Ionization processes of atoms and molecules: a Sturmian approach

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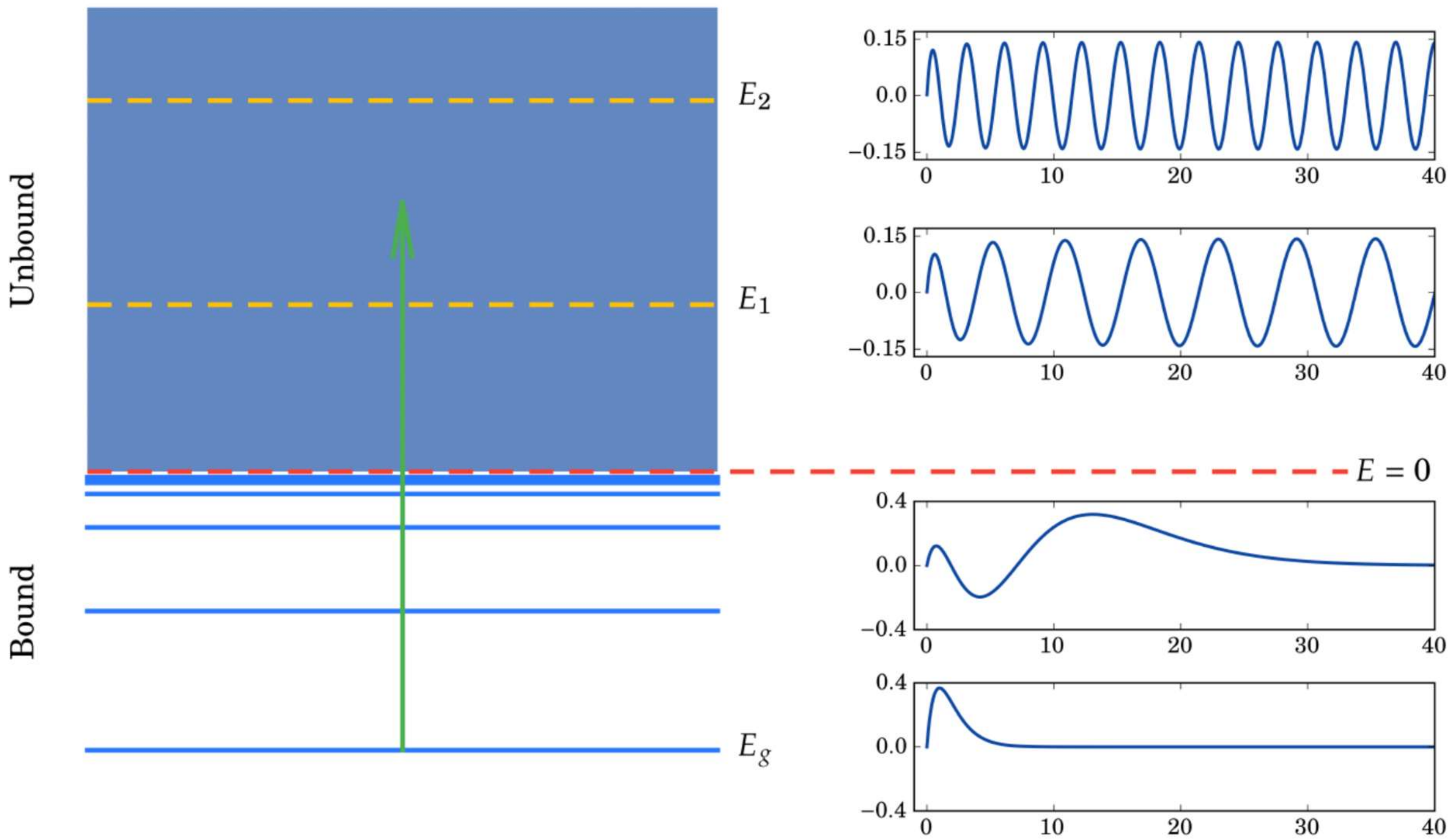
Hydrogen spectrum



"challenging the continuum" … is back !

PLAN

- **Ionization processes of atoms/molecules → N-BODY**

- **Generalized Sturmian Function (GSF) method implemented to study collision processes**

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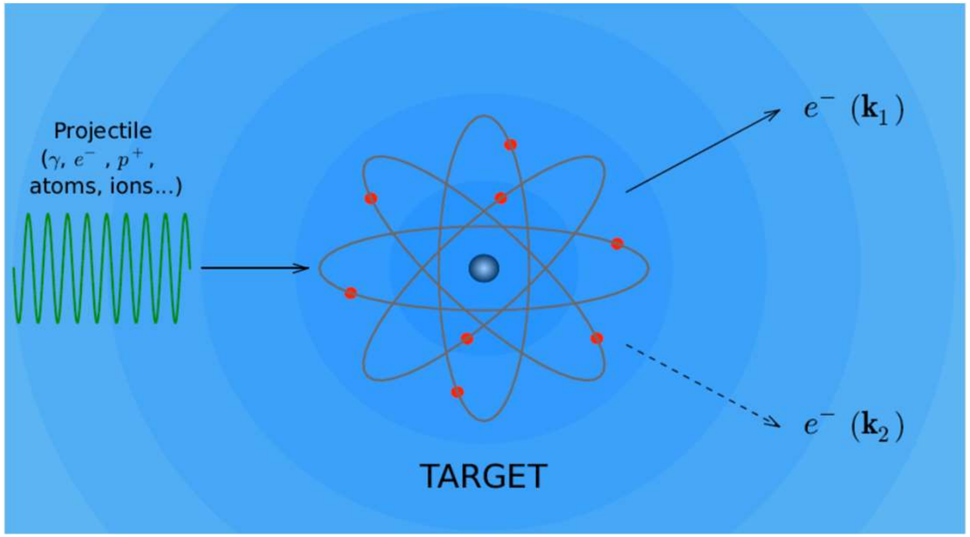
Ionization of atoms and molecules by photon or particle impact



TARGETS

- atoms (H, He, Be, Ne, Ar, Na, Mg, Au, …)
- molecules (H_2O, NH_3, CH_4, DNA basis, …)

Calculation of multidifferential cross sections

THEORY

↕

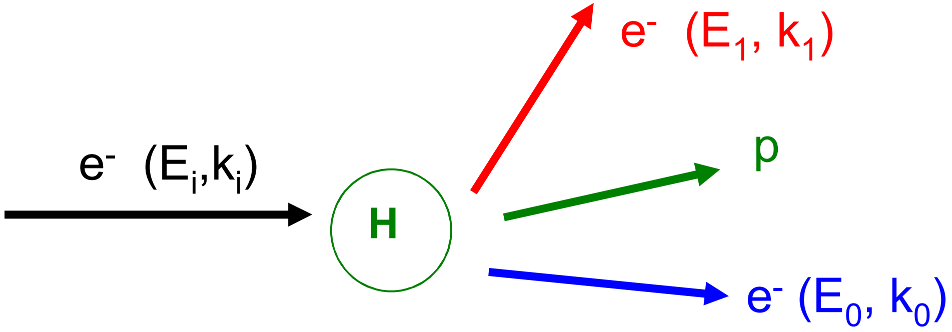
EXPERIENCE

WHY DO WE WANT DIFFERENTIAL CROSS SECTIONS?

