A Sturmian approach to structure and ionization processes of atoms and molecules

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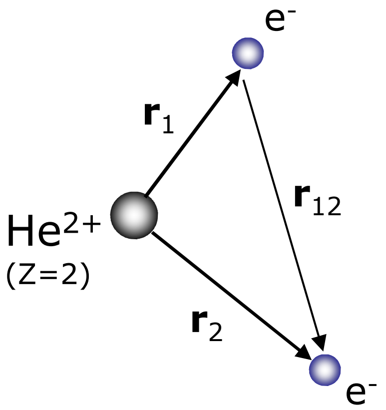
OUTLINE

- Context
- Method: Sturmian approach
- Examples (bound+ three body fragmentation)

Helium



Pure 3-body
Coulomb problem

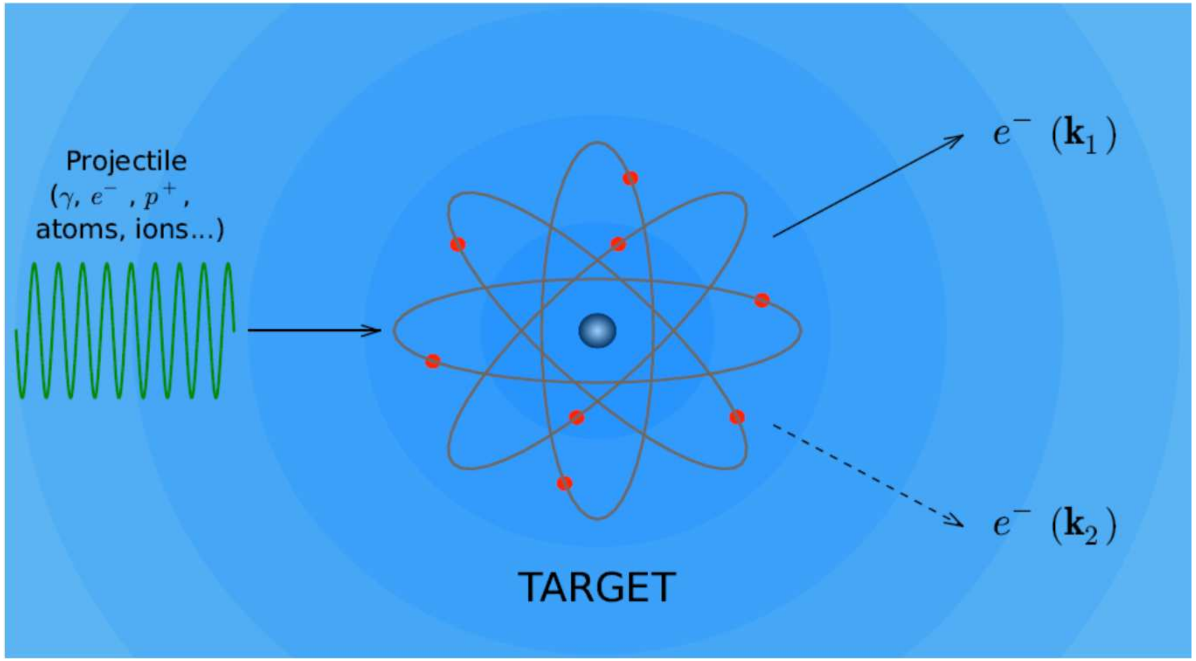
$$\left[T + \frac{q_1 q_3}{r_1} + \frac{q_2 q_3}{r_2} + \frac{q_1 q_2}{r_{12}} - E\right] = 0$$

Bound wavefunctions :

- **product of uncorrelated basis functions (e.g. ETO,GTO)**
- **explicitly correlated (r_{12}) basis sets**

FOCUS: Continuum states NOT bound states

Study of ionization of atoms and molecules by photon or electron impact



TARGETS : - atoms (H, He, Li, Be, Ar, Na, Mg, Cu, Au, …)
- molecules (H_2O, NH_3, CH_4 , DNA basis, …)

- **Development of theoretical tools (methods, wave functions)**
- **Calculation of multidifferential cross sections**

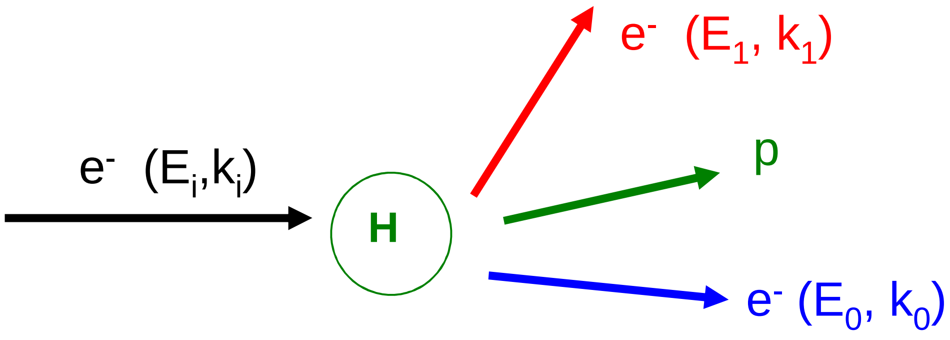
THEORY ←→ EXPERIENCE

SINGLE IONIZATION : (e,2e) on H

$$\boxed{e^- + H \longrightarrow p^+ + e^- + e^-}$$

Detection in coincidence:

Kinematically complete



e^- (E_i, k_i)

H

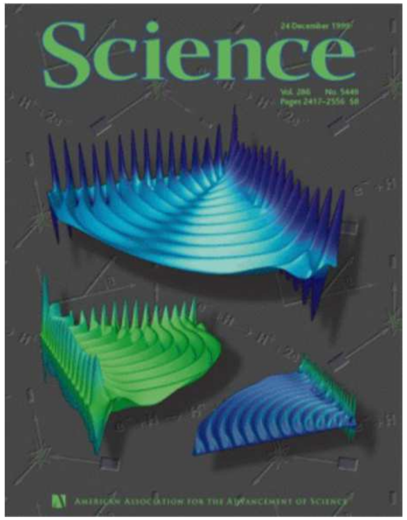
e^- (E_1, k_1)

p

e^- (E_0, k_0)

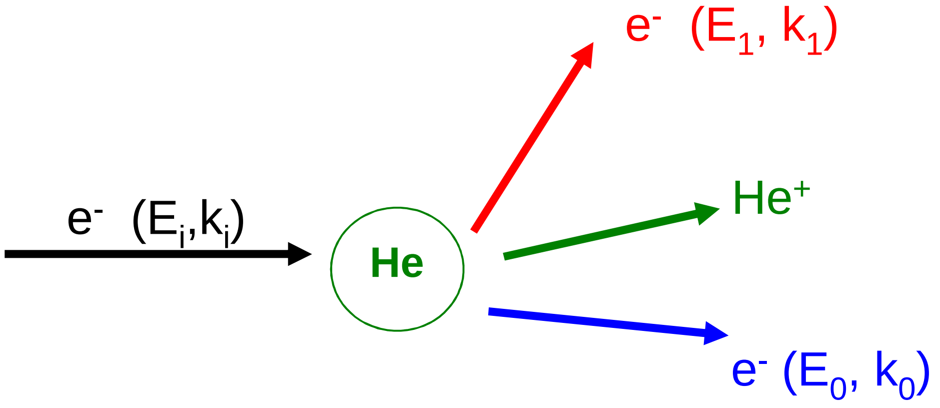
TDCS $$\frac{d^3\sigma}{d\Omega_1 d\Omega_0 dE_1}$$

- **Pure 3-body problem in final channel**
- **Solved numerically at the end of century**
- **Agreement between theories and experiments**



SINGLE IONIZATION : (e,2e)

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



e^- (E_i,k_i)

He

e^- (E_1, k_1)

He^+

e^- (E_0, k_0)

4-body problem

(6 interactions)

Detection in coincidence:

