Interaction of photons, positrons and electrons with molecules

Group of Atomic and Molecular Physics

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·Outline

- Where are we?
- Who are we?
- What do we do?
- Why do we do it?
- How do we do it?
- What do we get with it?

Where are we?





Araucária Angustifólia

(Paraná pine)



Pinhão (we eat)

Curitiba (kur yt yba = many pines)
Population:1.773.733 people (IBGE/2022)
http://www.curitiba.pr.gov.br/













Who are we?

Group of Atomic and Molecular Physics

Interaction of photons, positrons and electrons with molecules

Professors:

Alessandra de Souza Barbosa
Márcio Henrique Franco Bettega (group leader)
Milton Massumi Fujimoto
Sergio d'Almeida Sanchez
Thiago Corrêa de Freitas

Researchers:

Diego Farago Pastega
Giseli Maria Moreira
Leticia da Silva Maioli
Rafael de Oliveira Lima

Graduate Students (Doctorate):

Edvaldo Bandeira da Silva
Francisco Fernandes Frighetto
Jhenifer Martins Hummel Fófano
Luiz Vitorino dos Santos Dalagnol
Murilo de Oliveira Silva

Graduate Students (Master):

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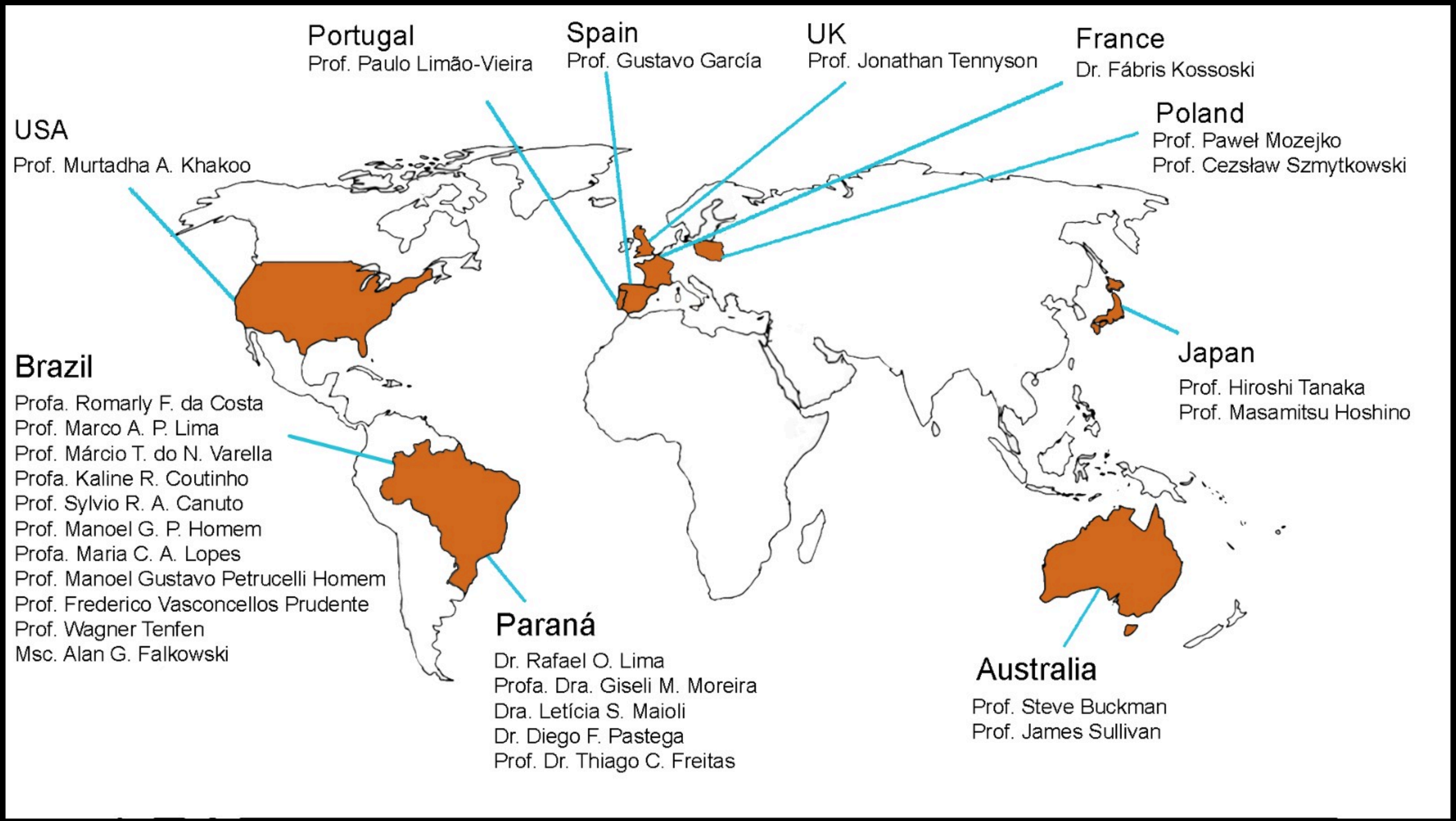
Eduardo Luis Puchalski da Silva Pereira
Levi de Andrade Lima
Pedro Alfieri Schadeck Randi
Valéria Liberti

Undergraduate Students:

Danilo Fernando Schafaschek
Elian Aristides Pinheiro
Gustavo Lanave Silvério
Lucas Nicolas Assad
Maria Gabrielle Goche
Pietra Sautchuk Puppi
Sidnei Guerino Fábris Júnior
Tiago Alexandre Correa

Who are we?

Collaborations



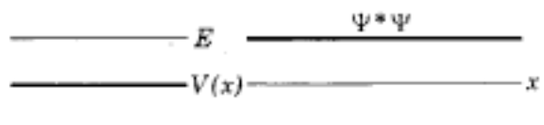
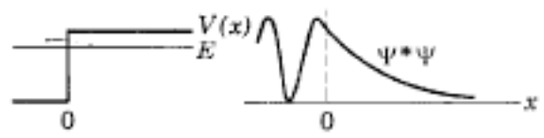
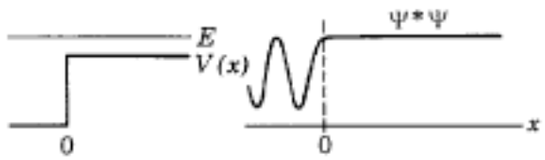
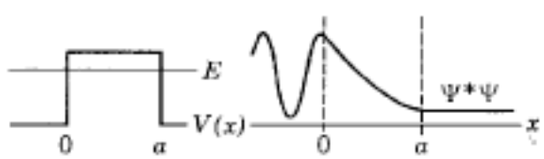
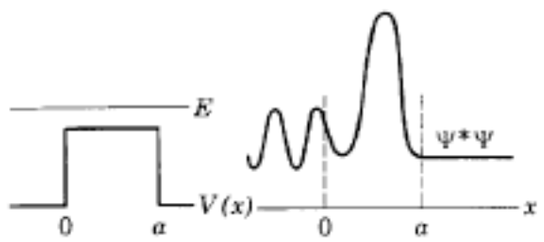
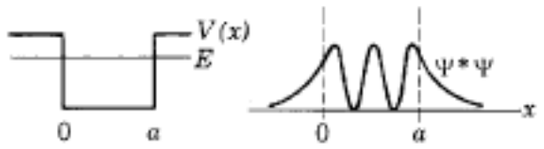
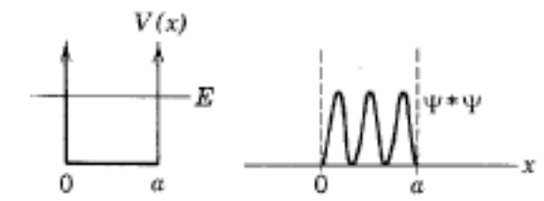
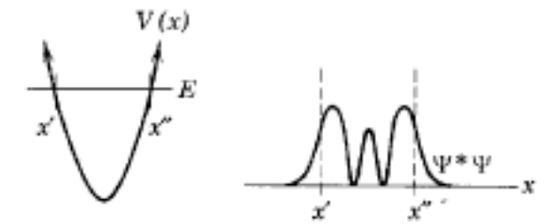
What do we do?

Research: Our group uses computers to study the processes involved in the interaction of photons, positrons and electrons with molecules (in gas phase). Our interests lie in the bound states (ground and electronic excited states) and in the continuum. In particular, we investigate electron and positron collisions with molecules using a variational method for the scattering amplitude. Through the scattering cross sections we are able to access the resonances (transient negative ions) formed during the collision in the case of electron scattering, and also bound and virtual states in the case of electron and positron scattering. We also investigate interactions of photons with molecules in order to help in the interpretation of the experimental VUV absorption spectra of molecules (excited states) and also molecular photoionization (continuum - also using a variational method).

What do we do?



Table 6-2. A Summary of the Systems Studied in Chapter 6

Name of System	Physical Example	Potential and Total Energies	Probability Density	Significant Feature
Zero potential	Proton in beam from cyclotron			Results used for other systems
Step potential (energy below top)	Conduction electron near surface of metal			Penetration of excluded region
Step potential (energy above top)	Neutron trying to escape nucleus			Partial reflection at potential discontinuity
Barrier potential (energy below top)	α particle trying to escape Coloumb barrier			Tunneling
Barrier potential (energy above top)	Electron scattering from negatively ionized atom			No reflection at certain energies
Finite square well potential	Neutron bound in nucleus			Energy quantization
Infinite square well potential	Molecule strictly confined to box			Approximation to finite square well
Simple harmonic oscillator potential	Atom of vibrating diatomic molecule			Zero-point energy

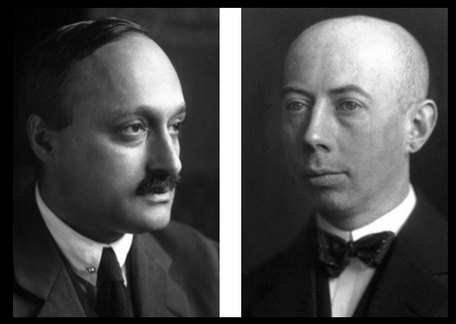
Continuum

Continuum and bound states

Bound states (átomo de H)

What do we do?

(Nobel prize 1925)



Experiência de Frank-Hertz (James Franck e Gustav Hertz)



Esse é um experimento de excitação eletrônica por impacto de elétrons



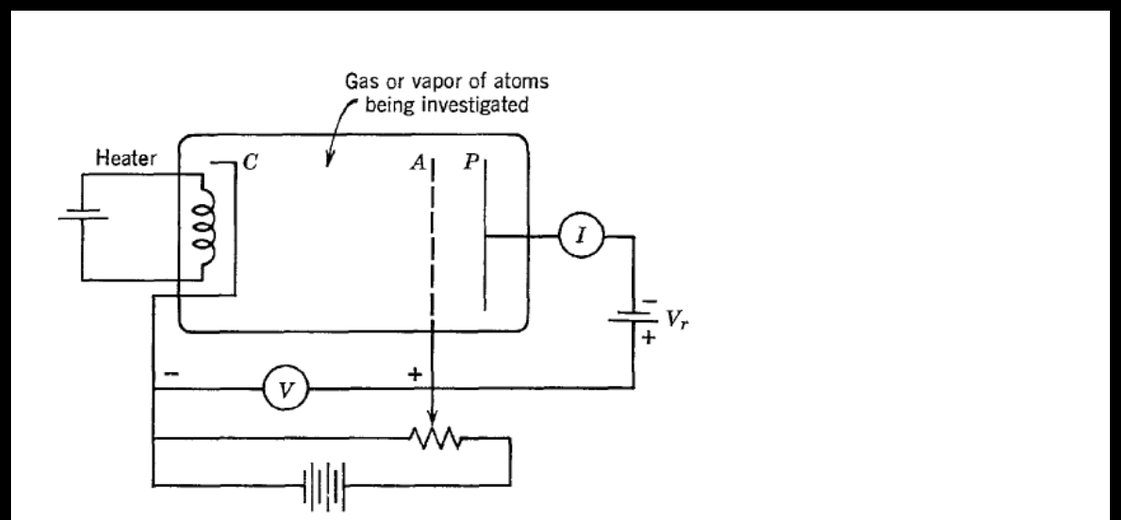


Figure 4-13 Schematic of the apparatus used by Franck and Hertz to prove that atomic energy states are quantized.

Quantização da energia:

Primeiro estado excitado: 4,9 eV acima do estado fundamental
Segundo estado excitado: 6,7 eV acima do estado fundamental
Potencial de ionização: 10,4 eV

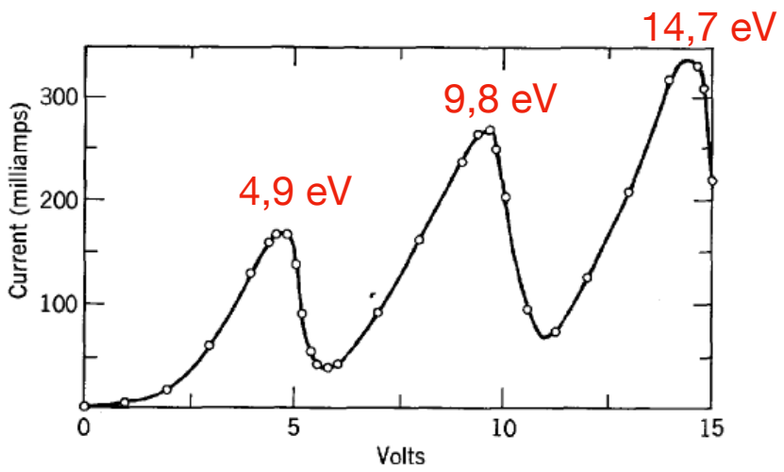


Figure 4-14 The voltage dependence of the current measured in the Franck-Hertz experiment.

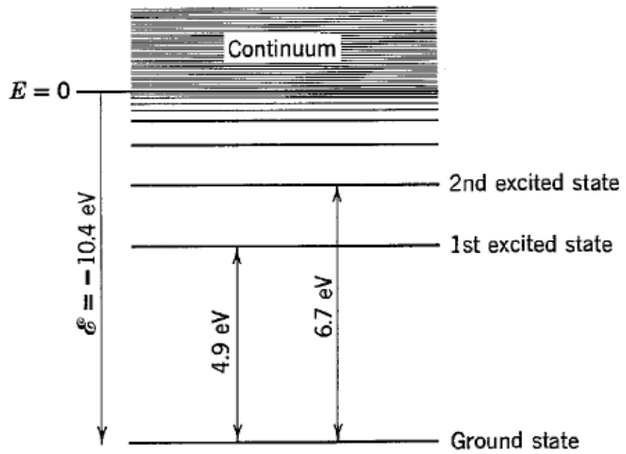
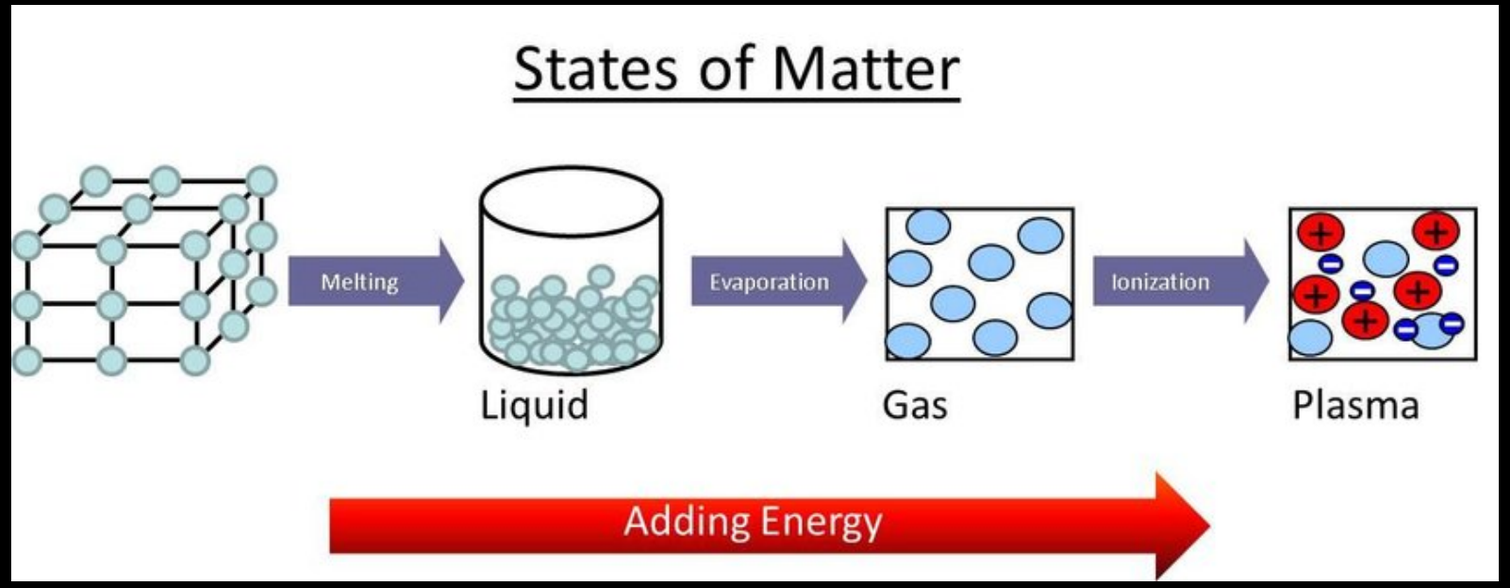


Figure 4-15 A considerably simplified energy-level diagram for mercury. Lying above the highest discrete energy level at $E = 0$ is a continuum of levels.

Motivation - plasma processing

✓"Why study plasma processing? Because we can't get along without computer chips and mobile phones these days."
Lecture Notes on Principles of Plasma Processing, F. F. Cheng, J. P. Chang, Plenum/Kluwer Publishers 2002

Plasma: matter heated beyond its gaseous state (atoms/neutral molecules neutras, ions, radicals, free electrons).