- **needed as database** for applications (e.g. plasmas or radiobiology)
- **test theoretical models in more details**
  - the collision dynamics
  - the wave functions
- **information/test on electronic correlation**

SINGLE IONIZATION : (e,2e) on H

$$e^- + H \longrightarrow p^+ + e^- + e^-$$



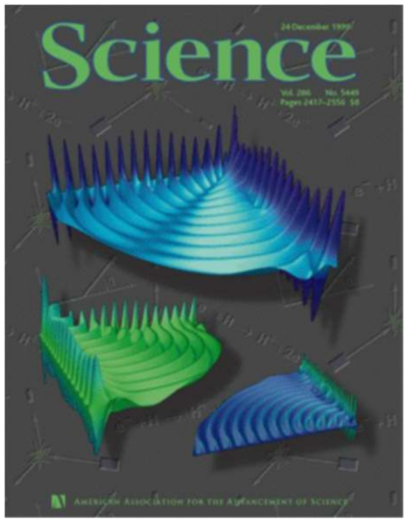
Detection in coincidence:

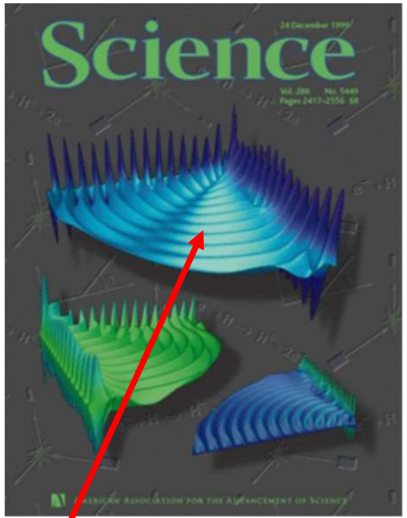
Kinematically complete

TDCS $\dfrac{d^3\sigma}{d\Omega_1 d\Omega_0 dE_1}$

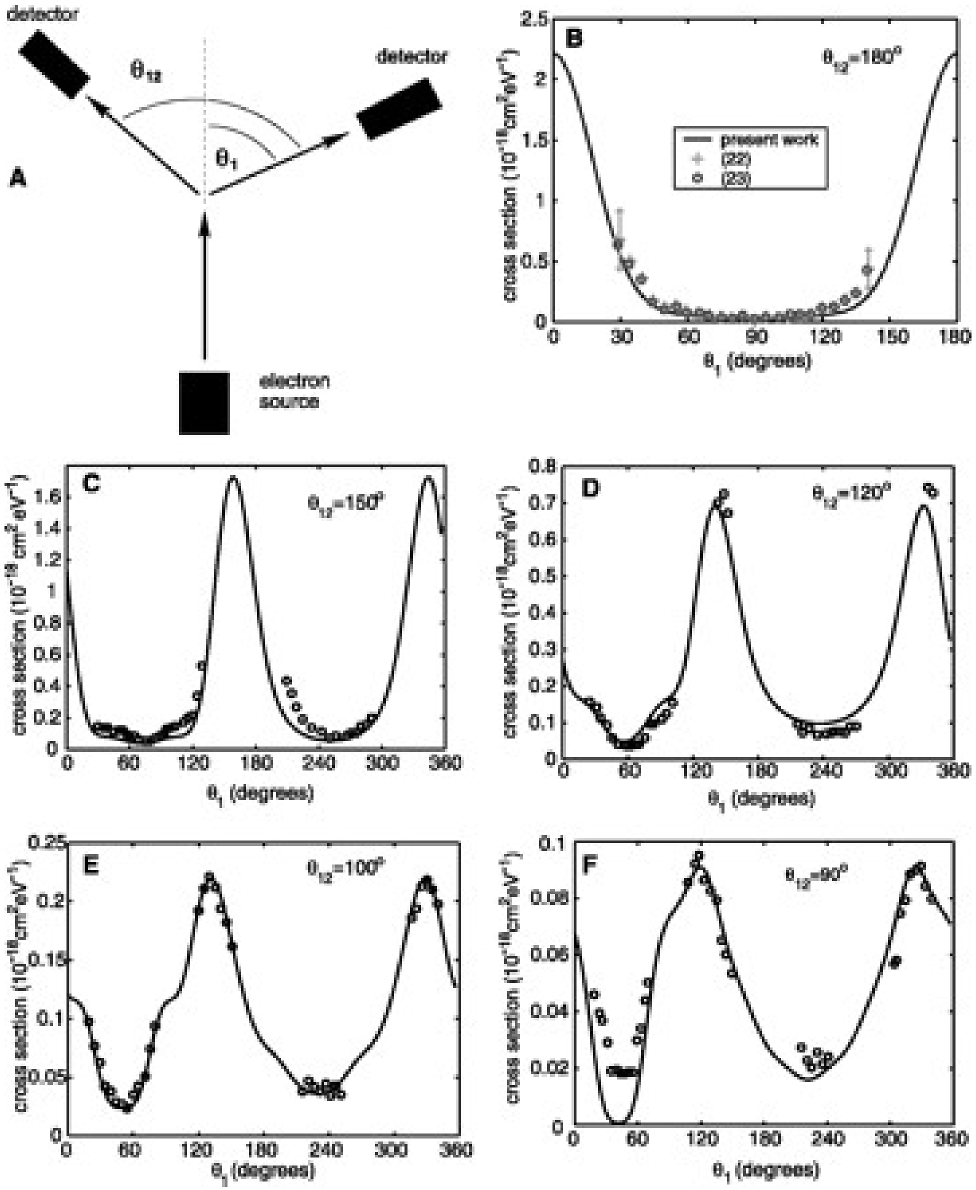
TCS σ

- **Pure 3-body problem in final channel**
- **Solved numerically at the end of century (24 Dec 1999 – Rescigno et al)**
- **Agreement between theories and experiments**

