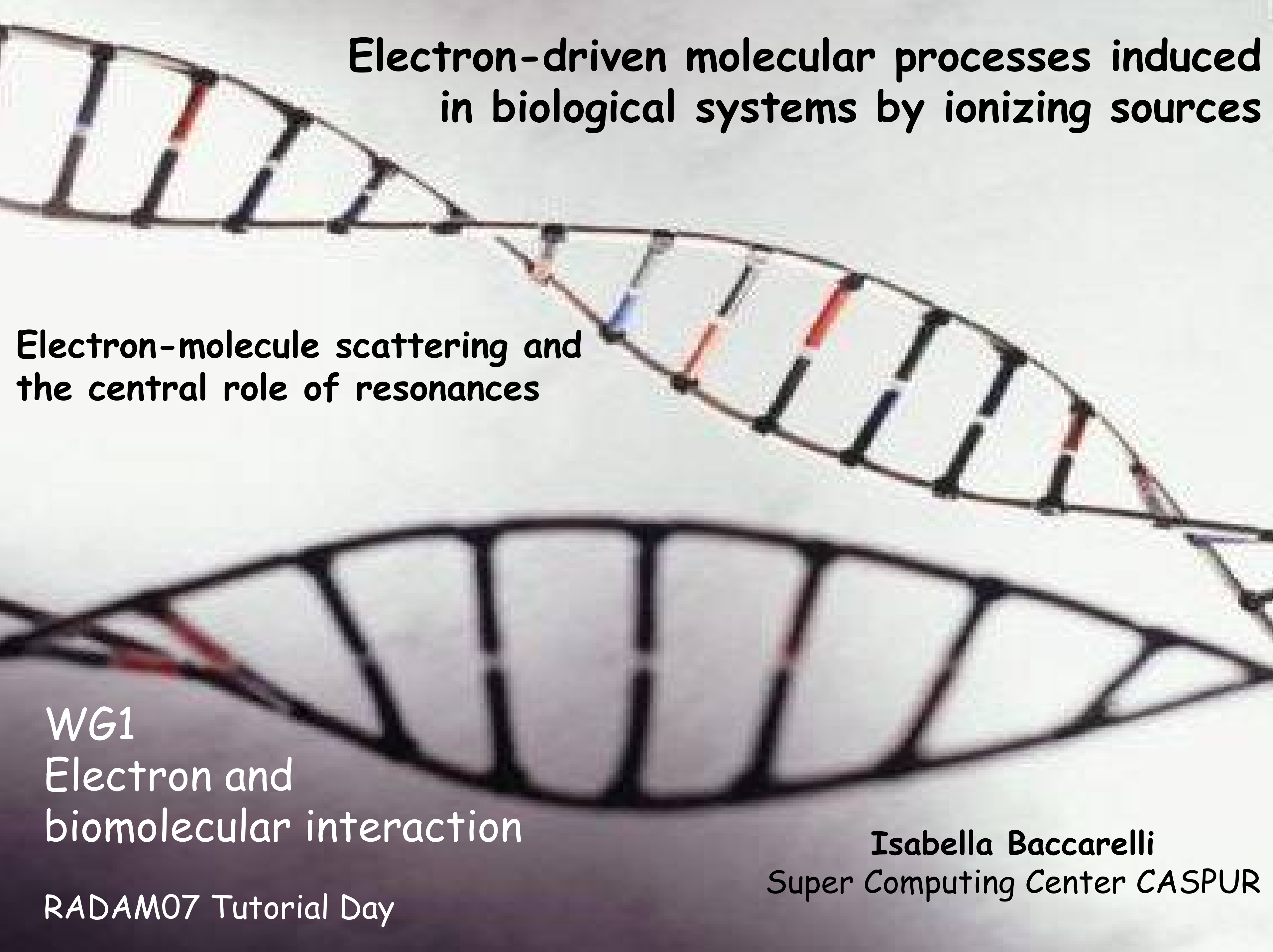

Electron-driven molecular processes induced in biological systems by ionizing sources

Electron-molecule scattering and the central role of resonances

WG1
Electron and biomolecular interaction

RADAM07 Tutorial Day

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Suite of codes to solve electron/positron-molecule scattering problem