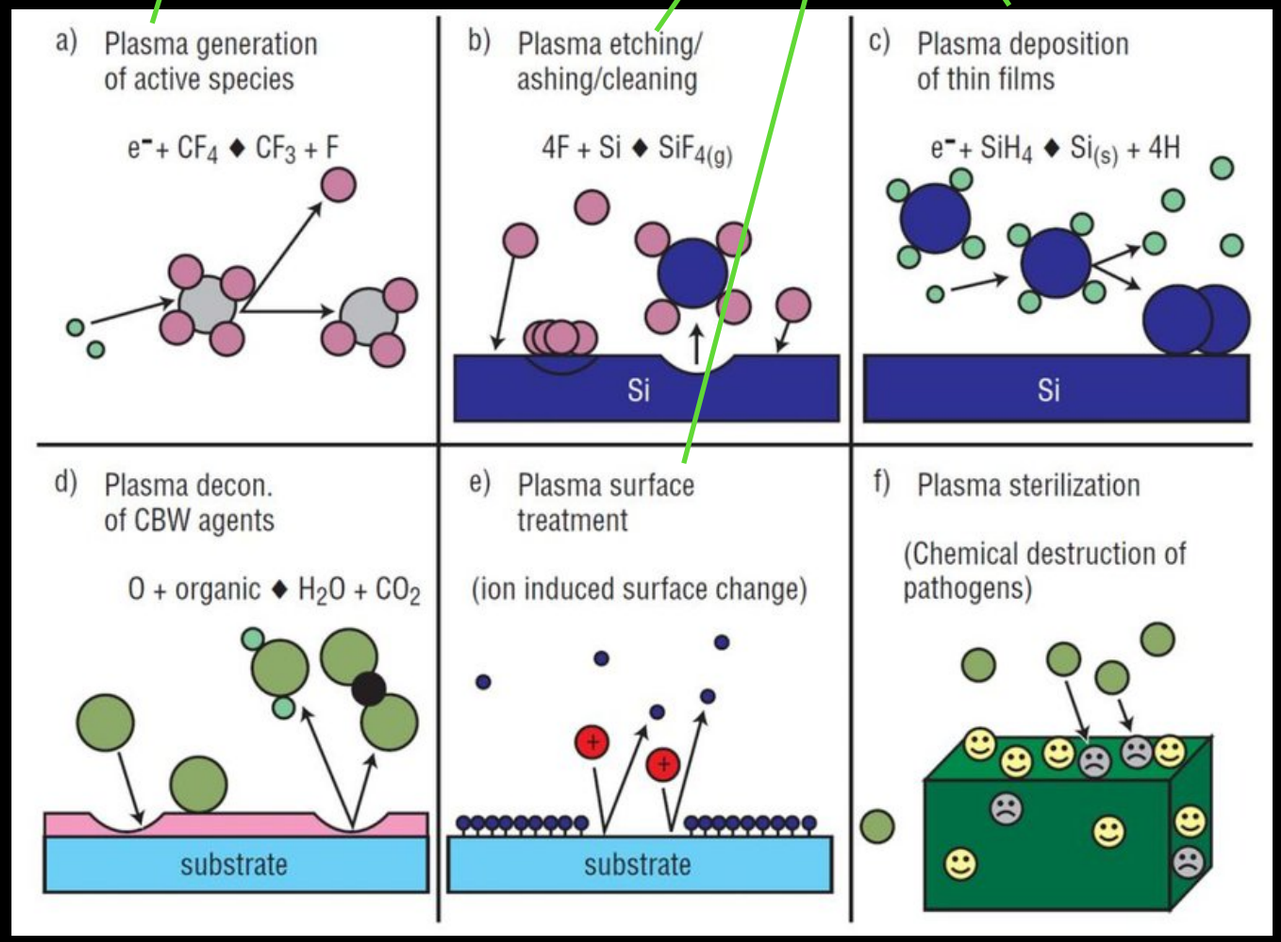


Our interest in is cold plasmas - electron temperature (at least) 10.000K (1eV = 11.600K).

Motivation - plasma processing

One can compute the energetics (thermodinamic thresholds) for these fragmentation processes

Important processes in microelectronic industry



S. Selwyn, H.W. Herrmann, J. Park, and I. Henins, Contrib. Plasma Phys. vol (2001) 6, 610–619

Franziska Grzegorzewski, Von der Fakultät III – Prozesswissenschaften der Technischen Universität Berlin zur Erlangung des akademischen Grades, 2011

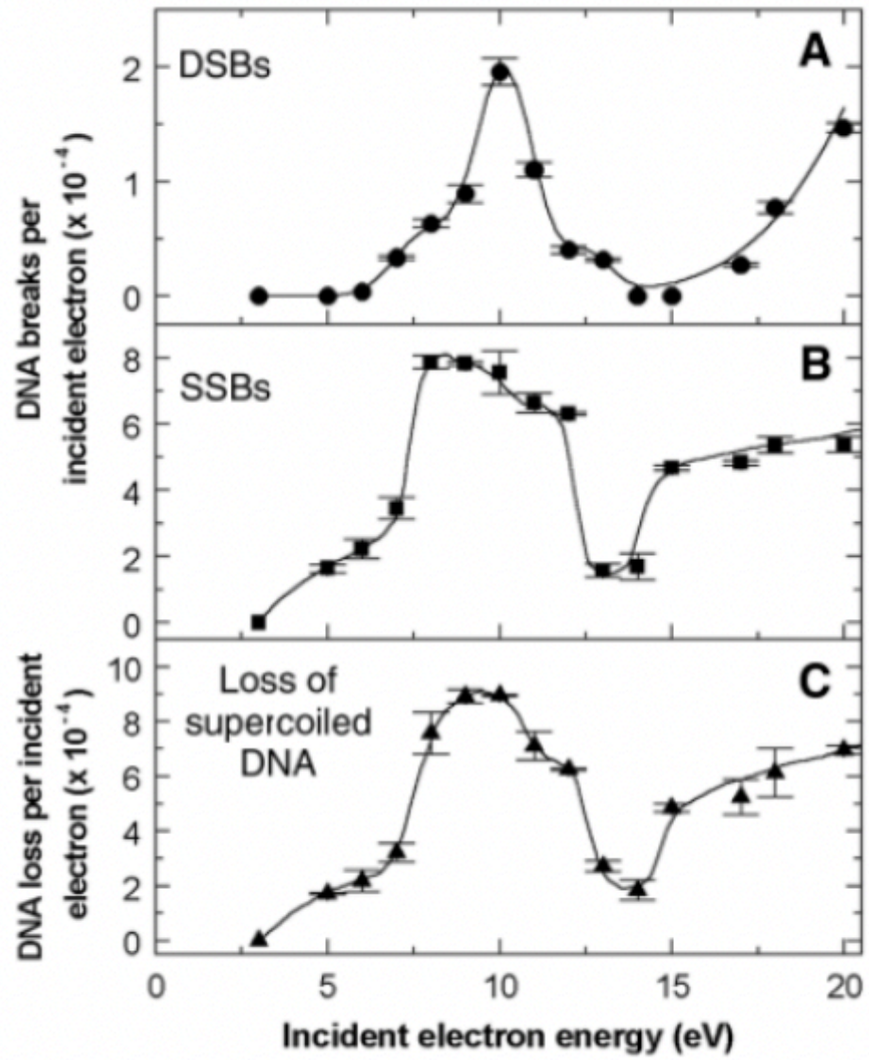
Motivation - DNA

3 MARCH 2000 VOL 287 SCIENCE 1658

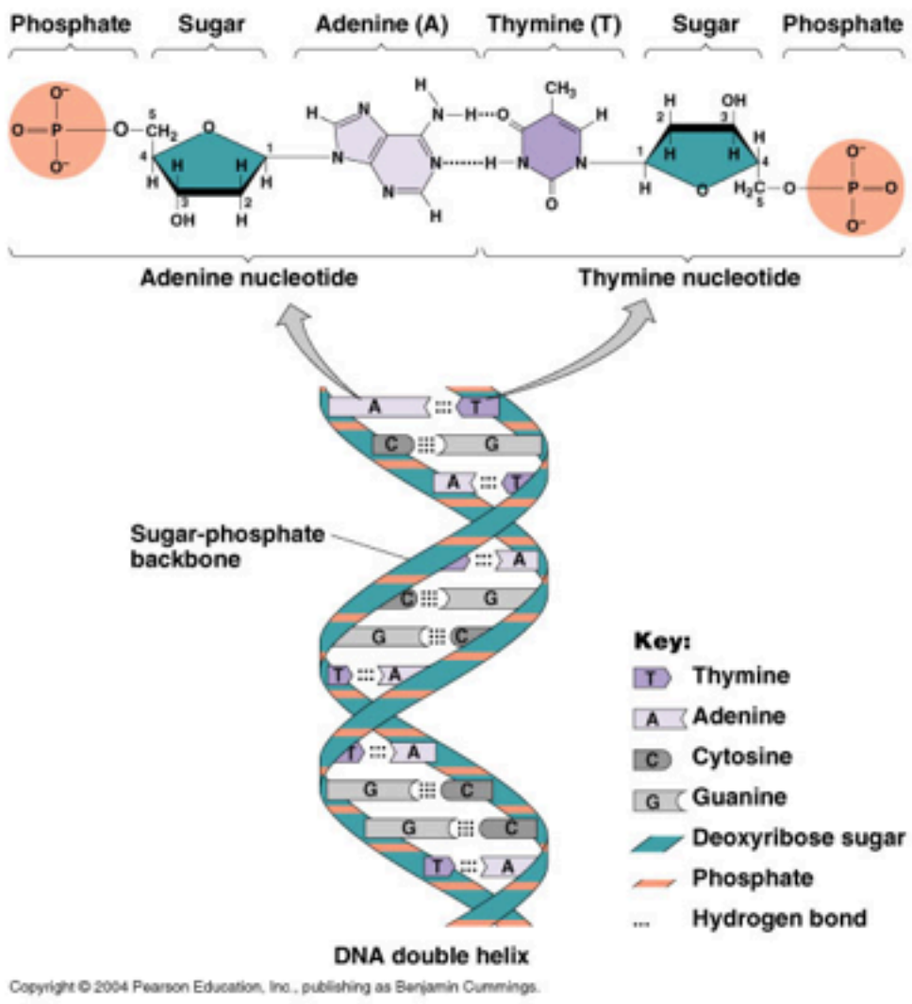
Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20 eV) Electrons

Badia Boudaïffa, Pierre Cloutier, Darel Hunting, Michael A. Huels,* Léon Sanche

DNA damage - single- and double-strand breaks in DNA are caused by secondary low-energy (up to 20 eV) electrons generated by the ionizing radiation (X-rays, γ-rays, β-rays).



Motivation - DNA



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✓ DEA to DNA initiates with the formation of a transient negative ion (shape, core-excited, or Feshbach resonances) ⟶ electron-molecule collision problem (gas phase).

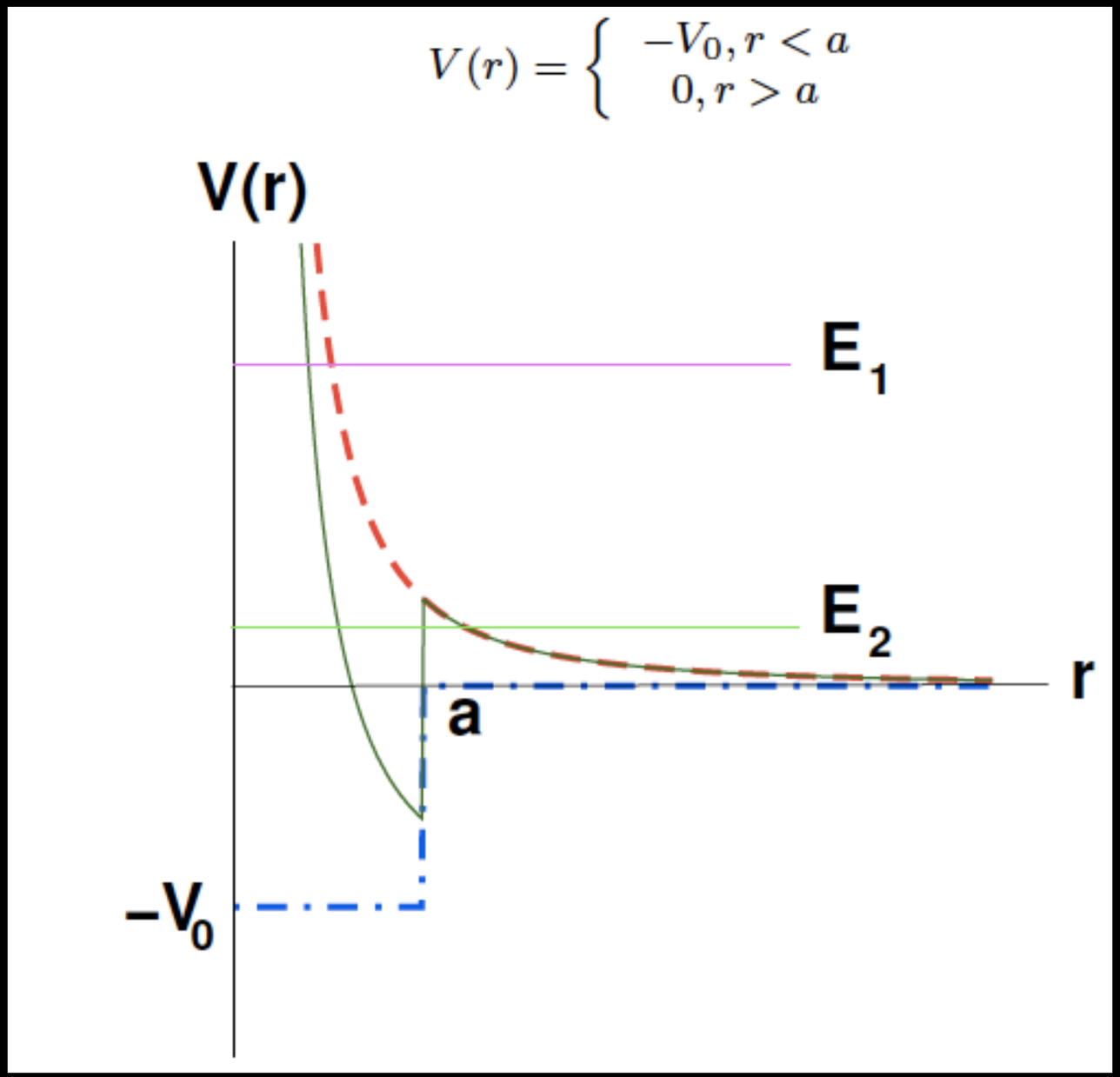
✓ Solvation: systems with water.

✓Gas phase ⟶ condensed phase: systems with hydrogen bonds.

✓ Shape resonance: the continuum electron occupies an empty MO (LUMO).

Motivation - DNA

Ressonância de forma



Motivation - DNA

VOLUME 93, NUMBER 6 PHYSICAL REVIEW LETTERS week ending 6 AUGUST 2004

DNA Strand Breaks Induced by 0–4 eV Electrons: The Role of Shape Resonances

Frédéric Martin,[1] Paul D. Burrow,[2] Zhongli Cai,[1] Pierre Cloutier,[1] Darel Hunting,[1] and Léon Sanche[1,*]

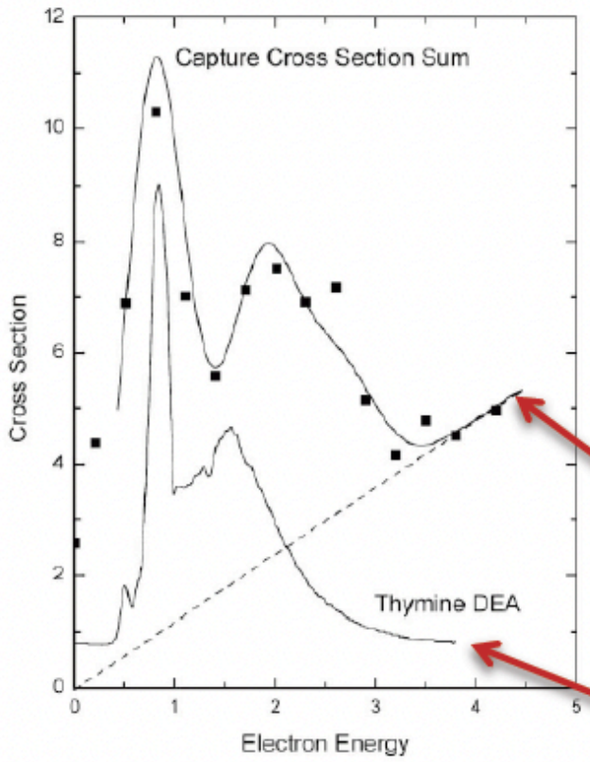


FIG. 2. Lower curve: the relative DEA cross section of thymine [10(b)], shifted by 0.2 eV to lower energy. Upper curve: A model of the electron capture cross section of DNA as a function of electron energy based on the resonance energies of the bases and their widths determined in gas-phase scattering studies. The curve has been shifted to higher energy by 0.41 eV, normalized to the SSB data and a linearly increasing background (dashed line) added. Closed squares: SSB yields from Fig. 1.

✓ The π^* shape resonances initiate the DEA to DNA.