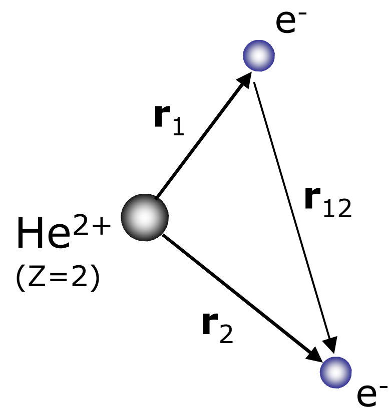




Hyperspherical front
(double continuum)



Helium

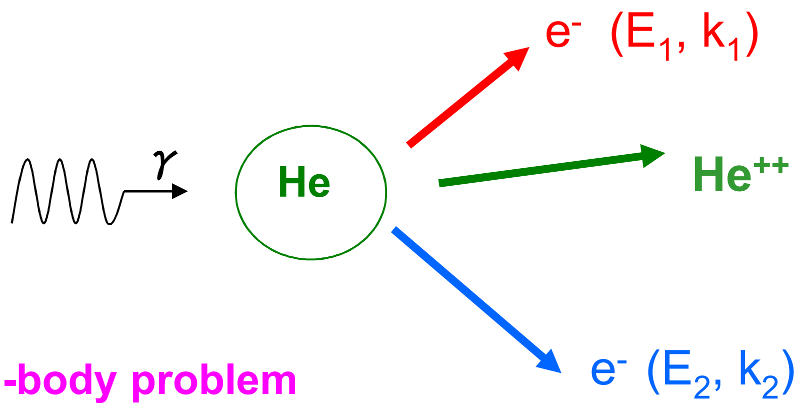


Pure 3-body Coulomb problem

FOCUS: Continuum states NOT bound states

DOUBLE IONIZATION : (γ,2e)

γ + He ⟶ He^{++} + e$^-$ + e$^-$



Detection in coincidence:

Kinematically complete FDCS

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE_2}$$

Pure 3-body problem

(3 interactions)

Double photoionization of He

γ + He → He^{++} + e^- + e^-

ECS (McCurdy et al, PRA, 2004)

GSF (Randazzo et al, EPJD, 2015)

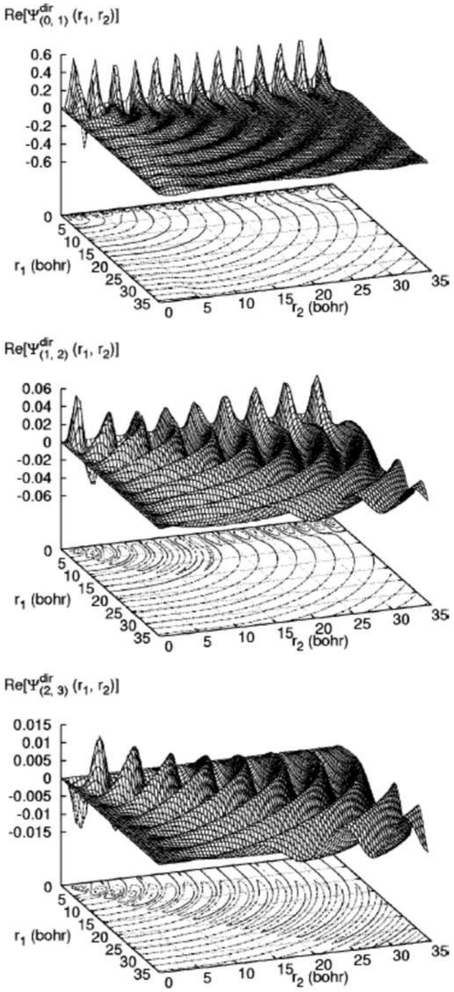
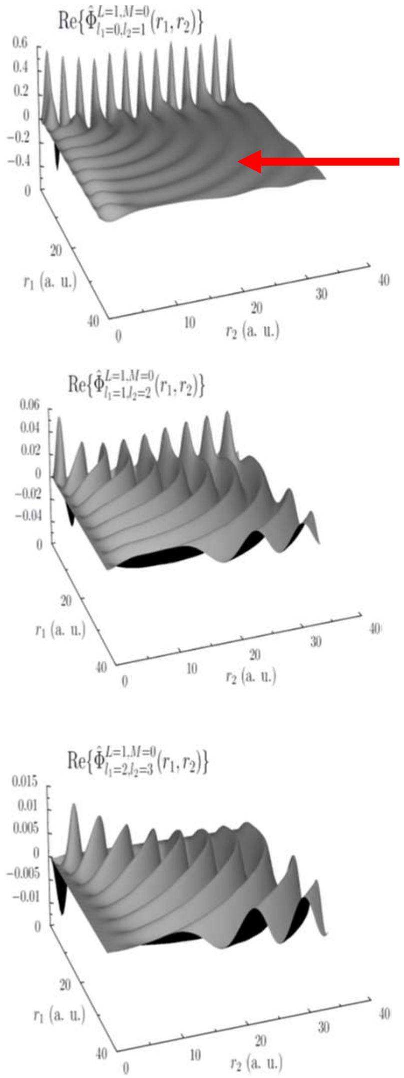


FIG. 3. Real part of direct contribution to the wave function at 20 eV. The panels from top to bottom show the contributions from the *kskp*, *kpkd*, and *kdkf* partial waves.

kskp

kpkd

kdkf



Double ionization

20 eV above threshold

Double photoionization (γ,2e) of He

TDCS for photon energy 20 eV above threshold

Equal energy sharing $E_1=E_2=10$ eV; different θ_1 values

(Randazzo et al, EPJD, 2015)

