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Heavy Particle Collision Processes

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HEAVY PARTICLE COLLISION PROCESSES

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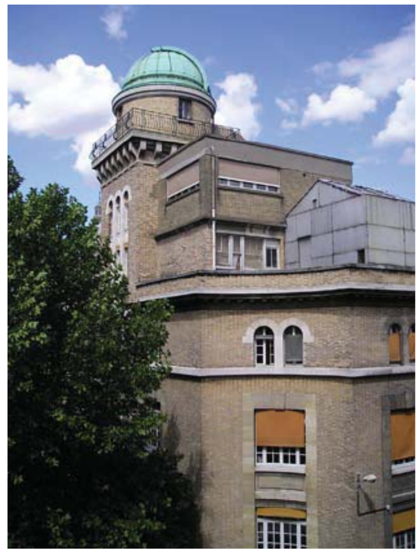


Heavy particle collision processes

I - Introduction

II - Three models for electron transfer

a) The Thomas mechanism

b) The Bohr-Lindhardt model

c) Resonant capture at low energy in homonuclear one electron collision systems

III - The quasi-molecular formalism

IV - The travelling asymptotic state basis set expansion : the intermediate energy domain

V - Capture in ion-molecule collisions

Electronic processes :

$$A^{q+} + B \longrightarrow \begin{cases} A^{q+} + B^{*} & \textit{excitation} \\ A^{(q-1)+} + B^{+} & \textit{capture (transfert)} \\ A^{q+} + B^{+} + e^{-} & \textit{ionization} \end{cases}$$

ex:

$$H^{+} + H(1s) \longrightarrow \begin{cases} H^{+} + H(2s) & \\ H^{+} + H(2p) & \ldots \\ H(1s) + H^{+} & \\ H(2p) + H^{+} & \ldots \\ H^{+} + H^{+} + e^{-}\,(\varepsilon_k) & \ldots \end{cases}$$

...

$$He^{2+} + He(1s^2) \longrightarrow He^{+} + He^{+}$$

$$Li^{3+} + He \longrightarrow Li^{2+} + He^{+}$$

$$Li^{+} + He^{2+}$$

$$H^{+} + H^{-}(1s^2) \longrightarrow H(nl) + H(n'l')$$

$$H^{-}(1s^2) + H^{+}$$

$$H^{+} + H + e^{-}\ (\varepsilon_k)$$

$$Kr^{34+} + Ar \longrightarrow Kr^{34+} + Ar^{n+} + n\ e^{-}$$

atomic units $\left\{ \begin{array}{l} m_e \\ e \\ \hbar \\ 4\pi\varepsilon_0 \end{array} \right. = 1$

Table A14.2 Atomic units.

Quantity	Unit	Physical significance	Value
Mass	m or m_e	Electron mass	$9.109\,38 \times 10^{-31}$ kg
Charge	e	Absolute value of electron charge	$1.602\,18 \times 10^{-19}$ C
Angular momentum	$\hbar$	Planck's constant divided by (2π)	$1.054\,57 \times 10^{-34}$ J s
Length	$a_0 = \dfrac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}$	Bohr radius for atomic hydrogen (with infinite nuclear mass)	$5.291\,77 \times 10^{-11}$ m
Velocity	$v_0 = \alpha c = \dfrac{e^2}{4\pi\varepsilon_0 \hbar}$	Magnitude of electron velocity in first Bohr orbit	$2.187\,69 \times 10^{6}$ m s^{-1}
Momentum	$p_0 = mv_0$	Magnitude of electron momentum in first Bohr orbit	$1.992\,85 \times 10^{-24}$ kg m s^{-1}
Time	$\dfrac{a_0}{v_0}$	Time required for electron in first Bohr orbit to travel one Bohr radius	$2.418\,88 \times 10^{-17}$ s
Frequency	$\dfrac{v_0}{2\pi a_0}$	Angular frequency of electron in first Bohr orbit (v_0/a_0) divided by (2π)	$6.579\,69 \times 10^{15}$ s^{-1}
Energy	$\dfrac{m_e e^4}{(4\pi\varepsilon_0)^2\hbar^2} = \dfrac{e^2}{4\pi\varepsilon_0 a_0} = \alpha^2 mc^2$	Twice the ionisation potential of atomic hydrogen (with infinite nuclear mass)	$4.359\,74 \times 10^{-18}$ J $= 27.2114$ eV
Wave number	$\dfrac{\alpha}{2\pi a_0} = 2\tilde{R}(\infty)$	Twice the Rydberg constant, i.e. twice the wave number corresponding to the ionisation potential of atomic hydrogen (with infinite nuclear mass)	$2.194\,75 \times 10^{7}$ m^{-1}
Electric field strength	$\dfrac{e}{(4\pi\varepsilon_0)a_0^2}$	Strength of the Coulomb field experienced by an electron in the first Bohr orbit of atomic hydrogen (with infinite nuclear mass)	$5.142\,21 \times 10^{11}$ V m^{-1}
Magnetic field strength	$\dfrac{\hbar}{ea_0^2}$		$2.350\,52 \times 10^{5}$ T

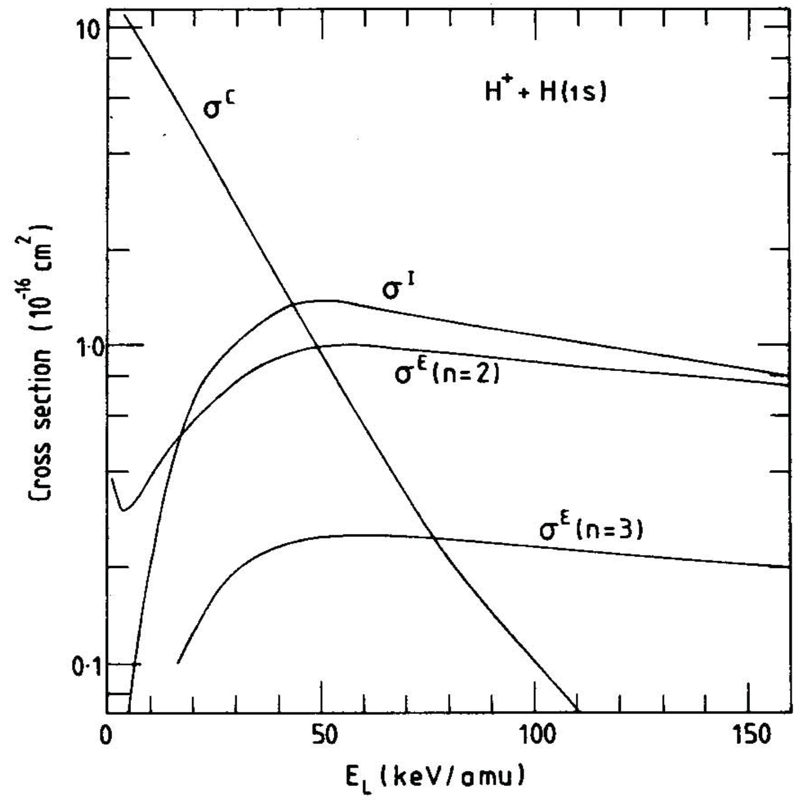
Velocity of ligth in vacuum

c = 1/α ≈ 137 u.a.

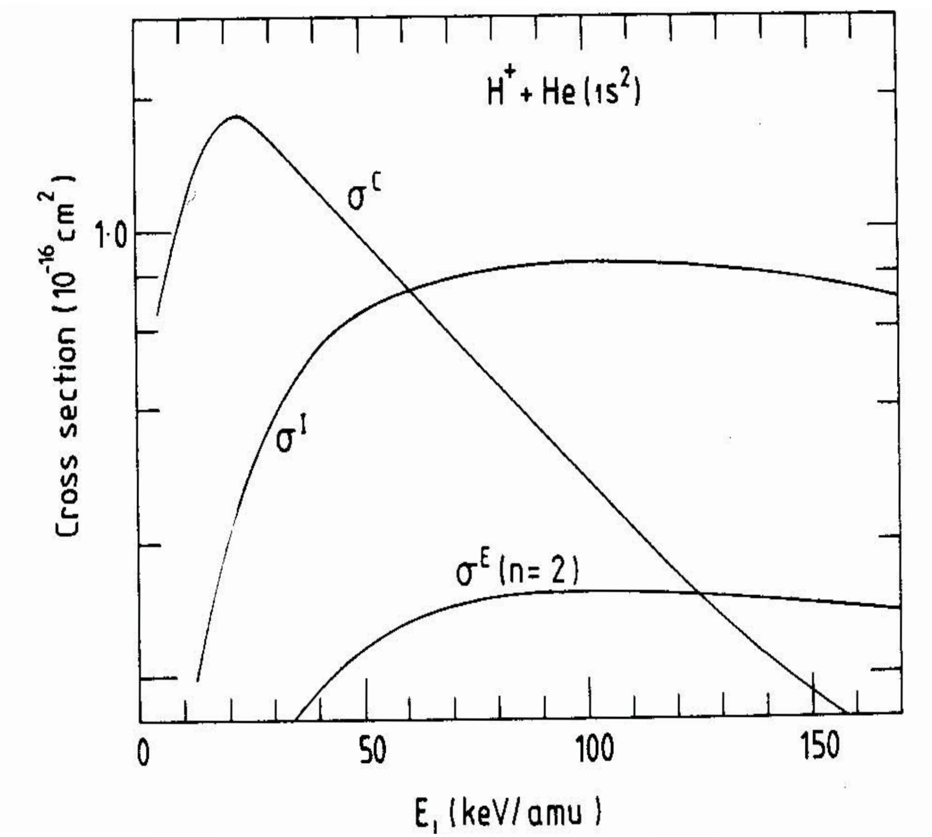
Typical structure and collision parameters for H + H (H_2) system

	energy ΔE	threshold velocity * $v_{thres} = \sqrt{\frac{2eE_{eV}}{\mu}}$	caracteristic time $\Delta E\ \Delta t > \hbar$	collision time ** $T_{coll} = a / v$	de Broglie wavelength $\lambda_{dB} = h / \mu v$
electronic transitions	$\approx$ 10 eV ($\approx$ 1 a.u.)	$v > 5\ 10^4$ m.s^{-1} ($\approx 2\ 10^{-2}$ a.u.)	$\tau \approx 5\ 10^{-17}$ s ($\approx$ 1 a.u.)	$T_{coll} < 2\ 10^{-16}$ s ($\approx$ 10 a.u.)	$\lambda_{dB\,l} < 10^{-11}$ m ($\approx$ 0.2 a.u.)
vibrationnal transitions	$\approx 10^{-1}$ eV ($\approx 10^{-2}$ a.u.)	$v > 5\ 10^3$ m.s^{-1} ($\approx 2\ 10^{-3}$ a.u.)	$\tau \approx 5\ 10^{-15}$ s ($\approx 10^2$ a.u.)	$T_{coll} < 2\ 10^{-15}$ s ($\approx$ 100 a.u.)	$\lambda_{dB\,l} < 10^{-10}$ m ($\approx$ 2 a.u.)
rotationnal transitions	$\approx 10^{-3}$ eV ($\approx 10^{-4}$ a.u.)	$v > 5\ 10^2$ m.s^{-1} ($\approx 2\ 10^{-4}$ a.u.)	$\tau \approx 5\ 10^{-13}$ s ($\approx 10^4$ a. u.)	$T_{coll} < 2\ 10^{-14}$ s ($\approx 10^3$ u.a.)	$\lambda_{dB\,l} < 10^{-9}$ m ($\approx$ 20 a.u.)

* $\mu = M_H/2 = 1.3 10^{-27}$ kg $\approx 10^3$ a.u. ** collision zone **a ≈ 5 Å (≈ 10 a.u.)**



Cross sections for the inelastic scattering of protons by atomic hydrogen in the ground state.

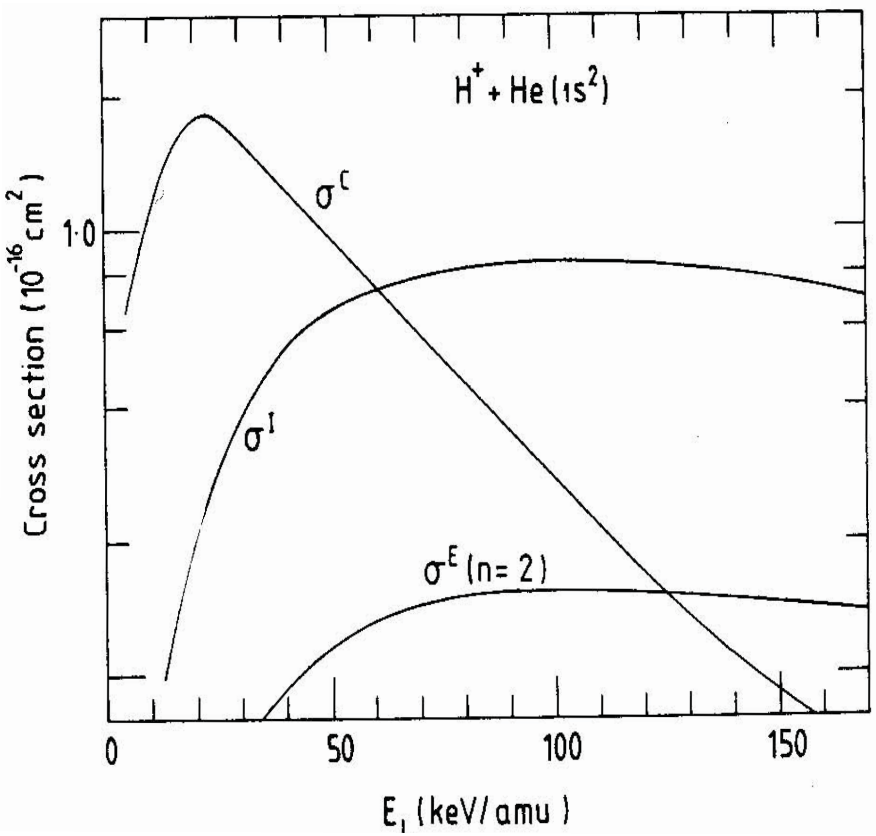


Cross sections for the inelastic scattering of protons by He^+ ions in the ground state.