Kinematically complete

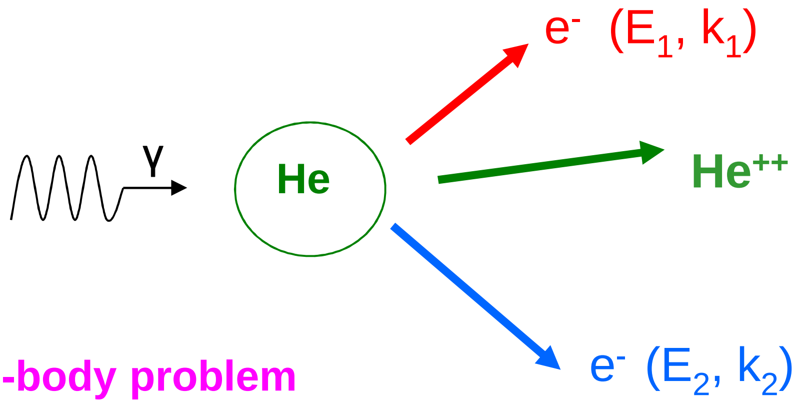
TDCS $\frac{d^3\sigma}{d\Omega_1 d\Omega_0 dE_1}$

$\downarrow$

TCS σ

DOUBLE IONIZATION : (γ,2e)

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



γ

He

e^- (E_1, k_1)

He^{++}

e^- (E_2, k_2)

Pure 3-body problem

(3 interactions)

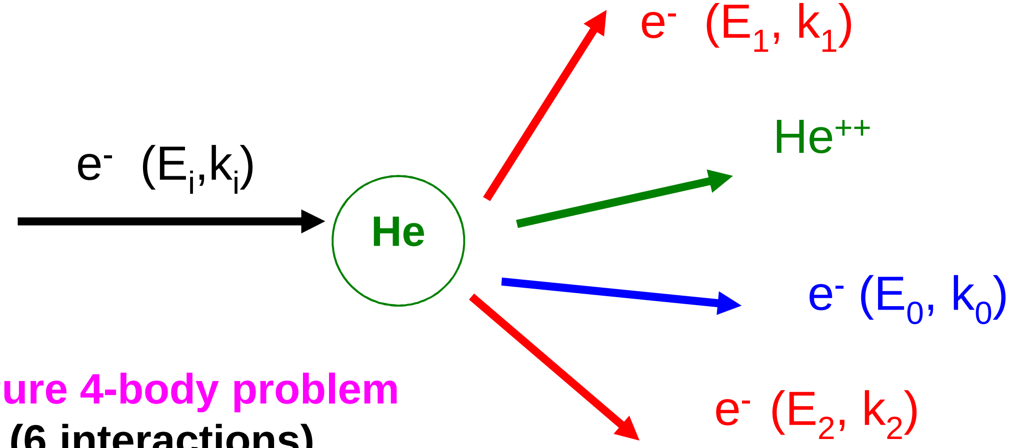
Detection in coincidence:

TDCS

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

DOUBLE IONIZATION : (e,3e)

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



e^- (E_i,k_i)

He

e^- (E_1, k_1)

He^{++}

e^- (E_0, k_0)

e^- (E_2, k_2)

Pure 4-body problem

(6 interactions)

Detection in coincidence:

FDCS

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

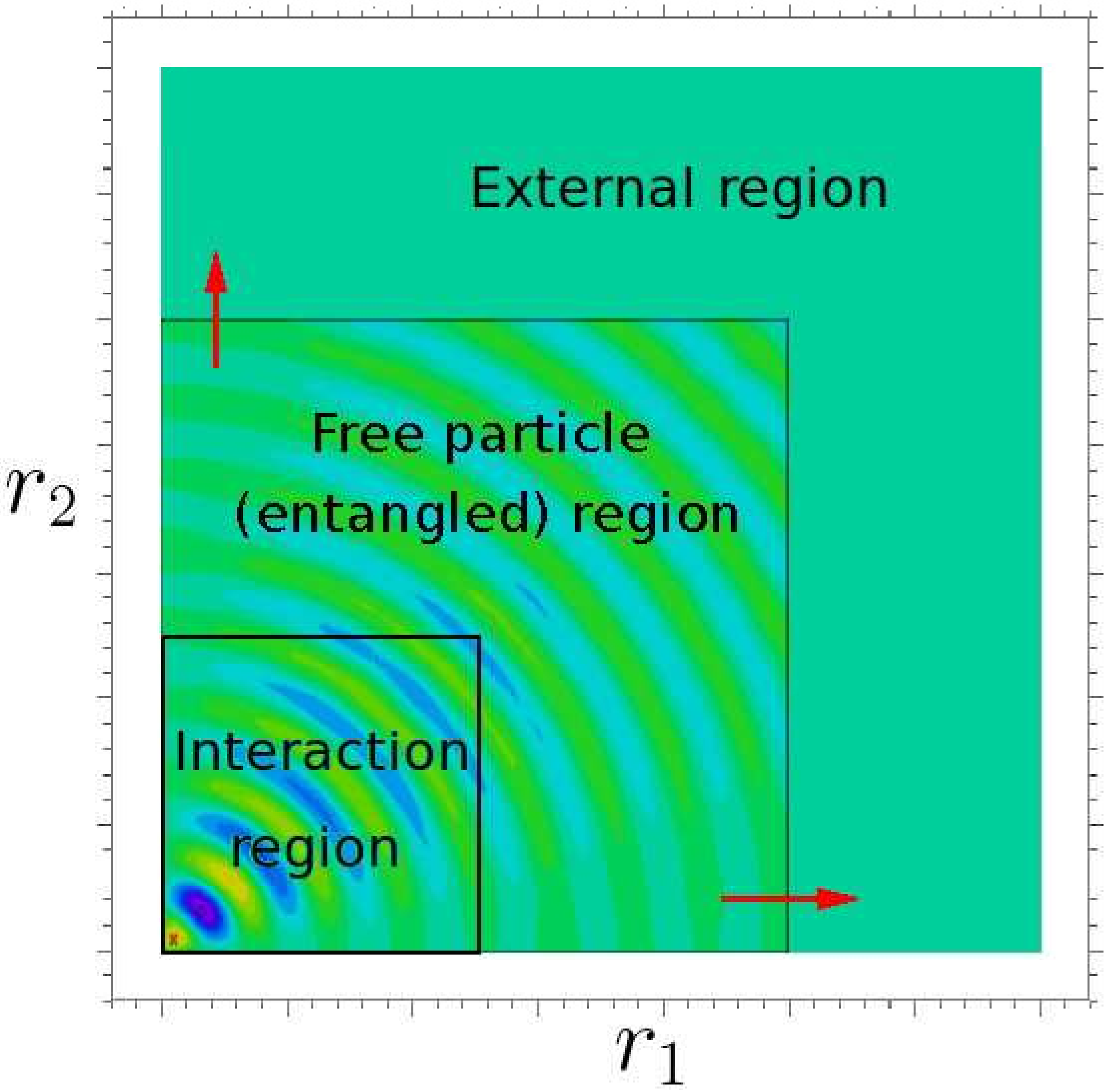
WHY DO WE WANT DIFFERENTIAL CROSS SECTIONS?

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

Electron Momentum Spectroscopy (EMS) technique: (e,2e) collisions

–> provide the F.T. of the target wave function: $|\Psi(p)|^2$

Three-body Scattering problem (ionization)



Recall Basic Quantum Mechanics (1/2)

Consider a two-body problem, reduced mass μ=1,
with a central potential U(r), generally with a Coulomb tail : - Z / r

$\Psi(\mathbf{r}) = \frac{1}{r} R_l(r) Y_l^m(\hat{r})$ → Radial equation: $\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + U(r) - E \right] R_l(r) = 0$