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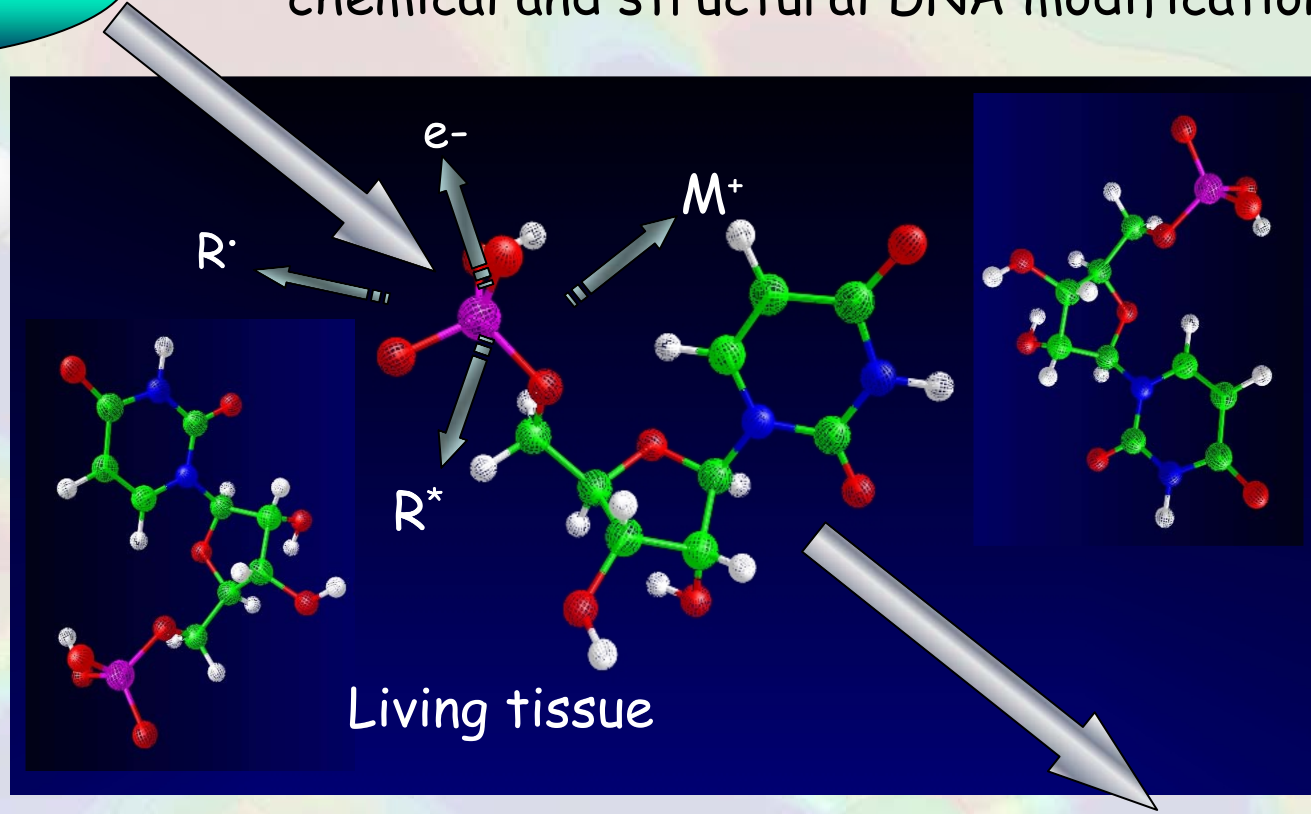
  Department of Chemistry
  University of Rome 'La Sapienza'
  Rome, Italy

- Prof. R.R. Lucchese
  Department of Chemistry
  Texas A&M University
  College Station, Texas

Ionizing radiation

Lethal effects of ionizing radiation: chemical and structural DNA modification

X rays
γ rays
α particles
β particles
Neutrons
Cosmic rays



The genotoxic effects, due to various DNA lesions, are <u>not only</u> produced by the direct impact of the initial high energy particles (direct ionization)

Role of SECONDARY SPECIES: excited atoms and molecules, radicals, ions, low-energy electrons (LEEs)

LEEs (1 eV < E < 20 eV): the most abundant among secondary species carrying most of the energy of the initial fast particles