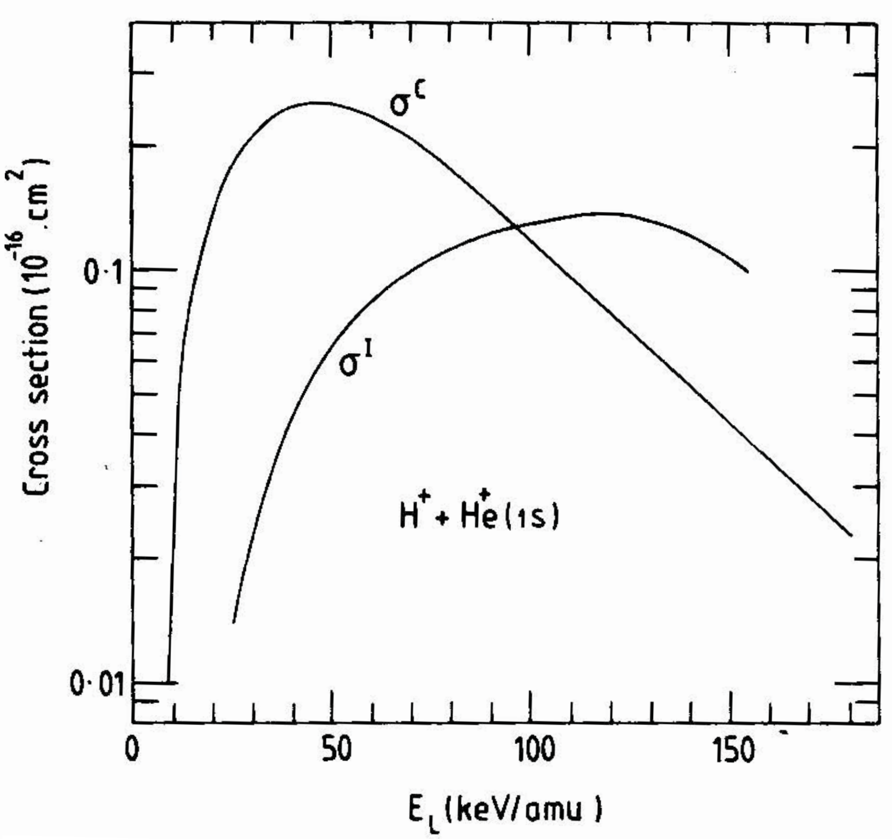
C= capture, E=excitation, I=ionization

$$E_{keV/amu} = 25\, v_{au}^2$$

from Charge Exchange and the Theory of Ion-Atom Collisions, Bransden and McDowelll



Cross sections for the inelastic scattering of protons by helium in the ground state.



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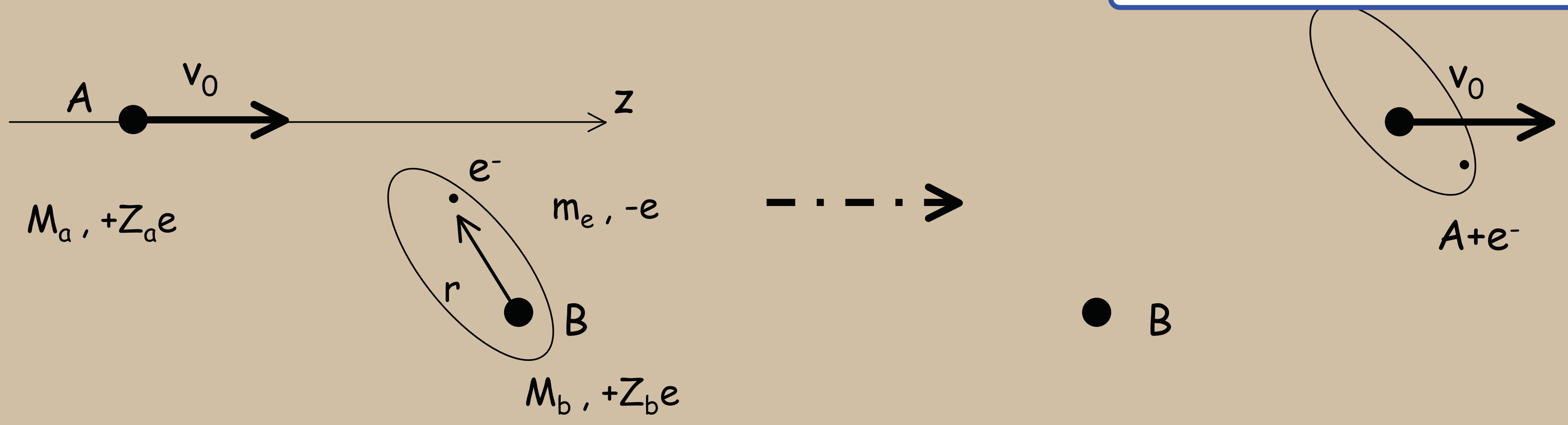


- **<u>single</u> scattering mechanism** => $\sigma^C \propto 1 / v_0^{12}$

  (matching of a part of the electron momentum distribution with v_0)

- **<u>double</u> scattering mechanism**

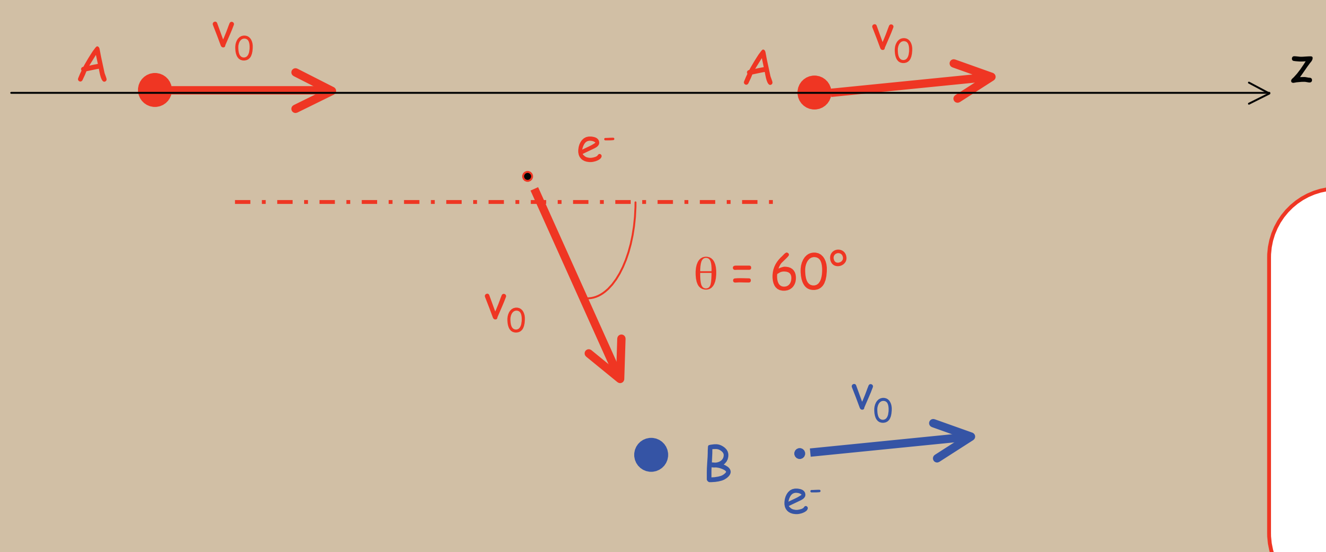
  classical model proposed by **<u>Thomas</u>** in 1927

  Proc. Roy. Soc. London A <u>114</u>, 561 (1927)

* target nucleus and electron assumed at rest (high velocity approx => $v_0 \gg 1$ a.u.)

* 2 binary collisions between charged particles (Rutherford scattering)

- 1st stage: between A and e^- to give v_0 to the electron
- 2nd stage: between e^- and B to bring e^- in the direction of the moving projectile A



Rem:

$$tg\theta_L = \frac{\sin\theta}{\cos\theta + \tau}$$

with = m_e/M_a or M_a/m_e

* <u>1st stage</u>

the electron gets $\approx v_0$ and is scattered at $\approx 60°$

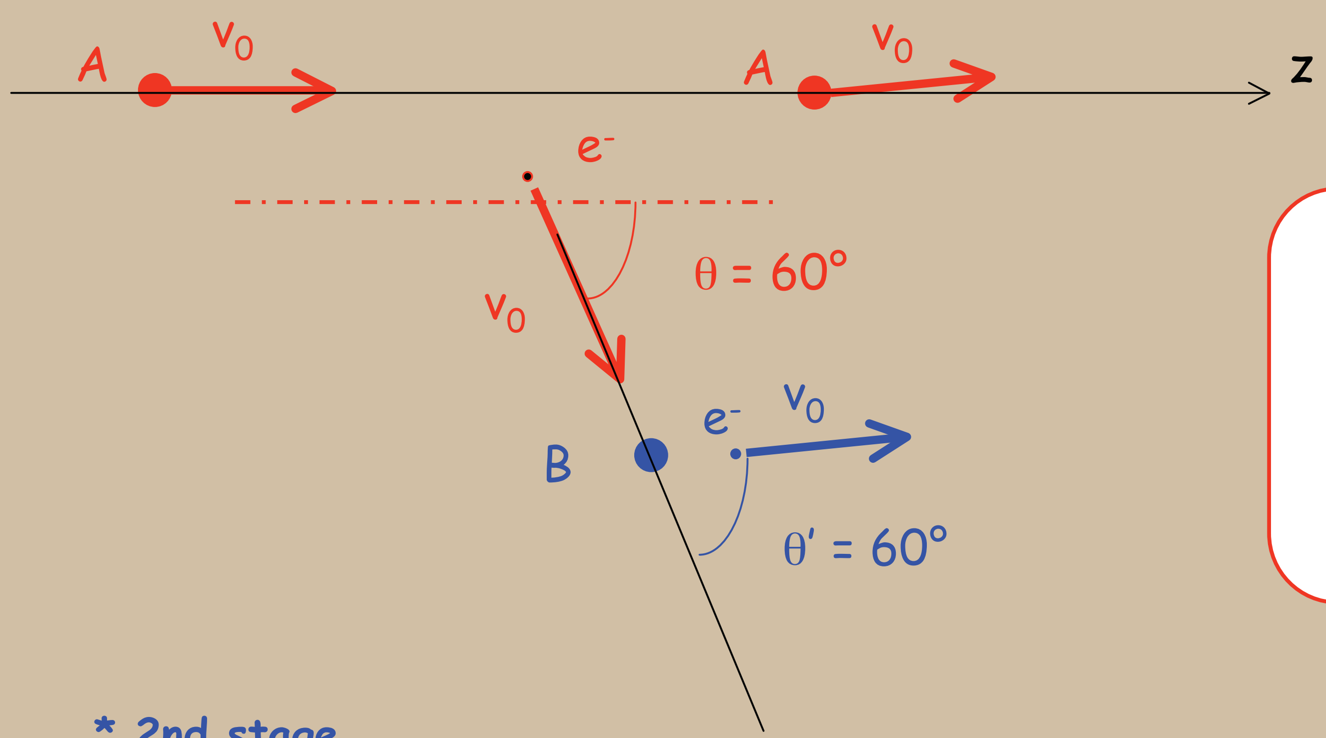
(insures energy and momentum conservation)

The probability for A to pass an electron at a distance b when travelling the distance Δl is

$dP_1 = 2\pi\ b\ db\ \Delta l$ (N density of atom B, b impact parameter)

with $b = \frac{Z_a}{\mu v^2} \mathrm{cotg}\ \theta/2$ (Rutheford) so that $\boxed{dP_1 \propto \frac{dv}{v^5}}_{v=v_0}$

IIa - The Thomas mechanism



Rem:

$$tg\theta_L = \frac{\sin\theta}{\cos\theta + \tau}$$

with $= m_e/M_a$ or M_a/ m_e

* **2nd stage**

the electron scattered by the target nucleus B and escape with the same velocity in the same direction than the projectile

$dP_2 \propto b'\, db'$

with $b' = \dfrac{Z_b}{\mu v^2} \cot g\, \theta'/2$ (Rutheford) so that $\boxed{dP_2 \propto \dfrac{d\theta'}{v^4}}$

So that finally $\quad dP = dP_1 \; dP_2 \propto \dfrac{dv \, d\theta'}{v^9}$

with $\; v \approx v_0 \;$ so that u the relative velocity of e^- with respect to A and $\; \mu u^2 < 2 Z_a/r$

so that dv is such $\quad v^2 \, dv \, d\Omega_v = 4/3 \, \pi \, (2 \; Z_a/ \mu r)^{3/2}$

$$\Rightarrow \qquad \boxed{dP \propto \frac{1}{v^{11}}}$$

valid in the relativistic regime (!) but the Thomas peak (angle) an be observed

$$tg\theta_{aL} = \frac{\sin\theta}{\cos\theta + M_a/m_e} = \frac{m_e \sin\theta}{M_a} \approx \frac{3^{1/2} m_e}{2 M_a} \approx 0.5 \text{ mrad} \qquad \text{for } A = H^+$$

PHYSICAL REVIEW A VOLUME 30, NUMBER 1 JULY 1984

Study of the Thomas peak in electron capture

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IIa - The Thomas mechanism

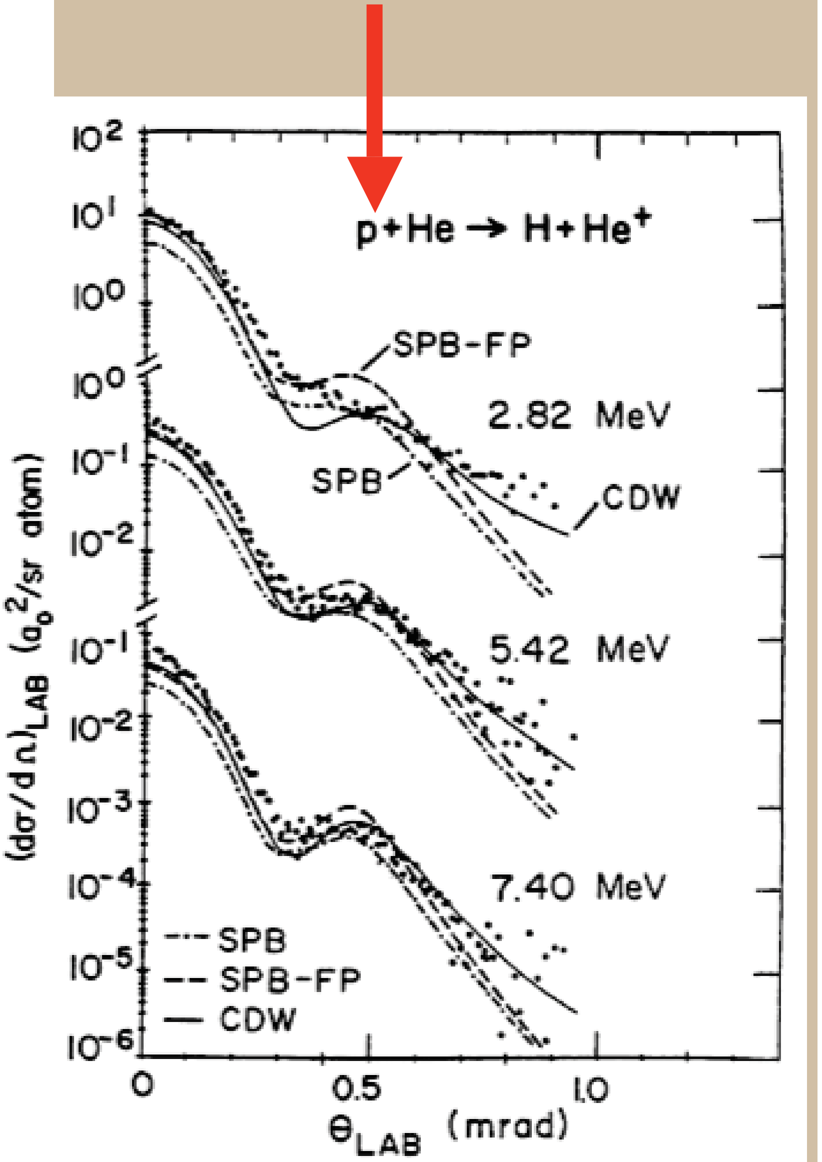

FIG. 4. Differential cross section vs scattering angle. Experimental results (dots, Ref. 20) are compared to strong-potential Born (SPB), strong-potential Born with full peaking (SPB-FP, Ref. 10), and continuum-distorted-wave (CDW, Ref. 22) theory.