Standard approach

Eigenvalue E

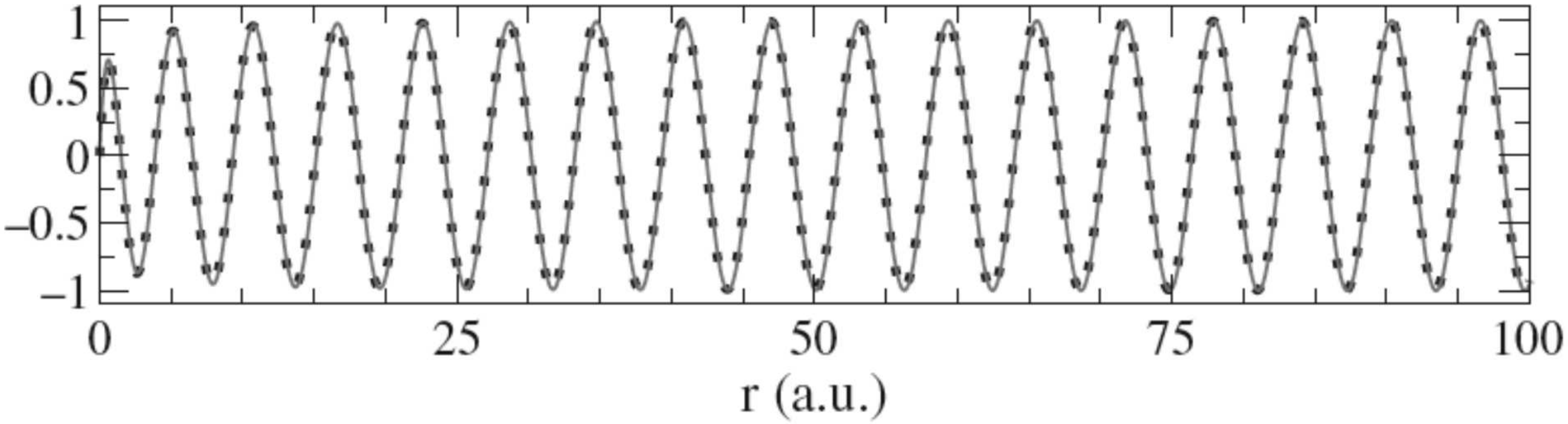
$R_l(r)$: eigenfunctions of the ENERGY

Complete and orthogonal set

Recall Basic Quantum Mechanics (2/2)

	Energy	r→∞ behavior
Bound states	$E_{n,l}$	$R_{n,l} \rightarrow e^{-Zr/n}$
Continuum states	$E = \dfrac{k^2}{2}$	$R_l \rightarrow e^{ikr - i\frac{Z}{k}\ln(2kr)}$

Highly oscillating !



Plane (or Coulomb) wave :

$$\boxed{\Psi(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}}}$$

SINGLE IONIZATION : (e,2e) of a molecule

Transition amplitude in the First Born Approximation:

$$T_{fi} \sim \left\langle \exp(i\vec{k}_s.\vec{r}_0)\underline{\Psi_f(\vec{k}_1,\vec{r}_1,..,\vec{r}_n)}\middle|V\middle|\exp(i\vec{k}_i.\vec{r}_0)\Phi_i\underline{(\vec{r}_1,..,\vec{r}_n)}\right\rangle$$

Simple continuum

Electron-target Interaction

Initial molecular state

Quantum Chemistry

Differential Cross Section

$$\frac{d^4\sigma(\alpha;\beta;\gamma)}{d\Omega_{Euler}\,d\Omega_0 d\Omega_1 dE_1} = \frac{k_0 k_1}{k_i}\left|T_{fi}\right|^2$$

Euler angles

DOUBLE IONIZATION : (e,3e) of He

$$\boxed{\frac{d^5\sigma}{d\Omega_0 d\Omega_1 d\Omega_2 dE_1 dE_2} = (2\pi)^4 \frac{k_0 k_1 k_2}{k_i} \left|T_{fi}(\underline{\mathbf{k}_0}, \underline{\mathbf{k}_1, \mathbf{k}_2})\right|^2}$$

Interaction

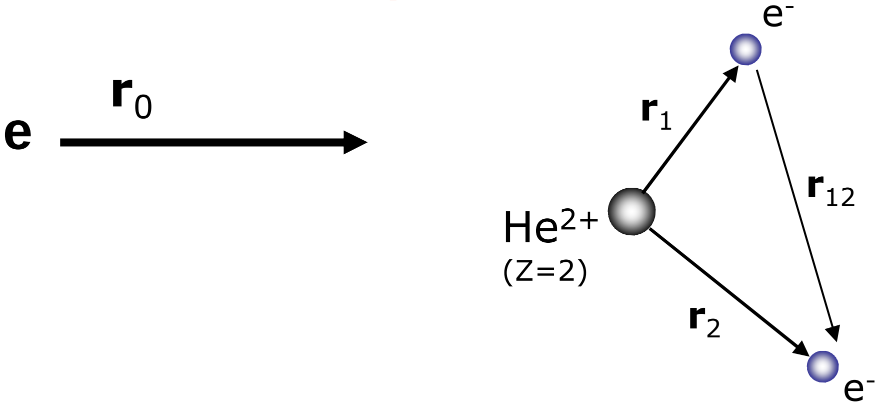
$$T_{fi} = \left\langle \frac{1}{(2\pi)^{3/2}} \underline{e^{i\mathbf{k}_0\cdot\mathbf{r}_0}} \, \underline{\Psi_f^-(\mathbf{r}_1, \mathbf{r}_2)} \left| -\frac{Z}{r_0} + \frac{1}{r_{01}} + \frac{1}{r_{02}} \right| \frac{1}{(2\pi)^{3/2}} \underline{e^{i\mathbf{k}_i\cdot\mathbf{r}_0}} \, \underline{\Psi_i(\mathbf{r}_1, \mathbf{r}_2)} \right\rangle$$

$\boxed{\to \int 9D}$

3-body CONTINUUM problem

(double continuum)

3-body BOUND problem
Ground state of He



Kinematically complete experiments → multiply differential cross sections

THEORY <-> EXPERIENCE

Need description 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)

Need to solve Schrödinger Equation

STURMIAN APPROACH

Like most other numerical approaches
it uses two-body basis functions (e.g. ETO,GTO, …)

Standard approach

U(r) : central potential

$$\Psi(\mathbf{r}) = \frac{1}{r} R_l(r) Y_l^m(\hat{r})$$

Radial equation:

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + U(r) - E \right] R_l(r) = 0$$

Eigenvalue E

$R_l(r)$: eigenfunctions of the ENERGY

Complete and orthogonal set

Sturmian approach:

$$\boxed{\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l\,(l+1)}{2r^2}+U_a(r)-E_s\right]S_{n,l}(r)=-\beta_{n,l}V_g(r)S_{nl}(r)}$$

$U_a(r)$: auxiliary potential (short or long range, usually related to the potential U to be solved)

$$\lim_{r\to\infty} rU_a(r) = Z$$

$V_g(r)$: generating potential (short range)

$$\lim_{r\to\infty} rV_g(r) = 0$$

E_s: externally fixed parameter

$\beta_{n,l}$: eigenvalues

$S_{n,l}(r)$: **Eigenfunctions of the potential**
(Generalized Sturmian Functions - GSF)

Complete and orthogonal (potential $V_g(r)$ weighted) set

Asymptotically:

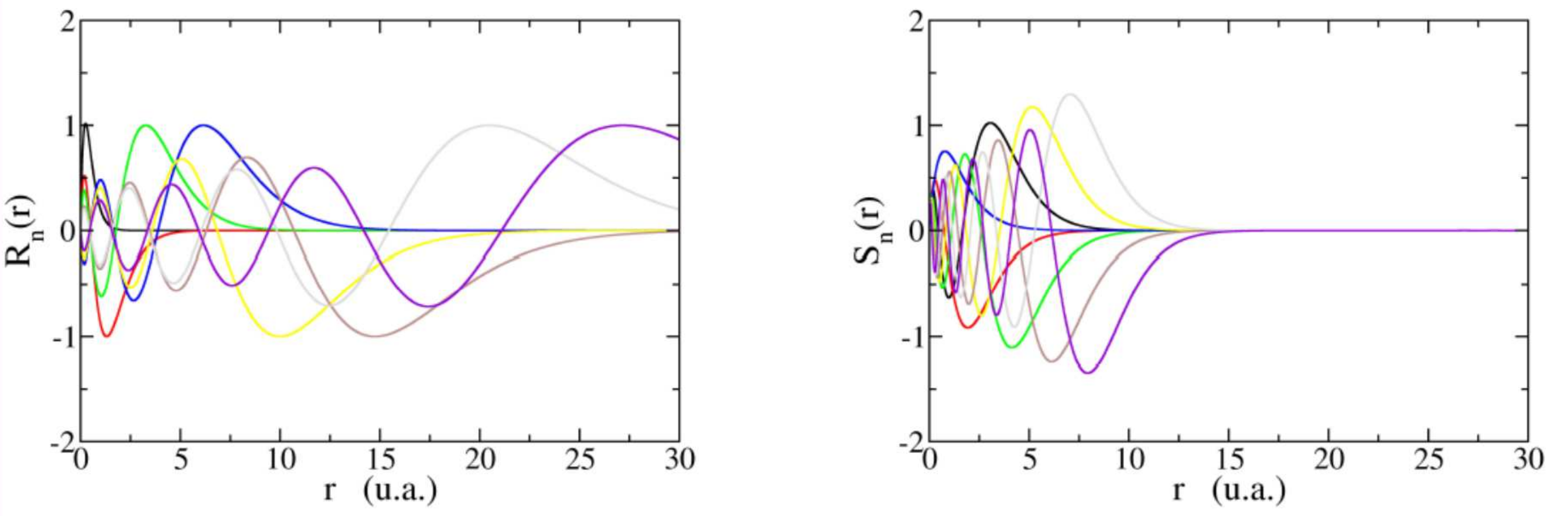
$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+U_a(r)-E_s\right]S_{n,l}(r)=0$$