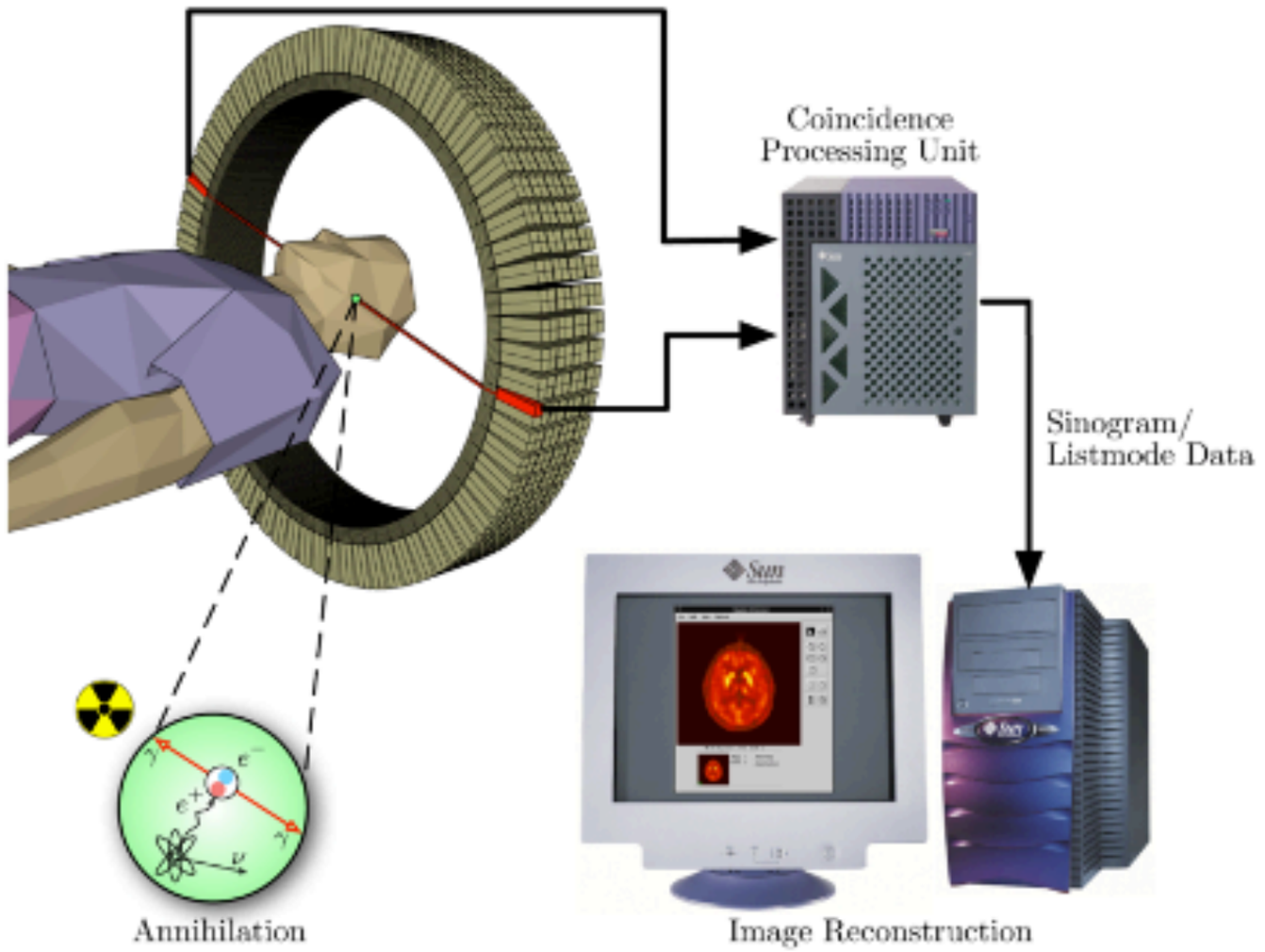
✓ Results obtained in gas-phase can help in the understanding of processes that occur in consensed phase.

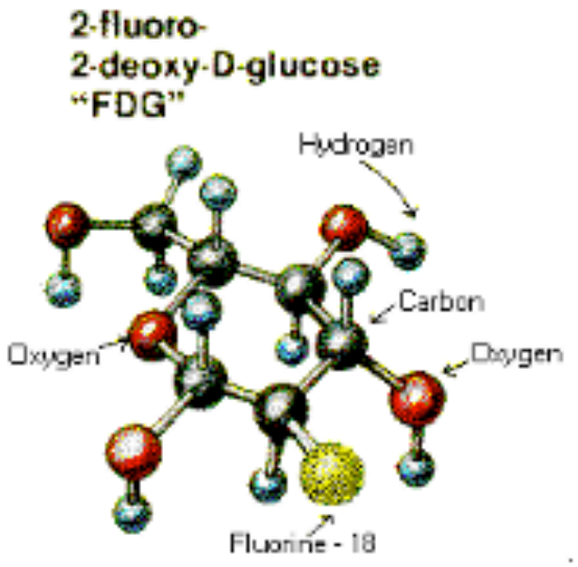
Model using resonances locations computed in gas-phase.

Gas-phase.

Motivation

✓ Positron Emission Tomography: imaging technique





What do we do? Why do we do it? How do we do it?

Photon-molecule interaction:

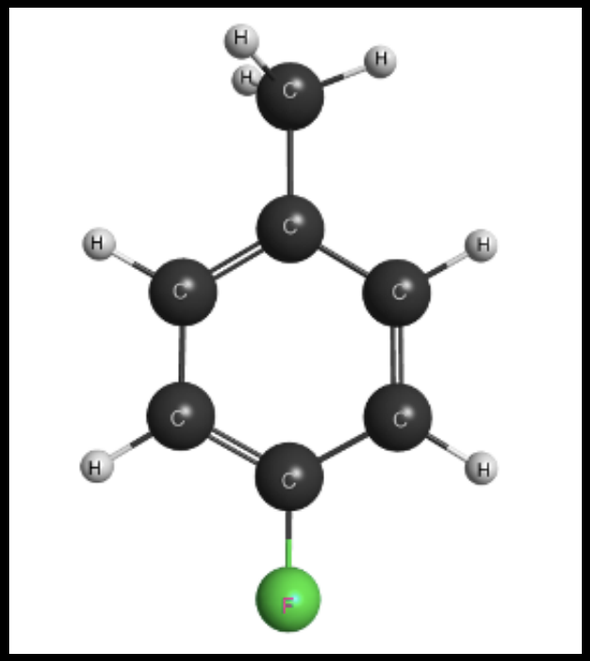
Main motivation: Plasma processing, prebiotic and biological molecules, fuels

Interest: Molecular photoionization, VUV spectra, electronic (ground and excited - singlet) states and vibrational excited states

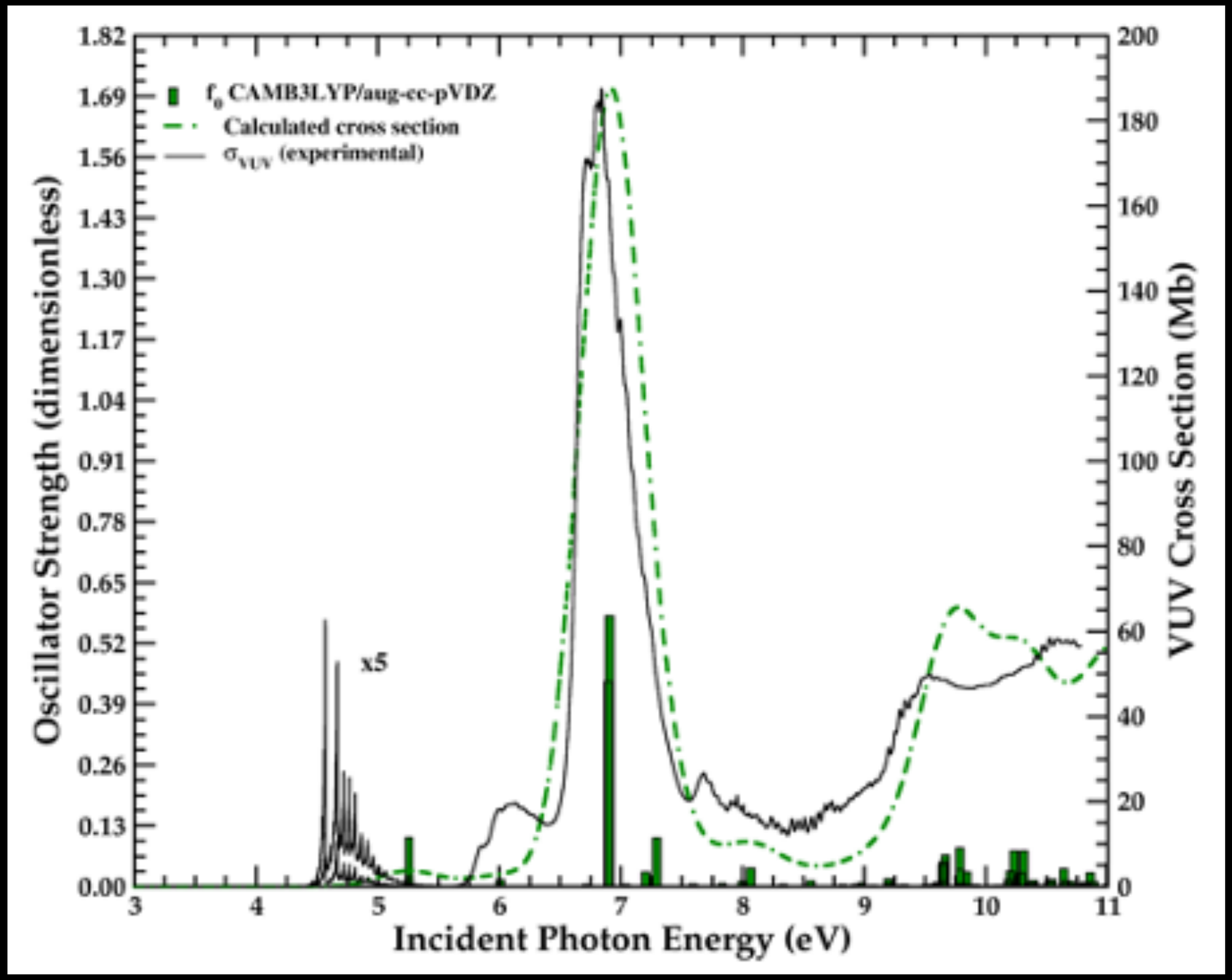
Theory: Schwinger iterative variational method (photoionization), electronic structure calculations (Hartree-Fock, DFT, TDDFT, EOM-CCSD)

VUV absorption spectra - electronic excited states calculations

4-fluorotoluene (4-C_7H_7F)



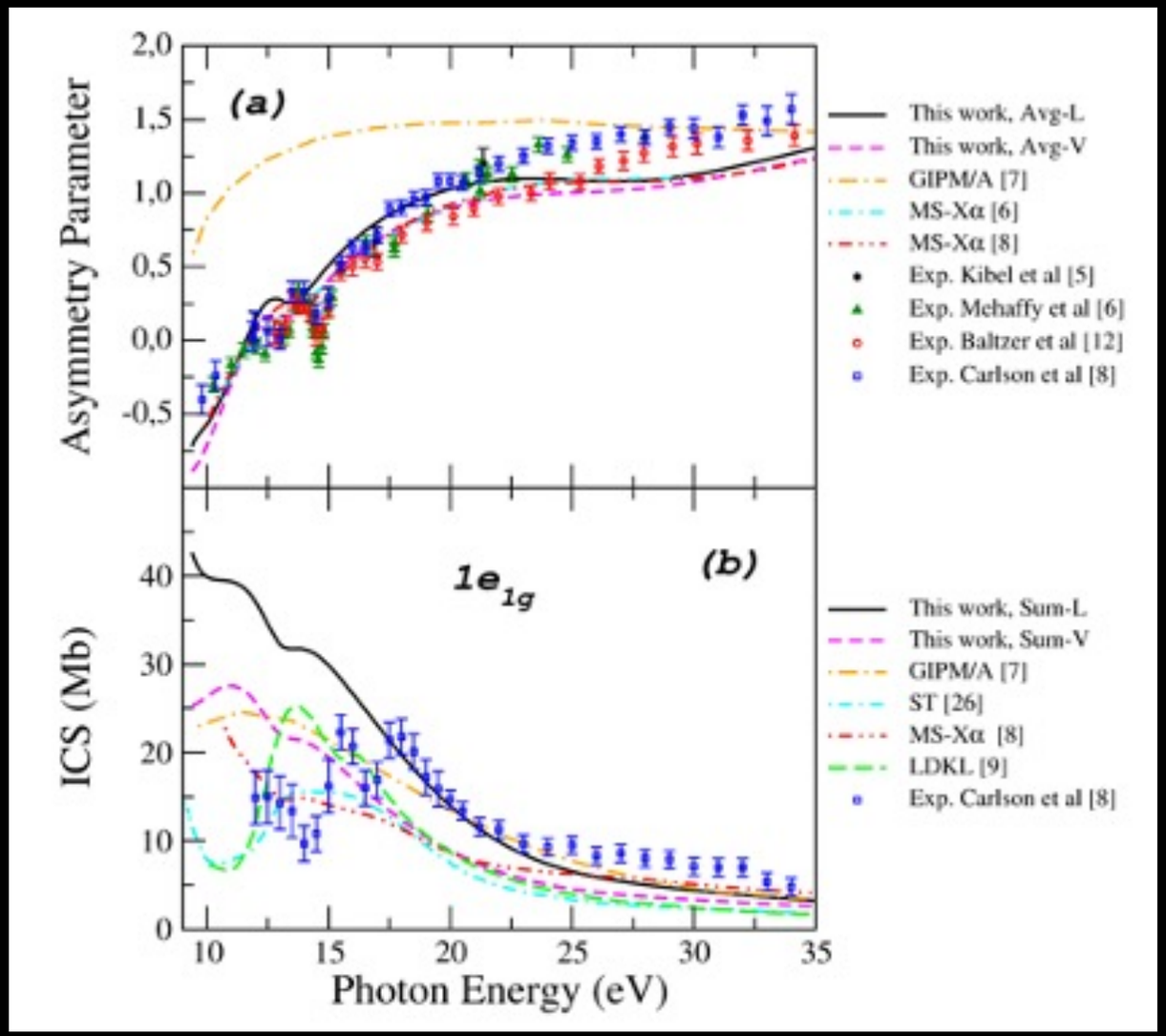
Basis set: aug-cc-pVDZ
Functional: CAMB3LYP
TDDFT level of theory
95 excited states

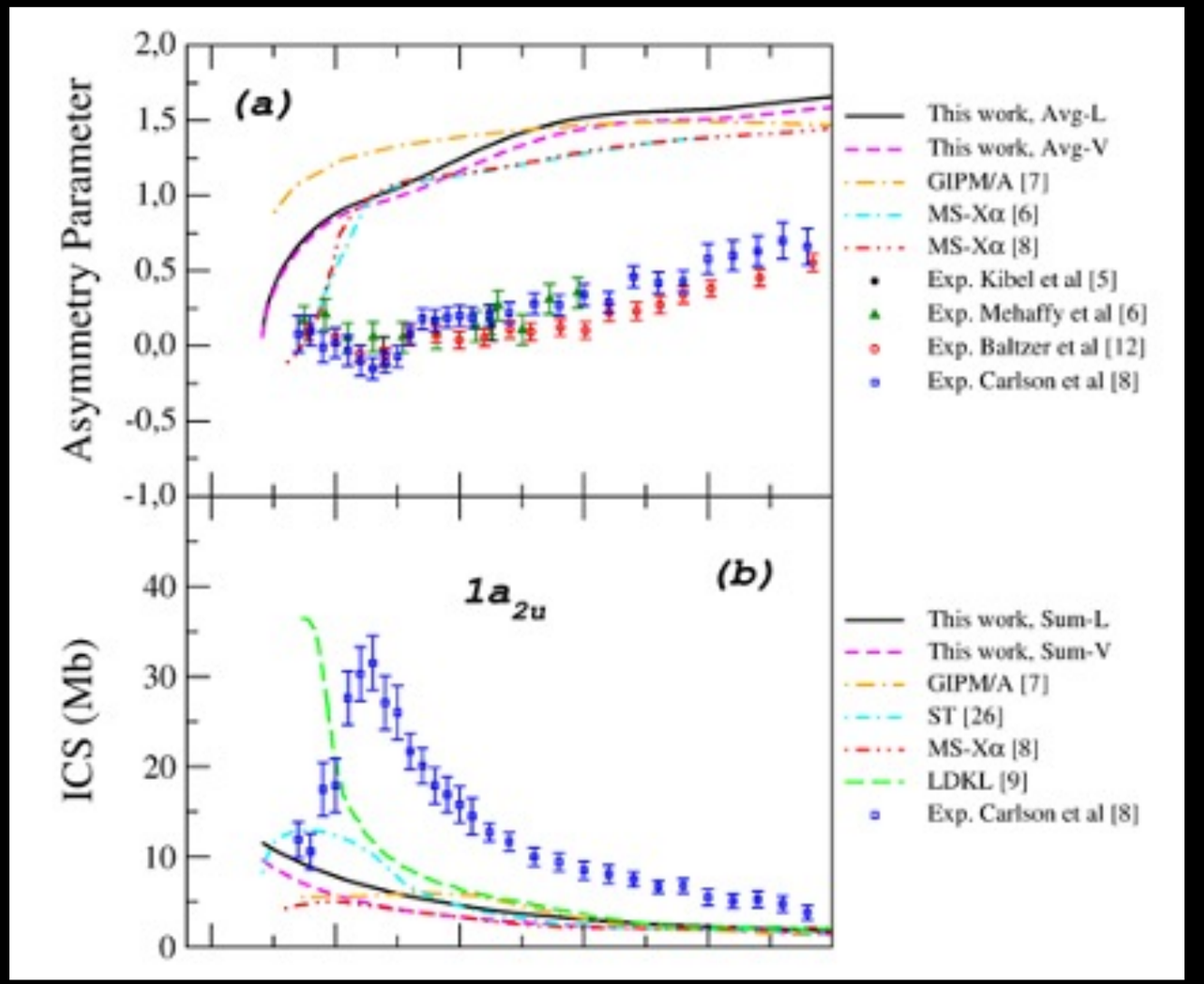


L.V.S Dalagnol, M.H.F. Bettega, S. V. Hoffmann, N. C. Jones, A.S. Barbosa, P. Limão-Vieira (unpublished)

$$\sigma(E) = \frac{\hbar q_e^2}{2m_e c\epsilon_0}\frac{\pi}{\Gamma\sqrt{2\pi}}\sum_{n=1}^{N_{\text{excited}}} f_{0n}^{i\to f}\exp\left[-\frac{(E-E_n)^2}{2\Gamma^2}\right] \qquad f_0^{i\to f} \equiv \frac{2m_e}{3\hbar^2 q_e^2}(E_f - E_i)\left|\langle\Psi_i|\vec{\mu}|\Psi_f\rangle\right|^2$$

Photoionization of Benzene Molecules
Is Benzene a benchmark ?