Low Energy Electrons in Radiation Damage

- LEEs are produced in large quantities in any type of material irradiated by high-energy particles
- in biological media LEEs can fragment molecules with the formation of highly reactive radicals and ions
- below 15 eV electron resonances (Transient Negative Ions, TNIs) play a dominant role in the fragmentation of all biomolecules investigated (below 16 eV DSB occurs exclusively via the decay of transient anions)

- DNA damage: TNIs (resonances) are LOCALIZED on the DNA's basic components (compare the results obtained with the basic constituents to the measured yields for the induction of SSB and DSB)

Electron-molecule collision

$e^-(E) + M$

$\rightarrow e^-(E) + e^-(E) + M^+$ — Ionization ($E > E_{threshold}$)

$\rightarrow e^-(E) + M,\ e^-(E') + M^*$ — Direct scattering

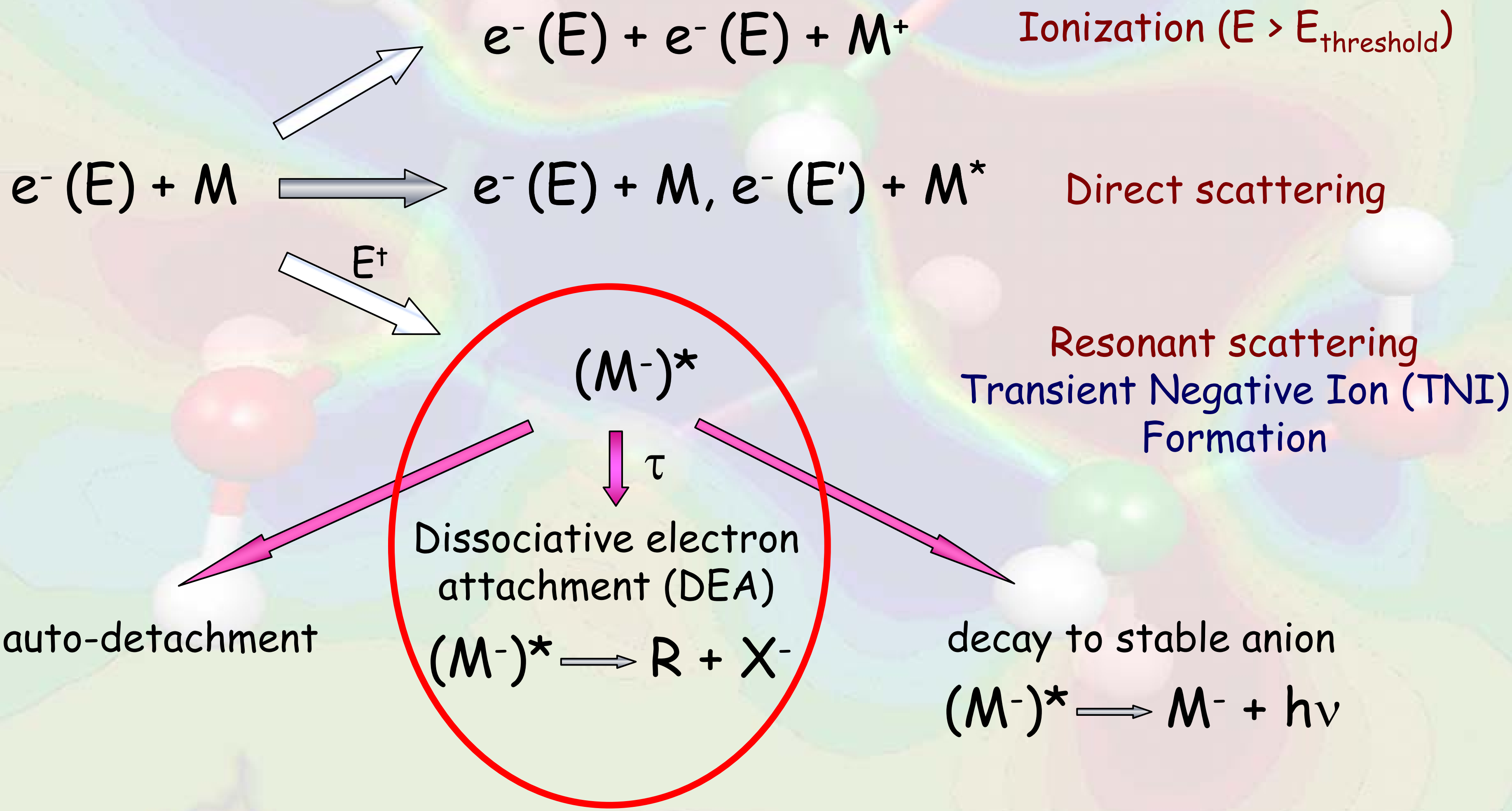
$M + E(M^*) - E(M)$

$A + B^*$

$A^- + (B^+)^*$

dipolar dissociation

Electron-molecule collision



Theoretical investigation of electron-induced processes relevant to radiation damage:

- need to describe electron-molecule collisions
  - need to describe resonance states

'Quantum chemistry' approach

(electronic structure calculation)

'Scattering' approach

(collisional processes)

Solution of the Schrödinger equation

Electron-molecule scattering

scattering is the effect of a collision (deviation from initial electron trajectory, energy loss, type and number of fragments eventually produced…)

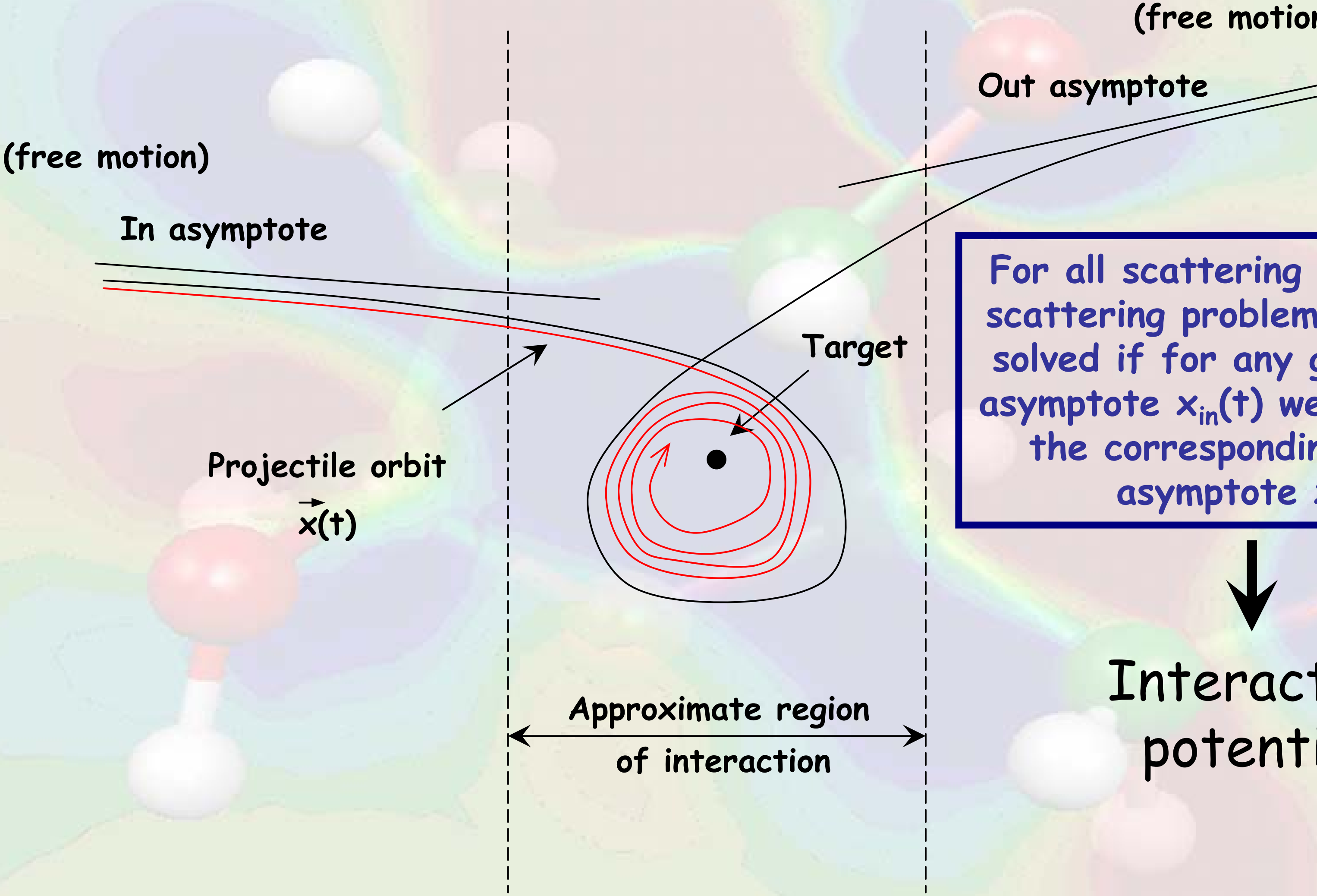
Quantum mechanical description of a scattering event