→ All $S_{n,l}(r)$: same asymptotic behavior dictated by $U_a(r)$

BOUND (E<0)

Same boundary conditions (for all n)

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

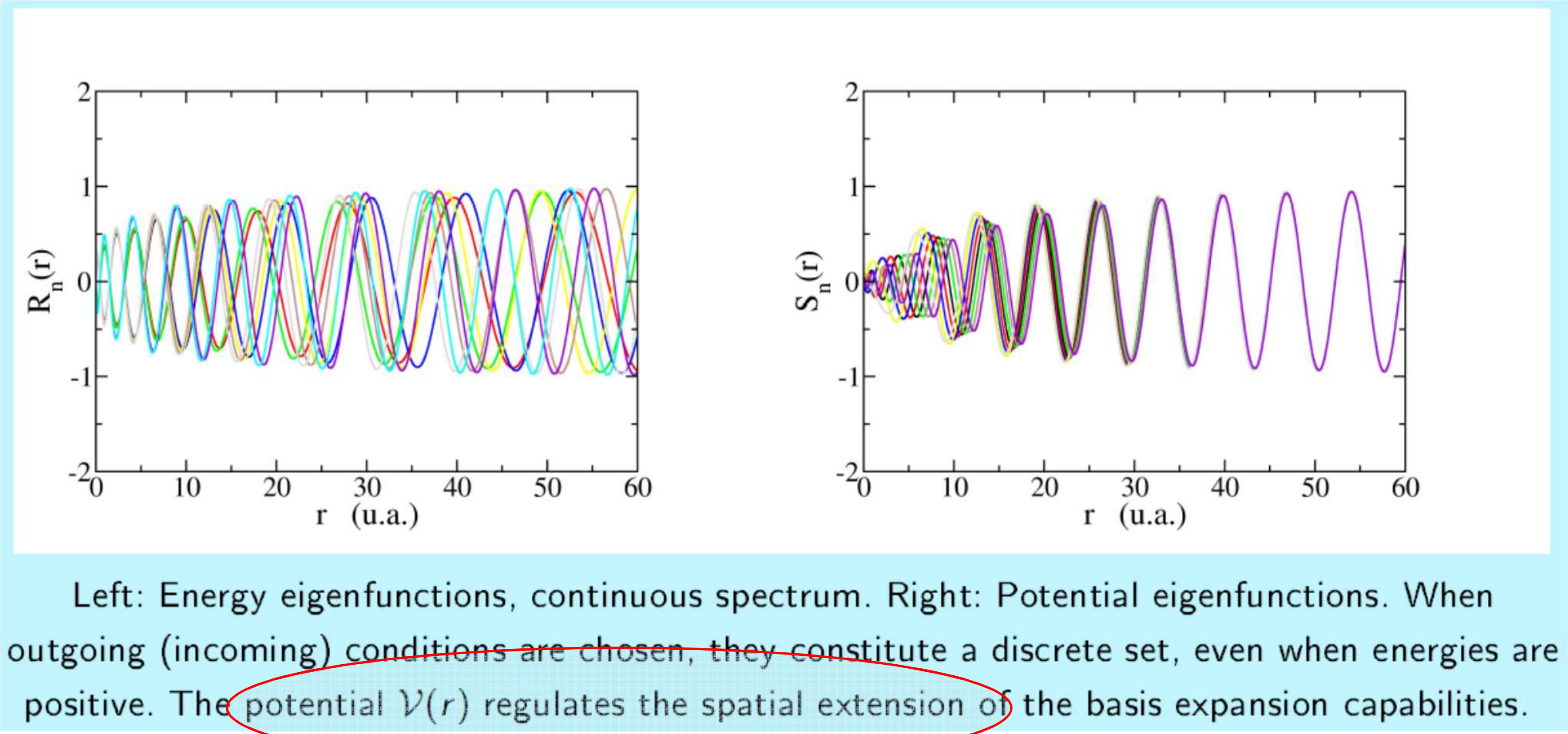


Left: Energy eigenfunctions: widely spread. Right: Potential eigenfunctions. The expansion power can be focused in the area of interest.

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

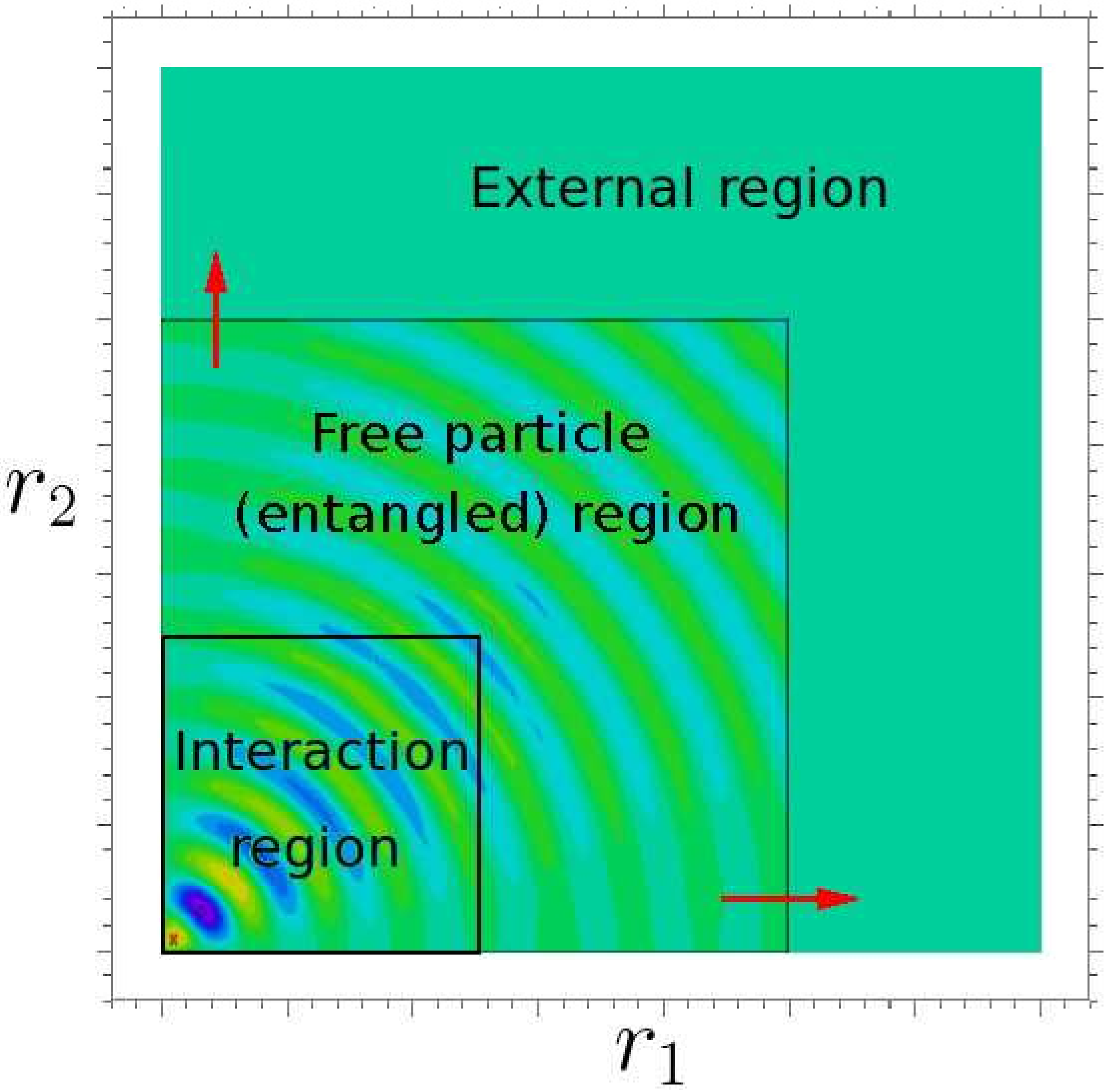
Same boundary conditions (for all n)

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



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 $\mathcal{V}(r)$ regulates the spatial extension of the basis expansion capabilities.