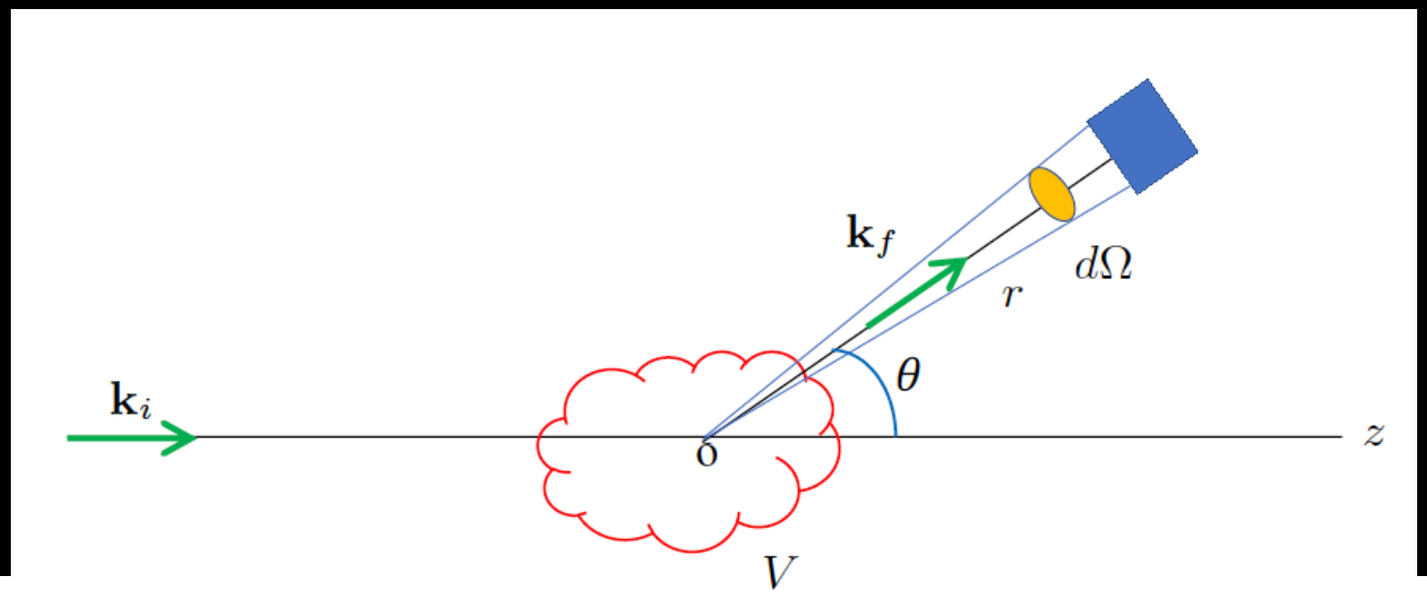
Theory agrees with theory/ Experiment agrees with experiment

How to approximate Theory from experiment?
- correlation, multichannel, vibrational motion

M. H. Ribas and M. M. Fujimoto (unpublished)

Espalhamento de pósitrons/elétrons por moléculas

Ilustração: espalhamento por um potencial (apenas canal elástico)



$$\psi^{(+)}_{\mathbf{k}_i}(\mathbf{r}) \xrightarrow[|\mathbf{r}|\to\infty]{} N\left\{e^{i\mathbf{k}_i\cdot\mathbf{r}} + f_k(\theta,\phi)\frac{e^{ikr}}{r}\right\}$$

$$\frac{d\sigma}{d\Omega}(k;\theta,\phi) = \frac{|\mathbf{j}_{out}|r^2 d\Omega}{|\mathbf{j}_{inc}|d\Omega} = |f_k(\theta,\phi)|^2$$

Problema de muitos corpos - interações de coulomb (atrativa para elétrons e repulsiva para pósitrons), troca (partículas idênticas - repulsiva) e polarização (atrativa)

Método multicanal de Schwinger (método variacional para a amplitude de espalhamento)

What do we do? Why do we do it? How do we do it?

Positron-molecule collision:

Main motivations: Plasma processing, biological molecules, PET scan

Interest: Elastic and inelastic scattering, multichannel coupling effect (singlet excited states), model potential for polarization effects

Theory: Schwinger multichannel method (variational method for the scattering amplitude), electronic structure calculations

How do we do it? -The Schwinger multichannel method

(e^-) K. Takatsuka and V. McKoy, PRA 24, 2473 (1981); ibid PRA 30, 1734 (1984)
(e^+) J. S. E. Germano and M. A. P. Lima, Phys. Rev. A 47, 3976 (1993).

- Variational approach for the scattering amplitude

- Formulated for applications to low-energy electron- and positron-molecule collisions

- Capable of addressing important aspects of these collisions as:
  -exchange interactions (*ab initio*)
  -effects arising from the polarization of the target by the incident electron/positron (*ab initio*): considering only single (virtual) excitations
  -electronic excitation (multichannel coupling): electronic excited states described at the MOB-SCI approach (single excitations - FSCI quality)

- (e^-) Pseudopotentials of Bachelet, Hamann and Schlüter [PRB 26, 4199 (1982)].

M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, PRA 47, 1111 (1993).

What do we do? What do we get with it?

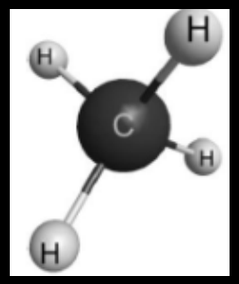
What are we missing?

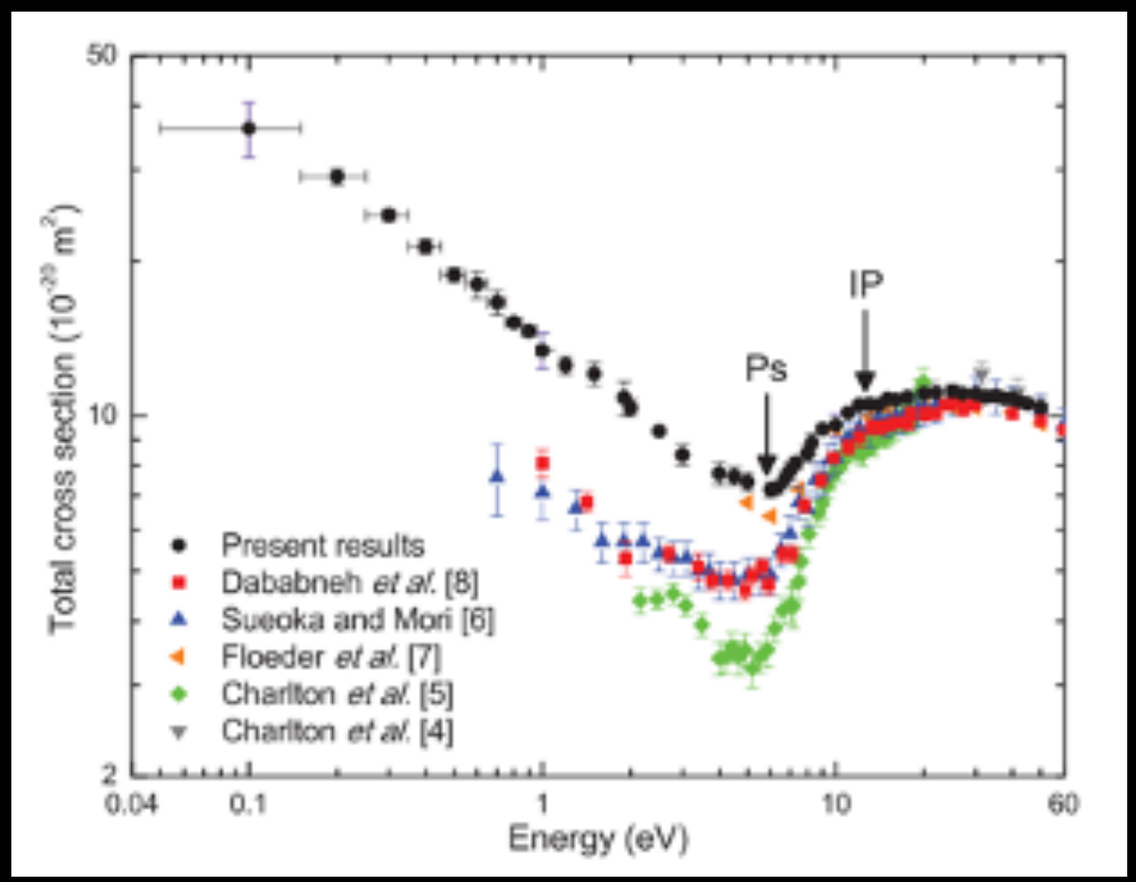
Experiment X experiment; experiment X theory; theory X theory

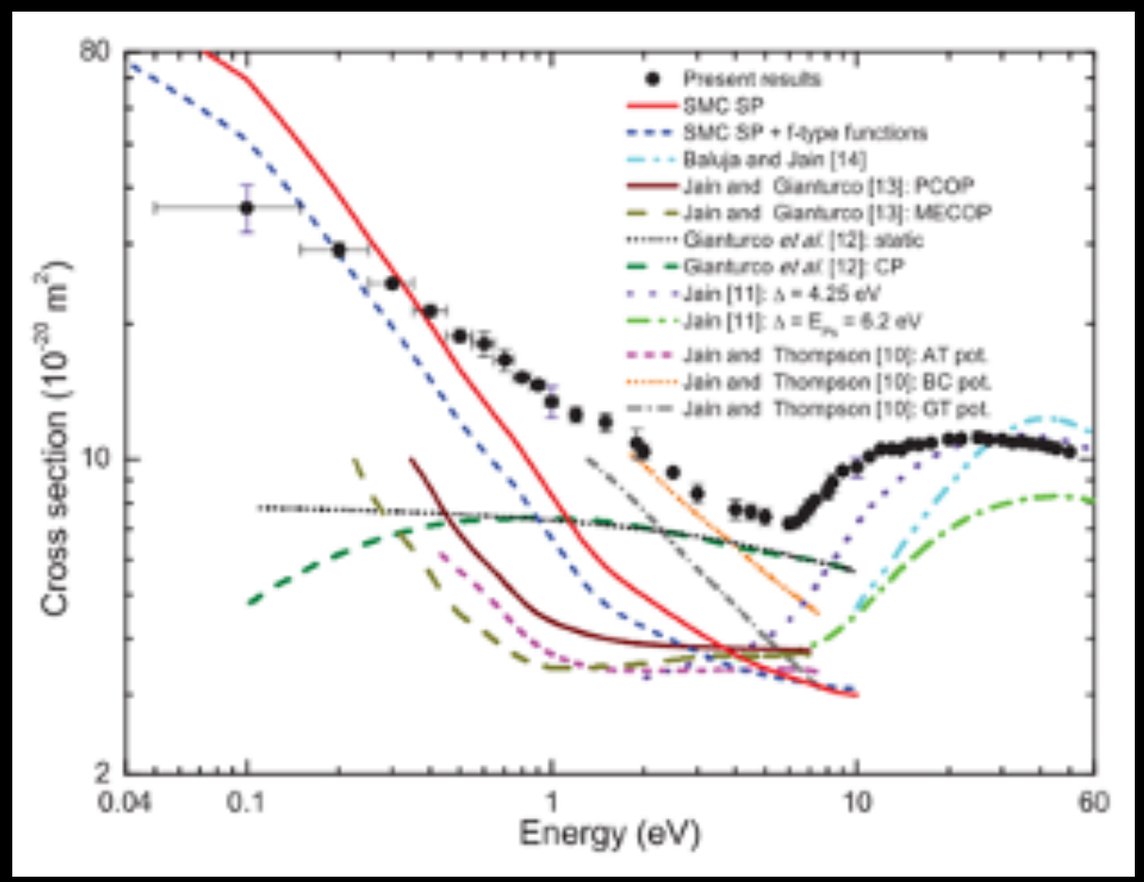
PHYSICAL REVIEW A **85**, 012707 (2012)

Positron scattering from methane

A. Zecca,[1] L. Chiari,[1,2] E. Trainotti,[1] A. Sarkar,[3] S. d'A. Sanchez,[4] M. H. F. Bettega,[4] M. T. do N. Varella,[5] M. A. P. Lima,[6] and M. J. Brunger[2,7]







Challenges for *ab-initio* calculations: polarization, Ps formation channel (not included)

What do we do? What do we get with it?

Positron-molecule interaction = static (repulsive) + polarization (attractive)

Balance between these two potentials is difficult to achieve.

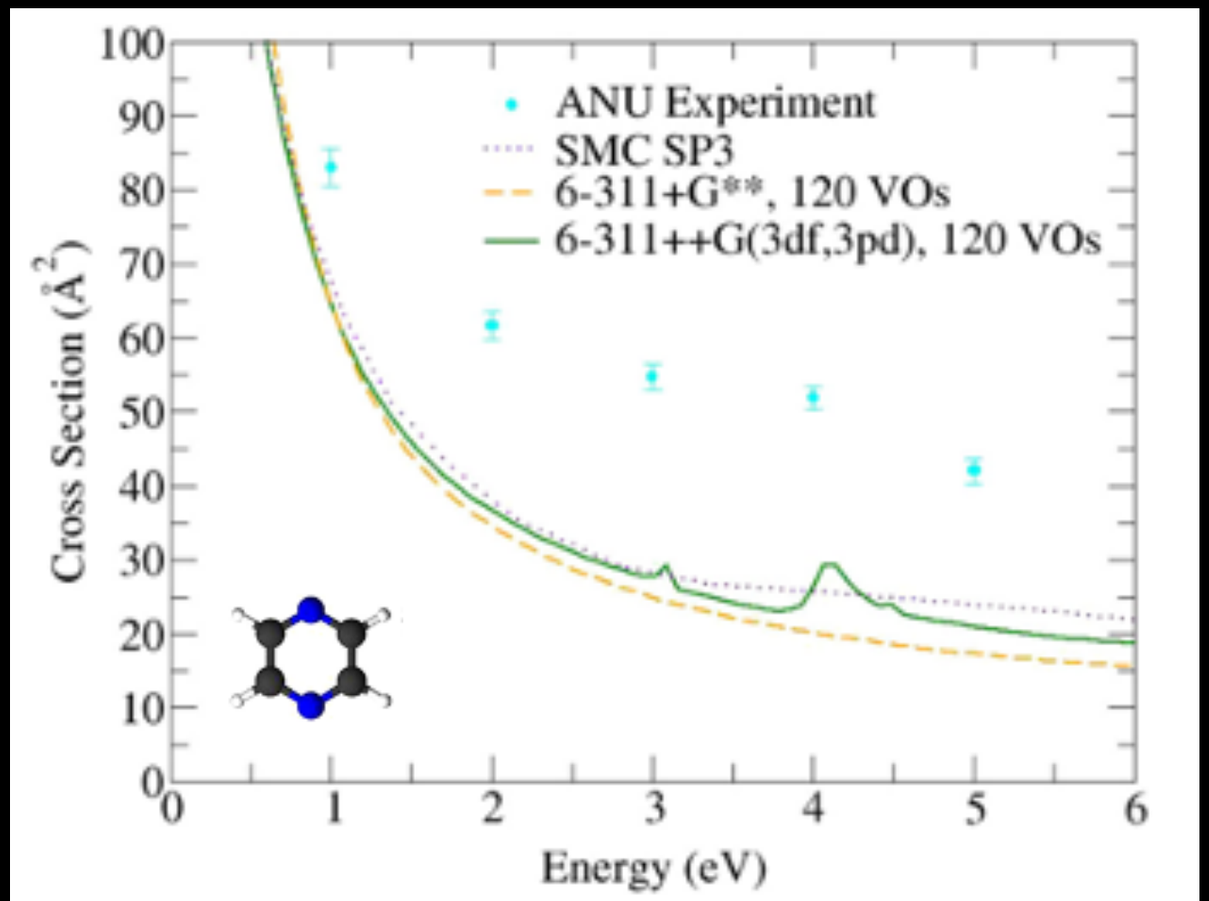


Fig. 6 Integral elastic cross sections for positron scattering from pyrazine using an SP model for the basis set and VOs indicated in the figure. The purple dotted curve corresponds to the SP3 SMC model by Moreira and Bettega [17] and the cyan dots are experimental results from Edwards *et al* [18]

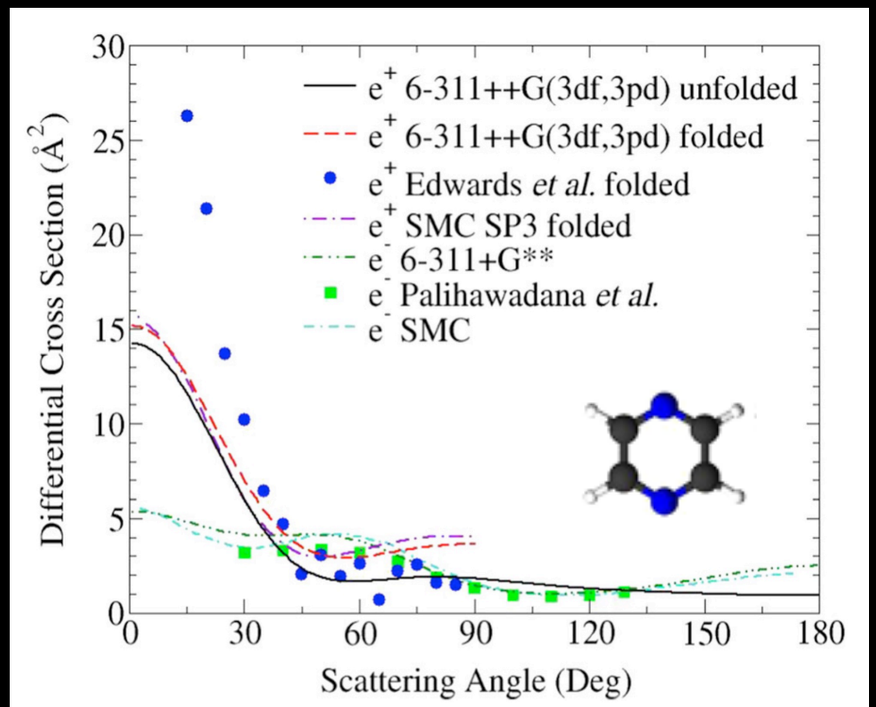


Fig. 4 Elastic differential cross section for electron and positron scattering from pyrazine at 3 eV. Experimental data: blue circles, positron data by Edwards et al. [18] (the measurement at 10° is outside the plotted range); green squares, electron data by Palihawadana et al. [32]. SMC SEP/SP results: purple dot-dashed curve, folded positron data by Moreira and Bettega [17]; cyan dot-dash-dashed curve, electron data by Winstead and McKoy [13]. R-matrix SEP/SP results: green dash-dot-dotted curve, electron scattering; black solid (unfolded) and red dashed (folded) curves, positron data. The basis sets used are indicated in the figure

V. Graves and J. D. Gorfinkiel, Eur. Phys. J D 76, 43 (2022)

What do we do? What do we get with it?