Cross section

probability for an event (caused by the collision) to take place

$$\vec{x}(t) \xrightarrow[t \to -\infty]{} \vec{x}_{in}(t) \equiv \vec{x}_{in}^{\,0} + \vec{v}_{in} t$$

$$\vec{x}(t) \xrightarrow[t \to +\infty]{} \vec{x}_{out}(t) \equiv \vec{x}_{out}^{\,0} + \vec{v}_{out} t$$



For all scattering purposes the scattering problem is completely solved if for any given incoming asymptote $x_{in}(t)$ we can calculate the corresponding outgoing asymptote $x_{out}(t)$

↓

Interaction potential

Classical representation of a scattering orbit

Classical representation of a bounded orbit

$$\vec{x}(t) \xrightarrow[t \to -\infty]{} \vec{x}_{in}(t) \equiv \vec{x}_{in}^{\,0} + \vec{v}_{in} t$$

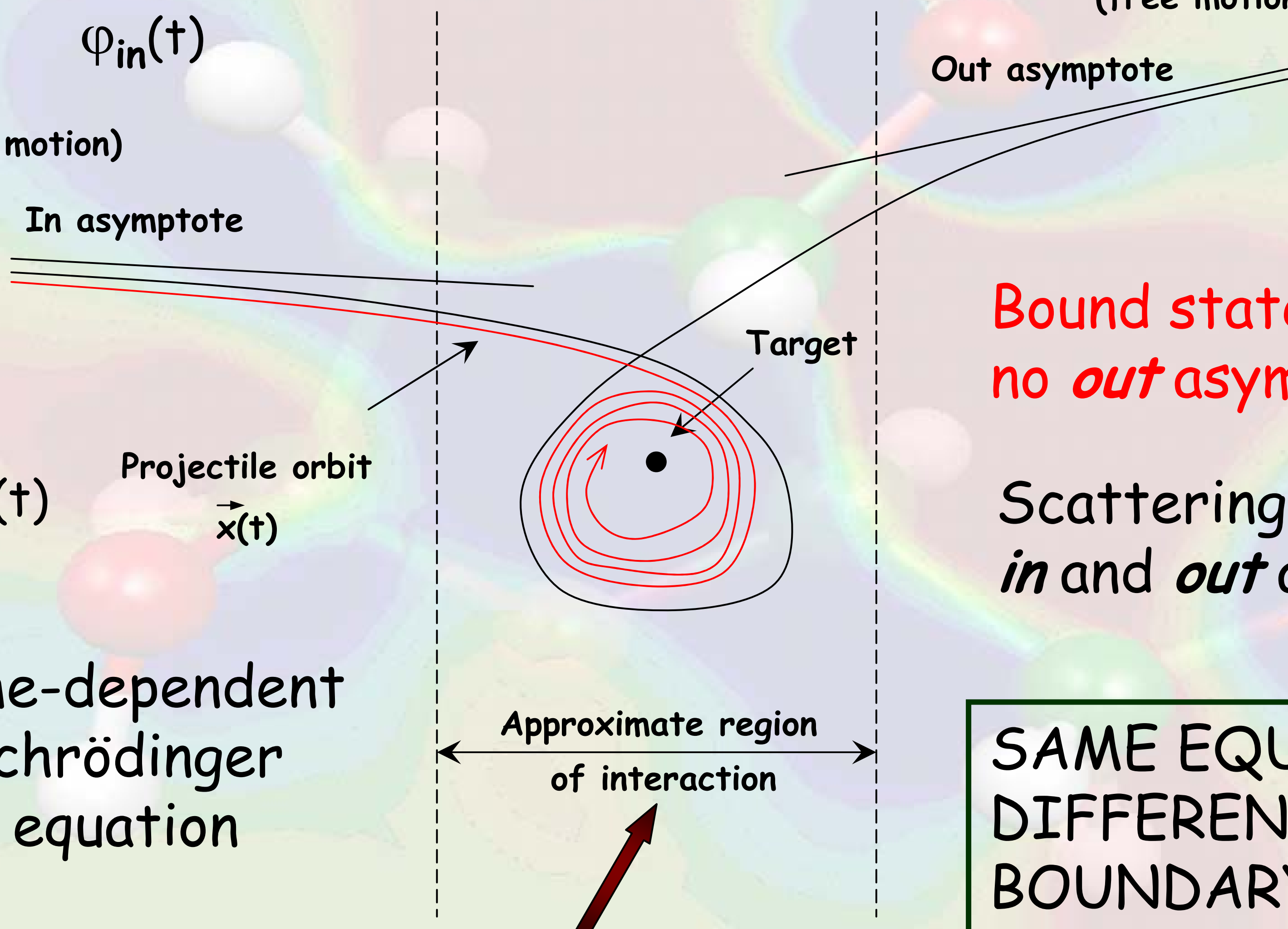
$$\vec{x}(t) \xrightarrow[t \to +\infty]{} \vec{x}_{out}(t) \equiv \vec{x}_{out}^{\,0} + \vec{v}_{out} t$$