Three-body Scattering problem (ionization)



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

- are solutions of a Sturm-Liouville differential equation
- form a complete and discrete set → BASIS SET
- have a unique and appropriate asymptotic behavior
  (with correct energy for continuum states
  or appropriate decay for bound states)
- can be constructed to properly represent the electron-nucleus cusp
- concentrate the effort in the inner part where interaction takes place
- solve the kinetic energy + main potential terms
- transform the Schrödinger equation into a matrix problem

→ VERY EFFICIENT BASIS
(require smaller computational resources)

REVIEW: Gasaneo et al, Adv. Quantum Chem., 2013

Coulomb Sturmian Functions

(more widely used)

Generating potential is a Coulomb potential

→ analytical solutions (hydrogen-like Sturmian basis)

$$R_{nl}(r) = \mathcal{N}_{nl}(2kr)^l \, \mathrm{e}^{-kr} \, F(l+1-n \mid 2l+2 \mid 2kr)$$

$$\left(-\frac{1}{2}\nabla^2 + \frac{k^2}{2} - \frac{\boxed{nk}}{r}\right) R_{nl}(r) = 0$$

- **If k=Z/n → hydrogen radial functions (bad ! - nodes)**
- **If k=constant → complete basis set (Shull and Lowdin)**
  fixed energy $E=k^2/2$ for all n
  BUT different asymptotic behavior

- Each eigenvalue is a different charge nk

→ e-N cusp condition NOT respected

- Span a larger domain

Generalized SF vs Coulomb SF

BOUND

Cusp

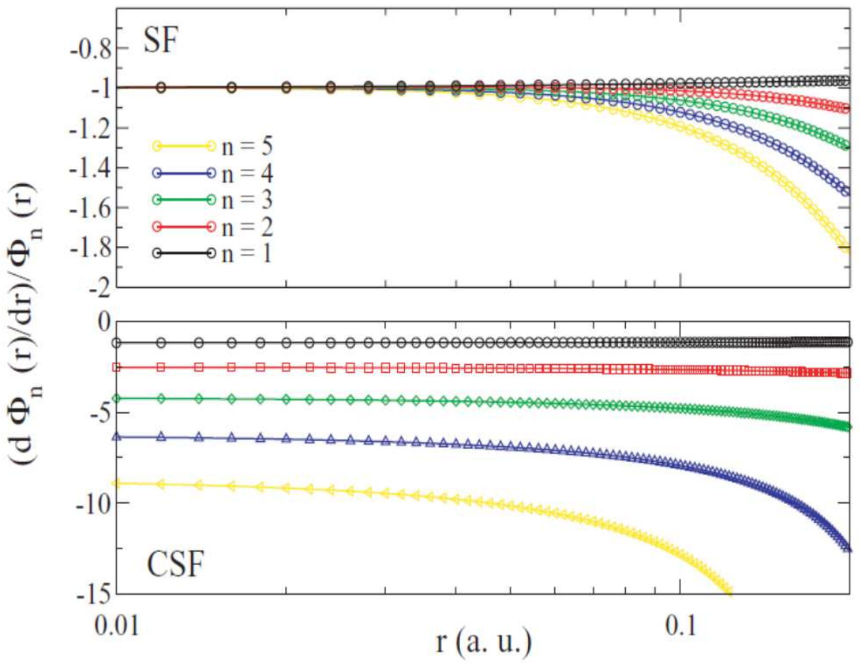


FIG. 2. (Color online) $\frac{1}{\Phi_n(r)}\frac{d\Phi_n(r)}{dr}$ as a function of r for the first five SF (top) and CSF (bottom).

Asymptotics

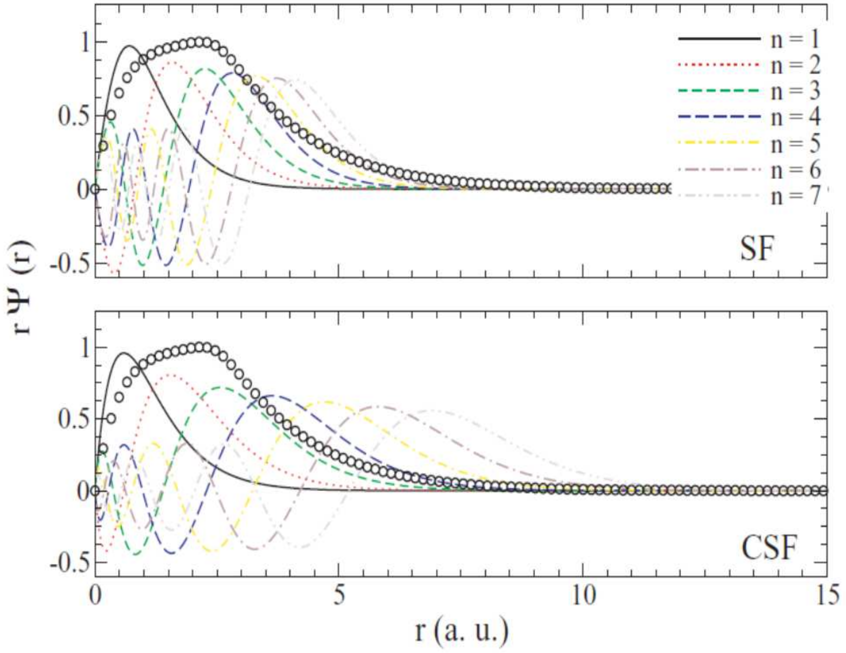
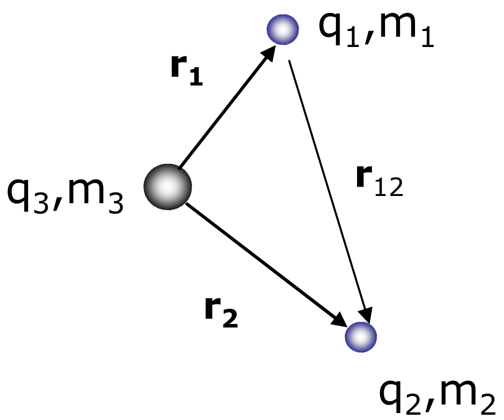


FIG. 1. (Color online) $r\Psi(r)$ (open circles) and seven asymptotically optimized SF (lines, top) and CSF (lines, bottom).

THREE-BODY CASE



$$\left[T + \frac{q_1 q_3}{r_1} + \frac{q_2 q_3}{r_2} + \frac{q_1 q_2}{r_{12}} - E\right] = 0$$

Uncorrelated product of two-body GSF:

$$\boxed{\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{l_1 l_2} \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} a_{n_1 n_2}^{l_1 l_2 LM} \mathcal{A} \frac{S_{n_1 l_1}(r_1)}{r_1} \frac{S_{n_2 l_2}(r_2)}{r_2} \mathcal{Y}_{l_1 l_2}^{LM}(\widehat{\mathbf{r}}_1, \widehat{\mathbf{r}}_2),}$$

- **Similar advantages** (inner part, matrix problem, …)
- **Several applications**

➢ **BOUND** - atomic states (ground and excited), resonances
- H_2^+ molecule
- confined systems