Model polarization potential (cheap)/improving the *ab-initio* description of polarization (too expensive)

Test case: hydrogen molecule

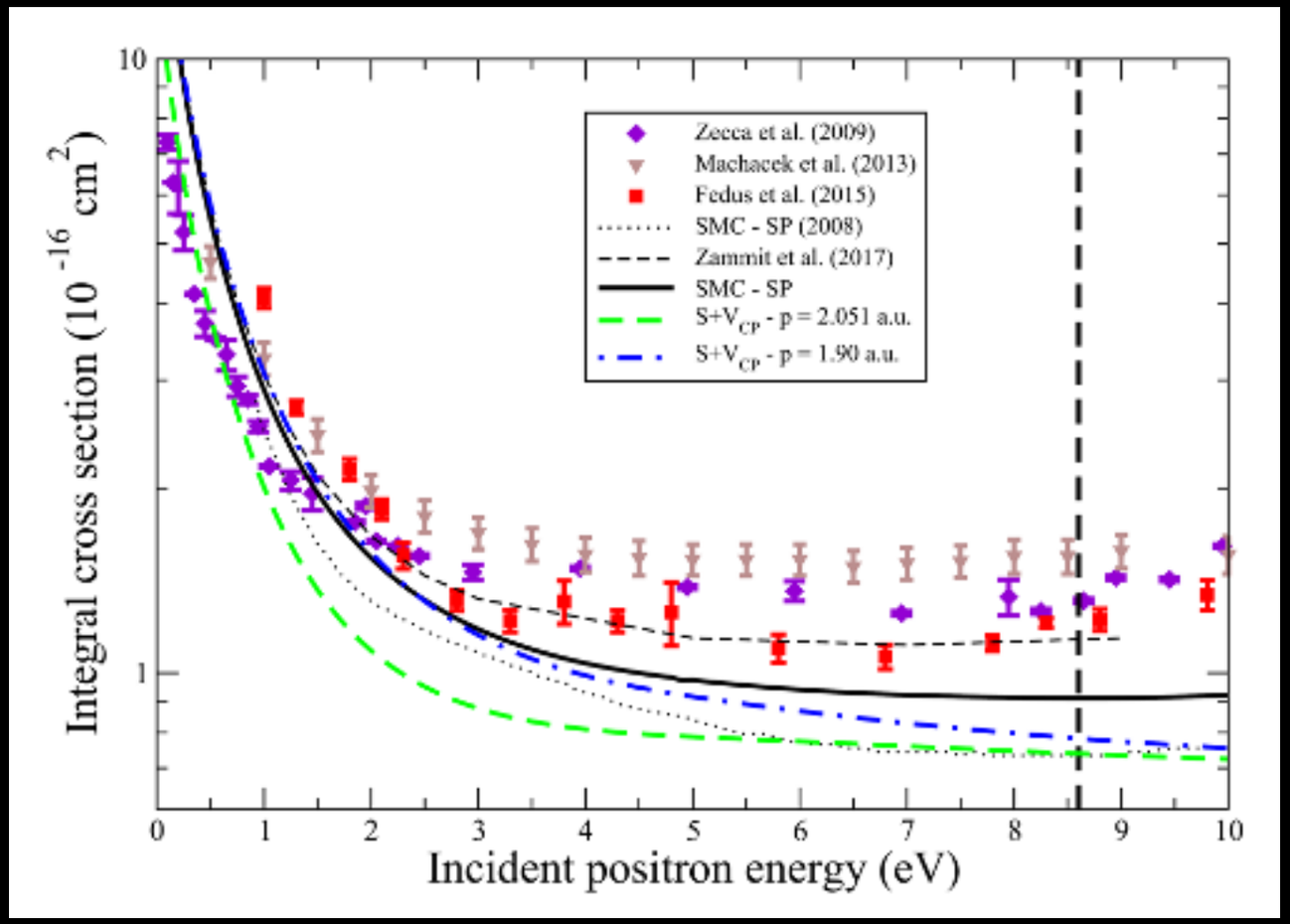


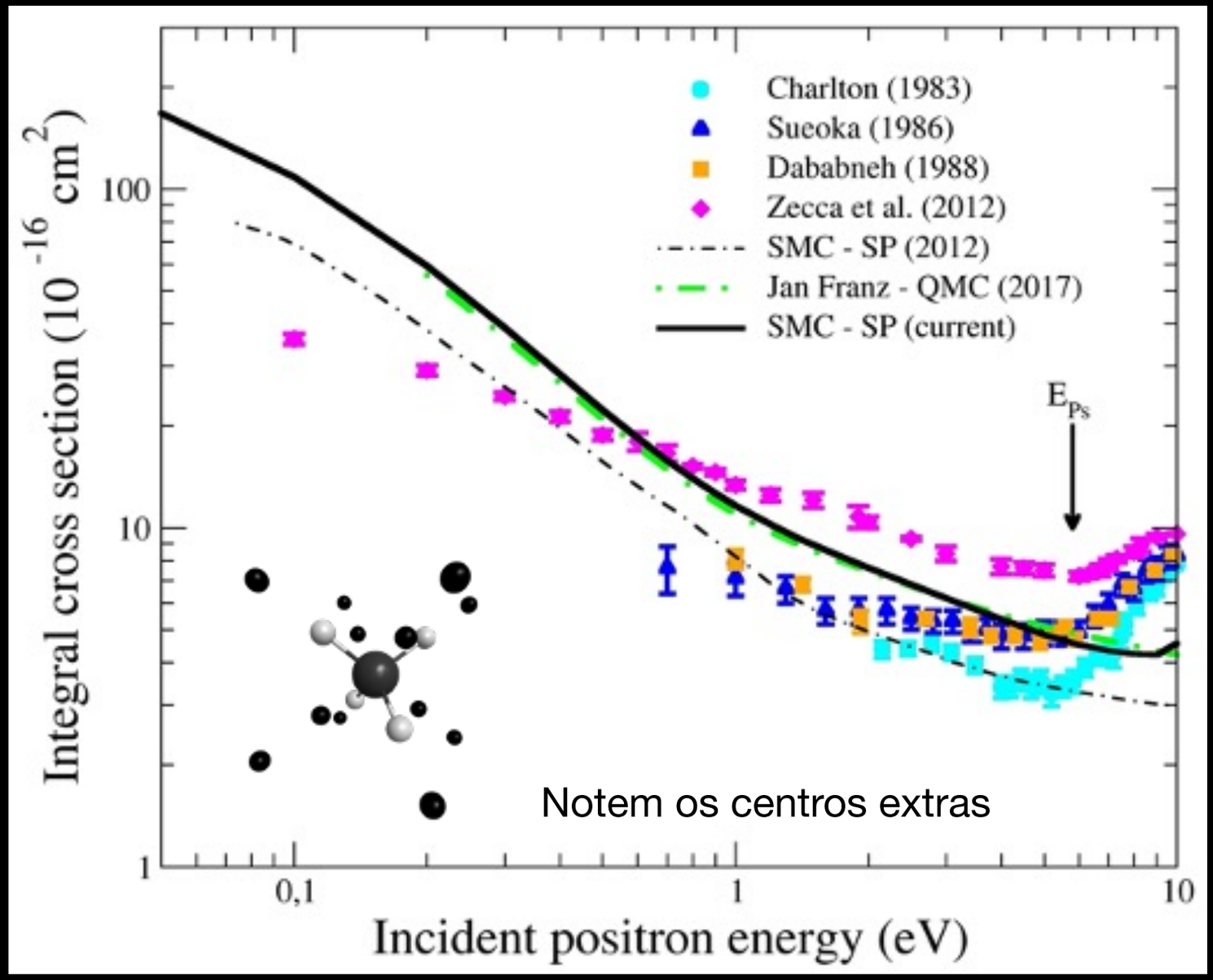
FIG. 5. ICS for positron scattering from hydrogen molecule. Our calculations in the *SP* approximation (solid black line) and $S + V_{CP}$ approximation with the cutting distances $\rho = 2.051$ a.u. (dashed green line) and $\rho = 1.90$ a.u. (dot dashed blue line) are compared with previous calculations of Sanchez *et al.* [55] (dotted black line) and Zammit *et al.* [56] (thin dashed black line) and experimental data from Zecca *et al.* [52] (purple diamonds), Machacek *et al.* [53] (brown down triangels), and Fedus *et al.* [54] (red squares) (the experimental data shown here are uncorrected for the forward scattering). The vertical dashed line corresponds to the energy at which the positronium channel opens ($E_{Ps} = 8.6$ eV) [52].

F. F. Frighetto, A. Souza Barbosa, S. Sanchez, Phys Rev A 108, 012818 (2023)

What do we do? What do we get with it?

Model polarization potential/improving the *ab-initio* description of polarization (too expensive)

Test case: methane (reaching the computational limits)



F. F. Frighetto, A. Souza Barbosa, S. Sanchez, Eur. Phys. J. D **77**, 206 (2023)

What do we do? Why do we do it? How do we do it?

Electron-molecule collision:

Main motivation: Plasma processing, prebiotic and biological molecules, fuels

Interest: Elastic and inelastic scattering, multichannel coupling effect (singlet and triplet excited states), model potential for the ionization channel

Theory: Schwinger multichannel method (variational method for the scattering amplitude), R-matrix method, electronic structure calculations (Hartree-Fock, DFT, post-Hartree-Fock methods, TDDFT)

What do we get with it? - elastic scattering: $TiCl_4$

Joint experimental and theoretical study on electron scattering from titanium tetrachloride ($TiCl_4$) molecule

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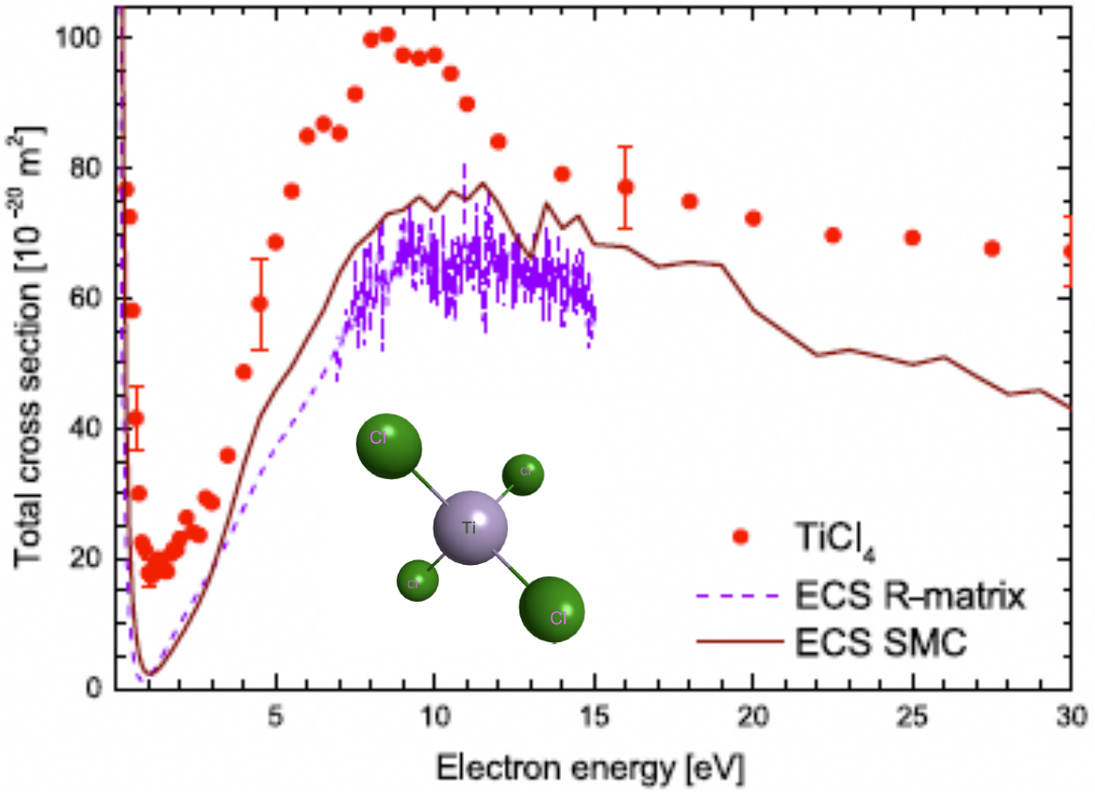
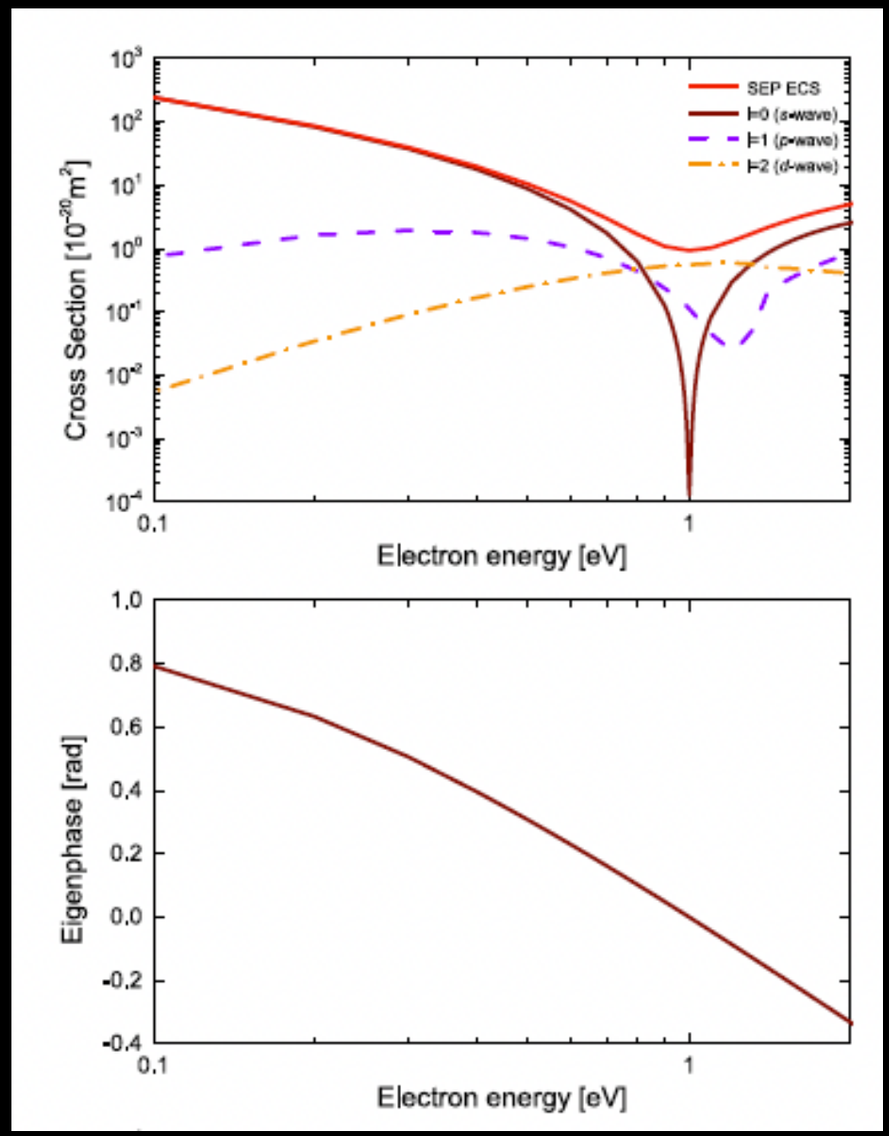


FIG. 6. Comparison of the experimental TCS with results of R-matrix (dashed violet line, ECS R-matrix) and SMC (full wine line, ECS SMC) calculations of the elastic integral cross section.

V=static + exchange + polarization

Ramsauer-Townsend minimum



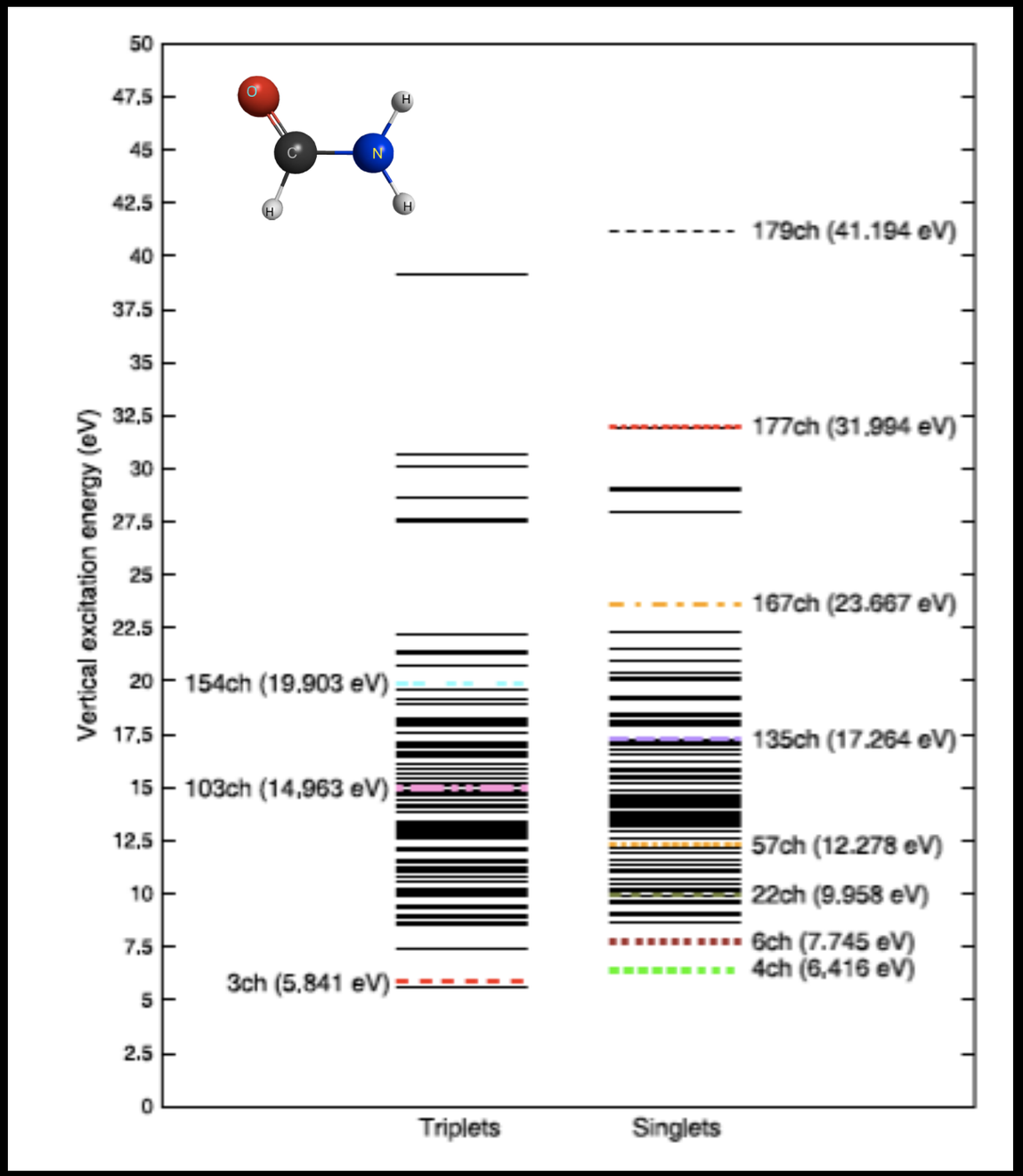
Sharp increase of the integral/total cross section at low-energy - virtual state (scattering length = -49,70 a_0)

What do we do? What do we get with it?