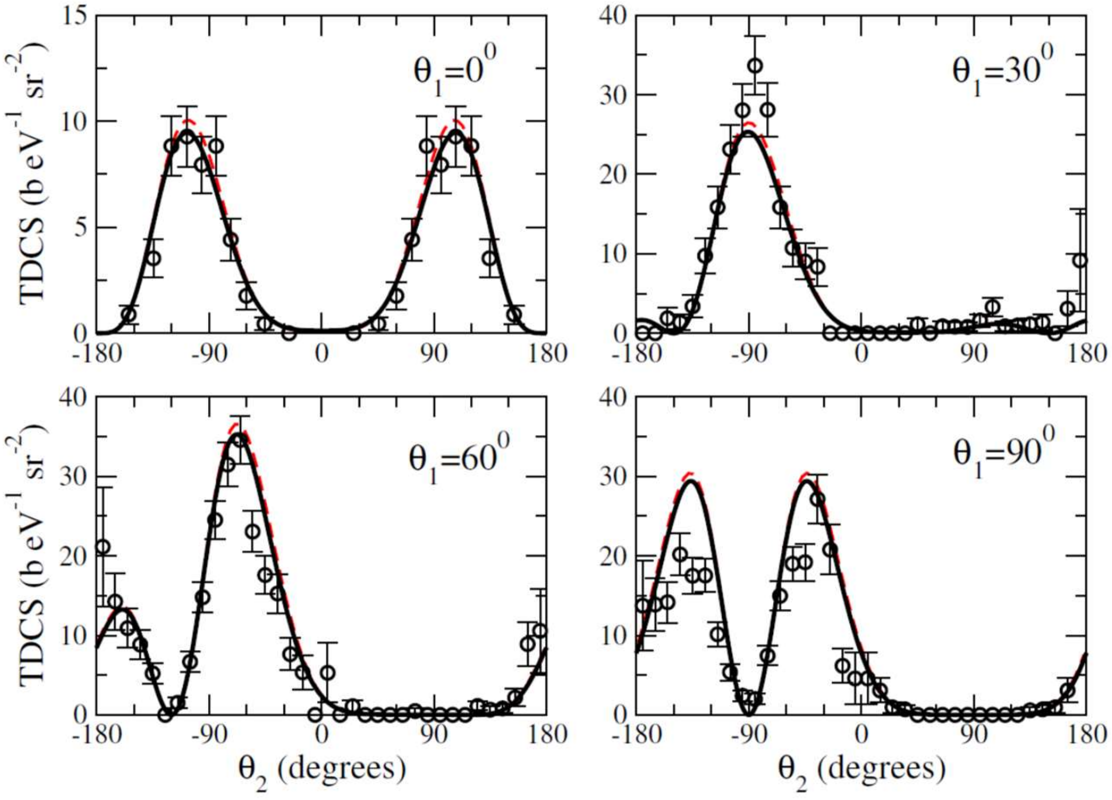


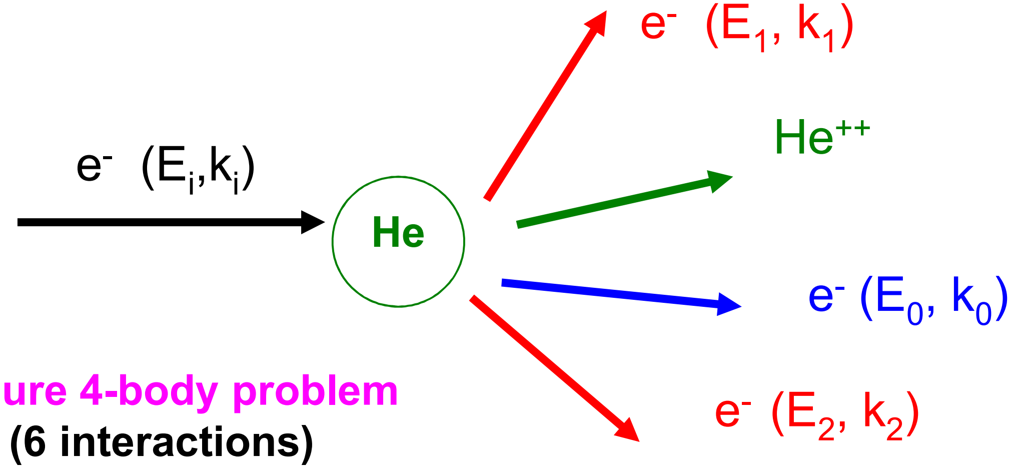
Figure 8: (Color online) TDCS for 20 eV and equal energy sharing at various geometries. Circles: absolute experimental values by Brauning *et al.* [14]. Red dashed line: ECS calculation [22]. Black solid line: present GSF results.

Absolute scale

Save 75% of memory storage

DOUBLE IONIZATION : (e,3e)

$e^- + He \longrightarrow He^{++} + e^- + e^- + e^-$



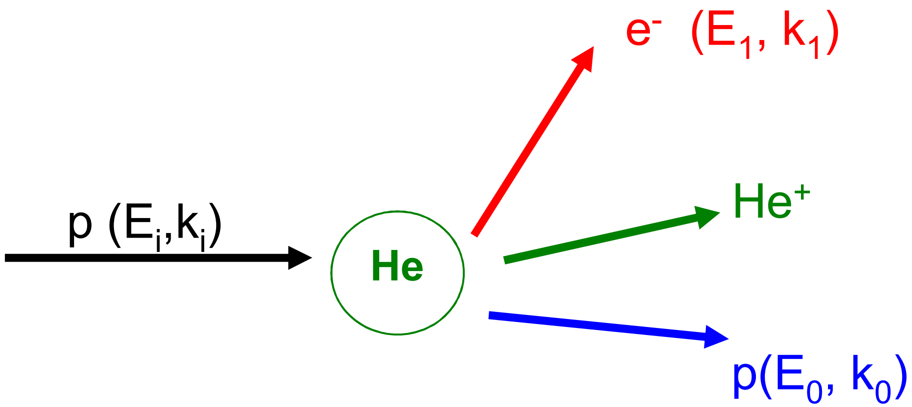
Pure 4-body problem
(6 interactions)

Detection in coincidence:
Kinematically complete
FDCS

$$\frac{d^5\sigma}{d\Omega_1 d\Omega_2 d\Omega_0 dE_1\, dE_2}$$

SINGLE IONIZATION : (p,2e)

$p + He \longrightarrow He^{+} + p + e^-$



4-body problem
(6 interactions)

Detection in coincidence:
Kinematically complete

TDCS

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_0 dE_1}$$

Complete experiments → multiply differential cross sections

→ transition matrix element

$$\langle \Psi_i | V | \Psi_f \rangle$$

6D, 9D integrals

Need description (wave function)
of charged particles in Coulomb interaction

- BOUND STATES (target)