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

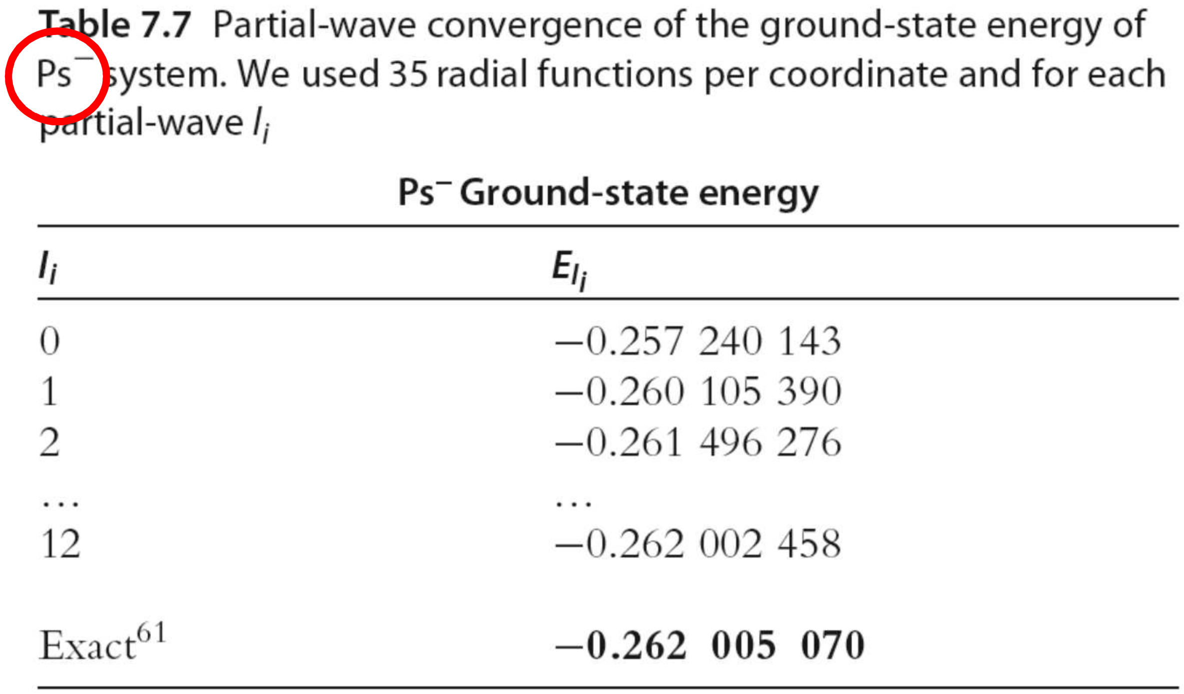


Table 7.7 Partial-wave convergence of the ground-state energy of Ps^- system. We used 35 radial functions per coordinate and for each partial-wave l_i

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

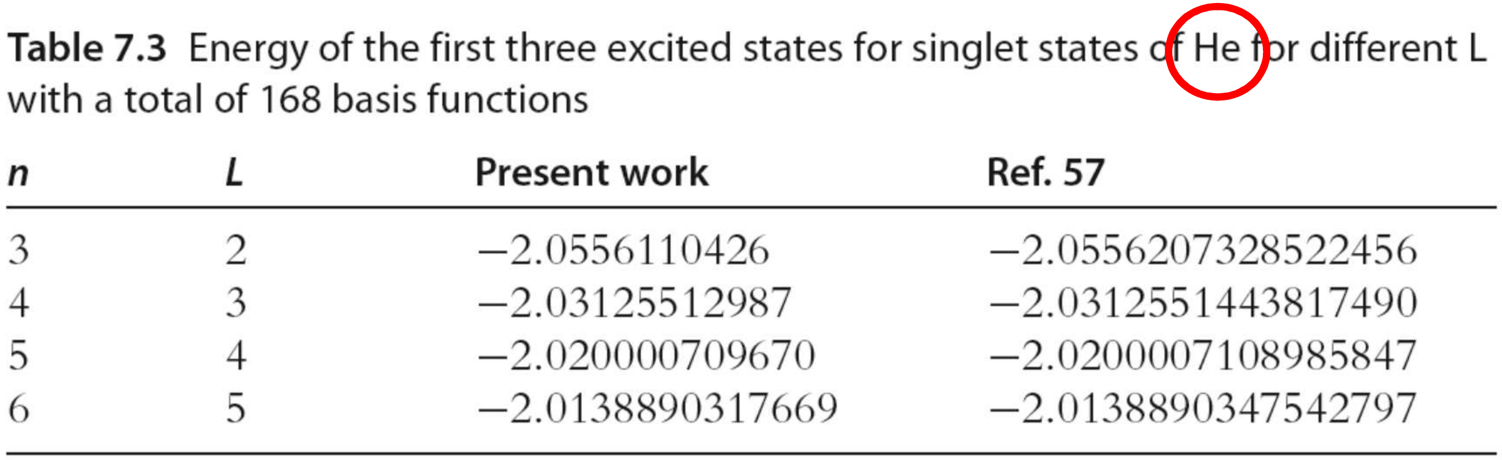


Table 7.3 Energy of the first three excited states for singlet states of He for different L with a total of 168 basis functions

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

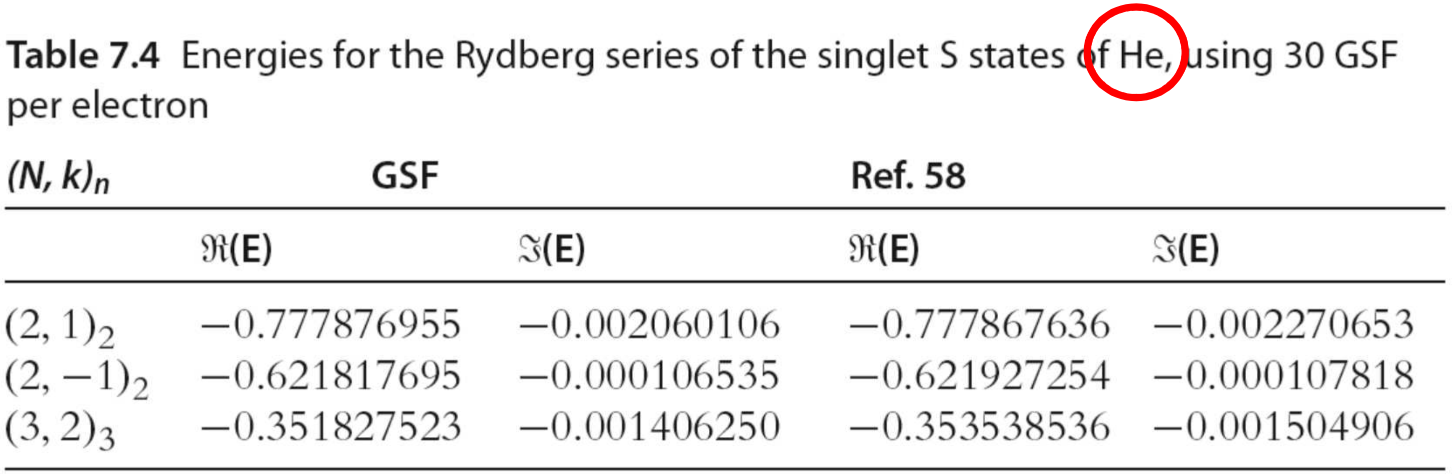


Table 7.4 Energies for the Rydberg series of the singlet S states of He, using 30 GSF per electron

$(N, k)_n$	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

Applications to ionization processes

1) **Double photoionization of He** (γ,2e)
2) **Double electron impact ionization of He** (e,3e)
3) **Single photoionization of molecules** (γ,e)
4) **Single electron impact ionization of molecules** (e,2e)

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

Extraction of amplitudes and cross sections directly from the scattering wave function

1) Double photoionization of He

γ + He → He^{++} + e$^-$ + e$^-$

State of the art

ECS (McCurdy et al, PRA, 2004)

GSF

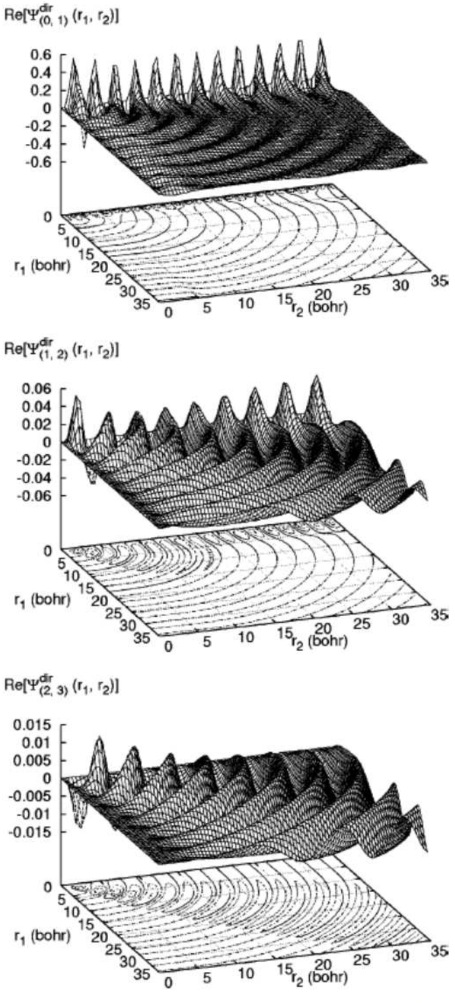
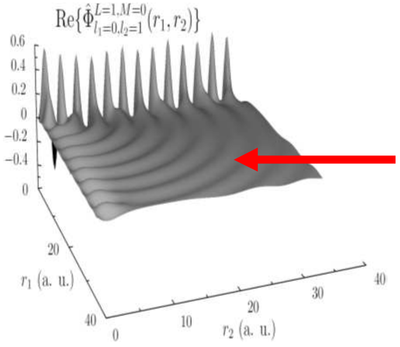