PHYSICAL REVIEW A **107**, 012806 (2023)

Electron scattering by formamide: Elastic and electronically inelastic cross sections up to 179 energetically open states

P. A. S. Randi,* G. M. Moreira,† and M. H. F. Bettega‡
Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-980 Curitiba, Paraná, Brazil



What do we do? What do we get with it?

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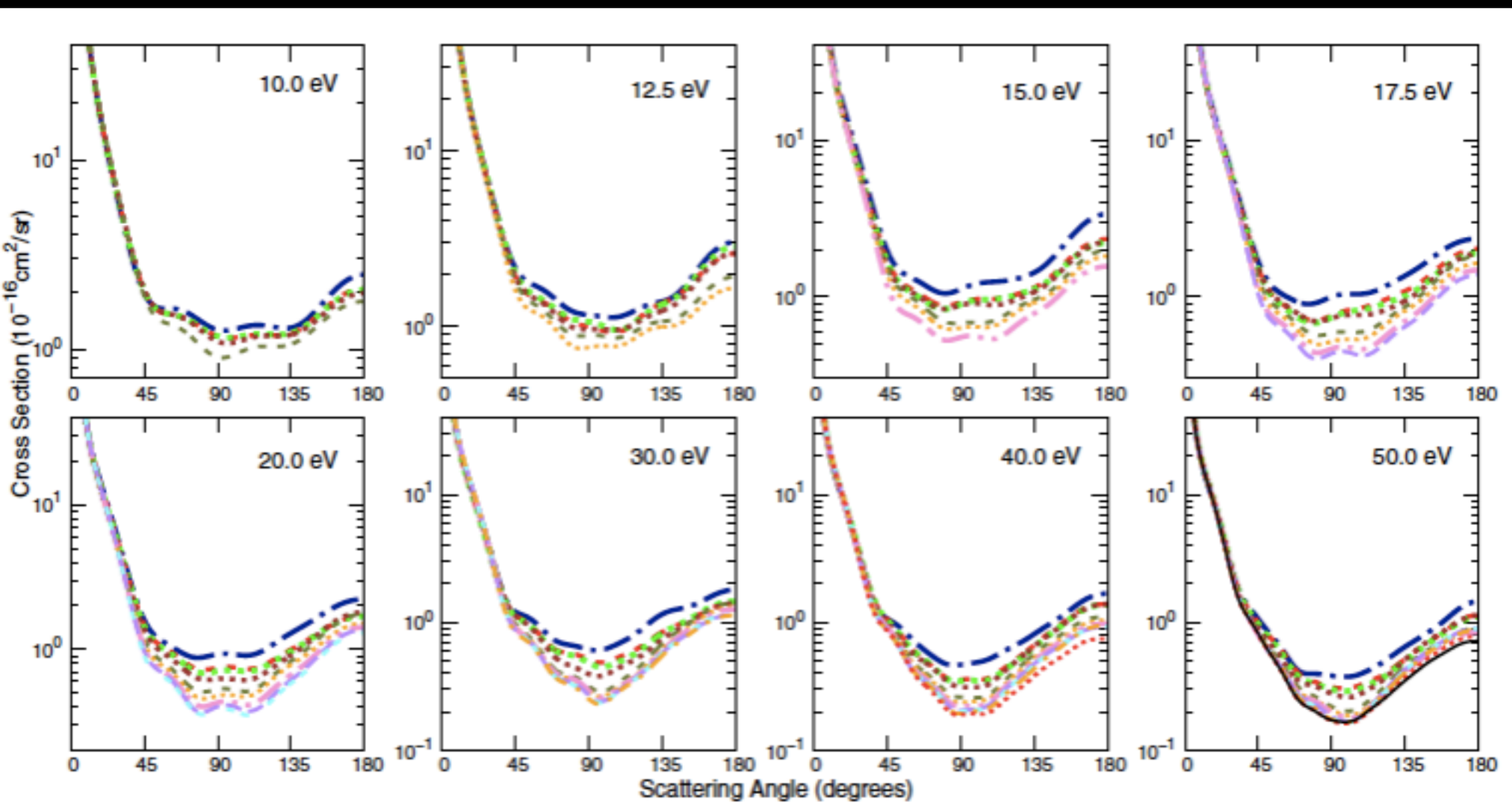

FIG. 3. Elastic differential cross section for the scattering of electrons by formamide calculated with different multichannel coupling schemes at 10, 12.5, 15, 17.5, 20, 30, 40, and 50 eV. Long-dash-dotted blue line, 1ch; dashed red line, 3ch; dotted green line, 4ch; dotted brown line, 6ch; dashed olive line, 22ch; dotted orange line, 57ch; dash-double-dotted pink line, 103ch; dashed purple line, 135ch; double-dashed cyan line, 154ch; dotted orange line, 167ch; dotted red line, 177ch; and solid black line, 179ch. The long-range dipole interaction between the incident electron and the molecule and the multichannel coupling effects are observed.

What do we do? What do we get with it?

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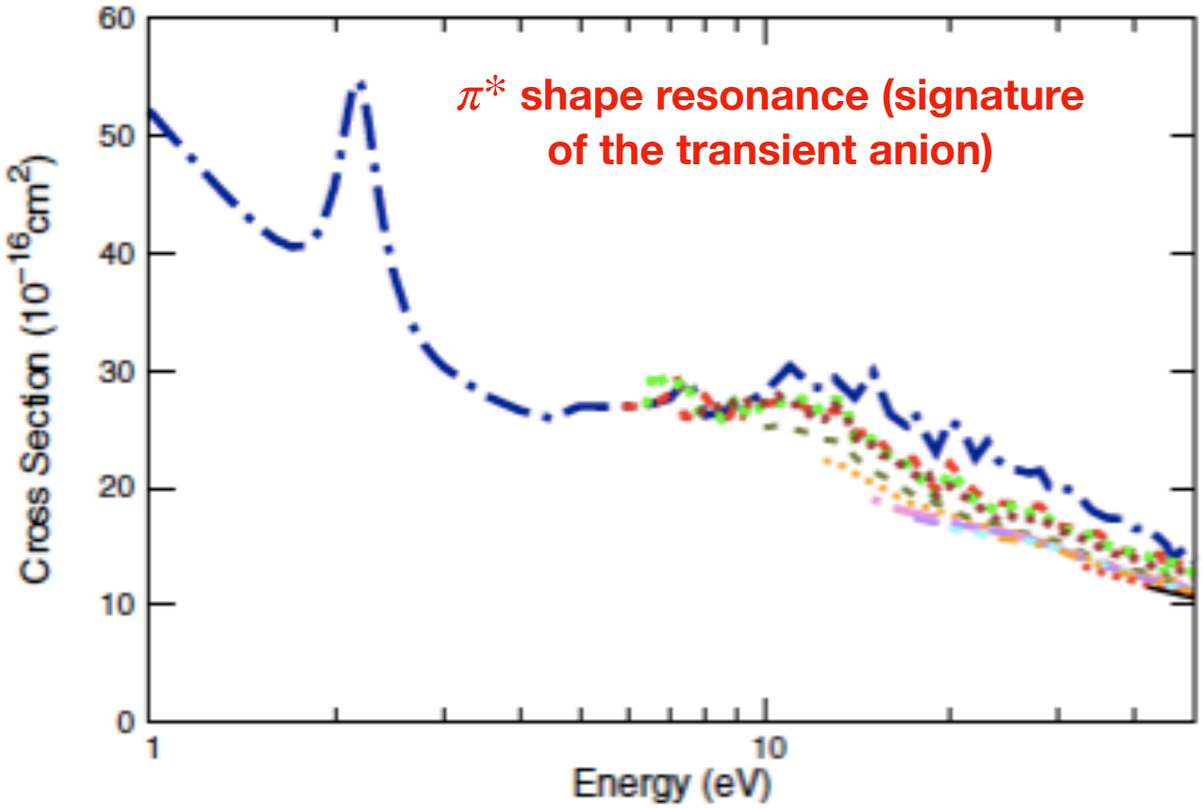

FIG. 6. Elastic integral cross section calculated with different multichannel coupling schemes without the Born-closure procedure. Dash-dotted blue line, 1ch; dashed red line, 3ch; dotted green line, 4ch; dotted brown line, 6ch; dashed olive line, 22ch; dotted orange line, 57ch; dash-double-dotted pink line, 103ch; dashed purple line, 135ch; double-dashed cyan line, 154ch; dotted orange line, 167ch; dotted red line, 177ch; and solid black line, 179ch.

What do we do? What do we get with it?

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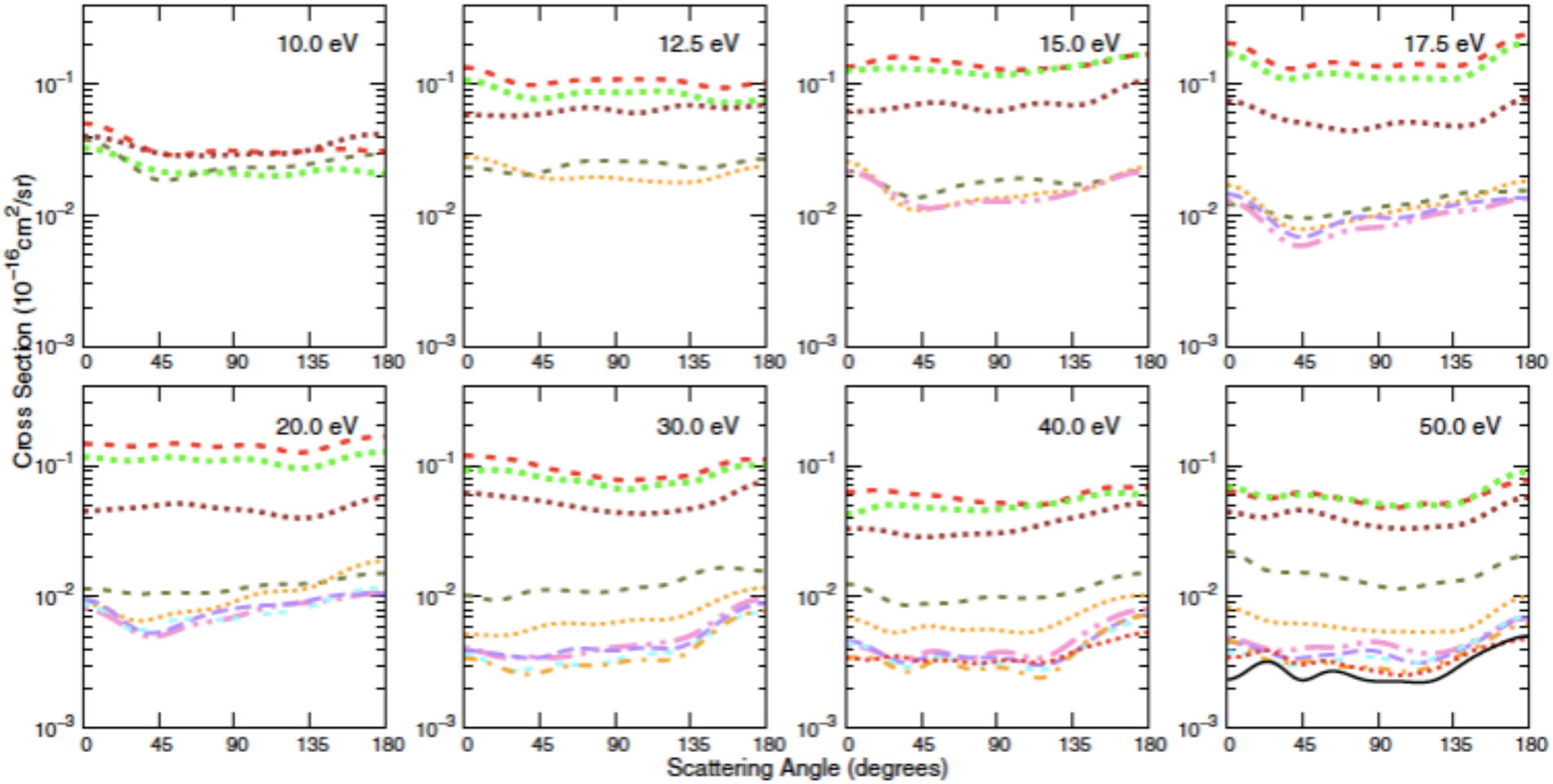


FIG. 8. Differential cross sections for the electronic excitation of the $1^3A'$ (5.572 eV) state of formamide for impact energies of 10, 12.5, 15, 17.5, 20, 30, 40, and 50 eV. Dashed red line, 3ch; dotted green line, 4ch; dotted brown line, 6ch; dashed olive line, 22ch; dotted orange line, 57ch; dash-double-dotted pink line, 103ch; dashed purple line, 135ch; double-dashed cyan line, 154ch; dot-dashed orange line, 167ch; dotted red line, 177ch; solid black line, 179ch.

Multichannel coupling

Continuity equation: $$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0$$

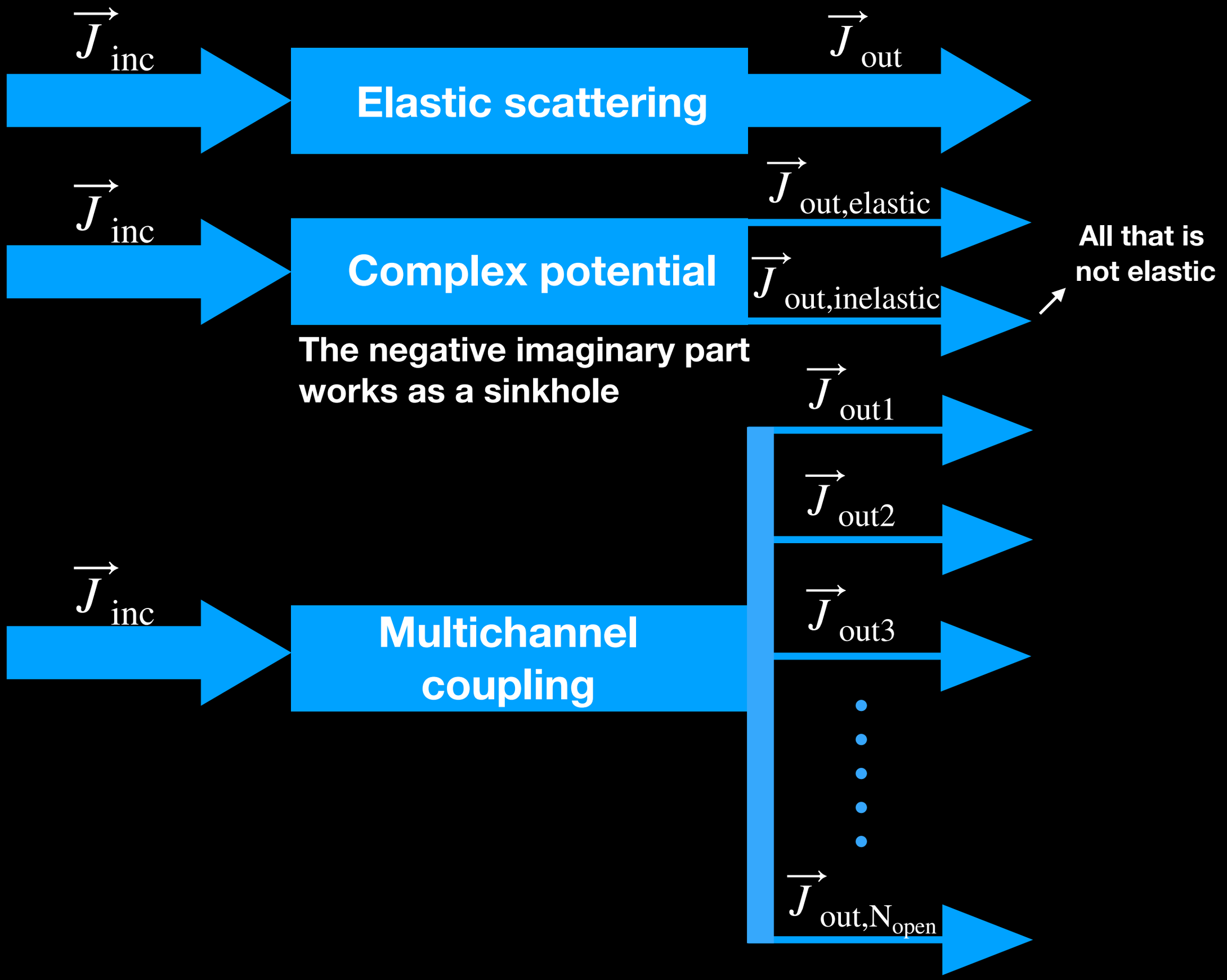
$$\rho = |\psi|^2 \quad \vec{J} = \frac{\hbar}{m} \mathrm{Im}\left(\psi^* \vec{\nabla} \psi\right)$$

ρ : probability density

$\vec{J}$: probability current (or probability flux)

Differential cross section: $$\frac{d\sigma}{d\Omega} = \frac{|\vec{J}_{out}| r^2}{|\vec{J}_{inc}|}$$

Multichannel coupling



What do we do? What do we get with it?