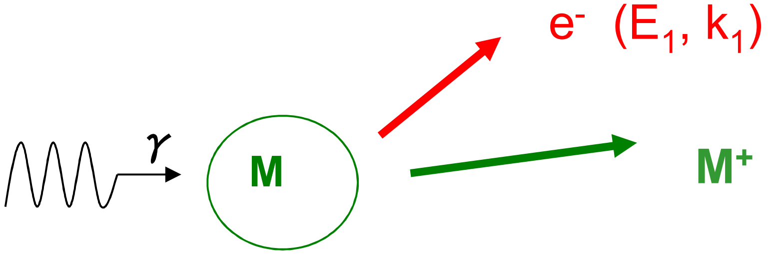
- CONTINUUM STATES (single or double)

(e.g. two electrons escaping from a positive nucleus – THREE-BODY)

N-Body → few body (2, 3 or 4)

Solve NR time-independent Schrödinger equation

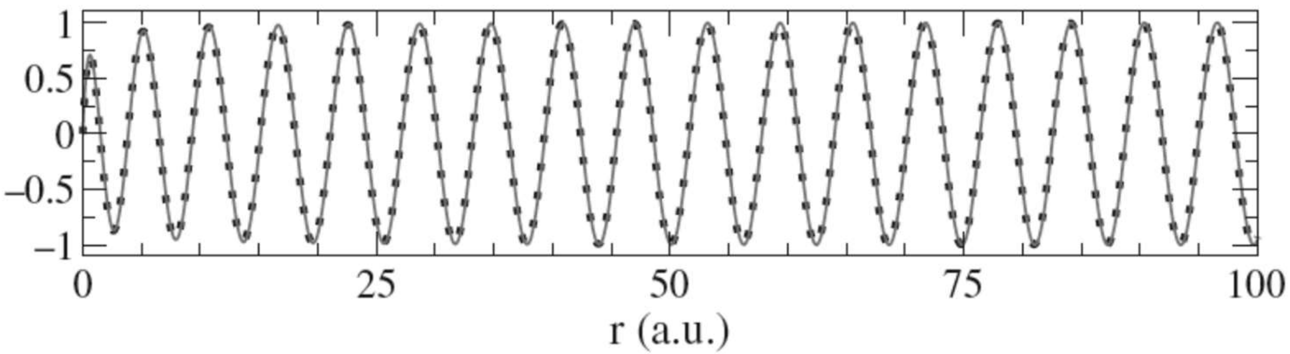
Continuum states



In the final state the ejected electron will « see » asymptotically a charge 1

Central potential U(r) with a Coulomb tail : - Z / r

$$R_l \rightarrow e^{ikr - i\frac{Z}{k}\ln(2kr)}$$



Contrary to the bound case here **the energy E is known.**
Highly oscillating and long-range.
How to represent the continuum?

The choice is crucial for efficiency !

GENERALIZED STURMIAN APPROACH

LIKE most other numerical approaches **it uses two-body basis functions**

BUT

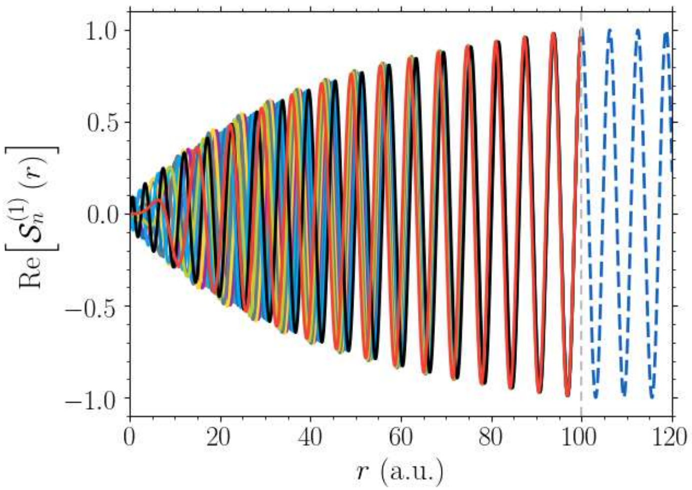
UNLIKE other methods the basis functions have **adequate asymptotic behavior**

Note: three body → also in hyperspherical coordinates

$$\rho = \sqrt{r_1^2 + r_2^2} \qquad \alpha = \arctan(r_1/r_2)$$

Generalized Sturmian Functions (two-body GSF): $S_{n,l}(r)$

- are (numerical) solutions of a Sturm-Liouville differential equation
- form a complete and discrete set → **BASIS SET** (index n)
  (spectral method)
- have a unique and appropriate asymptotic behavior
  (with correct energy for continuum states or expected decay for bound states)



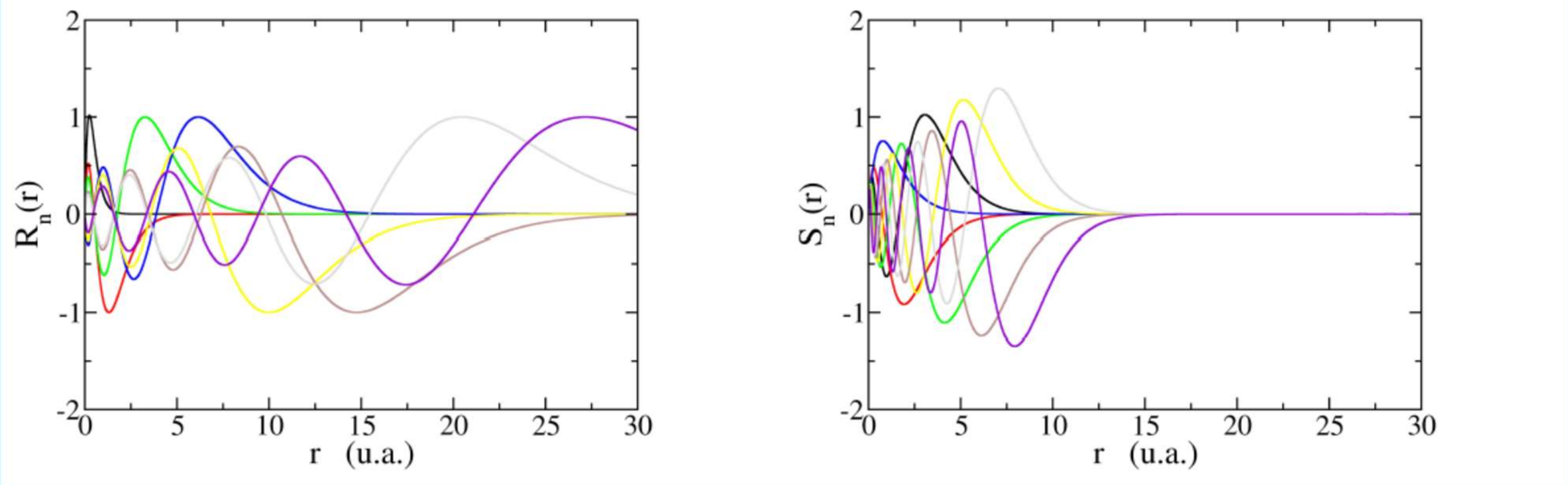
$$S_{n,l}(r) \rightarrow e^{ikr - i\frac{Z}{k}\ln(2kr)}$$