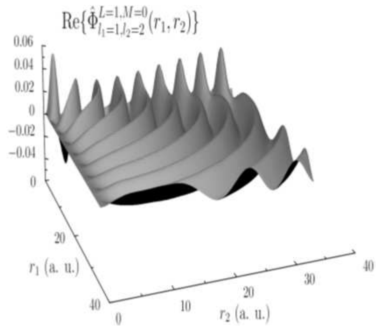
FIG. 3. Real part of direct contribution to the wave function at 20 eV. The panels from top to bottom show the contributions from the *kskp*, *kpkd*, and *kdkf* partial waves.

kskp



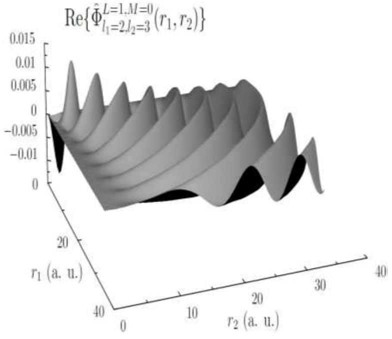
Double ionization

kpkd



20 eV above threshold

kdkf



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

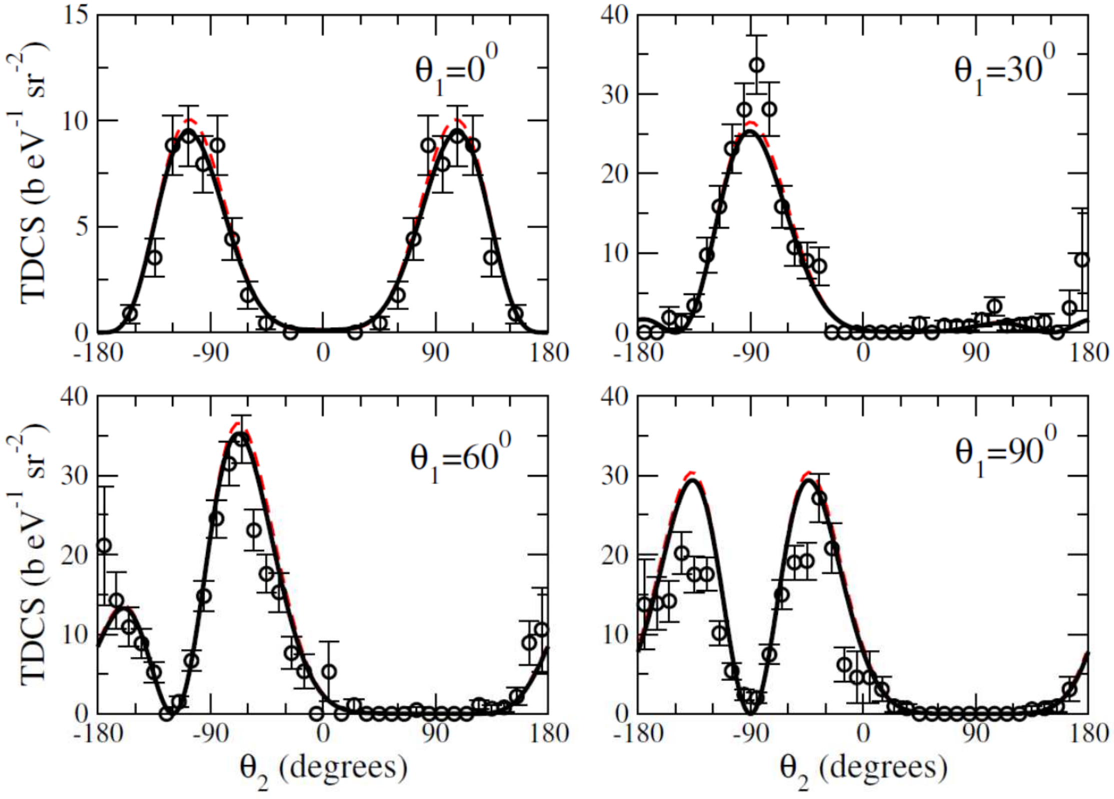


Figure 8: (Color online) TDCS for 20 eV and equal energy sharing at various geometries. Circles: absolute experimental values by Brauning *et al.* [14]. Red dashed line: ECS calculation [22]. Black solid line: present GSF results.

Absolute scale

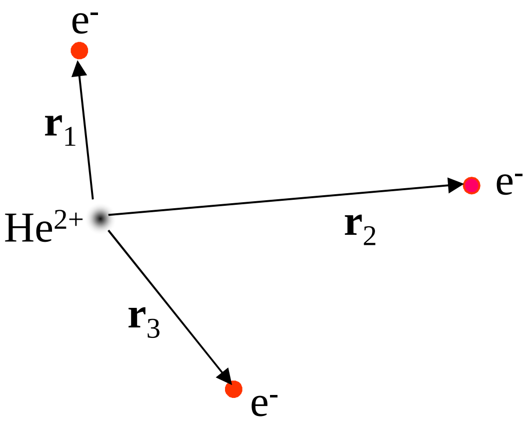
Save 75% of memory storage

2) Double ionization of He by electron impact

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

Four body problem

$$\left[H - E\right]\Psi\left(\vec{r}_1, \vec{r}_2, \vec{r}_3\right) = 0$$



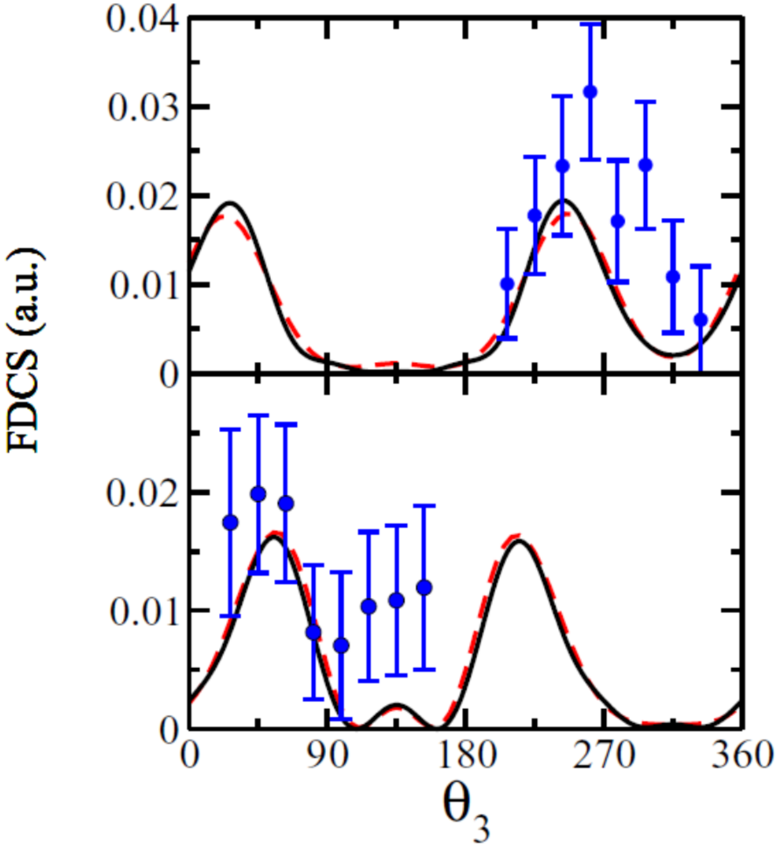
- If incident and scattered electron are fast, within the First Born Approximation → three-body problem
- Tests the double continuum **in a complete manner**

Absolute differential cross sections have been measured for (e,3e)

Ongoing debate for 15 years !

GSF calculation !!