PCCP

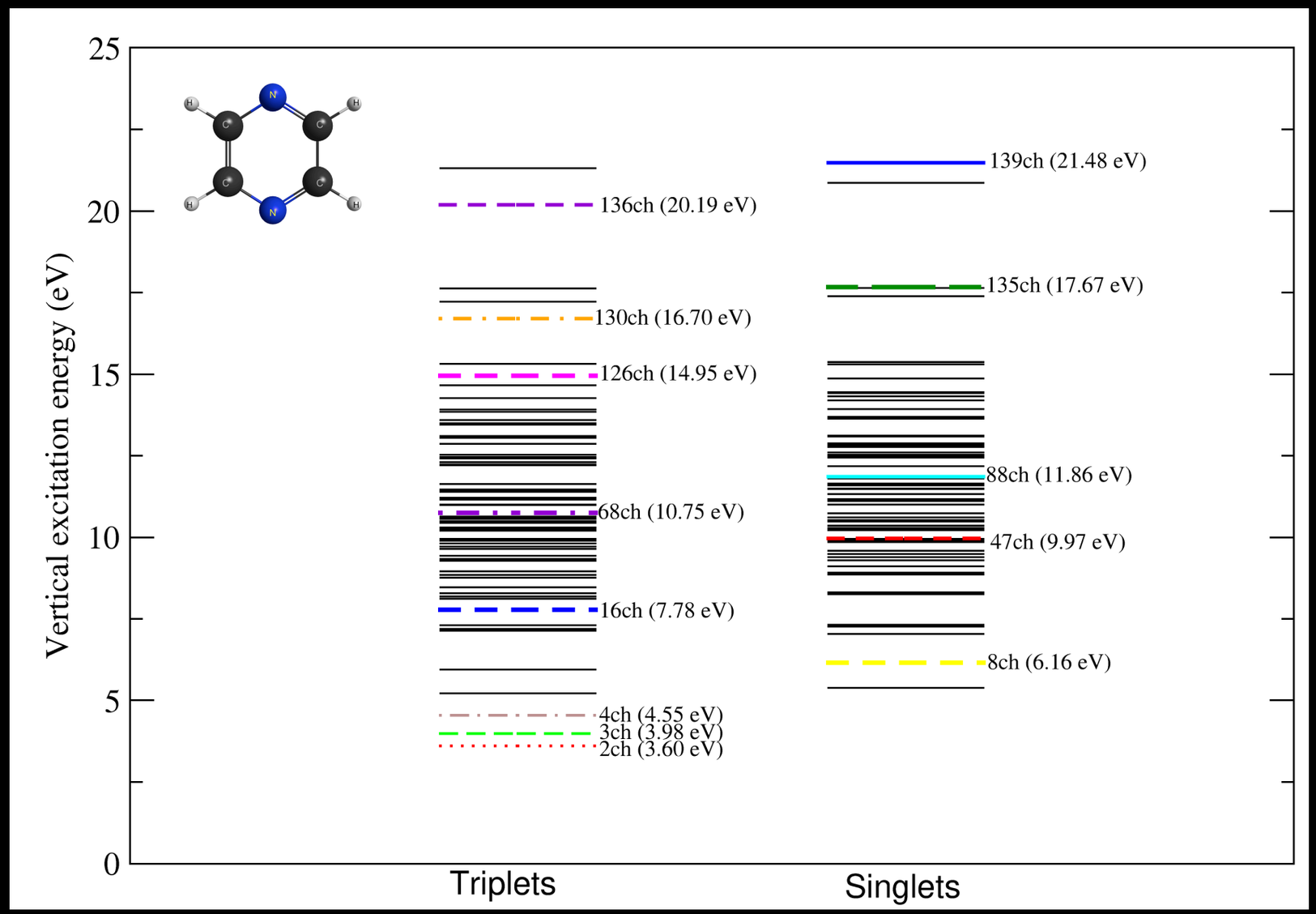
ROYAL SOCIETY OF CHEMISTRY

PAPER

Cite this: DOI: 10.1039/d3cp04619b

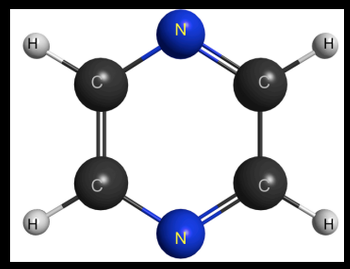
Elastic and electronically inelastic scattering of electrons by the pyrazine molecule

Murilo O. Silva,*[a] Giseli M. Moreira,[b] Jaime Rosado,[c] Francisco Blanco,[c] Gustavo García,[d] Márcio H. F. Bettega[a] and Romarly. F. da Costa*[e]



What do we do? What do we get with it?

Applications - multichannel coupling: $C_4H_4N_2$



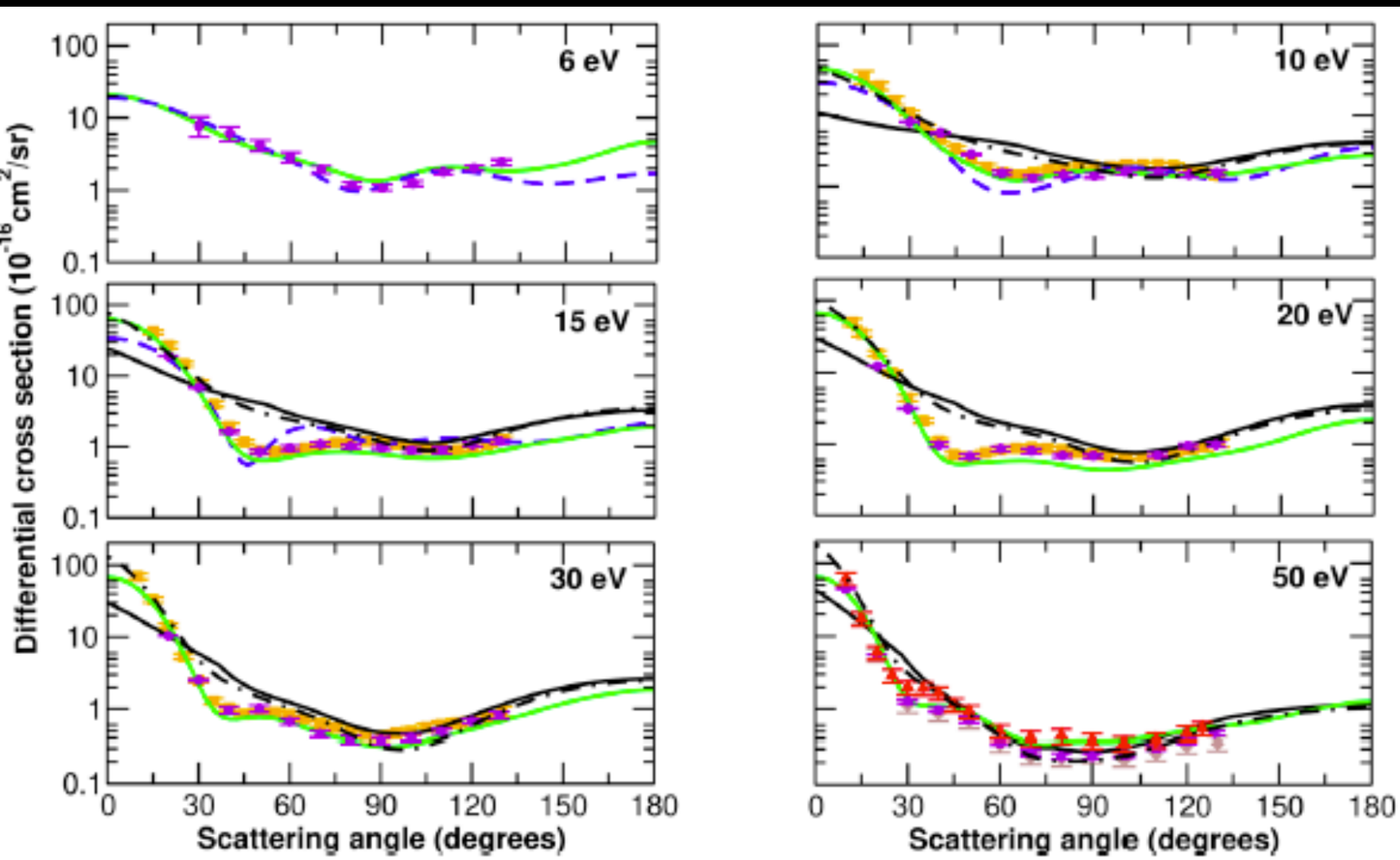
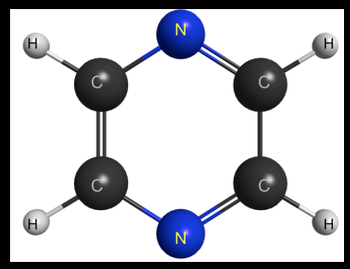


Fig. 4 Differential cross sections for elastic electron scattering by pyrazine at the impact energies of 6, 10, 15, 20, 30 and 50 eV. Solid green line, present SMC results obtained according to the best multichannel coupling scheme (4ch at 6 eV, 47ch at 10 eV, 126ch at 15 eV, 135ch at 20 eV and 139ch at 30 and 50 eV); black dashed-dotted line, present IAM-SCAR+I results; solid black line, IAM-SCAR results obtained by Sanz *et al.*;[2] dashed blue line, R-matrix results from Mašín and Gorfinkiel;[6] violet circles, experimental measurements reported by Palihawadana *et al.*;[8] measured data for the benzene molecule: orange squares, results reported by Cho *et al.*;[46] red up triangles, results reported by Sanches *et al.*;[47] brown diamonds, results reported by Kato *et al.*[48]

M. O Silva, G. M Moreira, M. H. F. Bettega and R. F. da Costa, PCCP (2024)

What do we do? What do we get with it?

Applications - multichannel coupling: $C_4H_4N_2$



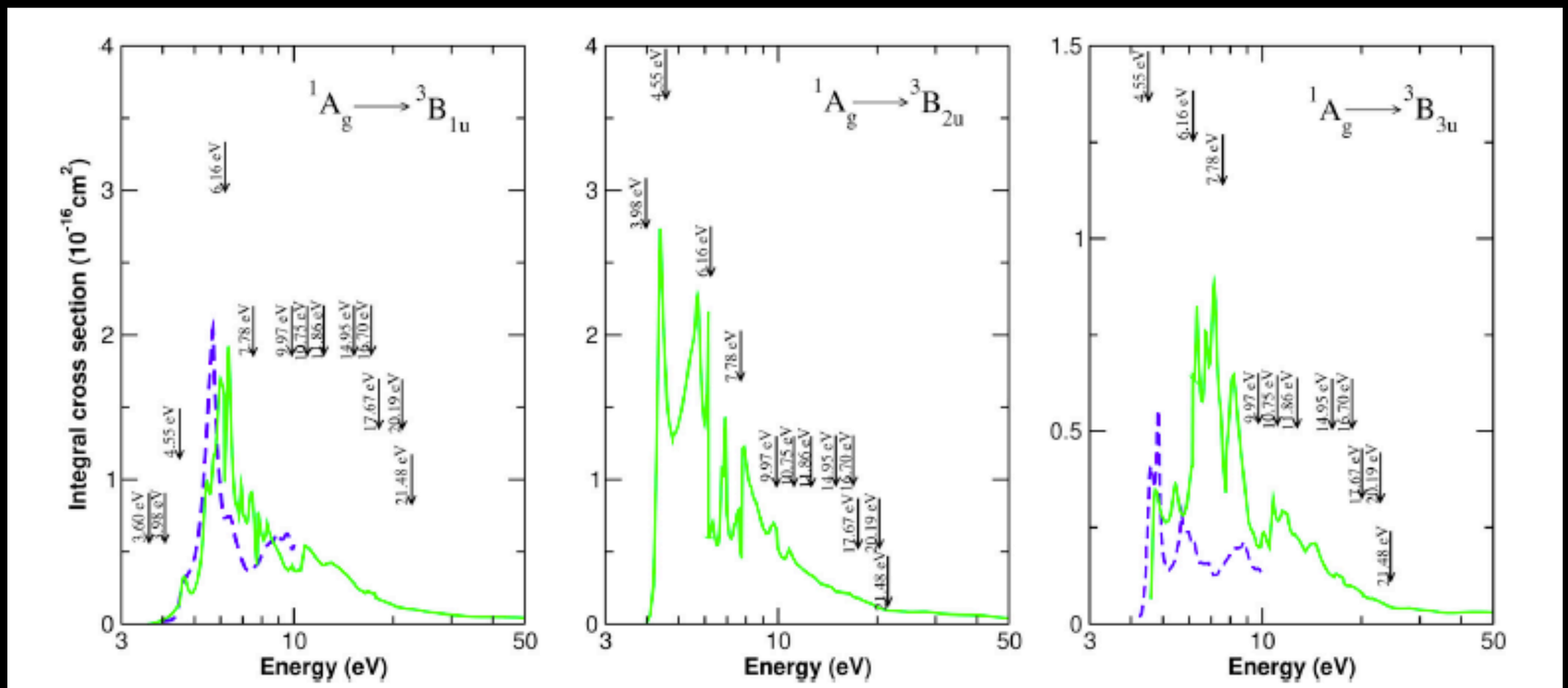


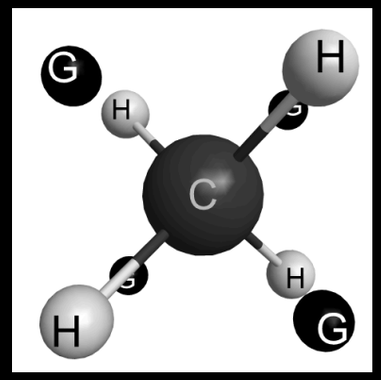
Fig. 7 Integral cross sections for the excitation from the ground state to the 1^3B_{1u} (3.60 eV), 1^3B_{2u} (3.98 eV) and 1^3B_{3u} (4.55 eV) excited states of pyrazine by electron impact. Solid green line, present SMC results; dashed blue line, R-matrix results from Mašín and Gorfinkiel.[6]

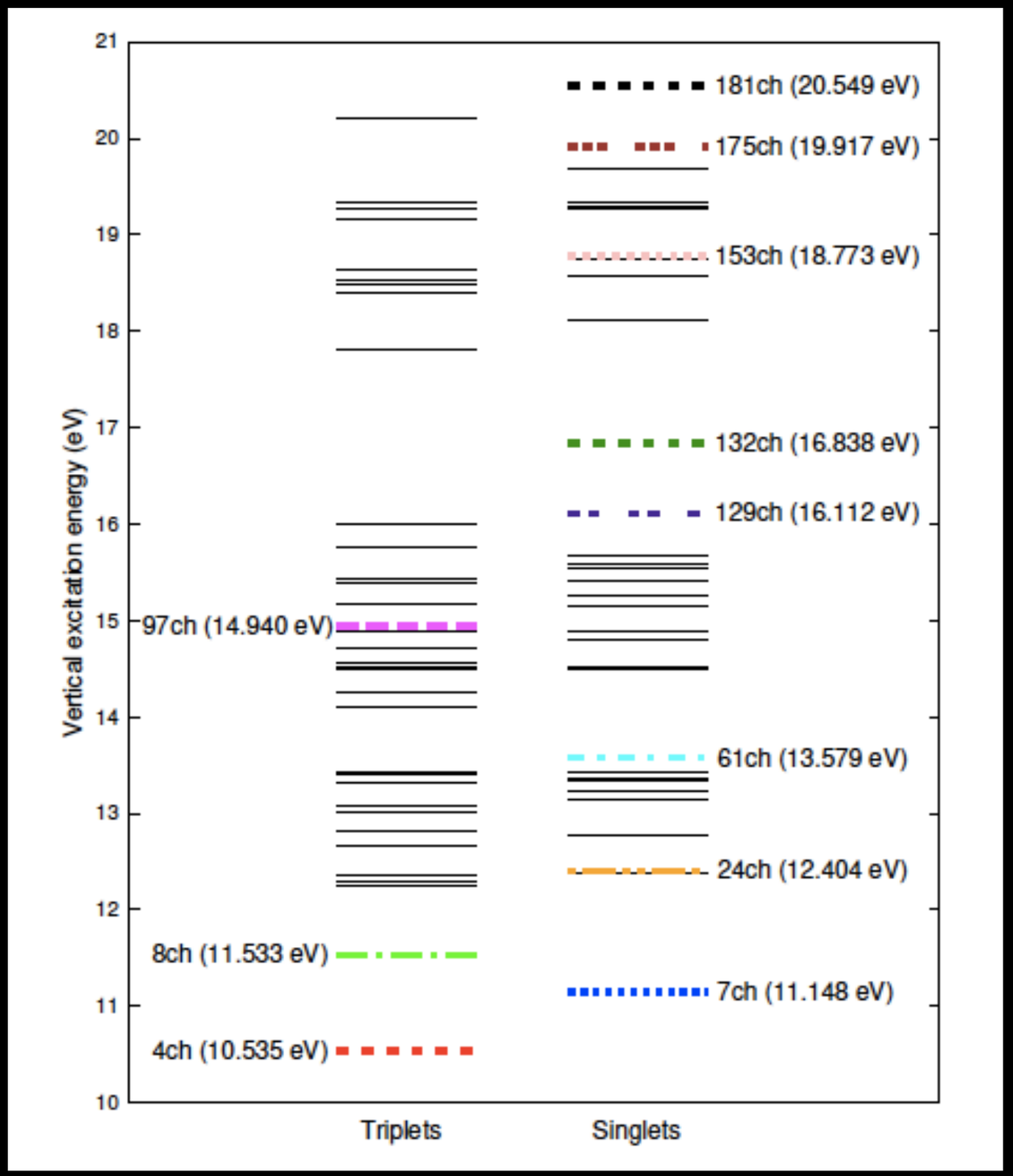
M. O Silva, G. M Moreira, M. H. F. Bettega and R. F. da Costa, PCCP (2024)

What do we do? What do we get with it?