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Another **classical** model working at intermediate to high energy

proposed by **Bohr and Lindhardt** in 1954

K. Dan. Vid. Sel. Mat. Phys. Medd. 28, 7 (1954)

* for fully stripped ion A colliding on hydrogenic ion B
* Capture can take place if two conditions are satisfied :
  - 1st condition : release of e^- by B
  - 2nd condition : capture of the e^- by A

$$y_m = -\frac{\sqrt{Z_b}}{\sqrt{Z_a}+\sqrt{Z_b}} R$$

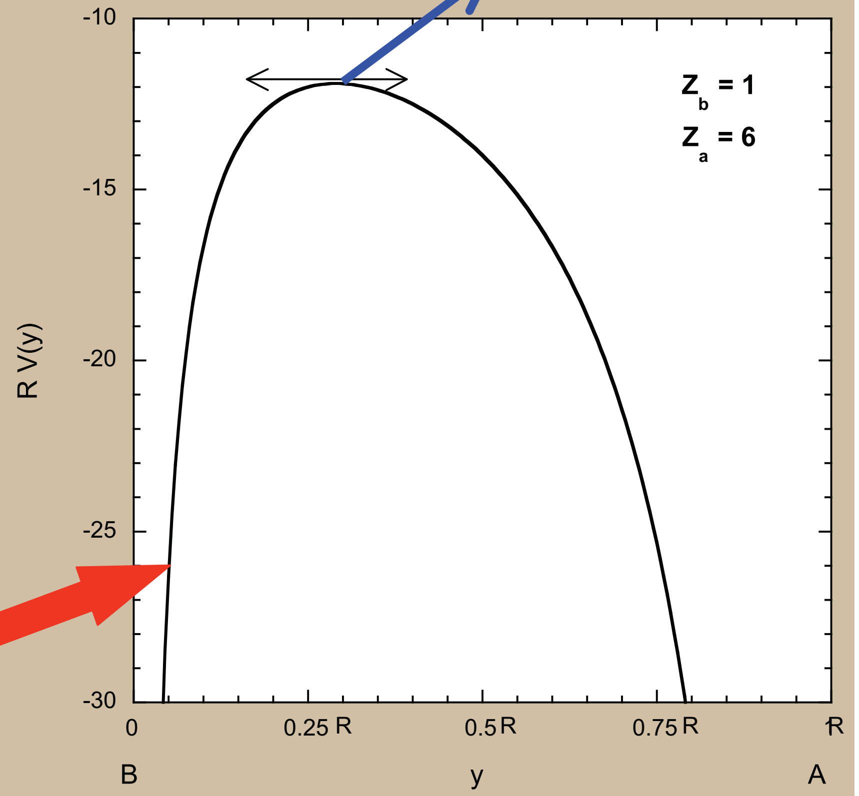
$$V(y_m) = -\frac{1}{R}\left(\sqrt{Z_a}+\sqrt{Z_b}\right)^2$$

Energy of the electron on B $\quad E_n = -\frac{1}{2}\frac{Z_b^2}{n^2}$

+ extra attraction term from A, in average $\quad -\frac{Z_a}{R}$

the total potential energy acting on the electron
(at y from B on the internuclear line **R**)

$$V(y) = -\frac{Z_b}{y} - \frac{Z_a}{R-y}$$



* 1st condition : **release**

the initial energy of the electron equal to the height of the barrier

$$R_1 = \frac{2n^2(Z_b + 2\sqrt{Z_a}\sqrt{Z_b})}{Z_b^2} \approx \frac{4n^2\sqrt{Z_a}}{Z_b^{3/2}} \quad \text{if } Z_a >> Z_b$$

* 2nd condition : **capture**

the electron has a kinetic energy $v^2/2$ with respect to the moving A: capture can occur if the attraction $-Z_a/R$ balances this term that is when $R < R_2$ with

$$R_2 = \frac{2Z_a}{v^2}$$

Then

- at high energy where $R_1 > R_2$ the geometrical cross section is $\sigma_1^C = \pi R_2^2$

but ionization may occur => σ^C weighted by the probability of ionizing the electron before capture takes place, approximate by the ratio between collision time R_2/v to the periodic time of the electron in the initial Bohr orbit a_n/v_n

$$\sigma_1^C = \pi R_1^2 \left[\frac{R_2}{v}\frac{v_n}{a_n}\right] = 8\pi Z_a^3 \left[\frac{v_n}{a_n}\right] v^{-7}$$

$$a_n = n^2/Z_b \qquad v_n = Z_b/n$$

- at low energy where $R_2 > R_1$ $\left(v^2 < \frac{1}{2}\sqrt{\frac{Z_a}{Z_b}}\, v_n{}^2 \right)$

$$\sigma_2^C = \pi R_1^2 \approx \frac{16\pi n^4 Z_a}{Z_b^3} \quad \text{or} \quad 16\pi Z_a \frac{a_n}{v_n^2}$$

Comparison with experimental data

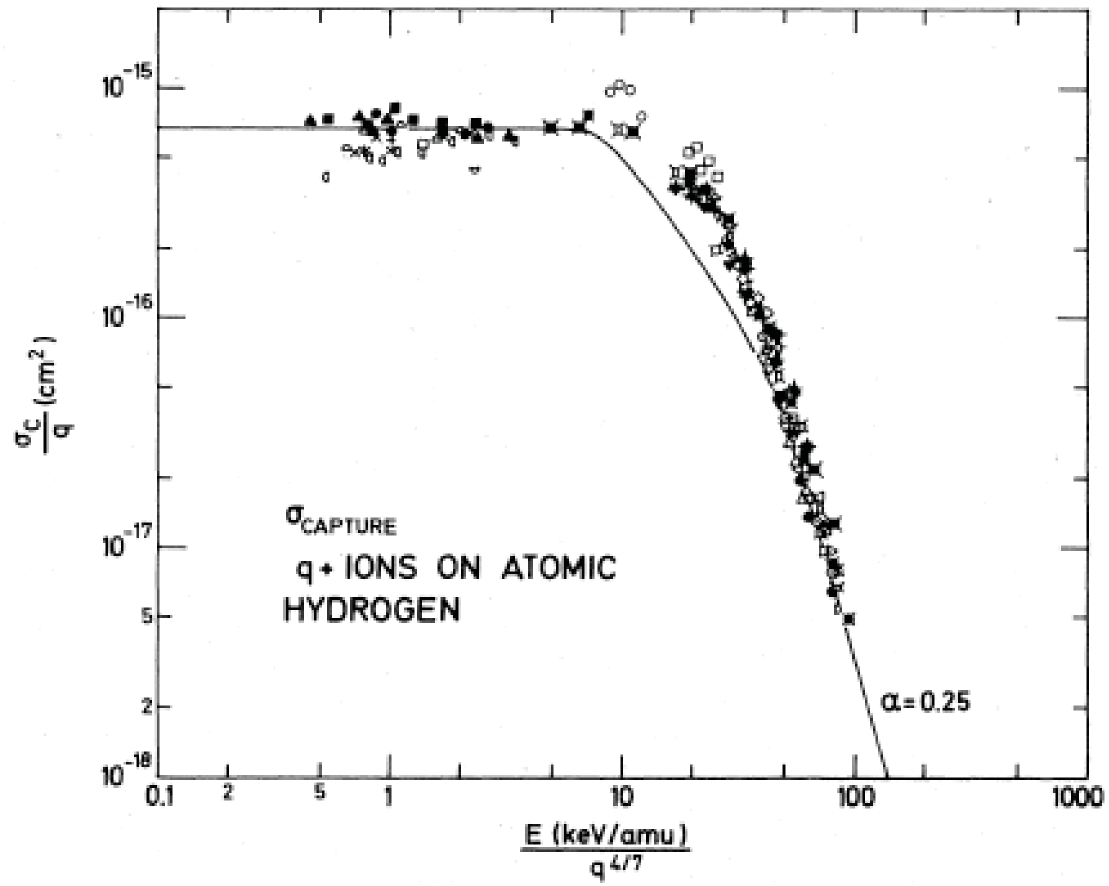


FIG. 3. Comparison between experimental data for the single-capture cross section for ions of charge $q \geq 4$ colliding with atomic H and the theoretical estimate [Eq. (17)]. The data were obtained by Crandall *et al.* (Ref. 7) (●: B^{4+}, ■: C^{4+}, ▲: N^{4+}, ▯: B^{5+}, ▭: C^{5+}, ▭: N^{5+}, ▯: O^{5+}, ×: O^{6+}, + : F^{6+}, *: Ar^{6+}), Phaneuf and Meyer (Ref. 8) (✚: C^{4+}, ✚ : N^{4+}, ✚: N^{5+}, ✚ : O^{4+}, ✚ : O^{5+}), Goffe *et al.* (Ref. 9) (■: B^{4+}, ✚: B^{5+}, ■ : C^{4+}, ⌑: C^{5+}, ✳ : C^{6+}), Kim *et al.* (Ref. 10) (⊖: Si^{5+}, ⊠ : Si^{6+}, ⊕ : Si^{7+}), and Gardner *et al.* (Ref. 11) (○: Fe^{4-7+}, □ : Fe^{6-10+}, ◇ : Fe^{6-10+}, ▽: Fe^{7-11+}, △: Fe^{8-12+}, ◁: Fe^{9-13+}, ▷: Fe^{9-12+}).

from Knudsen, Haugen, and Hvelplund, Phys. Rev. A **23**, 597 (1981))

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Resonant capture (C) vs. elastic scattering (E)

E : $H_A^+ + H_B(1s) \longrightarrow H_A^+ + H_B(1s)$

C: $H_A^+ + H_B(1s) \longrightarrow H_A(1s) + H_B^+$

at low velocities in a semiclassical treatment (**R** ≡ **R**(t) = **b** + **v** t)

so that

$$i\frac{\partial\psi(\vec{r},t)}{\partial t} = H_e\psi(\vec{r},t)$$

with

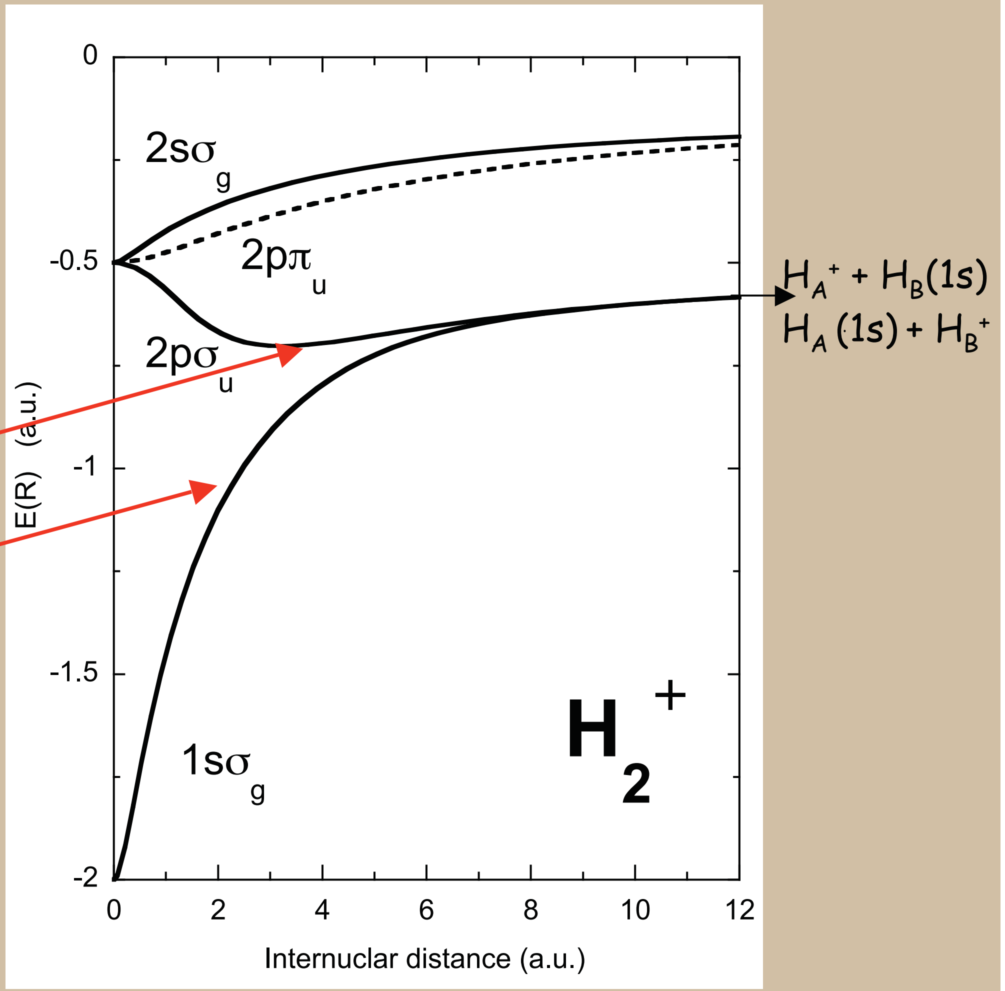
$$H_e = -\frac{1}{2}\Delta_r - \frac{1}{r_a} - \frac{1}{r_b} \quad \left(+\frac{1}{R}\right)$$

$$\phi_u \equiv \phi_{2p\sigma_u}$$

$$\phi_g \equiv \phi_{1s\sigma_g}$$

$$H_e\phi_{g/u}(\vec{r},R) = E_{g/u}(R)\,\phi_{g/u}(\vec{r},R)$$

$\phi_{g/u}$ are orthonormalized



$$\psi(\vec{r},t) = a_g(t)\phi_g(\vec{r},R)\, e^{-i\varepsilon_{1s}t} + a_u(t)\phi_u(\vec{r},R)\, e^{-i\varepsilon_{1s}t}$$

with

$$\phi_g(\vec{r},R) \approx \frac{1}{\sqrt{2}}(\varphi_{1s}(r_b) + \varphi_{1s}(r_a))$$

$$\phi_u(\vec{r},R) \approx \frac{1}{\sqrt{2}}(\varphi_{1s}(r_b) - \varphi_{1s}(r_a))$$

when $R \longrightarrow \infty$

so that

$$\psi(\vec{r},t) = \underbrace{\frac{1}{\sqrt{2}}(a_g(t) + a_u(t))}_{a_{1s}^E(t)}\, \varphi_{1s}(r_b)\, e^{-i\varepsilon_{1s}t} + \underbrace{\frac{1}{\sqrt{2}}(a_g(t) - a_u(t))}_{a_{1s}^C(t)}\, \varphi_{1s}(r_a)\, e^{-i\varepsilon_{1s}t}$$

when $R \longrightarrow \infty$

ESdt =>

$$i\frac{d}{dt}a_{g/u}(t) = a_{g/u}(t)\,(E_{g/u}(R) - \varepsilon_{1s})$$

with initial conditions $a_g(-\infty) = a_u(-\infty) = \dfrac{1}{\sqrt{2}}$

$$a_{g/u}(t) = \frac{1}{\sqrt{2}} \exp\left\{ -i \int_{-\infty}^{t} \left[E_{g/u}(R') - \varepsilon_{1s} \right] dt' \right\} \equiv a_{g/u}(t,b) \quad \text{since} \quad R' = \sqrt{b^2 + v^2 t'^2}$$

