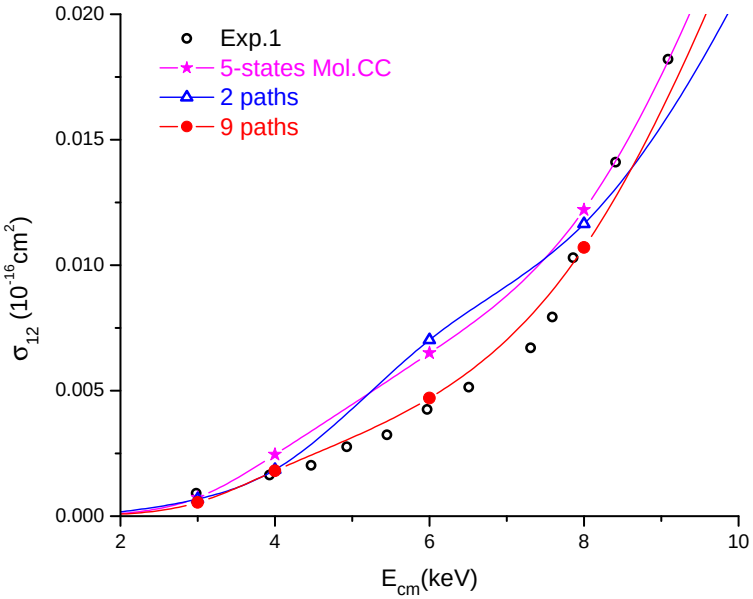


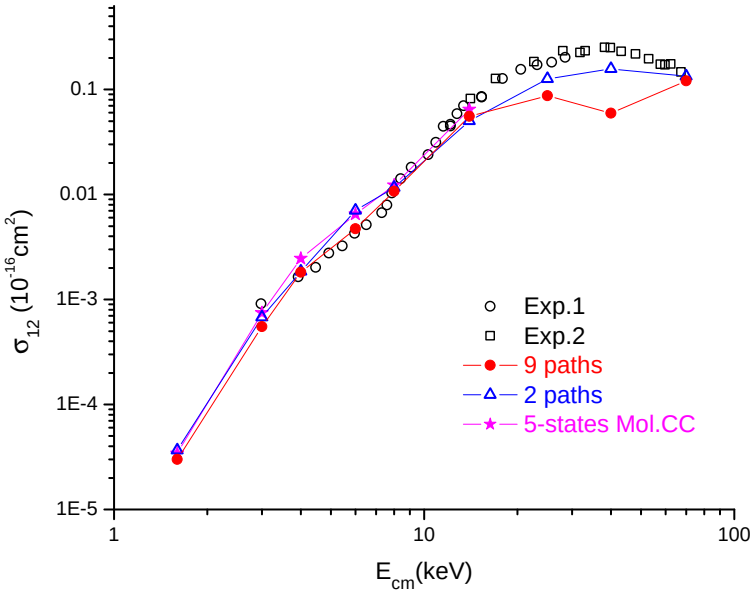
TRANSITION PROBABILITIES: $H^+ + He^+(1s) \rightarrow H(1s) + He^{2+}$



CROSS SECTIONS: $H^+ + He^+(1s) \rightarrow H(1s) + He^{2+}$

$$\sigma_{1,2}(E_{cm}) = \int_0^\infty \rho P_{1,2}(\rho) d\rho$$





Exp.1,2 - [B. Pearth et al, 1977,1983]

5-states Mol.CC-[T.G. Winter et al,1980]

Concluding remarks

- The application of hidden-crossings method for describing electronic transitions in ion-atom collisions is more complicated in dynamical adiabatic theory then in the standard adiabatic theory.
- This is because one has to deal with a series of branch points in the complex R-plane which change their positions when dynamical parameters (such as $\omega = \rho v$) are changed.
- The great advantage of this method is that electronic transitions caused by relative radial and angular motion of the nuclei can be treated on the equal footing, the property which is missing in the standard adiabatic approach.
- As the comparison with the close-coupling calculations show, the precision of the method is satisfactory.