$\varphi_{in}(t)$

(free motion)

(free motion) $\varphi_{out}(t)$

$\varphi\ (t)$



Bound state:
no *out* asymptote

Scattering state:
in and *out* asymptotes

Time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} |\varphi(t)\rangle = H |\varphi(t)\rangle$$

SAME EQUATION, DIFFERENT BOUNDARY CONDITIONS

- Scattering arises from the interaction potential
- Set the Potential ⟶ Solve the SE for the scattering ⟶ Derive S-matrix ⟶ Cross section
- Cross section measures the effect of scattering by connecting scattered (*out*) and incident (*in*) fluxes of particles

Differential and integral cross section

- In order to calculate cross sections we need to know the interaction potential between the incident electron and the molecular target: electrostatic + exchange + polarization (+ correlation)

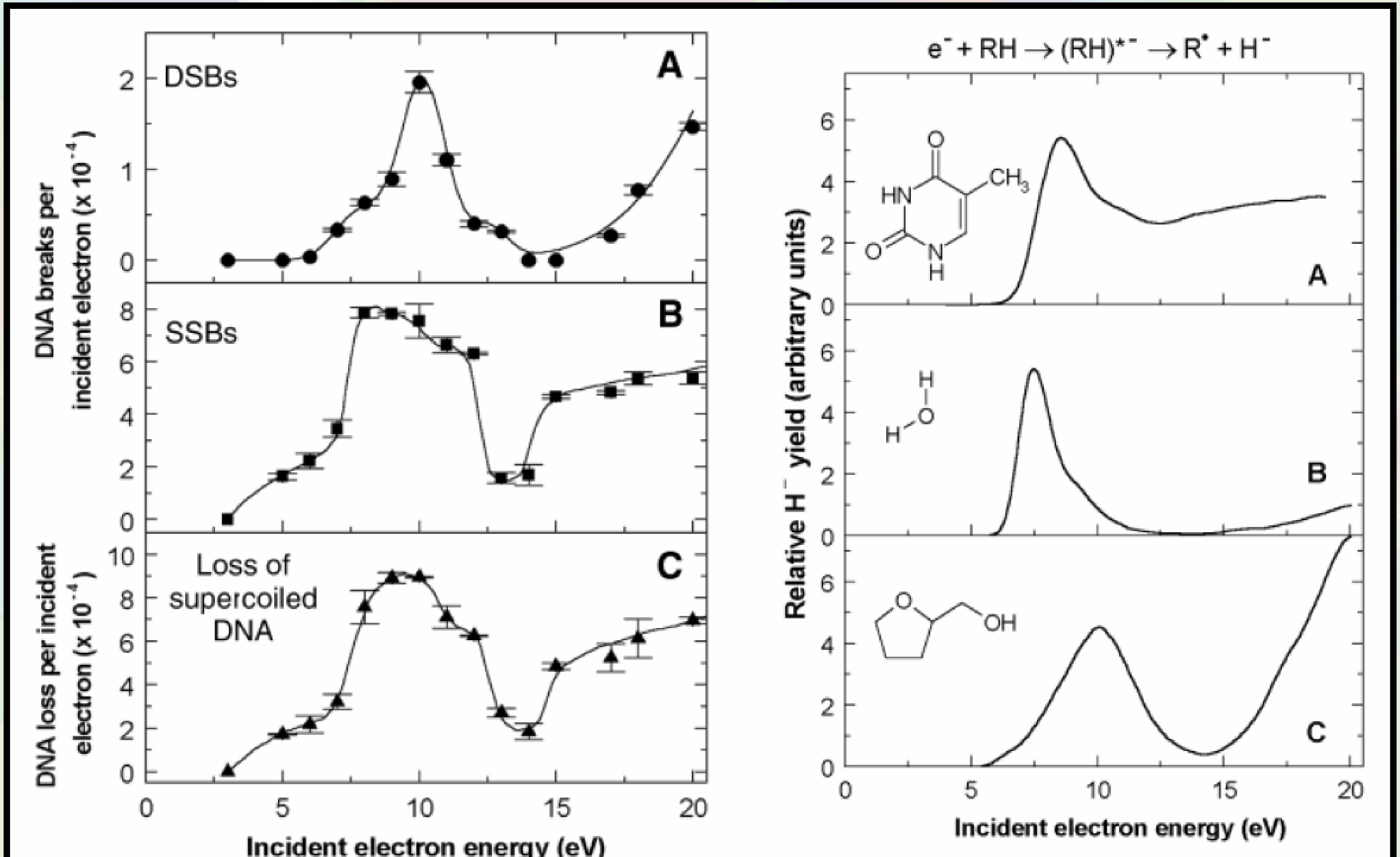
What is a resonance?

Experimental: peak in scattering cross section

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

Science **287**, 1658 (2000)



What is a resonance?

Experimental: peak in cross section

Quantum mechanical:

Resonance: quasi-bound state ⟹ finite-lived state

state with energy above the dissociation threshold for the system and a barrier hindering the immediate break-up

Energy at which the resonance appears (real positive number)

Width → Lifetime (complex number)

$$E_{res} = E - i\,\Gamma/2$$