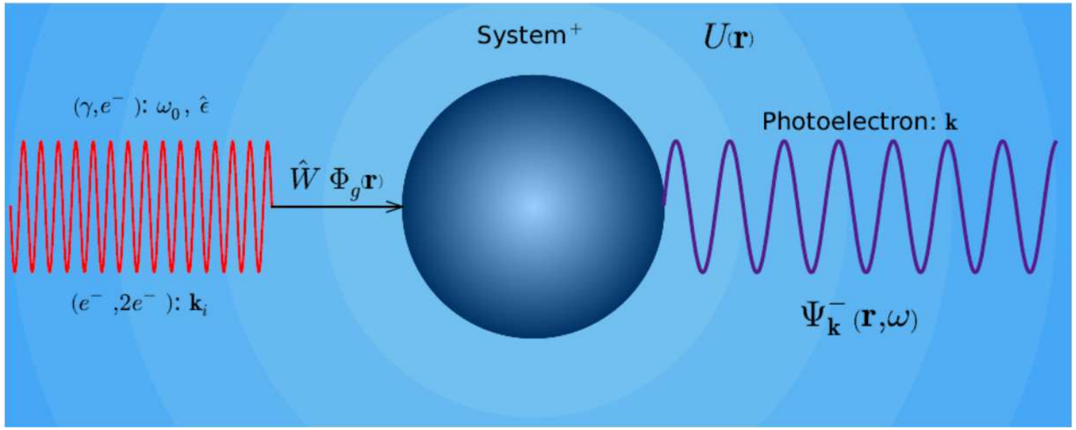
For the first time since 1999
two ab initio theories agree between each other (GSF and CCC)



$E_2=E_3=4$ eV
$\theta_2=135°$

$E_2=E_3=4$ eV
$\theta_2=315°$

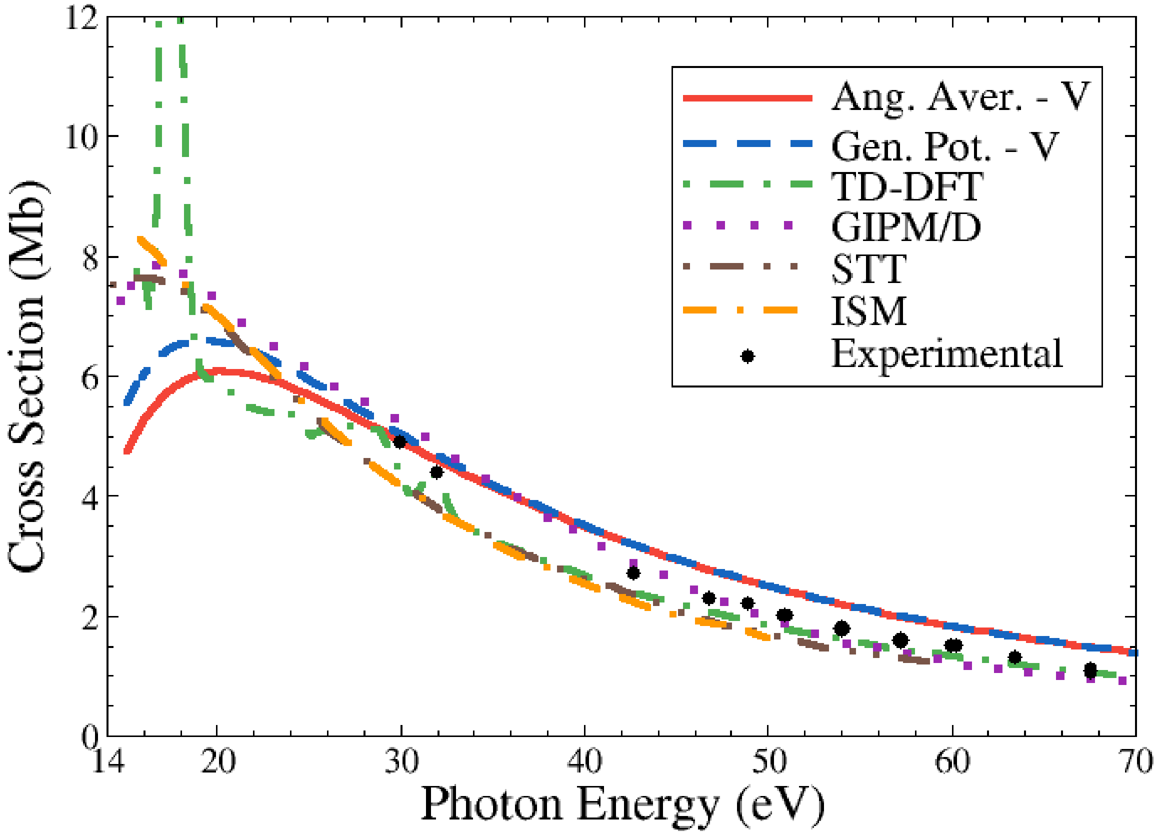
3) Single photoionization of molecules



- Multicenter nature, and generally non-central potential $U(\vec{r})$
- Orientation of the molecule

Need to describe accurately:

- the initial target
- the photoelectron (single continuum)



Inner valence

$3a_1$ of H_2O

Sturmian approach within

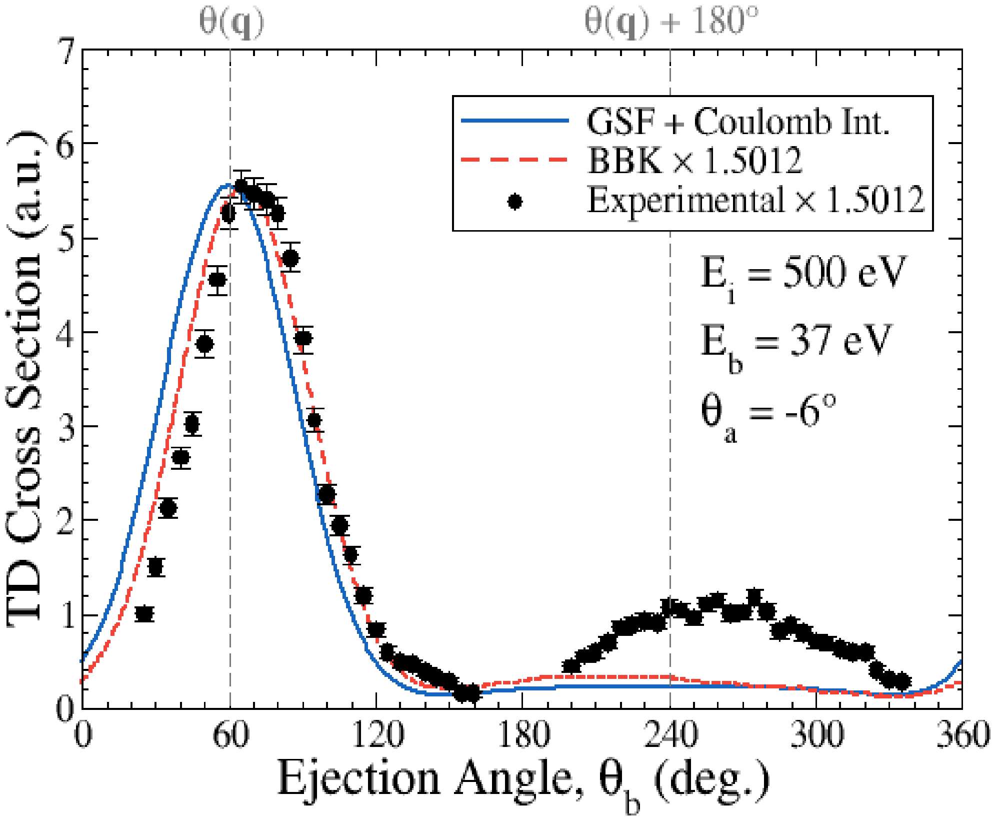
- one particle approx.
- OCE, FC, BO approx.
- model potential (static exchange approx.)
- first order perturbation theory

4) Single ionization of molecules by electron impact

$e^- + A \rightarrow A^+ + e^- + e^-$

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

TDCS



Outer valence

$1t_2$ of CH_4

Expt Data on relative scale

Take home message

Two-body Generalized Sturmian Functions (GSF) :

- **form a complete basis set {$S_n(r)$}**
- **are very efficient because appropriate boundary conditions can be imposed to the basis elements**
  - **→ concentrate in the region where it is interesting**
  - **→ smaller computational resources when compared to other benchmark numerical methods**
- **are able to build up efficiently the three-body wavefunctions**

Same tool for BOUND and CONTINUUM

REVIEW: Gasaneo et al, Adv. Quantum Chem., 2013

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Thank you for your attention !