- can be constructed to properly represent the electron-nucleus cusp
- concentrate the effort in the inner part where interaction takes place

BOUND (E<0)

Same boundary conditions (for all n)

$$S_{n,l}(r) \rightarrow e^{-ar}$$



Left: Energy eigenfunctions: widely spread. Right: Potential eigenfunctions. The expansion power can be focused in the area of interest.

Bound states

GROUND STATE

He: BEST ground state energy with uncorrelated product

$$-2.903\,712\,820$$
$$-2.903\,724\,377 \; [14]$$

Exotic systems e.g. positronium ion

Table 7.7 Partial-wave convergence of the ground-state energy of Ps^- system. We used 35 radial functions per coordinate and for each partial-wave l_i

Ps^- Ground-state energy	
l_i	E_{l_i}
0	−0.257 240 143
1	−0.260 105 390
2	−0.261 496 276
…	…
12	−0.262 002 458
Exact[61]	**−0.262 005 070**

EXCITED STATES

Table 7.3 Energy of the first three excited states for singlet states of He for different L with a total of 168 basis functions

n	*L*	Present work	Ref. 57
3	2	−2.0556110426	−2.0556207328522456
4	3	−2.03125512987	−2.0312551443817490
5	4	−2.020000709670	−2.0200007108985847
6	5	−2.0138890317669	−2.0138890347542797

DOUBLY EXCITED STATES

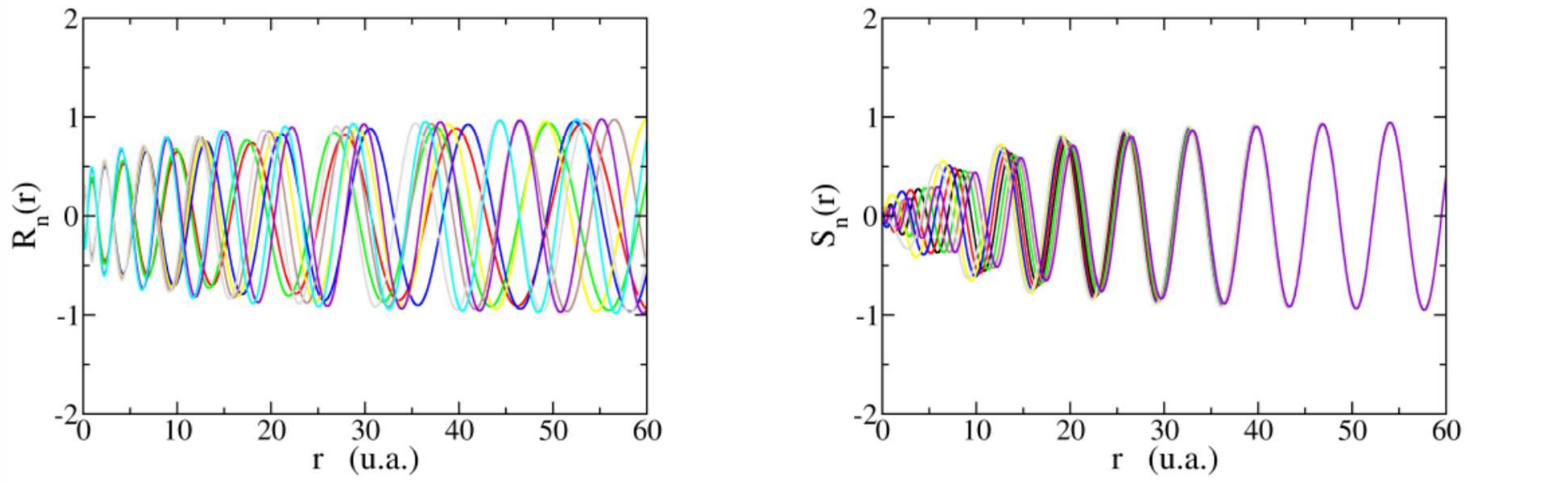
Table 7.4 Energies for the Rydberg series of the singlet S states of He, using 30 GSF per electron

$(N, k)_n$	GSF		Ref. 58	
	$\Re$(E)	$\Im$(E)	$\Re$(E)	$\Im$(E)
$(2, 1)_2$	−0.777876955	−0.002060106	−0.777867636	−0.002270653
$(2, -1)_2$	−0.621817695	−0.000106535	−0.621927254	−0.000107818
$(3, 2)_3$	−0.351827523	−0.001406250	−0.353538536	−0.001504906

Coulombic **CONTINUUM** states ($E=k^2/2 > 0$)

Same boundary conditions (for all n)

$$S_{n,l}(r) \to e^{ikr - i\frac{Z}{k}\ln(2kr)}$$



Left: Energy eigenfunctions, continuous spectrum. Right: Potential eigenfunctions. When outgoing (incoming) conditions are chosen, they constitute a discrete set, even when energies are positive. The potential $\mathcal{V}_g(r)$ regulates the spatial extension of the basis expansion capabilities.