$$E_{res} = E - i\,\Gamma/2$$

Quasi-bound states:

- 'bound' (L^2) techniques: optical potential, complex scaling… (i.e. making the Hamiltonian eigenvalues complex! Non-Hermitian Quantum Mechanics)

Peculiar Scattering states:

- 'poles' of S-matrix in the complex plane (like bound states!)
- Breit-Wigner analysis of scattering amplitudes (if possible)

Trapping mechanisms?

(i.e.: 'types' of resonances)

To better understand the possible origin of such a coupling between a discrete state and the continuum of a system, it is useful to distinguish between:

- Shape resonances (and core-excited shape resonances)
- (Fano-) Feshbach resonances

Shape resonances

- Resonances due to the **SHAPE** of the potential

Schematic example of a shape resonance

diatomic molecule with the total angular momentum, describing the relative rotational motion of the two nuclei, large enough to give rise to a centrifugal barrier

the resonance lifetime is related to the probability of tunnelling from the potential well to the other side of the barrier

Shape-resonances

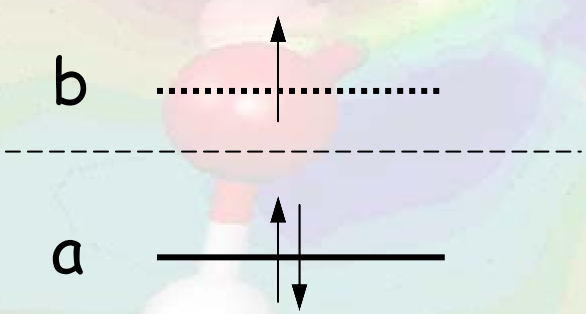
A shape resonance is a resonance which is not turned into a bound state if the coupling between some degrees of freedom (nuclear or electronic) and the degrees of freedom associated with the fragmentation (reaction coordinates) were set to zero (*V. Brems*)