=>

$$P^C(b) = |a_{1s}{}^C(+\infty)|^2 = \sin^2\left\{ \frac{1}{2} \int_{-\infty}^{+\infty} \left[E_g(R) - E_u(R) \right] dt \right\}$$

oscillates with unit amplitude versus
* b at fixed v or
* v (E) at fixed b(θ)

(but $\sigma^C(E) = 2\pi \int_0^\infty b\, P^C(b)\, db$ does not)

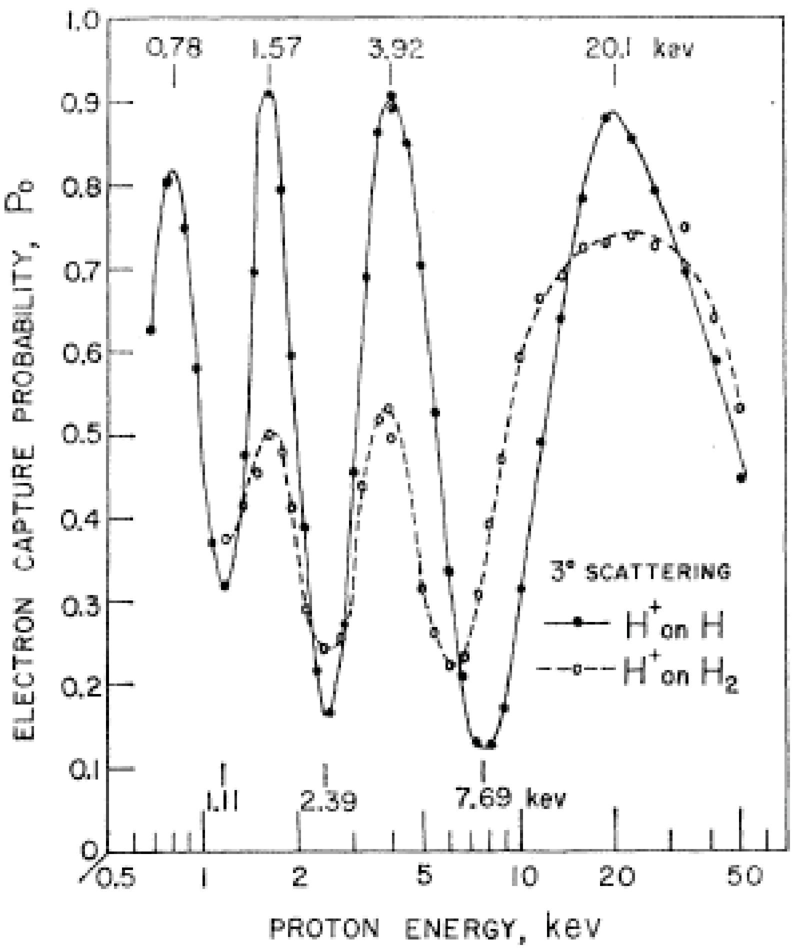


FIG. 3. The electron capture probability P_0 is plotted vs incident proton energy in kev for the combinations H^+ on H and H^+ on H_2. These data are for violent collisions in which the scattered particles emerge at 3°; laboratory coordinates.

from Lockwood and Everhart, Phys. Rev. **125**, 567 (1962)

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To solve generally the tdSE

$$i\frac{\partial\psi(\vec{r},t)}{\partial t}=H_e\psi(\vec{r},t) \qquad \text{with} \qquad \bar{H}_e=-\frac{1}{2}\Delta_r-\frac{1}{r_a}-\frac{1}{r_b}\quad(+\frac{1}{R})$$

and

$$\psi(\vec{r},t)=\sum a_i(t)\,\phi_i(\vec{r})\exp(-i\int_{-\infty}^{t}dt'\,E_i(R(t')))$$

one gets to coupled differential equations for the probability amplitudes $a_j(t)$ involving only **dynamical couplings** :

$$\left\langle \phi_j \middle| \frac{d}{dt} \middle| \phi_i \right\rangle$$

which can be written as

$$v_R\left\langle \phi_j \middle| \frac{\partial}{\partial R} \middle| \phi_i \right\rangle + i\dot{\theta}\left\langle \phi_j \middle| L_y \middle| \phi_i \right\rangle$$

radial couplings inducing transitions between states with same symmetry (Σ <-> Σ , Π<-> Π, …)

rotational couplings inducing transitions between states with different symmetry (Σ <-> Π, …)

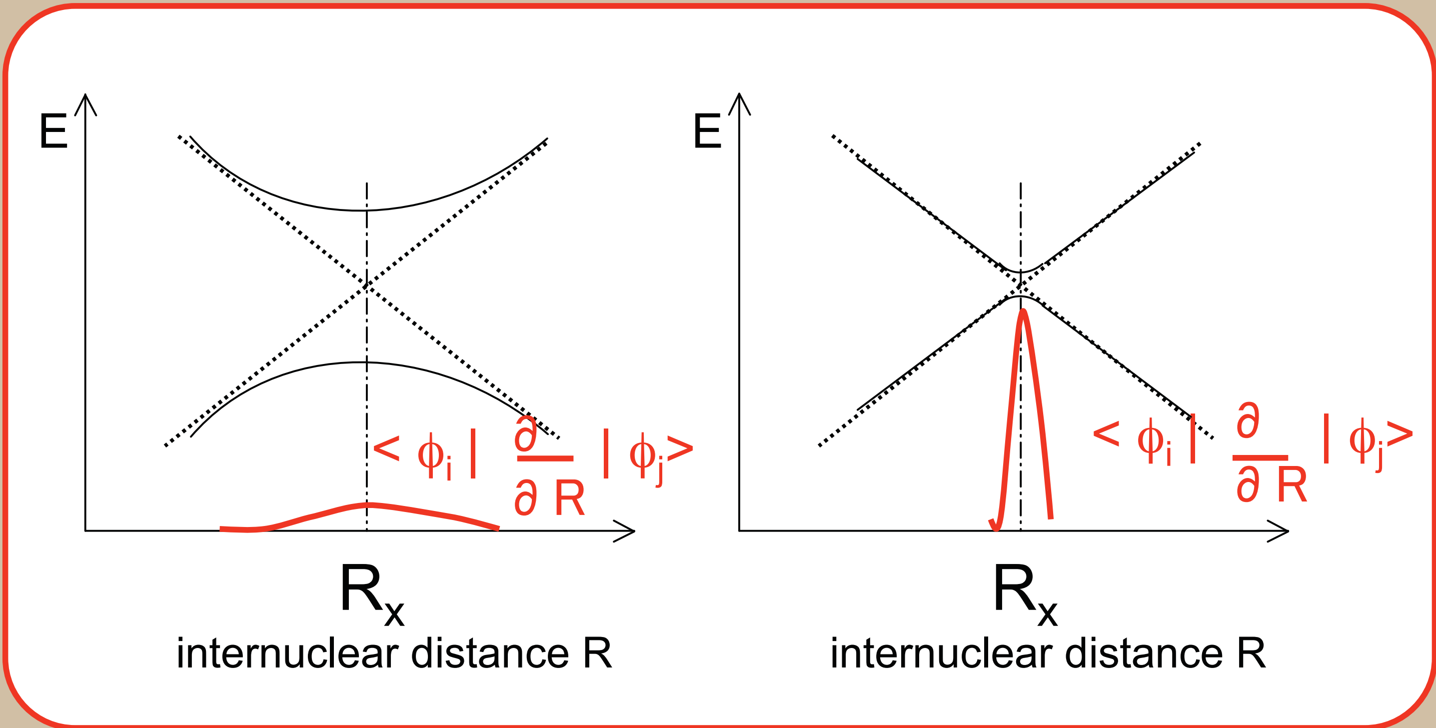
the basis set molecular functions can be chosen to

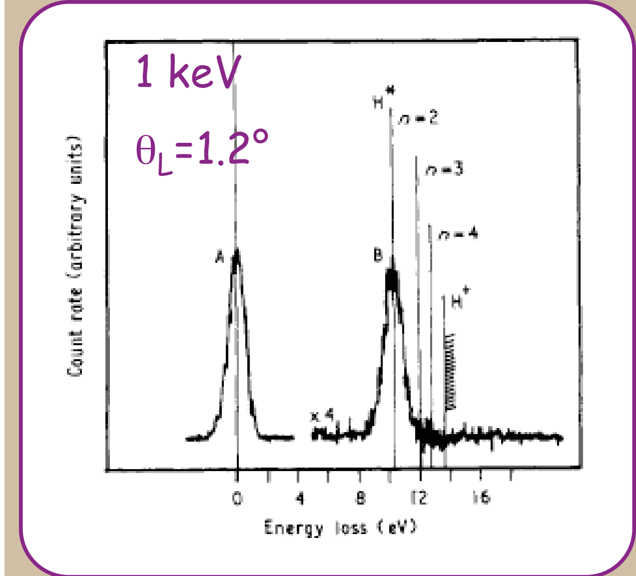
* such that $H_e \, \phi_j(\mathbf{r},\mathbf{R}) = E_j\,(\mathbf{R})\ \phi_j(\mathbf{r},\mathbf{R})$ **adiabatic representation**

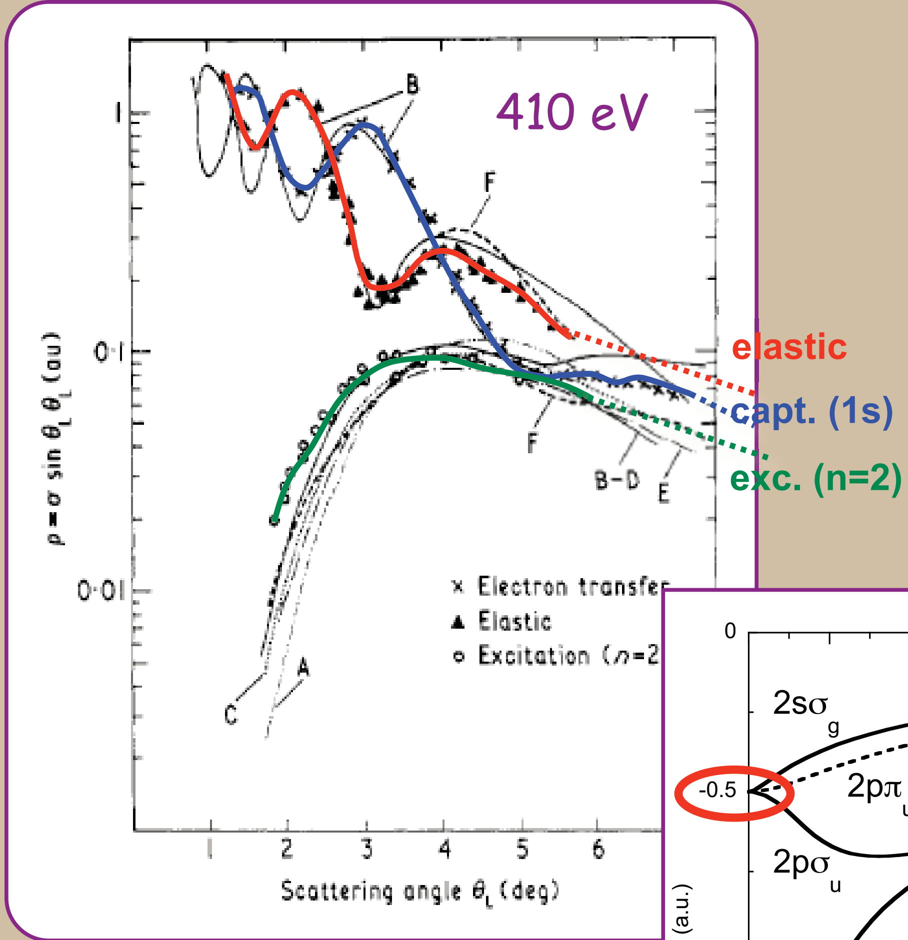
* or to minimize some of the dynamical couplings … **diabatic representations**

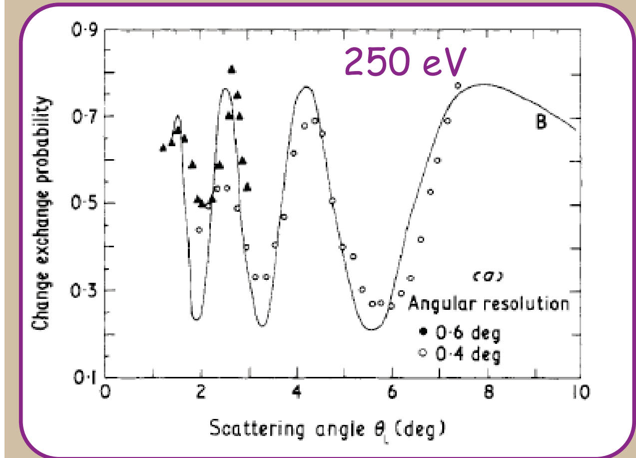
Best choice ?

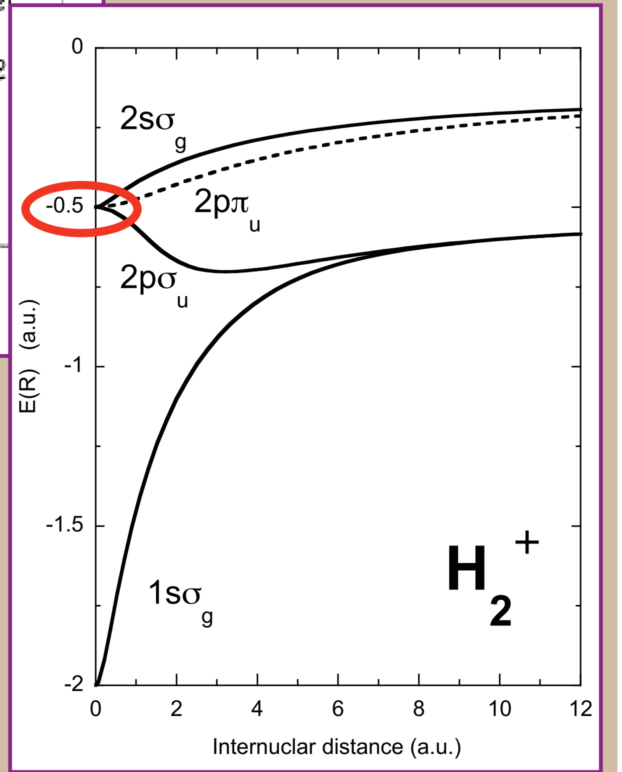
adiabatic representation vs. **diabatic representation**











$H^+ + H(1s)$

from Houver et al, J. Phys. B **7**, 1358 (1974).

N^{3+} + H(1s)

Figure 4. Potential energy curves of the NH^{3+} molecular ion. The outer full curves refer to the adiabatic energies of the $\sigma 1s_H$ and the $\sigma 3s_N$ states (avoided crossing at 9 a_0). These states are labelled, respectively, 1 and 2. The inner full curves (crossings at 9 a_0 and 4.2 a_0) refer to the diagonal elements of the diabatic potential matrix **V** with the origin of electronic coordinates on the N nucleus. The broken curves (crossing at 9 a_0) refer to the diagonal elements of **V** with the origin on the H nucleus.