Solve $(H-E)\Psi = 0$

Set $\Psi = \Psi_0 + \Psi^+_{sc}$

Initial state (Ψ_0)

Scattering function (Ψ^+_{sc})

→

Driven Equation

$$(H-E)\,\Psi^+_{sc} = W\,\Psi_0$$

Difficulties:

Coulomb boundary conditions (two-body and three-body)

GENERALIZED STURMIAN APPROACH

- **Efficient basis (smaller computational resources)**
  Adequate asymptotic conditions already built-in
  → concentrate the effort in the inner part where interaction takes place

- **ADVANTAGE: the extraction of amplitudes and differential cross sections directly from the scattering wave function Ψ^+_{sc}**
  (no need to evaluate a transition matrix element $\langle \Psi_i | V | \Psi_f \rangle$)

Applications to ionization processes

Single continuum (two-body)

1) **Single photoionization of atoms and molecules** (γ,e)
2) **Single electron impact ionization of molecules** (e,2e)
3) **Photodetachment of anions** (γ,e)
4) **Two-photon single ionisation** (2γ,e)

$$\Psi^+_{sc} = \sum_n a^l_n \; S^+_{n,l}(r)$$

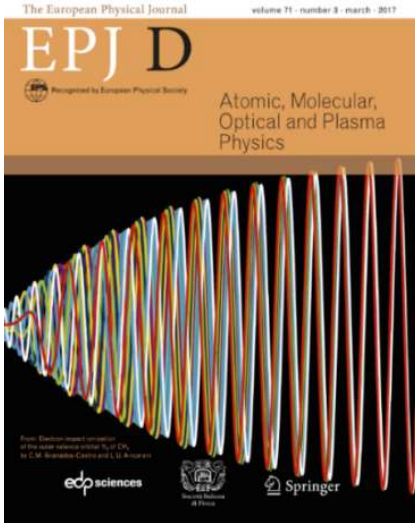
Double continuum (three-body)

5) **Double photoionization of He** (γ,2e) – pure 3-body
6) **Double electron impact ionization of He** (e,3e) – pure 4-body
7) **Double proton impact ionization of He** (p,p2e) – pure 4-body
8) **Double photoionization of molecules** (γ,2e)

$$\Psi^+_{sc}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{L\ l_1 l_2} \sum_{n_1} \sum_{n_2} a^{l_1 l_2 L}_{n_1 n_2} \mathcal{A} \frac{S^+_{n_1 l_1}(r_1)}{r_1} \frac{S^+_{n_2 l_2}(r_2)}{r_2} \mathcal{Y}^{L0}_{l_1 l_2}(\widehat{\mathbf{r}_1}, \widehat{\mathbf{r}_2})$$

What about molecules?

- N-BODY
- Multicenter nature
- Average over angular orientation



Calculations on small polyatomic molecules
like H_20, CH_4, NH_3

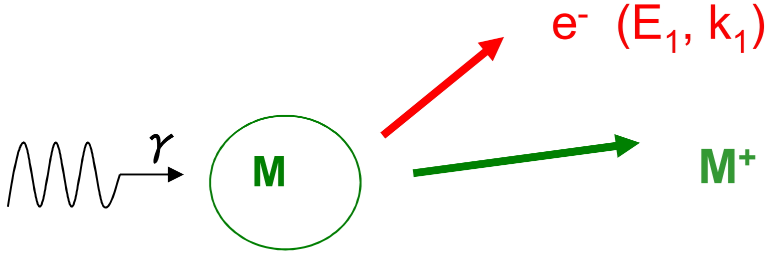
Granados et al, Adv Quantum Chem, 2016, **73**, 3
C. Granados and L.U. Ancarani, Eur.Phys.J D, 2017, **71**, 65
Randazzo et al, PRA, 2020

H_2O $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$

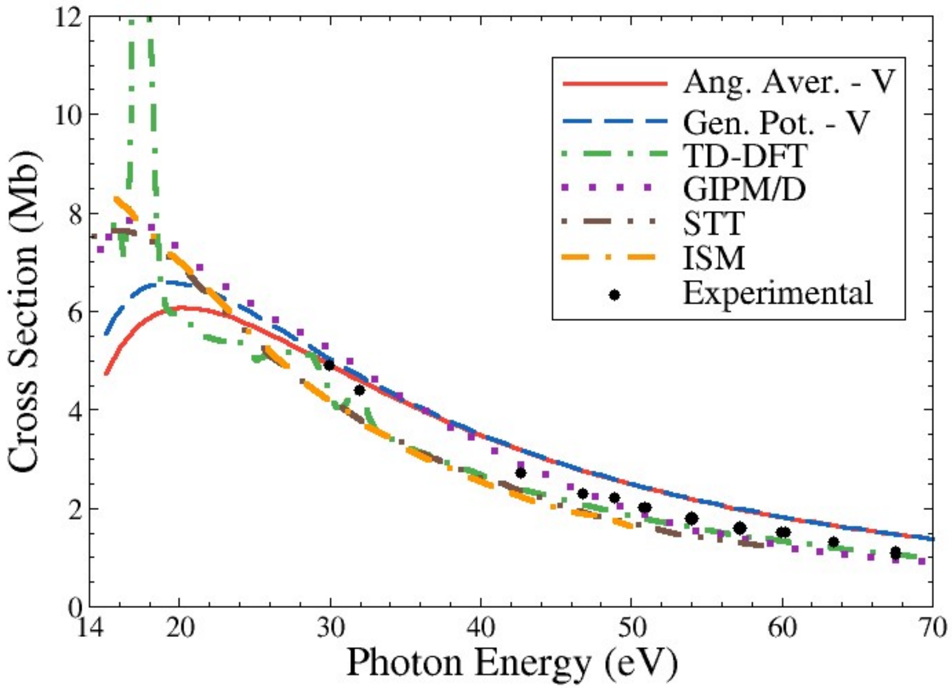
3 nuclei + 10 electrons :   approximations (BO, FC, OCE, …)
→ few body problem

1) Single photoionization

$\gamma + M \longrightarrow M^+ + e^-$



Photoelectron spectrum

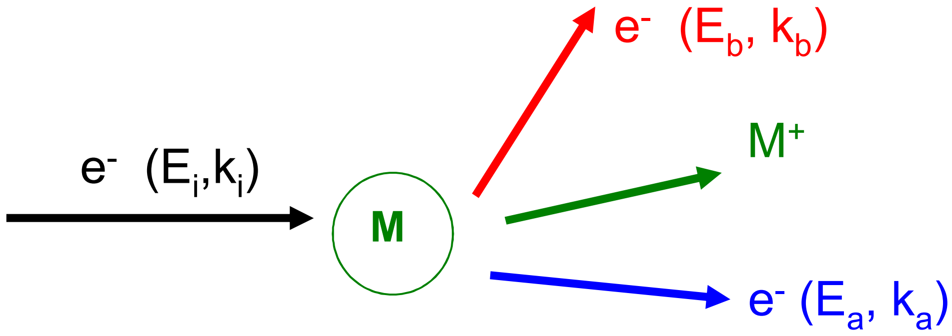


Inner valence

$3a_1$ of H_2O

(Granados et al,
Adv Quantum Chem, 2016)