- in one-dimensional systems resonances can only be shape resonances
- in a system with more than one degree of freedom this definition makes sense only if the separable model is a valid approximation (i.e. the two groups of degrees of freedom are supposed to be uncoupled)
- in the case of large coupling: distinction between different 'types' of resonances is less clear

Core-excited shape resonances

A shape resonance is a core-excited shape resonance if after the fragmentation one of the fragments is in an excited state (*V. Brems*)

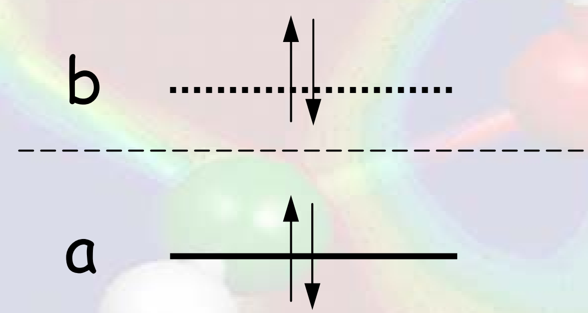
Shape resonance



$AB\ (a^2b^0) + e^-$

$\hookrightarrow AB^{-*}\ (a^2b^1) \longrightarrow A + B^-$

Core-excited shape resonance



$AB\ (a^2b^0) + e^-$

$\hookrightarrow AB^{-*}\ (a^1b^2) \longrightarrow A^* + B^-$

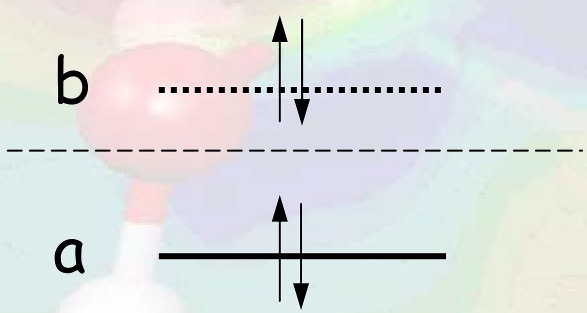
$\hookrightarrow AB^*\ (a^1b^1) + e^-$

Feshbach resonances

In contrast to a shape resonance, a Feshbach resonance is a resonance of a system with more than one degree of freedom which would turn into a bound state if the coupling between some degrees of freedom and the degrees of freedom associated with the fragmentation were set to zero

(*V. Brems*)

Core-excited shape resonance

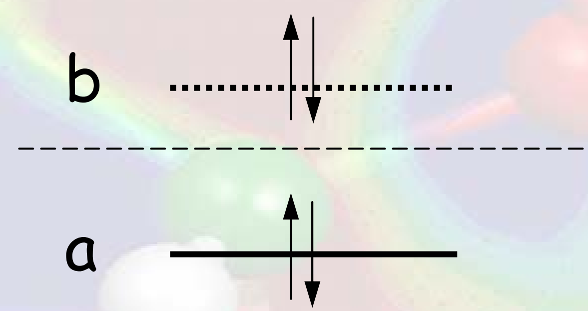


$AB\ (a^2b^0) + e^-$

↳ $AB^{-*}\ (a^1b^2) \longrightarrow A^* + B^-$

↳ $AB^*\ (a^1b^1) + e^-$

Feshbach resonance



$AB\ (a^2b^0) + e^-$

↳ $AB^{-*}\ (a^1b^2) \longrightarrow A^* + B^-$

✕ ↳ $AB^*\ (a^1b^1) + e^-$

Role of LEEs (and resonances) in Radiation Damage

Efficient way to transfer collisional (electronic) energy to nuclear motion eventually causing dissociation

Electron impact on DNA's basic components and surrounding molecules → TNI → Fragmentation channels → DNA Single- and Double-strand breaks

Transient Negative Ions: Resonances

Damaging effects of LEEs due to the interaction of LEEs with DNA components (1/3) and with molecules surrounding DNA (2/3) [attack of $OH^{\cdot}$ on the DNA chain]