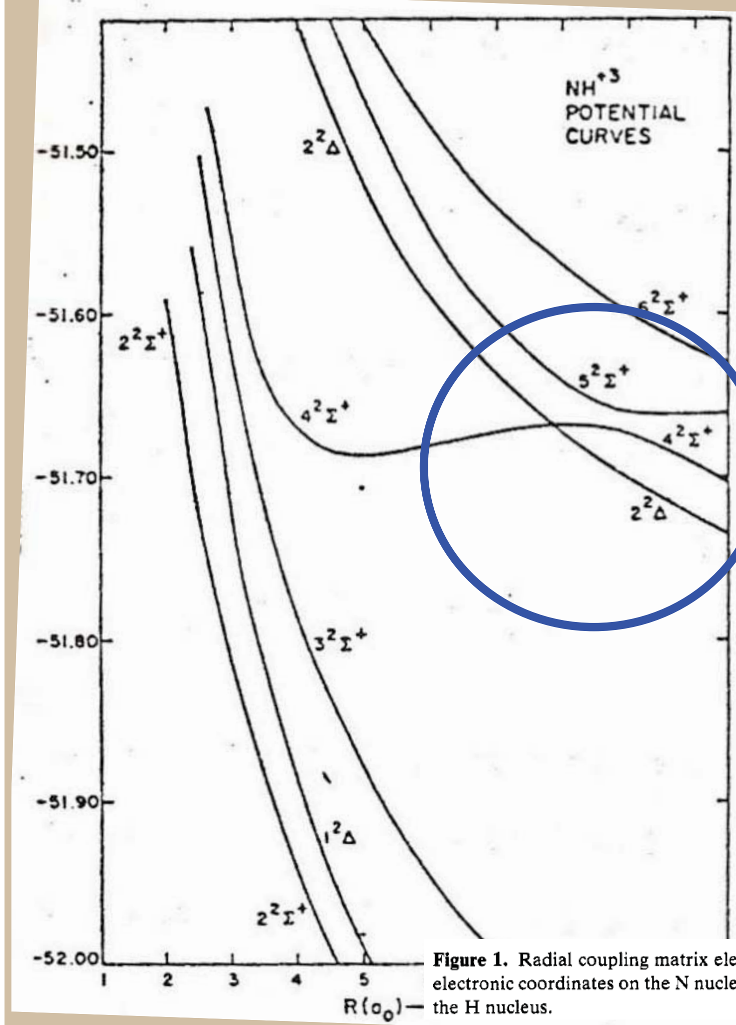


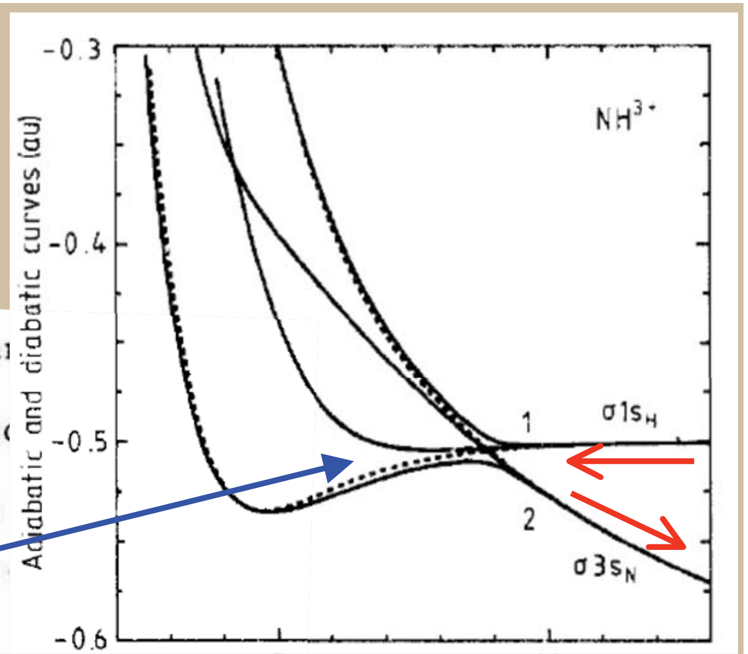
Fig. 9.8 - Potential e

of NH^{+3} as a function o

distances (Butler 53)

H(1s)

N^{2+}(3s)



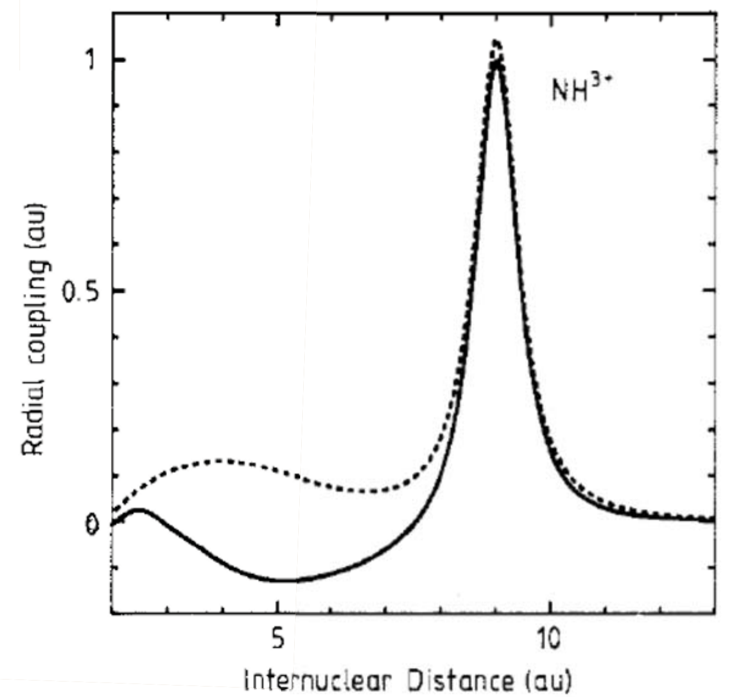


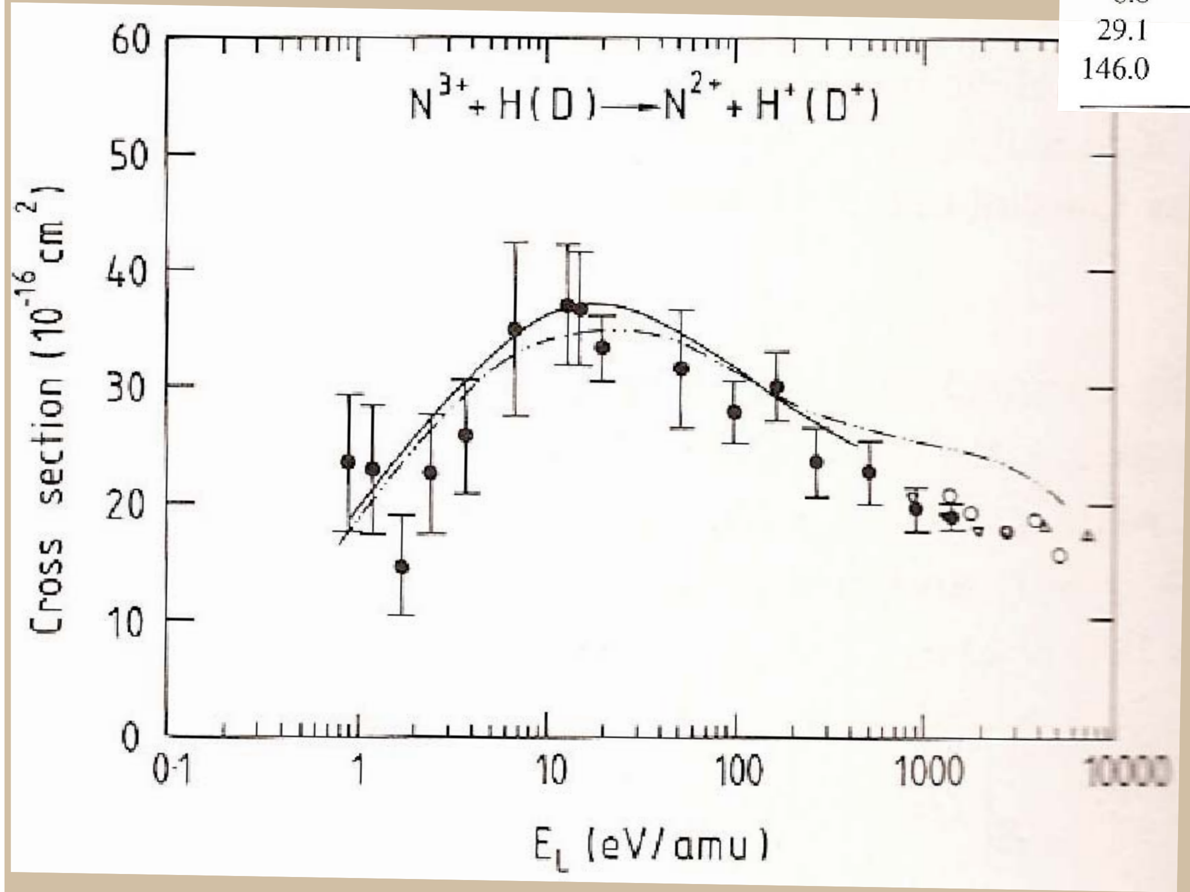
Figure 1. Radial coupling matrix element P_{12} for the system NH^{3+}. Full curve: origin of electronic coordinates on the N nucleus. Broken curve: origin of electronic coordinates on the H nucleus.

M Gargaud, J Hanssen, R McCarroll and P Valiron J. Phys. B: At. Mol. Phys. **14** (1981) 2259–2276.

N^{3+} + H(1s)

Table 4.2. Cross section for the reaction $N^{3+} + H(1s) \rightarrow N^{2+}(3s) + H^{+}$ (from Gargaud *et al.* 1981). A is origin at the H^{+} ion; B is origin at the N^{3+} ion; M is origin at the mid-point of the interionic line AB.

E_L(eV/a.m.u.)	Cross sections (10^{-16} cm^2)		
	A	M	B
8.8×10^{-3}	19.74	19.75	19.70
8.8×10^{-2}	7.75	7.73	7.70
8.8×10^{-1}	18.39	18.34	18.39
8.8	35.96	35.84	35.73
29.1	36.01	36.01	36.18
146.0	26.04	27.16	28.98



Heavy particle collision processes

I - Introduction

II - Three models for electron transfer

a) The Thomas mechanism

b) The Bohr-Lindhardt model

c) Resonant capture at low energy in homonuclear one electron collision systems

III - The quasi-molecular formalism

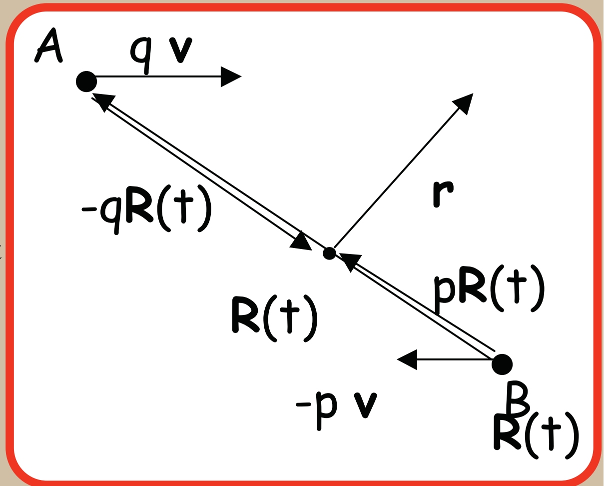
IV- The travelling asymptotic state basis set expansion : the intermediate energy domain

V - Capture in ion-molecule collisions

To solve the tdSE one can choose purely diabatic (asymptotic) states

$$i\frac{\partial\psi(\vec{r},t)}{\partial t} = H_e\psi(\vec{r},t) \qquad \text{with} \qquad H_e = -\frac{1}{2}\Delta_r + V^b(\vec{r}+p\vec{R}(t)) + V^a(\vec{r}-q\vec{R}(t))$$

and $\psi(\vec{r},t) = \sum^{N} b_n(t)\,\Phi_n^b(\vec{r},t) + \sum^{M} a_m(t)\,\Phi_m^a(\vec{r},t)$



$$\Phi_n^b(\vec{r},t) = \varphi_n^b(\vec{r}_b)e^{-ip\vec{v}.\vec{r}}e^{-i\varepsilon_n^a t - i\frac{1}{2}p^2v^2t} \qquad \Phi_m^a(\vec{r},t) = \varphi_m^a(\vec{r}_a)e^{+iq\vec{v}.\vec{r}}e^{-i\varepsilon_m^b t - i\frac{1}{2}q^2v^2t}$$

$$h^x\varphi_i^x(\vec{r}_x) = (-\frac{1}{2}\Delta_{r_x} + V^b(\vec{r}_x))\varphi_i^x(\vec{r}_x) = \varepsilon_i^x\varphi_i^x(\vec{r}_x)$$

$$b_m(-\infty) = \delta_{m,i} \qquad a_n(-\infty) = 0 \qquad \vec{r}_b = \vec{r} + p\vec{b} + p\vec{v}t \qquad \vec{r}_b = \vec{r} - q\vec{b} - q\vec{v}t$$

With such travelling states expansions and making use of the relations

$$\left.\frac{\partial}{\partial t}\right|_{\vec{r}} = \left.\frac{\partial}{\partial t}\right|_{\vec{r}_b} + p\vec{v}.\vec{\nabla}_{r_b} \qquad \left.\frac{\partial}{\partial t}\right|_{\vec{r}} = \left.\frac{\partial}{\partial t}\right|_{\vec{r}_a} - q\vec{v}.\vec{\nabla}_{r_a}$$

one gets rid of asymptotic spurious couplings and non galilean invariance

e.g. $\left\langle \varphi_n^b \middle| \vec{\nabla}_{r_b} \middle| \varphi_{n'}^b \right\rangle$

=> Coupled differential equations for the probability amplitudes

$$i\ \underline{\underline{S}}\ \underline{\dot{c}} = \underline{\underline{V}}\ \underline{c}$$

$$\underline{\dot{c}} = \frac{d}{dt}\underline{c} \qquad \underline{c} = \begin{pmatrix} b_1 \\ \vdots \\ b_N \\ a_1 \\ \vdots \\ a_M \end{pmatrix}$$

with, e.g.

$$S_{kl}^{ba} = \left\langle \varphi_k^b \middle| e^{i\vec{v}.\vec{r}} \middle| \varphi_l^a \right\rangle\ e^{-i(\varepsilon_l^a - \varepsilon_m^b + (q-p)v^2)t} = \left\langle \varphi_k^b \middle| e^{i\vec{v}.\vec{r}_m} \middle| \varphi_l^a \right\rangle e^{-i(\varepsilon_l^a - \varepsilon_m^b)t}$$

$$V_{kl}^{ba} = \left\langle \varphi_k^b \middle| V^b e^{i\vec{v}.\vec{r}} \middle| \varphi_l^a \right\rangle\ e^{-i(\varepsilon_l^a - \varepsilon_m^b + (q-p)v^2)t} = \left\langle \varphi_k^b \middle| V^b e^{i\vec{v}.\vec{r}_m} \middle| \varphi_l^a \right\rangle e^{-i(\varepsilon_l^a - \varepsilon_m^b)t}$$

...

$$\vec{r}_m = \frac{1}{2}(\vec{r}_a + \vec{r}_b)$$

and galilean invariance is fulfilled … but a lot of computations to be done …

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Good textbooks about collisions

Quantum Collision theory, C.J. Joachain (North-Holland) 1983.