2) Single ionization by electron impact

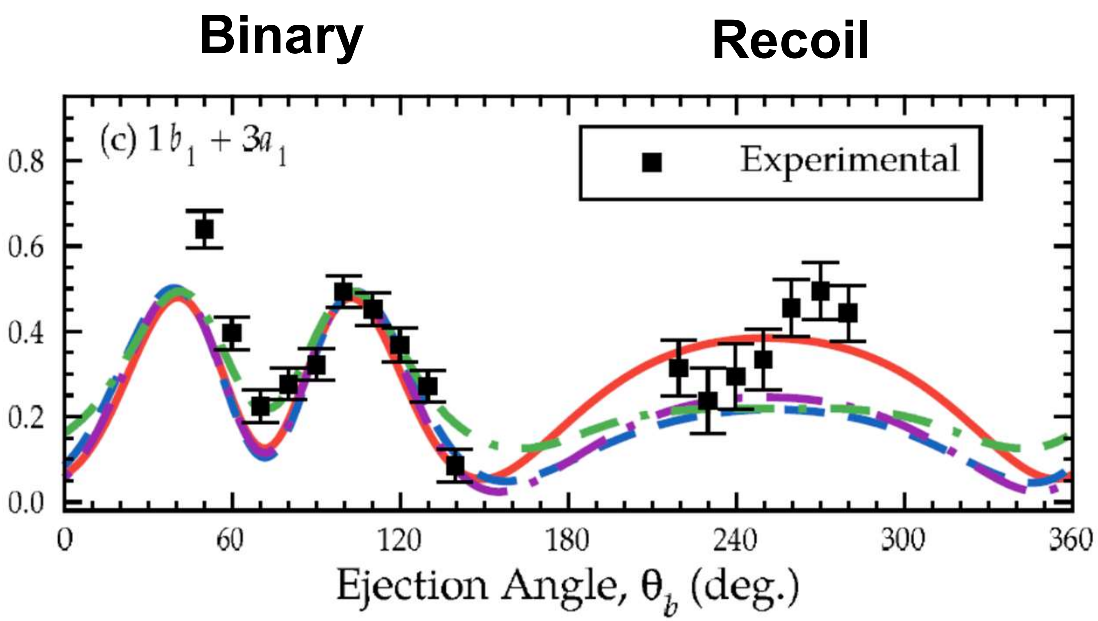


$e^- + M \rightarrow M^+ + e^- + e^-$

(e,2e) experiment

TDCS $\dfrac{d^3\sigma}{d\Omega_b d\Omega_a dE_b}$

Momentum transfer: $\mathbf{K}=\mathbf{q}=\mathbf{k}_i-\mathbf{k}_a$



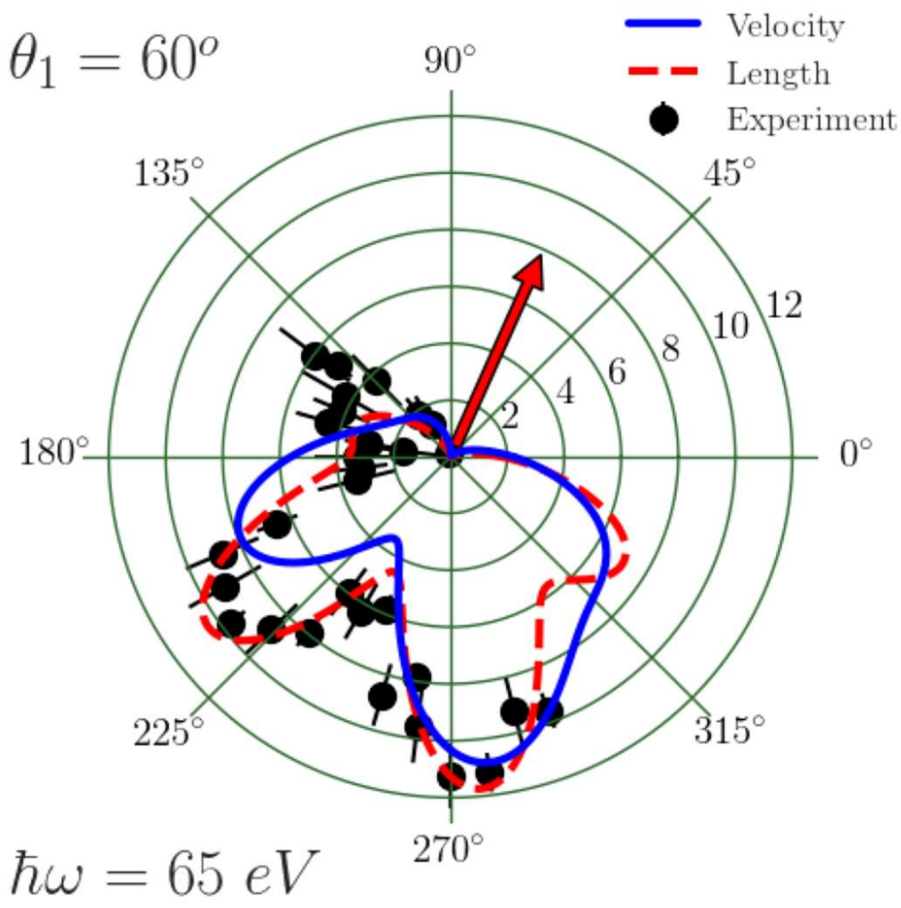
$1b_1$ and $3a_1$

E_i=250 eV
E_b=10 eV
θ_a=-15°

EXPT : Milne-Brownlie et al
PRA 69 (2004) 032701

3) Double photoionization

First measurements 2018 (photons of 63 and 65 eV) !!
First calculations 2019 (Randazzo et al, PRA, 2020)



$E_1=E_2=10$ eV
$\theta_1=60°$

Take home message

- **Ionization processes**
  → **N-body problem involving continuum states of given energy (highly oscillating + long range)**

- **Generalized Sturmian Functions (GSF)**
  - **computationally efficient because appropriate boundary conditions are built in the basis elements**
    → **concentrate the effort in the region where it is interesting**
  - **implemented to describe the single and double continuum of atoms and molecules**

Thank you for your attention !