Applications - multichannel coupling: CH_4

(not too many extra centers as in the positron scattering)





P. A. S. Randi, G. M Moreira, R. F. da Costa, and M. H. F. Bettega and, submitted to JAP

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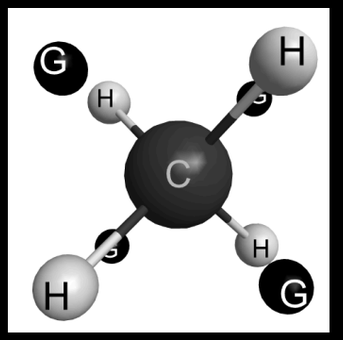

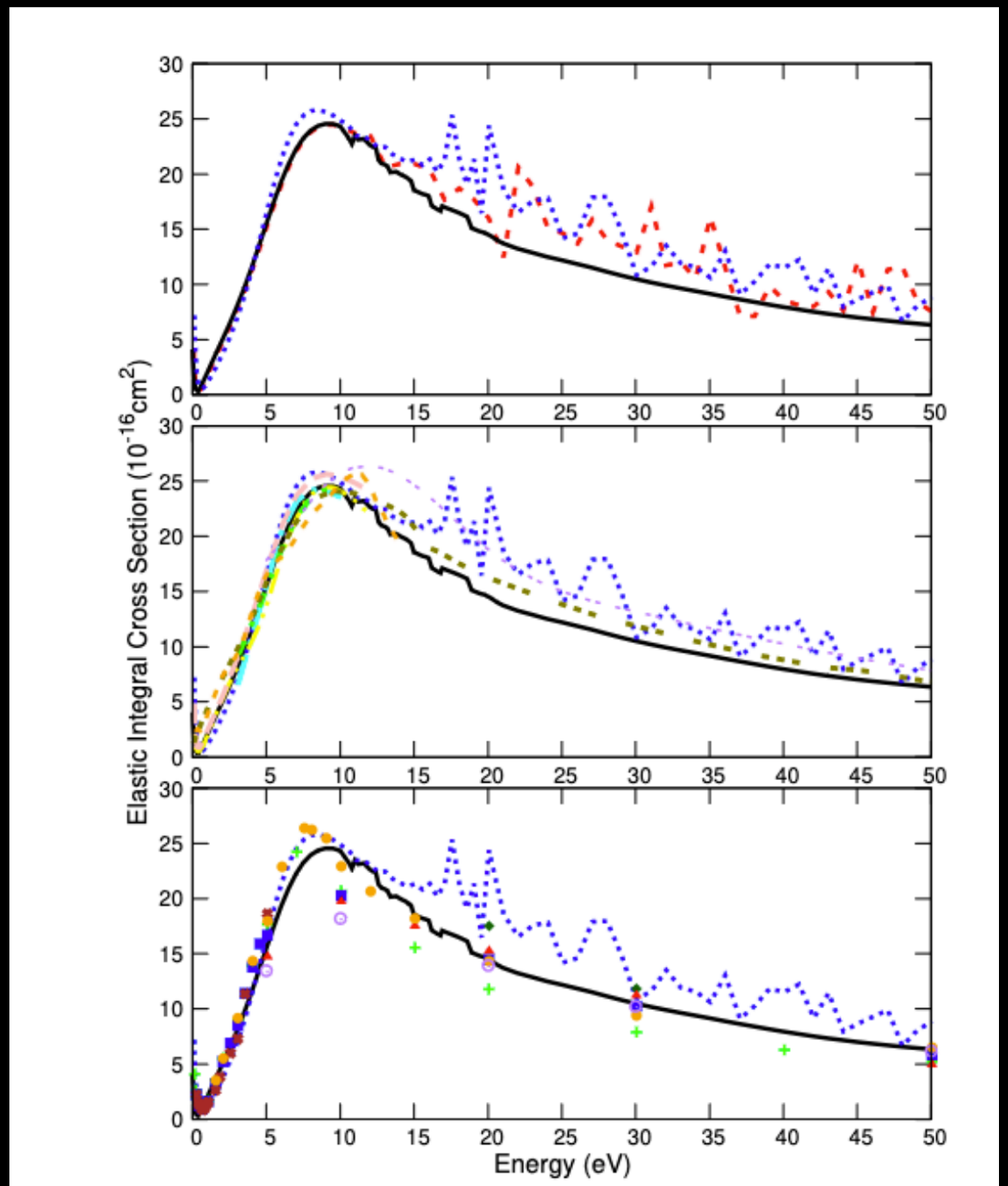

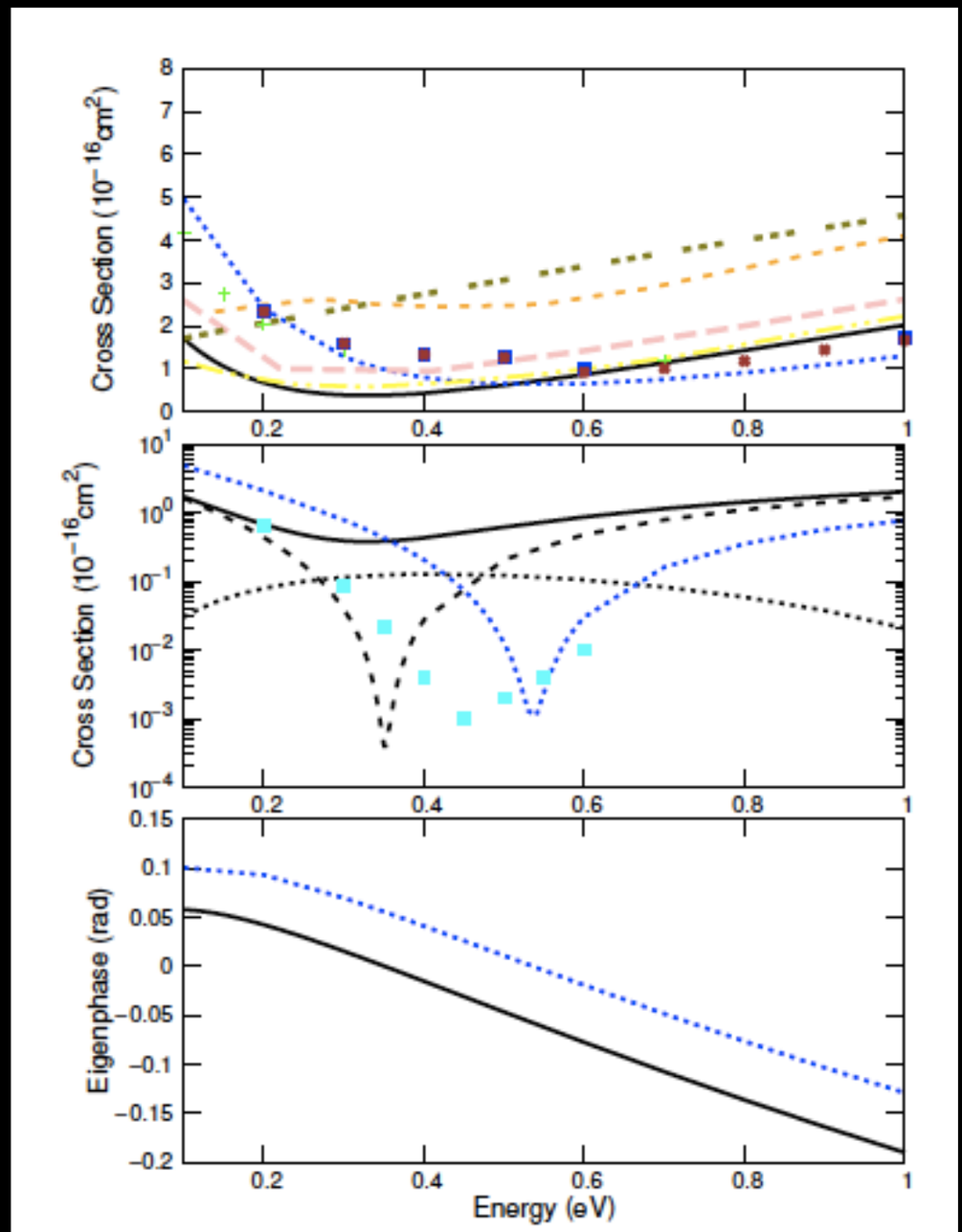

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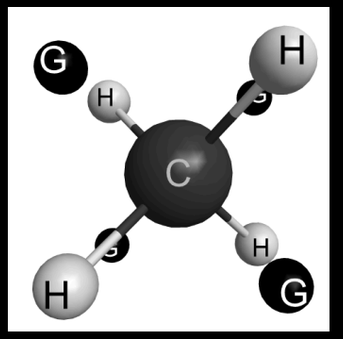
What do we do? What do we get with it?



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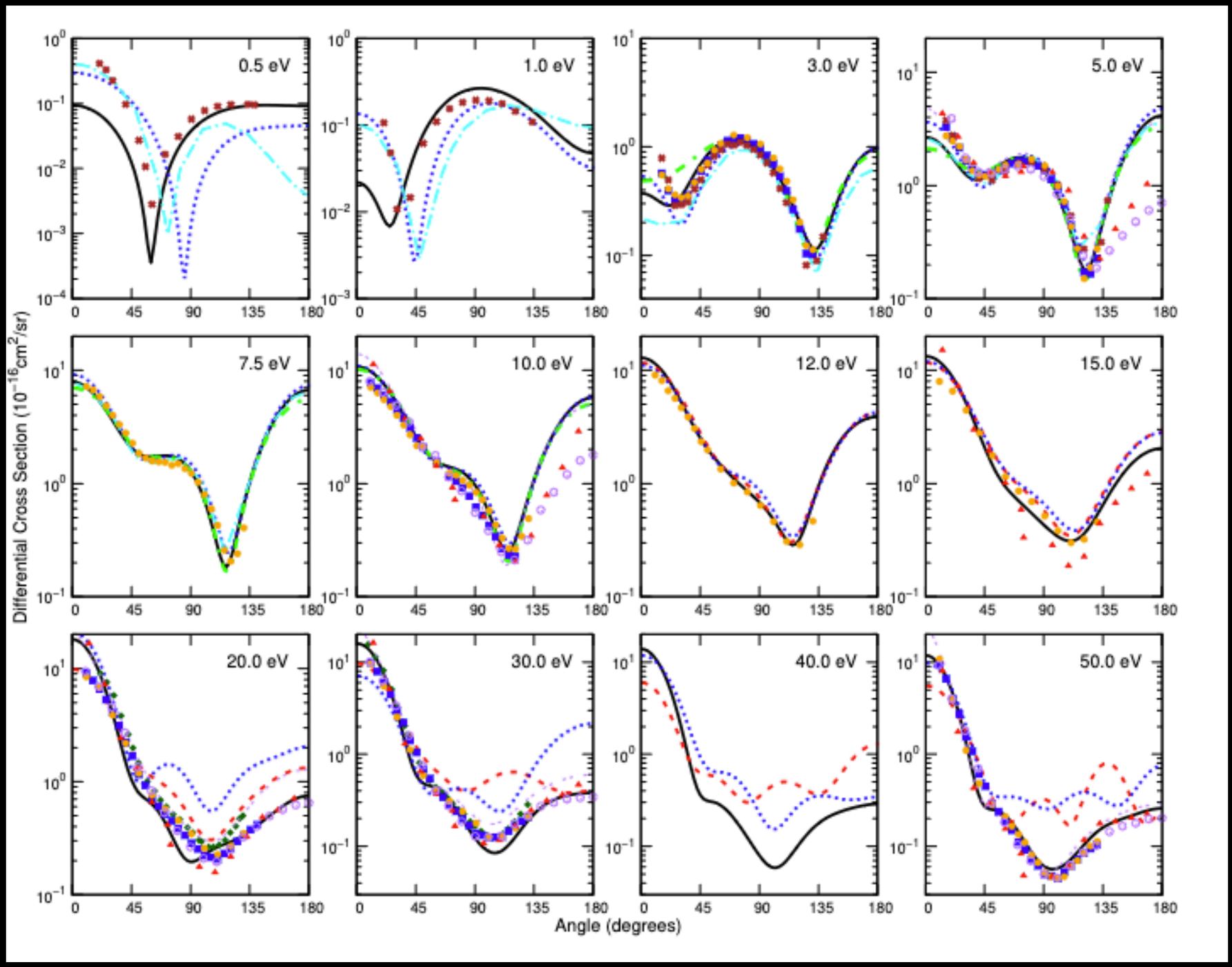

P. A. S. Randi, G. M Moreira, R. F. da Costa, and M. H. F. Bettega and, submitted to JAP

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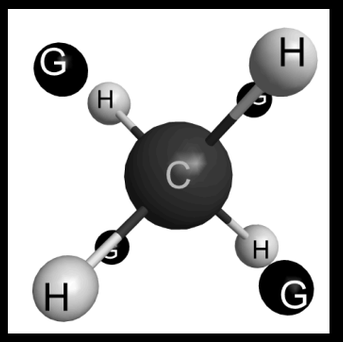

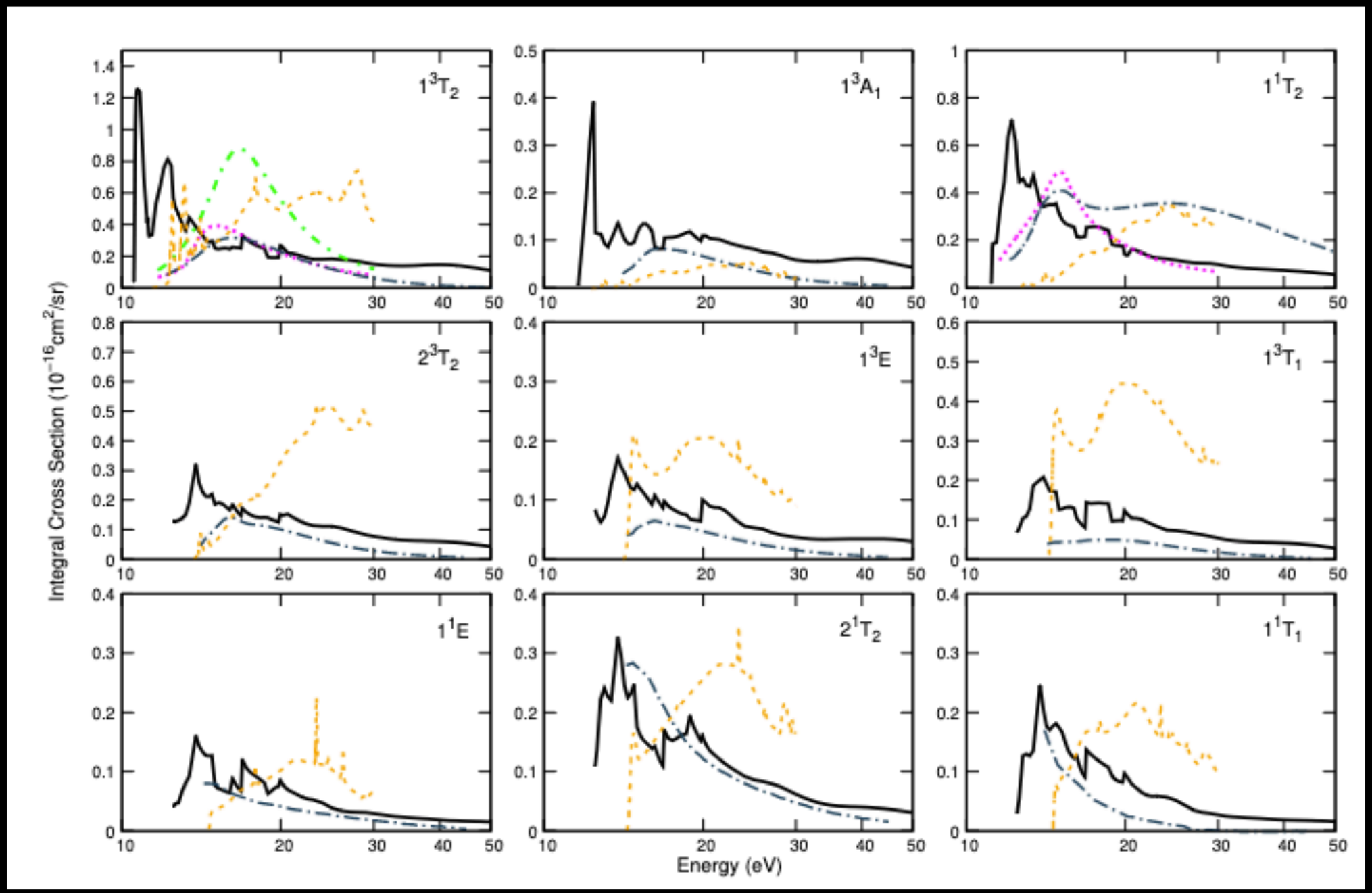

P. A. S. Randi, G. M Moreira, R. F. da Costa, and M. H. F. Bettega and, submitted to JAP

What do we do? What do we get with it?

The theory of electron-molecule collisions

N. F. Lane
Rev. Mod. Phys. **52**, 29 – Published 1 January 1980

The ultimate test of a theory, of course, is how well it describes the physical phenomena. In principle, this is determined by comparison with experimental measurement. However, measurements always contain some error, and often the amount of error is not well known. So, progress in understanding requires that theory and experiment proceed hand in hand. Error in theoretical

Acknowledgements

- Special thanks to Prof. Carlos Martins de Carvalho for computational support at LFTC-DFIs and LCPAD-UFPR

Theory

- The collision Hamiltonian: $H = (H_N + T_{N+1}) + V = H_0 + V$
- We know how to solve the target (Hartree-Fock): $H_N \Phi_\ell = E_\ell \Phi_\ell$
- The Lippmann-Schwinger equation:
  $A^{(\pm)} \Psi_m^{(\pm)} = V S_m;\ S_m = \Phi_m \exp(i\vec{k}_m.\vec{r}_{N+1})$
- The $A^{(+)}$ operator:

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(\hat{H}P + P\hat{H})}{2} + \frac{(VP + PV)}{2} - VG_P^{(+)}V$$

$$\hat{H} = E - H; \qquad P = \sum_{\ell \in \text{ open}} |\Phi_\ell\rangle\langle\Phi_\ell|$$

- $G_P^{(+)}$ is the free-particle Green's function projected on the P-space.
- Variational stability: $A^{(+)^\dagger} = A^{(-)}$

Theory

- The functional

$$[f(\vec{k}_{out}, \vec{k}_{in})] = -\frac{1}{2\pi}\left[\langle S_{\vec{k}_{out}}|V|\Psi^{(+)}_{\vec{k}_{in}}\rangle + \langle\Psi^{(-)}_{\vec{k}_{out}}|V|S_{\vec{k}_{in}}\rangle - \langle\Psi^{(-)}_{\vec{k}_{out}}|A^{(+)}|\Psi^{(+)}_{\vec{k}_{in}}\rangle\right]$$

- The scattering wave function is expanded in a basis of (N+1)-particle Slater determinants $\{|\chi_m\rangle\}$

$$|\Psi^{(\pm)}_{\vec{k}}\rangle = \sum_m a^{(\pm)}_m(\vec{k})|\chi_m\rangle$$

$\{a^{(\pm)}_m(\vec{k})\}$ are then variationally determined.

- The "working" expression for the scattering amplitude (in the body-frame) is

$$f(\vec{k}_{out}, \vec{k}_{in}) = -\frac{1}{2\pi}\sum_{m,n}\langle S_{\vec{k}_{out}}|V|\chi_m\rangle(d^{-1})_{mn}\langle\chi_n|V|S_{\vec{k}_{in}}\rangle$$

where

$$d_{mn} = \langle\chi_m|A^{(+)}|\chi_n\rangle$$

Theory

- Configuration state functions (CSFs):

  $|\chi_\mu\rangle = \mathcal{A}[|\Phi_1\rangle \otimes |\varphi_\mu\rangle]$ – direct space (static-exchange – SE – approximation);

  $|\chi_{\sigma\lambda}\rangle = \mathcal{A}[|\Phi_\sigma\rangle \otimes |\varphi_\lambda\rangle]\,(\sigma > 1)$ – polarization (plus the direct space – static-exchange plus polarization – SEP – approximation).

  $|\Phi_1\rangle$=target ground state (RHF);

  $|\varphi_\mu\rangle$=scattering orbital;

  $|\Phi_\sigma\rangle$=[hole $\rightarrow$ particle] virtual single excitation – singlet and triplet couplings.
- Single-particle basis $\rightarrow$ Cartesian Gaussian functions!
- Fixed-nuclei approximation.