Introduction to the theory of ion-atom collisions, M.R.C. McDowell and J.P. Coleman (North-Holland) 1970.

Charge exchange and the Theory of Ion-Atom Collisions, B.H. Bransden and M.R.C. McDowell (Oxford Science Pub.) 1992.

Molecular Collision Theory, M. Child (Academic Press, NY) 1974.

Ion-molecule collisions

Electronic capture

$$\mathrm{He}^{2+} + \mathrm{H}_2^+(1s\sigma_g) \rightarrow \mathrm{He}^+ + \mathrm{H}^+ + \mathrm{H}^+$$

(1 electron system)

$$\mathrm{Ar}^{2+} + \mathrm{H}_2^+(1s\sigma_g) \rightarrow \mathrm{Ar}^+ + \mathrm{H}^+ + \mathrm{H}^+$$

(resonant system)

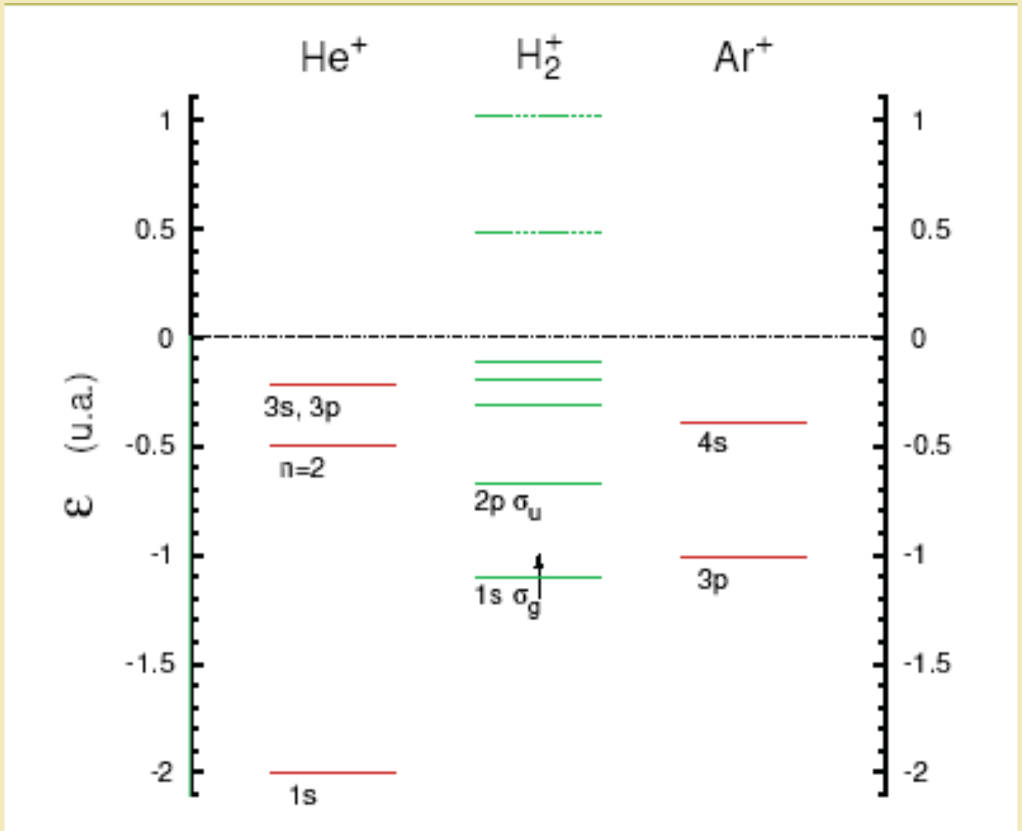
Recent experiments

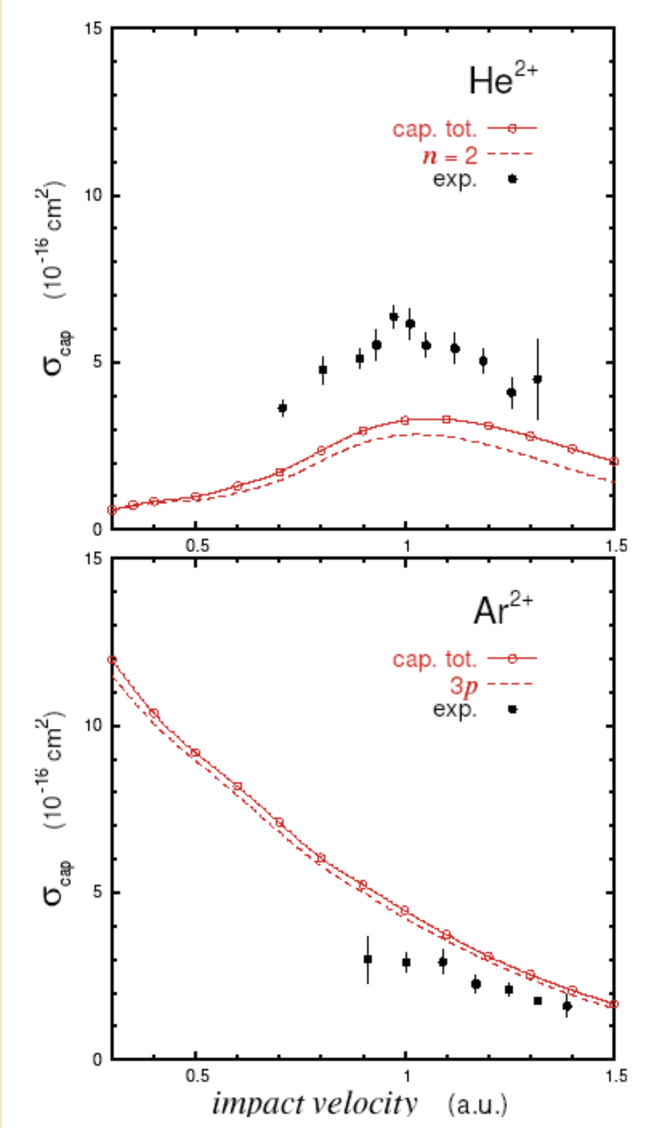
- ✓ Bräuning *et al*, J. Phys. B (2001)
  Total capture
- ✓ Reiser *et al*, HCI-2002, Caen
  Orientation effets (COLTRIMS)

Capture cross sections

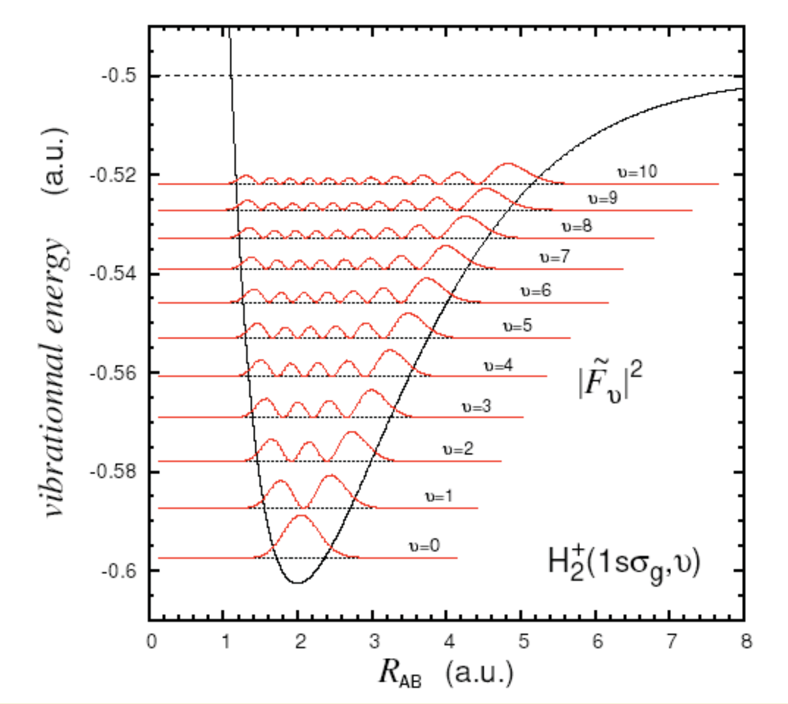
Franck-Condon approximation

$$\sigma^{v}_{cap}(\nu = 0) = \sigma^{v}_{cap}(R^{eq}_{\mathrm{AB}})$$



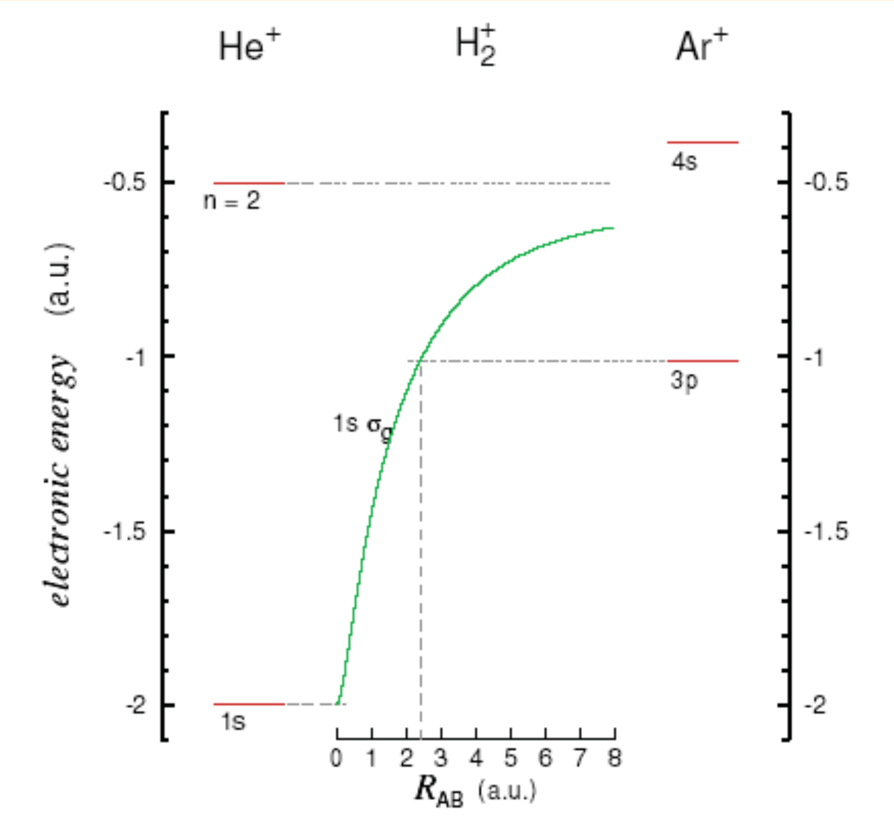


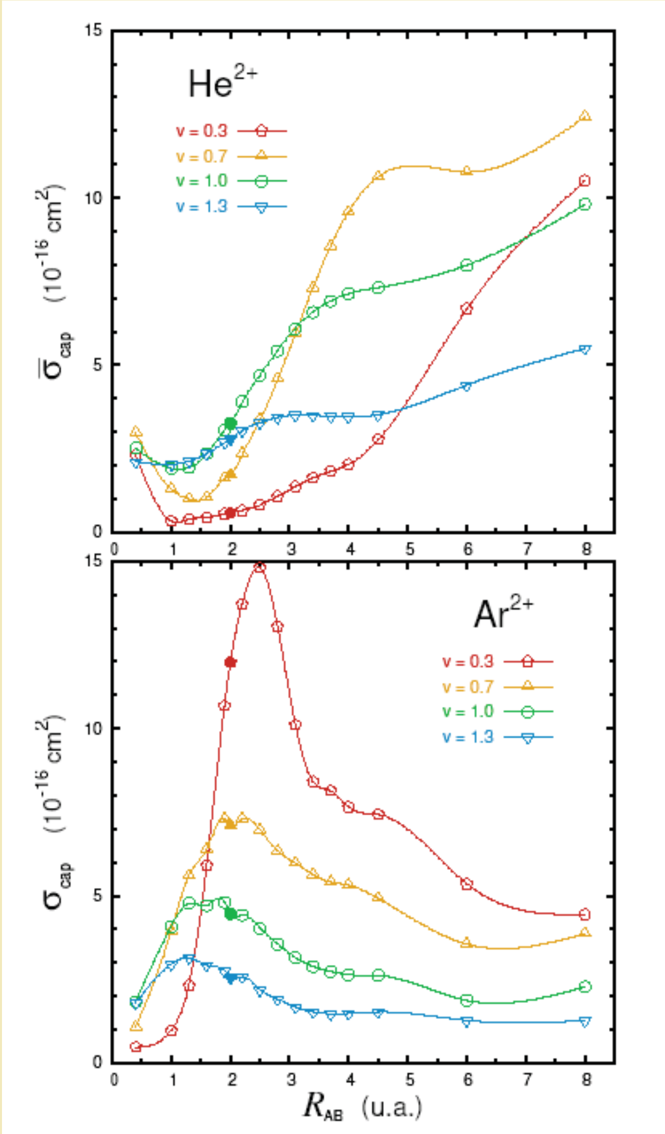
Effect of vibrational dof



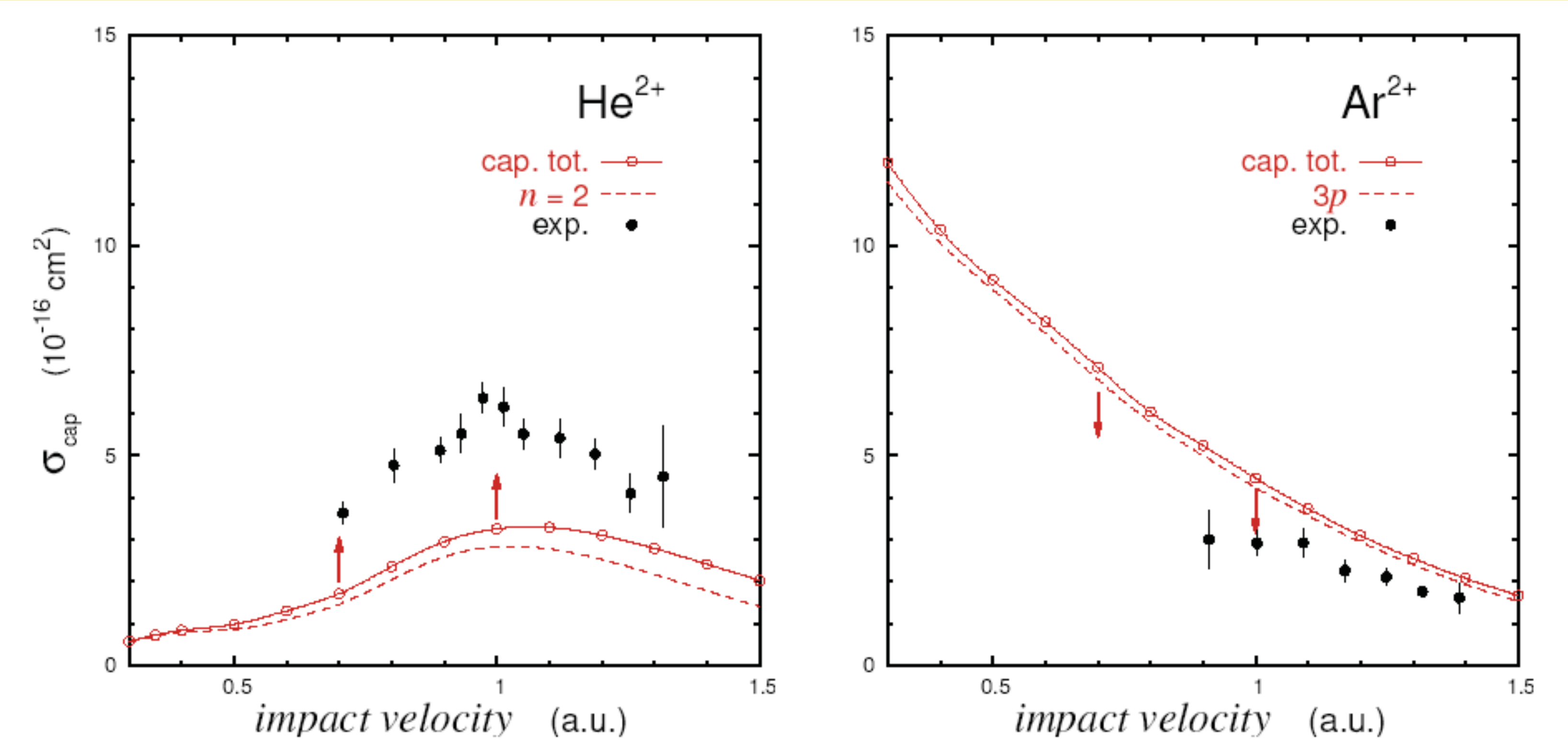
→ large values of R_{AB}

Differential cross sections vs. R_{AB}

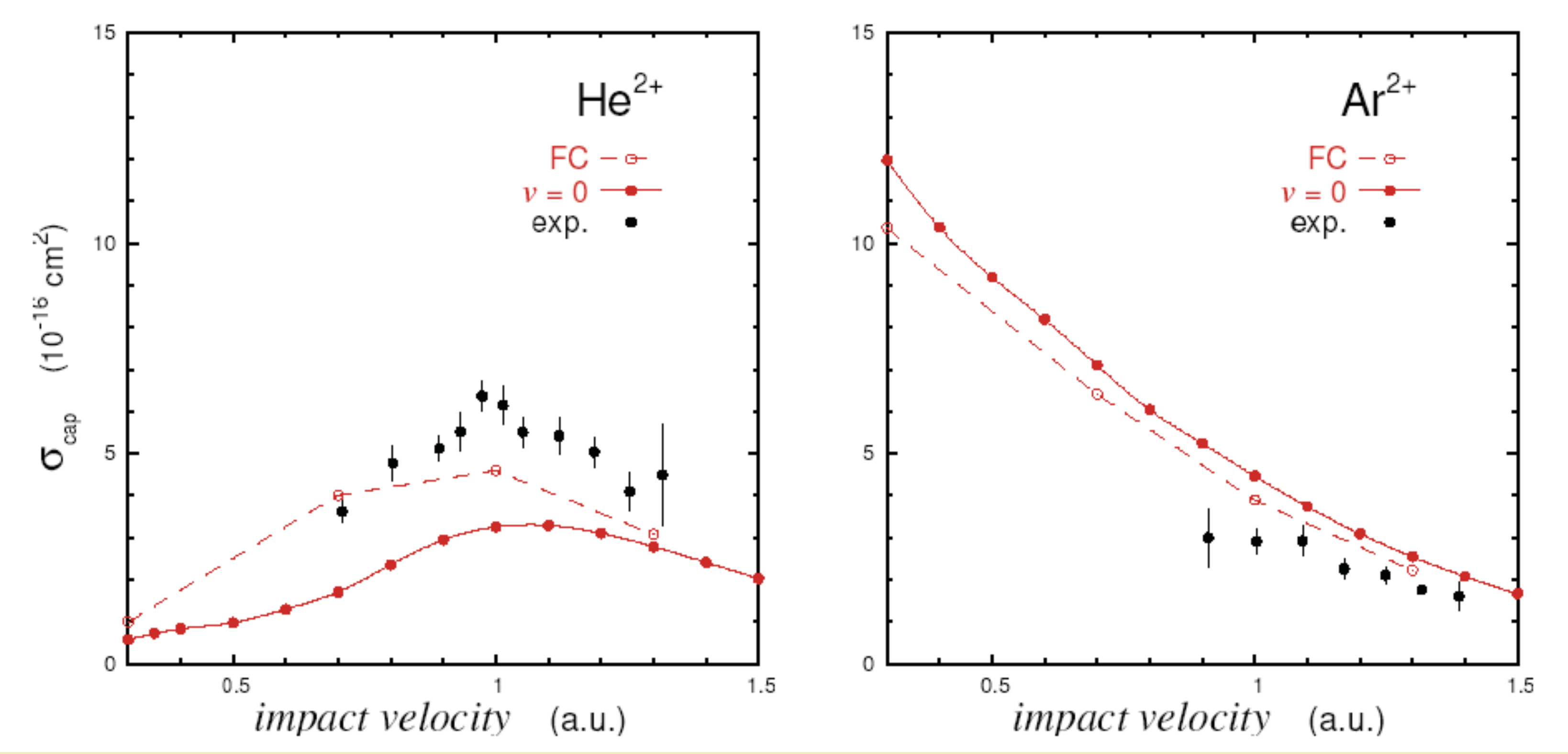




Capture cross sections



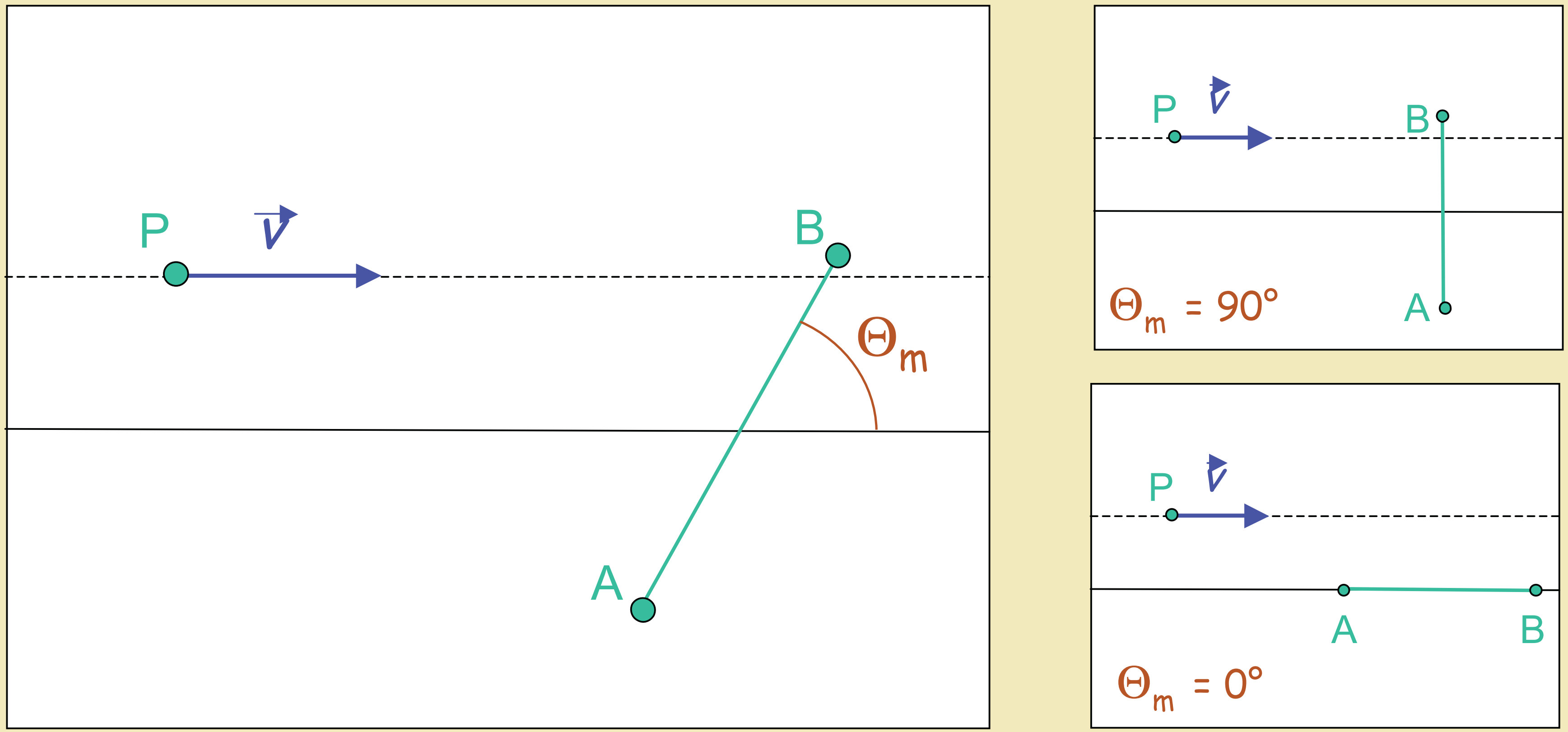
Unknown exp. vibr. distribution !



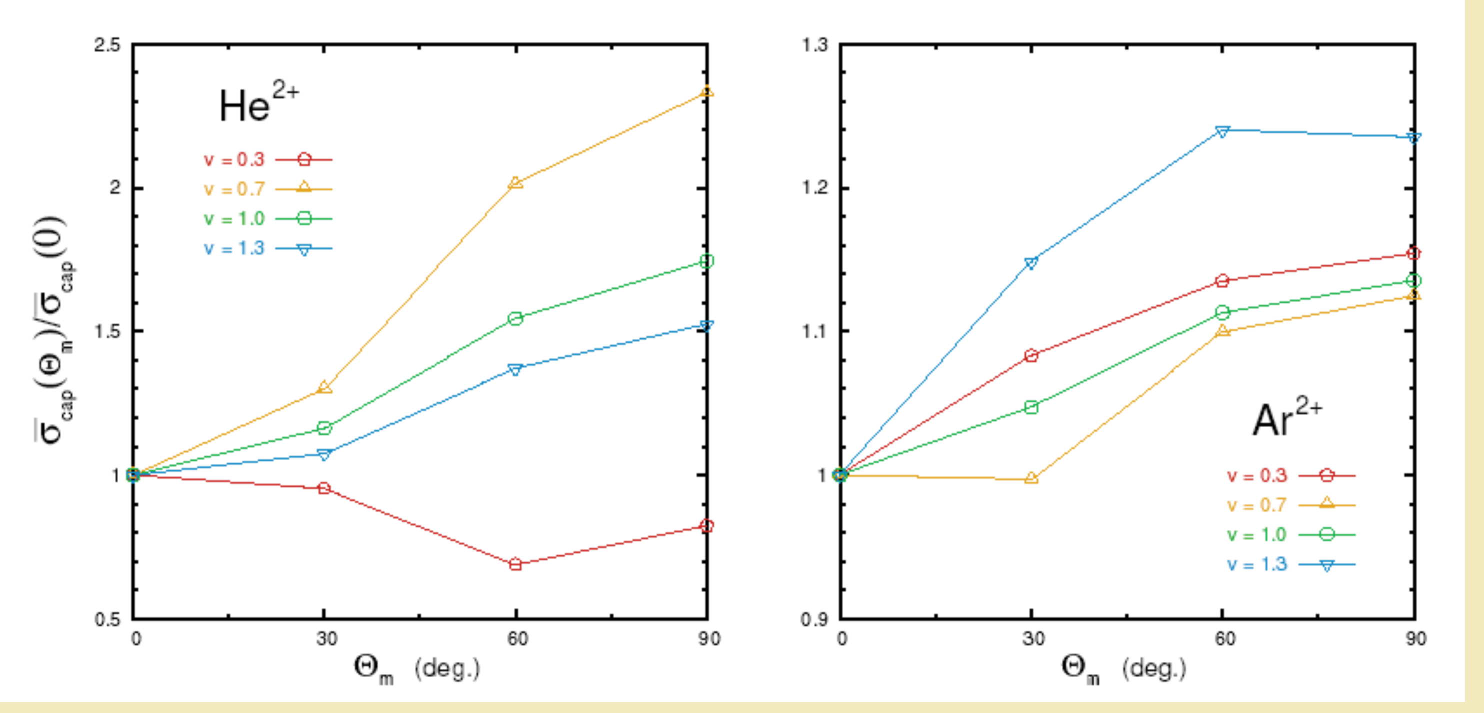
Example : **Franck-Condon** distribution

$$H_2 + h\nu \longrightarrow H_2^+ + e^-$$

Orientation effects



Differential cross sections vs. Θ_m

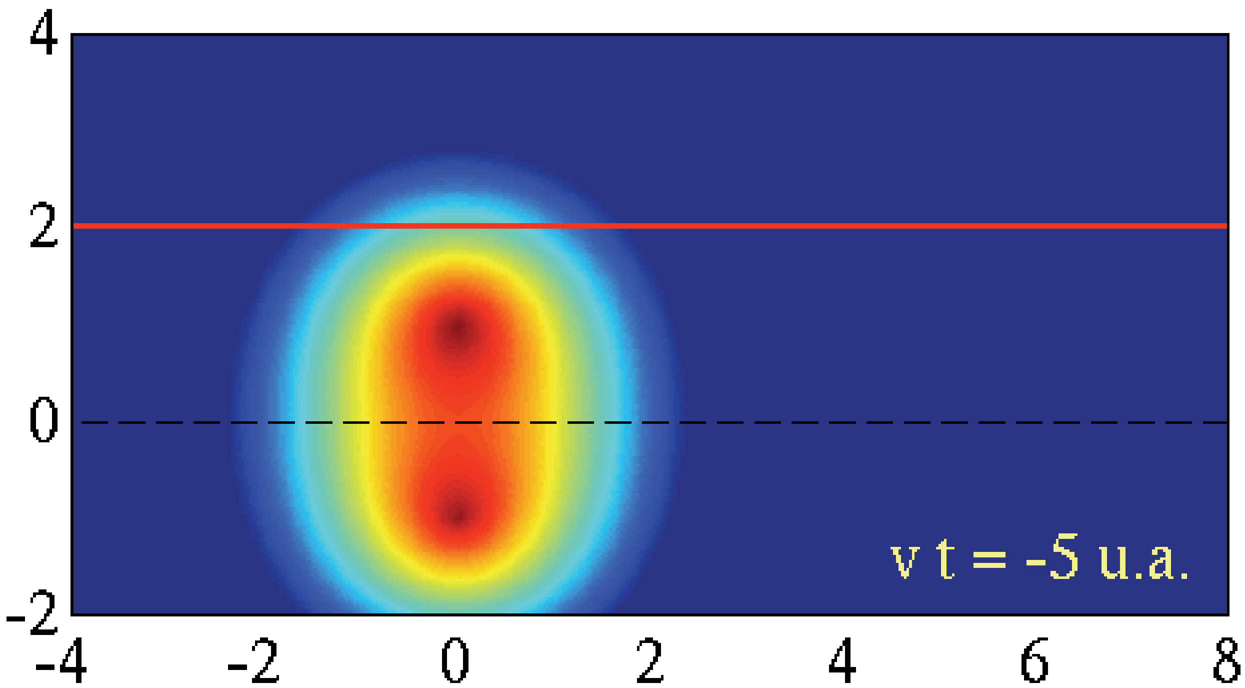


General tendancy : importance of 90° ⟺ **Steric factor**

Inversion for He^{2+} at v = 0.3 a.u. ⟺ **Dynamical effect**

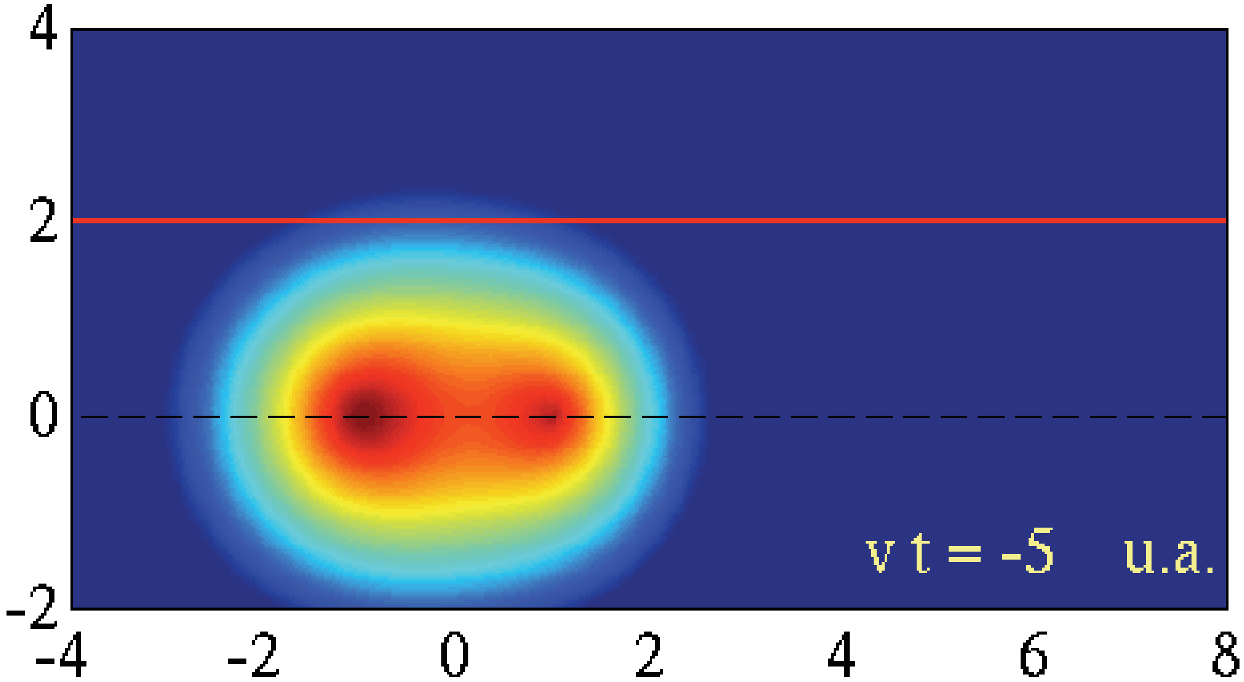
He^{2+} $v = 1.0$ a.u.

$\Theta_m = 90°$



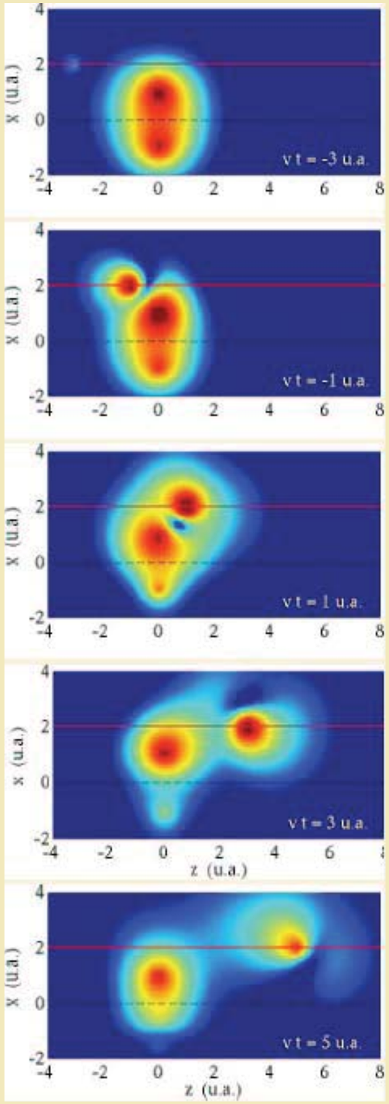
He^{2+} $v = 1.0$ a.u.

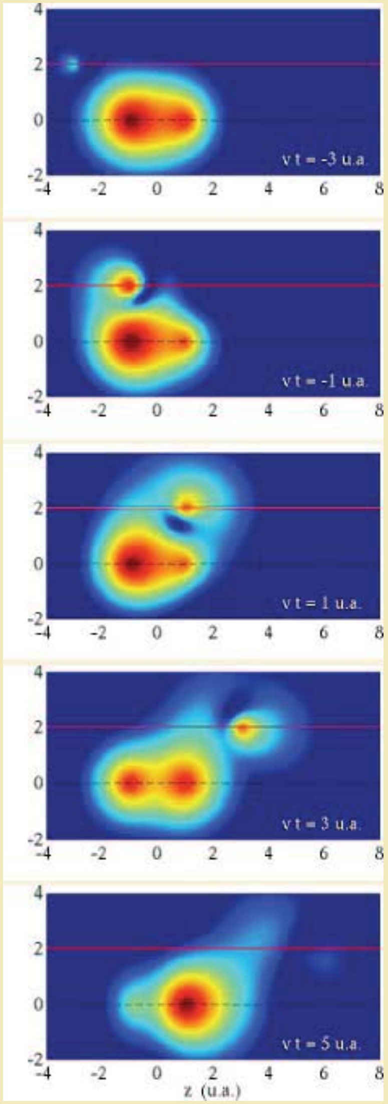
$\Theta_m = 0°$



He^{2+} $v = 1.0$ a.u.

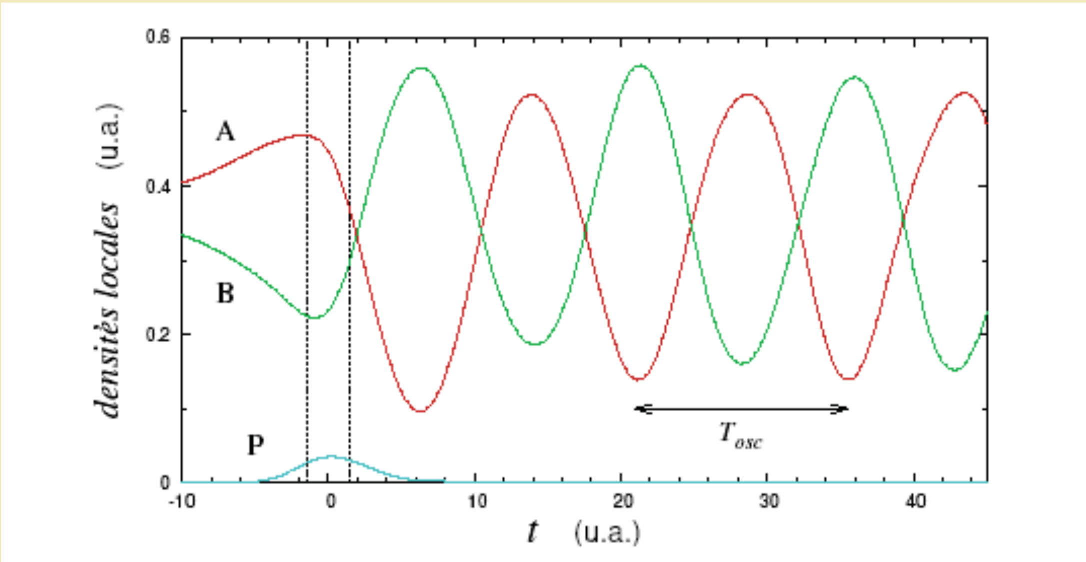
$\Theta_m = 90°$





$\Theta_m = 0°$

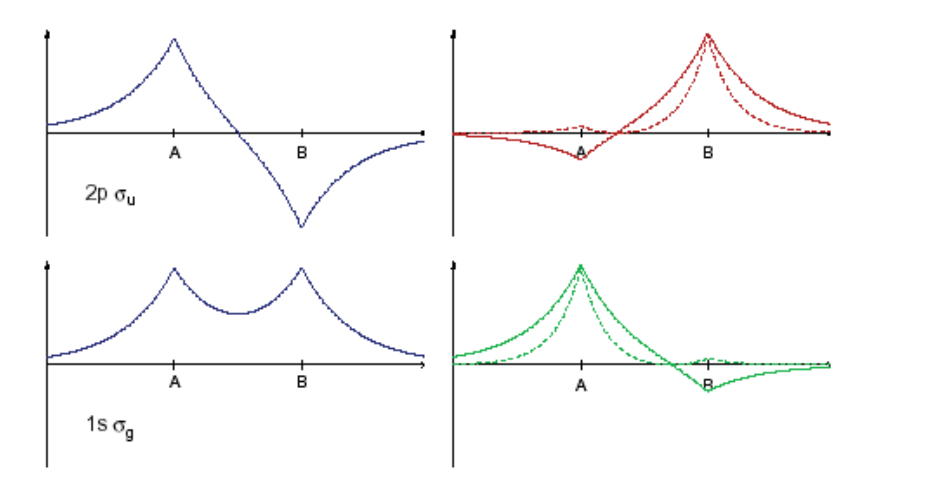
Oscillations



$T_{1/2} = T_{osc} / 2$
≈ 7.25 a.u.

Oscillations

Quantal interferences



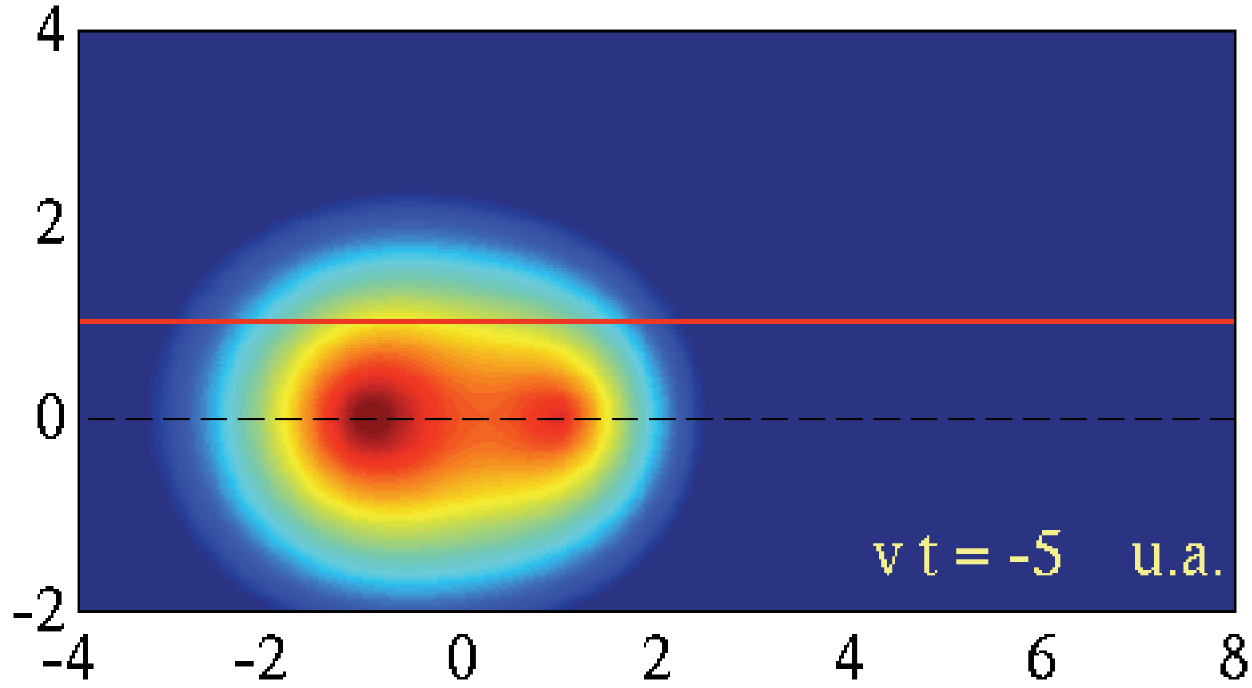
$T_{1/2} = \pi/\Delta E \approx 7.25$ a.u.

➡ Resonance :

$v = R_{AB}/T_{1/2}$
$= 0.28$ a.u.

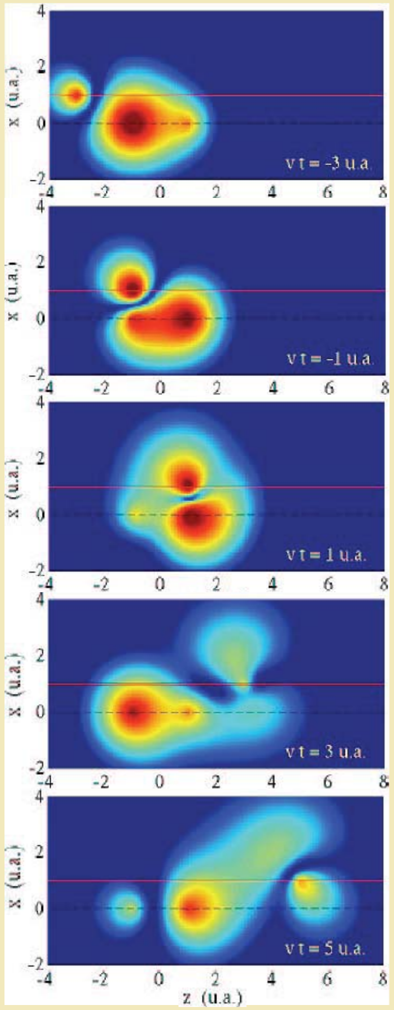
He^{2+} $v = 0.3$ a.u.

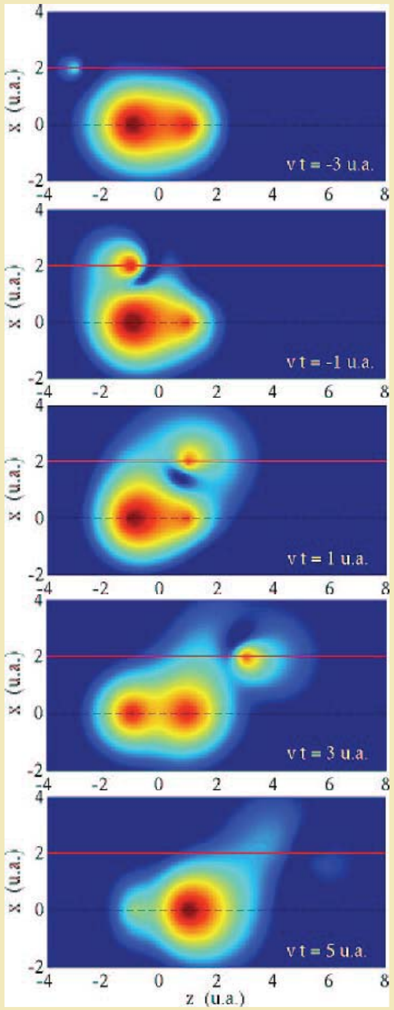
$\Theta_m = 0°$



He^{2+} $\Theta_m = 0°$

v = 0.3 a.u.





v = 1.0 a.u.